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Proceedings of the International Workshop on Structural Analyses Bridging Over between Amorphous and Crystalline Materials (SABAC2008)

(Eds.) Shin-ichi SHAMOTO and Katsuaki KODAMA

Nanomaterials Synthesis Group
Quantum Beam Science Directorate

July 2008

Japan Atomic Energy Agency

日本原子力研究開発機構

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Proceedings of the International Workshop on Structural Analyses Bridging Over between Amorphous and Crystalline Materials (SABAC2008)

January 10-11, 2008, Tokai-mura, Naka-gun , Ibaraki-ken, Japan,
Techno Community Square “RICOTTI”

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International workshop entitled “Structural Analyses Bridging over between Amorphous and Crystalline Materials” (SABAC2008) was held on January 10 and 11, 2007 at Techno Community Square “RICOTTI” in Tokai. Amorphous and crystalline materials are studied historically by various approaches. Recent industrial functional materials such as optical memory material, thermoelectric material, hydrogen storage material, and ionic conductor have intrinsic atomic disorders in their lattices. These local lattice disorders cannot be studied by conventional crystal structure analyses such as Rietveld analysis. Similar difficulty also exists in the structure analysis of nanomaterials. In this workshop, new approaches to the structural analysis on these materials were discussed.

This report includes abstracts and materials of the presentations in the workshop.

Keywords : Structural Analysis, Disordered Functional Materials, PDF Analysis

JAEA-Review 2008-031

アモルファスから結晶にわたる物質の構造解析に関する国際ワークショップ (SABAC2008) 講演集

2008 年 1 月 10-11 日, 茨城県那珂郡東海村テクノ交流館「リコッティ」

日本原子力研究開発機構量子ビーム応用研究部門
中性子物質科学研究ユニット

(編) 社本　真一、樹神　克明

(2008 年 5 月 8 日受理)

「アモルファスから結晶にわたる物質の構造解析に関する国際ワークショップ」 (SABAC2008) と題される国際会議が 2008 年 1 月 10、11 日にテクノ交流館「リコッティ」において開催された。　光メモリ材料、熱電材料、水素貯蔵材料、イオン伝導体など近年の工業的な機能材料にはその原子配列に乱れをもち、さらにその乱れがそれら物質の機能の本質を担っている場合がある。しかしこのような原子配列の乱れはリートベルト解析に代表される通常の構造解析手法を用いて調べることは不可能である。同様のことは機能性ナノ粒子に対しても言える。今回の国際会議ではこのような物質系の構造を調べるための新しい試みとその研究成果が報告され、活発な議論が行われた。

本報告書は本会議の講演要旨および講演で使用された発表資料を収録したものである。

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1. Preface

S. Shamoto

Neutron Materials Research Center, Quantum Beam Science Directorate,
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Amorphous material research is extending toward long range atomic correlations. Some functional crystalline materials have intrinsic atomic disorders. In the valley between them, we cannot apply periodic boundary condition. This fact makes it very difficult for us to explore this valley from structural point of view. In this sense, this valley may be called a hidden valley. There are, however, many modern functional materials such as hydrogen storage material, ionic conducting material, ferroelectric material, thermoelectric material, optical recording material, and nanomaterials in this valley. Because of these fruitful functional materials, this valley could be the Eden for material scientists. To explore the Eden, we need high intensity total scattering diffractometer, good algorism, and fast computing. High-intensity quantum beam facilities such as J-PARC will serve as the important bridge over between amorphous and crystalline materials to enhance the research activities. For example, the high-intensity neutron and X-ray beams enable simultaneous high-intensity and high-resolution diffraction measurements, leading to wide r-range atomic pair distribution function analysis. It gives us a possible chance to study form and size of crystalline domains in the disordered structure. In this workshop, new approaches in this interdisciplinary field are discussed by both amorphous and crystalline material scientists. I hope this workshop opens new scientific frontiers to be explored for many material scientists.

2. Opening Remarks

Y. Fujii
Director General, Quantum Beam Science Directorate

On behalf of the Quantum Beam Science Directorate of Japan Atomic Energy Agency (JAEA) hosting this Workshop, I'd like to say a few words.

First of all, we wish you a Happy New Year 2008 ! It's our great pleasure to welcome all of you to this Workshop here in Tokai. The Village of Tokai is the birth place of atomic energy research in Japan more than a half century ago. The first research reactor JRR-1 with its thermal power 50kW built in 1957 has been preserved as museum now while the most advanced 1MW spallation neutron source J-PARC will be turned on this year.

Second of all, let me briefly explain what is quantum beam and what is Quantum Beam Science Directorate for which I'm now responsible at JAEA. Recent technological advancement of controlling various beams such as neutron, ion, synchrotron radiation and laser has led us to highly sophisticated way to use their full capability in a wide variety of research fields from basic science, applied science to industrial and medical application. Such purpose-oriented excellently-controlled high-quality beams are recently called "quantum beams".

Our Quantum Beam Science Directorate was formed only two years and three months ago when the reorganized JAEA started in October 2005. The purpose of our Directorate is to promote material science, life science and industrial application by using various quantum beams complementarily based on JAEA-owned large-scale facilities such as JRR-3 reactor, J-PARC spallation neutron source here in Tokai, Ion-beam facility in Takasaki, Laser facility and SPring-8 synchrotron facility in Kansai, all well-coordinated and well-bridged-over Japan. In addition we are running several international cooperative research programs such as high-level Governmental Agreement for US-Japan Program on Neutron Scattering between ORNL/DOE and JAEA/MEXT, and institutional agreement on Quantum Beam Science and Technology between CAS/China and JAEA.

Third of all, let me say what most of us are doing is “Small Science at Large Facility”. The Small Science does not mean less important science at all, but important science which can be studied by a relatively small number of researchers, even by a single researcher. The Small Science is extremely important academically in basic and applied science as well as industrial and medical application.

The other extreme is Large Science. High energy physics experiment is typical one where several hundreds of researchers get together to pursue a single purpose to try to discover an unknown particle by using a large scale accelerator. That is “Large Science at Large Facility”. Our research of small science very much depend on reliable, stable and high-quality quantum beams provided by large-scale facilities such as reactor and accelerator. In order to stably operate such a large facility for small science, it’s essentially important to have government-level’s support as a national facility fundamentally important for promoting science and technology domestically as well as internationally. To secure such a reliable operation of various large facilities, we are now very keen on an establishment of so-called “Quantum Beam Platform” together with the Government.

Fourth and finally, I hope you enjoy this Workshop today scientifically and socially. I also hope that this Workshop is neither the first nor the last meeting on this kind of topics.

Thank you !

3. Taming the Structural Complexity

T. Egami

Joint-Institute for Neutron Sciences, Department of Materials Science and Engineering, Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, and Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Today's advanced materials are much more complex in the atomic structure than traditional materials, particularly at the nanometer-scale, whereas most of the existing methods of structural characterization are focused either on the long-range periodicity (crystallography) or the atomic environment (XAFS, NMR, etc.), and are not geared to assess the nano-scale atomic order. In my view there are only two quickly advancing techniques that has a true potential of covering the intermediate ranges, namely the high-resolution electron microscopy and the atomic pair-density function (PDF) approach with high-energy neutron or x-ray probes [1]. These two techniques are complementary, and should be used as such, and in either case sophisticated simulation and analysis are the key to the success of these methods. In this talk I review the state-of-the-art capabilities of the pulsed neutron PDF analysis, using the NPDF of the Lujan Center, Los Alamos National Laboratory, as the reference point. With the NPDF the PDF can be determined up to 30 nm, thus effectively bridging the atomic level structure and the long-range structure. Modeling the atomic structure over such a vast range of distances is a challenge, and much remains to be done. In some cases nano-scale domains are observed by the PDF, rendering relatively easy interpretation of the nano-scale structure [2]. Also it is easy to tell the size of nano-particles by the decay of the PDF amplitude. In multi-component systems often the chemical correlation plays an important role. Comparison of x-ray and neutron PDFs helps identifying the chemical order. The uses of isotopes for neutron PDF and the resonant scattering for x-rays allow at least the differential PDF to be determined. Finally the PDF method is now extended to the study of local dynamics through the dynamic PDF method. Some initial results by this technique will be presented and discussed.

References

[1] T. Egami and S. J. L. Billinge, Underneath the Bragg Peaks: Structural Analysis of Complex Materials, Pergamon, Amsterdam, 2003.

[2] J.-H. Chung, Th. Proffen, S.-I. Shamoto, A. M. Ghorayeb, L. Croguennec, W. Tian, B. C. Sales, R. Jin, D. Mandrus and T. Egami, *Phys. Rev. B*, **71**, 064410 (2005).

Taming the Structural Complexity: Increasing Relevance of Non-Crystallography

Takeshi Egami

Joint-Institute for Neutron Sciences,
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Oak Ridge National Laboratory, Oak Ridge, TN

Collaborators:

W. Dmowski	*Univ. of Tennessee, Dept. Mater. Sci. Eng.*
J.-H. Chung	*Korea Univ., Dept. Physics, Seoul, Korea*
I.-K. Jeong	*Pusan National Univ., Busan, Korea*
Th. Proffen	*Lujan Center, LANSCE, Los Alamos NL*

Many former students, including, **S. J. L. Billinge, D. Louca, R. J. McQueeney, E. Mamontov, S. Teslic,** *and postdocs/visitors,* **B. H. Toby, Y. Waseda, S. Nanao.**

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1

How periodic are the matters in the world?

- **70% of the surface of the earth is covered by ocean.**
- **Inside the earth is mostly molten liquid.**
- **Only bones are crystalline in our body.**
- **Only silicon chips are perfectly periodic.**
- **Even jewels are not; nitrogen in diamond adds to color.**
- **We now turn to more and more complex functional materials, which are not perfectly periodic.**
- **Materials with *competing interactions*; creates softness out of hard materials.**

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2

Competition is good for you

- Various functional properties are required for modern materials, requiring high-response.
- Atomic bonding (~1 eV) is too strong to produce high-response.
- Utilizing competing forces (divide and conquer) is the smart way of achieving high-response.
- Managing conflict and competition is the key to the smart materials.
- Electronic softness in hard materials.
- This often destroys lattice periodicity.

Bragg's Law

$$2d\sin\theta = n\lambda, \quad Q = 4\pi\sin\theta/\lambda = K$$

- Reduces the positions of 10^{23} atoms to a few numbers!!
- But, λ ~ 1 Å. Why can we determine the d value with the accuracy much smaller than the wavelength?
  - Actually we are measuring the periodicity of the lattice, not the atomic positions.
  - $L = N\lambda$, the coherence length, determines the accuracy. Since $N \sim 10^5$, highly accurate measurement is possible.
- The assumption of perfect periodicity is the key.

"Structure" of aperiodic matter

- Bragg's law does not work! What shall we do??
- Scattering?

$$\Psi_{scat}(\boldsymbol{Q}) = A\left(\sum_i e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i}\right)\Psi_{inc}$$

- By diffraction the phase information is lost.

$$I(\boldsymbol{Q}) = \left|\Psi_{scat}(\boldsymbol{Q})\right|^2 = |A|^2 NS(\boldsymbol{Q})$$

- Structure function = FT of PDF.

$$S(\boldsymbol{Q}) = \frac{1}{N}\sum_{i,j} e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}} d\boldsymbol{r}$$

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Atomic Pair-Density Function (PDF)

- But, most properties are determined by atom-atom interactions; absolute positions do not matter, correlation does;

$$\rho(\boldsymbol{r}) = \frac{1}{N}\sum_{i,j} \delta\left(\boldsymbol{r} - \left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)\right)$$

- For less-than-perfectly-periodic matter not only Bragg peaks but diffuse scattering has to be included (total scattering).
- The PDF method has long been used for the study of liquids and glasses.

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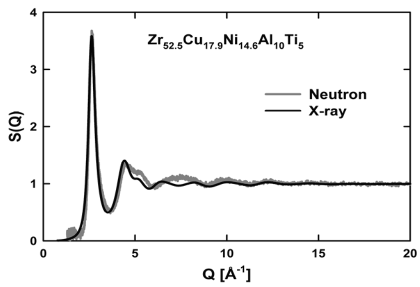
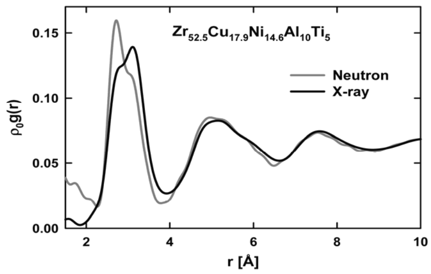
PDF of Bulk Metallic Glasses





- **PDF describes the distribution of distances between atoms, weighted by the atomic scattering factor.**

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Powder PDF Method

- **Powder averaging**

$$\rho(r) = \rho_0 g(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty [S(Q)-1]\sin(Qr)Qdq$$

- **Powder averaging is convenient and useful. Orientational information is lost, but all the diffuse scattering intensities are included.**
  - **Good practice to examine 1D PDF before studying diffuse scattering.**
  - **Diffuse scattering tells the periodicity, but not the atomic details (displacements….) unless studied over many Brillouin zones.**
- **Often crystals are not available, or powder samples are better than crystals.**

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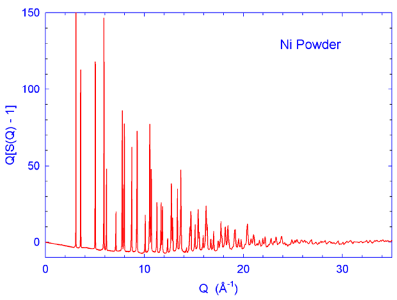
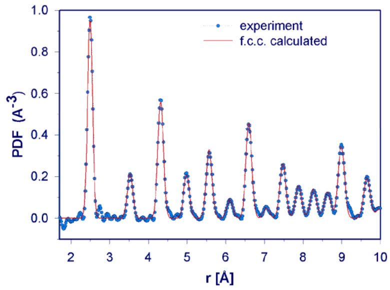
8

Local Structure by Atomic Pair-Density Function (PDF)



⇒ ***FT***



- *Distribution of distances between atoms, can describe local structural deviations.*
- *"Underneath the Bragg Peaks: Structural Analysis of Complex Materials", T. Egami and S. J. L. Billinge (Pergamon Press, Oxford, 2003).*

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High-Energy Probes

- **Termination of the integral**

$$\rho(r) = \rho_0 g(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty [S(Q)-1]\sin(Qr)Qdq$$

leads to errors (termination errors)

- **But since**

$$Q = 2k\sin\theta = \frac{4\pi\sin\theta}{\lambda}, \quad Q_{\max} < \frac{4\pi}{\lambda}$$

- **It is important to use a probe with a short wavelength, thus a high energy. Synchrotron-based radiation sources, spallation neutron sources and synchrotron radiation sources, resolved this difficulty.**

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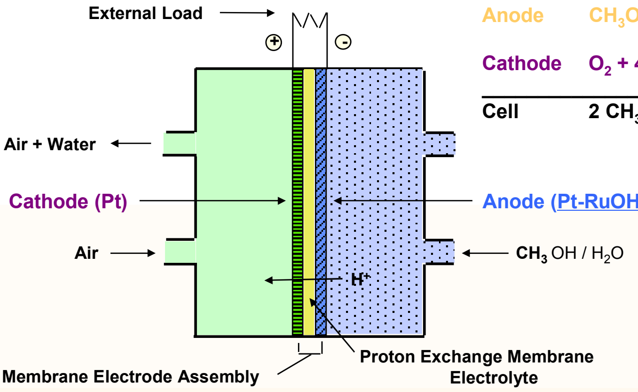
Direct Methanol Fuel Cell



Anode	$CH_3OH + H_2O$ □ $CO_2 + 6\ H^+ + 6\ e^-$
Cathode	$O_2 + 4\ H^+ + 4\ e^-$ □ $2\ H_2O$
Cell	$2\ CH_3OH + 3\ O_2$ □ $2\ CO_2 + 4\ H_2O$

Electrosorption of Methanol at Pt

$$CH_3OH + Pt \Rightarrow Pt\text{-}CO + 4\ H^+ + 4\ e^-$$

Oxygen transfer from RuOH

$$Ru + H_2O \Rightarrow Ru\text{-}OH + H^+ + e^-$$

$$Ru\text{-}OH + Pt\text{-}CO \Rightarrow Ru + Pt + CO_2 + H^+ + e^-$$

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Accepted mechanisms for pseudocapacitance in RuO_xH_y (or $RuO_2{\cdot}xH_2O$)...

$$RuO_x(OH)_y + \delta H^+ + \delta\ e^- \Leftrightarrow RuO_{x-\delta}(OH)_{y+\delta}$$

$$Ru^{4+}\text{–}O + H^+ + e^- \Leftrightarrow Ru^{3+}\text{–}OH$$

RuO_xH_y stores charge via the insertion of protons and electrons

Eqs imply that the $RuO_2{\cdot}xH_2O$ is an ionic compound, with protons inserting in the lattice. However, $RuO_2{\cdot}xH_2O$ is a metallic conductor, and electrons are fully or partially delocalized and there are no discrete ions.

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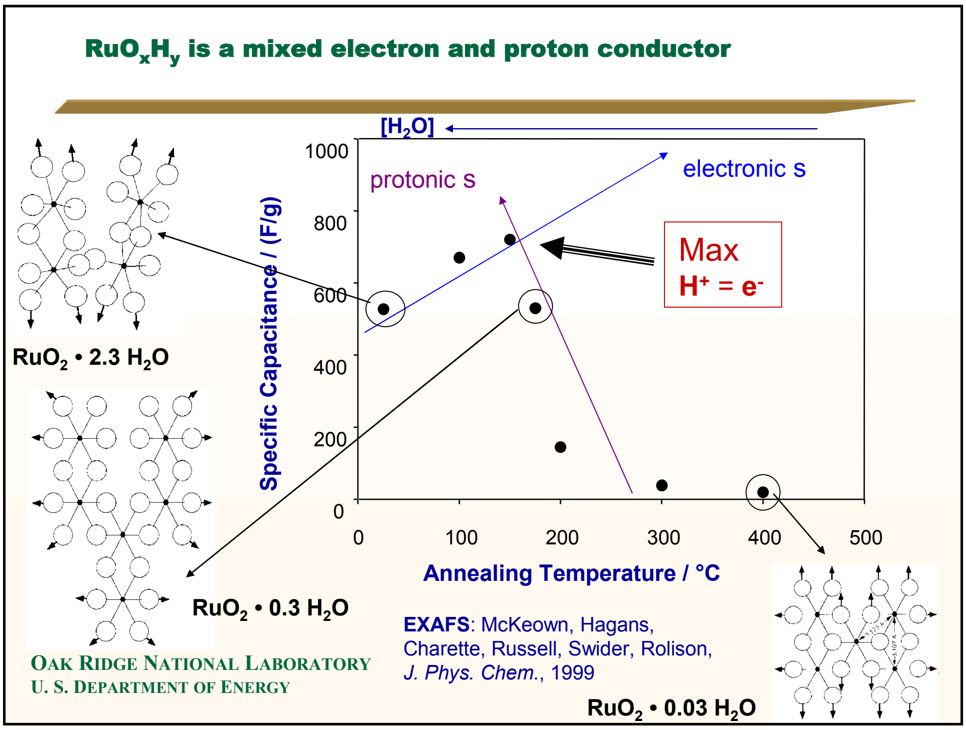
RuO_xH_y is a mixed electron and proton conductor
$[H_2O]$
protonic s
electronic s
Max
$H^+ = e^-$
Specific Capacitance / (F/g)
Annealing Temperature / °C
$RuO_2 \cdot 2.3\ H_2O$
$RuO_2 \cdot 0.3\ H_2O$
$RuO_2 \cdot 0.03\ H_2O$
EXAFS: McKeown, Hagans, Charette, Russell, Swider, Rolison, J. Phys. Chem., 1999
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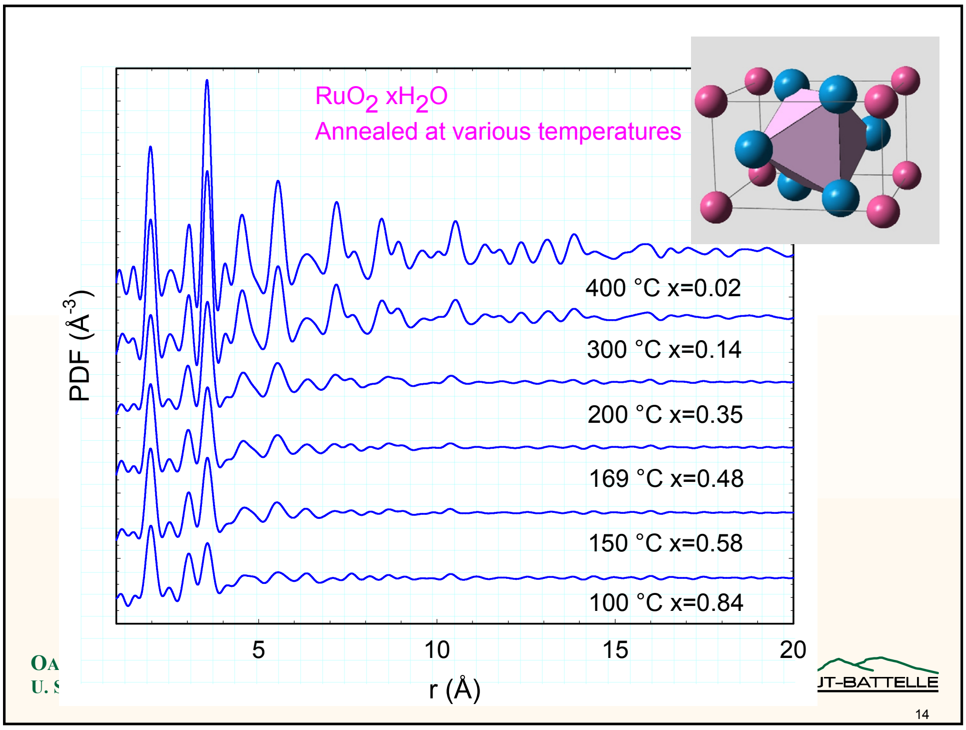
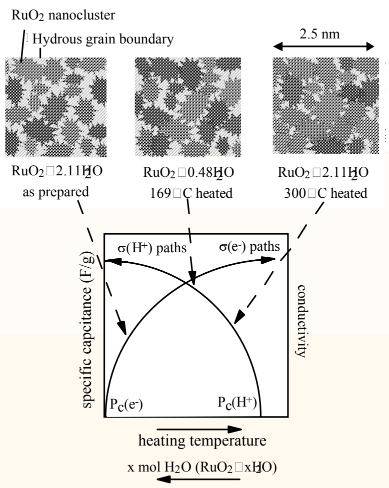

$RuO_2\ xH_2O$
Annealed at various temperatures
400 °C x=0.02
300 °C x=0.14
200 °C x=0.35
169 °C x=0.48
150 °C x=0.58
100 °C x=0.84
PDF ($Å^{-3}$)
r (Å)
14

Structure of hydrous RuO_2

$RuO_2{\cdot}xH_2O$ is composed of assemblies of small rutile-like ruthenium oxide nanocrystals or clusters having water (or protons) that is chemisorbed and physisorbed on the surface of the grains. Ruthenium-oxide nanocrystals are smaller and more dispersed for samples with high water contents.



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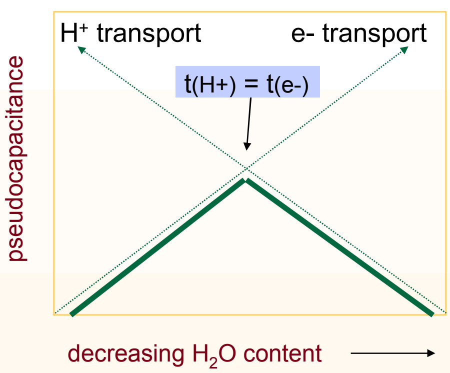
Conduction mechanism

- Electron conduction is supported by RuO_2 nanocrystals, while proton conduction is supported by the boundaries between nanocrystals.
- Due to the dispersive nature of the structure, separate percolation paths must be present between the RuO_2 nanocrystals and the hydrous part to provide paths for long-range electronic and protonic conduction, respectively.



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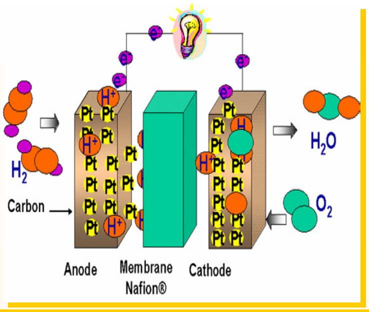
16

Polymer Electrolyte Membrane Fuel Cells (PEMFC) use carbon supported Pt-clusters for the oxidation of the fuel on the anode and the reduction of the oxygen on the cathode.

Efficient utilization of the Pt-based catalyst is crucial, as this metal is very expensive. Optimization has been reported through

- extreme dispersion (e.g. nanoparticles)
- metal alloying (e.g. Pt-Cr combinations).



Objectives of this research:

- decrease the Pt-content (and thus cost) of catalyst
- improve its Oxygen Reduction Reaction (ORR) activity

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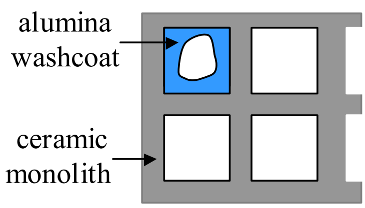
Motivation

- **Three-Way Catalyst**



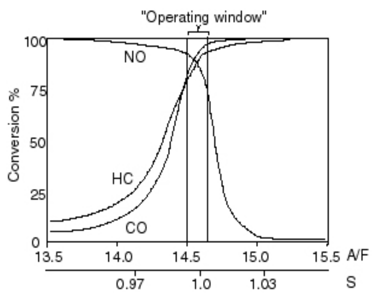
- Oxides: CeO_2, ZrO_2, La_2O_3
- Catalytic Metals: **Rh**, Pd, Pt

- **simultaneous oxidation**

  $CO, HC \longrightarrow CO_2$

- **and reduction**

  $NO_X \longrightarrow N_2$



Ceria: Oxygen Storage

fuel rich: $CO + CeO_2 \longrightarrow CO_2 + Ce_2O_3$

fuel lean: $Ce_2O_3 + O_2 \longrightarrow CeO_2$

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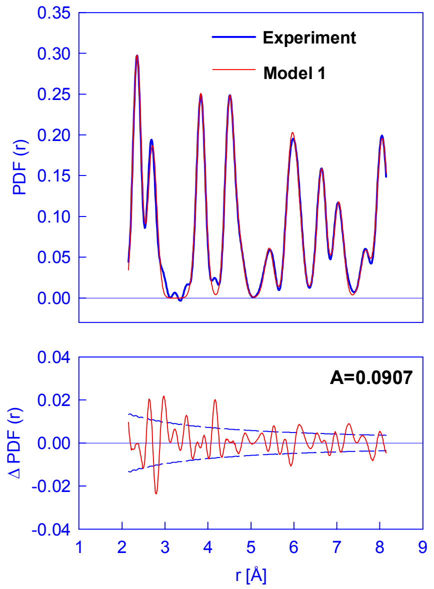

PDF of nano-powder ceria compared to the PDF calculated for the model with interstitial oxygen defects showing much better agreement. The difference is essentially due to noise. The results were confirmed by the Rietveld method.

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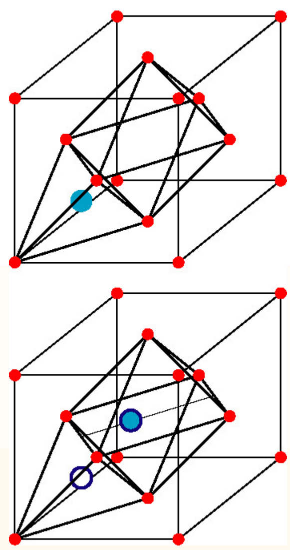
Interstitial Oxygen Model

- **Ce ions form f.c.c. sublattice.**
- **Regular site for oxygen is the tetrahedral site of f.c.c.**
- **Interstitial site is the octahedral site of f.c.c. which is more spacious.**
- **When a reduced sample is oxidized at a low temperature oxygen goes into the octahedral site.**



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Active oxygen

- Perfect ceria crystal is useless for oxygen storage.
- Active oxygen ions are interstitial oxygen ions at the octahedral sites, compensated by oxygen vacancies.
- Density of the defects (interstitials and vacancies) is roughly proportional to OSC.
- High temperature reduction followed by low temperature (~500° C) oxidation produces defect (active) oxygen ions.

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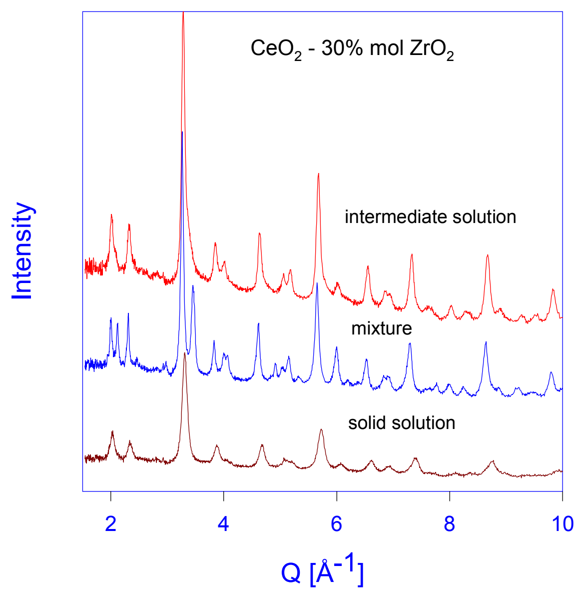
Diffraction pattern: Like solid solution.



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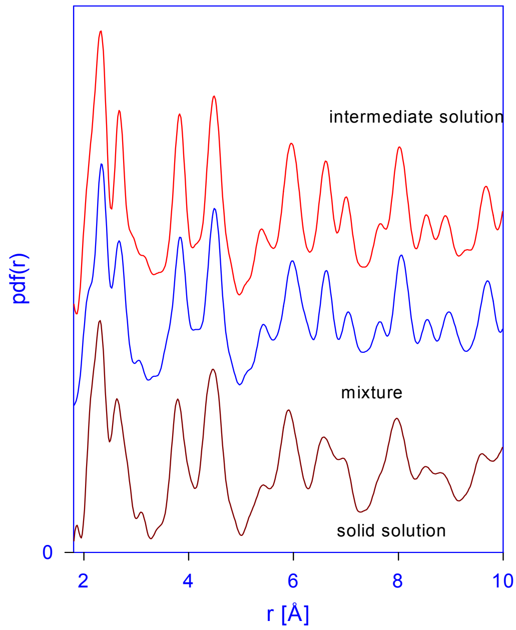
PDF: Looks phase segregated.



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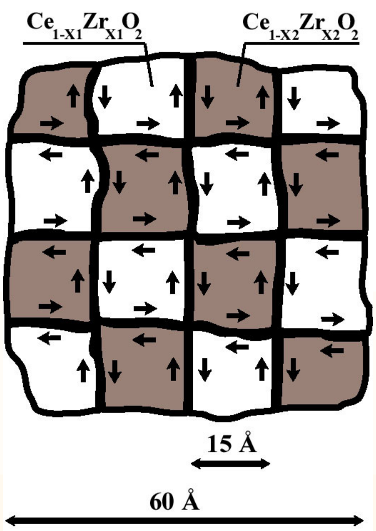
- Nano-domains inside a crystal.
- They provide pathways for oxygen.



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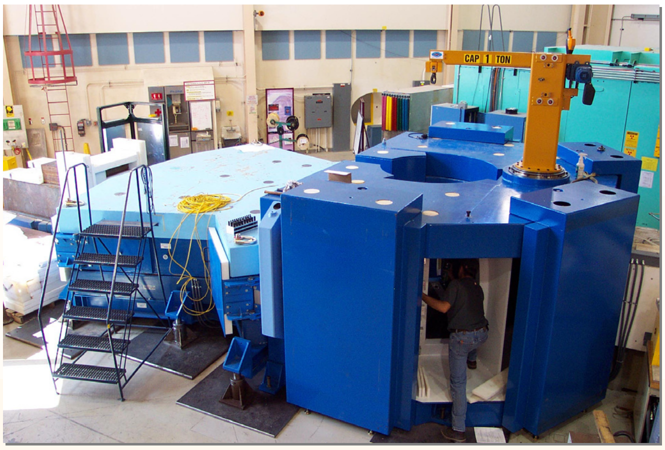
High-resolution pulsed neutron scattering with NPDF, LANSCE, LANL (Th. Proffen)



- High Q resolution ΔQ/Q = 0.0015, high real space resolution for PDF.

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Q-Resolution and the R-Range

- "Resolution" in PDF due to <u^2>:

$$g(r) = \int P(r'-r) g_0(r') dr', \quad P(r) = \sqrt{\frac{1}{u\pi}} \exp\left(-\frac{r^2}{2u^2}\right)$$

- Gives rises to the Debye-Waller factor;

$$D(Q) = \exp\left(-Q^2 u^2\right)$$

- In the same manner the Q-resolution produces the real-space envelope.

$$W(Q) = \exp\left(-r^2 \Delta Q^2\right)$$

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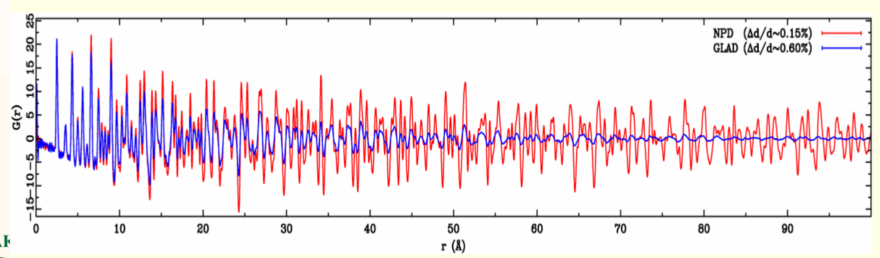
Requirement for Successful PDF Study

- Wide range of Q: Q_{max} > 35 Å^{-1} or more
- High intensity: Total count 10^7 or more
- High Q-resolution: $\Delta Q/Q < 10^{-3}$
- Pulsed neutron, or high-energy X-ray diffraction
  - Incident energy > 100 keV
  - Use of an image plate



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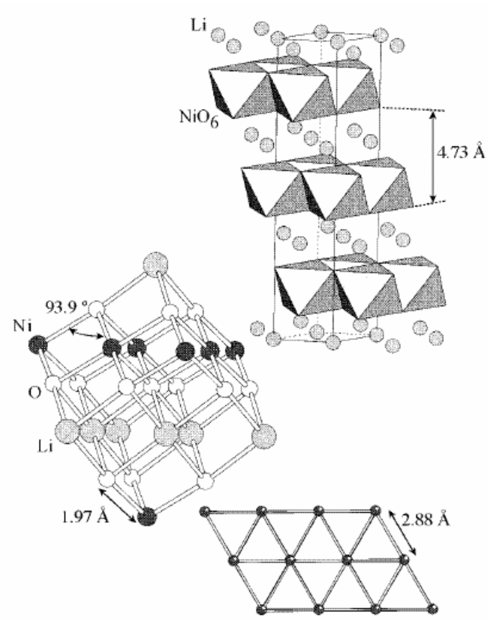
$Li^+Ni^{3+}O^{2-}_2$

- Ni^{3+}: d^7 (low spin state: $S = ½$)
- NiO_6 edge-sharing to form a 2-d layer of triangular **lattice**
- NiO_2^- layer separated by Li^+
- Ni spins frustrated in 2D triangular lattice.



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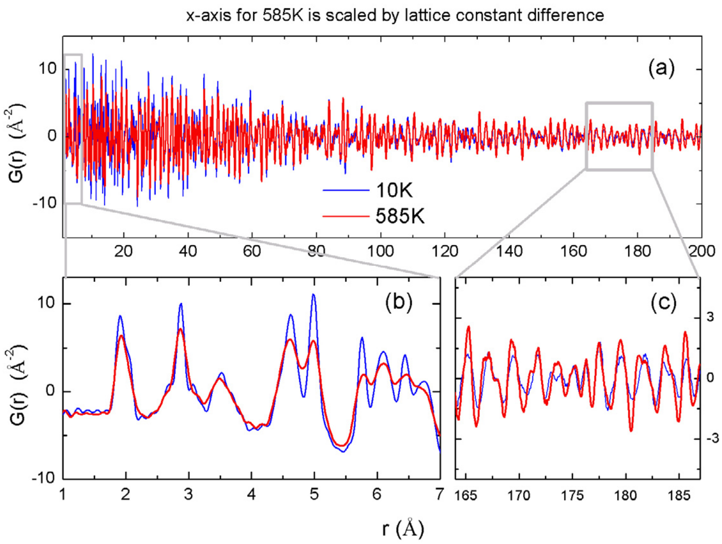
Temperature dependence in the PDF of $LiNiO_2$

PDF Obtained with the NPDF, LANSCE



- **The PDF height depends upon temperature differently at short and long distances.**

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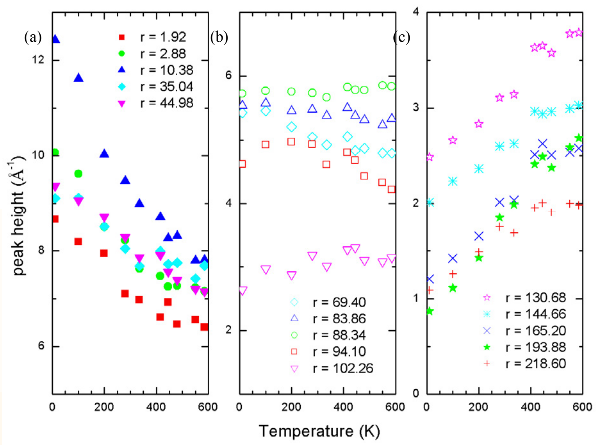
Temperature Dependence

- **For r < 60 Å peak height decreases with T.**
- **For r > 100 Å peak height increases with T.**
- **Local ordering vs. domain formation.**



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Relaxor Ferroelectrics and Dynamic PDF

- Relaxor ferroelectrics: Ferroelectrics with diffuse transition.
- Dielectric relaxation observed below T_{max}.
- Dielectric permittivity smoothly depends upon temperature and frequency; Widely used because of temperature stability.
- Seen only in disordered mixed-ion systems, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN).
  - Mixed valences; Mg^{2+}, Nb^{5+} in PMN, Zn^{2+}, Nb^{5+} in PZN, Pb^{2+}, La^{3+} in $(Pb,La)(Zr,Ti)O_3$ (PLZT).
  - Dilute impurities in high dielectric solid, such as $SrTiO_3$.

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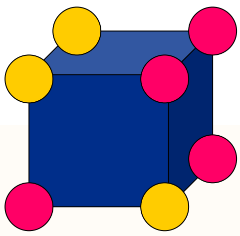
$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)

- Average structure is a simple perovskite, with polarization along (111) resulting in rhombohedral distortion.
- Pb polarization is locally along (100).
- Random Nb^{5+}/Mg^{2+} site occupation.
- Chemical ordering leaves one sublattice randomly occupied (Davies).
- Competition between local chemical disorder and ferroelectricity.



B site occupied by Nb^{5+} and Mg^{2+}.

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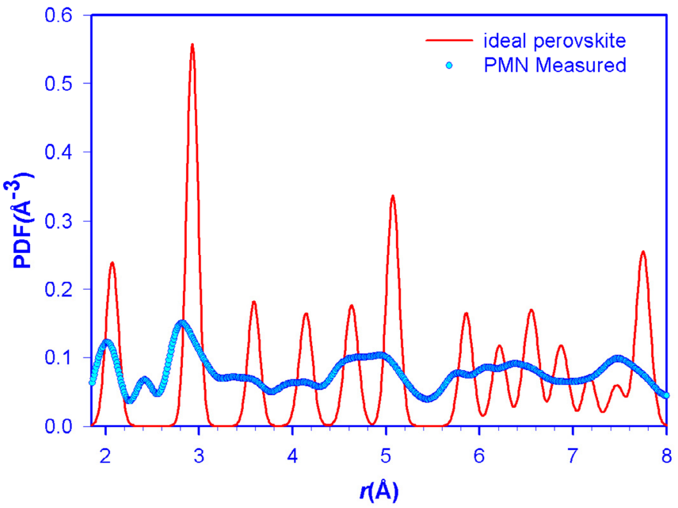

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PDF of PMN

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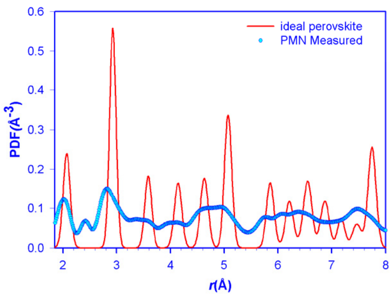
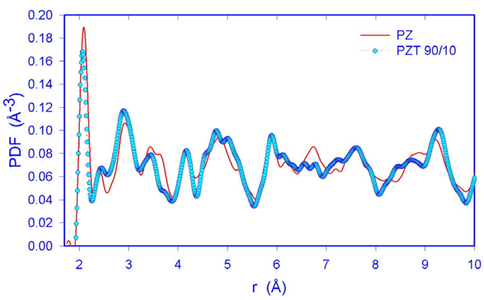
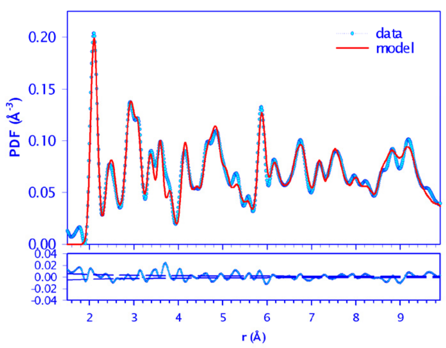
Pb polarization







- PDF of PMN

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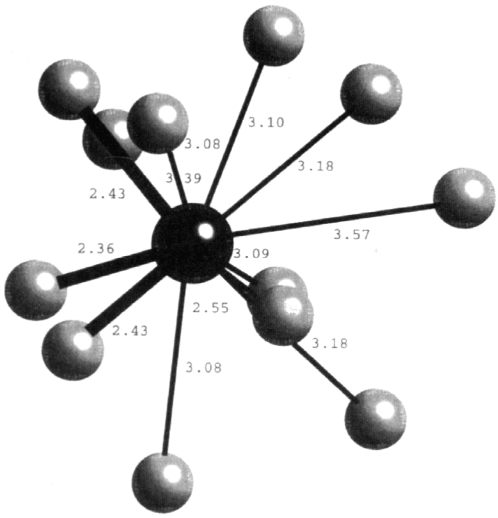
Pb^{2+} in $PbZrO_3$

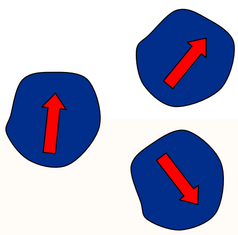


Pb is off-centered by 0.5 Å in the O_{12} cage

Lone-pair *s-p* electrons of Pb

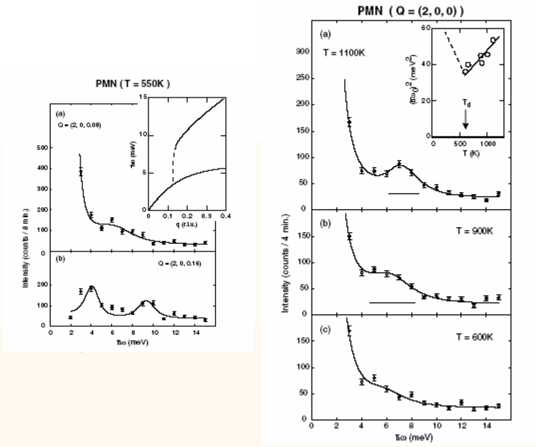
Origin of the Relaxor Behavior

- **Spin-glass behavior: Freezing temperature is ~230K for PMN.**
- **Formation of polar nano-regions (PNRs).**
- **Low-frequency relaxation behavior understood in terms of random interactions among the PNR, by spin-glass models (Kleemann, Glintchuk, Blinc…..).**



Phonon Water Fall

- LO phonons disappear at low Q below T_d.
- Water-fall between T_f anf T_d.
- Consistent with polar nano-regions (PNR).



P. Gehring et al., *PRL* **87**, 277601 (2000).

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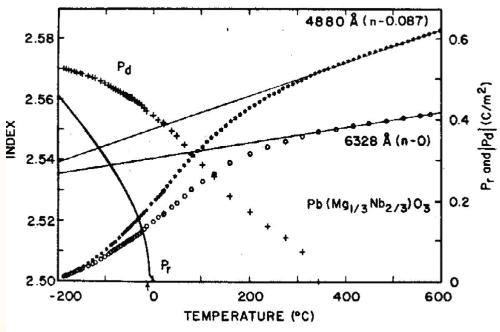
Burns Temperature

- At high-frequency (optical frequency) changes are observed at Burns temperature, Td ~ 600 K for PMN.
- PNR formed only below Td?



G. Burns and F.H. Dacol, Solid State Communications, 48 (1983) 853-856

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Origin of PNR

- **How to observe dynamics of NPR?**
- **How does it depend on T?**
- **Role of atomic level disorder?**
- **Interplay of dynamics and disorder?**

- **Neutron scattering experiment:**
  - Static PDF (instantaneous up to ~ 5 meV)
  - Dynamic structure factor
  - Dynamic PDF **– Dynamics of local structure.**

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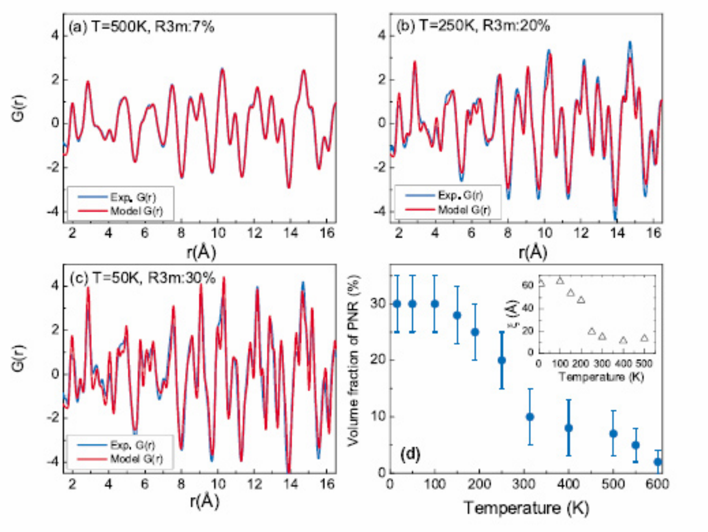

I.-K. Jeong, et al., *PRL* **94,** 147602 (2005).

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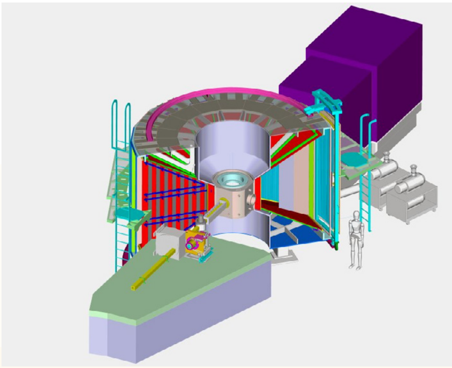
Dynamic PDF by Inelastic Neutron Scattering

- **Fourier-transform of $S(Q,\omega)$ is the** dynamic PDF.
- **$S(Q,\omega)$ has to be determined over large ranges of Q and ω.**
- **Measurement with** PHAROS **(inelastic chopper spectrometer) of LANSCE, Los Alamos NL.**
- **Powder sample 100 grams.**
- **Incident energy 250 meV, covering up to 20 Å^{-1}.**
- **Intensity corrected for absorption, background, multiple scattering and multi-phonon intensity.**



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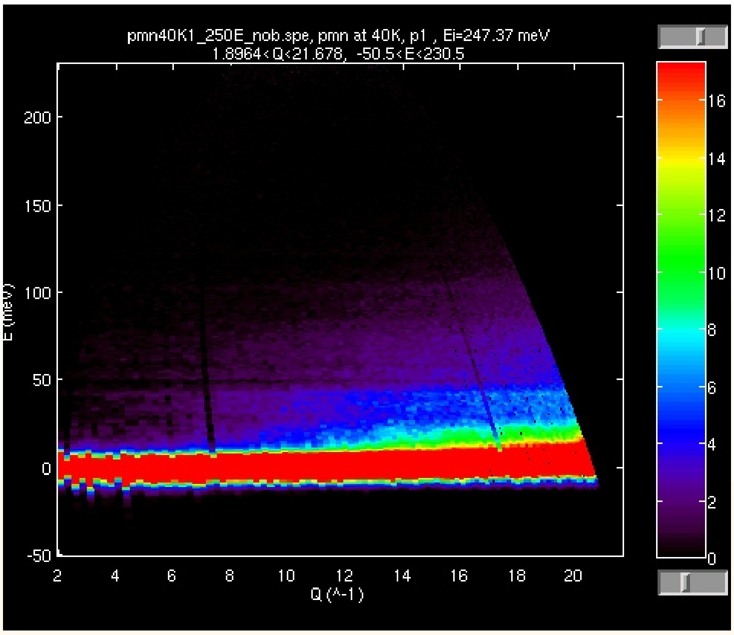

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T = 40 K

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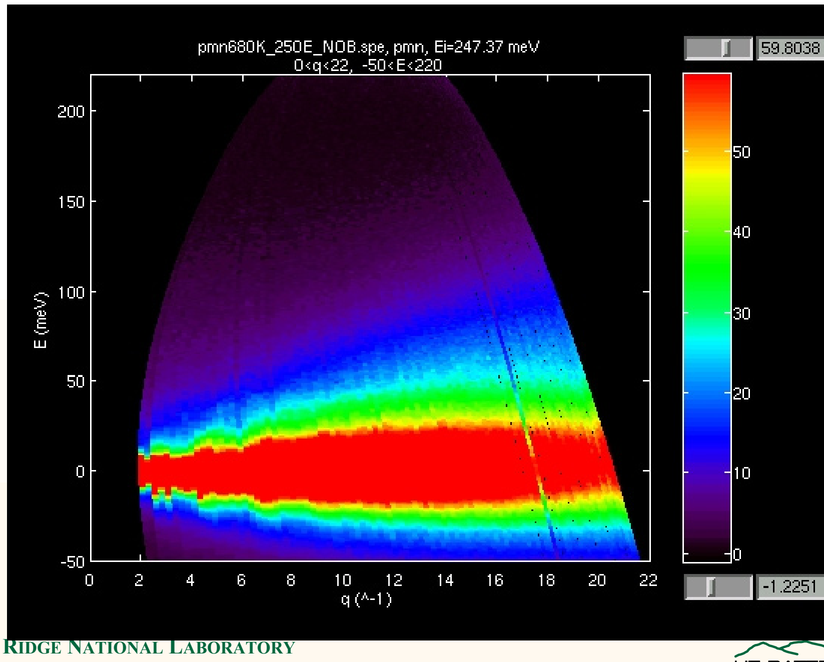

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T = 680 K

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Static PDF

- **Dynamic structure factor:**

$$S(\boldsymbol{Q},\omega)=\frac{1}{N\langle b\rangle^{2}}\sum_{\nu,\mu}b_{\nu}b_{\mu}\int\left\langle\left\langle e^{i\boldsymbol{Q}\cdot\left(\boldsymbol{R}_{\nu}(0)-\boldsymbol{R}_{\mu}(t)\right)}\right\rangle\right\rangle e^{-i\omega t}dt$$

- **Elastic structure factor describes the average structure:**

$$S(\boldsymbol{Q},0)=\frac{1}{N\langle b\rangle^{2}}\sum_{\nu,\mu}b_{\nu}b_{\mu}e^{i\boldsymbol{Q}\cdot\left(\langle\langle\boldsymbol{R}_{\nu}\rangle\rangle-\langle\langle\boldsymbol{R}_{\mu}\rangle\rangle\right)}$$

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Instantaneous PDF

- **Energy integrated structure factor describes the instantaneous (snap-shot) structure:**

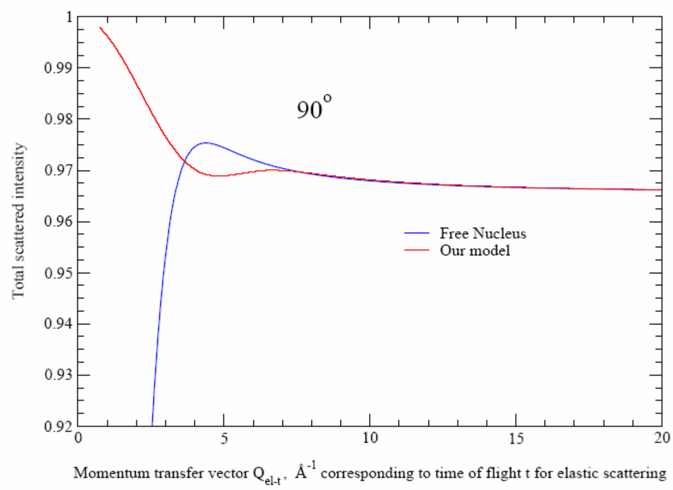
$$S_{total}(\boldsymbol{Q}) = \int_{-\infty}^{\infty} S(\boldsymbol{Q},\omega)d\omega$$
$$= \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \int\int \left\langle\left\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t))}\right\rangle\right\rangle e^{-i\omega t}dtd\omega$$
$$= \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \left\langle\left\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(0))}\right\rangle\right\rangle$$

Inelastic Correction

- **Actual measurement by powder diffractometer**

$$S_{Measured}(\boldsymbol{Q}(0)) = \int_{-\infty}^{\infty} S(\boldsymbol{Q}(\omega),\omega)d\omega$$

- **Correction by the Placzek approximation**
  - **Ballistic collision model, correct at high energies and large *Q*.**
  - **Inaccurate at low energies and low *Q*.**
  - **Particularly problematic at low *Q* (even for liquids) because of the elastic scattering.**
- **Correction by the Debye model**
  - **Calculate the *S*(*Q*(*ω*)) for the Debye model, and integrate for the phonons; mostly multi-phonon terms.**



- **Placzek correction is wrong at low *Q*.**

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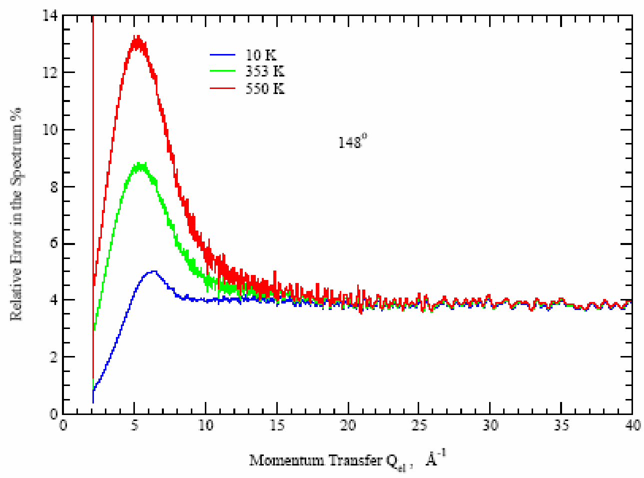

- **Error more serious at high angle and high T.**

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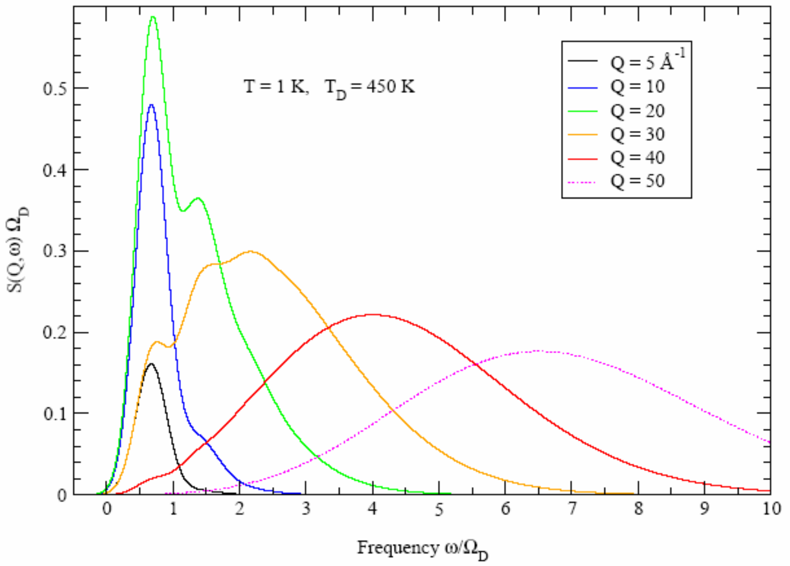

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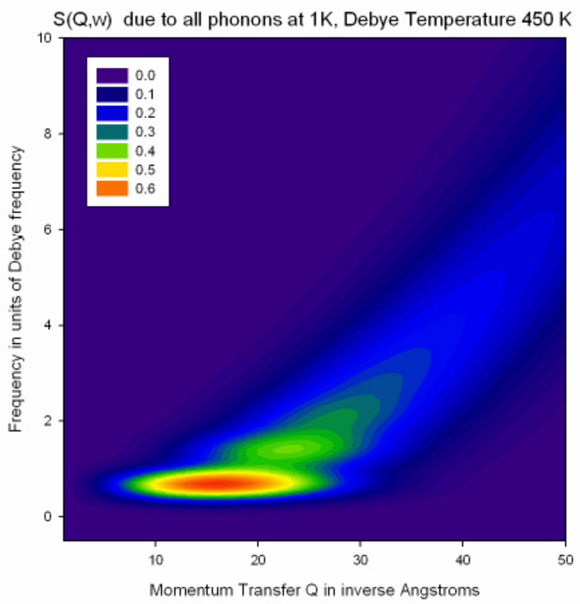

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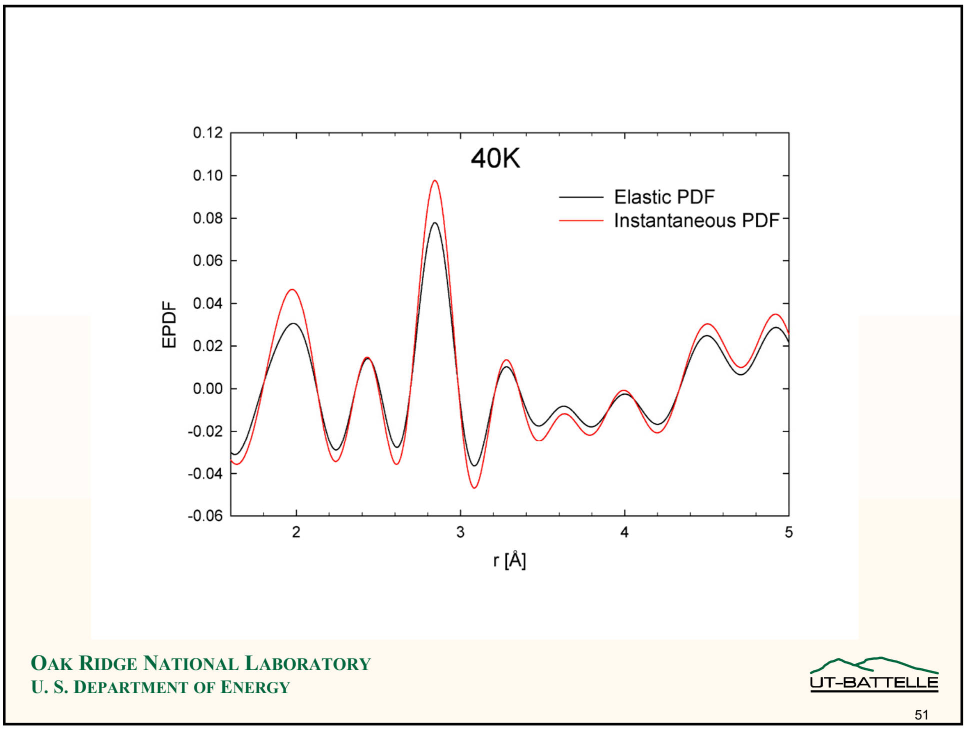
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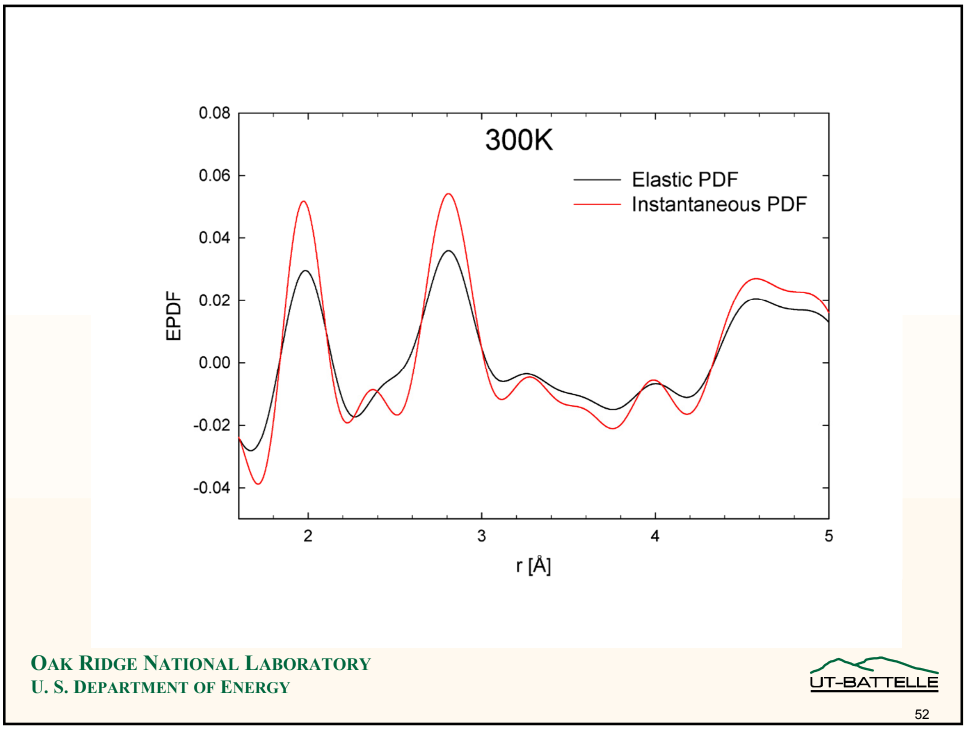
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Case In-Betwen

PHYSICAL REVIEW VOLUME 95, NUMBER 1 JULY 1, 1954

Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

LÉON VAN HOVE
Institute for Advanced Study, Princeton, New Jersey
(Received March 16, 1954)

A natural time-dependent generalization is given for the well-known pair distribution function $g(\mathbf{r})$ of systems of interacting particles. The pair distribution in space and time thus defined, denoted by $G(\mathbf{r},t)$, gives rise to a very simple and entirely general expression for the angular and energy distribution of Born approximation scattering by the system. This expression is the natural extension of the familiar Zernike-Prins formula to scattering in which the energy transfers are not negligible compared to the energy of the scattered particle. It is therefore of particular interest for scattering of slow neutrons by general systems of interacting particles: G is then the proper function in terms of which to analyze the scattering data.

After defining the G function and expressing the Born approximation scattering formula in terms of it, the paper studies its general properties and indicates its role for neutron scattering. The qualitative behavior of G for liquids and dense gases is then described and the long-range part exhibited by the function near the critical point is calculated. The explicit expression of G for crystals and for ideal quantum gases is briefly derived and discussed.

$$\rho(\mathbf{r},t)=\int S(\mathbf{Q},\omega)e^{-i[\mathbf{Q}\cdot\mathbf{r}-\omega t]}d\mathbf{Q}dt=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\delta\left(r-\left[\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t)\right]\right)$$

$$S(\mathbf{Q},t)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\left\langle\left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t))}\right\rangle\right\rangle$$

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Dynamic PDF

$$\rho(\mathbf{r},\omega)=\int\rho(\mathbf{r},t)e^{i\omega t}dt$$
$$=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\int\delta\left(r-\left[\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t)\right]\right)e^{i\omega t}dt$$

$$\mathbf{R}_\nu(t)=\langle\langle\mathbf{R}_\nu\rangle\rangle+\mathbf{u}_\nu(t),$$
$$\mathbf{u}_\nu(t)=\int\mathbf{u}_\nu(\omega)e^{-i\omega t}d\omega$$

$$\rho(\mathbf{r},\omega)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\delta\left(r-\left[\langle\langle\mathbf{R}_\nu\rangle\rangle-\langle\langle\mathbf{R}_\mu\rangle\rangle\right]+\left\langle\left\langle\mathbf{u}_\nu(\omega)-\mathbf{u}_\mu(\omega)e^{i\theta}\right\rangle\right\rangle\right)$$
$$+O(2\omega)+O(3\omega)+\ldots\ldots\ldots$$

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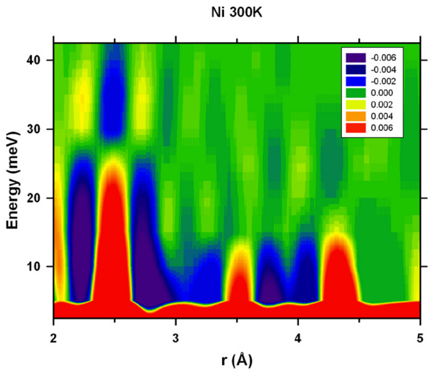
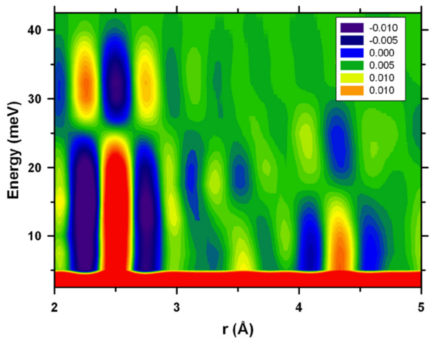
Phonons in Ni





Measured DPDF **Simulation**

- **Only local phonons near the saddle points are observed.**

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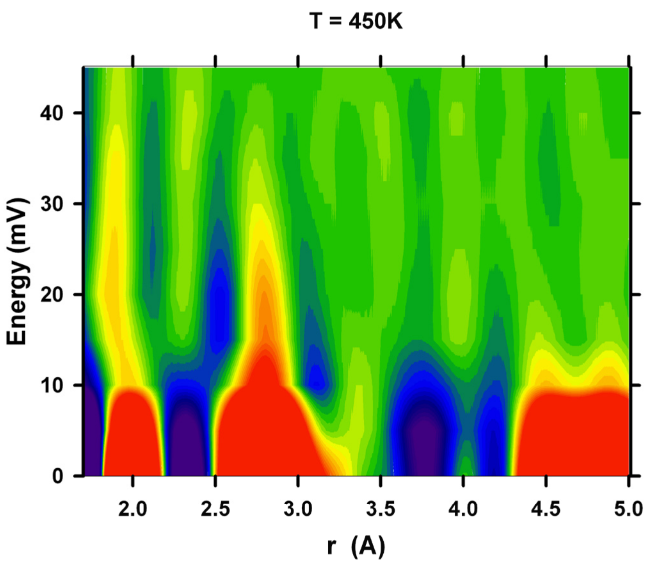
Dynamic PDF



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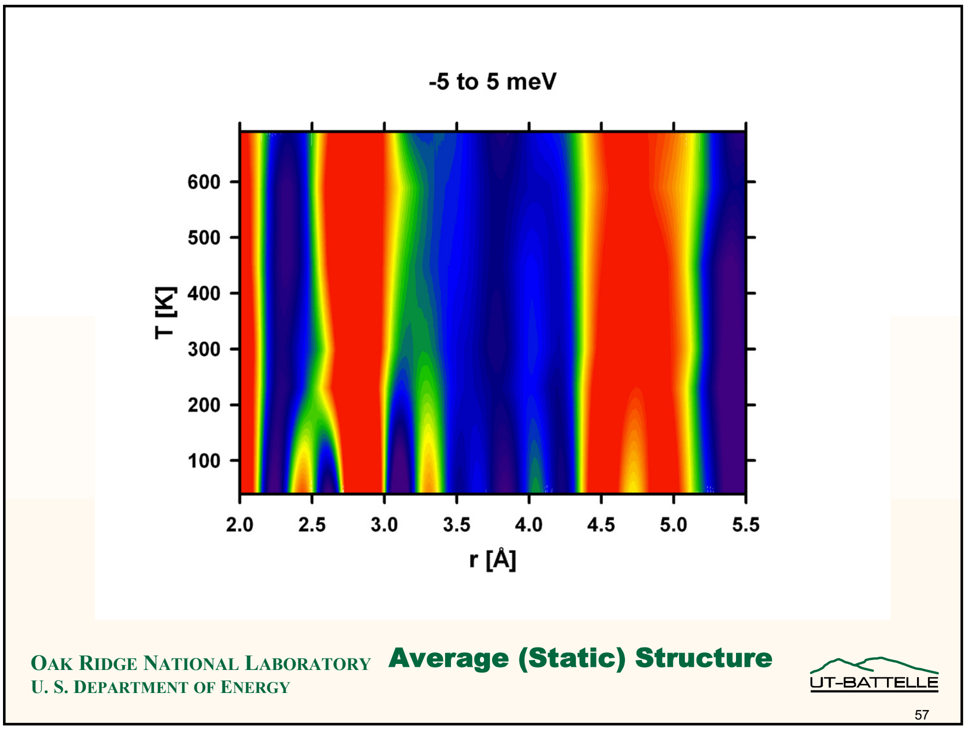
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Average (Static) Structure
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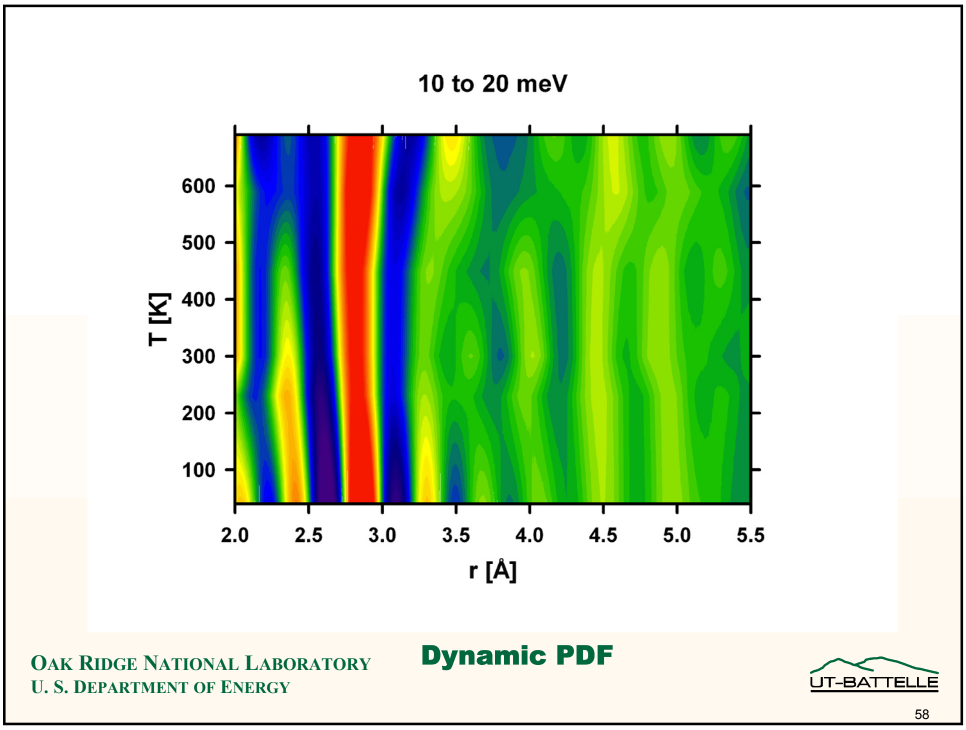
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Dynamic PDF Method

- **Describes local dynamics (lattice or spin).**
- **Local dynamics of atoms in liquids and glasses, certain types of chemical reaction, atomic transport in fast ionic conductors.**
- **Powerful tool for ARCS (SNS) and MERLIN (ISIS).**
- **Potential for wide use.**

Conclusions

- **Bragg's law saved us from hard work, but in the absence of periodicity we are forced to do hard work.**
- **Even for crystalline solids finding the lattice structure often is not enough to understand their properties, particularly for complex solids.**
- **Competing forces can create deviations from periodicity.**
- **Seeing atomic correlation is the best way to understand the structure of aperiodic systems.**
- **Static as well dynamic PDF determined by pulsed neutron or high-energy x-ray scattering are the powerful methods to investigate these complex materials.**