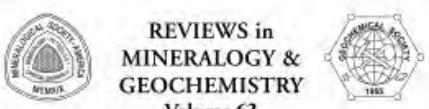


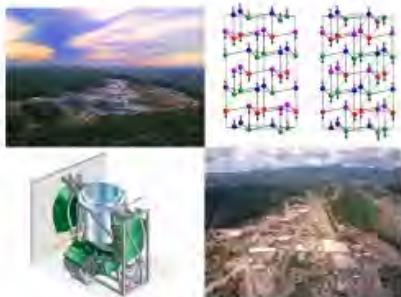
# Analysis of Disordered Materials Using Total Scattering and the Atomic Pair Distribution Function



REVIEWS in  
MINERALOGY &  
GEOCHEMISTRY  
Volume 63

**NEUTRON SCATTERING  
IN EARTH SCIENCES**

EDITOR: Hans-Rudolf Wenk



GEOCHEMICAL SOCIETY  
MINERALOGICAL SOCIETY OF AMERICA

Series Editor: Jodi J. Rosso

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Thomas Proffen

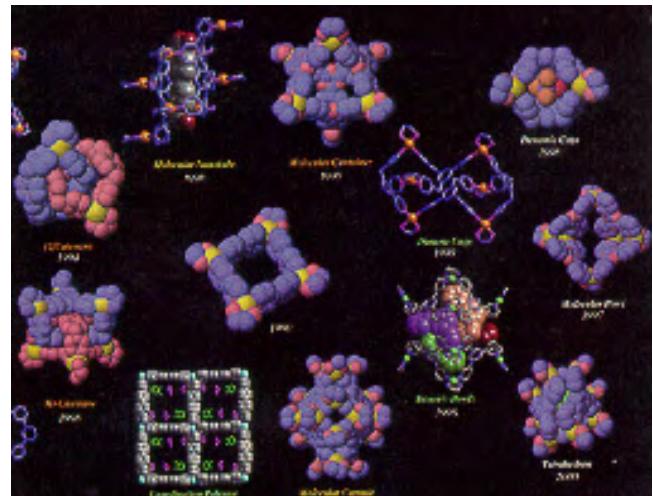
[tproffen@lanl.gov](mailto:tproffen@lanl.gov)

LA-UR 05-1010

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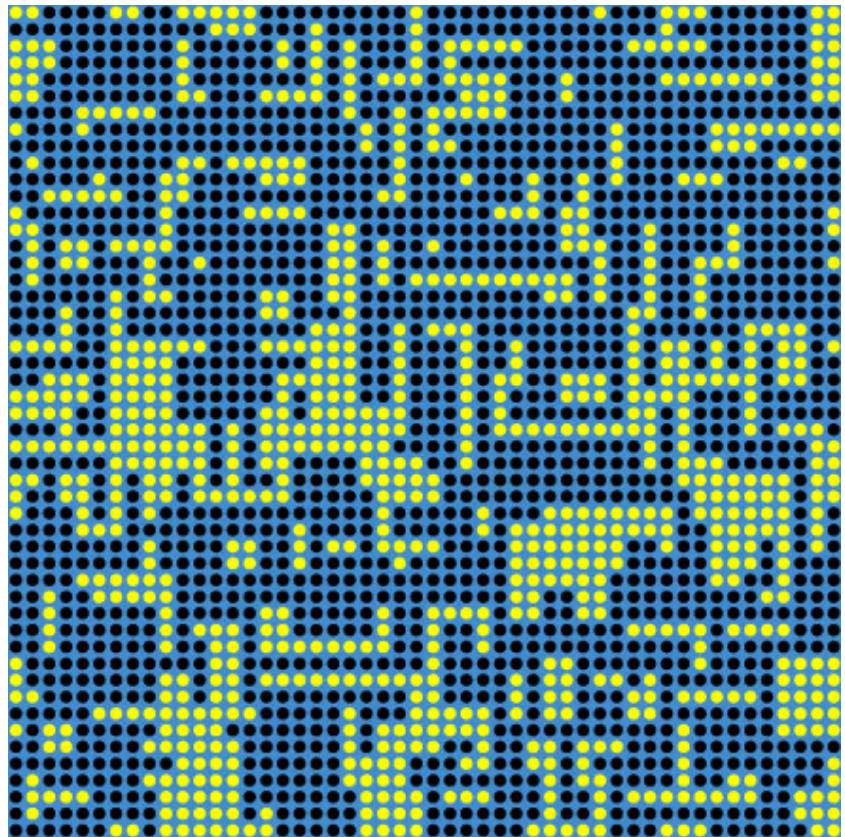
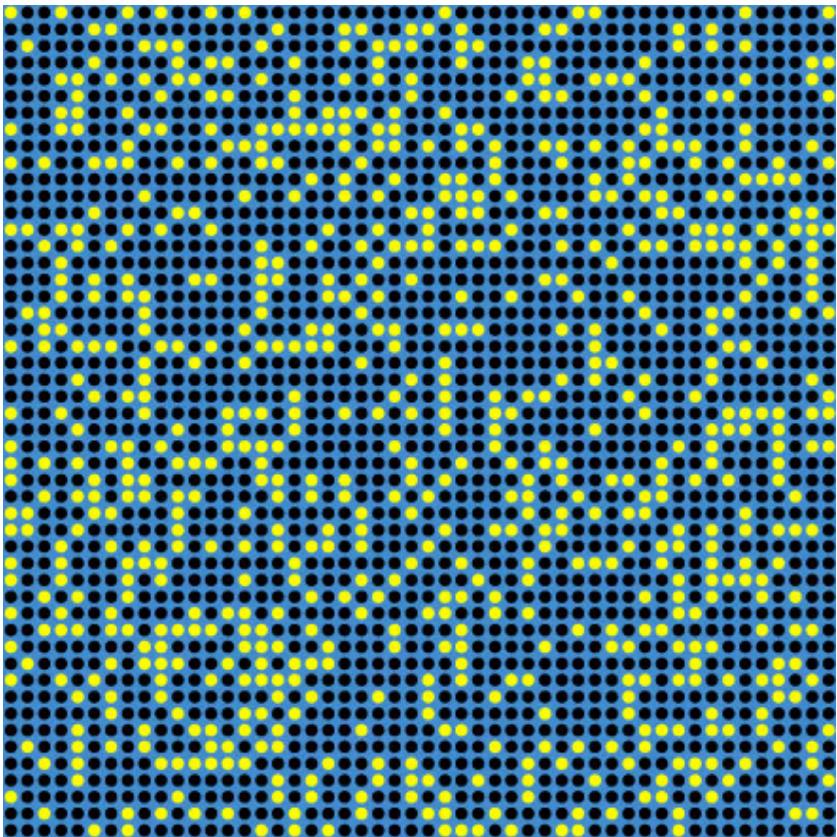
# The challenge of *real* materials

- Traditional crystallographic approach to structure determination is insufficient or fails for
  - Non crystalline materials
  - **Disordered materials:** The interesting properties are often governed by the defects or local structure !
  - **Nanostructures:** Well defined local structure, but long-range order limited to few nanometers (-> badly defined Bragg peaks)
- An approach to determine **local** and **nano-scale** structures is needed.



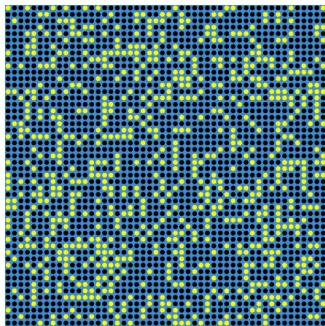
Nanostructures: *Science* (290) 2000

# Total scattering ?

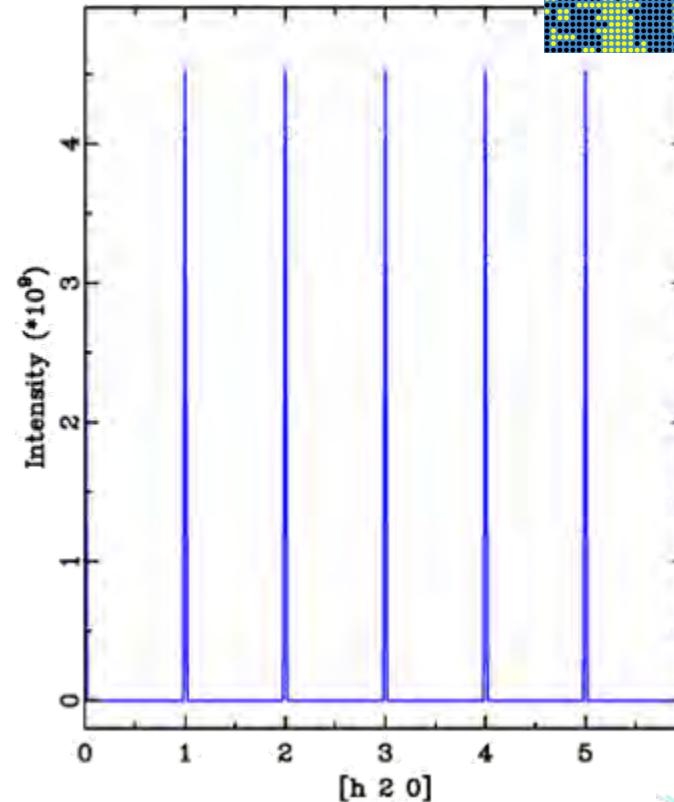
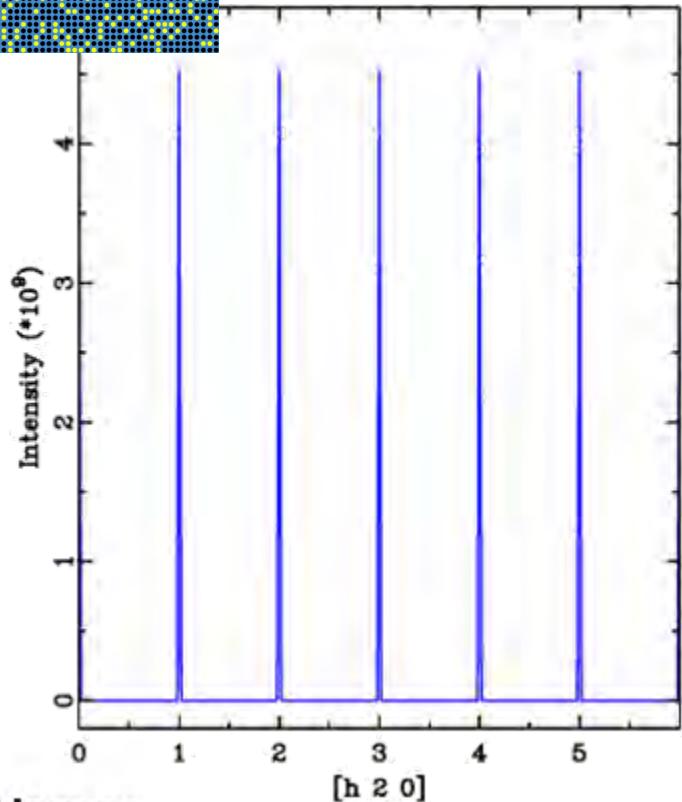
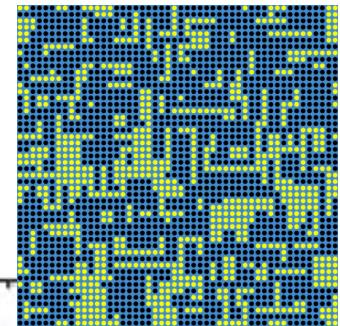


Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% vacancies !  
Properties might depend on vacancy ordering !!

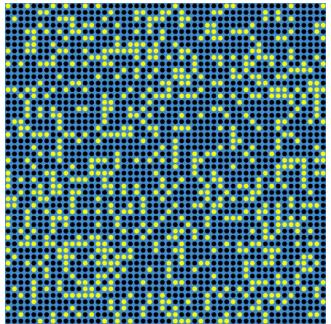
# Bragg peaks are blind ..



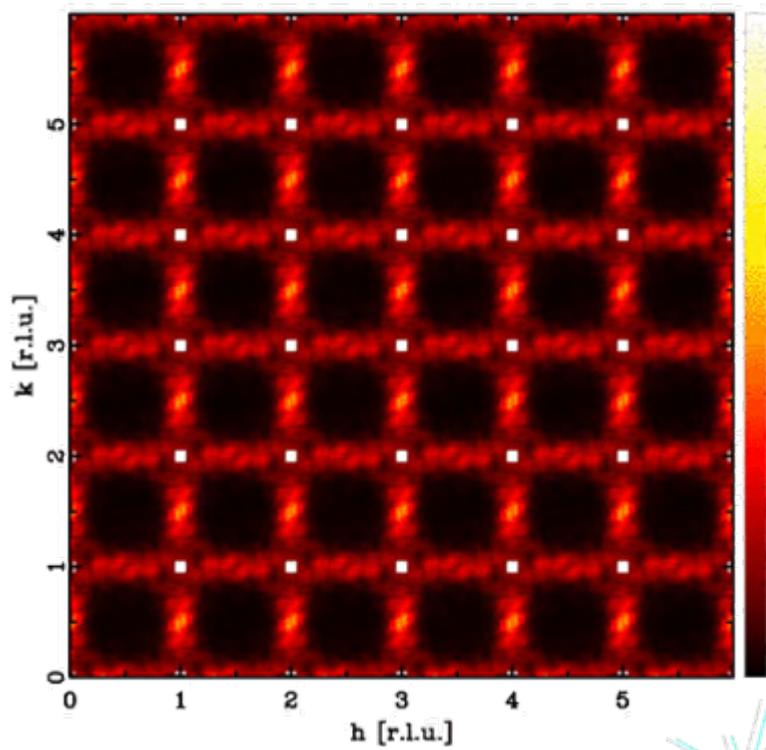
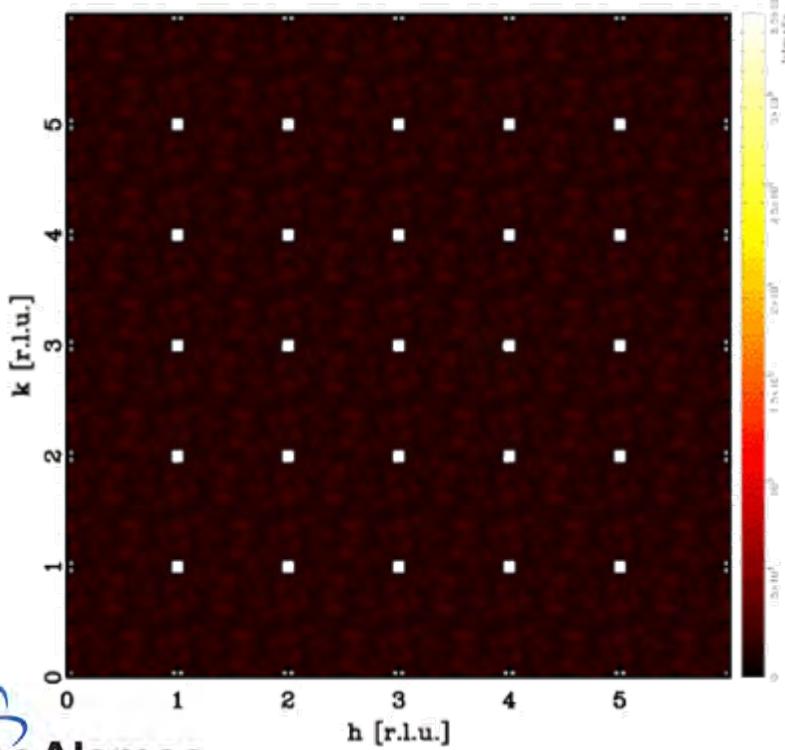
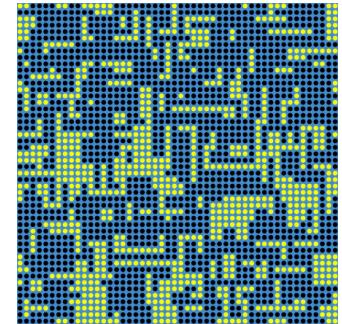
**Bragg scattering:** Information about the average structure, e.g. average positions, displacement parameters and occupancies.



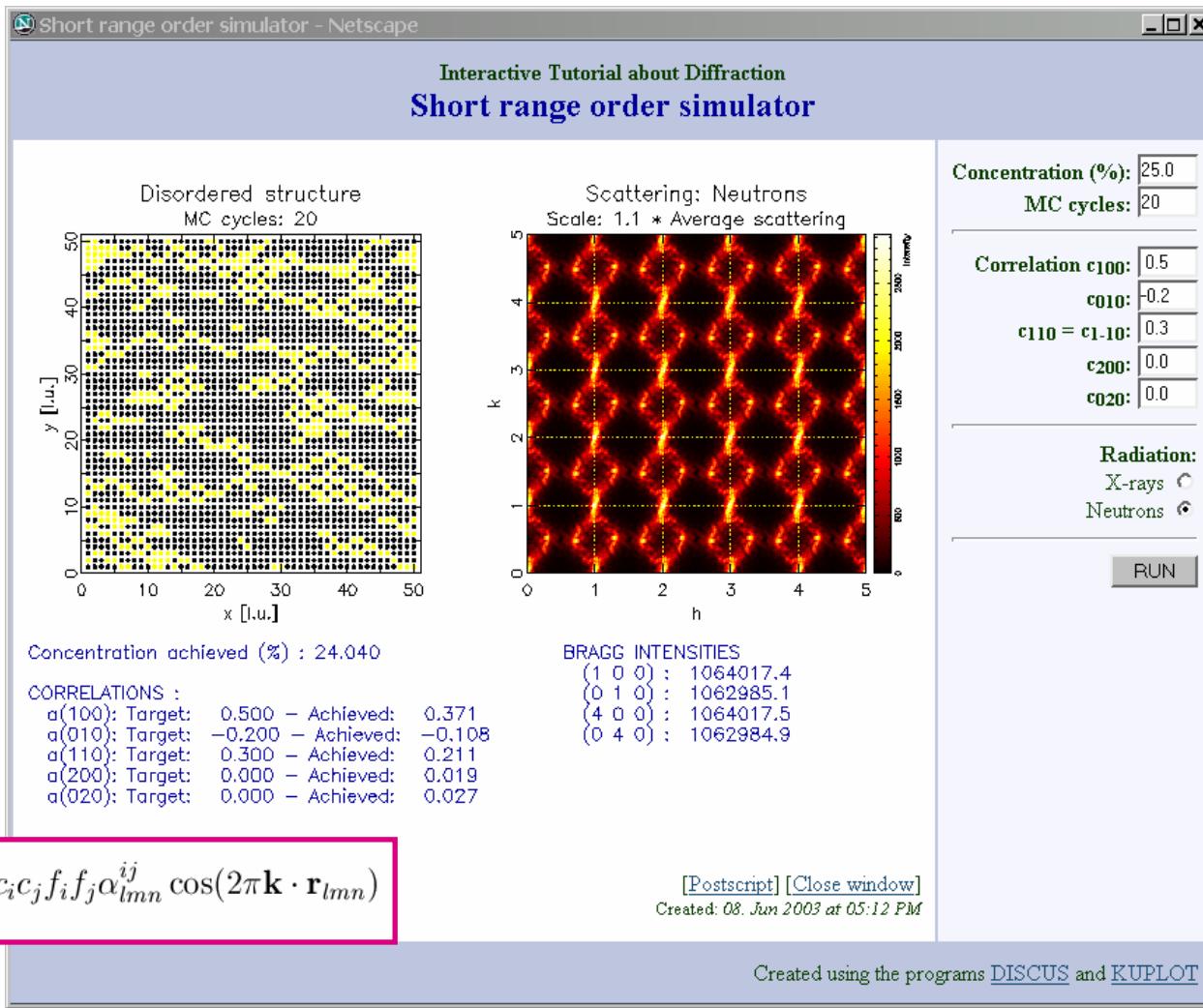
# Diffuse scattering to the rescue ..



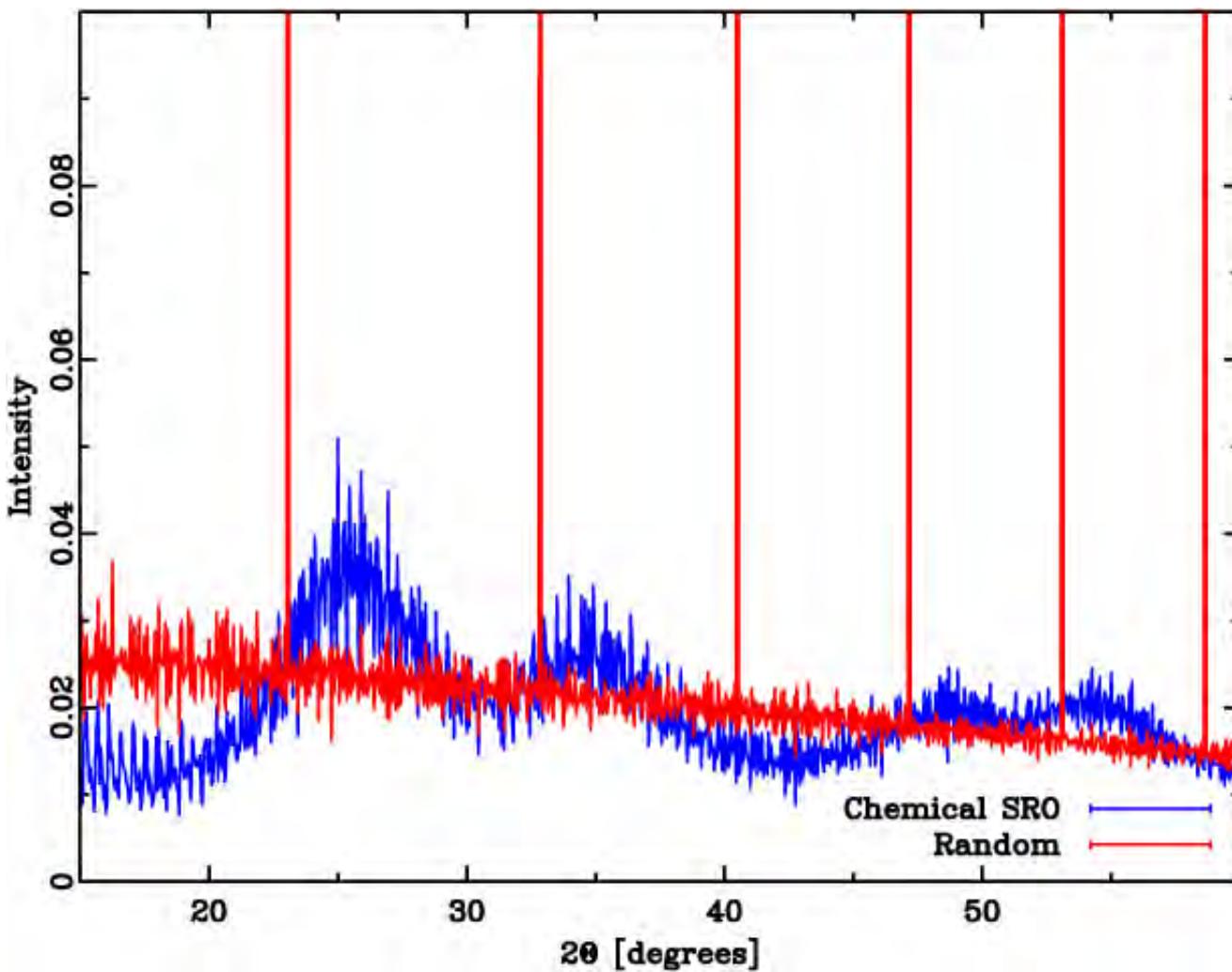
**Diffuse scattering:** Information about *two-body correlations*, i.e. chemical short-range order or local distortions.



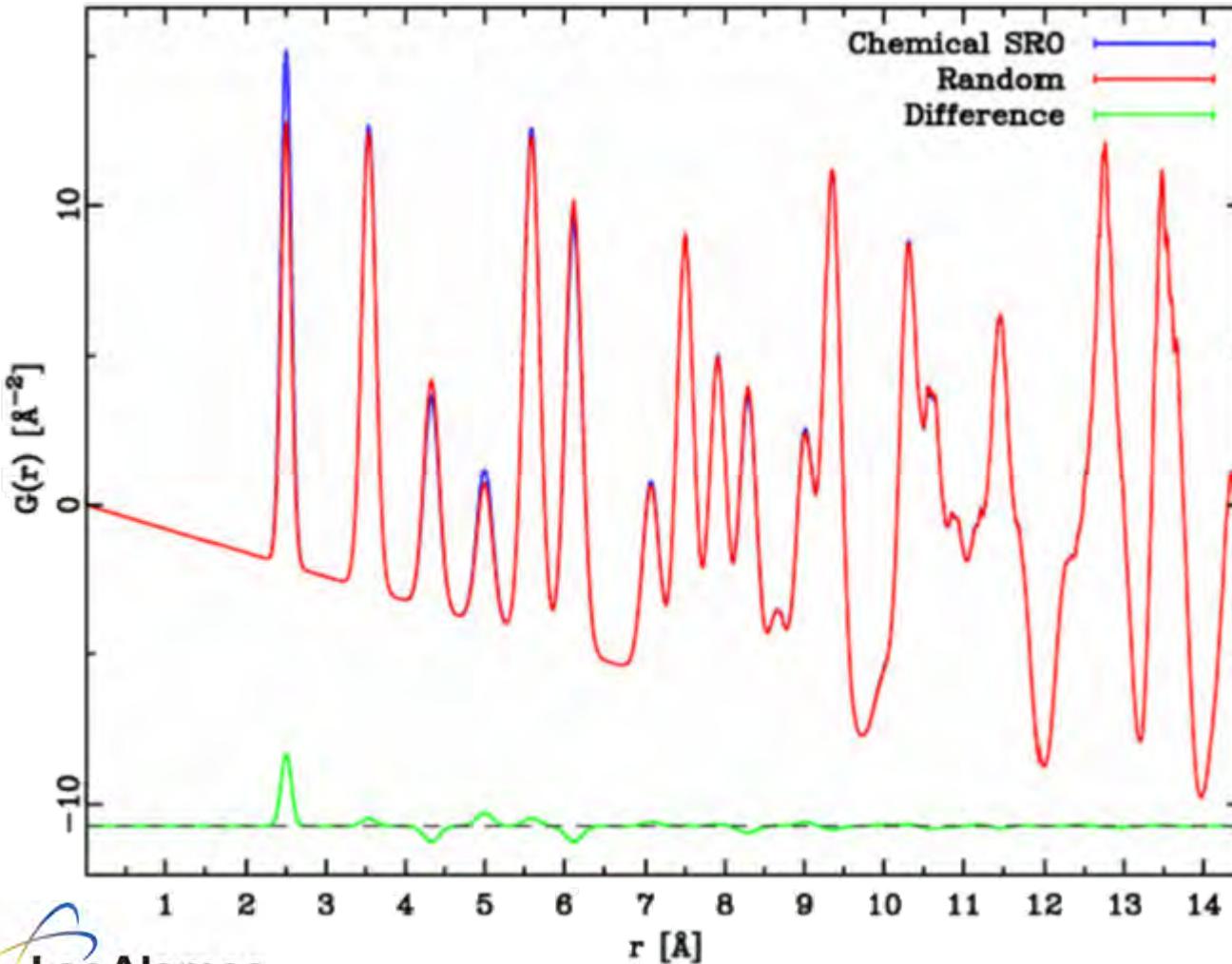
# See <http://www.totalscattering.org/teaching/>



# How about powder diffraction ?



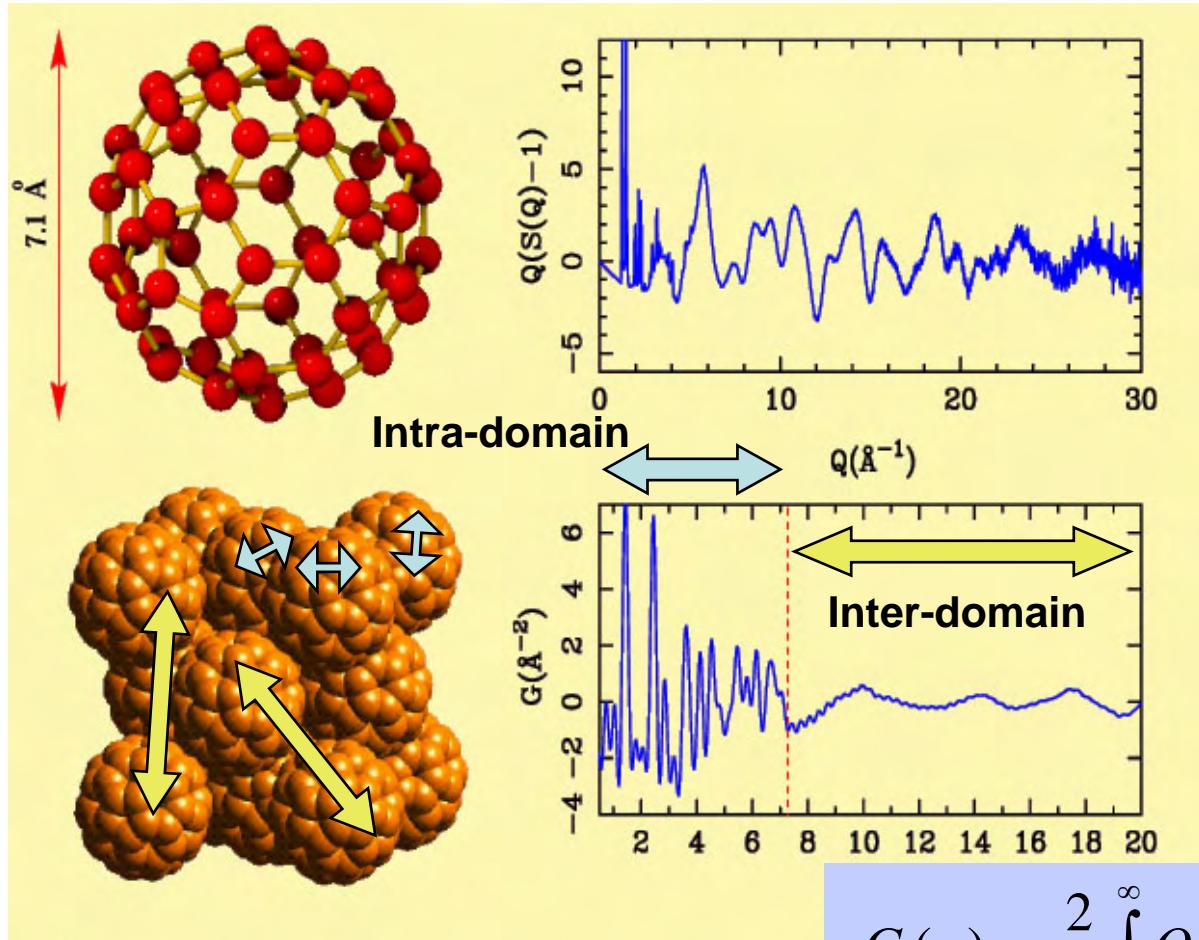
# Finally the Pair Distribution Function (PDF)



The PDF is the Fourier transform of the total scattering diffraction pattern !

Proffen, Z. Krist, 215,  
661 (2000)

# What is a PDF?



**Example:**  
**C<sub>60</sub> - 'Bucky balls'**

The PDF (similar to the Patterson) is obtained via Fourier transform of the **normalized total scattering S(Q)**:

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q [S(Q) - 1] \sin(Qr) dQ$$

$$Q = 4\pi \sin\theta/\lambda$$

# Instruments and Software

# What is required to obtain high quality PDFs ?

The PDF (similar to the Patterson) is obtained via Fourier transform of the **normalized total scattering**  $S(Q)$ :

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q [S(Q) - 1] \sin(Qr) dQ$$

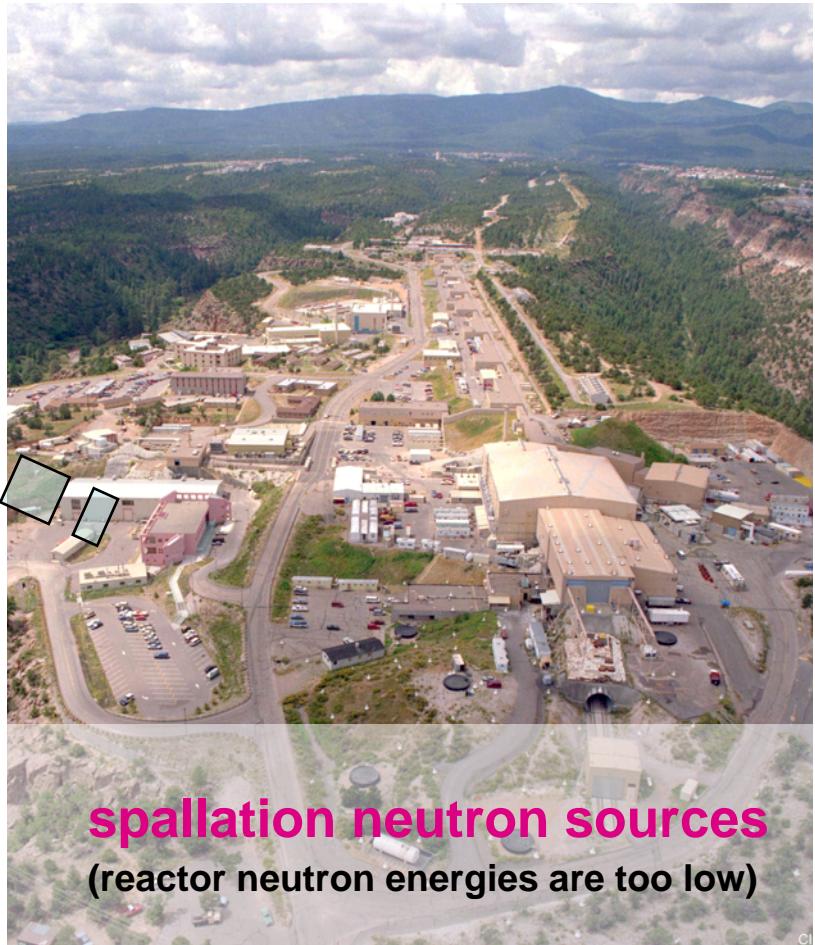
## **Requirements to obtain 'good' PDF:**

- High maximum momentum transfer,  $Q_{\max}$ .
- High Q-resolution.
- Good counting statistics @ high Q.
- Low instrument background

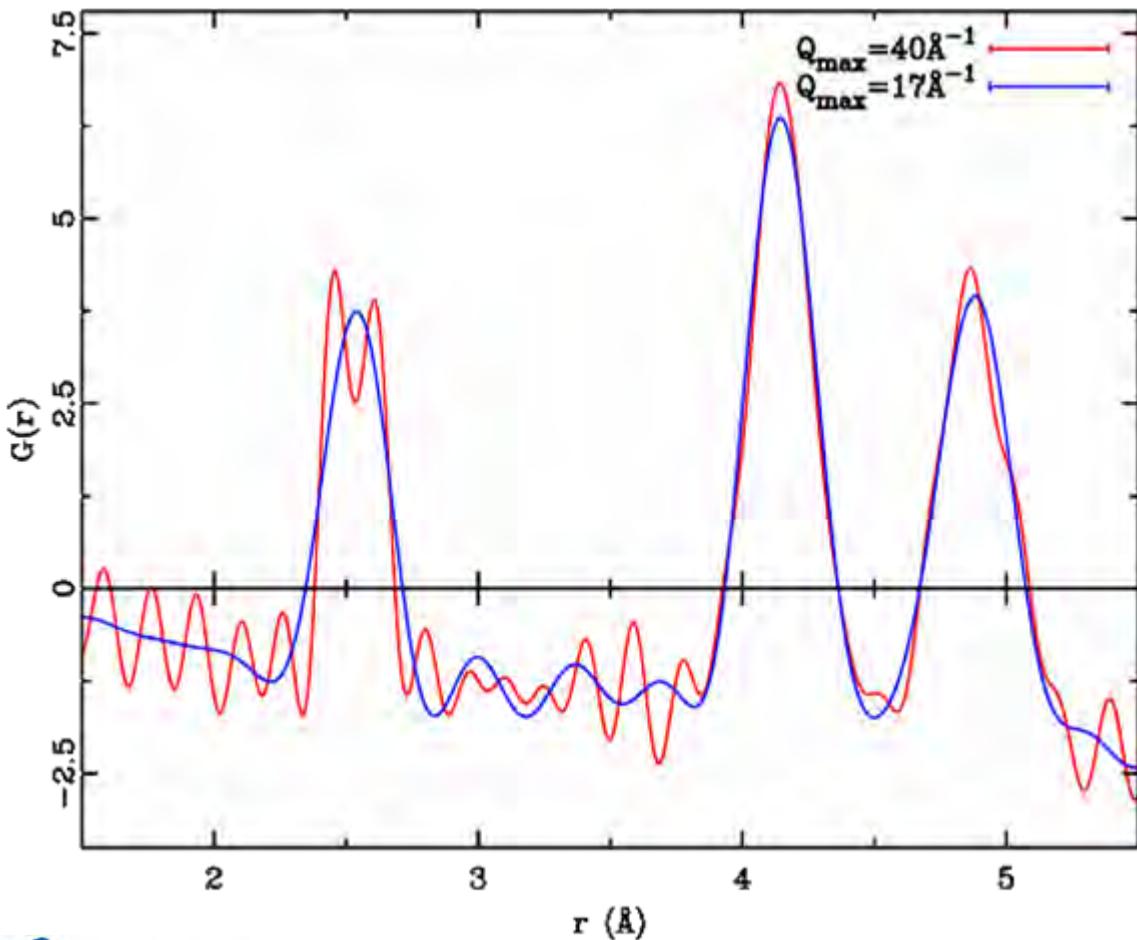
## **Where ?**

**Synchrotron sources**  
(high energy X-rays)

or



# What makes a good PDF: Influence of $Q_{\max}$ ...

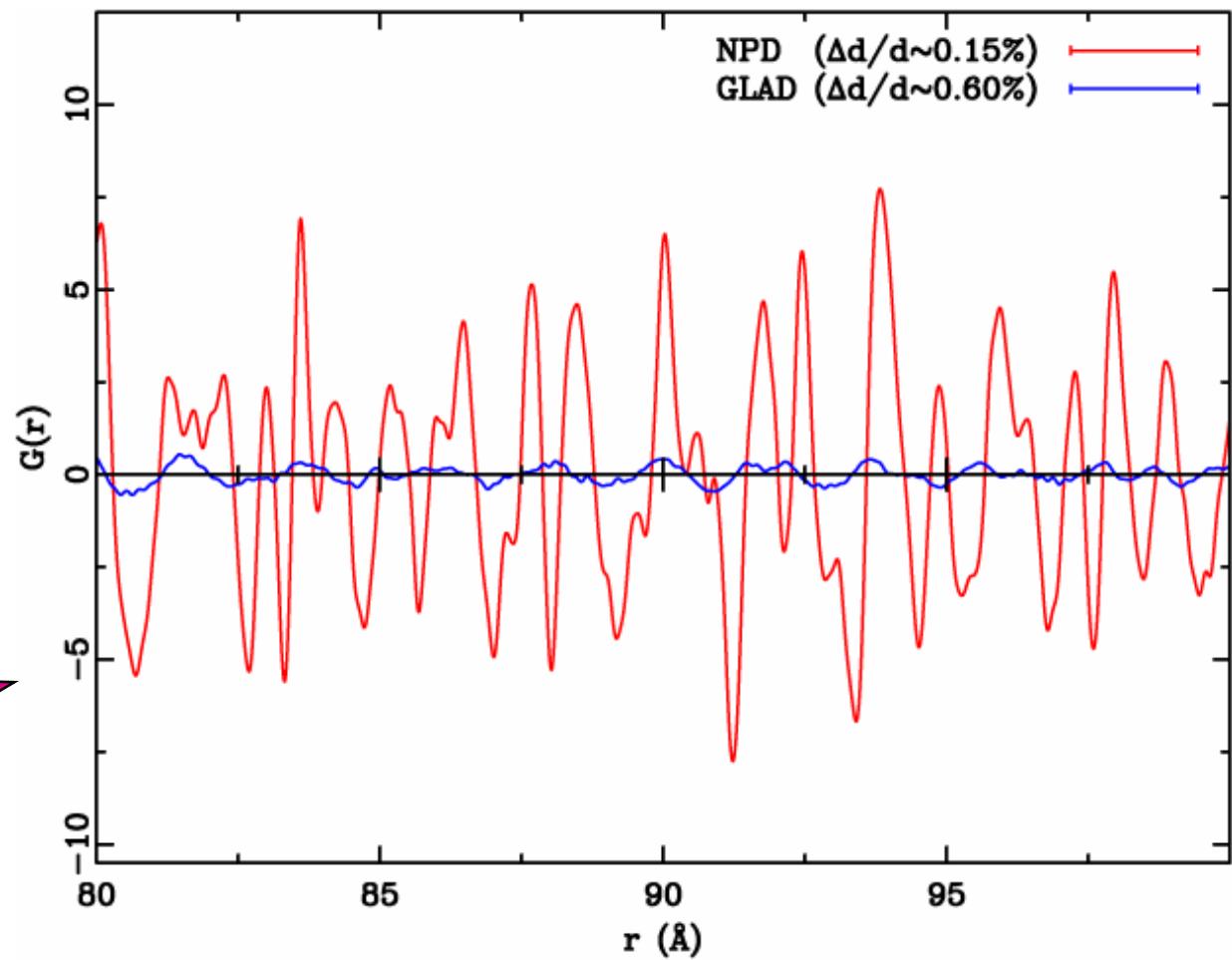


Termination of integral  
at  $Q_{\max}$  results in  
convolution of  $G(r)$  with  
 $\sin(Q_{\max} r)/r$ .

ZnSe<sub>0.5</sub>Te<sub>0.5</sub> data  
collected on GEM  
terminated  
at  $40 \text{ \AA}^{-1}$  and  $17 \text{ \AA}^{-1}$   
NN split unresolved  
at  $17 \text{ \AA}^{-1}$  !

# What makes a good PDF: Influence of Q resolution ...

Comparison of measurements of Nickel powder on instruments  
GLAD at IPNS and NPD at MLNSC.



High Q resolution: Large  $r$  range (PDF damped by  $\exp -(r\Delta Q)^2/2$ )

# NPDF: Overview

- **Specifications**

- Upgrade finished Sep. 2002
- L1: 32m,  $Q_{\max} = 50 \text{\AA}^{-1}$ ,  $\Delta d/d = 0.15\%$
- Typical PDF measurement 1 - 4 hrs
- Sample amounts down to 200 mg
- Ancillary: 10K-1500K, soon: 0.5K, 11T

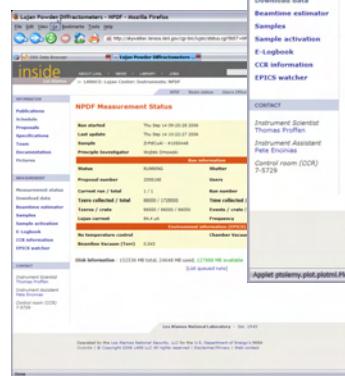


- **Science**

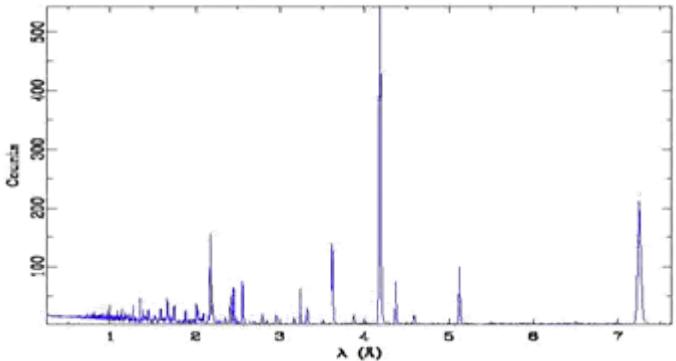
- 95% PDF studies, hard matter
- Many users *new* to PDF
- Oversubscription in 2006: ~1.6

- **Software**

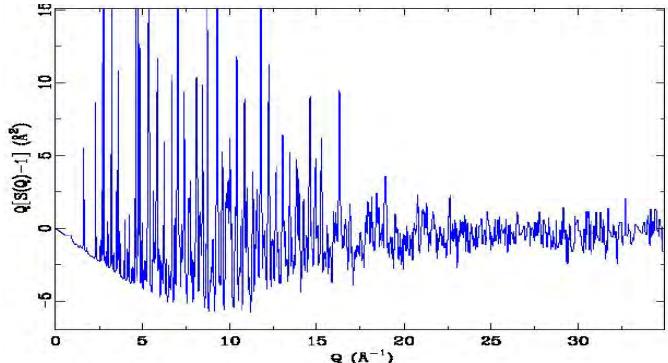
- Web based instrument interface
- Automatic creation of PDF
- Integration in SNS data portal (soon)



# Neutron data processing



Corrections,  
Normalization, ..

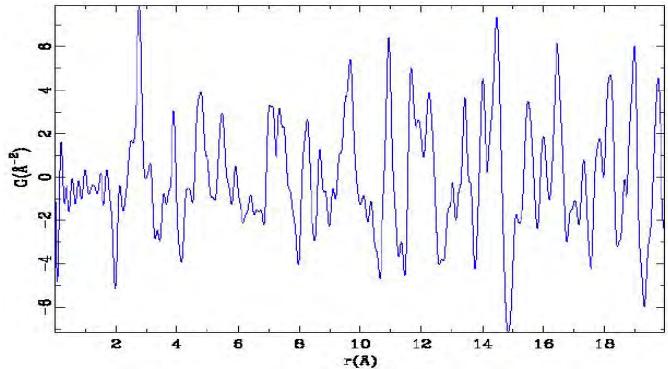
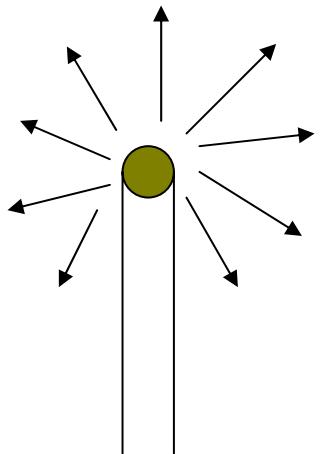


$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q)-1] \sin QrdQ$$

Cylindrical Time-Of-Flight geometry  
(energy dispersive)

Typical characterization runs

- Empty instrument (B)
- Empty Container (C)
- Empty Container background (CB)
- Vanadium (V)
- Vanadium background (VB)
- Sample (S)

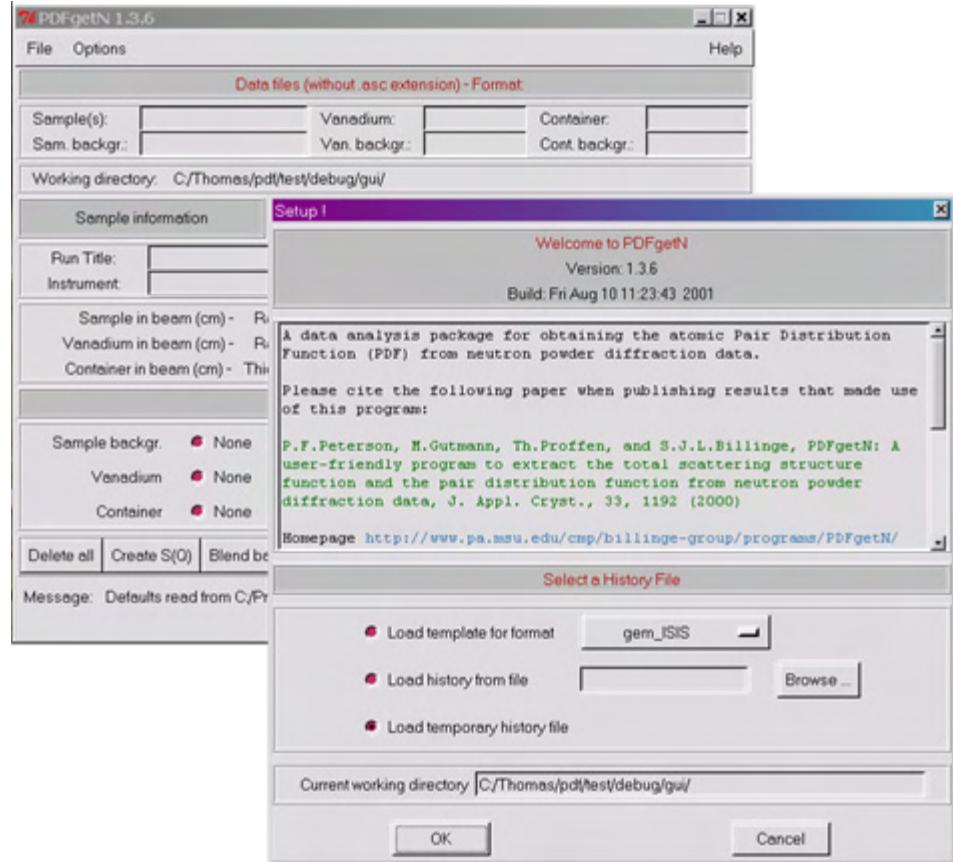


$$S_{corr} = [(S-SB) - \alpha(C-CB)]/[V-VB]$$

# PDFgetN

---

- Based on GLASS package.
- Graphical users interface & integrated plotting.
- Supports most TOF neutron powder file formats.
- Records all processing parameters as part of output files G(r) and S(Q).
- Runs on Windows 95/98/NT/2000 and UNIX



Peterson et al., *J. Appl. Cryst.* **33**, 1192 (2000)

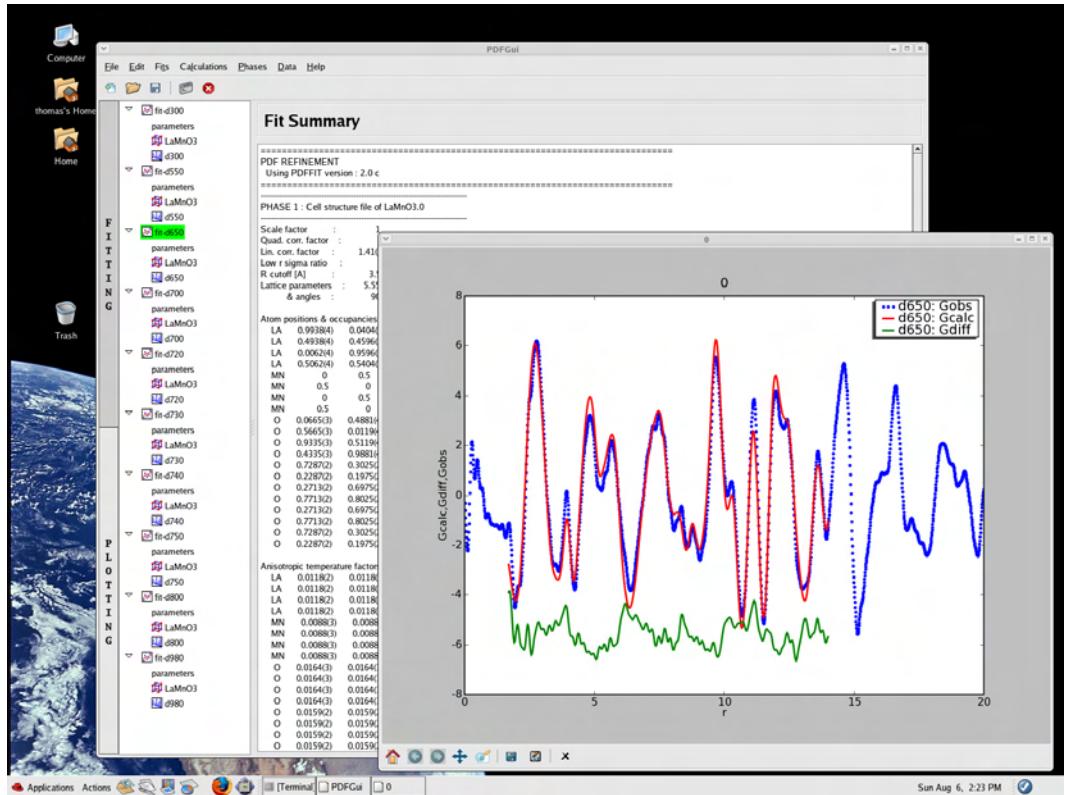
# How to model PDF data ?

---

- Single peak fitting
  - PDF peak position / widths as function of T,x,P,..
  - PDF peak widths as function of r  $\Rightarrow$  correlated motion, ..
- Modeling based on structural model
  - Comparison to average crystal structure
  - **DISCUS:** Large model systems, using e.g. RMC
  - **PDFFIT:** ‘Real space Rietveld’ (few unit cells)
- Compare to theoretical predictions
  - let the theorist do the work ..

# Next generation PDFFIT (under development)

- PDFFIT2 and PDFgui
- Part of the DANSE project.
- NSF award of ~\$12M.



[http://wiki.cacr.caltech.edu/danse/index.php/Main\\_Page](http://wiki.cacr.caltech.edu/danse/index.php/Main_Page)

# Downloads

---

<http://discus.sourceforge.net>

<http://pdfgetn.sourceforge.net>

DISCUS Package Home Page - Mozilla Firefox  
File Edit View Go Bookmarks Tools Help  
EPD3C10 DISCUS Package Home Page  
August 23, 2006

DISCUS SIMULATION PACKAGE

WELCOME TO THE DISCUS HOMEPAGE

Welcome to the new homepage for the DISCUS program package. We are now hosting the programs on Source Forge and hope you like the added features, such as mirror download sites all over the world.

The DISCUS package consists of four programs, each of which could be used independently or in combination. The first program in the package is DISCUS itself and the development started some 15 years ago by Reinhard Neder. DISCUS is a general program to generate disordered atomic structures and compute the corresponding experimental data such as single crystal diffuse scattering or the atomic pair distribution function (PDF). Features include symmetry operations, Monte Carlo simulation capabilities and the generation of domain structure to name just a few.

The second program is called PDFFIT. It is used for full profile refinements of the PDF based on an atomic structure. The program uses least squares and employs a very powerful way to implement constraints. Recently we have added a graphical users interface for simple refinements.

The next program is DIFFEV. This is a generic minimization program using an evolutionary algorithm. It is designed to work with the other programs in the package.

Finally the package contains a general plotting program called KUPLOT.

Thomas Proffen, Reinhard Neder and Simon Billinge

PDFgetN Home Page - Mozilla Firefox  
File Edit View History Bookmarks Tools Help  
Lujan Budget Lujan Forum  
PDFgetN Home Page UCSC - Directions to Core West ...  
December 4, 2006

PDFgetN Neutron Totalscattering Processing

WELCOME TO THE PDFgetN HOMEPAGE

Welcome to the new homepage for the PDFgetN program. We are now hosting the programs on Source Forge and hope you like the added features, such as mirror download sites all over the world.

PDFgetN is used to process scattering data from time-of-flight neutron (TOF) diffractometers (such as [INDF](#) at the [Lujan Neutron Scattering Center](#)) to obtain the normalized structure function,  $S(Q)$ , and the atomic pair distribution function,  $G(r)$ .

The program can read data from all TOF neutron powder diffractometers that can create GSAS type files. All processing parameters are set via web forms. Existing data can also be imported again into the program. The program is controlled via a graphical users interface but can also be used in batch mode. PDFgetN is based on the GLASS package developed at the [Intense Pulsed Neutron Source](#).

The PDFgetN team:  
Peter Peterson, Matthias Gutmann  
Thomas Proffen, Simon Billinge

# Examples

# Local atomic strain in $\text{ZnSe}_{1-x}\text{Te}_x$

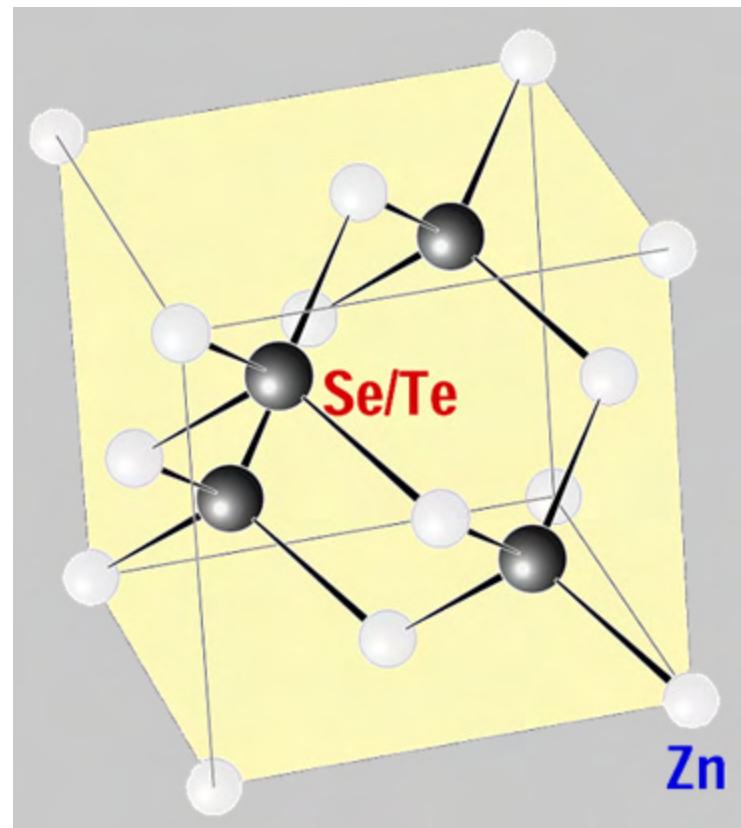


Simon Billinge  
Thomas Proffen (LANL)  
Peter Peterson (SNS)

Facilities: IPNS, Lujan  
Funding: DOE, NSF

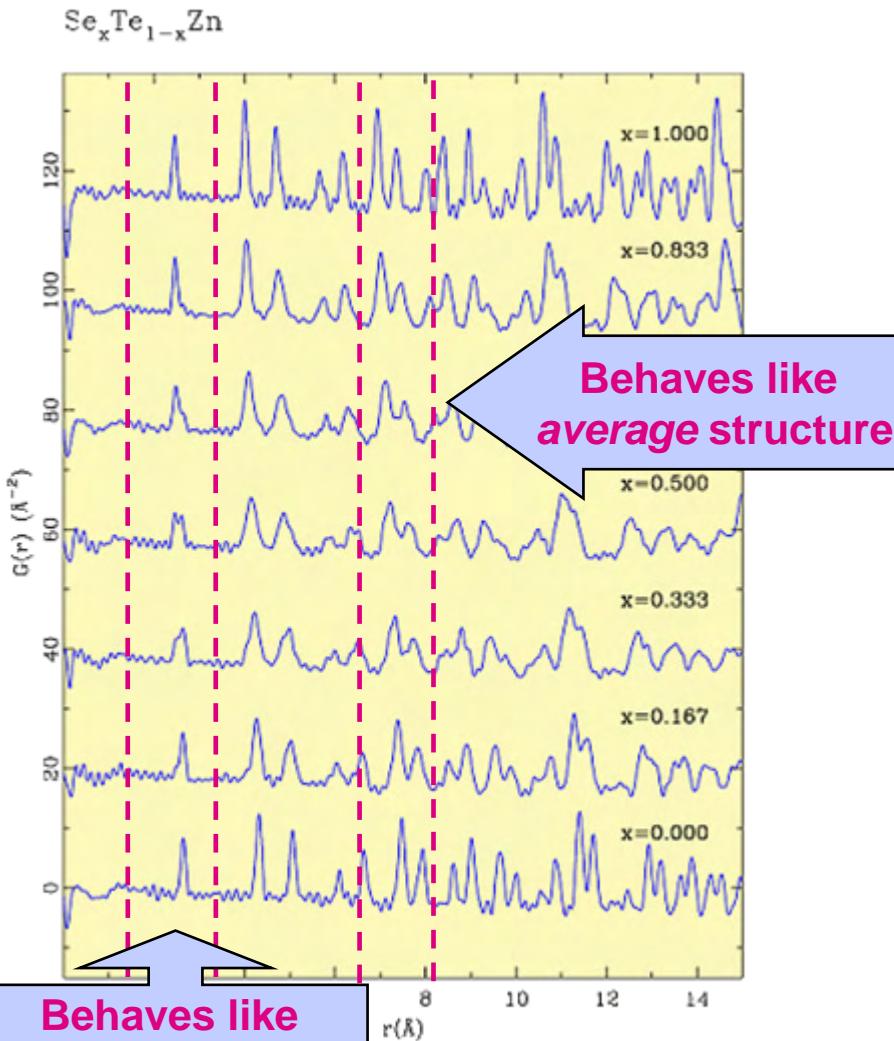
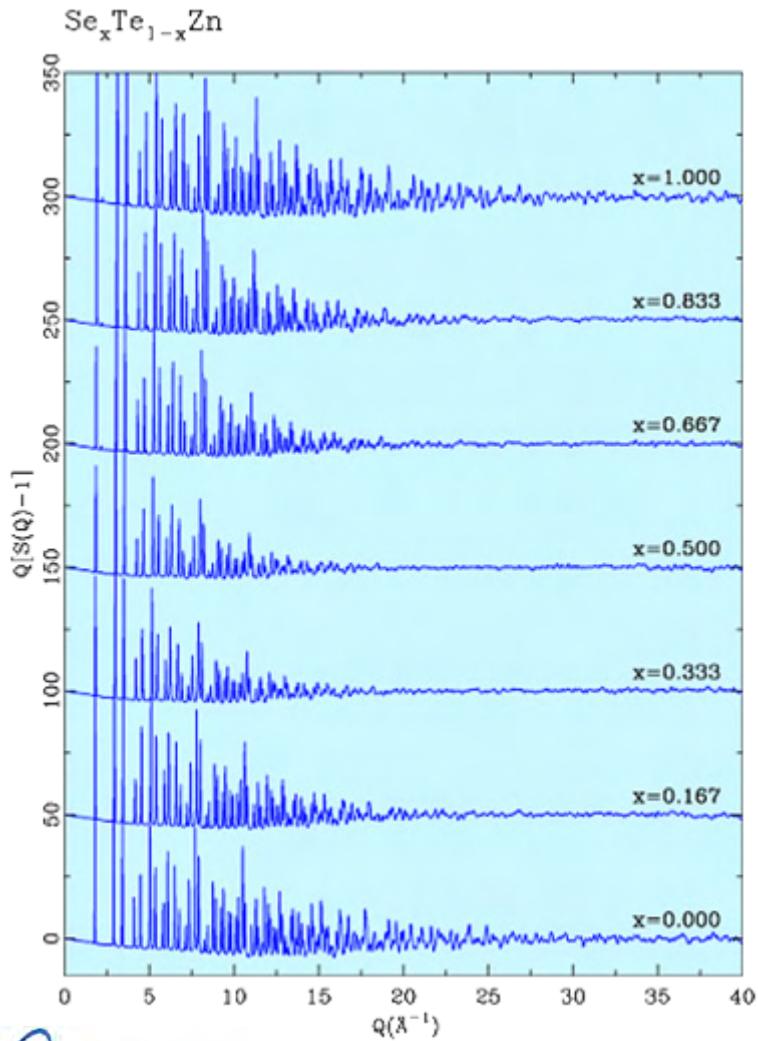
# ZnSe<sub>1-x</sub>Te<sub>x</sub> : Structure

- Zinc blend structure (F43m)
- Technological important : Electronic band gap can be tuned by the composition x.
- Bond length difference Zn-Se and Zn-Te ⇒ strain.
- Local structural probe required !



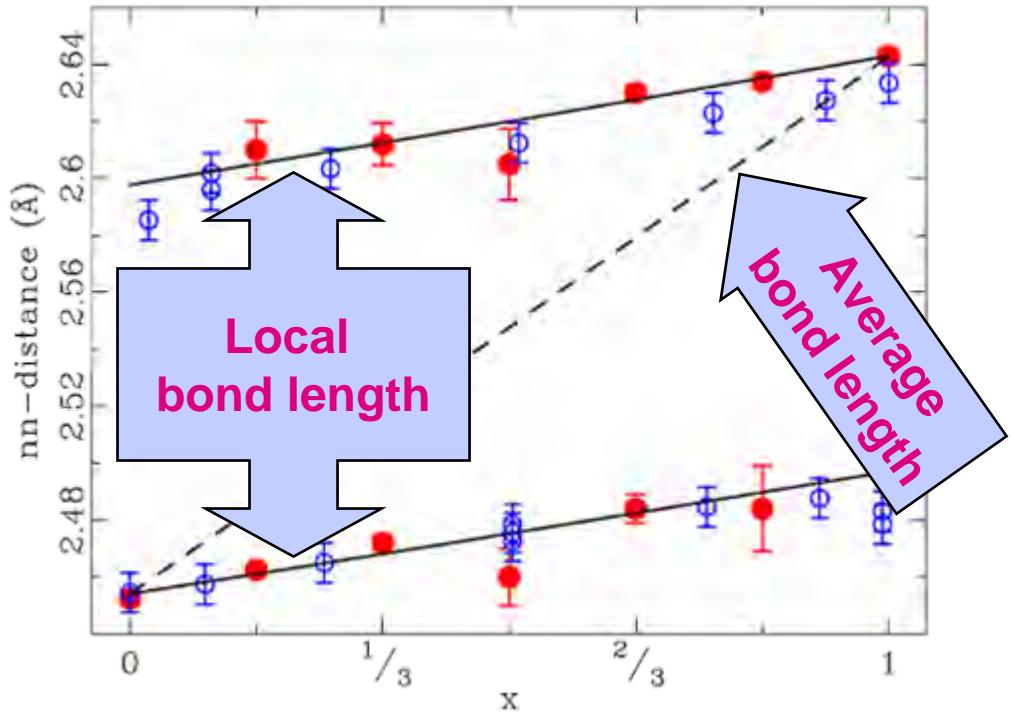
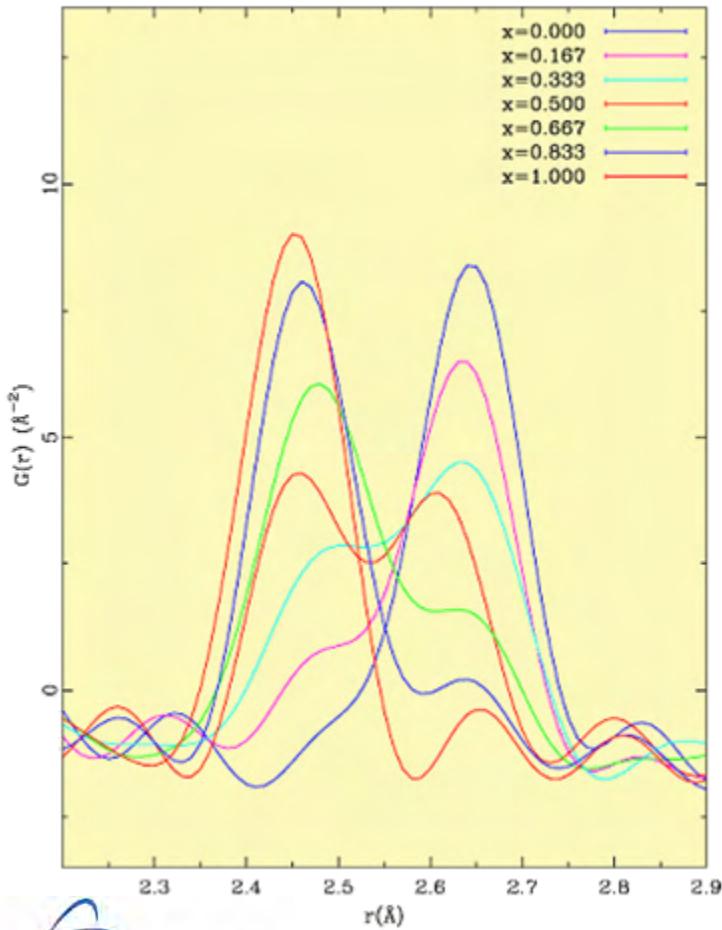
# ZnSe<sub>1-x</sub>Te<sub>x</sub> : Total scattering

Peterson et al., *Phys. Rev. B* **63**, 165211 (2001)



# ZnSe<sub>1-x</sub>Te<sub>x</sub> : Nearest neighbors and Z-plots ..

Se<sub>x</sub>Te<sub>1-x</sub>Zn



BLUE: XAFS from Boyce et al., *J. Cryst. Growth.* **98**, 37 (1989); RED: PDF results.

# Jahn Teller Distortion in LaMnO<sub>3</sub>

Simon Billinge  
Emil Bozin  
Xiangyn Qiu



Thomas Proffen

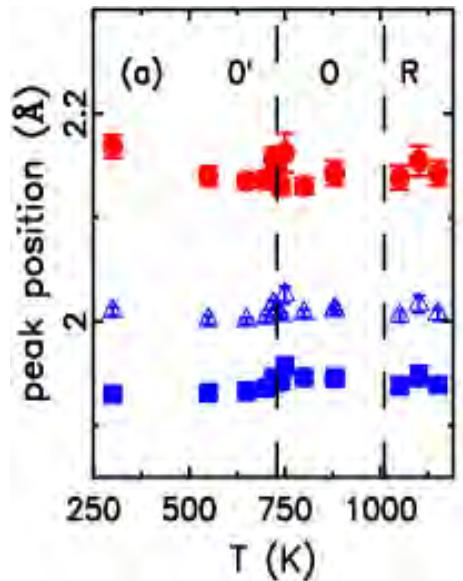
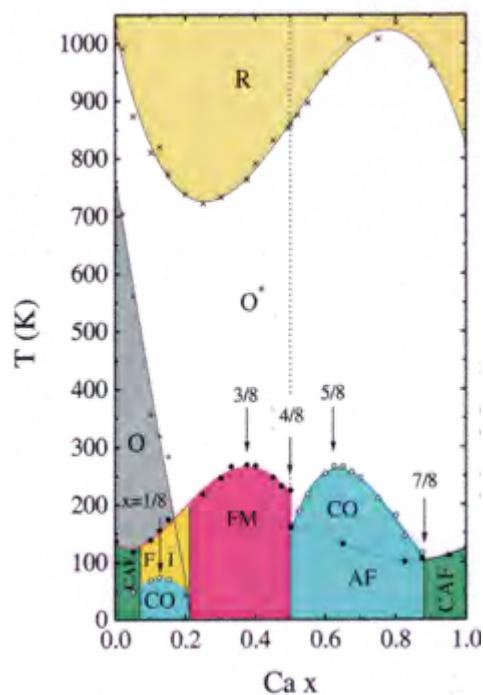


Facilities: Lujan  
Funding: DOE, NSF



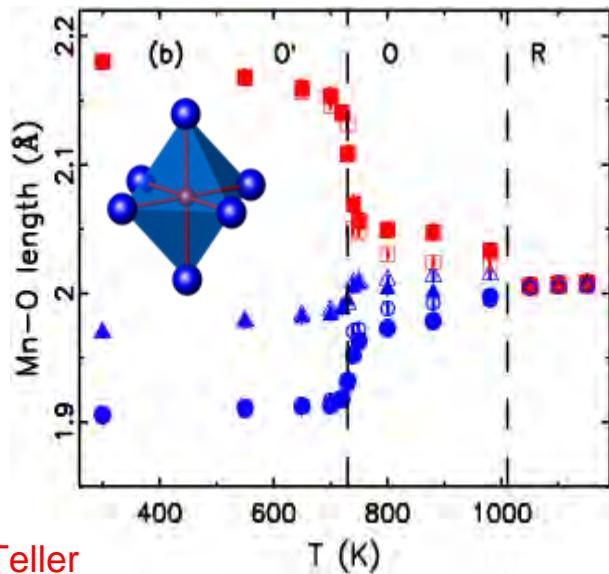
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# LaMnO<sub>3</sub>: Jahn-Teller distortion



Local structure

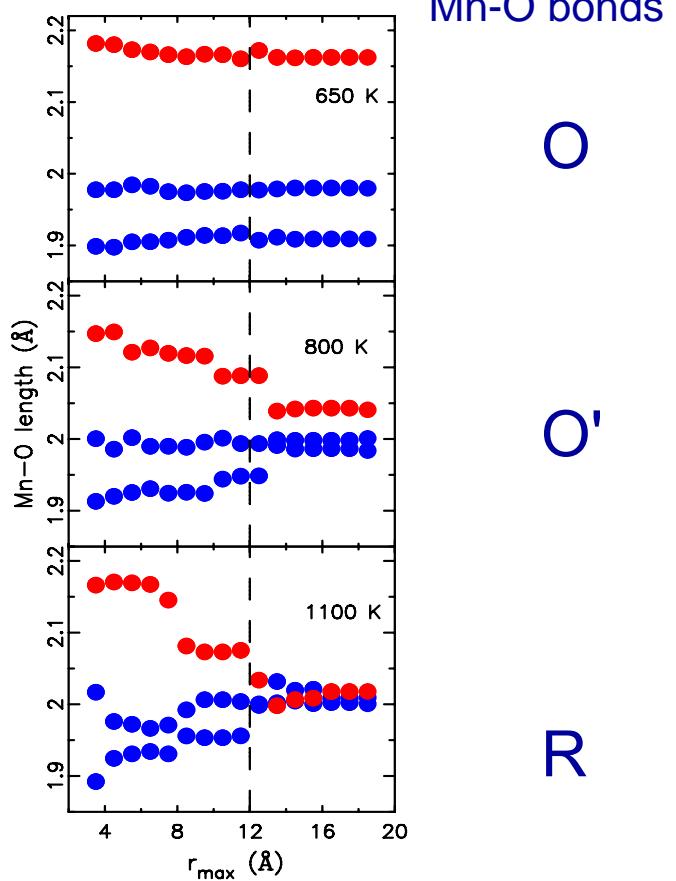
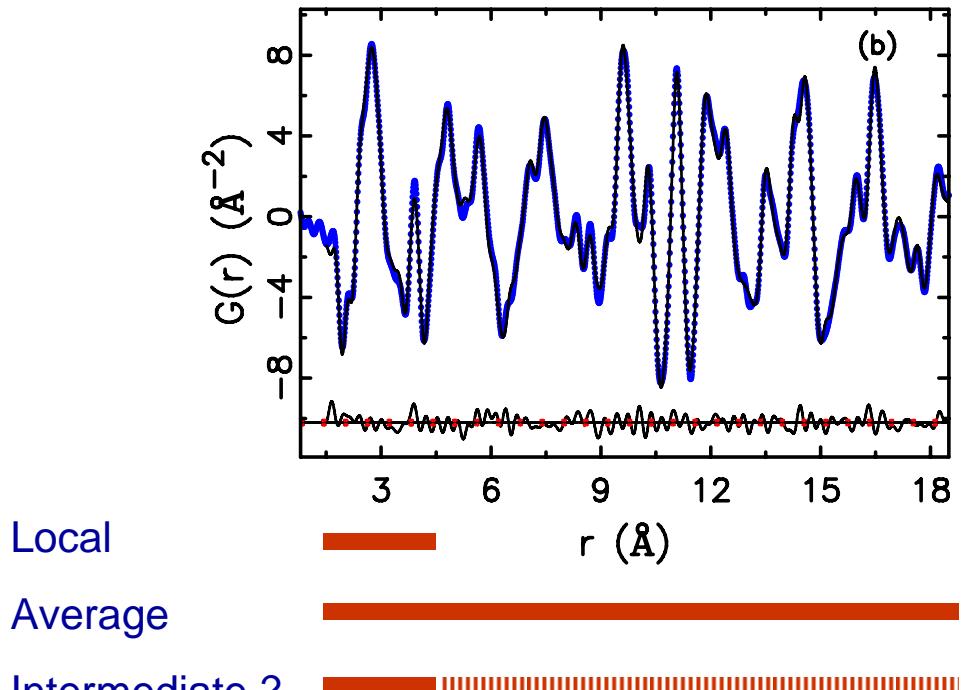
Jahn Teller  
Long Mn-O bond



Average structure

- Mn-O bond lengths are invariant with temperature, right up into the R-phase
- JT distortions persist locally in the pseudocubic phase
- Agrees with XAFS result: M. C. Sanchez et al., PRL (2003).

# LaMnO<sub>3</sub>: Jahn-Teller distortion



X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of LaMnO<sub>3</sub>**, Phys. Rev. Lett. 94, 177203 (2005).

# “Complete” Structure of Gold Nanoparticles

Katharine Page



Thomas Proffen

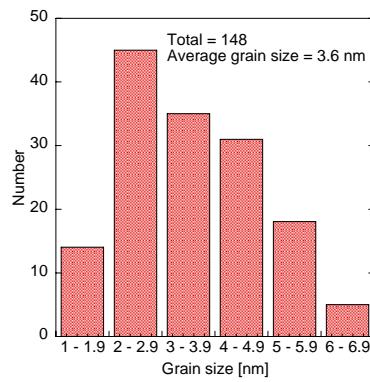
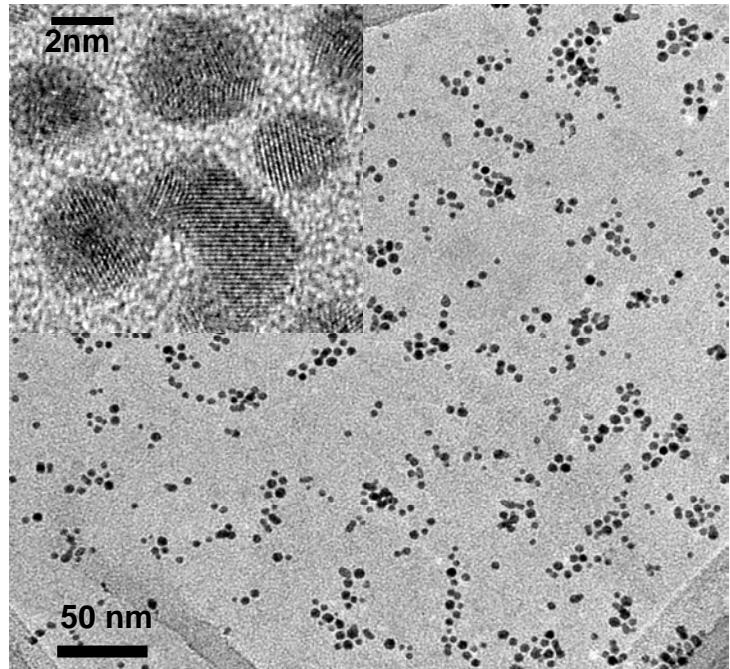


Ram Seshadri  
Tony Cheetham

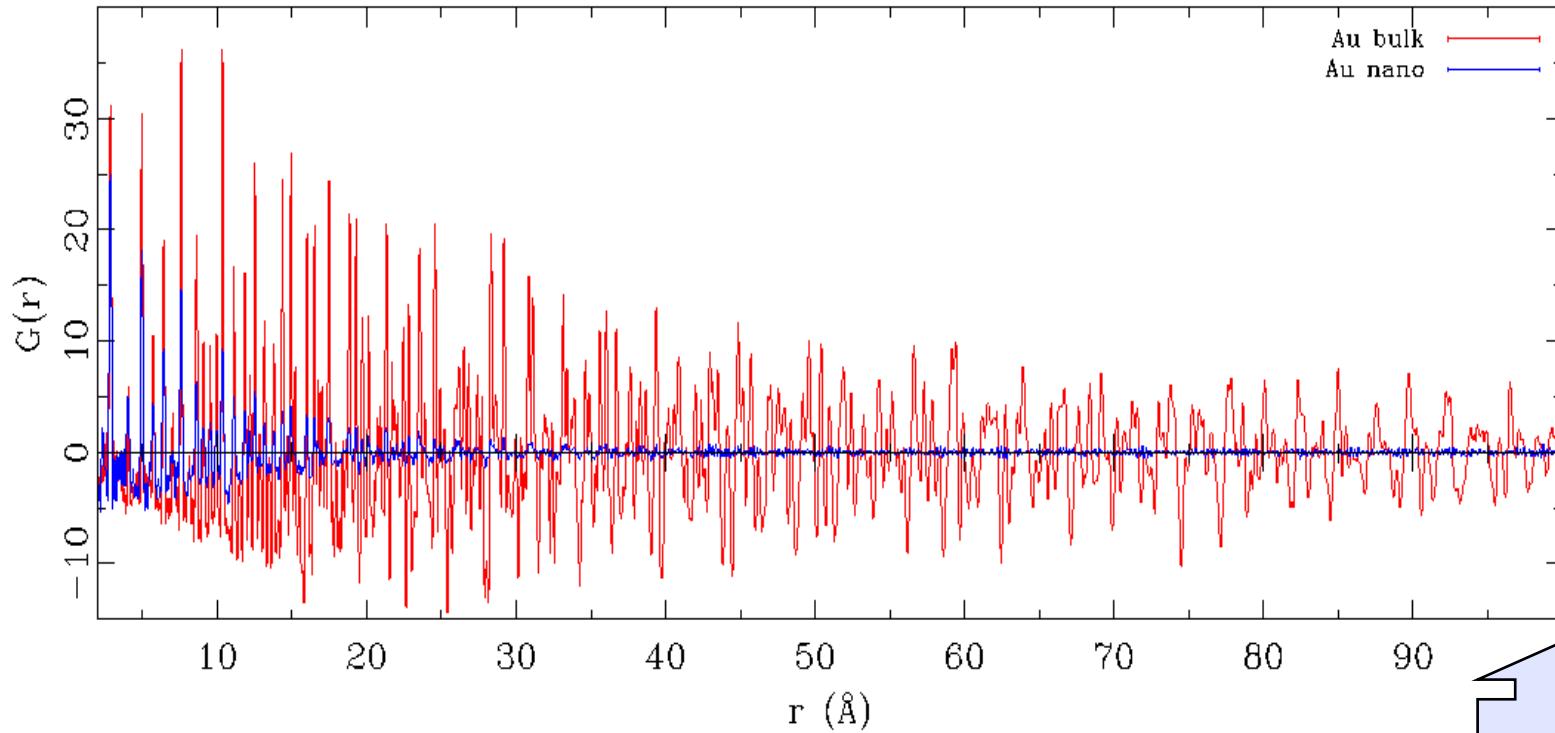
Facilities: Lujan  
Funding: DOE, NASA

# Example: Gold nanoparticles

- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.
- This study:
  - 5nm monodisperse Au nanoparticles
  - 1.5 grams of material
  - Neutron measurements on NPDF



# Au nanoparticles : Nano vs. bulk

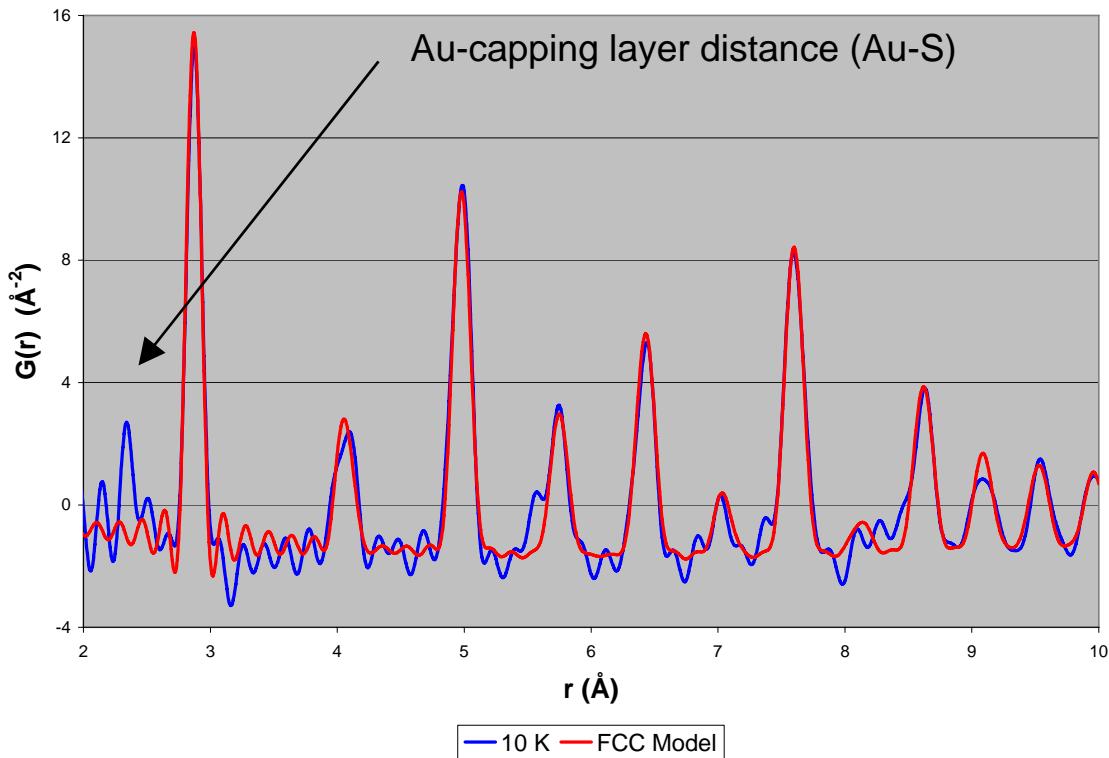


Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF.



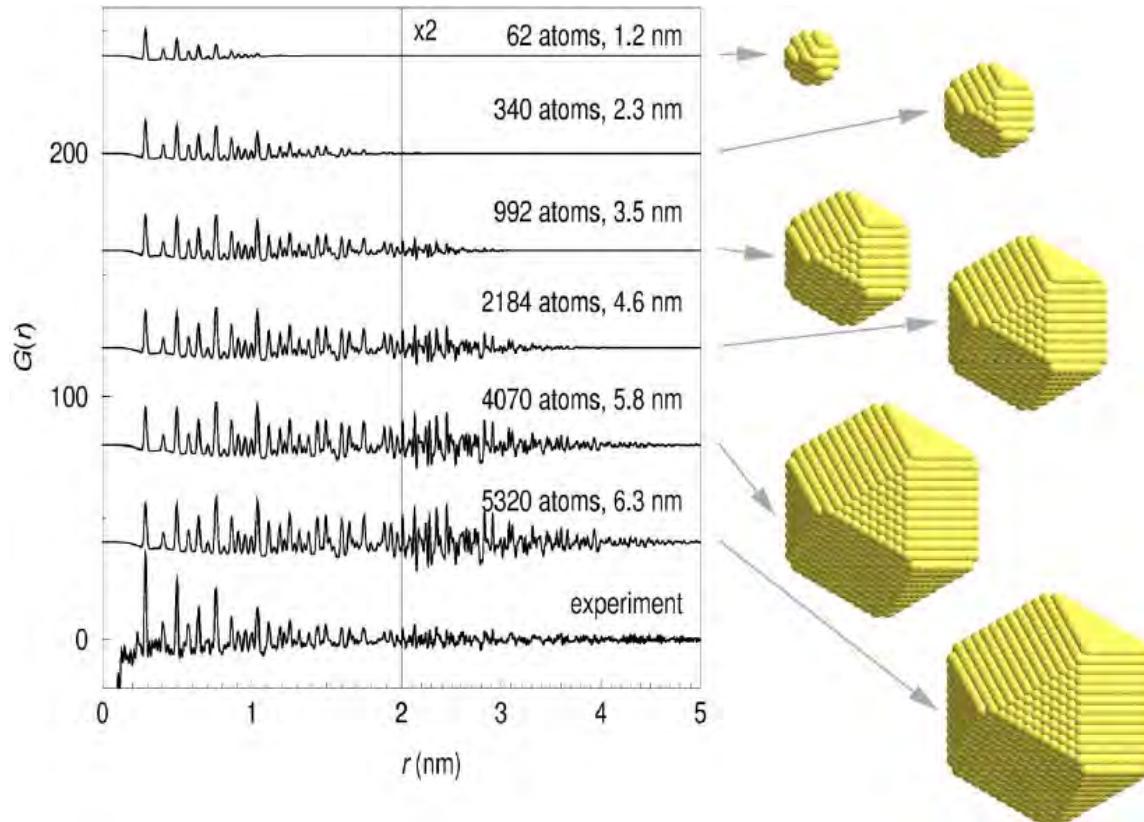
# Au nanoparticles : Structural refinements

- PDF from nano- and bulk gold refined using PDFFIT.
- Nanoparticles show “normal” gold structure.
- No indication of surface relaxations.
- $a_{\text{bulk}} < a_{\text{nano}}$
- Indication of Au-cap distances



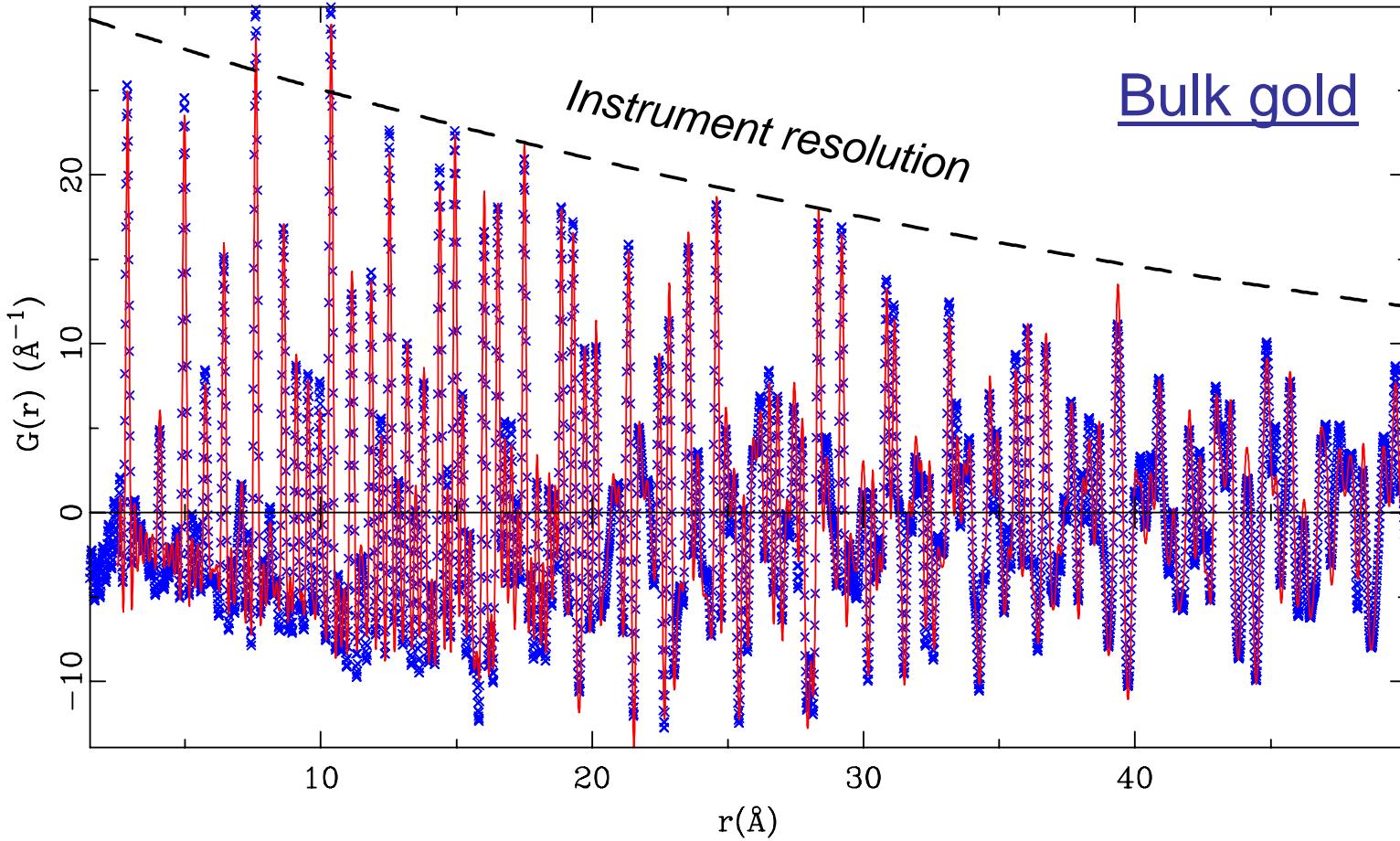
K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

# Au nanoparticles: Particle size

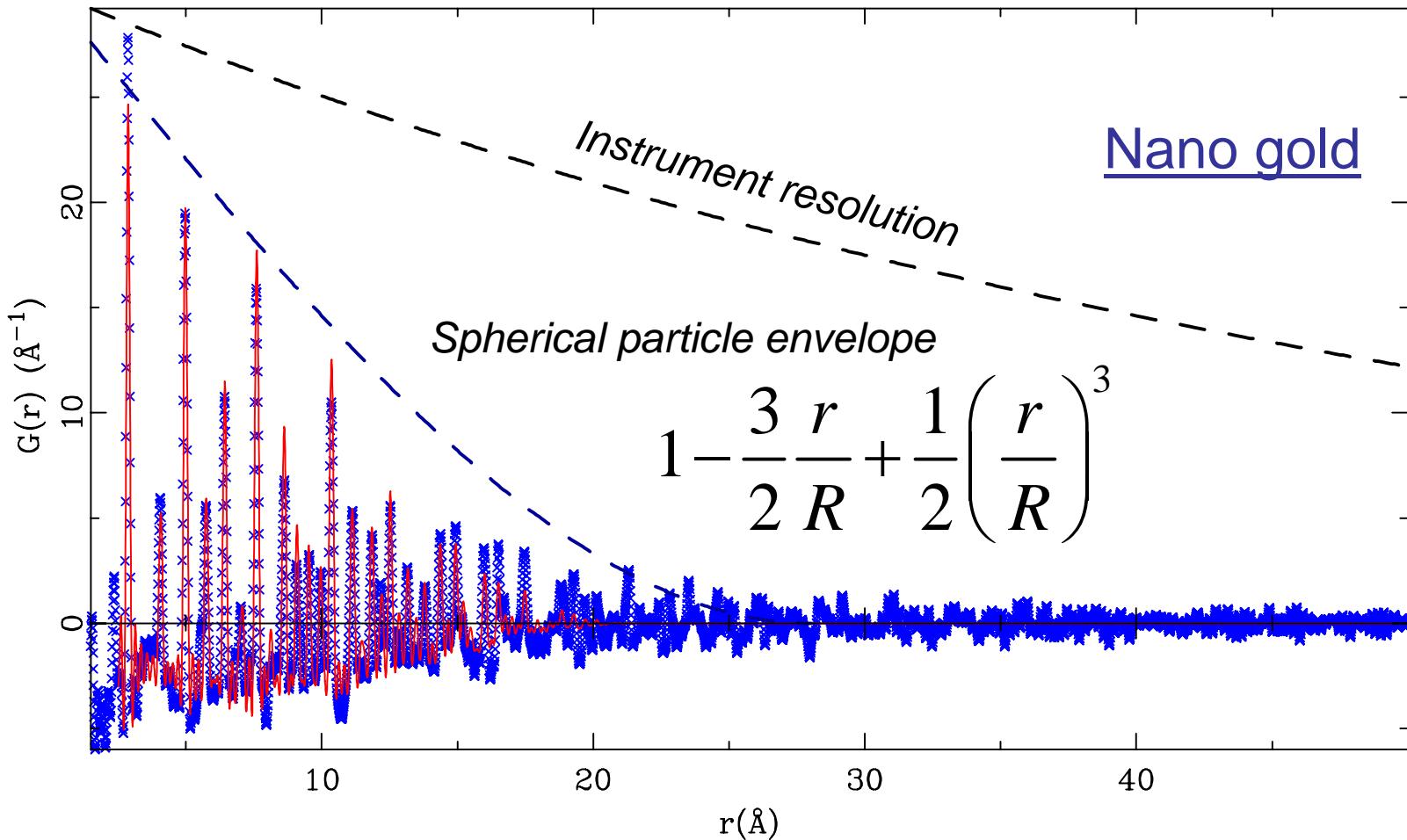


We're dealing with a length scale that can be simulated on an atom by atom basis, perhaps opening the door to extremely detailed refinements.

# Au nanoparticles: Particle size



# Au nanoparticles: Particle size



R.C. Howell, Th. Proffen and S.D. Conradson, **The pair distribution function and structure factor of spherical particles**, *Phys. Rev. B* **73**, 094107 (2006).

# Local structure in sandstone

Katharine Page  
Christina Herrera



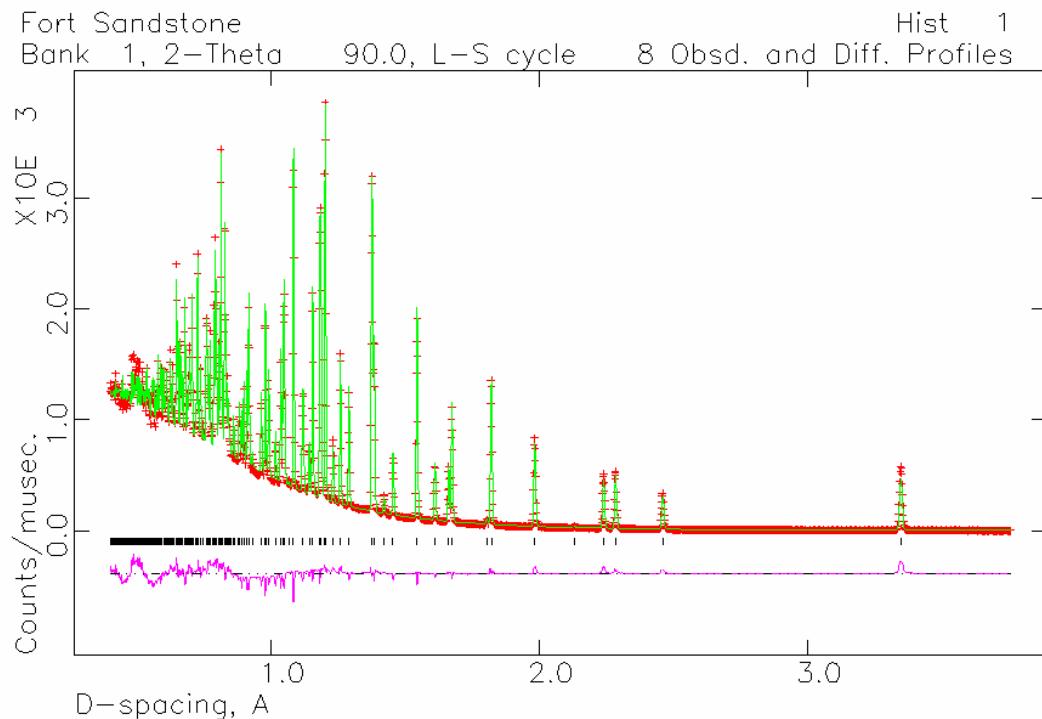
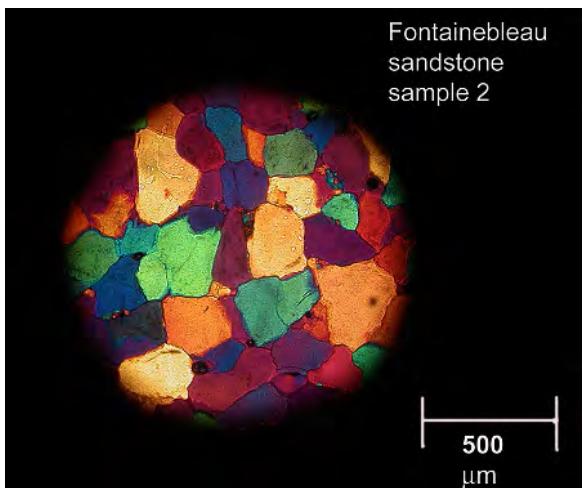
Thomas Proffen  
Sylvia McLain  
Tim Darling  
Jim TenCate

Facilities: Lujan  
Funding: DOE, NSF



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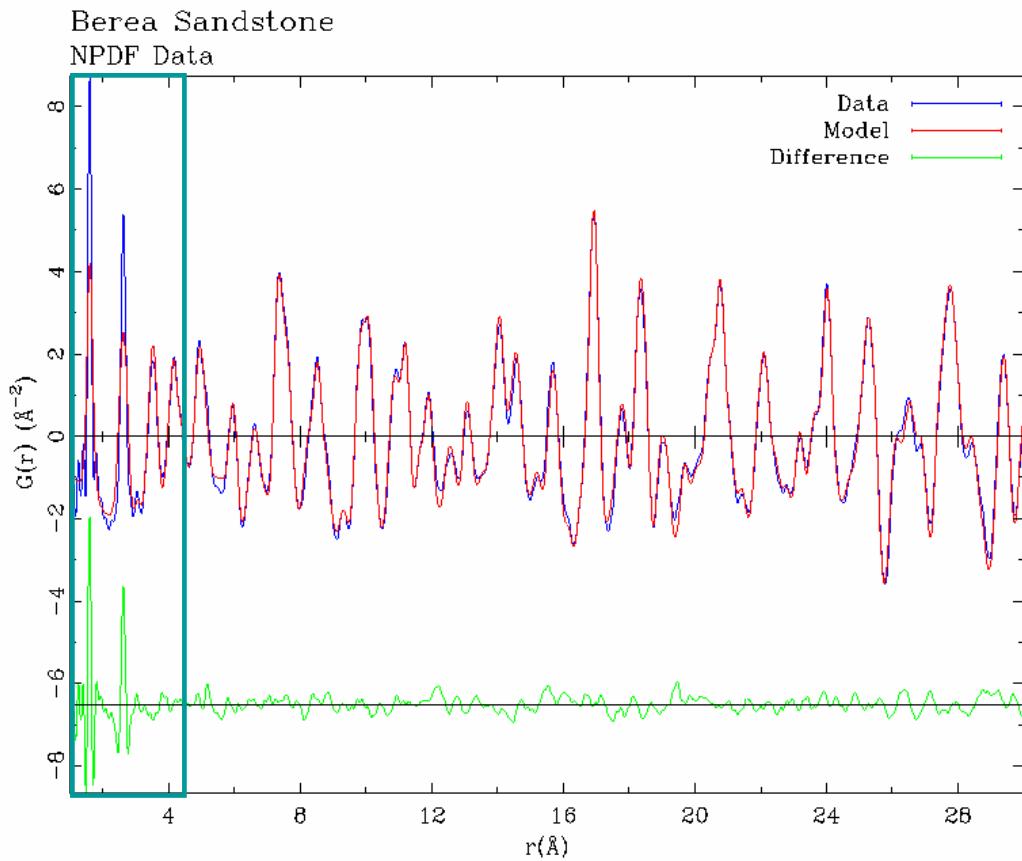
# Sandstone: Crystalline quartz ?



- Measured on NPDF
- High statistics data (24 hrs)
- Solid rock sample
- Ambient conditions – sealed to avoid taking up of water
- Motivation: Structural explanation for non-linear acoustic properties

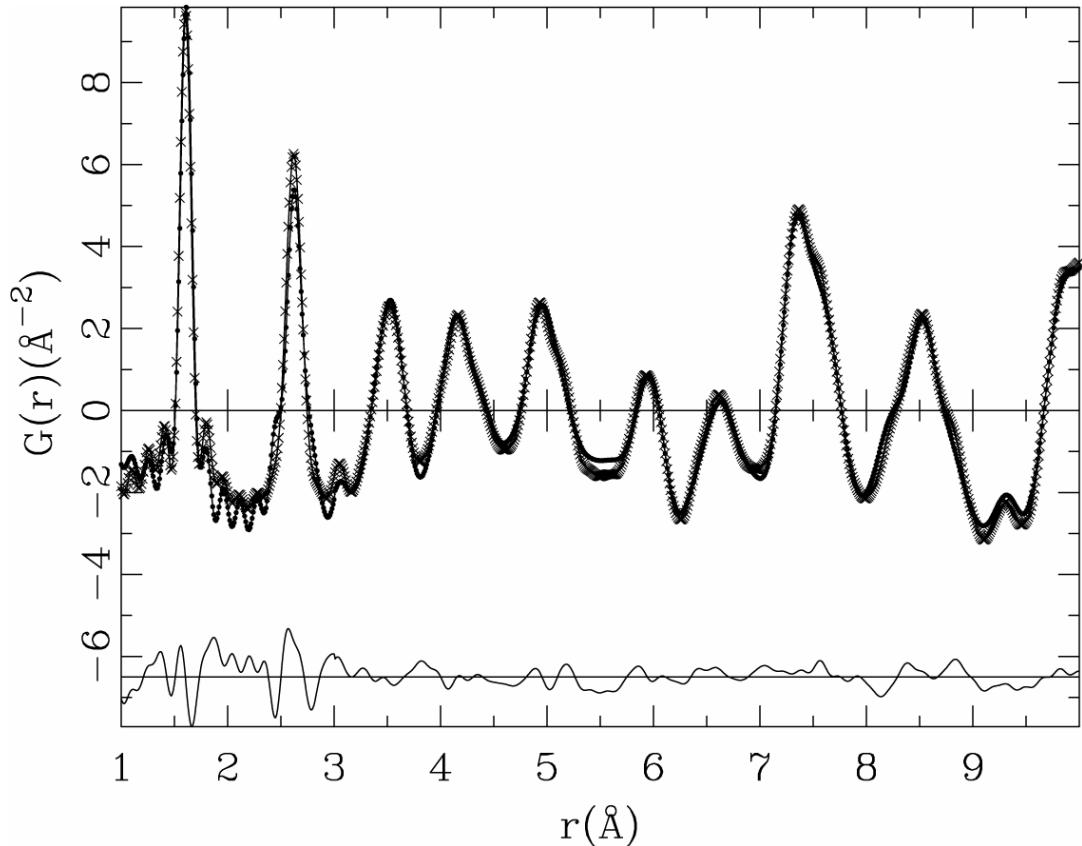
# Sandstone: Local structure

- Refinement of single phase quartz model.
- Good agreement above  $r > 3\text{\AA}$ .
- Missing “intensity” in first two PDF peaks corresponding to Si-O and O-O NN distances.



# Sandstone: Local structure

- Refinement of two phases :
  - Crystalline quartz
  - “Amorphous” quartz up to 3 Å
- Good agreement over complete range
- Amorphous regions “stress formed” by point like contacts at grain contacts ?



K.L. Page, Th. Proffen, S.E. McLain, T.W. Darling and J.A. TenCate, **Local Atomic Structure of Fontainebleau Sandstone: Evidence for an Amorphous Phase ?, Geophysical Research Lett.** 31, L24606 (2004)

# Nano-structured transition metal carbides

Katharine Page  
*(PhD work)*



Ram Seshadri  
Tony Cheetham

Thomas Proffen



**Facilities:** Lujan

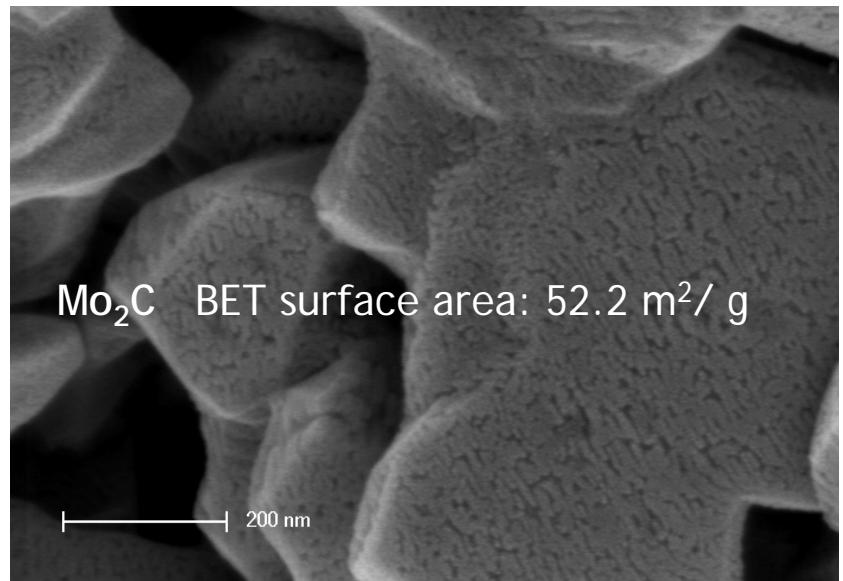
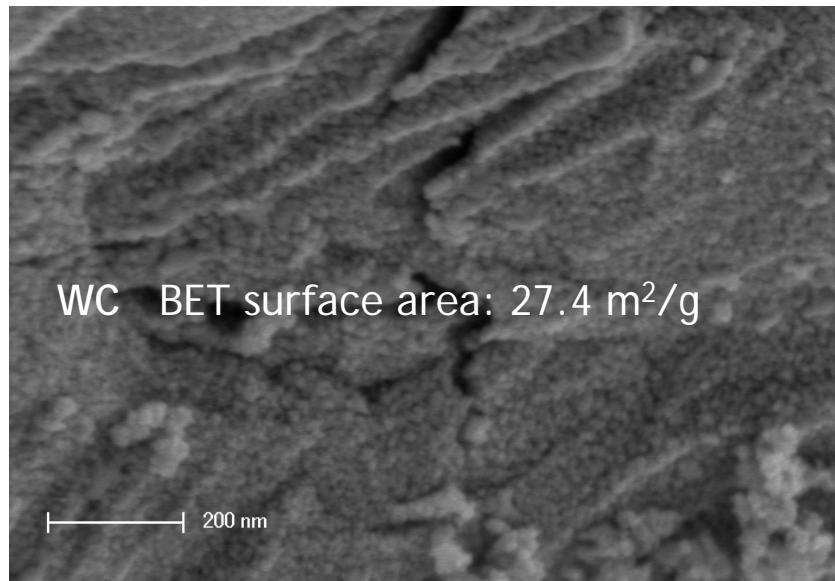


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# Nanostructures transition metal carbides

Catalytic activity of platinum group metals with greater thermal stability and resistance to poisoning.

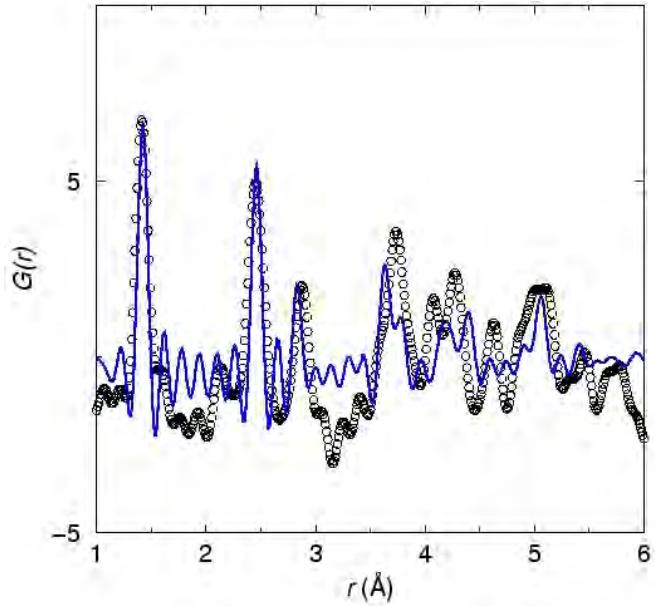
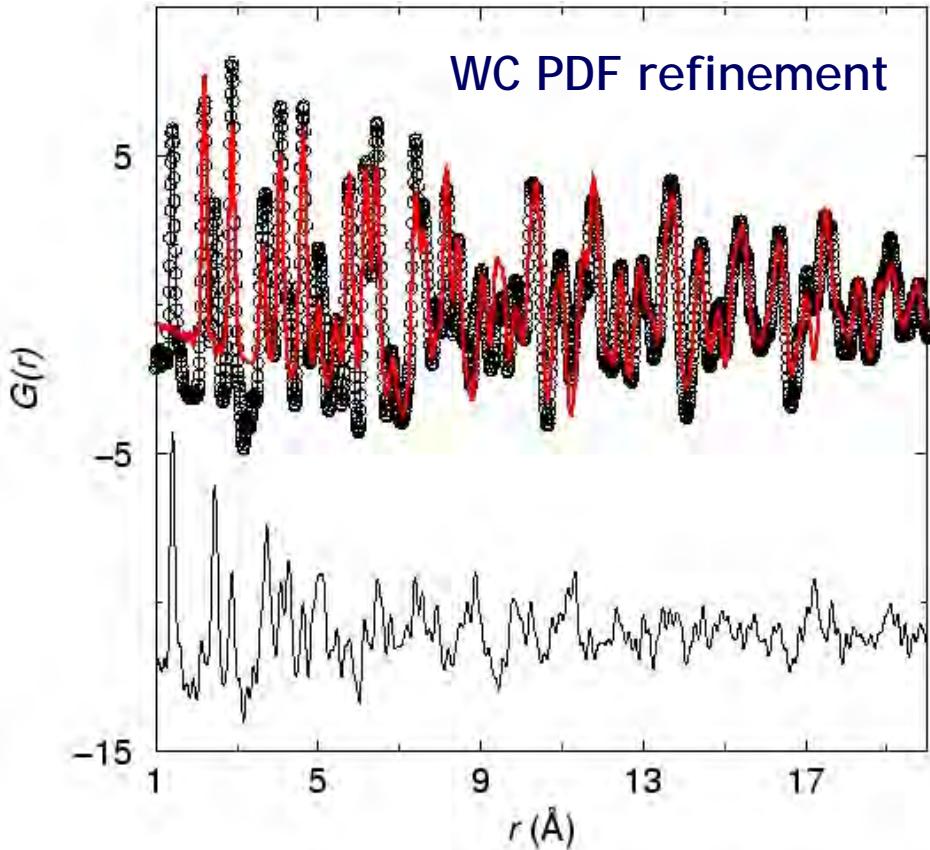
Nanostructured Mo and W carbide will provide higher surface area than traditionally prepared materials.



Prepared by treating molybdates/tungstates in a quartz tube with flowing 50%-H<sub>2</sub>/CH<sub>4</sub> at 10 mL/min at elevated temperatures.

## NPDF measurements

XPS studies suggest there is a significant contribution of non-carbide carbon.  
*It is known that graphitic carbon can block almost all of the active surface.*



The difference curve,  
fit with the graphite  
structure.

# Summary and more information

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- Analysis of total scattering gives valuable insight in **structure  $\Leftrightarrow$  properties** relationship
- High-resolution instruments open the door to medium-range order investigations
- Obtain structural information from disordered crystalline, amorphous or composite materials
- Fast powder measurements allow systematic exploration of local structure as function of  $T$ ,  $x$ ,  $P$

