研究炉利用における研究成果集（平成13年度）

2003年7月

（編）研究炉利用課

日本原子力研究 所
Japan Atomic Energy Research Institute
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研究炉利用における研究成果集（平成１３年度）

日本原子力研究所東海研究所研究炉部
（編）研究炉利用課

（2003年5月12日受理）

平成13年度、研究炉においてはJRR-3の7サイクルとJRR-4の41サイクルの共同利用運転が行われ、中性子散乱実験や放射化分析のための照射等様々な目的に利用された。本報告書は、実験あるいは照射利用を行った利用者（原研外を含む）から成果の提出を受け、これを分野別に取りまとめたものである。
Activity Report on the Utilization of Research Reactors
(Japanese Fiscal Year, 2001)

(Ed.) Research Reactor Utilization Division

Department of Research Reactor
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken

(Received May 12, 2003)

This is the fourth issue of the activity report on the utilization of research reactors in the fields of neutron beam experiments, neutron activation analysis, radioisotope production, etc., performed during Japanese Fiscal Year 2001 (April 1, 2001 - March 31, 2002).

All reports in this volume were described by users in JAERI and also users in the other organizations, i.e., universities, national research institutes and private companies, who had utilized our research reactor utilization facilities for the purpose of the above studies.

Keywords: JRR-3, JRR-4, Research Reactor, Neutron Scattering, Neutron Radiography, Neutron Activation Analysis, Neutron Beam, Irradiation
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はじめに

平成13年度には、JRR-3において7サイクルの共同利用運転、JRR-4において41サイクルの共同利用運転が行なわれ、これに伴いさまざまな利用が行われた。

本報告書は、利用者（原研外利用者を含む）から当該利用の成果の提出を受け、取りまとめたものである。

提出して頂いた成果の件数は、中性子散乱211件、中性子ラジオグラフィ8件、放射化分析16件、R1の製造1件、原子炉材料2件、即発ガンマー線2件、その他12件で合計252件であった。なお、本報告書では下記の報告書の中から一部を転載させて頂いた。

最後に、原稿を提出して頂いた利用者の皆様のご協力に感謝するとともに、今後も研究炉が有効に利用され、種々の研究がさらに進展されることを期待します。

研究炉利用課長
佐川 尚司

1) レポート番号：Vol.9（第9巻）
標 題 : ACTIVITY REPORT ON NEUTRON SCATTERING RESEARCH issued by ISSP-NSL, University of Tokyo
（東京大学物性研究所発行）
編 者 : Y.Oohara and M.Shibayama（藤井保彦，中島健次，大原泰明，）
発行年 : 2002年

2) レポート番号：UTRCN-G-31
標 題 : 原研施設利用共同研究成果報告書（平成13年度）
編 者 : 東京大学原子力研究総合センター
発行年 : 2003年
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1. Neutron Scattering  1) Structure · Excitation
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HYDROTHERMAL SYNTHESIS OF IRON PHOSPHATE CATHODE MATERIALS

1-1-1

Shigehisa Tajimi, Hirokazu Okawa, Kazuyoshi Uematsu, Kenji Toda and Mineo Sato

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ABSTRACT

Well crystalline Li3Fe2(PO4)3 with an orthorhombic Fe2(SO4)3-type structure was able to be synthesized by using two synthetic routes where hydrothermal reaction and successive heat treatment with low temperatures were employed. The sample prepared was found to show orthorhombic symmetry, contrary to the fact that a conventional solid state syntheses with high temperatures more than 1000°C gives monoclinic symmetry [1]. The sample showed two plateau potentials, 2.8 and 2.7 V vs. Li/Li+, upon discharge, and the total discharge capacity of the sample exhibited more than 80 mAhg⁻¹ under 0.5 mAcmin⁻².

INTRODUCTION

Intensive research is recently focused on LiCoO₂, LiNiO₂ and LiMn2O₄ as currently practical materials for a positive electrode material in rechargeable lithium batteries. Natural resources and environment considerations as well as material efficiency and performance are also very important for developing cathode materials. This makes us prompt a research on alternative cathode systems of iron compounds, which are quite attractive in viewpoint of natural abundance and environment issue.

Li₃Fe₂(PO₄)₃ has been reported to exhibit relatively high potentials, 2.7-2.8 V vs. Li/Li+, and good performance for a rechargeable lithium battery [2]. Usually, high temperatures are required in order to obtain well crystalline Li₃Fe₂(PO₄)₃ samples. We report here a new synthetic method for Li₃Fe₂(PO₄)₃ by using hydrothermal reaction and successive low temperature heat treatment.

EXPERIMENTAL

The starting materials for the hydrothermal reaction were LiOH, FeO(OH) and H₃PO₄. A mixture of these compounds in a molar ratio of 2:1:2 was placed in a Teflon vessel which was filled to a degree of 15% with water and enclosed in a stainless steel bomb. The mixture was heated at 220°C under autogenous pressure for 24h. The product was filtrated and dried in air, and then heated in an alumina crucible at various temperatures of 450-700°C for 24h in air. The crystal structure of sample was refined by the Rietveld method by neutron diffraction. Powder neutron diffraction pattern for the refinement was recorded using the PKD (HERMES) diffractometer installed at JRR-3M Guide Hall in the Japan Atomic Energy Research Institute (JAERI). An incident neutron wavelength \( \lambda = 1.8196 \text{Å} \) was obtained from a Ge(311) monochromator. The powder sample was enclosed in the cylindrical vanadium vessel and mounted on a double-axis diffractometer. The data were collected on thoroughly ground powders by a multi-scanning mode in the 2θ range from 5° to 155° with a step width of 0.05° and a monitoring time of 16 min. The powder patterns obtained were analyzed using the RIETAN2000 profile refinement program [3].

RESULTS AND DISCUSSION

After the hydrothermal reaction, the main crystalline product was identified to be LiFe(PO₄)(OH) by powder X-ray diffraction. The product also contained a small amount of some unidentified crystalline materials. In the next heat treatment, Li₃Fe₂(PO₄)₃ began to crystallize from 450°C, and a single phase of Li₃Fe₂(PO₄)₃ could be obtained over 525°C. Rietveld analysis for the neutron diffraction pattern was carried out on the data sets measured at room temperature for the sample fired at 700°C (Fig. 1). The fitting pattern shows well crystalline Li₃Fe₂(PO₄)₃ prepared by a two-step route of a hydrothermal reaction and a solid state reaction. DTA analysis showed no phase transition for the sample prepared by this method. In general, materials with the Fe₂(SO₄)₃-type structure such as Li₃Sc₂(PO₄)₃, Li₃In₂(PO₄)₃ and Li₃V₂(PO₄)₃ usually
have three kinds of structural modifications, monoclinic low-temperature form, monoclinic middle-temperature form and orthorhombic high-temperature form, where all transitions are reversible. In fact, the sample prepared by a conventional solid-state reaction at 1100°C showed two reversible transition points at 240 and 260°C. From these facts, the sample prepared by the new method may be a high-temperature modification with orthorhombic symmetry [4].

Figure shows the discharge/charge curves obtained at 0.5 mAhg⁻¹ for the sample heat-treated at 525°C. The insertion of lithium into the material actually occurs in two separate intercalation plateaus, at 2.8 and 2.7 V. The similar behavior are found for Li₃V₂(PO₄)₃ in our previous study. The Fe₄(SO₄)₄-type structure has three kinds of sites for lithium atoms. In the orthorhombic high-temperature, one site is fully occupied and the other two sites are partially occupied with 1/4 occupancy. Probably, the existence of such partially occupied sites, which inserted lithium ions can occupy, is responsible for the two separate potential plateaus. The sample showed a good cycle performance, about 85% capacity efficiency after 10 cycles (Fig. 2). Contrary to this, the sample prepared by the solid-state reaction exhibited a quite poor cycle performance, only 30% capacity efficiency after 3 cycles. The good cycle performance of the sample prepared by the new method could be attributed to high surface area given by the low temperature synthesis.

REFERENCES

Figure 2. Charge and Discharge curves of Li₃Fe₄(PO₄)₃

![Figure 2. Charge and Discharge curves of Li₃Fe₄(PO₄)₃](image1)

Figure 1. Neutron diffraction pattern fitting of Rietveld refinement for Li₃Fe₄(PO₄)₃ prepared by hydrothermal and solid state reactions

![Figure 1. Neutron diffraction pattern fitting of Rietveld refinement for Li₃Fe₄(PO₄)₃](image2)

Reliable factors:
Rwp= 5.18%, Rp= 4.09%, RR= 8.26%, Re= 5.29%, S=0.9802
RI=1.01%, RF= 0.47%
1.1.2

High-temperature neutron powder diffraction study of structural change in tricalcium phosphate

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Apatites and calcium phosphates are increasingly used as biocompatible materials for bone replacement and for the coating of bone prostheses. According to the literature, $\beta$-Ca$_5$(PO$_4$)$_2$ ($\beta$-TCP) transforms to $\alpha$-Ca$_5$(PO$_4$)$_2$ ($\alpha$-TCP) around 1125 °C [1], and $\alpha$-TCP transforms to a high-temperature phase, $\alpha^\prime$-Ca$_5$(PO$_4$)$_2$ ($\alpha^\prime$-TCP) around 1430°C [2]. The crystal structures of $\beta$- and $\alpha$-TCPs were determined, while the structure of $\alpha^\prime$-TCP has not been known yet. The purpose of this work is to study the $\alpha$-$\alpha^\prime$ phase transition of TCP, and to determine the crystal structure of $\alpha^\prime$-TCP.

High-purity $\alpha$-TCP was prepared by solid-state reactions from CaHPO$_4$ and CaCO$_3$. The neutron-diffraction measurements were performed in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in JAERI [3]. Diffraction data were collected in the $2\theta$ range from 20° to 150° in step interval of 0.1°, in the temperature range from 24°C to 1524°C. A furnace with MoSi$_2$ heater was placed on the sample table [4], and used for neutron-diffraction measurements at high temperatures. The temperature was kept constant within ±1.5°C during each data collection. The neutron-diffraction data were analyzed by Rietveld analysis using a computer program RIETAN-2000 [5].

Figure 1 shows the temperature dependence of neutron-diffraction pattern for TCP. All the neutron-diffraction peaks were indexed by $hkl$ of $\alpha$-TCP, indicating the single phase of $\alpha$ phase between 24°C and 1449°C. At 1474°C, the pattern exhibited both peaks of $\alpha$ (●) and $\alpha^\prime$ (○) phases. Therefore $\alpha$ and $\alpha^\prime$ phases coexisted at this temperature. The characteristic peaks of $\alpha$ phase (●) disappeared between 1474°C and 1499°C. The single phase of $\alpha^\prime$-TCP existed at 1499°C and 1524°C. During cooling, $\alpha^\prime$$\rightarrow$$\alpha$ phase transition was observed also between 1499°C and 1449°C. These results indicate that the $\alpha$-$\alpha^\prime$ phase transition occurred reversibly between 1449°C and 1499°C.

Fig.1 Neutron powder diffraction patterns of TCP obtained at different temperatures. Each diffraction pattern was measured keeping the sample temperature constant after heating.

Structural refinements of $\alpha$ phase were successfully done using a monoclinic structure (space group P2$_1$/a) for the neutron-diffraction data between 24°C and 1449°C. For the data obtained at 1499°C and 1524°C, structural refinements of $\alpha^\prime$ phase...
were successfully performed using a new monoclinic structure (space group $C2/c$). The data measured at 1474°C was successfully analyzed by the mixture of $\alpha$- and $\alpha'$-TCP.

Figure 2 shows the temperature dependence of unit-cell parameters (a) $a$-axis, (b) $b$-axis, (c) $c$-axis, (d) $\beta$ angle and (e) unit-cell volume $V$. The unit-cell parameters and unit-cell volume of $\alpha$ phase increased continuously with an increase of temperature between 1188°C and 1474°C. At 1474°C, the $\alpha$ and $\alpha'$ phases coexisted. The $a$-axis length and unit-cell volume $V$ of $\alpha'$ phase were larger than those of $\alpha$ phase, while the $c$-axis length and $\beta$ angle of $\alpha'$ phase were smaller than those of $\alpha$ phase. The $b$-axis length of $\alpha'$ phase was almost equal to that of $\alpha$ phase. The unit-cell parameters and unit-cell volume of $\alpha'$ phase increased between 1474°C and 1524°C. The unit-cell parameters and unit-cell volume obtained on heating exhibited fairly good agreements with those on cooling.

The $\alpha$-$\alpha'$ phase transition of TCP is of first order, because (1) the $\alpha$ and $\alpha'$ phases coexisted at 1474°C, (2) the $a$- and $c$-axis lengths, $\beta$ angle and unit-cell volume $V$ changed discontinuously at the $\alpha$-$\alpha'$ phase transition point.

![Graphs showing temperature dependence of unit-cell parameters](image)

Fig.2 Temperature dependence of unit-cell parameters (a) $a$-axis, (b) $b$-axis, (c) $c$-axis, (d) $\beta$ angle and (e) unit-cell volume $V$. Filled and open circles denote the data obtained on heating and cooling, respectively.

References
Magnetic energy of the dimerized singlet pair is lower than that of homogeneous antiferromagnetic system theoretically. Spin-Peierls (SP) transition is the magnetically induced transition from the paramagnetic state to the singlet ground state in an one-dimensional S=1/2 spin system with the lattice dimerization simultaneously. With the discovery of the first inorganic SP compound CuGeO$_3$ by Hase et al. in 1993 [1], many efforts to clarify the SP mechanism were performed theoretically and experimentally. The soft phonon mode which is expected in the standard SP transition by Cross and Fisher [2] has not been observed yet. In the case of organic SP compound MEM(TCNQ)$_2$ (T$_{SP}$=19 K), a soft phonon mode with the energy of 1.05 meV was observed by Raman scattering [3]. In the TTF-CuBDT (T$_{SP}$= 11 K) the energy of soft mode was also obtained to 1.4 meV by the analysis of X-ray diffuse scattering [4]. Then we expect to find the soft mode of CuGeO$_3$ with the energy of about 1 meV in considering the SP transition temperature of 14 K. Recently, the longitudinal optical phonon dispersion along the b-axis was determined [5], which mode behaves like the acoustic phonon branch with small energy difference. Inelastic neutron scattering experiments were performed to measure the low-lying phonon of CuGeO$_3$. ISSP-HER triple axis spectrometer was used for the experiment at C1-1 port of the guide hall at JRR-3M of JAERI in Tokai. The experimental condition with the horizontal and vertical focusing analyzer was used. The temperature dependence of the phonon spectrum at (0, 3, 0) was measured below 250 K. The full width at half maximum (FWHM) (-0.2 meV) and the central energy (-1 meV) of the phonon peak does not depend the temperature. Usually the temperature dependence of phonon intensity is described by the Bose factor, and the intensity decrease from 300 K to 175 K is consistent to the formula. However, below 150 K the integral intensity of phonon spectrum decreases significantly in discrepancy from the Bose factor curve as shown in Fig. 1. From the mode analysis the anomalous decrease of phonon intensity is speculated to stem from the structural fluctuation with lattice dimerization along the c-axis. The SP transition of CuGeO$_3$ is not displacive type which shows the soft phonon behavior but order-disorder.

References
Structural Change of B,C at High Temperatures

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Boron carbide B,C is an important high-temperature material with excellent mechanical properties. But, the structural change at high temperatures has not been known yet. Furthermore, there is an inconsistency in the temperature dependence of unit-cell parameters in the literature. Here we report the results of high-temperature neutron-diffraction measurements of B,C.

Neutron-diffraction measurements at high temperatures from 23 to 993°C were performed using the Kiken neutron diffractometer HERMES (T1-3) of JRR-3M research reactor of Japan Atomic Energy Research Institute, using a high-temperature furnace (λ=1.8196Å). We used an isotope-substituted boron carbide specimen with the composition of B_{0.807}C_{0.193} (99.68 % ¹¹B in boron), to prevent from the absorption by the ¹⁰B. Neutron-diffraction data were analyzed using a Rietveld program RIETAN.

We have successfully refined the unit-cell and structural parameters by the Rieweld analysis, assuming the B_{12+}(C1-B3-C1 chain) model with the space group of R₃m (Fig. 1). The reliability factors were R_w=9.22% and R=2.12% for the neutron-diffraction data analysis for the data measured at 23°C, and R_w=8.83% and R=2.91% at 993°C. The unit-cell parameters were a=5.6262(1) and c=12.1337(2)Å, and atomic coordinates were

- x(B1)=−x(B1)=0.1627(2),  z(B1)=0.5386(1),
- x(B2) =−x(B2)=−0.1074(2), z(B2)=0.1142(2),
- x(C1)=y(C1)=0.0 and z(C1)=0.3816(3), x(B3) =y(B3)=0.0 and z(B3)=0.5 at 993°C.

All the thermal parameters increased with an increase of temperature. The thermal parameters of B3 atoms were higher than those of others (Fig. 2). This would be ascribed to the void around the B3 site (Fig. 1). Probably due to the C1-B3-C1 chain structure, B3 has higher thermal parameter values. The U₁₁(B3) was higher than the U₁₁(B3) probably because the void exists in the x direction from the B3 site (Fig. 1).

Fig. 1 Crystal structure of boron carbide drawn based on the refined crystal parameters.

Fig. 2 Temperature dependence of anisotropic thermal parameters of boron carbide.

使用施設: JRR-3M, 装置: (KSD, HERMES), 分野: Structures & Excitations
In Situ Study of Structural Change of YTaO₄ at High Temperatures

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Stable phase of yttrium orthotantalate YTaO₄ at room temperature might be the monoclinic (M') form with a fergusonite structure that could be a fluorite-related structure. There are three polymorphisms for YTaO₄; two monoclinic forms of M'- and M-YTaO₄ and one tetragonal T-YTaO₄. However, the structural change of this material has not been known in detail yet. Here we report in situ neutron-powder-diffraction study of structural change and of YTaO₄ at high temperatures up to 1500°C.

Neutron-diffraction measurements were done using the Kinen neutron diffractometers HERMES (T1-3) and KSD (T1-2) of JRR-3M research reactor of Japan Atomic Energy Research Institute, using a high-temperature furnace (λ=1.8196 Å for HERMES and λ=1.53 Å for KSD). M single phase of the YTaO₄ was prepared by solid-state reactions. Each neutron-diffraction measurement was done keeping the sample temperature constant. The average heating and cooling rate including the measurements was 3.3°C/min and 0.19°C/min for HERMES and KSD measurements, respectively. Neutron-diffraction data were analyzed using a Rietveld program RIETAN.

Figure 1 shows temperature dependence of β angle refined through the Rietveld analyses where the average heating rate for the neutron-diffraction measurements was about 0.19°C/min. The β angle of M phase decreased with an increase of temperature up to 1200°C. The metastable M form transformed to more stable M' phase between 1200°C and 1300°C, leading to a discontinuous change in β angle. The stable M' phase changed into the high-temperature T form between 1500°C and 1550°C during heating. The discontinuous change in the β angle indicates that the M-to-M' and M'-to-T transformations are reconstructive.

In case of the higher heating rate we have succeeded in the observation of the reversible M-T transformation. As shown in Fig. 2, the β angle of M phase decreased with an increase of temperature up to 1400°C and became 90 deg., indicating the M-to-T phase transformation. The continuous behavior strongly suggests that the M-T transformation has a 2nd-order nature. In fact, the critical exponent was estimated to be about 0.5 when we apply the Landau’s theory.

Fig.1: Temperature dependence of β angle. Heating rate was about 0.19 K/min.

Fig.2: Temperature dependence of β angle. Heating rate was about 3.3 K/min.
Structures and Phase Transitions in Rb₂MoO₄ and Rb₂WO₄

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Many of the A₂BO₄-type ferroelectrics, for example, A₂CrO₄, A₂SO₄, Rb₂SeO₄, Cs₂SeO₄, Rb₂MoO₄ and Cs₂MoO₄ (A = K, Rb and Cs), undergo the same succession of phase transition: these transform from the parent high-symmetry phase (phase I, space group P6₃/mmc) to the orthorhombic phase (phase II, Pmcn) at high temperatures (T ~ 600 – 800 K) and retain the orthorhombic structure down to 2 K. On the other hand, in Rb₂WO₄, K₂WO₄ and K₂MoO₄, there is another intermediate incommensurate phase between phases I and II. In K₂SeO₄, as temperature decreases the crystal transforms from phase I to phase II and to a incommensurate phase (phase III), which is followed by a ferroelectric phase (phase IV). Among the A₂BO₄-type ferroelectrics, the low-temperature incommensurate phase was observed only in K₂SeO₄. However, we found new transition points at 200, 691 and 784 K in Rb₂MoO₄ with a differential scanning calorimeter and there were expected as a displacive-type normal-incommensurate phase transition such as K₂SeO₄ and as a high-temperature incommensurate one. In Rb₂WO₄, crystal structures still remains unclear.

In order to clarify the structures in Rb₂MoO₄ and Rb₂WO₄, we performed neutron powder diffraction experiments using the Kippen powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research (IMR), Tohoku University, installed at JRR-3M of JASRI.

Figure 1 shows neutron powder diffraction patterns for Rb₂MoO₄ at 20 and 290 K. The pattern was obtained at 290 K in the normal phase (space group Pmcn). The lattice parameters are a = 8.0955(7), b = 6.3758(6) and c = 11.1031(9) Å. The superlattice reflections were observed below 200 K and the structure is incommensurate with the wave vector q ~ c₀/3. However, we could not check for the presence of high-temperature incommensurate phase between phases I and II.

On the other hand, the crystal structure at 290 K of Rb₂WO₄ is not orthorhombic but monoclinic one (space group C2/m). And Rb₂WO₄ retains this structure down to 8 K.

![Neutron powder diffraction patterns of Rb₂MoO₄ at 20 and 290 K.](image)

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Phonon Dispersions of the Normal Phase in Rb₂CoCl₄

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Rubidium tetrachlorocobaltate, Rb₂CoCl₄, belongs to a family of A₂BX₄ type with the β-K₂SO₄ type structure such as Rb₂ZnCl₄. Three phase transitions are observed at temperatures T₁ = 294 K, T₂ = 194 K and T₃ = 66 K.

Samara pointed out an empirical law between the pressure coefficient dT/dp of the transition temperature and the mechanisms of the ferroelectric phase transition: a displacive type transition temperature has a positive coefficient with soft zone-boundary optic phonons, while an order-disorder type transition temperature has a negative coefficient. In Rb₂ZnBr₄, Rb₂ZnCl₄ and K₂ZnCl₄, the coefficients are positive, and soft modes have not been observed in the normal phase (above T₁). On the other hand, although the absolute value of the pressure coefficient is small in Rb₂CoCl₄, the coefficient is negative. Therefore, we expected that the underdamped soft modes will be observable in the normal and low-temperature phases.

In the previous report, we reported the observation of soft mode in the low-temperature phases by neutron scattering [1]. The existence of the mode is indeed quite certain. As the second step, in order to clarify the behavior of the mode in the normal phase, we performed inelastic neutron scattering experiments by using the triple-axis spectrometers (4G and C1-1) at JRR-3M of JASRI. Single crystals were grown from melt by the Bridgman method. Energy scans were done with the fixed incident neutron momentum k₁ = 2.57 Å at 4G and k₁ = 1.55 Å at C1-1. The data collections were carried out in the (a*, c*) scattering planes.

Figure 1 shows the phonon dispersion curves along the (0 0 ξ) direction in the normal phase.

![Fig. 1 phonon dispersion curves along the (0 0 ξ) direction in the normal phase.](image)

Although the behavior of the phonon dispersion was clearly observed, no softening of the branch was observed around ξ = 2/3. Furthermore, the anticrossing of the acoustic branch with an optic one was not observed. Although the pressure coefficient dT/dp in Rb₂CoCl₄ is negative, the order-disorder nature remained remarkably because the absolute value of the coefficient is small.

We arrived at the new conclusion that the transition mechanism is related to the ratio between the ionic radius of A⁺ and the average bond length B-X in the tetrahedral BX₄²⁻ ion, and the lattice distortive parameters.

References
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使用施設：JRR-3M，装置：GPTAS(4G) and HER(C1-1)，分野：1. Structures & Excitations
1-1-8 Crystal Structure in the Martensitic Phase of Ni$_{2.18}$Mn$_{0.82}$Ga Alloy

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We have made the powder neutron diffraction of an off-stoichiometric Heusler-type Ni$_{2.18}$Mn$_{0.82}$Ga alloy. It has a thermo-elastic martensitic transformation temperature of about 340K, coincident with the Curie temperature. A single crystal of this alloy shows a shape memory effect at 339 K. [1]

The diffractometer, HERMES, installed on T1-3 port of JRR-3M reactor was used. The wave length was 1.8196 Å. The measurements were made with increasing and decreasing temperature. We re-analyzed the crystal structure in the martensitic phase, using the computer program, RIETAN-2000. [2]

The results of the Rietveld analysis at 405K, at 324K and at 279K are shown in Figs. 1 (a) to (c). They were measured with decreasing temperature. We found that two structures coexist in the martensitic phase. One is an orthorhombic structure distorted from the cubic Heusler structure, and the other is a tetragonal one made from the shuffling of the 220 plane of the orthorhombic structure. This tetragonal structure coincides with the monoclinic one with 6 layers shuffling in the [110] direction of the orthorhombic structure, which we suggested formerly. [1,3]

The mutual relation of the cubic Heusler structure, the orthorhombic one and the tetragonal one is shown in Fig. 2. We see that the lattice constant, a(orth.), of the orthorhombic structure is slightly longer than a(cubic) of the cubic structure. The lattice constant, b(ortho.), is equal to a(cubic), and c(ortho.) is slightly shorter than a(cubic). We also see that the lattice constants, a(tetra.) and b(tetra.), of the tetragonal structure are equal to c(ortho.) of the orthorhombic structure. The value of c(tetra.) is longer than that of a(ortho.). The volumes of unit cell for these three structures are the same. The lattice spacing along [111] of each structure is also the same. In Fig. 2, we also see that the (220) plane of the orthorhombic structure is the same as the (202) plane of the tetragonal structure. These many common lattice spacing and planes will be the background of easy marten-

Fig. 1. Results of Rietveld analysis, (a) at 405 K, (b) at 324 K and (c) at 279 K.

使用施設：JRR-3M，装置：HERMES(T1-3)，分野：1.Structures & Excitations
b(ortho.) = b(cub.), a(tetra.) = b(tetra.) = c(ortho.)

d(c(111)) = d(o(111)) = d(t(111))

vol.(cub.) = vol.(ortho.) = vol.(tetra.)

---- cubic (mother)

--- orthorhombic (marten.)

--- tetragonal (marten.)

--- shuffling (mono.)

Fig. 2. Relation of three structures, the cubic structure, the orthorhombic structure and the tetragonal structure.

Fig. 4. Temperature dependence of each lattice constant with increasing temperature.

sitic transformation and of coexistence of three different structures. The temperature dependence of the mass fraction of each structure determined with increasing temperature and with decreasing temperature are shown in Figs. 3 (a) and (b). We see that there is a small hysteresis of the martensitic transformation temperature. We also see that the mass fraction of tetragonal structure in the martensitic phase is much larger than that of orthorhombic structure. This fact indicates that the tetragonal structure is more stable than the orthorhombic structure.

The temperature dependence of lattice constants of each structure measured with increasing temperature is shown in Fig. 4. We see the mutual relations of lattice constants, which we described above.

References
1-1-9 Structure Analysis of MeHPLN in Low Temperature Phase

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\textsuperscript{1}IMRAM, Tohoku University.
\textsuperscript{2}Graduate School of Science and Technology, Faculty of Science, Chiba University.
\textsuperscript{3}Department of Chemistry, Faculty of Science, Toho University.
\textsuperscript{4}Department of Basic Science, Graduate School of Arts and Science, The University of Tokyo

5-R-9-hydroxyphenalenon (R=I, Br, Methyl) is one of the ferroelectric groups containing hydrogen-bonds. These compounds are unique because they are classified in an isolated hydrogen-bond system that has only intramolecular hydrogen-bonds. Preliminary structure analysis of 5-Methyl-9-hydroxyphenalenon (MeHPLN) by X-ray and neutron at room temperature reveals that there is a local electrical dipole moment in the hydrogren-bond region.

X-ray structure analysis of MeHPLN in low temperature phase has already been carried out and the electron distribution in low temperature phase has been obtained. In order to compare this electron distribution and reveal the phase transition scheme of MeHPLN, structure analysis of MeHPLN by neutron diffraction in the low temperature phase was carried out.

Experiments were performed at JRR-3M in JAERI, utilizing the four circle diffractometer FONDER installed at T2-2 beam port. Neutron beam of which wave length is 1.5696 Å monochromized by Si monochrometer was used. The total number of collected Bragg reflections at 10K were 1536, including 681 superlattice reflections. After absorption correction, the parameters of positions, thermal factors and so on were determined by means of a least square method. The final reliable factor was $R=3.96\%$. Secondly the nuclear density was calculated by means of Maximum Entropy Method (MEM) and the final reliable factor was $R=4.06\%$.

Taking note of the hydrogen atom in the hydrogen-bond region, it is revealed that there are two types of distributions of electrons and nuclei (Fig.1). One of the independent molecule clearly shows ordering of the electron and nuclear distribution, whereas the hydrogen atom in the other molecule has almost the same electron and nuclear distribution as at room temperature. There is obvious discrepancy between electron and nuclear distribution in the ordered hydrogen atom (not shown here), indicating the static dipoloments with antiferroelectric order in the low temperature phase.

![Fig. 1. The nuclear distribution of the disordered hydrogen atom (upper) and ordered one (lower) in Hydrogen-Bond region](image)

使用施設：JRR-3M, 装置：FONDER(T2-2), 分野：1. Structures
Introduction

Ammonium-d4 hexachloroplatinate undergoes an order-disorder phase transition at 27 K whereas the un-deuterated crystal is cubic down to the lowest temperature examined (4K). The transition entropy of the deuterated crystal is larger than \( R (= 8.3145 \text{ J/K mol}) \). This suggests an interesting possibility that each of the protons and deuterons belonging to the ammonium ions are distributed over a set of positions dictated by the cubic symmetry. Multiple positions for a deuterium atom are a consequence of orientational disorder. For the hydrogenous ammonium compounds, the crystal symmetry is cubic even at the lowest temperature. Therefore, a multi-maximum proton distribution, if actually found, should be a characteristic of the ground state of the crystal. The low temperature heat capacity shows that the rotational motion of the ammonium ion is essentially in the ground state at 7 K (where the neutron experiment was performed) both for the hydrogenous and deuterated crystals. We have performed a low temperature neutron diffraction on ammonium hexachloroplatinate single crystals, using the diffractometer FONDER at JRR-3M.

Experiment

The sample \((\text{NH}_4)_2\text{PtCl}_6\) was prepared from ammonium chloride and hexachloroplatinate acid dissolved in water by slow evaporation of the solvent. Single crystals of an appropriate size (ca. 3.5mm) was chosen and fixed to the cold finger of a closed-cycle refrigerator mounted on the diffractometer. Diffraction data were collected at \( T = 7 \) and 35 K. The neutron wavelength was 1.5696 Å in the experiment at 7 K and 1.5683 Å at 35 K. In total 70 and 69 \((hkl)\) independent peak intensities were determined at \( T = 7 \) and 35 K, respectively. Because of the high symmetry of the crystal, several equivalent Bragg peaks occurred within the available ranges \((2\theta = 150 \text{ deg.})\) of the diffraction angle for many of the indices. The number of the peak intensities determined was ca. 400 before averaging the equivalent ones.

Result

All the peaks observed were consistent with the \( Fm\bar{3}m \) symmetry. The cubic lattice constant was 9.7466 Å and 9.7472 Å at 7 and 35 K, respectively. The lattice constant from high-resolution neutron powder diffraction is 9.7429 Å at 6 K in good agreement with the present values.

First the diffraction data were analyzed using the least squares program RADIUS. The least squares calculation converged smoothly, resulting in the following structural parameters.

\[
T = 7 \text{ K} \quad \text{RADIUS} \quad R_{\text{factor}} = 4.51\% \quad \text{Rw} = 4.93\% \quad \text{Scale} = 20.48(34), \text{Number of Reflections} 70
\]

\[
x \quad y \quad z
\]

\[
N \ 1/4 \quad 1/4 \quad 1/4
\]

\[
H \ 0.3175(34) \quad 0.3175(34) \quad 0.2870(35)
\]

\[
Pt \ 0 \quad 0 \quad 0
\]

\[
Cl \ 0.2390(2) \quad 0 \quad 0
\]
$U_{ij} \times 10^3$

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N-H distance 0.99(4) Å
Pt-Cl distance 2.329(4) Å

$T=35$ K RADIEL R-factor=4.32% Rw=4.79%, Scale=20.56(38). Number of Reflections 69

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$U_{ij} \times 10^3$

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N-H distance 1.00(5) Å
Pt-Cl distance 2.332(5) Å

**MEM Calculation**

Next we transformed the intensity data to the scatterer density in the unit cell by the Maximum Entropy Method (MEM). We divided the unit cell into 256x256x256 pixels and optimized the scatterer distribution in each pixel using the maximum of the information entropy compatible with the intensity data as the criterion for the most likely distribution. The negative scattering length of protons was taken into account by calculating their contribution separately from the scattering by other atoms. The results of the MEM calculation are shown in Fig. 1 and Fig. 2. Fig. 1 presents an ammonium ion with the nitrogen atom at the center and four hydrogen atoms surrounding it tetrahedrally. Interestingly, each of the four hydrogen atoms is distributed on a torus about 0.7 Å in diameter. The torus is very close uniform. As shown in Fig. 2, The representation could be a disk perpendicular to the three-fold axis. It could also be discreet three elongated maxima, depending on the threshold value used in the preparation of the image. This is in clear contrast to the delta function like distribution of the N, Cl and Pt. nuclei.

![Fig. 1 3D-map of nuclear density for N and H atoms obtained by MEM at 7K.](image1)

![Fig. 2 Contour map of Nuclear density for H atoms projected along $<111>$ axis at 7K.](image2)
Physon measurement on the antiferroquadrupolar Order compound Ho$^{11}$B$_2$C$_2$

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RB$_2$C$_2$ (R=rare earth) compounds, which have the tetragonal LaB$_2$C$_2$-type crystal structure, have been attracting many interests, because some of them shows strong antiferroquadrupolar (AFQ) interaction. DyB$_2$C$_2$ shows both of an AFQ ordering and an antiferromagnetic (AFM) ordering. The AFQ ordering temperature and the Néel temperature are $T_Q = 24.7$ K and $T_N = 15.3$ K, respectively, which is almost 10 times as high as those of the other system reported so far [1]. HoB$_2$C$_2$ also shows both of an AFQ ordering and an AFM ordering, but it is observed that an AFM transition occurs at $T_N = 5.9$ K and an AFQ ordering transition at $T_Q = 4.5$ K [2, 3]. $T_Q$ is lower than $T_N$ in HoB$_2$C$_2$, which is unusual for quadrupolar ordering compounds. TbB$_2$C$_2$ shows an AFM transition at $T_N = 21.7$ K but no AFQ transition at zero field. However it is confirmed by neutron diffraction that an AFQ ordered phase is induced by magnetic fields. These system which have both of an AFQ ordering and an AFM ordering shows complicated magnetic behavior.

In order to clarify the dynamical properties of RB$_2$C$_2$, we performed inelastic neutron scattering measurements on the single crystal Ho$^{11}$B$_2$C$_2$. Here B was replaced with enriched $^{11}$B isotope, because natural B is a strong neutron absorber. The measurements were made at room temperature by using TOPAN (6G) spectrometer installed at JRR-3M, JAERI. From the measurements, we investigated the phonon dispersion relations of Ho$^{11}$B$_2$C$_2$. Fig. 1 shows the phonon dispersion curves of Ho$^{11}$B$_2$C$_2$ at room temperature for the [0 0 k] direction. We obtained the dispersion relations for both LA and TA modes, and a possible TO mode. The phonon dispersions for the [h 0 0] direction were also examined, and the dispersion curves for transverse phonons were obtained. However, the sig-

Fig. 1. The phonon dispersion curves of Ho$^{11}$B$_2$C$_2$ at room temperature.

References
1-1-12
Crystalline-State Photoisomerization of α, β- Unsaturated Thioamide
Analysed by X-Ray and Neutron Diffractions

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The absolute asymmetric synthesis in the solid state has been extensively studied, in which the chiral product is produced from the achiral reactant in a chiral crystal environment. Among them, \(N,N\)-dibenzyl-1-cyclohexene-carbothioamide, 1, was photoisomerized to optically active β-thiolactam, 1-benzyl-4-phenyl-2-thioxoazetidine-2-thione-3-spirocyclohexane, 2, as shown in Scheme 1.

![Scheme 1](image)

When a crystal of 1 was exposed to UV light at 263 K, the cell dimensions were gradually changed with retention of the single crystal form. Since the crystal gradually decomposed after 330 h, the irradiation was stopped and the structure was analyzed by X-rays. The thioamide, 1, was converted by 65.0% to the thiolactam, 2. The thioamide and thiolactam molecules were observed as a disordered structure in the crystal as shown in Fig. 1. The disordered structure clearly indicates that the hydrogen atom of one of the benzyl groups is extracted by one of the olefin carbon atoms of the cyclohexenyl group and that the benzyl carbon atom makes a bond with another olefin carbon to form a thiolactam ring. The mechanism of the ring formation and the chirality of the produced thiolactam are well explained from the reaction cavity.

An important question still remains; which hydrogen atom is extracted by C3 when the crystal was exposed to UV light. Since the C-C bond is made between C2 and C8, H8A or H8B should be extracted by C2 within a molecule or in the neighboring molecules. The intramolecular H8A atom is probably extracted by C3, since the interatomic distance is the shortest. This indicates that the extracted H and original H3 atoms, H3A' and H3B', should occupy the positions upside and downside the cyclohexane ring. Recently a new compound with deuterium atoms at the positions of H8A and H8B were prepared. Large crystals suitable for neutron analysis were obtained. The crystal structures before and after photoirradation were analyzed by neutron diffraction with FONDER. The structure after irradiation gave a definitive answer to the question, that is, the intramolecular hydrogen is transferred in the process of the four-membered ring formation.

![Fig. 1](image)

使用施設：JRR-3M、装置：FONDER(T2-2)、分野：1. Structures & Excitations
1-1-13

The ordering of the $e_g$ electrons and $e_g$ orbitals of manganese ions play essential roles in determining the physical properties in the hole-doped perovskite manganites. The charge ordering and orbital ordering are strongly coupled to or compete with the ferromagnetic (FM) metallic interactions mediated by the double exchange mechanism. As a result, the manganites exhibit a great variety of the charge/orbital ordered states depending on the hole concentration and the one-electron band width.

One of the important aspects of the charge/orbital ordering is the introduction of the low dimensionality in the physical properties through the strong anisotropy of the $e_g$ orbitals. It would be interesting to examine whether the dimensionality of the crystal structure influences the character of the charge/orbital ordering. Previous studies on the charge and orbital ordering, however, are performed mainly against the cubic or bi-layered manganites.

Accordingly, we studied the charge and orbital ordering in single-layered manganites Nd$_{1-x}$Sr$_{1+x}$MnO$_4$ with $x = 0.75$ and 0.78, which have the lowest dimensionality of crystal structure among perovskite-derived manganites, using a neutron diffraction technique. The samples are single crystals grown by the floating zone method. The neutron diffraction measurements were performed using a triple-axis spectrometer GPTAS with $k_i = 2.57\,\text{Å}^{-1}$ and $3.81\,\text{Å}^{-1}$.

The $x = 0.75$ sample has a tetragonal $I4/mmm$ structure through all temperature range measured. With decreasing temperature, superlattice peaks due to lattice modulations appear below $T_{\text{CD}} \sim 270\,\text{K}$ where the in-plane resistivity $\rho_{ab}$ exhibits a steep rise [1]. Figures 1(a) and 1(b) show profiles of the superlattice reflections measured along the [110] and [110] directions at $T = 10\,\text{K}$. Superlattice reflections appear at $Q = (h, k, 0) \pm (\frac{1}{4}, \frac{1}{4}, 0)$ with $h + k = \text{even}$. The $Q$ dependence of the intensities indicates that the related lattice modulations consist chiefly of a transverse component. These nuclear superlattice reflections can be interpreted as arising from the stripe charge/orbital order within the MnO$_2$ planes as presented in Fig. 3(a). This charge/orbital order consist of $d(3x^2 - r^2)$ and $d(3y^2 - r^2)$ orbitals, and resembles that observed in a highly doped region in cubic manganites like La$_{1/3}$Ca$_{2/3}$MnO$_3$ [2]. The charge/orbital order also produces magnetic superlattice peaks. Figure 1(c) shows a profile of the magnetic peaks along the [110] directions. Strong magnetic peaks are observed at $Q = (h/2, k, 0)$ and $(h, k/2, 0)$ with $h, k = \text{integer}$, while weak magnetic peaks appear at $Q = (h/2, k, 0) \pm (\frac{1}{4}, \frac{1}{4}, 0)$ and $(h, k/2, 0) \pm (\frac{1}{4}, \frac{1}{4}, 0)$. These magnetic peaks are consistent with a spin structure shown in Fig. 3(a), where zig-zag FM chains run along the $d(3x^2 - r^2)/d(3y^2 - r^2)$ or-
Fig. 2. Profiles of the magnetic Bragg reflections in the $x = 0.78$ sample along the [001] direction for (a) $k = 0.5$, (b) $k = 1.5$ and (c) $k = 2.5$ at 10 K.

orbitals, though there is still an ambiguity in the spin directions.

The $x = 0.78$ sample has a tetragonal $I4/mmm$ structure at room temperature, while it shows a transition to an orthorhombic $Immm$ structure with $a > b$ below $T_N = 150$ K. We observed antiferromagnetic (AFM) Bragg reflections below this transition temperature (Fig. 1). The magnetic peaks appear at $(h, k/2, l/2)$ with $k,l = \text{integer}$. The magnetic structure that satisfies the observed peak positions is so-called C-type AFM structure. It contains FM chains within the MnO$_2$ planes as depicted in Fig. 3(b) [3].

The C-type AFM structure has been observed in cubic and bi-layered manganites in similar doping region [4, 5], and it has been proposed that this AFM structure is induced by a one-dimensional ordering of the $d(3z^2 - r^2)$ orbitals. In the present single-layered crystal, the FM chains of the C-type AFM structure are parallel to the $a$-axis, which is longer than the $b$-axis. This relation between the magnetic and the crystal structure implies that the C-type AFM structure in the $x = 0.78$ sample has its origin in an ordering of the $d(3z^2 - r^2)$ orbitals extending along the $a$-axis (Fig. 3(b)). The orbital and magnetic order also affects the transport properties. $\rho_{ab}$ shows a sudden drop below $T_N$ [1]. This anomaly in the resistivity can be interpreted as that the electron transfer is enhanced within the FM chains due to the double exchange interactions.

The present results indicate that the type of charge/orbital order in single-layered manganites shows an interesting switching within the MnO$_2$ layers around $x = 3/4$: a stripe-type charge/orbital order for $x \leq 3/4$ and a rod-type orbital order for $x > 3/4$. Because same types of orbital orders are observed in cubic and bi-layered manganites in similar doped regions, the orbital order is not much affected by the dimensionality of crystal structure, but strongly depends on the hole concentration.

References
1-1-14

研究テーマ：Pr$_{1-x}$Sr$_x$MnO$_3$ の A 型反強磁性相における電荷秩序
表題：Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ におけるストライプ的電荷秩序

Stripe-type charge ordering in the A-type antiferromagnet Pr$_{0.5}$Sr$_{0.5}$MnO$_3$

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A drastic increase of the conductivity accompanied by a ferromagnetic (FM) transition, or a colossal magnetoresistance (CMR) effect, in perovskite manganites has attracted enormous interests. Recent studies have revealed that the checkerboard-type (CE-type) charge ordering which appears at $x \sim 1/2$ is essential to this dramatic change of the transport property. The CE-type charge ordering is stabilized in systems with a narrow one-electron band width $W$ such as Pr$_{1-x}$Ca$_x$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$. On the other hand, the CMR phenomenon is not limited to the narrow $W$ manganites, and is indeed observed in systems with wider $W$ such as Pr$_{1-x}$Sr$_x$MnO$_3$, Nd$_{1-x}$Sr$_x$MnO$_3$, and La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ with $x \sim 0.5$. An important characteristics of these compounds is they show a highly conductive A-type antiferromagnetic (AFM) state around $x = 1/2$, where a planar ordering of the $d(x^2 - y^2)$ orbitals is established. This orbital ordering mediates the FM coupling and fairly large mobility of carriers within the orbital-ordered planes [1, 2]. The scenario for the CMR phenomenon based on the CE-type charge ordering is clearly irrelevant in this case, and another microscopic mechanism ought to be invoked.

To find what causes a drastic change in the transport property in wide $W$ manganites with the A-type AFM state, we have performed a neutron diffraction study on a single crystal of a cubic A-type antiferromagnet Pr$_{0.5}$Sr$_{0.5}$MnO$_3$. This material exhibits a first-order phase transition from a FM metal to an A-type AFM less-conductive state at $T_N \sim 140$ K (Fig. 1(c)), and it exhibits a significant MR below $T_N$ [3]. The neutron diffraction measurement was performed using the triple axis spectrometer GPTAS installed at the JRR-3M reactor in JAERI with an incident neutron momentum $k_i = 3.83$ Å$^{-1}$. The crystal has a distorted cubic structure with $a \sim 3.8$ Å, and we employ the cubic notation in indexing with the FM layers of the A-type AFM structure perpendicular to the [010] direction.

First, we surveyed the $(h, 0, l)$ scattering plane. Figure 1(a) presents a map of the scattering intensities around (002) at 7 K. Apart from an intense fundamental nuclear Bragg re-

Fig. 1. (a) Intensity maps around (0, 0, 2) at $T = 7$ K. Two ring-shaped scatterings are due to the Al sample cell. (b) Temperature dependence of the intensity at $(0, 0, 2, 3)$. The background (BG) intensity measured at $(0, 0, 2.475)$ is also shown. Open symbols and closed symbols denote the data for cooling and for heating, respectively. (c) Temperature dependence of the resistivity.

使用施設：JRR-3M，装置：GPTAS(4G)，分野：1. Structures & Excitations
reflection at (002) and A-type AFM Bragg reflections at (±0.5, 0, 2) and (0, 0, 1.6), anisotropic diffuse scatterings are clearly observed around (0, 0, 2 ± 0.3) (white arrows). The profiles are elongated towards the [100] direction, indicating the correlation length along the modulation vector $q = (0, 0, ±0.3)$ is much longer than that perpendicular to $q$. By examining the $Q$ dependence of the similar scatterings, we can conclude that these are attributable to longitudinal lattice modulations. A similar feature was also observed in the stripe-like charge ordering in a two-dimensional (2D) A-type AFM manganite La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ [4, 5].

In order to investigate the influence of newly found diffuse scattering on the transport property, we measured the temperature ($T$) dependences of the intensity at (0, 0, 2.3) (Fig. 1(b)). There is a strong correlation between the intensity and the resistivity (Fig. 1(c)), which establishes that the observed diffuse scattering arises from the charge ordering. Especially, the diffuse peak has large intensity in the A-type AFM state. In addition, we found that the correlation length of the charge ordering is well-developed below $T_N$. These observations verify that the charge ordering is intrinsic to the A-type AFM state. Since a similar charge ordering was observed in the 2D A-type AFM manganites, the existence of such charge ordering must be specific to the wide $W$ manganites independent of the spatial dimensionality.

The observed features of the charge ordering can be well explained by a model of the stripe-like charge ordering depicted in Fig. 2 for $q = 1/3$ r.l.u. In this model, Mn$^{4+}$ ions segregate within the metallic matrix of Mn$^{3+}$-like sites with $d(x^2 - y^2)$ orbitals, and form stripe-like objects along the Mn-O-Mn bond direction. The insulating Mn$^{4+}$ stripes block the hopping of the $e_g$ electrons, whereas the Mn$^{3+}$-like matrix retains the mobility of carriers, producing the high conductivity in the AFM state. In Fig. 2, the hole concentration of the Mn$^{4+}$ stripe is fixed to 1, while that of two Mn$^{3+}$ lines be 1/4, resulting in the overall concentration $x = 1/2$. In reality, some $e_g$ electrons may enter the line of Mn$^{4+}$ ions as depicted in Fig. 2 to disturb the correlation along the stripes resulting in the observed anisotropy in the correlation lengths.

References
Spontaneous rearrangement of the checkerboard charge order to stripe order in La$_{1.5}$Sr$_{0.5}$NiO$_4$

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One of the most fascinating examples of charge ordering may be a so-called stripe order discovered in the high-$T_c$ superconducting cuprates [1]. In hole-doped nickelates La$_{2-x}$Sr$_x$NiO$_{4+x}$, the static stripe order is observed for a wide hole concentration region 0.15 ≤ $n_h$ ≤ 1/2 [2, 3], where $n_h$ = $x + 2s$. The incommensurability $\epsilon$ of the stripe order is approximately proportional to the hole concentration, but the stripe order is most stabilized at the commensurate hole concentration $n_h = 1/3$ with $\epsilon = 1/3$. Considering the incommensurability effect, one can expect that another stable commensurate charge order may exist at $n_h = 1/2$. An early electron diffraction study, indeed, indicated the existence of a checkerboard-type charge order at $n_h = 1/2$ [4]. From our recent study on the highly Sr-doped nickelate system, however, we observed an incommensurate spin order with the incommensurability $\epsilon$ ~ 0.44 [3]. This result gives rise to a question whether the ground state of nickelates at $n_h = 1/2$ is the checkerboard-type charge ordering or stripe-type. In this study, we solve such a mystery of the charge ordering in the 50% doped nickelate by a neutron diffraction technique. We will demonstrate that the charge ordering shows an interesting rearrangement from checkerboard-type to stripe-type in the 50% Sr-doped nickelate.

A large single crystal sample was grown by the floating zone method, and pre-characterized by a resistivity measurement. The in-plane resistivity ($\rho_{ab}$) is almost metallic at high temperature ($\rho_{ab}(600 \text{ K}) \sim 2.5 \times 10^{-3}$ $\Omega \text{cm}$), but it increases monotonically as temperature ($T$) is lowered. The $T$ derivative of the resistivity $d \rho_{ab}/dT$ suggests that the $T$ dependence of the resistivity changes its slope twice at $T_{CO}^\perp \sim 480 \text{ K}$ and $T_{CO}^{\perp \perp} \sim 180 \text{ K}$. These anomalies in the resistivity may indicate that two different types of charge ordering are formed below the temperatures of two respective anomalies. The neutron diffraction experiments were performed using the triple axis spectrometer GPTAS with a fixed incident neutron momentum of $k_i = 3.81 \text{ Å}^{-1}$ and a combination of horizontal collimators of 40‘-40‘-40‘. The sample has a pseudo-tetragonal structure, and we employ an orthorhombic setting.

In order to find the signals due to possible charge orderings inferred by the anomalies of the resistivity, we surveyed reciprocal lattice positions around $(h,k,0)$ with $h + k$ = odd, where a superlattice peak due to the checkerboard-type charge order is expected. Figures 1(a) and (b) show the scan profiles along the [100] direction around $(5,0,0)$ and $(4,3,0)$ at several $T$‘s. In Fig. 1(c) is also shown the profile of the magnetic peak at $(1,0,0)$ measured along the [010] direction at 10 K. In Figs. 1(a) and (b), quite sharp peaks appear at commensurate positions at $(5,0,0)$ and $(4,3,0)$ below $T_{CO}^\perp$. These profiles clearly demonstrate that the checkerboard-type charge ordering is formed in our $x = 1/2$ sample below $T_{CO}^\perp$, being consistent with the early electron diffraction experiment [4].

More importantly, with further lowering $T$, another pair of satellite peaks emerges below $T_{CO}^\perp$ at both sides of the commensurate superlattice peaks for the checkerboard-type charge order, as indicated by arrows in Figs. 1(a) and 1(b) ($h + k = 5 \pm 0.13$ and $h + k = 4 \pm 0.13$, respectively). With use of the incommensurability of the magnetic reflections $\epsilon$ ~ 0.44, the satellite peaks are indexed as $(h \pm 2\epsilon,k,0)$ with $h + k$ = even. Thereby, we identify them as the charge and spin superlattice peaks from the stripe-type charge order with $\epsilon$ ~ 0.44. These observations lead us to conclude that the two types of charge order coexist at low tempera-
Fig. 1. Temperature dependencies of the profiles of charge order peaks: panel (a) at and around (5, 0, 0), panel (b) (4, 3, 0), and panel (c) that of a spin order peak (1, 0.44, 0). In the panel (a), the y axis is shifted by 100 counts for each data.

Fig. 2. Temperature dependencies of the peak intensities of the commensurate charge order peak (5, 0, 0) (a), stripe charge order peak (4, 13, 3, 0) (b). The background intensities measured at (4, 7, 0, 0) are also depicted. The inset in (b) is the temperature dependence of the peak intensity of the stripe spin order peak at (0.44, 1, 0).

In order to show an ordering process of these two charge orders, the T dependencies of the intensity of the commensurate peak at (5, 0, 0) and the satellite peak at (4.13, 3, 0) = (5 - 2x, 3, 0) are depicted in Fig. 2. With decreasing T, the intensity at (5, 0, 0) starts to grow around T_{CO}^{\text{COM}} \approx 480 \text{ K}. Further decreasing T, the intensity reaches a maximum around T_{CO}^{\text{IC}} \approx 180 \text{ K}, and then turns to decrease below T_{CO}^{\text{IC}}. The maximum of the commensurate component is well correlated with the onset of the satellite (incommensurate) components. The intensity of the satellite peak gradually develops below T_{CO}^{\text{IC}}. In addition, the stripe-type spin order sets in at much lower temperature T_N \approx 80 \text{ K} (see the inset of Fig. 2(b)). These T-dependent behaviors of the stripe-type charge and spin order manifest the marvelous stability of the stripe-type ordering at the very high hole concentration for n_h \approx 1/2 in the Sr-doped nickelate.

The incommensurate charge ordering in x = 1/2 can be understood in terms of a commensuration picture of the stripe ordering introduced in our previous study [3]. An important result of the commensuration is the energy gain by the spin exchange interactions. For the checkerboard-type charge ordered state, the exchange interaction between the nearest neighbor sites is unique, and there is only the one between Ni^{2+} and Ni^{3+} ions, which is expected to be quite small [5]. By contrast, when the charge order becomes incommensurate, Ni^{2+}\text{–}Ni^{2+} bond and/or Ni^{2+}\text{–}hole\text{–}Ni^{2+} bond may be introduced in the commensuration region, depending on whether the holes enter the metal site or the oxygen site. Because the exchange interaction for these bonds is much stronger than that between Ni^{2+} and Ni^{3+}, the energy gain due to the spin exchange interactions is larger in the stripe state, and favors the stripe ordering. The present observation suggests the importance of the role of the spin exchange interactions in the charge ordering in the Sr-doped nickelate system.

References
Phonon density of states for filled Skutterudite, $\text{Ba}_{0.1}\text{CoSb}_3$

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The Skutterudite is a name of a group of $\square\text{MX}_3$-type unique minerals in which $\square$, M and X refer to the vacancy, metal, Co, Rh and Ir, and anions, P, As and Sb, respectively. The crystal structure of this mineral is regarded as formed from the cubic perovskite structure as shown in figure 1. By the partial filling of the vacancy site with relatively heavy cations, i.e., Ba, La, Ce or Th, these crystals become promising thermo-electric materials suitable to generate electric power by the Seebeck effect in the temperature range from 500K to 700K[1].

![Crystal structure of Ba$_{0.1}$CoSb$_3$, Skutterudite, being cubic, Im-3m(225).](image)

Fig.1 Crystal structure of Ba$_{0.1}$CoSb$_3$, Skutterudite, being cubic, Im-3m(225).

The ever reported figure of merit, Z, times temperature, ZT, of these crystals exceeded the value of 1.0 in above temperature range[2]. One of the characteristic physical phenomena is a dramatic decrease of the thermal conductivity in the range from 1/2 to 1/4 less than the matrix by the partial site filling. That is mainly responsible for the extra-large ZT values. Dramatic decrease of the thermal conductivity has been explained in terms of the "rattling" of the "filled" heavy cation, which sits in a roomy 2a(000) site as shown in Fig.1. Twelve Sb atoms coordinate to a heavy atom. Metallic transport property of these crystals is also a characteristic feature. CoSb$_3$ octahedrons are slightly squeezed in [111] and its equivalent directions. The Co-Sb-Co distance and the bond angle are 2.595 Å-2.595 Å and 121 degree, respectively, being suitable for the metallic transport and weak magnetic coupling between the 3d electrons due to the Kanamori-rule. The "rattling" of the filled heavy cations corresponds to the local and low energy vibration mode in the Skutterudites. It has been accepted that the "rattling" mode causes significant decrease either of the mean free path of phonons and of the thermal conductivity. Present work was motivated to ensure this prediction experimentally.

Unfilled and filled Skutterudite powder samples were synthesized. The phonon density of states are measured by JRR-3M AGNES at temperatures from 12K to the ambient. Figure 2 shows parts of the DOS curves. Some new modes are seen at about 15 and 18meV in the filled Skutterudite, being consistent with the prediction[3].

![DOS curves](image)

Fig.2 Observed DOS of Skutterudites at room temperature by AGNES. New peaks, hopefully the "rattling mode" at E=15 and 18meV appeared in the filled Skutterudite.

References
Electron doping effects in conducting Sr₂FeMoO₆

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The carrier doping by chemical substitution is a powerful tool for investigation of strongly correlated electron systems, especially the perovskite-like 3d and 4d transition metal oxides. Most of the 3d transition metal oxides with integer filling, e.g., LaMnO₃ and LaCoO₃, are insulating due to the strong on-site Coulomb repulsion U. With substitution of the divalent Sr²⁺ ions for the trivalent La³⁺ ion, however, these compounds become ferromagnetic metal due to the double-exchange mechanism.

Recently, ordered double-perovskite molybdenum oxides A₂MMO₆₆ (A is a rare-earth metal and M is a 3d transition metal) begin to attract current interest of material scientists in the application point of view. Among the double-perovskite molybdenum oxides, Sr₂FeMoO₆ is most extensively studied, because high-quality single crystals can be obtained by the floating-zone method. Sr₂FeMoO₆ is ferrimagnetic and metallic with critical temperature T_C = 400 K. On the basis of a LDA band calculation, the conduction band is dominated by the Mo4d level, while Fe3d-electrons behave as local spins. We have investigated the electron-doping effects on the properties in the conducting double-perovskite (Sr₂La₄)FeMoO₆.

A stoichiometric mixture of commercial SrCO₃, La₂O₃, Fe₂O₃, Mo and MoO₃ was well ground, and pressed into a rod and sintered at 1200 C for 2 h in a flow of Ar gas. The crystal is grown at a feeding speed of 20 mm in an Ar atmosphere. Black and shiny crystals, typically 4 - 5 mm in diameter and 20 mm in length, were obtained. The actual chemical composition of the melt-grown (Sr₁₋ₓLaₓ)FeMoO₆ crystal was determined by the inductively coupled plasma (ICP) method, and is almost the same as the ideal values; Sr : La : Fe : Mo = 1.692 (1.7 : prepared value) : 0.316 (0.3) : 1.024 (1.0) : 0.972 (1.0). The crystal symmetry at room temperature (≤ T_C) is tetragonal (I4/mmm; Z = 2).

We have measured neutron powder diffraction patterns of Sr₂FeMoO₆ and (Sr₁₋ₓLaₓ)FeMoO₆ with the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute, Tokai, Japan. Neutrons with wavelength 1.819 A were obtained by the (331) reflection of Ge monochromater, and 12'-B-Sample-18' collimation. Melt-grown crystal ingots (5 g) were crushed into a fine powder and were sealed in a vanadium capsule with helium gas, and mounted at the cold head of the closed-cycle He-gas refrigerator.

Magnitudes of the respective moments are determined by the Rietveld fitting (RIETAN-97B), in which we assume a collinear magnetic structure with spin direction along c. Several impurity peaks, which are inevitably introduced from the skin region of the crystal ingot, were observed and were removed from the pattern. The obtained moments are \( \mu_{Fe} = 4.2(2) \mu_B \) and \( \mu_{Mo} = - 0.5(2) \mu_B \) at \( x = 0.0 \), and \( \mu_{Fe} = 3.8(2) \mu_B \) and \( \mu_{Mo} = - 0.8(2) \mu_B \) at \( x = 0.3 \). At \( x = 0.0 \), both the moments are suppressed as compared with the ideal values (5.0 \( \mu_B \) and - 1.0 \( \mu_B \) for the Fe²⁺ and Mo⁵⁺ ions, respectively). This is partly due to the disorder of the B-site ions. With increase of \( x \), absolute magnitude of \( \mu_{Mo} \) increases from -0.5(2) \( \mu_B \) at \( x = 0.0 \) to -0.8(2) \( \mu_B \) at \( x = 0.3 \). This enhancement of \( \mu_{Mo} \) indicates that the doped electrons occupy mainly the Mo4d down-spin band, consistently with the LDA band calculation.
Phase separation and ferromagnetic transition in B-site substituted Mangnaites

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The charge-ordered insulating (COI) phase, which is frequently observed in half-doped manganites (e.g., R$_{12}$Ca$_{0.2}$MnO$_3$, R = Nd, Pr, Sm and Tb), is amenable to the external perturbations, such as, magnetic field, external pressure and chemical pressure. This amenability of the COI state reflects a strong competition of the COI state with the ferromagnetic metallic state due to the double-exchange mechanism.

By contrast, Raveau et al. have found that 3% substitution of the perovskite B-site of Pr$_{12}$Ca$_{0.2}$MnO$_3$ by another transition metals, e.g., Cr and Co, induces a ferromagnetic transition at low temperature. This B-site substitution effect on the COI phase is rather complicated, since the B-site impurity is usually considered to be disadvantageous to the metallic state. Here, we should take into account the phase separation phenomena, that is, coexistence of the COI and ferromagnetic metallic phases, in addition to these microscopic effects between the dopant and Mn. For example, Nd$_{12}$Ca$_{0.2}$Mn$_{1.8}$Cr$_0.2$O$_3$ consists of ferromagnetic and charge-ordered microregions of the order of 10 nm, as was confirmed by dark field image of the superlattice reflection from the COI region.

We have systematically investigated the B-site substitution effects on the structural and magnetic properties in Nd$_{12}$Ca$_{0.2}$Mn$_{1.8}$M$_{0.2}$O$_3$ (M = Al, Zn, Sc, Fe, Ni, Co and Cr). The ground state of the non-doped Nd$_{12}$Ca$_{0.2}$MnO$_3$ is charge-ordered insulator with CE-type antiferromagnetic spin ordering. We found that all the compounds transformed into two-phase state with decreases of temperature below 200 K. With further decreases of temperature below 100 K, the Cr-, Co- and Ni-doped compounds show the ferromagnetic transition, while the other compounds show only the CE-type component. We have discussed interrelation between the phase separation and the ferromagnetic transition in these B-site substituted manganites.

![Graph of neutron powder pattern](image)

Fig. 1: Prototypical examples of neutron powder pattern (cross) of Nd$_{12}$Ca$_{0.2}$Mn$_{1.8}$Al$_{0.2}$O$_3$ at (a) 300 K, (b) 180 K and (c) 50 K. Solid curves are the results of Rietveld refinement with one [(a)] or two [(b) and (c)] distorted perovskites. Inset of (b) and (c) shows the powder pattern in the low angle region.
Neutron Structural Analysis of Tb$_{1-x}$Ca$_x$MnO$_3$

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Perovskite-type doped manganites, R$_x$A$_{1-x}$MnO$_3$, where R and A are trivalent rare earth and divalent alkaline-earth ions, respectively, have three dimensional networks of the MnO$_6$ octahedra. In this structure, variation of the averaged ionic radius r$_0$ of the perovskite A-site modifies the one-electron bandwidth W of the eg band through the variation of the Mn-O-Mn bond angle (chemical pressure). Actually, Radaelli et al. have experimentally confirmed this trend at a fixed-x (≈ 0.3). Thus, the insulator-metal crossover at the fixed-x has been understood in terms of W-control by the chemical pressure. A similar chemical pressure effect is expected even in the hole-doping procedure, i.e. substitute of the A$^{2+}$ ions for the R$^{3+}$ ions.

So far, many and theoretical studies have been carried out on such phase separation problem to clarify the origin of the colossal magnetoresistance (CMR). For example, Mori et al. performed an electron diffraction measurement on La$_{0.55}$Ca$_{0.45}$MnO$_3$ and found a coexistence of the FM metallic and charge-ordered insulating (COI) microdomains of the order of 10 nm. The coexistence of the different phase has been confirmed also by the synchrotron radiation (SR) x-ray diffraction as well as the NMR measurements. Recently, Machida et al. have investigated the lattice and magnetic structures of the phase separated state of Nd$_{0.55}$(Sr$_{0.17}$Ca$_{0.83}$)$_{0.55}$MnO$_3$, and argued possible mechanism for the phase separation. Their scenario, the lattice structural change at the charge-ordering transition (CE-type orbital-ordering) causes the internal stress into the domain, and induces the secondary phase in the surrounding area. Similarly, the C-type orbital-ordering can couple with the Jahn-Teller-type lattice distortion, and may cause the phase separation.

We have investigated the structural and magnetic properties of Tb$_{1-x}$Ca$_x$MnO$_3$ by means of neutron powder diffraction experiments. We chose Tb compound in order to perform the neutron diffraction experiments and reveal the magnetic property of the narrow band system. First, we derived a magnetic phase diagram against hole concentration x and temperature. We observed the magnetically phase separated states around the phase boundaries between the CE-type and C-type and between the C-type and G-type antiferromagnetic (AFM) phase. Secondly, we observed the metal-insulator behavior in the wide x region above $T_N$. We rather found that the chemical pressure effects well explain the observed metal-insulator behavior. Lastly, we compared the present magnetic phase diagram with that of the layered system.

Fig.1: Neutron diffraction patterns of Tb$_{1-x}$Ca$_x$MnO$_3$ at 10-K. Hatched reflections indicate the magnetic Bragg reflections. Inset shows the schematic illustration of the CE, C, and G-type spin structure.

使用施設：JRR-3M、装置：HERMES、分野：1 Structure & Excitation, 2 magnetism
Modulated Structure of the Composite Crystal [(Ca<sub>1-x</sub>Sr<sub>x</sub>)(CO<sub>3</sub>)<sub>0.62</sub>CoO<sub>2</sub>]

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Layered composite crystal cobaltite [Ca<sub>2</sub>CoO<sub>3</sub)]<sub>0.62</sub>CoO<sub>2</sub> has recently attracted much interest owing to its superb thermoelectric properties. Partial substitution of the Sr ions for the Ca ions was found to further enhance the thermoelectric power-factor due to a substantial decrease in electric resistivity. In order to elucidate the origin of such a change from a structure point of view, we have performed the structure analysis by means of a four-dimensional superspace group approach.

Polycrystalline samples of [(Ca<sub>1-x</sub>Sr<sub>x</sub>)(CO<sub>3</sub>)<sub>0.62</sub>CoO<sub>2</sub>] were prepared by the standard solid-state reaction method. Neutron powder diffraction (ND) data were collected at room temperature using HERMES diffractometer, installed at the JRR-3M reactor in JAERI. The ND data were analyzed using a Rietveld refinement program PREMOS 91 [1] designed for modulated structure analyses.

As shown in Fig. 1, the non-doped compound consists of a CdI<sub>2</sub>-type CoO<sub>2</sub> sheet (subsystem 1) and a tricapped rock salt-type Ca<sub>2</sub>CoO<sub>3</sub> block (subsystem 2) alternatively stacked parallel to the c-axis [2]. Both the subsystems have common monoclinic a- and c-axes but mutually incommensurate b-axes (b<sub>1</sub> and b<sub>2</sub>). With increasing the Sr content x, the a-, b<sub>1</sub>- and c-axis lengths continuously increased while the b<sub>1</sub>-axis length gradually decreased from 2.8201(3) Å (x = 0) to 2.8170(3) Å (x = 0.20).

Figure 2 shows the modulation of the Co-O distances in the CoO<sub>2</sub> subsystem plotted against a complementary coordinate t'. As is clearly recognized, the modulation amplitudes are significantly reduced with x. The decrease of resistivity can be thus understood in terms of the reduction of the displacive modulations in the conducting paths.

**Fig. 1** Fundamental structure of [(Ca<sub>2</sub>CoO<sub>3</sub>)<sub>0.62</sub>CoO<sub>2</sub>]

**Fig. 2** The Co-O distances in the CoO<sub>2</sub> subsystem plotted against a complementary coordinate t'.

References
Phase Transitions and Structures of CH₃NH₃PbCl₃

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A Methylammonium compound, CH₃NH₃PbCl₃, performs a cubic-orthorhombic transition around 170K[1,2]. In the perovskite cubic phase, a methyl-ammonium (MA) ion occupies disordered orientations to satisfy the O₆ symmetry. In the intermediate phase, satellite reflections have been observed[3], however, no further structural study has been reported.

In order to clarify the ordering mechanism of MA ions, we have been investigating the compound by neutron powder-diffraction methods. The crystal was milled and dried before canning in a vanadium cell, which was set on a goniometer. The measurements were carried out with using HERMES of IMR in JRR-3M. The wave length of neutron was 1.8196A. The scattered intensity was obtained for 1500 points with a 0.1° step, each 50min. A profile fitting program RIETAN-94[4] was used to determine the crystal structure.

The cubic structure at 180K (phase I: Pm3m, Z=1) has been successfully analyzed; Rp=2.64%, Rf=8.56%, S=1.172, d=1.725, although the background was very high because of protons of MA.

The temperature dependence of the diffraction intensity is demonstrated in Fig. 1, where indexes are referred to the cubic phase. Super-lattice reflections (h/2 k/2 l) or (h/2 k l) appear below 170K, and increase their intensity with lowering the temperature. This suggests that the phase III is orthorhombic. The structure analysis was almost successful with Pnma, Z=4; Rp=5.05%, S=2.13, d=0.713, Rf=7.52%. The atomic parameters for protons are not fully refined as yet.

The lattice parameters are plotted in Fig.2, where a/1.414, b/2 and c/1.414 are compared with the cubic a. The intermediate phase was difficult to be recognized. The rotation and the tilting of PbCl₃ octahedron take place through the phase transition. The orthorhombic structure is a modification from Cmcm. In order to analyze the mechanism of the ordering process of MA ions, more detailed investigation is desirable.

References
Relation between Crystal Structure, Thermodynamic Stability, and Electrode Characteristics of LiMn_{2-x}M_xO_4 (M = Ni, Zn) as a Cathode Active Material for the 4V, 5V Class Lithium Secondary Battery

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The relation between crystal structure, thermodynamic stability and electrode characteristics of the spinel LiMn_{3-x}M_xO_4 (M= Ni, x=0, 0.1, 0.3, 0.5 Zn; x=0, 0.05, 0.10) was investigated.

1. LiMn_{1.5}Ni_{0.5}O_4 as a Cathode Active Material for 5V Class Li Secondary Battery

LiMn_{1.5}Ni_{0.5}O_4 as a 5V class cathode material were prepared by changing synthesized method and heat treatment. We investigated the dependence of their properties, crystal structure and cathode performance on oxygen content.

Oxygen content of the samples (sol-gel method and annealed at high PO_2) increased in comparison with the sample (solid-state method).

The charge-discharge curves of the samples (solid-state method) appeared at 4.1V and 4.7-5.0V plateaus. On the other hand, the 4.1V plateau is disappeared (sol-gel method or annealed at high PO_2). The discharge capacity with respect to cycle number of the 5V region in LiMn_{1.5}Ni_{0.5}O_4 (sol-gel method) electrodes shows especially good cycle performance.

The neutron-diffraction intensity profiles of LiMn_{1.5}Ni_{0.5}O_4 using HERMES were analyzed by Rietan 2000. From the results, the samples are assigned to the ordered form (space group P4_32). The amount of impurity phase decreases by annealing at high PO_2 or sol-gel method. Furthermore, the distortion of Mn,Ni(12d)-O octahedral site was restrained with increasing oxygen content.

2. LiMn_{2-x}M_xO_4(M=Ni, Zn) as a Cathode Active Material for 4V Class Li Secondary Battery

We investigated the relation between electrode performance and electronic state of LiMn_{2-x}M_xO_4 (M = Ni, Zn) as cathode active materials for 4V class lithium secondary battery.

The cycle performance is improved by substitution of Mn with Ni or Zn. The neutron-diffraction intensity profiles of LiMn_{2-x}M_xO_4 (M=Ni: x=0, 0.1, 0.3; M=Zn: x=0, 0.05, 0.1) were analyzed over a wide range at room temperature and 200K sing HERMES. A refinement was carried out by assuming a cubic unit cell(space group: Fd-3m) by Rietan2000. From the results of room temperature and 200K, the phase transition (cubic to orthorhombic) were restrained by substitution of Zn, Ni for Mn. The bond lengths of Li-O, (Mn, M)-O [M=Ni, Zn] and Madelung energy decrease with increasing M content. The bond lengths of (Mn, M)-O dependence of temperature is decreased with
increasing M content, x(M=Zn, Ni). Hence, the crystal structure is more stable by the substitution of Zn, Ni for Mn.

We obtained the electron density distribution by XRD using MEM/Rietveld method.

Moreover, we investigated the electronic states of LiMn$_{1.75}$M$_{0.25}$O$_4$ (M=Mn, Ni, Zn) using First-principles calculation by DV-Xa method. The net charges of each atom, the bond overlap populations of Li-O, Mn-O, Ni-O and Zn-O were calculated. From the results, Li is high ionicity and the covalent bonding of Mn-O of LiMn$_{1.75}$M$_{0.25}$O$_4$ (M= Ni, Zn) is stronger than that of LiMn$_2$O$_4$. As a results of the DOS, the oxygen 2p orbital and Mn 3d orbital gives the overlap and the overlap of LiMn$_{1.75}$M$_{0.25}$O$_4$ is larger than that of LiMn$_2$O$_4$.

Furthermore, the standard enthalpies of formation, Δ$_f$$H^0$, and the enthalpy change of reaction, ΔH, were calculated from the heat of dissolution. Thermodynamic stability was examined by these parameters. These thermodynamic data was compared with the calculated one of samples to partially replace Mn by Ni or Zn. When Δ$_f$$H^0$ and ΔH decreased, it brought to a good cycle performance.

Accordingly, it is suggested that the stability of the host structure brought to improvement for the cycle performance.
Martensitic Transformation of Ni$_{2.18}$Mn$_{0.82}$Ga Single Crystal

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We have made the neutron diffraction of an off-stoichiometric Heusler-type Ni$_{2.18}$Mn$_{0.82}$Ga single crystal. It has a thermo-elastic martensitic transformation temperature of about 340K, coincident with the Curie temperature. The diffractometer, FONDER, installed on T2-2 port of JRR-3M reactor was used. The Q-scan at 416 K, 344 K and 302 K was made with decreasing temperature. The intensity map in Q-space was measured at 297 K, after cooling down from 400 K to room temperature under magnetic field of 1.5 T.

We determined previously the crystal structure of the martensitic phase using the Rietveld analysis of the powder diffraction patterns obtained by HERMES. Two structures coexist in the martensitic phase. One is an orthorhombic structure distorted from the cubic Heusler structure, and the other is a tetragonal one made from the shuffling of the 220 plane of the orthorhombic structure. This tetragonal structure is equal to the monoclinic one with 6 layers shuffling, which we suggested formerly [1,2]. The temperature dependence of mass fractions of three structures and the mutual relation of the lattice constants determined with increasing temperature are shown in Figs. 1 and 2. We see that there are several coincidences in the lattice constants of three structures.

The single crystal on the sample holder is shown in Fig. 3. The length of the crystal is about 6 mm. From the measurements by FONDER, we found that the single crystal at 416K has a cubic Heusler structure of single domain, where the direction of the crystal growth is [001]. As the examples, Q-scans along (1.8 0 0) to (2.2 0 0) around 200 peaks of cubic Heusler structure are shown in Figs.4 (a) to (c) for three temperatures. We see that 200 peak at 416 K becomes to have two satellites near (1.9 0 0) and (2.1 0 0) at 344 K. At 302 K, the (2.1 0 0) satellite grows up and the other two...
peaks disappear. The (1.9 0 0) peak corresponds to the lattice constant, a(ortho.) of the orthorhombic structure. The (2.1 0 0) peak corresponds to c(ortho.) of orthorhombic structure or a(tetra.) of tetragonal structure. Figure 4 indicates that at 344K near the martensitic transformation temperature, both of the orthorhombic structure and the tetragonal one begin to appear in addition to the cubic Heusler structure. However, at 302 K sufficiently lower than the martensitic transformation temperature, only the tetragonal structure remains. This fact is consistent with the result of powder neutron diffraction, that the mass fraction of tetragonal structure in the martensitic phase exceeds 90 % at low temperatures. The fact indicates that the tetragonal structure is more stable than the orthorhombic structure.

The magnetic field of field cooling was applied along the direction of crystal growth. By searching the crystal direction using FONDER, we found that the direction of the crystal growth in martensitic phase is tetragonal [001] direction. The intensity maps around the tetragonal (200) peak and the tetragonal (002) peak at 297 K are shown in Figs. 5 (a) to (c). In the (h0l) reciprocal plane around tetragonal (002) peak shown in Fig. 5 (c), we see three tetragonal (002) peaks and a weak orthorhombic (020) peak. In the (hk0) reciprocal plane around tetragonal (200) peak shown in Fig. 5 (a), we also see two tetragonal (200) peaks and nearby three tetragonal (202) peaks, which are equal to orthorhombic (220) peaks. From these three pictures, we conclude that field cooling under the magnetic field of 1.5 T could not produce a martensitic phase of single domain.

Fig. 5. Intensity maps in Q-space of single crystal, (a) (hk0) reciprocal plane around tetragonal (200), (b) (h0l) one around tetragonal (200) and (c) (h0l) one around tetragonal (002).

The plural number of tetragonal domains and the small amount of orthorhombic structure exist.

References
Crystal structure of Trivalent Ion Conductive Perovskite: Y₄(Ta₃₋xWₓ)O₉

1-1-24

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Introduction
It has recently been shown that non-stoichiometry and ordering of A-site cation in the perovskite-based oxides can influence the electronic conduction and structural phase transition of materials such as lithium conducting A-site deficient perovskites [1]. Quite recently, we have reported some possibilities of high trivalent ion conduction in Y₄(Ta₃₋xWₓ)O₉ (YTWO), which possesses an highly A-site cation-deficient perovskite structure [2]. The higher trivalent ionic conductivity for YTWO may be attributed to the larger number of A-site vacancies in the solid. However, there are a number of unclarified points regarding crystal chemistry of highly A-site cation-deficient perovskite, YTWO. The present report therefore aims at presenting basic crystallographic data on YTWO by the powder neutron diffraction pattern analysis.

Experimental
The perovskite, Y₄₀Ta₁₈W₈₂O₃, was prepared by a conventional solid state reaction. Starting materials were a stoichiometric mixture of Y₂O₃, Ta₂O₅ and WO₃. The mixture was pressed into a pellet and heated in a platinum boat at 1200°C for 30 min in air. The completion of the reaction and the phase purity of samples were confirmed by the powder X-ray diffraction and fluorescence X-ray method. Thermo gravimetric analysis and differential thermal analysis were used to check the absence of the phase transition. We performed neutron powder diffraction experiments on the Kinenk powder diffractometer for high efficiency and high resolution measurements, HERMES [3], of Institute for Materials Research(IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. The fine powder sample was sealed in a vanadium cylinder. Rietveld structure refinement was carried out with the program RIETAN2000 [4].

Result and Discussion
The synthesis of the A-site deficient perovskites, Y₄(Ta₃₋xWₓ)O₉, was first reported by Studer, Montfort and Raveau [5]. They refined the structure of orthorhombic Y₀₆Ta₀₁₈W₀₈₂O₃ in the space group Cmnm (a = 0.5298, b = 0.5377 and c = 0.3774 nm) without a tilting of (Ta, W)O₆ octahedra. However, it is unreasonable if we take account of the fact that the powder neutron diffraction data collected from the single phase x = 0.06 samples. Preliminary Rietveld analysis indicated that the superstructure peaks could not be indexed on the basis of the space group Cmnm. Figure 1 shows the powder neutron diffraction pattern fitting for the solid solution system, Y₀₆Ta₀₁₈W₀₈₂O₃. All of the patterns matched with that of orthorhombic space group Pnma and the calculated profile show good agreement with observed pattern. A monoclinic distortion model (Space group P2₁/n; Rwp = 9.45%) with a long-range ordering of the B-site cations and same tilt system was rejected by the Rietveld analysis. The refined crystallographic data obtained from Rietveld refinement is given in Table 1. The orthorhombic Pnma structure is a distorted form of ideal cubic perovskite. The distortion mechanism is a tilting of essentially rigid (Ta, W)O₆ octahedra. It occurs when the A-site cation is too small for its 12 coordinate cavity in the cubic perovskite structure. This distortion is the predominant for perovskites with tolerance factors smaller than 0.98. In the
A-site deficient perovskites $Y_a(Ta_{3-x}W_x)O_3$, the tolerance factor is 0.91 and the coordination number of the yttrium ion is effectively lowered from 12 to 8. In addition, neutron diffraction pattern analysis confirmed the disorder arrangement of A-site cations. The yttrium ions are statistically distributed only over 6% of a single 4c site with 94% vacancy in the space group Pnma. In this structure, trivalent yttrium ions can move easily through many A-site vacancies. Therefore, $Y_{0.06}Ta_{0.18}W_{0.82}O_3$ with the average structure showed the 800 times higher ion conductivity than an isostructural $La_{0.33}TaO_3$ with the order structure [2].

![Graph](image)

Fig.1 The powder neutron diffraction pattern fitting for the solid solution system, $Y_{0.06}Ta_{0.18}W_{0.82}O_3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>y</th>
<th>z</th>
<th>$B_{eq}(\times 10^2 \text{nm}^2)$</th>
</tr>
</thead>
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<td>Y</td>
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<td>1/4</td>
<td>-0.006(4)</td>
<td>1.34(4)</td>
</tr>
<tr>
<td>Ta</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>2.36(5)</td>
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<tr>
<td>W</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>2.36(5)</td>
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<tr>
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<td>4c</td>
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<td>1/4</td>
<td>0.064(3)</td>
<td>1.07(4)</td>
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<tr>
<td>O(2)</td>
<td>8d</td>
<td>0.281(2)</td>
<td>0.031(1)</td>
<td>0.717(2)</td>
<td>0.98(3)</td>
</tr>
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</table>

**Table 1. Structural parameters and reliable factors of the $Y_{0.06}(Ta_{0.18}W_{0.82})O_3$**

Space group: Pnma (No. 62)
Lattice parameters (nm): $a = 0.5373(3)$, $b = 0.7547(5)$, $c = 0.5297(3)$
Reliable factors: $R_w = 6.51\%$, $R_p = 5.08\%$, $R_1 = 2.50\%$, $R_f = 1.52\%$
Shear-Induced Transformations in the Lamellar Phase Formed in Nonionic Surfactant-Water System

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In recent years, much attention has been paid to the effects of shear flow on the structure of a lamellar phase by using various scattering techniques. In the previous studies, we have measured small-angle neutron scattering (SANS) on a nonionic surfactant C₁₆H₃₃(OCH₂)₃OH (C₁₆E₇)-water system at 48 and 55 wt% of C₁₆E₇ at 55 and 70°C under shear flow for the shear rates \( \dot{\gamma} = 10^{-3} \text{ to } 10^{2} \text{ s}^{-1} \) much lower than those for other studies reported so far. We have found specific shear rate dependences in both the position and the intensity of the first reflection. In the present study, measurements have been made at 40 wt% of C₁₆E₇ at 70°C which is close to the low concentration limit of the lamellar phase.

Measurements of SANS were carried out at the instrument SANS-U of Institute for Solid State Physics of University of Tokyo in JRR-3M at Tokai with a Couette shear cell.

Figure 1 shows examples of the observed diffraction patterns for different shear rates. At the shear rates 0.1 - 0.3 s⁻¹, the diffraction peak is shifted to the higher scattering angle. With the further increase in the shear rate, the peak position is moved to the lower scattering angle. These results indicate that the repeat distance \( d \) takes a minimum at the shear rates 0.1 - 0.3 s⁻¹. Similar results have been obtained in our previous studies. However, the decrease of \( d \) in the present study is much more pronounced than in the previous study. Moreover, the shear rate giving a minimum of \( d \) \( (d_{\text{min}}) \) is slightly lower than the previous one (0.3 - 1 s⁻¹).

In Figure 2, \( d_{\text{min}} \) is plotted against the concentration together with the \( d \) value and the film thickness at rest obtained from the analysis of SANS. This figure demonstrates that \( d_{\text{min}} \) depends on concentration only slightly, suggesting phase separation induced by shear flow.

Figure 1  Examples of diffraction patterns at 48 wt% and 70°C for gradient direction for different shear rates (indicated in the figure in s⁻¹).

Figure 2  Concentration dependence of the repeat distance \( d \) at 70°C for the shear rate of 0.003 (○) and 0.1 - 1 s⁻¹ (●) compared with \( d \) (△) and the film thickness (□) at rest obtained from SANS.
Jahn-Teller induced structural phase transition in TbVO₄

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The rare earth vanadates have proved ideal systems for study of structural phase transition involving lattice strains arising from the cooperative Jahn-Teller effect. The transition are driving by a coupling between the low-lying electronic energy levels of the rare earth ions and the lattice phonon. TbVO₄ has a tetragonal symmetry D₄h⁻¹-H₄amd of zircon structure at room temperature. The structural phase transition occurs at about 34K(Tc). It is known that the structure is an orthorhombic symmetry D₄h⁻¹-Fddd in the low-temperature phase. However, the structural property has been not adequately analyzed by appearance of multi-domains below Tc. Thus, we carried out neutron diffraction to re-study the structural modulation in the vicinity of tetragonal symmetry. The measurements were done at KSDL in JRR-3. At the present experiments, a specimen was made by fixing 9 small crystals with adhesive, whose size is about 1 x 1 x 5 mm³.

Fig.1 shows peak profiles of (4,0,0) and (0,4,0) fundamental reflections, taken at about 8K and 50K in TbVO₄. Since the structure is tetragonal at 50K, their intensities are approximately same. However, below Tc, the peak profiles of reflections are largely modified by the structural phase transition. It was found from Fig.1 that there are two kinds of orthorhombic domains in the used specimen and an angle γ between [100] and [010] of is not 90°. Because the peak profiles at 8K are refined by two Gaussian curves. This suggests that a structural distortion mode is a B₄₈ mode, not B₃₄ mode. Will et al. [1] argued from X-ray powder diffraction that there was no evidence for any discontinuous change in the cell volume at 32K(Tc) and the structural phase transition was of second order. In order to study the transitional order, we carried out measurements of the integrated intensity of (0,4,0) reflection, as shown in Fig.1. Fig.2 shows the peak profiles of the (0,4,0) reflection taken by the ω-scan at the respective temperature in the vicinity of the phase transition. It was interested in the peak profile taken at 31K, around which the phase transition occurs. This suggests that there is probably an semi-stable intermediate state related to the first-order structural modulation around Tc. Since the peak position in the low temperature
Fig. 2. Temperature dependence of the peak profiles of (0,4,0) reflection in the vicinity of the phase transition.

Phase is not cleared by the peak splitting, we first fixed the neutron detector at a maximum peak position of the (0,4,0) reflection at 50K. Second, we cooled the specimen till 8K. After that, we continuously measured the intensity, on heating. The results are shown in Fig. 3. It was found that the structural phase transition occurs at 33K and should be of first order, not second one. On the other hand, we first fixed the detector at a maximum peak position of the (0,4,0) reflection at 8K. Secondly, we continuously measured the intensity, on heating. The results are shown in Fig. 4. The phase transition was confirmed at 31K.

Fig. 3. Temperature dependence of the maximum peak intensity of (0,4,0) reflection taken at 50K in Fig. 2.

Fig. 4. Temperature dependence of the maximum peak intensity of (0,4,0) reflection taken at 8K in Fig. 2.

However, its (I-T) curve is characterized around Tc by a critical dispersion. In order to study the critical scattering, we carried out measurements of the intensity of (0,4,0) reflection observed in the intermediate phase, which is at \( \omega = 11.7^\circ \) in Fig. 2. Fig. 5 suggests that the intermediate phase occurs in a region from about 30.5K to 33K. The structural phase transition occurs at 33K, as shown in Figs. 3 and 4. Therefore, we considered that the large elastic strain induced at the phase transition by the Jahn-Teller effect is quickly transformed to a construction of the semi-stable intermediate phase in such narrow temperature region below Tc.

Fig. 5. Temperature dependence of the peak intensity of (0,4,0) reflection in the intermediate phase, which is observed at \( \omega = 11.7^\circ \) in Fig. 2.

Crystal structure and the structural phase transition in an itinerant 5f antiferromagnet $\text{UCr}_2\text{Si}_2$

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$\text{UT}_2\text{X}_2$ is one of the traditional 5f electron systems that the unusual magnetic and transport properties have been studied systematically for various compounds with different transition metal T and X=Si, Ge. In $\text{UCr}_2\text{Si}_2$ the small number of d-electrons and small distance between U atoms give rise to rather enhanced itinerant character of the 5f-electrons. Very recently, we have succeeded in growing single crystals of $\text{UCr}_2\text{Si}_2$ for the first time. The purpose of this study is to reveal the structural properties of $\text{UCr}_2\text{Si}_2$ by means of neutron scattering.$^2$

Polycrystalline samples were grown by arc-melting of stoichiometric amount of the starting materials. Single crystals were grown by the Czochralski-pulling method in a tetra-arc furnace under argon gas atmosphere. Powder diffraction patterns were measured by using HRPD ($\lambda$=1.8242 Å). The structural phase transition was studied in detail with a single crystal sample using triple axis spectrometers LTAS and TAS-2, respectively.

Figure 1 shows the neutron powder diffraction pattern of $\text{UCr}_2\text{Si}_2$. At 300 K the data were satisfactorily explained by the ThCr$_2$Si$_2$-type structure with the space group $I4/mmm$. At 100 K we observed clear splitting of the peaks, indicating the structural phase transition below $T_a$ = 210 K. We found that the observed diffraction pattern was well explained by the model calculation with space group $P\bar{1}$ (A-2). The obtained structural parameters after Rietveld refinement are listed in Table 1. The distortions due to the structural transition are very small.

Figure 3 shows the contour plot of the scattering intensities around the (2,0,0), (0,2,0),

![Figure 1: The high resolution neutron powder diffraction pattern of $\text{UCr}_2\text{Si}_2$ at (a) 300 K and (b) 100 K. The solid line is the calculated diffraction intensity after Rietveld refinement.](image1)

![Figure 2: The crystal structure of $\text{UCr}_2\text{Si}_2$ for (a) high-temperature tetragonal phase and (b) low temperature triclinic phase.](image2)
Table 1: Structural parameters of UCr$_2$Si$_2$. Numbers in parentheses following refined parameters represent the estimated standard deviations of the last significant digit(s)

<table>
<thead>
<tr>
<th>Space group</th>
<th>lattice parameter</th>
<th>atom (site)</th>
<th>position</th>
<th>B</th>
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<tr>
<td>14/mmm</td>
<td>$a=b=0.3913(1)$</td>
<td>U (2$a$)</td>
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<tr>
<td>300 K</td>
<td>$c=1.0507(5)$</td>
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<td></td>
<td>$\alpha=\beta=\gamma=90$</td>
<td>Si (4$e$)</td>
<td></td>
<td>0.38631(5)</td>
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<tr>
<td></td>
<td>$R_{wp}=5.21$</td>
<td></td>
<td>$R_e=3.97$</td>
<td>0.505441</td>
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<tr>
<td></td>
<td>$R_p=4.61$</td>
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<td></td>
<td>S=1.1299</td>
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<tr>
<td>P1</td>
<td>$a=0.3806(5)$</td>
<td>U (1$a$)</td>
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<tr>
<td></td>
<td>$b=0.3903(6)$</td>
<td>U (1$h$)</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>100 K</td>
<td>$c=1.0506(2)$</td>
<td>Cr(2$i$)</td>
<td>0.52134(0)</td>
<td>0.24977(2)</td>
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<tr>
<td></td>
<td>$\alpha=91.49(6)$</td>
<td>Cr(2$i$)</td>
<td>-0.0320(3)</td>
<td>0.24993(7)</td>
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<tr>
<td></td>
<td>$\beta=88.51(3)$</td>
<td>Si (2$i$)</td>
<td>0.01823(5)</td>
<td>0.38567(5)</td>
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<tr>
<td></td>
<td>$\gamma=90.74(1)$</td>
<td>Si (2$i$)</td>
<td>0.51053(9)</td>
<td>0.88644(4)</td>
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<tr>
<td></td>
<td>$R_{wp}=6.43$</td>
<td></td>
<td>$R_p=4.95$</td>
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</tbody>
</table>

Figure 3: The contour plot of the scattering intensity around (a) (2,0,0), (b), (0,2,0), and (c) (1,1,0) nuclear reflections. The panel (d) is the schematic view of the domain structure.

and (1,1,0) peak. The splitting of the peaks can be explained in terms of four domains as schematically shown in Fig. 3(d). On the other hand, the (0,0,2) reflection showed no change throughout the structural transition, namely all domains have a common c*-axis.

The angles $\alpha'$, $\beta'$, and $\gamma'$ are plotted as a function of temperature in Fig. 4 (a). The angles exhibit a clear jump with a hysteresis of 5 K and a two phase coexistence in the temperature range of 20 K. Figure 4 (b) indicates the volume fraction of the triclinic phase.

The volume fraction showed a very sharp jump with a hysteresis of 5 K. These behaviors are clear nature for the first-order transition.

References
Modulated Structure of the Composite Crystal \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2\)

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The compound known as \(\text{Ca}_3\text{Co}_4\text{O}_9\)\(^1\), \(^2\), \(^3\) has recently attracted much attention as a potential candidate for a thermoelectric material. However, the precise composition and the crystal structure have not yet been fully studied due to its incommensurate structure. We have revealed that the compound is classified as a composite crystal and its structure formula should be expressed as \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2\). In this report, we present the structure parameters of the compound on the basis of a four-dimensional superspace group approach using powder neutron diffraction data.

Neutron powder diffraction (ND) data were collected at 293 K by means of HRPD diffractometer (\(\lambda = 1.8226\) Å) installed at the JRR-3M reactor in JAERI. The ND data were analyzed using a Rietveld refinement program PREMOS 91\(^4\) designed for modulated structure analyses. The observed electron diffraction patterns demonstrated that the compound consists of two bace-centered monoclinic subsystems with different \(b\)-axis lengths. The superspace group of \(\text{Cn}(01p0)\) was then adopted on the basis of the observed systematic absences.

The observed, calculated and difference profiles for the ND data. Short vertical lines below the patterns indicate the peak positions of main (upper) and satellite (lower) reflections for the two subsystems. A satisfactorily good fit was achieved and the final \(R_{wp}\) factor was 10.6 %.

Figure 1 shows the observed, calculated and difference profiles for the ND data. Short vertical lines below the patterns indicate the peak positions of main (upper) and satellite (lower) reflections for the two subsystems. A satisfactorily good fit was achieved and the final \(R_{wp}\) factor was 10.6 %.

Figure 2 shows the fundamental structure (atomic site modulations are not shown for clarity) viewed in perspective from the \(b\)-axis. The closed circles represent the Co atoms, and the shaded and open circles are the Ca and O atoms. The fundamental structure consists of a CoO\(_2\) sheet (subsystem 1) and an ordered tripled NaCl-type Ca\(_2\)CoO\(_3\) block (subsystem

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Figure 1: Observed, calculated and difference patterns of the powder neutron diffraction data for \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2\) measured at 293 K.
2), stacked parallel to the c-axis. The CoO2 sheet is composed of edge-shared CoO6 octahedra forming a triangular lattice as seen in the CdI2-type structure. No substitution of the Ca sites with Co in the [Ca4CoO3] subsystem was noticed. The most interesting finding is a buckled atomic arrangement in the Ca2CoO3 subsystem. That is due to the x coordinates of the Co2 and O3 atoms in the middle-layer of Ca2CoO3 subsystem being slightly shifted toward -x direction from the center of the regular NaCl-type sites. Lattice parameters were refined to be \(a = 4.8339(3) \text{ Å}, b_1 = 2.8238(2) \text{ Å}, b_2 = 4.5582(2) \text{ Å}, c = 10.8436(7) \text{ Å}\) and \(\beta = 98.14(1)^\circ\). The resulting \(b_1/b_2\) ratio of 0.6195(1) corresponds to the stoichiometry of the sample, [Ca2CoO3]0.6195CoO2.

![Figure 2: The refined fundamental structure of [Ca2CoO3]0.62CoO2 projected in perspective from the b-axis.](image)

In the real structure, however, periodic difference between the subsystems causes atomic displacive modulations. Figure 3 exemplifies the modulation of the Co1-O distance \(d_{\text{Co1-O}}\) plotted against \(t' = -(b_1/b_2)x_2 + x_4 = -0.6195x_2 + x_4\) in the superspace. Any section with different \(t'\) value corresponds to a different phase of the modulation wave in the structure. The Co1-O bond lengths have periodical alteration with the interval of \(t' = 1.0\) because these atoms belong to the [CoO2] subsystem. Despite their large difference in modulation amplitudes, the mean bond distances are in the range of 1.87-2.02 Å.

Both the Co1 and Co2 atoms and their oxygen networks could be responsible for electric conduction. However, strong modulation and long bond distances observed in the Co2-O networks would prevent carrier transfer. A recent band calculation made on \(\gamma\)-Na\(_2\)CoO2 demonstrated that electric conduction occurs between the Co sites directly in the CdI2-type CoO2 layers. 5) Judging from the similarity between \(\gamma\)-Na\(_2\)CoO2 and [Ca2CoO3]0.62CoO2, the electric conduction would mainly occur within the CoO2 sheet in the present compound. The [Ca2CoO3] block can be thus regarded as a charge reservoir which supplies carriers into the CoO2 sheet.

![Figure 3: Co1-O distances, \(d_{\text{Co1-O}}\) plotted against a complementary coordinate, \(t' = -(b_1/b_2)x_2 + x_4 = -0.6195x_2 + x_4\) in the superspace.](image)

References

Diffuse Neutron Scattering from AgBr

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Correlation effects between the thermal displacements of atoms play an important role to explain the oscillatory diffuse scattering in solid electrolytes, AgI and CuI. The correlation effect is specific in solid electrolytes which have large thermal vibrations. In order to obtain the dynamical correlation among atoms in AgBr, diffuse neutron background intensity of AgBr has been measured from 8 K to 450 K using a neutron diffractometer HRPD installed at JRR-3 in JAERI. A powder sample of AgBr in a vanadium container with 10 mm in diameter was used. The incident neutron wave length of 1.823 Å was used. Neutron diffraction data were collected for 1° over the 2θ range of 20° to 150°. Fig. 1 shows the powder diffraction intensities of AgBr at 8 K and 450 K. Several sharp Bragg lines and a large diffuse scattering were observed at 450 K. The peaks of the oscillatory diffuse scattering appear at 2θ~40°, 53° and 98° in Fig. 1. The oscillatory characteristic in the diffuse scattering at 8 K is not clear. The values of thermal parameter $B_{Ag}$ and $B_{Br}$ at 450 K are 4.739 Å² and 3.959 Å², respectively. The values of $B$ at 8 K are about 1/100 of those at 450 K. The temperature dependence of the oscillatory diffuse scattering from AgBr, which was predicted with the correlation effect, was confirmed by the measurement.

Crystal of AgBr is assumed to belong to the rock-salt structure with a space group Fm3m. Silver and bromine atoms occupy 4(a) and 4(b) sites, respectively. The peak positions at 2θ~53° and 98° in diffuse scattering at 450 K in Fig. 1 are related to the reciprocal of the distance between first nearest neighbor atoms. The distance in AgBr is 2.899 Å at 450 K. The main contribution to the oscillatory diffuse scattering of superionic conductors was from the correlation among the displacements of cation and anion atoms. It is suggested that the main contribution of AgBr would be from the correlation among the displacements of silver and bromine atoms. The estimated value of the thermal correlation among AgBr is 0.742. However the peak at 2θ~40° does not appear from the correlation between first nearest neighbor atoms. The peak could be explained by the correlation between second nearest neighbor atoms. The distance between second nearest neighbor atoms (Ag-Ag and Br-Br) is 4.101 Å. The estimated value of the thermal correlation among Ag-Ag and Br-Br is 0.471. The peak at 2θ~40° is almost in agreement with the calculated value. Most influences on diffuse scattering above third nearest neighbor atoms could be disregarded. The value of thermal correlation depends on interatomic distance and crystal structure.

Figure 1: Observed neutron powder diffraction intensity for AgBr at 8 K (broken line) and 450 K (solid line).

原子炉：JRR-3M
装置：HRPD(1G)
分野：中性子散乱（構造）
Neutron Diffraction Study of Sr$_2$YC$_{2}$CoO$_7$

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Crystal structure of Sr$_2$YC$_{2}$CoO$_{6+δ}$ has been analyzed using neutron powder diffraction to compare with that of Sr$_2$YC$_{2}$FeO$_{6+δ}$\textsuperscript{1).} These compounds consist of nanometer-scale sequence of alternating double CuO$_2$ sheets as those in high-$T_c$ superconductors, and (Fe,Co)O$_4$ sheet similar to that in the Sr(Fe,Co)O$_{2+δ}$ magnetic compound with brownmillerite-type structure. Sr$_2$YC$_{2}$FeO$_{6+δ}$ exhibits superconductivity around 50 K when it is annealed under N$_2$ atmosphere and subsequently under O$_2$ atmosphere, while Sr$_2$YC$_{2}$CoO$_{6+δ}$ with the same annealing process does not exhibit superconductivity. Neutron diffraction can distinguish between Cu and Co because the scattering length of Cu differs from that of Co, while X-ray diffraction can hardly do so. Then, we can analyze the mutual substitution of Cu and Co.

Samples were prepared by the solid state reaction of stoichiometric amount of SrCO$_3$, Y$_2$O$_3$, CuO and Co$_3$O$_4$ powders. We prepared three kinds of samples: as-synthesized sample, and the samples which were N$_2$-annealed and oxidized under high oxygen pressure. Neutron powder diffraction experiments were carried out using a high-resolution powder diffractometer, HRPD, installed in JRR-3M. Intensity data were collected at room temperature and then were analyzed using the Rietveld refinement program RIETAN\textsuperscript{(2)} on the basis of the orthorhombic Sr$_2$YC$_{2}$GaO$_7$-type structure model\textsuperscript{(3)}.

Neutron diffraction study indicates that Cu is hardly substituted for Co in Sr$_2$YC$_{2}$CoO$_{6+δ}$, while it is easy to substitute Cu for Fe in Sr$_2$YC$_{2}$FeO$_{6+δ}$ and the N$_2$-annealing suppresses this substitution. Sr$_2$YC$_{2}$CoO$_{6+δ}$ without N$_2$-annealing already has the ordered distribution of the Cu and Co atoms, and this distribution does not change by N$_2$-annealing and oxidation under high oxygen pressure. The $δ$ value does not deviate substantially from unity by the annealing process in all Sr$_2$YC$_{2}$CoO$_{6+δ}$ samples, although the annealing process is very effective on the control of oxygen content, $6 + δ$, in Sr$_2$YC$_{2}$FeO$_{6+δ}$. These results show that enough amount of oxygen can not be supplied onto the CoO$_2$ sheet to exhibit superconductivity in Sr$_2$YC$_{2}$CoO$_{6+δ}$.

The Co and oxygen atoms on the CoO$_2$ sheet have large thermal vibration in all Sr$_2$YC$_{2}$CoO$_{6+δ}$ samples. This indicates that the arrangement of the CoO$_4$ tetrahedra is disordered although the four coordination of the Co atom is stable. The disorder of the arrangement is not also influenced by the annealing process.

References


Crystal Structure Study on Defective Silicalite by Neutron Diffraction

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Zeolites are used in the industry as catalysts. Performance of catalysts is strongly related to the crystal structure and the concentration of point defects in the zeolite crystal, because the point defects in the crystal often behave as active sites for reaction. Artioli et al.1) determined the crystal structure of silicalite by neutron diffraction experiments. However, information for concentration of the defect is insufficient. Therefore we study the crystal structure and defect concentration of silicalite with neutron diffraction measurements.

Silicalite powder samples were stirred in D_{2}O water at 353 K for H-D exchange. IR measurement of this sample was carried out for checking the H-D exchange. After this checking the fully deuterated sample was dehydrated at 673 K under He-gas flow. The sample was sealed in a special quartz tube without air exposure. The neutron powder diffraction pattern of the deuterated silicalite sample was observed with the High-Resolution Powder Diffractometer (HRPD) installed at the JRR-3M in JAERI.

Measurements were carried out at low temperature of 15 K in order to minimize the diffraction effect due to thermal vibration of atoms. Data were collected between 5 deg. and 150 deg. in diffraction angle with an equal step of 0.05 degree. Diffraction intensities of deuterated silicalite were obtained by subtracting the diffraction data of the blank quartz-tube(empt) from that of the sample.

A typical diffraction pattern of deuterated silicalite is shown in Fig. 1. We refined the observed data with a Rietveld method by using a RIETAN-2000 program package. Obtained results of the refinement are rather good. More detailed analysis of the diffraction data is being conducted in the current studies.

References

![Graph](image_url)

Figure 1: A typical diffraction pattern of deuterated silicalite measured at 15 K.
Magnetic Properties of CaMn$_{1-x}$Ru$_x$O$_3$

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Numerous studies have been reported in recent years for perovskite manganites because of their interesting properties such as the CMR (colossal magnetoresistance) effect. One of the compounds, CaMnO$_3$, has an orthorhombic crystal structure (space group Pnma) and is an insulating antiferromagnet below a Neél temperature ($T_N$) of about 130 K. Recently, it was found that ferromagnetism and metallicity are developed for CaMn$_{1-x}$Ru$_x$O$_3$ where the Mn ion is substituted by Ru in CaMnO$_3$. CaRuO$_3$ ($x=1$) has the same Pnma structure and exhibits metallic conductivity with a tendency toward magnetic order at low temperatures. The Curie temperature reaches a maximum value of 210 K for CaMn$_{0.6}$Ru$_{0.4}$O$_3$ ($x=0.4$). In this work, magnetic properties of this compound have been investigated.

The sample was prepared by the solid-state reaction in air. Magnetization measurements revealed a ferromagnetic transition at around 210 K. Figure 1(a) shows powder neutron diffraction patterns at room temperature measured with a high resolution powder diffractometer (HRPD). Though the previous X-ray diffraction measurements$^1$ led to an orthorhombic Pnma (No.62) structure, the present Rietveld analysis using the program RIETAN-2000 provided a better result for a monoclinic structure of $P2_1/n$ (No.14) with the lattice parameters of $a=5.3168(2)$, $b=5.3974(2)$, $c=7.5548(3)\AA$, and $\beta=89.977(9)^{\circ}$.

Figure 1(b) shows an experimental result at 4 K. It is seen that some magnetic peaks, such as that pointed by the arrow, are developed at low temperatures. From a preliminary analysis, this pattern could be fitted assuming ferrimagnetic spin alignment of the Mn and Ru moments with 1-3 $\mu_B$. In the previous work,$^1$ coexistence of ferromagnetic and antiferromagnetic phases was observed in the same sample. A further detailed analysis for the present data is in progress.

![Figure 1: Neutron powder diffraction patterns of CaMn$_{0.6}$Ru$_{0.4}$O$_3$ at (a) room temperature and (b) 4 K. The arrow shows a representative magnetic Bragg peak.](image)

References

Jahn-Teller distortion and orbital ordering in $\text{La}_{0.875}\text{Ca}_{0.125}\text{MnO}_3$

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Much attention has been paid to the rich phase diagram of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A}=\text{Ca}$ and $\text{Sr}$) system$^{1,2}$). There is the interplay between the super exchange and the double exchange interactions controlled by the orbital degree of freedom$^3)$. We have studied the Ca-doped manganites in the ferromagnetic insulating region ($0.08 \leq x \leq 0.18$) to identify the low temperature phase detected by the ultrasonic measurements$^4)$. In this study, we report the temperature variation of Mn-O bond lengths of $\text{La}_{0.875}\text{Ca}_{0.125}\text{MnO}_3$.

Polycrystalline samples of $\text{La}_{0.875}\text{Ca}_{0.125}\text{MnO}_3$ were prepared by a solid state reaction. Stoichiometric mixture of $\text{La}_2\text{O}_3$ (99.9%), $\text{CaCO}_3$ (99.9%) and $\text{Mn}_2\text{O}_3$ (99.9%) powders was pressed into pellets and calcined in air at 1273 K for 48 h and 1773 K for 36 h with an intermediate grinding. The Curie temperature $T_c$ was determined to be 170 K by the magnetization measurement under magnetic field of 50 Oe$^{5})$. Neutron diffraction measurements were carried out at several temperatures between 10 K and 293 K using HRPD ($\lambda =1.8196 \text{Å}$). The measured intensities were analyzed by a program RIETAN$^6)$, assuming the space symmetry Pmab (No.62) and collinear spins at Mn sites below $T_c$. The longest unit cell edge was assigned to the b-axis.

There is good agreement between the observed and calculated intensities in all data sets. As an example, the observed, calculated and difference profiles at 10 K were shown in Fig.1. Figure 2 shows the temperature variation of the Mn-O bond lengths. Mn-O(1) monotonically decreases with decreasing temperature, while small elongation and contraction were observed for Mn-O(2) and Mn-O(2') below 100 K, respectively. Such changes lead to the breathing type Jahn-Teller distortion of MnO$_6$ octahedra in the a-c plane, suggesting partial ordering of $3x^2-r^2/3z^2-r^2$ orbitals of Mn$^{3+}$. This distortion occurs well below $T_c$.

**Figure 1:** Observed, calculated and difference neutron diffraction profiles of $\text{La}_{0.875}\text{Ca}_{0.125}\text{MnO}_3$ at 10 K.

**Figure 2:** Temperature variation of Mn-O bond lengths in $\text{La}_{0.875}\text{Ca}_{0.125}\text{MnO}_3$.

References

Static Structure Factor and Self-diffusion Coefficient of Molten Tin in the Wide Temperature Range

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The understanding of diffusion phenomena and its temperature dependence in liquids both in microscopic and macroscopic point of view is one of the most difficult problem of condensed matter physics because the temperature dependence of many body interaction should be taken into account. Especially, in the case of group IVB elements such as Pb, Sn, Ge and Si, the electron-ion interaction induces the complicated interatomic interaction and liquid structures.

Recently, the evaluation scheme of effective pair interatomic potential directly from the static structure factors is proposed by Reatto et al.1 This method solves the inverse problem by the predictor-corrector method with the application of molecular dynamics simulation. Munegi et al.2 reported that the effective pair interatomic potential can be obtained from static structure factors with a high accuracy in combination with the large scale molecular dynamics simulation and the accurate experimental S(Q). In this study, the effective potential of liquid tin was calculated by the inverse problem scheme and the diffusion coefficient was evaluated from the molecular dynamics simulation in which the obtained effective pair potential is applied. The calculated self-diffusion coefficient was compared with the experimental one measured under low gravity condition.

The static structure of liquid tin was measured with the use of neutron scattering and small angle X-ray scattering. The low Q region (0.4 Å⁻¹ - 2.0 Å⁻¹) of S(Q) was measured carefully by the small angle X-ray scattering at the temperature of 573 K, 773 K and 1073 K. The S(Q) in the high Q range (1.5 Å⁻¹ - 10.4 Å⁻¹) was measured by the neutron scattering at the temperatures of 573 K, 773 K, 1073 K 1473 K 1673 K and 1873 K respectively. The neutron scattering experiment was performed with the use of triple axis spectrometer (TAS-1). The fused silica ampoule was used for the experiments at temperatures lower than 1073 K. For the experiments at the temperature higher than 1073 K, the glassy carbon ampoule was developed. The sample was placed in a high temperature radiation furnace with Nb foil heating element (at the highest 2100 K). The counting time at each temperature was typically 8-12 hours. Neutron and X-ray scattering data were treated using a standard procedure, which includes subtraction of cell intensities and correction for absorption.

The effective pair interatomic potential of liquid tin was evaluated with the use of solution scheme of inverse problem from the static structure factor which was measured by the small angle X-ray and the neutron scattering. In this scheme, the predictor-corrector method is applied to solve the effective pair potential, which is the combination of the integral equation theory and the computer simulation. The effective pair interatomic potentials were calculated by the inverse problem scheme at 573K, 773K and 1073K respectively at which the structure factors of liquid tin in the low Q range were measured. The convergence of evaluation procedure was quite well and the molecular dynamics simulation applying the obtained interatomic potential well reproduces the experimental static structure.
factor at each temperature, as shown in Fig.1. The obtained interatomic potential at 1073K is applied also to the molecular dynamics simulation at higher temperature than 1073K. Good agreements were found between molecular dynamics simulations and experiments.

Figure 1: The static structure factor of liquid tin.

The self-diffusion coefficient was evaluated from the molecular dynamics simulation, in which the obtained interatomic potential was applied, from the slope of mean square displacement. In the case of liquid tin, the self-diffusion coefficient was measured with high accuracy with the use of low gravity in space in the wide temperature range. The self-diffusion coefficients calculated from the molecular dynamics simulation are shown in Fig.2 together with the experimental data which were measured both under normal gravity (1g) and low gravity. The low gravity circumstances have been known to be ideal for the measurements of diffusion coefficient of melts with high melting temperatures due to the absence of convection. As a result, an agreement between low gravity data is rather excellent. On the other hand, diffusion data on the ground differs each other considerably depending on data sources probably due to the convection, though data of Bruson et al. is rather close to the low gravity data.

The obtained self-diffusion coefficients from the present molecular dynamics simulations are extremely in good agreement with the self-diffusion data under low gravity in the wide temperature range. The quantitatively good agreement between the present diffusion coefficient and the microgravity data indicates that this scheme is valid for the quantitative prediction of the self-diffusion coefficient in liquids with shoulders, such as liquid tin, by using the pair potential derived from the $S(Q)$ of liquids.

Figure 2: Self-diffusion coefficient of liquid tin.

References
Lattice dynamics of tetragonal PbTiO$_3$

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PbTiO$_3$ occupies an important position in ferroelectric perovskites. First, PbTiO$_3$ undergoes a single phase-transition from a cubic to tetragonal ferroelectric phase at $T_C=763$ K. Cohen$^1$ pointed out that the covalent nature of Pb 6s and O 2p states is responsible for the stability of the tetragonal phase. Second, PbTiO$_3$ is the end member of relaxor ferroelectrics (1-x)Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-xPbTiO$_3$ (PZN-PT) system. The introduction of $x=0.1$ PbTiO$_3$ enhances piezoelectric and dielectric constants. Recent neutron scattering studies for PZN show that the low-lying TO phonon branch drops sharply near the Brillouin-zone center. The limited data for PbTiO$_3$$^4$, however, does not permit a detailed comparison of the lattice dynamics of PbTiO$_3$ and PZN. In this report, we present the phonon dispersion relations for the tetragonal PbTiO$_3$ measured at room temperature.

Figure 1 demonstrates the difference of phonon dispersion relations between PbTiO$_3$ and PZN. A large splitting between the zone-center TO phonon modes in PbTiO$_3$ is consistent with Raman scattering$^5$ and dielectric constant measurements$^6$. The $\Sigma_2$ TO phonon frequency exhibits the maximum at [0.3 0.3 0], whereas the $\Delta_1$ TO phonon frequency increases toward [1 0 0]. The low-frequency TO mode at the M point corresponds to an oxygen octahedron rotation along the z axis. On the other hand, the isotropic TO phonon dispersion relations in PZN are mainly due to the compositional disorder at the B site. PbTiO$_3$ and PZN have the isotropic dispersion relations for the TA phonon branches. The TA phonon frequencies for PbTiO$_3$ are higher than the values for PZN in the entire zone.

In PZN the well-defined TO peak is absent around the zone center. For PbTiO$_3$ the low-lying TO phonon mode are expected to be temperature dependent. High-temperature neutron scattering experiments are now progressing.

References
Structural Transition in LiErO$_2$

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The crystal structure of ternary lithium oxides, LiRO$_2$ ($R$ = rare earths), are grouped into four type structures ($\alpha, \beta, \gamma, \delta$-type). A ternary lithium oxide, LiErO$_2$, has a tetragonal $\alpha$-type structure (space group: $I4_1/amd$) at room temperature. Its magnetic susceptibility and specific heat showed that a first-order phase transition and an antiferromagnetic transition occurred at ca. 200 K and 4.2 K, respectively).

In order to determine the crystal structures at low temperatures, powder neutron diffraction patterns of LiErO$_2$ were measured at 150 and 250 K using a High Resolution Powder Diffractometer (HRPD) in the JRR-3M reactor with a neutron incident wave length ($\lambda = 1.82268$ Å). The Rietveld analyses were performed with the neutron diffraction data.

Figure 1 shows the observed and calculated diffraction patterns. The crystal structure at 250 K was determined to be the tetragonal $\alpha$-type structure with the space group, $I4_1/amd$ ($a = 4.4291(2)$ Å and $c = 10.2210(5)$ Å; $z = 4$). Data collected at 150 K indicates that the crystal structure at this temperature transforms from $\alpha$-type to $\beta$-type structure. The Rietveld analysis of the crystal structure at 150 K using a monoclinic $\beta$-type structure with the space group, $P2_1/c$ (No. 14), gives a good agreement with experimental data ($a = 6.0761(6)$ Å, $b = 6.1617(4)$ Å, $c = 6.1546(6)$ Å, and $\beta = 118.479(4)^\circ$; $z = 2$). The crystal structure at 250 K and 150 K are illustrated in Fig. 2.

References


Figure 1: Powder neutron diffraction patterns of LiErO$_2$ at (a) 250 K and (b) 150 K.

Figure 2: The crystal structure of LiErO$_2$ at (a) 250 K and (b) 150 K.
Measurement of internal strain in Si single crystal by neutron diffraction method

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The monochromator of RESA in JRR-3M of Japan Atomic Energy Research Institute is Si(311) single crystal. This monochromator has been bending with the piano wire. The intensity of neutron is increased with this bend mechanism. However, the internal strain of monochromator bent with this mechanism has not been examined in detail until now.

Then, we gave the bend load to the Si(311) single crystal with a piano wire, and examined the distribution of internal strain. This single crystal is 200mm in length, 20mm in height, and 5mm in thickness. This shape was processed by the wire electrical discharge machine.

Fig. 1 shows the measurement method of bend mechanism. The slit used by this experiment is 10mm in length, and 0.5mm in width. The wavelength is 0.209613nm. Four kinds of the applied strain (200, 300, 400, and 500 μ strain) were added to the sample. Figure 2 shows the relationship between intensity and applied strain. As the intensity increases, the applied strain increases. However, the change of intensity between 400 and 500 μ strain is little. Figure 3 shows the relationship between distribution of internal strain and applied strain. Like Fig. 2, the change of internal strain between 400 and 500 μ strain is little. The internal strain varies a little for the applied strain of 200 and 300 μ strain. However, the applied strain of 400 and 500 μ strain is constant. This phenomenon influences the change of intensity in Fig. 2. In other words, the intensity keeps increasing until the internal strain becomes uniform. Moreover, the intensity studies when the internal strain becomes uniform, and the single crystal causes destruction afterwards.

Figure 1: Bend mechanism and measurement method

Figure 2: The relationship between intensity and applied strain

Figure 3: The relationship between distribution of internal strain and applied strain
Stress Measurement in Thin Steel Plate by Means of Neutron Image Plate

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Stress Measurement using neutron diffraction technique is a useful tool for the purpose of the investigation on the behavior of practical materials, especially that of inside material. A lot of researches have been made so far on both fundamental matters and application problems. In the conventional neutron stress measurement method, a zero dimensional neutron detector is generally used. A use of two dimensional detector such as, for example, a neutron image plate enables us to obtain huge amount of diffraction data at a stretch. The feature of a lot of data expects us more precise and detailed stress analysis. The present study was made to find the possibility of the neutron image plate for the stress measurement, and as the first step a tensile stress measurement for thin steel plates was performed.

The material used was steel, JIS S50C. The specimen was processed to have a geometry of 150mm length, 15 mm width and 2 mm thickness. It was then heat-treated for stress release under the condition of 650 deg C for 30 mins. For an application of stress measurement, a steel plate jointed on a stainless steel using self-heated sintering method (SHS method) with mixed powder of nickel and aluminum. the thickness of the steel was 2 mm as same as the above tensile test. The residual stress in the steel emerged after the joint process was measured by the present neutron image plate method.

Fig.1 shows the relation between the stress obtained by the present method and applied stress. The stress measured was calculated by means of so-called the coso method. The applied stress was calculated multiplying the strain detected by the strain gauge method and the Young’s modulus of the specimen. It can be seen that the slope of the line is about 0.8 and the intersection which means the initial stress of this method is about -450MPa. The initial stress in the figure was caused by the difference of absorption of each diffracted beam from each deepness of the specimen. Since the penetration depth of the neutron beam is generally large than that of x-ray beam, a theoretical understanding on such initial stress is necessary for the stress measurement. As a simple approach, we used Fig.1 as a calibration curve for a steel having thickness of 2 mm in order to the residual stress measurement of SHS sample.

![Graph: Stress obtained with IP, MPa vs Applied stress, MPa]

Figure 1: The relation between the stress obtained by the present method and applied stress.

Fig.2 shows the neutron diffraction pattern obtained from the SHS sample (211 diffraction from the steel layer). The stress was calculated from the diffraction image through the same method as the above tensile test), which was also plotted in Fig.1. As the stress obtained in this case also involved the initial stress, it should be corrected to obtain
the residual stress in the SHS sample. The stress at the transverse axis dropped from the cross point shown in Fig.1 can be estimated as the residual stress in the SHS sample, because the initial stress was removed from the raw data. The stress resulted in about 35 to 50 MPa, which is reasonable from the prediction of thermal expansion coefficient between the materials of each layer of SHS sample.

The present method is useful for the residual stress measurement of thin plate with higher accuracy. This is also applicable for layers put into other materials as the very deep penetration of neutron beams. This method has also possibility to be able to evaluate stress distribution in practical materials through the analysis of diffraction image diffracted from allover the depth of the material using the stress gradient analysis developed in the field of the x-ray stress analysis. The effect of the initial stress discussed above should be considered for this purpose, which is the authors’ next main theme.

Figure 2: The neutron diffraction pattern obtained from the SHS sample (211 diffraction from the steel layer).
Neutron diffraction study for locating proton in cryptomelane-type MnO$_2$ crystal

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Manganese dioxides form a family of the typical mixed-valence compounds and are represented by the chemical composition (A,H)$_x$MnO$_{2-x}$. H$^+$ is responsible for cation exchange, being variable with the extent of Mn$^{3+}$ substitution. The cation uptake mechanism depends on the crystal structure and the preparation routes, showing different degree of cation exchange and redox process. A cryptomelane-type manganic acid (CMA) having the 2 x 2 tunnel structure with the diameter of 0.28 nm has been studied by chemical and thermal analyses, ESCA, ESR, MASNMR, XRD and chemical thermodynamics of cation exchange.1, 2, 3) Very high selectivity for K$^+$, Rb$^+$, and Ba$^{2+}$ ions can be interpreted on a basis of cation exchange with the H$^+$ in the tunnel. The objective of the present work was to locate H$^+$ ions responsible for the cation exchange.

Samples were prepared by mixing MnCO$_3$ and BrOK at 8 and 20 mol % as the K$^+$ content and heating at 700 °C. Then, K$^+$ in the product was leached for H$^+$ by conc HNO$_3$. These H$^+$ form CMAs were immersed in LiOH to prepare the Li$^+$ form, and then Li$^+$ was removed by contact with DNO$_3$ solution in D$_2$O. DNO$_3$ was prepared by percolating DCI solution in the NO$_3^-$ form Dowex 1-X8 column. D$^+$ form samples were dehydrated by heating at 60 °C overnight. Measurements were conducted by means of High Resolution Powder Diffractometer (HRPD) installed at JRR-3M in JAERI. Figure 1 shows a diffraction pattern of deuterated cryptomelane-type MnO$_2$ measured at 10 K. We continue Rietveld refinement for this diffraction pattern by using a software package of RIETAN-2000 in current studies.

References

Figure 1: Diffraction pattern of deuterated cryptomelane-type MnO$_2$ measured at 10 K.
Neutron Powder Diffraction Study on BaF$_2$ at High Temperature

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Barium fluoride is a CaF$_2$-type crystal structure. Since CaF$_2$-type crystals have a order-disorder transition at high temperature of 80% of its melting temperature, this crystal became a super ionic conductor above the transition temperature. This transition temperature is closely related to the thermal vibration amplitude of fluoride atoms. To clarify the thermal vibration of BaF$_2$ at high temperature, we measured temperature dependence of intensities of diffraction lines of BaF$_2$ powder.

Neutron diffraction experiments were carried out by using High-Resolution Powder Diffractometer (HRPD) installed at JRR-3M in JAERI. BaF$_2$ powder sample was contained in a vanadium sample holder that its dimension was 50 mm height and 8 mm diameter. This sample holder was mounted in a ILL high temperature furnace. Measurement temperatures were 295 K, 650 K, 600 K, 850 K, 1000 K, 1150 K and 1350 K. Wavelength of used neutrons was 1.16 Å.

Diffraction patterns of BaF$_2$ measured at 295 K and 1350 K are shown in Fig. 1. From this figure one can see that the intensities of diffraction lines above 120 deg. are weakened. These diffraction patterns were refined by Rietveld method using a software package of RIETAN-2000. Results of refinements based on CaF$_2$ model were very good for all measured temperature except 1350 K. Temperature dependence of thermal parameter related to thermal vibration amplitude is shown in Fig. 2. Open and solid circles indicate the thermal parameter of Ba ion and F ion, respectively. Temperature dependence of thermal parameter for Ba ion has a linear relationship with temperature. While the thermal parameter of F ion increases with increasing temperature above 500 K. Since Ba-ion occupants a m3m symmetry site that has an inverse symmetry, it is well understood that thermal vibration of Ba-atom is harmonic. While anharmonic thermal vibration of F-atom became strong above 500 K.
Neutron Diffraction Study on Metane-Ethane Hydrate

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Clathrate hydrates are inclusion compounds where a variety of guest molecules can be occluded in a host lattice formed from an ice-like hydrogen bonded network. The host lattice forms in such a way that polyhedral cavities are created. Two common atomic arrangements that result are cubic and designated as structure I and structure II. Structure I consists of two types of polyhedra, the smaller polyhedra are formed from twelve pentagonal faces and the larger polyhedra are formed from twelve pentagonal faces and two hexagonal faces. Structure II also consists of two types of polyhedra, similar to structure I the smaller polyhedra are formed from twelve pentagonal faces, however, the larger polyhedra are formed from twelve pentagonal and four, instead of two, hexagonal faces. To clarify the structure of metane-ethane hydrate, we conducted neutron diffraction studies.

Figure 1: Comparison of the observed neutron powder diffraction data (+) with the calculated pattern (solid line) and corresponding difference pattern based on the 30 variable refinement.

Figure 2: Structure of C₃H₈ hydrate based on the refined atomic coordinates.

Neutron powder diffraction data were collected on the High Resolution Powder Diffractometer (HRPD) at the JRR-3M research reactor at JAERI. Wavelength of neutrons was 1.1635 Å. For temperature control a closed-cycle He refrigerator equipped with two temperature sensors was used. Samples in sealed vanadium cans were removed from storage in N₂(l) and immediately attached to the precooled cold-tip of the refrigerator under a glovebag filled with He gas. During this process the sample did not warm above 100K. Diffraction patterns were collected at 12, 40, 100, 130, 160, 190, 220, and 250 K.

The software package, GSAS, was used for the Rietveld refinements with a rigid body constraints. Structural refinements on the neutron powder diffraction data confirmed that hydrate samples synthesized with propane gas crystallize as structure type II hy-
hydrate. Figure 1 shows the comparison of the observed neutron powder diffraction pattern with the calculated structural model. There were no extra diffraction peaks indicating the presence of ice. The high back is due to incoherent scattering from the H atoms associated with the guest molecule. The structure type II hydrate at 12 K shown in Figure 2.

Figure 3: The atomic displacement parameters for the C$_3$H$_8$ guest molecules in the eight large cages of structure II compared to the small cage guest molecules (CH$_4$ only) and large cage guest molecules (CH$_4$ and C$_2$H$_6$) in mixed methane-ethane hydrate that crystallizes as structure II and the CH$_4$ molecules in both the small and large cages of structure I methane hydrate.

The atomic and molecular displacement parameters, U, for the D and O atoms in the host lattice and the guest C$_3$H$_8$ molecule are also determined. The atomic and molecular displacements help to describe the positional disorder found in gas hydrates. The propane molecule has similar positional disorder as the D and O atoms in the host lattice as evidenced by the similar U(T=0) intercepts. Figure 3 compares the molecular displacement parameters for the C$_3$H$_8$ molecules in the large cages of the structure II propane hydrate with the CH$_4$ molecules in both the large and small cages of the structure I methane hydrate and the CH$_4$ molecules in the small cages of the structure II mixed methane-ethane hydrate. Figure 3 suggests that this mixed cage has more positional disorder, most likely due to the sharing of different guest molecules, than small or larger cages occupied by a single guest molecule. Figure 3 also indicates that the guest molecules in the large cages have more positional disorder than the guest molecules in the small cages. The large error for the C$_3$H$_8$ molecular displacement parameters are most likely due to the shape of the molecule and the resulting rigid body. Figure 4 shows the methane, ethane, and propane molecules and the corresponding rigid bodies for comparison.

Figure 4: Methane, ethane, and propane molecules and the corresponding rigid bodies.

Atomic coordinates and atomic and molecular displacement parameters of the structure II propane hydrate have been determined from Rietveld refinements of neutron powder diffraction data collected at 12 K. The C$_3$H$_8$ molecules, located in the eight larger polyhedral cavities of a deuterated host lattice, were described using rigid-body constraints. From temperature dependence of lattice parameters, the instantaneous CTE was calculated and compared to that of a structure I hydrate, prepared with only CH$_4$ as the guest molecule, and a structure II hydrate, prepared with a mixture of CH$_4$ and C$_2$H$_6$ as the guest molecules, and D$_2$O ice from the literature. The thermal expansion behaviour of the three hydrates is similar and does not show the negative thermal expansion behaviour displayed by D$_2$O ice. The temperature dependence of the atomic and molecular displacement parameters suggests that the C$_3$H$_8$ guest molecule has similar positional disorder to the D and O atoms of the host lattice and to other gas hydrates formed from only one type of guest molecule.
Neutron Diffraction Study on Trimethylene Oxide Deuterate

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Trimethylene oxide (TMO) hydrate is of great interest because it forms structure I and II hydrate depending on stoichiometry. To clarify the crystal structure of two different types, TMO deuterates were studied with a neutron diffraction technique that was well suited for studying materials composed of light element. TMO deuterates were prepared by mixing TMO and deuterium oxide, and these solutions were added drop wise to vanadium cans suspended in liquid nitrogen, respectively. Each can was then capped and placed in to a freezer at 240 K for two weeks for annealing.

Neutron diffraction experiments of TMO deuterates were conducted by High-Resolution Powder Diffractometer (HRPD) installed at JRR-3M in JAERI. Diffraction data were collected at 10, 40, 70, 100, 130, 160, 190, 220 and 250 K. Wavelength of used neutrons was 1.1635 Å.

(GSUS) software program. Figure 1 shows a diffraction pattern of the structure-II of TMO deuterates measured at 40 K. In this figure, solid line indicates the result of Rietveld refinement.

Figure 1: Diffraction patterns of structure-II TMO deuterates measured at 40 K.

Diffraction patterns were analyzed using the General Structure Analysis System (GSAS) software program. Figure 1 shows a diffraction pattern of the structure-II of TMO deuterates measured at 40 K. In this figure, solid line indicates the result of Rietveld refinement.

An illustration of crystal structure of the structure-I TMO deuterate is shown in Fig. 2. From these measurements and analysis, it is found that structure-I TMO deuterate exhibits a structural transition above 146.5 K attributed to a change in motion of the guest molecules. The motion could be an additional degree of freedom representing rapid rotation and/or reorientation.

Figure 2: Crystal structure of structure-I TMO deuterate at 40 K (a) and high temperature (b). Carbons 1 and 3 closest to hexagonal face at 40 K. At higher temperature these carbons turn inward.
The Use of Rigid Body Constraints in Rietveld Refinements of Neutron Diffraction Data of Clathrate Hydrate


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A characteristic feature of the clathrates is the rotational disorder of the guest molecules. The rotational disorder is dynamics and persists even to low temperature. Complete freezing out of the rotations of guest molecules has not been observed in any case.

Rietveld refinement of neutron powder diffraction data is a well established approach to determine crystal structure of many materials. In practice, extraction of as much of this information as possible requires high quality diffraction data and particular attention to details of the refinement model to accommodate the intrinsic disorder of the clathrate and rotational disorder of the guest molecules. The rigid body formalism is a well established that can be used to model the rototational disorder of the guest molecules in the Rietveld refinement method.

Figure 1: Temperature dependence of the atomic and rigid body displacement parameters for CO2 hydrate.

Figure 2: Root mean-square displacement amplitude of the disordered CO2 rigid body occupying the large case of CO2 hydrate at 100 K.

Neutron powder diffraction data were collected as a function of temperature for hydrates of methane, carbon dioxide, tetrahydrofuran and trimethylene oxide by High Resolution Powder Diffractometer(HRDPD) installed at JRR-3M. Wavelength of neutrons was 1.1635 Å. These diffraction data were refined by Rietveld method using the General Structure Analysis System(GSAS) software. Figure 1 shows the resulting root-means square displacement probability of the large cage guests in the carbon dioxide hydrate, and Fig. 2 shows the root-means square displacement of CO2 rigid body in the small and large cages as compared to the atoms making up the host lattice.

The temperature dependence of the root-means square displacement can provide a measure of the positional disorder of the guest molecules in its cage, and can be further correlated with dynamical pictures given by quasi-elastic neutron scattering method.
Structure Study on Tetrahydrofuran Deuterate by Neutron Powder Diffraction


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Studies of natural gas hydrate have been motivated by their potential as an energy source and have dominated research interests in the class of water-based inclusion compounds known as clathrate hydrates. However, numerous experimental and theoretical studies of tetrahydrofuran (THF) hydrate and other easily-synthesized clathrate hydrates have made a significant contribution to the state of knowledge of the crystal structures and guest-host/guest-guest interactions.

Crystal structure of the THF-deutrate and its temperature dependence were studied with neutron diffraction measurements at 7, 75, 140, 205 and 265 K using High-Resolution Powder Diffractometer (HRPD) installed at the JRR-3M reactor hall. The diffraction data were refined by Rietveld method using the GSAS software program.

Figure 1: Diffraction pattern of THF deutrate measured at 265 K. Refinement result indicates by a solid line.

Figure 2: Temperature dependence of the lattice parameter for THF deutrate from this study. The error bars are smaller than the symbols themselves. For comparison, lattice parameters on THF hydrate obtained from the kiterature are plotted. Diamond–von Stackelberg and Meunten; square-Bertie and Jacobs; triangle–Sargent and Calvert.

Comparison, lattice parameters on THF hydrate obtained from the kiterature are plotted. Diamond–von Stackelberg and Meunten; square–Bertie and Jacobs; triangle–Sargent and Calvert. From the temperature dependence of the lattice parameter, it is found that the thermal expansivity of THF deutrate was shown to be greater than that of ice Ih in the same temperature range, as observed in previous studies of other clathrates. From 7 to 140 K, the volume of the small cage decreases slightly and that of the large cage increases, and between 140 and 205 K the trend is reversed.

References

原子炉: JRR-3M 装置: HRPD(1G) 分野: 中性子散乱 (構造)
1. Neutron Scattering  2) Magnetism
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Spin-Wave Excitations in the Metallic Ferromagnetic State of the CMR Manganite Sm$_{0.55}$Sr$_{0.45}$MnO$_3$

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In the colossal magneto-resistive (CMR) phenomena of manganites, several degrees of freedom, i.e. lattice, charge/orbital and spin interplay and as the result many interesting properties appear. Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ is a typical CMR compound showing a drastic metal-insulator transition at the Curie temperature $T_C \approx 130$ K. [1] In order to reveal the important role of magnetism, we performed an inelastic neutron-scattering (INS) study, particularly, on the spin-wave excitations in the metallic and ferromagnetic state. A cylindrical single crystal (0.4 cc) was mounted on the triple-axis spectrometers TOPAN and HET at JRR-3M. We succeeded in establishing the ferromagnetic dispersion along [ξ, 0, 0] throughout the cubic Brillouin zone ($\Gamma \to X$). In the small-$q$ region, the spin-wave excitation is isotropic and follows the ferromagnetic $q^2$-proportionality (the left inset of Fig. 1). However, the dispersive relation is remarkably suppressed beyond the half point toward $X$. The data points over the entire zone are well explained by applying a 3D Heisenberg model with exchange interactions up to fourth neighbour ($J_1 = 0.82$ meV, $J_4 = 0.49$ meV and $J_2 = J_3 = 0$, the curve in Fig. 1). The dominant spin interaction is, therefore, parallel to the linear Mn-O-Mn bonding axes with the spin-spin distances of $a_{ab}$ and $2a_{ab}$. The result strongly suggests the anisotropic Mn orbitals extending along the cubic ridge direction. Upon raising temperature, the collective excitations at $X$ point suddenly dissipate at $T_C$ (the right inset of Fig. 1). It is newly found that the spectral weight transfers to the quasielastic scattering and connects to the diffuse component with the antiferromagnetic propagation vector $Q = (1/2, 0, 0)$. [2]

Combined with other experiments from the X-ray [3] and Raman scattering [4], the spin dynamics in Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ should connect intimately to the directional orbitals of $e_g$-electrons.

References
In 1996 Isobe and Ueda reported the existence of the spin-Peierls (SP) transition at \( T_{\text{SP}} = 35 \text{ K} \) in inorganic \( \text{NaV}_2\text{O}_5 \) [1]. In contrast to the first inorganic SP system \( \text{CuGeO}_3 \) the temperature dependence of the magnetic susceptibility for \( T > T_{\text{SP}} \) can be well described by the theoretical Bonner-Fisher curve with \( J = 560 \text{ K} \) for a uniform \( S = 1/2 \) chain. The presence of superlattice reflections were confirmed at \( h+1/2, k+1/2, l+1/4 \) for \( \text{NaV}_2\text{O}_5 \) by X-ray diffraction [2]. Yoshihama et al. confirmed the existence of the magnetic excitation gap of 9.8 meV at \( T = 7 \text{ K} \) by inelastic neutron scattering [2,3]. More recently the crystal structure of \( \text{NaV}_2\text{O}_5 \) at room temperature was found not to correspond to the space group \( P2_1/nm \) with two kinds of \( V \) sites with \( V^{4+} \) and \( V^{5+} \), as originally thought, but a \( Pnma \) structure with only one site of \( V^{4+} \) [4]. It is now believed that the transition of \( \text{NaV}_2\text{O}_5 \) at 35 K is related the onset of a charge-ordered phase and not a spin-Peierls transition. This low-temperature phase has a singlet ground state below 35 K.

The inelastic neutron scattering measurements were performed using the ISSP-PONTA triple axis spectrometer installed at JRR-3M of JAERI in Tokai. The measurements were performed using the fixed final energy mode with \( E_f = 14.7 \text{ meV} \) using a horizontal and vertical focusing analyzer. Aligned small single crystals (0.34 g) of \( \text{NaV}_2\text{O}_5 \) were mounted \((h, k, 0)\) zone in a micro cell filled with Fluorinert 75 as pressure transmitting fluid. The high pressure was obtained using a clamped-type pressure cell designed by Onodera et al. [5]. The high-pressure cell was set on the cold tip of a gas-helium circulation type cryostat and cooled down to 4 K. The quoted pressure of 0.90 GPa was determined from the measured lattice constant of NaCl single crystal at 4 K.

Fig. 1. Neutron scattering intensity profiles at \( Q = (3, -0.5, 0) \) at 0.9 GPa for \( T = 4 \text{ and } 35 \text{ K} \).

As shown in Fig. 1 the data at 35 K shows an increased intensity at the lower energies due to magnetic diffuse scattering from the sample. The peaks at 5, 6.5 and 12 meV are perhaps phonon scattering from the pressure cell structural materials. The magnetic scattering signal was obtained by subtracting the neutron scattering intensity at 35 K from that at 4 K and then making a correction for the diffuse magnetic scattering using the Lorentzian fit around elastic position \( E = 0 \text{ meV} \) as shown in Fig. 2. The transition temperature \( T_{\text{C}} = 26.2 \text{ K} \) was determined from the temperature dependence of the neutron scattering intensity at \( (6, 0, 0) \) Bragg peak. The data obtained at \( Q = (h, -0.5, 0) \) with \( h = 3, 2.75 \) and 2.5 were fitted to Lorentzian and Gaussian functions and the full width at half maximum of Gaussian fitted peaks at 9 meV are 1.4, 0.9 and 2.9 meV, respectively. We cannot distinguish whether these peaks have a real intrinsic broadening or if they consist of...
Fig. 2. Subtracted neutron scattering intensity at 35 K from that at 4 K at Q = (3, -0.5, 0) at 0.9 GPa. The solid lines are Lorentzian and Gaussian-fit results.

hand, the central energy of these peaks are about 9 meV and the spin excitation gap $E_g$ at 0.9 GPa lie within a bandwidth of 0.1 meV along inter-chain direction parallel to $\alpha^*$-axis. This can be compared to the ambient pressure bandwidth of 3 meV and $E_g$ of 10 meV [3]. This experimental result should be related to the crystal structure change from (2xa, 2xb, 4xc) to (2xa, 2xb, c) above 0.9 GPa observed by X-ray scattering [6]. The pressure dependence of $E_g$ and $T_C$ in NaV$_2$O$_5$ is opposite to that for CuGeO$_3$ [7]. When the ratio of $E_g$ to $T_C$ is normalized, the pressure dependence of $E_g$ is smaller than that of $T_C$ as shown in Fig. 3 and this result may be related to the fact that in NaV$_2$O$_5$ we have a charge order transition and not spin-Peierls transition as originally thought.

References

Fig. 3 P-T phase diagram of the phase transition temperature and the plot of spin gap energy normalized at ambient pressure. Solid line is the guide to eyes.
A quaternary oxide Ba$_3$TbRu$_2$O$_9$ has a 6H-perovskite structure with space group P6$_3$/mmc. Its magnetic susceptibility and specific heat measurements showed that the magnetic transition occurred at 9.5 K [1].

In order to determine the magnetic structure, powder neutron diffraction measurements were performed at 2 and 15 K, and at room temperature using the Koken powder diffractometer for high efficiency and high resolution measurements, HERMES, installed at JRR-3M reactor with a neutron incident wave length (\(\lambda = 1.8196\) Å). Crystal and magnetic structures were determined by the Rietveld analysis.

Figure 1 shows the observed and calculated diffraction patterns. The Rietveld analyses of data collected at 15 K and room temperature indicate that Ba$_3$TbRu$_2$O$_9$ adopts the 6H-perovskite structure (Fig. 2(a)). In this structure, the cation sites within the face-sharing octahedra are occupied by Ru$^{4+}$ ions, and those within the corner-sharing octahedra are occupied by the Tb$^{3+}$ ions.

The data collected at 2 K show a number of low angle peaks, which are not observed above 15 K. They are the magnetic peaks due to an antiferromagnetic ordering of Tb$^{3+}$ ions. These peaks are indexed in the crystallographic unit cell with odd values of \(l\), however, the (00l) peaks are negligibly weak. These facts indicate that two Tb$^{3+}$ ions occupying the 2a Wyckoff positions have antiparallel magnetic moments with each other, and that the direction of ordered moments is parallel to the c axis. The magnetic structure of Ba$_3$TbRu$_2$O$_9$ is illustrated in Fig. 2(b). In this magnetic structure, the magnetic moments of the Tb$^{3+}$ ions order ferromagnetically in the c plane, and these ferromagnetic sheets are stacked antiferromagnetically along the c axis. The ordered magnetic moment of Tb$^{3+}$ ions is determined to be 6.84(4) \(\mu_B\). This value is reasonable for Tb$^{3+}$ (4$f^7$).

On the other hand, the ordered moments of Ru ions were not determined. This may be due to an absence of long range magnetic ordering of the Ru ions.

References
Neutron Scattering of $\text{BaVS}_3$ Oriented Crystals

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Origin of the metal-insulator transition ($T_M = 70$ K) of $\text{BaVS}_3$ (hexagonal $P6_3/mmc$) is still mysterious in spite of a long history of investigations. Pure Peierls instability expected from the one-dimensional arrangement of V atoms is now doubted because in fact the conduction between the chains and the conductivity are nearly isotropic [1]. On the other hand, pure Mott instability due to the strong electron correlation was also refused because a symmetry breaking, i.e., superlattice formation, was found at $T_M$ by recent X-ray diffraction measurements of single crystalline $\text{BaVS}_3$. According to the results the chemical V site separates into 2 sites as a manner of $V_L - V_R - V_L - V_R$ along the $c$ direction. To resolve this complex situation we performed neutron scattering experiments of single crystals. The main purpose of this study is to get information on the spin and charge states in the ground state below $T_X = 30$ K by probing the detailed magnetic structure.

Single crystals of $\text{BaVS}_3$ were synthesized by a Te flux method. The shape of the crystal is like a fine needle with the hexagonal $c$ direction along the long axis. The crystals is typically in several mm length and 0.1 - 0.4 mm diameter. The mass is less than 1 mg. For neutron scattering experiments about 1000 pieces of crystals are collected and oriented along the $c$ axis on thin Al plates. Hence hexagonal $a$ axes of the crystals are expected to orient at random. To fix the crystals we used conventional adhesive paste diluted in acetone. Neutron scattering experiments were performed with a triple-axis spectrometer ISSP-POINTA-5G installed at JRR-3M in JAERI. Measurements were carried out at a incident energy $k_i = 2.67$ Å$^{-1}$ with a collimation sequence open-80'-80'-80'.

All results obtained so far are consistent with the magnetic modulation vector $\mathbf{q} = (0.226, 0.226, 0)$ determined from powder diffraction experiments [3]. One of preliminary results is shown in Fig. 1, which are difference profiles between data measured at 10 K and 50 K. The value of the horizontal axis was normalized by hexagonal $a^*$, although the lattice is slightly distorted to orthorhombic below $T_X = 420$ K. Top and bottom figures corresponds to elastic diffraction profiles measured at $L = 1/2$ and 0, respectively. Although the experimental accuracy is not enough to determine the precise magnetic structure due to high back ground originating in scattering from protons included in the adhesive paste, no appreciable magnetic peak at $L = 1/2$ indicates that the V site separation revealed by the X-ray measurements does not correspond to explicit separation of the spin (or charge) state, for example, to 0 $\mu_B$ and 1 $\mu_B$. This suggests a nearly uniform spin and charge state even below $T_X$.

Efforts to reduce the back ground and low-energy and high-resolution experiments are now in progress.

Fig. 1 Difference profiles between 10 K and 50 K

References
Atomic and Magnetic Order in RbCo$_{1-x}$Mg$_x$F$_3$ System

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RbCo$_2$F$_2$ crystallizes in the cubic perovskite structure (space group Pm-3m) and antiferromagnetically orders below $T_N$=100K. For the RbCo$_{1-x}$Mg$_x$F$_3$ system $T_N$ decreases with increasing $x$ and ferrimagnetic order with the hexagonal structure appears for $0.3<x<0.68$. In order to clarify the crystal and magnetic structure of the RbCo$_{1-x}$Mg$_x$F$_3$ system, especially to inspect the possible presence of atomic order, we made specific heat, magnetic susceptibility, magnetization and neutron diffraction measurements. In this report we present the result of powder neutron diffraction measurements for $x=0.33$, 0.40, and 0.50 samples.

Figure 1 shows the powder neutron diffraction pattern taken at room temperature and the result of Rietveld analysis for $x=0.33$. The hexagonal BaTiO$_3$-type structure (space group P6$_3$/mmc) gives the best fit to the data. In this structure Co and Mg atoms occupy 2a and 4f sites. For $x=0.33$, 13% of 2a site and 42% of 4f site are occupied by Co atoms, therefore, Co atoms prefer 4f site.

Deviation from the dashed line, which is the expected value for random occupation, increases with decreasing $x$.

Relation between the atomic order and the saturation moment in the ferrimagnetic phase will be discussed based on the super-exchange interaction path among 2a and 4f sites in the forthcoming paper.

Figure 2 shows the occupation factor of Co atoms as a function of Co concentration $x$.

Reference

A study of a pseudo-binary alloy system Fe$_{65}$(Ni$_{1-x}$Mn$_x$)$_{35}$ was initiated by Shiga to investigate the magnetic state of an iron atom in fcc lattice long before the discovery of spin-glass.\textsuperscript{1)} Besides the knowledge of the electronic state of the constituent atoms he reported that the alloy is an antiferromagnet in the composition range 0.3<\textit{x}<1.0, and a ferromagnet for 0\textit{x}<0.3. Many experimental works on the Fe$_{65}$(Ni$_{1-x}$Mn$_x$)$_{35}$ and the related systems followed.

A previous neutron scattering study\textsuperscript{2)} showed that ferromagnetic clusters exist in ferromagnetic and spin-glass phases. The origin of anomalous temperature variation behavior of spin-wave stiffness and spin-wave intensity observed in this and other spin-glass materials is attributed to the presence of magnetic clusters. Recently, we found that magnetic clusters with antiferromagnetic correlation coexist with ferromagnetic clusters in the alloy of \textit{x}=0.22. This observation showed that the magnetic phase diagrams based on the macroscopic measurements is insufficient to describe the magnetic state of competing interaction systems.

In order to clarify the microscopic magnetic state of the present system, we made a neutron diffraction study of Fe$_{65}$(Ni$_{1-x}$Mn$_x$)$_{35}$ with x=0.05–0.22. Figure 1 shows the temperature variation of amplitude and line width of the magnetic diffuse pattern measured around (110) which is an antiferromagnetic Bragg point for fcc structure. We remark that the magnetic scattering arising from antiferromagnetic as well as ferromagnetic clusters (not shown here) develop far above the spin-glass transition temperature. The present observation showed that ferromagnetic and antiferromagnetic clusters coexist in wide temperature range. Time evolution of these clusters is currently studied by means of time-resolved SANS technique.

\textbf{References}

Spin density distribution in CeB$_6$


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The Kondo compound CeB$_6$ with a cubic CaB$_6$-type structure has attracted much attention because of its complicated magnetic phase diagrams [1–5]. It shows the successive phase transitions from the paramagnetic state to the antiferro-quadrupolar (AFQ) ordering at $T_Q = 3.3$ K, and to the antiferromagnetic ordering at $T_N = 2.3$ K. The phases are usually denoted as phases I, II and III, respectively.

Our previous polarized neutron diffraction (PND) work on CeB$_6$ has revealed the spin density distribution of CeB$_6$, deduced by the maximum entropy method (MEM) using PND data, under an applied magnetic field in parallel to [110]-axis. So we tried to investigate the spin density distribution of CeB$_6$, under an applied magnetic field in parallel to different axis from the former one.

Single crystals of CeB$_6$ were grown by a floating zone method. $^{11}$B-isotope enriched single crystals of about $5 \times 6 \times 1$ mm$^3$ in size were used for the PND experiments. The PND experiments were carried out on the triple-axis spectrometer, PONTA, installed at JRR-3M reactor at Tokai JAERI. The PND data were collected at 1.7 K under an applied magnetic field of 5.9 T in parallel to [100]-axes, with the incident neutron energies of 80 meV. The effects of the incomplete polarization (neutron polarization $P_n \sim 95\%$) and the statistical uncertainty estimations were taken into account.

The magnetic form factors, $\mu_f$, derived from the observed PND data are shown in Fig. 1. The new data set for $H/[100]$ was combined with the old one for $H/[110]$ by scaling to the $(001)$ reflections, which are common to both data sets.

As shown in Fig.1, the observed form factors are unusually scattered. If the spin densities are localized on Ce site, the magnetic form factor of Ce in CeB$_6$ should have to be almost spherical in reciprocal space. As a matter of fact, any theoretical calculation based on the spin localization model at Ce site had never succeeded in reproducing the observed magnetic form factors as shown in Fig. 1. Under these circumstances, a new approach is highly desirable.

The spin density reconstruction by MEM analysis was carried out under the constraint of simple cubic crystal symmetry (space group: $Pm3m$) with a computer program ENIGMA [6] using $80 \times 80 \times 80$ pixels. The total magnetic moment of unit cell is fixed on the total +0.8 $\mu_B$; which is the measured magnetic moment at 1.6 K. In MEM analysis, it is assumed that positive density is +1.1 $\mu_B$ and negative density is $-0.3 \mu_B$ after checking several combinations of positive and negative moments like +0.9 $\mu_B$ and $-0.1 \mu_B$, etc. Therefore, it has

Figure 1: The observed magnetic form factors with solid circles with error bars for each reflection. The calculated values from the obtained MEM spin density are also plotted.
to be admitted that some ambiguities are remaining in the assumption of the component of antiferro-magnetic moment in the total spin density. Among them, the result with the least reliable factor, 0.98 %, is obtained as the final result of this work. Fig. 2 is the equi-contour surface (±0.3 μB) of total spin density of CeB₆. For the convenience, boron network of CeB₆ is also shown in the figure.

The MEM spin density of CeB₆ is just striking. Although the most of the spin density moment were found to be localized at Ce atomic sites, we found that the magnetic moments exist not only at Ce-site but also at between B₄ octahedral and at the center of triangle bonding in the B₆ octahedral. The significant negative density was also found at the center of B₆ octahedron. The amounts of each magnetic moment are as follows; Ce-site: +0.444(2) μB; the midpoint between B₄ octahedron: +0.018(1) μB, the center of triangle surface in the B₆ octahedron: +0.021(1) μB; the center of B₄ octahedron: −0.013(1) μB. The spin density at Ce site has the spiny squarish deformation. This characteristic feature can be interpreted as the averaged feature of Og type AFQ moment, which should show the spiny deformation toward (111) direction. The calculated magnetic form factors based on the MEM spin density distribution in CeB₆ show very good accordance with the observed values as shown in Fig. 1. The present unexpected peculiar ferromagnetic spin density feature is the first example of spin density localized at non-atomic site. At the present stage, the meaning of the present results are not fully understood but it can be said that both the Boron atom's network as well as Ce atoms contribute to the magnetic properties of CeB₆.

References


Orbital Ordering in La$_{0.5}$Sr$_{1.5}$MnO$_4$

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La$_{0.5}$Sr$_{1.5}$MnO$_4$ is a layered manganite with average valence of 3.5 at each Mn site. Recent studies have indicated a real space ordering of two distinct Mn sites below $T_{CO} = 217$ K, with the two sites identified as Mn$^{3+}$ and Mn$^{4+}$ in the $ab$ plane and the oxygen atoms in the $ab$ plane are 1% breathing model like movement towards one set of Mn atoms, identified as the higher valent Mn$^{4+}$ sites. The resonant X-ray scattering (RXS) experiment suggested orbital ordering that alternating $3x^2-r^2$ and $3y^2-r^2$ orbitals at each Mn$^{3+}$ site below $T_{CO}$. However, the contradictory result that the "forbidden" nuclear and magnetic reflections were observed with polarization analysis experiment.

In order to check these points, we investigated the orbital ordering scheme of La$_{0.5}$Sr$_{1.5}$MnO$_4$ by means of the polarization analysis.

Single crystal was grown by the floating zone method. The polarization analysis measurements were performed at JRR-3M reactor at Tokai JAERI. The energy of the incident neutrons is 14.7 meV. The data was taken at 8 K under an applied magnetic field of 10 Gauss by Helmholtz coil in parallel with $<$0 0 1$>$-axis of single crystal specimen. The procedures for correcting the incomplete polarization (neutron polarization $P_n \approx 96\%$) will be published elsewhere.

The final experimental results of the nuclear and magnetic intensity are shown in Fig.1 and 2 with diamond. The bars indicate the statistical uncertainties. These observed intensity in Fig.1 suggest that distortions of oxygen atoms can not be explained by the suggested model. Magnetic reflections in Fig.2 can be explained by the minority stacking. In order to compare the RXS experiment suggested orbital order configuration of the eg electron with the experimental results, we calculated the intensity of magnetic reflection. The best-fitted orbital ordering is suggested by RXS and two domain state are taken into account in La$_{0.5}$Sr$_{1.5}$MnO$_4$.

![Figure 1: Intensity of the observed nuclear diffractions.](image1)

![Figure 2: Comparison between the observed (diamond with bars) and calculated (square) diffraction.](image2)
Neutron Diffraction Study of Magnetic Structure in Ca₃Co₂O₆

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Ca₃Co₂O₆ with the rhombohedral K₂CdCl₆ structure contains linear chains consisting of alternating face-sharing CoO₆ trigonal prisms and CoO₆ octahedra. The chains along the c-axis are separated by calcium cations, forming a triangular lattice in the c-plane. The magnetic susceptibility of Ca₃Co₂O₆ exhibits two anomalies at 25K(=T₁) and 10K(=T₂) [1]. From the experimental results reported previously, the following two models can be given as the possible magnetic structure between T₁ and T₂. One is a ferromagnetic (FR) structure made up of ferromagnetic Ising spin chains and the other is a partially disordered antiferromagnetic (PDA) structure, where 2/3 of the ferromagnetic Ising spin chains order antiferromagnetically each other and the remaining 1/3 are left incoherent with the other chains as illustrated in ref. [2]. To clarify which magnetic structure is realized, we measured the temperature dependence of the integrated intensity of (110) peak. It is a crucial point in determining the magnetic structure because (110) reflection includes no magnetic component in the case of PDA, while it does a finite magnetic component in the case of FR structure.

The neutron diffraction experiment was performed for an uncrushed sintered pellet of Ca₃Co₂O₆ using the HQR diffractometer (T1-1) in the temperature range of 2-32K under applied magnetic fields of 0-2T after ZFC.

Figure 1 shows the temperature dependence of the integrated intensities of the (110) peak. The intensity at 0T shows no increase below T₁, indicating that Ca₃Co₂O₆ realizes the PDA state below T₁ similar to Ca₃CoRhO₆ [2]. The intensity at 2T is larger than that at 0T due to a field-induced FR state characterized by a plateau at 1/3 of the saturation magnetization [1]. The decrease in the intensity at 2T below T₂ is probably attributed to the spin freezing suggested by the difference between ZFC and FC below T₂ in the magnetic susceptibility [1].

References
The magnetic structure of Pt3Fe

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The PtFe alloys with containing about 25% of iron have the cubic Cu3Au structure for which corners and centers of the unit cell are occupied by iron and platinum atoms, and have an antiferromagnetic structure. In Fig.1 temperature variations of magnetic peak intensities are shown, the peak intensity at (.5,0,0) reciprocal lattice point which is observed in high temperature phase (<180K) is reduced when the peak at (.5,0,0) observed in low temperature phase (<90K) appears.

In 1960's, Bacon proposed the magnetic structure at the high temperature phase as shown in Fig.2. The (110) ferromagnetic sheets couple antiparallel. In low temperature phase, he proposed that there is a wrong placed iron atom in the cubic face which couple ferromagnetically with the nearest neighbour iron atoms [Fig.3]. In this case, the model of Fig.3, the magnetic scattering at (.5,0,0) is expected to be a short range order. The elastic scattering peak of (.5,0,0) is apparently a Bragg peak. In Fig.2 the magnetic moments of irons in (001) planes couple unparallel each other, while the coupling along the [001] axis is parallel despite the lattice parameter of [100] is equal to [001]. Thus, this model is considered to be very unstable.

We conducted neutron scattering experiment to check if the Bacon's model is really correct. At 100K, strong inelastic scattering is observed at (.5,0,0) both Pt75Fe25 and Pt76Fe24 samples. Based on the Bacon's model, latter sample is thought to have less wrong placed iron atoms in the cubic face because the (.5,0,0) magnetic peak intensity is extremely weak. This result indicates that the model of the low temperature phase is not come from the wrong placed iron atoms and spin correlations which appears at the low temperature phase is already developed in the high temperature phase. Now we propose the new magnetic structure model for the low temperature phase which makes magnetic scattering peaks at (.5,0,0) and (.5,5,0) without thinking the wrong placed iron atoms [Fig.4].

![Figure 1: Temperature variations of magnetic peak intensities (.5,5,0) & (.5,0,0)](image-url)
Fig. 2 Bacon's magnetic structure of Pt3Fe in high temperature phase

Fig. 3 Bacon's magnetic structure of Pt3Fe in low temperature phase

Fig. 4 The new magnetic structure of Pt3Fe in low temperature phase

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Spin-dynamics in PdMn spin-glass alloy

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The PdMn alloy with Mn content below 5 at.% shows ferromagnetic behavior at low temperature, but the alloy with higher Mn content displays typical characteristics of a spin-glass; a cusp type anomaly and remanent magnetization in susceptibility measurements, but no obvious peak around the freezing temperature in the specific heat. In neutron scattering measurements, satellite diffuse peaks had been observed at the \((1 \pm \delta, 0, 0)\) positions accompanied with the atomic short range order peak at \((100)\).

For examining dynamics of PdMn spin-glass alloy we measured temperature dependence of the neutron magnetic diffraction intensity with changing the window of the energy resolution.

We used PdMn single crystal with Mn concentration of 18 at.%. The single crystal was grown by the bridgeman method by using a furnace with carbon electrode. Neutron diffraction measurements were carried out at the C1-1 and T1-1 triple axis spectrometers of JRR-3M, Tokai, Japan.

Neutron diffraction patterns obtained at 12 K by scanning along the line connecting the \((000)\) and \((200)\) points in reciprocal space are given in Fig1. The nuclear scattering contribution coming from the broad atomic short range order peak centered at \((100)\) has been subtracted using the data measured at 102 K (\(>>T_{f}\)) for obtaining magnetic diffuse peaks.

The temperature dependence of the ‘elastic’ intensities for three different energy-resolution experiments is shown in Fig2. The scattering vector \(Q=(0.78,0,0)\) corresponds to the center of one of the incommensurate magnetic peaks for this sample. These energy-resolutions determined by the vanadium incoherent scattering in each measurement are given in the Fig2.

Experimental data show that the kink of the intensity variation approaches to \(T_{f}\) obtained by the magnetic susceptibility measurements as increasing the energy-resolution, that is to say decreasing the speed of the incident neutron. This is the same phenomenon observed in the spin-dynamics of CuMn [Ref1,2]. Thus, the origin of the spin-glass like behavior in PdMn alloys can be ascribed to the dynamics of the fluctuating spin-density-wave clusters just as observed in CuMn alloys.
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Fig. 1. Neutron magnetic intensity around (100)
obtained at 12 K. The atomic short-range order peak
at 102 K has been subtracted out.

Fig. 2. Temperature dependence of the 'elastic'
component of the satellite peak intensities studied at
(0.78, 0, 0) point in three different energy-resolution.

使用施設：JRR-3M，装置：T1-1、C1-1，分野：2.Magnetism
Sample Dependence of Frustration System in Mn$_3$Pt Alloy

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The ordered alloy Mn$_3$Pt has a Cu$_3$Au-type lattice structure, in which Pt and Mn atoms occupy at the corner and face center of fcc structure, respectively. This alloy is antiferromagnet with the first order AF-AF magnetic transition at $T_c=400K$ below Neel temperature ($T_N=475K$). High temperature phase and low temperature phase are named as F-phase and D-phase, respectively. The magnetic structures are triangular below $T_c$ and collinear between $T_c$ and $T_N$. The magnetic structure of F-phase has a special feature that one third of all Mn atoms have no magnetic moments. This may be reasonable if we consider the molecular field of the Mn site surrounded by eight n.n Mn atoms. To investigate the dynamics of these spins, we performed inelastic neutron scattering measurements at T1-1 (HQR) triple axis spectrometer. In the F-phase, inelastic diffuse scattering was observed along Brillouin zone boundary of fcc structure. The distribution of inelastic diffuse scattering indicates that Mn spins are dynamically fluctuating with some spin correlation. Since the dynamical fluctuation comes from the symmetrical configuration of Mn spins, this fluctuation would relate to the atomic long-range order parameter. Thus, two stoichiometric samples, 75 at. % of Mn, with the different atomic long-range order parameter $x$ were prepared by means of different heat treatments. The atomic long-range order parameter $x$ was determined by comparing the observed intensity ratios of (100) to (200) nuclear Bragg peaks in neutron scattering measurements. SampleA and SampleB were estimated to be $x=0.99$ and $x=0.55$, respectively. The constant Q scan of each sample studied at $Q=0.25$ in the RLP are given in Fig.1. These data show that inelastic scattering is observed only in the F-phase. In the SampleA, inelastic scattering distributes toward a high-energy region. However, in the SampleB, quasi-elastic scattering is observed around the center of $E=0meV$. In the SampleB with $x=0.55$, the Mn spins would be pinned due to the substitution of Mn and Pt atoms. In the case of the SampleA with $x=0.99$, Mn spins are fluctuating with high frequency due to the high symmetry of the n.n Mn spins.

Fig.1. Constant $Q=0.25$ scans in the sampleA and sampleB at the D- and F-phase. Open and filled circles represent the data for the F-phase and the D-phase, respectively.
Neutron powder diffraction for frustrated $^{110}$CdFe$_2$O$_4$

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CdFe$_2$O$_4$ has a normal spinel structure, and the magnetic ions construct the corner sharing tetrahedra. This structure is the same as pyrochlore and C15 inter-metallic Laves Phase compound. Therefore we considered that CdFe$_2$O$_4$ is one of substance of the frustration system, because magnetic susceptibility data is similar to the data of ZnFe$_2$O$_4$. Using powder neutron scattering measurement with isotope $^{110}$CdFe$_2$O$_4$, we obtained diffuse scattering at around 30$^\circ$ (See Fig. 1) which is different from the angle of ZnFe$_2$O$_4$. It indicates that the first neighbor Fe$^{3+}$ ions couple antiferromagnetically and frustration occur between these Fe$^{3+}$ ions. The lattice constants and $u$-parameter are difference between CdFe$_2$O$_4$ and ZnFe$_2$O$_4$: (CdFe$_2$O$_4$ ; 8.715 Å, ZnFe$_2$O$_4$ ; 8.52 Å), (CdFe$_2$O$_4$ ; $u$=0.3925, ZnFe$_2$O$_4$ ; $u$=0.3852). Considering the results of ZnFe$_2$O$_4$ and $^{110}$CdFe$_2$O$_4$, it is worth while to notice that the position of Q where magnetic diffuse scattering goes out changes such largely, just replaced Zn to Cd. ZnFe$_2$O$_4$ takes 95$^\circ$ between the nearest neighbor Fe$^{3+}$ angle and the interaction is week ferromagnetic (almost paramagnetic), on the other hand CdFe$_2$O$_4$ takes 99$^\circ$ between the nearest neighbor Fe$^{3+}$ angle and the interaction is antiferromagnetic. Therefore, we consider that the nearest neighbor Fe-O-Fe super exchange interaction (antiferromagnetic) become dominant and the interaction changed dramatically. Temperature dependence of the diffuse scattering at the strongest intensity still exists around 60K (See Fig. 2), though that of ZnFe$_2$O$_4$ extinguishes around 30K.
Magnetic Neutron Scattering Measurements in Frustrated ZnFe₂O₄ Single Crystal

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ZnFe₂O₄ is one of geometrical frustration substance, and the data of elastic neutron scattering had already reported. This report is summarized about the energy spectra at several reciprocal space. There are two kinds of spin motions in ZnFe₂O₄. Even though very high-energy resolution, the energy spectrum of antiferromagnetic diffuse scattering are elastic peaks. In ferromagnetic diffuse scattering positions, there are inelastic peaks. With increasing temperature, the inelastic peaks gradually shift toward E=0 meV and they become quasielastic peaks at high temperature. Fig. 1 shows the |Q| dependences of the inelastic peak center and the line width (FWHM), which were determined using “damped harmonic oscillator (DHO) peak”

\[ S(Q, \omega) = A \frac{k_f^2}{k_i} \frac{\omega}{\omega_0^2 \Gamma_2} \left( 1 - \exp\left( -\frac{\omega_0}{kT} \right) \right) \left( \omega^2 - \omega_0^2 \right)^2 + \omega^2 \Gamma_2^2 \]

where, A is proportionality coefficients, \( \omega_0 \) is peak center, \( \Gamma \) is FWHM, \( T \) is temperature. \( k_f \) and \( k_i \) are incident and scattered neutron wave vectors, respectively. The horizontal axis |Q| is written by the distance from 1 1/2 0. The data show that there is very soft dispersion relation originated from strong diffuse scattering position in low temperature. In addition, there is a energy gap. The inelastic peak center has still finite energy at 15K. We consider that they concerns with frustration.

Fig. 1 The |Q| dependences of the inelastic peak center and the line width (FWHM), which were determined using “damped harmonic oscillator (DHO) peak”. The horizontal axis |Q| is written by the distance from 1 1/2 0. Though fitting curves were calculated by actual temperatures T, the peak center and the FWHM don’t almost change.

Fig. 2 Diagram of reciprocal space for ZnFe₂O₄. The open circles labeled with alphabet indicate positions where we observed energy spectrum. The solid circles indicate nuclear reflections and the solid lines denote Brillouin zone boundaries of the fcc structure.
Neutron Diffraction Study on Single Crystal HoB$_2$C$_2$

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HoB$_2$C$_2$ shows both of an antiferro-quadrupolar (AFQ) ordering and an antiferromagnetic (AFM) ordering. Complicated magnetic behavior of the systems which have both of an AFQ ordering and an AFM ordering have been attracting many interests, but HoB$_2$C$_2$ is striking because $T_Q$ is lower than $T_N$. It is reported that an AFM transition occurs at $T_N = 5.9$ K and an AFQ ordering transition at $T_Q = 4.5$ K in HoB$_2$C$_2$ from magnetization and heat capacity measurements$^1,2$. Hence, in the field-temperature phase diagram of HoB$_2$C$_2$, we obtained a new intermediate phase, phase IV, between $T_Q$ and $T_N$.

The neutron diffraction measurements using powdered Ho$_{11}$B$_2$C$_2$ sample shows that the magnetic structure below $T_Q$ is described by four propagation vectors of $k_1$=[1 0 0], $k_2$=[0 1 1/2], $k_3$=[0 0 0] and $k_4$=[0 0 1/2].$^3$ On the other hand, phase IV, between $T_Q$ and $T_N$, is a magnetic state with long periodicity. From our preliminary measurements on the single crystal sample, we saw three type of magnetic components around the (1 0 0) magnetic Bragg point: the (1 0 0) Bragg peak which appears below ~ $T_Q$, the (1+$\delta$ 0 $\delta$) satellite peaks, and the small uniform scattering intensity observed in the region whose vertices are the satellite peaks. In order to clarify the nature of magnetic structure in phase IV, we further investigated neutron diffraction measurements on the single crystal Ho$_{11}$B$_2$C$_2$ using TOPAN (6G) spectrometer installed at JRR-3M, JAERI.

In Fig. 1, we show the magnetic scattering profiles around the reciprocal lattice point (1 0 0) at various temperatures. The temperature region where the (1+$\delta$ 0 $\delta$) satellite peaks appear corresponds to phase IV in zero field. The uniform scattering intensity is also observed in the phase IV, but it remains at the temperatures higher than $T_N$. The satellite peaks are broader than resolution, especially along the c'-axis. The estimated correlation length along the c'-axis is about between 11 and 14 Å. This indicates that phase IV is a short-range magnetic ordered state.

![Graph](image)

Fig. 1. Magnetic scattering profiles around the reciprocal lattice point (1 0 0) at various temperature of the single crystal Ho$_{11}$B$_2$C$_2$. (a) Profile along (H 0 0.04), and (b) along (1.11 0 L). In order to catch the satellite peaks, the vertical c'-axis was tilted by 5.7°.

References

U₃Pd₂₀Si₆ crystallizes in a cubic crystal structure of space group Fm-3m, where U atoms occupy two different sites (4a and 8c). This structure is isomorphous as that of the rare earth compounds R₃Pd₂₀X₆ (R = rare earth, X = Si, Ge) which have been studied extensively due to their unique crystal structure where both of U-sites are under rather high cubic symmetry. Macroscopic measurements show that it undergoes successive phase transitions at Tₚ = 19 K and Tₖ = 2 K. Neutron diffraction measurements revealed that U ions at 4a site order antiferromagnetically whereas those at 8c site are paramagnetic, and that later ions order ferromagnetically below Tₖ. Temperature dependences of magnetic susceptibility, specific heat and elastic constant indicate that the 5f-electron state of U atoms in this compound are well localized. Actually, inelastic neutron scattering experiments revealed the existence of well-defined crystal field excitations as well as spin wave excitations. Currently, study of U-based metallic compounds is one of major subjects in the condensed matter physics because more than a few U-based materials show unusual properties such as unconventional superconductivity. However, 5f-electron state in these materials is less understood compared to those of 3d and 4f electrons in materials because of its intermediate nature between those of the 3d- and 4f-electron cases. Therefore, it is worth while to do a detailed study of the 5f electron state of U₃Pd₂₀Si₆ as a reference material since such typical localized electron behaviors are rather rare in U-based metallic compounds. We have performed a polarized neutron diffraction experiment on U₃Pd₂₀Si₆ to study magnetic form factor of the U atoms, which gives direct information on the 5f-electron state in this material.

A single crystal sample of U₃Pd₂₀Si₆ (~ 4 x 2 x 0.5 mm³) was placed in a superconducting split-coil magnet with [0 1 -1] axis vertical to the scattering plane. The experiment has been done with the triple-axis spectrometer.
PONTA(5G) installed at JRR-3M reactor, JAERI. A polarized incident neutron beam with the wavelength of 1.015 Å produced by a Cu$_2$MnAl polarizer was used. The condition of the collimators is open-40'-sample-80'-open. The experiment was performed at 1.5 K where the 8c site U ions order ferromagnetically. A magnetic field of 0.6 T was applied along the [0 1 -1]-axis to make a single domain sample. Polarization of the incident beam was 0.93.

Fig. 1 depicts the magnetic amplitudes $\mu f$ of U atom at 4a site of U$_2$Pd$_{30}$Si$_6$ as a function of $\sin \theta / \lambda$, where $\mu$ and $f$ are magnetic moment and form factor, respectively. Here, we neglect the effect of the ferromagnetic component of U atoms at 8c site because they order antiferromagnetically and the induced moment is considered to be small. In Fig. 1, the calculated form factor of a U$^{4+}$ free ion based on the dipole approximation is also shown by a solid line. Its value at $\sin \theta / \lambda = 0$ is normalized to the magnetization value per 4a site U atom. The observed form factor values are rather close to the free ion values as many of U-based metallic compounds including some unusual uranium compounds such as the heavy-electron super conductor UPt$_3$. However, it can be also seen that the data show some scattering around the calculated form factor. It may indicate an anisotropy of the 5f-electron distribution due to the crystal field.

Reference
8) N. Aso et al., 312-313 (2002) 897.
Anisotropy of Magnetic Form Factor in UGe$_2$

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UGe$_2$ is a heavy-fermion ferromagnetic compound with a Curie temperature of 52 K$^{1,2}$. Recently, superconductivity in a single crystal of this material was discovered by Saxena et al. under high pressure~(−1.3 GPa)$^3$. It crystallizes in the base-centered orthorhombic structure (Cmmm)$^4$. The magnetization along the $a$-axis, which is the direction of easy axis, shows a spontaneous magnetic moment of 1.43$\mu$B, whereas the $b$- and the $c$-axis are hard directions for magnetization$^{1,2}$. Thermal expansion and transport properties also show strong anisotropy$^{5-9}$. We have already measured the magnetic form factors in the $[0kl]$ plane at 2K (ferromagnetic phase) at ambient pressure and 1.4GPa by applying a magnetic field of 2 T along the $[100]$ direction, namely the $a$-axis. They are similar to that of free ion U$^{3+}$ and U$^{4+}$, and no anisotropy of the form factor was found at ambient pressure in the experimental error$^{10}$. In order to obtain the information on the three dimensional extent of $5f$-electrons in UGe$_2$, we have performed polarized neutron scattering experiments to measure the magnetic form factor in the $[h0l]$ plane of the field induced moment of U atoms at 60K (paramagnetic phase) at ambient pressure by applying a magnetic field of 6 T along the $[010]$ direction, namely the $b$-axis. This is because the $b$-axis is hard direction for magnetization and it is difficult to measure the magnetic form factor in the $[h0l]$ plane in the ferromagnetic state.

The single crystal sample of UGe$_2$ used in the experiment is nearly parallelepiped with the shortest axis oriented to the $c$-axis ($10 \times 3.5 \times 0.5$ mm$^3$). It was placed in a superconducting split-coil magnet with hard magnetization $b$-axis vertical to the scattering plane, and magnetic field was applied along the $b$-axis. The experiment has been done with the triple-axis spectrometer PONTA(5G) installed at JRR-3M reactor, JAERI. An incident neutron beam polarized along $b$-axis with the wavelength of 1.015 Å was produced by the Cu$_2$MnAl polarizer. A set of collimators of OPEN-80'-80'-OPEN (2-axis mode) was used.

![Image](image_url)

Fig. 1. The magnetic amplitudes $\mu$ of UGe$_2$ as function of sin$\theta$/$\lambda$. The closed circles and squares denote the observed $\mu$ associated with scattering vector parallel to [100] and [001] direction, respectively. The open circles denote with $\mu$ associated with the other scattering vectors.
The analysis has been done based on the assumption that the magnetization is localized on the uranium site. Figure 1 shows the magnetic amplitude $\mu_f$ of UGe$_2$ as a function of $\sin \theta \alpha$, where $\mu$ and $f$ are magnetic moment and the magnetic form factor of 5f-electrons, respectively. It can be seen that there is a large anisotropy of magnetic form factor in UGe$_2$. The $\mu_f$ is more expanded along the [100] direction than along [001]. The observed anisotropy of $\mu_f$ may imply that the density of 5f-electrons in UGe$_2$ is elongated along the $a$-axis. In order to clarify the state of 5f-electron in UGe$_2$ more accuracy, further experiments and analysis are necessary.

Reference
1) A. Menovsky et al.: in *High magnetic Field in High Field Magnetism*, edited by M. Date (North-Holland Publishing Company, 1983)
5) P. Boulet et al.: J. Alloy and compounds 247 (1997) 104
1-2-18  

Neutron Scattering of Ferroelectric-antiferromagnetic YMn$_2$O$_5$ Single Crystal  

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Rare earth manganese oxides RMn$_2$O$_5$ (R=Sm-Lu, Y or Bi) are ferroelectric below $T_{CE}$=40 K, where a spontaneous polarization appears along $b$-direction of orthorhombic structure ($Pbam$). The origin of the ferroelectricity is presumably related to the magnetic long-range order reported in these oxides. In support to this, the ferroelectric Curie temperature $T_{CE}$ (25-39 K) is close to the antiferromagnetic Néel temperature of the Mn$^{3+}$ and Mn$^{4+}$ moments (about 45 K).  

We are trying to confirm a conjecture that the ferroelectric spontaneous polarization is induced by the magnetic long-range order. In our previous neutron scattering measurement, the magnetic structure of YMn$_2$O$_5$ changes at $T_{CE}$=39 K from incommensurate (1/2 0 1/4) to commensurate (1/2 0 1/4) with respect to the lattice period.[1] The aim of this study is to know the details of both the crystal and the magnetic structures.  

Neutron diffraction measurement of YMn$_2$O$_5$ was performed by a 4-circle diffractometer (FONDER) installed in the guide hall of the JRR3M at JAERI. Nuclear Bragg reflections were collected at 25 K and 48 K, and magnetic Bragg reflections at 25 K. The condition of the measurement is tabulated in Table I.  

No lattice distortion was observed in the nuclear Bragg reflections at 25 K. Parameters of the crystal structure at 25 K and 48 K can be refined as $Pbam$. The estimated $R$-factors were 4.53 % and 4.81 %, respectively.  

Magnetic structure is estimated by refining spin components of 16 manganese ions in the magnetic unit cell. The possible model of the magnetic structure is shown in Fig. 1. This model is obtained on the assumption that there are only the x components of the spins.  

![Fig. 1: The possible magnetic structure of YMn$_2$O$_5$](image)

<table>
<thead>
<tr>
<th>Table I: numbers and reciprocal range of the collected reflections.</th>
<th>25 K</th>
<th>25 K</th>
<th>48 K</th>
</tr>
</thead>
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<td></td>
<td>magnetic</td>
<td>nuclear</td>
<td>nuclear</td>
</tr>
<tr>
<td>numbers</td>
<td>498</td>
<td>298</td>
<td>325</td>
</tr>
<tr>
<td>$h$</td>
<td>0~8.5</td>
<td>0~8</td>
<td>0~8</td>
</tr>
<tr>
<td>$k$</td>
<td>0~10</td>
<td>0~10</td>
<td>0~10</td>
</tr>
<tr>
<td>$l$</td>
<td>0~5</td>
<td>0~4</td>
<td>0~5</td>
</tr>
</tbody>
</table>

Reference

[1] I. Kagomiya, H. Kimura, Y. Noda and K. Kohn:  
Metamagnetism of TbRu$_2$Ge$_2$ with a two-dimensional modulated magnetic structure.

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The ternary compound TbRu$_2$Ge$_2$ with the tetragonal ThCr$_2$Si$_2$-type structure orders antiferromagnetically below $T_N$=37 K. The antiferromagnetic structure has been reported to be a one-dimensional long period modulation with the propagation vector $Q=(0.233, 0, 0)$ [1]. Recently, however, pulsed neutron study showed that it becomes a two-dimensional square-wave modulation at low temperatures [2]. The compound shows a multi-step (at least 6-step) metamagnetic process along the c-axis at low temperatures. This process had been explained on the basis of a one-dimensional model [3]. It should be, however, explained by a two-dimensional model. Neutron diffraction study under magnetic fields on a TbRu$_2$Ge$_2$ single crystal compound has been carried out to determine magnetic structures of field-induced magnetic phases. The experiments have been performed on the triple-axis spectrometer PONTA installed at JRR-3M in JAERI, Tokai. The single crystal was mounted in a cryomagnetic system so that the c-axis was vertically oriented to make scan in the a*-b* reciprocal plane. Magnetic fields were applied up to 2.2 T along the c-axis and temperature was down to 1.6 K.

Figure 1 shows the neutron diffraction patterns scanned along the low symmetry line, (1-τ, k, 0) (τ=0.7647) under various magnetic fields. Many magnetic satellites are seen under all magnetic fields, which can be indexed by the fundamental period τ, such as (1-τ, nτ, 0) (n=integer). Along the symmetry lines such as the (1, k, 0) line, many magnetic satellites are also observed such as (1, nt, 0). This fact indicates that field-induced magnetic structures are two-dimensional ones. Detail analysis is now in progress.

References
Unusual Magnetism in the Strongly Correlated 5f-Electron System

\[ \text{URu}_2\text{Si}_2 \]

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The heavy-electron superconductor \(\text{URu}_2\text{Si}_2\) has attracted particular interest for its curious, second-order, phase transition at 17.5 K (\(\equiv T_c\)) \(^1\), where antiferromagnetic (AF) order with an extremely small ordered moment (\(\mu_{\text{ord}} = 0.03 \pm 0.01 \mu_B/\text{U}\)) is observed \(^2\). Recent experiments of neutron scattering \(^3\) and \(^{29}\text{Si}\) NMR \(^4\) performed under hydrostatic pressure have revealed that inhomogeneous AF order with a normal size of moment (\(\mu_{\text{ord}} \approx 0.25 \mu_B/\text{U}\)) is induced by pressure \(P\), at least, in the range 0.3 – 0.83 GPa. Simple extrapolation to ambient pressure strongly suggests that the tiny AF moment is ascribed to 1% volume fraction of this AF phase. The true nature of the 17.5 K transition is thus attributed to an unidentified, nonmagnetically ordered phase which occupies the rest 99% of the crystal. In order to clarify the nature of this unusual two-phase competition, we have embarked upon the study of uniaxial stress effects \(^5\).

The single crystalline \(\text{URu}_2\text{Si}_2\) was prepared in a tri-arc furnace using the Czochralski technique, and annealed in an evacuated sealed quartz tube at 1000 °C for one week. The crystal was shaped into a plate (\(5 \times 5 \times 1\) mm \(^3\)) with (110) basal planes. The uniaxial stress \(\sigma\) was applied by means of a top-loading type of piston device installed in a \(^4\)He cryostat. The elastic neutron scattering measurements were performed on the triple axis spectrometer GPTAS(4G) at the JRR-3M reactor, by using neutrons with momentum of 2.660 Å\(^{-1}\). Double PG(002) filters and 40°-80°-40°-80° horizontal collimation were adopted.

Figure 1 shows the \(\sigma\) dependence of \(\mu_{\text{ord}}\) obtained from the (111) magnetic Bragg reflections at 1.4 K. For zero-stress cooled process, we found the \(\mu_{\text{ord}}(\sigma)\) curve showing a clear hysteresis loop. Considering the previous results of NMR \(^4\), \(\mu_{\text{ord}}\) measures not the true moment value but the AF volume fraction. The observed hysteresis thus indicates that the process of the AF volume evolution is irreversible; i.e., the AF phase is metastable and separated from the hidden order by a first order phase transition.

![Fig. 1 Uniaxial-stress dependence of the volume-averaged AF staggered moment of URu2Si2.](image)

**References**


As one of model materials of triangular lattice antiferromagnet with a partially released geometrical frustration, recently we have studied an isosceles triangular Ising antiferromagnet \( \text{CoNb}_2\text{O}_6 \). The system exhibits slow domain-growth-kinetics that time evolution of the correlation length is well fitted to power law with anomalously low growth exponent \( n \approx 0.2 \) in the antiferromagnetic (AF) phase [1]. To investigate how domain-growth-kinetics characteristic to the isosceles-triangular geometry of frustrated spins in \( \text{CoNb}_2\text{O}_6 \) is modified on substitution of a small amount of \( \text{Mg}^{2+} \) non-magnetic impurities, we have studied \( \text{Co}_{0.5}\text{Mg}_{0.5}\text{Nb}_2\text{O}_6 \) sample with \( x = 0.01 \). It turned out that as a result of strong suppression of domain-growth-kinetics, 1 \% substitution of non-magnetic impurities prevents system from AF ordering and serves apparent incommensurate state down to the temperature of \( T = 0.2 \) K, in which thermodynamically equivalent four types of AF-domain arrange quasi-regularly along the b axis with phase shift of \( \pi/2 \) [2]. These suggest that 1 \% substitution of non-magnetic impurities is too much to study impurity effects on domain-growth-kinetics. Therefore, as a next step we performed further neutron scattering experiments at GPTAS(4G) and HER(C1-1), choosing the sample with \( x = 0.005 \), which seems to be suitable to study non-magnetic impurity effects on domain-growth-kinetics.

In Fig. 1, we show the time evolution of the correlation length along the a axis (\( \zeta_a(t) \)) and the b axis (\( \zeta_b(t) \)), obtained from the (h 1/2 0) and (3 k 0) transverse scans, respectively. As was in the sample with \( x = 0.00 \), both \( \zeta_a(t) \) and \( \zeta_b(t) \) are fitted to the power law with growth exponent \( n \approx 0.2 \) and ac susceptibility reflecting the number of spins on domain wall also shows power law decay with \( n \approx -0.2 \). As is clearly seen in Fig. 1, \( \xi_a(t) \) is not affected by non-magnetic impurities, whereas \( \xi_a(t) \) is strongly suppressed by only 0.5 \% substitution of non-magnetic impurities, as applied magnetic field does for the sample with \( x = 0.00 \). These findings indicate that a small amount of non-magnetic impurities suppress domain-growth-kinetics not in the a direction but in the b direction. Experimentally observed anisotropic suppression of domain-growth-kinetics due to non-magnetic impurities was confirmed by our Monte Carlo simulation with cluster heat bath method, and can be explained by estimating activation energy of domain wall as anisotropic suppression by external magnetic field was explained for the sample with \( x = 0.00 \).

Fig. 1 Time evolution of \( \xi_a(t) \) and \( \xi_b(t) \) at \( T = 1.5 \) K under zero magnetic field.

References
Neutron Diffraction Study on Mn$_2$RuGa Alloy

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$^1$Shibaura Institute of Technology
$^2$IMR, Tohoku University

We have found that Mn$_2$RuGa alloy have an ordered b.c.c. structure; the Curie temperature and saturation magnetization are 450 K and 23 emu/g (= 1.15 $\mu_B$ per a chemical formula) at 4.2 K, respectively. We have made neutron diffraction experiments for powdered Mn$_2$RuGa alloy at temperature between 10 K and 500 K by using HERMES. For analysis of neutron data, we have assumed 4 sites in a unit cell and these atomic coordinates are as follows: 4a (0, 0, 0), 4b (1/2, 1/2, 1/2), 4c (1/4,1/4,1/4) and 4d (3/4, 3/4, 3/4). When we assume each site being occupied by different kind of atoms, three kinds of atomic structure factors are easily obtained:

$$ F = 4|f_a - f_b| \pm i(f_a - f_b) $$ for $h, k, l$ all odd,

$$ F = 4(f_a + f_b - f_c - f_d) $$ for $(h+k+l)/2$ odd,

$$ F = 4(f_a + f_b + f_c + f_d) $$ for $(h+k+l)/2$ even,

where $f_a$, $f_b$, $f_c$, and $f_d$ are nuclear scattering amplitude of atoms on each site. Unfortunately, nuclear scattering amplitude of Ga and Ru atoms are nearly equal. Therefore we cannot distinguish Ga and Ru. Scattering amplitude $b_{Mn} = -0.373$, $b_{Ga} = 0.729$ and $b_{Ru} = 0.722$ in $10^{-12}$ cm are used in the Rietveld analysis.

Fig. 1 shows observed neutron diffraction pattern for Mn$_2$RuGa ($z = 0.33$) alloy at 480 K ($> T_C$). It is remarkable that the 200 line is absent in the observed diffraction pattern. This result suggests that Mn atom occupies mainly the 4a and 4d sites, and Ga and Ru the 4b and 4c sites. We assumed a fictitious atom with the average neutron scattering amplitude of Ga and Ru atom, and analyzed by the Rietveld refinement. The site occupancy obtained by the analysis are shown in Table 1.

![Fig. 1. Observed (+) and calculated (line) neutron diffraction patterns for Mn$_2$RuGa alloy at 480 K. The difference between the observed and calculated intensities is shown by the lower curve.](image)

Table 1. The site occupation for the Mn$_2$RuGa alloy from observed by Rietveld analysis

<table>
<thead>
<tr>
<th>Mn$_2$RuGa</th>
<th>site</th>
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<th>Ru/Ga</th>
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<tr>
<td>4a</td>
<td>0.900</td>
<td>0.100</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>0.049</td>
<td>0.951</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>0.334</td>
<td>0.666</td>
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</tr>
<tr>
<td>4d</td>
<td>0.717</td>
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</tbody>
</table>

Mn$_2$RuGa alloy using KSD diffractometer. The field was applied parallel to scattering vector. The 111 and 200 intensities decrease with applied field. It is suggested that the alloy has a collinear ferrimagnetic structure. For detailed analysis of neutron diffraction data, we assumed that magnetic moment $\mu_a$ is plus, $\mu_c$ and $\mu_d$ are minus direction, and $\mu_b = 0$ because the occupancy of Mn atom in the 4b site is little, where $\mu_a$, $\mu_b$, $\mu_c$ and $\mu_d$ are the average magnetic moments per atom for the 4a, 4b, 4c and 4d sites, respectively. We easily determined values of the magnetic moments of Mn atoms for each site, and obtained that $\mu_a = 4.15\mu_B$ (it means 4.6 $\mu_B$/Mn atom), $\mu_c = 0.63\mu_B$ (1.9$\mu_B$/Mn atom) and $\mu_d = 2.37\mu_B$ (3.3$\mu_B$/Mn atom) at 10 K.

We have made neutron diffraction experiments under a magnetic field for the

使用施設：JRR-3M. 装置：HERMES(T1-3) and KSD(T1-2). 分野：2. Magnetism
New pseudo binary intermetallic compounds \((\text{Mn}_{1-x}\text{Pd}_x)_2\text{Ga}\) of \(\text{Ni}_2\text{In}\) \((\text{B}_2\text{B})\) type structure are found in the range of \(0.3 \leq x \leq 0.6\). Magnetization at \(T = 4.2\) K and \(H = 9.5\) kOe increases with increasing \(x\) up to \(x = 0.5\) and it reaches maximum value of 70 emu/g. In the higher \(x\) range \(x \geq 0.5\), the magnetization decreases with increasing \(x\). The \(x\) dependence of Curie temperature changes in the similar manner with \(x\) dependence of magnetization but shows a minimum at \(x = 0.35\). The temperature dependence of magnetization \(\sigma\) shows a concave in the all range of \(x\). For example, the \(\sigma - T\) curve for \(x = 0.4\) is shown in the Fig. 1.

We have carried out the neutron diffraction experiments to determine the magnetic structure of \((\text{Mn}_{1-x}\text{Pd}_x)_2\text{Ga}\) with \(x = 0.4\) using HERMES installed in the JRR-3M in JAERI. The atom arrangement corresponding to minimum values of disagreement factor \(R\) is as follows: in the \(\text{Ni}_2\text{In}\) type structure, the \(2(a)\) site is entirely occupied by Mn, the \(2(d)\) site by Pd and residual Mn randomly and \(2(c)\) site by Ga. A preferred occupation of Pd on the \(2(d)\) site is observed. We observed the neutron diffraction patterns for \(x = 0.4\) at several temperatures. Fig. 2 shows a part of the diffraction patterns for \(x = 0.4\) in the low Bragg angle region at \(T = 13\) K and \(170\) K. In the patterns at \(T < 170\) K, the \((001)\) and \((111)\) magnetic reflection is observed, indicating the presence of antiferromagnetic component lying in the basal plane. The detailed analysis is now in progress.

Fig. 2. Neutron diffraction patterns at temperature 13 K and 170 K for \(x = 0.4\).

Fig. 1. The \(\sigma - T\) curve at several magnetic field for \(x = 0.4\).
Neutron diffraction study on the magnetic structure of GdB₂C₂

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There are two purposes in this study. One is to see performance of our powder neutron diffractometer, HERMES[1], for very heavy neutron absorber, GdB₂C₂. The other is to see the magnetic structure of GdB₂C₂ as a compound of tetragonal R₂B₂C₂ family in which antiferroquadrupolar and magnetic interactions compete.

Tetragonal R₂B₂C₂ compounds are known as in which antiferroquadrupolar(AFQ) interaction is very strong. For example, AFQ ordering temperature of DyB₂C₂ is 24.7K about one order higher than other type of AFQ ordering compounds[2]. The magnetic unit cell below the Neel temperature, 15.3K, is two times large compared with the chemical one along the c-axis, and two rare earth layers are in it perpendicular to the c-axis. The magnetic moments lie in the c-plane, and the direction oscillates as 0-70-0-70 degrees along the c-axis. This structure is considered to come from competing of AFQ and antiferromagnetic(AFM) interactions. In order to study quadrupolar interaction in these compounds, we wanted to know the magnetic structure due to purely magnetic interaction, and chose GdB₂C₂ in the present study, because Gd has no quadrupolar moment and the interaction is purely magnetic.

Magnetic structures of Gd compounds are very hard to study because of heavy absorption of neutrons by Gd atoms. Absorption cross section for 1 A neutrons is tremendous for Gd as it being 44890 barns. The size is about 64 times larger than B and 20 times larger than Cd. So usually we have to use an isotope for neutron scattering experiment though it is very expensive. But it is true that when we use a very high efficient diffractometer and reflection geometry we can obtain diffraction patterns even for very heavy absorber. Therefore in the present study we try to obtain data of GdB₂C₂ using natural Gd for neutron diffraction experiment by the HERMES diffractometer.

In the present experiment a powder sample of GdB₂C₂ was pasted on an aluminum plate using epoxy resin. And
reflection geometry of the sample plate was used with a fixed inclination angle of 20 degrees to the incident beam direction. Diffraction data were taken by step scanning of counter bank with a stepping angle of 0.1 degrees.

Temperature dependence of the magnetic susceptibility measured on a single crystal of GdB$_2$C$_2$ shows that it is antiferromagnetic with $T_N=46.5$K and the magnetic moments are in the $c$-direction[3].

Neutron diffraction patterns obtained for GdB$_2$C$_2$ at 2.2K and 60K as shown in Fig.1. We can see magnetic peaks of 101, 210 and 211. There should be 100 magnetic peak around 19, degrees but it was cut by the sample itself because sample inclination angle is 20 degrees. Intensities of 001 and 002 reflections are emphasized because preferred orientation exists as the $c$-plane being parallel to the sample plate. We concluded that the simple magnetic structure shown in Fig.2 is realized in GdB$_2$C$_2$ which comes from purely magnetic interaction, and this is the fundamental feature of the magnetic interaction in the RB$_2$C$_2$ family at least for medium members of rare earth ions except for the end members, CeB$_2$C$_2$ and TmB$_2$C$_2$[4].

![Fig. 1](image)

Fig. 1. Neutron diffraction patterns of GdB$_2$C$_2$ obtained on HERMES at 2.2K(upper) and 60K(lower).

![Fig. 2](image)

Fig. 2. Magnetic structure of GdB$_2$C$_2$ below $T_N$ with $k=(100)$. The octagon with black and white circles is B-C layer.

References

Magnetic Structure of $\beta$-Na$_{0.33}$V$_3$O$_5$ at Low Temperature

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$\beta$-Na$_{0.33}$V$_3$O$_5$ is a mixed valence system of $V^{4+}$($S=1$) and $V^{5+}$($S=0$) with the mole ratio $V^{4+}$: $V^{5+}$=1.5. It undergoes structural phase transition at 136 K accompanied by charge ordering, and magnetic long range ordering phase transition at $T_C$=24 K[1]. In Fig. 1(a), the crystal structure is shown. It belongs to the monoclinic ($\beta$=109.6°) system and has the C2/m symmetry at room temperature. The extinction rule of magnetic Bragg reflection requires the position of the magnetic moments to choose C-face centered lattice, as shown in Fig. 1(b), where the lattice unit along b axis is taken to be 6b in accordance with the observed propagation vector of 1/6b as in the magnetic Bragg peaks at (h, k+1/6, l) h+k=odd. The purpose of the present study is to get information of the direction of magnetic moments on the linear chain vanadium sites, where the conjecture is examined that there exists an easy axis lying in ac plane.

Experimental

We performed polarization analysis measurement with $\beta$-Na$_{0.33}$V$_3$O$_5$ single crystal with the size of $8 \times 5 \times 3$ mm$^3$ on the triple axis spectrometer ISSP PONTA, installed at the SPring-8 beam port in the JRR-3M reactor hall. The wavelength was chosen to be 2.67 Å using PG(002) monochromator. Collimations of open, 80', 80', open were chosen in order from upper stream, and PG filter were inserted before the monochromator to suppress the contamination of higher order wavelength beam. A He-gas closed type cryostat were used to achieve 7 K at the lowest. The scattering plane was chosen to be (h00), and a Helmholtz coil was mounted around the sample table to provide horizontal(P/Q) or vertical field(P.1.Q), Q being the scattering vector at the sample position. The degree of polarization of the incident beam was 95 % for horizontal field and 97 % for vertical field, which were estimated from the measurement of nuclear fundamental reflections at (600) and (020), respectively.

Result

In Table 1, the depolarization corrected peak intensities of (0, 5/6, 0) Bragg reflection are summarized. The intensity with P/Q configuration is almost purely SF and shows that this reflection is of magnetic origin. The small, but finite, NSF intensity is probably due to the imperfect parallelity of P and Q in the experiment. And the intensity from SF process decreases when the configuration is changed to P.1.Q, and the intensity is found in the NSF process. This is the e-component of magnetic moment modulated with the period of 6b. This e-component amounts to about 20 % of the moment parallel to a’, which is seen in the SF intensity in P.1.Q configuration. This support the conjecture that the magnetic moments on the linear chain site have an easy axis in ac plane, and the newly obtained information is that this axis is directed at an angle of 20±2° from a’ axis, the axis in the ac plane and perpendicular to the c axis, as shown in Fig. 2.

Table 1: Depolarization corrected peak intensities at (0, 5/6, 0) Bragg reflection.

<table>
<thead>
<tr>
<th></th>
<th>NSF (cnts/sec)</th>
<th>SF (cnts/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Q</td>
<td>0.029(0.006)</td>
<td>0.45(0.01)</td>
</tr>
<tr>
<td>P.1.Q</td>
<td>0.088(0.007)</td>
<td>0.36(0.01)</td>
</tr>
</tbody>
</table>

Fig. 2: The direction of the easy axis lying in ac plane.

β-Na$_{0.33}$V$_2$O$_5$ is a compound belonging to the beta-vanadium oxide family, expressed as β-A$_x$V$_2$O$_5$ (A=Li, Na, Ag, Ca, Sr, etc.). In these compounds (we often call them "beta-vanadates"), metallic atoms can crystallize as monovalent or divalent cation between the V$_2$O$_5$ layers with a wide composition range of x[1]. A systematic study varying the concentration of cations revealed that in the case of A = Li, Na, Ag, phase transition related to a magnetic long range ordering commonly takes place at $x \approx 0.33$[2]. The purpose of the present study is the determination of the magnetic structure of β-Na$_{0.33}$V$_2$O$_5$, which will lead to comprehensive understanding of the transport property of β-vanadates from microscopic view point.

**Experimental**

Based on the extinction rule of the magnetic Bragg reflections in (hk0) plane previously revealed in the 2000 fiscal year on ISSP PONTA, we performed diffraction experiment with β-Na$_{0.33}$V$_2$O$_5$ single crystal on the four axis diffractometer FONDER, installed at the T2-2 beam port on the T2 thermal neutron guide tube. The size of the sample was 8×5×3 mm$^3$. The wavelength was chosen to be 1.5729 Å using Si(422) monochromator. The λ/2 contamination was about 1.2 %, which was estimated by comparing the observed (010) reflection (absent position) with fundamental (020) reflection. With the aid of a He-gas closed type cryostat, we gathered magnetic Bragg reflections at 8 K, well below the magnetic ordering temperature 24 K.

**Result**

One of the important results we obtained was an information related to the easy axis of the antiferromagnetic spin ordering. When the collinearity of the magnetic structure is assumed as has been suggested by the polarized neutron diffraction experiment on PONTA, the orientation factor expressed as $κ \times (S \times κ)$ remains outside the phase part of the structure factor, so we can determine the direction of the easy axis by comparing intensities from equivalent magnetic Bragg reflections with different scattering vector Q. As the polarized neutron analysis measurement performed on ISSP PONTA left a question about the sign of the angle 20(+2)° between the easy axis and a' axis, which is the axis in the ac plane directed perpendicular to the c axis, magnetic reflections at such Q with nonzero component of both h and l need to be observed. In Fig. 1(a), the reflections from (3, 1/6, 1) and (3, 1/6, -1) are shown, where the signal from the former reflection is smaller than the statistical error of the background while that from the latter is clearly seen. On the other hand, the angle between a' axis and the projection of the scattering vector (3, 1/6, 1) on the ac plane is 22.3°, and the angle between a' axis and the projection of (3, 1/6, -1) is 30.1° as shown in Fig. 1(b). So if we assume the easy axis is directed at an angle of 15° from a' axis in counterclockwise manner, it leads to the smaller value of $κ \times (S \times κ)$ with $κ/5(3, 1/6, 1)$, thus the weaker signal at (3, 1/6, 1) is explained.

Figure 1(a): Bragg reflections at (3, 1/6, 1) and (3, 1/6, -1). (b): Configuration of scattering vector on the crystal structure.

Powder Neutron Diffraction Measurements of TbPdSn

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TbPdSn is one of the equiatomic ternary Tb compounds which crystallize in the orthorhombic (Pnma) TiNiSi-type structure. The compound has three magnetic phases ($T_1$=23 K, $T_2$=12.2 K, $T_3$=2.5 K) and exhibits a multi-step metamagnetic transition in the lowest temperature phase, when magnetic field is applied along the easy magnetization direction of the b-axis [1].

It has also been revealed from the neutron diffraction measurements at 1.8 K that there are two kind of magnetic reflections with different propagation vectors, $\mathbf{Q}_1 = (1, 0, 0.45)$ and $\mathbf{Q}_2 = (0, -0.4, 1)$ [2]. In this work, powder neutron diffraction measurements have been performed to examine the temperature dependence of the magnetic reflections in detail.

Neutron diffraction measurements were made by using the HQR spectrometer of JRR-3M of JAERI at Tokai in the temperature range from 3.8 K to 22 K.

Figure 1 shows the powder diffractions at Phase II ($T_2<T<T_1$) and Phase I ($T_1<T<T_0$). Using a model of two kinds of propagation vectors, we have indexed the magnetic reflections as shown in Fig. 1 and summarized them in Table 1. Obtained propagation vectors are in good agreement with those of single crystal measurements. At 3.8 K and 10 K (Phase II), some reflections could not be indexed by assuming only $\mathbf{Q}_1$ and $\mathbf{Q}_2$. These peaks seem to origin from higher order magnetic reflections.

Further diffraction measurements are in progress to clarify the magnetic structure in each phase in the compound.

Table 1. The propagation vectors of TbPdSn at 3.8 K, 10 K, 16 K and 22 K. ($a = 7.1735$ Å, $b = 4.5861$ Å, $c = 7.9099$ Å)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\mathbf{Q}_1$</th>
<th>$\mathbf{Q}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>(1.005, 0.093, 0.449)</td>
<td>(0.004, 0.425, 0.949)</td>
</tr>
<tr>
<td>10</td>
<td>(1.000, 0.103, 0.441)</td>
<td>(0.004, 0.413, 0.960)</td>
</tr>
<tr>
<td>16</td>
<td>(0.980, 0.144, 0.401)</td>
<td>(0.024, 0.365, 0.969)</td>
</tr>
<tr>
<td>22</td>
<td>(0.978, 0.176, 0.404)</td>
<td>(0.017, 0.361, 0.970)</td>
</tr>
</tbody>
</table>

References


Fig.1. Powder neutron diffraction data for TbPdSn at 3.8 K, 10 K, 16 K and 22 K.

JRR-3M. T1-1. 2. Magnetism
Phonon Dispersion in the heavy-electron compound URu$_2$Si$_2$

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The second-order phase transition at $T_o = 17.5$ K in the tetragonal heavy-electron compound URu$_2$Si$_2$ is one of the most interesting issues in this material. Recent NMR measurement under pressure revealed the coexistence of antiferromagnetic and paramagnetic regions below $T_o$, where the two regions are spatially separated [1]. However, the nature of the intrinsic order parameter in the paramagnetic region below $T_o$ has not been identified yet. Regarding the intrinsic order parameter below $T_o$, the importance of the orbital degrees of freedom of the 5f electrons has been argued. Among the various scenarios, one of the candidates for the order parameter below $T_o$ is a quadrupole of the 5f electrons [2, 3].

If the phase transition at $T_o$ is an antiferroquadrupolar (AFQ) ordering with a wave vector $Q$, the transverse acoustic (TA) phonon with a propagation vector $q$ and a polarization vector $u$, coupled to the quadrupole moment with the same symmetry, may show a softening near $T_o$ at $q = Q$. From the previous inelastic neutron experiments in the $(h k 0)$ scattering plane [4], however, no tendency of the softening was observed in TA phonon branches for $q \parallel [1 0 0]$ and $u \parallel [0 0 1]$ and for $q \parallel [1 1 0]$ and $u \parallel [1 1 0]$ in the Brillouin zone. For further check on the possibility of the softening due to the AFQ ordering, we have measured the temperature dependence of the dispersion curves of URu$_2$Si$_2$ for other propagating directions of phonons by inelastic neutron scattering.

Single crystal of URu$_2$Si$_2$ used in this study was the same crystal as was used in the previous experiment. The inelastic neutron scattering experiments have been done using the triple axis spectrometer TOPAN (6G) at the JRR-3M, Tokai. Pyrolytic graphite (002) crystals were used as monochromator and analyzer. For suppressing higher-order contaminations, a pyrolytic graphite filter was placed between sample and analyzer. The constant-$Q$ scans were performed in the $(h 0 l)$ scattering plane with a fixed final energy of 14.7 meV. The horizontal collimation was set to be (open)-60°-60°-(open). The sample was cooled in a closed-cycle refrigerator.

![Fig. 1. The TA phonon dispersion of URu$_2$Si$_2$ for $q \parallel [0 0 1]$ direction at 294 K (x) and 21 K (c).](image)

Figure 1 shows the TA phonon dispersion curve of URu$_2$Si$_2$ for $q \parallel [0 0 1]$ and $u \parallel [1 0 0]$. The observed dispersion curve also depends only little on temperature. Thus the large anomaly related to the phase transition at $T_o$ seems to be absent in the TA phonon branches along the $[\xi 0 0]$, $[\xi \xi 0]$ and $[0 0 \xi]$ symmetry directions.

References
The effects of an orbital angular momentum on several physical properties in solid are one of open questions in recent solid-state physics. As one of the effects, we have paid attention influence of the lattice distortion to the direction of magnetic moment through the orbital moment in CoO. The orbital angular momentum of Co$^{2+}$ ion in CoO is not quenched.

Above the Neel temperatures, MnO, CoO and NiO have the rocksalt structure, below their Neel temperatures, they all are distorted and have the type-II fcc magnetic structure, that is, the ferromagnetic sheets of the magnetic moments in the (111) planes, stacked antiferromagnetically along the [111] directions.

However, there are differences between them in the directions of their distortions and magnetic moments. MnO and NiO contract rhombohedrally along [111] direction and the directions of their moments are parallel to [112] direction within the (111) plane. However, only CoO contracts tetragonally along the [001] direction and the moments are parallel to [1,1,2,7].

Fortunately, the tetragonal distortion of CoO is second order like, that is, the magnitude of the distortion increases gradually as the temperature decreases from $T_N=290[K]$ to about 100[K] and saturates below about 100[K]. So, we can obtain the relation between the magnitude of the distortion and the directions of the magnetic moments in CoO by measuring the powder pattern at several temperatures from $T_N=290[K]$ to 100[K].

The results are shown in fig.1 and 2. Fig.1 shows the temperature dependence of integrated intensities at the several reciprocal lattice points and fig.2 shows the temperature dependence of the direction of the magnetic moments by estimating from ratio of the intensities with Watson-Freeman's form factor of Co$^{2+}$ ion. The direction of the moments approaches to the one within the (111) plane as the distortion decreases and does to the [001] direction as the distortion increases. This result is consistent with the cases of MnO and NiO. In other words, the tetragonal contraction yields component within the (111) plane of the magnetic moment. We consider this component as the orbital moment and now investigate the experiments to proof the expectation.
Magnetic Excitations in the quantum system NH$_4$CuCl$_3$

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NH$_4$CuCl$_3$ has a monoclinic structure (space group $P2_1/c$). The crystal structure is composed of planar dimers of Cu$_2$Cl$_4$, which are stacked on top of one another to form infinite double chains parallel to the crystallographic $a$-axis. The double chains are located at the corners and center of the unit cell in the $bc$-plane, and are separated by NH$_4^+$ ions [1].

The notable feature of magnetic properties in NH$_4$CuCl$_3$ is the magnetization plateaus of the one-quarter and three-quarters of the saturation magnetization between $H_1 = 5.0$ T and $H_2 = 12.8$ T, and between $H_3 = 17.9$ T and $H_4 = 24.7$ T for $H || a$, respectively [1]. Because the magnetization plateaus was also observed in the powder sample, the origin of the plateau can be attributed to quantum effect.

In order to investigate the magnetic excitations in NH$_4$CuCl$_3$, neutron inelastic scattering experiment was performed on deuterated ND$_4$CuCl$_3$ using the C1-1 ISSP-HER spectrometer installed at JRR-3M, Tokai. It was confirmed that ND$_4$CuCl$_3$ and ND$_4$CuCl$_3$ exhibit the same magnetic properties. The constant-$Q$ mode was taken with a fixed final neutron energy $E_f$ of 4.4 meV. In order to gain intensity, the horizontal focusing analyzer with the applicable collimations was used. A PG-filter and a Be-filter were used to suppress the higher order contaminations. We stacked four single crystals of ND$_4$CuCl$_3$ with a total volume of approximately 1 cm$^3$.

The samples were mounted in an ILL-type orange crystal with its $a^*$- and $c^*$-axes in the scattering plane.

Figure 1 shows the constant-$Q$ energy scan profile in ND$_4$CuCl$_3$ for $Q = (0, 0, 1.6)$ at $T = 1.6$ K. Two excitations are clearly observed near $E = 1.8$ and 3 meV. The scan profile was fitted with two Gaussians as shown by the solid line in Fig. 1. It was confirmed that the origin of both excitations is magnetic from their temperature dependence.

Figure 2 shows the dispersion relations $\omega(Q)$ in ND$_4$CuCl$_3$ for $Q = (h, 0, l)$ and $(0, 0, l)$. Two excitations were observed in all scans. Both excitation branches are less dispersive. We also measured along $Q = (h, 0, 2h+1)$ and $(h, 0, -2h+1)$, which are most dispersive and less dispersive directions, respectively, in isostructural compounds KCuCl$_3$ and TICuCl$_3$ [2]. However, the remarkable difference compared with $Q = (h, 0, 1)$ and $(0, 0, l)$ was not observed.

The magnetic excitations at $Q = 0$ in NH$_4$CuCl$_3$ have been already investigated by the ESR measurements [3]. Two singlet-triplet excitations were observed. Their zero field excitation energy excitations were observed at 388 GHz (1.60 meV) and 708 GHz (2.93 meV), which are the same as the excitation energies at $Q = (0, 0, 1)$. Thus, we infer that the two magnetic excitations observed in the present measurements correspond to two singlet-triplet excitations observed by the ESR measurements. Since NH$_4$CuCl$_3$ undergoes magnetic ordering at zero field, there exists a gapless excitation. The gapless ESR excitation expressed by $\omega_f = H$ was observed. Thus, we expect that one more excitation exists below 0.5 meV.

![Fig. 1 Constant-Q energy scan profile in ND$_4$CuCl$_3$ for $Q = (0, 0, 1.6)$ at $T = 1.6$ K.](image)

![Fig. 2 Dispersion relations $\omega(Q)$ in ND$_4$CuCl$_3$ for (a) $Q = (h, 0, 1)$ and (b) $Q = (0, 0, l)$.](image)

Reference

Cs₂CuBr₄ has an orthorhombic crystal structure with space group Pnma. Magnetic Cu²⁺ ions make a distorted triangular lattice in the bc-plane as shown in Fig. 1. The magnetic properties of the present system were investigated by means of the specific heat and the magnetization measurements [1]. Cs₂CuBr₄ undergoes magnetic ordering at $T_N = 1.4$ K, which is more than twice as large as $T_N = 0.62$ K in the isostructure Cs₂CuCl₄ [2]. It was found that Cs₂CuBr₄ exhibits the magnetization plateau at approximately one third of the saturation magnetization in the ordered state for the magnetic field parallel to the $b$ and $c$-axes [1]. The magnetization plateau should be stabilized by the quantum fluctuation.

In order to investigate the magnetic excitations of Cs₂CuBr₄ in the paramagnetic phase, we have performed neutron inelastic scattering experiments. The measurements were performed on the triple axis spectrometer HER installed at JRR-3M, Tokai. All measurements were performed in the fixed-$k_F$ mode. The second, the third and the forth collimators were chosen as open-80'-80'. The sample was mounted in an ILL-type orange cryostat with its $a^*$ and $b^*$-axes in the scattering plane.

Figure 2 shows the dispersion relation of Cs₂CuBr₄ along the $b^*$ direction measured at $T=1.5$ K. Thick gray curve is the guide for eyes. The dispersion has the maximum and minimum at around $Q=(0, 0.8, 0)$ and $(0, 0.5, 0)$, respectively. This dispersion behavior is similar to that in Cs₂CuCl₄ [3]. The excitation energy at $Q=(0, 0.8, 0)$ is about three times as large as that in Cs₂CuCl₄. This indicates that the exchange interactions in Cs₂CuBr₄ are about three times as large as those in Cs₂CuCl₄. Now precise neutron elastic and inelastic scattering measurements below $T_N = 1.4$ K are in progress.

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Neutron Diffraction Studies of Two-Dimensional Magnetic Modulation in TbRu$_3$Ge$_2$

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Rare-earth compound, TbRu$_3$Ge$_2$ crystallizes in the tetragonal ThCr$_2$Si$_2$ type structure, in which only Tb ions are simply arranged in the body centered tetragonal lattice and bear the magnetic moment. The compound exhibits a successive magnetic transition: $T_\text{N}=37\text{K}$, $T_\text{I}=30\text{K}$ and $T_\text{II}=4.3\text{K}$. At the high temperature phase (HTP) of $T_\text{I}>T>T_\text{N}$, two domains with $Q_1=(q_1, 0, 0)$, $q_1=0.235$ and with $Q_2=(q_2, 0, 0)$, $q_2=0.247$ coexist with equal amounts, and at the intermediate temperature phase (ITP) of $T>T_\text{II}$, the $Q_2$ domain disappears and only $Q_1$ domain is retained. The magnetic structures in these regions are one-dimensional expressed with $Q=(q, 0, 0)$ along the $a$-axis [1]. On the other hand, at the low temperature phase (LTP) of $T<T_\text{II}$, many magnetic satellites are observed on low symmetry lines in the $a^*-b^*$ reciprocal plane as well as on the high symmetry lines in pulsed-neutron diffraction experiments [2]. The existence of those satellites suggests that the spin configuration is not one-dimensional, which has been reported so far [3], but two-dimensional. Since there are some difficulties in the precise estimation of satellite intensities for pulsed-neutron experiments, reactor neutron experiments are necessary.

Figure 1 gives a contour map of distribution of Bragg neutron intensities in the $a^*-b^*$ reciprocal plane obtained from $k$-scanning data for every 1/17$a^*$ step at 1.6K. The diffusive Debye-Scherrer rings in the figure are due to scattering from Al of a cryostat and the sample holder. The other peaks can be indexed with odd harmonics components of main satellites from the (2 0 0) or (1 1 0) nuclear reflection. The satellites on the high symmetry lines are indexed with fundamental $Q=(q, 0, 0)$, $q=4/17$ and its odd harmonics, while those on the low-symmetry lines are indexed with $Q=(mq, nq, 0)$, where $q=4/17$, and $m, n$=odd. The reflections on the low-symmetry lines disappear around 4.3K, which is in agreement with $T_\text{II}$ indicative of susceptibility anomaly at low temperatures. Those patterns can be described as a model of a $17a \times 17a \times c$ magnetic unit cell containing two paramagnetic sites. The paramagnetic sites correspond to node positions of long-period magnetic waves, and also, the positions are strongly frustrated. Intensity data are still insufficient, because satellites on low-symmetry lines are usually smaller by several hundred times than those on high-symmetry lines.

Electronic structures of Sr$_{1-x}$La$_x$RuO$_3$

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Polycrystalline samples of Sr$_{1-x}$La$_x$RuO$_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5) were synthesized by a conventional solid state reaction method. All of the sintered pellets were analyzed at room temperature, using an X-ray diffractometer with step scanning. The powder XRD patterns show a single-phase compound with the Pnma type space symmetry (No.62) for every sample. The sample for x=0.5 also was analyzed at room temperature, using a neutron diffraction study. Neutron scattering measurements were carried out on the ISSP triple-axis spectrometer HQR installed at T1-4 experimental port in JRR-3M in JAERI (Tokai).

No impurity peak was detected in the present powder XRD or neutron diffraction measurements, and all samples of Sr$_{1-x}$La$_x$RuO$_3$ had the GdFeO$_3$ type orthorhombic perovskite structure. All three lattice constants, a, b, and c, increase with increasing x, although Sr$^{2+}$ (0.144 nm) is replaced with La$^{3+}$ (0.136 nm). There is however an anomaly around x=0.3 in the lattice constant. This must be because electronic structures and magnetic properties change at x=0.3.

The average net charges evaluated for [Sr$_{2}$Ru$_2$O$_8$]$^{16+}$ and [Sr$_{2}$La$_2$Ru$_2$O$_8$]$^{33+}$ clusters at x=0.0 and 0.5 are +2.28e and +1.93e for Ru, +1.55e and +1.97e for Sr, and +4.63e and +4.43e for O, respectively. There must be a small covalent component in the bonding between a cation and an anion. Total DOS and partial DOS of SrRuO$_3$ (x=0.0) and Sr$_{1-x}$La$_x$RuO$_3$ (x=0.5) are illustrated in Fig.1 together with energy level diagrams. All of the theoretical lines in Fig.1 are the results computed by broadening discrete MO energy eigenvalues, using Gaussian function of 0.5 eV full width at half maximum (FWHM) for easy visualization of the DOS. As shown in Fig.1 (a), the filled band located from -10 eV to 0 eV is mainly composed of Ru 4d and O 2p orbital at x=0.0. This indicates that the electronic structure around Fermi level consists of Ru 4d and O 2p orbital which are hybridized. Figure 1 (b) demonstrates the energy levels at x=0.5. The electronic structure around Fermi level consists of Ru 4d, La 4f, O 2p orbital which are also hybridized.

There is an energy difference between up and down spin in Ru 4d partial DOS which forms FM states. The energy difference between up and down spin in Ru 4d partial DOS in SrRuO$_3$ (x=0.0) is larger than that in Sr$_{0.8}$La$_{0.2}$RuO$_3$ (x=0.5). This means that FM states are suppressed with increasing x. The unoccupied DOS located above Fermi level is mainly made up of Ru -O and Sr -O hybridization, even though La -O hybridization is included at x=0.5 as shown in Fig.1 (b). The La - O hybridization above Fermi level affects the magnetic local environment around Ru and the local charge state of Ru. Moreover, the local electron densities throughout the Ru - O network and the charge distribution with increasing x are likely to fluctuate by this hybridization. Such a fluctuation weakens somewhat the Ru - O hybridization and also the FM interactions between Ru 4d spins. As a result, FM states in Sr$_{1-x}$La$_x$RuO$_3$ are suppressed.

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Fig.1. Energy level diagrams and total and partial density of states of (a) SrRuO$_3$ (x=0.0) by [Sr$_{2}$Ru$_2$O$_8$]$^{16+}$ cluster and (b) Sr$_{0.8}$La$_{0.2}$RuO$_3$ (x=0.5) by [Sr$_{2}$La$_2$Ru$_2$O$_8$]$^{33+}$ cluster.
Neutron Diffraction Studies on Ho$_7$Rh$_3$ Single Crystal

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The rare earth compound Ho$_7$Rh$_3$ crystallizes in the hexagonal (P6$_3$mc) Th$_2$Fe$_3$ type structure. From magnetic measurements, we found that there are two magnetic phase transitions; a paramagnetic to antiferromagnetic (A.F.) at $T_N = 34$ K and the A.F. to ferrimagnetic at $T_C = 22$ K. In the Ferrimagnetic Phase, small spontaneous magnetization in the c-plane and a metamagnetic transition along the c-axis were observed. We have made neutron diffraction studies to determine the magnetic structure of Ho$_7$Rh$_3$ and found that Ho$_7$Rh$_3$ has an incommensurate helical structure with the propagation vector $Q = (0, 0, 0.38)$ at 1.5 K. In this work, more detailed studies have been made using single crystal samples.

Single crystalline samples were prepared by the Czochralski method using a tri-arc furnace. Neutron diffraction measurements were made in the $a^*-c^*$ reciprocal plane using the HQR spectrometer of JRR-3M of JAERI at Tokai in the temperature range from 1.5 K to 42 K.

Figure 1 shows the magnetic and nuclear reflections in the $a^*-c^*$ reciprocal plane. The magnetic reflections appear at the positions indexed with the propagation vector $Q = (0, 0, 0.38)$. Therefore, magnetic structure at 1.5 K is helical along the c-axis. Further, a new reflection peaks $(1, 0, \pm 0.16), (1, 1, \pm 0.16)$ and $(2, 0, \pm 0.16)$ were found. Figure 2 shows the $(0 0 0)$, $(0 0 2)$ and $(1 0 -0.15)$ reflection peak intensities as a function of temperature. $(1 0 -0.15)$ reflection peak intensity disappears at $T_C$ and the other two peaks disappear at $T_N$. This indicates that the $Q_2 = 0.16$ component relates to the ferromagnetic structure below $T_C$. The $Q_2$ component of $(0 0 0)$ reflections does not change with temperature up to $T_N$. Incommensurate structure of Ho$_7$Rh$_3$ is considered to be almost the same as commensurate one of Tb$_2$Rh$_3$[1]. More precise investigation using single crystals is in progress.

The ternary intermetallic compounds $U_2TSi_3$ and $Ce_2TSi_3$ ($T = Pd, Rh, Ru$) crystallize in a derivative of the hexagonal AlB$_2$-type structure with the magnetic atoms (U, Ce) fully ordered on the aluminum site 1a (0, 0, 0) and the non-magnetic atoms (T/Si) both on the boron site 2d ($1/3$, $2/3$, $1/2$). These systems are of particular interest because of complex magnetic properties, which depend on the degree of structural disorder of T and Si atoms, can vary between simple spin-glass behavior ($U_2PdSi_3$), spin-glass behavior with extended short-range ferromagnetic correlations ($U_2RhSi_3$), absence of spin-glass behavior ($U_2RuSi_3$), long-range antiferromagnetic order ($Ce_2RhSi_3$) and coexisting different types of short-range antiferromagnetic correlations ($Ce_2PdSi_3$) [1].

$Ce_2PdSi_3$ has a high degree of structural disorder and the competition between ferromagnetic and antiferromagnetic Ce - Ce exchange interactions leads to two successive magnetic phase transitions at $T_{N1} = 3.7$ K and $T_{N2} = 2.4$ K with two different kinds of coexisting antiferromagnetic short-range correlations. The dominating magnetic Bragg peaks can be indexed [2] with an incommensurate magnetic propagation vector $k_1 = [0, 0, 0.21]$. On PONTA spectrometer have performed elastic and inelastic neutron scattering experiments on three different $Ce_2PdSi_3$ samples to study magnetic correlations and crystal field excitations. Two polycrystalline samples were prepared by arc-melting and annealing for 5 days at 900°C by using high quality Ce-4N material, "PC(4N)", and normal quality Ce-3N material, "PC(3N)". Additional measurements were performed on a $Ce_2PdSi_3$ single crystal "SC" already used in [3]. The magnetic susceptibility data shown in Fig. 1 reveal a strong sample dependence of magnetism in $Ce_2PdSi_3$ [4], the magnetic phase transition at $T_{N1} = 3.7$ K is most

Fig. 1 Temperature dependence of magnetic susceptibility (ZFC, H=0.010T) for different $Ce_2PdSi_3$ samples.

Fig. 2 PONTA neutron diffraction data showing the sample dependence of the strongest magnetic Bragg peak of $Ce_2PdSi_3$.
pronounced in the high-quality sample "PC(4N)", smeared out in the medium quality sample "PC-3N" and completely absent in the single crystal "SC". The elastic neutron diffraction data shown in Fig. 2 confirm these results: The incommensurate magnetic Bragg peak (0, 0, 0.24) is observed with a similar peak shape in both polycrystalline samples but is absent in the single crystal. Typical inelastic neutron scattering pattern measured for Ce₂PdSi₃ "PC(4N)" are shown in Fig. 3. Compared to 2 K, the broad crystal field excitation near 12 meV shifts to slightly smaller energy (10 K) and decreases in intensity (50 K).

References
Magnetic properties of hexagonal LuMnO$_3$ and their doping effect

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Hexagonal manganeseites RMnO$_3$ (R is rare earth) are rare compounds in the sense that ferroelectricity and magnetism coexist in one compound.[1] In these compounds, the Mn ions, each of which is surrounded by three in-plane and two apical oxygen ions (a MnO$_3$ polyhedron), form triangular-lattice layers. As to their ferroelectricity, it is known that the triangular lattice of the Mn ions has a superstructure (a trimerization of Mn ions), and this distortion leads to the absence of centrosymmetry of the crystal (the space group $P6_3cm$) and the appearance of ferroelectric polarization perpendicular to the layers. Concerning their magnetism, the ordering pattern of the Mn moments is the so-called 120° structure, where the Mn moments lie within a layer and neighboring Mn moments in a layer are aligned by 120° different directions.

The main purpose of the present study is to pursue the doping effect in hexagonal RMnO$_3$. We tried several different types of doping into hexagonal RMnO$_3$, and found that $R^{11+}$ can be replaced with Zr$^{4+}$, i.e., nominal electron doping into the Mn site (the formation of Mn$^{2+}$ ion). Associated with this doping, it is found that magnetic susceptibility is enhanced and Weiss temperature, $|\theta|$ is suppressed. To investigate the spin structure of Zr-doped samples, neutron powder diffraction measurements were performed using the Kingen powder diffractometer for high efficiency and high resolution measurements (HERMES) installed at the JRR-3M reactor at the Japan Atomic Energy Research Institute, Tokai, with wavelength 1.8196Å. The samples used in the present study are LuMnO$_3$ and Lu$_{0.8}$Zr$_{0.2}$MnO$_3$, both of which are made by conventional solid state reaction.

The powder diffraction patterns of LuMnO$_3$ and Lu$_{0.8}$Zr$_{0.2}$MnO$_3$ at 300 K and 10 K are shown in Fig. 1. As can be seen, the magnetic Bragg peaks observed for LuMnO$_3$ (shown by arrows) at 10 K are substantially suppressed for the Zr-doped sample. Considering the fact that $|\theta|$ is also suppressed with Zr doping, we conclude that the interaction between Mn$^{3+}$ and Mn$^{2+}$ is ferromagnetic, and the system becomes a spin-glass state for the Zr-doped sample, because of the coexistence of antiferromagnetic (between Mn$^{3+}$ and Mn$^{2+}$) and ferromagnetic interactions.

Another notable feature (though barely seen in Fig. 1) is a broad peak around the (100) peak (~20°, forbidden in LuMnO$_3$), most strongly observed around $T_N$, which can be assigned to a magnetic diffuse scattering. What is striking is that this magnetic diffuse scattering survives at least up to 220 K (~3 $T_N$) for LuMnO$_3$. For the Zr-doped sample, the magnetic diffuse scattering exists even at the lowest temperature. This indicates that Zr doping changes the long-range ordering of the Mn moments into short-range clusters, consistent with a spin-glass picture above.

Reference

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Fig. 1 Neutron diffraction patterns of (a) LuMnO$_3$ and (b) Lu$_{0.8}$Zr$_{0.2}$MnO$_3$ at 100 K and 300 K
Field Cooling Effect in Magnetic Neutron Scattering of ZnCr$_2$O$_4$ Crystal II

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Normal spinel ZnCr$_2$O$_4$ is a typical example of a geometrically frustrated system. It has a first-order antiferromagnetic transition at $T_N=12(\pm1)$ K. We wish to make clear how the frustration is relaxed at the transition. For this purpose we will going to know the spin structure below $T_N$. Magnetic Bragg reflections of the type $(h/2, k/2, l/2)$ and $(h/2, k/2, l/2)$ have been observed. However, the magnetic structure has not been clear. Because the presence of antiferromagnetic domains makes the problem difficult to be solved, it is effective to investigate the effect of magnetic and magnetoelectric field cooling in controlling the domains. According to our previous study, a magnetic field cooling approximately along the [110] brings a remarkable change in the integrated intensity, while that along the [100] is not effective. The purpose of this study is to obtain the further information of the effect of magnetic field cooling.

We used the PONTA diffractometer installed at JRR-3M in JAERI with the incident wavelength 2.358 Å. A single crystal sample was set so that the [111] direction of the phase was vertical. The integrated intensities of the reflections on the (111) reciprocal plane as depicted in Fig. 1 are compared after cooling from about 100 K to 2.6 K in the following conditions. (1)Cooling in magnetic field of 6 T applied along the [111] (MFC). (2)Cooling in both magnetic (6 T) and electric (about 2 kV/cm) fields applied simultaneously (MEFC). The fields are along the [111], and along the [110], respectively. We confirm the position of the nuclear Bragg (220) before every measurement run.

The intensities of the reflections E~F and H after MFC or MEFC increase as compared with the intensities on the ZFC. On the other hand, the intensities of the A~D after MFC or MEFC is lower than them in ZFC. Figure 2 shows profiles of the A, E and H with MFC.

The results are expressed by the difference of the integrated intensities after MFC or MEFC and ZFC, $\Delta I = |I_{ZFC} - I_{MFC}|/I_{ZFC} \times 100$. The $\Delta I$ estimated at the A~D and E~G reflection is about 50%, while the $\Delta I$ of H is about 30%. Difference between MFC and MEFC of any reflections is not clear. Remarkable changes of the integrated intensities with the MFC or MEFC along the [111] and no effect of [100] cooling are is an evidence that unique axis of the spin structure is along the [111].

Collecting a lot of magnetic reflections with the field cooling is necessary in order to solve the spin structure. We are now preparing an experiment to record further more magnetic reflections on (111) reciprocal plane and some other reciprocal planes.

Fig. 1 (111) reciprocal plane of ZnCr$_2$O$_4$

Fig. 2 Profiles of magnetic Bragg reflections after ZFC and MFC.
Cold neutron scattering study of La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.05$-$0.20$

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Cold neutron inelastic scattering measurement for the 113-type La(Ca)-Mn-O perovskite single crystals grown by one of the present authors (Tomioka) is carried out using AGNES. Low energy and nearly dispersionless magnon mode was discovered in the present system by Hennion et al. [1] and Moussa et al. [2]. The low energy magnon mode was found in the q-range close to the gamma-point in the charge ordered anti-ferromagnetic phase (CAF) of La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.05$ and 0.08 in the energy range less than 2 meV. There are two kinds of separated magnon branches in the system, i.e., the low energy branch and the ferromagnetic one both of which have gaps of approximately 1 meV and 3 meV at the gamma point, respectively. The latter one has a close similarity with that in the La-Mn-O system [3]. Previously, low energy excitation mode was observed in the powder samples of the same system with $x=0.08$-$0.20$ in the ferromagnetic insulator phase (FI) by AGNES [4].

Present work shows low energy excitation in the q-range close to 1/2 0 1/2 point, the zone boundary, and 020 point at temperatures from Curie point down to 18 K. Care must be taken for the present Puma crystal setting. (The b-axis of this setting corresponds to the c-axis of Hirota's crystal). It is interesting that the low energy mode was observed in the vicinities either of the zone boundary and the zone center, an indication of relatively weak and local interplanar magnetic coupling. It is pointed out that similar nearly flat low energy mode is observed either in the CAF and FI phases.

Figure 1 (a) and (b) show observed inelastic scattering intensities in the samples with $x=0.15$ and 0.20. The energy values of the peaks are seen at E=1.0 meV and 0.9 meV in the $x=0.15$ and 0.20 samples, respectively. The same peak is found at E=1.2 meV in the $x=0.05$ sample, decreasing with increasing hole density.

Fig.1 Temperature dependent inelastic scattering intensity of $x=0.15$ (a) and 0.20 (b) samples.

References

使用施設：JRR3M，装置：AGNES(Ca-11)。分野：2. Magnetism
Magnetic Structure and the Anomalous Hall Effect of SrFe$_{1-x}$Co$_x$O$_3$

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SrFe$_{1-x}$Co$_x$O$_3$ with distorted perovskite structure has the helical spin ordering at $x \sim 0.0$ [1] with the modulation vector is along [111] [2]. For $x > 0.2$, the system has the ferromagnetic moment below the temperature $T_C$ [1, 2]. Sintered samples of the compound were prepared and then, annealed at 320 °C under the oxygen pressure of 60 atm. Their resistivities $\rho$, Hall resistivities $\rho_H$ and magnetizations $M$ have been measured as functions of temperature($T$) and magnetic field ($H$) to search effects of the possible nontrivial spin structure (or effects of the spin chiral ordering, where the chirality $\chi$ is locally defined as $\chi \equiv S_1 \cdot (S_2 \times S_3)$ for three spins $S_1$, $S_2$ and $S_3$) on $\rho_H$, which have been often argued [3, 4], since the observation of the very striking $T$- and $H$-dependences of $\rho_H$ of Nd$_2$Mo$_2$O$_7$ [5, 6, 7].

The Hall resistivity $\rho_H$ was measured as follows. First, it was measured at the lowest $T$ ($\sim 5$ K) after zero field cooling with $H$ being kept constant, by rotating the sample with respect to the $H$ direction and then, by increasing $H$ stepwise to take the $\rho_H$-$H$ curve. Then, $H$ was turned to zero by the oscillating mode, and $T$ was raised above $T_C$. After lowering $T$ to the next measuring value, $\rho_H$ was measured by the processes stated above. These processes were repeated many times to obtain the whole $\rho_H$-$T$ curves. The same samples were used in the measurements of $\rho_H$ and $M$ to avoid the ambiguity introduced by the effects of the demagnetization field. $T$ and $H$ were changed in the same order in both measurements $\rho_H$ and $M$ not to introduce possible ambiguities due to the hysteretic effects. Neutron data were taken with the T1-1 triple axis spectrometer at JRR-3M.

Figure 1: Magnetization $M$(top) and the Hall resistivity $\rho_H$(bottom) of SrFe$_{1-x}$Co$_x$O$_3$ are plotted against the applied field $H$ at various fixed $T$ values.

The $M$-$H$ curves taken with increasing $H$ after the zero field cooling are shown in the top of Fig. 1 for the sample with $x=0.5$, for example. For the sample $\delta=0.14$ and $T_C$ is $\sim 100$ K. Because $M$ in the low field region ($H<\sim 2$ T) decreases with decreasing $T$ below $\sim 50$ K and because the significant hysteresis of the $M$-$T$ curves was also observed below $\sim 70$ K(not shown) at $H=1$ T with varying $T$ up and then, down, we think that the system has the reentrant spin glass phase. This idea is supported by the neutron data: The profiles of the reflections of the magnetic components become diffuse-like with decreasing $T$, as shown in the top of Fig. 2 for the 100 reflection at 10 K. (In the bottom panel, the increase of the profile
width can be seen with decreasing $T$.)

Considering that $M$ does not exhibit the saturating behavior up to 5 T even at 5 K and that the hysteric behavior of $M$-$T$ curves can be observed even at $H>1$ T, we think that nontrivial local spin structure is realized even in the reentrant spin glass phase at low $T(< 70 \text{ K})$. The structure can probably be derived by adding ferromagnetic component to the helical structure similar to that observed for $x=0$. The hysteric behavior is most significant for $x=0.4 \sim 0.6$. In the bottom of Fig. 1, the $H$-dependence of $\rho_H$ is shown for $x=0.5$, for example. The data have been fitted by the equation $\rho_H = R_0 H + 4\pi R_a M$, which is used for ordinary ferromagnets. Satisfactory fits have been obtained in the $T$-region where the hysteric behavior of the $M$-$T$ curves is not seen (See the fitted line at 200 K, for example.) In contrast, in the low $T$ region where the hysteric behavior is significant, we cannot get satisfactory fits (See the line at 5 K, for example.) It is remarkable in the $T$-region where the good fits cannot be found, coincides with the region of the glassy behavior of $M$.

In Fig. 3, the $T$-dependences of $R_a$ obtained by the fittings are shown for various $x$ values. In the relatively high $T$ region, $R_a$ decreases, as for ordinary ferromagnets, with decreasing $T$. However, for $x=0.4 \sim 0.6$, where the glassy behavior appears most significantly, $R_a$ increases with lowering $T$, in the glassy phase.

As one of the candidate mechanisms of the deviation of $\rho_H$, we note the possible coupling of $M$ and proposed by Tatara and Kawamura [4]: The coupling induces the uniform component of $\chi$, which induces a new component of $\rho_H$, in addition to those treated by the classical theories.

References

Magnetic Structure and the Anomalous Hall Effect of Nd₃Mo₂O₇

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Nd₃Mo₂O₇ consists of individually formed networks of corner-sharing Mo₄⁺ and Nd₄⁺ tetrahedra and exhibits a ferromagnetic transition at temperature $T_C=93$ K, where the Mo-moments primarily order. The ordering of the Nd-moments becomes significant below ~30 K. The low $T$ magnetic structure is non-collinear for both the Mo- and Nd-moments [1]. Unusual behavior of the Hall resistivity ($\rho_H$) of Nd₃Mo₂O₇ has been reported by the authors' group [2]: Above 30 K, the data of $\rho_H$ is well described by $\rho_H=R_0 H+4\pi R_4 M$ as for ordinary ferromagnets, where $R_0$ and $R_4$ are the ordinary and anomalous Hall coefficients, respectively, and $M$ is the total magnetization. However, below ~30 K, the expression no more works and instead, $\rho_H=R_0 H+4\pi R_4 M_{Mo}+4\pi R'_4 M_{Nd}$ ($R_4, R'_4<0$) has been found to describe the experimental results rather well, where $M_{Mo}$ and $M_{Nd}$, and $R_4$ and $R'_4$ are the net magnetizations and the anomalous Hall coefficients corresponding to the Mo- and Nd-moments, respectively. The existence of the two components in $\rho_H$ is supported by the doping effect studies [3]. $R_4$ and $R'_4$ are found not to exhibit significant decrease as $T$ approaches zero in contrast to the case of ordinary ferromagnets. None of classical theories can describe these results. A new proposal has been made that the ordering of the spin chirality $\chi$ which is locally defined as $\chi=S_1 \cdot S_2 \times S_3$ for three spins $S_j$ ($j=1$~$3$) contributes to the Hall resistivity [4].

Here, neutron scattering studies in the applied magnetic field $H/(||[011])$ up to 5.7T have been carried out to clarify the relationship between the order of $\chi$ and the behavior of $\rho_H$. The neutron measurements were carried out by using the triple axis spectrometer HQR(T1-1) of JRR-3M of JAERI, where double axis condition was adopted. The crystal was oriented with the [011] axis vertical. In the zero and finite magnetic field $H/(||[011])$, the neutron elastic scattering intensity has been measured on a single crystal of Nd₃Mo₂O₇ at various $Q$-point at 113 K ($>T_C$) and 1.6 K ($<T_C$). The magnetic scattering intensity $I_{mag}$ was obtained by taking the differences between the observed integrated intensities at two temperatures, where the absorption and extinction corrections were made, though the results of the analyses do not sensitively depend on the extinction corrections. At 1.6 K, the Mo-moments align along the direction nearly parallel to the [001] or other equivalent axes, but have the slight tilting by the angle $\alpha=3(\pm 3)^°$ towards the local principal axes, while the Nd-moments are along...
their principal axes with their net magnetization being antiparallel to that of the Mo-moments. The results indicate that there exists the relatively strong axial anisotropy at the Nd sites.

We have determined the magnetic structure at 1.6 K as a function of $H$, where the Mo-Mo and Mo-Nd exchange fields and the single ion anisotropy of the Mo- and Nd-moments are considered as the parameters and so chosen that they can reproduce the $H$-dependence of the observed magnetic scattering intensities, the examples of which are shown in Figs. 1(a)-1(d). The obtained ordering patterns at 1.6 K in the field $H=5.7$ T indicates that the Mo-moments align along the direction nearly parallel to $H//[001]$ but they are tilted from the direction by the single ion anisotropy and the Mo-Nd exchange interaction. For the two Nd sites with the principal axes (parallel to the corresponding lines connecting the center of gravity with the sites) perpendicular to $H$, the magnitude and directions of the Nd-moments hardly change. With increasing $H$ up to 5.7 T, because the anisotropy is very large. For the other Nd-sites, the population of the moments with the anti-parallel component to $H$ decreases with keeping di-

rectional vectors along the principal axes and the average magnitude of the moments also changes. We have also determined the magnetic structures under the conditions $H//[001]$ and [111] by using the same parameters as used for $H//[011]$.

In the chiral order mechanism of $\rho_H$, the spin chirality $\chi$ makes the fictitious magnetic flux of the Mo- and Nd-moments, $\Phi_M^\|_M$ and $\Phi_N^\|$, respectively. We calculate them at 1.6 K as a function of $H$ by using the $H$-dependent magnetic structure determined here. Their components parallel to $H$, $\Phi_M^\|_M$ and $\Phi_N^\|$, is proportional to the anomalous Hall conductivity, $\chi$ which is approximately considered to be proportional to the anomalous Hall resistivity here. They are shown in Fig. 2 for $H//[001]$ for two effective magnetic fields, $H_{aniso}^{Mo}=4.9$ T and 0 introduced to consider the single ion anisotropy of the Mo-moments. The curves of $\Phi_M^\|_M$ shown in Fig. 2 do not agree with the experimentally observed $\rho_H$ [2] shown by the open circles in Fig. 2. The observed curves of $\rho_H$ cannot be described by the combinations of $\Phi_M^\|_M$ and $\Phi_N^\|$, either, though the anomalous Hall resistivity can basically be described, as stated above, by the sum of two components from $M_M$ and $M_N$. These results indicate that the chiral order mechanism does not describe the behavior of $\rho_H$ of the present system.

References
The tetragonal LaB$_2$C$_2$ type RB$_2$C$_2$ (R=rare earth) system shows various and characteristic magnetic and quadrupolar behaviour caused by coexistent competition among antiferroquadrupolar (AFQ) and antiferromagnetic (AFM) interactions and magnetic anisotropy by crystalline electric field (CEF) effects [1, 2]. Of this system, DyB$_2$C$_2$ undergoes an AFQ ordering at $T_Q$=24.7 K and a further transition to an AFM state with a weak ferromagnetic component at $T_C$=15.3 K. HoB$_2$C$_2$ exhibits an AFQ ordering at $T_Q$=4.5 K under zero magnetic field as well, even though a magnetic ordered state exists between $T_Q$ and $T_N$=5.9 K ($> T_Q$) [2]. Note that the strict ground state by CEF in the RB$_2$C$_2$ system is a doublet which has no degree of freedom of quadrupolar moments.

We think that the AFQ orderings in RB$_2$C$_2$ require a quasi-doublet or quasi-triplet ground state with very small energy gap between the strict ground states and the first excited states. Thus, to understand the mechanism of AFQ orderings in RB$_2$C$_2$, it is indispensable to make clear the low-lying CEF levels of this system. For this purpose, we performed inelastic scattering experiments on the triple axis spectrometer TOPAN at the JR3M reactor of JAERI.

Since level schemes in DyB$_2$C$_2$ and HoB$_2$C$_2$ are expected to be too complicated to clarify, the sample for the present experiments was a polycrystalline sample of Nd$^{111}$B$_2$C$_2$ because Nd has a simple level scheme with only five doublets. The experimental conditions were as follows; collimation was B-60-S-PG-60-B, $E_f$=14.7 meV, the sample dimension was $\phi$12mm x 15mm.

Fig.1 shows energy spectra with $Q$=2Å$^{-1}$ at $T$=12.5 K and room temperature. We observed obvious excitations at $\epsilon$=7.5 meV and 17.5 meV with a small shoulder around 21 meV at $T$=12.5 K. These three excitations are magnetic ones because of its $T$ and $Q$ dependence. The relatively sharp peak at 22 meV at room temperature is a phonon component because of its $Q$-dependence.

We have already confirmed that the excitation at 17.5 meV at $T$=12.5 K consists of two excitation at about 16.5 meV and about 18 meV by high resolution experiments on the CAT spectrometer at KENS. Thus, we were able to determine the level scheme with five doublets: 0-7.5 meV-16.5 meV-18 meV-21 meV. Using this level scheme and results of detailed magnetic measurements, we can obtain accurate CEF parameters in NdB$_2$C$_2$; furthermore, CEF parameters for the other RB$_2$C$_2$ compounds can be probably expected through extrapolation from the parameters for NdB$_2$C$_2$.

Fig. 1. Energy spectra of a polycrystalline sample of Nd$^{111}$B$_2$C$_2$ at $Q$=2Å$^{-1}$ obtained on TOPAN. Open and closed circles show spectra at $T$=12.5 K and room temperature, respectively.

References
La-dope effect on the magnetic structure in tetragonal TmB$_2$C$_2$

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DyB$_2$C$_2$ undergoes an antiferroquadrupolar (AFQ) ordering at $T_Q=24.7$K and a further transition to an antiferromagnetic (AFM) state with a weak ferromagnetic component at $T_C=15.3$K [1]. HoB$_2$C$_2$ exhibits an AFQ ordering at $T_Q=4.5$K as well, even though a magnetic ordered state exists between $T_Q$ and $T_N=5.9$K($>T_Q$) [2]. Various and anomalous behaviour observed in RB$_2$C$_2$ is thought to be caused by coexistent competition between AFQ and AFM interactions [1, 2]. Thus, understanding roles of AFM interactions in RB$_2$C$_2$, as well as those of AFQ interactions, must be indispensable.

The fundamental magnetic coupling in RB$_2$C$_2$ is thought to be $k=(1,0,0)$ type one: the coupling in the c-plane is antiferromagnetic and that along the c direction is ferromagnetic. TmB$_2$C$_2$ which is the heavier end of this system, however, has a $k=(1,0,1/2)$ type AFM structure below $T_N=16.5$K. Since TmB$_2$C$_2$ has the largest unit cell, particularly the longest c, we expected that the distance between magnetic atoms probably plays important roles to determine its magnetic coupling. Under this expectancy, we tried to determined magnetic structures in La-doped TmB$_2$C$_2$ compounds because La-dope reduces the unit cell.

We performed neutron powder diffraction experiments of a powder sample of Tm$_{0.85}$La$_{0.15}$B$_2$C$_2$ on Kinken powder diffractometer HERMES at the JRR-3M reactor in JAERI. Neutrons with a wavelength of 1.8196Å were obtained by the 331 reflection of the Ge monochromator and 12' blank sample-22' collimation.

Figure 1 shows powder patterns of Tm$_{0.85}$La$_{0.15}$B$_2$C$_2$ at 2.2K and 30.1K. The lattice constants $a$ and $c$ were determined as $a=5.3312(5)$Å, $c=3.4856(6)$Å at $T=30.1$K, while $a=5.3234(3)$Å, $c=3.4596(2)$Å for TmB$_2$C$_2$ at 25K; reduction is 0.15% for $a$, and 0.75% for $c$. As shown in Fig.1, we observed the sharp 101/2 magnetic Bragg peak at 2.2K, indicating that the magnetic structure is basically the same as that in TmB$_2$C$_2$. However, broad scattering was also observed around the (1,0,0) position. Magnetic origin of this diffuse scattering is evident because it was not observed at 30.1K. The fact that diffuse scattering was observed around (1,0,0) which is the same position of the fundamental coupling in RB$_2$C$_2$ indicates that reduction of the unit cell develops the fundamental (1,0,0) correlation, though the (1,0,0) correlation is a short range one.

From the present experiments, we can conclude that the distance between magnetic atoms is an important factor to determine magnetic couplings in RB$_2$C$_2$.

Fig. 1. Powder diffraction patterns of Tm$_{0.85}$La$_{0.15}$B$_2$C$_2$ at 2.2K and 30.1K observed on HERMES.

References

PrFe₃P₁₂ crystallizing in a cubic structure with Im 3 exhibits heavy-electron phenomena and a phase transition at $T_A = 6.5$ K. This low-temperature phase is suppressed by external magnetic field and disappears around $H = 5$ T. No magnetic reflection was seen in neutron powder diffraction below $T_A$, in spite of a cusp of magnetic susceptibility at $T_A$ like an antiferromagnetic (AF) ordering. At outside of the low-temperature phase in the $H$-$T$ phase diagram, the heavy-electron phenomena which is novel for Pr-based compounds were observed. X-ray diffraction experiments revealed a crystal-lattice modulation characterized by the wave vector $q = (1, 0, 0)$ with a dominant Fe-ion longitudinal displacement in the low-temperature phase. The superlattice formation is caused by the Fermi-surface nesting predicted in the band structure study. In order to investigate a role of Pr-ion 4f electrons in the phase transition, we measured neutron diffraction from a single-crystal sample under magnetic field.

The experiments with neutron wavelength of 2.35 Å were performed by a spectrometer PONTA (5G). Sample temperature was controlled down to $T = 1.5$ K and magnetic field was applied up to $H = 5.8$ T in the [0, 1, -1] direction.

Figure 1 depicts profiles thorough the reciprocal-lattice points $Q = (1, 0, 0), (1, 1, 1)$ and $(3, 0, 0)$. As the result of $(3, 0, 0)$, superlattice reflections at $Q = (h, k, l)$ with odd numbers of $h + k + l$ were detected below $T_A$ at $H = 0$. On the other hand, intensities at $(1, 0, 0)$ and $(1, 1, 1)$ do not show observable temperature dependence thorough $T_A$. These reflections at $H = 0$ are ascribed to the crystal-lattice modulation as observed by the X-ray diffraction experiment. Applying external magnetic fields below $T_A$, in addition to ferromagnetic intensities at $Q = (h, k, l)$ with $h + k + l = $ even, the superlattice-reflection intensities also increase with increasing magnetic field as shown in Fig. 1. At the phase boundary of $H = 5$ T and $T = 1.6$ K, these intensities suddenly disappear.

We analyzed the observed superlattice-reflection intensities by taking into account the crystal-lattice modulation and a field-induced AF structure of the Pr ions. The model based on the Fe-ion coordinate represented as $(1/4 + \delta, 1/4 + \delta, 1/4 - 2\delta)$ is adopted for the crystal-lattice modulation as in the previous X-ray study. For the magnetic structure, we assumed two different magnetic moments $\mu_1$ and $\mu_2$ induced at the corner and body-centered Pr-ion sites in the unit cell along the applied-field direction. Calculated superlattice intensities with varied $\delta$ and $\mu_1 - \mu_2$ reproduce the magnetic-field-dependent intensity pattern. Evaluated magnetic-field dependences of these parameters are shown in Fig. 2. The value of $\delta \equiv 0.2 \times 10^{-3}$ at lower magnetic field is very close to the X-ray diffraction result. The AF amplitude $(\mu_1 - \mu_2)/2$ increases up to 0.06 $\mu_B$/Pr just below the critical magnetic field of 5 T. Above this magnetic field, the lattice modulation and the AF structure vanish and the uniform ferromagnetic structure appears.

The theoretical work on the phase transition of PrFe₃P₁₂ suggested a split of a non-magnetic
研究テーマ：PrFe₆P₁₂における低温秩序相の磁気特性と電子状態
表面：PrFe₆P₁₂におけるPrイオン4f電子状態の四重極秩序
doublet crystal-field state Τ₂₃ due to coupling
between the Pr-ion state and the tetragonal Fe-ion
lattice distortion 6, 7. Because the Fe-ion
arrangements around the corner and body-center
Pr-ion sites are different, the two Pr-ion states
align on these sites with the wave vector q = (1, 0, 0),
and the different size of magnetic moments
are induced on these sites. Therefore, we
conclude that PrFe₆P₁₂ exhibits antiferro-
quadrupolar (AFQ) ordering of Pr-ion 4f-electron
states below Τₐ.

It is novel that the low-temperature phase
of PrFe₆P₁₂ is produced by a coupling between the
AFQ ordering of 4f-electron states and the gap
formation by Fermi-surface nesting with the
crystal-lattice modulation by the wave vector 2Kₚ
≡ (1, 0, 0).

![Graph](image)

Figure 1. Neutron diffraction profiles at 
Q = (1, 0, 0), (1, 1, 1) and (3, 0, 0) at 1.6 K and 4.8 T (solid circles)
or zero field (open squares). Background intensities
measured at 10 K and at zero field was subtracted.

![Graph](image)

Figure 2. Magnetic-field dependences of the Fe-ion
displacement parameter δ and the antiferromagnetic
amplitude (μ₁ - μ₂)/2 at 1.5 K.

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Neutron Diffraction Study on TbPtSn

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Magnetic properties have recently been reported of Tb equiatomic ternary compounds with the orthorhombic TiNiSi structure, TbNiSn, TbPdSn and TbRhGe [1-3]. Neutron diffraction and bulk magnetic measurements on single crystals have indicated that their magnetic properties are characterized by successive magnetic phase transitions below 20 K, incommensurate magnetic structures and metamagnetism along the b-axis in the ordered states. In the present study, we report the results of bulk magnetic measurements and the powder neutron diffraction experiments on isomorphic compound TbPtSn.

Ingots of TbPtSn compound were prepared by arc-melting the constituent elements. Neutron diffraction measurements were carried out by using the HQR spectrometer of JRR-3M of JAERI at Tokai in the temperature range from 1.5 K to 30 K.

The magnetic susceptibility shows that there are two anomalies at \(T_N = 14 \text{ K}\) and \(T_1 = 2.4 \text{ K}\) (Fig.1). The magnetization curve indicates the metamagnetic transitions at 30 kOe and 50 kOe at 1.8 K.

The powder diffraction patterns at various temperatures are depicted in Fig.2. It is indicated that a change in magnetic structure occurs between 10 K and 11 K. With regard to the magnetic transition at \(T_1 = 2.4 \text{ K}\), there is not strong evidence to conclude that a different magnetic phase exists below \(T_1\) from the neutron diffraction. An analysis is under way to examine the magnetic structure at the lowest temperature.

![Fig.2. Powder diffraction pattern of TbPtSn.](image)

![Fig.1. Temperature dependence of magnetic susceptibility of TbPtSn.](image)

References


JRR-3M, HQR (T1-1), 2. Magnetism
Paramagnetic Scattering from NiO

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It is essentially important to investigate the paramagnetic spin dynamics in NiO, which is a prototypical antiferromagnetic insulator classified into the strongly correlated electron systems. Although the local electronic structure observed by the photoelectron spectroscopy does not show a significant change near the magnetic ordering temperature, the information is totally absent on the low energy dynamical response of the localized, mutually interacting moments in the paramagnetic state in NiO. In order to reveal the characteristics of the spin dynamics, the paramagnetic scattering experiments have been carried out. The preceding experiments with the time-of-flight inelastic spectrometer have shown rather sharp, intense inelastic scattering.[1] For a further detailed study, experiments have been carried out on the triple-axis spectrometer PONTA (5G) at JRR-3M.

In the present study, the paramagnetic (and critical) scattering from a single crystal NiO were measured in the temperature range from 300 to 614 K (1.17\(T_N\)). The measurements were mostly made with the conventional constant-\(k_f\) mode with \(E_f=14.7\) meV. A preliminary polarized neutron experiment was also carried out and the magnetic inelastic signals were confirmed with sufficient intensity. The inelastic magnetic scattering is centralised around the antiferromagnetic zone centers such as \(Q=(0.5, 0.5, 0.5)\) or \((0.5, 1.5, 1.5)\). The observed magnetic response is characterized by the large energy width extending over a energy of 30meV. It is possible to construct an intensity map from a series of constant-E measurements. The map observed around \(Q=(0.5, 1.5, 1.5)\) and at \(T=555\) K (1.06\(T_N\)) is shown in Fig. 1. A peak of the zone-boundary TA-phonon has been observed around 26meV but its intensity can be subtracted without distorting the contour.

The observed scattering function has been analyzed assuming the conventional double-Lorentzian-formed \(S(Q, \omega)\). As seen in the figure, the rod-like intensity distribution corresponds to the large spectral width \(\Gamma_q\). It is important to note that the coefficient \(\Delta\) is as large as 800 meVÅ\(^2\), when the \(q^2\)-dependence of \(\Gamma_q\), i.e., \(\Gamma_q=\Delta q^2+\Gamma_0\) is assumed. It is interesting to investigate the origin of this large spectral width in the paramagnetic NiO, because the large spectral width is considered to be a characteristic of the metallic systems [2], and also because of the particular situations in NiO such as the type-II AF structure in the FCC lattice.

References
Disordered Pt-rich Pt-Mn alloys have been known to exhibit spin-glass behavior similar to the Cu-Mn alloys. The magnetism of the alloys is explained by the same mechanism as that in Cu-Mn alloys, i.e., dynamically fluctuating SDW clusters with broad distribution of relaxation times [1]. In the disordered alloys, short-ranged SDW causes magnetic diffuse scattering at (1±δ,0,0) and its equivalent positions. Recently, neutron diffraction measurements have revealed two ordered phases in the alloys with Mn concentration around 14.4 at.% [2]. Below the order-disorder transition temperature, a Cu₃Au type ordered structure appears and at low temperature, an ABC₆ type ordered structure with a unit cell $2 \times 2 \times 2$ as large as that of the fundamental fcc cell was found to be stable. In this work, we studied magnetic structure in Pt-14.4 at.%Mn with ABC₆ type ordered structure.

Single crystal diffraction measurements were performed using FONDER installed at T2-2, JRR3-M in Tokai, JAERI. Figure 1 shows the contour map around at $(0 \ 1 \ 1/2)$ on [001] plane with $l = 1/2$. Two magnetic peaks are observed at $(-1/4 \ 1 \ 1/2)$ and $(0 \ -3/4 \ 1/2)$ with broad magnetic diffuse scattering elongated along [110] at T=7.5K. As temperature is raised, intensities of the magnetic peaks decrease rapidly and almost disappear at T=20.5K though the diffuse scattering remains same intensity. It survives even at R.T. with much broader distribution. The observed magnetic peaks and diffuse scattering are explained as follows; peaks at $(-1/4 \ 1 \ 1/2)$ and $(0 \ -3/4 \ 1/2)$ are due to a long-ranged magnetic order on ABC₆ type ordered structure, whereas diffuse scattering along [110] is due to the short-ranged SDW newly appeared around $(0 \ 1 \ 1/2)$ for smaller Brillouin zone in the ordered structure. The present results show coexistence of the magnetic long-range order and SDW clusters in the alloy.

Fig.1 The contour map around at $(0 \ 1 \ 1/2)$ on [001] plane with $l = 1/2$ at 7.5K and 20.5K.

References
Evidence of the anisotropically developed antiferromagnetic spin fluctuation in CeFe$_2$ under high pressures

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Itinerant electron system CeFe$_2$, with the lowest $T_c=230$K and the smallest $M_s=2.3\mu_B$/f.u. at 4.2K among C15 cubic Laves phase RFe$_2$ family, is located near an instability of ferromagnetism. Because the Fe3d–Fe3d ferromagnetic exchange interaction competes with an antiferromagnetic spin correlation with propagation vector $q=(1/2, 1/2, 1/2)$ and an energy of $\sim 3$meV due to Ce4f–Fe3d hybridizations [1]. Therefore, it is of interest to know how this system does behave under hydrostatic pressure. Magnetization measurements on single crystal CeFe$_2$ under high pressures up to 8kbar indicated that the magnetization along the each principal axis is quite anisotropically suppressed at 5K even in the cubic symmetry by applying the hydrostatic pressure [2]. To clarify the origin of this anomalous behavior, we performed the neutron scattering experiment on single crystal CeFe$_2$ under pressures.

Neutron scattering experiments for single crystal CeFe$_2$ were performed under ambient pressure and 15 kbar below 270 K both in the double-axis and triple axis modes using a Triple-Axis Spectrometer (5G-PONTE) at JRR-3M reactor of JAERI.

Fig.1(a) shows the (111) peak intensity in the triple-axis mode as a function of temperature under $P=15$ kbar. Here, the triple-axis mode was fixed to zero energy transfer $\Delta E=0$. In this figure, the upper part than the dotted line indicates the contribution of magnetic scattering to the (111) peak intensity, in which the nuclear scattering contribution is the smallest. As is recognizable in Fig.1(a), the (111) peak intensity under 15 kbar begins to decrease significantly around $T^{*}\sim 110$ K with decreasing temperature without any transition and the magnetic contribution to the peak intensity becomes only half of that under $P=1$ bar at $T=4.2$ K. In addition, any other magnetic elastic peak has not been found in the reciprocal (110) plane. This indicates that the suppression of magnetization is not attributed to the long range antiferromagnetic ordering and the Fe static magnetic moment under $P\sim 15$ kbar shrinks only half of that under $P=1$ bar. Subsequently, we carried out the linear scan around $<1/2, 1/2, 1/2>$ reciprocal lattice point in the double-axis mode without energy analyzer. Therefore, in this mode, the observed scattering intensity contains both the contributions from elastic and inelastic magnetic scattering. As is seen in Fig.2(b), a small clear peak under $P\sim 15$ kbar in double-axis mode is recognizable around the $<1/2, 1/2, 1/2>$ reciprocal lattice point. We can see an appreciable magnetic contribution in the $<1/2, 1/2, 1/2>$ intensity. It should be noted that we observed no magnetic contribution on the $<1/2, 1/2, 1/2>$ reciprocal point in the double-axis mode under 1 bar, except for the $\lambda/2$ contamination of the (111) reflection. Therefore, the above result can be interpreted as one of the evidence that the antiferromagnetic spin fluctuation with a propagation vector $q = (1/2, 1/2, 1/2)$ develops in CeFe$_2$ under 15 kbar.

References

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Fig.1(a) The (111) peak intensities in the triple-axis linear scan with $\Delta E=0$ under $P=1$ bar and 15 kbar as a function of temperature for CeFe$_2$, and (b) the scattering intensity in double-axis linear scan without energy resolution under $P=15$ kbar around the $<1/2, 1/2, 1/2>$ reciprocal lattice point.
Antiferromagnetic Phase Transition in KMnF₃ by means of Neutron Diffraction Camera

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A neutron diffraction camera method is often convenient to easily check quality of a used specimen. We can also get visual images of diffraction spots and diffuse scattering in a reciprocal lattice space around a special crystal axis by using the camera method. Since a sheet-like neutron detector, imaging plate (IP), is developed, the neutron camera method is more powerful for investigations of crystal and magnetic structures. We tried to study magnetic phase transitions in a perovskite-type compound KMnF₃, using the Neutron diffraction camera.

We carried out measurements of some diffraction spots of KMnF₃ at T2-2 experimental station in JRR-3. A tentative neutron camera was equipped on a magnet, called to be "SAIKORO", which was set on a camera goniostage and gives maximum magnetic field of about 8kOe. A single crystal having a size of about 2 x 2 x 4mm³. The used neutron wavelength at T2-2 was 1.5627 Å. A functional DC-magnet called to be "SAIKORO" was set on a camera goniostage. The magnet gives a maximum magnetic field of about 8kOe. A small CIT-type cryostat was inserted in a pole gap of the magnet by hanging from a side-flange of the magnet. Size of focused incident Neutron beam was about 10mm in vertical and 6mm in horizontal.

Figure 1 shows a rotational visual image around a pseudo-cubic axis [001] of KMnF₃ taken at 40K with exposure time of 30 minutes and rotational angle of 6 degrees. Thus, in the figure, a (1,1,0) nuclear fundamental reflection is in a 0-layer, while magnetic reflections of (1/2,1/2,1/2) and (1/2,1/2,-1/2) are in a 1/2-layer and -1/2-layer, respectively. KMnF₃ shows successive magnetic phase transitions at about 88K and 83K. An uni-axial antiferromagnet occurs in the region from 88K to 83K. On the other hand, an antiferromagnet having weak ferromagnetic component occurs below 83K. Crystal structural phase transitions also occur at about 83K, 93K and 185K.

In order to study a magnetic filed effect to the magnetic structure, we carried out measurements of integrated intensity of the (1/2,1/2,1/2) magnetic reflection as functions of magnetic field and temperature. During the experiments, the magnetic filed was applied to be parallel to pseudo-cubic [100] of KMnF₃. The [100] axis is a magnetic easy axis. The exposure time was 15 minutes and the rotational angle 3 degrees at each measurement. Some results are shown in Figure 2. At the respective temperature from 60K to 100K, the data were taken by vertically sifting the IP-sheet cassette, whose front was screened by a Cd-
plate having a window to measure only the \((1/2,1/2,1/2)\) magnetic reflection. The window width was 10mm in vertical and the

Fig.2. Visual image of the \((1/2,1/2,1/2)\) magnetic reflection in K\(\text{MnF}_3\), taken at the respective temperature from 60K(left) to 100K(right) with exposure time (15min.) and rotational angle (3°).

 cassette was shifted by12mm. The applied magnetic field was 8kOe. Figure 3 (a) and (b) represent peak profiles of the visual images of \((1/2,1/2,1/2)\) magnetic reflection under the applied magnetic field of 0Oeand 8kOe, as like those in Fig.2, respectively.

Fig.3. Peak profiles of the \((1/2,1/2,1/2)\) magnetic reflections; (a)H=0Oe and (b)H=8kOe.

Fig.4. Intensity of the \((1/2,1/2,1/2)\) magnetic reflection in K\(\text{MnF}_3\) under the applied magnetic field, as shown in Figs.3(a) and (b).

In the figure, an ordinate refers to total counts / total vertical pixel numbers in each horizontal pixel of the imaging plate (IP), while an abscissa to the horizontal channel number in IP.

We measured total counts of the \((1/2,1/2,1/2)\) magnetic reflection at the respective temperature, as shown in Figs.3 (a) and (b). The results are shown in Fig.4. The data denoted by open circles and solid circles are taken under the applied magnetic field of 0Oe and 8kOe, respectively. We found the magnetic field effect to the temperature dependence of the intensity. Although we need to accurately measure the intensity, it was confirmed that there are two magnetic transition at about 83K and 90K. Furthermore, the antiferromagnetic diffuse scattering was also found in region from about 90K to 100K. Thus, the neutron camera gives a possibility to study crystal and magnetic diffuse scattering, though ordinary neutron detectors of counter-type are very useful and functional than the neutron camera method. In Fig.4, we are interested in new modulation of the intensity at about 73K under the applied magnetic field of 8kOe.
Correlation between the structural and antiferromagnetic phase transitions in ZnCr$_2$Se$_4$

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ZnCr$_2$Se$_4$ has a normal-type spinel structure shown in Fig. 1, where arrows will be described later. The structure is mainly characterized by 8 tetrahedra of ZnSe$_4$ (A-site) and 16 octahedra of CrSe$_6$ (B-site) in its cubic structural unit cell having a lattice constant of about 10.50 Å. It is well known that Cr$^{2+}$ ions preferably locate in the B-sites in the spinel structure. The CrSe$_6$ chain is made along [110] by owing two Se$^{2-}$ ions between the neighbor octahedra. These chains are also isolated each other by the ZnSe$_4$ tetrahedra. ZnCr$_2$Se$_4$ is a semiconductive antiferromagnet having the spiral spin order of Cr$^{2+}$ below about 20K. More recently, Hidaka et al. [1] argued from neutron powder diffraction that Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ with $x=0.15$ and 0.30 show a new antiferromagnetic transition at about 23K and 24.5K, in addition to the ferromagnetic transition at about 410K and 415K, respectively. It was also found that Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ with $x=0.50$ and 0.60 show an antiferromagnetic phase transition at about 24K and 28K, respectively, in addition to a ferromagnetic phase transition at about 420K. However, the antiferromagnetic phase was not observed in Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ with $x > 0.75$. Temperature dependence of lattice constants taken by X-ray powder diffraction suggested that a structural phase transition in ZnCr$_2$Se$_4$ occurs at about 20K to be of first order from a cubic to tetragonal symmetry [2]. Thus, we carried out to re-study a correlation between structural and magnetic phase transition in ZnCr$_2$Se$_4$. The measurements were done at HQR in JRR-3. At the present experiments, a [-110] edge of the octahedral shape of the present crystal was set up to be parallel to a vertical rotation axis of the diffractometer. That is, the cubic axes of [001] and [110] were in a horizontal plane. From neutron powder diffraction [1], it was found that substituted spinels Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$, $0.0 \leq x \leq 0.3$ show the incommensurate magnetic reflections having an cubic symmetry index of $(h \pm q_x, k, l \pm q_y)$ with $q_x \approx 0.470$ at 2.5K. Thus, we carried out measurements of integrated intensity of $(0,0,q_y)$ magnetic peak as a function of temperature, to determine the antiferromagnetic phase transition temperature. It was found that the magnetic phase transition occurs at about 21K ($T_{N}$) and a magnetic diffuse scattering appears above $T_{N}$, as like neutron powder patterns [1].

In order to study a thermal modulation of an incommensurate periodicity of the spiral spin order along C axis, we simultaneously measured

![Graph](ZnCr2Se4.png)
peak profiles of the (2,2,2) fundamental reflection and the satellite-like (2,2,2 ± q) magnetic reflections by a k - scan along a reciprocal lattice axis of C* at respective temperature. Figs. 2(a), (b) and (c) show the peak profiles of the (2,2,2−q), (2,2,2) and (2,2,2+q) as a function of temperature, we did a Gaussian curve-fitting to the peak profiles of the reflections in Figs. 2(a), (b) and (c). The results are shown in Fig.3, where q = (q1 + q2)2. Therefore, it was considered that an incommensurate periodicity of the spiral spin order is slightly modulated along C axis.

![Fig.2. Temperature dependence of the peak profiles of the fundamental reflection of (2,2,2), and magnetic reflections of (2,2,2−q) and (2,2,2+q), respectively. It was found that, on heating, the anti-ferromagnetic reflections of (2,2,2−q) and (2,2,2+q) reduce the intensity and inversely shift the peak position each other to the (2,2,2) reflection, while the peak position of (2,2,2) reflection does not depend on temperature. To accurately obtain the q and q, as a function of temperature, we did a Gaussian curve-fitting to the peak profiles of the reflections in Figs. 2(a), (b) and (c). The results are shown in Fig.3, where q = (q1 + q2)2. Therefore, it was considered that an incommensurate periodicity of the spiral spin order is slightly modulated along C axis.](image)

Fig.3. Temperature dependence of q, q1, and q2, refined by the Gaussian curve-fitting to the peak profiles shown in Fig.2(a), (b) and (c).

However, the temperature dependence of q, q1, and q2 shows a first-order transition at about 21K, as like the first-order property of the structural phase transition. Thus, we argued that the structure phase transition at Tc mainly results from a construction of spiral magnetic long-range order along C axis. We could often observe an unusual rod-like magnetic diffuse scattering, when the crystal was cooled gradually by passing through the structural phase transition. The diffuse scattering was passed through a reciprocal lattice point of (h, h, h+q) to be approximately parallel to [111]. The rod-like magnetic diffuse scattering disappeared above Tc. This means that there is two-dimensional anti-ferromagnetic spin order appears in a single [111] plane but its planar spin order perfectly disappears between adjacent [111] planes.


Magnetic excitation in Pt-Mn spin glass alloy

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The mechanism of spin-glass behavior in Cu-Mn and Pt-M or Pd-M alloys (M represents 3d metal) has been explained by a dynamical fluctuation of short-ranged SDW [1]. In these alloys, the SDW does not develop to long-ranged because of the absence of atomic long-range order. Recently, in Pt rich Pt-Mn alloys, ABC₆ type ordered phase is found to exist around 14.4 at.\%Mn [2]. By long annealing, long-range order of the structure develops in the alloys. However, magnetic susceptibility shows clear spin-glass behavior in both ordered and disordered alloys. In the susceptibility data for the ordered 14.4 at.\%Mn alloy, antiferromagnetic transition is found with T_N = 20 K along with the spin-glass behavior. From the diffraction measurements, the static magnetic structure is shown to consist of antiferromagnetic long range order and short-ranged SDW in the alloy. In the data, magnetic peaks for the long range order appear below T_N with diffuse scattering for the short-ranged SDW remaining even at R.T.. The diffuse scattering is elongated along [110] and [1\bar{1}0] on (001) plane at around (1/2 1/2 0) and also observed at equivalent positions with the symmetry of ABC₆ type structure.

In order to understand magnetism in the ordered alloy, we have performed inelastic neutron experiment using TOPAN in JRR3M in Tokai, JAERI. In fig.1, inelastic patterns of the diffuse scattering at around (1/2 1/2 0) are shown. Their intensities increase at temperature higher than T_N and show a maximum at 40 K, whereas the elastic component increases with decreasing temperature (fig.2). The results indicate that in the ordered alloy, a dynamical structure is governed by the short-ranged SDW though static structure forms antiferromagnetic long range order.

![Fig.1 Inelastic patterns at 1.5 meV.](image)

![Fig.2 Temperature dependences of elastic and inelastic components.](image)

References

Magnetic structure analysis of KCuF$_3$

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KCuF$_3$ is one of the typical example of the one-dimensional antiferromagnet with $S = 1/2$. In spite of the pseudo-cubic crystal structure, it forms antiferromagnetic quantum linear chains along the c-axis as a result of the orbital ordering of Cu$^{2+}$ holes. It turns into a long-range ordered state at low temperature owing to the very weak inter-chain exchange interaction. The magnetic structure below $T_N$ is a type-A ordering with the spins lying in the c-plane due to the very weak XY-like anisotropy. By neutron diffraction measurements, the spin direction in the c-plane was proposed to be parallel to [100] in a unit cell of a perovskite structure [1]. On the other hand, magnetic resonance studies have shown that due to the Dzyaloshinsky and Moriya (DM) interaction, it has an eight-sublattice magnetic structure and substantial easy direction is along [110] and its equivalent axis [2]. In this study, neutron diffraction measurements with a single crystal KCuF$_3$ have been performed by using Four-circle Off-center-type Diffractometer FONDER in JRR-3M at Tokai JAERI, to confirm the spin structure reported by resonance measurements and investigate Cu$^{2+}$ orbital ordering based on the actual magnetic structure.

A single crystal sample grown by a precipitation method with about 13 mm$^3$ in volume was used in the experiment. There are two different crystal types in KCuF$_3$ which are named (a) and (d) type respectively owing to the difference of the displacement of flourines in the sequence along the c-axis. We examined the nuclear reflections belonging to both types and found that the sample is almost (a) type. The Néel temperatures for (a) and (d) types are 39 and 22 K, respectively. In the sample, $T_N$ is found to be 39 K confirming that the sample is mainly (a) type.

Over 80 magnetic reflections up to 8 Å$^{-1}$ have been measured below and above $T_N$ and differences between them are regarded as magnetic scattering. The obtained magnetic form factors are shown in fig.1 in which absorption and Lorents factor were corrected. For full analysis, accurate ratio of (a) type to (d) type in volume and distances between Cu – F of Cu – F$_6$ octahedron should be known for the sample. Powder diffraction measurements for the same sample are now in plan for these structural parameters.

![Fig.1 Observed magnetic form factor at 8 K.](image)

**References**

Antiferromagnetic Phase Transition in Substituted Spinel of

\[ \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4; x = 0.50 \text{ and } 0.60 \]

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\( \text{ZnCr}_2\text{Se}_4 \) and \( \text{CuCr}_2\text{Se}_4 \) have a normal spinel-type structure, which is mainly characterized by a strong preference of \( \text{Cr}^{3+} \) ions to locate in the octahedral site. \( \text{ZnCr}_2\text{Se}_4 \) spinel is an antiferromagnetic insulator or semiconductor below 20K. The magnetic structure is mainly characterized by a spiral spin order of \( \text{Cr}^{3+} \) ions. \( \text{CuCr}_2\text{Se}_4 \) is a ferromagnetic metal below 420K. \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) show an ideal solid solution and non-modification of the normal spinel structure. The magnetic and electronic properties of \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) depend on Cu-concentration \( x \). It is known that an antiferromagnetic semiconductor occurs in \( x < 0.10 \) and their Néel temperature \( (T_n) \) is about 20K, while an ferromagnetic metal occurs in \( 0.2 \leq x \leq 1.0 \) and their Curie temperature \( (T_c) \) is about 380~420K.

More recently, Hidaka et al. [1] argued that the substituted spinels with \( x = 0.15 \) and 0.30 show a new antiferromagnetic transition at about 23.0K and 24.5K, in addition to a ferromagnetic transition at about 410K and 415K, respectively. We considered that the magnetic phase diagrams should be re-studied to interpret a complex correlation between the magnetic and electronic properties in \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \). Because it has been known that the substituted spinels with \( x = 0.15 \) and 0.30 are not the anti-ferromagnet but semiconductive spin glass and metallic conical ferromagnet, respectively. Thus, we carried out measurements of some magnetic reflection in \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) with \( 0.50 \leq x \leq 1.0 \), using a high-resolution neutron diffractometer, HERMES, in JRR-3. The used wavelength of incident neutron beams was about 1.820 Å. The partial powder diffraction patterns of \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) with \( x = 0.50, 0.60 \) and 0.75 are shown in Figs. 1(a), (b) and (c), respectively. In the figures), the thin and thick solid-lines represent the data taken at about 2K and 40K, respectively.

![Fig. 1. Peak profiles of Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ with $x = 0.50, 0.60$ and $0.75$, taken by neutron powder diffraction.](image)

Notations of (1,1,1), (2,2,0), (3,1,1) and (2,2,2) mean an index for fundamental reflections, while a notation 'M' a magnetic reflection. The magnetic reflections appear only in the antiferromagnetic phase below $T_n$. The magnetic reflection having a strongest intensity in Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$.

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\(\text{Cu}_2\text{Cr}_2\text{Se}_4\) with \(x = 0.50\) and 0.60 was observed at about \(2\theta = 4.69\) and 4.90 degrees at 2K, respectively. However, we could find only weak magnetic reflections at about \(2\theta = 5.0\) degrees in \(\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Cr}_2\text{Se}_4\) as shown in Fig. 1(c). Therefore, we considered that the antiferromagnetic phase transition in \(\text{Zn}_{x}\text{Cu}_2\text{Cr}_2\text{Se}_4\) occurs in the region of \(0.0 \leq x < 0.75\). Furthermore, the magnetic diffuse scattering denoted with MD was also observed at 40 K in Figs. 1(a), (b) and (c). The magnetic diffuse scattering decreased its intensity as increasing the specimen temperature and disappeared above about 70K.

In order to index such the magnetic reflections, we deduced the counts of the powder patterns taken at 2K from those taken at 40K in \(\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Cr}_2\text{Se}_4\). The resulting difference curve is shown in Fig.2. In the figure, all of the peak-profiles were the magnetic reflections. Furthermore, the magnetic diffuse scattering (MD) can be confirmed by negative counts in the figure. Since the magnetic reflections are related to the spiral spin-configuration, the satellite-like magnetic reflections could be indexed by \((h \pm 4, k, l)\) with \(Q = 0.470\) as shown in Fig. 2. The calculated peak positions of the magnetic reflections are shown with thick vertical lines in Fig. 2. The value of \(Q\) in \(\text{Zn}_{x}\text{Cu}_2\text{Cr}_2\text{Se}_4\) is 0.493, in contrast with 0.470 for \(\text{Zn}_{0.2}\text{Cu}_2\text{Cr}_2\text{Se}_4\) with \(0.0 \leq x \leq 0.50\).

We carried out measurements of an integrated intensity of the magnetic reflection having the index \((Q,0,0)\) in Fig. 1(a) and (b), in order to find transition temperature in \(\text{Zn}_{x}\text{Cu}_2\text{Cr}_2\text{Se}_4\) with \(x = 0.50\) and 0.60. The results are shown in Figs. 3(a) and (b). Since the magnetic diffuse scattering occurs above the phase transition, it is not easy to separate the intensity between the magnetic reflection and the magnetic diffuse scattering in the vicinity of the transition temperature.

![Fig.3.Temperature dependence of the intensity of the magnetic reflection in for Zn_{x}Cu_{2}Cr_{2}Se_{4}; x=0.50 and 0.60.](image)

Thus, we approximately determined the transition temperature by calculating a derivative point of the intensity curve shown in Figs. 3(a) and (b). The results suggested that the magnetic transition occurs at about 25K in \(\text{Zn}_{x}\text{Cu}_2\text{Cr}_2\text{Se}_4\) with \(x = 0.50\) and 0.60. We also measured the magnetization of the present spinels using a SQUID magnetometer. The results showed the antiferromagnetic phase transition occurring at 24K and 28K for \(\text{Zn}_{x}\text{Cu}_2\text{Cr}_2\text{Se}_4\) with \(x = 0.50\) and 0.60, respectively.

Magnetic structure and $H$-$T$ phase diagram in a localized $5f$ system $U_3\text{Pd}_{20}\text{Si}_{6}$

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Actinide based intermetallic compounds attract strong interests because of the variety of their magnetic and electronic properties. The $5f$ electrons in most of uranium intermetallic compounds exhibit itinerant character, which is due to strong hybridization with conduction electrons. Up to now only a few uranium compounds have been reported as localized $5f$ systems. Recently we have found a new uranium intermetallic compound $U_3\text{Pd}_{20}\text{Si}_{6}$. The localized character was suggested by the Curie-Weiss behavior in magnetic susceptibility. The purpose of this study is to clarify the crystal and magnetic structure and the $H$-$T$ phase diagram in $U_3\text{Pd}_{20}\text{Si}_{6}$.

Powder diffraction data were measured using HRPD at $\lambda = 1.162$ Å with the collimation of $6^\circ$-$12^\circ$-$6^\circ$. Single crystal diffraction and inelastic scattering were measured using triple-axis spectrometers TAS-1, TAS-2, and LTAS. The sample was cooled by using a conventional dilution refrigerator (DR) or a liquid-He-free DR$^3$ with a liquid-He-free 10 T magnet.$^4$

Figure 1 shows the crystal structure of $U_3\text{Pd}_{20}\text{Si}_{6}$. Uranium atoms occupy two different crystallographical sites, $4a$-fcc site and $8c$ simple cubic site which has a half unit of the crystallographical unit cell. The space group is $Fm\overline{3}m$. The structural parameters obtained by neutron diffraction have been published elsewhere.$^5$ Upon cooling down the sample, magnetic peaks were superposed at odd integer nuclear reflections, (111), (311), etc as shown in Fig. 2(a). Therefore the propagation vector is $[111]$. These magnetic peaks are explained in terms of the antiferromagnetic ordering on $8c$ site. The propagation vector [111] can be described as $[1/2 1/2 1/2]$, when the indices are denoted by the $8c$ simple cubic cell. The magnetic ordering on $4a$ site can be ruled out, because the magnetic scattering only at the odd integer reflections can not be explained by any kind of magnetic ordering on $4a$ site. Below $T_C = 2$ K we observed additional magnetic intensities at all nuclear reflections (Fig. 2(b)). This is due to the ferromagnetic ordering on $4a$ site. The moment size was determined to be $1.83 \pm 0.05 \mu_B$ for $8c$ site. The moment on $4a$ site $1.1 \mu_B$ for $H = 0$ is strongly suppressed and recovered in the magnetic field up to $1.6 \mu_B$ for $H = 10$ T. This suppression would be a result of the strong frustration of $4a$ site due to the coupling with $8c$ site.

![Figure 1: The crystal structure of $U_3\text{Pd}_{20}\text{Si}_{6}$.](image)

原子炉：JRR-3M 装置：TAS-2(T2-4) 分野：中性子散乱（磁性）
Figure 2: (a) The powder diffraction profile of $U_2Pd_{25}Si_6$. (b) The temperature dependence of the (111) and (022) peak intensities.

Figure 3 shows the $H-T$ phase diagram of $U_2Pd_{25}Si_6$ determined by neutron diffraction.\textsuperscript{6} For $T_C < T < T_N$ only 8$c$ spins exhibit antiferromagnetic ordering. The magnetic easy axis is along (100) for 8$c$ spins. Below $T_C = 2$ K, the ferromagnetic ordering on 4$a$ site coexists with 8$c$ antiferromagnetic ordering. The collinear structure is realized in the ground state. Our neutron diffraction experiments with magnetic field unambiguously revealed the collinear interaction between 4$a$ and 8$c$ spins. The origin of this collinear interaction is an open question. It can not be explained with Heisenberg interaction which is cancelled out within the inter-site nearest neighbor pairing. The cancellation of the dipole field is also clear. Therefore we conclude that the higher-order exchange and/or quadrupole interaction would be the origin of this unusual collinear interaction.

With applying field, we observed spin flop of 8$c$ site at $H_C \sim 5T$ against the uniaxial anisotropy induced by this collinear interaction. This is a new type of spin flop related to the higher-order interaction in the coexistence of ferromagnetic and antiferromagnetic sublattice ordering.

The existence of the metamagnetic behavior in $U_2Pd_{25}Si_6$ was reported for the first time in magnetization measurement.\textsuperscript{7} The present study revealed the origin of the metamagnetic transition by means of neutron scattering on a single crystal under high-field.

References
Magnetic structure in an itinerant 5f antiferromagnet UCr$_2$Si$_2$

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UT$_2$X$_2$ is one of the traditional 5f electron systems that the unusual magnetic and transport properties have been studied systematically for various compounds with different transition metal T and X=Si, Ge. In UCr$_2$Si$_2$ the small number of $d$-electrons and small distance between U atoms give rise to enhanced itinerant character of the 5f-electrons. In fact, this compound shows strong anisotropic susceptibility which obeys Curie-Weiss law with effective moment 2.54 $\mu_B$/U much smaller than uranium free ion. The electronic specific heat 80 mJ/K$^2$mol is the signature for the heavy fermion with medium mass enhancement. There is an antiferromagnetic ordering below $T_N = 27$ K. The magnetic entropy was roughly the half of Rhn2. The purpose of this study is to clarify the magnetic structure of UCr$_2$Si$_2$ by means of neutron scattering.$^1$

The neutron scattering experiments were carried out using the triple axis spectrometers LTAS and TAS-2. The energy was 4.66 meV and 14.7 meV for LTAS and TAS-2, respectively. We used Be and/or PG filters to remove the higher order contaminations.

The antiferromagnetic peaks were searched with polycrystalline sample with use of LTAS. At 8 K we observed antiferromagnetic peaks at the scattering angle of the (-1/2,1/2,0) and (-1/2,1,1) peak positions as shown in Fig. 1.

Figure 2 (a) shows the contour plot of the magnetic scattering intensity around the (-1/2,1,0) magnetic reflection in the $(h,k,0)$ scat-

![Figure 1: The powder diffraction pattern of UCr$_2$Si$_2$ at $T= 8$ K and 34 K.](image1)

![Figure 2: (a) The contour plot of the scattering intensity around (-1/2,1,0) magnetic reflections. (b) The position of the magnetic (close circles) and nuclear (open circles) reflections in the $(h,k,0)$ scattering plane.](image2)
Figure 3: The temperature dependence of the antiferromagnetic Bragg intensities.

We observed splitting of the magnetic peaks. This splitting is due to the domain structure associated with the structural transition of UCr$_2$Si$_2$. UCr$_2$Si$_2$ has a triclinic structure below $T_a = 210$ K. From the peak position, we conclude that the antiferromagnetic wave vector is $Q = [-\frac{1}{4}, \frac{1}{4}, 0]$. It should be noted that the wave vector $[-\frac{1}{4}, \frac{1}{4}, 0]$ is not equivalent to the $[\frac{1}{2}, \frac{1}{2}, 0]$ in the low temperature triclinic structure. The $a^* - b^*$ reciprocal plane and the position of the antiferromagnetic reflections are shown in the schematic view graph in Fig. 2 (b).

The magnetic peak intensities were measured as a function of temperature. The peak intensities showed a clear nature of the magnetic order parameter as plotted in Fig. 3.

The observed integrated intensities of the magnetic reflections were compared with model calculations, using the following equation,

$$I_{mag}(Q) \propto |F_{mag}(Q)|^2 f^2(Q) (\sin \alpha)^2 L(\theta),$$

where $F_{mag}$ is the magnetic structure, $f$ is the magnetic form factor of uranium U$^{3+}$ free ion, $\alpha$ is the angle between the ordered magnetic moment and the scattering vector $Q$ and $L$ is the Lorentz factor.

The experimental results are well explained by the model calculation with the ordered moment of uranium 0.65 $\mu_B$/U parallel to the [0,0,1] direction. The weaker intensity at the $(-\frac{1}{2}, \frac{1}{2}, 0)$ antiferromagnetic peak than the expected one from the model calculations is most probably due to the extinction, since this reflection is rather strong. The obtained magnetic structure is displayed schematically in the inset of Fig. 4. The obtained moment size is consistent with that of typical itinerant 5f antiferromagnet, UGa$_5$$_3$, UPtGa$_5$ and UNiGa$_5$. The direction of the moment is consistent with the uniaxial anisotropy in magnetic susceptibility, where the c-axis is the easy axis.

References

Magnetic Excitations in an itinerant 5\textit{f} antiferromagnet UPt$_2$Si$_2$

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The wide variety of behaviour exhibited by 5\textit{f} electrons is one of the most intriguing problems in strongly correlated electron systems. The spectrum, encompassing localised, heavy fermion, non-fermi liquid and itinerant aspects, depends on the strength of the hybridization with valence and ligand electron states. Materials in the UT$_2$Si$_2$ system play an important role in our understanding as the hybridisation can be controlled by varying the transition metal element T. In this respect the unusual transition at $T_0 = 17$ K and the superconductivity in UR$_2$Si$_2$ are especially interesting with, on the other hand, UPt$_2$Si$_2$ ($T_N = 37$ K, $M = 1.7 \mu_B$) being considered as an example of an antiferromagnet with localised 5\textit{f} states. The susceptibility 1) and specific heat 2) of the latter material were understood in terms of the crystalline electric field (CEF) levels suggested by a previous neutron scattering study on a polycrystalline sample 3) whilst the large drop of the resistivity at $T_N$ and the anisotropic behaviour remained unexplained 3). The purpose of this study is to reveal the magnetic excitations of UPt$_2$Si$_2$ in single crystalline samples.

Single crystalline samples were grown by the Czochralski-pulling method in a tetra-arc furnace under argon gas atmosphere. The magnetic excitation was measured with three single crystal rods aligned within the accuracy of 0.3 degrees on a triple axis spectrometer LTAS with fixed $E_f = 3.5$ meV.

Figure 1 shows the crystal structure of UPt$_2$Si$_2$. UPt$_2$Si$_2$ has the CaB$_2$Ge$_2$-type structure with space group P4/nnm. The uranium magnetic moments order antiferromagnetically below $T_N = 37$ K.

Figure 2: The intensity of the (100) antiferromagnetic Bragg peak and the inelastic component at $\Delta E = 0.4$ meV in UPt$_2$Si$_2$, denoted by close and open circles, respectively.
Figure 3: The inelastic scattering profile at $Q = (100)$ and $(1.3 0 0)$, denoted by circles and triangles, respectively. The spectra were measured at 3.1 K (close symbols) and 38 K (open symbols), respectively.

The magnetic structure can be described by the antiferromagnetic stacking of the ferromagnetic basal plane along the $c$-axis as shown in Fig. 1. The uranium moment 1.67 $\mu_B$/U is parallel to the $c$-axis.

The temperature dependence of the $(100)$ antiferromagnetic Bragg intensity is plotted in Fig. 2. The intensity exhibits a clear nature of the magnetic order parameter. The intensity at the neutron energy loss $\Delta E = 0.4$ meV increases with elevating temperature and showed a maximum at $T_N$. It means that there is a low energy magnetic excitation.

The existence of the low energy component of the magnetic excitation is clearly demonstrated by the inelastic scattering profile shown in Fig. 3. On the $(100)$ antiferromagnetic zone-center we observed pronounced quasi-elastic peak at $T = 38$ K, slightly above $T_N$. This quasi-elastic scattering can be fitted by Lorentzian line shape with the full width of 0.15 meV. This excitation decreases in intensity with decreasing temperature. At $Q = (1.3 0 0)$ a weaker and broader quasi-elastic scattering with width of 0.4 meV was observed. Figure 4 shows the magnetic excitation spectra of UPt$_2$Si$_2$ measured as a function of $Q$. It is clearly seen that the low energy quasi-elastic scattering has a maximum intensity around the antiferromagnetic zone center $(100)$. We concluded that this low energy quasi-elastic component is spin fluctuations of the heavy quasi-particles due to hybridization between $5f$ and conduction electrons. Very recently similar low energy excitation has been observed in the heavy fermion superconductors UPd$_2$Al$_3$ 4, UPt$_3$ 5, and $5f$ itinerant antiferromagnet $UGa_5$. 6 It is also found even in the localized $5f$ antiferromagnet, $U_3Pd_2Si_8$. 7 Therefore, the existence of the low energy quasi-elastic component due to quasi-particles is a general feature in uranium intermetallic compounds, because $5f$ electrons in uranium has rather strong hybridization effect.

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Neutron Scattering Study of the Magnetic and Crystal Structures in Itinerant-5f Antiferromagnets UNiGa₅ and UPtGa₅

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Very recently we succeeded in growing single crystals of uranium intermetallic compounds UTG₅ (T: Fe, Co, Ni, Ru, Rh, Os, Ir, Pt). These are iso-structural compounds of heavy fermion superconductors Ce₁₁S and/or PuCoGa₅ with the HoCoGa₅-type tetragonal structure with space group (P4/mmm), as shown in Fig. 1.¹ This crystal structure can be described by a stacking of uniaxially distorted UGa₃ layer with the AuCu₃-type structure and a transition metal layer along the [0,0,1] direction. UTG₅ (T: Ni, Pd, Pt) are typical itinerant 5f antiferromagnet, while the other compounds exhibit Pauli-paramagnetic behavior.²,³ We revealed the crystal and magnetic structures of UNiGa₅ and UPtGa₅.⁴

Polycrystalline samples were synthesized by arc-melting and subsequent annealing. Single crystals were grown by the Ga self-flux method. The detail of sample preparation technique has been published elsewhere.²,³ Neutron scattering experiments were carried out using HRPD and TAS-1.

Figure 2 shows a powder diffraction pattern of UNiGa₅ at 8 K. The profile was satisfactorily analyzed by the HoCoGa₅-type structure. The structural parameters have been published elsewhere.⁴ The UGa₃ layer is more compressed in UPtGa₅ than in UNiGa₅ due to the larger ionic radius of Pt.

Figure 3(a) shows the result of the (h, h, h) scan for UNiGa₅ at 10 and 90 K, below and above $T_N$ (=86 K), respectively. We observed clear antiferromagnetic reflections with half integer reflection indices such as (1/2,1/2,1/2) and (3/2,3/2,3/2). These data indicate that the antiferromagnetic propagation vector in UNiGa₅ is [1/2,1/2,1/2]. On the other hand, the antiferromagnetic peak of UPtGa₅ was observed at the Bragg points with half integer 1/2 Therefore we conclude that the propagation vector in UPtGa₅ is [0,0,1/2]. No magnetic scattering was observed at (0,0,1/2), indicating the direction of the magnetic moment to be along the [0,0,1] in UPtGa₅.

![Figure 1: Crystal structure of UTG₅.](image1)

**Figure 1: Crystal structure of UTG₅.**

![Figure 2: Crystal structure of UTG₅.](image2)

**Figure 2: Crystal structure of UTG₅.**
Figure 3: Elastic neutron scattering profile in the (a) \((h,h,h)\) scan in UNiGa5 and (b) \((1,0,1)\) and \((0,0,0)\) scans in UPtGa5. Inset: The positions of the nuclear (solid squares) and magnetic (open circles) peaks.

From the propagation vector, the magnetic structures can be proposed as shown in Fig 4. In UNiGa5 the uranium moment has the \(\text{N}\)el-type structure. Namely adjacent spins orient along the opposite direction. On the other hand, magnetic moments of uranium atoms in UPtGa5 are aligned ferromagnetically in the \((0,0,1)\) plane and stacked antiferromagnetically along the \([0,0,1]\) direction \((\uparrow\downarrow)\). Fig 4 is the integrated intensities of the antiferromagnetic reflections. The experimental results are well explained by the model calculation with the moment parallel to the \([0,0,1]\) direction. The magnetic moments were estimated to be 0.9±0.1 \(\mu_B/\text{U}\) and 0.24±0.03 \(\mu_B\) in UNiGa5 and UPtGa5, respectively. The Ni and Pt moment should be negligibly small.

The magnetic structures in UNiGa5 and UPtGa5 are considerably different. The nearest-neighbor interaction has opposite sign. At present we have no definitive explanation for the unusual difference in magnetic structure. We believe, however, that the \(5f\) and Ga-\(4p\) hybridized band plays a significant role for the antiferromagnetic propagation vector. It is well known that the magnetic ordering is closely related to the electronic and orbital configuration. Therefore it might be possible to find out a configuration which gives rise to the cross over of the interaction in the basal plane between antiferromagnetic and ferromagnetic, when the \(p-f\) hybridization changes with stress due to the difference in ionic radius.

References
Magnetic structure of the coupled edge-sharing CuO$_2$ chains in Ca$_2$Y$_2$Cu$_5$O$_{10}$

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An interesting feature in the edge-sharing CuO$_2$ chain, in which copper spins are coupled by the nearly 90° Cu-O-Cu interaction, is that the magnetic moments can be induced at oxygen sites because of a strong Cu $d$-O $p$ hybridization in the CuO$_2$ chains. An existence of the magnetic moments in the CuO$_2$ chains is predicted theoretically in Li$_2$CuO$_2$. 1) and observed experimentally in La$_8$Ca$_8$Cu$_{24}$O$_{41}$. 2)

From a powder diffraction study, 3) a possibility of a small amount of the magnetic moments at oxygen sites is suggested. However, the number of the magnetic Bragg peaks used for the magnetic structural analysis is only 5 and errors of the magnetic intensities are rather large because the magnetic intensities are weak except an intense (0,0,1) peak. As the result, the statistics are not enough to analyze the data quantitatively. In this study, we performed neutron diffraction measurements using a single crystal in order to elucidate the magnetic moment at oxygen sites in the ferromagnetic edge-sharing CuO$_2$ chains Ca$_2$Y$_2$Cu$_5$O$_{10}$.

The single crystal of Ca$_2$Y$_2$Cu$_5$O$_{10}$ was grown using a traveling solvent floating zone method in air. The dimensions of the rod shaped crystal were ~6×25 mm$^3$. The neutron scattering experiments were carried out on the 3-axis spectrometer TAS-2.

The magnetic Bragg reflections are expected at (even, even, odd) and (odd, odd, even) from the magnetic structure determined by the powder diffraction studies. 3, 4) If the magnetic moments are localized at Cu sites and point along the $b$ axis, the magnetic Bragg intensity should decrease monotonically with increasing $Q$, mainly due to the magnetic form factor and the Lorentz factor.

Figure 1 shows an elastic scan along $[h, h, 1]$ measured at 9 K. The integrated intensities of a number of magnetic peaks were obtained from $\theta$-2$\theta$ scans as shown in Table I. Along [0, 0, 1] and [2, 2, 1], the magnetic intensities decrease with increasing $Q$. On the other hand, along [1, 1, 1] the magnetic intensities shows a modulation and has a maximum at (1,1,2). This behavior is similar to that observed along $[h, 0, 1]$ in La$_8$Ca$_8$Cu$_{24}$O$_{41}$.

![Figure 1: Elastic neutron scan of Ca$_2$Y$_2$Cu$_5$O$_{10}$ along [0, 0, 1] (a), [1, 1, 1] (b), and [2, 2, 1] (c) measured at $T$=9 K. The data at $T$=35 K were subtracted as background.](image-url)
Table 1: Observed integrated ($I_{\text{obs}}$) and calculated intensities ($I_{\text{calc}}$) of magnetic Bragg reflections on Ca$_2$Y$_2$Cu$_3$O$_6$. The measurements were performed at $T=9$ K. $I_{\text{Cu}}$ represents the intensity calculated by assuming the magnetic moments only at the Cu sites.

<table>
<thead>
<tr>
<th>$(h,k,l)$</th>
<th>$I_{\text{obs}}$</th>
<th>$I_{\text{calc}}$</th>
<th>$I_{\text{Cu}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,1)</td>
<td>105(4)</td>
<td>152</td>
<td>90.6</td>
</tr>
<tr>
<td>(0,0,3)</td>
<td>18.3(2)</td>
<td>19.8</td>
<td>22.9</td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>8.0(2)</td>
<td>5.4</td>
<td>8.5</td>
</tr>
<tr>
<td>(0,0,7)</td>
<td>4.3(2)</td>
<td>4.4</td>
<td>3.6</td>
</tr>
<tr>
<td>(0,0,9)</td>
<td>1.6(1)</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>4.8(1)</td>
<td>6.2</td>
<td>10.2</td>
</tr>
<tr>
<td>(1,1,2)</td>
<td>9.0(1)</td>
<td>8.9</td>
<td>8.6</td>
</tr>
<tr>
<td>(1,1,4)</td>
<td>10.1(1)</td>
<td>10.0</td>
<td>5.6</td>
</tr>
<tr>
<td>(1,1,6)</td>
<td>5.1(1)</td>
<td>4.4</td>
<td>2.9</td>
</tr>
<tr>
<td>(1,1,8)</td>
<td>1.4(1)</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>(2,2,1)</td>
<td>2.4(1)</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>(2,2,3)</td>
<td>1.6(1)</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>(2,2,5)</td>
<td>1.0(1)</td>
<td>0.58</td>
<td>0.93</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td></td>
<td>2.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

As shown in Table 1, a simple model that assumes magnetic moments only at the Cu sites does not describe the modulation of the intensity along [1,1,1]. One possibility to explain the modulation would be that the Cu moments do not point exactly along the $b$ axis but between the $a$ and $b$ axes. However, this structure also requires the similar modulation of magnetic intensities along [2,2,1]. Therefore, it is more plausible that moments induced on the oxygen sites present in the magnetically ordered phase as described below.

The result of a least-square fitting shows that the moment at the oxygen site is $14\pm2\%$ of that at the Cu site. The fitted magnetic intensities agree reasonably well with the observed ones as shown in Table 1. Assuming that the total moment in a CuO$_2$ unit is $\sim0.9\mu_B$, which is determined from the powder diffraction measurement, the ordered Cu moment is estimated to be $\sim0.7\mu_B$ and the O moment is $\sim0.1\mu_B$. Although there is an ambiguity in the absolute value of the magnetic moment, a ratio between copper and oxygen moments should be quite accurate. Note that the absolute value of the ordered moment in Cu$_2$Y$_2$Cu$_3$O$_6$ ($\sim0.9\mu_B$) is larger than in La$_5$Ca$_9$Cu$_{24}$O$_{41}$ ($\sim0.2\mu_B$) probably because the interchain coupling along the $b$ axis is larger so that the quantum fluctuation is more suppressed. The fraction of the oxygen moment in the CuO$_2$ unit is $22\pm4\%$, which is similar to that in La$_5$Ca$_9$Cu$_{24}$O$_{41}$ ($\sim17\%$). This fact suggests that the covalency between the Cu and O ions in the CuO$_2$ chain is similar in both compounds.

![Figure 2: A proposed model for the magnetic structure in the CuO$_2$ chain. Closed and open circles represent copper and oxygen ions, respectively.](image)

References

SANS Study of Slow Dynamics in Concentrated Spin Glasses

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Although the problem of slow dynamics, or long time relaxation phenomena, has long been a central issue of the spin-glass research, the experimental studies on slow dynamics have been limited to macroscopic measurements. In order to clarify the mechanism of slow dynamics, the application of microscopic experimental method such as time-resolved neutron scattering technique has been needed. In the previous neutron scattering studies on concentrated spin-glass alloys we showed that the magnetic clusters play an important role for the reentrant spin-glass (RSG) transition and that a wide variety of spin dynamics observed in various RSG materials can be attributed to the differences in the size and the number of magnetic clusters. Based on this finding, we speculate that the mechanism of slow dynamics might be closely related to the time evolution of magnetic clusters which can be detected by small-angle neutron scattering (SANS) experiment.

We have made time-resolved SANS experiments on several kinds of concentrated spin glass materials of which characteristics in the stationary state had been clarified in the previous neutron scattering experiments. In this report, we present a result of the time-resolved SANS experiment of a typical spin glass alloy Fe_{0.70}Al_{0.30} in magnetic field. Results in zero magnetic field of the present sample and other RSG alloys have already been reported elsewhere.

Fe_{0.70}Al_{0.30} alloy used in the present experiment transforms to the ferromagnetic phase below 510K then enters the paramagnetic phase below 160K and finally it enters the spin-glass phase at 70K. Microscopic characterizations of the magnetic "phases" of the present alloy system was extensively investigated by elastic and inelastic neutron scattering measurements.

Time-resolved SANS experiments were made utilizing the SANS-J spectrometer installed at the JRR-3M reactor of JAERI-Tokai. The incident-neutron wavelength and band-width are \lambda=0.45-0.65nm and \Delta\lambda/\lambda=0.10-0.14, respectively. The momentum-transfer range of 0.03<q<2 nm^{-1} was covered by changing the sample-detector length between 1.35 to 10m. Sample was rapidly cooled to the RSG phase in zero field. After the waiting time t_w magnetic field was applied and a series of time-resolved SANS patterns was taken up to 20hrs with a typical time window of 10-30mn. Observed SANS patterns (scattering intensity as a function of momentum transfer q) are well traced by a Lorentzian (LOR) function

\[ I(q) = \frac{A}{q^2 + \kappa^2} \]

within the q range of 0.06<q<0.3 nm^{-1}. Based on a simple model, the LOR form is attributed to the scattering from magnetic clusters with correlation length of 1/\kappa.

In Fig.1, we show the time variation of \kappa measured under (a) H=0 Oe and (b) H=500 Oe at representative temperatures. In zero field the time variation of \kappa is more pronounced as temperature increases, however the initial value (\kappa at time=0) does not change so much with temperature. Under H=500Oe, the initial value and the time variation behavior are quite different from those in zero field. At T=10K, the initial value is nearly same as that in H=0. At high temperatures the initial value is remarkably larger than that of at H=0, which means \kappa suddenly increases by the application of field. Time variation of

原子炉：JRR-3M 装置：SANS-J(C3-2) 分野：中性子散乱（磁性）
\( \kappa \) either in \( H=0 \) Oe or in \( H=500 \) Oe is well traced by a simple function

\[
\kappa(t) = \kappa_0 + A \exp \left( -\frac{t}{t^*} \right)
\]

with a temperature dependent characteristic time \( t^* \). In Fig. 2 we show \( 1/t^* \) as a function of temperature. Detailed analysis and discussion including the results of macroscopic measurements will be presented elsewhere. 8)

**References**


![Figure 1:](image1)

![Figure 2:](image2)
Relationship between the Magnetic Structure and the Anomalous Hall Effect of 
\( \text{Cu}_{1-x}\text{Zn}_x\text{Cr}_2\text{Se}_4 \)

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In the study of the magnetic and transport properties of \( \text{Nd}_2\text{MnO}_2 \), we have reported that its Hall resistivity \( \rho_H \) cannot be described by the equation \( \rho_H = R_0 H + 4\pi R_a M \) used for ordinary ferromagnets, where \( H \) and \( M \) are the applied magnetic field and the uniform magnetization, respectively, and \( R_0 \) and \( R_a \) are the ordinary and anomalous Hall coefficients, respectively. Instead, an equation \( \rho_H = R_0 H + 4\pi R_a M_{Mn} + 4\pi R_a' M_{Nd} \), which has two individual contributions from the Mn and Nd-moments, \( M_{Mn} \) and \( M_{Nd} \), respectively, can describe the \( T \)- and \( H \)-dependences of \( \rho_H \). Although the equation seems to be a simple extension of the ordinary equation, the \( T \)-dependences of the anomalous Hall coefficients \( R_a \) and \( R_a' \) obtained for the present system cannot be understood by the classical theories. Then, a question arises how this unusual behavior of \( \rho_H \) is related with its non-collinear magnetic structure reported by the present authors’ group. It is interesting to study effects of the ordering of the spin chirality \( \chi \) on the behavior of \( \rho_H \), the possibility of which has been pointed out by Ohgushi et al.

Here, the spinel type ferromagnet \( \text{Cu}_{1-x}\text{Zn}_x\text{Cr}_2\text{Se}_4 \) has been adopted as a candidate, which has the non-trivial spin structure but simpler magnetic behavior than that of \( \text{Nd}_2\text{MnO}_2 \) in the sense that it has only one magnetic elements. The transport and magnetic properties as well as the magnetic structures have been studied. At \( x=0 \), it is a collinear ferromagnet with Curie temperature \( T_C \approx 450 \) K and at \( x=1.0 \), it has the helical structure with the Neel temperature \( T_N \approx 20 \) K, and from measurements of the \( M-H \) curves, the conical structure is expected for the intermediate \( x \) region below the characteristic temperature \( T_m (\sim 150 \) K), at which the slope \( -dM/dT \) begins to increase gradually with decreasing \( T \). For \( x=0.5 \), we have reported the anomalous sign change of \( \rho_H \) at around \( T_m \).

Polycrystalline samples which are confirmed to be the single phase by X-ray diffraction are used. The Hall resistivity \( \rho_H \) was measured by the four probe method. Neutron diffraction studies have been carried out at JRR-3M of JAERI for three samples with \( x=0.3, 0.5 \) and \( 0.7 \). Other details of the sample characterizations and physical measurements are described elsewhere.

In the analyses of the \( T \)- and \( H \)-dependences of \( \rho_H \), we have used the equation \( \rho_H = R_0 H + 4\pi R_a M \), and the \( R_a \) values obtained here are shown in Fig. 1. \( R_a \) of the sample with \( x=0 \), which has the collinear magnetic structure, approaches zero, as in the
Figure 2: Neutron diffraction patterns of Cu$_{0.3}$Zn$_{0.7}$Cr$_3$Se$_4$ taken at 13 K, room temperature and 420 K. The arrows show the incommensurate magnetic superlattice reflections which indicate the conical magnetic structure.

In the case of ordinary ferromagnets, while for the other samples, the sign change takes place at around $T_m$ ($\sim 150$ K), suggesting the possible effects of the non-trivial magnetic structure to the behavior of $\rho_H$.

In Fig. 2, the neutron diffraction patterns taken at 420 K ($T > T_C \sim 390$ K), at room temperature and at 13 K are shown for $x = 0.7$, for example. (The wave length $= 2.4436$ Å.) At 13 K, additional reflections can be seen at the angles which correspond to the reciprocal points, $(0,0,Q_0), (1,1,1-Q_0)$ and $(1,1,1+Q_0)$, with the incommensurate vector $Q_0 \sim 0.440$ in the unit of reciprocal lattice $a^*$, indicating that the magnetic structure is non-trivial. The peak intensity of the superlattice reflection at $(0,0,Q_0)$ gradually increases with decreasing $T$ below 150 K. This gradual growth of the superlattice peak or the non-trivial magnetic structure seems to be related to the gradual increase of the magnetization $M$ and the anomalous sign change at around $T_m$ with decreasing $T$. Considering that the magnetic structure of Cu$_{1-x}$Zn$_x$Cr$_3$Se$_4$ changes from the collinear to the helical one with the modulation vector along [001], as $x$ changes from 0 to 1 $^5$), we adopt a model that the structures of the present samples are conical with the modulation vector along [001] and with the magnetic moments within a $z$-plane directing the same direction (See inset of Fig. 2 for the details, where $\theta$ and $\delta\Phi$ are the tilting angle of the moments from the $z$ axis and the difference of azimuthal angles between the neighboring $z$-planes, respectively). Then, by fitting the calculated intensities to the experimentally obtained integrated intensities of the magnetic reflections, values of the fitting parameters, $\theta$, $\delta\Phi$ and the absolute value of the ordered moment $\mu_a$ of Cr atom are obtained. The results are as follows. $\theta = 14.5^\circ$, $\delta\Phi = 50.3^\circ$, $\mu_a = 2.6\mu_B$, for $x = 0.3$, $\theta = 22^\circ$, $\delta\Phi = 42.1^\circ$, $\mu_a = 2.49\mu_B$, for $x = 0.5$, and $\theta = 32^\circ$, $\delta\Phi = 39.6^\circ$, $\mu_a = 2.57\mu_B$, for $x = 0.7$.

One of the interesting things is that the sign change of $\rho_H$ takes place along with the appearance of the conical structure confirmed here by the neutron diffraction. Because the present samples are in the polycrystalline form, we cannot directly argue the effects of the non-trivial structure. However, it is interesting to mention that for the larger value of $\theta$, the larger absolute value of $R_e$ at $T \to 0$ was observed, which may indicate that the spin chirality locally defined by $S_1 \cdot S_2 \times S_3$ for three spins $S_1$, $S_2$ and $S_3$, contributes in the present polycrystalline samples. To clarify the relationship between $\rho_H$ and the spin structure, we have to use single crystals and study the detailed behavior of $\rho_H$ in various magnetic field directions.

References
Neutron diffraction study of antiferromagnetic order in UGa$_3$ under pressure

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The nature of 5f-electrons exhibits various attractive physics. One of the unique characters is the large spin-orbit interaction and the resulting large orbital moment. Many intermetallic actinide compounds exhibit itinerant 5f-character, due to the strong hybridization with the conduction electrons. The UX$_3$ systems have AuCu$_3$-type cubic structure and show a great variety of magnetic properties depending on the ligand element. In this study we have tried to discuss the contribution of the orbital magnetic moment in UGa$_3$ by changing the strength of hybridization with applied pressure. The UGa$_3$ orders antiferromagnetically at $T_N = 67$ K with a small magnetic moment of 0.6 – 0.8 $\mu_B$. The itinerant character of UGa$_3$ has been revealed by previous experimental results$^{1,2}$. The moment direction of UGa$_3$ is still controversial, although many experiments were performed.

The neutron diffraction measurements were carried out on the triple-axis spectrometers TAS-1 and TAS-2 installed at the research reactor JRR-3M. The scans were performed in the $(h,l,l)$ scattering plane. Quasi-hydrostatic pressure was applied by McWhan-type clamp cell up to $P = 2.2$ GPa. We found that the Néel temperature $T_N$ decreases with the rate of $dT_N/dP = -9.9 \pm 0.4$ K/GPa. This pressure dependence of $T_N$ is in good agreement with the value obtained by magnetic susceptibility measurements, $dT_N/dP = -11 \pm 2$ K/GPa$^3$. Furthermore, we observed that the magnetic moment ($\mu$) drastically decreases with increasing pressure, from $\mu \sim 0.6 \mu_B$ at 0 GPa to $\mu \sim 0.3 \mu_B$ at 2.2 GPa. These features support the itinerant nature of antiferromagnetism.

![Figure 1](image.png)

**Figure 1**: The ratio of intensities at 0.8 GPa (solid triangles), 1.7 GPa (open squares) and 2.2 GPa (solid circles) to those at 0 GPa. The calculated angle factors are also plotted for $\mu[[111]}$ (solid line), $\mu[[111]}$ and $[[111]}$ (dashed line), and $\mu[[100}$ (dotted line). All of the data are normalized to the value at $(1/2, 1/2, 1/2)$.

Figure 1 shows the pressure dependence of the integrated intensity divided by the value at ambient pressure. The magnetic peak intensities are measured at 3 K. All the data are plotted by normalizing the intensity at $(1/2, 1/2, 1/2)$ to be unity. The experimental results for the other Bragg points obviously deviates from unity, indicating the changes in relative intensity with pressure. It suggests the modification of the domain population and/or change in moment direction. The intensity of the magnetic peak $I_M$ is described
as follows,
\[ I_M = K \mu^2 L(\theta) \sum_{\tau} \{ f(\tau) \}^2 \{ 1 - (\hat{\tau} \cdot \hat{\mu})^2 \} \delta(Q - \tau). \] (1)

The term \( 1 - (\hat{\tau} \cdot \hat{\mu})^2 \) is referred to as the angle factor, where \( \hat{\tau} \) and \( \hat{\mu} \) is a unit vector along the reciprocal lattice vector and the moment, respectively. If all the domains are equally populated, the relation of \( 1 - (\hat{\tau} \cdot \hat{\mu})^2 = 2/3 \) holds independent of \( Q \) and \( \mu \). This situation is realized at ambient pressure. In a single-domain sample the angle factors are strongly affected by the direction of \( Q \) and \( \mu \). The calculated angle factors are also plotted in Fig. 1. We found that the experimental results at 0.8 GPa are well reproduced and that the sample has a single domain with the moment along the [011] direction. A possible explanation for the presence of a single domain is a small residual uniaxial component in our pressure cell. At 2.2 GPa the uranium moment seems to be parallel to the (111) directions. In the present scattering geometry, both the [111] and [111] axes are perpendicular to the uniaxial pressure. The calculated angle factor for [111] is the average for these equivalent directions. The reorientation of the magnetic moment under high pressure is a highly interesting result, however the mechanism of this phenomena remains an open question. It can be easily imagined that the orbital moment and its suppression under pressure play a significant role.

Figure 2 shows the magnetic scattering amplitude \( \mu_f(Q) \) in the ordered antiferromagnetic state at 0 GPa and 2.2 GPa. The values of \( \mu_f(Q) \) at \( P = 0 \) GPa are obtained based on the constant angle factor \( \sin^2 \alpha = 2/3 \) for all magnetic peaks, while those at 2.2 GPa are obtained from the averaged angle factor for (111) directions. Using the dipole approximation\(^5\), we may write
\[ \mu_f(Q) = \mu \times (\langle j_0 \rangle + C_2 \langle j_2 \rangle), \] (2)
where the functions \( \langle j_i \rangle \) are the spherical Bessel function. The coefficient \( C_2 \) is given as \( C_2 = \mu_L / (\mu_L + \mu_S) \), where \( \mu_L \) and \( \mu_S \) are orbital and spin moment, respectively.

The dotted line in the figure is the curve reported by Hiess \textit{et al}., in the form of 
\[ \mu_f(Q) = 0.63 \times (\langle j_0 \rangle + 2.52 \langle j_2 \rangle), \]
which suggests \( \mu_L / \mu_S = -1.66 \). Our experimental data at ambient pressure are in good agreement with the their results\(^6\). This result indicates that the contribution from orbital moment plays dominant role in the magnetic moment of UGa\(_3\). The dashed line is the temporary fitting curve in the form of 
\[ \mu_f(Q) = 0.3 \times (\langle j_0 \rangle + 3.0 \langle j_2 \rangle), \]
which suggests \( \mu_L / \mu_S = -1.5 \). The statistical errors in our preliminary results at \( P = 2.2 \) GPa are not small enough to distinguish the spin and orbital contribution reliably, although there is an indication that the spin and orbital moments are further compensated under pressure, as predicted in Ref. 6. We need further experiments to obtain a reliable result of the form factor under pressure.

\[ \begin{align*}
\mu_f(Q) \quad & \text{(amu)} \\
\sin^2 \theta/\lambda (\AA^{-1}) \\
\end{align*} \]

Figure 2: The magnetic scattering amplitude \( \mu_f(Q) \) as a function of \( \sin^2 \theta/\lambda \) for UGa\(_3\) both at 0 GPa and 2.2 GPa.

References
Neutron Scattering Study on the Antiferroquadrupolar Order of DyB$_2$C$_2$ under Magnetic Fields

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RB$_2$C$_2$ (R = rare earth) compounds, which exhibit various magnetic properties, have been attracting a great deal of interest, because the interactions between quadrupolar moments representing the asphericity of the 4f-charge distribution play significant roles in the physical phenomena. In particular, DyB$_2$C$_2$ is the first compound with a tetragonal symmetry showing an antiferroquadrupolar (AFQ) ordering.\(^{1,2,3}\) This compound undergoes successive transitions from a paramagnetic phase (I) into an antiferroquadrupolar (AFQ) ordered phase (II) at $T_Q = 24.7$ K, and further into a coexisting phase (III) of the AFQ and antiferromagnetic (AFM) orders at $T_N = 15.3$ K. Below $T_N$, a strange AFM structure occurs, which is represented by four propagation vectors of $\mathbf{k}_1 = (100)$, $\mathbf{k}_2 = (101/2)$, $\mathbf{k}_3 = (000)$, $\mathbf{k}_4 = (001/2)$.

Neutrons can disclose the AFQ ordering through the observation of field-induced antiferromagnetic peaks, reflecting the existence of distinct easy axes on the two AFQ sublattices. In order to get new experimental evidence for the AFQ order in DyB$_2$C$_2$, we performed neutron scattering experiments under magnetic fields on the triple-axis spectrometer TAS-2 installed at the thermal neutron guide of JRR-3M of Japan Atomic Energy Research Institute (JAERI).

The single crystals of Dy$^{115}$B$_2$C$_2$ were grown by the Czochralski method with a tetra-arc furnace. Since natural boron is a strong neutron absorber, B in the sample was replaced with enriched $^{11}$B isotope whose absorption cross section is negligible small. The scattering plane was chosen in the $a^*-c^*$ reciprocal lattice plane in order to look for the $(h 0 l)$ type reflections, since the propagation vector of the AFQ ordered structure which is consistent with the magnetic structure below $T_N$ is expected to be $\mathbf{k} = (001/2)$ or $(101/2)$. Magnetic fields were applied vertically to the scattering plane, i.e. along $[010]$ direction, using a He-free type 10 T superconducting magnet developed by JAERI.\(^4\)\(^5\) The details of the reciprocal lattice space investigated are already reported in the previous work.\(^6\)

The application of magnetic fields up to 2.5 T causes the appearance of 101/2, 101 and 103/2 reflections in addition to the nuclear ones, though 001/2 was not observed. These results are consistent with the previous ones.\(^6\) The rocking curves of 101/2 and 101 taken at 19 K for several fields up to 2.5 T are shown in Fig. 1. The scan in the paramagnetic phase at 30 K for $H = 2$ T is also shown together (mascles). As can be seen from Fig. 1, the 101/2 reflection develops rapidly with increasing fields, while no peak is recognized in zero field nor at 30 K for $H = 2$ T within experimental accuracy in the present measurements. The 101 reflection also exhibits a distinct increase with magnetic fields up to 2.5 T. Because the 101/2 and 101 reflections are derived from the components of induced magnetic moments parallel and perpendicular to applied magnetic field, respectively, the intensity of 101/2 is much larger than that of 101.

Figure 2 shows integrated intensities of the 101/2 and 101 peaks. The background components were subtracted from the data. The arrows with $T_N$ and $T_Q$ indicate the transition temperatures determined from the specific heat measurements. When a magnetic field is applied with $H = 2$ T, 101/2 and 101
peaks appear below $T_Q$. On the other hand, we have already confirmed that magnetic reflections do not exist in the AFQ ordered phase for $H = 0$, which indicates that transition occurring in zero field is not associated with magnetic dipole order. Therefore we can easily conclude that the appearance of the observed peaks is attributed to AFM components of Dy dipole moments induced by applied magnetic fields restricted by the underlying AFQ order.

The next step of our study is to determine the quadrupolar ordered structure and the symmetry type of the quadrupolar order parameter. For this purpose, neutron scattering experiments in the $[1\ 1\ 0]$-c* scattering plane under magnetic fields along [1\ 1\ 0]-axis are now in progress.

References

Determination of the Magnetic Structures of Exotic Spin-Density Waves in Cr(001)/Sn Epitaxial films

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Metal Chromium (Cr) is very famous for the incommensurate spin-density-wave (SDW) below the Néel temperature of 311 K1. The magnetic properties are drastically modified by circumstances such as impurities, temperature, internal stress and so on. Therefore thin films and multilayers of Cr exhibit a variety of magnetic properties quite different to those of bulk Cr2.

Recently we have reported exotic SDW states observed in epitaxial Cr(001)/Sn multilayers in which monatomic Sn layers are periodically inserted in the Cr(001) epitaxial films3, 4, 5. Unpolarized neutron diffraction measurements revealed that in the multilayers SDWs with complicated waveform were stabilized at low temperatures. The most exotic feature of the SDWs is that their wavelength is not controlled by the nesting vector of the Fermi surface but by the artificial periodicity introduced by the embedded Sn monatomic layers. The constraint of the wavelength of the SDWs is thought to be the pinning of antinodes at Cr/Sn interfaces.

We could successfully elucidate the existence of unique SDWs in the Cr/Sn multilayers by unpolarized neutron experiments. However, the determination of the spin orientation in the films is not easy by unpolarized neutrons because it is difficult to normalize intensities at different reciprocal points accurately, especially when one scattering vector is located in in-plane and the other in out-of-plane. Such scattering condition is essential to separate the in-plane and out-of-plane component of spins. We have performed polarized neutron scattering experiments with polarization analysis in order to directly determine the spin orientation of the multilayers.

Figure 1: Structure of Cr(001)/Sn epitaxial films with monatomic Sn spacer layer. Several films with different artificial period (A) were synthesized. The sample with A = 16.0 nm was used in this study.

15 bilayers of [Cr(16.0 nm)/Sn(0.2 nm)] were epitaxially deposited on a MgO(001) substrate with a 5-nm-thick Cr buffer layer by using ultrahigh-vacuum (UHV) deposition. The structure of sample is schematically drawn in Fig. 1. The MgO[001] and the bcc Cr[001] directions are normal to the sample plane, and the MgO[110] and the Cr[010] are parallel each other. We denote the Cr[001] direction as L and the [010] direction as K hereafter.

Polarized neutron diffraction measurements were performed on TAS-1 at JRR-3M in JAERI. The Cu Heuser(111) monochromator and analyzer were employed to produce monochromatic polarized neutron of 14.7 meV and to analyze the diffracted neutrons, respectively. Scans were performed along the L and K directions through the (001) and (010) reciprocal points, where the nuclear peaks of the
The reciprocal plane of bcc Cr structure are forbidden (Fig. 2).

Fig. 3(a) shows the scan along the $L$ direction through (010) point at 290 K. In bulk Cr the satellite peaks from the SDW state appear at $(0, \pm \delta, 1)$, $(0, 0, 1 \pm \delta)$, $(0, 1 \pm \delta, 0)$ and $(0, 1, \pm \delta)$. The incommensurability $\delta$ is defined in bulk Cr as $1 - |\tilde{Q}|$ where $\tilde{Q}$ is the nesting vector of Fermi surface. Since we do not observe such extra satellite peaks, the commensurate antiferromagnetic (CAF) structure is realized in the Cr/Sn multilayer at 290 K.

When neutrons are scattered by magnetic materials, neutron is only sensitive to components of magnetic moment perpendicular to the scattering vector. In addition the direction of neutron spins parallel to the magnetic moments is conserved while that perpendicular to the moments is flipped during the scattering process by magnetic interaction.

In this experiments direction of neutron spins was maintained by a weak vertical magnetic field parallel to the sample plane. Therefore intensities of non-spin-flip (NSF) neutrons in Fig. 3 (a) and (b) are proportional to the square of in-plane component of magnetic moments ($M_{//}$) and that of spin-flip (SF) neutrons to the square of out-of-plane one ($M_{\perp}$).

The intensity ratio between SF and NSF in Fig. 3(a) is approximately 4. This indicates that the ratio of $M_{\perp}$ to $M_{//}$ is 2, which suggests that $\vec{M}$ is not aligned to the principal axis of bcc lattice but is inclined to the sample plane. Another probable explanation of the ratio is coexistence of domains in which directions of $\vec{M}$ are different.

With decreasing temperature the CAF structure gradually transforms to the SDW state accompanied with 6 satellite peaks as shown in Fig. 3(b). The SF/NSF intensity ratio of each satellite peak is almost the same and does not remarkably differ from the CAF structure at 290 K. This suggests that the satellite peaks do not come from independent SDWs of different wavelength but that they can be assigned to the Fourier components of a single SDW with a highly distorted sinusoidal waveform.

References

Investigation of the Magnetic Structure of a TbB$_{50}$-type B$_{12}$ Cluster Compound

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Magnetic properties of rare earth boride compounds such as the hexaborides have been an extensively researched topic over the years.$^{1,2}$ Recently a striking discovery was found in the magnetically dilute higher boride compounds; the magnetic transition discovered in the REB$_{50}$ and isostructural REB$_{44}$Si$_2$ compounds.$^{3,4}$ The transition temperature of TbB$_{50}$ for example ($T_N = 17$ K) is actually comparable to that of the much more magnetically dense TbB$_6$ in which the magnetic interaction is further mediated by conduction electrons. It has been indicated that the magnetic interaction along the B$_{12}$ chain is critical for the magnetic transition to appear which is a new phenomena in the boron compounds.$^{3,4,5}$

In this work, we report on the investigation of the magnetic structure of Tb$_{11}$B$_{44}$Si$_2$ in an attempt to further elucidate the nature of this new magnetic transition found in borides.

Because this is such a boron-rich system especial care was taken in preparing the $^{11}$B isotope compound. Usually the borothermal reduction of rare earth oxide under vacuum is used for for our boride synthesis.$^9$ However, in this case since BN crucibles are used, it was found that a small amount of natural isotope ratio boron enters the sample, which is sufficient to hinder the neutron diffraction measurements due to the extremely large cross section of $^{10}$B.

We used an arc-melt method to directly synthesize Tb$_{11}$B$_{44}$Si$_2$ from the elements. Terbium metal powder (99.9 %), Si powder (99.9 %), and $^{11}$B powder (isotope purity of 99.54 %) were used. Arc melt was performed under argon gas. We were successful in obtaining the Tb$_{11}$B$_{44}$Si$_2$ phase (with REB$_{50}$-type structure) as characterized by a high resolution powder x-ray diffractometer (Rigaku Co.; RINT2000) with Cu K$_\alpha$ radiation. Chemical analysis of the samples was done with ICP (inductively coupled plasma atomic emission spectroscopy) after the samples were dissolved in nitric acid for 16 hours at 110 °C. No significant impurity elements were detected, but an impurity phase of B$_2$O was observed. This impurity phase had never been observed before for our higher boride samples, but was unavoidable with the present synthesis technique, which was especially employed to avoid $^{10}$B introduction into the sample.

Magnetic susceptibility was measured by using a Quantum Design SQUID magnetometer from 300 K to 2 K.

Neutron diffraction measurements were done using the high resolution powder neutron diffractometer (HRPD) installed at JRR-3M. The sample was mounted in a closed cycle $^4$He gas refrigerator. Neutrons of wavelength of 1.8230 Å were used.

The temperature dependence of the magnetic susceptibility of Tb$_{11}$B$_{44}$Si$_2$ is plotted in Fig.1. A drop in the susceptibility is observed at 16 K, indicating the antiferromagnetic transition. The transition temperature is similar to that previously observed for TbB$_{44}$Si$_2$.$^6$

Refinement of the neutron diffraction patterns by RIETAN2000$^7$ was attempted. Although the refinement is not optimum yet, the lattice parameters we obtain in the present cycle for Tb$_{11}$B$_{44}$Si$_2$ (4 K) were determined as follows: $a=16.71$ Å, $b=17.65$ Å, $c=9.547$ Å.

The obtained neutron diffraction difference pattern of Tb$_{11}$B$_{44}$Si$_2$ from 300 K to 4 K is
plotted in Fig.2. The striking feature is that the relatively large peaks originating from B₂O, indicated by the asterisks, disappear at 4 K. There appears to be no trivial explanation for this behavior, since the samples are sealed in cells and in any case an evaporation of B₂O at low temperatures is not reasonable. At present it is not clear whether this is an intrinsic phenomena or is due to some artifact of measurement we have not yet considered, but the behavior is interesting and bears further investigation.

To summarize, we have investigated the magnetic structure of Tb₁₁B₄₄Si₂ of the REB₅₀ system, which display magnetic transitions mediated by a new interaction mechanism in borides. We have found that it is indicated that there is no long range ordering in this new magnetic system. An interesting behavior was observed for impurity B₂O peaks which disappeared at low temperature and bears further investigation.

References

No significant additional peaks due to magnetic ordering could be observed to appear for the 4 K neutron diffraction pattern. Since the magnetic transition temperature of Tb₁₁B₄₄Si₂ is 16 K it is indicated that the transition observed in the REB₅₀ systems is not of long range order character, which is valuable new information on these exotic compounds.
Magnetic $P$-$T$ phase diagrams of CeSb and CeBi

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The heavier Ce-monopnictides, CeSb and CeBi exhibit highly unusual and anisotropic magnetic properties as well as Kondo-effect like transport properties in spite of their simple NaCl-type crystal structures and low-carrier-density$^1$. The magnetic properties of these compounds were mainly explained by a fundamental microscopic analysis based on the anisotropic $p$-$f$ mixing effect between the Ce 4f electrons and the neighboring pnictogen 5p valence-holes with $\Gamma_8$ symmetry$^2$. CeSb is well known with its complicated magnetic phase diagrams below 2 GPa or 10 T revealed by the extensive neutron diffraction studies$^3$. Magnetic structures consist of a stacking of ferromagnetic (001) planes with a given sequence. The magnetic moments, which are perpendicular to the ferromagnetic planes, are originated from $\Gamma_8$-like state of Ce-ions with the moment of 2 $\mu_B$. Non-magnetic (001) planes with the $\Gamma_7$ Ce-ions appear in the so-called AFP phases below 1 GPa. The developments of high pressure techniques on the measurement of transport properties revealed new features of the phase diagram of CeSb up to 8 GPa$^4$. A huge enhancement and a sharp drop of the resistivity appear at $T_H$ and $T_L$ above about 2 GPa. This brought forward new problems to be solved, that is, the apparent discrepancy of the phase diagram at around 2 GPa, or whether the magnetic orders exist or not above 2 GPa. On the other hand, in contrast to CeSb case, there have been few reports on the $P$-$T$ phase diagram of CeBi so far. Nevertheless, the resistivity data show an unusual hump and an inflection point at $T_H$ and $T_L$, and give the similar phase diagram to that of CeSb above about 2 GPa. Thus, systematic neutron diffraction studies beyond 2 GPa are inevitable to confirm the $P$-$T$ phase diagrams of these compounds. In this paper, we briefly present our neutron diffraction studies up to 4.6 GPa.

Fig. 1 shows the $P$-$T$ phase diagram of CeSb obtained in this work together with the data of the previous neutron diffraction$^3$, the resistivity measurements$^4$ and X-ray diffraction$^5$. Below 1 GPa, the lowest temperature phase AF-IA with the stack (↑↓↓↓), all the AFP phases and the highest temperature phase AF-I with the (↑↑) are confirmed in our measurements. The transition temperatures are identical with that in ref.$^3$. However, above 1 GPa, AF1 and AF2 phases exist in very narrow temperature ranges and disappear at about 2 GPa. Furthermore, $T_{AF-I A}$ and $T_{AF-F-1}$ shift to considerably higher temperatures of 31 K and 38 K. Above 2 GPa, AF-I and AF-IA phases were clearly observed as higher and lower temperature phases. The new phase boundaries of $T_{AF-I A}$ and $T_{AF-F-1}$ are smoothly connected through the all $P$-$T$ area investigated in this work. These results solve the problems mentioned above. Fig. 2 shows the $P$-$T$ phase diagram of CeBi together with the resistivity data. In marked contrast to CeSb case, the phase diagram consists of only two magnetic phases AF-I and AF-IA. The lower temperature phase AF-IA disappears at around 2 GPa.

As shown in fig. 1 and fig. 2, AF-I phase clearly relates to the unusual enhancement of the resistivity at $T_H$ and the development of AF-IA phase leads to the rapid decrease of the resistivity at $T_L$. These results indicate that the mechanism of the carrier scattering or the carrier number itself is highly different between the two magnetically ordered phases.
The sudden shrinking of the crystal lattice is observed at $T_3$, which agrees well with $T_H$. The origin of this shrinking is clearly evidenced by the direct observation of the modulation of 4f electron orbital on CeSb, the planes with the $\Gamma_3$-like state of Ce-ions, which have small effective ionic size due to the p-f mixing effect, appear in the lattice of Ce ions with $\Gamma_7$ CEF ground state. It should be pointed out that in CeSb non-magnetic $\Gamma_7$ planes disappear at about 1 GPa and the phase diagram above 2 GPa bears a close resemblance to the phase diagram of CeBi above ambient pressure, which has no non-magnetic plane. As pointed out for lighter monopnictides CeP and CeAs in ref 7, 8), this behavior is probably understood in terms of the common physical basis for the whole Ce-monopnictides system. In this idea, although the difference of the CEF splittings or pnicgen atoms between the compounds should be considered, the carrier density can be a common physical parameter. That is, the application of pressure increases the carrier density. As a result of this, the p-f mixing effect is highly enhanced. Indeed, the carrier number are estimated to be about 0.04 and 0.06 per Ce for CeSb and CeBi, respectively 9) and the calculated energy gain of the p-f mixing effect in CeBi is much larger than that in CeSb 2). However, the future development of theoretical works is highly desired to elucidate the problems such as the correspondence between the unusual enhancement of the resistivity and the magnetic orders, or the strong stabilization of the AF-I phase by applied pressure in spite of the small difference of the energy between the AF-I and the AF-IA phases at ambient pressure 2).

Figure 1: The magnetic P-T phase diagram of CeSb.

Figure 2: The magnetic P-T phase diagram of CeSb.

References
Crystal and Magnetic Structure of the Antiferromagnetic Iron Sulfide BaPr$_2$FeS$_5$

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A quaternary iron sulfide BaPr$_2$FeS$_5$ has a tetragonal crystal structure with space group, $I4/mcm$, at room temperature. Its magnetic susceptibility and specific heat showed that the antiferromagnetic transition of the Fe$^{2+}$ ions occurred at 40 K and another anomaly occurred at 150 K.

In order to determine the magnetic structure, powder neutron diffraction patterns of BaPr$_2$FeS$_5$ were measured at 10, 100 and 200 K using a HighResolution Powder Diffractometer (HRPD) in the JRR-3M reactor with a neutron incident wave length ($\lambda = 1.82268$ Å). The neutron diffraction data were analyzed with the Rietveld method.

Figure 1 shows the observed and calculated diffraction patterns for BaPr$_2$FeS$_5$ at 10, 100 and 200 K. The patterns calculated using the crystal structure with the space group of $I4/mcm$ at 100 and 200 K are in good agreement with the observed ones, which indicates that no structural transition occurs between 100 and 200 K. The lattice parameters were refined to be $a = 7.8297(5)$ Å, $c = 13.5914(9)$ Å at 100 K and $a = 7.8352(5)$ Å, $c = 13.6028(10)$ Å at 200 K. Compared with the pattern at 100 and 200 K, additional magnetic Bragg peaks appear in the pattern at 10 K. This result indicates that the Fe$^{2+}$ ions in BaPr$_2$FeS$_5$ has a long-range magnetic ordering. The magnetic structure of Fe$^{2+}$ at 10 K was determined to have a collinear antiferromagnetic structure which has dimensions $\sqrt{a} \times \sqrt{a} \times c$ in terms of the tetragonal chemical cell. The magnetic moment of Fe$^{2+}$ is estimated to be $2.78(2)$ $\mu_B$ and determined to lie in a parallel direction with the $c$-axis. The schematic magnetic structure is illustrated in Fig. 2.

Figure 1: Powder neutron diffraction profiles for BaPr$_2$FeS$_5$ at 10, 100 and 200 K.

Figure 2: The magnetic structure of BaPr$_2$FeS$_5$ at 10 K.
Neutron Diffraction Study on Ordered Perovskites $\text{Ba}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tm, Yb}$) and $\text{Sr}_2\text{YbRuO}_6$

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The ordered perovskite-type compounds $\text{Ba}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tm, Yb}$) and $\text{Sr}_2\text{YbRuO}_6$ showed magnetic transitions at around 45 K. In order to determine their magnetic structures, powder neutron measurements were performed at 100 and 10 K with a High Resolution Powder Diffractometer (HRPD) in the JRR-3M reactor with a neutron incident wave length ($\lambda = 1.8226\text{Å}$).

Neutron diffraction profiles measured at 100 K show that the crystal structures of these compounds are monoclinic with space group $P2_1/n$, and the $\text{Ln}^{3+}$ and $\text{Ru}^{5+}$ ions are structurally ordered at the B sites of the $\text{ABO}_3$ perovskite-type structure.

The data collected at 10 K show a number of low angle peaks, which are not observed at 100 K. (Fig.1) They are magnetic peaks due to an antiferromagnetic ordering of both $\text{Ln}^{3+}$ and $\text{Ru}^{5+}$ ions. Their magnetic structures were determined by the Rietveld method.

The magnetic structure of $\text{Ba}_2\text{YbRuO}_6$ at 10 K is illustrated in Fig.2. In this magnetic structure, the magnetic moments of the $\text{Yb}^{3+}$ and $\text{Ru}^{5+}$ are ordered antiferromagnetically, respectively. In the $ab$ plane, the magnetic moments of $\text{Yb}^{3+}$ and $\text{Ru}^{5+}$ are coupled ferromagnetically. The direction of the magnetic moments is along the $c$ axis. The ordered magnetic moments are listed in Table 1.

The magnetic structure of $\text{Sr}_2\text{YbRuO}_6$ is the same as that of $\text{Ba}_2\text{YbRuO}_6$, except for the difference in the direction of the magnetic moments (canted from the $c$ axis about 20°). For $\text{Ba}_2\text{TmRuO}_6$, it is found that the magnetic moments of $\text{Tm}^{3+}$ and $\text{Ru}^{5+}$ are coupled ferromagnetically rather than ferromagnetically in the $ab$ plane.

### Table 1: Ordered magnetic moments ($\mu_B$) of $\text{Ba}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tm, Yb}$) and $\text{Sr}_2\text{YbRuO}_6$.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ln}^{3+}$</th>
<th>$\text{Ru}^{5+}$</th>
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<tbody>
<tr>
<td>$\text{Ba}_2\text{YbRuO}_6$</td>
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<tr>
<td>$\text{Sr}_2\text{YbRuO}_6$</td>
<td>0.92(6)</td>
<td>3.0(2)</td>
</tr>
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原子炉：JRR-3M
装置：HRPD(1G)
研究分野：中性子散乱（磁性）
Spin fluctuations in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$ ($y = 0, 0.03$)

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$\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_3$ is an antiferromagnetic insulator showing strong ferromagnetic spin fluctuation in the paramagnetic state. This system changes to a ferromagnetic metal by substituting a small part of the Mn ion by Cr ion. We studied ferromagnetic spin fluctuation of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ (PCMCO) comparing with that of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_3$ (PCMO) and also studied ferromagnetic ordering of PCMCO with the small-angle neutron scattering instrument (SANS-J) installed in the JRR-3M. The instrument was operated with either $\lambda = 0.35$ or 0.65 nm.

The scattering cross-section of PCMCO consists of coherent and diffuse scattering components. The coherent scattering component is dominant below the ferromagnetic transition temperature $T_C = 140$ K in the $q$ region lower than about 0.2 nm$^{-1}$. This component has the $q^{-4}$ dependence (Porod law) indicating that the boundary of ferromagnetic domains appearing below $T_C$ is sharp in scattering length density. On the other hand, the diffuse scattering component becomes larger than the coherent scattering component above $T_C$ in the $q$ region larger than about 0.5 nm$^{-1}$.

Fig.1(a) shows the temperature dependence of the scattering cross-section of PCMCO at $q = 0.071$ nm$^{-1}$. Below $T_C$ the scattering cross-section normally increases owing to the development of the ferromagnetic long range order. However, as shown in Fig.1(b) the diffuse scattering cross-sections of PCMCO at $q = 1.31$ nm$^{-1}$ shows anomalous behavior. With increasing the temperature, the scattering cross-section starts to increase at about $T_N$ and remains finite even in the temperature region much higher than $T_C$. This result indicates that the strong ferromagnetic spin fluctuation persists in the paramagnetic state of PCMCO as that of PCMO. In principle, the ferromagnetic spin fluctuations of both systems are expected to be due to the double exchange interaction between Mn spins. The magnitude of the ferromagnetic spin fluctuation of PCMO is slightly lower than that of PCMCO. However, both spin fluctuations have similar Lorentzian $q$ dependence with about 30 nm in correlation length.

![Figure 1: Temperature dependence of the scattering cross-sections of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$ ($y = 0, 0.03$) at (a) 0.071 and (b) 1.31 nm$^{-1}$.](image)

References

The dispersion of the crystalline electric field (CEF) excitation in a single crystal PrCu₅ has been investigated to understand the enhanced nuclear magnet due to the hyperfine coupling to f electrons associated with the RKKY interaction between f electron spins. The enhancement causes the ordering temperature at 2 mK which is several thousand times higher than that of pure nuclear spin systems.

We have reported the dispersion of CEF along the h00, 0k0, and other axes in the (h0l) plane of the single crystal (40 mm in length, 5 mm in diameter, monoclinic notation; a = 0.509 nm, b = 1.015 nm, c = 0.809 nm β = 91.33 degree).1) Recently we measured the dispersion of CEF at 00l (0.8<l<2.9) positions in the (h0l) plane. Figure 1 shows the accumulated dispersion relations at low temperatures which clearly show the followings; (1) The CEF excitations are at the energy about 1.7, 2.7, 5.0, 7.4, and 8.9 meV, some of which are different from the previous data from polycrystals.2) (2) The first excitation at about 1.7 meV was not observed along the a-axis, Q=(100), which indicates the x-polarization of the f electron moment. This is consistent with the report that the Van-Vleck susceptibility along the a-axis is larger than the other orientations. (3) Similarly the 7.4 and 8.9 meV excitations are considered to have y-polarization, but the 2.7 and 5.0 meV levels have a polarization with x, y, z-components. (4) We found the minimum energy at the forbidden Bragg point (010). The data and the temperature dependence might suggest that Q=(010) would be the antiferromagnetic propagation vector for the nuclear magnetic ordering of PrCu₅. (5) The first excited level splits into two modes around the ferromagnetic Bragg points 020 and 002. The splittings could be explained in terms of the mode splitting of the optical and acoustic mode in a non-Bravais lattice.

References
Field-induced Antiferroquadrupolar Ordering in The Tetragonal TbB$_2$C$_2$ Compound

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In RB$_2$C$_2$ system (R=rare earth), coexistence of antiferroquadrupolar (AFQ) and antiferromagnetic (AFM) interactions brings variety and anomalous magnetic properties. In particular, DyB$_2$C$_2$ is the first tetragonal AFQ order compound with the high $T_Q$ value of 24.7 K$^{1,2}$. In addition, HoB$_2$C$_2$ also shows an AFQ order transition at $T_Q$=4.5 K which realized under the magnetic ordered state of $T_N$=5.9 K$^{3,4}$. In this report, we show the evidence of another AFQ order compound in RB$_2$C$_2$ system, TbB$_2$C$_2$.

Because of the large spin-orbit coupling in f electron systems, the effects of the AFQ order in DyB$_2$C$_2$ and HoB$_2$C$_2$ are revealed in their magnetic structures. In the AFQ+AFM ordered state, the magnetic moments which lie in the c-plane make an twice a period along the [001] direction with the characteristic coupling angle $\phi$ of about 70$^\circ$$^4$ and 77$^\circ$$^2$ in HoB$_2$C$_2$ and DyB$_2$C$_2$, respectively. These magnetic structures are originate in the four different propagation vectors: the two dominant $k_1$ = (100), $k_2$ = (011/2) and the two additive $k_3$ = (000) and $k_4$ = (001/2).

TbB$_2$C$_2$ is an antiferromagnet with $T_N$=21.7 K under $H$=0$^9$. The magnetic structure is described by dominant $k_2$ = (011/2) with an additive $k_4$ = (001/2) and a long period component of $k_1$ = (1±$\delta$±$\delta$) ($\delta$ = 0.13), which differs from the characteristic magnetic structure under the AFQ+AFM ordered states$^{5}$. However, it is notable that the long period component $k_1$ in TbB$_2$C$_2$ is common to that between $T_N$ and $T_Q$ in HoB$_2$C$_2$ where AFQ interactions supposed to play an important role$^6$. In addition, the magnetization processes of TbB$_2$C$_2$ reveal

Figure 1: Magnetic field dependence of rocking curves of the (a) 100, (b) 101/2 and (c) 001/2 magnetic reflections up to 2.0 T taken at 3.9 K.

resemblant characteristics as those of DyB$_2$C$_2$ and HoB$_2$C$_2$. It is, therefore, highly probable that an AFQ order is realized in TbB$_2$C$_2$ under magnetic fields, though there is no AFQ order under $H$=0$^9$. Thus, the aim of this work is to confirm the field-induced AFQ order in TbB$_2$C$_2$ by means of neutron diffraction under magnetic fields.

A single crystalline sample was grown by the Czochralski method with enriched $^{11}$B isotope. The neutron diffraction experiments were carried out on the triple-axis spectrometer TAS-2. The spectrometer was operated in the triple-axis mode with elastic condition. The incident energy was fixed at 13.7 meV and
two PG filters were used to reduce higher order contamination. Magnetic fields applied along the [010] direction were generated by a liquid-He-free type 10 T superconducting magnet developed by JAERI.  

Figure 1 shows magnetic field dependence of the rocking curves of magnetic Bragg reflections, (a) 100, (b) 101/2 and (c) 001/2 up to 2.0 T taken at 3.9 K. The small humps observed on the low angle side of main peaks are attributed to the existence of other grains. Under zero field, the intense 101/2 and the weak 001/2 magnetic reflections were observed, while no peak was found at (100). These results were consistent with the previous ones. The application of magnetic fields causes the appearance of a new antiferromagnetic reflection of 100 even at 0.5 T where the broad transition was observed in the magnetization process along the [010] direction. This result indicates that the (100)-type antiferromagnetic component is also needed for the field-induced ordered state in TbB2C2. The intensity of the weak magnetic reflection of 001/2 also exhibits an increase against magnetic fields up to 2.0 T. In contrast, the most intense 101/2 reflection decreases by just about 8% from zero to 2.0 T.

Including a field-induced ferromagnetic component which overlaps nuclear peak, the reflections above 0.5 T are associated with the following four propagation vectors; the two dominant \( k_1 = (100), k_2 = (011/2) \) and the two additive \( k_3 = (000), k_4 = (001/2) \). This indicates that the field-induced magnetic structure of TbB2C2 is basically the same as the characteristic structures of DyB2C2 and HoB2C2 in the AFQ+AFM ordered state.

The magnetic moments of dominant components \( k_1 \) and \( k_2 \) are reported to be 5.5 \( \mu_B \) and 4.4 \( \mu_B \) in DyB2C2, 5.15 \( \mu_B \) and 3.56 \( \mu_B \) in HoB2C2. In contrast, the ratio at 1.5 T in TbB2C2 is roughly estimated from the integrated intensity to be \( \mu_{k_1} \approx \mu_{k_2} = 2.3 \mu_B \): 5.6 \( \mu_B \). The magnetic moment for \( k_3 \) in TbB2C2 is far larger than that for \( k_1 \), which is different in the case for DyB2C2 and HoB2C2. The discrepancy among these compounds originates from an angle \( \phi \). The characteristic angle \( \phi \) is deduced to be 130° in TbB2C2, while those angles are reported to be 77° and 69.6° in DyB2C2 and HoB2C2, respectively. The schematic magnetic structure of TbB2C2 under magnetic fields are shown in Fig. 2.

Although the coupling angles \( \phi \) are different, the fundamental structure of the field-induced phase in TbB2C2 is common to those of the ground states in DyB2C2 and HoB2C2, where the AFQ and AFM order coexist. The characteristic magnetic structure in TbB2C2 under magnetic fields is hardly explained by only magnetic interactions as well as those in DyB2C2 and HoB2C2. We believe, therefore, that TbB2C2 is the first material which shows a field-induced AFQ ordering.

References

Spin dynamics of hole doped Haldane system Nd$_{2-x}$Ca$_2$BaNiO$_5$

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The one-dimensional (1D) Heisenberg $S = 1$ chains and $S = 1/2$ ladders have been extensively studied as disordered nonclassical systems after Haldane’s prediction in 1983 $^{1,2}$. It has been well established that the spin gap state still survives in the hole doped ladder compound, and that the spin-gapped phase is favorable for superconductivity $^{2,3}$. Studies of hole doped Haldane system have only recently been realized experimentally in the compound Y$_{2-x}$Ca$_2$BaNiO$_5$ $^{4,5}$, but the resistivity of this system behaves like an insulator and the carriers do not induce metallic behavior. The key picture in the hole doped Haldane system is that induced holes create excitations below the Haldane gap with an incommensurate structure factor. Surprisingly, increased hole doping does not yield a proportional increase in the shift of the peaks from antiferromagnetic zone center (AFMZC).

In this study, we prepared the single crystals of Nd$_{2-x}$Ca$_2$BaNiO$_5$ ($x = 0, 0.05, 0.10, 0.20$) by the floating zone method to elucidate the spin dynamics of hole doped Haldane chains. Nd$_2$BaNiO$_5$ has shown the same behavior as the Haldane gap obtained in the pure Haldane system Y$_2$BaNiO$_5$ above the Néel temperature ($T_N$), and its behavior is different from that of CsNiCl$_3$ in which the Haldane gap is lost below $T_N$. In other words, the Haldane state coexists with antiferromagnetic state below $T_N$, which was recently recognized as a unique model of Haldane-gap quantum spin chain in a strong staggered applied field $^{6,7}$. An effective staggered exchange field acting on 1D chains is generated by 3D magnetic long-range ordering in the auxiliary sublattice of magnetic rare earth ions, which occurs at $T_N$ of several tens of kelvin.

Elastic and inelastic neutron measurements were done on the TAS-1 triple axis spectrometer at JEARI. Neutron beams of fixed final energy $E_f = 14.7$ meV were used with pyrolytic graphite filter to eliminate the higher order contaminations. The sample was mounted with the (H, 0, L) reciprocal space parallel to the scattering plane of the triple axis spectrometer. The data from each samples were normalized with the integrated intensity of the (200) Bragg reflection.

Magnetic phase diagram was determined by measuring the temperature dependence of susceptibility and magnetic Bragg peak. A spin-glass like phase in Nd$_{2-x}$Ca$_2$BaNiO$_5$ has been observed at the temperature between 3 and 25K as the hole concentration is changed. This is much higher than that ($\sim$ 3K) in

![Figure 1: Constant E scans at E = 5.5 meV and T = (2 + T_N) for three different hole concentrations.](image-url)
$Y_{2-x}Ca_xBaNiO_5$. $T_N$ equals to $T_N$ above $x = 0.10$. This suggests that a spin-glass like state and an antiferromagnetic (AFM) state coexist, and holes create ferromagnetic cloud around the holes in the AFM state caused by Nd ions.

The spectrum weights of peaks which can be explained by the incommensurate spin modulation were observed by inelastic neutron scattering at AFMZO $\{ q = (1.5, 0, 0) \}$ for $E = 3 - 7 \text{ meV}$ above $T_N$ in Nd$_{2-x}$Ca$_x$BaNiO$_5$ (Fig. 1). These peaks have so broad structure. Because observed temperature is relatively high temperatures for the incommensurate spin modulation, we must observe them over $T_N$. The incommensurability $\varepsilon$ which was calculated by two Gaussians centered at $1.5 \pm \varepsilon$, was larger than that of $Y_{2-x}Ca_xBaNiO_5$ (Fig. 2). How do we account for the inelastic incommensurate spin modulation? The key picture is that induced holes in Haldane chains create the weak ferromagnetic (FM) interaction coupling around holes. The nature of the inelastic incommensurate spin modulation might be caused from the structure factor of the spin part of the hole wavefunctions.

The result is a new excitation spectrum around $11 \text{ meV}$ below $T_N$ (Fig. 3). This excitation have the dispersion different from the Haldane mode parallel to the chains (the Haldane gap increases at low temperatures). We have not determined what this excitation is caused by. The first possibility is partially due to a weak, previously unobserved Nd crystal-field (CF) excitation. The second possibility is due to the induced holes in the Haldane chains.

References

1. Neutron Scattering  3) Superconductivity
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Phonon Density of States of $\beta$-ZrNBr

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Fermi chopper at TOF-type spectrometer AGNES at C3-1-1 of JAERI-JRR3M in Tokai reduces neutron flux to about 1/100 of incident flux. This low flux density is compensated by 199 counters installed at AGNES, which is enough for quasielastic scattering studies of compounds with hydrogen atoms. On the other hand, it is still challenging to study inorganic compounds at AGNES, because of the neutron flux. Among many compounds with light atoms, nitrides are suitable candidates for the study at AGNES, since a nitrogen atom with light mass has relatively large total bound scattering cross section, i.e., 11.5 barn. From this point of view, we have tried to study layered nitride superconductors at AGNES in a wide range of temperature [1]. At low temperature, we found multiple elastic scattering at Al cell and sample dominated scattering intensity. Here, we report high temperature measurement of $\beta$-ZrNBr.

Novel layered superconductors, Li$_x$ZrNCl ($T_c$=15 K), Li$_x$ZrNBr ($T_c$=13 K), and Li$_x$ (THF)$_2$HfNCl ($T_c$=25.5 K), have been discovered by Yamanaka et al. [2]. The conducting layer consists of double honeycomb lattice of [(Hf, Zr)N]$_2$. The conduction band is partially filled by electrons, which are supplied from alkali metals. It is recently that recently discovered high-$T_c$ MgB$_2$ [3] has similar band structure to the present double honeycomb lattice superconductors but contrasts with that in the sign of doped carriers.

Figure 1 shows powder diffraction patterns of pristine $\beta$-ZrNBr at $T$= 270 and 600 K by AGNES. On heating, anisotropic intensity decrease can be seen for 00 $\bar{2}$ scattering in addition to c axis elongation, corresponding to weak van der Waals force in bromine layers. Generalized phonon density of states, GPDS, of $\beta$-ZrNBr is shown in Fig. 2. Sample weight, measuring time and counter number are 3.8 (8.5) g., 40 (55.2) h and 199 (119) for the measurement at 600 (270) K, respectively. Nitrogen atoms contribute 85 % in the total

GPDS intensity for $\beta$-ZrNBr. Even at 50 meV, hardening of optical phonon upon cooling can be seen in Fig. 2, showing the potential of AGNES for nitride studies.

References
Relation among crystal structure, stripe order and superconductivity in (La,Ba,Sr)CuO$_4$

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Since the discovery of charge and spin-stripe order in lamellar copper oxides [1] the interplay between stripe correlation and superconductivity has attracted considerable attention. However, no evidence of CDW order was so far obtained by diffraction measurements except for the low-temperature-tetragonal (LTT) phase of La$_{1.8}$Nd$_{0.2}$Sr$_{1.8}$CuO$_4$, while SDW order is stabilized at the hole concentration of ~1/8 irrespective of crystal structure. It is therefore important to clarify whether the static and/or the dynamical stripe correlations commonly exist in the high-$T_c$ superconductors.

In order to elucidate the relationship between the crystal structure and the stripe order, we have performed neutron-scattering measurements on La$_{1.875}$Ba$_{0.125}$Sr$_{0.8}$CuO$_4$ (LBSCO) single crystals, in which the crystal structure can be controlled by varying the Ba and Sr concentration. Most of measurements are done using triple-axis spectrometers TOPAN and HER at JRR-3M, JAERI (Tokai).

We found the clear evidence of stripe order in the samples with $x=0.05, 0.065$ and 0.075. Superlattice peaks from the charge stripe order observed in the LTT and low-temperature-orthorhombic (LTO) phases dramatically degrade towards the LTO, while the well-defined SDW order remains even in the LTO phase. (Fig. 1)

Furthermore, both the CDW and SDW peak intensities were found to begin appearing at the structural transition temperature ($T_d$) with similar temperature dependence to that of the order parameter of the (0 1 0). (Fig.2) The coincident appearance of the CDW and SDW orders below $T_d$ is also observed for the $x=0.05(T_d=37K)$ and 0.085 ($T_d=30K$) samples. These results clearly demonstrate a structural effect on the charge and spin orders in the copper oxides.

References
Magnetic Excitation Spectra of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$

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In the study of the superconductivity of Cu oxides, the detailed wave vector($q$)- and energy($\omega$)-dependences of the magnetic excitation spectra $\chi''(q, \omega)$ present important information. The spectra may also present information on the role of the fluctuating or dynamical "stripes" in the occurrence of the superconductivity. If they have significant effects on the electron system, we may have to consider $\chi''(q, \omega)$ essentially in the charge ordered background.

We have been studying the detailed structure of $\chi''(q, \omega)$ of YBa$_2$Cu$_3$O$_y$ (YBCO$_y$ or YBCO) and reported that the magnetic excitation spectra of YBCO$_y$ ($y \geq 6.5$) can be well understood without effects of dynamical "stripes" [1, 2]. In the study, an expression $\chi(q, \omega) = \chi^0(q, \omega) \{1 + J(q) \chi^0(q, \omega)\}$ is used for the dynamical susceptibility with the exchange coupling $J(q) = J(\cos q_x a + \cos q_y a)$ and the Lindhard function $\chi^0(q, \omega)$ of the electron system. The effective band parameters $t_0$, $t_1$ and $t_2$, which can reproduce the Fermi surface shape are used. Other details can be found in refs. 1 and 2. What we just want to emphasize here is that consideration of the quasi particle broadening is important to suppress the antiferromagnetic ordering and to reproduce the $(q, \omega)$- and temperature($T$)-dependence of the spectra.

The above results suggest that effects of the dynamical "stripes" is not important for the occurrence of the high-$T_c$ superconductivity and that the effects can be seen only in La214 systems such as La$_{2-x}$Ba$_x$CuO$_4$, La$_{1.6-x}$Nd$_{0.4}$Sr$_{x}$CuO$_4$, and other related systems with $x \sim 1/8$. To study this point in detail, we have deliberately adopted La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ which has the static "stripe" order. In the present crystal, the first order transition to the low temperature tetragonal(LTT) phase takes place at $\sim 70$ K and the superlattice reflections related to the magnetic and charge order appears at $\sim 60$ K with decreasing $T$ ("stripe" order).

We have measured the spectra $\chi''(q, \omega)$ to find how effects of the "stripes" appears in $\chi''(q, \omega)$. The data present useful information to study the existence or non-existence of effects of dynamical "stripes" in Cu oxides which exhibit high-$T_c$ superconductivity.

In Fig. 1, the magnetic excitation spectra of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ taken along $(0.5, k, 0)$ at several energies $E$ are shown at 10 K and 83 K. At 10 K, the "stripe" order exists and the sharp spin wave-like excita-
tions can be observed at the incommensurate (IC) points, \((0.5,0.5\pm 0.5,0)\). The peak intensity is larger for the smaller \(E\). At 83 K, because the magnetic order does not exist, the peak width becomes broader than at 10 K and the low energy peak diminishes.

Figure 2 shows the profiles taken at \(E=5\) meV at several temperatures. We can see that the IC nature survives up to the \(T\) region much higher than the temperature \(T_{\text{CO}}\) of the "stripe" order.

Figure 3 shows the \(T\)-dependence of the incommensurability \(\delta\) (top) and the intrinsic width of the IC peaks (bottom). One of the interesting points is that \(\delta\) changes from \(\sim 0.10\) to \(0.12\) at around \(T_{\text{CO}}\). If the periodicity of the one dimensional charge order determines \(\delta\), it is equal to 0.12 even at \(T>70\) K. However, \(\delta=0.12\) has been observed only in the region of the static order, indicating that \(\delta\) is rather determined by the Fermi surface effect above 70 K, than the periodicity of the "stripes". The LTT phase may stabilize the "stripe" order and the change of \(\delta\) takes place just below the transition to the LTT phase.

The robust nature of the IC structure against the \(T\) increase (and equivalently in some sense, the rather small width of the IC peaks) indicate(s) that the energy broadening of the electrons should be much smaller than that of \(\text{YBCO}_y\). This feature is seen in the published data of \(\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4\) and \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\), too [3, 4]. The large broadening of the quasi particles, which is one of the characteristics of high-\(T\) systems, is less significant in \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) (LSCO) system. It is possibly attributed to the existence of the dynamical "stripes" in LSCO.

References
Neutron Scattering Study on in-plane phonon modes of \( \text{YBCO}_{6.5} \)

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The \( T_c \)-suppression found in \( \text{La}_{2-x}\text{Ba}_x\text{Cu}_4\text{O}_y \) and \( \text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{Cu}_4\text{O}_y \) at around the hole carrier concentration \( p(=x)\sim1/8 \) is called the "1/8 anomaly", and considered to originate from the formation of the one dimensional charge order or "stripes" in the \( \text{Cu}_2\text{O}_2 \) planes. To study whether the fluctuations of the "stripes" or the dynamical "stripes" have important roles in realizing (or suppressing) the superconductivity, we have searched effects of dynamical "stripes" on the physical quantities of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) (YBCO, \( \text{YBCO}_y \)) and reported that magnetic excitation spectra of YBCO can be understood without effects of dynamical "stripes" in the region of \( y\geq0.5 \) [1, 2]. The present paper reports results of phonon measurements.

Mook et al. [3, 4] measured the in-plane longitudinal modes of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) (YBCO) system, which have the energies of \( \sim(43\sim52) \) meV and are assigned as the \( B_{2u}/B_{3u} \) modes at \( \Gamma \) point. They reported the anomalous wave vector \( q \) dependence of the broadening of one of the modes (\( B_{3u} \) one), which vibrates perpendicular to the \( b \)-axis, as the experimental evidence for the existence of the dynamical "stripes" along \( b \). Anomalous \( q \) dependence of the integrated intensity of the phonon peak has also been reported by their group.

We have measured other in-plane longitudinal phonons, which are also assigned as the \( B_{2u}/B_{3u} \) modes at \( \Gamma \) point [5]. (Hereafter, we just call these branches \( B_{2u}/B_{3u} \) modes.) As shown in Figs. 1(a) and 1(b), the atomic motions of the \( B_{3u} \) (\( B_{2u} \) mode in the \( \text{Cu}_2\text{O}_2 \) plane are mainly perpendicular(parallel) to the chain direction(\( b \)-direction), and the amplitude of the chain oxygen motion is larger for the \( B_{3u} \) mode than for the \( B_{2u} \) one.

Neutron measurements were carried out with spectrometer ISSP-PONTA at JRR-3M of JAERI on single crystals of \( \text{YBCO}_{6.5} \) (\( T_c\sim50 \) K), \( \text{YBCO}_{6.7} \) (\( T_c\sim62 \) K), and \( \text{YBCO}_{7.0} \) (\( T_c\sim91 \) K). Oxygen numbers \( y \) of the crystals were controlled by the annealing temperature. The horizontal collimations were \( 40'-40' \)-\( 40' \)-\( 80' \), and to eliminate the higher order contamination the Pyrolytic Graphite (PG) filter was put after the samples. Calculated profiles obtained by convoluting the Lorentzian type phonon profiles with the resolution function, were fitted to the energy-scan profiles at constant reciprocal points \( q=(3+h,0,0) \).

Figure 1(c) shows the energy scan profile of the \( B_{2u}/B_{3u} \) phonons taken for \( \text{YBCO}_{6.5} \) at \( h=0.2 \) and at \( \sim7 \) K. The \( h \) value is
close to the twice of the incommensurability, $2\delta$, of the magnetic scattering peak. Similar data taken for YBCO-7 at $\sim 7$ K are shown in Fig. 2 for several $h$ values. Two peaks can be observed in each profile: The higher energy mode has the smaller widths and larger intensities than the lower energy one. The large broadening or large smearing observed for the lower energy mode might be attributed to an effect of the dynamical "stripes". However, the smearing is found in the wide region of $h$, suggesting that it is not related to the value of $2\delta$. It is insensitive to the carrier number $p$ or $y$. Moreover, it seems to be insensitive to the temperature $T$, too. These facts cannot be explained by considering effects of the dynamical "stripes", which should be stronger in the region of $p\sim 1/8$ and at lower $T$. Instead, we simply attribute the smearing to the oxygen deficiency at the chain sites, assigning that the lower energy mode is the $B_{3u}$ one, which has the larger amplitude of the chain oxygen vibration than the $B_{3u}$ one. (We think that there exist, even in the sample with $y=7$, enough amount of oxygen deficiency to bring about the observed smearing of the mode.)

In Fig. 3, dispersion curves obtained for YBCO-7 at 7 K and 295 K are shown, where just the smooth $q$-dependence can be observed for all the samples at all temperatures. This result is contrasted to that reported by Mook et al. [3, 4], where an anomaly was observed at $q=2\delta$.

In summary, although the smearing of $B_{3u}$ phonon mode has been found, its $h$, $y$- and $T$- dependences indicate that the dynamical "stripes" cannot be considered to be the origin of the smearing. Instead, it is attributed to the chain oxygen deficiency. No anomalous feature has been found in the dispersion curves.

References

Observation of a gapped excitation in the overdoped La$_{2-x}$Sr$_x$CuO$_4$


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The superconducting phase of high-$T_c$ cuprates are generally classified in the underdoped, optimally doped and overdoped regions, according to the carrier-doping level and $T_c$. Various concepts (e.g., pseudo-gap, quantum critical point, Fermi-liquid,...) are proposed to explain the curious phase diagram. La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) is a suitable and unique system for the experimental study over the entire superconducting phase, due to the large capacity for Sr doping. Although low-energy spin fluctuations from the underdoped to optimally doped phases ($0.07 \leq x \leq 0.18$) have been well studied with inelastic neutron scattering (INS), [1, 2, 3] no detailed investigation has been performed in the overdoped phases except for the heavily overdoped sample with $x = 0.25$ (gapless). [2] Therefore, we explored magnetic excitations of the lightly overdoped superconducting phase in $0.18 < x < 0.25$.

Single crystals of La$_{1.86}$Sr$_{0.20}$CuO$_4$ were grown by the TSFZ method. We confirmed the Sr concentration with respect to $T_c$($= 30$ K) and the structural phase-transition temperature. The five cylindrical crystals (5 mm each) were assembled, finally giving the total volume of 2 cc. INS experiments were performed on the triple-axis spectrometer TOPAN installed at the JRR-3M.

Our new finding is a gapped behavior in the low-energy excitation spectra as shown in Fig. 1. In the superconducting state, no magnetic response was observed at $\omega = 3$ meV (Fig. 1(b)), in contrast with the finite incommensurate scattering at $\omega = 4$ meV (Fig. 1(c)). Further, the incommensurate response of $\omega = 3$ meV appears in the normal conducting state (Fig. 1(a)). This gap-type excitation is similar to those observed in optimally doped $x = 0.15$ and 0.18, [1, 2] but different with the gapless energy spectra in the underdoped ($x = 0.10$ [2] and 0.07, [3]) and heavily overdoped phases ($x = 0.25$ [2]). Through the comparison between the gapped superconductors, the peak-width was found to broaden gradually with keeping a saturated incommensurability ($\approx 0.12$) as the doping level deepens. The analysis for the resolution-deconvoluted intensity, or $\chi'(\omega)$ is now in progress, which will clarify the relation between the superconductivity and spin fluctuations in terms of the spectral weight.

References
Magnetic field effect in lightly doped La$_{2-x}$Sr$_2$CuO$_4$

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Extensive neutron elastic scattering studies have been performed on lightly doped La$_{2-x}$Sr$_2$CuO$_4$ (0 < x < 0.055) in order to clarify the static magnetic properties in the spin-glass regime. It is revealed that the static spin correlations in the spin-glass phase show a one-dimensional diagonal spin modulation, in which the direction of the modulation is rotated away by 45° from that in the superconducting phase.\(^1\)\(^2\)

In this study we examined magnetic field effect of the static magnetic correlations in lightly doped La$_{2-x}$Sr$_2$CuO$_4$. One important point is to clarify whether the diagonal incommensurate (DIC) structure is dominated by the charge disproportion or a magnetic origin. Another point is to understand the magnetic anisotropy in doped La$_2$CuO$_4$ from a microscopic point of view. The neutron-scattering experiments were carried out on the cold neutron three-axis spectrometers LTAS and the thermal neutron three-axis spectrometer TAS2, using single crystals of La$_{2-x}$Sr$_2$CuO$_4$ (x=0.014 and 0.024) grown by the traveling

\[
\text{La}_{1.988}\text{Sr}_{0.014}\text{CuO}_4
\]

\[
\text{LTAS, } H//c, T=4 \text{ K}
\]

Figure 1: Magnetic elastic intensity around the diagonal incommensurate positions (1,0,0) and (0,1,0) at 4 K in La$_{1.988}$Sr$_{0.014}$CuO$_4$ as a function of magnetic field. The scan trajectories are shown in the inset of (a). Open circles in (c) are the data measured at 0 T after a magnetization cycle. Magnetic field is applied perpendicular to the CuO$_2$ plane. Background intensities measured at a high temperature have been subtracted. The lines are guides to the eyes.
solvent floating-zone method.

Figure 1 shows the magnetic field dependence of the magnetic elastic intensity around DIC positions (1,±ε,0) and (0,1±ε,0) in La$_{1.988}$Sr$_{0.014}$CuO$_4$, which exhibits a coexistence of a Néel ordered phase and a spin-glass phase at low temperatures. The magnetic signal, which develops below ~30 K, originates from the spin-glass phase. The incommensurate peaks are antisymmetric because of the twin structure as shown in the inset of Fig. 1(a). As shown in Figs. 1(a) and 1(c), the magnetic intensity at (1,±ε,0) are almost constant between 0 and 6 T and gradually decreases above 6 T.

It is known in pure La$_2$CuO$_4$ that applying the magnetic field perpendicular to the CuO$_2$ plane, the magnetic structure factor of the (100) reflection becomes zero because a spin reorientation transition from La$_2$CuO$_4$-type to La$_2$NiO$_4$-type occurs. The decrease in intensity in La$_{1.988}$Sr$_{0.014}$CuO$_4$ probably originates from this spin reorientation transition. This transition is ascribed to the Dzyaloshinskii-Moriya (DM) antisymmetric exchange terms generated by the small rotation of the CuO$_4$ octahedra. Because of the DM terms, the magnetic anisotropy is weakly Ising-like and has an easy-axis along the b axis. Therefore, it is suggested that the DIC spin structure in the spin-glass phase also has an Ising-like anisotropy.

The magnetic intensity at (0,1±ε,0) is almost magnetic field independent as shown in Figs. 1(b) and 1(d). The magnetic signal at (0,1±ε,0) is considered to be a tail of (0,1±ε,1), which is broad along the c axis. The instrumental resolution elongated vertically integrates the tail effectively. The (011) magnetic Bragg peak should decrease under magnetic field. Whereas the (010) magnetic intensity increases. Since the both contributions compensate with each other, the intensity at (0,1±ε,0) may be almost unchanged.

Figure 2 shows the magnetic field effect in La$_{1.976}$Sr$_{0.024}$CuO$_4$, which shows no long-range AF order but a spin-glass behavior below ~25 K, with field perpendicular to the CuO$_2$ plane. The magnetic intensity at (1,±ε,0) decreases monotonically with increasing magnetic field. The tendency is similar to that in La$_{1.988}$Sr$_{0.014}$CuO$_4$, although there is a decrease in intensity between 0 and 5 T and the intensity at 10 T becomes almost half of that at 0 T. This means that the averaged critical field becomes smaller with hole doping. The transition is very broad in the spin-glass phase probably because the cluster size is finite and distributed so that the critical field is also distributed. In this experiment, it is found that the transition temperature, the peak width, and peak positions are almost unchanged under magnetic field although the magnetic intensity decreases. This result indicates that the DIC structure is probably dominated by the charge disproportion.

![Diagram](image-url)

Figure 2: Magnetic elastic intensity around the diagonal incommensurate positions (1,±ε,0) at 4 K in La$_{1.976}$Sr$_{0.024}$CuO$_4$ as a function of magnetic field. Magnetic field is applied perpendicular to the CuO$_2$ plane. Background intensities measured at a high temperature have been subtracted.

References
Magnetic field effect on the static magnetic order in the electron-doped superconductor Nd$_{1.86}$Ce$_{0.14}$CuO$_4$

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Extensive neutron-scattering studies have been performed on the high-$T_c$ superconductors in order to clarify the interplay between the superconductivity and magnetism. Especially in the hole-doped cuprate superconductor La$_{2-x}$Sr$_x$CuO$_4$ and related systems, static and dynamic properties of spin correlations are studied in considerable detail.

In the electron-doped cuprate superconductor, however, the number of neutron-scattering studies is limited. In this study we examined magnetic field effect of the static magnetic correlations in Nd$_{1.86}$Ce$_{0.14}$CuO$_4$ ($T_c \sim$25 K). Since the coherence length is $\sim$100 Å in the electron-doped system, which is several times larger than that in La$_{2-x}$Sr$_x$CuO$_4$, large magnetic field effect can be expected. Furthermore, the upper critical field $H_{c2}$ is less than 10 T in the electron-doped system so that normal state properties can be easily studied.

The neutron-scattering experiments were carried out on the three-axis spectrometer TAS2, using a large single crystal grown by the traveling solvent floating-zone method. The ($\frac{1}{2}\frac{1}{2}0$) magnetic Bragg intensity, which mainly originates from the order of both the Cu and Nd moments at low temperatures, shows no magnetic field dependence when the field is applied perpendicular to the CuO$_2$ plane up to 10 T above $H_{c2}$, as shown in Fig. 1. This result is much different from that reported in the hole-doped superconductors, in which the quasi-static magnetic order is enhanced under magnetic field. This suggests that the interplay between magnetic order and superconductivity in this system is much different from that in the hole-doped system.

Figure 1: Neutron elastic intensity around the commensurate position ($\frac{1}{2}\frac{3}{4}0$) in Nd$_{1.86}$Ce$_{0.14}$CuO$_4$ under magnetic fields $H=0$ and 10 T and at $T=15$, 45, and 75 K. Magnetic field is applied perpendicular to the CuO$_2$ plane. The solid lines are the results of fits to a Gaussian function for the zero field data.
Measurements of the In Plane Longitudinal Phonons of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$

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The suppression of the superconducting critical temperature $T_c$ observed in La$_{2-x}$Ba$_x$CuO$_4$ and La$_{2-x}$Nd$_x$Sr$_2$CuO$_4$ systems at around the hole carrier concentration $p(=x)\sim 1/8$ is considered to originate from the formation of the one dimensional-like charge ordering or "stripes" in the CuO$_2$ planes.

To clarify whether the fluctuations of the "stripes" or the dynamical "stripes" have important roles in realizing (or in suppressing) the superconductivity commonly to every high-$T_c$ system, we have studied effects of dynamical "stripes" on the physical quantities of YBa$_2$Cu$_3$O$_y$ (YBCO, YBCO$_y$) and reported that magnetic excitation spectra of YBCO can be understood without effects of dynamical "stripes"$^1,2$.

The present paper reports results of phonon measurements on single crystals of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$, which has the "stripe" ordered state in the low temperature tetragonal (LTT) phase. Mook et al.$^3,4$ measured the in-plane longitudinal modes of YBa$_2$Cu$_3$O$_y$ (YBCO$_y$) system. These phonons have the energies of $\sim$43~52 meV and can be assigned as the $B_{2u}$/B$_{3u}$ modes at $\Gamma$ point. They reported the anomalous wave vector ($q$) dependence of the broadening of one of the modes (B$_{3u}$ one), which vibrates perpendicular to the b-axis, as the experimental evidence for the existence of the dynamical "stripes" along b. Anomalous $q$ dependence of the integrated intensity of the phonon peak has also been reported by their group.

Similar studies have also been carried out by the present authors' group for similar longitudinal modes ($B_{2u}$/B$_{3u}$ modes at $\Gamma$ point) of YBCO$_y$ with the energy dispersions between $\sim$20 and $\sim$35 meV, where, in contrast with the results of Mook et al.$^3,4$, significant effects of the dynamical "stripes" have not been found$^5$. Considering these results, we have deliberately adopted La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$, which has the "stripe" order at low $T$, to study how significantly we can see effects of the "stripes" on the phonon modes. Neutron data were taken with the TAS-1 spectrometer at JRR-3M.

Figures 1(a)-1(c) show the temperature ($T$) dependences of the peak intensities of the superlattice reflections observed at (0.5±0.5,0,0) (a), (2+28,0,0) (b) and (1,0,0) (c) in the reciprocal space of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$. The data at the point $Q$=(1,0,0) shows that the LTT phase appears suddenly (by the first order transition) at about 70 K with decreasing $T$. The data at (0.5±0.5,0,0) and (2+28,0,0) show that the ordering of the mag-

Figure 1: $T$ dependences of the peak intensities of the superlattice reflections observed at (0.5±0.5,0,0)(a), (2+28,0,0)(b) and (1,0,0)(c) in the reciprocal space of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$. 

原子炉：JRR-3M 装置：TAS-1(2G) 分野：中性子散乱（超伝導）
nertic moments and charges, respectively, appear at around 60 K with decreasing T.

Figures 2(a)-2(d) show the transfer energy (E) dependence of the neutron scattering intensity measured at several temperatures at Q=(4.25,0,0), where in-plane longitudinal modes are mainly detected. A broad peak can be seen at around 30 meV and a clear peak can also be observed at around 41 meV. The former peak can be assigned to be the modes which correspond to the B2u/B3u modes observed in our study on YBCO system. It also corresponds to the the in-plane longitudinal mode of La2−xSrxCuO4, as can be found by comparing the energy dispersions of the present system and La1.9Sr0.1CuO4 (See Fig. 3). An effect of the "stripe" formation can be seen as the increase of the width of the peak at around 30 meV: At 90 K (above the temperature of the charge ordering T_{CO}), the peak is relatively sharp and we can therefore see the dip-structure at E~35 meV. It can also be seen at 60 K (~T_{CO}), but cannot be observed at 35 K and 10 K. This result indicates that the broadening increases with the charge order rather than the sudden increase at the transition to the LTT phase.

A rather significant change of the observed spectra is also found in the T-dependence of the peak intensity at E~41 meV. Although the peak intensity seems to be T-dependent even below 35 K, we cannot distinguish, at this moment, if the observed change is induced by the structural transition at 70 K or by the charge ordering.

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Low Temperature Scattering in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$

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The magnetic phase diagram of $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ (LCLO) bears strong similarity to the more familiar superconducting compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO). At low doping both compounds are antiferromagnets. The boundary of the antiferromagnetic (AF) phase is slightly renormalized in LCLO to $x = 0.03^3$, compared to $x = 0.02$ for LSCO. Beyond the AF phase boundary, both compounds have spin-glass phases which are quantitatively similar to each other$^4$. Reentrant spin-glass behavior within the AF phase is also present in both compounds. A key difference is that for concentrations $x > 0.055$, LSCO becomes a superconductor while LCLO remains an insulator for all dopings.

Recent results by Matsuda et al. for LSCO ($x < 0.02$) have demonstrated first-order phase separation into AF and incommensurately spin-ordered regions at low temperature$^3$. Although previous reports at higher doping ($x = 0.10$) for LCLO reported the absence of an incommensurate spin structure$^4$, the strong similarities between the magnetic phase diagrams leaves the behaviour inside the AF phase as an open question.

We conducted high-resolution elastic neutron scattering studies at the cold neutron beamline LTAS. The sample was a single crystal of $\text{La}_{2}\text{Cu}_{0.98}\text{Li}_{0.02}\text{O}_4$ grown by the Travelling Solvent Floating Zone method at Stanford University. As expected, the sample exhibits antiferromagnetic order below a mean transition temperature of $T_N = 125$ K. Our experiment reveals several indications of exciting low-temperature magnetic behaviour.

Figure 1 presents a scan at the AF (100) peak position. The instrumental resolution as measured by $\lambda/2$ is indicated by the dashed line. As is apparent, the width of the peak is broader than resolution at all temperatures below the ordering temperature. This may either indicate that the increased disorder experienced in this system limits the magnetic order to being quasi-long-range, or as suggested by some, the presence of a second component to the scattering function, indicating the presence of topological "skyrmonic" spin structures surrounding the doped Li sites$^5$.

![Figure 1: Antiferromagnetic (100) Bragg peak showing a temperature independent width which is broader than the instrumental resolution.](image)

In Fig. 2 we present a measurement of the antiferromagnetic order parameter. The onset of AF order is easily visible at high temperature, marked by the sudden increase in intensity. At low temperature, as highlighted in the inset, a fraction of the intensity is lost. In the low-doped LSCO samples studied by Matsuda et al.$^3$, a similar loss of intensity is observed at $T \sim 30$ K and correlates with the appearance of incommensurate peaks in a diagonal stripe geometry.
Intrigued by the possibility of similar incommensurate correlations in LCLO, we undertook a detailed survey around the commensurate position in a sample of La$_2$Cu$_{0.98}$Li$_{0.02}$O$_4$. In Fig. 3, we present a series of scans at the (0,1,0.2) position in reciprocal space. The (0,1,0) peak is forbidden by the magnetic structure factor in the La$_2$CuO$_4$ spin configuration. Yet, it is very clear from the scans that a broad magnetic scattering rod forms at low temperature. The intrinsic width of the peak is difficult to determine because of the multiple twin domains in our sample. At present our data do not enable us to distinguish between broad scattering at the commensurate position, and incommensurate scattering with a reduced incommensurability. What we have been able to establish is that, if the low-temperature magnetic scattering is incommensurate, then the incommensurability is at most half that observed in samples of LSCO at the same doping level.

The physics of La$_2$Cu$_{1-x}$Li$_x$O$_4$ in the low-doping regime has revealed strong similarities but also intriguing differences with La$_{2-x}$Sr$_x$CuO$_4$. Contrasting the two systems is an exciting means of exploring the different ways in which their common parent responds to perturbations of the Mott insulator. Many of the ambiguities in our current analysis are directly attributable to the multi-twin domain nature of our sample. A second round of experiments are planned both within the Néel phase and in the spin-glass regime that lies at higher doping once single-domain samples can be produced.

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Search for Antiferromagnetic Fluctuations in Bismuth-Based Superconductors

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It is widely believed that antiferromagnetic fluctuations play an important role in the physics of high-temperature superconductivity. The undoped parent compounds, such as $\text{La}_2\text{CuO}_4$, are antiferromagnetic insulators. Upon doping the $\text{CuO}_2$ sheets with a few percent of holes, these materials become metallic and superconducting, with "strange" metallic behavior in the normal state. Neutron scattering studies have demonstrated that dynamic antiferromagnetic correlations are a robust feature of both superconducting and normal states\textsuperscript{1, 2, 3, 4, 5, 6}.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) has been the only single-layer hole-doped high-temperature superconductor that has been studied systematically via neutron scattering, since it is relatively straightforward to grow the required large single crystals. Detailed studies have revealed many interesting properties, such as an incommensurate magnetic response\textsuperscript{1, 2, 7, 8}. The only other high-$T_c$ family of materials for which sizeable crystals over a wide range of hole-doping have been available for neutron scattering studies is the structurally more complicated bi-layer system $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (YBCO)\textsuperscript{3, 4, 5, 6, 9}. The magnetic response of YBCO appears to be rather different from that of LSCO. In particular, it was found that the magnetic response is gapped and incommensurate only at high energies, and that there exists a magnetic resonance (at 41 meV for optimally doped YBCO) in the superconducting state.

To better understand the connection between antiferromagnetic correlations and high-temperature superconductivity, it will be necessary to study additional materials. Neutron scattering experiments require sizeable samples, a fact that has presented a significant obstacle toward this end. We have succeeded with the growth of sizeable crystals of the single-layer and double-layer Bi-based superconductor $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ (Bi2201). The sample shown in Fig. 1 consists of 6 co-aligned single crystals with total volume of 1.1 cm$^3$. Initial crystal checks demonstrated the single-grain nature of the individual crystals. Small pieces from these crystals show excellent superconducting properties, with an onset of $T_c \sim 36$K, which compares well with the highest values achieved in LSCO.

In light of the differences observed for LSCO and YBCO, a study of the magnetic response of Bi2201 should yield valuable new information about the connection between superconductivity and antiferromagnetic order and fluctuations. We have begun to pursue neutron scattering measurements to search for antiferromagnetic fluctuations in Bi2201. Specifically, we carried out inelastic neutron scattering measurements on the TAS-1, TAS-2, PONTA, and TOPAN triple-axis instruments at the JAERI JRR-3M research reactor. To our surprise, unlike for LSCO, these measurements reveal no obvious features in the 3-12 meV range, both below and above the superconducting transition temperature. The incommensurate low-energy magnetic scattering may be broader than in LSCO, and therefore harder to detect. Alternatively, the magnetic fluctuations may be gapped, perhaps with a gap much larger than that of optimally-
doped LSCO (about 6 meV). We note, that the experiment is made difficult by the fact that the scattering in Bi2201 results in a very high “background,” in large part due to significant low-energy phonon scattering, a result of the complex crystal structure of Bi2201. Figure 2 shows a comparison of our data with data for LSCO to demonstrate the strong difference. We note that we counted as long as 1 hour per point in our inelastic scans. We recently learned that a similar search for antiferromagnetic fluctuations in optimally-doped Bi2201 by Prof. Keimer's group (MPI, Stuttgart, Germany) has failed to discern an antiferromagnetic signal as well.\(^{11}\)

While inelastic neutron scattering experiments reveal a \((\pi, \pi)\) resonance in YBCO\(^{4, 5, 9}\), this feature has not been seen in LSCO. We conducted a search in optimally doped Bi2201, but did not find any evidence for a magnetic resonance peak.

In optimizing the crystal growth, it was very helpful to aim for a sample composition that resulted in the highest possible superconducting transition temperature and in very sharp transition widths. On the other hand, underdoped Bi2201 should exhibit more prominent antiferromagnetic fluctuations. While it has not been possible so far to obtain single crystals at half-filling (i.e., undoped CuO\(_2\) sheets), we have managed to grow samples that are very underdoped and non-superconducting. We have also succeeded in growing antiferromagnetically ordered samples of Y-substituted Bi2212, Bi\(_{2.06}\)Sr\(_{2.15}\)Y\(_{0.71}\)Cu\(_2\)O\(_8\). Our measurement indicates that T\(_N\)=450 K, to our knowledge the first such measurement on this system. Our goal for the near future then is to continue our search for antiferromagnetic correlations in lightly doped Bi2201 and expand the work to Bi2212 near half-filling.

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Mechanism of high-$T_c$ superconductivity mediated by spin fluctuations is one of the central topics in highly correlated electron systems. Studies of spin correlations in the hole-doped high-$T_c$ cuprates such as La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and YBa$_2$Cu$_{O_y}$ have intensively been carried out by neutron scattering experiments, and show an intimate relation between low-energy spin fluctuation and superconducting transition temperature. However, due to the difficulties in growing large single crystals, no systematic study has been done on the electron-doped system.

Quite recently, we have succeeded in growing large single crystals of Pr$_{1-x}$LaCe$_x$CuO$_4$ (PLCCO) and inducing the superconductivity after an oxygen-reducing procedure by heat treatment. Therefore, we have carried out neutron-scattering measurement using TAS-1 and TAS-2 triple-axis spectrometers in order to investigate the relation between spin correlations and the superconductivity.

Reduced $x=0.11$ sample shows bulk superconductivity with the onset temperature of 26K. No evidence of antiferromagnetic order was found in the superconducting sample. On the other hand, a clear magnetic Bragg peak appears below ~200K in the as-grown sample which does not show superconductivity down to 2K. These results imply that superconductivity concomitantly appears with the degradation of a magnetic ordering.

Furthermore, we observed clear commensurate spin fluctuations at the antiferromagnetic zone center of (1 0 0) (orthorhombic notation) in both as-grown and reduced $x=0.12$ samples (Fig. 1), analogous to the result for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. Therefore, the commensurate spin fluctuations seem to be robust with respect to electron-doping, while the incommensurability of spin fluctuations in the LSCO system dramatically change by hole-doping.

Figure 1: Constant-$\omega$ spectra at $\omega=4$meV for (a) as-grown and (b) oxygen-reduced Pr$_{0.89}$LaCe$_{0.11}$CuO$_4$.

References

Charge-Spin Self-Organization in Superconducting Cuprate


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For a long time high-temperature superconductivity (HTSC) has been thought to occur in a homogeneous crystal via a purely electronic mechanism involving spin excitations [1]. However, lately this view is being challenged by the observation of the spin-charge stripes [2] and observation of various lattice effects [3], including the possible role of phonons [4-6]. Since HTSC occurs in an antiferromagnetic Mott insulator doped with holes, from the beginning it has been a major puzzle how to reconcile the localization tendency due to spin correlation with high supercurrent mobility. A possible solution is to have electronic phase segregation [3] such as the stripe phase formation. However, the stripe phase was observed only for an insulating compounds [2] and its presence in the superconducting phase is highly controversial. In addition our recent study of phonon dispersion [4,5] suggests there are two kinds of stripe phases, one that involves the Néel antiferromagnetic state and the domain boundary dressed with holes (classical stripes) [7] and the other that has the spin-ladder spin-singlet resonant state (quantum stripes) [8,9]. Our phonon results support the latter picture.

Inelastic neutron scattering measurements were carried out with a triple-axis-spectrometer TAS-1 at JAERI-3 reactor at JAERI, Tokai. The sample was a collection of single crystals of YBa$_2$Cu$_3$O$_{6.95}$ prepared by the melt-extraction method. If dynamic doubling of the unit cell exists as suggested by the phonon measurement, we expect quasielastic scattering that peaks around $h = n + 0.5$, in the unit of the reciprocal lattice, $a^* = 2\pi/a$. Since the stripes in the adjacent CuO$_2$ layers are likely to be out-of-phase due to Coulomb repulsion they are likely to be seen around $l \sim 1.5$ ($\sim 1.9$ Å$^{-1}$). Indeed as shown in Fig. 1 some intensity was seen at the expected $Q$ space $Q = (3.5, 0, 1.5)$ above $T_c = 93$ K, for $T = 100$ and 110K. The data were taken with the energy transfer of 4 meV, and were processed to temperature averaged background and smoothed. The data summed over $l = 1.2 - 2.2$ are shown in Fig. 2. While the statistical fluctuation is too severe to derive definite conclusions, clearly the data at $T_c$ are anomalous, and it appears that dynamic doubling of the unit cell in the CuO$_2$ plane is taking place above $T_c$. The results are consistent with the presence of the cell doubling phase transition at low temperatures that are terminated by the appearance of super-conductivity, a quantum-critical point.
(QCP) scenario pictured for the charge density waves [10].

Further research on this subject is warranted to improve statistics and confirm the temperature dependence.

References:

Fig. 1: Differences r.w.t. total average.

Fig.2: $h$-dependence of difference intensities integrated over $l=1.2-2.2$. 
Low-Energy Spin Fluctuations in the Ni-substituted La$_{2-x}$Sr$_x$CuO$_4$

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It is widely believed that the large magnetic interaction between Cu$^{2+}$ spins ($S = 1/2$) plays an important role for the high-$T_c$ superconductivity in cuprates. A Ni-substitution for Cu could produce a magnetic impurity of $S = 1$ on the Cu-O$_2$ plane, giving rise to a moderate suppression of $T_c$ compared to the doping of non-magnetic Zn ($S = 0$). In the recent inelastic-neutron-scattering (INS) study for a Ni-substituted optimally doped YBa$_2$Cu$_3$O$_{7}$, a reduction of energy scale of the resonance peak is reported.\(^1\) Therefore, it is interesting to clarify the antiferromagnetic spin fluctuations of Ni-doped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with respect to the energy spectrum in the wide energy range.

Single crystals of Ni-2% substituted LSCO ($x = 0.15$ and 0.17) were grown by the TSFZ method. The sample volume was about 1.5 cc each. INS experiments were performed at the triple-axis spectrometer TAS-2 installed along the thermal beam port of the guide hall. As a first step, we searched how the Ni impurities modify the low-energy spin excitation in the optimally doped LSCO with an energy gap of 6 meV.\(^2\) Figure 1 shows the low-energy spin fluctuations of La$_{1.85}$Sr$_{0.15}$Cu$_{0.98}$Ni$_{0.02}$O$_4$ at well below $T_c$. No clear energy-gap behavior is seen down to 1.2 meV, though the intensity of Fig. 1(a) is not sufficient yet. Similar Q-spectra were obtained in La$_{1.83}$Sr$_{0.17}$Cu$_{0.96}$Ni$_{0.02}$O$_4$ as well. These results are in contrast with the impurity-free optimally doped LSCO ($x=0.15$) in which the spin excitations below 3 meV completely disappear in the superconducting state.\(^2\) As for the gap-less behavior, it is similar to the Zn-2% substituted La$_{1.85}$Sr$_{0.15}$CuO$_4$;\(^3\) while the $\omega$-dependence of $\chi(\omega)''$ is intermediate between pure LSCO and Zn-doped case (not shown). The qualitative and/or quantitative difference between Ni- and Zn-impurity compounds will be clarified with progressing analyses. We are planning further high-energy experiments.

![Figure 1: Low-energy incommensurate scattering of Ni-2% doped La$_{1.85}$Sr$_{0.15}$CuO$_4$ ($T_c$ onset = 28 K) in the superconducting state. (a) $\omega = 1.2$ and 2 meV with the $E_1$-fixed mode. (b) $\omega = 4$ meV with the $E_1$-fixed mode. The curves are drawn as a guide to the eyes. The inset shows the scan direction in reciprocal lattice space based on the high-temperature tetragonal notation.]

References

1. Neutron Scattering

4) Amorphous \cdot Liquid
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NSE and SANS Studies on the Temperature and Pressure Dependencies of the Curvature Elasticity of Amphiphilic Membranes

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In a mixture of water, n-decane and AOT (diocyl sulfosuccinate sodium salt), a water-in-oil droplet microemulsion is formed at ambient temperature and pressure at oil rich region. In this system, it has been reported that a phase decomposition is induced by applying either temperature or pressure from a one-phase droplet to a two-phase coexistence of a dilute and a dense droplet phases. In order to understand this phase transition, temperature and pressure dependencies of curvature elasticity of amphiphilic membranes like the bending modulus $\kappa$ should be clarified.

In this study, we investigated the static and dynamic properties of amphiphilic membranes by means of small-angle neutron scattering (SANS) and Neutron Spin Echo (NSE) in a dilute droplet system. We modified a NSE data analysis procedure proposed by Farago et al. [1, 2], and could obtain the temperature and pressure dependencies of $\kappa$. The temperature and pressure dependencies of $\kappa$ showed that the mechanisms of the temperature-induced phase transition were different from those of the pressure-induced one. This result is consistent with the previous result at dense droplet region [3].

A mixture of 5.4% vol. of AOT (99% purity, purchased from Sigma Inc.), 4.6% vol. of D₂O (99.9 at-% D purchased from Isotec Inc.) and 90% vol. of C₁₀D₂₂ (99.9 at-% D, purchased from Isotec Inc.) was prepared. This composition leads the volume fraction of droplets being 10%.

SANS experiments were carried out at the SANS-U. Temperature was varied from 283 to 353 K with a step of about 3 K. Pressure was varied from 0.1 to 66.5 MPa with a step of about 5 MPa using a high-pressure cell. The mean radius $R₀ = \langle R \rangle$ and the polydispersity index of droplets $p = (\langle R^2 \rangle - \langle R \rangle^2)^{1/2}$ can be deduced from the obtained SANS spectra using a model proposed by Gradzielski et al. [9, 10]. $p = 0.16$ and $R₀ = 32$ Å were obtained independent of pressure. With increasing temperature, $R₀$ decreased from 32 to 28 Å and $p$ increased from 0.16 to 0.18.

NSE experiments were performed at the ISSP-NSE. Temperature was varied from 283 to 308 K with a step of 5 K. Pressure was varied from 0.1 to 60 MPa with a step of about 20 MPa. A new high-pressure cell was developed using non-magnetic stainless steel and inconel.

Obtained $I(Q,t)/I(Q,0)$ was analyzed by a model proposed by Milner and Safran [4], which is taken the membrane fluctuation into account. From the fitting to $I(Q,t)/I(Q,0)$ using a single exponential decay function, we could...
obtain diffusion coefficient $D_{\text{eff}}$. The $D_{\text{eff}}$ includes two decay components, $\lambda_1$ and $\lambda_2$, corresponding to the membrane fluctuation and the translational diffusion of droplets, respectively. In Figure 1, $Q$ dependencies of $D_{\text{eff}}$ at various conditions are shown. Lines are the fitting results according to Milner and Safran's model, and $\lambda_1$ could be obtained. In order to explain the obtained parameters, we developed the expression of $\kappa$, which Farago et al. have proposed by using Helfrich's bending free energy [2]. In the Free energy expression, there are three key parameters, spontaneous curvature $C_0$, bending modulus $\kappa$ and saddle-splay modulus $\tilde{\kappa}$. In the Farago's procedure, some assumptions are necessary to estimate each parameter, because there are only two equations related to these three parameters. In this study, we found the expression to estimate $\kappa$ without any assumptions.

$$\kappa = \frac{1}{6 \frac{k_B T}{8 \pi p^2} + \frac{\lambda_2 R_0 \left(23 \eta' + 32 \eta\right)}{24}}.$$  \hspace{1cm} (1)

Here, $\eta$ and $\eta'$ are the viscosities of inside and outside of a droplet. In Figure 2, the temperature and pressure dependencies of $\kappa$ are shown. It is clear that AOT monolayers become flexible with increasing temperature, while they become rigid with increasing pressure. This tendency is consistent with the result obtained by Nagao et al. [3] for the same system at dense droplet region.

The temperature and pressure dependencies of the rigidity of monolayers may be interpreted by the behavior of head-area $a_H$ of AOT molecules. We can roughly calculate the head-area $a_H$ by dividing the surface area per drop by the number of surfactant per drop. In Figure 3, the temperature and pressure dependencies of $a_H$ are shown. $a_H$ increased from 52 to 64 Å² with increasing temperature while it kept almost constant at about 52 Å². This fact can be interpreted as the density of AOT molecules in monolayers decreases with increasing temperature while it increases with increasing pressure. Therefore, we can imagine the following microscopic pictures; the density of AOT molecule in membrane decreases with increasing temperature because of the head-head repulsion due to the dissociation of counterion; on the other hand, it increased with increasing pressure because of the decrease of the steric volume of tail of AOT molecules. These pictures are consistent with those obtained from another NSE experiment at dense droplet region by Nagao et al. [3]

References

1-4-2

Dynamic Anomalies Accompanied by the Semiconductor-Metal Transition in Liquid Chalcogen

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Recently, sound attenuation measurements for fluid mercury [1] and liquid Te-Se mixtures [2] revealed that the sound attenuation coefficient $\alpha$ shows anomalous increase in their metal-nonmetal (M-NM) transition region. From the frequency dependence of $\alpha$, their relaxation time is estimated to be of the order of nano-seconds. These anomalies may be related to the fluctuations between the metallic and non-metallic region in the liquid, and it is interesting to study the space-and time-structure of the fluctuations. Neutron spin-echo (NSE) is a powerful technique which gives information on the intermediate scattering function $I(Q,t)$. However, to our knowledge, there is no NSE measurement under such high temperature conditions.

In the present work, we developed a new electric furnace which can be used for NSE measurements up to ~ 600°C. In order not to disturb the magnetic field around the sample, we used non-inductive resistance heaters. By using this furnace, we measured NSE signals for liquid Te-Se mixture at 500°C as shown in Fig.1. Unfortunately, the scattered intensity from the sample $I_{sample}$ is relatively small compared with the background intensity $I_{BG+cell}$, and the statistical error in $I_{sample}$ is very large. However, the echo signal in $I_{sample}$ can be recognized as shown in the Fig. 1(a). It should be noted that the echo signal $I_{sample}$ in Fig. 1(b) (Fourier time $t=1.47$ ns) is strongly damped compared to $I_{sample}$ in the Fig. 1(a) ($t=0.147$ ns). Fig. 2 shows the intermediate scattering function $I(Q, t=0.03A^{-1})$ for liquid Te-Se mixture at 500°C. From these data, the relaxation time $\tau$ is roughly estimated to be ~ 0.2ns.

References

Figure 1: The absorption-corrected NSE signals from liquid Te-Se mixture at 500°C. The momentum transfer is $Q = 0.03A^{-1}$. The solid squares, the open circles and the closed circles indicate the $I_{BG+cell+sample}$, $I_{BG+cell}$ and $I_{sample}$, respectively. The precession coil currents are (a) 1A and (b) 10A, which correspond to the Fourier times $t = 0.147$ and 1.47 ns, respectively.

Figure 2: Intermediate scattering function $I(Q = 0.03A^{-1}, t)$ for liquid Te-Se mixture at 500°C. The solid line indicate $\exp(-t/\tau)$ with $\tau = 0.20$ns.

使用施設：JRR-3M，装置：NSE(C2-2)，分野：4 Amorphous & Liquid

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Neutron Spin Echo Investigations on Dynamics of Lipid Bilayers in the DPPC/D₂O/CaCl₂ System

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In the dipalmitoylphosphatidylcholine (= DPPC)/water system, the liquid crystalline phase Lα appears above the main-transition temperature Tₘ (about 41°C). The result obtained from neutron spin echo (NSE) experiments on the sample with a lamellar repeat distance d₀ = 54 Å could be explained by a mode with a relaxation rate determined mainly by the friction between the two layers constituting the bilayer[1]. d₀ varies greatly with an addition of salt in the DPPC/water system. In order to study the dynamics further in undulation of lipid bilayers, NSE experiments were carried out on the dilute lamellar phase of the DPPC/D₂O /CaCl₂ system with d₀ longer than 300 Å in order to avoid the effect on the single membrane dynamics from neighbouring sheets of membranes.

In small angle neutron scattering (SANS) experiments using SANS-U, we observed the peaks corresponding to d₀ for lipid samples in which DPPC dispersed in D₂O solutions with 7mM CaCl₂ as shown in Fig. 1 though we had not observed such peaks for the samples with d₀ larger than 280Å in small angle X-ray scattering (SAXS) experiments using BL15A at PF in KEK and BL40B2 at SPring8. The disappearance of diffraction peaks in SAXS reflects the X-ray form factor of a bilayer for the lamellar peak which approaches to zero because the undulation of the bilayer increases with d₀. The SANS profiles l(Q) were fitted to the following equation given by Nallet et al.[2] as shown in Fig. 1.

Fig. 1. SANS profiles l(Q) obtained using SANS-U for DPPC/D₂O samples with 7 mM CaCl₂ at 52°C. The lines are fitting curves to Eq. (1).

Fig. 2. DPPC concentration dependence of the lamellar repeat distance d₀ obtained from the fitting to Eq. (1). The solid line is a fitting curve to inverse proportion to DPPC concentration.
\[ I(Q) = I_o/Q^2(\xi_0^2 + 1) + I_s/((Q - 2\pi/d_i\xi_3)^2 + 1) + I_o \]  

where \( \xi_0 \) and \( \xi_3 \) are the correlation length of the concentration fluctuation of DPPC and the membrane, respectively. The lamellar repeat distance \( d_i \) obtained by the fitting are shown in Fig. 2. \( d_i \) is roughly in inverse proportion to DPPC concentration as shown in Fig.2.

![Graph showing the relationship between \( I(Q,t) \) and \( t \) in the NSE experiment for a lipid sample with 7.7 wt% DPPC dispersed in D_2O solutions with 6.8mM CaCl_2 at 52°C.](image)

The scattering vector \( Q \) and time \( t \) dependent intermediate functions \( I(Q,t) \) obtained from the NSE experiments using ISSP-NSE were well fitted to the following equation,

\[ I(Q,t) = I(Q,0)\exp[-(\Gamma t)^{2/3}] \]  

as shown in Fig. 3. The relaxation rates \( \Gamma \) obtained from the fitting to Eq.(2) increased as \( Q^3 \) over the range of \( Q \) from 0.05 Å\(^{-1}\) to 0.13 Å\(^{-1}\)[3]. So with the case of the non-ionic surfactant \( n \)-dodecyl pentaoxyethylene glycol ether (\( C_{12}E_5 \ )) \( n \)-octane / D_2O system[4], these NSE results supported the theory presented by Zilman and Grahe[5]. They considered an ensemble of membrane plaquettes at random orientations and used the Helfrich bending free energy to describe membrane undulations in sponge and lamellar phases and predicted a stretched exponential relaxation of \( I(Q,t) \) as follows Eq.(2) where \( \Gamma \) is given by

\[ \Gamma = 0.025\gamma(k_BT/\kappa)^{1/2}(k_BT/\eta)Q^3. \]  

Here, \( \kappa \) is the bending modulus of the membrane and \( \eta \) the viscosity of the surrounding medium. Figure 4 shows an example of the temperature dependence of \( \kappa \) estimated in the lipid system using their theory. The values of \( \kappa \) seem to depend strongly on \( d_i \) though \( d_i \) is longer than 300Å.


![Graph showing the dependence of the reduced bending modulus \( \kappa \) of the membrane on the temperature \( T \) obtained from NSE experiments for the lipid sample in which DPPC was dispersed in D_2O solutions with 7 mM CaCl_2.](image)
1-4-4 Fast Relaxation in Glass-forming Electrolyte Aqueous Solutions

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Introduction

Some of electrolyte aqueous solutions are vitrified easily by cooling. According to previous neutron diffraction studies [1,2], the cations are strongly coordinated by water molecules and the hydrogen-bond network is partly broken by the added ions. We have studied structural and dynamical properties of these solutions by using neutron scattering technique. The purpose of the present work was to search for the evidence for the fast relaxation (sometimes called β relaxation) in aqueous solution glasses. The origin of the fast relaxation is still unknown and one of the most important problems in physics of glasses.

Experimental

The neutron scattering experiments were performed using a direct geometry chopper-type TOF spectrometer AGNES [3]. The elastic energy resolution of this spectrometer was 0.12 meV. Two solutions LiCl-6H₂O and CaCl₂·13H₂O were prepared by mixing the salts and purified water. The glassy samples were prepared by rapid cooling (2 K min⁻¹) and the crystalline sample (only for CaCl₂·13H₂O) by annealing the glassy sample at ca. 200 K. The data were collected at every 20 K in the temperature range 20—300 K. The duration of each measurement was 2—4 h.

Results and Discussion

Figure 1 shows the temperature dependence of the elastic scattering intensities of LiCl-6H₂O and CaCl₂·13H₂O. The elastic intensity was calculated by integrating the data with scattering angles of 89—120° (Qₑ = 2.36 Å⁻¹) over energy region between -0.2 and 0.2 meV. The data of the crystalline and glassy solids lie on a straight line as expected from the Debye-Waller factor exp(-<u²>Q²) of a harmonic oscillator (<u²> ∼ T). In the supercooled liquids, however, excess decrease of elastic intensity was found for both samples. This is a strong evidence that the electrolyte aqueous solution glasses exhibit fast relaxation as most fragile glasses such as polymer and molecular glasses do.

Fig. 1 The temperature dependence of the elastic scattering intensities of LiCl-6H₂O (upper) and CaCl₂·13H₂O (lower).

References
1-4-5 Medium-Range Order in Electrolyte Aqueous Solution Glasses

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Introduction

The glasses of electrolyte aqueous solutions are typical hydrogen-bond network glasses. According to previous neutron diffraction studies on LiCl solutions [1,2], the cations are strongly coordinated by water molecules and the hydrogen-bond network is partly broken by the added ions. The coordination is known to be stronger as the ionic radius of cation becomes smaller. We have been studying the boson peak of solution glasses with neutron scattering and low-temperature heat capacity measurements [3,4]. We found boson peaks in LiCl, BeCl₂, MgCl₂, and CaCl₂ solution glasses and revealed that the boson peak intensity strongly depends on cations.

The purpose of this work is to find the relation between the boson peak intensity and the medium-range order of amorphous structure. We have measured the neutron diffraction of several electrolyte aqueous solution glasses. The use of neutron is essential since we can investigate the structure of hydrogen-bond network not overshadowed by the scattering from cations and Cl⁻ ions.

Experimental

The neutron diffraction experiments were performed by using HERMES diffractometer [5] belonging to Institute for Materials Research, Tohoku University. HERMES is installed at the thermal neutron guide (T1) of JRR-3M research reactor of Japan Atomic Energy Research Institute (JAERI). Incident neutrons with wave length of 1.8196 Å was selected by Ge(331) monochromator. The diffraction data were collected at scattering angles of 3—152.5°, corresponding to 0.18—6.70 Å⁻¹ of momentum transfer Q, with a step of 0.5°.

The sample solutions, LiCl·4D₂O, LiCl·6D₂O, BeCl₂·9D₂O, BeCl₂·13D₂O, MgCl₂·13D₂O, and CaCl₂·13D₂O, were prepared by mixing the corresponding salts and heavy water in appropriate mass ratios. For MgCl₂·13D₂O solution, 30% of BeCl₂·13D₂O was added to suppress crystallization; this solution is called MgCl₂·13D₂O hereafter in this report. The liquid samples were confined in cylindrical aluminum or gold-plated copper cans (1.0 mmφ x 60 mmH). The gold-plated can was used only for BeCl₂ solutions to avoid the corrosion of the can. These cans were set in a CTI cryostat. The background scattering from the cell and the cryostat was corrected by the established method.

The measurement was carried out at 275 K (liquid state) and 130 K (glassy state). The glassy samples were prepared by cooling the sample liquid with a cooling rate of ca. 3 K min⁻¹. The duration of the measurement was 6—9 h for each.

Results and Discussion

Figure 1 shows the neutron diffraction pattern of the three solution glasses at 130 K.

![Figure 1 Neutron diffraction pattern of the three solution glasses and amorphous ice [6].](image-url)
The data of other solution glasses are not plotted in Fig. 1 to avoid the confusion due to data overlap. The data of vapor-deposited amorphous ice [6] was plotted together for comparison. As shown in Fig. 1, the structure of the solution glasses is much different from that of amorphous ice and also from each other.

To estimate the correlation length of disordered structure, the low-\(Q\) side data of the first sharp diffraction peak (FSDP) was fitted to the Lorentzian form

\[
I(Q) = aQ^2 / [(Q/\Omega_c)^2 + \Delta Q^2] + b
\]

The half width \(\Delta Q\) is approximately related to the correlation length \(\Omega_c\) by

\[
\Omega_c = 2\pi / \Delta Q
\]

This method is the same as that used in oxide glasses by Sokolov et al [7]. Figure 2 shows typical results of the fitting.

Figure 3 shows the relation between the correlation length thus obtained and the intensity of the boson peak determined by the heat capacity measurements [3]; the boson peak appears as a hump of \(C_p/T^3\). \(T_p\) in Fig. 3 is the peak temperature of the hump. Though the plotted data are scattered, there is a clear tendency that the solution glass with larger \(\Omega_c\) gives larger boson peak intensity. This relation was pointed out also in oxide glasses [7]. The oxide glasses have covalent-bond networks while the solution glasses have hydrogen-bond networks. We may conclude that the boson peak intensity of the network glasses is dominated by the correlation length of disordered structures.

References
Neutron Scattering Study on Dynamics of Methanol Molecules in MCM-41

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We have investigated dynamics of partially deuterated methanol (CD$_3$OH) molecules confined in mesopores of MCM-41 by using quasi-elastic neutron scattering (QENS). In the present system, QENS spectra mainly consist of the contribution by hydrogen atom of hydroxyl group. It is expected that dynamics of hydroxyl and methyl groups in the methanol are revealed separately by combining present experiments with previous ones conducted for methanol (CH$_3$OH) confined in MCM-41. MCM-41 is one of the most suitable sample to study confined liquids, since it has highly controlled cylindrical channels with very narrow pore size distribution.

Three kinds of MCM-41 (C10, C14 and C18) were prepared, whose pore diameters were 2.14, 2.84 and 3.74 nm, respectively. For the neutron scattering measurements, we prepared three kinds of samples having different amounts of adsorbate for each MCM-41. (1) Pore-filled sample: the mesopores are filled with methanol; (2) monolayer sample: the pore wall are covered with monolayer methanol molecules; (3) dry sample: there are no methanol in the pore. QENS measurements were carried out by using time-of-flight type spectrometer AGNES installed at the JRR-3M reactor of Japan Atomic Energy Research Institute. The wavelength of neutron beam was 4.22 Å, the momentum transfer (Q) range 0.68-1.87 Å$^{-1}$, and the temperature range 100-297 K.

The line widths of QENS spectra obtained decreased in the order: bulk > pore-filled > monolayer samples. This means that the motion of methanol molecules becomes slower in the above order. In the dry sample, quasi-elastic broadening was not observed. In order to discuss the effect of pore sizes on the dynamics of methanol molecules, QENS spectra were analyzed by fitting with a linear combination of delta and Lorentzian functions. The delta function component is due to immobile molecules near the pore wall. Figure 1 shows Q-dependence of the half width at half-maximum $\Gamma$ of the Lorentzian functions for the pore-filled samples at 295 K. As shown in figure 1, $\Gamma$ values for CD$_3$OH decrease rapidly at high-Q region by confinement, while those for CH$_3$OH decrease slowly. This signifies that the motion of hydroxyl groups in methanol molecules is strongly limited by confinement. Detailed analysis is now in progress.

![Figure 1](image-url)

Figure 1. Q-dependence of $\Gamma$ for the pore-filled samples at 295 K. (a) CD$_3$OH (this work), (b) CH$_3$OH (previous work').

References

§1. Introduction

Dynamics of ferrofluid have been studied by the neutron spin echo (NSE) method by Lebedev et al.\(^1,2\)

We have firstly applied NSE method for the Bragg reflection of moving magnetite particle crystal in ferrofluid. Bragg reflection of moving particle brings Doppler shift of neutron velocity at scattering. The Doppler shift is caused not only by translational motion but also librational and rotational motions of the particle crystal. NSE signal by Doppler shift at Bragg reflection directly gives the information of the velocity of moving fine crystals.

In order to study the size of clustering particles in ferrofluid, neutron small angle scattering on the same sample for NSE experiment was measured at three temperatures. There is a tendency for magnetite particles to make clusters with each other with increasing temperature above the room temperature.

§2. NSE for Doppler Shift Velocity

Doppler shift at Bragg reflection from a moving crystal with the velocity vector \(v\) is governed in the Laboratory frame by the following two equations.\(^3\)

\[
\begin{align*}
\nu_1 - \nu_0 &= \frac{\hbar r}{m} \\
\frac{m\nu_1^2}{2} - \frac{m\nu_0^2}{2} &= \hbar r \cdot v
\end{align*}
\]

which represent the momentum and the energy conservation law. Here, \(\nu_0\) and \(\nu_1\) are incident and scattered neutron in the laboratory frame, \(r\) the reciprocal vector of the Bragg reflection. The conventional single Bragg law for a crystal at rest splits into the following two laws for a moving crystal.\(^3\) For the incident neutron, 2\(d\sin \theta_0 = \lambda_0 (1 - f)\), 2\(d\sin \theta_1 = \lambda_1 (1 + f)\), where \(\theta_0\) and \(\theta_1\) are the angle of incidence and of reflection, \(\lambda_0\) and \(\lambda_1\) are the wavelengths of the incident and the reflected neutron in the laboratory frame, and \(d\) the interlayer spacing of the moving crystal. The factor \(f\) is defined as

\[
f = \frac{2\mathrm{m} \cos \beta}{\hbar r}
\]

Here \(\beta\) is the angle between \(r\) and \(v\).

For the case of \(v < \nu_0\), (also for \(f < 1\)), we estimate the Doppler shift, \(\delta \nu = \nu_1 - \nu_0\) as follows from equation (2.2).

\[
\delta \nu = \frac{\hbar r \cdot v}{\nu_0} = \frac{\hbar r}{m\nu_0} f.
\]

The shift of Bragg angle, \(\delta \theta = \theta_1 - \theta_0\), is also estimated to be,

\[
\delta \theta \approx 2f - \frac{\delta v}{\nu_0}.
\]

Let us consider NSE method at Bragg reflection of a moving particle crystal. The difference of Larmor precession angle before and after scattering is given by,

\[
\Delta N = N_0 - N_1 = \frac{7\pi}{2 \nu} \left\{ \frac{H_0}{\nu_0} - \frac{H_1}{\nu_1} \right\},
\]

where \(\gamma L = 2.916\) kHz/On, \(N\) is the number of Larmor precessions, \(I_0\) and \(I_1\) the length of the magnetic field \(H\) before and after the scattering, respectively. The the scattered Doppler velocity shift, \(\delta v\) at Bragg reflection of a moving particle crystal gives additional shift of Larmor precession.

\[
\delta N = N_0 \frac{\delta v}{\nu_0}.
\]

Then, NSE signal is given by the normalised summation of cosine functions of each \(\Delta N\), which is the Fourier transformation of the velocity distribution of Doppler shift.

\[
P_{NSB} = P_{0} \cos(2\pi \Delta N) = < \cos(N_0 \frac{\delta v}{\nu_0}) >.
\]

Usually NSE signal is plotted against spin echo Fourier time for inelastic scattering.\(^4\) For Doppler shift scattering, number of Larmor precession, \(N_0\) is the Fourier parameter. For a fixed velocity of \(v\), \(\delta v\) distributes following eq.(2.4) by all the space angles \(\beta\). If the velocity of the particle crystal distributes such as Maxwellian function one should again product the Maxwellian distribution function on the cosine distribution function of \(\beta\). Then, it is not so easy to get the distribution function of particle velocity directly from \(P_{NSB}\) but the velocity distribution can be estimated by simulations if we suppose some distribution function of Doppler shift velocity.

§3. Experimental

More than 90 % of water in the magnetite ferrofluid of PW-40 Matsumoto oil Co. Ltd. Japan is replaced by heavy water by a distillation method. Neutron spin echo at Bragg reflection as well as small angle scattering
studies were carried out on magnetite particles in the ferrofluid stabilized by ionized oleic acid in heavy water which is dispersed in heavy water of which magnetite concentration is about 40 wt% The particle diffraction patterns of the magnetite in ferrofluid were taken for sample thicknesses of 2 mm, 2.5 mm and 3 mm in thin aluminum containers with rectangular parallelepipeds using the ISSP 5G PONTA NSE spectrometer at JRR-M reactor at JAERI with monochromatic polarized neutron of 0.2353 nm and the velocity of 1681 m. Rather high back ground is due to the high incoherent cross-section of hydrogen in the ionized oleic acid. NSE measurements were carried out for the ferrofluid sample with the thickness of 2 mm at the Bragg peaks of (111) (29 = 60.4°) reflection of aluminum container, (311)(29 = 55.4°) reflection of magnetite up to the number of Larmor precession a order of 10^5 s. In these NSE spectra, the background intensity for each Bragg intensity were subtracted. The effects of depolarization in NSE polarization of (311) magnetite Bragg reflection through ferrofluid were corrected by normalizing it by the NSE polarization of the (111)aluminum reflection of the sample container.

Small angle scattering experiment on the same ferrofluid was carried out in order to check the clustering state of magnetite particles in the weak applied field of 0.001 T. using reflectometer post of MINE with a wavelength of 1.20 nm at JRR-3M reactor of JAERI.

§4. Experimental Results

![Figure 1](image1)

**Fig. 1**. Small angle scattering of the heavy water based magnetite ferrofluid at 296.5 K, 318 K, and 335 K where fitted curves are spherical radius of 28.7 nm, 30.3 nm and 33.6 nm, respectively.

In Fig. 1 small angle scattering of the heavy water based magnetite ferrofluid at 296.5 K, 318 K and 335 K were fitted with a spherical radius of small angle scattering on the same sample used for the NSE experiment. Obtained particle radius are 29 ± 5 nm, 30 ± 5 nm and 37 ± 4 nm at 296.5 K, 318 K and 335K, respectively. At smaller q region less than 0.04 nm^-1 deviations from the theoretical curves indicate the existence of some clustered particles in the weak magnetic field of 0.001 T. Though the particle size in the ferrofluid at 296.5 K and 318 K has the similar value of 30 nm, the scattered intensity at 318 K decreases to 64% of that at 296.5 K in the fitting, which also suggests a proceeding of clustering at 318 K.

![Figure 2](image2)

**Fig. 2**. NSE signals for magnetite Bragg reflection (311) in the ferrofluid at temperatures 293 K and 323 K, which are normalised by NSE signal of Al(111) Bragg reflection. Theoretical curves are fitted with a simple exponential decay function.

In Fig. 2 normalized NSE visibilities are plotted against the number of Larmor precession at three temperatures of 293 K and 323 K. The observed NSE signals at 293 K and 323 K show rather simple decay with increasing of the number of Larmor precession up to 967 turns. If we apply the Lorentzian distribution function of the Doppler shift velocity, we can estimate order of velocity from the exponential decay constant of NSE signal as a function of the precession number as shown in the theoretical curves in fig. (2). The estimated velocity distribution is 1.0 ± 0.2 m/s, 1.7 ± 0.3 m/s at 293 K and 323 K, respectively.

We estimate velocity of the surface part of a free rotating sphere of magnetite by the following equation, supposing rotational kinetic energy of the sphere is equal to 3k_BT/2.

\[
v = \sqrt{\frac{15k_BT}{2M}}
\]

where \(k_B\) is the Boltzmann constant, M the mass of particle. Here rotational kinetic energy of the sphere is equal to 3k_BT/2 is used. Then the estimated velocity for the magnetite particle radius 29 nm and at 293 K is 8.4 m/sec. The observed velocity of 1 m/s which is less than that of the free Brownian motion is due to viscosity including particle particle interaction. For further interpretation of the spin echo signal, precise distribution function of particle velocity must be supposed.

4) F. Mosei, Neutron Spin Echo (Springer-Verlag, 1979)
Introduction

Recently, we examined rheology of aqueous suspensions of poly(methyl methacrylate-co-styrene) (MS) particles having partially screened surface charges [1]. The electrostatic shell due to these charges enhanced the zero-shear viscosity \( \eta_0 \), indicating that the shell behaved as a part of the hard-core radius in long time scales where \( \eta_0 \) was measured.

However, under fast shear, the MS particles exhibited no thickening characteristic to hard-core particles [1]. Thus, the electrostatic shell was argued to behave as a soft object under fast flow thereby suppressing the dynamic clustering/thickening of the particles.

In this study, a rheo-SANS experiment was conducted to confirm this argument and identify the structural origin of the thinning behavior.

Experimental

For a suspension of monodisperse MS particles in deuterated water, the rheo-SANS measurement utilizing the Couette cell was made at the SANS-U beam line at the Neutron Scattering Laboratory, Institute for Solid State Physics, University of Tokyo. The incident neutron wavelength was 0.7 nm, and the sample-to-detector distance was 4.0 m. The particles had a radius of 45 nm and the volume fraction of 0.5. The non-Newtonian viscosity \( \eta_t \) was measured at 25°C together with the SANS intensity \( I(q) \) in the velocity-vorticity plane.

Results and Discussion

As shown in Fig.1, \( \eta_t \) of the MS suspension strongly decreased with the shear rate (\( \dot{\gamma} \)). Correspondingly, the dependence of \( I(q) \) on the wave vector \( q \) changed with \( \dot{\gamma} \). However, this change was just moderate, as demonstrated in Fig.2 where the \( I(q) \) data under the fastest shear (\( \dot{\gamma}=100 \text{ s}^{-1} \)) are compared with the azimuthally isotropic data in the quiescent state (dotted curve): The \( I(q) \) peak under the shear just moderately shifts to a low-\( q \) side but the data at larger \( q \) are insensitive to \( \dot{\gamma} \). This result suggests that the particles form no huge clusters under the shear (possibly due to their electrostatic repulsion) to exhibit no thickening.

The moderate peak shift reflects a weak distortion of the spatial distribution of the particles under the shear that could result in the thinning. Thus, we estimated a magnitude of distortion \( \gamma \) from the peak shift value and evaluated a thermodynamic viscosity \( \eta_t \) from this \( \gamma \) [2]. This \( \eta_t \) (dotted curve in Fig.1) was close to the \( \eta_t \) data, suggesting that the thinning reflects the weak \( \dot{\gamma} \) dependence of the particle distribution.

References
Structure Factors of Liquid Ge at High Temperatures and Electron-Ion Correlation

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There are several single-element liquids with anomalous static structures that have a shoulder near the first peak of the structure factors. Liquid Ge is one of such liquids and has attracted attention because of the semiconductor-metal transition on melting. The tetrahedral unit in crystalline and amorphous phases and the relatively low coordination number in the liquid phase around the melting point are in contrast with simple liquid metals.

Many researchers have attempted to interpret the structure of liquid Ge as a mixture between tetrahedral units and the metallic phase, and tend to emphasize the persistence of covalent bonding even in the liquid state. On the other hand, theoretical studies have pointed out a metallic character in the bonding. This ion-ion potential, which has a hard-sphere core with a positive step, reproduced the shoulder in the structure factor. This suggests the existence of two characteristic lengths in liquid metals.

From the viewpoint of the homogeneous metallic phase, it is suggested that the shoulder appears at $Q = 2k_F$ corresponding to the diameter of the free-electron Fermi surface, and the atomic configuration is modulated by the Friedel oscillations. There were some differences between earlier X-ray data and neutron data in the low-$Q$ region, with regard to the height of the first peak, and the height and position of the second peak. The aim of this study is to report the exact structural data of liquid Ge by neutron diffraction to high temperature region and provide the electron-ion correlation around Ge$^{4+}$ ion from the diffraction data.

Neutron diffraction was carried out at several temperatures (1000, 1100, 1250, 1500 and 1550°C) under atmospheric pressure of He by HERMES spectrometer system. The spectra were accumulated with two initial angles of 3.0° and 3.5°. The series of solar slits at the front of the counters is suitable for reducing the scattering intensity from the background. The wavelength of neutron beam was 1.8196 Å.

The purity of Ge sample was 99.9999 wt% and the sample was inserted into the cylindrical cell made of glassy carbon. The diameter of the cell was 9.8 mm and its wall thickness was 0.2 mm. The furnace was a 1800°C-Furnace constructed by A S Science Products, Ltd, and was provided by NSDA. The heater consists of two concentric cylinders made of 0.05mm thick niobium foils. The temperature of the sample was measured by a W-Re thermocouple.

The helium gas was introduced to keep the liquid sample stable in the carbon cell. Glassy carbon is known to absorb hydrogen, which considerably increases the inelasticity of the neutron scattering. The scattering intensity from the carbon cell at room temperature is compared with that at 1000°C after being normalized by the monitor counts. The observed spectrum at 1000°C does not appear to include the large inelastic contribution which tends to incline the centroid of the interference function.

The observed structure factors of liquid Ge are shown in Fig. 1. The accumulated monitor counts are $16.6 \times 10^5$, $2.0 \times 10^6$, $8.8 \times 10^6$, $16.6 \times 10^6$ and $2.0 \times 10^6$ at 1000, 1100, 1250, 1500 and 1550°C. Several researchers have previously measured $S(Q)$ of liquid Ge within 100°C above the melting point (937°C) and their structure factors also exhibit the characteristic shoulder in the high-$Q$ region of the first peak. In our data at 1000°C, the first peak is located at 2.53 Å and its peak height is about 1.42, which is consistent with the data of Bellissent-Funel and Bellissent. and Altholz and Hoyet, but slightly small.
when compared with the data of Waseda and Suzuki\(^9\) and Salmon\(^9\). The shoulder appears at around 3.3 Å\(^{-1}\) in accordance with data in the literature\(^6\),\(^7\),\(^8\). The second peak is located around 5.1 Å\(^{-1}\), similar to the data in refs. 3, 8 and 9, but the peak height is rather low compared with the results of these studies. The temperature dependence of the structure factor is not large, but a clear tendency is evident as shown in Fig. 2. The height of the first peak decreases slightly with increasing temperature and the position moves to the high-Q side. At the highest temperature, the peak position becomes 2.60 Å\(^{-1}\). The shoulder becomes inconspicuous and almost disappears at 1550°C. This temperature dependence seems to follow the prediction of the MD simulation at 2000 K\(^7\) where the structure factor resembles that of a simple liquid metal and the first peak is located around 2.7 Å\(^{-1}\).

Fig. 1 Structure factors of liquid Ge at several temperatures.

The neutron diffraction data presented in this work are expected to include both the density and temperature dependences of $S(Q)$. Both the position of the principal peak and that of $k_F$, the Fermi momentum, are roughly proportional to $n^{1/3}$, where $n$ denotes the density of the liquid. Given that the density decreases as the temperature increases, and taking into account the results shown in Fig. 2, we can postulate that our results are dominated by the temperature dependence of $S(Q)$.

Fig. 2 Temperature dependence of the structure factors around first peak region.

References
Introduction

It is well known that anomalies in various physicochemical properties of alcohol-water mixtures appear in a water-rich region. These anomalies become enhanced with increasing the size of hydrophobic group of alcohols and have been explained by the formation of molecular aggregates or microinhomogeneities in the mixtures. n-butoxyethanol-water mixtures undergo phase separation at a lower critical solution temperature (LCST) of 49 °C[1]. A small-angle neutron scattering (SANS) experiment of the mixture has revealed concentration fluctuations in the mixture at temperatures even below the LCST[2], suggesting that microinhomogeneities on a mesoscopic scale precede the macroscopic separation. The neutron spin echo (NSE) technique is a powerful tool to investigate the dynamics of systems in timescale of 0.1-100 ns in mesoscopic spatial structure of 1-100 nm, and has been widely used in the field of soft materials, such as micelles, microemulsion, and polymers. In this study, NSE measurements have been carried out to reveal the dynamics of the molecular aggregation in a n-butoxyethanol-water mixture, in particular, whether such an aggregation is stable like micelles or transit structure in the NSE timescale.

Experiment

An NSE spectrometer is equipped at the C22 cold neutron guide port of JRR-3M, JAERI. The scattering vector \( Q \) covered was 0.01 - 0.10 Å\(^{-1}\). The Fourier time was varied from 0.15 to 15 ns. The measuring time was about 8 h for each \( Q \) range at fixed temperatures. A plate of Grafoil was measured for resolution correction.

Deuterated n-butoxyethanol (over 98 atom%D, Aldrich), C\(_4\)H\(_9\)O\(_2\)D, whose hydroxyl part is deuterated since the hydroxyl hydrogen of the alcohol exchanges with water hydrogen, and D\(_2\)O (99.95 atom%D, CEA) were used without further purification. The sample solutions were 4 and 9 mol% n-butoxyethanol in D\(_2\)O and sealed in a quartz cell of 2 mm thickness. The temperature was controlled to within ±0.1 °C with a thermostat to circulate water.

Results and Discussion

The NSE method measures the energy transfer of neutrons at an extremely high energy resolution as a phase shift in the Larmor precession of each neutron spin in a magnetic field. The intermediate correlation function \( I(Q, t) \) is defined by the following equation as a function of the wave vector \( Q \) and Fourier time \( t \).

\[
I(Q, t) = N^{-1} \sum_{\mathbf{H}} \left\{ \exp[iQ \cdot \mathbf{\tau}(t)] \exp[iQ \cdot \mathbf{\tau}(0)] \right\}
\]  

(1)

Here, \( N \) is the number density. The bracket means an ensemble average. In the case of neutron quasielastic scattering, \( I(Q, t) \) can be obtained directly from the amplitude of the NSE signal at the spin echo condition. The \( I(Q, t) \) obtained from NSE experiments was fitted to the following equation on basis of the Brownian motion,

\[
I(Q, t) / I(Q, 0) = \exp(-\Gamma t)
\]  

(2)

where \( \Gamma \) is the relaxation rate. Figure 1 shows the \( Q \)-dependence of the relaxation rate. The diffusion
coefficient $D$ was obtained from the following equation,

$$\Gamma = DQ^2$$  \hspace{1cm} (3)

The values of $D$ have been summarized in Table 1. These values seem to reflect the motion of molecular aggregates because they are $\sim 10^2$ times smaller than those of pure water and alcohol. The apparent activation energy, $E_a$, of the diffusion process is obtained from temperature dependence of the diffusion constant by using the following equation.

$$D = D_0 \exp \left( - \frac{E_a}{k_B T} \right)$$  \hspace{1cm} (4)

where $D_0$ is constant.

The values of $E_a$ at $x_{BE} = 0.04$ and 0.09 were obtained as about 25 and 23 kJ mol$^{-1}$, respectively, which is larger than the hydrogen bonding energy deduced from the translation of water molecule (19 kJ mol$^{-1}$) in pure water [3]. This implies that the hydrogen bonding is strengthened due to hydrophobic hydration in the mixtures.

At a temperature near LCST, the correlation length of concentration fluctuations obtained from the SANS increases with temperature. It has been proposed that this increase in correlation length is related to an increase in the alcohol content in a micelle-like model or to an increase in contents of both water and alcohol in a mixed aggregate model [2]. The values of $D$ obtained from the present NSE measurements increase with increasing temperature in spite of an increase in the correlation length obtained from SANS [2]. This discrepancy cannot be explained by the Stokes-Einstein model where a stable aggregation moves independently as a micelle of surfactants. A model proposed from these results is that the molecule aggregation is preserved only for short time (about nanoseconds) characterized by the wavelength of the neutron used.

The present conclusion on the dynamics of the molecular aggregation in the $n$-butoxyethanol-water mixture should be confirmed by further NSE experiments under different pressures and compositions, which are now in progress.


<table>
<thead>
<tr>
<th>$x_{BE}$</th>
<th>$D \times 10^{11}$ (m$^2$s$^{-1}$)</th>
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<tr>
<td>0.04</td>
<td>8°C</td>
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<td></td>
<td>25°C</td>
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<td>37°C</td>
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Table 1. Diffusion constants ($D \times 10^{11}$ / m$^2$s$^{-1}$) of BE/water mixtures

Fig. 1. $Q$-dependence of the relaxation rates $\Gamma(Q)$ in the $n$-butoxyethanol-water of 0.09 mole fraction at various temperatures.
Hydrogen-Bonded Structure in Concentrated Aqueous DL- and L-Alanine Solutions

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Optical activity of amino acid molecule plays an important role in various biological systems. Chemical properties of the L-amino acid and the D,L-racemic mixture (equimolar mixture of D- and L-amino acid molecules) are identical, however, the solubility for water is known to be slightly different between L- and D,L- compounds. This solubility difference becomes much enhanced when the solvent is substituted by heavy water. In fact, solubility of L-Alanine to D$_2$O is ca. 17% lower than that for D,L-Alanine (3 mol% D,L-Alanine in the saturated solution). This difference in the solubility may be related to the different intermolecular hydrogen bonds in the crystalline state.$^{1}$ On the other hand, no direct information has been reported on the effect of different optical activities of solute molecules to the intermolecular hydrogen-bonded structure in the aqueous solution.

In this paper, we describe results of neutron diffraction measurements on concentrated aqueous D,L- and L-Alanine solutions with different H/D isotopic ratio in order to obtain direct structural information on the intermolecular hydrogen bonds in solutions involving solute molecules with different optical activities.

D,L- and L-Alanine (natural abundance) were dissolved into D$_2$O and H$_2$O/D$_2$O mixtures to prepare six kinds of aqueous 2.5 mol% D,L- and L-Alanine solutions.

1) (D$_2$-ND$_2$CH$_2$CHOOH)$_{0.025}$(D$_2$O)$_{0.975}$ (96.1% D)
2) (D$_2$-ND$_2$CH$_2$CHOOH)$_{0.025}$(H$_2$O)$_{0.975}$ (33.9% D)
3) (D$_2$-ND$_2$CH$_2$CHOOH)$_{0.025}$(D$_2$O)$_{0.075}$ (66.0% D)
4) (L-ND$_2$CH$_2$CHOOH)$_{0.025}$(D$_2$O)$_{0.975}$ (96.1% D)
5) (L-ND$_2$CH$_2$CHOOH)$_{0.025}$(H$_2$O)$_{0.975}$ (33.9% D)
6) (L-ND$_2$CH$_2$CHOOH)$_{0.025}$(D$_2$O)$_{0.075}$ (66.0% D)

The sample solutions was sealed into a cylindrical quartz cell with 11.8 mm in inner diameter and 1.1 mm in thickness. Neutron diffraction measurements were carried out on the ISSP 4G diffractometer installed at the JRR-3M research reactor, JAERI. The incident neutron wavelength of $\lambda = 1.096 \pm 0.003$ Å was employed. Scattered neutrons were collected over the angular range of 3 ≤ 2θ ≤ 115°, corresponding to 0.30 ≤ Q ≤ 9.67 Å$^{-1}$. Measurements of scattering intensities were made in advance for a vanadium rod, an empty cell and a background. After corrections for background and absorption, observed neutron count rates were converted to the normalized scattering cross section.

Observed scattering cross sections for the six aqueous 2.5 mol% Alanine solutions are shown in Fig. 1. Although cross sections for the D,L- and L-Alanine solutions with the same H/D isotopic ratio seem very similar, a systematic difference in the lower-Q region can be observed between the D,L- and L-Alanine solutions with the highest D content.

![Figure 1](image-url)
The difference in cross sections, $\delta(Q) = [\text{D,L-Alanine solution}] - [\text{L-Alanine solution}]$ are indicated in Fig. 2. Experimental data points are somewhat scattered due to the statistical uncertainties, however, no significant difference in the scattering cross sections for D,L- and L-Alanine solutions can be observed for the $^1$H$_2$O (35.9 % D) and $^0$H$_2$O (66.0 % D) solutions within experimental errors. On the other hand, the residual structure is evident in the D$_2$O (96.1 % D) solutions in which larger difference in the solution structure is expected from the solubility data as mentioned above.

![Image of Fig. 2](image)

**Fig. 2** Observed difference function between scattering cross sections for aqueous 2.5 mol% D,L- and L-Alanine solutions with different D content.

Observed scattering cross sections in Fig. 1 were carefully re-normalized by applying the least squares fitting analysis of the intramolecular interference terms of Alanine and water molecules in the range of $3.0 \leq Q \leq 9.6$ Å$^{-1}$. The re-normalized difference function, $\Delta I(Q)$, for the D$_2$O solutions (Fig. 3a) was then Fourier transformed to obtain the difference distribution function $\Delta g(r)$ (Fig. 3b). The structural feature appearing around $r = 2$ Å is identified, which implies that the difference in the intermolecular structure between D,L- and L-Alanine solutions is present at this radial distance.

Figure 4 represents partial distribution functions, $g_{HH}(r)$, $g_{XH}(r)$ and $g_{XY}(r)$ (X: N, O, C) observed for the aqueous 2.5 mol% L-Alanine solution. These distribution functions were obtained by the Fourier transform of partial structure factors, which were derived from a combined analysis of observed intermolecular interference terms. A well defined first peak at $r = 2$ Å in the present $g_{XH}(r)$ function is attributable to the hydrogen-bonded O-H(D) interaction among solvent water molecules. The position of this intermolecular O-H(D) peak corresponds well to the negative peak observed in the $\Delta g(r)$ function shown in Fig. 3b. The negative intensity of the peak in $\Delta g(r)$ implies that the hydrogen-bonded structure is more pronounced in the L-Alanine solution, which may be consistent with the lower solubility of the L-Alanine molecule.

Further data analysis involving the least squares refinement of the observed partial structure factor is now in progress.

![Image of Fig. 4](image)

**Fig. 4** Partial distribution functions, $g_{HH}(r)$, $g_{XH}(r)$ and $g_{XY}(r)$ (X: N, O, C), observed for the aqueous 2.5 mol% L-Alanine solution.

References
Super- and subcritical water receives much attention recently as an environmentally benign solvent to often induce a chemical reaction at noncatalytic conditions. In order to understand and control the chemical reaction in this unique solvent, it is essential to elucidate the molecular motion of water and aqueous solutions at super- and subcritical conditions. In general, a chemical reaction proceeds first through the encounters of the reacting molecules. Therefore, since water acts not only as a medium but also as a reactant in the hydrothermal regime, it is of primary interest to characterize the diffusion dynamics of water. In this study, we determine the diffusion constant of high-temperature and high-pressure water at its neat and solution states by means of the quasielastic neutron scattering. Since super- and subcritical water is a good solvent for organic compounds, we employ the aqueous solution of benzene to assess the motional behavior of water at the solution state.

The samples prepared were $H_2O$, $C_6H_6$, and their mixture with the benzene mole fraction of 0.05. Pure benzene was also examined to compare the diffusion behaviors of water and organic solvents at high-temperature conditions. All the samples were sealed in quartz capillaries at packing fractions of 60%. The experimental temperature was 290 °C. At this temperature, the pressure is around 10 MPa. The quasielastic neutron scattering measurements were performed using the AGNES facility. The spectra were fit to the Lorentzian form at each momentum transfer $Q$.

The quasielastic linewidth $\Gamma$ is shown in Fig. 1 as a function of $Q^2$. From the jump diffusion model, the diffusion constant was found to be 9.6, 5.3, and $6.5 \times 10^4$ cm$^2$/s for neat $H_2O$, neat $C_6H_6$, and $H_2O$ in the mixture, respectively. These values are one order of magnitude larger than the typical value of the diffusion constant at ambient conditions. When neat $H_2O$ and $C_6H_6$ are compared, the ratio of the diffusion constant is similar to the ratio of the viscosity. Since $H_2O$ is smaller in molecular size, this means the breakdown of the hydrodynamic law and shows the apparent expansion of the water molecule due to the hydrogen bonding. When neat $H_2O$ is compared to the mixture, the diffusion constant is observed to become smaller when 5% of benzene is added. This is related to the weakening of the hydrogen bonding of water upon addition of the nonpolar compound. Actually, the proton chemical shift of $H_2O$ was found, as a consistent and complementary observation, to shift upfield upon addition of benzene.

![Fig. 1. The quasielastic linewidth $\Gamma$ as a function of the momentum transfer $Q$.](image-url)
Liquid As-Te mixtures show the semiconductor to metal transition with increasing temperature. Recent EXAFS[1] and neutron diffraction[2] studies reveals that the network structure of threefold coordinated As and twofold coordinated Te atoms is transformed into the twofold chain structure in the high temperature (metallic) region. In this region, the occurrence of the fluctuation of the interchain correlation is expected. Hence the structural investigation over the scale of over ten angstroms is important. In order to study this structural change, we have performed the neutron small angle scattering measurements for liquid As$_{20}$Te$_{80}$ and As$_{30}$Te$_{70}$ by using SANS-U spectrometer equipped at JRR-3M in JAERI Tokai.

The samples were sealed in the standard silica cell of 5mm thick. The camera distance was set to be 4m. The scattering intensity was accumulated for about six hours for each sample and each temperature. The scattering intensity from the mixtures was very weak and the intensity from silica cell dominates the data in low Q region (Q < 0.01Å$^{-1}$). Hence we can use the data only over the Q range, 0.01 < Q < 0.1Å$^{-1}$. Figure 1 shows the I(Q) for liquid As$_{20}$Te$_{80}$ at 400, 450, 500 and 550 °C. The I(Q) increases slightly with decreasing the Q value and becomes nearly constant at Q ~ 0.03Å$^{-1}$, which suggests that the density or concentration fluctuation of the 100Å scale. The I(Q) increases with increasing temperature. Hence the structure has certain temperature dependence. Figure 2 shows the I(Q) for liquid As$_{30}$Te$_{70}$ at 400 and 500 °C. The weak scattering intensity seems to arise from the silica cell. So scattering from this sample could not be observed.

By other measurements, some structure

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Fig. 1. The I(Q) for liquid As$_{20}$Te$_{80}$ at 400, 450, 500 and 550 °C.

Fig. 2. The I(Q) for liquid As$_{30}$Te$_{70}$ at 400 and 500 °C.
Liquid As-Te mixtures show the semiconductor to metal transition with increasing temperature. Recent EXAFS[1] and neutron diffraction[2] studies reveals that the network structure of threefold coordinated As and twofold coordinated Te atoms is transformed into the twofold chain structure in the high temperature (metallic) region. In this region, the occurrence of the fluctuation of the interchain correlation is expected. Hence the structural investigation over the scale of about ten ångstroms is important.

In order to study this structural change, we have performed the neutron scattering measurements for liquid As_{10}Te_{90}, As_{20}Te_{80}, and As_{30}Te_{70} by using HERMES spectrometer equipped at JRR-3M in JAERI Tokai.

The measurements have been performed with the usual procedure. The scattering intensity was accumulated for about ten hours for each sample and each temperature. After the correction of absorption, scattering from the silica cell and multiple scattering and after the normalization of the efficient of detectors, the structure factor $S(Q)$ for liquid As-Te mixtures was derived as shown in Fig. 1. The obtained $S(Q)$ has enough accuracy for investigation especially in low $Q$ region ($Q < 4\text{Å}^{-1}$).

The obtained $S(Q)$ is nearly the same to that from HIT-II over the middle and high $Q$ region. It is notable that a small but clear prepeak at about $Q = 1.5\text{Å}^{-1}$ appears in the $S(Q)$. The prepeak is clearer for As_{20}Te_{80} than that for As_{10}Te_{90}. For As_{30}Te_{70}, the position of the prepeak shifts toward low $Q$ area. And the decrease of peak strength was observed both for As_{20}Te_{80} and As_{30}Te_{70} with increasing temperature. The appearance of the prepeak and its behavior is consistent with the model of structure change[1].

It is notable that at higher temperature another prepeak appears in very low $Q$ region ($Q \sim 0.5\text{Å}^{-1}$), which suggests the creation of the large scale fluctuation caused by the structural transition. As the result, the HERMES spectrometer is very useful for the structural study of the liquid having intermediate range correlation.

In order to investigate the relation between the metal-non metal transition and the structural change, the neutron scattering measurements for the sample of eutectic composition and over the wide temperature range is planned.


![Fig. 1. The structure factor $S(Q)$ for liquid As_{10}Te_{90}, As_{20}Te_{80} and As_{30}Te_{70} at just above the melting point (solid lines) and at about 550 °C (dotted lines).](image-url)
The Origin of FSDP in AgI-Ag2O-V2O5 Glasses

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The superionic conducting glasses have high ionic conductivity at ambient temperature. The investigation on the structural features is very important for understanding of the conduction mechanism of the superionic conducting glasses. It is worth noting that the most of the superionic conducting glasses show pre-peak in low Q region, that is called FSDP. The origin of the FSDP of superionic conducting glasses is considered to be due to the density fluctuation of glass network. In the previous study, new FSDP was observed in 10AgI-3Ag2O-2V2O5 glass from the elastic neutron scattering experiment\(^1\) in contrast to the total neutron scattering experiment. In the present study, the elastic neutron scattering experiments were performed for the glasses having different AgI concentration in order to confirm the origin of FSDP in the superionic conducting glasses.

The measurements were performed on the triple-axis spectrometer TAS-2 at JRR-3. The incident neutron wavelength of 0.245 nm is employed. The elastic neutron scattering intensity \(I(Q, \omega = 0)\) was recorded in the range \(1 \leq Q \leq 45\) \(\text{nm}^{-1}\) at room temperature. Powdered glass sample filled into a cylindrical vanadium container of 10 mm diameter was used for neutron diffraction.

The elastic scattering intensities for several AgI concentration at room temperature are shown in Fig.1. Only 10AgI-3Ag2O-2V2O5 glass has FSDP at around 4 nm\(^{-1}\). The FSDP is formed by the addition of high concentration of AgI into 3Ag2O-2V2O5 host glass. It is considered that the origin of FSDP is due to the medium range Ag-Ag, Ag-I and/or I-I correlation. The existence of medium range interionic correlation suggests the formation of ordered microdomain, such as AgI cluster. However, AgI microdomain does not increase linearly with AgI concentration based on the composition change of FSDP. The threshold of microdomain formation seems to lie on the 30 to 50 mol\% of AgI from the limited data. The investigations on the detailed composition change of FSDP and the contribution of low energy inelastic scattering to FSDP are necessary for the elucidation of the dynamical structure of AgI microdomain.

Figure 1: Elastic neutron scattering in low Q range for several AgI concentration of silver vanadate glasses.

References


原子炉：JRR-3M 装置：TAS-2(T2-4) 分野：中性子散乱（液体・不規則物質）
1. Neutron Scattering  5) Polymer
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1-5-1 Polysaccharides Induced Crystallization of TMV Particles

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Addition of polymers into colloidal rod system induces an aggregation of rod particles. The effective attractive interaction between the rod particles are explained by simple entropic interaction, so-called depletion.

Recently it is found that chondroitin sulfate (Chs) a kind of polysaccharides induces the aggregation of tobacco mosaic virus (TMV) at very low concentration. The TMV concentration where TMV starts to aggregate for Chs addition is about 1/1000 compared with that for PEO addition, or theoretical prediction based on the depletion interaction. The purpose of this study is to elucidate this enhancement of the depletion interaction induced by the polysaccharides. Especially, we focus our attention on the effect of electrostatic interaction on the inter-TMV distance.

The SANS profiles for the TMV and Chs mixture as a function of Chs concentration $\rho_{\text{Chs}}$ is shown in Fig. 1. In the low Chs concentration region ($<1.0$ mg/ml), the scattering profiles shows monotonic curves, indicating that no regular ordered structure is appeared in the suspension. At $\rho_{\text{Chs}} = 1.0$ mg/ml, a Bragg peak suddenly appears at $q=0.014$ Å⁻¹, indicating formation of the raft-like aggregates. The repeat distance of the raft-like aggregates is 45 nm which is about 2.5 times larger than the bare diameter of the TMV particle. The peak position is shifted to the higher $q$ side as increasing $\rho_{\text{Chs}}$ and obeys a power law of $\rho_{\text{Chs}}^{1/4}$ as shown in Fig. 2. In order to explain this behavior, we assume that the total inter-TMV interaction is expressed by sum of the electrostatic interaction (DLVO theory) and the depletion interaction. The obtained peak position as a function of $\rho_{\text{Chs}}$ is shown in Fig. 2 with solid line. The theoretical calculation well describes the $\rho_{\text{Chs}}$ dependence of the peak position, although the theoretical values are somewhat shifted to the higher $q$ side. Thus the observed experimental results are well explained by the depletion and electrostatic interactions.

Fig. 1 SANS profiles for the TMV and Chs mixture as a function of $\rho_{\text{Chs}}$

Fig. 2 Relationship between Bragg peak position and $\rho_{\text{Chs}}$ observed in TMV and Chs Mixture. Solid line indicates theoretical prediction.
Structural Analysis of Metastable Phases of Triacylglycerols

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Osaka University, Graduate School of Science

Triacylglycerols (TAGs) are main components of natural fats and oils and widely used as raw materials for industrial products. One of the important characteristics of TAGs is polymorphism. In addition to the stable phase, many metastable phases appear by changing crystallization conditions.

Although the metastable states are more significant than the stable state from scientific and industrial points of view, our knowledge of their structures is still deficient, because these phases contain various kinds of disorders and X-ray diffraction method is not so effective for such highly disordered states. In this study, we tried to deduce structural information about the α and sub-α phases using selectively deuterated specimens (\(d^{6}\)-tristearin [\(C_3D_3(O_2C(CH)_{18}CH_3)\)]).

Fig. 1 shows the powder diagrams of tristearin in β, α, and sub-α phases measured with HERMES. In the ordered phase β, the second-order reflections due to subcell structure around 3.0 Å\(^{-1}\) are observed as sharp and intense peaks as well as the first-order reflections around 1.5 Å\(^{-1}\). The relative intensity of the second-order reflections is markedly strong compared with that in X-ray diffraction, which makes it possible to deduce the information about the nature of disorder in lateral direction and the dynamical properties for hydrocarbon segments.

The second order reflections in the metastable states α(at 283K) are almost smeared. Since the acyl chains in α are packed in a loose hexagonal subcell, the significant intensity decrease can be ascribed to the effect of activated molecular motions on the Debye-Waller factor.

The sub-α phase transformed from α by cooling exhibits the (200) and (110) reflections of the pseudohexagonal subcell around 1.5 Å\(^{-1}\) (Fig. 2) and shows a significantly broadened profile in the second-order reflection region. It is suggested that hydrocarbon chains make the O\(_\perp\) like lateral packing with neighboring chains but the structural correlation decreases rapidly with distance.

In the region of q < 0.5 Å\(^{-1}\) shown in Fig. 2, three intense reflections due to long spacings, (002), (003) and (004) reflections, are observed in the α phase. The deuteration of glycerol backbone results in the significant intensity increase in the (002) and (004) reflections. On the transition from α to sub-α, the intensity of the (004) reflection decreases, which suggests that the subcell structural change induces a small shift of glycerol backbones towards the lamellar interfaces.

Fig. 1. The diffraction diagram of tristearin

Fig. 2. The diffraction diagram in low q range.
Analysis of Aggregation Structure of Natural Aluminum Silicate Nanofiber Gel and Its Polymer Hybrids


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Imogolite is one of aluminosilicate nanotube with a chemical formula of Al₂O₃SiO₂(H₂O)₅, consisting of hollow nanotubes with an external diameter of about 2.5 nm and a length from several hundred nanometers to a micrometer. Since imogolite has a high aspect ratio, the dispersion of imogolite in polymer matrix can improve the physicochemical properties of matrix polymers. Poly(vinyl alcohol) (PVA) was chosen as a matrix polymer since both PVA and imogolite dissolve in water. Small angle neutron scattering (SANS) experiment was performed in order to reveal the structure of imogolite gel and (PVA/imogolite) hybrid gel.

Raw material of imogolite gel was collected from the pumice bed in Kitakami area, Iwate, Japan. Imogolite gel purified of contaminants was dispersed in a weak acidic solution (pH=5.0-6.0) by applying a 42 kHz ultrasonic wave for a week. PVA with degree of polymerization of 1730 was used for the preparation of hybrid gel (PVA/imogolite) hybrid gel was prepared by mixing the solutions of imogolite and PVA. Weight fractions of imogolite in hybrid gel were 0, 0.5 and 1.0%. (PVA/imogolite) hybrid gel in the (D₂O/DMSO-d6) (20:80) solvent were prepared. These gels were rapidly cooled from 353K to 253K and were maintained at 253K for 24hr. The neutron scattering experiment was performed with the SANS-U (ISSP) installed at JRR3-M reactor of JAERI (Tokai).

Figure 1(a)(b) shows SANS profiles of imogolite and (PVA/imogolite) hybrid gel. Even though the change of scattering length density of the solvent, no distinct feature was not observed for the scattering from imogolite gel. Since the hydrogen is present at the surface of imogolite, the scattering length density of imogolite increase and that of D₂O decreased due to the hydrogen-deuterium exchange reaction. Thus, the imogolite in D₂O gave very weak scattering. (PVA/imogolite) gel in D₂O showed broad scattering at q=ca.0.3 nm⁻¹. A large increase in scattering at higher q region was observed for the hybrid gel.

Dynamics of a glass-forming polymer near $T_g$, as Revealed by Thermal Neutron Spin Echo Technique

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Dynamics of a glass-forming polymer has been studied near the glass transition temperature using a spin echo option of thermal neutron triple axis spectrometer (PONTA) at JRR-3M reactor. In this study we carried out measurements of intermediate scattering function $I(Q,t)$ in a wide $Q$ range up to $3.5$ Å$^{-1}$ and in a time window of 0.012 to 0.143 ns. The sample used in the experiment is deuterated polybutadiene (PB-d$_6$) with glass transition temperature $T_g = 170$ K.

The elastic scattering intensities of PB-d$_6$ show inter-chain and intra-chain correlation peaks at 1.5 and 2.9 Å$^{-1}$, respectively, as shown in Fig. 1. The measurements of $I(Q,t)$ were done at $Q = 1.5$, 2.2, 2.9 and 3.5 Å$^{-1}$, covering both of the correlation peaks. The observed normalized intermediate scattering functions $I(Q,t)/I(Q,0)$ at 200 K are shown in Fig. 2 after correcting for the resolution function, which was evaluated from a measurement of PB-d$_6$ at 10 K. By fitting a decay function to $I(Q,t)/I(Q,0)$ we have evaluated the decay rate $\Pi(Q)$ as a function of $Q$. The decay rate $\Pi(Q)$ normalized to $\Pi(Q = 1.5$ Å$^{-1}$) is plotted in Fig. 1, where $\Pi(Q)/\Pi(Q = 1.5$ Å$^{-1}$) observed by Richter et al. [1] in a low $Q$ range below 2 Å$^{-1}$ is also included. It is interesting to point out that $\Pi(Q)/\Pi(Q = 1.5$ Å$^{-1}$) shows a minimum at around $Q = 1.3$ Å$^{-1}$ corresponding to the inter-chain correlations while no minima are observed at around the intra-chain correlation peak ($Q = 2.9$ Å$^{-1}$). This suggests that the dynamics of PB-d$_6$ in a spatial scale of 2.9 Å$^{-1}$ is not affected by the intra-chain potential, and intra-chain atoms move as a rigid body although they have some degrees of freedom.

![Fig. 1. Elastic intensity of PB-d$_6$ at 170 and 298 K and normalized decay rate $\Gamma(Q)/\Gamma(Q=1.5$ Å$^{-1}$).](image1)

![Fig. 2. Normalized intermediate scattering function $I(Q,t)/I(Q,0)$ of PB-d$_6$ at 200 K.](image2)

Role of Local Dynamics in the Gas Permeability of Glassy Substituted Polyacetylenes. A Quasielastic Neutron Scattering Study

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The local dynamics of 10 substituted polyacetylenes in the glassy state have been investigated in a time range of picoseconds to several tens of picoseconds using a quasielastic neutron scattering spectrometer AGNES installed at the cold neutron guide C3-2-1. We focused our attention on a relationship between the local mobility and the gas permeability of these polymers.

Even in the glassy state, these polymers show quasielastic scattering components, suggesting that certain stochastic motions occur in the glassy state. The dynamic scattering laws $S(Q,\omega)$ of the quasielastic components were well fitted to the sum of two Lorentzians, i.e., the narrow (slow) and broad (fast) components as shown in Fig. 1. It was found that both the relaxation rate $\Gamma_n$ and the fraction $A_n$ of the narrow (slow) component show positive correlations with oxygen permeability coefficient ($PO_2$), suggesting that the local mobility of the matrix polymers plays an important role in gas permeability. We then defined local flux $F$, which is the product of $\Gamma_n$ and $A_n$, as a measure of the local mobility to find that $F$ is proportional to the diffusion coefficient of $O_2$ gas ($DO_2$), i.e., $F \propto DO_2$ (see Fig. 2). To explain and discuss this relation, we have proposed a random gate model, where mobile side groups in the matrix polymer act as a gate for gas diffusion.

This study has been published in Ref. [1]

§1. Dynamical Features in the $\gamma$ and $\alpha$ phases

We have reported lattice and molecular vibrational modes of oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) in oriented crystal phases of $\gamma(T<271.0)$ and $\alpha(271.0<T<286.5K)$ as well as in the liquid phases ($T>286.5K$) by neutron incoherent inelastic scattering method using TOF spectrometer, AGNES in JRR3M.\cite{1,2} Since oleic acid molecule consists of a couple of finite polyethylene chains connected by ethylene double bond carbon and makes a dimer along the chain axis connected by hydrogen bonds between carboxyl group in liquid and crystal phases, hierarchical excitations of local modes of finite polyethylene unit have been observed.

Recently we have observed clear difference in the Raman scattering spectra in the $\gamma$ and $\alpha$ phases as shown in Fig. 1. In the Raman spectra in Fig. 1, lattice phonon bands at 3.5meV and around 2meV in the $\gamma$ phase overdump to bands at 3meV and 3.3meV, respectively in the $\alpha$ phase. The enthalpy and entropy changes of the $\gamma$ to $\alpha$ phase were reported as $\Delta H=8.76$ kJ/mol and $\Delta S=32.2$ kJ K$^{-1}$/mol, respectively indicating that the $\alpha$ is a kind of disordered phase.\cite{3}

Kobayashi\cite{3} suggested that the terminal methyl groups which are the lamellar interface of the bimolecular layer of phase $\gamma$ induce interface melting in the $\alpha$ phase. In order to study the interface melting in the $\alpha$ phase, we have observed quasielastic as well as low energy excitation spectra of oriented oleic acid in the $\gamma$, $\alpha$ and liquid phases using neutron incoherent scattering of hydrogen.

§2. Quasielastic Scattering

Figure 2 shows $S(E)$ of oleic acid in the $\gamma$ and liquid phases. Usually for a quasielastic scattering a Lorentzian function of the energy transfer is supposed. But in the $\alpha$ phase, the motion of hydrogen is rather complexed by mixing of translational and rotational coupled motion of finite zigzag chain. Here, in figure 2 in the $\gamma$ phase, very small amount of quasielastic scattering below $300\mu eV$ is observed. On the contrary, the tail of quasielastic scattering in the $\alpha$ phase spread out up to $3meV$. Of course in the liquid phase, the wider quasi elastic scattering than that in the $\alpha$ phase is observed by free translational motion of zigzag chain. Thus the smearing out and overdamp of phonon bands observed in the Raman scattering of oleic acid in the $\alpha$ phase in the figure 1 can be explained by a random motion of hydrogen atoms of which most violent motion comes from terminal CH$_3$-molecule of zigzag chain.

Viscoelastic effects on the dynamics of concentration fluctuations in dynamically asymmetric polymer blend


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Recently, it has been found that the dynamical asymmetry between constituent components in a mixture causes the coupling between stress and diffusion during phase separation processes of the mixture due to the asymmetric stress division. This coupling is called "viscoelastic effects" and has been found to cause shear-induced phase separation in polymer solutions and non-exponential decay in dynamic scattering near equilibrium. Doi and Onuki (DO) have formulated the Time-Dependent-Ginzburg-Landau-type dynamic equation including the dynamical coupling between stress and diffusion. We aim to confirm the DO theory can well-describe the viscoelastic effects on the dynamics of SD in dynamically asymmetric polymer blends as well as to explore how the viscoelasticity affects the growth of the concentration fluctuations in the early stage SD in dynamically asymmetric polymer blends.

The blend sample used in this experiment is deuterated polybutadiene (DPB, Mw = 3.74 x 10^{4}, Mw/Mn = 1.28) / polyisoprene (PI, Mw = 8.5 x 10^{4}, Mw/Mn = 1.1) = 50/50 (wt/wt), where Mw and Mn are, respectively, weight-averaged and number-averaged molecular weight. The DPB/PI has lower critical solution temperature type and upper critical solution pressure type phase diagram. The spinodal temperature of the DPB/PI at 0.1 MPa is 314.2 K. We measured the time changes in SANS intensity of the mixture after the onset of the pressure drop from 100 MPa to 0.1 MPa at 38.5 K with the SANS-U spectrometer of the Institute for Solid State Physics of the University of Tokyo in JRR-3M at Tokai.

The scattered intensity increases with time at all-observed q-region. The time changes in the scattered intensity can be well described with Cahn-Hilliard-Cook theory and we obtained the q-dependencies of the growth rate and Onsager kinetic coefficient A(q). Fig. 1 shows the q-dependence of A(q). The q^{2}-dependence can be observed at large q-region. Doi-Onuki predicted the following q-dependence of A(q):

\[ A(q) = A(0)/(1 + q^{2} \xi_{\infty}^{-2}) \]  \hspace{1cm} (1)

where A(0) and \xi_{\infty} are, respectively, A(q) at q = 0 and the viscoelastic length within which the growth of the concentration fluctuations is suppressed by viscoelastic effects. We can well fit the data with eq. (1) and obtained \xi_{\infty} = 79.9 nm. This indicates that the viscoelastic effects have important role in the dynamics of phase separation processes in dynamically asymmetric polymer blends.

\[ A(q) \text{ / \ m^2 s}^{-1} \]

![Graph of A(q) vs. q/\text{nm}^{-1}](image)

Fig. 1 q-dependence of A(q)

JRR-3M, SANS-U, Polymer
1-5-8
高分子の結晶構造
Crystal Structure of Polymers
NEUTRON AND X-RAY STRUCTURE ANALYSES OF POLY(PYRIDOBISIMIDAZOLE) PIPD

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Poly(pyridobisimidazole) PIPD is a fully conjugated polymer with the highest tensile strength, whose chemical structure is shown in Fig. 1. Neutron and X-ray structure analyses of this polymer were carried out. Neutron diffraction has several advantages in comparison with X-ray diffraction: the position of the hydrogen atom can be easily determined, the carbon and nitrogen atoms can be easily distinguished, and furthermore, it is easy to measure the diffraction at low temperature.

Neutron diffraction on the equator were measured by a powder diffractometer HERMES at JRR-3M installed in JAERI at 10, 100, 200, and 295K. X-ray diffraction was measured by an imaging plate at room temperature and the integrated intensities were estimated digitally.

All the reflections could be indexed by the unit cell reported by Klopf & Lammers. In Fig. 2, the temperature dependence of the cell parameters a, b, and c measured by neutron diffraction are shown. Two molecular chains pass through the unit cell. From the neutron structure analysis, it was clarified that the crystal assumes the statistical structure between two molecules of the pyridine rings with different orientations. By the constrained least-squares refinements, R-factors reduced to 15.6, 13.0, 16.5, and 10.5% for 12 intensity data at 10, 100, 200, and 295K, respectively. Three dimensional structure was clarified by X-ray data (R = 16.5% for 17 reflections). The crystal structure of PIPD is shown in Fig. 3. The space group is the P2_1/a-C_5. The OH bonds extend to outside of the molecule and form the intermolecular hydrogen bonds. The molecule is virtually planar differing from poly(p-phenylenebenzobisoxazole) and poly(p-phenylenebenzobisthiazole),


Fig. 1.

Fig. 2.

Fig. 3.
Small Angle Neutron Scattering (SANS) measurements have been performed on poly(vinyl alcohol) (PVA) gels in a mixture of deuterated dimethyl sulfoxide (DMSO-d₆) and D₂O with volume ratio 60:40 at various temperatures during the melting process. It was previously revealed [1] that the crosslinking points of PVA gel at 25°C are crystallites and the size has been estimated to be about 70 Å in radius under an assumption of sphere shape of a crystallite. In this study, we have evaluated the structure changes around the crosslinking points during the melting process of the gel.

SANS measurements were carried out on SANS-U spectrometer at a beam port (C1-2) of JRR-3M reactor, Tokai. The gel samples were prepared as follows. A homogenized PVA solution at 100°C was quenched to 27°C to stand for 24 hour to gel. The measurements were carried out at 27°C, 45°C, 60°C, 70°C, 80°C, 90°C, and 100°C.

Figure 1 shows SANS intensity \( I(Q) \) of the PVA gel at 27°C as a function of \( Q \) in double logarithmic form. The scattering intensity \( I(Q) \) can be well described by the Ornstein-Zernike (OZ) formula [eq. (1)] in the \( Q \) range below about 4 x 10² Å⁻¹.

\[
I(Q) = \frac{I(0)}{1 + \xi^2 Q^2}
\]

where \( \xi \) is a correlation length and \( I(0) \) is the scattering intensity at \( Q = 0 \). The solid line in the figure is the best fit of the OZ formula to the observed \( I(Q) \). In the high \( Q \) range above 6 x 10⁻² Å⁻¹, the scattering intensity \( I(Q) \) decreases with increasing \( Q \) according to a power law with an exponent \( n \).

The correlation length \( \xi \) and exponent \( n \) are plotted against temperature in Figure 2. It is noted that the exponent \( n \) is close to -4 at 27 to 70°C, which is the so-called Porod's law, suggesting the smooth surface of crystallites (crosslinking points) [1].

The melting temperature of the gel has been estimated to be about 75°C. Above the melting temperature of the gel, the exponent \( n \) gradually increases to -3. It reveals that the surface of...
研究テーマ：PVA化学架橋ゲルのシネレシスにおける微視的構造変化
表題：ポリビニルアルコールゲルの融解過程における小角中性子散乱測定

crystallites becomes rougher. The correlation length $\xi$ corresponds to an average distance between the nearest neighboring crosslinking points, at least below $T_m$. The value is 139 Å at 27 ℃ and after showing a minimum (152 Å) at 45 ℃, it decreases with increasing temperature. It is not physically acceptable that the average distance between the nearest neighboring crosslinking points decreases because the number of crystallites must decrease during the melting process.

In order to solve this problem, we calculated distance distribution function $P(r)$, which is defined by inverse Fourier transformation of scattering intensity $I(Q)$ [2],

$$P(r) \sim \left( \frac{2}{\pi} \right) \int rQI(Q)\sin(rQ)Q dQ \quad (2)$$

$$\sim 4\pi r^2 \gamma(r)$$

where $\gamma(r)$ is a pair correlation function. For calculation of eq. (2), it is necessary to extrapolate the observed scattering curves both to the lower and higher $Q$ ranges. This was made by employing the functions of $OZ$ formula and power law for the lower and higher $Q$ ranges, respectively. The calculated $P(r)$ at 27 and 90 ℃ are shown in Figure 3 (a) and (b), respectively. The broad peak and/or shoulder are observed in $P(r)$ at 27 ℃. Following the previous analysis [1], the broad peaks at 70 Å and 180 Å can be assigned to the intra- and inter-crystallite correlations, respectively. In order to separate two contributions, we fitted the observed $P(r)$ in the small $r$ range with a model function for the intra-crystallite correlation. This model function was calculated under the assumption that shapes of the crystallites are sphere and the distribution of sizes of crystallites (radius) can be represented by a Gaussian. The inter-crystallite correlation $P_{\text{int}}(r)$ was obtained by subtracting $P_{\text{intra}}(r)$ from the total $P(r)$. The results are shown in Figure 3 (a) by dotted and dashed lines, which correspond to the intra-crystallite correlation $P_{\text{intra}}(r)$ and inter-crystallite correlation $P_{\text{int}}(r)$, respectively. In Figure 3 (b), we can find the $P_{\text{int}}(r)$ clearly, and the value is about 80 Å. It is close to the correlation length $\xi$. It indicates that $\xi$ corresponds to the average size of crystallites (intra-correlation of crystallites) when the temperature is above $T_m$. The power law exponent $n$ is -2.5, suggesting that the crosslinking points don’t have even rough surface at this temperature. The detailed analysis is now in progress.

Structural Analysis of Weakly-Charged Polymer Gels including Local Hydrophobic Micro-Aggregations in Mixed Solvents.

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Introduction

We have studied the copolymer gels consisting of 12-acyroyloxydodecanoic acid (ADA) and acrylic acid (AA) as a crosslinked protein model, which includes groups capable of hydrophobic and ionizable interactions and hydrogen bonding. The ADA (Fig. 1) has a long-alkyl-side chain and an ionizable carboxyl group, which probably contribute to hydrophobic chain assembly and hydrogen bonding between the ADA side chains, respectively. First, the effect of the hydrophobic interaction and the hydrogen bonding has been identified by equilibrium swelling measurement in 1-propanol/water (PrOH/W) and propionic acid/water (PAC/W) mixed solvents. The PrOH and PAC have the almost same “log P”¹, the logarithmic partition equilibrium coefficient, which shows the hydrophobicity of the solvent. So, we can ignore the difference of hydrophobic interaction effect, when discussing the solvent effect of PrOH and PAC. Fig. 2 shows the swelling ratio, S, of ADA/AA gels in PrOH/W and PAC/W systems as a function of solvent composition, x (φ = PrOH or PAC mol% in organic solvent/water mixtures). The remarkable shrinking (S, ≈ 2) at x = 0 mol% proved the hydrophobic association of the long-alkyl-side chains, in which the hydrogen bonding of the carboxyl groups also occurred. The interesting feature was the fact that the S, of the PAC/W system was larger than that of the PrOH/W system at x < 15 mol% and then the order was inverted at x > 15 mol%. This seems to be due to the difference of hydrogen bonding capability of the carboxyl group in PrOH/W and PAC/W solvents. The aim of this study is to clarify the origin of the difference from a microscopic viewpoint by means of small-angle neutron scattering (SANS).

Experimental

The ADA²/AA gels were heat-polymerized in ethanol for 24 h at 60 °C. The monomer composition of ADA in ADA/AA gel was 32.7 mol% and the net monomer concentration was 5 M. SANS measurements (with SANS-U spectrometer at ISSP, Univ. of Tokyo, at λ = 7 Å, at room temperature) were carried out for 1.0 and 1.5 h for 1 and 4 m sample-to-detector distance conditions,
respectively. The solvents of the samples were replaced by deuterated ones, i.e., combinations of D_2O, deuterated 1-propanol (d-PrOH), and deuterated propionic acid (d-Pac).

Results and Discussion

Fig. 3 shows I(q) of ADA/AA gels in d-PrOH/W (a) and d-Pac/W (b) as a function of x in double logarithmic plots. I(q)'s for both systems had a broad scattering peak at x = 0, 2, and 5 mol%, indicating the existence of local periodic hydrophobic micro-aggregations. However, the x dependence of the peak position was different. That is, as shown more clearly in the Kratky plot in the inset, the peak maximum for the d-PrOH/W system (Fig. 3a) shifted to lower q region (54.4 to 59.0 Å in the real space) with increasing x, while that for the d-Pac/W system hardly changed (ca. 55.0 Å). Also, the peak height for the d-PrOH/W system decreased remarkably with increasing x. These differences were explained as follows. The Pac, a kind of acid, attacks the hydrogen bondings between hydroxyl groups at the end of the long alkyl groups and destroys them, following quick disorganization of the hydrophobic aggregation of long-alkyl-side chains. This is reflected to the quick reduction of the peak height in Fig. 3a. On the other hand, the PrOH gradually destroys the hydrophobic aggregation, corresponding to the peak change in Fig. 3b. So, as shown in Fig. 2, the gel at the Pac/W system swelled more quickly with increasing x than that at the PrOH/W system. However, the increase of Pac also reduces the pH in the system, leading to suppression of dissociation of the carboxyl groups on the AA. Therefore, at higher x, S, of the Pac/W systems becomes lower than that of the PrOH/W systems, as shown at x > 15 mol% in Fig. 2.

Summary

As described above, the ADA/AA gels have the local hydrophobic micro-aggregations in the water-rich solvents. The increase of the organic composition (PrOH or Pac) in the solvent tends to destroy the aggregations. Here, because the effect of disorganization by Pac is stronger than that by PrOH, the S, for the Pac/W system is larger than that for the PrOH/W system at the low x region. However, since Pac is an acid, it reduces the degree of ionization of acrylic acid, leading to a lowering of S, which becomes effective for x > x_c (15 < x_c < 25 mol%) and an inversion of S, takes place. This result proved that a slight difference in the nature of solvent can lead to a significant difference in forming higher order structure of proteins. The more detailed results and discussion have already published in the full paper^3.

References

Small Angle Neutron Scattering Studies on Structural Inhomogeneities in Temperature Sensitive Polymer Gels: Irradiation Cross-linked Gels vs Chemically Cross-linked Gels

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Introduction
Polymer gels are gigantic molecules consisting of long branched polymer chains immersed in a solvent. Due to restriction of the chain motion by cross-links, gels possess a very complicated structure and dynamics compared to the corresponding polymer solutions. Poly(N-isopropylacrylamide) (PNIPA) gel is a typical example of polymer gels and is usually synthesized by conventional radical polymerization starting from the constituent monomer and cross-linking agents (chemical gels). Another approach to make gels is γ-ray irradiation (γ-ray gels). The resultant gels are more or less homogeneous comparing to that prepared by the conventional method since cross-links are expected to be introduced randomly in space. In our previous report [1], we demonstrated that the neutron scattering functions varied from Lorenz to a power-law behavior with increasing cross-linking density for both types of polymer gels. The scattering functions were successfully reproduced by theoretical structure factor proposed by Panyukov and Rabin (PR theory), which allowed us to evaluate molecular parameters, such as degree of cross-links, interaction parameters and degree of inhomogeneities. In this report, we address the physical significance of the concept of the cross-linking saturation threshold (CST), which defines the maximal achievable density of cross-links in a gel.

Experimental
Poly(N-isopropylacrylamide) (NIPA) gels having different cross-link densities were prepared by polymerizing NIPAm monomer with cross-linker, methylene-bisacrylamide (BIS) in water at 20°C. The concentrations of BIS, C_{BIS} were varied from 0 to 35 mM, while that of NIPAm (C_{NIPA}) was kept to 690 mM. The cross-linking density for the γ-ray gels was controlled by varying the radiation time (0 ~ 16 Mrad).

Small angle neutron scattering (SANS) measurements were carried out with SANS-U spectrometer of the Institute for Solid State Physics, University of Tokyo in Tokai. The wavelength of neutron beam was 7.0 Å.

Results and Discussion
Due to non-cancel-out fluctuations of polymer gels, the scattering functions for both the chemical and γ-ray gels exhibited a positive deviation at lower wave vector with increasing the cross-linking degree. As demonstrated in our previous works [1, 3], the scattering functions for PNIPA gels were successfully reproduced by the PR theory. As a consequence, we obtained the degree of
polymerization between cross-links, $N$, and the Flory's interaction parameter, $\chi$. Figure 1 shows the values of $N$ evaluated by the PR analysis as a function of cross-linking density for the chemical gels (open circles) and the $\gamma$-ray gels (filled circles). As expected, $N$ decreased with the degree of cross-linking and approached an asymptotic value for both the chemical and $\gamma$-ray gels. The limit, $N_{\text{CST}}$, is called the cross-linking saturation threshold (CST), which can be considered as a point where the number of cross-links introduced to the gel becomes equal to the number of binary contact of monomers.[2, 3] Because of this physical limitation, any additional cross-linking is no longer formed above the CST. Although the results for higher doses were not shown here for the $\gamma$-ray gels, a volume shrinking of gels was observed for 16 Mrad, which is located far below the CST. Thus, it can be concluded that the efficiency of the cross-linking formation for the $\gamma$-ray gels is much higher than that for the chemical gels and a less number of cross-links is required to form a gel.

Figure 2 shows the $C_{\text{RS}}$ and irradiation dose dependence of the inhomogeneity-correlation length at sample preparation, $\Xi$, for the chemical gels (open circles) and the $\gamma$-ray gels (filled circles).

Reference
Fluorinated polymers have attracted much attention because of their unique characteristics such as high hydrophobicity, lipophobicity, chemical stability and biocompatibility. The combination of fluorinated polymers with hydrophilic polymers may lead to a new class of polymeric amphiphiles.\textsuperscript{1,2} We have already found that vinyl ether based fluorine-containing amphiphilic block copolymer possesses peculiar properties such as high surface activity and "fluorophilicity" in the solubilization of fluorinated dyes in aqueous media. To understand more about this series of block copolymers, here we examined their micelle structures in aqueous media in detail. We utilized small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS) techniques.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Chemical structure of amphiphilic block copolymers}
\end{figure}

F3: $R = \text{OCH}_2\text{CF}_3$, $m = 78$, $n = 23$
F5: $R = \text{OCH}_2\text{CF}_2\text{CF}_3$, $m = 74$, $n = 22$
F7: $R = \text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_3$, $m = 79$, $n = 19$
F0: $R = \text{CH}_2\text{CH}_3$, $m = 70$, $n = 22$

Figure 1 shows the chemical structure of the block copolymers (F3, F5, F7) used in this study. In comparison with the fluorine-containing block copolymers, non-fluorine-containing block copolymer (F0) was also prepared. All samples had approximately the same chain lengths both in hydrophilic segments and in hydrophobic segments.

Figure 2 shows the SANS profiles for 3.2 x 10\textsuperscript{4} mol/L block copolymer solutions in D\textsubscript{2}O. A strong scattering in small angle region suggested a formation of micelles in all cases. The profiles of F0, F5, and F7 showed clear q\textsuperscript{-1} dependence in the lower angle region, indicating the formation of rod-like micelles, while the profile of F3 showed much gentler slope, indicating a possibility of coexistence of rod-like and spherical micelles.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{SANS profiles for the block copolymer in D\textsubscript{2}O}
\end{figure}

Figure 3 represents the SAXS profiles of the copolymer solutions measured under the
same conditions as SANS experiments. The micelle formations were also confirmed by a strong x-ray scattering in the small angle region. In these cases, a clear second maximum of the scattering due to an intra-particle structure such as core-shell structure was observed around $q = 0.04 \sim 0.08 \text{ Å}^{-1}$.

![SAXS profiles for the block copolymer aqueous solutions](image)

**Figure 3.** SAXS profiles for the block copolymer aqueous solutions

To analyze these scattering data, we assumed both core-shell rod-like micelle and core-shell spherical micelle models, and calculated the theoretical profiles for SANS and SAXS. Radii of the core ($R_c$) and the radii of the whole micelle ($R_m$) in the cross section of spherical micelles and rod-like micelles were assumed to be the same in our models. The solid lines shown in figures 2 and 3 were the fitting curves. They reproduced both experimental data quite well with the same fitting parameters in all cases, which strongly supported the accuracy of the proposed model. The fitting parameters are listed in table 1.

DLS results of the copolymer micelle solutions are consistent with the above considerations. Hydrodynamic size distributions of the block copolymer micelles were bimodal in all cases. Hydrodynamic radii ($R_h$) of the micelles obtained by double exponential fitting for the time correlation functions were also listed in table 1. Particles of hydrodynamic radius ($R_h = ca.110 \text{ Å}$) can be considered as spherical micelles and those of $500 \text{ Å}$ or larger $R_m$ as rod-like micelles.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\Phi$</th>
<th>$R_c$</th>
<th>$R_m$</th>
<th>$R_{h,rod}$</th>
<th>$R_{h,sphere}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F3</td>
<td>0.1</td>
<td>53</td>
<td>110</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>0.7</td>
<td>53</td>
<td>110</td>
<td>600</td>
<td>100</td>
</tr>
<tr>
<td>F7</td>
<td>0.8</td>
<td>55</td>
<td>110</td>
<td>1100</td>
<td>150</td>
</tr>
<tr>
<td>F0</td>
<td>0.4</td>
<td>55</td>
<td>120</td>
<td>650</td>
<td>150</td>
</tr>
</tbody>
</table>

$\Phi$: volume fraction of the rod-like micelle

$R_c$: cross-sectional radius of the micelle core

$R_m$: cross-sectional radius of the overall micelle

$R_{h,rod}$: hydrodynamic radius of the rod-like micelle

$R_{h,sphere}$: hydrodynamic radius of the spherical micelle

It was revealed that F3 mainly formed spherical micelles, F5 and F7 mainly formed rod-like micelles, while F0 formed both spherical and rod-like micelles. Based on these results, we supposed that rod-like micelles are more likely to be formed in the highly fluorinated block copolymers, while the size of spherical micelle and radius of rod-like micelles are almost unchanged regardless of the number of fluorine atoms per monomer unit.

**References**


Neutron Spin Echo Study of the Dynamics of Tethered Polyelectrolyte Chains on Solid Substrate in Aqueous Media

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In 1999, we performed a systematic Neutron Spin-Echo (NSE) experiment on polymer micelles in aqueous solution. Amphiphilic diblock copolymers were synthesized and their aqueous solutions were measured by NSE to elucidate the dynamic character of polymer micelles, especially the dynamics of "corona" part of the polymer micelle. We found that there were two dynamic modes existed in the system and the time-correlation functions obtained by NSE were well reproduced by a double exponential function. The decay rate $\Gamma$ both for the fast and slow modes showed an excellent linearity as a function of the square of $q$ (the scattering vector). By independent experiments by SANS and SAXS, the size and shape of the micelle were evaluated. Also, by a dynamic light scattering technique, we evaluated the translational diffusion coefficient of the micelle in water solution. From systematical analyses of these data, it was concluded that the slow mode by NSE corresponded to the translational diffusion of the whole micelle and the fast mode was considered to be a dynamic mode of corona, i.e. hydrophilic polymer chains on the micelle surface. However, the unknown factor was a contribution from "unimer" which is a single polymer chain in the solution. In this study, we have synthesized a novel corona system without unimers, and the dynamics of the corona, i.e. the tethered polyelectrolyte chains has been further investigated.

By following the scheme shown in Figure 1, we have synthesized polyelectrolyte grafted colloidal silica particle. This graft-polymerization reaction was confirmed by IR, ESCA, and $\zeta$-potential experiments. The graft polymer chains have sulfonic acid groups, hence this is a polyelectrolyte grafted colloidal particles. The 1.64 vol.% dispersion was measured by NSE. The $q$ range was from 0.03 to 0.065 Å$^{-1}$. Due to the unexpectedly weak scattering intensity, the time correlation function obtained had not enough statistics but it was fitted by exponential function. $\Gamma$ vs. $q^2$ plot showed an excellent linearity up to $Q=0.05$ and smaller $\Gamma$ value was found at $Q=0.065$. There is a possibility that the dynamics of corona chains contributed to NSE data at this higher $Q$ regions.

Figure 2 An example of NSE data for polyelectrolyte grafted colloidal silica particles in aqueous dispersion.

References
Molecular Weight Dependence of Interfacial Broadening at (Polystyrene/Deuterated Polystyrene) Bilayers below Bulk Glass Transition Temperature by Neutron Reflectivity

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Molecular motion at polymer surfaces is quite different from that in the interior bulk region due to the free energy difference between surface and bulk. The purpose of this study is to elucidate the depth region, in which segmental mobility is enhanced, based on interdiffusion experiments using (polystyrene/deuterated polystyrene) (h-PS/d-PS) bilayers at a temperature above surface glass transition temperature, $T_g^s$, and below bulk glass transition temperature, $T_g^b$.

h-PS and d-PS with various molecular weights were anionically synthesized. Thin films of h-PS and d-PS were prepared by the spin-coating method on silicon wafers. (hPS/dPS) bilayers were prepared by a floating technique as follows. The perimeter of the h-PS film was scored with a blade, and then, floated off onto the surface of distilled water. The h-PS film was picked up onto the d-PS film by attaching the d-PS film from the air side. For interdiffusion experiments, the bilayers were annealed at 365 K, which was above $T_g^s$ and below $T_g^b$ for 152 hrs. The interfacial broadening of the bilayer by annealing was monitored using dynamic secondary ion mass spectroscopy (DSIMS) and neutron reflectivity (NR). The incident beam of oxygen ions with 4k eV and ca. 30 nA was focused onto a 200 µm x 200 µm area of the specimen surface. The incident angle was 45 deg. NR measurements were made using the multilayer interferometer for neutrons (C3-2-2, MINE) at the Institute for Solid State Physics, University of Tokyo. The incident neutrons possess the long wavelength of 1.26 nm and the resolution of 5.1 %. The reflectivity was calculated based on the scattering length density profile along the depth direction by using Spreadsheet Environmental Reflectivity Fitting.

Figure 1 shows the molecular weight dependence of interfacial thickness for (h-PS/d-PS) bilayer films annealed at 365 K for 152 hrs. While the interfacial thickness was smaller than 1 nm before the annealing, it was discernibly evolved after the annealing below $T_g^b$. Hence, it is clear that segmental mobility at the interfacial region, which used to be surface layer, is much enhanced in comparison with the bulk. Also, the interfacial thickness was almost constant below $M_n$ of 75k and then slightly decreased with increasing molecular weight. This $M_n$ dependence might be explained in terms of the temperature difference between $T_g^s$ and 365 K.

![Figure 1 Molecular weight dependence of interfacial thickness for (h-PS/d-PS) bilayers after annealing at 365 K for 152 hrs.](image-url)
Chain End Distribution near the Surface in Polymer Films by Neutron Reflectivity

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Manifestation of surface functions for polymeric materials is closely related to its surface aggregation structure and thermal molecular motion. One of our goals is to rationalize the distribution of chain end groups in the vicinity of the surface and its role for various surface functionalities. In this report, chain end distribution near the surface under hydrophobic and hydrophilic atmosphere is studied by neutron reflectivity.

The polymer used in this study was symmetric (tridecafluoro-1,1,2,2-tetrahydro-oyctyl dimethylsilyl-terminated poly(styrene-d4-block-styrene-block-styrene-d4) triblock copolymer [Rf-P(dSt-St-dSt)-Rf] synthesized via living anionic polymerization. Figure 1 shows the chemical structure of Rf-P(dSt-St-dSt)-Rf. The number average molecular weight (Mn), the molecular weight dispersity (Mw/Mn), PS weight fraction, and functionality was 25.7 k, 1.09, 0.744, and 2.02, respectively. Two Rf-P(dSt-St-dSt)-Rf films were coated from toluene solution onto a silicon wafer with native oxide layer by a spin-coated method, and then annealed at 423 K for 24 hrs under vacuum in order to remove any sample preparation history. One of the films was further annealed under water vapor atmosphere at 373 K. At that time, the relative humidity was 100%. NR measurements were made with the multilayer interferometer for neutrons (C-3-2-2, MINE). The incident neutrons possess the long wavelength of 1.26 nm with the resolution of 5.1 %. The reflectivity was calculated based on the model scattering length density profile along the depth direction by using spreadsheet environment reflectivity fitting (SERF).

Figure 2 shows the scattering vector, q, dependence of neutron reflectivity for the Rf-P(dSt-St-dSt)-Rf films annealed under vacuum and water vapor. The solid curves denote the best-fitted reflectivity calculated on the basis of model scattering length density, (b/V), profile along the direction normal to the surface shown in the inset. Since both (b/V) values at the surface were higher than that of its interior region, it seems reasonable to consider that fluoroalkylsilyl end groups are preferentially partitioned to the surface. Also, the surface concentration of chain ends is strongly dependent on the environment such as vacuum and water vapor.

Figure 1 Chemical structure of Rf-P(dSt-St-dSt)-Rf.

Figure 2 The scattering vector, q, dependence of reflectivity for the Rf-P(dSt-St-dSt)-Rf films. The inset shows the model scattering length density, (b/V), profile along the direction perpendicular to the film surface. See detail in the text.
1-5-16 Complex Microphase Transitions in an ABC Triblock Terpolymer

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Introduction Polyisoprene-b-poly(D6-styrene)-b-poly(vinyl methyl ether) triblock terpolymer (abbreviated to PI-b-DPS-b-PVME) is an extremely interesting system, because DPS and PVME have a lower critical solution temperature (LCST)-type phase diagram, while PI and DPS (or PVME) have an upper critical solution temperature (UCST)-type phase diagram. Namely, with increasing temperature the segregation power between PI and DPS decreases and DPS tends to mix with PI. However, PVME is still immiscible with PI while miscibility between DPS and PVME decreases with temperature. Therefore, it is quite interesting to investigate the phase behavior of this terpolymer. Order-disorder transitions with temperature based on the competition of three components of PI-b-DPS-b-PVME makes the phase behavior extremely rich but complex. However, it can be investigated by using a combined small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) analysis, because they give different contrast for the three components and, therefore, the complementary information.

Experiment PI-b-DPS-b-PVME (Mn=4.1x10^3, 2.1x10^4 and 3.4x10^3 for each block, respectively) triblock terpolymer sample cast from toluene solution. SANS-U (λ=7.0Å, SDD=4.0m) equipped with a heating stage controlled by TEMCON was used. The SANS data were obtained for a heating and a cooling cycle by 5K step for each between room temperature and 487 K. The SAXS measurement was performed for the cooling cycle from 493 to 300 K.

Results Figure 1 shows the temperature dependence of Bragg spacing D (D is related to qm by D=2π/qm) calculated from SANS(○) and SAXS(□) measurement. At below 410K, both D shows the same behavior and it means the distance between PI phase and PI phase. This results suggest that spherical micro-domains of PI phase are not packing in the matrix of DPS/PVME mixed phase. At temperature above 410 K, D(SANS) decreases sharply, on the other hand, D(SAXS) increases because of the difference of scattering contrast between SANS and SAXS. This results means mixed phase of DPS/PVME is separated each other, and PVME forms spherical morphology. Figure.2 shows the phase behavior model of PI-b-DPS-b-PVME.
1-5-17

Small-Angle Neutron Scattering Study on Droplet Density Dependence of Static Structure in a Ternary Microemulsion System

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A mixture of AOT (Aerosol-OT; diocyl sulfosuccinate sodium salt), D₂O, and oil forms stable water-in-oil droplet microemulsion in the vicinity of room temperature as shown in Figure 1. The arrow indicates the same water to AOT molar ratio line and it has been believed that the size of droplet is almost constant and only droplet concentration \( \phi \) (the volume fraction of D₂O plus AOT) is different. [1] Seto et al. [2] investigated the static structure of the system by means of small-angle x-ray scattering (SAXS) technique in the droplet concentration region of 0.45 \( \leq \phi \leq 0.65 \) with the water to AOT molar ratio of 40.8. They concluded that the mean droplet radius \( r \) and the polydispersity index became small with increasing \( \phi \). However, their analysis depended on the model of the structure factor \( S(Q) \). Thus, their result on the droplet structure had an ambiguity.

Small-angle neutron scattering (SANS) technique has an advantage in determining structures comparing with SAXS; the contrast variation method can be used. In general, an observed scattering intensity can be expressed by the product of \( P(Q) \) and \( S(Q) \);

\[
I(Q) = nP(Q)S(Q).
\]

In the case of water-in-oil droplet structure, only the form factor is changed when deuterated oil (film contrast) is used instead of protonated oil (bulk contrast) while the structure factor is the same. In case of polydisperse droplets, \( P(Q) \) can be written as,

\[
P(Q) = \int F(Q,r)h(r)dr,
\]

here, \( h(r) \) is a distribution function and \( F(Q,r) \) is

\[
F(Q,\tau_c) = \left[ \frac{4\pi}{3} \tau_c^3 \Delta \rho f(Q\tau_c) \right]^2
\]

for bulk contrast and,

\[
F(Q,\tau_c) = \left[ \frac{4\pi}{3} \Delta \rho \left( \tau_c^3 f(Q\tau_c) - (\tau_c + \delta)^3 f(Q(\tau_c + \delta)) \right) \right]^2
\]

for film contrast. \( Q \) is momentum transfer, \( \tau_c \) and \( \delta \) radius of droplet core and thickness of droplet shell, \( \Delta \rho \) the neutron scattering amplitude density difference, respectively. The function \( f(x) \) is

\[
f(x) = 3 \sin x - x \cos x \over x^2.
\]

Hereafter, a Relative Form Factor, \( R(Q) \), is introduced as a ratio of the scattering

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phasdiagram.png}
\caption{A triangle phase diagram of AOT, D₂O, and n-decane system at ambient temperature and pressure.
}
\end{figure}
function of bulk and of film contrast as follows;

\[ R(Q) = \frac{I_{\text{bulk}}(Q)}{I_{\text{film}}(Q)} = \frac{p_{\text{bulk}}(Q)}{p_{\text{film}}(Q)}. \]  \hspace{1cm} (6)

With this relation, we can determine the shape of droplets independent of \( S(Q) \). Fit parameters are core radii \( r_c \), thickness of droplet shell \( \delta \), and the root mean square deviation from the mean of droplet \( \Delta r \) \( (\Delta r^2 = \langle r^2 \rangle - \langle r \rangle^2) \). The polydispersity index \( p \) is determined as \( p = \Delta r / r_c \).

A SANS experiment at ambient temperature and pressure was done using SANS-U with 7Å of incident neutron beam. The covered \( Q \) range was 0.005\( \leq Q \leq 0.15 \)Å\(^{-1}\). Mixtures of AOT/D\(_2\)O/decane, whose composition was 0.05\( \leq \phi \leq 0.75 \) at water to AOT molar ratio being 32.5, was measured for both the bulk and film contrast.

In Fig. 2, observed SANS profiles from bulk contrast samples are shown. With increasing \( \phi \), a pronounced peak due to the structure factor grew. Dividing SANS profiles of bulk contrast by those of film contrast, \( R(Q) \) below \( \phi=0.6 \) were almost the same as shown in Fig. 3. From this plot, it is clear that the droplet shape is unchanged below \( \phi=0.6 \) and it deforms at \( \phi>0.6 \). Solid lines indicated in Fig. 3 are fit result according to Eq. (6). Here, Gaussian form was used for the radius distribution function, \( h(r) \). In Fig. 4 obtained fit parameters are shown. \( r_c \) and \( r_r \) (shell radius of droplet) were constant below \( \phi=0.56 \), where the close-packed structure of spheres occupies, and it decreased above this value. On the other hand, \( p \) decreased below \( \phi=0.56 \) monotonically and then it increased. Evaluated structure factor showed that at low \( \phi \) region, the concentration fluctuation was dominant for \( S(Q) \) and droplets were well aligned at high \( \phi \) region.

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**References**


Temperature and Pressure-Induced Phase Transition in Aerosol-OT, Water, n-Hexane Microemulsion System

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An anionic surfactant AOT (Aerosol-OT; dioctyl sulfosuccinate sodium salt) is typical amphiphile forming a stable microemulsion mixing with water and oil. Because AOT has positive spontaneous curvature at room temperature, it forms water-in-oil type structure. With increasing temperature, the head-head repulsion increases due to the dissociation of counterion from head groups of AOT, and spontaneous curvature changes to negative. Thus, the structure of the system shows a sequence of a phase transition from w/o droplet (positive spontaneous curvature), to lamellar (zero curvature) and finally, to o/w droplet (negative) with elevating temperature. In the case of applying pressure, a pressure-induced phase transition from a dense w/o droplet to a lamellar structure has been observed in AOT, water, and n-decane system by means of small-angle neutron scattering (SANS). \[1,2\]

A measurement of dynamics by means of neutron spin echo (NSE) showed that temperature and pressure dependencies of bending elasticity of membranes were quite different, although static structure appeared were almost the same. \[2,3\] From these results we have concluded that pressure effects mainly affected to the packing property of tail of amphiphile molecules. Therefore, interactions among tail of amphiphile and oil molecules are quite important to understand nature of self-assembling in microemulsion system.

Eastoe et al. indicated that phase behavior obtained with changing the carbon number, C, of n-alkane showed different temperature and pressure dependence below and above C=5. \[4\] However, the origin of the different phase behavior is not clear.

In this report we demonstrated SANS results obtained in AOT/water/n-hexane (C=6) with almost the same composition of sample as previous results in AOT/water/n-decane. \[1,2\]

A SANS experiment was conducted on SANS-U spectrometer of JRR-3M, JAERI, Tokai. Sample used is a mixture of 20 vol.% of AOT, 40 vol.% of water, and 40 vol.% of n-hexane. The incident neutron wavelength was 7.0Å with the wavelength distribution of about 10%, and the sample to detector distance was set to be 2m. The source aperture was 20mm\(^4\) 4m apart from the sample position and the sample silt was 3mm\(^4\). The covered momentum transfer, Q, was ranged over 0.014 to 0.14Å\(^{-1}\). Temperature and pressure were controlled using a high-pressure cell for SANS. \[5\]

Temperature and pressure range were from 298K to 333K and from 0.1MPa to 100MPa, respectively.

In Figure 1, obtained phase diagram in temperature and pressure plane is shown. The phase boundary between droplet phase and lamellar shows negative straight line and the slope indicates -2.6MPa/K. This value is quite different from the previous value (-1.7MPa/K) obtained in AOT / water / n-decane by means of SAXS. \[6\]

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Figure 1: Obtained phase diagram in temperature-pressure plane in AOT/D_{2}O/n-hexane. Open circles were points experimentally accessed, and full circles and triangles obtained phase transition point, respectively. The slope is -2.6 MPa/K.

In Fig. 2, pressure variation SANS profile is shown. With increasing pressure a phase transition from the dense w/o droplet to the lamellar structure can be clearly found as the case of decane as oil. In order to analyze such the profiles, we utilized Teubner and Strey model for a broad peak profile at lower Q originated from the dense w/o droplet, and a model proposed by Nallet et al. for a sharp peak profile at higher Q originated from the lamellar structure. Fitting results to those equations are shown in Fig. 2 as solid lines.

From the fitting to those theoretical models, we can obtain the mean repeat distance \( d \) and the correlation length \( \xi \) for both dense droplet phase and lamellar phase. A pressure dependence of \( d \) is shown in Fig. 3(a) for 3 temperature conditions, and temperature dependence is shown Fig. 3(b). This showed that the phase behavior with varying temperature and pressure in the system is almost the same as the case of \( n \)-decane as oil.

Figure 2: Obtained pressure variation SANS profile in AOT/D_{2}O/n-hexane. The same volume of water and oil was mixed with 20 vol.% of AOT. Temperature was set to be 319.2K. The broad peak appeared at \( Q=0.05 \AA^{-1} \) broaden with increasing pressure and finally at \( P=100MPa \) it was disappeared. A lamellar peak at \( Q=0.06 \AA^{-1} \) was appeared above \( P=50.2MPa \).

Figure 3: (a) Pressure and (b) temperature dependence of \( d \).

References
Small-angle Neutron Scattering Study on Thermal Phase Behavior of NIPA-PEG Diblock Copolymer

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The self-aggregation of block copolymers has attracted much attention both for its intrinsic scientific interest and for its technological importance. We prepared the block copolymer consisting of poly(N-isopropylacrylamide) and poly(ethylene glycol) (NIPA-b-PEG) by using ceric ammonium nitrate (IV) as a redox initiator. NIPA polymer is one of the most studied thermo-reversibility responsible polymer which shrinks dramatically in water around 33°C, which is attributed to the microscopic coil-globule transition. Therefore NIPA-b-PEG aqueous solution shows unique phase behavior with varying temperature.

We employed pinhole small angle neutron scattering (PSANS) in order to investigate the microscopic structure for NIPA-b-PEG in D2O with spectrometer SANS-J at JAPAN Atomic Energy Research Institute in Tokai. The details for PSANS measurements samples are shown in Table 1. For PSANS measurements, we used a wavelength of 0.65 nm with \( \Delta \lambda/\lambda = 14\% \) and two detector positions of 1.5 and 10 m, and q-profiles are obtained gradually increasing temperature from 10°C to 34°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Block ratio (m:n)</th>
<th>Conc. % (w/v)</th>
<th>( M_n )</th>
<th>( M_g/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2:1</td>
<td>7</td>
<td>30000</td>
<td>1.23</td>
</tr>
<tr>
<td>2</td>
<td>1:3</td>
<td>5</td>
<td>9200</td>
<td>1.20</td>
</tr>
</tbody>
</table>

At lower temperature below 20°C, Ornstein-Zernike (OZ) type scattering, which is typical for the semi-dilute polymer solution, was observed. It is interesting to note that excess scattering was observed in addition to OZ-type scattering component in a q-region of \( q \leq 0.3 \, \text{nm}^{-1} \) above 17°C in spite of Sol state. This excess scattering cannot observe for NIPA homopolymer and NIPA Gel in swelling state. We consider that NIPA and PEG chains segregate with themselves for increasing hydrophobicity of NIPA segment, and the microscopic structure will affect gelation mechanism and structure around high temperature region.

The OZ-type scattering is characterized by two parameters of the forward scattering in-
tensity $I(q=0)$ and a correlation length $\xi$. Figure 1 shows a plot of $I(q=0)^{-1}$ and $\xi^{-2}$ vs inverse absolute temperature $1/T$. The excess scattering (shadow region) was observed above the vicinity of 17°C. We can guess the OZ-type scattering component parameters $I(q=0)_{OZ}^{-1}$ and $\xi_{OZ}^{-2}$ by estimating their along the dashed line level from 17°C to 22°C in Figure 1, because of $I(q=0)_{OZ}^{-1}$ and $\xi_{OZ}^{-2}$ are proportional to inverse absolute temperature in mean field theory. Therefore we can decompose PSANS profiles into OZ-type scattering component and excess scattering component by subtracting the guessed OZ-type scattering component from measurement PSANS profile.

Figure 1: Temperature dependence of inverse forward scattering intensity and squared inverse correlation length, which were estimated by using a so-called OZ-plot for sample No. 1.

Figure 2 shows the decomposition results for PSANS profiles with sample No.1. The excess scattering component was analyzed by adapting the Debye-Bueche (DB) theory of scattering for a heterogeneous system to the case of polymer solution, which is contribution from long-range concentration fluctuations appear in inhomogeneous solutions. The spatial scale of the density fluctuations due to inhomogeneous is estimated by the correlation length $\xi_{DB}$ in DB theory. The two different correlation lengths for fitting parameters ($\xi_{OZ}$ and $\xi_{DB}$) listed in Table 2. We think that variation trend of the parameter $\xi_{DB}$ is not consistant with Sample No.1. and No.2., because of the NIPA-PEG segregation morphology is different with two samples.

On the other hand, in gel and demixing state we discussed the observed power-low q-behaviors based on the mass and surface fractals and Porod low. Above 30°C, Porod ($q^{-4}$) region was shown that is the scattering for reflecting on the microstructure of aggregated NIPA rich domain. The two phases surface structure was characterized by Porod plot and we estimated the characteristic interface thickness and the specific surface area. Details will be discussed in future.

Figure 2: Decomposition of PSANS profiles into OZ-type scattering component and excess scattering component for sample No. 1.

| Table 2: Summary of two correlation lengths. |
|-------------------|------|------|------|------|
| Temperature (°C)  | $\xi_{OZ}$ (nm) | $\xi_{DB}$ (nm) | $\xi_{OZ}$ (nm) | $\xi_{DB}$ (nm) |
| 17                | 3.3  | 7.0  | 2.9  | 5.7  |
| 18                | 3.4  | 6.4  | 3.0  | 5.7  |
| 19                | 3.4  | 6.4  | 3.0  | 5.7  |
| 20                | 3.6  | 6.3  | 3.0  | 5.7  |
| 22                | 3.6  | 6.3  | 3.1  | 6.4  |
Phase Diagram for Polystyrene/Poly (vinyl methylether) Blend and Dynamical Symmetry-Asymmetry Crossover Line

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The polymer blend of polystyrene (PS)/poly (vinyl methylether) (PVME) is characteristic to have a large contrast of glass transition temperature $T_g$, i.e., $T_g$ for PS or PVME is $T_g^{PS} = 100^\circ C$ or $T_g^{PVME} = -22^\circ C$, respectively. Simultaneously, this blend has a phase diagram of the lower critical solution temperature (LCST) for its mixing behavior, where a critical point is about $145^\circ C$, for the blend with symmetric molecular weights of $M_n = 50K$. Therefore, two $T_g$'s for PS and PVME appear in a single phase. A calorimetric measurement by DSC determines a single glass transition temperature for the blend $T_g^{mix}$, which appears somewhere in a single phase.

The concept of dynamical asymmetry, on the other hand, is recently introduced in order to explain the viscoelastic effect observed in the two components system. 2) Originally the dynamical asymmetry is attributed to the difference in size between two components. For example, the blend of polymer/solvent or colloid/solvent belongs to this group. Even for a blend with identical molecular sizes between two components, if there is one-sided interactions among identical molecules, again we can find the dynamical asymmetry in the blend. The polymer blends with a large contrast of $T_g$ belongs to this second group of dynamical asymmetry, changing a degree of asymmetry as temperature changes (thermoreversible dynamical asymmetry).

In the case of PS/PVME blend, in a temperature region higher than $T_g^{PS}$, PS and PVME chains are free from vitrification, showing the dynamical asymmetry between two components. However, the thermo-reversible dynamical asymmetry appears as temperature decreases into an intermediate temperature region between $T_g^{PS}$ and $T_g^{mix}$. The thermal concentration fluctuations, inducing PS-rich or PVME-rich regions, accelerate the dynamical asymmetric picture; PS-rich regions relax more slowly and PVME-rich regions relax faster. The characteristic length scale for the dynamical asymmetry might be in a same order of the correlation length $\xi$ of the thermal concentration fluctuations.

![Figure 1: Forward Scattering $S(q = 0)$ for d-PS/PVME (50/50) blend determined according to a Ornstein-Zernike formalism.](image)

According to this motivation, by small-angle neutron scattering (SANS), we tried to determine a dynamical symmetry-asymmetry crossover, which should appear somewhere in a single phase. Deuterated polystyrene (d-PS) was employed in order to have a strong scattering contrast for neutron scattering. The molecular weights of d-PS and PVME are about 50K. We performed SANS measurements over a wide temperature-range in a sin-
ngle phase from above $T_{g,mix}$ to $T_{g,PS}$. Forward scattering intensity $S(q = 0)$ was determined from a small q-region according to a Ornstein-Zernike formalism.

Figure 1 shows the results for the blend of a volume fraction of PS, $\phi_{PS} = 0.5$. In a temperature region higher that $T_g$ for pure PS, inverse of forward scattering intensity $S(q = 0)^{-1}$ is well reproduced by using a random phase approximation model (RPA) with a same interaction parameter $\chi$ ($\sim A + B/T$). However for the blend of $\phi_{PS} = 0.5$ below about 80$^\circ$C, $S(q = 0)$ is suppressed anomalously more than expected from the higher temperature region, which was already reported in ref.2. The anomalous suppression becomes more obvious as temperature decreases more, or as PS becomes richer in the blend. Finally at $T = T_{g,mix}$, $S(q = 0)$ freezes and dose not show temperature-change anymore.

We attribute this anomalous suppression to appearance of thermo-reversible dynamical asymmetry. In order to explain our idea, we introduce a viscoelastic network-like region richer-in PS, assisted by thermal concentrations fluctuations with a correlation length $\xi$. In this network-like region, polymer chains moves cooperatively and more slowly as compared with a PVME-richer region. In the temperature region below 80$^\circ$C but still above $T_{g,mix}$, the relaxational modulus $G(t)$ originated from this network-like domains becomes non-decaying and have a life time longer than the characteristic relaxational time of the thermal concentration fluctuations without a vitrification effect. In such a case, the non-decaying modulus $G$ shifts a critical point to higher temperature (Cahn's Discussion). Therefore, $S(q = 0)$ apparently suppressed more than expected in case without non-decaying $G$. On a basis of this discussion, we define the crossover temperature of dynamical asymmetry $T_A$ as the temperature from which $S(q = 0)^{-1}$ deviates from a linear decrease according to $T^{-1}$ observed in a higher temperature region.

Figure 2 shows the phase diagram of the PS/PVME blend, indicating a spinodal point $T_s$, a cloud point $T_c$ and the calorimetric glass transition temperature for the blend $T_{g,mix}$. In Figure 2, we further add the crossover line from dynamical symmetry to asymmetry $T_A$ in this phase diagram. The temperature $T_A$ slightly decreases as a volume fraction of PS decrease. If we induce a shear-field to the blend just below $T_A$, as marked by a crossed circle for $\phi_{PS} = 0.5$, we could observe an abnormal butterfly pattern as a shear-induced phase separation. ^4

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3) private discussion with prof. Kawakatsu.
Elastic incoherent structure factors for poly(styrene) and poly(vinyl methyl ether) mixtures

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We investigated elastic structure factors for poly (styrene) (PS) and poly(vinyl methyl ether) (PVME) mixtures by use of low energy triple axis spectrometer (LTAS). Because of large incoherent scattering cross-section of hydrogen atom, we mainly observed the elastic incoherent structure factor (EISF) due to the hydrogen atom. In this study, we try to pursue the local motion of the system through EISF due to the hydrogen atoms. We used four samples such as neat PVME, deuterated PS (dPS) and PVME mixture, protonated PS (hPS) and PVME mixture, and neat hPS. If the motion of the system is vibrational, the dependence of EISF is described by the Debye-Waller factor, i.e., $S(q, \omega = 0) \sim \exp(- < u^2 > q^2)$, where the quantity $< u^2 >$ is the mean square displacement and $q = \frac{4\pi}{\lambda} \sin(\frac{\theta}{2})$ is the magnitude of the scattering vector $q$. However, even at low temperature of ca. 10 K, the observed scattering did not obey the Debye-Waller representation and had a peak corresponding to the coherent scattering for all the samples. This result suggests that the effect of the coherent scattering is not negligible. Therefore, in order to reduce the effect of the coherent scattering from the observed scattering, we evaluated $< u^2 >$ by using the same procedure as that carried out by Kanaya et al. Namely, we divided it by the scattering at the lowest temperature (ca. 10 K). And from plot of the logarithm of the divided intensity $\ln[S(q, \omega = 0)_{\gamma}/S(q, \omega = 0)_{\gamma = \infty, 10K}]$ against $q^2$, we obtained $< u^2 >$ at each temperature. Figure 1 shows the temperature dependence of $< u^2 >$ for each sample. $< u^2 >'$s of neat PVME and dPS/PVME linearly increase with increase of temperature below 90 K. Above 90 K, they deviate upwards from linear relationship. The quantity $< u^2 >$ for hPS shows linear relation against temperature below 200 K and deviates from the linearity above it. On the other hand, the $< u^2 >$ for hPS/PVME appears to deviate from linear relationship at both temperatures of 90 K and 200 K. Thus, for dPS/PVME we see the motion of PVME, while for hPS/PVME we see both the motions of hPS and PVME. In comparison of the $< u^2 >$ of PVME with that of dPS/PVME, the $< u^2 >$ for the latter is larger than that for the former, indicating PVME in the mixture moves in larger space or with larger free volume. This result supports our "interstices model" in the miscibility and glass transition temperature behaviors for this mixture.  

![Graph showing temperature dependence of mean square displacement](image)

Figure 1: Temperature dependence of mean square displacement for various samples.

References
2) M. Naoki and H. Takeno, to be submitted.
Small-angle neutron scattering and dielectric studies on poly(styrene) and poly(vinyl methyl ether) mixtures

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By using small-angle neutron scattering (SANS) and dielectric spectroscopy techniques, we investigated the static mixing behaviors and local molecular motions for poly(styrene) (PS) and poly(vinyl methyl ether) (PVME) mixtures. From SANS measurements, we can obtain the interaction parameter between different components $\chi$, which is a key parameter to understand miscibility of polymer mixtures. However, the $\chi$ parameter obtained by SANS is believed to include all factors which influence the miscibility of polymer mixtures, and the physical content is ambiguous. On the other hand, dielectric spectroscopy measurements can give information on the local molecular motion such as side group motion. In this study, by combining SANS and dielectric spectroscopy techniques, we try to understand the physical content of the $\chi$ parameter in terms of local molecular motions.

We used two kinds of PVME samples, one of which was purchased from Aldrich (coded as PVME-no6) and the other is from Scientific Polymer Products (coded as PVME-sp2). We evaluated the $\chi/\nu_0$ for deuterated PS (dPS) and PVME mixtures by a best fit to SANS data in the single phase state with theoretical curve obtained by de Gennes$^1$, where $\nu_0$ is the reference volume. Figure 1 shows plot of the $\chi/\nu_0$ against reciprocal temperature for dPS/PVME-no6 and dPS/PVME-sp2. The $\chi/\nu_0$ increases with decrease of reciprocal temperature, i.e., increase of temperature, indicating the system has a lower critical solution temperature (LCST) type of phase diagram. The $\chi/\nu_0$ value for dPS/PVME-no6 mixture is larger than that of dPS/PVME-sp2 mixture. If we compare composition dependence of the $\chi/\nu_0$ for dPS/PVME-no6 mixture at a constant temperature, then the $\chi/\nu_0$ has a minimum at (70/30) or (80/20) mixture. For dPS/PVME-sp2 the $\chi/\nu_0$ monotonically decreases with increase of content of PS. The latter result is consistent with the SANS results by Han et al.$^2$

On the other hand, in the dielectric measurements, a local molecular motion of PVME ($\beta_\alpha$ process), which may be related to side group motion, was found to be largely affected by blending PS, i.e., the dielectric loss peak shifts toward high temperature. Thus, side groups of PVME is predicted to strongly correlate with PS. Moreover, the magnitude of the shift significantly depends on the composition. We compare the composition dependence of the $\chi/\nu_0$ obtained by SANS with that of relaxation time $\tau$ for the $\beta_\alpha$ process in the dielectric spectroscopy measurements. We estimated the difference between the temperature position at a given $\tau$ value ($\log \tau = -4$ and -4.5) in the $\beta_\alpha$ process of PVME and that of the mixture, $\Delta T_{\beta_\alpha}$. Figure 2 shows comparison between the composition dependence of the $\chi/\nu_0$ and that of $\beta_\alpha$. Interestingly, there is a strong correlation between the $\chi/\nu_0$ and $\Delta T_{\beta_\alpha}$. If we see dPS/PVME-no6 mixture, $\Delta T_{\beta_\alpha}$ is found to increase, when the $\chi/\nu_0$ decreases. Moreover, $\Delta T_{\beta_\alpha}$ has a maximum around stoichiometric mixture in the repeating units, while the $\chi/\nu_0$ has a minimum at almost the same composition. Both results indicate that correlation between PVME and PS is the strongest at the same composition. Thus, side groups
of PVME are considered to play an important role in miscibility of this mixture. Dielectric measurements for PS/PVME-sp2 mixture are in progress now.

References

Figure 1: Temperature dependence of the $\chi/\nu_0$ parameter for dPS/PVME-no6 and dPS/PVME-sp2.

Figure 2: Comparison between composition dependence of the $\chi/\nu_0$ estimated by SANS and that of the difference between the temperature at a given relaxation time ($\log \tau = -4$ and -4.5) for neat PVME and that of mixtures.
Small-Angle Neutron Scattering Study of Long-Chain Branched Polyethylenes

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In order to investigate a blending effect of a little number of long branchings of polyethylene in a molten state, we employed small-angle neutron scattering (SANS) with a spectrometer SANS-J at JRR-3M reactor of JAERI. A heating cell, filled with nitrogen gas to avoid thermal degradation, was installed on SANS-J to heat sample specimens. To get a strong scattering contrast for SANS, we specially prepared mixtures of hydrogenous polyethylene (H-PEs) and a deuterated high-density polyethylene (D-HDPE). Measuring temperatures were 125 and 160°C or 125 and 150°C for the mixture with a H-PE fraction of 0.2 or 0.5, respectively. The melt structure of the long chain branched linear low-density polyethylene (LCB-LL) in the D-HDPE was compared with that of other H-PEs in the D-HDPE.

<table>
<thead>
<tr>
<th></th>
<th>Mw</th>
<th>Mn</th>
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<tr>
<td>LLDPE</td>
<td>88000</td>
<td>44000</td>
<td>17.8</td>
</tr>
<tr>
<td>LCB-LL</td>
<td>74800</td>
<td>34800</td>
<td>20.6</td>
</tr>
<tr>
<td>LDPE</td>
<td>60700</td>
<td>18900</td>
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<tr>
<td>D-HDPE</td>
<td>100400</td>
<td>24300</td>
<td>-</td>
</tr>
</tbody>
</table>

*: The number of short-chain branching
**: The number of CH₃

The SANS profiles of the mixtures of D-HDPE/LLDPE and D-HDPE/LDPE in a melt state show an asymptotic decrease according to q⁻², over a whole q-region detected by SANS (Figure 1, 2). These asymptotic q-behavior of q⁻² originate from a local segmental distribution in a Gaussian chain. This result indicates that the LLDPE and the LDPE mixes with the D-HDPE on a molecular length scale.

On the other hand, the profile of the D-HDPE/LCB-LL exhibits two q-regions; in a lower q-region, close to q⁻⁴ and in a higher q region close to q⁻², respectively (Figure 3). The q-behavior of q⁻⁴ originates from an interfacial structure of phase-separated macromdomains between LCB-LL and D-HDPE (Porod law).

The LCB-LL has about the same number of short-chain branching and is about the same of molecular weight with the LLDPE. Therefore the LCB-LL was estimated to have similar miscibility with the D-HDPE to the
LLDPE. However the LCB-LL showes the worse miscible than the LLDPE. Furthermore the LCB-LL had worse miscible than the LDPE that had a lot of long-chain branching.

These results indicate that just a little number of long-chain branching has remarkable effect on the miscibility of polymers.

References

Figure 1: Logarithmic plot of SANS profiles obtained for D-HDPE/LLDPE (80/20) (diamonds at 160°C and squares at 125°C, respectively).

Figure 2: Logarithmic plot of SANS profiles obtained for D-HDPE/LDPE (80/20) (diamonds at 160°C and squares at 125°C, respectively).

Figure 3: Logarithmic plot of SANS profiles obtained for D-HDPE/LCB-LL (80/20) (diamonds at 160°C and squares at 125°C, respectively).
1-5-24  
研究テーマ：リン脂質膜のラメラ構造の圧力依存性  
表題：リン脂質 DPPC 水溶液/エタノール系の圧力誘起相転移  
Pressure-induced interdigitation of DPPC aqueous solution with small amount of ethanol.

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An aqueous dispersion of dipalmitoyl-sn-glycerol-3-phosphatidylcholine (DPPC) exhibit a rich structural polymorphism depending on their environmental conditions such as temperature and pressure. A fluid lamellar phase (L₀) is a basic structural element of biological membranes characterized by lipid bilayers. Two thermotropic lamellar phase transition have been observed below the fluid lamellar phase; a gel-to-gel (Lₙ′/Pₚ′) pretransition and a gel-to-liquid crystalline (Pₚ′/L₀) main transition. In the gel phases, the lipophilic chains of phospholipid molecules are extended and ordered, whereas the chains are conformationally disordered in the fluid lamellar phase. By applying pressure up to about 150 MPa, it transforms to an interdigitated gel phase (Lₙβ). This structure is the same as the one induced by adding ethanol, [1] however, the microscopic origins of these transitions must not be the same. [2]

The purpose of the present small-angle neutron scattering (SANS) experiment at SANS-U is to clarify the effect of pressure on phospholipids. Because the maximum pressure of our high-pressure cell was about 100 MPa, we prepared aqueous solutions of DPPC with

Fig. 1 T-P phase diagram of DPPC / D₂O / C₂H₅OH. Open circles indicate measured points.

adding small amount of ethanol (between 0.7 M and 1.2 M) in order to decrease the phase transition pressure. [3]

Comprehensive set of SANS profiles of these solutions were collected in the range of 25 ≤ T ≤ 60 °C and 0.1 ≤ P ≤ 100 MPa. Figure 1 is a phase diagram determined by the present experiment. Observed SANS profiles were analyzed using the model proposed by Lemmich et al. [4] It was confirmed that the pressure-induced phase is the interdigitated phase (Lₙβ) from the thickness of phospholipid layers. (See Table 1.)

A new phase, in which a large single peak appeared at around Q = 0.07 Å⁻¹ was found at 45 ≤ T ≤ 55 °C and 15 ≤ P ≤ 60 MPa, being among Pₚ′, Lₙ, and Lₙβ phases. The observed
Table 1. Thickness of phospholipid layers at each phase.

<table>
<thead>
<tr>
<th>phase (condition)</th>
<th>thickness / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>L° (42°C, 0.1 MPa)</td>
<td>43.5</td>
</tr>
<tr>
<td>P° (30°C, 0.1 MPa)</td>
<td>47.3</td>
</tr>
<tr>
<td>L° (25°C, 0.1 MPa)</td>
<td>47.1</td>
</tr>
<tr>
<td>L° (42°C, 100 MPa)</td>
<td>32.7</td>
</tr>
<tr>
<td>swollen gel (48°C, 40 MPa)</td>
<td>47.5</td>
</tr>
</tbody>
</table>

Fig. 2 Typical SANS profiles of L° (squares), L° (circles), P° (diamonds), L° (triangles), and the swollen gel phase (full triangles).

SANS profiles of this phase is shown in Fig. 2 comparing with profiles of other phases. The characteristic repeat distance of this phase was about 90 Å, which was 1.3 times larger than that of P° phase. The thickness of phospholipid layers of this phase was estimated to be 47.5 Å, which was almost the same as those of L° and L°. Thus, here we characterize this new phase as a swollen gel phase; only the amount of interlamellar water increases, and the structure of the phospholipid bilayer is the same as that of the P° phase.

The kinetics of the phase transition to the L° phase was investigated by using the time-resolved SANS on pressure-jump. The measurements were done at T = 27 °C (from L° to L°), 40, 42 °C (from P° to L°) and 48, 50 °C (from the swollen gel phase to L°). In Fig. 3, a typical time-evolution of the SANS profile is shown. The growing process of the interdigitated phase was characterized by a two-state mechanism; the Bragg reflection of a low-pressure phase shrunk, while the peak from the L° phase increased. From the time dependences of the peak intensities, a relaxation time of the phase transition was estimated. At all the conditions, it was larger than 500 sec. This result indicates that the transition process to the L° phase is much slower than the transitions to the other structures. [5]

References

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1. Neutron Scattering  6) Biology
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Oligomeric forms of the light-harvesting complexes from photosynthetic bacteria
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Light-harvesting (LH) complex serves as a highly efficient molecular machinery for the collection and transfer of solar energy to photochemical reaction centers in photosynthetic organisms. In purple photosynthetic bacteria, the LH complexes are classified into either of two major types, namely, the core (LH1) and peripheral (LH2) complexes, both comprising two small polypeptides α and β along with bacteriochlorophyll (BChl) and carotenoid molecules. Several resolved LH2 complexes reveal an annular structure of 9 or 8 αβ heterodimers, while electron projection structures from 2D crystals show that the LH1 complexes are composed of larger rings than LH2 containing 16 αβ subunits. The LH1 complex is characterized by a near-infrared absorption at approximately 880 nm (referred to as B880) in detergent n-octyl β-D-glucopyranoside (OG). In this study, we report the preliminary results of characterization of the B880 complexes dissolved in deuterated OG using SANS and compare with the calculated scattering profiles and radius of gyration of the LH2 complexes.

SANS measurements were conducted at room temperature (~22°C) with SANS-U(C1-2) at JRR-3M. Neutron wavelength was 7Å. Both native and carotenoidless B880 complexes from Rhodospirillum rubrum were dissolved in 1% deuterated OG solution (D2O). The SANS data were analyzed by using standard Guinier procedure. Calculations of the scattering profiles and radius of gyration for the LH2 complexes were carried out using the CRYSON program.

Figure 1 shows the scattering profiles of native B880 and carotenoidless (B873) LH1 complexes. From small q range measurement, the radius of gyration was determined to be 65Å. A shoulder was observed at approximately q=0.07Å⁻¹ for both the complexes. Similar result was reported for a deuterated LH1 complex solubilized in 0.8% OG, 17% D2O. This feature was considered to arise from the internal structure, or packing of subunits within the large LH1 particles. To examine this possibility, we compare with the calculated scattering profiles of the smaller LH2 complexes based on their crystal structures. Figure 2 shows the scattering curves over a large q range for two LH2 complexes containing 9 and 8 αβ heterodimers. Radii of gyration for the 9 and 8 αβ heterodimers are 30.3Å and 28.9Å, respectively. Clear difference can be found in the position of the first scattering maximum, which corresponds to number of the subunit and may be used as a useful measure of the size for the ring-like oligomeric structure of light-harvesting complexes. Further detailed data analysis is in progress.

Small-Angle Neutron Scattering of Lipophorin

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Lipophorin in the insect blood is a sphere-like particle with a particle weight of about 6.0x10⁵ and contains two apoproteins and 40-50% (w/w) lipid. Lipophorin is a unique lipoprotein that serves as a reusable shuttle to transport a variety of lipid classes, including diacylglycerol, cholesterol, and hydrocarbons between tissues. The apoproteins and phospholipids work as a vehicle to load and unload the above lipids. We have already proposed a model of three layered lipophorin (diameter = 168Å) based on small-angle X-ray scattering results, which was supported by the small-angle neutron scattering work with H₂O/D₂O contrast variation. The model consists of an inner core of hydrocarbons surrounded by a layer of diacylglycerol and apolipoporhin-II (M₉=8x10⁵), and a spherical micellar arrangement of the outer hydrophilic surface formed by apolipoporhin-I (M₉=2.5x10⁵) and polar phospholipid headgroups¹,²,³. In the present study, we reared American cockroach on deuterated amino acid mixtures for partially deuterating apolipoporphins. The prepared lipophorin was subjected to small-angle neutron scattering analyses with H₂O/D₂O contrast variation (Fig.1). They gave several parameters different from those obtained by the non-treated lipophorin. The model refinement is now in progress.

Fig.1 Small-angle neutron scattering curves of the cockroach lipophorin reared on deuterated amino acids.

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1-6-3 Structure analysis of ganglioside/dipalmitoyl phosphatidylcholine vesicle using inverse contrast variation


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1. Introduction Gangliosides, glycosphingolipids containing sialic acid residues, locate mainly on the outer surfaces of cell membranes, and are abundant in the tissues of the central nervous system. Recent studies suggest that these molecules not only locate on outer-leaflet of cell membrane but also form lipid microdomains with other particular lipids and proteins in neuronal cells. The microdomains are assumed to have a significant role as a molecular device to localize specific proteins which are evolved in cell-surface signal transduction such as src-family kinases and G proteins. Although the physiological functions of the microdomains is one of the current hot topics in cell biology, the biophysical studies of the formation and functionality of the microdomain are rather poor. Thus, we have carried out small-angle neutron scattering (SANS) measurements to elucidate characteristics of monosialoganglioside (GM1) dipalmitoyl phosphatidylcholine (DPPC) mixed vesicle as a model of the microdomains.

2. Experimental Here we employed the inverse contrast variation method in the solution neutron scattering methods. As is well known, inverse contrast variation method can avoid a lowering of data statistics that occasionally occurs in the use of the solvent contrast variation method. For this purpose, we dissolved the mixed vesicles in 99.9+ atom % D2O solvent with 50 mM Hepes adjusted to pH 7. The contrast of the vesicle was varied by changing the molar ratio of DPPC/deuterated-DPPC (d-DPPC). The molar contents of GM1 to DPPC are 0.1 [M/M]. The molar ratios of [DPPC]/[d-DPPC] were 1/0, 0.3/0.7, 0.7/0.3 and 0/1. To prepare small unilamellar vesicles (SUV), we used a high-power ultrasonicator with a probe. SANS experiments were carried out by using a SANS spectrometer installed at C1-2 beam port at JRR-3M, Tokai, Ibaraki, Japan.

3. Results and Discussion Fig. 1 shows the scattering curves from the SUV samples with different inverse contrasts. The insert in Fig. 1 shows the scattering curves of the above samples. In spite of the samples with different contrasts for neutron, all scattering curves for X-ray agree well, indicating that the SUV samples with different molar ratios of DPPC/d-DPPC have a same structure. Thus, the variation of the scattering curves depending on the DPPC/d-DPPC ratio in Fig. 1 is attributed to the change of the contrast. As we successfully measured the GM1/DPPC=0.1/1 SUV vesicle at 5 different contrasts, in other words, at 5 different phases (four from neutron, one from X-ray), we can determine the internal structure of the vesicle. The detailed analyses using the shell-model fitting procedure considering a polydispersity will be seen in elsewhere.

![Fig. 1. SANS curves of GM1/DPPC SUV samples with different inverse contrasts at 25 °C. The insert shows X-ray scattering curves of those SUV samples.](image-url)
The origin of non-gaussianity in q dependence of incoherent elastic neutron scattering

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²Chiba Institute of Technology
³Institute for Chemical Reaserch, Kyoto University

A protein takes its unique structure, and structural flexibility is considered to be essential for its function and activity. Thus, the understanding of the protein dynamics is important to reveal the molecular mechanisms of vital phenomena. Neutron scattering is a good tool for studying protein dynamics, because neutron scattering can give us information on both energy and the geometry of the atomic motions.

We measured the incoherent elastic neutron scattering for Staphylococcal nuclease(SNase) under the various temperatures with the use of the triple axis spectrometer, GPTAS. The purpose of the measurement was to reveal the dynamical transitions(so-called glass transition) of SNase and to analyze the q-dependence of EISF. The energy resolution was 1meV, corresponding to the picosecond time scale motions. The measured q-range was from 3.1 to 6.4 Å⁻¹.

The q-dependence of EISF can be approximated a Gaussian in low q region, while the deviation from the Gaussian becomes remarkable in rather wide q region. We considered that dynamical heterogeneity of SNase is an origin of the non-Gaussianity appeared in high q region. We assumed that the mean square displacements of hydrogen atoms in SNase can be described with a Gaussian distribution. Under the assumption, the non-gaussianity is reasonably explained in terms of the width of the Gaussian. The distribution becomes broader as temperature increases.

In the case of myoglobin, the origin of non-gaussian behavior was explained as two site model[1]. In the model, each hydrogen atom in a protein jumps between two sites of different free energy. In the case of bacteriorhodopsin, the non-gaussianity was interpreted as two distinct motions, that is a higher amplitude motion and a lower amplitude motion[2]. In the case of SNase we could not separate into two distinct motions. In the two site model the mean square displacement of each atom is the same, that is not reasonable. It is suggested that the heterogeneity of protein dynamics is one of the origin of non-gaussian in q dependence of incoherent elastic neutron scattering. MD simulation of SNase also gives Gaussian-like distribution in mean square displacement.(J. Smith and J Hayward, personal communication).

References
1-6-5 Structure of Short and Long Chain Phosphatidylcholine mixtures in Trehalose Solutions

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Trehalose is a natural cryoprotectant. Thus, in order to reveal the mechanism, many studies of the effect of trehalose on model biomembranes have been performed. Based upon the results of such studies, a following hypothesis has been proposed [1]: The presence of trehalose reduces the interfacial area between the lipids and the aqueous phases. To examine above hypothesis, we have investigated the interaction between trehalose and phosphatidylcholines (PCs), which are one of the major phospholipid components of biomembranes. In this study [2], we studied the structure of a binary mixture of short PC (dihexanoyl-PC (diC₆PC) ) and long chain PC (dihexadecyl-PC (DHPC) ) in trehalose solutions.

DHPC and diC₆PC were dissolved in chloroform and mixed to achieve the molar fraction of DHPC : diC₆PC = 4:1. The solvent was evaporated under a stream of oxygen free dry nitrogen. The dried lipid samples were hydrated in 100 % D₂O containing various concentrations of trehalose by shaking on a Vortex mixer. The total lipid concentration was 25 mM. Small angle neutron scattering (SANS) measurements were performed with the SANS-U spectrometer at JRR-3M reactor at the Japan Atomic Energy Research Institute. The wavelength of the neutron beam was 7 Å. The samples were contained in a rectangular quartz cell with 1 mm optical path length. The data corrections were carried out at about 25 °C.

Figure 1 shows the SANS curves for the PCs mixtures in trehalose solution. For the mixtures in pure D₂O and 0.4 M trehalose solution, Bragg diffraction peak is observed (d = 52 Å), indicating that a phase separation between multilamellar vesicles of DHPC interdigitated gel bilayers and micellar structures occurs in the mixtures. On the other hand, in high trehalose concentrations, no Bragg diffraction peak is observed. For the cases of 1.6 M trehalose concentration solution, we estimated that the membrane thickness is about 42 Å from the analysis using Kratky-Porod plot of the scattering curve. The value is interpreted as suggesting that, in the DHPC/diC₆PC mixture, DHPC does not form the interdigitated structure but a normal bilayer structure. This result supports the hypothesis proposed by Koyanova et al. [1]. We assume that the structure of the DHPC/diC₆PC mixtures in high concentration trehalose solutions is a bilayer structure with edge of the disk and that the diC₆PC molecules cover the edge of the DHPC bilayer disk.

![Figure 1 SANS curves of the mixtures of DHPC and diC₆PC in trehalose solution with various concentrations.](image)

References

Neutron scattering study on self-assembly of keratin molecules in water

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The aim of this study is to clarify structural changes of proteins in apoptosis. Once apoptotic trigger is pulled in a hair cell, the cell begins to produce enormous amount of keratin proteins. Then, SS cross-linking is induced between the molecules and keratin proteins are finally gelated. This type of apoptosis is unusual in normal body but often occurs in cancer, AIDS and Alzheimer disease. Keratin fibril consists of 2 types of keratin, i.e., Type I (~45kDa, acidic) and Type II (~56kDa, basic). It is known that keratin assembles spontaneously as dimer, tetramer, octamer, and multimer, and finally forms 10 nm filaments. However, the organization process and structure of keratin in aqueous solution has not been well understood. We also confirmed the presence of keratin multimers in water by SANS measurement. In this study, we synthesized gene-expressed Type I and Type II keratins and chemically modified the cysteine residues to the s-carboxymethyl alanyl disulfide (R-SCH2COO⁻, CMAD), and investigated the structure of keratin proteins in aqueous solution by small-angle neutron scattering (SANS).

SANS was undertaken at SANS-J situated at the end of a cold-neutron guide tube from the JRR-3 reactor. For the present experiment, neutron wavelength \( \lambda = 7 \) Å was used. The distance \( (L) \) from the sample to the two-dimensional position-sensitive detector (PSD) was set at 10 m. We previously measured the keratin solutions (10 mM Tris-HCl buffer solution, pH7) by SNAS. The profiles of Type I and Type II showed a straight line which had a slope of ca. -1 (Fig.1-a inserted in Figure 1). This means that Type I and Type II exist as rod-like molecules. However, we could not observe the self-assembled profile between Type I and Type II. In this study, we added 50 mM NaCl to the buffer to control the electro-static repulsion between CMAD residues and to promote the hydrophobic interaction between them. Figure 1 shows the scattering profiles of Type I and Type II, equal molar mixture of Type I and Type II and the theoretical profile when there are no interactions among them. The scattering intensity profile of Type I and

![Graph](image)

Figure 1. Scattering profiles of Type I and Type II keratins in 10 mM Tris-HCl buffer solution (pH7) containing 50 mM NaCl.

Type II mixture showed the increase of the intensity in the smaller q region and the decrease in the wider q region. This profile was different from that of Type I and Type II respectively, and was also different from the theoretical profile assumed there were not any interactions between them. This result suggested that two types of keratin molecules might self-assemble in the existence of a higher salt concentration without SS cross-linking formation. We are now discussing the structure of keratin protein in various conditions.

Reference
1) F. Ikkai and S. Naito, Biomacromolecules 2001,3(3), 482-487.
2) S.Naito et al., JAERI-Review 2001-005, 14.
Small-Angle Neutron Scattering Measurements of TroponinC on the Thin Filament

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Muscle contraction occurs via sliding of two types of the filaments past each other. These filaments are actin-based "thin" filaments and myosin-based "thick" filaments. The molecular mechanism of the muscle contraction and its regulation is one of the most important problems in biophysics, as it is a typical example of energy transduction mechanisms of living organisms. In vertebrate skeletal and cardiac muscles, muscle contraction is regulated via the interactions between the thin filament proteins, troponin (Tn) C, TnI, TnT, tropomyosin, and actin. These interactions are triggered by binding of Ca²⁺ to TnC. As a first step toward understanding these interactions, we investigated the structure of TnC on the thin filament with and without Ca²⁺.

Neutron scattering was employed to do this. Structural information of a selected component within a protein complex can be obtained with this method, when it is combined with the strategies of selective deuteration and contrast matching. We prepared the deuterated (d-) TnC by expressing the protein in E. coli in D₂O medium containing deuterated algal peptone. The purified d-TnC was exchanged into the native thin filaments by CDTA treatment. The native thin filaments containing d-TnC were then exposed to neutrons under the condition where the contrast of the other components of the thin filaments were matched out with 40% D₂O.

Small-angle neutron scattering measurements of these samples with and without 1.1 mM CaCl₂ were done with the Small-Angle Neutron Scattering Instrument (SANS-J) at the guide hall of the reactor JRR-3M in Japan Atomic Energy Research Institute. Neutrons with the wavelength of 6.5 Å(Δλ/λ = 12.98%) were employed. Figure 1 shows the extracted scattering curves of d-TnC on the thin filaments with and without Ca²⁺. These curves showed distinct changes with and without Ca²⁺, indicating that there are conformational changes of TnC on the thin filaments.

![Figure 1: The extracted neutron scattering curves of d-TnC on the thin filaments with and without Ca²⁺.](image)

Since these curves were obtained from the samples of the very high concentration (the concentration of the thin filament was about 160 mg/ml), a simple analysis, such as the analysis by the Guinier plots, to derive the radius of gyration of d-TnC cannot be applied. Analysis of these scattering curves by model calculation is now underway. Supported by Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology, the Japanese Government.
Analysis of the Muscle Structure from Neutron Fiber Diffraction Measurements Using the Contrast Variation Method

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One of the important features of neutron scattering is that it is relatively easy to do the contrast variation measurements by changing D_2O content in the solvent. The contrast variation method is applicable not only to neutron solution scattering, but also to low-resolution neutron crystallography and neutron fiber diffraction as well. We have explored the possibilities of neutron fiber diffraction combined with the contrast variation measurements. We measured the neutron fiber diffraction patterns of frog sartorius muscles under the relaxed state where no tension of the muscle is produced, in various D_2O concentrations. It was shown that under both states, there were reflections having different matching points, indicating that there is a variation of the scattering length density in the unit cell of the muscle structure. Calculation of the projected density map of the unit cell to the plane perpendicular to the axis of the muscle, using the equatorial reflections showed that it was possible to select the correct neutron phase of these equatorial reflections. The maps using this correct phase combination showed that the (projected) density of the thick filament region and that of the thin filament region are different.

We also performed similar measurements of the muscles under the rigor state where the myosin heads bind tightly to actin, and found that the contrast dependence of the scattering amplitudes of the observed reflections was similar to that under the relaxed state.

Here we performed again the contrast variation measurements of muscle under relaxed state to measure particularly the intensities of meridional reflections. These reflections arise from the muscle structure projected to the axis of the muscle. The measurements were done with the Small-Angle Neutron Scattering Instrument (SANS-J) at the guide hall of the reactor JRR-3M in Japan Atomic Energy Research Institute. Figure 1 shows the diffraction patterns of muscle under the relaxed state in H_2O and D_2O. The meridional reflections up to 5th order can be observed. The analysis of these patterns is now in progress. Supported in part by Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology, the Japanese Government.

![Figure 1: Neutron fiber diffraction patterns of frog sartorius muscle in (a) H_2O and in (b) D_2O. The axis of the muscle is horizontal.](image)

References


原子炉: JRR-3M 装置: SANS-J(C3-2) 分野: 中性子散乱(生物)
Enzymes have their specific activities to produce "products" from "substrates." To study molecular mechanisms of functions of the enzymes, it is important to study the structures of the complexes formed by the enzymes and the substrates. Particularly, since hydrogen atoms may play essential roles in enzyme activities, it is important to know the structure of the enzyme-substrate complex including the hydrogen atoms. Neutron crystallography, which can locate the hydrogens, is one of the important methods to investigate these problems.

Lysozyme has a $\beta(1 - 4)$ glucosaminidase activity with the ability to hydrolyze a mucopolysaccharide component of some bacterial cell walls releasing N-acetyl amino sugars derived from glucosamine and muramic acid\(^1\). As a model of the enzyme-substrate complex, we prepared a complex of hen egg-white lysozyme (HEWL) and tri-N-acetylgalactosamine (NAG$_3$). NAG$_3$ is one of the competitive inhibitors of HEWL, and can be regarded as a substrate analogue. Crystals of HEWL-NAG$_3$ complex were prepared by co-crystallization\(^3\). A solution containing 30 mg/ml HEWL in 50 mM sodium acetate (pH 4.3) in D$_2$O was mixed with a solution containing NAG$_3$ and NaCl to make 1:1 complex of HEWL and NAG$_3$. Crystals were formed in about two weeks, and the crystals grew only to the size of about 3 mm$^3$. The sizes of the crystals were significantly smaller than those of the crystals of HEWL without NAG$_3$\(^4\),\(^5\).

One of the crystals was set to measure the diffraction patterns with BIX-2\(^6\). The space group of the crystals was $P4_12_12_1$, and the cell parameters were $a = b = 7.91$ nm, $c = 3.66$ nm. The oscillation method of 0.4 degrees has been employed. Figure 1 shows an example of the collected diffraction patterns of the crystal of HEWL-NAG$_3$ complex. Diffraction spots of at least 0.25 nm resolution have been observed. Exposure time per one frame has been 24 hours. Since the size of the crystal was small, the more exposure time was needed per a frame than the cases of HEWL. The resolution of the diffraction was also worse, presumably because the presence of NAG$_3$ made each molecule in a crystal more disordered. So far, the data of 20 degrees of rotation range were collected, and the data collection is currently underway.

Figure 1: An example of Neutron diffraction patterns of the crystal of HEWL-NAG$_3$ complex. Exposure time per one frame has been 24 hours.

References
Neutron diffraction experiments of fully deuterated B-DNA crystal

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The neutron diffraction is a very powerful method to determine the detailed structure of biological materials including hydration and hydrogen positions. We are trying to solve the structure of B-DNA duplex by using the neutron diffractometer BIX-3 with a large single crystal of fully deuterated B-DNA decamer (CCATTAATGG). In a neutron diffraction experiment, in order to avoid the high background coming from the incoherent neutron scattering of hydrogen atoms, DNA sample was synthesized by fully deuterated nucleotides and crystallized in D$_2$O solution. A large single crystal was obtained by using the phase diagram information for MgCl$_2$-DNA systems at 6°C for 2 months, in which the size of obtained crystal was $2.0 \times 2.0 \times 0.3$ mm. To measure this crystal by BIX-3, we developed the crystal cooling device.

Fig.1 shows a preliminary neutron diffraction pattern of DNA crystal by use of the crystal cooling device. The exposure time was 4 hours. The wavelength of the incident neutron beam was 2.33Å. The insert shows a used crystal.

Fig.2 shows a scheme of the crystal cooling device which consists of two component parts. Cold dry air, which was obtained from a low temperature circulator (-20°C), cooled the whole of the sample capillary. To prevent the condensation on the surface of sample capillary, the cold gas stream is coaxially surrounded by a little warm and dry stream of air (~10°C). By using this device, the temperature of sample position was kept at 6±1°C for a long time measurement (more than 2 weeks).

The collection of a complete data set of Bragg reflections is presently scheduled.

Fig.1 A preliminary neutron diffraction pattern from the grown single crystal. The exposure time is 4 hours. The insert shows a used crystal.

Fig.2 The developed crystal cooling device for the neutron diffractometer BIX-3.

References
Neutron Crystallography of Human Lysozyme

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The most important information from neutron crystallography is that of hydrogen atoms and hydration waters at physiological temperatures. Wild-type human lysozyme (MW 14,700) was selected for our neutron structure determination because it has been studied by many other biophysical methods as one of the most typical examples of stable globular proteins. The activity of human lysozyme is hydrolysis of polysaccharides.

Human lysozyme was obtained using high-yield yeast strain, *Pichia pastoris*. Crystals for neutron experiment were grown in D\(_2\)O-based buffer solution at 20 °C. The size of the single crystal used for the neutron structure determination was 3.0 mm \(\times\) 1.0 mm \(\times\) 0.7 mm. Diffraction data were collected with the monochromatic neutron diffractometer BIX-3 equipped with a neutron imaging plate at room temperature. The total measuring time was 55 days. Crystal shows no degradation even after the relatively long measuring time.

The neutron diffraction data have been analyzed up to 1.8 Å resolution. R-factor was 19.7% (R\(_{free}\) = 23.57%). Number of H atoms determined was 955. Number of hydration waters determined was 55. H/D exchange ratio for each amide proton was obtained. In the obtained lysozyme structure, we observed many hydrogen bonds and hydrogen atoms even on the terminal methyl groups of the buried hydrophobic residues. Human lysozyme has many basic amino acids, 14 arginines and 5 lysine residues in the relatively small number of amino acid residues, 130. Those bulky residues are positively charged at the pH condition of 4.3 for the diffraction experiment. Deuterium atoms were well-observed when the deuterium atoms of ND\(_3\) groups form hydrogen bonds with negative charges like carboxyl groups both on main and side chains.

Regarding to intra-molecular interactions, deuterium atoms in one arginine and 3 lysine residues form hydrogen bonds with negatively charged residues existing on some secondary structures far along the primary structure. These hydrogen bonds make two helixes interact or a loop region clip on a stable secondary structure. Hydrogen and deuterium atoms in such residues are well-observed in the nuclear density map.

On the other hand, 5 of the 14 arginine residues and 2 of 5 lysine residues form direct hydrogen bonds with neighboring lysozyme molecules in the crystal. Also in these cases, many hydrogen and deuterium atoms in those residues were clearly observed in the nuclear density map.

After deionization, protein was freeze-dried and used for the following crystallization.
High population of these large and flexible residues may contribute to the high solubility of the protein and also to the relatively easy crystallization of lysozyme molecule.

The authors tried to re-adjust an EBP-Si monochromator for BIX-3, which was 2 plates of 5 mm thickness, by the incident beam width of 20 mm with \( \theta \) of 22 deg, but the gain factor compared to single plate was only 1.1. After checking many points, the authors found the possibility that the bender iron holders might shield incident and reflected beam. From an experiment as Fig. 1, the maximum loss of intensity was about 20 %.

Reference

1. Neutron Scattering  7) Fundamental Physics
   Neutron Optics
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Echo Condition in Time Beat Neutron Spin Interferometry

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1 Research Reactor Institute, Kyoto University, Kusumagawa, Senmon-cho, Ono-shi, Osaka 590-0084, Japan

§1. Introduction

Neutron resonance spin echo method (NRSE) has been developed by Gähler and Golub et al.,\(^1,\)\(^2\) where spin echo phases are created by radio frequency (RF) flippers. As a modified version of NRSE, they apply the echo of time beat for a TOF neutron spectrometer, MIEZE instrument.\(^3,\)\(^4\) In the MIEZE spectrometer the sample is downstream of the analyzer leaving the signal indifferent to magnetic field and spin flips in the sample. Following their principle, we have developed neutron spin interferometry using these radio frequency flippers.\(^5-7\) In this paper we have firstly demonstrated the difference of time beat depending on the positions of neutron spin depolarizer.

The time beat of neutron intensity at detector position is created by the coherent superposition of the same spin eigenstates of neutrons with different energy states, which are produced with two radio-frequency flippers and polarization analyser.

![Diagram](https://via.placeholder.com/150)

Fig. 1. Arrangement of a time beat neutron spin interferometer with RF spin flippers. The splittings in total energy are given by the exchange of quanta with energies \(\omega_1, \omega_2, \omega_3\) by RF flippers.

§2. Quantum beat

A simple cold neutron spin interferometry using radio frequency flippers (RF flipper) is shown in Fig. 1, which is similar to the MIEZE spectrometer.

A time beat neutron spin interferometer with RF spin flippers which is installed in C3-1-2 cold guide, JRR-3M, JAERI. These RF flippers consists of two coils, that is, one creates a magnetic field \(B_z\) parallel to the quantized axis and another one creates an oscillating field \(B_d(t)\) perpendicular to the quantized axis. Assuming the resonance condition for the RF flipper and expressing the oscillating field as \(B_d(\sin \omega t + \Delta)\), the frequency of the oscillating field, \( \omega \) is given by,

\[
\hbar \omega = 2 \mu B_d
\]

where \(\mu\) is the neutron magnetic moment. The RF flippers function as \(\pi/2\) and \(\pi\) when the amplitude \(B_d\) satisfies Eqs. (2.2) and (2.3), respectively,

\[
\frac{l}{v} (\mu B_d) = \frac{\pi \hbar}{2}
\]

\[
= \pi \hbar
\]

where \(l\) is the length of the RF-flipper and \(v\) the neutron velocity.

We consider the case of the following conditions as regards the magnetic fields of the system,

\[
B_{z,1} = B_{z,2} = B > B_{z,3} = B_y
\]

where \(B_{z,i}\) are the magnetic field in z axis of the \(i\) th RF flipper and \(B_y\) the guide field, respectively. The three RF flippers function as \(\pi/2, \pi\) and \(\pi/2\) in turn.
polarized neutron is split into the two spin eigenstates with energy difference with $\hbar \omega_0$ by the first RF $\pi/2$-flippers. The spin state and energy difference of these partial waves are reversed by the second RF $\pi$-flippers. The third $\pi/2$-flipperv supersplits into two $\uparrow$ and two $\downarrow$ spin neutron states which can be selected by analyser to give two $\uparrow$ spin states with different energy, giving rise to quantum beat of neutron intensity.

The time beat of neutron intensity at the detector position at $t_d = t_0 + t_1 + t_2 + t_3$ is given by Eqn (2.5). Here $t_0$ is the time when the neutron is incident on RF $\pi/2$-spin flipper, and $t_1$ is given by $L_1/u$.

$$|\psi_0(+)|^2 = \frac{1}{2} + \frac{\cos[(2\omega_{l_3} - \omega_{l_1})L_3 + \Delta_0 + \Theta]}{2}$$

where the effect of $B_y$ is neglected and the wavelength dependent phase is given by

$$\Theta = -\frac{(\omega_{l_1}L_1 - (2\omega_{l_2} - \omega_{l_3})(L_2 + L_3))}{u}$$

where $L_1$ the length between the first and second RF flippers, $L_2$ the length between the second RF flipper and the sample, $L_3$ the length between the sample and the detector. The phase difference by the momentum difference, which is in quite analogous situation to the Larmor precession. Accordingly, this term induces a phase dispersion depending on the velocity resolution of the incident neutrons. Condition $\Theta = 0$ is required in order to observe the interference pattern with high visibility.\(^{6,9}\)

This condition is equivalent to the time focussing in the MIEZE spectrometer by Gähler et al.\(^{2,10}\)

Figure 2 shows a typical time dependent interference pattern with frequencies of 100, 330 and 400 KHz using a fast time analyser.

These figures show that the time beat appears as a function of the neutron detection time $t_d = t_0 + t_1 + t_2 + t_3$ with frequency $2\omega_{l_3} - \omega_{l_2}$.

Consequently we would observe a time interference in the time spectra. We should note that the time beat only appears at the position of the time echo where detector should be located. The positional dependence of the visibility of oscillating time spectra is shown in Fig. 3.\(^{11,12}\) Here we have recognized for the high frequency time beat, half width of the beat visibility at detector position is only ±1cm. So detector should be very thin such as a LiF solid scintillator of which thickness is below than 0.5mm.

**Acknowledgements**

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8) D. Yamasaki, private communications.
We have made three improvements for our Mieze spin echo method using RF flipper[1] with regards to neutron intensity, a new RF flipper applicable to pulsed neutron source and precise polarization control of a neutron beam.

The bender system at C312 port supplies neutrons to beam ports of three channels called CH1, CH2 and CH3 [2]. Neutron intensities increase by about 3 times by replacing the supermirror of the bender with new 3Q supermirrors, which is supported by NOP. Typical parameters and neutron intensities for the three channel beam ports are summarized in Table 1 [3]. The new resonance spin echo system of Mieze type is installed at CH2, which supplies neutrons with wavelength longer than 8.2 Å.

Table 1: Three channel beams at C312 port and typical parameters of the three channels.

<table>
<thead>
<tr>
<th>Beam port</th>
<th>CH1</th>
<th>CH2</th>
<th>CH3</th>
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<tbody>
<tr>
<td>Bent angle</td>
<td>14.5</td>
<td>24.1</td>
<td>35.1</td>
</tr>
<tr>
<td>Intensity</td>
<td>$3.0 \times 10^6$</td>
<td>$1.0 \times 10^6$</td>
<td>3000</td>
</tr>
<tr>
<td>Beam size</td>
<td>42×8</td>
<td>42×7</td>
<td>42×3</td>
</tr>
<tr>
<td>Wavelength</td>
<td>&gt;7.2 Å</td>
<td>&gt;8.2 Å</td>
<td>8.8 Å</td>
</tr>
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</table>

Neutron intensity reduction in the Mieze spectrometer caused by the long traveling would be prevented by a short neutron guide tube, which is set between the first and second RF flippers.

Radio frequency(RF) flippers applicable to wide band neutrons from pulsed source have been developed [4]. Resonance spin echo methods including the Mieze type will be suitable for a pulsed neutron source, replacing the conventional RF flippers with the new RF flippers.

A precise method of neutron polarization control has been developed from the viewpoint of magnetic mirrors and a spin flipper. We obtain a high neutron polarizability of 0.98. Using this polarization technique we can develop an interesting TOF method with spin flip chopper[5]. A TOF data in CH2 beam port at C312 port is shown in Fig. 1. The flight path length and pulse width are 2.0 m and 500 μsec, respectively. Neutron counts in the background region are about 77/CH averaged over 20 channels. Unique performance of spin flip chopper is that the pulse characteristics is controlled by electric circuit.

We are going to make two preliminary applications using this spin echo method to two scattering phenomena. They include neutron inelastic reflection from a polymer with lamellar structure and incoherent inelastic scattering by hydrogen atoms.

References
The authors have established a new type of cold-neutron interferometer based on a pair of etalons coated with multilayer mirrors. Neutron interferometry is a powerful technique for studying fundamental physics. A large dimensional interferometer for long wavelength neutrons has the advantage to increase the sensitivity to small interactions. Though such a kind of interferometer was realized by using multilayer mirrors[1], the range of experimental application was limited due to the small spatial separation between the two coherent beams.

We used etalons in order to enlarge the spatial separation between two parallel waves in neutron spin interferometer[2]. The present interferometer consists of several neutron optical components; a neutron polarizer, π/2 spin flipper coil, π spin flipper coil, phase-shifter coil, π/2 spin flipper coil, a spin-analyzer mirror, and a pair of etalons (Figure 1). By depositing neutron multilayer mirrors on the parallel planes of an etalon we can produce an optical component which divides the incident neutrons into two parallel paths. And then the two paths are recombined after the reflection off the second etalon. Using etalons with an air gap of 9.75μm in spacing we have observed interference fringes with the contrast of 60%. The experiment was performed using the cold neutron beam line ‘MINE’ at the JRR-3M reactor in JAERI. The beam had a wavelength of 8.8Å and a bandwidth of 2.4% in FWHM. In the viewpoint of geometrical optics the pair of etalons is equivalent to a Jamin interferometer, which is the oldest type of interferometer of visible light.

The present results have demonstrated the feasibility of developing a cold neutron interferometer with a large path separation to carry out high precision measurements and new types of experiment.

References

Figure 1: Experimental setup of the interferometer and an interferogram.
Neutron Diffraction Measurement of Residual Strain of Partial Penetration Welds for ITER Vacuum Vessel

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The vacuum vessel (VV) of ITER is a double-walled "doughnut" structure made of stainless steel SS316L with D-shaped cross section. The development of the partial penetration welding by through-wall electron beam welding (EBW) is carried out for the T joint of the outer shell (40-60mm plates) and the rib, because it has advantage from distortion and cost points of view. In this study, neutron diffraction measurement of residual strain of this new welding had been carried out in order to investigate an applicability of the welding to the VV. The configuration of weld and the measurement positions of residual strain are shown in Fig. 1. RESA (Neutron Diffractometer for REsidual Stress Analysis) in the JRR-3 is used for the measurement. Major issue of this measurement is to obtain sufficient neutron intensity within practical exposure time, because the test piece is thick. The neutron intensity was obtained during measurement of strain in two directions. The test condition and results are shown in Table 1 and Fig. 2, respectively. The exposure time of each step is 10 min. These results show that the neutron intensity of measurement in toroidal direction is enough high. But in poloidal direction, the intensity was less than 1/10 of that in toroidal direction. This is because the path-length-difference. The path length of measurement in toroidal direction was about $\sqrt{2} \times 5$ mm but it will be the same as poloidal measurement when the measurement depth is 40 mm (full-depth). It can be concluded that the slit of $3 \times 3$ mm was too small to obtain sufficient intensity or an exposure time of 10 min was too short. Further survey to find practical test parameter is required.

Figure 1: The configuration of weld specimens and the measurement positions

Table 1: Test conditions

<table>
<thead>
<tr>
<th>Structure</th>
<th>Wave length (Å)</th>
<th>Slit (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC (220)</td>
<td>2.09989</td>
<td>3W x 3H</td>
</tr>
</tbody>
</table>

Figure 2: Obtained neutron intensity
Strain Measurement in Laser Peened Stainless Steel

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Shot peening treatment has been widely adopted to improve the surface properties such as hardness and strength. Recently, a new technique for the surface treatment was developed by using pulse laser. The laser peening is a promising new technique for the surface treatment of the reactor internals in light water reactors.

In the present study, strain distribution in a stainless steel SUS316NG treated by the laser peening was measured by neutron diffraction method.

The 0.2\% proof strength and the tensile strength of the material are 279 MPa and 572 MPa, respectively. The specimen was peened by pulsed laser after annealing at 900 °C for 30 min. The energy, beam diameter and number of pulse were 200 mJ, 0.8 mm and 3600 pulse/cm\(^2\).

The neutron diffraction from Fe 111 was used for strain measurement. The wave length used was 0.20955 nm. The slit used was 0.35 mm in width and 10 mm in height. The direction of the lattice strain measured was x, y and z direction as shown in Fig. 1. The arrows indicate laser path.

Figure 2 shows the change of strain with depth from specimen surface. The strains of x and y direction near the surface is compressive. The compressive strain in both direction increases with depth. When the depth is larger than about 1mm, the strain becomes nearly constant.

---

Fig. 1. Coordinate.

Fig. 2. Change of strain with depth.
Residual Stress Measurement and Verification of Quenched Steel
Based on Neutron Diffraction Method and Numerical Analysis

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Introduction
Many measurement methods of residual stress have been developed in industry technology such as X-ray diffraction, rapid drilling, ultrasonic method and so on. These techniques have only capability to measure residual stresses near the surface of machine parts. Recently, neutron diffraction method has been developed to measure the residual stress of materials. One of main peculiarities of neutron diffraction is the capability to measure residual stresses in inside of materials. Using the neutron diffraction technique, many researches for measuring of residual stress in inside space have been carried out and its effectiveness has been verified. From results of some research, we can know measurement of the standard lattice spacing of strain-free materials \(d_0\) is very important to increase measuring preciseness and reliability. However, in manufacturing process incorporating temperature history and microstructure variation, complex thermal mechanical behavior results in macro and micro residual stresses and phase transformation as well as texture in materials. When each material point or different area after manufacturing has different microstructure, the measurement and analysis of residual stresses will be difficult, so that it is an open problem and important object how to determine the standard lattice spacing \(d_0\) of strain-free materials to different structures, in which the micro-residual stresses due to variation of phase transformation are main source of internal stress in materials.

This paper presents the measurement with neutron diffraction method for evaluating the residual stresses of quenched steel with large phase transformation. The influence of microstructure due to phase transformation during quenching process on standard lattice spacing \(d_0\) was given. The measurement accuracy is verified by comparison between simulated values of the residual stresses with measured results by XRD and neutron diffraction.

Measurement Method of Residual Stress
Measurement method based on neutron diffraction. Figure 1(a) presents the schematic of neutron diffraction equipment, which was installed in the thermal neutron guide tab T2-1 port of JRR-3M reactor in JAERI. For precise stress analysis, standard lattice spacing of strain-free materials \(d_0\) must be accurately measured and estimated. Powder diffraction method is a general way of determining the parameter \(d_0\). However, for engineering materials especially those involving large plastic deformation or phase transformations often have preferred crystallographic orientation or non-homogenous distribution of phase or composition, the measured \(d_0\) by powder diffraction method could not coincide with the true original lattice spacing of the material with variable phase and texture. In this measurement, we performed a technique proposed by Minakawa to estimate the \(d_0\) from the measured average lattice space by rotating specimen method shown by Fig.1(b). Rotation target is used to increase the gains contributing to the diffraction peak in different directions. In this way, an average result of lattice strain could be obtained to eliminate the influence of textures and crystal direction formed in materials processing. The residual strains were measured in three mutually perpendicular directions in which were the expected principal axes. Follow equations give the principles for stress measurement with neutron diffraction method by measuring Young's modulus from tensile test and initial lattice spacing \(d_0\).

\[
\sigma = \frac{E}{(1 + v)(1 - 2v)} \{\varepsilon + v(\varepsilon_x + \varepsilon_y)\} \\
\lambda = 2d_0 \cdot \sin \theta \\
\varepsilon = \frac{d - d_0}{d_0} = -\cot \theta \Delta \theta \\
\]

Here, \(E\), \(v\), and \(\sigma\) indicate young's modular, Possier's ratio and principle stress, respectively. \(\lambda\), \(\theta\), and \(\varepsilon\) indicate the...
wavelength, neutron beam angle and the strain on crystallographic plane, respectively. $d_0$ and $d_0'$ are the interplanar spacing and standard lattice spacing of strain-free materials, respectively. For the measured specimen of S45C carbon steel material, strains on (110) and (200) crystallographic plane were measured in neutron diffraction. Residual stresses are calculated from measured strains using diffraction elastic constants measured experimentally.

Specimens for tension test A round disk with 30 mm diameter and 10 mm thickness were used in residual stresses measurement. The specimens of S45C carbon steel were measured before and after heat treatment by quenching in water. The quenching process is heating at $850^\circ$C for one hour and then cooling in $20^\circ$C water.

Measurement method based on X-ray method The stress filed in the quenched parts under examination is usually assumed to be two dimensional with $\sigma_x$ and $\sigma_y$ as the principal stresses in the surface. In the direction $\Phi$ on the plane of the sample can be calculated directly from the slope by the sin$^n$ method. According to the Bragg’s law, the X-ray measured strain can be represented by a relative change in the interplanar spacing of specified crystal planes to define wavelength $\lambda$, the initial lattice spacing $d_0$ and lattice constant $a_0$ in the unstrained or stress-free condition, respectively, whilst $d_{0}$ and $a_{0}$ are those for the stressed condition in the planes perpendicular to the direction $\psi$, and 20 corresponding diffraction angles of the plane. It is already known that the stress-free lattice spacing can be roughly estimated at a definite $\Psi^*$ position where the measured strain is always zero.

Measured and Simulated Results
The measured $d_0$ in (110) and (200) plane of the tensile specimen before and after water quenching are given in Table. 1. It is obvious that the lattice spacing of strain free material in different positions is different. Due to the non-homogeneous distribution of martensite from surface to center for a quenched disk, the initial lattice space decreases a little from surface to center. This result confirmed that the initial lattice space varies as the material phase changes.

From the measured $d_0$, the strain of lattice could be determined. From the measured stress train curve in tensile test, elastic constants including Young’s modulus and Poisson’s ratio were obtained and also listed in Table 1. The residual stresses were calculated from the above parameters.

Based on metallo-thermo-mechanical theory, finite element simulation on quenching process of disk are carried out with the same size of the disk model. Under three types of heat transfer coefficient boundaries, the simulated results were given [3]. Comparison of residual stresses on the surface of specimens based on neutron diffraction measurement and thermo-mechanical simulation as well as X-ray method is presented in Fig. 2.

![Fig. 2 Comparison of the measured residual stresses with computed values](image)

Summary
Neutron diffraction studies has been conducted to ascertain the level of residual stresses in heat treated disk. Results of these experiments indicates that changes in lattice parameters associated with heat treatment may be attributed to phase transformation and microstructure change in the materials. The results of the simulation were compared with measured residual stresses based neutron diffraction and X-ray methods. From these results, we obtained some useful conclusions:

1. From the results in research, we can know that effect of the standard lattice spacing $d_0$ of strain-free materials on residual stresses measurement was very large, so it is important to determine micro-residual stress due to distribution of microstructure after quenching process.
2. The distribution of residual stresses near surface agrees well with calculated value, when $d_0$. Young’s modulus and Poisson’s ratio can be measured by using quenched tensile specimen with enough small size and almost same distribution of micro-structure, such as martensite.
3. The measured residual stresses confirmed the micro-residual stresses generated due to variation of phase transformation are main source of internal stress in materials of heat-treated parts.

References
Evaluation of Fatigue Damage in SiC Particulate
Reinforced Aluminum Alloy by Neutron Diffraction

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Structural materials fracture when they are subjected to cyclic loading, even if the load is less than the static strength. This phenomenon is known as fatigue failure. For engineering components, clarification of fatigue properties and development in inspection procedures to detect fatigue damage are very important to obtain a good reliability.

In this study, the neutron diffraction method was used to measure the change of the phase strains of the composite during the fatigue process.

The materials used were aluminum alloy reinforced by silicon carbide particles (SiCp/Al 2024). The volume fraction of SiC particles of the composite is 20% and their average size is 3µm. The 0.2% proof strength is 465 MPa and the tensile strength is 625 MPa. The neutron diffractions from Al 200 and SiC 116 were used for stress measurement.

Figure 1 shows the change of the slope of the relation between applied stress and measured strain obtained from Al200 diffraction. The slope increases with stress cycles. On the other hand, the slope obtained from SiC116 diffraction decreases with stress cycles as shown in Fig. 2. Debonding of the interface between the matrix and the particle was initiated during fatigue process. The strain in the SiC particles was reduced by the debonding. The specimen was broken at N=7500 cycles.

Fig.1. Change of slope in Al phase.

Fig.2. Change of slope in SiC phase.
Feasibility study on nondestructive measurement of residual stress profile in carburized bearing rings using neutron diffraction method

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Feasibility study on nondestructive measurement of residual stress profile in carburized and quenched bearing rings was carried out using neutron diffraction apparatus, RESA at JRR-3M.

The measurement condition is as follows, λ=0.2098885nm, diffraction plane=(110), diffraction angle range (2θ)= 60.5 - 64 degree, slit for incident beam=2mm×2mm, measurement depth=0, 2, 4, 6, 8, 12mm from outer surface. The test sample was SAE9315 carburized and quenched ring, size of which was φ160, φ136 and 50mm in O.D., I.D. and width. No strain d0 was measured with random rotation method using each depth cubic sample cut from above measured ring.

Figure 1 shows the apparatus and actual measurement. Figure 2 shows result of axial residual stress measurement. The strain values are all positive and no significant difference is found between the surface and core. This means that the residual stress of surface layer in carburized steel ring is tensile although it has normally compressive residual stress. Figure 3 shows that the residual stress of surface layer in axial direction is actually compressive with X-ray measurement method. The result different from the forecast was obtained in this measurement. To develop the measurement analysis technique of quenched steel in the future is important. Neutron diffraction method is attractive for residual stress measurement because of non-destructive measurement.

Figure 1 Neutron diffraction apparatus and actual measurement.

Figure 2 Profile of axial residual stress in bearing ring measured by neutron diffraction method.

Figure 3 Residual stress of surface layer in axial direction measured by X-ray diffraction method.
Residual strain of W/Ta Joint Material for Spallation Neutron Source

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Residual strain near the boundary of Tungsten and Tantalum was measured. Both materials are candidate for a target of spallation neutron source. Tungsten has a good neutron yield as a solid target; however, a disadvantage for usage is brittleness due to irradiation by protons and neutrons, and a corrosive property in water under radiation. So Tungsten is recommended to be cover with cladding material. Tantalum has also a high atomic number so that good material for target except for a high atomic density decaying heat. The property of Tantalum had shown remarkable a loss of ductility after proton bombardment but recently a different data was disclosed from Julich Laboratory. They examined a spent target of ISIS and concluded that Tantalum, which received a damage of 13-dpa, had enough ductility to use as target. The reason is hinted to high purity in chemical composition. So the idea is to make Tantalum -cladded Tungsten target. We chose a HIP, Hot Isostatic Pressing, process to joint them together.

The size of solid target is 55x28x76mm. The thickness of cladding tantalum is less than 1mm. This is a real size suitable for KENS target at KEK. The preferable condition for HIP was to avoid re-crystallization of Tantalum in the deeper diffusion length of Tantalum into Tungsten and was found to be 200MPa in press at 1500°C during 3 hrs. Target blocks were manufactured, examined by non-destructive inspection. We found no gap between HIPped boundary by means of ultra-sonic microscope.

This study aims at examining the residual stress near the boundary jointed by HIP. The
Tantalum into tungsten is expected to be 4 μm as shown in Fig. 2.

The residual strains were measured by RESA. Preparation was done by Measurement of the wavelength of incident beam, Determination of center of distributed incident-beam intensity, and Measurement of powder diffraction of both materials. The strain-free lattice length at (110) was decided to be 2.239602×10⁻¹⁰ m for Tungsten and 2.336669×10⁻¹⁰ m for Tantalum, respectively.

Figs. 3 and 4 show strains to the component of radial direction and hoop direction, respectively. It is found that near the jointed boundary all of measured strain components showed tension varied in 1000 to 5000×10⁶.
1. Introduction

Fiber reinforced materials have found considerable applications in the improvement of the performance characteristic on engineering materials. However, there is a large difference in the thermal expansion coefficient between the matrix and the fiber. The main cause of thermal stress in such composites is the thermal expansion mismatch between the matrix and the fiber. In this study, the thermal residual stress in the continuous tungsten fiber embedded in the copper matrix was measured by the neutron diffraction method.

2. Conditions of the Neutron Stress Measurement

The specimen used in this investigation is tungsten-fiber (100μm in diameter) reinforced copper composite. This composite was produced by a unidirectional solidifying method. The volume fraction of the tungsten fiber is about 10%. This specimen was annealed at 973K for 2 hours before stress measurement. The thermal residual stresses due to the difference of the coefficient of thermal expansion between the matrix and the fiber were generated in the composite.

Figure 1 shows the coordinate system of this composite. The axes $x_1$ and $x_2$ are parallel to and $x_3$ axis is normal to the specimen surface, with $x_1$ axis being defined as parallel to the fiber direction. The angles $\varphi$ between the $x_1$ axis and the $x_2$ axis are defined as shown in Fig. 1.

Table 1 shows the conditions of neutron stress measurement. The stress-free lattice spacing of each {hkl} was measured from the bundled tungsten-fiber specimen annealed at 973K, by using the rotating sample attachment.

<table>
<thead>
<tr>
<th>Measurement apparatus</th>
<th>RESA in JAERI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron wave length $\lambda$, nm</td>
<td>0.209783 nm</td>
</tr>
<tr>
<td>h k l plane and initial lattice spacing $d_0$, nm</td>
<td>W(110) $d_0 = 0.223807$</td>
</tr>
<tr>
<td></td>
<td>W(200) $d_\varphi = 0.158214$</td>
</tr>
<tr>
<td></td>
<td>W(211) $d_\varphi = 0.129151$</td>
</tr>
<tr>
<td>Diffraction angle, deg.</td>
<td>W (110) $2\theta = 55.9$</td>
</tr>
<tr>
<td></td>
<td>W (200) $2\theta = 83.0$</td>
</tr>
<tr>
<td></td>
<td>W (211) $2\theta = 108.6$</td>
</tr>
<tr>
<td>Young's modulus $E$, GPa</td>
<td>402.7</td>
</tr>
<tr>
<td>Poisson's ratio $\nu$</td>
<td>0.28</td>
</tr>
</tbody>
</table>

In this study, two types of neutron stress measurement method were used to investigate the thermal residual stress in the fiber phase of the Cu/W composite. The one is the usual triaxial measurement method by using Hopke's equation, and the other is the $\sin^{2}\varphi$ method which is commonly used in X-ray stress measurement with the assumption of the plane stress condition. The fundamental equation of $\sin^{2}\varphi$ method is given by the following equation:

$$
\sin^{2}\varphi = \frac{E}{\rho} \frac{d_0}{d_\varphi} \frac{d_\varphi}{d_0} \frac{E}{\rho} \frac{d_0}{d_\varphi}
$$
\[
\varepsilon_{\nu} = \frac{1 + \nu}{E} (\sigma_{11} - \sigma_{33}) \sin^2 \psi + \frac{1 + \nu}{E} \sigma_{33} - \frac{\nu}{E} (\sigma_{11} + \sigma_{22} + \sigma_{33}).
\] (1)

If the plane stress condition is held in the sample, we can regard as the stress \(\sigma_{33} = 0\). Thus, this equation means that \(\varepsilon_{\nu}\) linearly relates against \(\sin^2 \psi\), and the longitudinal stress \(\sigma_{11}\) is determined from the slope of the \(\sin^2 \psi\) diagram. However, when the stress component of \(\sigma_{33}\) cannot be ignored, the \(\sin^2 \psi\) method leads to the result in the stress value of \(\sigma_{11} - \sigma_{33}\).

3. Results of Neutron Stress Measurement

Figure 2 shows the relationship of the neutron diffraction intensity of three types of hkl plane against \(\psi\) tilt angle. From this result, it is obvious that the tungsten fiber has a heavy 110 texture along its longitudinal direction. Therefore, the specimen must be adequately tilted for the measurement of \(\sin^2 \psi\) method.

![Graph showing the relationship between neutron intensity and tilt angle](image)

**Fig. 2: Diffraction intensity of three (hkl) planes against \(\psi\) angle by neutron diffraction.**

**Table 2:** Combinations of the \(\psi\) tilt angle between the measurable plane and the 110 oriented plane.

<table>
<thead>
<tr>
<th>Measurable plane</th>
<th>(\psi) tilt angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0, 60, 90</td>
</tr>
<tr>
<td>200</td>
<td>45, 90</td>
</tr>
<tr>
<td>211</td>
<td>30, 54.7, 73.2, 90</td>
</tr>
</tbody>
</table>

Table 2 shows the combinations of the \(\psi\) tilt angle between the measurable 110, 200 and 211 plane in the 110 textured tungsten fiber. All of these \(\psi\) tilt angles were employed in neutron stress measurement by using \(\sin^2 \psi\) method.

Figure 3 show the typical \(\sin^2 \psi\) diagram described the lattice spacing vs. \(\sin^2 \psi\) in 200 plane. Owing to the heavy 110 texture, the measurement result in the point of \(\sin^2 \psi = 1.0\) \((\psi = 90°)\) could not be obtain due to the very weak 200 diffraction. However, the points of the others lie on a line of least square approximate, and this line shows a good linearity in this case. Therefore, the stress in 200 plane might be calculate from the slope of this line by using \(\sin^2 \psi\) method.

![Graph showing \(\sin^2 \psi\) diagram for 200 plane](image)

**Fig. 3: \(\sin^2 \psi\) diagram for 200 plane.**

The results of neutron stress measurement by using the triaxial measurement method as well as the \(\sin^2 \psi\) method are shown in Table 3. From these results, it can be confirm that all of the stress values are compressive, and the longitudinal stress \(\sigma_{11}\) along the fiber takes the maximum value. The stresses for 200 and 211 planes could not be calculated by the triaxial measurement method, because the diffraction peak in \(\psi = 0\) (deg.) did not appear from the tungsten fiber which has a strong 110 texture. On the other hand, the \(\sin^2 \psi\) method gave the stress value from the slope of the \(\sin^2 \psi\) diagram for each plane of 110, 200 and 211. However, we must note that the results from the \(\sin^2 \psi\) diagram lead to the stress value \(\sigma_{11} - \sigma_{33}\) in the triaxial stress state.

**Table 3** Results of neutron stress measurement.

<table>
<thead>
<tr>
<th>Triaxial measurement method (MPa)</th>
<th>(\sin^2 \psi) method (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl (\sigma_{11}) (\sigma_{22}) (\sigma_{33}) (\sigma_{11} - \sigma_{33})</td>
<td>hkl (\sigma_{11}) (\sigma_{22}) (\sigma_{33}) (\sigma_{11} - \sigma_{33})</td>
</tr>
<tr>
<td>110 -467 -219 -150 -268</td>
<td></td>
</tr>
<tr>
<td>200 - - - -215</td>
<td></td>
</tr>
<tr>
<td>211 - - - -209</td>
<td></td>
</tr>
</tbody>
</table>

**References**
1. Neutron Scattering  8) Instrument
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1-8-1 Characteristics of Deuterated Diamond-like Carbon as Neutron Mirror

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Deuterated diamond-like carbon (D-DLC) was fabricated on silicon wafer and the characteristics as a neutron mirror was measured. The UCN confinement experiments need free surface neutron mirrors to confine UCN in an experimental equipment, though neutron mirrors are usually flat. D-DLC was developed to use as a mirror material of UCN bottle for neutron electric dipole moment (EDM) experiment.

Usually, diamond-like carbon is deposited by the radio frequency plasma chemical vapor deposition (RF-CVD). As usual DLC thin layers made by this method contain a lot of hydrogen, D-DLC has been developed with deuterated hydro-carbon as source gas to eliminate hydrogen in the layer. D-DLC has the advantage as neutron mirror because deuterium has the positive potential and the small absorption cross-section for neutrons.

The surface roughness of D-DLC was measured by the scanning white light interferometry. They have the roughness of Ra = 0.3 - 0.6 nm, and are good enough for monolayer mirrors. The neutron reflectivity measurement shows that the critical wavelength of the total reflection is 59.9 - 62.2 nm. It is almost same with that of natural nickel, 58.0nm, which is usually used as a good material of neutron mirrors. The neutron reflectivity is about 1.0 in the total reflection range. These results show that performance of D-DLC as neutron mirror is completely satisfactory.

The measurements of ERDA & RBS show the number densities of elements in D-DLC layers. The number density of carbon is 6.3 - 6.5 x 10²² C/cm³ and that of deuterium is 4.2 - 4.7 x 10²² D/cm³. The density calculated from these numbers is 1.4 g/cm³ and it is a little smaller than that of usual DLC layer. The number density of hydrogen in unit area is 1.4 - 3.2 x 10⁴⁴ H/cm². This is same with the typical numbers of usual neutron mirrors. So D-DLC is not the solution of the surface hydrogen problem of the UCN bottle experiments.

Though D-DLC is not ideal for UCN bottle, it is a promising neutron mirror. It has a good neutron reflectivity with high quality mirror surface and high potential. It also has a possibility of making a free shape mirror, because DLC is already used on complicated surfaces like molds and tools in manufacturing engineering. It will be useful for neutron guide tubes, neutron benders and focusing devices, because they require many kinds of mirror surfaces, for instance, spherical or parabolic surfaces on both sides of very thin substrates.

Neutron Reflectivity of D-DLC
Development of a new spin echo spectrometer using multilayer spin splitters II.

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1 Japan Atomic Energy Research Agency

Modified neutron spin echo (MNSE) methods, in which neutron spin precession is realized other than Larmor precessions, allow us to construct compact NSE spectrometers and hence to combine NSE with other spectrometers. Especially, one of the MNSE methods, Mieze[1], is applicable to measure quasi-elastic scattering accompanying neutron spin-flip process, since in Mieze spectrometer neutron spin echo is realized after spin analyzer. One of the MNSE methods is realized by using the multilayer spin splitters (MSS's), which are composed multilayer consisting of a magnetic mirror, gap layer, and a non-magnetic mirror[2]. When a neutron in a superposing state of magnetic field parallel and anti-parallel states is incident to the MSS, then a phase proportional to the gap layer thickness is introduced since parallel and anti-parallel components are reflected by the different multilayers. The phase shift is equivalent to the Larmor precession angle. The most important feature of the spectrometer is its compactness. In the spectrometer, since Larmor precession magnets are replaced by pairs of multilayer spin splitters, then total size, required electric power are much reduced.

MSS is fabricated with vacuum evaporation system in Res. React. Inst. Kyoto Univ. The magnetic and non-magnetic mirrors consist of permalloy/Ge and Ni/Ti. The d-spacing for both multilayer is 110Å. The gap layer is made of Ge with thickness of 3500Å. The experiments are carried out at C3-1-2 beam port (MINE) of JRR-3M reactor in Japan Atomic Energy Agency. The wavelength of neutron is 12.5Å. The arrangement of the MSS-NSE spectrometer is shown in Fig.1. The incident neutron is set into the superposing state by the polarizer (P) and the first $\pi/2$-spin flipper ($\pi/2$-1). Then it is incident to the pair of MSS in (+) configuration (DMSS1). This configuration is important to deal with the neutrons scattered by the sample, since the phase difference due to the beam divergence is cancel out after the second reflection. The phase introduced by the first pair of MSS's is canceled by the second pair of MSS's (DMSS2) after the $\pi$-spin ($\pi$) flipper. The neutron is detected after the phase analysis with $\pi/2$-2 and spin analyzer (A). To measure the spin echo signal, a phase shifter coil is inserted and the neutrons are counted via the flipper coil current.

The NSE signal for the set-up shown in Fig.1 is presented in Fig.2, and expresses the clear oscillation. In the next step, we are planning to measure the quasi-elastic scattering from some typical samples.

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References


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Figure 1: The arrangement for MSS-NSE method.

Figure 2: NSE signals for the arrangement shown in Fig.1.
Characteristics of Photostimulable Phosphor SrBPO₅:Eu²⁺ for Neutron Imaging

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The neutron imaging plate (NIP) has made a great success in the field of neutron scattering study but the NIP is sensitive to not only neutron but also gamma ray. Therefore, it is difficult to discriminate neutron signal from gamma ray one when the NIP is read out. To overcome the problem, the authors have been studying a SrBPO₅:Eu²⁺ material as a new neutron storage phosphor consisting of light materials.

The SrBPO₅:Eu²⁺ powder sample was prepared by firing raw materials (SrCO₃, H₃BO₃, (NH₄)₂HPO₃, and EuCl₂·6H₂O) in a muffle furnace in a nitrogen atmosphere at 600°C for 2 hours and at 800°C for 2 hours. The authors found that this phosphor shows photostimulated luminescence (PSL) at 390 nm by illumination of 635 nm laser light after neutron irradiation without adding any neutron sensitive materials such as Gd.

Table 1: The neutron and gamma-ray sensitivities (Sₙ and Sγ) of SrBPO₅:Eu²⁺ and BAS-ND

<table>
<thead>
<tr>
<th>items</th>
<th>SrBPO₅:Eu²⁺</th>
<th>BAS-ND</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sₙ</td>
<td>1.66×10⁻²</td>
<td>1.24</td>
</tr>
<tr>
<td>Sγ</td>
<td>3.47×10⁻⁵</td>
<td>2.19×10⁻²</td>
</tr>
<tr>
<td>Sγ/Sₙ</td>
<td>2.09×10⁻³</td>
<td>1.77×10⁻²</td>
</tr>
</tbody>
</table>

unit: Sₙ (PWL/mm²/neutrons), Sγ (PWL/mm²/gamma)

The concentration of Eu in the samples was changed. It can be seen that the total PSL output was proportional to the irradiation time. Results of linear fitting of the data are also shown in the figure. The slope is proportional to the neutron sensitivity. The optimal concentration of Eu in the samples was 2%.

The authors have also investigated the neutron and gamma sensitivities of the SrBPO₅:Eu²⁺ (2%) sample. Table 1 lists measured neutron and gamma-ray sensitivities of samples compared with those of a BAS-ND neutron imaging plate (Fuji film Co. Ltd.), where the neutron wavelength and gamma-ray energy are 0.5 nm and 662 keV (¹³⁷Cs gamma-ray source), respectively. One can see that the neutron sensitivity of the SrBPO₅:Eu²⁺ sample is two orders of magnitude lower than that of BAS-ND, while the gamma-ray sensitivity is three orders lower. These results may come from the fact that the BAS-ND sheet contains Gd atoms which has a very large neutron cross section and consists of relatively heavy materials (BaFBr:Eu²⁺). However, the Sγ/Sₙ ratio of the SrBPO₅:Eu²⁺ sample is ten times better than that of BAS-ND. The low Sγ/Sₙ ratio is favorable for reducing the gamma-ray influence on the signal.

Figure 1 shows the total PSL output as a function of the neutron irradiation time when the concentration of Eu in the samples was changed.

Figure 1: The total PSL output as a function of the neutron irradiation time, where the concentration of Eu in measured samples was changed.

Table 1: The neutron and gamma-ray sensitivities (Sₙ and Sγ) of SrBPO₅:Eu²⁺ and BAS-ND

<table>
<thead>
<tr>
<th>items</th>
<th>SrBPO₅:Eu²⁺</th>
<th>BAS-ND</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sₙ</td>
<td>1.66×10⁻²</td>
<td>1.24</td>
</tr>
<tr>
<td>Sγ</td>
<td>3.47×10⁻⁵</td>
<td>2.19×10⁻²</td>
</tr>
<tr>
<td>Sγ/Sₙ</td>
<td>2.09×10⁻³</td>
<td>1.77×10⁻²</td>
</tr>
</tbody>
</table>

unit: Sₙ (PWL/mm²/neutrons), Sγ (PWL/mm²/gamma)
Comparison Between Symmetric Diffraction Geometry And Fully Asymmetric Diffraction Geometry (FADG) Of Bent Perfect Silicon Monochromator

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²Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
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Reflectivity properties of the fully asymmetric diffraction geometry (FADG) of the bent perfect Si(111)-crystal were experimentally studied. The obtained results are compared with those corresponding to the symmetric diffraction geometry. Both these parameters were measured on the dependence of curvature of the cylindrically bent Si(111)-crystal slab, using the crystal slabs of the same dimensions (200x40x4 mm³) and the width of the incident beam of 13 mm, 0.209nm wavelength and 1.5 m monochromator to Neutron Imaging Plate distance. It has been found (fig. 1) that the peak intensity of symmetric geometry was about 1.5 times higher with respect to the FADG case, but in case of FADG the irradiated crystal volume was smaller by a factor of 1.9 than symmetric one. FWHM for FADG was relatively independent to the curvature. The FWHM for FADG affected only by thickness of monochromator crystal. It shows the condensation of incoming beam had been occurred.

Concerning the focusing properties, each system has its own advantage. Using the FADG system, it is very easy to make a narrow (comparable to the crystal thickness) parallel-diffracted beam without any Soller collimator. Due to a larger incident angle for white beam with respect to the surface of the crystal slab the irradiated monochromator volume in the FADG case is correspondingly smaller than in symmetric case. However, thanks to the spatial condensation (Fankuchen effect) a high monochromatic beam density may be obtained with the FADG¹. In case of wide beam, FADG may become better -high intensity and parallel beam- than symmetric geometry.

Figure 1: Intensity (upper) and FWHM (lower) as a function of curvature for Symmetric and Fully Asymmetric diffraction geometry.

References

Improvement of the polarized neutron beam flux in TAS-1 spectrometer by doubly focusing Heuser monochromator

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2Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Our research group is currently making efforts to install the CRYogenic Polarization Analysis Device (CRYOPAD) on TAS-1 spectrometer at JRR-3M reactor in collaboration with French neutron scattering scientists1. We will be able to carry out the zero-field spherical neutron polarimetry (SNP) by using the CRYOPAD1. The zero-field SNP experiments enable us to measure both the longitudinal and transverse components of the final polarization vector, which is impossible by conventional uniaxial polarization analysis2. In the elastic mode CRYOPAD offers a sensitive method for the determination of complicated AF order and the measurement of form factors in special class of AF compounds, in which the magnetic and nuclear scattering occur in the same reflections3. In the inelastic mode CRYOPAD can elucidate that the transverse components may contain direct information on the spin-lattice correlations, e.g. involving the Dzialoshinskii-Moriya interaction4.

However, the great improvement of the incident polarized neutron flux is indispensable for utilizing the advantage of CRYOPAD. Therefore, we had to design a new Heuser monochromator. The exact geometry of the primary spectrometer has been optimized using the Monte-Carlo ray-tracing simulation.

Figure 1: The new TAS-1 Heuser monochromator.
software McStas\textsuperscript{5).} The magnetic circuit of the monochromator has been optimized by 3D finite-element calculations (PHOTO Series-MAG). A new doubly focusing Heusler monochromator has 140 mm wide and 100 mm height. The Heusler crystals are saturated by a vertical magnetic field closed by a C-shaped iron yoke on the rear side of the monochromator. Old Heusler monochromator was 75 \times 70 \text{mm}^2 (width \times height) area and had no focusing mechanism. As displayed in Fig.1, the new monochromator consists of 35 crystal plates mounted in 7 columns, pivoting around vertical axes to provide variable horizontal focusing. Moreover, the five plates in each of the columns are glued on BN supports inclined by angles corresponding to the vertical focusing, optimized and fixed at \(E_g=30.5\) meV.

Figure 2(a) shows the calculated result of neutron beam distribution at sample position for old set-up, and Fig. 2(b) gives one for new set-up. Monte-Carlo simulation results also indicate that, by enlarging the monochromator size and equipment with doubly focusing mechanism, the neutron flux at sample position is about six times larger than old monochromator set-up as shown in Fig.3.

Next step is to build a new Heusler analyzer which gather the scattered neutron beam as much as possible. We have already started the design of a new Heusler analyzer.

![Figure 3: The calculated scattering angle dependence of the neutron beam flux at sample position; (open circle) for old monochromator set-up and (closed circle) for new monochromator set-up.](image)

**References**


\textsuperscript{1} Dr. P. Tasset (ILL) and Dr. L.P. Regnault (CEA-Grenoble)
Beam Enhancement by a Pre-Crystal in the Precise Neutron Optics

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We are working on the development and application of the neutron interferometry, where we sometimes feel the lack of the neutron intensities. Therefore, we tried to realize a convenient method to enhance the neutron flux on the experimental table. Here, on the premise that the concave crystal that is conventionally used in usual diffraction-work is not suitable for our present purpose of precise neutron optics, because the neutron beams forcibly gathered will not contribute the intensity of the Si-reflected beam.

We tried a pre-crystal of asymmetric reflection, where, as the incident beam of the width \( W \) is reflected as the beam width of \( w \), we can expect the reflected beam enhanced by \( W/w \), Fig.1(a).

![Figure 1: Si Asymmetric Pre-Crystal (C1); Beam Path with Si analyzing crystal C2 (a) and Beam Condensation (b).](image)

We measured the intensity \( I_p \) of Si-plate of 2mm thickness put in the neutron beam reflected by the pre-crystal and the intensity \( I_o \) of Si-plate put in the incident beam, "original beam" in Fig.1(a), without the pre-crystal. We compared, then, if the ratio of \( I_p/I_o \) is larger than unity or not. The FWHM and the ratio of the background noises to the peak intensity of the rocking-curve were also compared. Wavelengths, \( \lambda \) in the following tables, of 1.5, 1.56, 1.74, 2.0 and 2.3A were used.

At first, we tested the asymmetric reflection of a silicon perfect crystal, because it is rather easy to make up into an expected shape. Although all of those pre-crystal with silicon single crystal with asymmetric reflection gave the condensed neutron beam as expected, Fig.1(b), they showed very large beam-divergence and did not supply any enhanced beam intensity for the following reflection by a silicon crystal, Table 1.

<table>
<thead>
<tr>
<th>C1</th>
<th>( \lambda )</th>
<th>( I_p/I_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Plate-111-Bragg</td>
<td>1.5</td>
<td>0.74</td>
</tr>
<tr>
<td>( \sim )Laue</td>
<td>2.3</td>
<td>0.68</td>
</tr>
<tr>
<td>Si Block-220-Bragg</td>
<td>1.52</td>
<td>0.14</td>
</tr>
<tr>
<td>( \sim )</td>
<td>1.56</td>
<td>0.27</td>
</tr>
<tr>
<td>( \sim )</td>
<td>1.74</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The reason for the above results were supposed that, as predicted in the textbook of the dynamical diffraction, quite the same factor, \( W/w \), affects on the beam-divergence of the diffracted beam from the asymmetric crystal just as the beam condensation.

Next, we tried the asymmetric reflection of imperfect single crystals, such as Cu-based alloys, Ni-based super alloy, in addi-
tion to the highly oriented pyrolytic graphite (HOPG), in order to avoid the dynamical effect against the beam divergence mentioned above. On the HOPGs, in addition to the flat HOPG plates as the reference, we tried the asymmetric angle of 11deg. and 15deg., which were made of HOPG platelets of 10mm width set in the aluminium frames, ground by emery paper and polished with special cloth as smooth as possible, Fig.2.

![Figure 2: Asymmetric Pre-Crystal made of HOPG-Platelets Set in an Aluminum Frame.](image)

Although we have not systematically tested, the distance between the pre-crystal and the Si plate was found very important parameter, i.e., the shorter the better.

We succeeded in the enhancement of the Si-reflected beam in several cases, Table 2. The best case was the flat HOPG with 2.0Å wavelength and 40nm distance, giving the enhancement of around 3 times.

With shorter wavelengths and longer distance, they gave weaker reflections. With this pre-crystal method, we could not only get stronger intensity but also reduce the ratio of the background noise and the FWHM. Here, it seems rather strange to gain intensity with a flat HOPG. It may be explained with the idea of some kind of integration of coherent part within the original beam by the pre-crystal.

On the other hand, both of asymmetric HOPGs of 11deg. and 16deg. gave only 2 times or less even with 2.0Å wavelength and 40nm distance, while they really concentrated the width of the incident beam as expected.

We tested some conditions of 1st and 2nd slits, i.e. before- and after the pre-crystal.

1) With the same cross-section of the 2nd slit to the 1st, the reflected intensity is larger more than 115%.
2) With the fixed height of 7mm of the 1st slit, the same intensity is obtained with the reduced width of 2mm of the 2nd slit.
3) With the same height, the reflected intensity increases with the increasing width up to 4.5mm, and then saturated.
4) When we chained the HOPG’s reflections successively, we could not get more intensity than 80-90% of the one-piece reflection, as usually said.
5) The thicker HOPG’s of two or three HOPG platelets, in addition, gave the same intensity as the one-piece case, just as reported that 2mm is the optimum thickness for thermal neutron reflection as a monochromator by the maker’s reports.

Further investigation is in progress.

References
Development of Electrostatic Levitation Furnace for Neutron Diffraction

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2Advanced Science Research Center, JAERI, Tokaimura, Ibaraki 319-1195
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Liquid structure obtained from scattering experiments is necessary for the prediction of the physico-chemical properties. However, there are only limited studies for high-temperature liquids because of the lack of suitable container material for diffraction experiments. In addition, the diffraction intensity of the liquid is much weaker than that of the solid. Moreover, the subtraction of the sharp background peaks of the container material from the sample intensity affects the precision of structural data. Recently, contact-less techniques were applied to materials research. Also, the structure of liquids at high temperatures is frequently studied by levitation methods in combination with synchrotron radiation. However, x-ray is diffracted at the surface and the angle dependence of diffraction intensity is sensitive to the sample position. Therefore, the stability of the sample position is important for precise measurements. Additional difficulties arise when the shape of the sample departs from that of a sphere. This complicates the corrections of diffraction intensity in order to obtain accurate structure factor, S(k). It is not always easy to obtain a complete spherical liquid sample in many levitation techniques. However, electrostatic levitation (ESL) offers a spherical shape which has the advantage to ease data corrections such as the absorption correction. Neutron is of great advantage in obtaining bulk structural data because of its high permeability that minimizes the diffraction intensity at the surface of oxidized sample at high temperatures. If ESL is adopted for neutron diffraction experiments, it is possible to obtain more precise diffraction data for high temperature liquids. In this report, we present the result of the first neutron diffraction experiment carried out with ESL with poly-crystalline alumina.

Neutron diffraction experiment was performed with the HRPD (High Resolution Powder Diffractometer) of JRR-3M in JAERI. The neutron wavelength was 1.823 Å. The neutron collimation setup was open-(M)-20°-(S)-6° in order to make the incident neutron intensity stronger.

The design of the ESL for neutron diffraction experiments was reported earlier. Fig. 1 shows the ESL at HRPD. The furnace had a 0.25 m diameter and a 0.35 m height. The sample position was controlled independently in X,Y,Z directions. A levitated charged sample (Fig. 2) was held at a constant position by a 720 Hz feedback control loop. Stability of the sample position was estimated to be better than ±0.1 mm along the three axes. The sample was a 3 mm diameter alumina sphere coated by platinum with a thickness of a few ten angstroms. During levitation, ultraviolet light was irradiated to the sample to maintain charges through photoelectric emission. The sample could be kept levitated for more than 12 hours. The pressure inside the furnace was about 5×10⁻⁴ Pa. A cadmium slit was located at 50 mm from the sample position to adjust the incident neutron beam size to eliminate sharp background intensity from the copper electrodes. The slit width was set to be 3 mm, corresponding to sample size.

As shown in Fig. 3, there are no sharp Bragg peaks in the background data. As for the intensity from the sample, peaks of platinum were not observed because the diffraction.
tion intensity of the platinum coating was far weaker in comparison with that of alumina. Another neutron diffraction experiment of levitated alumina was performed by an aerodynamic levitation technique\(^5\). The background intensity of our data was weaker than that of the other study because of the absence of sharp peaks. In addition, the baseline of the alumina intensity was flatter than that observed elsewhere\(^3\). As for the peak width, narrower sharp peaks were observed. Observed peaks in the present study are in reasonable agreement with the literature\(^5\).

This preliminary work illustrated that neutron diffraction and the ESL is a good combination for structural study of liquid state at very high temperatures without any containers.

![Figure 2: Horizontal view of the levitated alumina specimen during the experiment. The white sphere is 3 mm diameter alumina which is levitated between the copper electrodes (above and below the sphere).](image)

![Figure 1: The developed electrostatic levitation furnace at HRPD.](image)

![Figure 3: The intensities of levitated alumina specimen and background.](image)

References

5) N. Madsen et al., Acta Cryst., B49(1993)973
Development of Neutron Reflectometer for Air/Water Interface with Imaging Plate

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For the water surface system, such as a lipid monolayer on water, polymer monolayers, and monolayer-polymer complex, the reflectivity measurement is the unique technique to evaluate their nanostructure on water directly, not in dried state\(^1,2\). We have been continuing the project for construction of NR for water surface. In 1999, we had succeeded in detecting a neutron reflection from water (\(D_2O\)) by LTAS (C2-1) in JRR-3M. By using an imaging plate (IP), the off-specular reflection was also detected. Last year, we developed a novel NR optical system as shown in Fig.1. We used 3Q-supermirrors to change the incident neutron beam in combination with monochromator tilt. By this system, NR profile from free surfaces can be obtained without changing sample surface position in vertical direction.

By using this system, we carried out a reflectivity measurement for silicon wafer. A typical example is shown in Fig.2. The wavelength of neutron was chosen to be 3.4\(\AA\). The slit width was 0.5mm and 0.3mm for the slits at before monochromator and before sample position, respectively. The distance between these two slits was 1.5m. The size of Si wafer was 20mmx20mm, and the accumulation time was 30sec for 2theta from 0 to 0.5 degree, 300sec for 0.5 to 3.0 degree, and 5000sec for over 3 degree. This NR profile for Si wafer showed a typical decay for flat and smooth surface and the statistics is also enough under these experimental conditions. The reflectivity down to the order of \(10^{-5}\) was detected and the measurable Q range was found to be more than 0.15 \(\AA^{-1}\). For the measurements on monolayers and self-assemblies on water surface, the reflectivity down to \(10^{-8}\) should be detected and the Q range should cover up to 0.3\(\AA^{-1}\), which might be possible with minor modification of this system such as a reduction of background intensity.

![Figure 1 New optical setup of LTAS as a reflectometer for water surface.](image)

![Figure 2 NR profile for Silicon wafer by LTAS.](image)

Reference
Off-specular reflection from Ni/Ti multilayers

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²Kyushu University, Hakozaki, Higashi, Fukuoka 812-8581

Multilayer mirrors of Ni/Ti with periodical d-spacing in nanometer range, may be utilized for neutron focusing and imaging devices. However, due to the interface roughness of Ni/Ti multilayers, vertical correlation give rise to off-specular (diffuse) scattering which leads to decreasing the resolution of these optical devices. For evaluating and reducing the intensity of diffuse scattering in a rough interface, theoretical and experimental study has been conducted.

Rocking curves of Ni/Ti multilayer with d=100 Å and 20bi-layers were measured at small 2θ angles. The measurements were carried on a reflectometer of the LTAS (C2-1) using cold neutron with a characteristic wavelength of 3.8 Å.

The measurement performed at the second \((qz=0.0303\AA^{-1})\) and third \((qz=0.0641\AA^{-1})\) Bragg peaks of sample are shown in Fig.1 together with the calculations obtained with DWBA model. The calculation method is based on the extension of DWBA for layered system which has been performed by Holy et al. In Fig.1, we have found a good quantitative agreement between the calculation and measured curve. The diffuse scattering is strongly structured, the striking feature being the large constructive interference occurring at the maximum of the second Bragg peak. The best fit gives 50 Å and 0.2 for the correlation length \(\xi\) and the \(h\) exponent, respectively. The vertical correlation length \(\xi_z\) is estimated as 500 Å, corresponding to one forth of the total thickness of the multilayer. In addition, due to the effect of measurement background, the diffuse neutron scattering is covered under the background at the wing curve, therefore the calculation gives lower intensities than the

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References

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原子炉：JRR-3M 装置：LTAS (C2-1) 分野：中性子散乱 (装置)
The characteristic of the very small-angle neutron scattering instrument using thin type ch-cut Si

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We are attempting the development of very small-angle neutron scattering instrument which used ch-cut Si of 111 symmetrical reflection. The contents of the development are increase of incidence neutron intensity, the improvement of the profile of the rocking curve of the 2nd crystal which is the basic characteristic, etc. We have used symmetrical 5 bounce - 5 bounce reflective arrangement using the elements of the slab thickness of 10 mm - 10 mm (medium thick type) or 10 mm - 30 mm (thick type) on neutron wavelength of 0.25 nm. Among these, thick type has been used in order to remove the reflective neutron from back surface simply. The $S/N$ ratio was about $4.3 \times 10^4$ in medium thick type, and was about $9.8 \times 10^3$ in thick type. From these facts, the influence of thermal diffuse scattering (TDS) from slab can be considered as a factor of the background which determines a $S/N$ ratio. Then, in order to reduce TDS, the ch-cut Si optical elements for 3 bounce - 3 bounce symmetrical reflection for wavelength 0.2 nm of the 2 mm slab thickness were made as test pieces, and the basic characteristic of very small-angle neutron scattering instrument using it was measured. A schematic layout of new ch-cut Si optical element is shown in Fig. 1.

The experiment was carried out using the PNO instrument installed in JRR-3M in Japan Atomic Energy Research Institute. An example of an obtained rocking curve of the 2nd crystal is shown in unit of $q$ in Fig. 2. The peak intensity of rocking curve is about 1300 cps, $FWHM$ is about 1.38 sec, and a $S/N$ ratio is about $1 \times 10^5$. Compared with the former, Fig. 2 shows that the improvement of $S/N$ ratio is more than twice. Based on this result, the experiment using ch-cut Si of thinner slab is under plan. On the other hand, the deviation from the measured data and theoretical curves is observed in the region of $q > \sim 2 \times 10^{-4}$ nm$^{-1}$. The reason is considered to be the influence of back surface reflection. Then, wrapping processing of back surface or vacuum evaporation of Cd to the back surface is considered to remove back surface reflection.

![Schematic layout of thin type ch-cut Si](image1)

Figure 1: Schematic layout of thin type ch-cut Si.

![Rocking curve example](image2)

Figure 2: A example of 2nd Si rocking curve in unit of $q$ with theoretical curves.

原子炉：JRR-3M
装置：PNO(3G)
分野：中性子散乱（装置）
A new single crystal diffractometer for biological macromolecules (BIX-3M)

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Hydrogen atoms occupy about half of the atoms in a protein molecule, and water molecules of hydration always surround a protein. There is no doubt that they play an important role in physiological functions. They are indispensable substances in many naturally-occurring processes. In addition, H atoms are intimately involved in the folding and stabilization of protein structure through hydrogen bonds. Therefore, the determination of accurate positions of hydrogen atoms of a protein and its hydration water molecules is an important information for understanding the mechanism, function, and stability of many important proteins.

A neutron diffractometer (BIX-3) at JRR-3M of the JAERI has been applied to the structure determination of rubredoxin from Pyrococcus furiosus (1.5Å resolution)\(^1\), its 3-point mutant (1.6Å)\(^2\) and sperm whale myoglobin (1.5Å)\(^3\). Those results led to increase of activity of the neutron protein crystallography. Therefore a much higher performance is now required to shorten the measurement time and/or get more accurate diffraction data.

We have constructed a new single-crystal diffractometer for neutron protein crystallography (BIX-3M) at 1G-A site of JRR-3M of the JAERI. Since BIX-3 has been already installed at 1G-A site, the layout of the monochromator house is also changed so that the two diffractometers are located at the opposite sides of the monochromator house. The main architecture of BIX-3M is based on that of BIX-3 (Figure 1). The details of the architecture and the performance of BIX-3 is discussed elsewhere\(^4,5\).

BIX-3M uses an elastically-bent perfect-Si (EBP) crystal monochromator and a neutron imaging plate (NIP) as BIX-3. To shield the neutron- and γ-background from the environment in the reactor hall the diffractometer is covered by a cylinder which consists of two layers, 50mm thick B\(_4\)C + resin against neutron (outside) and 50mm thick lead against γ-ray (inside). In addition, several optimizations of the monochromator and modifications from BIX-3 are carried out as follows,

1. 2.6Å is used instead of 2.35Å as the wavelength for the incident neutron which gives a larger intensity on the detector and larger separation between Bragg reflections.

2. A super mirror guide composed of Ni/Ti multi-layers (3.6Q) is installed inside of a flight tube to increase the intensity by reflecting thermal neutrons on the walls of the guide.

Figure 1. BIX-3M without cylinder shield (right), the NIP and laser module (left top), and the reading rod and erasing lamp (left bottom). The neutron beam comes from the right side. During data collection the NIP is located at the top position (white arrow). In the reading procedure the NIP cylinder moves down and is scanned by the laser with a reading rod rotating. After the reading the NIP is initialized by an erasing lamp and moves up to the top position.
Table 1. Comparison of the specification of BIX-3M and previous BIX-3.

<table>
<thead>
<tr>
<th></th>
<th>BIX-3M</th>
<th>Previous BIX-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochromator</td>
<td>EBP-Si (111) / (311)</td>
<td>EBP-Si (111) / (311)</td>
</tr>
<tr>
<td>Wavelength</td>
<td>2.60Å / 1.36Å</td>
<td>2.35Å / 1.23Å</td>
</tr>
<tr>
<td>Beam size at monochromator</td>
<td>80 mm × 44 mm</td>
<td>40 mm × 44 mm</td>
</tr>
<tr>
<td>Flight tube</td>
<td>with 3.6Q super mirror</td>
<td>without super mirror</td>
</tr>
<tr>
<td>NIP size</td>
<td>450 mm × 980 mm</td>
<td>450 mm × 980 mm</td>
</tr>
<tr>
<td>Camera constant (radius)</td>
<td>200 mm</td>
<td>200 mm</td>
</tr>
<tr>
<td>d-min</td>
<td>1.4Å / 0.7Å</td>
<td>1.2Å / 0.6Å</td>
</tr>
<tr>
<td>(along the horizontal line)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total gain</td>
<td>1.69</td>
<td>1</td>
</tr>
</tbody>
</table>

(3) The neutron beam size from the reactor is 80mm × 44mm. However, only the bottom half of it has been used for the previous BIX-3 at the monochromator position. After the modification of the monochromator house, a new monochromator composed of three elastically-bent perfect-Si plates is used to cover the full size of the beam.

The comparison between BIX-3M and previous BIX-3 is summarized at Table 1. The peak intensity of BIX-3M at the sample position is measured to be about 1.25 times larger than previous BIX-3. As the reflectivity of the sample is proportional to the 3rd power of the wavelength, the final gain for the integrated intensity of the Bragg spots are estimated to be 1.69 times larger. Supposing that 800 frames are measured for one data set with 60 min/frame under those conditions, only 22.5 days is necessary for BIX-3M whereas 36 days are required in the case of previous BIX-3.

On the other hand, the background also increases to be at most 1.56 times in the low-resolution range. Thus in that region intensity (S) / background (B) ratio is almost same as in previous BIX-3. However, in the high-resolution range the increment of the background is less than 1.56 times so that it is concluded that data quality (S/B) in BIX-3M is better than in previous BIX-3. The BIX-3M is scheduled to be shifted closer to the monochromator by about 25cm. This yields an additional gain factor of 1.5.

Figure 2 shows an example of the diffraction images from a protein crystal taken by BIX-3M.

In conclusion, as mentioned above, BIX-3M shorten the collection time of diffraction data sets. In addition, since it is still difficult to get large crystals of proteins and other biological macromolecules, a higher performance of BIX-3M increases the possibility to apply neutron crystallography to such biomacromolecules.

References

2) T. Chatake et al., submitted paper.
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1. Neutron Scattering  9) Others
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Structural Phase Transition in Pyrochlore Compound Cd₂Re₂O₇

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Cd₂Re₂O₇ is the first superconductor (Tc ~ 1 K) which have been found among cubic pyrochlore oxides [1]. Peculiar interplay between geometrically frustrated antiferromagnet and superconductivity is expected to realize in this system. The electrical resistivity measurements, and 4C-XRD experiments have revealed the existence of the second order phase transition around 200 K [2]. The results of Re-NQR experiments have suggested the breaking of symmetry of three-fold axis in the temperature range of 5~100 K [3]. Now, we are interested in the relationship between the structural changes and electrical resistivity at low temperatures, especially in the shift of oxygen and its effect to the band structure.

We have performed 4-circle neutron diffraction experiments on spectrometer FONDER, which is installed at T2-2 beam port of the thermal guide at the JRR-3M research reactor of JAERI. The wavelength of neutron was 1.5648 Å. ¹¹⁵Cd was used to avoid the absorption of neutron. The size of the single crystal was 3.0mm × 3.5mm × 2.0mm; which was enough small compared to the beam diameter (10mm).

Figure 1 shows the peak-profile of the Bragg reflection (040) measured by ω-scan (scan speed ~ 0.2 deg./min). A single peak was measured at ω = 17.77° and at T=250 K (peak width; Δ = 0.166(7)°). With lowering temperatures at 50 K, an additional peak appeared at around ω=17.98°. This peak might come from the contribution of a new domain, which was produced owing to the structural phase transition at around 200K. The superlattice peak of (020) reflection was also measured at below 150 K. The intensity of the reflection was rather weak (the counts of the peak was about 30cts); although, it seemed for us that the peak was also split for this reflection. The crystal structure analysis comparing with the synchrotron X-ray data is now in progress.

Fig. 1 The peak profile of (040) Bragg reflection at 50 K (a) and 250 K (b).

[2] Z. Hiroi et al., cond-mat/0203178
[3] O. Vyaselev et al., cond-mat/0201215
Introduction

Normal spinel LiMnMO₄ (M:Co [1], Cr [2]) and inverse spinel LiNiVO₃ [3] with 4.5 – 5 V plateau have been investigated as post 4 V cathodes. We introduced that phospho-olivine LiMPO₄ with a theoretical capacity of 170 mAh/g should be a strong candidate for a new high-voltage cathode with superior capacity in the previous report.

In this report, the structure of ordered-phospho-olivine LiCoPO₄ and fluoride phosphate Li₂CoPO₄F (the latter previously unreported) were identify by Neutron diffraction and the cathode properties were compared using coin cells.

Experimental

Conventional solid-state reactions were employed to synthesize the phospho-olivines. LiCoPO₄ were prepared from stoichiometric amounts of reactants Li₂CO₃, P₂O₅, and CoO. The mixtures were presintered at 500 °C for several hours. After firing at 780 – 820 °C for 2 days with an intermittent grinding, the mixtures were quenched using liquid nitrogen. Moreover, obtained LiCoPO₄ was mixed with LiF and heated at 780°C for 78 hours in vacuumed quartz tube. Both obtained powders, LiCoPO₄ and Li₂CoPO₄F were indexed as orthorhombic in the space group Pnma by XRD (Rigaku RINT2100HRL/PC), using monochromatized CuKα radiation. Neutron diffraction data were taken at powder diffractometer, HERMES [4], at JRR-3M reactor in Japan Atomic Energy Research Institute. The structural parameters were refined by Rietveld analysis using Rietan 97β [5].

We fabricated the cathodes for electrochemical characterization by blending powders of the active material LiMPO₄ with acetylene black (Denki Kagaku Co., Ltd.) and F-210L PTFE Teflon binder (Dalkin Industry Ltd.) in a weight ratio of 70 : 25: 5. We measured the cathode properties in a coin-type cell (type 2032 made from SUS316) with a nonaqueous electrolyte (1M LiPF₆/Ethyl Methyl Sulfone, Tomiyama Pure Chemical Industries, Ltd.) and polypropylene separator (Celgard 3501) against a Li metal anode.

Results and discussion

Interatomic distances for LiCoPO₄ obtained from Rietveld refinements of neutron diffraction are shown in Table 1. According to Shannon’s ion radii in MO₄, M-O interatomic distances in Table 2 suggest every transition metals have 2+ high spin state in initial LiMPO₄ olivine matrix.
Table 1. Interatomic distances for LiMPO₄

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>M-O (1)</td>
<td>2.150</td>
<td>2.23</td>
<td>2.25</td>
<td>2.150</td>
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<td>M-O (2)</td>
<td>2.084</td>
<td>2.14</td>
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<td>M-O (3) x2</td>
<td>2.187</td>
<td>2.13</td>
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<td>M-O (3) x2</td>
<td>2.080</td>
<td>2.30</td>
<td>2.30</td>
<td>2.150</td>
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<tr>
<td>Average</td>
<td>2.151</td>
<td>2.205</td>
<td>2.310</td>
<td>2.110</td>
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Table 2. Shannon's Ion radii in MO₆

<table>
<thead>
<tr>
<th>6-fold coordinated ion radii [7]</th>
<th>Co⁺⁺</th>
<th>Mn⁺⁺</th>
<th>Fe⁺⁺</th>
<th>Ni⁺⁺</th>
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</thead>
<tbody>
<tr>
<td>High Spin</td>
<td>2.145</td>
<td>2.23</td>
<td>2.18</td>
<td>2.09</td>
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<tr>
<td>Low Spin</td>
<td>2.05</td>
<td>2.07</td>
<td>1.98</td>
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Table 3. Interatomic distances for Li₂MPO₄,F

<table>
<thead>
<tr>
<th>M-O bond length[Å]</th>
<th>Li₂CoPO₄,F</th>
<th>Li₂NiPO₄,F [8]</th>
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<tr>
<td>M (1) O (2) x2</td>
<td>1.9960</td>
<td>2.011</td>
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<td>M (1) O (6) x2</td>
<td>2.0872</td>
<td>2.070</td>
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<tr>
<td>M (1) F (2) x2</td>
<td>2.1637</td>
<td>2.081</td>
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<td>M (2) O (6) x2</td>
<td>2.0092</td>
<td>2.013</td>
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<td>M (2) O (4) x2</td>
<td>2.0606</td>
<td>2.036</td>
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<tr>
<td>M (2) F (1) x2</td>
<td>2.1552</td>
<td>2.082</td>
</tr>
<tr>
<td>Average</td>
<td>2.0382</td>
<td>2.032</td>
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</table>

On the other hand, the interatomic distance for Li₂MPO₄,F indicates that Co has 2+ low spin state in initial Li₂CoPO₄,F matrix as shown in Table 3. The quasi-open circuit voltage charge-discharge profiles of identified LiCoPO₄ and Li₂CoPO₄,F are shown in Fig.1. It found that the fluoride phosphate Li₂CoPO₄,F is a new 5-volt class cathode as LiCoPO₄ and the open circuit voltage is higher than that of LiCoPO₄.

References

Structure and Battery Properties of Calcite-type MBO₃ (M: V, Fe)

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Polyanionic compounds such as NASICON-type Fe₂(SO₄)₃ and Li₂Fe₂(PO₄)₃ [1] have engendered much interest as rare metal free cathodes for next generation lithium secondary batteries. However, there have been few studies as anode. The skeleton structures built up from both MO₆ octahedra and XO₄ polyhedral anion, allow both the redox potential energy and electrochemical properties to be tuned by the combination of M and X. The corner sharing 3D matrix should be suitable anode for not only lithium-ion batteries but also sodium-ion batteries.

In this paper, we tried to design the polyanionic anode with much lighter BO₃ group and synthesize it with suitable low redox potential as anode by chemical substitution in FeBO₃.

Figure 1 shows XPS spectra of Fe 2p for the typical iron anode and cathodes with ferric ion and various polyanions. The stronger the X-O bonding (S-O > Mo-O = W-O > B-O), the weaker is the Fe-O bonding and hence, the larger the open circuit voltage (OCV). The 1.8 eV difference in the Fe 2p binding energy of ferric sulfate and ferric borates, reflects a 2 V difference in the OCV. The theoretical capacities estimated by Fe³⁺/Fe²⁺ redox reaction are 234 mAh/g (856 mAh/cc) for calcite FeBO₃ and 293 mAh/g (1272 mAh/cc) for norbergite Fe₃BO₉, respectively. However, the 1.6 V mean voltage on lithium intercalation into ferric borates is unfortunately still too high as anode for lithium-ion batteries [2].

The OCV for rhombohedral Fe₂(SO₄)₃ is about 1 V higher than that of V₂(SO₄)₃ [3]. On the analogy of this, we tried to replace the redox couple from Fe³⁺/Fe²⁺ to V³⁺/V²⁺ in FeBO₃. Mixed V₂O₅ and H₃BO₃ were preheat at 670 °C for 24 h and calcined at 1200 °C for 24h in Ar-H₂ (5%) to avoid oxidation of V³⁺. The XRD profile of obtained VBO₃ powder is well refined by Rietveld analysis (REITAN97-β [4]) based on the crystal parameters of FeBO₃ with R-3c space group as shown in Fig.2.

The charge/discharge profile in Fig.3 shows the reversible capacity of VBO₃ is 420 mAh/g.
研究テーマ：リチウム2次電池正極活物質の構造解析

表題：カルサイト型MBO₃の構造と電池特性

and the mean voltage of VBO₃ is 1 V lower than that of FeBO₃ as we expect. Looking at the redox potentials, VBO₃ should have the best performance as an anode material, when compared to the iron borate.

Fig.2 Observed, calculated and difference plots for X-ray diffraction pattern of FeBO₃ and VBO₃.

Fig.3 Charge and discharge curves of FeBO₃ and VBO₃.

References:


JRR-3M, HERMES(T1-3), 9. Others
Residual Strain Measurement of the Three Layers Material, 
[WC-10mass%Ni]-[SUS304]-[WC-10mass%Ni]

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The thermal residual stress in the three layers material, [WC-10mass%Ni]-[SUS304]-[WC-10mass%Ni] has been investigated by RESA. The sample was 40mm in diameter and the thickness of each layer was about 4 mm. A photograph of the sample is shown in Fig. 1.

![Figure 1: Photograph of the three layers sample.](image)

The raw materials of the composite [WC-10mass%Ni] are powders of W, C and Ni with an average size of 5-8μm, and the middle layer is made of a plate of SUS304. The sample was made by Self-propagating High-temperature Synthesis / Static Pseudo Isostatic Compaction (SHS/SPIC) equipment, which is shown in Fig. 2.

![Figure 2: Scheme of a SHS/SPIC equipment.](image)

The green compact, which was formed beforehand to three layers by cold isotropic press, was wrapped by carbon sheet and was pressed isostatically by commercial sand. The pressure was 25 MPa. The carbon sheet was ignited by an induction heating. Then, the combustion wave of about 1800 K propagated toward the center of the sample with a speed of 1-100 mm/s. The sample cooled down rapidly after the combustion wave passed. The SEM image of the composite material, [WC-10mass%Ni], is shown in Fig. 3, where the white region is WC and the black region is Ni. As shown in Fig. 1, the middle [SUS304] layer is forced out from the edge. The situation is quite different from the case of the three layers material, [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni], of which the middle layer was made from Ni in powder state. In this case the middle [Ni] layer shrinks inside the edge.\(^1\)\(^2\)

![Figure 3: SEM image of [WC-10mass%Ni].](image)

The wavelength of neutron beam was 2.0995 Å. As the size of slits for incident and reflected beams were 2 mm × 2 mm respectively, we were able to observe the small area of the sample. On the mid plane of the [SUS304] layer, we observed 200 reflection, for axial, radial and hoop directions, from the small area of SUS304 at 0, 10, 15, 16, 17 and 18 mm positions apart from the center. On the interface between [WC-10mass%Ni] and [SUS304],
we observed 200 reflection, for axial, radial and hoop directions, from the small area of SUS304 at 0, 15 and 18 mm positions apart from the center. For the estimation of the strain, we obtained the standard lattice spacing, \( d_0 \), using the 200 reflection of the single layer material, [SUS304(plate)], made by the same synthesis method. During the observation of the reflection, the sample was rotated around the \( \chi, \phi \) directions using two small motors on the goniometer, to obtain the average lattice spacing for all directions.

The 200 reflection peak for axial direction from the center of mid plane of the [SUS304] layer and that from the center of the boundary between [SUS304] layer and [WC-10mass%Ni] layer, are shown in Fig.4 (a) and (b), as the examples of the peaks of 200 reflection of SUS304. In Fig.4 (b), we also see the Ni 200 reflection peak on the right hand side, which comes from the Ni region of composite [WC-10mass%Ni] layer. To estimate the stress, we used Young’s modulus of 113.6 GPa and the Poisson ratio of 0.262, which were obtained from the 200 reflection of SUS304 under tensile test.  

![Figure 4: Data plot and the Gauss fitting of the 200 reflection of SUS304 for axial direction. (a) from the center the mid plane of the [SUS304] layer and (b) from the center of the boundary of two layers.](image)

SUS304 feels a weak tensile stress in the radial and hoop directions and a weak compressive stress in the axial directions. We see that the stresses of [SUS304] change drastically at the radial position of 14-18mm from the center, especially on the mid plane. They have a tendency to become more compressive.

As a result of the previous measurements by RESA, we found that the middle [Ni] layer of the three layers [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni], experiences almost no strain. The reason of the difference of the strain between the [SUS304] middle layer and the [Ni] middle layer is presumably due to the difference of the state of the original material. When the original materials are all powders, there is no macro strain in any place of the sample. We conclude that the original materials in the powder state has a great advantage to synthesize a plural layers material by SHS/SPIC equipment. We are able to avoid the occurrence of the crack or the fracture of the materials.

References
Deformation Behavior of Ferrite-Cementite Steels Examined by Neutron Diffraction

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1. Introduction
We have reported changes in ferrite [110] lattice spacing along the tensile direction by in-situ neutron diffraction during tensile deformation to investigate deformation mechanism in pearlitic steels1). In this study, in-situ neutron diffraction during tensile deformation was performed for two pearlitic steels with different cementite volume fractions. Lattice plane strains in ferrite and cementite along the tensile and its perpendicular directions were determined to examine stress partitioning between the two constituent phases.

2. Experimental procedures
Chemical compositions of tested steels are shown in Table 1. Samples with fully pearlitic structure were prepared by the following heat-treatments: B03 and B04 austenitization at 1273K for 0.6ks and isothermal transformation at 823K for 1.2ks followed by air cooling for B03 and B04, and austenitization at 1173K for 3.6ks and hot rolling at 1143K followed by air cooling for SK5. Tensile specimens with a gauge length of 120mm, width of 3mm and thickness of 2mm were prepared. In-situ neutron diffraction profiles were obtained during tensile deformation by using RESA, JRit-3M at Japan Atomic Energy Research Institute. Tensile load was applied in a step by step manner and in-situ neutron diffraction spectra were recorded during a temporary stops of the loading (creep mode). Changes in lattice plane strains for ferrite [110] and cementite [212] were measured.

Table 1: Chemical compositions of steels used (mass%)

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<tr>
<th>steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
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<tr>
<td>B03</td>
<td>0.58</td>
<td>0.04</td>
<td>1.5</td>
<td>0.005</td>
<td>—</td>
<td>0.004</td>
</tr>
<tr>
<td>B04</td>
<td>0.77</td>
<td>0.04</td>
<td>1.5</td>
<td>0.005</td>
<td>—</td>
<td>0.004</td>
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<tr>
<td>SK5</td>
<td>0.85</td>
<td>0.25</td>
<td>0.4</td>
<td>0.009</td>
<td>0.004</td>
<td>—</td>
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</table>

3. Results and Discussion
Figure 1 shows nominal stress-strain curves for the pearlitic steels. It is known that yield stress (YS) of pearlitic steel is dependent on lamellar spacing (S0), while work-hardening and tensile strength (TS) is dependent on cementite volume fraction (fS). As seen, YS and TS are found larger in B04 than in B03 because of smaller S0 and larger fS for B04.

Figure 1: Nominal stress-strain curves for B03 B04 and SK5.
Figure 2: Ferrite(110) diffraction profiles at various applied stresses for B03.

Figure 2 shows ferrite(110) peak at various stresses for B03. A peak shifts to lower angle with increasing of the applied stress. Figure 3 shows stress estimated from lattice plane strains in ferrite and cementite as a function of the applied stress($\sigma_a$) for B04. After the onset of plastic flow, i.e., yield strength of 500MPa, stresses in ferrite($\sigma_a$) and in cementite($\sigma_\theta$) differs from each other. The following stress equilibrium condition holds among $\sigma_a$, $\sigma_a$, $\sigma_\theta$ and $f_\theta$.

$$\sigma_a=\sigma_a(1-f_\theta)+\sigma_\theta f_\theta$$  \hspace{1cm} (1)

Such stress partitioning leads to large work-hardening in a pearlitic steel\(^9\). Under $\sigma_a$ of 800MPa, $\sigma_a$ and $\sigma_\theta$ are estimated to be 613 and 2500MPa respectively. In SK5 steel, the maximum stress of cementite was determined to be 2700MPa.

References
In Situ Neutron Diffraction Experiment during Tensile Deformation for a TRIP Type Multi-Phase Steel

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[Introduction]

Trip type multi-phase steels are characterized by an excellent combination of strength, ductility and response to high-speed deformation. The stress-induced martensitic transformation of retained austenite is known to contribute to such favorable properties, but the transformation behavior during deformation has not been made clear. Recent development of neutron diffraction experiment enables us to find deformation and transformation behavior in situ during deformation.

[Experimental Procedures]

A steel was prepared by a laboratory process at Sumitomo metal industries Ltd.. Chemical analysis for the steels showed 0.10C, 1.2Si, 1.3Mn, 0.01P and < 0.01S in mass%. Hot rolled (TMCP) sheets with 2 mm in thickness were made. Their microstructure consisted of ferrite, bainite and retained austenite. The angle of the diffraction neutron with wavelength of 0.2096724 nm was performed during step-wise tensile testing by using RESA at JAERI. The gauge volume of neutron diffraction was 15 \times 3 \times 2 \text{ mm}^3 so that the average lattice strains in bulk specimen were evaluated. Plate specimens were extended step by step and neutron diffraction profiles for austenite (111) and ferrite (110) planes were obtained at each step.

[Results and Discussion]

The change in diffraction intensity related to austenite volume fraction revealed that the onset of stress-induced martensitic transformation took place at approximately 400 MPa. The change in (111) austenite lattice plane spacings were measured along longitudinal and vertical directions with respect to the applied stress. The spacings measured were transformed to strains using the spacing before loading as a reference distance. The results are depicted in Fig.1. The change is apparently divided into three regimes; (i) elastic deformation below 400 MPa, (ii) stress partitioning between austenite and ferrite caused by the preferential plastic flow in the ferrite matrix and (iii) stress-induced transformation contributes to the change in stress partitioning. The data from ferrite (110) peak verify these conclusions. The higher flow stress of retained austenite and formation of strong martensite are speculated to yield larger uniform elongation.

![Figure 1: Lattice plane strain of (111) austenite as a function of applied stress.](image)

原子炉: JRR-3M
装置: RESA(T2-1)
分野: 中性子散乱 (その他)
In situ observation of deformation and recovery behavior by neutron diffraction in an Fe-Mn-Si shape memory alloy

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[Introduction]

The shape memory effect in Fe-Mn-Si based alloys generates by the stress induced transformation from austenite (γ: fcc) to epsilon martensite (ε: hcp) and its reverse transformation on heating. The transformations are caused by the forward and backward movement of Shockley partial dislocations. The variant selection of stress induced ε-martensite was restricted to a few orientations with respect to the tensile direction. The details of the transformations and then the improvement of shape memory have not been made clear. In this study, changes in lattice plane strains and volume fractions of the constituents were measured in situ by neutron diffraction during tensile straining.

[Experimental Procedures]

An Fe-28Mn-6Si-5Cr shape memory alloy was used (numerals refer to mass chemical composition). Round bars with 35mm in diameter were made through an industrial process and austenitized at 1273K for 3.6ks in a muffle type furnace followed by quenching into water with ice. Tensile specimens were prepared from the bars using a spark-cutting machine. The neutron diffraction experiments were performed with RESA at modified JRR-3M. The (111) and (200) diffraction peaks of γ and the (10\bar{1}1) of ε were measured by the angle dispersion method at several steps of loading. A gauge volume for neutron diffraction was $10 \times 3 \times 6$ mm$^3$. Tensile load was kept constant during $0\text{-}28$ scan with a point counter. Diffraction angles were determined by a curve fitting with a Gauss function for the measured profiles.

[Results and Discussion]

Fig.1 shows the changes in lattice plane strain for γ(111) and (200) along vertical (axial) and horizontal (transversal) directions. Both of them increase linearly up to approximately 250MPa. After that, γ(111) deviates from the linear increase but γ(200) maintains the linearity. This suggests the stress-induced transformation, i.e., movement of partial dislocation occurs preferentially in (111) family grains. At the same time, integral intensities of ε(10\bar{1}1) in the both directions were increased gradually with straining, but their increasing rates were different from each other.

![Figure 1: Changes in lattice plane strain for each planes.](image)

原子炉：JRR-3M 装置：RESA(T2-1) 分野：中性子散乱（その他）
Textured measurement by neutron diffraction for pearlite steel wires

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1. Introduction
Heavily drawn pearlite steel wires are known to show the highest strength in commercially available materials. The reason of the ultra-high strength is however unclear. We have found that the yield strength anisotropy in a drawn pearlitic steel wire by compression tests along five different directions1. This anisotropy is much influenced by heat treatment. Here, the reason of the anisotropy is speculated either residual phase stress in cementite and the ferrite matrix, ferrite texture or the both. First, we measured the residual phase stress by neutron diffraction and found a good correspondence with the yield strength anisotropy2. Then, we secondly examined the ferrite texture in this study. Here two samples, P2 and P4 explained in chapter 2, were used because the strong anisotropy were observed in P2 but scarcely in P4.

2. Experimental procedure
A hypereutectoid steel with chemical compositions of 0.85C, 0.24Si, 0.82Mn, 0.011P, 0.01S, 0.02Al and 0.05Cr in mass percent was used in this study. Hot-rolled rods with 11mm in diameter were patented through an industrial process to produce fully pearlitic structure. They were then drawn to wires with 5.5mm in diameter, where reduction in area was 75 percent (P2). After that, some of the drawn wires were aged at 698K for 0.6ks (P4: Zn-plating simulated heat). Specimens size of 5.5 × 5mm were prepared for texture measurement by using RESA at JRR-3, JAERI. Figure 1 shows geometrical arrangements for measurement, ferrite (110) radiation was employed. The angles φ and χ are defined as depicted in Fig.1. The scanning with respect to φ and χ was performed at 5° intervals, and the measured ranges of φ and χ were from 0° to 180° and from 0° to 90°, respectively. Texture was evaluated by 110 pole figure.

Figure 1: Geometrical arrangements for texture measurement.

3. Result and Discussion
Figure 2 shows a part of the 110 pole figure of a P2 specimen. Pole densities were projected onto a plane perpendicular to the extrusion direction using the mean pole densities as units. The concentric distribution around the center is observed, where the maximum intensity is 6.8. Another concentric-circular distribution is found at approximately 60° declined from center. This apparently shows the formation of 110 fiber texture of ferrite phase.
Figure 3 shows a part of the 110 pole figure of a P4 specimen. The pole figure of the P4 specimen is similar to that of P2 specimen, where, the maximum intensity is 6.2. Consequently, the texture evolved by the drawing was hardly changed by the annealing at 698K.

Figure 2: 110 pole figure of a P2 specimen.

Figure 3: 110 pole figure of a P4 specimen.

According to the results by the neutron stress measurement, the phase residual stress are generated by the drawing and relaxed by the subsequent annealing. They are balanced among pearlite colonies as well as between cementite and ferrite. Because the ferrite matrix was totally compressed along the drawing direction for P2, the residual phase stresses were concluded to bring the yield strength anisotropy. The strong fiber texture is thus found to give minor influence.

Texture measurement is usually conducted by X ray diffraction, however, the quantity of information is not satisfactory in the case of small specimen. In this study, detail texture measurements were performed by using neutron diffraction.

References
Development of optical devices for cold neutrons


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Recently, we have developed optical devices for cold neutrons and have demonstrated the capability of focusing and polarizing a neutron beam by magnetic lenses that do not attenuate the neutron beam. We have designed and fabricated compound Fresnel-type refractive lenses for cold neutrons. Fresnel lens made of single-crystal MgF₂ are better than vitreous silica due to its higher purity and much reduced microstructure. For the convenience of fabrication, an array of parallel prisms of triangular cross section was assembled to form a compound refractive prism. This development lays an important groundwork for the eventual design of two-dimensional compound refractive lenses. Additionally, such a one-dimensional neutron prism may have potential applications such as energy analyzers for time-of-flight neutron spectroscopy.

Figure 1: Setup of the experiment.

Figure 2: The intensity profiles for wavelength of 4, 8, 12, and 15 Å.

Setup of the experiment is shown in Fig. 1. The intensity profiles for wavelength of 4, 8, 12, and 15 Å are shown in Fig. 2 as a part of the results. The wavelength resolution (∆λ/λ) of neutron beam is 13%. Neutron beam was refracted by the prism. Refracted angle depended on wavelength of neutrons, therefore the prism works as a spectroscopic. There is a little of reflected component on the parallel surfaces to the beam at around ∆x = 0. No component of the high-energy time-independent (delayed) neutrons is observed. In order to understand these results quantitatively, we performed numerical simulations of the refractive prism, taken into account the effects of prism geometry, beam collimation, small-angle scattering and neutron transmission from the MgF₂ single crystals. Obviously, the detailed experimental results cannot be explained solely by the effects included in the simulation. Other factor due to stray scattering have to be investigated further.

We also designed and fabricated compound Fresnel-type refractive lenses for cold neutrons. One device consisted of 49 pieces of Fresnel lens made of MgF₂. Focusing function and performance was evaluated. As a
Figure 3: The size of focused beam depending on lens-detector distance at wavelength 14.4 Å.

Figure 4: The picture of the detector. One of the covers is opened.

In order to make sure the function of these optical devices, 2-dimensional survey must be required after a exit of these devices. To make experiment progress efficiently, 2-dimensional neutron detector has been highly required to develop the neutron optical devices. We are developing the 2-dimensional detector based on neutron scintillator reading out with wavelength shifting fiber crossing each other 6). The picture of the detector is shown in Fig. 4. The typical result is shown in Fig. 5, which is image of cadmium slit slanting. Width of opened lines of cadmium slit is 0.5 mm. Distance between slits is 5 mm. Now, spatial resolution was about 0.5 mm in FWHM and detecting efficiency was about 10% for cold neutrons. The detecting efficiency should be increased for practical application.

Figure 5: Image of cadmium slit slanting. Width of opened lines is 0.5 mm. Pixel size in the image is 0.5 mm × 0.5 mm.

References

Residual Strain Measurement of S45C Round Bar Hardened by Induction

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The residual strain of the S45C round bar hardened by induction heating was measured by neutron diffraction apparatus, RESA. The diameter of the bar was 20 mm and the length was 60 mm. The surface of the bar was hardened by induction heating of 50kHz. The temperature of the surface was increased up to 950 °C. After heating for 8.5 s, it was cooled down to 26.9 °C with the water. The depth of the hardened layer was 1 ~ 3 mm. It is expected that the martensitic phase occurs in this layer, whereas the inner region is not hardened in the ferritic phase.

The sample installed on the goniometer of RESA is shown in Fig. 1. We determined the wave length of neutron beam precisely for each machine time, using Si poly-crystal. It was about 2.10 Å. We used a peak of 110 reflection of the S45C sample. On the circular cross section at the center of the bar, the strain for the axial, radial and hoop directions at each position of 0, 2, 4, 6 and 10 mm from the surface was measured.

Figure 1: Sample installed on the goniometer of RESA.

The 110 reflections of the two round bars of the same size were measured for the estimation of standard lattice spacing, d_0. One is heat treated to obtain the martensitic phase for the whole of the sample, and the other is not heat treated and in ferritic phase. During the observation of the reflection, the sample was rotated around the χ, φ directions using two small motors on the goniometer, to obtain the average lattice spacing for all directions. The value of d_0 for (110) plane of martensitic phase was 2.0311 Å and that of ferritic phase was 2.0289 Å. We could not observe the separation of the peaks which is expected for the tetragonal structure of martensitic phase.

Figure 2: Strain versus applied stress obtained from the 110 reflection, (a) for a heat treated specimen and (b) for a non heat treated specimen.

The Young’s modulus and the Poisson ratio of a heat treated specimen and of a non heat treated specimen were measured by RESA, using the tensile test equipment. The heat treated specimen was cooled down with water-
solution of polymer. The 110 reflection was used. The results are shown in Figs. 2 (a) and (b). We see the linearity of the data in Fig. 2 (b) is good, whereas the data in Fig. 2 (a) are dispersed. The dispersion is presumably due to the existence of the defects, the grain boundary of the texture and so on, caused by rapid quenching. The Young's modulus, E, for martensitic phase is 214.7 GPa and that for ferritic phase is 196.4 GPa. The Poisson ratio, ν, for martensitic phase was 0.341 and that for ferritic phase was 0.295. For the values of E and ν at the region where the martensitic phase and the ferritic phase coexist, we use the average value weighted by the volume fraction of each phase. The volume fractions was estimated by finite element method (FEM). 1)

The typical observed reflection peaks for three directions from the position at 2mm from the surface on the central circular cross section of the bar are shown in Figs. 3 (a) to (c). We see that for axial direction shown in Fig. 3 (a) the data points are scattered remarkably in spite that we expend 40 minutes for one datum point. This is because the path length of the neutron beam inside the sample is long for the measurement of axial direction.

The calculated residual stress for three directions at each position of the circular cross section at the center of the bar is shown in Fig. 4. Near the surface where the material is hardened, the residual stress for radial direction is tensile and large, whereas the stresses for axial and hoop directions are compressive. We see that at the inner position the stress is small.

The residual stress at each position on the central axis of the bar, which was also measured by RESA, will be published elsewhere.

References

Figure 3: Reflection peaks from the position at 2mm from the surface on the central circular cross section (a) for axial direction, (b) for radial direction and (c) for hoop direction.

Figure 4: Residual stress at each position on the central circular cross section of the heat treated round bar.
Measurement of Residual Stress in the Neutron Cold Moderator Cell for High Intensity Proton Accelerators II

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Residual stresses in the side wall of an aluminum alloy neutron cold moderator cell for Japanese spallation neutron source (JSNS) 1 was investigated by neutron diffraction method as the sequel to the previous study 2 on the front wall. Diffraction strain measurement was performed in the same conditions as that of the previous study, but the size of Cd masks aperture restricting gauge volume were chosen 4mm 3 to suit the wall thickness of the side wall. Figure-1 shows horizontal and vertical cross sectional views of the cell, and measurement region in the side wall is a hatched area. Each strain component in x, y and z directions for 10 gauge volumes were measured as change in the Al(111) lattice plane spacing.

Figure-2 shows the estimated residual stress distribution in the side wall of the moderator cell. The stresses in all three coordinates exhibit compressive stress state throughout the measured range, but show a slight increase response toward tension in between z=6mm and z=12mm, and then take a maximum compression peak at z=10mm. Contrary to this, the stress response of the front wall in the previous study in the same range assumed a minimum compression value around z=10mm.

References
1) The Joint Project for High-Intensity Proton Accelerators, ed. the Joint Project Team of JAERI and KEK, JAERI-Tech 2000-003.

Figure 1: Fig.1 Cross-sections of the neutron cold moderator cell for high-intensity proton accelerators. A view in the top shows a horizontal-section along the weld seam.

Figure 2: Fig.2 Residual stress distributions in the base metal near weld of the A7N01-T6 moderator cell.
Measurement of residual stress distribution vicinity of the crack on peened surface of type 304 stainless steel by neutron diffraction method

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Shot peening (SP) deforms and hardens a metal surface plastically with particles of metal or glass. As a result, compressive residual stress appears and the surface properties are improved. Cracks, not only those caused by SCC, in compressive residual stress fields are difficult to propagate unless an external load is applied. The cracks on the peened material, consequently, will not propagate without the external load. So residual stress measurement by neutron diffraction was discussed to the peened materials.

The materials used in this research were stainless steel Type-304. The specimens were 10 mm wide, 50 mm long, and 3 mm thick. These were extended under a strain range of 0.4 % and soaked in an autoclave for 500 hours, at a temperature of 562 K, in which the concentration of dissolved oxygen was 8 ppm.

RESA was used in the measurement of lattice strain. The 111 diffraction of γ-Fe in type-304 steel was used in the measurement of strain. The wavelength, λ was 0.20731. Measurements were performed in steps of 0.1 mm to a depth of 0.5 mm and in steps of 0.2 mm to a depth of 1.0 mm-depth. Cadmium masks were inserted in both the incoming beam and the diffracted beam to define a sampling volume of 0.2x0.2x10 mm³. The stresses were obtained from Hooke’s law using lattice strains in three directions. For 111 diffraction the Young’s modulus, E₁₁₁, was 249 GPa and the Poisson’s ratio, ν₁₁₁ was 0.28.

The results of surface residual stress vicinity of crack on the surface obtained from before and after peened specimen are shown in Fig. 1. In the case of before peened specimen, residual stresses were almost 0 MPa since they were released by crack progress. In the case of after peened specimen, residual stress were compressive and at about 500 MPa and 400 MPa. These compressive stresses decreased rapidly and changed to tensile at a depth of 0.5 mm. The surface residual stresses were nearly same in spite of flat or notched.

The values of residual stress obtained by x-ray diffraction are also shown in Fig. 1. It was found that the result for residual stress as obtained by neutron diffraction almost agreed with those from x-ray diffraction.

According to the principle of superposition, the load on the crack surface controls the stress intensity factor K at the crack tip. The sum of load on the crack surface and K decreases if a compressive residual stress exists at the surface. As the result, the crack growth rate in the depth direction will decrease. The prevention effect of crack propagation on the surface is greater than that in depth direction since the compressive residual stress will prevent the crack from opening. As the result, crack propagation on the surface was arrested. These results means if compressive stress slightly exist at the surface, crack progress is prevented.
The possibility of internal stress measurement of the King-size sample

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We performed evaluation about the possibility of an internal residual stress measurement using king-size aluminum alloy material. As for the engine of the airplane, the ship, and the automobile, many aluminum alloy material is used for the purpose of the lightening, the cooling performance and the lifetime improvement. In order that to improve the radiation effect of engine temperature, it is performed that expand surface area or a cooling water passage is puffed up etc. Therefore, big space is located in the inside of engine, and there are few neutron pass lengths than an actual size pass length. This measurement used the RESA equipment. This engine is the water-cooled type, which is made by the aluminum alloy, the specific gravity is about 2.88. The void ratio in the engine, which was found from the weight, is about 50%. The neutron absorption coefficient $\mu$ is about $0.125 \text{cm}^{-1}$ as for $0.21 \text{nm}$ neutron wavelength. The incidence neutron intensity of RESA is about $3 \times 10^5 \text{n/cm}^2/\text{sec}$, and the slit of incidence and reflection used $3 \text{mm} \times 3 \text{mm}$. The measurement position and size of engine is shown in Fig. 1.

![Figure 1: The size and a measurement position of engine.](image)

In an internal residual stress measurement, we have to do a neutron diffraction measurement about 3 axial directions of X, Y, and Z. The neutron total pass length in the engine to get the diffraction of the measurement position is 191 mm at the X-axis, 55 mm at the Y-axis, and 309 mm at the Z-axis. $I/I_0$ with consideration to the void ratio is 0.3 in measurement of the X-axis, at the Y-axis is 0.71 and at the Z-axis is 0.15. The measurement neutron wavelength of RESA used for 0.2098 nm. The measurement index and the diffraction angle thought the gauge volume as important, selected Al (220) near right-angled, and diffraction angle was used at the 94.28 degrees. Al (220) diffraction pattern of the measuring points in A and B are shown in Fig. 2.

![Figure 2: Al (220) diffraction pattern of the measuring points A and B.](image)

The neutron diffraction pattern by gauge volume of doing about 27 mm$^3$ is good gauss distribution position A. But in a certain measurement part, a diffraction pattern position B might not be obtained at all. It is interpreted that this is in order that having measured for the space part to the gauge volume. In the case of a huge aluminum sample, at RESA, it proves that an internal strain can be measured with a $3 \text{mm} \times 3 \text{mm}$ incidence neutron beam size. Moreover, in order that to measure the position, which cannot be viewed with a sufficient precision, when considering the method of doing incidence neutron beam to a measurement position in the precision of less than $\pm 1 \text{mm}$ with the working drawing or the 3-dimensional drawing by the ultrasonic scanner etc., it proves that it is also practical use.
2. Neutron Radiography
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研究テーマ：中性子ビーム利用技術に関する開発研究
表　題：パルス中性子ラジオグラフィ用電子撮像システムの開発

パルス中性子ラジオグラフィ用電子撮像システムの開発

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パルス中性子ラジオグラフィの中性子飛行時間撮影法では中性子散乱実験装置で要求される程度の時間分解能は必要としないが、高計数特性（高時間分解能）と高空間分解特性を兼ね備えた中性子シンチレーション検出器の開発が必要とされている。本研究では、中性子用蛍光体の前面及び後面にX-Yの直交した2方向に配置された波長変換光ファイバ群から出力される微弱光をマルチチャンネル光電子増倍管で受光し、検出点のX-Yアドレスを30ns以下で出力する電子回路の試作を行った。

システムの試作において、波長変換ファイバの断面形状が角型と丸型との場合で比較し、蛍光体との接触面積が大きくなる角型の方が効率の点において優れていることを確認した。また、回路の入力信号となる光電子増倍管からのパルス出力を中性子蛍光体として広く使用されているLiF:ZnS(Ag)を用いて確認した。これらの結果から、今後検出器の大面積化に伴い大規模化が予想されるエンコーダ部分の設計に必要な基礎データを取得した。

今後は熱中性子ラジオグラフィ装置を用いて、空間分解能と計数特性の観点から最適な読み出しレイアウトの検討を進める。回路は高速のプログラムループ素子を使用し、将来の大型システムの基幹要素となるものである。

フェーズコントラストイメージング

ピンホールを用いた中性子フェーズコントラスト(PC)イメージングの予備実験を冷中性子ラジオグラフィ装置場で中性子イメージングプレートを用いて実施した。ベン先部を撮影した結果では、図1に示すとおりオリジナル画像では曲線管及びピンホールのバリ等によるアーティファクトが観察されたが、背景補正後の画像にはボール部及びインク部をはっきりと観察できた。

図1 PCイメージング
上：オリジナル画像、下：背景補正
中性子ラジオグラフィを用いたストロボ撮影技術に関する研究

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大強度陽子加速器の中性子散乱施設のうちパルス中性子ラジオグラフィ装置(PNR)のストロボ撮影で必要とされる検出器の開発を行った。現在 JRR-3M 中性子ラジオグラフィ装置に設置されている中性子線損失システムは高エネルギーで撮影された写真を光学レンズにより接続したのであるが、大強度陽子加速器の核破壊中性子源から発生されるパルス中性子ビームには高エネルギーや中性子およびγ線が含まれることから鋳型コンバータとカメラを光ファイバーを用いて接続する等カメラの遮蔽を十分に行う必要がある。

本年度は光ファイバー接続を導入した撮影システムを熱中性子ラジオグラフィ装置に仮構築し、模擬撮影により問題点の検出を行った。鋳型コンバータ（シンチレータ部分）とカメラ部分を光ファイバー接続するための 20cm 長のファイバーバンドルはプラスチック光ファイバ（三菱レイヨン製エスカ 1mmφ）を用いて試作した。シンチレータは高輝度の LiF-ZnS(Ag)をファイバーバンドル中性子入射端面側にシリコンゲルで取付け、冷却型 CCD カメラでファイバーバンドル出射端を撮影した。その結果、シンチレータの発光を直接カメラで撮影した場合の輝度15380に対して、ファイバーバンドル出射端での輝度が 8930 となり、ファイバーバンドル使用による輝度の低下は 60%程度であることが分かった。また、二次元のイメージを確認するためフィルム法で使用されるマークの撮影を行った。撮影結果を図1に示す。マーカーのレイアウトは図に示す通りであり、形状はプラスチックに鉛でできた文字が埋められている。従って、中性子による透過画像では文字部分の輝度が高い状態となる。マーカーのあり、なしを示す a) 及び b) を比較しても良く分からないが、両画像を用いた背景補正により得られた画像 d) ではマーカーの位置がはっきりと確認できる。しかし、文字の位置は凡そ確認できるが形状 "A" をとらえるところまでは至っていない。また、バンドル製作に伴う画像歪みの影響が確認された。

今後は、イメージ領域を広げるために入射側をテーブラー状に拡大する方策を開発する。

図1 ファイバーバンドル使用撮影画像

原子炉：JRR-3M 装置：TNRF, CNRF 分野：中性子ラジオグラフィ（その他）
研究テーマ：中性子ビーム利用技術に関する開発研究
題：再帰型2液相分離系水溶液における濃度ゆらぎの空間発展の可視化

2-3
再帰型2液相分離系水溶液における濃度ゆらぎの空間発展の可視化

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1-プロパノール水溶液は組成・温度によらず一様に混合しているが、これに少量の塩(KCl)を添加する、ある温度範囲（例えば 40℃〜60℃の間）で2液相に分離する。本研究ではこの特異な相分離過程における濃度ゆらぎの空間・時間発展を中性子ラジオグラフィにより可視化した。

可視化は冷中性子ラジオグラフィ装置において磁通コンバータと SIT 管カメラを組合わせた実時間撮像システムを用いて行い、画像をリアルタイムでレーザーディスクに記録した。レーザーディスクに記録された画像はフレームグラーポードによって 8bit(256 階調)の 640x480pixels 画像に変換された後、IP-Lab Spectrum により画像解析された。

光学用石英ガラスセル内に封入した KCl 添加のプロパノール水溶液を室温から 80℃まで変化させながら濃度ゆらぎから相分離にいたる過程でのゆらぎ構造の空間発展を可視化した。図1に水溶液の透過画像を示す。石英ガラスセルは殆ど中性子に対して透明であり、溶液部のみが可視化された。その結果、相分離温度（50℃）で相分離に伴う2相間の透過率の違いが可視化画像上で段階状に確認できた。（図2 参照）

水溶液の温度をパラメータとした可視化実験により、昇温過程においても降温過程においても同じ50℃で相分離が起こることを確認した。その際、温度変化過程の違いによる相の界面位置の変化は見られなかった。さらに、塩の添加量を1ミリ mol 程度減じて添加して行った実験では相

図1 水溶液透過画像

図2 中性子透過率

原子炉：JRR-3M 装置：CNRF 分野：中性子ラジオグラフィ（その他）
研究テーマ：中性子ラジオグラフィによる沸騰流のポイド率計測
表題：中性子ラジオグラフィによる沸騰開始点の計測
2-4

中性子ラジオグラフィによる沸騰開始点の計測

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図 1 ポイド率の計測実験用水循環ループ

Instantaneous Void Fraction (dT=0.89ms)

図 2 非時変ボイド率の計測

図 3 沸騰開始点の計測

当研究グループでは、中性子ラジオグラフィ（NRG）を用いて狭い流路内を流れる熱的および時間分解能で可視化し、瞬間ボイド率分布および時間平均ボイド率分布を計測してきた。平成13年度は、NRGを熱流体計測に応用して計測されるボイド率分布から沸騰開始点を計測した。

実験は、JRR-3M熱中性子ラジオグラフィ実験施設（TNRF-2）を利用した。ボイド率分布計測実験には、沸騰流NRG実験用絞形流路（流路間隔が3mmおよび5mm、加熱面100mm、流路幅30mm、加熱幅20mm）を用いた。図1にこの試験体と水循環ループの概略図を示す。このループ内を水が流れ、試験体の中で沸騰が始まる。

図2に瞬時ボイド率を計測した一例を示す。図2は、約1000フレーム毎秒で記録したNRG画像を画像処理して得られたボイド率の分布を示しており、これは動画撮影用画面の1コマを示している。沸騰開始点は、実験の時間と逆方向に画像処理を行って統計的に評価を行った。図2条件での沸騰開始点を測定した結果を図3に示す。図3から、沸騰開始点の統計的分布と変動幅が分かり、これらのデータから沸騰開始点計算式を導出した。

本成果により、狭縫矩形加熱長矩形流路体系でのボイド率を解析的に計算可能となり、除熱限界を高精度で計算できるようになった。

次ステップとして、将来型原子炉の炉心を模擬した実験装置を模擬した実験で流路内に2相流のボイド率計測を行い、ボイド率の3次元分布を計測するための技術開発を進めている。

参考文献
2-5 JRR-3M 冷・熱中性子を用いたラジオグラフィ技術の高度化－III

Development of Advanced Neutron Radiography Techniques Using Thermal and Cold Neutrons from JRR-3M, Part III

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1. 研究の目的
本研究は、これまでに開発した中性子ラジオグラフィ高感度撮像技術と熱中性子ラジオグラフィ画像の定量化法（エスケーリング法）を応用して、超安全・超小型原子炉 RAPID-L の自己作動型反応度制御装置の基礎の特性を調査するとともに、更なる中性子ラジオグラフィ技術の革新を目指して、熱中性子ラジオグラフィ高感度撮像法を用いた気液二相流計算における技術的課題を明らかにし、また、画像処理による流体計測の新しい可能性を追求するものである。以下にそれぞれの研究の概要を述べる。

(1) 超安全・超小型原子炉 RAPID-L の自己作動型反応度制御装置の特性
超安全・超小型原子炉 RAPID-L は、図 1 に示すようなウラン密化物燃料リチウム冷却スラウドであり、電気出力 200 kW の両面及び火災基盤用原子炉として開発されている。この原子炉では、無人化技術を実現するために、自己作動型反応度制御系（LEM 及び LIM）を有する。
LEM(Lithium Expansion Module) は、図 2 に示すように、Li-6 を満たしたリザバーと封入管なり、Li-6 の液面は封入管の途中にくるようにし、封入管の下部は不活性ガスで欠けされている。この Li-6 の液面は、水銀温度計のようにリザバーの温度上昇により下降する。そのため、炉心出力の上昇に伴う冷却材出入口温度の上昇によりリザバー内の Li-6 が膨張して液面が炉心内に下降し、

図 1 RAPID-L 概念図
図 2 LEM 概念図

JRR-3M 7R(TNRF2)、中性子ラジオグラフィ装置、熱流体工学
中性子吸収材としての Li-6 が炉心に入ることにより負の反応度を増加する。LIM（Lithium Injection Module）は、図 3 に示すように、封入管はフリーズシールにより区切られ、上部には Li-6 とカーバーガスが、下部（炉心）部は真空に保たれる。カーバーガスは適度に加圧される。炉心温度が上昇しフリーズシールが溶融すれば、Li-6 が炉心部に注入され、負の反応度を急速に増加し、炉を停止する仕組みである。本研究では、この LEM および LIM の作動特性を中性子ラジオグラフィにより可視化し確認することを目的とする。

(2) 高速度撮像法による気液二相流計測の検討

高速度撮像法の流体計測への応用における技術的課題に関しては、すでに平成 10 年度までの共同利用研究により、ボイド率や気泡の速度など、物理量の計測に有用であることを示し、また、撮像速度と気液二相流のボイド率の計測誤差との関係などについて調べた。しかしながら、これらの物理量は時間平均値に限られており、瞬時の物理量の計測においては、高速で動く流体粒子の画像のフレームの新たな誤差が生じる可能性がある。中性子ラジオグラフィに関しては、画質の劣化、とくに画像のエッジのポケは、コンバータの平行度、物理内部乱、幾何学的不明確、運動の不明確、撮像系のノイズによる考えられ、これまで検討されているが、運動する流体粒子の速度の影響については明らかにされていない。そこで、本研究では、気泡を模擬した穴を明けた回転円盤を用いて、瞬時ボイド率計測に対する気泡速度の影響を調べることを目的とする。

(3) 画像処理による流体計測法の開発

本研究では、中性子ラジオグラフィにより得られた画像を処理することにより、溶融金属二相流の液相内の速度場を PIV 法を用いて計測することを目的とする。
溶融金属二相流は、液体金属冷却高速炉の炉心溶融事故時の溶融炉心内のスチームの沸騰現象を模擬したものである。この現象を解析するための SIMMER-III コードでは気泡挙動に関する構成式がいくつか使われているが、これらの構成式の検証のデータを取得することが本来の目的である。

2. 研究の方法および成果

2.1 超安全・超小型原子炉 RAPID-L の自己作動型反応度制御装置の特性

(1) LEM の作動特性

図 4 に実験装置の概要を、図 5 に Ta 製および SUS 製の 2 種類の LEM 試験体および実験条件を示す。先に述べたように LEM 試験体上部には Li（本実験の場合は、通常の Li を用いた）を封入し、下部は Ar＋He のカーバーガスを封入した。この試験体を加熱することにより Li の液面は下降するので、この液面の動きを可視化し、液面の位置と温度との関係を求めることが本実験の目的である。この実験では、LEM 試験体内の Li の液面を精度良く測定する必要があり、また、液面は温度上昇によりゆっくりと動き、バケラシ系に CCD カメラを用い、コンバータとしては "LiF/ZnS:Ag（成形オプトニクス NR コンバータ）を用いた。

図 4 LEM 可視化実験装置および撮像条件
図5 LEM試験体および実験条件

図6 Ta試験体の画像

図7 SUS試験体の画像

フィルター（8近傍平均）→処理後の画像（解像度0218mm/画素）の画像処理を施したものである。これらの画像より、いずれのLEM試験体も所期の作動特性を満たしていることが確認された。

(3) LIMの作動特性

LIMの場合、フリーズシールの清浄に伴って液体Liが急速に移動するため、可視化実験では動画の撮影が必要である。このような実験装置を用いた。撮影にはSTI管カメラを用い、コンバータとしてはLiF/ZnS:Ag（化成オプトンクスNRコンバータ）を用いた。LIM試験体を図9に示す。この試験体のフリーズシールは材質がアルミニウムであり、660℃で作動する設計である。
実験では、試験体を可搬型加温装置内に収納し、
約600℃まで昇温した後、一旦温度上昇をやめ、
撮像系を作動させた後、再び温度上昇を開始し、
フリーゼシールが作動して Li が下部のシリンダー
内に移動を終わるまで続けた。このようにして
得られた画像を図10に示す。この場合、1コマ
1/30秒の時間で進める。従って、Li の移動
は、約6コマ、すなわち約0.2秒で完了してい
ることが示され、所期の作動特性を満たしている
ことが確認できた。

2.2 高速度撮像法による気泡二相流計測の検
討
この研究では、図11に示すような、気泡を模
擬した適当な大きさと深さの穴をいくつか明け
たステンレス鋼製円盤を回転させて、この動きを
可視化して画像を処理することにより、瞬時のボ
イド率を求め、これと円盤の回転から求められる
瞬時のボイド率とを比較することにより、瞬時ボ
イド率の計測誤差の評価を行った。この実験では、
円盤の回転速度は0から350rpm（接続速度
0から1.5m/sに相当）とした。また、この
計測誤差に及ぼすイメージ・インテンシファイア
のゲート時間の効果も調べた。

撮像系としては、イメージ・インテンシファイ
アーガー（Photoron C6276-01MOD）付きの高速度ビデ
オ（Photoron FastCam-Ultima）を用い、コンバ
ータにはLi/ZnS:Ag（化成オプトニクス NR コン
バータ）を用いた。

得られた画像の例を図12に示す。この図で、

回転速度が350rpmの場合は、明らかに残像
がみられる。従って、この画像をもとに得られた
瞬時ポイド率分布は、図13に示すように、静止
した円盤のボイド率分布とは異なる。ここで、ボ
イド率は、Mishimaらによるスケーリング法を
用いて計算した。

次に、静止した円盤の画像を時間平均してボイ
ド率分布とえた結果を図14に示す。この図か
図14 静止した円盤の時間平均ポイド率

図15 静止した穴の周りのポイド率分布

図16 回転円盤の時間平均ポイド率

図17 動く穴の周りの時間平均ポイド率分布

これらの結果を検討した結果、瞬時局所のポイド率の計測誤差は主にコンバータの光電管特性に依存し、1.5m/sのときのピークのポイド率の値に対して20%程度の誤差を含む。従って、現在の撮像系では、瞬時局所のポイド率分布の計測誤差評価においてはコンバータの光電管特性に依存する。
2.3 画像処理による流体計測法の開発

本研究では、中性子ラジオグラフィにより得られた画像を処理することにより、溶融金属二相流の液相内の速度場をPIV法を用いて計測することを目的とする。用いた試験部の概略を図18に示す。これを中性子ラジオグラフィ設備に設置し、試験部内の溶融金属内の気泡挙動を可視化した。溶融金属にはPb/Bi合金を、気相として窒素ガスを用い、試験部容器下部のノズルより注入した。溶融金属にはトレーサとして直径約1〜1.5mmのAuCd₃粒子を混入させた。実験中Pb/Biの温度は150°Cとした。

撮影系には、SIT管カメラ(Hamamatsu C2741:30fps)と高速度ビデオ(Photonon FastCam-ULTIMA)を用い、コンバータには"LiF/ZnS:Ag"(化成オプトニクスNRコンバータ)を用いた。

得られた画像の原画像、原画像を処理して得られたトレーサ粒子の画像及び気泡の画像を図19に示す。これらの画像を求める際には、原画像から気泡とトレーサ粒子を分離する必要があるが、これらは、図20のようなロジックを用いた。すなわち、原画像から2スケーリング法によりピクセル率を求め、ピクセル数が一定の領域は気泡として、他の部分は液相としてトレーサ粒子像を得た。このトレーサ粒子の画像に密度相関によるPIV法を用いて速度場を求めた。

図21は、PIV法により得られた速度ベクトル場の結果に対する画像積分時間の影響を示す。こ
ように、画像積分時間が短い場合、速度ベクトルの変動が大きく、流れのシステムティックな挙動が隠されてしまうことが分かる。また逆に積分時間が非常に長い場合、二次流れのような変動成分は平均化されてしまう。従って、流れの変動の時間スケールに応じて適切な画像積分時間を設定する必要がある。

以上の結果より、中性子ラジオグラフィにより得られた画像を処理し、PIV法を用いることにより液相速度計の計測が可能であることが示された。

3. 得られた結果の評価

本研究により、中性子ラジオグラフィの流体計測への新しい応用例が示されたほか、高速度撮影によるポイド率計測において、計測誤差に対する気泡の画像のブレの影響が明らかになり、また、コンパラータの光減衰特性の重要性が明らかになった。さらに、流体計測への応用の可能性を広げる技術開発としては、PIVによる液相速度ベクトル場の計測法が提案され、その有効性が示された。これらの成果は、いずれも、熱中性子による中性子ラジオグラフィ技術の高度化およびその流体計測への応用に対して有益な知見を提供するものと考えられる。今後は、さらに、中性子ラジオグラフィと画像処理法とを組み合わせた流体計測技術の高度化とともに新しい要素として、パルス中性子の利用技術の開発のための基礎的研究を行う予定である。

4. 成果の公表

本研究により得られた成果の一部あるいは全部を、国際会議あるいは雑誌に公表したものは以下のとおりである。


(2) Y. Saito, T. Hibiki, K. Mishima, K. Moriyama, and J.


2-6

厚い水性試料の中性子ラジオグラフィー
Neutron radiography of thick hydroxenous materials
with use of an imaging plate neutron detector.

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1. はじめに
核磁気共鳴等の研究から生体内の水構造は病変に応じて変化することがわかった。生体においてその
重要な構成成分である水が中性子に対するクロス
セクションが非常に大きいため中性子ラジオグラフ
ィーの応用が困難であった。
中性子ラジオグラフィーを用いて病変のイメージング
ができれば診断および治療に非常に有用である。
また恶性腫瘍の治療に中性子照射が用いられるが中
性子ラジオグラフィーを利用しての照射部位での線
量の正確な測定は治療においに役立つであろう。
放射線中止の大きな水性試料の中性子ラジオグラ
フィーでは、放射線の影響が無視できない。またバッ
クグラウンドの低減には、中性子遮蔽材の放射の研究
が必要である。様々な遮蔽材の後方散乱、厚い水
性試料に関する中性子ラジオグラフィーの空間分解
能の向上に関する研究を行った。

2. 実験
1) 中性子入射側からイメージングプレート(1P),
試料の周りに密接して配置し、ビッカースの中央から一
方的に試料を設置し、試料からの後方散乱を撮像した
(図1)。試料として、面積は種々であるが、SiC
(5 mm t), Si₃N₄ (5 mm t), S₁ 単結晶
(10 mm t), ポロンゴム (10 mm t), 砂糖
B₄C (5 mm t), リチウムタイル (10 mm t),
アルミ (1 mm t), すず (0.5 mm t X 2),
鉛 (0.5 mm t), パラフィン (4.3 mm t),
水晶セリ中の水道水 (1, 2, 4, 10 mm t) を
使用した (表1)。
IP は、γ線用 (γ IP), およびGd をコンバーター
として 50 %、発光物質を 50 % 含有する 145
μ m 厚の中性子用 (IP-ND) を使用した。

研究施設・装置  JRR-3M, 中性子ラジオグラフィー装置
研究分野  構造解析

図1. 試料とIPとの設置位置
中性子はJRR−3 M素中性子ラジオグラフィー装置N. 2を使用し3秒照射した。

表1；試料のサイズ

<table>
<thead>
<tr>
<th>材料</th>
<th>W(mm)</th>
<th>L(mm)</th>
<th>T(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>40</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>Si3N4</td>
<td>58</td>
<td>58</td>
<td>5</td>
</tr>
<tr>
<td>Si crystal</td>
<td>40</td>
<td>120,150</td>
<td>10</td>
</tr>
<tr>
<td>B rubber</td>
<td>104</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>B4C</td>
<td>100</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>Li tile</td>
<td>100</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>Al</td>
<td>250</td>
<td>300</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>100</td>
<td>100</td>
<td>0.5X2</td>
</tr>
<tr>
<td>Pb</td>
<td>42</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>Paraffin</td>
<td>60,63</td>
<td>40</td>
<td>4.3</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

2) 200 mlビーカー内の水および5cm厚パラフィンブロックの90度散乱像を撮影した。試料を中性子照射野の外側縁に設置し、I P−NDを試料の側方に約5cm離して中性子照射野外に設置した。

3) 試料とIP−NDとの間隔を大きくしたときに、距離による透過像の変化を研究するために、イメージングプレート感受性面を中性子ビームと平行方向（試料とは垂直方向）に設置して200mlビーカー内の水および4mm厚クオーツセル中の水の透過ラジオグラフィを撮影した。

4) 試料とIP−NDとの間隔を15mmとして透過ラジオグラフィを撮影した。

3. 結果および考察

1) 試料からの散乱部位のphotostimulating luminescence(PSL)値の、試料から離れたところの中性子照射部位でのPSL値に対する比（測定散乱強度比）を表2に示した。測定散乱強度比は、パラフィンと水を除いて、γ線IPでの測定値の方が、中性子IPでの測定値より高かった。（中性子用IPでの測定散乱強度比/γ線用IPでの測定散乱強度比）は、特にPb、0.89、B4C、0.79、Sn、0.98で顕著であり、中性子との反応による電離線の散乱が顕著に認められた。パラフィン、1.18、水、1.02、1.06（図2，図3，4mm，1.09，1.07（1〜10mm）では、中性子用IPでの測定値のほうが高く、中性子の散乱の寄与が高いという予測の通りであった。

図2. 4mm厚クオーツセル中の水の後方散乱像（IP-ND）。

図3. 4mm厚クオーツセル中の水の後方散乱プロファイル。

JRR3M中性子ラジオグラフィー装置でのneutrons/γは、6.25 X10^4（neutrons/cm^2・mR）であるが、γ線用IPでの測定散乱強度がどの程度中性子用IPでの測定散乱強度に反映しているかは不明である。中性子IPでの測定散乱強度比のプロファイルとγ線用IPでの測定散乱強度比のプロファイルが類似しているのは興味深い結果であった。

この結果より中性子用イメージングプレートを使用する際には中性子だけでなくガンマ線に対しても散乱および放射の少ない遮蔽が必要と考えられる。ガンマ線用の遮蔽材料では中性子照射によるその材料からのガンマ線の放射が高く単純には、中性子用イメージングプレート使用時のガンマ線の遮蔽には困難がある。ガンマ線および中性子の散乱および
表2. 試料からの後方散乱部位のPSL値の、試料から離れたところの中性子照射部位でのPSL値に対する比（測定散乱強度比）

<table>
<thead>
<tr>
<th></th>
<th>中性子用IP</th>
<th>ガンマ線用IP</th>
<th>IP-β/γIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>水 1mm</td>
<td>1.102</td>
<td>1.079</td>
<td>1.02</td>
</tr>
<tr>
<td>水 2mm</td>
<td>1.135</td>
<td>1.071</td>
<td>1.06</td>
</tr>
<tr>
<td>水 4mm</td>
<td>1.167</td>
<td>1.072</td>
<td>1.09</td>
</tr>
<tr>
<td>水 10mm</td>
<td>1.158</td>
<td>1.084</td>
<td>1.07</td>
</tr>
<tr>
<td>濃縮B4C 5mm</td>
<td>1.141</td>
<td>1.450</td>
<td>0.79</td>
</tr>
<tr>
<td>ボロンラバー 10mm</td>
<td>1.149</td>
<td>1.226</td>
<td>0.94</td>
</tr>
<tr>
<td>リチウムタイル</td>
<td>1.137</td>
<td>1.188</td>
<td>0.96</td>
</tr>
<tr>
<td>すず 1mm</td>
<td>1.249</td>
<td>1.280</td>
<td>0.98</td>
</tr>
<tr>
<td>鉛 0.5mm</td>
<td>1.419</td>
<td>1.599</td>
<td>0.89</td>
</tr>
<tr>
<td>SiN4</td>
<td>1.186</td>
<td>1.158</td>
<td>1.02</td>
</tr>
<tr>
<td>SiC</td>
<td>1.154</td>
<td>1.170</td>
<td>0.99</td>
</tr>
<tr>
<td>Si crystal</td>
<td>1.178</td>
<td>1.194</td>
<td>0.99</td>
</tr>
<tr>
<td>Al</td>
<td>1.120</td>
<td>1.124</td>
<td>0.99</td>
</tr>
<tr>
<td>パラフィン4.3mm厚</td>
<td>1.233</td>
<td>1.049</td>
<td>1.18</td>
</tr>
</tbody>
</table>

放射線の測定とともに遮蔽としてどのような物質を

2）90度散乱；水試水を満たした200mlビーカー内

な水による散乱像は、ビーカーを中心にした散乱

強度の高い部分があり、彗星の尾のように入射反対

側へ低い散乱強度の部分がみられた（図4）。

パラフィンブロックでは、中性子入射側前線から強

度の高い散乱像が広く入射側に拡がっており、入射

反対側へ入射側よりやや低い散乱強度の部分が狭

い面積で認められた（図5）。

3）200mlビーカー内の水では試料直後の画像上

での水の幅は68mm、200mm離れた部での水の幅

は68mmで200mm離してもほとんど画像上では

像の広がりの変化はみられなかった（図6）。4mm

厚のクオーツ中の水でも画像上の幅は試料直後で1

3mm、200mm離れた所で12mmであった。

後方散乱に関してもIPを試料の中性子入射側に水

平に設置して同様の実験を行ったり、IPの残像の影

響で正確なデータを得ることに至っていない。

4）4mm厚の水と中性子用IPの間隔を変えたの

透過ラジオグラフィでの試料透過部位のPSL値の、

試料から離れたところの中性子照射部位でのPSL値

に対する比（測定透過強度比）は、0mm；

図4. 200mlビーカー内の水による90度散乱

像（IP－ND）。照射3秒。図の右側が中性子入射

側。黒マークビンはビーカー後中心位置。

図5. 5cm厚パラフィンブロックの90度散乱像

（IP－ND）。照射3秒。図の右側が中性子入射側。

黒マークビンはパラフィン前線。
図6. 200mlビーカー中の水の試料からの中性子の変化による中性子透過像（1P－ND）。図の左側が中性子入射側。

Sn1mm厚の中性子1Pによる透過像では、試料と15mm間にして撮影した像の方が、Sn板の保持に使用したプラスチックテープの像が鮮明に認められた（図8）のに対して、1Pを密接に撮影した像（図9）ではそれが認められなかった。

1.20gのラジウムの中性子1Pの透過像では、試料との間隔を0mm、10mm、30mmと変えても撮影したが、画像上では変化が認められなかった。

4. まとめ

1P－ND使用により試料による中性子後方散乱像、および90度散乱像が撮影できた。使用した1P－NDは中性子だけでなくγ線にも高い感度があるため、1P－NDを使用してより鮮明な透過中性子ラ

図7. 試料からの間隔0mm、15mmのSn1mmの中性子透過像（1P－ND）。図の右側部分が試料部分のプロファイル。

図8. 試料からの間隔15mmのSn1mmの中性子透過像（1P－ND）、白線はスペーサーの透線像。

図9. 試料からの間隔0mmのSn1mmの中性子透過像（1P－ND）
ジオグラフィー像を得るためには、試料からのγ線を含めた中性子の散乱の状況を知ることが役に立つであろう。

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(3) 加藤一夫、松本元一、新村信夫、松林政仁。イメージングプレートを用いた中性子ラジオグラフィーの散乱線およびガンマ線の影響。中性子ラジオグラフィー高度技術の開発と応用専門研究会、2001年、熊取、10月
Development of Advanced Neutron Radiography Using Imaging Plates at JRR-3M TNRF and CNRF

Nagoya Univ., Engineering

Masayoshi Tamaki, Yuusaku Masunaga, Sinnpei Taguchi,
Kazuhiko Iida, Makoto Okada
はじめに

本研究では、イメージングプレートの開発、散乱中性子及びガンマ線の影響を除去することで中性子ラジオグラフィ技術による計数解析精度を高めること、定量解析する上での中性子ラジオグラフィの固有の問題を解決することを目的とし、さらに、イメージングプレートに取り入れた新概念を冷却型 CCD 撮像系に用いてシステムの定量化向上に関する手法の開発を目指した。

具体的には、Jet Propulsion Laboratory の中性子ビームを利用することのラジオグラフィの高精度化技術の開発を目指して、イメージングプレート技術の NR 技術への展開、CCD 冷却型固体撮像素子の利用による広帯域性デジタルラジオグラフィの開発などの基礎実験を実施した。以下に概要をまとめる。

(1) イメージングプレート関係

(1-1) 中性子ラジオグラフィ用イメージングプレートの開発と特性評価

まずカドミウムのステップウェッジを撮像し、中性子透過率を求めて比較した。さらに、中性子透過率を指数関数的減衰からずれる原因がコンバータの性能、特にコンバータの放射する二次放射線にあると考え、これを確認するための実験および解析を行った。

実験：中性子ラジオグラフィ実験は、日本原子力研究所 JRR-3M の TNRF において、極性中性子を用いて行った。撮像試料としては中性子の散乱による影響が現れにくい、厚さが約 0.1 mm で変化する Cd 製のステップウェッジ及び厚さ約 0.9 mm の Cd 製シャープウェッジを用いた。照射時間は Gd 直接法では 1 sec、Dy 直接法では 3 sec、Dy 間接法では 3 sec とした。

この実験では、被写体と検出媒体を密着させず撮影することで入射中性子ビームの非平行による影響を考えないこととした。またこの検出系を L1 タイプで組み、照射孔内での中性子の散乱による影響を最小限にした。

まず上記の IP 撮影法により、Cd のステップウェッジを撮像し中性子の透過率を求め、各手法における直接性の比較を行った。次に Gd のシャープウェッジ像を撮像し、フィッティング関数を用いて解析した。IP の読み取りは BAS 2000 を用い、画素サイズを 100 μm × 100 μm とした。

結果：Fig. 1 に、前述した 3 手法によって Cd のステップウェッジの NR 像から計算した中性子透過率を示す。Gd をコンバータとして用いた場合に比べ、Dy を用いた場合の方が直線性に優れ、透過率が 10^{-3} 程度までは指数関数的減衰の傾きが分かった。

考察及び今後の課題：IP を用いた中性子ラジオグラフィの手順は、コンバータとして Dy を利用した手法は Gd を利用したものがより直線性に優れていることが確認された。しかし、放射化によって Dy から放出される β 線、γ 線のエネルギーは大きく、空間分解能を劣化させ、定量化を損なう原因となっている。そこで、中性子の透過率が 10^{-3} 以下のように低いときには、画像の取り扱いに問題があると考えて、測定結果に誤差を生じてしまうので、定量化的解析を行うためには、コンバータの性能を考慮して、適切な補正を行う必要がある。

(1-2) 新 Dy 入りイメージングプレートの開発

中性子コンバータとしてジスプロジウム (Dy) を用いた手法は、照射場において γ 線の影響を受けないため、中性子用 IP (BAS-ND) に比べて定量化解析において IP のダイナミックレンジを考慮すれば、より低い透過率での定量化解析が期待できる。
さらに中性子ラジオグラフィにより定量解析を行うためには、中性子の散乱成分を除去することが重要であること、従来の研究が明らかにされている。

IP は薄い PSL 体保護膜、(中性子コンバータ+PSL 体)、PET 製支持体、の順に 3 層の構造をしており、保護膜の方向から中性子を入射させる。PSL 体中のコンバータに捕獲されなかった中性子は、支持体層を通り抜けるか、またはここで散乱される。この散乱成分が再び PSL 体に入射し、コンバータに捕獲されるという現象が生ずる。また、コンバータ後方からの中性子がコンバータに入射することがある。これらの IP 支持体側からの後方散乱中性子の影響を除くため、(コンバータ+PSL 体) と支持体との間に強中性子吸収体層を挿入した IP（図 2）を新たに考案・試作し従来の手法と実験的に比較した。

図 2 Dyステップ ウェッジの実験値と理論値（冷中性子）

実験及びデータ処理：中性子ラジオグラフィ実験は日本原子力研究所 JRR-3M にある CNRF 、TNRF2 ビーム孔を用いて行った。従来の IP と比較・評価するために従来の 3 つの IP-NR 手法及び中性子遮蔽体層 (Gd2O3) の上に Dy2O3+PSL 体を均一に塗布した新しい IP の 4 手法を用いて行った。Dy2O3 をコンバータとして練りこんだ IP では照射直後 IP 画像をいったん消去して 2 時間 30 分間化粧光させた。それぞれの手法において被写体として評価用ステップウェッジ状の Dy, Cd を用いた。IP レーダー (BAS-1800, BAS-2000) で読み取ったデジタル画像データから NR 画像の特性、中性子透過率などを評価した。

被写体である Dy の断面積は全断面積に占める散乱断面積の値が一割程度で無視できないために全断面積による透過率の理論値と吸収断面積のみによる透過率の理論値を求めて示した。実際の被写体内で散乱された中性子のうちのいく分か IP に吸収されないことを考えれば、実験値はそのことをよく表わしている。シミュレーション等を用いて正確に評価することが今後の課題である。また表 1 にそれぞれの手法におけるシャープウェッジの空間分解能を示す。Dy をコンバータとして用いると分解能が悪くなっているが、これは B 線のエネルギーが高いためである。他方、Dy を用いた新 IP は B 線の影響を消去できるので図 2 で示したところ中性子透過率を定量的に評価できる利点を持つことが確認できた。

表 1 それぞれの IP における空間分解能

<table>
<thead>
<tr>
<th></th>
<th>IP－NR 手法</th>
<th>転写法</th>
<th>新 IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>半径幅 (μm)</td>
<td>BAS</td>
<td>135</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>thermal</td>
<td>170</td>
<td>350</td>
</tr>
</tbody>
</table>

(1-3)成果の公表

1) M. Tanaki (Invited Talk)

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radiography."
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(2) 冷却型CCD撮像系関係

(2-1) C-CCD式ラジオグラフィ用コンバータの開発

冷却型CCD(C-CCD)撮像装置はダイナミックレンジ、直線性、及び無歪位置検出に優れている。このC-CCDカメラを用いる中性子ラジオグラフィの定量性向上を目指した。CCDカメラによる中性子ラジオグラフィの定量性を改善する成分として、散乱中性子成分、γ線成分とCCD素子の長時間撮影による暗電流があげられる。本研究ではそれらの成分除去する方法を数々に行った、またその他の定数を妨げる成分としてコンバータからCCDカメラまでの間に入ってくるまわりごみ成分の評価を行った。そしてこれらの手法を組み合わせた統合実験を行い総合的にシステム評価を行った。

実験及び解析: 実験は日本原子力研究所JRR-3M熱中性子ラジオグラフィ装置で行った。
1) 乱中性子成分除去実験ではハニカムコリメータを用いて散乱中性子成分を除去した。X-γ駆動装置を用いて、ハニカムコリメータを16通り移動させ、ハニカムコリメータの位置をずらした画像を16枚撮影した。得られた16通りの画像を重ね合わせることによって、ハニカムコリメータの影を消去した。
2) γ線成分除去実験では、Gd2O2ZnS(Ag)を原料とした中性子コンバータとZnS(Ag)を原料としたγ線コンバータを製作した。2種類のコンバータで得られた画像データをγ線に対する感度比をかけて引き算することにより、γ線成分を除去した。
3) よりこま成分除去実験では、コンバータから出てくる光を遮蔽するカバーを製作した。カバー有りとカバー無しのデータの引き算することにより、よりこま成分を除去した。この方法は、暗電流を同時に除去できる。
4) 1)、2)、3)の実験を組み合わせて統合実験をおこない評価した。

結果および考察:
1) 統合実験で得られたFeステップの画像を図に示す。

解像処理による画像比較

2) 画像から評価したFeステップの透過率を理論値で規格化して次図に示す。最も統合実験の透過率曲線が理論値に近づいた。γ線コンバータを用いた結果が理論値より下がり方がなるのは、γ線感度比が高く評価されたことによると考えられる。
3) 今回予定していた全ての手法を取り入れた統合実験で、これらの手法の有効性を示し、本研究の目的はほぼ達成できた。
実験及び解析： 実験は日本原子力研究所 JRR-3M
熟中性子ラジオグラフィ装置 (TNRF-2) で行った。
原子炉から中性子線を照射開始から CCD カメラ
を用いて、二分間撮影し、一分おき、再度二分間
撮影した。この方法でまず五枚撮影した。照射開
始 105 分後から、再度二分ずつ五枚撮影した。
計十枚の撮影が終わってから照射を終了させた。
照射終了直後から二分間撮影し、一分間空け、再
度二分間撮影という方法で二十枚の画像を撮影
した。
また、コンパータからの蛍光を遮蔽する事によ
り、コンパータ以外から入ってくる放射線と光の
みを撮影し、CCD カメラの暗電流成分の除去とノ
イズ成分の除去をした。
得られた画像から、中央値フィルタ法を用いて、
画像処理を行い 153Dy と 154Dy、156Dy それぞれの画像
を分離した。
結果：153Dy と 154Dy、156Dy それぞれの画像を図に
示した。

中性子ラジオグラフィの原理とは、中性子線から
コリメータで引き出された平行の中性子ビームを被
写体にあて、照射をした中性子をコンパータと撮
像機とを組み合わせて中性子画像を得るという仕組
みである。この中性子ラジオグラフィにおける、定
量的解析を向上させる方法は幾つか存在するが、本
実験ではコンパータに着目した。γ 線の影響を受け
ない間接法を採用し、半減期と放射化断面積の観点
から Dy_{2}O_{3}+2ZnS(Ag) コンパータを用いた。この Dy
には、三つの同位体が存在しそれぞれの異なる特性
をもっている。153Dy と 154Dy の崩壊特性について表
にまとめた。また 153Dy と 154Dy は、154Dy の (n, γ)
反応によって、生成されるという特性を利用し、中
性子ラジオグラフィの新システムの構築をめざした。

165Dy と 165mDy の崩壊特性

<table>
<thead>
<tr>
<th>物質</th>
<th>半減期</th>
<th>記号</th>
<th>mGdB</th>
<th>反応度</th>
<th>γ線と相関</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>133m</td>
<td>β</td>
<td>10%</td>
<td>γ(3.7eV)</td>
<td>0.05/0.05</td>
</tr>
<tr>
<td>Dy</td>
<td>133m</td>
<td>γ</td>
<td></td>
<td></td>
<td>1.8/1.8</td>
</tr>
<tr>
<td>Dy</td>
<td>133m</td>
<td></td>
<td></td>
<td></td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>Dy</td>
<td>238m</td>
<td>γ</td>
<td>90%</td>
<td>γ(214eV)</td>
<td>0.00/0.00</td>
</tr>
<tr>
<td>Dy</td>
<td>238m</td>
<td>β</td>
<td>22%</td>
<td>γ(233eV)</td>
<td>1.0/1.0</td>
</tr>
</tbody>
</table>

また 156Dy のみの画像から崩壊関数を導き出し、
その図の示す曲線半減期を求めた。
導き出された半減期が、2.30 時間となり、文献
値の 2.33 時間と合致したと言える。これらの実
験結果から Dy 入り中性子コンパータの新システ
ムが構築できたと言える。
１６５Ｄｙの崩壊特性

（２－３）成果の公表

1）田口晋平、他：日本原子力学会「２０００年秋の大記念」（青森学会）
「冷却型ＣＣＤカメラを用いた中性子ラジオグラフィの開発」
2）田口晋平、他：日本中性子科学会「第一回年会」（仙台学会）
「冷却型ＣＣＤカメラを用いた定量的中性子ラジオグラフィ手法の開発」
3）Shinpei Taguchi et al.: 7th World Conference on Neutron Radiography (イタリア, 2002・9・発表予定) [Development of Quantitative Techniques of Digital Neutron Radiography using Cooled CCD-camera].

（３）今後の計画

以上のようにこの３年間で得られた成果を生かして、次年度以降に計画しているパルス中性子ラジオグラフィ技術の開発に生かしていく。
2-8 多色発光蛍光体を用いた中性子・γ線ラジオグラフィの研究
Neutron-γ-ray Radiography Using Multi-color Scintillator

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1. はじめに
中性子ラジオグラフィとγ線ラジオグラフィは互いに相補的な情報を得ることができる。原子炉からはこれらの放射線が同時に放射されているので、同時に透過像を得ることが期待できる。一方、（株）東芝の日塔等が、Gd系の赤色蛍光コンパータを開発し、従来のGd系緑色蛍光コンバータと組み合わせて、中性子とX線（γ線）の透過像を、カルテフィルムを用いて取得し、その有効性を実証した1）。カルテフィルムでは実時間性にかけるため、我々は、従来から行なってきた電子顕微鏡法による同時取得を試みた。大別して静止画と動画の観察のためのシステムを開発した。静止画は、さらに冷却型モノクロ CCDと光学カルテフィルタを用いる方法と、冷却型カラーCCDを使用する方法を開発した。動画では、高速に切り換える可能な液晶カルテフィルタと高感度TV用CCDを使用する方法と、3板式高感度カラーCCDを使用する方法を開発した。以下、順を追って報告する。

2. 2色発光コンバータ
2.1 2色発光コンバータ

Fig.1に2色発光コンバータ1）の概略図を示す。このコンバータは、Gd2O2S(Tb)とGd2O2S(Eu)の2層構造になっており、第1層では熱中性子に対応する検出断面積が大きいGdで熱中性子が吸収され、同時に電子が放出される。この電子によりEuが励起され、赤色に発光する。γ線の吸収でもEuが励起され、赤色に発光する。同様なことが第2層でも起こる。しかし、第2層の蛍光体がTbであるため緑色に発光する。Fig.2に発光スペクトルを示す。

ここで、第1層の厚みを厚さごとの熱中性子を吸収する厚みに設定し、したがって第2層ではγ線の発光成分が多い思うようにする。ここで、γ線は各層で検出されるのに対し、熱中性子は第1層で多く検出される。したがって、熱中性子成分の抽出では赤色画像中のγ線成分を緑色画像によって除去し、γ線成分の抽出では緑色画像中の熱中性子成分を赤色画像によって除去すれば良い。

JRR－3M 7R 中性子ラジオグラフィ装置、非破壊検査、イメージング

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Rob(i,j)=In(i,j)·An(i,j)·Bn(i,j)·Za(i,j)
+Iγ(i,j)·Aγ(i,j)·Bγ(i,j)·Za(i,j)·D(i,j)······(1)

ここで、
In(i,j): 熱中性子強度
Iγ(i,j): γ線強度
An(i,j): 熱中性子に対する被検体透過率
Aγ(i,j): γ線に対する被検体透過率
Bn(i,j): 熱中性子が第1層で吸収される割合
Bγ(i,j): γ線が第1層で吸収される割合
Za(i,j): 赤に対する光学フィルタの透過率
D(i,j): CCDの効率を考慮した係数
である。また、被検体を設置していない赤画像(赤のジェディング画像)[Resd(i,j)]は式(2)のように示される。

Rshd(i,j)=In(i,j)·Bn(i,j)·Za(i,j)
+Iγ(i,j)·Bγ(i,j)·D(i,j)······(2)

第2層からの出力でも第1層と同じようなことが起こり、緩フィルタを設置した時のCCDからの出力（緑画像）[Gobj(i,j)]、及び被検体を設置していない緑画像（緑のジェディング画像）[Gshd(i,j)]はそれぞれ式(3)と(4)で示される。

Gobj(i,j)=In(i,j)·An(i,j)·Bn(i,j)·Za(i,j)
+Iγ(i,j)·Aγ(i,j)·Bγ(i,j)·Za(i,j)·D(i,j)······(3)

Gshd(i,j)=In(i,j)·Bn(i,j)·Za(i,j)
+Iγ(i,j)·Bγ(i,j)·Za(i,j)·D(i,j)······(4)

ここで、
Bn(i,j): 熱中性子が第2層で吸収される割合
Bγ(i,j): γ線が第2層で吸収される割合
Za(i,j): 緑に対する光学フィルタの透過率
D(i,j): CCDの効率を考慮した係数
である。これに5種類の画像データを用いて次の計算を行い中性子画像N(i,j)とγ線画像γ(i,j)を求めることができる。

N(i,j)= [Rob(i,j)·D(i,j)·k1·Gobj(i,j)·D(i,j)]/ [Rshd(i,j)·D(i,j)·k1·Gshd(i,j)·D(i,j)] = An(i,j)······(5)

γ(i,j)= [Gobj(i,j)·D(i,j)·k2·Rob(i,j)·D(i,j)]/[Gshd(i,j)·D(i,j)·k2·Rshd(i,j)·D(i,j)]=Aγ(i,j)······(6)

ここで、k1とk2は係数であり、
k1=[Bγ(i,j)·Za(i,j)]/[Bγ(i,j)·Za(i,j)]
k2=[Bn(i,j)·Za(i,j)]/[Bn(i,j)·Za(i,j)]
であるが、実際の処理では目視により各値を決定している。これについては、3.1.2節にて詳しく述べる。以下のような記述では、(5),(6)をそれぞれ、つぎの(7),(8)で表記する。

n = Red - k1·Green ·······(7)
γ = Green - k2·Red ·······(8)

ここで、
n: 赤中性子線画像
γ: γ線画像
Red: 赤画像
Green: 緑画像
である。

3. 静止撮像撮像システム

CCDにモノクロとカラーの冷却型2種類を使用した。それぞれ、フルフレーム型で解像度と感度が高いこと、一度の測定で2色の画像が取得できることの長所がある。カメラカメラは自作した。

3.1 ジェジオロ・C C D 撮像

Fig.3に撮像システムの概略図を示す。Table 1に実験を行なったJRR-3MのTNTF2のフィールド特性を示す。赤と緑の線の画像は回転交換式光学フィルタと冷却型モノクロ CCDカメラによって撮像される。まず、アクリル板（厚さ5, 10, 15mm）でローラー線量比を変化させ、熱中性子とγ線の発光成分の強度比の依存性を調べた。

![Fig.3 Schematic view of the imaging system](image)

Table 1 Characteristic of the TNTF2

<table>
<thead>
<tr>
<th>Thermal neutron</th>
<th>n/γ</th>
<th>Cd ct</th>
<th>L/D</th>
<th>Radiation field [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 × 10⁹ [n/cm²/s]</td>
<td>62.5 [n⋅cm⁻²⋅μSv⁻¹]</td>
<td>130</td>
<td>H:176</td>
<td>V:153</td>
</tr>
<tr>
<td>255 × 305</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CCDからのデータは14Bitのデジタルデータとして取得され、オフラインでパソコンで処理された。

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3.1.2 透過画像

Fig.4 に、この実験で使用した被検体を示す。

Fig.4  Schematic view of object

Fig.5 に、10 mmのアクリル板を使用して取得された赤画像及び緑画像を示す。赤、緑両方の画像とともに熱中性子成分及びγ線成分のどちらも含まれているが、赤では熱中性子成分、緑ではγ線成分が多く含まれているのがわかる。

これらの画像から、つぎに中性子とγ線の成分を分離抽出するが、ここで$k_1$と$k_2$の決める方で述べる。これらは現在目視によって最適値を決めており、その例としてγ線を抽出する場合をFig.6 に示す。

Fig.5  Raw red and green images

(a) $k_2=0.45$

(b) $k_2=0.52$ (best)

(c) $k_2=0.60$

Fig.6  Dependency of γ ray image on the coefficient $k_2$ value.

目視評価の際、ASTM インジケータのPb 部分、アクリルステップやステップ被検体のポリエチレン部分を評価の対象とした。$k_2=0.45$の場合、アクリル部分に影が残っているため、熱中性子が残っていることが確認できる。そのため係数が小さい事がわかる。また、$k_2=0.60$の場合、アクリル
部分やBN部分が白く反転していることから、係数が大きい場がわかる。このようにして、係数を判定し(7)、(8)の式をそれぞれ。

\[ n = \text{Red} - 0.74 \cdot \text{Green} \cdots \cdots (9) \]
\[ \gamma = \text{Green} - 0.52 \cdot \text{Red} \cdots \cdots (10) \]

とし、それぞれ中性子線画像、\( \gamma \)線画像を抽出した。その結果をFig.7に示す。

Fig.7より、\( \gamma \)線成分を抽出した画像では、BNやアクリル、ポリエチレンが透過しやすいのがわかる。また万歩計は電池の部分で減衰しているのがわかる。逆に中性子画像では、Pbは透過し、アクリルのステップウェッジや万歩計の内部が見て取れるような透過画像になっている。

以上より、画像解読算により静止画での中性子線成分と\( \gamma \)線成分が、抽出されていることが確認できた。

### 3.1.3 アクリルの厚さの検討

熱中性子、\( \gamma \)線ラジオグラフィの同時撮像を行う場合、2つの画像を最大限に有効に活用するためには、2つの画像のN/Sの和が最低となるのが望ましい。そこで、撮像時間が一定で、N/Sの和が最低となる熱中性子成分と\( \gamma \)線成分の強度比(\( n/\gamma \))を求めるため、被検体の前にアクリル板を設置し、設置なし、5mm、10mm、15mmと変化させた。Fig.8に相対標準偏差と\( n/\gamma \)との関係を示す。

![Fig.8 Relation of the sum of relative standard deviation and n/\( \gamma \).](image)

Fig.8よりアクリルの厚さが10mmの時に最良な画像が得られることがわかる。

### 3.2 カラーC C D撮像

#### 3.2.1 撮像システム

中性子と\( \gamma \)線の強度が時間的に変化するような場では、赤色画像と緑色画像を同時に取得できると良い。また、将来の中性子線源であるパルス中性子源でも、パルス毎に強度が異なる時には、同時取得は有効である。そこで、カラーコードチップを搭載した冷却型カメラを製作し、中性子-\( \gamma \)線ラジオグラフィを試みた。撮像素子はProgressive Scan CCD Image Sensor ICX085AK（SONY製）であり、有効画素数1300(H)×1030(V)、画素サイズ6.7(μm)×6.7(μm)、受光面サイズ2/3インチである。カラーコードの色フィルタは
原色フィルタであり、高い色再現性を示し、画像処理に適している。このカラーCCDを組み込んだカメラの側面をFig.9(a)に、正面をFig.9(b)に示す。カメラ部の底面にはベルチュ素子用冷却水のためのコネクタと、CCD表面の露銅防止用乾燥室素のためのコネクタがある。

Color CCD Chip Peltier Element

Dried Nitrogen Circulating Water

(a) Side view. (b) Top view.

Fig.9 Cooled color CCD camera.

3.2.2 通過画像

実験は、同様に被検体の前方に厚さ10mmのアクリル板を設置して撮像を行った。Fig.10に被検体を示す。被検体を露出時間87.8[sec]で8フレーム撮像した。この8フレームに対して暗電流補正を施しフレーム間フィルタリングを行った原画像（カラー画像）をFig.11に示す。カラー画像の赤色成分と緑色成分を分離した画像をFig.12に示す。これらの画像から、熱中性子成分とγ線成分を抽出した画像をFig.13に示す。

同じ係数を用いて、池の破繊体のデータにつな

Fig.10 Inspecting objects: Step-wedges of acrylic resin and ion and ASTM indicators.

Fig.11 Pre-processed raw color image with acrylic resin plate of 10 mm thick.

(a) Red component.

(b) Green component

Fig.12 Separated images.

しても処理した。被検体は、プラスチック製のおもちゃ（ピカチュウ）、9[v]の電池、PIC(マイコン)である。撮像条件は同じである。ただし、4フレ
ーム撮像し、4フレームに対して暗電流補正を施しフレーム間フィルタリングを行なって、γ線によるインパルス性ノイズを除去した。熱中性子とγ線成分の画像に分離するために前回使用した係数を用いて画像間演算した結果を図11に示す。図より熱中性子成分とγ線成分の画像に分離できているのがわかる。また、γ線成分の画像から9行の電池が6つの層になっていることや電池の内部の配線を可視化できている。このことから、同じ撮像条件であれば、同じ係数を用いて熱中性子とγ線成分の画像に分離することができることがわかった。

4. 動画映像撮像システム

静止画実験によって開発された画像間演算法を動画に応用するために、実時間演算処理が可能な動画信号処理装置を開発した。また、動画用カメラとしては、高速に透過光のスペクトルを選択できる電圧制御の液晶フィルタを用いたものと、RGBに対応した3つの中CCD型を有する3極板式カラーカメラで、(株)東芝により特別に高感度化がなされたものを使用した。

4.1 液晶フィルタ方式撮像

4.1.1 撮像システム

高感度なカラーCCDカメラを実現すべく、Fig.15に示す動画用液晶カメラを構築して使用した。2色発光コンバータからの光を、液晶フィルタとモノクロCCDカメラにより時分割に色分離して取得する。液晶フィルタは、透過スペクトルを電気信号により瞬時に選択ができる光学フィルタである。Fig.16にこの撮像系を使った信号処理システムの概略図を示す。CCDで取得された画像は、10(12)bitデジタルデータとして実時間処理装置に取り込まれ、暗電流・ジェーディング補正、ディジタルフィルタ、フレーム間演算、リカーネンブフィルタ、及び擬似カラー化処理をリアルタイムで施され、モニタとVTRに出力される。な
30フレーム/秒のフレームレートで撮像し、赤フレーム、緑フレーム、ダミーフレームの周期で取り込み、熱中性子及びγ線の画像は10フレーム/秒で出力される。

被検体は、厚さ（3mm, 6mm, 10mm）の異なる鉛板、厚さ（50μm, 100μm, 150μm, 200μm）の異なるカドミウム板、ATSMインジケータ3種、100円ライタ、厚さ4mmの星型アクリル板であり、これらをAl板に貼り付け水平に移動させて撮像した。Fig.18に赤フレームと緑フレームの画像を示す。

(a) Red Frame Image  (b)Green Frame Image

Fig.18 Raw red and green frame images.

イメージ・インテンシファイア（II）を使用しているため、解像度の低い画像となっている。また、赤色画像と緑色画像との相違点を認識しやすいが、ASTMインジケータの鉛とアクリルを組み合わせたものにおいて、緑色画像のほうがアクリル部分の影が薄く、鉛部分の影が濃いことがわかる。また100円ライタの本体部分はプラスチックであるため赤色画像のほうが、影が濃いことがわかる。ここでは、静止画と同様に、式(7)、(8)を用いて、係数を目視によりk1=0.75、k2=0.80と決定し、以下の式(11)、(12)を用いて実時間で画像間演算を行った。

\[ n = \text{Red} - 0.75 \times \text{Green} \cdots (11) \]

\[ \gamma = \text{Green} - 0.80 \times \text{Red} \cdots (12) \]

その結果をFig.19に示す。

(a) Neutron frame image  (b) γ ray frame image

Fig.19 Derived thermal n and γ ray frame images.

ASTMインジケータがどちらの画像も見難くなっている。しかし、他の被検体は確認することができる。星型のアクリル板は中性子線成分の画像に見られ、γ線成分では透過していることが確認できる。100円ライターやカドミウム板についても同じことが言える。逆に、鉛は、熱中性子線成分の画像では透過して見ることができない。
が、γ線成分の画像では吸収されて見ることができない。以上のことより、リアルタイムで熱中性子とγ線通過像が表示できたと言える。

4.2 3板式高感度カラーCCD撮像[9,12]

4.2.1 撮像システム

（株）東芝が開発した3板式高感度カラーCCDカメラを使用し、赤と緑のビデオ信号を12bitのデジタル信号に変換して、実時間信号処理装置で画像処理した。

4.2.2 透過画像

実験で使用した被検体をFig. 20に示す。

![Fig.20 Layout of the objects](image)

アクリル10mmを用いて取得した赤色および緑色画像をFig.21に示す。次に、実時間処理を行った中性子画像・γ線画像のフレーム画像をFig.22に示す。このときの係数k1、k2はそれぞれ0.4と0.6であった。

![Fig.21 Raw red and green frame images](image)

![Fig.22 Derived neutron and γ-ray frame images](image)
Fig.22 の中で、部分を注目してみると、中性子画像ではプラスタックの輪郭ははっきり現れているのに対し、γ線画像では内部の電池のほうがよく見えている。また、インジケータを比較すると、上と下のインジケータの鉛部分が中性子画像ではほとんど見えないのに対し、γ線画像では検出できていることがわかる。以上より、中性子画像とγ線画像に分離可能であることが分かった。液晶フィルタを用いた画像と比較してみると、カラー CCD カメラ利用時のほうが被検体の輪郭が鮮明であり、分解能が向上していることが分かる。つまりに階調分解能を評価した。これは被検体のない部分での出力の揺らぎである標準偏差で比較した。256 階調で表示した場合、モノクロ CCD の標準偏差は約 0.5 であったが、カラー-CCD では約 4.9 に改善されていた。

5. まとめ

(株)東芝が開発した 2 色発光コンバータを利用した中性子・γ線の同時ラジオグラフィのために静止画像と動画のシステムを開発し、JRR-3M の TNRF-2 において実験し、各種システムの特性を評価した。静止画像には、モノクロとカラーの冷却型 C C D カメラを使用し、γ線によるホイート・ノイズの除去法や、赤色と緑色の画像から中性子とγ線の画像を抽出する手法を開発した。画像は前者の方が優れていた。

この手法を実時間で実行する動画システムを開発し、液晶フィルタと 3 板式カラーコンバータを使用する 2 種のシステムを開発し、実時間表現が出ることを実証した。また、画質は後者が勝っていた。

この中性子・γ線同時ラジオグラフィの画質は、根本的にγ線線量に依存しており、高い線量が望ましい。しかし、TNRF-2 の照射場は中性子線用に低く整備されているため、やむおえずアクリル板上でγ線を低減させて同時撮像した。

動画においては、まだ十分な性能が得られていない。しかしながら、静止画においては、1 台の C C D カメラだけでなく、これまでもない、画像ずれるのない中性子とγ線のラジオグラフィを表示することに成功した。

今後は、中性子・γ線・CT の応用を進めるとともに、動画の改善を継続して行く予定である。

最後になりましたが、この研究においてキーポイントとなる 2 色発光蛍光コンバータや 3 板式カラー C C D カメラを提供いただいた、(株)東芝の日塔光一氏と小長井担当氏に感謝する次第です。

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成果の公表

上記参考文献の(2)から(12)は、この研究で得られた成果を公表したものです。
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3. Neutron Activation Analysis
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研究テーマ：広域環境モニタリング試料の微量元素分析
表 題：フィッショントラック法を用いた微量核分裂性物質の分析

3-1 フィッショントラック法による天然ウラン含有粒子の検知

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1 日本原子力研究所 環境科学研究部 分析科学研究グループ

IAEAは保障措置強化・効率化策の一環として保障措置環境試料分析法を導入した。これは、原子力関連施設の内外で採取した環境試料（スワイプ、植物、水、土壤試料等）中に含まれる極微量
核物質の同位体組成を調べることにより、未申告の原子力活動及び核物質を検知するものである。現在、原研ではスワイプ材上に捕集された極微量のウラン及びプルトニウムの同位体組成分
析法の技術開発を行っている。本研究はスワイプ試料中の極微量ウラン検出のためのパーティクル分析法開発の一端である。

パーティクル分析では、試料中の核物質を含有する数 μmの粒子一個一個について、二次イオ
ン質量分析法（SIMS）により同位体分析を行っている。しかしながら、現状ではサブミクロンサイズの粒子を検知・分析することが難しいため、フィッショントラック法の応用を検討している。

本報告では、天然ウランを含む粒子を用いた予備実験について述べる。

原研施設内で採取したスワイプ試料から吸引
法により粒子を回収した。これらの粒子の中には
天然ウランを含む粒子が存在することが、他の実
験から既知である。捕集された粒子はポリカーボ
ネット溶液と混合し、これをフィルム状に乾燥させる。粒子をポリカーボネットに閉じ込めた形の照
射試料とした。このポリカーボネットは固体飛跡
検出器の役割を果たす。試料はポリエチレン袋に
封入し、熱中性子フューチェンス 9 × 10^14cm^-2で照射
した。この際、試料中の 238Uの誘導核分裂によ
り、ポリカーボネット中に核分裂片による飛跡
（フィッショントラック）が形成される。このフ
ィッショントラックを明瞭にするため、照射した
試料を放射能減衰させた後、55℃の 6N-NaOH
中に10分間エッチング処理した。試料は純水で
十分に洗い、乾燥させた後、顕微鏡観察した。

図1 天然ウランによるフィッショントラック

図1は、デジタルマイクロスコープ（3,000倍）
でフィッショントラックを観察した写真である。
このような、ウランを含む微小粒子を顕微鏡下で
検知することができた。今後は本法の有効性につ
いて、粒子径とウラン濃縮度の面から検討を進める。
また、環境試料にフィッショントラック法を
適用し、検知された粒子をビックアップし、表面電離型質量分析法（TIMS）により粒子の同位
体分析を行う予定である。

原子炉：JRR-4 装 置：気送管 分 野：放射化分析（環境科学）

- 377 -
研究テーマ：中性子放射化分析法の環境影響元素・物質研究に対する新利用法と高度化技術の開発
表題：臭素同位体比（Br-81/Br-79比）測定法の開発による土壌浸透水の野外・長期間追跡への利用

3-2 土壌水を追跡するための臭素同位体比測定法の開発

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1. はじめに
農耕地地での浸透水の動きを正確かつ精密に把握することを目的に、安定同位体でラベルしたBr-79あるいはBr-81を利用するトレーサ手法について、土壌のサンプリング法、土壌水および土壌の分析法（放射化分析等）などの基礎的事項の検討を行った。

2. 実験方法
90atm%Br-79および90atm%Br-81の臭化アンモニウム試料を水溶化した後、自然存在比レベルの臭化アンモニウム溶液と混合して臭素同位体存在比の異なる溶液を作成した。試料液0.1mLをろ紙に吸収させ、検量線を作成用試料とした。また前作で小麦を栽培していた圃場から、ハンマーで打ち込み式採土器を用いて、直径5cmの塩化ビニール製容器に入れ、表層腐植質層をクロボ土壌を充填し、長さ29.5cmの側壌カラムを作成した。土壌カラムにおおも通常同位体の比の100mgL⁻¹臭化アンモニウム溶液10mLを1カラムに一斜添加した。採取した100mLカラムに日10〜20mLカラムに採取した浸透水を100μLをろ紙に吸収させ、照射試料とした。

3. 結果および考察
1) 臭素の同位体比に対し、生成放射能をプロットすると0〜8μgの範囲において、Br-79でBr-80の37keV、Br-81でBr-82の554keVおよび776keVの光電ピークについて相関係数0.99以上の1次回帰直線（検量線）を書くことができた。

カプセル内位置が異なる試料から作成した2本の検量線の差はほとんどなかった。測定時間500秒でBr-82の測定を行うことににより、0.01ngのBr-81含量の差を定量できると考えられた。2) カラムからの浸透水を照射した場合に、Br-80m、Br-82ともに大きな妨害ピークが無く、両核種の光電ピークが明瞭に現れた。経時的試料採取の結果、浸透水中の臭素同位体の差が明らかに認められた（図1）。両同位体の合計は、臭素全量にほぼ一致した（図2）。3) 土壌についてもBr-79とBr-80の分析を非破壊放射化分析法で行えることができ確認できた。
以上の結果は、臭素の同位体をトレーサ試験に適用できる可能性が高いことを示した。

4. 図1 カラム浸透水のBr-79とBr-81

4. 図2 カラム浸透水の臭素同位体合量と全臭素の比較

参考文献
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研究テーマ：ヨウ素同位体核種の陸水・土壌・地層・植物系における広域的・地球化学的な分布と挙動
表題：放射性ヨウ素の土壌蓄積性と浸透性の把握

3-3
ヨウ素の野外環境中の土壌・水系における分布と移行

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目的：再処理工場から大気に放出される長寿命131Iの地表へ落下後の土壌・水系における影響解明のため、非放射性ヨウ素131Iを指標とするヨウ素の土壌水・水における動態解明、特に土壌への蓄積や土壌からの溶出・浸透について、野外で実証的に解明する。

方法：つくば市農業環境技術研究所内水田、畑地および林地の実験圃場（図1）において、第1帯水層下の常緑森林土壌（水深0〜6m）の深度別土壌のほか、降水、かんがい水、田面水、深度別土壌水（水深0〜2.5m）、第1帯水層地下水を4年間にわたり継続的に採取した。

水田圃場の浸水システムと土壌断面を写真1に示した。

水試料中のヨウ素はICP-MS法を主体とし、一部試料は放射性分析法で分析し、クロスチェックを行った。土壌中ヨウ素は放射性分析法（化学分離法）により定量した。

結果：1）表層土壌中ヨウ素含量は、畑地や林地が水田より1桁以上高かった。しかし、両圃場とも下層ほどに減少し、さらに還元環境となる地下水面下、水田との差異はほとんどなかった（図2）。

水田の場合、夏季かんがい期には還元化が著しい作土層より下にある、かんがい層下には地下水面より上となる比較的酸化的な50〜89cm層（2Bw層）のヨウ素濃度は作土層の4〜5倍と高く、上層から浸透してきたヨウ素が吸着・集積したことを示唆していた。

2）土壌水中ヨウ素濃度は、土壌中ヨウ素含量とは逆に水田が畑地や林地より著しく低い傾向を示していた（かんがい期）。これは土壌のたん水化で還元的環境となり、ヨウ素が溶出したためと推定された。

また、還元化が進んだ層ほど高く、20cm＞50cm＞100cm＞100cm以上であった（図3）。

水田では、かんがい期、特に土壌の還元化が進むかんがい後期にないと、かんがい期に蓄積していた分も含めて、排水路や地下水層へヨウ素が流出していくことが示唆された。その結果、表層土壌中のヨウ素含量が畑地や林地よりも著しく低い傾向を示していると考えられた。

3）畑地・林地の土壌水中ヨウ素濃度は、水田のような季節変動は見られず、畑地表層（20cm）が平均2.2μg/Lと高かった以外、畑地0.4μg/L、林地0.2μg/Lと前後し、降水量の平均1.6μg/Lより1桁近く低かった（図3）。降水中伴って供給されたヨウ素のほとんどを表層土壌が吸着・蓄積した結果、畑地・林地の表層土壌のヨウ素濃度が高レベルであったと推定された。畑地が畑地より表層土壌中ヨウ素含量が低いのは、畑地は機械耕作等の影響で透水性が林地より悪く、大雨時には冠水して還元的になり、土壌からのヨウ素溶出率が増加するためと推定された（図2）。

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2）第39回理工学における同位元素・放射線研究発表会要旨集（2002）、p22
研究テーマ:ラジオアイソトープ技術者の養成
表 題:実習 放射化分析

3-4 貝殻中の鋼・ナトリウムの放射化分析

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本研究は、R 1 技術者の養成を目的とする研修コースの中で実習教科として行うものである。本報告では、平成 13 年度の研究をもってた成果として、国内原子力技術および放射線利用に関係する人材養成を行った基礎実習およびアジア・太平洋地域開発途上国の原子力分野人材養成への国際援助として JICA 与協力して行った原子力基礎技術コースにおいての実習を以っての放射化分析について報告する。

原子力の基礎として中性子核反応の理論や応用を理解することは重要である。放射化分析の実際を経験させることはこれらの知識の理解を深めるのに大変重要であり、結果としてガンマ線スペクトル解析による放射能測定法および非密封 R 1 の安全取扱法を習得させることになる。

平成 13 年度は基礎実習の JICA 原子力基礎技術コースの中で 3 回の放射化分析実習を行った。分析実習は海水産の大アサリであり、炭酸カルシウムをマトリックスにして微量元素を含有する。分析目的核種は、放射化生成核種のガンマ線スペクトルで主成分となるナトリウム 24、放射化生成物が陽電子変換を伴い陽電子消滅ピークを主要放射線ピークとする鋼 64 である。照射条件は研究炉の気冷管で 2～5 分間照射とし、ナトリウムと鋼の標準試料と共に大アサリ貝殻の照射を 3 回行った。

鋼の分析:

鋼 64 の陽電子消滅放射線は、他の放射化生成核種からの高エネルギーガンマ線や宇宙線が物質にもたらす電子対生成による放射線と同一放射線であるから、鋼 64 の分析に化学分離を必要とした。簡単な鋼の化学分離法として金属亜鉛により銅イオノンを還元させて鋼の沈殿分離を行った。この化学分離の操作は、30 分間の所要時間で 0.1ppm Cu 濃度に対して 5% の精度で分析された。本実習は、生成核種を同定および定量することにより核反応の理解を深め、R 1 実験における放射線被ばくに対する工夫、除染、サーベイ等、一連の安全取扱いの基礎を習得させるものとして有効であった。

本実験による研修生の被ばく線量は、線源が 10 Bq 位に対し最大 1μSv 程度であった。
安定同位体による土壤有機物中重金属の標識化

環境中の無機元素（Cd, Se, Zn, Cu等）の動態解明や影響評価に資するために、野外での使用が可能である安定同位体（SI）による環境物質の標識化法と中性子放射化分析によるこれら安定同位体の高精度測定法を開発する。本年度はモリブデン、セレンの安定同位体の中性子放射化分析法による高精度検出条件とセレン、カドミウムのSIによる土壤有機物（フルボ酸）中の無機元素の標識化を行う。

堆肥を混ぜた淡色黒ボク塩化から抽出精製したフルボ酸をカチオン交換樹脂、アニオン交換樹脂でイオン交換後、Se-74またはCd-114で標識化した（表1）。放射化は日本原子力研究所研究炉JRR-3Mで、5.2×10^11（m/s）の熱中性子束を600秒間照射し、1日間冷却後、Ge検出器と波高分析器により、生成した放射性核種のγ線スペクトルを計測（300～1500秒）した。

1）Mo-98とSe-74の両元素とも12000～500000 ngでγ線ピーク面積と相関係数0.98以上での検出限界が得られ、SIトレーサとして利用できることが示された。5.2×10^11（m/s）の中性子束を600秒間照射し、1日間冷却、300秒のγ線計測時間でMo-99（半減期66 h, 181 keV, 739 keV）は約100 ng、Se-75（半減期120d, 136 keV, 264 keV）は約10 ngまでの定量が可能であった。

2）Cd-114はH型の樹脂で陽イオン交換したフルボ酸がOH型の樹脂で陰イオン交換したフルボ酸に比べて約3.4倍量のCd-114が結合した。Se-74は陰イオン交換したフルボ酸が陽イオン交換フルボ酸よりも約2倍量のSe-74と結合した（図1）。

表1 安定同位体によるフルボ酸の標識化

<table>
<thead>
<tr>
<th>項目</th>
<th>具体内容</th>
</tr>
</thead>
<tbody>
<tr>
<td>フルボ酸5000 μg/mLの水溶液調製</td>
<td>↓</td>
</tr>
<tr>
<td>イオン交換(Amberlite CG120 or CG400)</td>
<td>↓</td>
</tr>
<tr>
<td>イオン交換フルボ酸(+Cd-114, Se-74各1000 μg/mL)</td>
<td>↓</td>
</tr>
<tr>
<td>カラム吸着(Amberlite XAD-7)</td>
<td>↓</td>
</tr>
<tr>
<td>洗浄(+H2O)</td>
<td>↓</td>
</tr>
<tr>
<td>漬離(10% NH3 soln.)</td>
<td>↓</td>
</tr>
<tr>
<td>濃縮・回収(凍結乾燥)</td>
<td>↓</td>
</tr>
<tr>
<td>安定同位体標識化フルボ酸</td>
<td>↓</td>
</tr>
</tbody>
</table>

図1 イオン交換したフルボ酸（FA）への同位体元標示量

原子炉: JRR-3
装置: 気送管
分野: 放射化分析（農・水産物）
研究テーマ：広域環境モニタリング試料の微量元素分析
表題：広域環境モニタリング試料の微量元素分析

3-6
広域環境モニタリング試料の微量元素分析（2）

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はじめに
大气中に放出された極微量の放射性核種や大气汚染物質の挙動、分布などを評価するために、これらの直接的な情報が得られないため、大気汚染の量や組成についてモニタリングすることが重要である。本研究では大気汚染の捕集と、放射性分析法で元素分析を行った。捕集はエアーサンプラーによる方法で行われ、松葉表面に付着したものを洗い落として採取した。大気汚染は植物の葉の表面に付着やすいことが知られている。特に松葉は常緑樹であるため、数年前の松葉を探取することにより、長期間にわたって蓄積された大気汚染の入所が可能となる。

これら2つの方法で捕集した大気汚染の元素分析の結果、大気汚染の発生源や環境中における挙動、分布について調べることを試みた。

実験方法
大気汚染の捕集に使用したエアーサンプラーは、ハイポリュームエアーサンプラーおよび粒径の分级が可能な8段階のアンダーセンサンプラーである。また、降雨開始から雨下がりにおいてメンブランフィルターを3透し、雨水にけん溝している大気汚染（以下、「けん溝汚染」とする）を集めた。ハイポリュームサンプラーによる捕集は2001年の5月～8月にかけて行い、天候の変化に応じて2～6日間毎にフィルターを交換した。アンダーセンサンプラーは2001年1月～2月の1ヶ月間行った。また、松葉は2001年1月に採取した。これら全てを原研東海研内で行った。

エアーサンプラーで大気汚染の捕集と捕集したフィルターの一部を切り取り、それを照射試料とした。松葉表面に付着した大気汚染は、水またはアセトンで洗浄を反復して洗い落とした。その洗浄液を蒸発させて蒸発残分を集め、照射試料とした。それをJRR-3Mの出来で10分間、あるいはPN-2で10分間照射した。比較試料として日本地質調査所製のJB-1a, JA-1, JA-3, JG-1aを用いた。

結果と考察
図1は、ハイポリュームサンプラーで捕集した大気汚染について定量した元素の内、いくつかについて示したものである。晴天時に捕集したものは（白色）と雨天時に捕集したもの（灰色）に分類して示した。また、けん溝汚染中の元素濃度を同時にエアーサンプラーで捕集した試料のヒストグラムの横に青色で示した。採取時期の違いによって各元素濃度の変動幅は4倍以上あり、極端に濃度が高くなる時期もあった。単純にけん溝汚染が降雨によって大气から洗い流されたものであると考えず、けん溝汚染の元素濃度を降雨の影響を含めた汚染濃度と同様に分類して示した。これにより、雨天時の汚染濃度を比較することができると考えられる。この考えをもとに元素濃度の比較から定量元素を3つに分類した。

グループ1：雨水に可溶な成分に含まれるもの（Na, CI, V, As, V）。けん溝汚染の試料の方がアーサンプラーのものよりも2倍以上濃度が低い。特にCIについては全てのけん溝汚染試料から検出することができなかった。
グループ2：雨水に難溶な成分に含まれるもの（Al, Fe, Sc, Th等）。けん溝汚染の試料の方がアーサンプラーのものよりも濃度が高かった。
グループ3：測定した傾向を示さないもの（Zn, Br）。

得られた結果から、晴天時に雨天時における大気汚染の元素濃度組成の違いについては、Na, Cl, Vでは平均して雨天時の方が晴天時よりも低いことが分かった。

アンダーセンサンプラーで捕集した汚染試料、4～5μm以下の部分に2つのビーグを持つ粒径分布をしていた。粒径が大きい粒子に多く含まれるSc、および粒径が小さい粒子に多く含まれるVの元素濃度比をアンダーセンサンプラーの各段について求め、松葉から採取した汚染試料の大きさをV/Sc比率で示した。図2に粒径に対するV/Sc比率を示す。松葉を水またはアセトンで超音波洗浄して得た試料のV/Sc比率も図中に示した。V/Sc比率と判別すると、雲洗浄、アセトン洗浄とともに洗い落とした汚染試料は粒径が2μm以上の大きな粒子で、洗浄方法の違いによって付着している成分の粒径に違いが見られなかった。
図1 ハイボリュームサンプラーより採集した大気浮遊塵および雨水にけん満した大気浮遊塵の元素濃度

図2 分散された大気浮遊塵および松葉付着成分のV/Sc濃度比
多重ガンマ線分析法による高感度多元素同時定量の応用

-古代中国青銅器の分析

初川雄一、篠原伸夫、藤幡葉、大島真澄
物質科学研究室原子核科学研究グループ

ガンマ線の同時測定を用いた多重ガンマ線分析法を中性子放射性分析法と組み合わせることにより高感度の元素定量法を開発してきた(1)(8)。今回多重ガンマ線分析法を利用し、古代中国製造の青銅器の微量元素分析を行ったので報告する。分析した試料は殷代(紀元前1500年頃から紀元前1050年頃)の青銅器で有数の酒器(図-1)であり、この底部を削ることにより41.206gの粉末を採取した。照射は原研・研究炉において短(5秒)・中(1分)・長時間(3時間)の3種類の照射を同一の試料に対して行い、それぞれ異なる半減期を持つ核種の分析を試みた。特に主要成分であるCuからの生成する46 Cu(半減期12.7時間)からの放射線が少なくなるように測定を行った。試料と一緒に純Cu箔(2.396mg)、標準岩石試料JB-1a、及びAg、Au、Irの標準溶液試料を5枚まで同様に照射させたものを標準として原子炉にて照射した。原子炉における中性子原射後に試料は試験され、多重ガンマ線分析装置GEMINIにおいて多重ガンマ線の同時測定を行った。定量は同時照射した標準試料のガンマ線強度との比から得た。また測定時にGe検出器やデータ収集系において発生するデッドタイムの補正は測定試料と同時に132 Baの標準線源を測定し、そのピークの数え落としを除いて同様に計算した。得られた結果を表1に示した。

文献
(3) Y. Toh et al., Health Phys., 83 (2002), 110-113

![図1 分析に用いた古代中国の青銅器](image)

<table>
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<th>元素</th>
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<th>ppm</th>
<th>誤差</th>
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表1 青銅器試料の微量元素分析結果

原子炉：JRR-3、JRR-4
装置：気送管

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図1 実験圃場（つくば市農環研究内）の位置

写真1 水田圃場

図2 土壌中ヨウ素の深度分布

図3 土壌水試料中の平均ヨウ素濃度
3-8

宇宙物質の中性子放射化分析 (3)

Neutron activation analysis of the extraterrestrial materials

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1 はじめに

平成11年度から13年度にかけて、標記課題で原研設施を利用した共同研究を行った。この間に行った研究は2つに分類できる。1つは宇宙物質の非破壊中性子放射化分析（機器中性子放射化分析）（INAA）であり、もう一つは目的元素を絞って高感度な分析を行う放射化学的中性子放射化分析（RNAA）である。どちらにおいても、いくつかの異なる種類の隕石について、その元素含有量を正確に求め、その元素存在に基づいて、それらの隕石が形成された太陽系初期の物質の進化について考察することを目的とした。中性子放射化分析法は宇宙物質の元素分析法としてはもっとも有効な分析法であり、今後も宇宙物質の元素分析を行う上で、中性子放射化分析法を積極的に利用していいく予定である。

本報告では、隕石中に微量に存在する希土類元素をRNAAで定量する新しい方法についてのべ、ついでその方法を用いてパラサイト隕石中のラマン石に存在する希土類元素をした結果について述べる。また INAAの例として、このラパサイト隕石中の金属部分の組成を求めた例についてのべる。これらの記述によって、中性子放射化分析が隕石試料の分析にどのように利用され、どのような成果が得られるかが明らかになるものと期待される。

地球や火星など太陽系の岩石型惑星は、原始太陽系星雲からの凝縮・集積・熱成作用の結果による部分を経て今日に至っている。上に述べたパラサイト隕石は分離した隕石の1つであり、惑星の成因や内部構造の進化を推定する上で重要な隕石である。このパラサイトを構成するかんらん石中の微量元素存在度の存在度をもとに、これらの物質が太陽系初期にどのような変遷を経たかを議論することができる。特に希土類元素の相対存在度は、結晶化・溶融による部分過程を考察するのに適している。

2 微量希土類元素のRNAAによる定量法の確立

岩石中の微量な希土類元素(REE)の分析には、一般に中性子放射化分析法(NAA)および同位体
希釈質量分析法（MS-ID）が用いられている。MS-ID は感度の点で優れた分析法であるが、前処理にともなう誤差や試薬等からの汚染の可能性がある。NAA は、正確な点で優れており、特に中性子照射後に化学分離操作を行うユ RNAA を用いると、感度良く分析できる。岩石中の微量希土類元素を RNAA を用いて定量する場合、放射化学的妨害元素であるスカンジウム等を分離・除去する必要がある。本研究ではイオン交換分離法を用いた分離法を検討し、標準岩石試料に用いた。

（実験操作）
標準岩石試料 JP-1（かんらん岩）約 80mg を石英管に封入し、日本原子力研究所の原子炉 JRR-3（1 × 10^{21} n/cm^2/sec）で 100 時間、中性子照射した。約 1 週間冷却後、焼体とともにつぼ中アルカリ熔融し、水酸化物およびフッ化物沈殿を生成して上澄みを分離した。沈殿を塩酸に溶かし、陽イオン交換樹脂に吸収し、希土類元素と分離される。溶出液から水酸化物沈殿として希土類元素を捕集し、濃縮水酸素に溶解して、陽イオン交換カラムに通した。このカラムでは Sc が樹脂に吸着し、希土類元素は溶出する。この陽イオン交換樹脂にによる分離を 2 回繰り返した。溶出液から水酸化物沈殿として希土類元素を回収し、少量の硝酸に溶解して一部を化学収率測定用に保存し、残りを乾燥させて密封し、ガンマ線測定用試料とした。（Fig.1）

（ガンマ線スペクトル測定）
ガンマ線の測定には、京都大学 RI 研究施設のガルマニウム半導体検出器および、日本原子力研究所の多重ガンマ線検出装置（GEMINI）を使用した。これは 12 台のガルマニウム検出器を球形に配置した装置で、複数のガンマ線を同時に測定し 2 次元マトリックスに展開するため、高いエネルギー分解能を持つ。各ガルマニウム半導体検出器はガルマニウム酸ビスマス（BGO）シンチレータ検出器で囲まれ、反時計回りに配置する。コンプトン散乱によるバックグラウンドを低減している。この装置を用いて、京都大学の装置では Sc のコンプトン散乱によるバックグラウンドのため検出できなかった 197Yb, 134Eu を測定することができた。

（化学収率測定）
RNAA においては、目的元素の担体を添加してから放射化学分離操作を行うが、化学収率を求めて放射能測定値を補正する。化学収率の測定法としては従来、再放射化法を用いてきたが、この方法は場所や時間の制約が大きい。誘導結合プラズマ発光分析法（ICP-AES）は操作の簡便性、安全性、経済性などの点で優れた分析法である。感度や汚染の可能性の点では NAA に劣るものの、RNAA の化学収率測定に利用する場合は、担体として加える元素の量を ICP-AES の最適分析条件にあわせることができるので、正確な測定が可能である。したがって本研究では、ICP-AES を用いて RNAA の化学収率を測定する方法の検討を行なった。

分析感度および相互干渉を考慮し、La, Nd, Eu, Ho, Yb の元素を定量元素として選んだ。標準元素として Cd を加え、これら 5 元素とと共に測定した。各元素間の相互干渉の程度を見積もりため、各元素ごとの標準溶液について、複数の波長で発光強度を測定した。その結果から最も干渉の少ない波長を測定波長として選定した。各元素における干渉は 1 ppm あたり 0.007 ppm 以下であり、測定濃度領域（0.5 ～ 2 ppm）では約 1 ％の補正を行なった。また、定量精度を求めるため、試薬を調製した同一の溶液を練り返して測定した。20 ～ 50 試料の一連の分析における分光強度の変動は 10 ％であり、標準溶液の補正を行なうと 6 ％になった。RNAA の化学収率測定の際には、1 時間ごとに標準試料を測定して分光強度の補正を行なった。収率測定の結果はそれぞれの試料で 20 ～ 60 ％であった。放射化学分離操作における希土類元素間での分離は見られなかった。

（結果）
標準岩石試料 JP-1 の希土類元素存在度を Cl コンドライト隕石の存在度で規格化したバターーンを Fig.2 に示す。定量値は RNAA による文献値にと良い一致を示している。しかしこ地質調査所（GSJ）から公表されている参考値と比較すると、軽希土類元素で系統的に低い値が得られた。おぞ
らく地質調査所の値は汚染のため高い値を示す
測定値も含まれているのではないかと思われる。

3 パラサイト隕石かららん石中の超微量
希土類元素の RINAA による定量

パラサイトは石鉄隕石の一種で、鉄-ニッケル合金（metal）かららん石（olivine）が主成分である。鉄-ニッケル合金は分化した小惑星のコア（核）の主成分であり、かららん石はマントル物質であると考えられるが、パラサイトは小惑星のコア-マントル境界で形成されたと考え
が広く受け入れられているが、その形成過程は不明である。

パラサイトのかららん石中の希土類元素存在度は、マントル物質であるかららん石が隕石母天体内部で分離・結晶化した時の元素の分配状態を
反映していると思われる。しかし、希土類元素はかららん石の結晶に入りにくいため、存在度が低く、正確な解析は困難である。また、パラサイト
は落下後かなりの年月が経過してから発見されることが多い、その間の風化の影響が著しい。地球表層の岩石や土壤は隕石に比べ希土類含有量
が高く、わずかな汚染でも高い定量値が得られる。また、地球表面の物質の希土類元素存在度はコンドライト隕石に比べて相対的に軽希土類に富むため、規
格化したパターンに影響を及ぼす。

これまでに、RINAA と MS-ID による測定結果
の報告例がある。初期の RINAA による測定では
コンドライトレベルの希土類元素が含まれて
ると報告された 3)。MS-ID による測定は、試料
を酸処理して分析したものであり、RINAA によ
る値より 1 から 2 倍低い値が得られた 39)。その
ため RINAA による定量値は地球表面の汚染が完
全に除去できていなかったとされる。MS-ID に
よる定量値を CI コンドライト隕石の値で規格化
した希土類元素存在度パターンは、軽希土類元素
と重希土類元素に富む中希土類付近に極小をも
tつ「V 字型」パターンを示している。このような
微量の希土類元素を分析した例は他にないたため、
パラサイトのかららん石中の希土類元素はこの
ようなパターンを示すものとされ、分別過程の説
明が試みられている。しかし、これをかららん石
の結晶構造から説明することは無理があるよう
に思われる。

本研究では、あらかじめ確立した極微量希土類
元素の定量法をパラサイト隕石に応用し、からら
ん石本来の希土類元素存在度を求め、その規格化
パターンから母天体でのかららん石の晶出過程
を考察した。

（実験）

パラサイトの塊を手綱で砕き、かららん石の結晶
の塊を取り出した。顕微鏡下でブラインダー
を使用し、金属部分と隕石部分に特定した結晶を剝離
取った。直径約 0.5mm の粒を集め、約 80mg を
石英管に封入し、中性子照射した。照射後、化学
分離操作に、洗浄のため塩酸で 10～20 分表面
を溶かした。実験操作、ガンマ線スペクトル測定、
化学吸収測定は前述の方法と同様である。

（結果と考察）

希土類元素存在度を CI コンドライト隕石の値
で规格化したパターンを Fig.3 に示す。定量結果
から次の 2 種類のパターンが得られた。(1)軽希
土類に乏しく重希土類に富む右上がりの直線的
なパターン。(2) 軽希土類から中希土類にかけて
ほぼ平坦で重希土類に富むパターン。(1)の La の
値は上限値が得られたのみだが、もし重希土から
中希土の直線上に位置するするとコンドラライ
ト含有量の 10⁻⁴～10⁻² になり、本手法でもほとん
ど定量不可能である。地球表面の物質は相対的
に軽希土類元素に富むので、もし地球起源物質の
汚染を受けた相対的に軽希土類の存在度が高
くなるはずである。よって(1)のパターンがから
らん石本来のパターンで、(2)のようなパターン
を示す試料は地球起源物質による汚染を完全に
除去できていないと思われる。これまでの文献値
もおそらく汚染を受けた見かけのパターンであ
ろう。このパターンは、かららん石が平衡状態で
晶出した場合の、分配係数を仮想されるパターン
と整合的である。これによりパラサイトの
母天体からかららん石が平衡状態で晶出したこ
とを示唆している。

4 パラサイト隕石金属中の RINAA

鉄-ニッケル合金からなる鉄隕石は、ppm レベル
の鉄亜鉛亜を含み、その微量元素組成の違いを
もとにグループ別に分類され、隕石天体のマグ
マの進化史が議論されている。ハラサイト隕石も同様に金属部分の微量元素存在度をもとに、メイングループとそれ以外に分類されている。メイングループ・ハラサイトは、鉄隕石のIIIABグループと同じ（成因の）母天体から分化したものと考えられている。

（実験）

ハラサイト隕石の金属部分をダイヤモンドカッターで切断し、2～3mm角の塊を切り出した。顕微鏡下でグラインダーを使用し、付着している銅などを削って除去し、金属部分だけを取り出した。20～100mgの塊をポリエチレン袋に封入し、照射用試料とした。立教大学原子炉TRIGAII原子炉（1.5×10^{19}n/cm²sec)で100秒中子照射し、照射後約60秒後に100秒間ガンマ線スペクトル測定を行い、Cu, Ge, Rhを定量した。その後、同じ試料を30分照射して約1日後に約1000秒測定し、Ga, As, Auを定量した。数ヶ月冷却後、さらに6時間照射し、数日後に約5000秒測定し、Fe, Co, Ni, Irを定量した。

（結果）

Fe, Ni, Co, Cu, Ge, Ga, Au, As, Irおよび、パラサイト隕石ではいまでの報告例のなかったRhの定量値が得られた。Fig.4, 5はそれぞれ、AuとNi, Ga, Geの相関図である。ほとんど分析値は、報告されているパラサイトの値の範囲内にある。Fig.6には、パラサイトおよび鉄隕石中の鉄元素存在度をニッケルの百分比で規格化した値を、鉄隕石(IIIAB)の値と共有に示した。パラサイトの値と鉄隕石の値を比較すると、Co, Cuの値には差があく、Au, Asでは明らかにパラサイトの方が高い値を示している。Irでは鉄隕石間でばらつきが大きくなり、パラサイトのそれはその最も低い値に近い。これらの傾向はパラサイト隕石の金属部分はIIIAB鉄隕石と同じ起源を持ち、より分化が進んだ母天体のコアであるという推定を支持する。

References

研究成績（発表論文）

（共同研究の期間にJRR-3M, JRR-4を用いて得られた成果を報告したもの）

1. 海老原充（1999）放射性同位体は地球外物質の分析にどのくらい効果か？鉱物学雑誌28, 131–138.
Fig. 1 Procedure of radiochemical separation for REE

Fig. 3 CI chondrite normalized REE abundances in pallasite olivine

Fig. 4 Logarithmic Au-Ni diagram for pallasite metal

Fig. 5 Logarithmic Ge-Ga diagram for pallasite metal and Hf isotopes

Fig. 6 Ni-normalized elemental abundances in pallasite metal and iron meteorite

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3-9

南九州の四万十帯に関するI N A AとF T年代測定 

INAA and FTD for sedimentary rocks from the Shimanto Terrane of South Kyushu, Japan 

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齋木達郎

Tatsuo Suzuki
Faculty of Education, Kagoshima University

1. 緒言

南九州は地質学的には西南日本外帯に属し、鹿児島県はそのなかでもほとんどが四万十帯に含まれる。四万十帯は白亜系とみられる四万十帯北帯と第三系とみられる四万十帯南帯に分けられている（例えば、宇都ほか、1997）。薩摩半島や南隣地山脈をなすものはほぼ四万十帯南帯に属する堆積岩類であり、それを新第三紀以降の火山岩類が覆っている。とくに第四紀のいわゆるシラスなどは大規模に火成流に厚く覆われている。薩摩半島地域などの四万十帯については、近接地域に横木（1962a・1962b）や米田・岩松（1987）があるが、この地域には通産省資源エネルギー庁（1981）による調査研究があるだけで従来その地質構造のみならず堆積岩類の詳細についての研究は不充分であった。その地質構造については宮崎県・大分県で近年詳しく調査されている（寺岡・奥村、1992；など）。このようなもののか、また鹿児島湾形成にともなう鹿児島沖積などがあるために、それにとどまらないもののか、ということについても良好な指標が不足するために地層の追跡が不充分で、未だ明らかに通っているとはいえない。この地域においては堆積岩類の詳細な性質を検討することがそのような問題解決に有功であると考えられる。

一方、機器中の子放射性化分析（INAA）によりは、多数の試料について多くの元素同時分析が可能であるので、堆積岩類のキャラクタリゼーションが容易にできると期待できる。またフィッシングのトラック年代測定の際によれば、汚染性のジルコン・アンバイトを含めてその起源を論審するデータが容易に得られるだけでなく、その地域の発生についてのデータも得られると期待できる。これらの観点から南九州地域の基盤をなす古期岩類と、とくに四万十帯における堆積岩類の検討を行ってきている。現在まだ進行中の部分も多いが、今後も得られた結果をここで報告する。

2. 分析試料

南九州に広く分布する四万十帯から、鹿児島県下の阿久根市、日置郡吹上町、日置郡金峰町、川辺郡川辺町、鹿児島市、川辺郡知覧町、高森郡吹上町、川辺郡笙沙町から頁岩・砂岩を採取した。砂岩試料はとくに厚層の砂岩層を選んでいる。今回のINAAによる分析値を報告するものは、砂岩8点、頁岩4点の合計12点である（Table 1）。また日置郡東市来町江口浜、川辺郡笙沙町高崎から花崗岩質岩巖を見出してフィッシングのトラック年代測定用の試料とした。

Table 1. 分析試料

<table>
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<tr>
<th>Sp No.</th>
<th>岩石名</th>
<th>取り場</th>
</tr>
</thead>
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<tr>
<td>S01</td>
<td>細粒砂岩</td>
<td>阿久根市大川表川内</td>
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<tr>
<td>H71</td>
<td>頁岩</td>
<td>日置郡吹上町北平</td>
</tr>
<tr>
<td>S07</td>
<td>細粒砂岩</td>
<td>日置郡吹上町北平</td>
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<td>H68</td>
<td>頁岩</td>
<td>日置郡金峰町町田</td>
</tr>
<tr>
<td>H63</td>
<td>頁岩</td>
<td>日置郡金峰町町田</td>
</tr>
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<td>S08</td>
<td>細粒砂岩</td>
<td>日置郡金峰町厚野</td>
</tr>
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<td>中粒砂岩</td>
<td>日置郡金峰町江辺門前</td>
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<td>H77</td>
<td>頁岩</td>
<td>日置郡金峰町金峰</td>
</tr>
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<td>S03</td>
<td>中粒砂岩</td>
<td>日置郡金峰町江辺</td>
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<td>S09</td>
<td>中粒砂岩</td>
<td>日置郡金峰町新川</td>
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<td>S90</td>
<td>中粒砂岩</td>
<td>阿久根市美しが隠</td>
</tr>
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<td>S06</td>
<td>細粒砂岩</td>
<td>川辺郡笙沙町高崎</td>
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<td>Eg-Zr</td>
<td>花崗岩質岩巖</td>
<td>日置郡東市来町江口浜</td>
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<td>Kz-Zr</td>
<td>花崗岩質岩巖</td>
<td>川辺郡笙沙町高崎</td>
</tr>
</tbody>
</table>

3. 中性子放射性化分析

中性子放射性化分析による元素定量のためにおり、この試料作成法は以下のようにおこなった。採取した微細数kg以上の原岩試料をまず数cm 
大にして、さらにジョークラッチャーで微細数数mm大小にする。これを縮分器で縮分して数
Fig.1. I NAAにおけるデータ解析の流れ

Fig.2 四万十帯砂岩・頁岩のI NAAによるランタノイド組成パターン
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<th>Element or Nuclide</th>
<th>SB5</th>
<th>H71</th>
<th>SB7</th>
<th>H68</th>
<th>H63</th>
<th>S88</th>
<th>S82</th>
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<td>Na2O (%) Na-24</td>
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<td>4.22</td>
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<td>3.34</td>
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<td>±0.017 ±0.027 ±0.018 ±0.021 ±0.012 ±0.013 ±0.015</td>
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<td>Fe2O3 (%) Fe-59</td>
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<td>Rb (ppm) Rb-86</td>
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<td>171.47</td>
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<td>53.94</td>
<td>70.96</td>
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<td>Sm (ppm) Sm-153</td>
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<td>3.68</td>
<td>6.24</td>
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<td>0.881</td>
<td>1.11</td>
<td>0.890</td>
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<td>4.89</td>
<td>3.96</td>
<td>4.50</td>
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<td>7.50</td>
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<td>8.43</td>
<td>12.87</td>
<td>14.06</td>
<td>12.45</td>
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<td>2.84</td>
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Standard = AGVI

--- 393 ---
Table 2. 四万十帯砂岩・頁岩のI N A Aによる元素組成（続き）

<table>
<thead>
<tr>
<th>Element or Nuclide</th>
<th>Constituent</th>
<th>H77</th>
<th>SB3</th>
<th>SB9</th>
<th>SB9</th>
<th>SB6</th>
<th>WAG</th>
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<td>3.89</td>
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<td>3.84</td>
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<td>±0.014</td>
<td>±0.018</td>
<td>±0.024</td>
<td>±0.018</td>
<td>±0.012</td>
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<td>±0.026</td>
<td>±0.025</td>
<td>±0.029</td>
<td>±0.037</td>
<td>±0.048</td>
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<td>Hf (ppm) Hf-181</td>
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<td>±0.082</td>
<td>±0.114</td>
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<tr>
<td>Th (ppm) Pa-233</td>
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<td>7.13</td>
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<td>7.72</td>
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<td>U (ppm) Np-239</td>
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<td>±0.24</td>
<td>±0.485</td>
<td>±0.853</td>
</tr>
</tbody>
</table>

Standard = AGV1
100 g程度にする。さらに研磨して数g程度にしたものをメノミ製ポットミルで微粉末とする。この粉末試料を110℃1夜乾燥し、ポリエチレン製の薄手の袋に100mgから200mg程度を秤量して照射試料とする。目的試料20個から30個にUSGS（アメリカ合衆国地質調査所）の標準岩石試料G-2・AGV-1およびGSJ（文部省工業技術院地質調査所・現産業技術総合研究所）の標準岩石試料JR-1・JB1aを加えて順序をチェックして照射用キャプセルに詰める。これを日本原子力研究所東海研究所の研究用原子炉JRR-3M・JRR-4の中性子フルエニオン合わせて時間を調節して目的に適した照射施設で中性子照射をおこなう。今回はJRR-4のTパイプ350kW出力時で90分、100kW出力時で5時間、またJRR-3MPN2では15分間の照射をおこなった。JRR-4のTパイプでは水中で照射するため水分に注意が必要であり、3号炉蒸気管でインナーとして使用されるパイアールに試料を詰めその口を接合して封じることで目的を達した。照射後3日ないし1週間程度冷却後、中性子核種定量のため、また2週間ないし1ヶ月後に長寿命核種の定量のための測定をおこなった。ガンマ線スペクトル測定では中性子核種に関しては、大学開放研の実験室での他種類に関しては鹿児島大学と共用したR1実験室において実施した。

ガンマ線スペクトロメトリーは、プロフーウラディスクに保存したスペクトルデータを用いて、まずネットカウント計算（GSPAN：銅木，2011）、ついで放射能計算（ACTCLQ80・銅木，未公表）、元素定量計算（CONSET7：銅木，未公表）の計算プログラムを使用しておこなった。その解析に必要な計算プログラムとデータファイルをフローチャートとしてFig.1に示した。

定量化計算ではSiO₂成分の試料の架橋開始が急激に変化するUSGS（アメリカ合衆国地質調査所）のAGV1のデータ（Potts et al., 1992）を標準値とし、GSJ（旧工業技術院地質調査所・現産業技術総合研究所）のJR1・JB1aを位置補正のためのワーキングスタンダードとして使用している。

得られた分析結果をTable 2に示す。USGS（アメリカ合衆国地質調査所）の標準岩石試料の堆積岩試料であるMAG・SGRについての分析結果を併せて示したが、現在知られるデータ（Pottsほか、1992）と良く一致している。Table 2の試料の配列順序はTable1に従って、ほぼ北から南の順である。ランタノイドのMasuda-CorryellプロットをFig.2に示した。

これらのデータからは、砂岩・頁岩の相違はあるが、大略似たような元素組成であり、まだ特徴づけるためには充分とはいえない。しかし詳細に見ると砂岩のなかでも区分できる可能性はあると見られる。また四方十帯中の鹿児島南部29,000年前に噴出した無有石灰の大規模火成岩堆積物である火成岩堆積物のINAAによる元素組成（銅木，2002）はほぼ同じものであることは極めて示唆的にみ、今後の重要な研究課題である。さらに広域に試料を収集し、この地域の地質の帯状構造と微量元素組成に関連があるのかどうかなどを詳細に検討する必要があると思われる。

4. フィッシュ・トラック年代測定
鹿児島県日置郡東亜町江口浜、川边町笠沙町高崎に分布する十帯状相関層から見出した花崗岩質岩屑からジルコン・フッ化物・フライムによってフィッシュ・トラック年代測定を試みた。中性子照射はJRR-3MPN1で20分間おこなった。また内部デイテクターとして使用したのは雲母は46％HF 23℃12分間、ジルコンはNaOH・KOH・LiOH・H₂Oの共融液（Zaun and Wagner, 1985）200℃6～8時間で данングして適正なトラックを検出された。なお年代測定値の算出にあたっては、モニターガラスとしてCN1を、年代標準試料としてフィッシュ・キャニオン・タフのジルコン（FC3）を使用したゼータ法に沿った。

今回の測定では、江口浜の試料では7.5Maが、笠沙町高崎の試料からは70.1Maの年代値が得られた。その詳細はBG値による校正法（Suzuki, 2000）との相互検討のうえ別に報告する。笠沙町高崎のジルコン試料では測定困難なグレインもあるが計測できないトラック密度ではないが、江口浜の試料では良好なトラックが検出でき、両者ともほぼ信頼できる結果であるといえる。従ってその地質的解釈が必要である。これらの試料はともに白亜紀の堆積岩層に含まれる堆積物であるから、その生発年代値は白亜紀以前の堆積物である。従って笠沙町高崎の試料はその堆積時に割れてしまい、江口浜の試料では核のイオン連にある若返ったと考えざるを得ない。実際、江口浜局所の四方十帯層には14Maの花崗岩質の貫入が見られるほか、一部にはそれ以上ない活動と見られる石英脈などもある。薩摩半島における金鉱床生成に関わる鉱化作用の時期のひとつが7Maにあることを併せて考える。
ときこの測定結果は極めて興味深し。その解釈の是非はこの地域を含む広域での砂岩中の堆積層の年代測定によって明らかになると思われる。現在その測定を準備中である。

5. まとめと今後の課題

南九州とくに鹿児島県薩摩半島地域の四万十帯の堆積岩類から砂岩-頁岩を採取してその放射化分析による元素組成分析を試み、水質の分析値を検討し、この地域の堆積岩類の特徴を明らかにした。またこれらの堆積岩類の供給源に関わる問題解決に有効な花崗質岩類試料のフィッショントラック年代の一部を報告した。

これらの調査・研究を通じて広域に広がって南九州四万十帯の地域学的特徴、とくに中生代白亜紀以降の堆積史・変成史を明らかにしていきた

6. 謝辞

一部の試料採取については、鹿児島大学教育学部地学教室（当時）の畠 木・春田幸作・税所教授の諸氏の助力があった。また試料の中性子照射とそのガンマ線測定については、東京大学原子力研究総合センター東海分室開放出研究室・鹿児島大学共同利用 RI 実験室にお世話になった。これら関係各位に深謝の意を表する。

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3-10 中性子放射化分析による環境汚染指標生物ダンゴムシの検討
川西幸子、野川憲夫、澤郷浩之、森 実

Biological Monitoring of Pollution on Armadillidium vulgare (Latreille)
by instrumental Neutron Activation Analysis

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1. 研究の目的と意義
大気環境汚染、特に粒子状物質汚染調査の一環として、環境指標により得るもの検討することに、人を含む生態系への環境汚染の影響を把握する目的で必要である。陸生等節類の Armadillidium vulgare (Latreille) は乾燥に耐え、食性が広く、主として落ち葉や朽ち木、あるいは生葉、野菜、節足動物の死骸なども食べる。行動範囲も狭く、寿命は普通 2 ～ 3 年である。地域の環境状況を反映している可能性がある。このテーマに関係する文献は、山本ら1）（福岡県衛生公害センター）が、重金属 Cd, Cu, Pb, Zn を原子吸光で測定し、Cd, Cu, Zn について生物濃縮を認めていた。また、Drobose ら2）は陸生等節類の他種 Porcelio scaber, Qniscus asellus において、生態污染物の体内実験を行い、Co をカセアスに添加し、500 μ g/g 以上で毒性よりも摂取抑制が出ると報告している。本研究はまず汚染元素を採取するかどうか、また採取した場合の汚染元素の保持能力をトレーサー実験により検討した。次に、都市部を中心として近郊各地から、試料を集め、中性子放射化分析により、保存元素の分析を行い、汚染マップを作成した。

2. 実験方法
2.1 代表試料の検討
汚染元素の例として、Sb のアイソトープによるトレーサー実験を行った。114 Sb（半減期 60 日、中性子放射化した金属 Sb 粒子を玉水に溶解し NaOH で中和した溶液）を馬鈴薯（一辺約 1.5 cm 立方体）に添加した飼料で 3 日間飼育し、無添加飼料に切り替え、死亡まで経過を 3 日間観察した。放射能の体内残量は各段階で個体を水洗し、コブラ（クワンダム）5003 自動ガンマカウンター（PACKARD）で測定した。

2.2 粉末後体保持元素量の検討
馬鈴薯飼料（一辺約 1.5 cm 立方体）に Cu, Co, Sb, Zn, Ba 各 10 ppm, Sc, Fe 各 5 ppm, pH 6.4 調整試薬を添加して飼育 3 日後の個体を、無添加試料で飼育した対照個体と共に、中性子放射能分析により、この 7 元素を定量比較した。

2.3 吸収部位（胃脳部と他部位）の検討
フィールドの廃棄物堆卸近傍 2 個所、A (区) および B (川崎市)地点より採取した 3 個体の平均値を中性子放射化分析（RSi）により算出した。

2.4 東京都 23 区および近隣市町のフィールド調査
（2000年 5月 23日～2000年 6月 30日）1 区および B (川崎市) において 1 ～ 3 個体で、原則として成虫、雌、5 個体を目安に採取したが、見つからない個体は死亡、幼生を含めた。また、その近傍の食餌堆棄をコロナに採取した。採取試料は水洗し、水紙、キムワイドで拭き取り、シートカーテーで恒量するまで乾燥後、二重のポリエチレン袋装入、更にローズ（No. 51 A）を挟んで閉じ、中性子放射化分析により、各群の 7 元素を定量した。
3. 分析結果と考察
3.1 汚染元素の保持能力

Sb による室内アイソトープ実験の結果は、多量に摂取した場合を除いて、40～80%保持したまま死に至っている。一方、低量摂取の場合は、生きてきて 5%保持して死亡した。いずれの例数も少なくな、数値的に結論を出すことは出来ないが、傾向が読み取れる。少なくとも、高い保持量が示された場合、汚染の検知に役立てと思われる。

3.2 吸収部位の検討
フィールドで採取していると、死亡があり、特に甲殻の残骸が見られることがある。この部位で汚染調査が出来ればよし、確実な検討ではないが、甲殻部に汚染元素が浸透しているかどうかを調べた。この 7 種の元素で、他の部位と共に浸透している元素は Ce 以外すべてに認められ、Ba 濃度が他部位より高く、付近の土壌の濃度よりも高かった。このことは初期の甲殻が残る場合、生でなくても環境調査が出来る可能性がある。

3.3 東京都 23 区および近隣市部のフィールド調査
東京都 23 区および近隣 25 市部、合計 48 地域の 59 個所で Arndallidium vulgaris を採集した。この 7 元素の一部、Co と Sb につき、地域上に濃度分布として表わしたのが図 1 である。ただし、あくまでもそのスポットの反映であり、地域を代表する数値ではないことを注意としている。また、個体と同所の集成分の関係を調べた。これらの結果から、次のようことが考えられる。

(1) 高濃度地点と環境汚染負荷

(2) 生物濃縮
食餌源と個体の汚染濃度を比較した結果は、ばらつきは大きいが、Zn、Ba、Co が個体に濃縮されている。特に、[港区-1] は Zn 元素全てで集を上まわり、最高 30 倍にもなっている。これらは分析試料として、集植物に対して二次試料であるが、生物濃縮を示し、1 個～2 年の過去を含めた現在を反映している試料として意味があると考えられる。

(3) 分析方法としての意義
文献 1) における Cd、Cu、Zn の分析法は原子吸光法であった。Zn 以外の元素条件はなかったが、今回の Pb 吸収分析は次の点に有用であると思われる。① 試料の前処理がなくして済むため、試料の量が少なく済む。1 回の分析に必要最小量は前者数 g に対して後者 20～30 mg (1 個体) 即ち 1/100 で出来ます。このことは生態系に影響を与えないで済む。[死骸の甲殻は試料になる] ①また、そのため一度に多くの試料数 (100 倍) を分析できる。③ 条件が合致する多種の微量元素を同時に分析できる。特に、今日、注目されつつあるレアメタル汚染を解明するために役立つと思われる。

4. まとめ
室内実験およびフィールド調査から、陸生等脚類の Arndallidium vulgaris は環境汚染指標生物となり得ると考えられる。中性子放射性分析法を用いて分析することにより、容易に多数の検体を扱え、広域の調査が出来ることが確かめられた。この方法による環境汚染濃度の東京都 23 区近隣市部調査は、限定された地点であるが、予想以上に、汚染の実態が示された結果になった。この 7 元素 Co、Ce、Sb、Sc、Fe、Zn、Ba の分析は照射 20 分、クーリング期間 7 日後および37 日後に測定する条件で適当であることが分かった。

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地衣類を環境指標として用いるための基礎研究
Basic study for using lichen as an environmental index

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1. はじめに
地衣類は藻類と菌類の共生体として知られる複合生物であることはよく知られている。日本では正月の生け花にウメノキゴケのついた梅の枝が使われたり、山地の台のぼりにはサルオガサがよく見られたりと人々の目によく触れそのものであった。また一方、ロンドンの大気酸ガス濃度と地衣類の生育状況の調査などから、知られているように、大気汚染には非常に弱い生物であることもある知られている。しかし、火山の噴気が噴出している地域のようにほかの植物が生育していない場所にも生じ、極地から熱帯まで世界中に分布しているので、環境指標として適しているのではないかと考えて本研究に着手した。地衣類の共生藻類が光合成によって生成する養分を菌類に与え、菌類はすみかを藻類に提供することで成立し、環境から酸の変化を吸収できる生长可能のはずで、以前は日本各地に普通に見られた生物であった。ところが近年非常に減少しており、当初は環境と地衣類の組成について調査し、環境指標として地衣類を用いる可能性を研究する目的で開始したのであったが、少しでも試料のあるうちに組成の傾向を明らかにすることが急務であると考えるようになった。そのため、なるべく多くの元素について熱中性子放射化分析により、地衣類の組成を明らかにし、元素組成の種によく差異、種類によるちがい、場所による違いを調

べることを本研究の目的とした。

地衣類は大きく分けて樹枝状地衣、葉状地衣、固着地衣の3種類あり、固着地衣は木の幹や岩石、建築物などの基質に密に浸入して存在し、葉状地衣も基質と分離は簡単ではない。そこで、樹枝状地衣を中心として葉状の地衣のうちでも広く分布しているウメノキゴケなどを試料として放射化分析により元素組成の傾向を明らかにした。

2. 実験について
試料
樹枝状地衣は空気の清浄な地域でしか生育していないので、山梨県、長野県、北海道などで採取したものが多かった。採取した地衣類の数はおよそ90、種は10種あまりであった。

そのうち樹枝状地衣ではハナゴケ Cladonia rangiferina、ミヤマハナゴケ Cladina stellaris、ワラハナゴケ Cladina arbuscula、トゲニバリ Cladia aggregata、ショクダイゴケ Cladonia crispate ホグロハナゴケ Cladonia amauraocraea、ワラハナゴケモドキ Cladina mitis、葉状地衣ではウメノキゴケ Parmotrema tinctorum、キウメノキゴケ Flavoparmelia caperata、マツゲゴケ Rimelia clavulifera などを分析した。

採取した地衣類を超純水（Mill-Q＞15MQ）で洗浄し、乾燥して標本を作製し、一部をとり、種の同定を行った。一部を精製して放射化分析用の試料とした。

研究施設と装置名：立教大学原子炉、JRR-3M、PN-1
研究分野：中性子放射化分析、環境科学
原子炉照射と測定
半減期の短い核種を用いる元素（Na, K, Mg, Al, Cl, Ca, V, Mn, As, Br, Iなど）については立教大学の原子炉の回転試料槽で5分間照射し、直ちに測定した。比較的長い半減期のもの（Cr, Fe, Co）はF孔で1時間照射し、筑波大学に持ち帰りアイソトープセンターでガンマ線の測定をした。
また、Fe, Co, Csについては日本原子力研究所のJRR-3Mの気送管PN-1で20分照射して約20日後、筑波大学アイソトープセンターでガンマ線測定を行った。

3. 結果と考察
立教大学の原子炉の回転試料槽で5分間照射した試料のγ線スペクトルの1例を図1に示す。試料は恐山周辺で採取した植枝状地衣のヤマトハナソウトとゴケ Cladonia carassensis subsp. japonica で、多くの元素ともに他の地域で採取した地衣には見られないと素が390±40 ppm検出された。

![Gamma-ray Energy (keV)](image)

図1. 立教大学原研のTRIGA-II回転試料槽で5分間熱中性子照射した恐山付近に生育するヤマトハナソウトとゴケ Cladonia carassensis subsp. japonica のγ線スペクトル

一般に地衣類中の元素はその地衣の種、採取場所などによって、変動があるが、同じ場所で採取した別の種類の地衣類中の元素濃度を比較した。
次に示す図2は北海道、美瑛で採取した植枝状の地衣、ショクダイゴケ、ホクロハナゴケ、ハナゴケ、ワラハナゴケモドキの4種を分析した結果である。図3には石鎚山周辺で採取した葉状地衣のウメノキゴケ、マツケゴケ、キウメノキゴケの結果を示した。元素濃度は植枝状、葉状を比較すると、一般に葉状地衣の元素濃度が高く、特にカルシウムとマンガンで顕著である。カルシウムはウメノキゴケとキウメノキゴケでは2.5%、4.5%含まれることがあり、マツケゴケとは異なる機能を持つことが予想される。これは他の地域で採取したものについても同様の傾向であった。
また、火山地帯における土壌、筑波山神社の鋼屋根からの下に生育するマツケゴケに45.2ppmの銅が検出されたことなど多くの興味ある結果が得られた。
指標として地衣類は生育環境を反映する元素組成をすることがわかった。
図2 北海道美瑛で採取した樹枝状地衣類ショクダイゴケ、ホグロハナゴケ、ハナゴケ、ウラハナゴケモドキの元素濃度（ppm）

図3 石鎚山周辺で採取した葉状地衣類ウメノキゴケ、マツケゴケ、キウメノキゴケの元素濃度（ppm）
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アビアスキュラー菌根の形成が宿主植物の各種元素の吸収に及ぼす影響

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Influence of arbuscular mycorrhizal colonization on uptake of various elements by host plant.

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1. 論言

高等植物の根の組織内あるいは表面において植物と糸状菌共生関係を営んでいるものを菌根と言ぶ。菌根は陸上植物の約80%に認められ、特にアブラナ科やアカザ科を除く農作物や草本植物はアビアスキュラー菌根(AM)を形成する。

AMの形成によって根の周りにはAM菌の外生菌糸が伸長する。この外生菌糸にはN, P, Zn, Cuなどの植物養分を植物に輸送する能力がある(AMES et al. 1983; KOTHARI et al. 1991; LI et al. 1991)。さらに近年では、AM菌の外生菌糸がNa, Sr, Seなどの植物非必須元素を植物に輸送することも明らかにされた(SUZUKI et al. 2001)。このため、AM菌の外生菌糸による元素輸送は宿主植物の様々な元素の吸収に重要な役割を果たしていると考えられる。

AMの形成が植物養分の吸収に及ぼす影響については、Manschner and Dell (1994)などの観察にまとめられおり、AMの形成は植物の養分吸収を改善することが報告されている。しかし、植物非必要性であるMgについての知見など、いくつかの植物養分の吸収に対するAMの形成による影響はまだ明らかにされていない。一方、非必須元素の吸収に対してAMの形成が及ぼす影響はほとんどの元素について明らかにされていない。また、ZnやMnなどいくつかの元素については、AMの形成によって元素吸収が増加する場合と増加しない場合のあることが報告されている(JACKSON et al. 1973; KOHTHARI et al. 1990; LAMBERT et al. 1991; 佐藤・鈴木 1995; 鈴木ら2000)。このような現象は、AMの形成が宿主植物の養分や非必須元素の吸収に影響を及ぼす機構を外生菌糸の元素輸送能のみで説明できないことを示唆している。このため、AMの形成が宿主植物の元素吸収に及ぼす影響を解析するためには、外生菌糸の元素輸送能よりもAMの活性（たとえばAMの発達状態）の点から検討を加えることが重要である。

しかしAMの形成が宿主植物の元素吸収に関連のある現在までに報告された知見については、宿主植物とAM菌の組み合わせ、植物の生育状態、AMの発達状態などがそれぞれの実験において異なることや、同時測定の対象となった元素数が少ないなどの問題点があるため、既往の知見を利用してAMの形成が宿主植物の養分や非必須元素の吸収に及ぼす影響をAMの発達状態のようなAMの活性の点から解析することは容易ではない。

そこで本研究では、植物の生育期を栄養生長期、生長生長期の前半（開花期）、生長生長期の後半（開花期と結実期）の3つの生育時期に分け、それぞれの時期において採取したAMの発達状態が異なる植物体を放射化分析することによって、AMの形成が宿主植物の様々な元素の吸収に及ぼす影響についてAMの存在、AMの発達状態、植物の生育期の点を踏まえた解析を行った。

研究施設・装置：JRR-3M(PN-1, 2); JRR-4(気管管)。研究分野：中性子利用分析・放射化分析

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2. 試料および方法

宿主植物としてマリーゴールド (Tagetes patula L., 品種名: ボナシスブルー)、接種 AM 菌として Glomus etunicatum (Becker and Gerdemann)を使用した。試験区は前年度に採取した AM 菌を接種菌として用いた AM 区、共生能力が低下した前年度に採取した AM 菌を接種菌として用いた LAM区、無接種の対照区の 3 試験区を設けた。栄養土にはオートクレーブ滅菌（121℃, 1 時間）した川砂（利根川砂）を使用した。川砂は 400g を内径 9cm のポットに充填した。各ポットにはマリーゴールドの種子を 4 粒播種し、播種後 6 日目と 8 日目にはそれぞれの AM 菌の胞子を約 200 胞子播種した。また、対照区では AM 区で用いた胞子をオートクレープ滅菌（121℃, 15 分）したものを使い約 200 胞子播種した。

栽培は気温 25℃、満度 65%、照度 15,000Lux（明期 16 時間、暗期 8 時間）に調節したバイオトン内で行った。栽培期間中は 1 日 2 回ポットの重量を測定し培土の水分量を最大容水量の約 55%に維持するために蒸留水を与えた。また、播種後 7 日目に 1 ポットあたり 1 個体に間引きを行い、播種後 8 日目からは毎日液肥を与えました。栄養の組成は別報 (Suzuki et al. 2001) に示した。植物体は各試験区ともに 21 ポットずつ栽培し、播種後 29 日、50 日、68 日目にそれぞれ 7 ポットずつ採取しました。各採取した植物体は各個体ごとにより、栄養生長期、播種後 50 日日目と 68 日目は生理生長期の前半（開花期）と後半（開花期と登熟期）にそれぞれ相当した。栄養生長期の試験区では、栄養土は根部と地上部に分け、地上部は直ちに新鮮土を測定した。根部は蒸留水で洗浄し、ベーパータオルで湿って発芽する水分を取り除いた後新鮮土を測定した。採取した植物体は 4 個体を放射化分析に用い、残る 3 個体を AM 形成の測定に用いた。

放射化分析に用いる植物体の根部は、付着する培土を含まず取り除くために、さらに超音波洗浄を行った。地上部については蒸留水で洗浄した。

ただし、播種後 50 日目と 68 日目の場合は地上部をさらに茎葉部と花弁部に分けて蒸留水で洗浄した。洗浄した根部、茎葉部、花弁部は 80℃で 48 時間かけて乾燥した。また、AM 形成率の測定は別報 (Suzuki et al. 2000) に示した方法によって行った。

乾燥した植物体は粉碎器を用いて粉砕した。粉砕した植物体、培土、種子、標準試料から約 20〜50mg を秤量し、ポリエチレン袋に封入した。また、液肥については 1mL をポリエチレン袋に分取し、ディスペンサー中で乾燥したものをそのまま密封した。各試料を封入したポリエチレン袋はさらに別のポリエチレン袋に入れ、これに放射照射試料とした。

放射化分析は測定対象の核種を半減期別に短寿命核種、中寿命核種、長寿命核種に分け、それぞれの測定を次のような手順で行った。短寿命核種の場合、試料を日本原子力研究所東海研究所の原子炉 JRR-4 の気温管で 10〜30 秒照射し、1 分間冷却後、ガラス製半導体検出器を用いて 3 分間観測した。中寿命核種と長寿命核種の場合では、試料を日本原子力研究所東海研究所の原子炉 JRR-3M の NU-1 あるいは NU-2 で 10 分間照射した。そして、1 分間冷却後、中寿命核種の測定をガラス製半導体検出器を用いて 3000 秒間行なった。また、長寿命核種の測定は 4 週間以上冷却後にガラス製半導体検出器を用いて 65000 秒間行った。

各測定結果はポップフェローニ法による多重検定を行い、有意差があると断定した。

3. 結果および考察

3.1 植物生長期と AM 形成

各生育時期における対照区、LAM 区、AM 区の植物体新鮮重と AM 形成率を表 1 に示した。播種後 29 日目では地上部と根部の新鮮重に差は認められなかった。また、LAM 区と AM 区では AM の形成は認められたが、両試験区の AM 形成率は 10% 未満でありほとんど同じであった。このため、栄養生长期における AM の形成は未発達であり、AM の
影響も被検重に現れなかったと考えられる。

播種後 50 日目では、地上部の被検重が AM 区で最も高くなかった。しかし、根部の被検重は 3 つの試験区間でほとんど同じであった。AM 形成率は対照区よりも AM 区が最も高くなった。播種後 68 日目では、地上部の被検重と AM 形成率は播種後 50 日目の場合と同様の傾向を示した。しかし、根部の被検重については LAM 区が 3 つの試験区間の中で最も小さくなった。播種後 50 日目と 68 日日ににおける植物地上部の被検重は AM 形成率の高かった AM 区において対照区や LAM 区よりも有意に増加したことから、生殖生長期の前半と後半における AM の発達が植物地上部の被検重の増加に寄与したためと考えられる。一方、播種後 50 日目と 68 日日ににおける根部被検重には対照区と AM 区の間で試験区間差が認められなかったことから、生殖生長期の前半と後半における AM の発達が植物地上部の被検重にほとんど影響を及ぼしていないと考えられる。しかし播種後 68 日日ににおける LAM 区の根部被検重が対照区よりも有意に低下した点については、播種後 50 日日に LAM 区の根部被検重が対照区とほぼ同じであったことから、AM が未発達であることが根部被検重の低下に直接的に影響を及ぼしていないと考えられる。むしろ、AM が未発達であることと植物の生育状態が生殖生長期の後半であることとの関係が根部被検重の低下に強い影響を及ぼしていると考えられる。

3.2 放射化分析

放射化分析の結果、実験に用いた培土からは Na, Mg, Al, Cl, K, Ca, Sc, Cr, Mn, Fe, Co, Zn, Sc, Sr, Cs, Ba, La, Ce, Sm, Eu, Yb, Lu, Hf, Th の 24 元素が検出された。また、液肥からは Na, Mg, Cl, K, Ca, Mn, Fe, Zn, Br の 9 元素が検出された。表 2 に培土の元素含有率と各採取日までに与えた施肥に伴う元素栄養量を示した。植物体内からは、培土から検出された元素から Ba と Hf を除く 22 元素に Br を加えた 23 元素が検出された。また、種子からは Na と K が検出された。図 1 に種子と植物体の各元素の含有率をまとめ植物体 1 個体あたりの含有量として示した。植物体中の Mg, Ca, Br を除く 20 元素の含有量は施肥に由来する元素含有量を上回っていたため、これらの元素の植物体内含有量の大半は培土に由来すると考えられる。Mg と Ca については、植物体内含有量が施肥に由来する元素含有量の範囲内であったことから、培土に由来する量は少ないと考えられる。Br については、培土を測定する場合には検出度の低下のために培土の Br 含有率を求められなかったため、培土の Br 量を土壤や岩石の Br と Cl の濃度比が 1:20〜1:52 であることに基づいて推定し（結田 1990）、施肥由来の Br 量を差し引いた植物体中の Br 含有量が培土中の Br に由来すると判断した。

各元素の含有量は 3 つの試験区間で比較しその結果を試験区間差の有無に基づいて 7 つの型に分類した。表 3 に各元素の含有量分類結果と多変量分析の結果から導いた考察を示した。また、各分類型の番号は数字の增加と共に元素吸収に対する AM の影響が小さくなるように配列した。

播種後 29 日目の場合では Cr の含有量が LAM 区において最も少なくなり、対照区と LAM 区の間では有意差が認められた。Cr 含有量の試験区間での違いは VI型に属したことから、Cr 吸収は AM が未発達であるために低下した可能性があるが、播種後 29 日目における AM 形成分には LAM 区と AM 区の間で違いが認められていなかった。このため、LAM 区と AM 区における AM の発達状態には AM 形成率のような指標では評価できない活性の違いがあるのかもしれない。また、Cr 以外の元素の含有量には試験区間での違いがほとんど認められなかった（含有量の試験区間での違いは VI型に属する）。このため AM の形成は栄養生長期における Cr 以外の元素の吸収に対してほとんど影響を及ぼさないと考えられる。

播種後 50 日目に 68 日目では各元素の含有量に試験区間の違いが認められ始めた。播種後 50 日目...
の場合、各元素の含有量の試験区間での違いは種類の型に分類することができた。I型にはCoとLaが該当した。Coの含有量はLAM区とAM区よりも対照区において高くなり、Laの含有量は対照区よりもLAM区とAM区において高くなった。しかしLAM区とAM区の間ではCoとLaの含有量に違いは認められなかった。このため、生殖生長期の前半においてはAMの発達状態よりもAMの存在がCo吸収を低くさせ、一方でLa吸収を増加させていると考えられる。II型に属するCr、Mn、Zn、Cs、CeとIV型に属したNa、Mg、Euについては、AM区における含有量が最高であり、対照区とAM区との間で有意差が認められた。このため生殖生長期の前半において、これらの元素の吸収に対するAMの影響はAMが発達した場合のみ現れると考えられる。V型に属したScについてはAM区における含有量が最も高かった。しかし、有性差はAM区と対照区との間で認められず、むしろLAM区とAM区の間で有意差が認められた。このため生殖生長期の前半におけるSc吸収はAMの存在よりもAMの発達状態による影響を強く受けていると考えられる。Al、K、Ca、Cr、Fe、Br、Rb、Sr、La、Sm、Yb、Thの12元素はV型に属していたので、生殖生長期の前半におけるこれらの元素の吸収にはAMの存在とAMの発達状態はほとんど影響を及ぼさないと考えられる。

播種後68日目の場合、各元素の含有量の試験区間での違いは種類の型に分類できた。分類型の数は播種後50日目と同じであったが播種後68日目ではI型とIV型に属する元素が多く、代わってII型とV型に属する元素が現れた。CrはII型に属した唯一の元素であり、その含有量はLAM区と対照区とAM区の順に増加した。このため、生殖生長期の後半におけるCr吸収はAMの存在とAMの発達状態の両方から影響を受けていていると考えられる。また3つの試験区のCr含有量の相対度はAMが未発達である場合にCr吸収の低下、発達した場合にはCr吸収の増加を引き起こしている可能性も示している。しかし

CIは播種50日目ではIII型に属していることから、CI吸収の低下にはAMが未発達であることと植物の生育が生殖生長期の後半に属したことを関係していると推測される。III型に属した元素はNa、Sc、Zn、Br、Sr、La、Ce、Sm、Eu、Yb、Laの11元素であり、播種後50日目よりその元素数は増加した。これらの11元素がIII型に属したことは、生殖生長期の後半におけるAMの発達が元素の吸収を高めていると考えられる。特にBr、Sr、La、Sm、Ybは播種後50日目ではAM形成の影響を受けることが考えられるIII型に属していたので、AM区においてこれらの元素の含有量が増加する要因をAMの発達だけで説明することはできない。このため、AM区におけるこれらの元素の吸収の増加にはAMの発達と植物の生育状態の関係が重要であると考えられる。V型に属した元素はAl、Ca、Mn、Fe、Csであり、この5元素の含有量はいずれもAM区で最も高かった。これらの元素の生殖生長期の後半における吸収はAMの存在よりもAMの発達状態による影響を強く受けていると考えられる。特にAl、Ca、Feは播種後50日目ではV型に属していたので、播種後68日目のAM区におけるこれらの3元素の吸収の増加にはAMの発達と植物の生育状態との関係が重要であると考えられる。一方、MnとCsは播種50日後ではIII型に属していたので播種後68日目のV型に属したことは、MnとCsの吸収がAMの発達状態と植物の生育状態との関係によって変化しやすいことを示している。このためLAM区とAM区との間で含有量に著な違いを示さないV型の元素の吸収についてはAMの影響を解析するためには、植物の生活状態の一部だけでなく植物の生育状態の全体を通じた解析が必要であると考えられる。V型にはCrとRbが並び、両元素の含有量はLAM区において最大になっていた。このため生殖生長期の後半においてAMが未発達であることにはCrとRbの吸収の低下と関係があると思われる。またIV型に属した元素はMg、K、Co、Thの4元素であり、その数は播種後50日目よりも
少なくないため、細胞型に属したCoやMgは被種50
日後ではそれぞれ1型と4型に属したので、Coや
Mgの吸収は生長生長期の後半においてAMの存在
やAMの発達状態による影響を受けにくくなる
と考えられる。KとThについては植物の生育史の
各時期のいずれにおいても細胞型に属したことから、
これらの元素の吸収は植物の生育史の全体を通して
AMの存在やAMの発達状態の影響を受けにくいと
考えられる。しかし、本実験よりも施用量が少
ない条件において栽培したマリーゴールドでは、
AM菌を接種したマリーゴールドのKとThの含有
量が無接種の場合よりも高くなることが報告されて
いる（鈴木，2000）。このためKとThの吸収につい
てはAMの形成と植物の生育史との関係にさらに
施用量に影響を及ぼす可能性があると考えられる。
以上の結果から、植物体から検出された23元素
の吸収に対するAMの形成の影響を次のように
総括した。
1) KとTh以外の21元素の吸収は植物の生育
史を通じていずれかの時期においてAMの
形成による影響を受けると考えられた。
2) AMが十分に発達していない栄養生長期では、
Crを除くほとんどの元素の吸収にAMの形
成は影響を及ぼさないと考えられた。
3) 生長生長期の前半では、AMの発達はNa、Mg、
Cl、Mn、Zn、Cs、Ce、Euの吸収の増加と関
係があると考えられた。また、生長生長期の
後半ではAMの発達はNa、Sc、Zn、Sr、
La、Ce、Sm、Eu、Yb、Luの吸収と関
係があると考えられた。
4) 生長生長期の前半においては、AMの発達よ
りもAMの存在がCo吸収の低下とLu吸収の
増加に寄与していると考えられた。
5) 生長生長期の後半におけるC1吸収はAMの
存在とAMの発達状態の両方から影響を受け
ていると考えられた。特に、AMの発達状
態の違いはC1吸収の増加と低下といった異
なった結果をもたらすと考えられた。
6) 生長生長期の前半におけるSc吸収および後半
におけるAl、Ca、Mn、Fe、Csの吸収はAM
の存在よりもAMの発達状態による影響を
強く受けると考えられた。さらに、これらの
元素の吸収傾向を生長生長期の前半と後半で
比較することによって、これらの元素の吸収
はAMの発達状態と植物の生育史との関係
によって変化やすいと考えられた。

4. 要約
アーバスキュラー菌根(AM)の形成が植物による
様々な元素の吸収に及ぼす影響を明らかにするため
に放射化学分析法を用いた解析を行った。実験には宿
主植物としてマリーゴールド（Tagetes patula L.）
の種を用いたGlomus etunicatumを用いた。様々な
元素の吸収に対するAMの形成による影響は、AM
の発達状態が異なるマリーゴールド（無接種の対照
区、AMの発達していないLAM区、AMが発達した
AM区）の元素含有量を比較して解析した。また上
述のマリーゴールドは栄養生長期、生長生長期の前
半（開花期）、生長生長期の後半（開花期と発熟期）
の3つの時期に分けて採集し、様々な元素の吸収に
に対する植物の生育史による影響も考慮して解析を行
った。放射化学分析は日本原子力発電所のJRR-3Mと
JRR-4の原子炉を利用して行った。

植物体からはNa、Mg、Al、Cl、K、Ca、Sc、Cr、
Mn、Fe、Cu、Zn、Br、Rb、Sr、Cs、La、Ce、Sm、
Eu、Yb、Lu、Thの23元素が検出された。KとTh
以外の21元素の吸収については植物の生育史を通
じていずれかの時期においてAMの形成による影
響を受けると考えられた。そして、AMの形成に
影響する影響はAMが十分に発達していない栄養生長期
よりもAMが発達した生長生長期において顕著に
認められると考えられた。特に、生長生長期の前半
におけるNa、Mg、Cl、Mn、Zn、Cs、Ce、Euの吸
収と生長生長期の後半におけるNa、Sc、Zn、Br、
Sr、La、Ce、Sm、Eu、Yb、Luの吸収は、AMの発
達によって増加すると考えられた。また、生長生長期
5. 引用文献


Jackson, N.E., Miller, R.H. and Franklin, R.E.: The influence of vesicular-arbuscular mycorrhizae on uptake of \(^{90}\text{Sr}\) from soil by soybeans., Soil Biol. Biochem., 5, 205-212, 1973


依藤敏昭・鈴木源士：根と共生して作物を強くする菌根菌の活かし方, p.24～25, 農文協, 東京, 1995

結田庚一：農業生態系における微量元素および農業の動態, 微量元素・化學物質と農業生態系, p.112～135, 農林水産省農業環境技術研究所編, 姜賢堂, 東京 (1990)

6. 成果の公表

【学術論文】

鈴木弘行：アーバスキュラーギキョウ根を形成した植物の有害微量元素吸収, そのメカニズムとphytoremediationへの応用, 土と微生物, 投稿中

表1 種29日、50日、68日後に採取した各試験区の植物体地上部と根部の新鮮重およびAM形成率①

<table>
<thead>
<tr>
<th>試験区</th>
<th>地上部(g)</th>
<th>根部(g)</th>
<th>AM形成率(%)</th>
<th>地上部(g)</th>
<th>根部(g)</th>
<th>AM形成率(%)</th>
<th>地上部(g)</th>
<th>根部(g)</th>
<th>AM形成率(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>対照区</td>
<td>1.40 a</td>
<td>1.16 a</td>
<td>0</td>
<td>6.11 a</td>
<td>2.84 a</td>
<td>0</td>
<td>7.66 a</td>
<td>3.85 b</td>
<td>0</td>
</tr>
<tr>
<td>LAM区</td>
<td>1.27 a</td>
<td>1.01 a</td>
<td>7</td>
<td>6.24 a</td>
<td>2.87 a</td>
<td>18</td>
<td>8.03 a</td>
<td>3.02 a</td>
<td>26</td>
</tr>
<tr>
<td>AM区</td>
<td>1.54 a</td>
<td>1.18 a</td>
<td>9</td>
<td>6.96 b</td>
<td>2.96 a</td>
<td>51</td>
<td>9.56 b</td>
<td>3.43 ab</td>
<td>46</td>
</tr>
</tbody>
</table>

① 植物体地上部と根部の新鮮重は植物体7個体の平均値、AM形成率は植物体3個体の平均値。
② 表中の同一英文字はボンフェローニ法による多重検定において危険率5％水準では試験区間に有意差がないことを示す。
<table>
<thead>
<tr>
<th>元素</th>
<th>含量 (mg kg⁻¹)</th>
<th>ポット中の元素量 (mg)</th>
<th>施肥由来の元素量 (µg ポット⁻¹)</th>
<th>播種29日後</th>
<th>播種50日後</th>
<th>播種68日後</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>10.5×10³</td>
<td>4.20×10³</td>
<td>5.88×10³</td>
<td>1.18×10³</td>
<td>1.68×10³</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>10.8×10³</td>
<td>4.32×10³</td>
<td>2.52×10³</td>
<td>5.04×10³</td>
<td>7.20×10³</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>59.2×10³</td>
<td>23.7×10³</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>300</td>
<td>120</td>
<td>405</td>
<td>811</td>
<td>1.16×10³</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>21.0×10³</td>
<td>8.40×10³</td>
<td>8.40×10³</td>
<td>16.8×10³</td>
<td>24.0×10³</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>17.8×10³</td>
<td>7.12×10³</td>
<td>8.40×10³</td>
<td>16.8×10³</td>
<td>24.0×10³</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>14.2</td>
<td>5.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>21.8</td>
<td>8.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>766</td>
<td>306</td>
<td>42.0</td>
<td>84.0</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>31.4×10³</td>
<td>12.6×10³</td>
<td>81.9</td>
<td>164</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>10.4</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>186.6</td>
<td>74.2</td>
<td>8.4</td>
<td>16.8</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>N.D.⁺</td>
<td>(2.3〜6) †⁺</td>
<td>0.4</td>
<td>0.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>96.1</td>
<td>38.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>125</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>5.4</td>
<td>2.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>365</td>
<td>146</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>14.3</td>
<td>5.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>38.4</td>
<td>15.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>2.9</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>1.4</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>6.4</td>
<td>2.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>0.3</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>5.4</td>
<td>2.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>3.3</td>
<td>1.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

⁺: 検出限界以下。 †⁺: 文献による推定値（檜原 1990）

- 412 -
図1 各試験区の植物体中の元素含有量の変化
（〇：対照区, ●：LAM区, ▲：AM区, 図中の値と誤差線は植物体4個体の平均値と標準偏差を示す。）
<table>
<thead>
<tr>
<th>分類型</th>
<th>対照区 vs LAM区</th>
<th>対照区 vs AM区</th>
<th>LAM vs AM区</th>
<th>多重検定の結果からの考察</th>
<th>各分類型に対応する元素</th>
<th>検査日数</th>
</tr>
</thead>
<tbody>
<tr>
<td>I型</td>
<td>*</td>
<td>*</td>
<td>NS</td>
<td>AMの存在は含有量の試験区間差に影響を及ぼしているが、AMの発達状態は影響を及ぼしていない。</td>
<td>Co, Lu</td>
<td>検査9日後</td>
</tr>
<tr>
<td>II型</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>AMの存在とAMの発達状態が含有量の試験区間差に影響を及ぼしている。</td>
<td>Cl</td>
<td>検査50日後</td>
</tr>
<tr>
<td>III型</td>
<td>NS</td>
<td>*</td>
<td>*</td>
<td>AMの存在とAMの発達状態が含有量の試験区間差に影響を及ぼしているが、その影響はAMが発達した場合に限られる。</td>
<td>Cl, Mn, Zn, Ca, Ce</td>
<td>検査68日後</td>
</tr>
<tr>
<td>IV型</td>
<td>NS</td>
<td>*</td>
<td>NS</td>
<td>目型と同様であるがAMによる影響は目型よりも弱い。</td>
<td>Na, Mg, Eu</td>
<td></td>
</tr>
<tr>
<td>V型</td>
<td>NS</td>
<td>NS</td>
<td>*</td>
<td>AMの存在よりもAMの発達状態の違いが含有量の試験区間差に影響を及ぼしている。</td>
<td>Sc</td>
<td></td>
</tr>
<tr>
<td>VI型</td>
<td>*</td>
<td>NS</td>
<td>NS</td>
<td>AMの存在は含有量の試験区間差に影響を及ぼしている。しかし、その影響はAMが発達していない場合に限られる。</td>
<td>Cr</td>
<td></td>
</tr>
<tr>
<td>VII型</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>AMの存在とAMの発達状態は含有量の試験区間差にほとんど影響を及ぼしていない。</td>
<td>Na, Mg, Al, Cl, K,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca, Sc, Mn, Fe, Co,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zn, Br, Rb, Sr, La,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ce, Sm, Eu, Yb, Lu,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca, Th</td>
<td></td>
</tr>
</tbody>
</table>

1) ボンフェローニ法による多重検定の結果；*：危険率5％水準で試験区間に有意差があることを示す。NS:有意差なし。
3-13
中国で採取された風成堆積物の放射化分析
Neutron Activation Analysis of aeolian sediment samples in China

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北海道大学大学院地球環境科学研究科
Kazuhito Toyoda, Yoshitsugu Shinozuka, Atsushi Watanabe, Kiyoshi Hasebe
Graduate school of Environmental Earth Science, Hokkaido Univ.

I 中国東北部と中国中央部の黄土高原に採
取された風成堆積物

【緒言】近年、風成堆積物は季節風変
動や乾燥変動など過去の環境変動の指標と
なるものとして注目されている。特に、中
国内陸部の黄土高原を中心に広い範囲に
堆積している風成堆積物は、タクラマ
ガン砂漠やゴビ砂漠などの内陸部の乾燥地
域から舞い上がった風成塵が、偏西風など
により運搬され、過去に連続的に降雨して、
堆積したものとされている。しかし、その
正確な起源地や運搬経路については現在で
も不明な点が多い。

本研究では図1に示した、黄土高原に位
置する「蘭州」で採取された風成堆積物
に加え、文献値の少ない中国北東部の大連
近郊の「大連山」及び内モンゴル地域に近
い「天山」についても無機化学分析を行い、
その化学組成から、その地域的な特徴と約
1万年前から現在までの時代変化について
検討をおこなった。

【実験】Ti、Al、Fe、Mg、Caなどの試料
中の主成分元素はICP発光分析で測定し、Hf
、Rb、Cs、Coや希土類元素などの微量元素
の定量は日本原子力研究所の原子炉にて中
性子放射した後、γ線測定をおこなった。
分析した試料の数はバルク分析では3地点
から主に採取された計200試料、堆積後
の風化作用によるCaなどの溶出の影響を除
くために、塩酸により炭酸塩相などを除去
した溶液成分については3地点計90試料
である。さらに風成の運搬過程で粒度に
よる分別をうけるという観点から、3地点
それぞれ8試料ずつをふるいにより粒度別
に分離をおこない、同様に無機化学分析を
おこなった。

【結果と考察】バルク分析の結果に文献
値を合せて比較すると、中国北東部と内陸
部の黄土高原とでは風成堆積物の無機化
学組成は明らかに異なることがわかった。

黄土高原の「蘭州」ではMgやFeに比較的富
んだ玄武岩質の礦物を多く含むのに対して、
中国北東部の「天山」及び「大連山」では
Hf、Ybなどに相対的に富み、花崗岩質の礦
物を多く含む、というように地域的な特徴
をもつ。

次に粒度別に分離した試料を比較すると、
遠方より運搬されたと考えられる20μmよ
りも細粒成分の化学組成は3地点でやや
重なる範囲の値を示すのに対して、63μm
よりも粗粒成分の化学組成は地域的な化
学組成の違いが顕著にみられた。このこと
より、地域的な特徴は試料採取地点に起源
する物質の寄与が大きいためと考えられ、

JRR-3 PN、JRR-4 Tパイプ、γ線スペクトロメトリー、堆積物の放射化分析

－415－
一方、細かい粒度の成分については、各地域
で起源地が同じであることが推測できた。
この共通の起源地については、タクラマカ
ン砂漠などの化学組成の文献値が今後報告
される事で、本研究のデータはその同定に
貢献すると考えている。
さらに酸抽出残渣のいくつかの化学組成
の時代変化は浮遊性有孔虫の酸素同位体比
時代区分と同期しているように見える（図
2）。粒度別試料の結果とこの化学組成の
変遷を考えて合わせると、過去約12万年間
で、風成塚試料中には氷期はより遠方を
起源とする成分が多く含まれ、間氷期には
試料採取地点の近隣地域を起源とする成分
の寄与が相対的に増加したと考えられる。
つまり、寒冷な時期には偏西風によって
大陸内部の乾燥地域より、細粒物質が大量
に運搬されるのに対し、温暖な時期には夏
季季節風が活発化し大陸内部は比較的湿潤
で、風成塚の運搬量が減少し、遠方からの
寄与が減少したことが記録されていると推
測できる。
ただし、現時点では3つのコアの測定試
料の数が少なく、より確かな考察をするに
はもう少し垂直化学分布データの時間分解
能を高める必要がある。その後に、本研究
内容について学術雑誌に投稿したいと考え
ている。

図1. 試料採取地点

図2. 中国北東部（天山）時代変化（炭酸塩層抽出残留豊）。
天山のコーヒーサンプルでは温暖期（土壌層）でHf/Th比、Yb/Sc比が増大している。
II 古カトマンズ湖のラピバーワンコア中の無機化学成分の垂直分布
【予報】ヒマラヤ山脈の南斜面に位置するカトマンズ盆地で採取された218m長のラピバーワンコアはインドモンスーンの変動とヒマラヤ山脈の上昇の双方の過去300万年の歴史を記録していると考えられる。これらは日本の気候変動に大きく連動しているので興味深い。

前述と同様に機器中性子放射化分析を用いて、ラピバーワンコアの深度7m～41mの部分から約0.2mおきに採取された164個の試料中の長寿命核種の測定を行い、微量成分10元素と鉱含有量の定量を行った。河成層である深度12m以浅の試料は深度12m以深に比べてハフニウム含有量、セリウム含有量、及びトリウム／スカンジウム比が高く、花崗岩質屑屑物の寄与が大きいと推定された。

一方、深度12m～41mの試料についてはトリウム／スカンジウム比の値が0.9～1.2の間を狭やかに変動している。これが気候変動に伴う風成層の寄与の大きさの変化を意味しているかどうか興味のあるところである。また、深度22m～31mの鉱含有量の変動がやや激しく、酸化還元状態の大きな変動を示していると考えられる。

またセシウム含有量のみが時代を経るにつれて著しく減少している。これについてはICP発光分析などで他のアルカリ元素含有量が測定された後に考察したい。今後は、短寿命核種の測定に加えて、既に採取されている深度41m以深の試料についても機器中性子放射化分析を行っていきたい。

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カツオドリ（*Sula leucogaster*）の有機態ハロゲン（Cl, Br, I）

3-14 Extractable Organohalogens (EOX) in Brown Booby (*Sula leucogaster*)

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1. はじめに

人工有機塩素化合物（DDTs, PCBs, CHLs等）は、生産系の高次生物に高濃度に濃縮されることとが知られ、特に海洋生態系の高次生物である海生哺乳類や海鳥において成長が高い程度で蓄積していることが明らかにされている。しかしながら、近年上記の対象化合物以外に未知の有機塩素化合物を含む有機ハロゲン化合物が見出されている。これらの化合物は高濃度で生物や土壌・底質中に存在していることが次第に明らかにされ、未検討の有機ハロゲン化合物による環境汚染が懸念されている。

それら未知有機塩素化合物の環境中における蓄積レベルと蓄積特性に関する検討結果は、未知化合物の検出・同定や環境汚染物質の評価を行う上で有力な情報となることが期待される。そこで本論文では、海洋生態系の高次捕食者である海鳥カツオドリ（*Sula leucogaster*）を対象に、未知有機塩素化合物の存在レベルと蓄積性について、上記の代表的な人工有機塩素化合物と比較検討した。

有機ハロゲン（Extractable organohalogens: EOX）は機器中性子放射化分析法で測定した。なお未知有機ハロゲン化合物の蓄積濃度は、機器中性子放射化分析で得られた有機ハロゲン濃度とGC-MS, GC-ECDで得られた個別有機ハロゲン化合物濃度を比較検討する目的によって求めた。

2. 試料と方法

試料は、1993年夏季に沖縄県沖ノ神島において許可のもとに採集された鶴5検体、幼鳥2検体、成鳥2検体、合計9検体を個別化合物の分析に、さらに上記の試料のうち5検体（鶴2検体、幼鳥1検体、成鳥2検体）をEOX分析に供した。分析には皮下脂肪を用い、有機溶媒による抽出の後、カラムクロマトグラフィーによる妨害物の除去後、GC-MS, GC-ECDにより個別化合物を定量した。一方、有機溶媒による抽出の後、無機ハロゲンを除去し、放射線分析法により有機ハロゲン化合物を計測した。なおEOXとして有機塩素化合物（EOCl）、有機塩素化合物（EOBr）及び有機塩素化合物（EOI）を測定した。EOX分析は、調製した有機溶媒抽出液を試料容器に入れ、日本原子力研究所の原子炉JRR-4を用いた。なお、放射線化については中性子束约3.7×10^5n/cm^2/sで、2分間照射し生成した放射性核種（Cl（1642 keV, 2167keV）, Br（517keV, 668keV）, I（443keV）をγ-スペクトロメトリーにより計測した。

3. 結果と考察

分析対象の人工有機塩素化合物（DDTs, PCBs, CHLs=総合物質として30種程度）が全ての試料から検出され、濃度順位はPCBs>DDTs>CHLs>HCHs>HCBであった。これらは今日知られている代物的な環境残存性の強い人工合成有機塩素化合物である。一方、これら未知有機塩素化合物に由来する総塩素量とEOC濃度を比較すると前者が90%以下であった。このことはカツオドリ体内に蓄積している有機塩素化合物の内に90%以上が、未知の有機塩素化合物であることを意味している。即ち、未同定の有機塩素化合物が比較的高濃度で存在していることが明らかとなった。Fig.1に各試料のEOX組成、Fig.2に既知と未知有機塩素化合物に由来する各既知塩素化合物化合物の割合を示した。
EOClおよび未知EOClの組成割合を示す。本研究で得られたカツオドリ中の未知EOC組成は、先に検討したキアシシギの場合が平均73％に比べ大きい割合を示し、カツオドリには比較的高い濃度の未知EOCの有機塩素化合物が蓄積していることが明らかとなった。

鳥類の飼育定法が確立されていないため、野生鳥類の成長に伴うPCBs、DDTsなどPOPsの体内蓄積変動に関する情報は少ない。そこで本研究では、特に、標識によって飼が明らかにされている試料を用い既知・未知有機塩素化合物を含むEOCの蓄積性について明らかにした。その結果、EOCの濃度順位はEOCl＞EOBr＞EOIであり、成長段階におけるハロゲン間の存在割合に大きな相違は見られずEOClが最も高濃度であった。成長に伴うEOCの蓄積に関して、PCBs等に由来する既知EOC濃度（脂肪酸当量）は雛から幼鳥にかけて濃度低下が見られ、その後次第に体内濃度は上昇した（Fig. 3）。

この濃度の一時的な低下は、急速な成長による希釈効果によるものと考えられる。既知EOCと同様な蓄積傾向をEOIも示した（Fig.3の上段図）。一方、未知EOCとEOBrについては、雛から幼鳥期にかけて一時的な濃度低下は見られたものの、既知EOCほど顕著な成長に伴う濃度上昇は見られなかった（Fig.3の下段図）。既知・未知EOC、EOBr及びEOIは上述のようにそれぞれ特徴的な蓄積パターンを示した。
Fig. 3. Relationships between age and concentrations of known EOCI, unknown EOCI, EOBr and EOI in adipose tissue of brown booby collected at Nakanokami Island, South Ryukyus.
以上の結果、EOXは必須性の化合物より構成されることが考えられる。それに対して未知EOClとEOBrは蓄積性が低いことから必須性であることが推定される。これらEOX濃度は比較的高いことから毒性など生物影響についてもさらに検討する必要がある。

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3-15
岩石の酸性変質と二次鉱物の生成に伴うランタノイドの移動
Mobility of lanthanides accompanying rock alteration and formation of secondary minerals in acidic environment.

1. はじめに
火山地域においては、酸性の火山ガスや沸水などの火山性流体により岩石が酸性変質を受け、広範囲にわたる火山変質帯が形成される場合がある。このような変質帯においては、岩石成分の分解、溶脱、運搬が継続的に行われ、火山地域における物質循環における重要な役割を担っている。しかしながら岩石の変質過程は、単純な岩石成分の溶脱現象だけでなく、その地質や環境に応じた二次鉱物の生成過程とが密接に関わっているため、複雑な相互関係があることから、未だその体系的理
解には至っていない。したがって岩石の変質現象の理解を深めるために、複雑に重なり合った様々な物理化学現象を理解し、個々の現象の詳細を明らかにしていくことが求められている。その中で本研究は、火山地域において広く見られる硫素変質帯中に一般的に認められる変質二次鉱物“アルナイト”に着目し、そこに微量に含まれるランタノイドをトレーサーとして用いることにより、通常の主成分元素の挙動のみでは知り得ない変質過程の詳細を、アルナイトの生成過程を通じて捉えようとするものである。

アルナイト（alunite：明礬石）は KAl_3(SO_4)_2(OH)_6 で示される二次鉱物であり、火山性の酸性変質帯には広く見られる変質鉱物である。アルナイトの K を Na あるいは Ca で置換したものはそれぞれ、ナトリオアルナイト (natroalunite)、フアンジャイト (huangite) と呼ばれ、これらはアルナイトグループ鉱物と総称される。また、カリウムの一部をナトリウムおよびカルシウムで置換した (Na, Ca, K)Al_3(SO_4)_2(OH)_6 の組成で示される鉱物は南石 (minamiliite) と名付けられ、群馬県草津白根火山地域の奥万座が発育地となっている。このように天然において産出するアルナイトは、アルナイトの生成過程におけるK, Na, Ca 組成の固溶体として幅広い組成を持って産出する。

これまでの研究の上に、アルナイトに微量に含まれるランタノイドの周辺岩石（母岩）に対する存在度パターンは、相対的に軽ランタノイドに富み、アルナイトに特有のパターンを示すことが示唆されており、アルナイトの生成過程におけるランタノイドの相互関係が内蔵する可能性が示されている。このような相互関係を解明することは、アルナイトの生成過程を理解する上で重要な役割を果たすものである。

そこで本研究では、アルナイトグループ鉱物中に含まれるランタノイド並びに、ランタノイドとその存在度の相関性が期待される Sr および Ba に着目し、アルナイトの生成過程に介在する、これら元素が関与する化学的現象を明らかにすることを第一の目的とした。

2. 実験
本研究を進めることにあたり、大きく分けて二つの実験を行った。ひとつは天然に産するアルナイトの分析であり、もうひとつは、実験室内で人工的にランタノイドを添加したアルナイトを合成する実験である。

2.1 天然産出アルナイトの分析

試料

研究施設と装置名：JRR-4 S・T、下り、上り、気冷管
研究分野：地球化学的試料の放射化学分析
本研究で用いたアルナイト試料は、群馬県草津白根火山地域で採取した17試料であり、その内訳は草津白根山の山頂火口湖である水釜から2試料、万座空洞泉周辺から4試料、奥万座源泉泉周辺から11試料である。採取試料のいくつかは、色調の違いにより組成あるいは組織が明らかに異なると判断される複数の部分から成っており、このような場合には色調により試料を分け、それぞれ異なる試料として取り扱った。また、草津白根山の基盤岩を成す高井溶岩の比較のために用いた。試料採取地点はFig.1に示してある。

取り上げられたアルナイト試料は、風乾後、粉碎し、粉末X線回折法(XRD)による鉱物種の同定を行い、浸出分析法およびフィッチャル素酸分解法を用いたICP発光分析法および磁光度法により主成分元素の定量を行った。

ランタノイド並びにストロニチウム、バリウムの定量には非破壊中性子放射化分析法を用いた。日本原子力研究所以東海研究所のJRR-4を中性子源として用い、高純度ガラス製半導体検出器を用いるγ線の測定を行い、4096ch波高分析器を用いてγ線の計測を行った。なお、いくつかの試料のランタノイドの定量のみ初数値(TRIGA-II)を中性子源として用いた。中性子照射からγ線測定まで測定は、既報6-7に準じた。

2.2 実験室におけるアルナイトの合成
まず、希硫酸に過剰量のランタノイド酸化物を溶解させ、室温におけるランタノイドの混合酸和溶液を調製した。次に、この酸和溶液を以下に述べる三通りの実験を行った。

カリウム-ランタノイド-硫酸複塩の生成実験
ランタノイドはカリウム、ナトリウムなどのアルカリ金属と硫酸複塩を形成することが知られている。そこでアルナイトの合成実験に先立ち、混合ランタノイド酸和溶液と硫酸カリウム溶液を所定の温度、時間で反応させることでカリウム-ランタノイド-硫酸複塩の合成を試みた。実験手順は以下の通りである。

先に用意した酸和ランタノイド硫酸水溶液と、室温における酸和硫酸カリウム水溶液を同体積ずつ取り、テフロン製の密閉容器内で、25℃、40℃、80℃、120℃で各々7日間、および室温において49日間反応させた。所定の反応日数終了後、反応溶液は0.1μmのメンプランフィルターを用いて通過した。通過液中のランタノイドを定量し、出発溶液に含まれるランタノイド濃度との濃度差から元素ごとに固相への分配比を求めた。

水熱合成法によるアルナイトの合成
アルナイト生成に伴いアルナイト中に取り込まれるランタノイドの相互分離現象を実験的に確かめるため、以下の手順によりランタノイド添加系でのアルナイト合成実験を行った。
表 1 ピラニテ試料の主成分およびSr, Ba濃度分析値

<table>
<thead>
<tr>
<th>Sample name</th>
<th>MI21</th>
<th>MI22</th>
<th>KAR1</th>
<th>KAR2a</th>
<th>KAR2b</th>
<th>KAR3</th>
<th>OKU1</th>
<th>OKU2</th>
<th>OKU3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Mizugama</td>
<td>Mizugama</td>
<td>Manza-Karabuki</td>
<td>Manza-Karabuki</td>
<td>Manza-Karabuki</td>
<td>Manza-Karabuki</td>
<td>Okumanza</td>
<td>Okumanza</td>
<td>Okumanza</td>
</tr>
<tr>
<td>(wt.%) SiO₂</td>
<td>2.67</td>
<td>0.08</td>
<td>12.44</td>
<td>60.45</td>
<td>35.39</td>
<td>47.34</td>
<td>1.92</td>
<td>3.89</td>
<td>18.17</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.45</td>
<td>2.19</td>
<td>0.70</td>
<td>0.29</td>
<td>0.50</td>
<td>0.58</td>
<td>2.06</td>
<td>2.62</td>
<td>1.02</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.51</td>
<td>4.59</td>
<td>8.56</td>
<td>3.27</td>
<td>4.98</td>
<td>4.18</td>
<td>2.36</td>
<td>5.18</td>
<td>6.52</td>
</tr>
<tr>
<td>CaO</td>
<td>0.09</td>
<td>1.71</td>
<td>0.11</td>
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| ppm | Sr | 1.1E+03 | 1.5E+03 | 3.7E+03 | 3.4E+02 | 4.8E+02 | 3.5E+02 | 4.1E+02 | 2.2E+03 | 1.2E+03 |
| ERR(%) | 3.4 | 3.7 | 2.5 | 8.7 | 6.8 | 23.6 | 5.5 | 7.8 | 4.8 |
| Ba | 3.5E+02 | 4.2E+02 | 6.9E+02 | 8.0E+02 | 4.9E+02 | 1.5E+02 | 1.1E+02 | 1.2E+02 | 3.3E+02 |
| ERR(%) | 10.9 | 11.6 | 10.4 | 4.6 | 6.5 | 19.5 | 13.8 | 40.1 | 10.3 |

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| ppm | Sr | 6.6E+02 | 1.2E+03 | 7.4E+02 | 4.0E+03 | 4.7E+03 | 1.2E+03 | 7.0E+02 | 4.0E+03 | - |
| ERR(%) | 5.7 | 4.0 | 4.4 | 3.8 | 3.4 | 5.3 | 5.7 | 4.3 | - |
| Ba | 3.3E+02 | 4.4E+02 | 1.5E+02 | 4.1E+02 | 4.9E+02 | 2.6E+02 | 1.5E+02 | 3.0E+02 | - |
| ERR(%) | 6.8 | 7.4 | 13.1 | 7.8 | 4.1 | 11.8 | 12.1 | 7.0 | - |

ERR(%) : Errors in gamma ray counting.
したアルナイト中のラタンノイドを定量し、アルナイトの生成に伴うラタンノイドの相互関係を求めた。

合成実験試料の分析操作

複数合成実験ならびに水熱合成実験における生成物（図相）は、乾燥、粉碎して XRD によりその化学種の同定を行った。また、各出発原料（出発溶液）中、および複数合成実験後の液相中のラタンノイド組成は、ICP発光分析法により行った。

水熱合成実験により得られた合成物中のラタンノイド組成は天然試料の場合と同様に、JRR-4 を中性子源とした非破壊中性子放射分析法により求めた。

3. 結果と考察

3.1 草津白根地域産出の天然アルナイト

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<th>Sm</th>
<th>Eu</th>
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<td>3.7</td>
<td>12.9</td>
<td>11.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OKU6c</td>
<td>1.3E+01</td>
<td>2.7E+01</td>
<td>1.8E+01</td>
<td>4.2E+00</td>
<td>8.7E-01</td>
<td>ND</td>
<td>ND</td>
<td>2.4E-01</td>
<td>9.2E-01</td>
<td>ND</td>
<td>1.4E-00</td>
<td>1.1E+00</td>
</tr>
<tr>
<td>ERR(%)</td>
<td>2.4</td>
<td>4.0</td>
<td>20.7</td>
<td>5.3</td>
<td>2.4</td>
<td>25.6</td>
<td>11.2</td>
<td>4.9</td>
<td>15.4</td>
<td>11.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OKU7</td>
<td>3.3E+00</td>
<td>6.6E+00</td>
<td>4.1E+00</td>
<td>1.0E+00</td>
<td>2.1E+00</td>
<td>ND</td>
<td>ND</td>
<td>4.4E-01</td>
<td>1.2E+00</td>
<td>ND</td>
<td>1.3E+00</td>
<td>ND</td>
</tr>
<tr>
<td>ERR(%)</td>
<td>1.1</td>
<td>1.7</td>
<td>10.2</td>
<td>0.9</td>
<td>1.7</td>
<td>12.8</td>
<td>16.2</td>
<td>9.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAKAI</td>
<td>1.1E+01</td>
<td>2.2E+01</td>
<td>1.2E+00</td>
<td>3.4E+00</td>
<td>1.1E+00</td>
<td>ND</td>
<td>ND</td>
<td>5.2E-01</td>
<td>3.5E-01</td>
<td>ND</td>
<td>2.6E+00</td>
<td>4.1E-01</td>
</tr>
<tr>
<td>LAVA</td>
<td>ERR(%)</td>
<td>2.8</td>
<td>5.0</td>
<td>27.9</td>
<td>5.9</td>
<td>5.1</td>
<td>12.1</td>
<td>16.0</td>
<td>7.0</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| ERR(%) | Errors in gamma-ray counting. |

* 立体炉を利用しての分析値

主成分並びにストロンチウム、バリウムの定量結果を Table 1 に示した。また、ラタンノイドの定量結果を Table 2 に示した。分析試料中の重ラタンノイドの含有濃度が全体的に低かったため、中性子放射分析法による定量がそれほど困難ではない。Yb、Lu が検出限界以下となるものが多かったことがわかる。

XRD 測定の結果、全ての試料にアルナイトの存在を確認し、ナトリウムの含有量の多い試料にはナトリオルナイトが、カルシウム含有量の多い試料にはニトリオルナイトがそれぞれ含まれていた。また、ケイ酸の含有量が多い試料には、石英あるいは石英の合成ピクルが認められた。したがって、XRD による鉱物の同定結果は主成分分析結果とよく一致している。

天然アルナイトのラタンノイドパターン
Table 2 に示した各アルナイト試料のラントナイド定義値を、この地域の基盤岩として知られる高井溶岩中のラントナイド定義値を規格化することで得られたランタンノイド存在度パターン（Masuda-Coryell plot）を Figs. 2, 3, 4 に示した。これを見ると、試料ごとにランタンノイドの含有濃度に違いはあるものの、何れの試料も重ランタンノイドに比較して軽ランタンノイドに相対的に富んだ類似のパターンを示すことが分かる。また、その傾向は試料の採取位置に依らずに共通のものである。したがって、これはアルナイトに共通のランタンノイド存在パターンであると考えられる。

Table 1 を見て分かるとおり、今回分析した試料の中には数 10 wt.%から大きいものでは 60 wt.%を越える SiO₂ 濃度を示すものがある。このような SiO₂ 濃度の高い試料は XRD の結果から、アルナイトと共に蛋白石、あるいは非晶質シリカのようす、理想的には SiO₂のみから成る変質鉱物が共存している試料であることが分かっている。そのため、純粋なアルナイトにおけるランタンノイドの挙動を見極めるために、Fig. 5 に SiO₂の濃度が 10 wt.%未満であった 7 試料のみのランタンノイドパターンを示した。

これをみると、やはり試料ごとにランタンノイド濃度に違い
があるが、試料間のランタノイド濃度差は、重ランタノイドよりも軽ランタノイドで大きいように見ることが出来る。すなわちアルナイトの生成に伴うランタノイドの相互別現象は、軽ランタノイドにおいてより大きいと考えられる。また、パターンの形状はTb—Dy付近でブロットの変曲点に連続性を欠き、この前後でランタノイドの挙動に差異があることが示唆される。すなわち、Tbより軽いランタノイドでは、やや急形になりながら、軽いほど相対的濃縮傾向が強くなるような連続的な変化を示すのに対し、Dyより重いランタノイドでは、元素間での明瞭な分別が認められない。

以上の点を整理すると、アルナイトにおけるランタノイドの分別現象は、Tb—Dyを境界としてその前後で異なっており、その差異の生じる原因としての何らかの物理的・化学的現象がアルナイトの生成過程に関与していると考えられる。また、軽ランタノイドにおいて、軽い元素ほど相対的に濃縮傾向を示し、その濃縮傾向の強さが原子番号と共にほぼ連続的に変化することから、それにはおそらくイオン半径に依存するような何らかの分別現象が関与しているものと考えられる。

ストロンチウム、バリウムおよびランタノイド含有濃度間の相関性

Table 1を見ると、ストロンチウムの含有量は300 ppm程度から多いものは4,000 ppmを越えるものまで非常に幅広い範囲にわたっている。数千 ppmに達するストロンチウム濃度は一般的な火山岩中の存在量に比較して極めて高い。一方、バリウムは100〜800 ppmの範囲にあり、ストロンチウムに対して試料間での濃度のばらつきは若干小さく、また一般的な火山岩と比較して特異的に高い値ではない。以上より少なくともストロンチウムは明らかにアルナイト中に濃縮していると言えることができる。

Fig.6にストロンチウム濃度とバリウム濃度の相関図を示す。ここからは、両元素の濃度間には有意な相関性は無いように見えるが、一方で図中の直線A、Bで示したように複数の孤立した相関性が存在している可能性も否定できない。ここで古万座産出のアルナイト試料の中でケイ酸の濃度が10 wt.%未満のものに対する回帰直線（相関係数0.90）が直線Aであり、ケイ酸濃度が10 wt.%以上のものに対する回帰直線（相関係数0.54）が直線Bである。万座空洞産および水釜産出のアナルbite試料は分析数が少なく、かつ、万座空洞産出ではケイ酸濃度の低い試料がひとつしか得られなかったことから、どこその相関性について論議することはできないものの、少なくとも万座産出の分析試料を見ると、ケイ酸濃度の低い、すなわち、不純物の少ないアルナイト試料においては、ストロンチウム濃度とバリウム濃度との間には有意な相関性があると見ることが可能である。

ストロンチウムとバリウムのようなアルカリ土類は、単に
純にはアルナイトグループ物質で同じアルカリ土類であるカルシウムを置換していると想像される。もし両元素がアルナイトグループ物質中のカルシウムの一部を置換しているのであれば、アルカリ金属濃度に対してカルシウム濃度が高い試料、すなわち、ミナミサイトを多く含む試料ほどそれらの含有量は高くなるはずである。しかしながら、実際には最もカルシウム濃度が高いOKU1のストロンチウム、バリウム濃度は全試料中でかなり低濃度の部類に属し、OKU1を除外してもカルシウム濃度との間には相関性は認められない(Fig. 7)。したがって両元素はカルシウムとの単純な置換により取り込まれているものではない。

ストロンチウムとバリウムを含むアルナイト類似物として、walthierite (Ba₆Al₃(PO₄)₃(OH)₃)、gorceixite (Ba₂Al₂(PO₄)(PO₃OH)(OH)₂)、goyazite (SrAl(PO₄)(OH)₃(H₂O))などが知られているが、一般にイオン半径の大きいストロンチウム、バリウムは対となる亜イオンとして硫酸イオンよりもリン酸イオンあるいはホスホ酸を好む。一方、奥万座産出のアルナイト中に、微量な crandallite (CaAl₂(PO₄)(OH)₂(H₂O)) の結晶が存在することが報告されており 6)。また、今回の成層白根火山地域産出の天然アルナイト試料の分析値においても、軽ラタンノイド濃度とリノ酸濃度の間に良好な正の相関性が認められる(Fig. 8)。このことから、crandallite のカルシウムサイトをラタンノイドに置き換えた組成に属する florecite ((La,Ce,Nd)Al₃(PO₄)₃(OH)₃) のようなリン酸塩物質中にラタンノイドが取り込まれている可能性が高い。したがってストロンチウムやバリウムもリン酸を伴った試料を形成し、アルナイト中には共存している可能性が高いと思われる。そこで Fig. 9 に奥万座産出のアルナイト試料におけるリノ酸濃度とストロンチウム、バリウム濃度との相関図を示した。これを見ると、ケイ酸濃度が低い、純度の高いアルナイト試料においては、両元素濃度共にリン酸濃度との間に比較的良い相関性（相関係数 r > 0.9）を有し、あるいはストロンチウムとバリウムがリン酸と対になってアルナイト中に取り込まれていることを示す結果となった。さらに同じく奥万座産出のアルナイト試料について、ストロンチウム濃度とリン酸濃度との相関性（Fig. 10）を求めたところ、ケイ酸濃度の大小にかかわらず、全ての試料を通じて良好な相関性（相関係数 r > 0.9）が認められ、ストロンチウムと軽ラタンノイドがアルナイトの生成過程において挙動を共にしていることが示された。

以上の結果より、火山地域における岩石の酸性変質に伴って生成するアルナイト中に微量に含まれるストロンチウム、バリウムは、アルナイト類似の含リン酸塩物として存在している可能性が高いと言える。またその際、軽ラタンノイドもストロンチウムに付随して含リン酸塩物質中に取り込まれているものと考えられる。

3.2. アルナイト合成実験

![Fig. 9 奥万座産出アルナイト試料の P-Sr および P-Ba 相関図](image-url)
## 飽和ラントナイト硫酸水溶液の組成

室温にて13元素の酸化ラントナイトを希硫酸に溶解することで得られた飽和ラントナイト硫酸水溶液の組成をTable 3およびFig. 11に示した。Fig. 11から分かるように、約5 mol dm\(^{-3}\)の硫酸濃度の元で、ラントナイトの溶存濃度は軽ラントナイト、重ラントナイトの両極で高く、その中間で低いものとなった。ここでCeの溶解度がLa、Ndに比較して極端に小さいが、これは、今回用いたCe以外の酸化ラントナイト試料が4+3値のLa\(_2\)O\(_3\)であったのに対して、Ceのみ4+4値の酸化物(Ce\(_4\)O\(_2\))であったためである。

### カリウム-ラントナイト硫酸塩の生成に伴うラントナイトの相互分別

反応実験終了後の反応液の漏汁中に含まれるラントナイト濃度と出発原料中のラントナイト濃度との差から固相中に取り込まれたラントナイトの物質量を求め、それを出発原料中に存在していたラントナイトの物質量で規格化することで得られた各元素の分配比をFig. 12に示した。これをみると、何れの反応条件においても固・液間でラントナイトの相互分別が生じていることが分かる。しかしながら、その分別状況は反応温度により異なっている。室温と25℃における分配パターンは一致し、

![Graph](image-url)

**Table 3 飽和ラントナイト硫酸水溶液の組成**

<table>
<thead>
<tr>
<th>成分</th>
<th>(\text{SO}_4)</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>対数</td>
<td>(mol/dm(^{-3}))</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>濃度</td>
<td>5.3</td>
<td>856</td>
<td>54.4</td>
<td>414</td>
<td>128</td>
<td>85.6</td>
<td>77.4</td>
<td>78.3</td>
<td>61.7</td>
<td>104</td>
<td>121</td>
<td>192</td>
<td>325</td>
<td>486</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

40℃におけるパターンも軽ラントナイトにおける分配比が小さくなるものの、やはり同様のパターンと見なすことが出来る。また、そのパターン形状は天然のアルナイトに見られるラントナイトパターンと良く一致する。一方、80℃、120℃における分配パターンは、非常にばらつきが大きく、明らかに40℃以下で見られた分配パターンとは異なっている。しかしながら、再後端のTmからLuに
4. まとめ
本研究より、岩石の酸性変質に伴うアルナイトの生成過程に関して、以下の点が明らかになった。
（1）天然産出のアルナイトに共通のランタノイド存在度パターンが見出された。この存在度パターンはアルナイトに特徴的なものであり、軽ランタノイドほどアルナイト中に取り込まれやすい。
（2）天然産出のアルナイトにおいては、軽ランタノイド、ストロンチウム、バリウムおよびリチウムの含有量の間には、相互に正の相関性が認められ、軽ランタノイドの一部はストロンチウム、バリウムと共にアルナイト類似のリン酸塩鉱物中に取り込まれている可能性が高い。
（3）実験室で合成したカリウム-ランタノイド-硫酸複塩ならびに、ランタノイドを添加した合成アルナイトにて認められるランタノイドの分配比のパターンは、天然産出のアルナイトの存在度パターンと類似しており、天然産出アルナイトに特有のランタノイド相互分配現象は、上記複塩が生成することにより生じる可能性が強く示唆された。
（4）火山地域における岩石の酸性変質に伴うアルナイトの生成は、カリウム-ランタノイド-硫酸複塩が生成することにより生じる環境の元に生じているものと考えられる。

引用文献
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研究成果

学位論文等
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学会発表等
1. はじめに

平成12年度と13年度は、JRR-3M、JRR-4の気送管及び水力照射設備を使用し、1）熟外中性子放射化とコンプトンサプレッションγ線スペクトル測定による生体試料中の微量ヨウ素の定量、2）k0法による多元素標準物質、及び3）底質標準物質の分析を実施した。

2. Non-destructive determination of trace amounts of iodine in biological samples by epithermal neutron activation and Compton suppression gamma-ray spectrometry

The importance of iodine in radiation protection, medicinal, nutritional and epidemiological research studies demands an accurate determination of traces of iodine in biological materials. Radioactive nuclides such as $^{35}$Cl and $^{24}$Na produced from matrices interfere in the trace determination of iodine in biological materials when $^{125}$I (half-life 24.99 min) is applied for NAA of iodine. The interference, however, can be reduced by employing epithermal activation and Compton suppression γ-ray spectrometry because the resonance integral of iodine is larger than those of Cl and Na, and the emitting γ-ray energy of $^{125}$I is lower than those of $^{35}$Cl and $^{24}$Na. In the present study, epithermal neutron activation analysis in conjunction with Compton suppression spectrometry has been examined for the determination of iodine in various biological samples.

A sample was irradiated at JRR-4 pneumatic tube using Cd filter for 10 s to 5 min together with an iodine standard. The γ-ray spectra were measured by a Compton suppression spectrometer using a Ge-BGO detector system.

When compared with the case of thermal neutron activation, radioactivity of $^{35}$Cl and $^{24}$Na induced by the epithermal neutron activation using Cd filter at JRR-4 PN irradiation facility decreased by factors 8.5 and 7.0, respectively, however, the induced radioactivity of $^{125}$I decreased by only factor 1.8. The Compton background counts at $^{125}$I 443 keV region suppressed by factors 4.3, and 11 for $^{35}$Cl and $^{24}$Na, respectively, by the Compton suppression γ-ray spectrometry compared to the single mode γ-ray measurement. The detection limits of iodine in biological samples by 1) conventional thermal neutron activation and normal γ-ray measurement, 2) epithermal activation and normal γ-ray measurement, and 3) epithermal activation and the Compton suppression γ-ray measurement were 2600 ppb, 450 ppb and 14 ppb, respectively. More than 35 ppb of iodine in various materials such as human diets, bovine muscle, non-fat milk powder, oyster tissue and human thyroid were determined. The analytical results agreed well with other reported values.

3. Multi-element determination for the characterization of SMELs samples by k0-INAA

Three types of Synthetic Multi-Element Standard (SMELs), which were spiked with a total of 33 elements into a phenol-formaldehyde resin, have been prepared at IRMM, Geel and INW, Gent for QC/QA of k0-NAA. Co-operative analysis of the SMELs has been carried out by several laboratories to characterize the elemental concentration of the spiked elements. We were determining the elemental concentrations in the SMELs by k0-INAA using the NAA facilities of the JRR-3M reactor at JAERI.

Samples (50 to 100 mg) were sealed in high-purity polyethylene film and irradiated for 10 s to 20 min in the pneumatic tube irradiation.
facility of the JRR-3M with a neutron flux higher than $10^{11}$ n cm$^{-2}$ s$^{-1}$. After cooling during periods corresponding to the half-lives of the measured radionuclides, gamma-ray spectra were measured using calibrated high-purity Ge detectors and the spectra obtained were analyzed by the HYPERMET-PC program. Elemental concentrations in the samples were calculated by the KAYZERO program using the parameters obtained for the calibration of the detector and the neutron spectrum. In the detector calibration, detection efficiency and P/T curves for the Ge detectors were measured using calibrated gamma-ray sources. The solid angle and coincidence summing correction parameters for the samples were calculated by the SOLCOI program. The neutron spectrum parameters of the irradiation channel such as alpha, f and Fe were measured by irradiating Au-Al wires (IRM530) and Zr foils.

Elemental determination of the spiked elements were also carried out by comparative standardization irradiating standard samples for the corresponding elements together with samples. Analytical results of the SMELSSs by the $k_0$ and comparative standardization will be reported.

4. $k_0$ 法による底質標準物質の分析

中性子放射化分析法（NAA）は、多元素を高感度で且つ正確に定量することができるから標準物質の認証値を決めるための必要不可欠な分析法となっている。De Corteらによって開発された $k_0$-NAA 法は、比較標準試料を使用しないで多元素を 3.5%以下で正確さで定量することができる。独立行政法人産業技術総合研究所計量標準総合センター（NMIJ/AIST）では、有害金属分析用の標準物質として港湾水の二種類の底質試料を調製し、現在その共同分析が行われている。筆者らはこの共同分析に参加し、$k_0$-NAA により、これらの標準物質の多元素定量を行った。

定められた方法によって乾燥させた二種類の底質試料約 0.1 g を高純度のポリエチレン袋中に入りとり、三重に封入した。中性子モニターとして Al-Au 合金（IRM530, Au: 0.1%）0.015 g, Zr 板（純度 99.7%, 厚さ 0.1 mm）0.1 g をポリエチレン袋に封入し、中及び長寿命核種の測定の場合は試料と同時に、また半減期が分オーダーの短寿命核種測定の場合は、試料とは別に中性子照射をした。分析は、測定する核種の半減期に応じ、短寿命、中寿命及び長寿命核種に分けて行った。中性子照射には JRR-4 を使用し、短寿命核種測定の場合は気冷管で 10 sec, 中及び長寿命核種測定では TB-パイプで 2～20 min 照射した。γ 線スペクトル測定は、あらかじめ検出効率とピーク対全数 (P/T) 比測定によって校正した高純度 Ge 検出器を使用して行った。得られたγ 線スペクトルを HYPERMET-PC プログラムによって解析し、$k_0$ 法の解析プログラム KAYZERO/SOLCOI によって元素濃度を定量した。

本分析により、短寿命核種測定では Mg, Al, Cl, Ca, Ti, V, Mn が、中寿命核種測定では Na, K, As, Br, La が、そして長寿命核種測定では Sc, Cr, Fe, Co, Zn, Rb, Ba, Cs, Ta, Th 等の合計 22 種類以上の元素が定量された。また、既に多くの定量値が報告されている底質（NIES No.1）と River Sediment（NIST SRM1465）標準物質も分析し、定量値の正確さを評価した。

5. 成果の公表

3. 米沢四郎, 松江秀明, Sri Wardani: “$k_0$-機器中性子放射化分析法による底質標準物質の多元素定量”, 第 63 回分析化学討論会, 2002 年 5 月, 姫路市で発表。
4. 松江秀明, 米沢四郎: "$k_0$ 法に基づく即発 γ 線分析及び中性子放射化分析による底質標準物質の多元素定量", 第 46 回放射化学討論会, 2002 年 9 月, 札幌市で発表。
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4. Production of Radio Isotopes
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イットリア微小球の原子炉照射実験
Reactor Irradiation Experiment for Yttria Microspheres

1. はじめに

諸外国では、放射性微小球を血管造影剤とともにカテーテルをとおして直接肝腫瘍近傍に送込み、γ線利用により異常部を切除することなく腫瘍部のみ治療する内用療法が行われている。Y(半減期:64.10h)は、最大エネルギーが約2.3MeVの純β線放出核種であり、ガラス微小球(Y_2O_3-Al_2O_3-SiO_2など)は化学的耐久性が高く、持続的に照射を続けることができ、注入カプセル設計・製作、原子炉照射、放射性核種分析、および放射線測定、微小球の消去処理及び注入試験などを実施したので報告する。

2. 実験方法

最初に、微小球の原核カタログ製品であるY製造用ターゲット(Y_2O_3粉末)をそれぞれ約50mgづつ高純度石英アンプルに封入し、原子炉(IRR-3M)の水力照射で(熱中性子束:9×10^13 n·cm^{-2}·s^{-1})で1〜1.5時間照射した。アンプル中の照射密度試料の外観および移動度を比較し、それぞれ、6M塩素酸溶液と30%過酸化水素水で加温溶解後、一部を高純度アルミウム検出器で測定した。また、同時に照射したフラックスモニターから熱中性子照射量を求め、Yの生成量を計算した。前処理で開発した東京理工社製のガラス微小カーリーメータを用い、石英アンプルに封入したまま非破壊によりYの放射能を測定し、この値を基準として通常測定用のキャビンテック社製放射線量計を校正した。

高純度アルミウム製カプセル内に微小球を注入カプセルに移し替えるための専用装置を用い、遠隔操作により試験した後、図のような「自動注入装置」により注入実験を行った。

3. 結果および考察

照射した微小球は、Y_2O_3粉末と比べ難溶性であり、動物実験に適用可能と考えられる。Yの放射能は、1および1.5時間照射後でそれぞれ6.1および11MBq/kgであり、Yの放射性核種純度は99.9%以上であった。

アルミウム製カプセルを十分に乾燥させると微小球が移動しやすくなり、注入カプセルへの充填率は80〜97%であった。今後、動物注入実験に向けシステムの最適化を図る予定である。

*1 Japan Atomic Energy Research Institute; *2 Shinizutech Co., LTD.; *3 Radiation Application Development Association; *4 Tokyo Nuclear Services Co., LTD.
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5. Irradiation Test of Reactor Materials
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研究テーマ：核融合炉プランケット照射試験に関する技術開発
表 題：耐放射線小型モータの開発

5-1

JRR-4を用いた小型モータの照射試験

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国際熱核融合実験炉（ITER）では、原型炉用プランケットを開発するために、試験用プランケットを取付け、核融合反応で発生した中性子を実際に利用して、発電と燃料生産の実証試験が行われる。試験用プランケット開発の一環として、試験用プランケットの設計データを取得するため、JMTRを用いた炉内機能試験が計画されている。炉内機能試験では、ITERの運転を模擬するために、小型モータで供給された中性子吸収体を回転させることにより、熱中性子束をパルス状に可変できる照射試験体の開発が必要となる。このため、耐放射線性小型モータを開発し、照射試験を行った。

モータの開発においては、γ線照射環境で使用されていた小型ACサーボモータ（従来品）の基本設計を用い、コイル用巻線及びコイル用成形・固定材には、耐放射線性に優れたポリイミド鋼線（導体線径0.18mm）及びMgO, Al2O3等の絶縁材を含有したシリコン樹脂を用いた。また、マグネット及びベアリング潤滑剤には、各々Nd-Fe及び耐放射線性のポリフェニルエーテルを用いた。試作モータの基本性能は、出力6kW、定格トルク13g-cmであり、照射試験に必要なトルク（10g-cm以上）を満足している。

従来品と開発品のACサーボモータの耐放射線性を比較するため、JRR-4の炉ブームを利用して照射試験を実施した。試料容器には、従来品と開発品のACサーボモータを各1台装荷し、炉停止後にモータを運転し、回転数を測定して正常に動作していることを確認した。開発品のACサーボモータは、JMTRでの照射試験に比較することで減速ギヤの寿命を明らかにするため、減速ギヤを取外して照射試験を行った。

照射試験の結果を図1に示す。JMTRで照射した開発品（ギヤあり）は、JRR-4で照射した従来品（ギヤあり）よりも、耐放射線性が1桁以上向上したことが明らかになった。また、JMTRの照射試験を比較すると、同じ開発品であっても、「ギヤなし」の耐放射線性が向上していた。この原因は、減速ギヤの有無の差異が見られると考えられる。このため、潤滑剤の有無の差異を考慮に入れれば、更に耐放射線性が向上すると考えられる。

参考文献
Tritium Release from Neutron-Irradiated Li\textsubscript{2}O Sintered Pellets: Fluence Dependence

Takaaki Tanifuji, Daiju Yamaki and Shiro Jitsukawa

1. Introduction

Li\textsubscript{2}O is one of the principal candidates for tritium breeding materials in the fusion reactor system. In the solid breeding materials, various kinds of irradiation defects are produced by exposing to high energy radiations during the fusion reactor operations. These irradiation defects are considered to affect the tritium release behavior from and the tritium inventory in the solid breeding materials. Many researchers have investigated the production and reduction behavior of the point defects in Li\textsubscript{2}O such as F\textsuperscript{+} center and Li colloid, and effects of the defects on tritium release behavior from Li\textsubscript{2}O by using methods of ESR, optical absorption and so on.

In the present study, the neutron fluence dependence on the tritium release behavior from sintered Li\textsubscript{2}O with various bulk density (71-89\%T.D.) was investigated. Various fluence of thermal neutron irradiation (4x10\textsuperscript{20}-2x10\textsuperscript{23} n/m\textsuperscript{2}) was performed to investigate the effects of irradiation defects on the tritium release behavior.

2. Results and Discussion

A: Lower density region (71-86\%T.D.)

Figure 1 shows the tritium release rate from sintered Li\textsubscript{2}O with 71\%, 81\% and 86\%T.D. in the constant heating rate (2K/min.) tests. It is shown that the temperature of the tritium release peak shift to higher temperature with increase of neutron fluence, that is, 620K for 4x10\textsuperscript{20} n/m\textsuperscript{2}, 640K for 2x10\textsuperscript{21} n/m\textsuperscript{2}, 660K for 2x10\textsuperscript{22} n/m\textsuperscript{2} and 680K for 2x10\textsuperscript{23} n/m\textsuperscript{2}. From the comparison between fig.1 and 2, it is found that the temperature of the peaks in the intermediate density region (87-89\%T.D.) is higher 50K than that in the lower (71-86\%T.D.) for the same neutron fluence by approximatively specimens. This results suggest that the rate determining step in the intermediate region is different from that in the lower.

As shown in figure 3, in the lower density region (71\%-86\%T.D.), the open and closed porosity show 25\% and 3.5\% for 71\%T.D., and 11\% and 3\% for 86\%T.D., respectively, that is, the ratio of the closed to the open porosity between 0.14-0.27. This

![Fig. 1. Fluence dependence for tritium release rate from sintered Li\textsubscript{2}O pellets of 71-86\% TD during a temperature ramp of 2 K/min.](image)
large open porosity ratio to the closed is considered to
the small contribution of interconnected pores to the
tritium release, and to become make the cause of the
constant temperature of the peak in this density
region for same neutron fluence. In the intermediate
density region (87-89\%T.D), the ratio of closed to
open porosity between 0.57-1.8. The difference of the
temperature of the peaks between the lower and
intermediate density region is considered to be caused
by the change of the ratio of closed to open porosity.

It suggests that the rate determining step of the
tritium release in the intermediate density region is
considered as the advection through the open pores via
adsorption and desorption on the inner wall of the
poles, or the diffusion in the gas phase in the
interconnected pores[1].

3. Conclusion

The tritium release behavior from Li\textsubscript{2}O sintered
pellets with various densities (71-89\%T.D.) is
investigated by the constant heating rate tests. It is
clarified that there is a porosity dependence of the
tritium release rate in the density range over
87\%T.D., while no dependence is observed in the
density range under 86\%T.D., and there is a neutron
fluence dependence of the tritium release rate in the
density range under 89\%T.D. From these results, it is
considered that the rate determining step of the tritium
release changes with the density change, described as
follows: (1) lower density region (71-86\%T.D.): the
detrapping of tritium trapped in the point defects due
to the recovery of the defects; (2) intermediate density
region (87-89\%T.D.): the migration through the
interconnected pores via adsorption and desorption on
the inner wall of the interconnected pores, and the
diffusion in the gas phase in the interconnected pores.

It is clarified that the tritium release process
from sintered pellet consists of many elemental
mechanisms and is significantly affected by porosity
and neutron fluence. The production and reduction of
irradiation defects under high energy radiation such as
neutron are considered to play an important role in the
assessment of stability and tritium release
characteristics of solid breeding materials.

Reference
[1] T. Tanifuji, D. Yamaki, T. Takahashi, A. Iwamoto,
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6. Prompt Gamma-ray Analysis
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研究テーマ：環境関連物質の分析高度化研究
表 題：中性子即発γ線分析の研究
6-1
中性子即発γ線分析の研究
松江秀明、米沢伸四郎
環境科学研究部 分析科学研究グループ

1. はじめに

報告者らは、これまでに JRR-3M の冷及び熱中性子ビームを使用する中性子即発 γ 線分析法（PGA）を開発し、各種分野の試料分析に応用してきた。本年度は、冷中性子ビーム（第 1～3、7 サイクル）と熱中性子ビーム（第 4～6 サイクル）を使用し、1) k0 法による多元素定量法の検討、2) 底質標準物質の分析と、3) 大学との協力研究を実施した。

2. k0 法による多元素定量法の検討

k0 法による元素定量法のための k0 係数を冷及び熱中性子ビームで測定し、その評価を行った。表 1 に k0 係数の測定値を示す。PGA が有用な 27 元素について、ほぼ 3%以下の精度で k0 係数を測定し、1) 他の研究施設（ハンガリー IKI、米国 NIST）との比較、2) 核データによる計算値、3) 標準物質の分析によって評価した結果、非 1/4 元素（Sm、Cd、Gd など）を除きほぼ 10%の正確さで存在を確認した。

更に、k0 係数の汎用性を高めるため、中性子スペクトルによる k0 係数への影響の補正法の検討を行った。中性子エネルギーキーに対する中性子捕獲反応面積のデータベースである JENDL-3.2 と研究開発の鈴木正年氏より提供を受けた冷及び熱中性子ビームの中性子飛行時間法（TOF）により測定された中性子エネルギーよ分布スペクトルに基づき g 係数を数値計算し、この係数を用いた補正法の試を行った。これままでに、Cd については、その補正に成功したが、Sm と Gd については、満足な補正結果が得られていない。

3. 底質標準物質の分析

PGA は、正確さが優れていることや、他の方法では困難な元素の分析が可能であること等から標準物質の調製は不可欠な分析法となっている。本研究では、k0- PGA により新たに有害金属分析用として独立行政法人産業技術総合研究所計量標準体制センター（NMIJAIST）で調製された 2 種類の底質試料（港湾と湖）の多元素定量を行った。
k0-PGA では元素の絶対濃度を求めることができないため、標準添加法により Ti の絶対濃度を定量し、それらの値から各元素の絶対濃度を求めた。本分析により新元素を中心とした H、B、Si、K、Ti、Cr、Mn、Fe、Cd 等の 15 元素の定量を行うことができた。

4. 協力及び共同研究

JRR-3M の即発 γ 線分析装置を使用し、大学との協力研究（3 件）として、中性子ビームガイドを用いた高速電磁粒子の化学的挙動の研究（大同工業大学工学部）、廃棄物埋立によるホウ素汚染の機構解明（東京大学大学院 新領域創成科学研究科）、即発 γ 線分析法による地衣類の研究（筑波大学化学系）を実施した。

5. 成果の公表


原子炉: JRR-3M
装置: 即発 γ 線分析装置
分野: 即発 γ 線分析（分析化学一般）

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### 表1 塩素の1951 keV γ線に対する $k_{0,Cl}$ 測定値

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (keV)</th>
<th>Cold $k_{0,Cl}$</th>
<th>Cold Error</th>
<th>Thermal $k_{0,Cl}$</th>
<th>Thermal Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2223</td>
<td>1.86 ± 0.0058</td>
<td></td>
<td>1.80 ± 0.0045</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>478</td>
<td>359 ± 3.5</td>
<td></td>
<td>371 ± 31</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4944</td>
<td>0.000643 ± 0.0000077</td>
<td></td>
<td>0.000762 ± 0.000023</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>4505</td>
<td>0.00698 ± 0.0000140</td>
<td></td>
<td>0.00573 ± 0.000056</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>472</td>
<td>0.116 ± 0.00060</td>
<td></td>
<td>0.116 ± 0.0014</td>
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</tr>
<tr>
<td>Si</td>
<td>3540</td>
<td>0.0214 ± 0.000087</td>
<td></td>
<td>0.0218 ± 0.00010</td>
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</tr>
<tr>
<td>P</td>
<td>637</td>
<td>0.00481 ± 0.000080</td>
<td></td>
<td>0.00470 ± 0.000077</td>
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<tr>
<td>S</td>
<td>841</td>
<td>0.0576 ± 0.0012</td>
<td></td>
<td>0.0554 ± 0.0012</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>786+788</td>
<td>1.36 ± 0.0039</td>
<td></td>
<td>1.32 ± 0.0080</td>
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<tr>
<td>K</td>
<td>770</td>
<td>0.129 ± 0.00061</td>
<td></td>
<td>0.127 ± 0.00057</td>
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</tr>
<tr>
<td>Ca</td>
<td>1942</td>
<td>0.0464 ± 0.00061</td>
<td></td>
<td>0.0469 ± 0.0010</td>
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<tr>
<td>Ti</td>
<td>1381</td>
<td>0.592 ± 0.0062</td>
<td></td>
<td>0.5827 ± 0.0059</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>834</td>
<td>0.143 ± 0.0016</td>
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<td>0.140 ± 0.0012</td>
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<tr>
<td>Mn</td>
<td>314</td>
<td>0.151 ± 0.0062</td>
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<td>0.150 ± 0.00078</td>
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<tr>
<td>Fe</td>
<td>352</td>
<td>0.0272 ± 0.00069</td>
<td></td>
<td>0.0270 ± 0.00055</td>
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<tr>
<td>Co</td>
<td>277</td>
<td>0.624 ± 0.0052</td>
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<td>0.610 ± 0.0027</td>
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<tr>
<td>Ni</td>
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<td>0.0821 ± 0.00093</td>
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<tr>
<td>Sr</td>
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<tr>
<td>Cu</td>
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<tr>
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<td>0.169 ± 0.0012</td>
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<tr>
<td>Cd</td>
<td>558</td>
<td>62.1 ± 1.5</td>
<td></td>
<td>79.9 ± 0.84</td>
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</tr>
<tr>
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研究テーマ: 環境関連物質の分析高度化研究
表 題: 中性子ビームガイドを用いた高速荷電粒子の化学的挙動の研究

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中性子ビームガイドを用いた高速荷電粒子の化学的挙動の研究

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1. はじめに

JRR-3M の中性子ビームガイドを用いた中性捕獲反応によって生成する高エネルギー相に粒子の化学的挙動を追跡することを行ってきた。今年度は以下の2つの中性子捕獲反応について実験を行った。
(1) 10B(n,α)7Li 反応
(2) 56Fe(n,γ)57Fe 反応

2. 18B(n,α)7Li 反応

18B(n,α)7Li 反応で生成する高エネルギーグamma線のドップラー広がりを測定・解析することによりホウ素の化学的・物理的状態についての情報が得られることを、これまで示してき。今年度は地球科学、環境科学的な試料にこのドップラー広がり法を適用することを行った。平成14年3月に名古屋でサンプリングした黄砂に対して、JRR-3M の PGA 装置で 478keV・早い γ 線を測定した。この黄砂試料のドップラー広がりに仮想的な解析法を、我々が開発した方法を用いた(M.K.Kubo and Y.Sakai: J. Nucl. Radiochem. Sci., Vol.1, 83 (2000))。解析は γ7Li の物質中での減速定数 D を実験値として与える。D は物質の元素組成、密度によって決まる値である。理論的には LSS モデルを適用することにより計算される。この計算値との比較により、黄砂中のホウ素は、アルミシリンテートマトリックス中に存在するものであろうと結論した。

3. 56Fe(n,γ)57Fe 反応

56Fe(n,γ)57Fe 反応で生成する γ57Fe から放出される 14keV・早いメスバウアーγ線をブロープとする短寿命化学種の追跡についても研究した。これは JRR-3M の PGA 装置とメスバウアー分光器の組み合わせではじめて可能になる実験である。金属 (α-Fe)、合金 (ステンレスチール) では、メスバウアーシグナルが観測されたが、化合物ではシグナルが弱く、さらなる実験条件の改善が必要であることがわかった。

4. 成果の公表

γ57Li に関しては以下の、1)として学会発表を行った。
γ56Fe のメスバウアー実験については、2)のメスバウアー分光研究会シンポジウムで招待（依頼）講演として発表された。題目からわかるように、この研究は将来の環境分野加速器の建設を視野に入れた萌芽的な研究である。今後の発展が期待される。

1) 酒井陽一、大下一政、久保謙哉、松江秀明、米沢伸四郎、「黄砂の鉄とホウ素のメスバウアー分光法と仮想γ線ドップラー広がり法によるキャラクタリゼーション」 2002 日本放射化学年会 (9.2002 札幌) で講演
2) 久保謙哉、「大強度陽子加速器とメスバウアー研究」メスバウアー分光研究会会誌、No.3、22、(2002.3)

原子炉: JRR-3M
装置: 仮想γ線分析装置
分野: 仮想γ線分析（分析化学一般）

－449－
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7. その他

7. Others
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Comparison of Dosimetry by the Realistic Patient Head Phantom and by the Patient’s Brain, and the JCDS Calculation - A Clinical Dosimetry Study

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Introduction
Since the 1990s, University of Tsukuba and JAERI have been studying BNCT mainly as a curative therapy for malignant glioma. Using conventional BNCT in a 1990s clinical trial, we irradiated patients without a computational planning system, depending on gold wires as the neutron detector and semiconductor detector. We treated 9 cases with mixed thermal-epithermal neutron flux in BNCT 1). Subsequently, the JCDS was developed to calculate the BNCT dosimetry for more correctly with the epithermal neutron beam by JAERI 2). A realistic phantom model of a patient head was developed for use in applying the system to complex three-dimensional objects too. This realistic phantom has advantages for biomedical study, it provides a similar CT model for use in computational simulation and a model for the real radiation field condition in an in-vitro phantom experiment.

In this study, the realistic phantom was used to optimize the JCDS by correlating the data from the phantom measurement to that by the calculation, using the JCDS and the direct measurement in the patient’s brain obtained from actual BNCT operations.

Materials and Methods
A set of CT data (40 slices at a 5mm pitch) from a BNCT patient was used to produce the solid formative model phantom using the Rapid Prototyping Technique. With SURFACER (Imageware Company), the three-dimensional solid surface model was built from the point data extracted from the CT data on the computer. We then converted the original surface data into STL-type data for use in the stereolithography format, and input the transformed data to Magics RP (rapid prototyping software). At this stage the phantom surface was 3mm thick and the structure was empty; it could hold water. The SOLIFORM-500B (Teijin Seiki Company, Japan) utilizes ultraviolet rays to harden resin, and was used to make a more solid structure. The resin selected for the RPT was the TSR-810, an epoxy acrylate resin that provided a thin, hard layer.

A mixed thermal-epithermal neutron beam (thermal neutron beam mode 1: TNB-1) was applied to the neutron source in vivo in the clinical cases of BNCT irradiation. In an experiment, the realistic phantom was irradiated with the neutron beam in the same mode by a reactor power of 3.5MW. The measurement condition with the JCDS was corresponded to the experimental condition.

In the procedure of the intraoperative BNCT with TNB-1 mode, the thermal neutron flux distributions are calculated using gold wires which are directly placed on the brain surface. The thermal neutron flux was simulated using a simultaneous β-γ coincidence-counting device.

In the experiment using the realistic phantom, the thermal neutron flux distributions on the brain surface of the phantom were also measured by means of 31 gold foils (5mm in square 0.01mm in thickness ), which were located at the sites on the brain surface where the clinical dosimetry was measured . And the realistic phantom was settled the irradiation place with Patient Setting System 3, 4). Further, in order to verify the performance of JCDS by comparing with the data of the phantom experiments, the thermal neutron flux using the JCDS were calculated by simulating the realistic phantom experiment.

In this study, we try to compare with dosimetry by the realistic phantom, by the
clinical measurement, and by the JCDS calculation.

Results

The profiles of thermal neutron flux on the brain surface calculated using the realistic phantom showed close agreement with the measurements obtained by clinical dosimetry; a relatively high dose area at the parietal lobe was shown by both methods. Using JCDS, it may be possible that the pin-point peak is not calculated because the calculation is based on the average dose of each 1cm³ voxel size.

Discussion

Factors that may have led to the discrepancy between findings of the realistic phantom, JCDS and those determined by clinical dosimetry in BNCT are as follows: 1) Blood clot and cerebrospinal fluid overlying the brain surface during the irradiation; 2) Lack of data of the Lithium helmet (it’s quality of the material or geometry size and so on); 3) The accuracy of reappearance produced differences in the thermal neutron flux between JCDS and the realistic phantom. If these factors are more closely considered, the dosimetry data can be evaluated more exactly.

To reproduce more accurate irradiation in BNCT, we must evaluate the gold wires, which are settled in the realistic phantom to calculate the thermal neutron flux. And then these data are used to evaluate the actual dosimetry to the organ and so on.

Further optimization of the simulation technique will be needed in order for BNCT, and particularly intraoperative BNCT, to be applied as a more reliable and effective therapeutic modality.

Conclusions

In conclusion, use of an individual patient’s realistic phantom is one of the more effective methods by which to verify the JCDS data and the clinical dosimetry. This phantom can be used as an in vitro tool, arranging the cells in the phantom so that it approximately reproduces the real conditions of exposure to clinical radiation.

In the future, using these simulation techniques, we will be able to simulate the dosimetry for each patient at the experimental stage and obtain much more reliable and effective therapeutic irradiation by BNCT.

REFERENCES:


Radiobiological Characterization of JRR-4 Neutron Beams

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Introduction
For evaluating the biological response of the tumor and healthy tissue to neutron beams, and for comparing the clinical results of BNCT at different institutions with accuracy, all of the physical dose components and their RBE values of each beam must be determined separately. In this study, physical dosimetry and in vitro cell survival assays were performed to determine the RBE of each dose component for the beams, which have not been previously characterized at JRR-4.

Materials and Methods
An epithermal neutron beam (epithermal neutron beam mode: ENB), a mixed thermal-epithermal beam (thermal neutron beam mode 1: TNB-1) and a thermal beam (thermal neutron beam mode 2: TNB-2) were used as the neutron source for in vitro and physical measurements. For determining the neutron flux, the activation of nickel and of gold foils with or without cadmium covers was measured. The neutron energy spectrum was also calculated using the Monte Carlo Code, MCNP 4B. The γ-ray dose was measured with a thermoluminescent dosimeter (TLD) that had a beryllium oxide as a thermoluminescent material and was covered with quartz glass (Panasonic 170LS).

V79 Chinese hamster cells in the stage of exponential cell growth were preincubated for 6h with 10B-enriched boric acid at 10B concentrations up to 15μg10B/ml medium. The cells in suspension in polyethylene cryotubes were irradiated with each neutron beam for the colony formation assay. The RBE values were calculated by comparing the D₀ value of subtracted each dose component to the D₀ of 150 cGy for 250 kVp X rays.

Results
The slopes with the survival curve of V79 cells for all dose components were steeper for ENB compared to TNB-1 and TNB-2 (Fig.1). Comparing the D₀ values for the separated response to boron neutron capture reaction in ENB, TNB-1 and TNB-2 to the D₀ value of 150 cGy for γ-rays, the corresponding RBE (²⁹⁶RBE_boron) values of 4.07 ± 0.22, 2.98 ± 0.16, and 1.42 ± 0.07 were obtained. The beam RBE (RBE_beam) values based on the D₀ values for R_beam were 1.22 ± 0.16, 1.23 ± 0.16, and 1.21 ± 0.16 for ENB, TNB-1 and TNB-2, respectively. The RBE (RBE_neutron) values based on the D₀ values for the high-LET dose components were 2.50 ± 0.32, 2.34 ± 0.30, and 2.17 ± 0.28 for ENB, TNB-1 and TNB-2, respectively.

Discussion
The surviving fraction of the neutron beam with or without the presence of ¹⁰B depended highly on the neutron beam used, according to the epithermal and fast neutron content in the beam. The most significant difference was seen in the survival fractions of the boronated cells, and the ²⁹⁶RBE_boron for ENB (3.99) was 2.8-fold higher than that for TNB-2. The energy range 1 keV to 0.5 MeV is important for the biological response to the dose components in BNCT (4). The neutron fluences determined by the gold activation method are used to estimate the absorbed dose from boron neutron capture and nitrogen capture reactions, for each of the three spectra. Since the foil activation technique only measures neutron energies in a restricted range, leading to a systematic error in the calculation of the RBE values for the different dose components. The RBE value for boron neutron capture reactions was, particularly in the beam with
Fig. 1  Survival curve of V79 cells incubated with 0 (◇), 5 (■), 10 (△), and 15 (●)
μg 10B/ml medium of 10B obtained after irradiation with ENB (a), TNB-1 (b) and TNB-2
(c) at JRR-4.

high epithermal content, considerably influenced by the determination of neutron
fluences which depend on the capture cross section of boron in the epithermal energy
range (≈ 10^3 barns). The previously reported RBE values for the boron capture
reaction and the high-LET dose components using in vitro endpoints ranged 2.3 – 3.7 and
1.9 – 3.7, respectively (1,2,3). The variation of reported RBE values for the
dose components in BNCT seems to be partially caused by the nonuniformity of
dose distribution, the inhomogeneity in subcellular boron distribution (1), and the
different experimental conditions. However, the data in this paper, by comparing different neutron beams with
uniform dose distributions and the same experimental conditions, indicate that the
neutron energy of a beam is the primary factor for the variation of RBE values.
Further investigation is needed to evaluate the in vivo and in vitro in-phantom
radiobiological effect with variable neutron beams to assess the clinical results from
individual BNCT trials as well as the other particle and ionizing radiation therapies.

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7-3
Comparative Study of the JCDS Calculation and Patient Brain Dose Measurements

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Department of Research Reactor, Tokai Research Establishment, JAERI²

Introduction
Intraoperative irradiation has been utilized with a thermal beam as part of the BNCT procedure to facilitate neutron penetration (1). In an intraoperative BNCT (IOBNCT) trial with a mixed thermal-epithermal beam at JRR-4, dose simulation has been found to play a minor role in IOBNCT because of difficulties in achieving the complicated simulation of 3-dimensional dose distribution in the postsurgical brain (4). The vascular boron dose (0.33 x blood boron dose) is determined based on activation of the gold wires that are arranged directly in the surgical field. Some of these are withdrawn and utilized for the calculation of irradiation time (2).

JAERI computational dosimetry system (JCDS), the dose planning system for BNCT, has been tested in the ongoing IOBNCT and will be put to practical use in the dose planning of IOBNCT with an epithermal beam. In the present study, the JCDS calculations of the clinically treated cases were compared to direct measurements in the patient’s brain.

Materials and Methods
Nine patients with malignant glioma underwent the IOBNCT with the mixed thermal-epithermal beam at JRR-4 using BSH as the boron compound. Irradiations were performed as the maximum vascular boron dose as 10.8 Gy, which is 80% of the previously reported tolerance dose to avoid radiation necrosis (3). Following the craniotomy, two sets of gold wire were placed on or inserted into the postsurgical brain for the direct measurement of thermal neutron flux. The irradiation time was calculated by extrapolating the clearance curve of the blood boron levels and thermal neutron flux measured by the set of gold wire that was withdrawn 15 minutes after the beginning of each irradiation (intra-irrad measurement). The rest of the gold wires were measured after the irradiation and were used for the retrospective evaluation of 2-dimensional thermal neutron distribution on the brain surface as well as around the postsurgical cavity (post-irrad measurement). The 3-dimensional dose distributions for the same cases were calculated by JCDS for the retrospective evaluation based on the actual head position of the individual treatment. The maximum thermal neutron flux in the irradiated volume and the mean target vascular dose by JCDS were compared to those obtained from the intra-irrad measurements and the post-irrad measurements. Case 1 was omitted from the comparison in the maximum vascular boron dose because the dose of this case had been planned as 13 Gy. The regional doses of the volume with radiation injury were also calculated.

Results
The slopes with the survival curve of TNB-2, respectively.

The maximum thermal neutron flux on the brain surface from the intra-irrad measurements and the post-irrad measurements averaged 2.20±0.32 and 2.33±0.37 (109 cm-2sec-1), respectively (Table 1). The vascular boron dose on the brain surface derived from the post-irrad measurements averaged 11.4±1.2 (9.6-12.7) Gy. From the JCDS calculation, the maximum thermal neutron flux in the irradiated volume averaged 2.21±0.33 (109 cm-2sec-1). The mean vascular dose of the brain in the target volume varied from 3.5 to 7.8 Gy and averaged 5.7 Gy.

Radiation necrosis was found in 4 of 9
cases (Case 1,2,5,6). The vascular dose of the volume with radiation necrosis averaged 5.9 Gy (3.0-9.3). No significant difference was seen in the target vascular dose between the cases with and without radiation necrosis. Oculomotor palsy was found in 3 of 9 cases (Case 1,2,5). The boron dose of the cavernous sinus in the case with and without oculomotor palsy was 4.28 Gy (3.5-5.0) and 2.08 Gy (1.1-5.1), respectively.

**Discussion**

The maximum boron vascular dose of 10.8 Gy derived from the intra-irrad measurement was equivalent to the target boron vascular dose of 5.7 Gy obtained by the dose calculation with JCDS, which should be considered as the reference dose in future BNCT dose-planning. The mean vascular dose in radiation necrosis (5.9 Gy) was similar to the mean target vascular dose, implying the presence of a high risk of radiation necrosis with dose escalation.

The difference between the intra-irrad and post-irrad measurements was caused primarily by the sampling error in the intra-irrad measurements, in which both the number and arrangement of the withdrawn gold wires were restricted by the intraoperative irradiation procedure. Moreover, the JCDS calculation showed considerable variation in the vascular boron dose in the target volume according to the individual case (3.5 to 7.8 Gy). This dose variation suggests the technical limitations of dose control with direct measurement; therefore, volume-dose control with a practical simulation system is needed for intraoperative irradiation.

Thermal neutron flux calculated by JCDS was found to be equal to or less than that of the measurement except for Case 8, in which the scheduled head position was modified by a technical problem. This difference between calculation and measurement may be related to the voxel size used in JCDS, and to the influence of surgical drapes and clots overlying the gold wires on the thermal neutron distribution. Further evaluation is recommended for the practical use of JCDS in IOBNCT, which requires the simulation of complex conditions such as the geometry of the postsurgical brain and the influence of surgical equipment.

**REFERENCES:**


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*Table 1: Thermal neutron flux (10^9 n cm^-2 sec^-1) and vascular boron dose (Gy) in nine cases. Data were calculated by gold wire measurements (intra-irrad, post-irrad) or JCDS. *The maximum vascular boron dose on the brain surface was planned as 13 Gy in Case 1.*

原子炉：JRR-4

装置：中性子ビーム設備

分野：
研究テーマ：超流動反応場の原子・分子研究

表

| 7-4 |

1.6 K ²He-³He量子混合体中における再結合反応、H+T→HT およびT+T→T₂への超流動の影響

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ヘリウムは反応性が無いかから、化学反応においては気相反応のモデレータとしての役割しか与えられてこなかった。しかしながら、凝縮相（液体、固体）は、非常に低温であること、そして大きい量子パラメータを持つことに加えて特に超流動現象がマクロに現れる唯一の物質として、多くの低温物理学者を魅了し続けている。一方、化学の観点から見ると、物質との相互作用が非常に小さいや低温であることから、凝縮相中の原子、電子、イオン等は二核体原子、スノーボールといった特異な化学相像やトンネル反応のような低温特有の化学現象が期待され、レーザ分光を中心とした研究が近年盛んになってきた。しかししながら、そのような特異な媒体中の化学反応に関する研究は全くなされていない。本研究は、²He(n,p)³He反応によって生成する水素原子とトリチウム原子との結合反応、H+T→HT およびT+T→T₂を³He-²He混合体中で観察したものである。図1に示すように³He-²He混合体溶液は温度、混合割合によって超流動（α）・常流動（α）相へと変化する。本報告は1.6 Kの実験結果である。したがって、α・γ間の転移点は³Heの割合が0.35にある。³Heの割合を0.1から0.95まで変化させた溶液をJRR-3M ガイドホール熱中性子ビーム（中性子束：3-4×10⁶ n cm⁻² s⁻¹）で約40時間照射した。生成したHT、T₂をラジオガスクロマトグラフで分離しそれぞれの相対収率を求めた。図2にこの相対収率[T₂/(H₂+T₂)]を[³He]を示す。図から明らかのように³Heの割合が0.95-0.35（n 増加）においては収率は一定であるのに対し、0.35付近から収率の急激な増加が観察されるこの変換点は相図のs・n転移点に相当する。二流体理論によれば、³He の割合は、実際にはs・n成分の混合体である²Heの割合によってその比は変化する。実験的に求められた0.35以下では³He・n成分の割合と0.35〜0.95でのn領域での収率を利用し、反応が²He成分及びn成分中で起こると仮定すると、³He成分中の§同位体効果（ΓHT/ΓT₂）は110±17，²He成分中では58±14となる。同じ温度領域での気相反応ではこのような大きな同位体効果は無く、本実験結果は、パルプ状のHT原子のトンネル反応によるためと考えられる。また²He・n成分中での気相のコヒーレンス性との関わりを示唆している。

図1 ³He-²He混合体溶液の相図

図2 T₂の相対収率の³He濃度依存性

原子炉：JRR-3M 装置：低温化学実験装置 分類：その他（放射化学）
研究テーマ：フィッショニオン・トラック年代表定
表　題：FT 年代表定のためのディテクターの開発

7-5 DAPプラスティックディテクターの特性とフィッショニオン・トラック年代表定への応用
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フィッショニオン・トラック (FT) 年代表定法は、鉱物(おそらくジルコンやアパタイト)中の $^{238}$U が一定の速さで自発的に核分裂し、その際できた放射性的密度が、その年代と U 濃度に比例するという原理的上に成り立っている。U 濃度は熱中性子照射によって誘導核分裂させた $^{235}$U の誘導 FT 密度から求められ、一般的に誘導 FT は、鉱物に寄着させた外部ディテクター上で測定される。このことから、照射後に分析するディテクターの取扱いには十分な配慮が必要である。

従来 FT 年代表定法では、外部ディテクターとして天然の鉱物の白雲母が使われてきた。最近、白雲母の放射化分析から Sc-46(半減期 84 日)と Ta-182(半減期 115 日)が突出して放射化されることが明らかになった。また通常の照射条件(JRR-5, 3.5MW 90 秒)において、放射能濃度は照射後 6 ヶ月経過しても 1000Bq/g を超え、放射線障害防止の観点からも白雲母は安全な材料とは言える難い。

今回、固体放射線計器の新材料として注目されているジアフルホケート (diallyl phthalate: DAP) 樹脂 1,2,3,4,5,6 を FT ディテクターとしてテストした。DAP 樹脂は、97%の DAP モノマーと 3%の IPP モノマーの混合物を重合させて作られるポリカーポネイトで(図 1)、核分裂片のように重荷電粒子のみに感度を示し、α 粒子に感度を示さない特徴がある。DAP のエッチングには 60℃の PEW-55 溶液 (15% KOH, 65%エタノール, 20%水) が用いられ、FT のエッチビットはシャフトになる(図 2)。

まず、改良点として最も重要な DAP の放射化の速度を調べた。JRR-4 炉(3.5MW)において熱中性子照射を 18 秒間行い、放射化分析を行った。照射後 24 時間後 Na-24 と Br-82 のピークがわずかに検出されたが、ほぼバックグラウンドと同程度であった。照射後 2 週間後再測定した際には検出ピークは全くなく、放射能濃度も検出限界以下であった。この結果から DAP 樹脂が放射化しない FT ディテクターとして極めて優れた特性をもつことが確かめられた。最近、DAP ディテクター上の FT 密度が画像処理により自動測定出来ることが報告され 7, DAP は白雲母ディテクターの代替として、今後広く利用されることが期待される。

![DAP: Diallyl phthalate (C14H14O4)](image)

図 1. DAP モノマーの分子構造 (Tsuruta, 2000)

![DAP 上のフィッショニオン・トラック](image)

図 2. DAP 上のフィッショニオン・トラック

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5) 小口・鶴田 (2001) 第 1 回先進放射線応用シンポジウム(大阪大学), 103-106.
In an odd-odd nucleus $^{186}$Re, a long-lived isomer (hereafter expressed as $^{186m}$Re) with spin and parity of $8^+$ is previously known. A half-life of $^{186m}$Re was measured as $2 \times 10^5$ y [1]. While a main path of neutron capture on $^{185}$Re is that to the ground state $^{186g}$Re, which has a cross section of $\sigma = 112$ mb, a small fraction for a $^{185}$Re $\rightarrow$ $^{186m}$Re path has been reported with a neutron capture cross section of 0.3 % with respect to that for the $^{185}$Re $\rightarrow$ $^{186g}$Re path. Recently, we have identified that a chain reaction of $^{185}$Re(n,$\gamma$)$^{186m}$Re(n,$\gamma$)$^{187}$Re via $^{186m}$Re plays an important role in production for both of $^{187}$Re and $^{187}$Os, which would perturbs the abundance ratios of those nuclei. A pair of $^{187}$Re/$^{187}$Os is famous for a nuclear chronometer to deduce an age of the Galaxy [2]. In order to obtain an absolute value, we have made a new neutron capture cross section measurement.

Natural rhenium foils with a thickness of 52 mg/cm$^2$ were irradiated by thermal neutrons derived from JRR-4 at JAERI. After 6-h irradiation, the samples were kept in the reactor pool for 4 months to reduce activities of $^{186g}$Re and $^{188}$Re. A neutron flux was estimated as $5 \times 10^{13}$ /s/cm$^2$ by a Co-Al flux monitor. Two HP-Ge detectors were used to measure emitted $\gamma$ rays. Figure 1 shows a $\gamma$-ray energy spectrum obtained 4 months after the neutron irradiation. Most of the peaks are assigned as $\gamma$ rays emitted after $\beta$ decays of $^{184}$Re. For these $\gamma$ rays, two components of half-lives of 38 d and 169 d are confirmed, which correspond to the ground state and the isomeric state at 188 keV, respectively. The $^{184}$Re was produced by a fast neutron induced reaction of $^{185}$Re(n,2n). Since the $^{184}$Re activities have the half-lives comparable as the present experimental conditions, relevant $\gamma$-ray peaks are enhanced. For the neutron capture to $^{186m}$Re, in spite of its very long half-life and the strong contaminant from $^{184}$Re decays, we have succeeded to observed a 137 keV $\gamma$ ray in $^{186}$Os emitted after $\beta$ decay of $^{186m}$Re. Detailed analysis is now in progress.

![gamma-ray spectrum](image)

**Fig. 1.** A $\gamma$-ray spectrum measured 4 months after neutron irradiation

**References**
7-7
悪性脳腫瘍に対する熱外中性子による中性子捕獲療法のための基礎的・臨床的研究
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【目的と意義】中性子捕獲療法（以下、BNCT）で利用されるα線は予め投与された硼（ほう）素素化合物（BSH）を取り込んだ組織内でのみで発生し、飛程が短いため（10μm）限局性に作用する。また、X・γ線と比べ細胞周期や組織内酸素濃度による影響が少なく、生物効果の大きい高エネルギーフォトン線であるという放射線生物学的特長を有しており、従来の方法で難治の悪性腫瘍に対する治療効果が期待されている。腫瘍に選択的に治療を行い、正常脳は障害が少ないことが特徴である。

筑波大学では1998年10月以来、日本原子力研究所の放射性原子炉施設（JRR-4）において、従来開頭照射BNCTで用いられてきた熱中性子に適応した高温熱中性子を加えた熱・熱外混合中性子ビームを用いたBNCTのPhase I/II臨床試験を行い、本治療法の有効性について検証を行っている。

【対象と方法】
1．対象患者の適応決定
本研究は筑波大学医の倫理委員会にて承認された。プロトコールについては日本原子力研究所の施設利用協議会ならびに医療照射専門部会で承認を受けた。患者適格性は組織学的に証明されたanaplastic astrocytomaまたはglioblastomaで、年令18-70才、Karnofsky Performance Scale（KPS）50%以上、過去に放射線治療・化学療法が行われていない、増強MR上の腫瘍辺縁が脳表から6cm以内という条件を満たすものである。対象となる患者は例ごとに筑波大学内の放射線治療検討会で適応について検討し、治療計画を医療照射専門部会委員に提示し、承認を得た。

2．治療の手順
患者はまず通常の初回手術において病巣の可及的全摘出を行った。中性子捕獲療法の際には照射に用いる硼素化合物BSHはBNCT照射開始予定時刻の12時間前から点滴静注した。当日は全身麻酔下に照射のための開頭手術を行い、開頭術野での照射中および照射中の熱中性子フラックス値と全血中10B濃度をもとにして算出した血管差素線量に対し、正常脳の耐容血管差素線量10.8 Gyを基準として照射時間を決定した。開頭術野を除く部分はフッ化リチウムサーモプラスチックで覆い、熱中性子を遮蔽した。照射終了後は開頭手術を行い、病院に搬入して術後管理を行った。

【治療結果の中期分析】
1999年10月より2002年7月までにJRR-4混合ビームを用いて開頭BNCTを行ったのは日本原子力研究所東海研究所、JRR-4号炉、生物に対する放射線効果
anaplastic astrocytoma (AA) 4，glioblastoma (GBM) 5 の初発例数 9 例で、年令は平均 51.6 才 (20-66)，男性 3 名，女性 6 名であった。K.P.S. は 80-100 の症例が多く，Case 4 は治療前日に DIC を併発していたため 40 であった。用いた薬剤中線量 (α線量) は 1 回照射で 10.8 Gy であり，各症例の照射条件によって多少の違いはあるが γ 線量 (7.4 Gy) と陽子線等の線量も含まれる。診断確定後の平均観察期間は 17.7 ヶ月 (3.3-33.8) で，9 例中 4 例が生存し観察中である。治療後 6 ヶ月の MR 上の最大増悪では Case 8 が播種性に再発し進行したのに対し，4 例で縮小が認められた。画像上腫瘍の残存がなかった 4 例で不変のまま経過した。再発を認めたのは 5 例 (Case 3, 4, 5, 6, 8) で，うち Case 4 は生存，Case 3 を除く 3 例が再発で死亡した。再発形式は局所再発が 1 例，遠隔または播種性再発が 4 例であった。解析時点で 9 例中 3 例 (Case 1, 2, 5) に放射線療法および動眼神経障害 (Case 5 では一過性) が認められた。生存期間中央値は GM で 15.4 M, AA で 16.0 M である。

【考察】
生存期間および生存率の算定については観察期間が短く，症例も少ないため現時点での評価は困難であるが，治療に対する早期反応については治療直後に播種性再発をきたした Case 8 を除き不変または縮小が見られている。glioblastoma の放射線治療では治療線量の増加により生存期間の延長が認められているが，70 - 80 Gy の高線量が照射された場合でも，照射野中心部から再発することが示されている [2]。X 線に陽子線を併用した 90 Gy までの dose escalation では，局所制御率および生存期間中央値が改善される一方で，辺線部分での再発や放射線療法を高率に認めた [3]。
術中 BNCT で得られる腫瘍線量はこれを上回るものと考えられており，治療早期の局所反応はその結果と考えられる。

熱外中性子子を取り入れた現在の熱・外照射合中性子ビームによる BNCT では深部の線量分布が増加する一方，従来の熱中性子ビームでは一般的でない N. III や N. VI の障害が見られた。通常 BNCT では腫瘍薬剤濃度の低い正常組織障害されにくいとされているが，高薬剤薬剤濃度の血液を含む海綿静脈洞部での中性子分布が増加することでこれらの障害が発生する可能性が考えられる。遠隔度の低い従来の熱中性子ビームでは，脳面の線量を測定することで照射条件が決定されたが，この方法は現在行っている熱・外照射中性子ビームの BNCT でも用いられている。熱外中性子子を含むビームでは，BNCT で発生する症例の放射線（腫瘍線量，γ線量，窒素線量，速中性子線量）と開頭術野の複雑な形状による複雑な線量分布 [4] を高精度でシミュレーションすることが重要であり，現在線量計画・位置決めシステムの検証を行っている [5]。

今後の方向としてはまず線量計画・位置決めシステムを用いて純粋な熱外中性子子を用いた臨床試験を開始してその安全性・効果を検証する。

さらに将来的には BNCT を boost 照射として位置付けて他の放射線治療と併用する方法や，薬剤の改良によって治療効果が改善することが望まれる。ガドリニウム化合物との併用などは動物実験レベルである程度実用化できるのではないかと考えている [6]。

1. Matsumura A, Shibata Y, Yamamoto T,


低温核偏極による局在モーメントと交換相互作用の研究
A Study of Exchange Interactions Between Localized Moments by Low Temperature Nuclear Orientation

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1. 研究の目的と意義

磁気異方性（magnetic anisotropy）は磁性研究における重要なテーマであり、特に磁性材料の開発研究における基テーマといえる。Nd₄Fe₄B（ネオマックス）は広く利用されている強磁性材料である。

Pr₄Fe₄BはNd₄Fe₄Bを上回る磁気異方性を持っており、磁気異方性の関数に含まれるNdの交換相互作用やその他の磁気異方性の明は一般的な磁性研究手段では難しい[1]。

この研究の目的は、放射性同位元素をプローブとする核磁気共鳴法（LNO）により、多重磁性イオンを含む（反）強磁性化合物における異常磁性イオン間の交換相互作用や個別の磁気構造を調べることである。研究の意義は、新しい磁性研究手段を確立すること。また、新しい機能を持った磁性材料を開発するのに重要な情報を提供することである。

磁場と低温により偏極した核の核磁気共鳴法（BF-NMRON）は、放射線反射の検出精度とNMRの測定精度を兼ね備えて、相対的な効率性の高い研究手段である[2]。この実験手段を用いる事例、例えばNbとCuのように不溶性で固体の希薄合金における核磁気構造を研究できる。しかし、実験手法が難しく、過去に3例の報告があるのみである。近年ナノ構造材料が開発されてきており、BF-NMRONのようなppmオーダーの検出精度と合金元素の幅広い組合せに適した微观的磁性研究手段を本稿において確立することが目的(2)である。その意義は、新しい希薄合金における核磁気相互作用の情報提供できること。

2. 研究の方法と結果

2.1 LNOによるRENi₄Al₃の磁気異方性研究

「磁気異方性希土類化合物（Pr₄Nd₄B）Ni₄Al₃におけるPr- Nd交換相互作用とそれらの磁気異方性」を研究テーマとして、多重磁性イオンを含む核磁気共鳴法のLNO実験をした。RENi₄Al₃（RE：希土類元素）は、YNi₄Al₃型の斜方晶の結晶構造を持つ[3]。PrNi₄Al₃やNdNi₄Al₃の単結晶試料を用いた磁性研究から、磁気異方性を反映した大きな磁気異方性が報告されている[3-5]。

この研究に使用した単結晶は、高周波炉を用いた回転引上げ法（Cz法）により作成した。原材料は純度3Nの希土類元素と4Nのニッケルである。タングステン坩埚を使用し、0.5気圧のアルゴンガス雰囲気中で育成した。結晶方位はX線ラウエ法により決定した。試料の形状は放電カッターで行った。

PrNi₄Al₃は、ネオ磁性元素が8.4Kの焼結させた、a軸が磁化容易軸である。温度2K、外部磁場約3Tで、a軸の磁化は磁気移動が観測される。1Tで磁化はMₚ(Pr) = 2.68μₛであり、Pr₄Al₃の飽和磁気モーメント3.20μₛの約85%である。b軸、c軸とも磁化阻却軸であり、Mₚ(Pr) = 0.21μₛである。SQIDにより磁化の測定結果をFig.1aに示した。中性子回折測定により磁気構造が調べられており、伝播ベクトルは(010)と報告されている[5]。

Fig.1bは、NdNi₄Al₃の磁化測定結果で、ネオ磁性は温度が9.6K、b軸が磁化容易軸であり、約4.2Tで磁気移動する。外部磁場7Tでb軸の磁化はMₚ(Nd) = 1.8μₛであり、Nd₄Al₃の飽和磁気モーメント3.27μₛの約半分である。7Tでa軸の磁化はMₚ(Nd) = 1.15μₛである。

研究施設・装置： JRR-3M 水力照射孔
研究分野： 核物性、固体物理、核物理
Fig. 1a Magnetization of PrNiAl₄ at 2 K.

Fig. 1b Magnetization of NdNiAl₄ at 2 K.

Fig. 1c Magnetization of Pr₆Nd₈NiAl₄ at 2 K.

PrとNdを混合したPr₆Nd₈NiAl₄では、ネルン温度は5.7Kに下降する。Fig. 1cに示すように、磁化はa軸だけで磁気転移を示す。60°の角を加えた77での磁化は、Mₐ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-
Fig.2c γ-ray energy spectrum of $^{142}$Pr, $^{147}$Nd, $^{54}$Mn, $^{60}$Co.

に作用するとした。崩壊が増すと核スピン方向の計数率が減少し、垂直方向の計数が増加する。

Fig.2c は崩壊のエネルギースペクトルである。
$^{147}$Nd の 531keV ピーク、$^{142}$Pr の 1576keV ピーク、他に$^{60}$Co（hcpCo）や$^{54}$Mn（Ni）崩壊を各々放出されたピークもである。

論文は新潟大学理学部とニュー・サウス・ウェールズ大学のキャンベラの$^3$He/$^4$He 希薄冷凍機を用いて行った。

Fig.3a は、$\text{Pr}_{0.8} \text{Nd}_{0.2} \text{NiAl}_x$ における $^{142}$Pr と $^{147}$Nd の $\beta(\theta)$ の温度依存性である。外部磁場を a 軸方向に印加した。温度が下がるに従い磁場が増加し、$^{142}$Pr の $\beta(\theta)$ は、a 軸方向（Pr/a）での崩壊線相関性（$\beta(\theta) < 1$）を示し、b 軸方向（Pr/b）で正の崩壊相関性（$\beta(\theta) > 1$）を示している。この結果は、Pr のモーメントが、a 軸方向に整列していることを示している。$^{147}$Nd の $\beta(\theta)$ も $^{142}$Pr と同様に変化しており、Nd のモーメントも a 軸方向に整列していることがわかる。

Fig.3b は、$\text{Pr}_{0.8} \text{Nd}_{0.2} \text{NiAl}_x$ における $^{142}$Pr と $^{147}$Nd の $\beta(\theta)$ の磁場依存性である。外部磁場を a 軸方向に印加した。$^{142}$Pr の $\beta(\theta)$ は、磁気スピンが起こる磁場で変化する。a 軸方向の Pr/a は崩壊線相関性（$\beta(\theta) < 1$）を示し、b 軸方向の Pr/b は正の崩壊相関性（$\beta(\theta) > 1$）を示している。この結果は、Pr のモーメントが、a 軸方向に整列していることを示している。つまり、Pr のモーメントはメタ磁性転移を示していると考えられる。

一方、$^{147}$Nd の $\beta(\theta)$ は、外部磁場の作用に伴って大きな変化を示す。a 軸の $\beta(\theta)$ は、低い磁場側と

Fig.3c Magnetic structure at fields, before, during and after the magnetic phase transition.

高磁場側で $\beta(\theta) < 1$ であり、磁気転移状態で $\beta(\theta) > 1$ になる。b 軸の $\beta(\theta)$ は、これに反対する振る舞い
をしてる。この変化は、スピノフロップ磁気転移により説明できる。

初めNdのモーメントは、Prのモーメントとの交換相互作用で、軸に整列している。Prの磁気構造は、面で平行な面内で強磁性的配列で、最近隣接面間で反磁磁性的である。(Fig.3c参照)Prのモーメントがメタ磁性転移すると、Ndのモーメントに作用して面間の反磁磁性的な交換相互作用の方向が反転し、面内の強磁性的な交換相互作用と競合することになる。結果的には、Pr-Ndの交換相互作用は弱められ、Ndのモーメントは自身の磁化容易軸であるb軸方向に整列するものと思われる。さらに外部磁場を増すごとNdのモーメントは外部磁場との相互作用で回転する。

2.2 BF-NMRによる110mAgの核磁気

BF-NMRによる核磁気時間の測定は、過去にAg中の110mAgの1例報告されているのみである[9]。新潟大学物理部では、希釈冷凍機に新たに12Tの超伝導磁石を設置し、BF-NMRの測定システムを構築している。

この測定手段で観測される放射性原子核の核磁気共振周波数は、主に外部磁場に支配される。よって、外部磁場強度を正確に校正することが重要である。そこではじめに磁場強度の校正のため、BF-NMRの共振周波数と核磁気時間が報告されている110mAg(Ag)の実験を計画した。実験試料は厚さ3μm程度のAg箔を原子炉からの熱中性子で1週間照射して110mAg生成した。

Fig.4a NSF-NMRON共振スペクトルである。縦軸は110mAgのβ崩壊後に放射される658, 764, 885, 937keVγ線の計数の和、横軸はRF磁場周波数である。共振中心周波数は54.64MHzであり、外部磁場が11.922Tであることがわかった。

RF磁場を共振周波数に合わせていった110mAg核を共振状態にしてから、RF磁場を切ると、核磁気過程が観測される。Fig.4bはその過程の曲線である。指数関数で解析した結果緩和時間を98(57)sと得た。これは過去の報告結果と一致する。試料温度は10(nK)である。110mAgのNMR測定の結果と比較するため核g因子で規格化した(1/μgT)を計算した。110mAgで(1/μgT) = 1.8(9.1)[1/Ks]、110mAgで(1/μgT) = 1.6(0.2)[1/Ks]であり、精度内で一致する。

3. 結果の評価と今後の方針

LTNOによるRE pairsの研究を通じ、「多重磁性イオンを含む反磁性化合物において希土類イオンは、固有の磁気構造と磁気異方性を持つ」場合があることがわかった。このような情報はユニークであり、LTNOが磁性研究における新しい実験手段になることがわかる。今後は(Pr,Nd)FeBのような实用材料の基礎的研楽に応用していきたい。

BF-NMRONによる核磁気やナイトショットの研究は、110mNb(Cu)、110mNb(Nb)、110mRh(Nb)と110mRh(Cu)なども行われた。NbのCuに対する固溶度は0.1%以下であり、一般のNMRデータが少なく、貴重なデータと考えられる。合金材料に微量に添加されている元素の微視的
研究成果として応用していきたい。

以上、この研究の目的は達成されたが、今後も同様の研究を継続し磁性に関するユニークな研究成果を公表することが重要であると考える。

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内部起源粒子線による石英中の常磁性格子欠陥の生成効率の研究

Paramagnetic lattice defects in quartz
created by internal alpha and alpha recoil particles

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(1) はじめに

電子スピン共鳴年代測定法は、第四紀と呼ばれる、人類が発生し、発展してきた、最近約200万年間の時代の年代測定法として注目され、サンゴ、鍍乳石、テフラ、断層粘土、化石の歯、骨、石膏などの試料に適用されてきた（Ikeya, 1993）。この方法は、自然放射線によって鉱物中に生成する熱的に安定な常磁性格子欠陥やラジカルが年代と共に蓄積することを利用している。すなわち、年代測定を行う試料のESR信号強度を測定した後に、自然放射線による被曝を模擬した人為ガンマ線照射を行い、信号の生成効率を求ることにより、自然放射線による総被曝量を求められる。この値を別に求めた自然放射線による年間被曝量で割って年代を算出する。

この年代測定法は信号の熱安定性から、その適用範囲が第四紀に限られると言われてきたが、花崗岩に含まれる石英中の酸素空孔に関連したESR（電子スピン共鳴）信号（E\textsubscript{1}中心）の強度と、花崗岩の年代の間に関係があることが見出され（Odom and Riak, 1989）、ESR年代測定が、第四紀だけでなく、10億年までの範囲で適用可能である可能性が示された。

筆者は、このE\textsubscript{1}中心とその前躯体である酸素空孔との関連を調べ、花崗岩中の石英についても珪素-珪素の結合が、ホール中心から供給されるホールを捉えることによってこのE\textsubscript{1}中心が生成することを示した。また、ガンマ線照射後300℃で15分間加熱することによって、酸素空孔の相対的な量をE\textsubscript{1}中心の信号強度として測定できることを提案した（Toyoda and Ikeya, 1991）。この方法を用いて、花崗岩の石英中の酸素空孔量と年代との関係があることを報告した（Toyoda et al., 1992; Toyoda et al., 1996）。

しかし、自然の花崗岩中の石英に生成する酸素空孔の生成過程については、微量に含まれるウラン、
トリウム及びその娘核種からのアルファ反応粒子のためか（Rink and Odom, 1991）、それとも外部からのベータ線、ガンマ線によって生成するのか（Toyoda et al., 1996）明らかではない。

(2)目的
アルファ反応粒子によって石英中に酸素空孔が生成するとの立場では、酸素空孔の生成量を理論計算によって行っている（Rink and Odom, 1991）。しかし、この生成量が、実際にESRで、E1中心として測定される酸素空孔量と一致するのかどうか、明らかではない。本研究では、人為的にアルファ及びアルファ反応核種を石英中に生成させ、これによってつくられる酸素空孔の量をESRによって実験的に測定しようとした。

(3)方法
石英内部からアルファ線及びアルファ反応核種を放出させるため、ホウ素をドープした石英を日本電波工業（株）に依頼して製作した。そして、自然の熱水作用で生成した石英をあわせ、15種類の試料を準備した。これらの試料に熱中性子を照射すると、熱中性子が$^{10}$Bと下記の反応をすることで、アルファ粒子及びアルファ反応粒子が内部で石英を照射することになる。

$$^{10}\text{B} + n \rightarrow ^4\text{He} + ^7\text{Li}$$

また、リチウムについても同様の次の反応があるのでこれについても考慮した。

$$^6\text{Li} + n \rightarrow ^4\text{He} + ^3\text{H}$$

照射後石英試料をESR測定することにより、生成した酸素空孔量を知り、理論計算と比較する。

(4)試料
準備した試料中のホウ素の含有量を、熱中性子発ガンマ線解析により定量した。また、各試料をフッ化水素酸で溶解後、ICP質量分析計によりリチウムの含有量を測定した。結果を表1に示す。

表1 本研究で分析した石英試料中のホウ素及びリチウムの含有量（ppm）。

<table>
<thead>
<tr>
<th>試料番号</th>
<th>リチウム濃度</th>
<th>ホウ素濃度</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.4</td>
<td>2.45</td>
</tr>
<tr>
<td>3</td>
<td>25.0</td>
<td>0.71</td>
</tr>
<tr>
<td>4</td>
<td>17.0</td>
<td>0.70</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>0.04</td>
<td>1.52</td>
</tr>
<tr>
<td>2037</td>
<td>14.1</td>
<td>2.33</td>
</tr>
<tr>
<td>11+x</td>
<td>14.1</td>
<td>1.25</td>
</tr>
<tr>
<td>11-x</td>
<td>16.4</td>
<td>0.71</td>
</tr>
<tr>
<td>11z</td>
<td>3.7</td>
<td>0.81</td>
</tr>
<tr>
<td>12+x</td>
<td>22.6</td>
<td>4.09</td>
</tr>
<tr>
<td>12-x</td>
<td>15.5</td>
<td>3.33</td>
</tr>
<tr>
<td>12z</td>
<td>2.3</td>
<td>0.46</td>
</tr>
<tr>
<td>13+x</td>
<td>40.5</td>
<td>7.81</td>
</tr>
<tr>
<td>13-x</td>
<td>32.8</td>
<td>6.58</td>
</tr>
<tr>
<td>13z</td>
<td>12.8</td>
<td>1.68</td>
</tr>
</tbody>
</table>

(5)熱中性子照射とESR測定
それぞれ粉末にした石英試料を、石英ガラス管あるいはアルミニウム管に封入し、原子炉JRR-3の気送管、PN-1を使用して熱中性子照射を行った。熱中性子のフレーガン率は、5.2×10$^{13}$ n/cm$^2$ s で、10分、30分、60分の照射を行った。

照射後60分間をおいてから、試料を分割し、装置で300℃で15分加熱を行った後に、各試料のESR測定を行った。日本電子製RE-3Xを用い、測定条件は、室温で、マイクロ波出力0.01mW、磁場変調幅0.1mT、g=2.001付近のSmTの幅の検出とした。測定の終定数は、信号強度の大きさによって設定した拡大率に対応させ、0.1から1秒、検出時間は4分から16分とした。

観測されたE1中心の信号のピーク値を測定し、測定時の信号の拡大率、試料の質量によって規格化した。試料の測定と同時にマンガンマーカーを測定したが、マーカーの信号強度は3%程度しか変化しなかったので、各々の試料の測定に際して、感度に変
理想的には、10 分、30 分、60 分のそれぞれの照射について、それぞれデータが直線上のにるはずであるが、残念ながらばらついた結果となってしまった。10 分のデータについては、多少右上がりの傾向が見えて取れるが、30 分及び 60 分についてはむしろ酸素空孔が多く生成しているはずの試料で ESR 信号強度が小さくなっている。ただ、左の部分については増加の傾向が見えて取れる。

予想に大きく反する結果が得られたのであるが、検討を重ねた結果、原因として次のようないことが考えられる。図 2 の右の酸素空孔が多く生成しているはずの試料は、ホウ素をより多く含んだ、人工水晶である。液体窒素温度での ESR 測定によって、石英中のアルミウムがホールを捉えたアルミウム中心の信号を測定してみると、これらの人工水晶において、信号強度が小さく、図では左の方に示される自然の石英のほうでアルミウム中心の信号強度は大きかった。石英中の E1 中心は、酸素空孔にホールが捉えられて生成する。従って、人工水晶では純度が高く、不純物としてのアルミウムの量が少なく、アルミウム中心が生成しにくいため、加熱によって供給されるホールが十分でなく、酸素空孔が十分に生成していてもそれが全部 E1 中心として ESR 測定で検出できなかった可能性がある。

筆者によって主張されてきた、酸素空孔の量を E1 中心の信号強度として測定する方法（Toyoda and Ikuya, 1991）は自然の石英の、不純物であるアルミウムを「十分に」含んだ石英を用いて提案されたものである。このような不純物の少ない人工水晶について、同様の現象が成立するかどうか、検討が必要である。

自然の石英中の酸素空孔を用いることによって、花崗岩の年代測定のほか、石器の加熱変質の測定（Toyoda et al., 1993）、風成塵の起源の推定（Ono et al., 1998）など地球科学的に興味深い研究課題が多い。したがって、自然の石英中の酸素空孔の生成過程の研究は重要であるが、この課題を取り組むためには、上に述べた基礎的な、酸素空孔と E1 中心の信
号の生成との関係に戻って、再度検討を重ねなければならないと考えられる。

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Paramagnetic defects in quartz created by internal alpha particles. 9th International Conference on Luminescence and Electron Spin Resonance Dating, Sep. 6-10, 1999, Complesso Monumentale del San Michele a Ripa in Trastevere, Rome, Italy.
Characteristic Measurements of the Multi-Leaf Collimator for Boron Neutron Capture Therapy at JRR-4

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Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan

Summary

The Multi-leaf Collimator, which can form various beam outlet shapes for Neutron Capture Therapy, was developed in Japan Atomic Energy Research Institute. This collimator consists of stacked movable leaves, which are made of polyethylene mixed with LiF, in a set of 60. By sliding the individual leaves, a proper beam outlet shape can be formed for a particular patient. By applying the new collimator to NCT, an adequate dose can be delivered to the target region with minimized dose delivery in the healthy tissue outside the target field.

Introduction

In the Neutron Capture Therapy (NCT), one of the primary concerns in irradiation is to deliver the highest possible dose to the target region while protecting the surrounding healthy tissues. Especially in epithelial neutron beam NCT, it is necessary to control the dose distribution in the radiation field because the high-energy neutron (epithelial to fast neutron) and secondarily-generated gamma-ray spread widely to the radiation field and surrounding tissues. In thermal neutron beam BNCT that has been performed in Japan, patient’s head outside of the target region was covered with a thermo-plastic plate mixed with enriched Lithium (Li-helmet) in order to focus the radiation field, and to shield the surrounding healthy tissues. However, to perform the epithelial neutron beam NCT, alternative techniques and equipment were required to control the irradiation dose distribution inside/outside of the target region due to the Li-helmet’s inability to shield the high-energy neutron. Thus the Multi-Leaf Collimator (MLC) for NCT, which can form various beam outlet shapes, was developed in JAERI. The MLC consists of a series of 60 movable leaves (the size of one leaf is 110×6×60mm), which are made of polyethylene mixed with LiF, stacked in layers, so that any proper shape of the beam outlet can be formed for a particular patient by sliding the individual leaves. Fig.1 shows the front view of the MLC.

In order to confirm the characteristic performance of the MLC, several experiments and calculations were carried out. This report describes the MLC performance and its applicability to actual NCT.

Movable Leaf : Height 6mm × Width 110mm × Thickness 60mm

Fig.1 The front view of the Multi-Leaf Collimator.

Materials and Methods

To verify the MLC’s characteristic performance, the results of experiments with the MLC were compared with the existing performance data of the conventional circular collimators, which have already been applied to the thermal neutron beam BNCT. Therefore, in the verification test, the MLC beam outlet was arranged to circular shapes, though the MLC is capable of forming a variety of beam outlet shapes. The beam spectrum in the experiments was set to ENB mode, which is scheduled to be applied in epithelial neutron beam BNCT in JRR-4. Thermal neutron flux and gamma-ray dose were measured around the beam outlet in free beam condition. Thermal neutron flux was measured by foil activation...
method. For measurement of the beam performance, the gold foils or gold wires were positioned in the center of the aperture. And to confirm the shielding effect and the leakage level of the stacked leaves, the detectors were positioned on the surface of the leaves, including the boundary lines of individual leaves.

To verify its applicability to NCT, water phantom experiments were performed to measure thermal neutron flux distribution around the irradiation field. The gold wires were placed radially in the phantom to measure two-dimensional distribution of thermal neutron flux around the radiation field. In addition, several calculations using MCNP-4C were carried out in order to evaluate various beam outlet shapes and the high-energy neutron behavior.

**Results and Discussion**

In free beam condition, the maximum thermal neutron flux in the aperture of the MLC’s outlet was 2.7x10^5 (cm^-2 sec^-1). It is approximately 90% compared with the performance of the conventional collimator whose shape has been optimized for the neutron beam collimation. Thermal neutron flux, high-energy neutron flux and gamma-ray dose on the surface of the stacking leaves were less than 1/10 compared with the value in the aperture of the outlet. In the phantom experiments, the two-dimensional distribution of thermal neutron flux was comparable to the distribution of the conventional collimator beam, though the rate of the thermal neutron flux was reduced approximately by 15%.

Fig.2 shows a phantom experiment simulation calculated with MCNP-4C, in which the MLC beam outlet was arranged to “L” shape. The distribution of high-energy neutron flux on the surface of the MLC is shown in Fig.3. This result indicates that the high-energy neutron beam can be controlled correspondingly to the beam outlet shape of the MLC, and that the outlet shape influences distribution of thermal neutron flux in phantom.

These verification results prove that the MLC is able to shield the high-energy neutron outside the aperture, and it is able to make an essential dose distribution to the radiation region. And the MLC has a potential to deliver a proper dose distribution to a complex target field while suppressing the irradiation dose to surrounding critical organs and tissues by changing the outlet shape.

![Fig.2 A simulation with MCNP-4C, in which the MLC beam outlet was arranged to “L” shape.](image)

![Fig.3 The high-energy neutron flux distribution on the surface of the MLC.](image)

**Conclusions**

By applying the Multi-Leaf Collimator to NCT, proper dose delivery can be executed to the target region while minimizing the dose to surrounding healthy tissues.

**Reference**

研究テーマ：核対中性子源材料の開発
表題：W/Ta 固体ターゲットの開発
7-11
核対中性子源用 W/Ta 接合材の残留歪み

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核対中性子源として開発した W/Ta 固体ターゲット接合部の残留歪みを測定した。W と T a の間に隙間があると、核発生する W の除熱が進まないので、熱抵抗となる隙間が無いように接合させて使用する。接合材を HIP 製作するに当たり、温度、圧力をパラメータにして R & D を実施した結果、再結晶化を防ぎ、拡散を大きくする点から、1500℃、2000 気圧で 3 時間がベストとわたかった。この条件で製作した接合強度を評価する目的で、接合境界部に残留している歪みを、中性子回折で測定した。接合モデル材は粉末から焼結した W, Ta であり、直径約 10 mm, 高さ 4.5 mm, 厚さ 1 mm の T a 箇に、はじめの精度に加工した T a と W の円筒を半割にし、もとの T a 箇に入れ、別の T a の蓋をし、HIP 处理してある。HIP 接合した W/Ta の残留歪みを中性子回折で測定した（図 1）。その結果、半径方向歪みは W 側でやや引張り、T a 側で引張り、円周方向歪みは W 側、T a 側とも同程度の引張りの残留歪みが残っていることが明らかになり、ターゲット伝熱接合界面の機械的状況がわかった。ターゲットは KENS で中性子源としてすでに使用中である。

図 1 W/Ta 接合材とビーム経路

図 2 半径方向歪みの測定例

3 号炉、RESA、1-(1)
Research Theme: Basic and Clinical Study for Boron Neutron Capture Therapy
Title: Intraoperative Boron Neutron Capture Therapy using Thermal/Epithermal Mixed Beam

Department of Neurosurgery and Anesthesiology, University of Tsukuba, Ibaraki, Japan
Department of Research Reactor, Japan Atomic Energy Institute, Tokai, Ibaraki, Japan

INTRODUCTION
A new clinical phase I/II trial has been conducted for intraoperative boron neutron capture therapy (IBNCT) using mixed thermal/epithermal neutron beam at Japan Atomic Energy Institute (JAERI). At JAERI, medical equipment such as operation room and remote anesthesia monitoring system has been implemented. The interim results of the clinical trial will be presented.

MATERIALS AND METHODS
From October 1999 to July 2001, 7 patients (4 glioblastoma; GBM, 3 anaplastic astrocytoma; AA) have been treated at JAERI with the new mixed neutron beam and IBNCT. BSH (100mg/kg) were given 12 hours prior to irradiation at JRR-4. In selected cases, the clearance of the blood boron concentration and tumor boron concentration were measured by administering 1g BSH at the first debulking surgery.

RESULTS AND DISCUSSION
The initial response (including two complete response (CR), two partial response (PR)) was 100% in patients having macroscopic residual tumor. Including patients with no residual tumor on MRI, the effective rate was also 100%. Because the patient's number is small, it is too early to discuss about the final results. However, all the patients treated by IBNCT showed better clinical survival if compared to RTOG classification by Curran (1993).

The median survival time (MST) in GBM was 19.8 months and 16.8 months in AA. There was one directly tumor related death among 7 cases. Other two patients died of pneumonia and pancytopenia 15.4 and 16.7 months after initial operation followed by BNCT, respectively. IBNCT with mixed thermal/epithermal neutron beam provide better primary radiation effect than conventional therapy in selected cases.

There have been recurrent tumors outside the irradiation field in three cases, which may suggest the necessity of using more powerful beam such as pure epithermal beam to cover wider area of the clinical target volume with more irradiation dose.


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付録

Appendix
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原研研究炉の利用設備一覧

1. JRR-3M
   1) 実験設備

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2）照射設備

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2. JRR−4
1）実験設備

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2）照射設備

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<td>Dパイプ</td>
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<td>Nパイプ</td>
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国際単位系（SI）と換算表

### 表1 SI基本単位および補助単位

| 長さ | メートル | m |
| 質量 | キログラム | kg |
| 時間 | 秒 | s |
| 電流 | アンペア | A |
| 無Dimension | ケルビン | K |
| 物質量 | モル | mol |
| 光度 | カンデラ | cd |
| 平面角 | ラジアン | rad |
| 立体角 | ステラジアン | sr |

### 表2 SIと用いる単位

| 長さ | 分、秒、時 | mm, m, km |
| 光強度 | リットル | L |
| 電子ボルト | eV |
| 原子質量単位 | u |

### 表3 固有の名称をもつSI導入単位

| 騒音レベル | デン | dB |
| 鍾 | デン | N |
| 力学 | ヌートン | N |
| 声音 | バスカル | Pa |
| ハム | ジュール | J |
| 唐 | ワット | W |
| 電子 | クローナ | C |
| 電気 | ボルト | V |
| 電子流 | ファラデ | F |
| 電位 | オーム | Ω |
| 電磁気 | サンダーバー | T |
| 電子 | ヴォルト | V |
| 電磁気 | ファラデ | F |
| 電磁波 | オーム | Ω |

### 表4 SIと互換的に維持される単位

| 長さ | デン | cm |
| 光強度 | デン | J |
| 電子 | デン | m |
| 電気 | デン | s |
| 電磁波 | デン | N |
| 電子流 | デン | A |
| 電磁波 | デン | s |
| 電磁波 | デン | S |

### 表5 SI換算表

| 長さ | 分、秒、時 | mm, m, km |
| 光強度 | リットル | L |
| 電気 | ボルト | V |
| 原子質量単位 | u |

### 拡算表

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<tr>
<th>力</th>
<th>MPa(=10 bar)</th>
<th>kgf/cm²</th>
<th>atm</th>
<th>mmHg(Torr)</th>
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### 計算例

1 cal = 4.1865 J（計量法）

### 放射能

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### 総計

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(96年12月26日現在)