9. Superconducting Properties of FeSe and FeTe

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Soon after the discovery of iron based superconductor LaFeAsO1-xFx with the superconducting transition temperature of Tc=26K by Kamihara et al., superconductivity in PbO-type FeSe at 8K was reported. The FeSe layer is analogous to the FeAs layer, which implies that FeSe has the simplest crystal structure in the iron-based superconductors. FeSe samples were prepared using the solid-state reaction in the quartz tube. The structural phase transition from tetragonal to orthorhombic was observed by high-resolution synchrotron X-ray diffraction. We observed the extremely huge pressure effect of the superconducting transition temperature. Surprisingly, the superconducting transition temperature Tc raised from13K to 27K at 1.48GPa. The Tc also raised by the substitution of Se by Te. However, FeTe is not superconducting. Recently we have succeeded to realize superconductivity in FeTe by S doping. Superconducting transition temperature is around 10K and upper critical field is estimated to be 70T. This result suggest that all of FeAs, FeP, FeSe, FeTe layers have potential of superconductivity. We will also report the valence band photoemission spectra and NMR measurements of FeSe. We think that the detailed investigation of FeSe and FeTe system will provide us the clues to understand the mechanism of superconductivity in iron-based superconductors.

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[2] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi and Y. Takano, Appl. Phys. Lett. 93, 152505 (2008)

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Superconducting Properties of FeSe and FeTe

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January 25, 2009, Veno, Tokyo, Japan

Crystal structures of Fe-based superconductors



G. Hägg and A. L. Kindstrom, Z. Phys. Chem. 22, 455 (1933).F. C. Hsu and M. K. Wu *et al.*, Proc. Nat. Acad. Sci. 105, 14262 (2008).

Introduction for iron-based superconductor

ZrCuSiAs-type structure

LaFeAsO_{1-x} $F_x (T_c = 26 \text{ K})^{[1]}$ NdFeAsO_{1- δ} ($T_c = 54 \text{ K})^{[2]}$





 $T_{\rm c}$ increased to 43 K under high pressure.^[4]

Y. Kamihara *et al., J. Am. Chem. Soc.* **13**0, 3296 (2008).
 H. Kito *et al., J. Phys. Soc. Jpn.* **77**, 063707 (2008).
 S. Matsuishi *et al., cond-mat*:0810.2351.
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Introduction for iron-based superconductor



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FeSe: Crystal structural transition around 70K

Transport properties of FeSe under pressure



Y. Mizuguchi et al., APL 93, 152505 (2008).



Magnetization properties of FeSe under pressure

Y. Mizuguchi et al., APL 93, 152505 (2008).



Y. Mizuguchi et al., APL 93, 152505 (2008).



H. Kotegawa et al., JPSJ 77, 113703 (2008).

Valence band photoemission spectra of FeSe









Intensity reduction at E_F starts above Tc.

Two possibilities:

- (1) Pseudogap formation above Tc as observed for FeAs compounds.
- (2) Tc of measured area indeed higher than bulk Tc.

R.Yoshida et al., cond-mat:0811.1507. JPSJ in printing.

Substitution effects of FeSe



Superconductivity was suppressed strongly by Co or Ni doping contrary to 1111 system.

Y. Mizuguchi et al., arXiv:0811.1123.





X-ray diffraction pattern & Rietveld refinement FeTe





An anomaly corresponding to a structural transition was observed around 80 K.

With increasing pressure, resistivity at 300 K decreased and the transition broadened.

Y. Mizuguchi et al., arXiv:0810.5191



$d_{\rm P}/dT$ plots of resistivity under pressure

We defined T_s as the maximum temperature in $d\rho/dT$. T_s clearly decreases with increasing pressure.

Y. Mizuguchi et al., arXiv:0810.5191



Magnetization and H_{C2} of $FeTe_{1-x}S_x$



Superconductivity was found in S doped FeTe using nontoxic elements. Y. Mizuguchi *et al.*, APL 94, 012503 (2009).



Y. Mizuguchi et al., APL 94, 012503 (2009).

Summary

- 1. High pressure enhanced the Tc of FeSe up to 27K. Latest data shows Tc over 30K under higher pressure.
- 2. Gap-like properties was observed above Tc by AIPES.
- 3. Superconductivity was discovered in S doped FeTe around 10K.
 - Y. Mizuguchi et al., APL 93, 152505 (2008).
 - S. Margadonna et al., Chem. Commn. 5607 (2008).
 - H. Kotegawa et al., J. Phys. Soc. Jpn., 77, 113703 (2008).
 - Y. Mizuguchi et al., APL 94, 012503 (2009).



Thank you...

10. High-Pressure Synthesis and Physical Properties of New Iron Based Superconductors

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Here we present a series of oxygen-deficient oxypnictide superconductors, LnFeAsO_{1-y} (Ln: lanthanide elements) with Ln=La, Ce, Pr, Nd, Sm, Gd, Tb and Dy has been prepared using high-pressure synthesis technique. We demonstrate that the lattice parameters, the superconducting transition temperatures (T_c) and the phase purity of the samples strongly depend on the synthesis pressure, in particular for heavier Ln's, such as Tb and Dy. Sharp superconducting transitions are observed at almost the same temperature both in resistivity and magnetic susceptibility measurements for each sample. It is demonstrated that the LnFeAsO_{1-y} superconductor containing Ln's (Nd, Sm, Gd, Tb and Dy) inherently possesses high- T_c exceeding 50 K while those with lighter Ln's (La, Ce and Pr) has been lower T_c 's. The *a*- and *c*-parameters decrease with atomic number of Ln while T_c is constant for Ln=Nd to Dy, which suggests that the lattice parameters themselves are not dominant factors to determine the maximum T_c .

Also we show our first hand result on Fe-isotope effect in Ba_{1-x}, K_xFe₂As₂ samples prepared by using high pressure synthesis technique. We have studied the effect of isotopic substitution on the superconducting transition temperature (T_c) by replacing ⁵⁴Fe by ⁵⁷Fe. We repeated experiment for eight set of samples and precisely determined and which demonstrate that iron isotope component α , ($T_c \sim M^{-\alpha}$) is negative.

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High-pressure synthesis and physical properties of new iron based superconductors

Ln La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

International Workshop on Iron Related high-Tc Superconductors (IRiSes2009)

<u>Parasharam M. Shirage</u>, K. Miyazawa, K. Kihou, M. Ishikado, H. Matsuhata, N.Takeshita, C. H. Lee, R. Kumai, Y. Tomioka, T. Ito, H. Eisaki,H. Kito, A. Iyo

National Institute of Advanced Industrial Science and Technology (AIST)

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Crystal structures of Fe-based superconductors



Ways to induce superconductivity in "1111" phase

F substitution LaFeAsO_{1-x}F_x

Y.Kamihara et al. JACS **130** (2008) 3296.



Oxygen deficiency *Ln*FeAsO_{1-y}

H.Kito, H.Eisaki, A.Iyo, JPSJ 77 (2008) 063707. Z,A. Ren et al. Europhys. Lett. 83 (2008) 17002.

Fe site substitution Ca(Fe,Co)AsF S. Matsuishi et al, JACS **130** (2008) 14428

Pressure N.Takeshita et al. JPSJ 77 (2008) Suppl. C, 131. H.Okada et al. cond-mat, arXiv:0810.1153.

Ln site substitution (Gd³⁺Th⁴⁺)FeAsO C. Wang et al. arXiv:0804.4290

High-pressure synthesis method



Cubic-anvil type high-pressure apparatus CAP-07, RIKEN

Merits of high-pressure synthesis

- **New materials** -high-pressure phase *Ln*FeAsO_{1-v}
- **Safety** -evaporation of toxic As is suppressed
- High productivity -short reaction time ~2 hrs (3~4 samples /day)
- High-purity samples -crystal structure analysis
- High-density samples
 -transport measurements
- Single crystal growth PrFeAsO_{1-v}, (Ba,K)Fe₂As₂



High-pressure synthesis of *Ln*FeAsO_{1-v}

Starting Materials: *Ln*As, Fe (powder), Fe₂O₃

• Precursors of *Ln*As are prepared in quartz tube.

•Oxygen content of samples are controlled by Fe/Fe₂O₃ ratio.

Conditions

Pressure: 2.0~5.5 GPa

Temperature: 1050~1150 °C

Time: 2 hours



High-pressure synthesis of AM_2X_2

A = Ba,K,Ca; M= Fe, Ni; X= As, P etc

Starting Materials: *BaAs*, KAs, Ca, Na, Fe (powder), As, P, etc.

• Precursors of *Ba*As are prepared in quartz tube while KAs in alumina tube.

Conditions

Pressure: 1.0 GPa

Temperature: 950~1150 °C

Time: 1-1.5 hours





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Oxygen-deficient NdFeAsO1-y



•No impurity peaks, indicates pure phase.

•212 diffraction peak systematically shift to higher diffraction angle with increase in oxygen deficiency.

•Indicates the shrinkage of lattice parameters.

XRD Patterns of Oxygen deficient NdFeAsO_{1-v}

Peaks are indexed on the basis of tetragonal ZrCuSiAs type crystal structure, P4/nmm symmetry

NdFeAsO_{1-v} lattice parameters as a function of 1-y



Lattice Parameters shrinks non-monotonously with oxygen deficiency.

-0.32 percentage change is lattice parameters, which is higher than substitution of F at O in LaFeAs(O_{1-x}F_x).

□Shrinkage of lattice parameter with 1-y is reasonable, as oxygen deficiency alters the charge distribution between NdO and FeAs.

 \Box (NdO)⁺¹ and (FeAs)⁻¹ changes to (NdO_{1- δ})^{+1+2 δ} and (FeAs)^{-1-2 δ}.

□Causes displacement of these layers closer to each other.



Real Oxygen content

- Real oxygen content is determined by Rietvelt analysis.
- Real oxygen content in sample is different form the nominal, real is 0.12 higher than nominal.
- The relation between the real oxygen content and aparameter is linear and which can be given by relation: 1-y =(6.637)a-25.373



Oxygen deficiency dependence of T_c

The temperature-dependence of the resistivity

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The electronic phase diagram



The *a*-axis length decreases as the oxygen deficiency increases, and superconductivity seems to develop discontinuously below a~3.964A.

The electronic phase diagram of oxygen-deficient NdFeAsO1-y samples synthesized by high-pressure technique.

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Structural parameters depend on the synthesis methods ?



For Ln = La and Nd, structural parameters are not dependent on synthesis methods. How about *Ln* =Sm, Gd,Tb and Dy?

Effect of synthesis pressure





XRD DyFeAsO_{0.7}



With increase in pressure from 2 Gpa to 5.5 Gpa

- 1. Impurity decreases
- 2. 212 peak shift to higher diffraction angle with decrease in lattice parameter
- 3. T_c increase
- HP technique is effective for synthesizing heavier *L_n*-based superconductors.



(Ln=Sm,Gd,Tb and Dy) samples against the *a*-axis lattice parameter at various pressures, sample prepared by high pressure synthesis technique.

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Powder XRD patterns of *Ln*FeAsO_{1-v}





Ln dependence of lattice parameters









The highest $T_{\rm c}$ obtained so far are around 53 K

K. Miyazawa et al. submitted to JPSJ.
J-W. G. Bos et al. Chem. Commun. 31 (2008) 3634.
Y.G. Shi et al. cond-mat. arXiv:0808.1948.
J. Yang et al. cond-mat. arXiv:0809.3582.
J. Yang et al. Supercond. Sci. Technol. 21 (2008) 082001.





For the lighter Ln's (La, Ce, Pr, Nd), T_c increases monotonously with decreasing the lattice parameters, then stays at the constant value around 53 K for the heavier Ln (Nd, Sm, Gd, Tb and Dy)

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Fe-Isotope effect

Prepared 16 set of Fe-54 and Fe-57 , $Ba_{0.6}K_{0.4}Fe_2As_2$ samples by using High Pressure Synthesis Technique. Our data shows highly reproducible results.

Iron isotope component α , ($T_c \sim M^{-\alpha}$) is negative and small : (α = -0.1 ±0.1) by 1 % drop in susceptibility. (α = -0.02 ±0.12) by susceptibility cross defination.

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- We have prepared high-purity oxygen-deficient *Ln*FeAsO_{1-y} samples by optimizing conditions using high-pressure synthesis method.
- T_c increases monotonously with decreasing the lattice parameters for the lighter Ln's (La, Ce, Pr, Nd), then stays at the constant value around 53 K for the heavier Ln (Nd, Sm, Gd, Tb and Dy).
- The *a* and *c*-parameters decrease with atomic number of *Ln* while T_c is constant for *Ln*=Nd to Dy, which suggests that the lattice parameters themselves are not dominant factors to determine the maximum T_c .
- Fe-isotope effect shows very small and negative effect.

11. Magnetism and Superconductivity in Actinide Compounds Related to Iron-Oxypnictide Structure

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Since the discovery of heavy fermion superconductivity in CeCu₂Si₂[1], a number of rare-earth and actinide compounds have been reported to exhibit unconventional superconductivity. More recently, transuranium-based superconductors such as PuCoGa₅ and NpPd₅Al₂ have also been reported. It is interesting to note that compounds with the ThCr₂Si₂-type tetragonal structure, which has similar crystallographic characteristics as oxypnictide superconductors, often show unconventional superconductivity (CeCu₂Si₂, URu₂Si₂, CePd₂Si₂ under pressure, etc). After reviewing the superconducting characteristics of these compounds, we mention the synthesis of actinide compounds with oxypnictide structure.

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Magnetism and Superconductivity in Actinide compounds related to ironoxypnictide structure

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- 1. role of *f*-electrons in RE-oxypnictide : structural tuning ? how about 5*f*-electrons ?
- 2. single crystal growth of Actinide oxypnictide UCuPO : AF ground state
- 3. What happens when 5*f*-electrons superconduct ? . New material : NpPd₅Al₂



	f-ele	ctron Heavy	y Fermion supe	erconductors	1911 Hg
	compound	T _c (K)	C _e / T (mJ/K ² mol)	Magnetic Ordering	1961 Nb ₃ Sn
1979	CeCu ₂ Si ₂	~ 0.5	~ 1000	complex	
	UPt ₃	0.45, 0.55	500	fluctuating AF at 5 K	1986 HTSC
	UBe ₁₃	0.9	1000	Curie-Weiss	
	URu ₂ Si ₂	1.4	60	hidden order at 17.5 K	
1990	UPd ₂ Al ₃	2.0	145	AF at 14.3 K.	
	UNi ₂ Al ₃	1.0	300	AF (SDW) at 4 K	
	Celn ₃ (p), CePd ₂	Si ₂ (p), CeRh ₂ Si ₂ (((
2001	CeCoIn ₅	2.3	500	Curie-Weiss	2001
	CeRhin _s (p)				MgB ₂
	Celrin ₅	0.4	500	Curie-Weiss	
2002	PuCoGa ₅	18.5	70	Curie-Weiss	
	PuRhGa ₅	8.5	70	Curie-Weiss	
	URhGe	0.15	150	Ferromagnetic at 10 K	
	CePt ₃ Si	0.5	300	AF at 2.3 K	2004
	PrOs ₄ Sb ₁₂	1.5	~ 500	paramagnetic	diamond
2006	6 CeRhSi ₃ (p), CelrSi ₃ (p), CeCoGe ₃ (p), Ulr (p)				
2007	NpPd ₅ Al ₂	4.9	200	Curie-Weiss	2008
	UCoGe	0.8	150	Ferromagnetc at 3 K	Fe-





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2.3

NpPd₅Al₂



Summary

1. role of *f*-electrons in RE-oxypnictide : structural tuning ? how about 5*f*-electrons ?

5*f*-electrons usually delocarize to participate in conduction. Also show magnetism with strong anisotropy

- 2. single crystal growth of Actinide oxypnictide UCuPO : AF ground state
- 3. What happens when 5*f*-electrons superconduct ? New material : NpPd₅Al₂
 - strong Pauli-limited superdoncutor 1st order H_{c2}
 - a new family of RE- and actinide-compounds
 UPd₅Al₂ : paramagnet, PuPd₅Al₂ : AF
 CePd₅Al₂ : AF, pressure-induced SC