

Characterizing complex materials using *total scattering* (focus on nano-particles)

Thomas Proffen
tproffen@lanl.gov



Total Scattering Group at the Lujan Center

We are using and **developing** total scattering methods to characterize disordered crystalline, nano- and amorphous materials.

- Members

- Thomas Proffen (NPDF)
- Joan Siewenie (NPDF)
- Anna Llobet (HIPD)
- **Katharine Page** (Postdoc)
- Graham King (Postdoc)
- Claire White (Postdoc Nov.)
- *Taylor Hood (Student)*
- *Paul Lauria (Student)*
- *Daniel Shoemaker (Student)*
- *Emily Tencate (Student)*

- Facilities

- Lujan Center
- Advanced Photon Source

The screenshot shows a web browser displaying the 'Total Scattering Group, Lujan Neutron Scattering Center' website. The page features a header with the Los Alamos National Laboratory logo and a search bar. The main content area is titled 'TOTAL SCATTERING GROUP' and describes the group's focus on structural analysis of complex materials. It includes a 'Welcome' section, a 'Recent Highlights' section with three items (Neutrons and X-rays United, 'Green' Concrete, The Package Matters), and a 'News and Announcements' section with several bullet points about workshops, conferences, and publications. On the left, there is a sidebar with links for 'Total Scattering', 'RESOURCES', 'CONTACT', and a 'Lead Scientist' section.

<http://totalscattering.lanl.gov>

Total Scattering ?



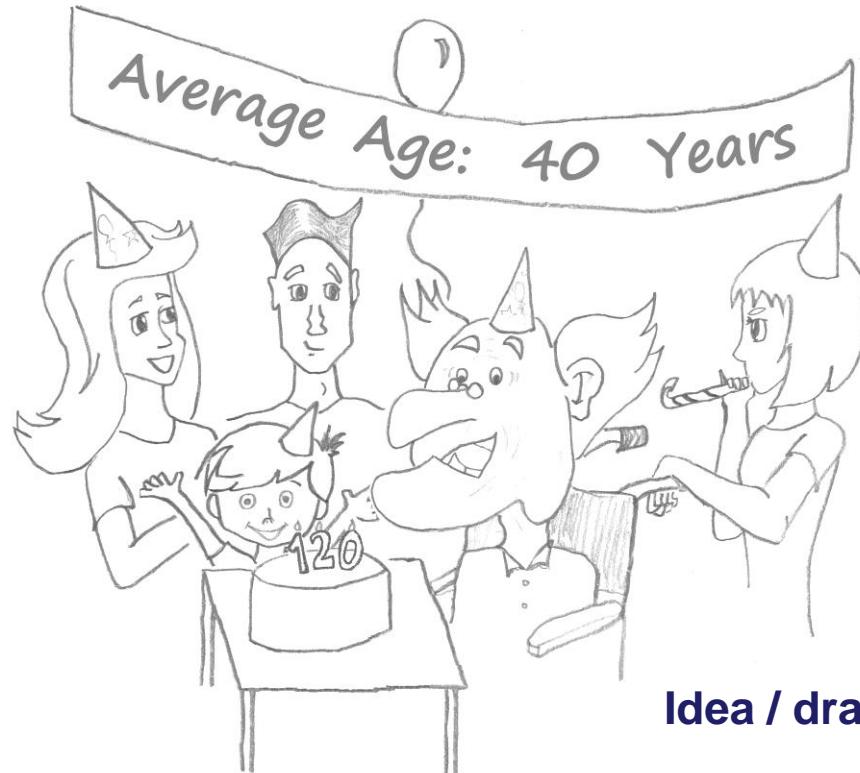
EST. 1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA

U N C L A S S I F I E D



Judging by the average ..

- Analysis of Bragg intensities yields the **average** structure of materials which can be deceiving !
- Consider going to a party where all you know is the average age is 40 ...

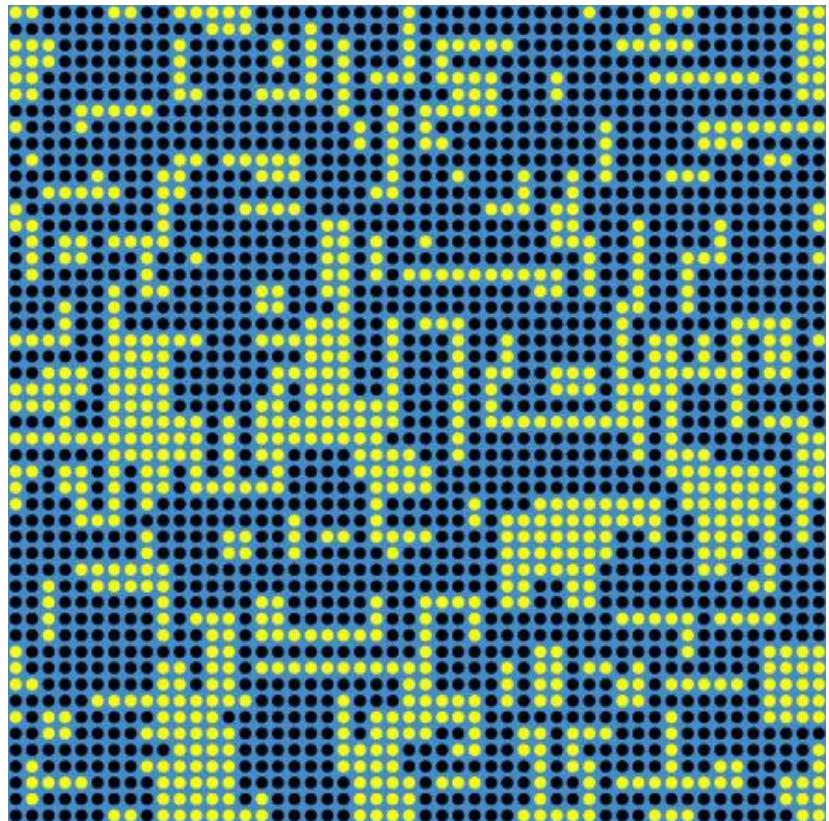
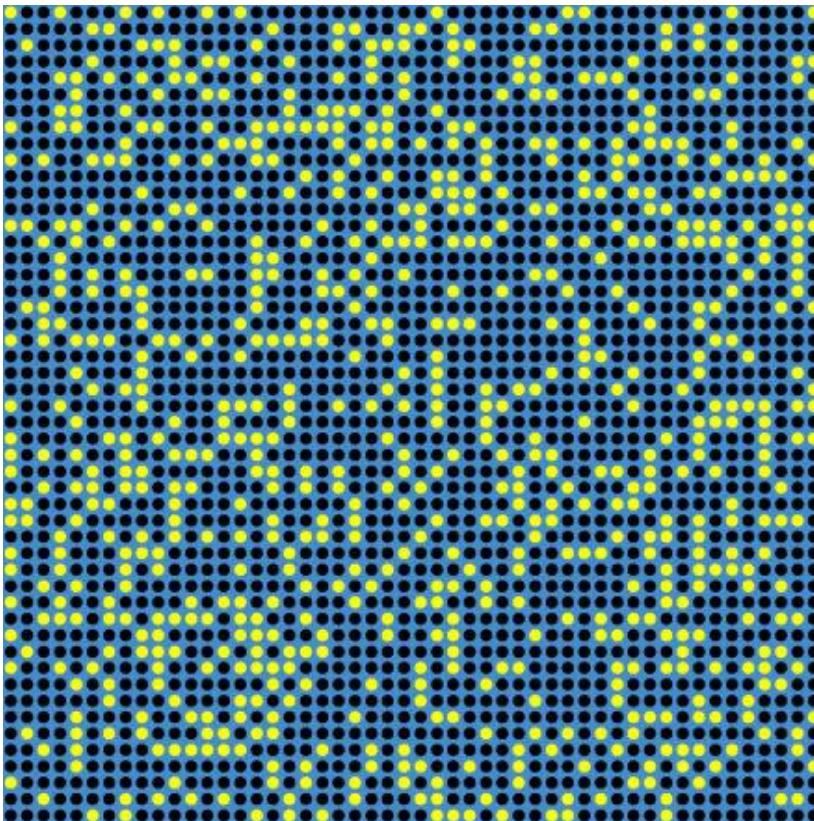


Idea / drawing by Emily Tencate

Emily's corner soon coming to <http://totalscattering.lanl.gov>

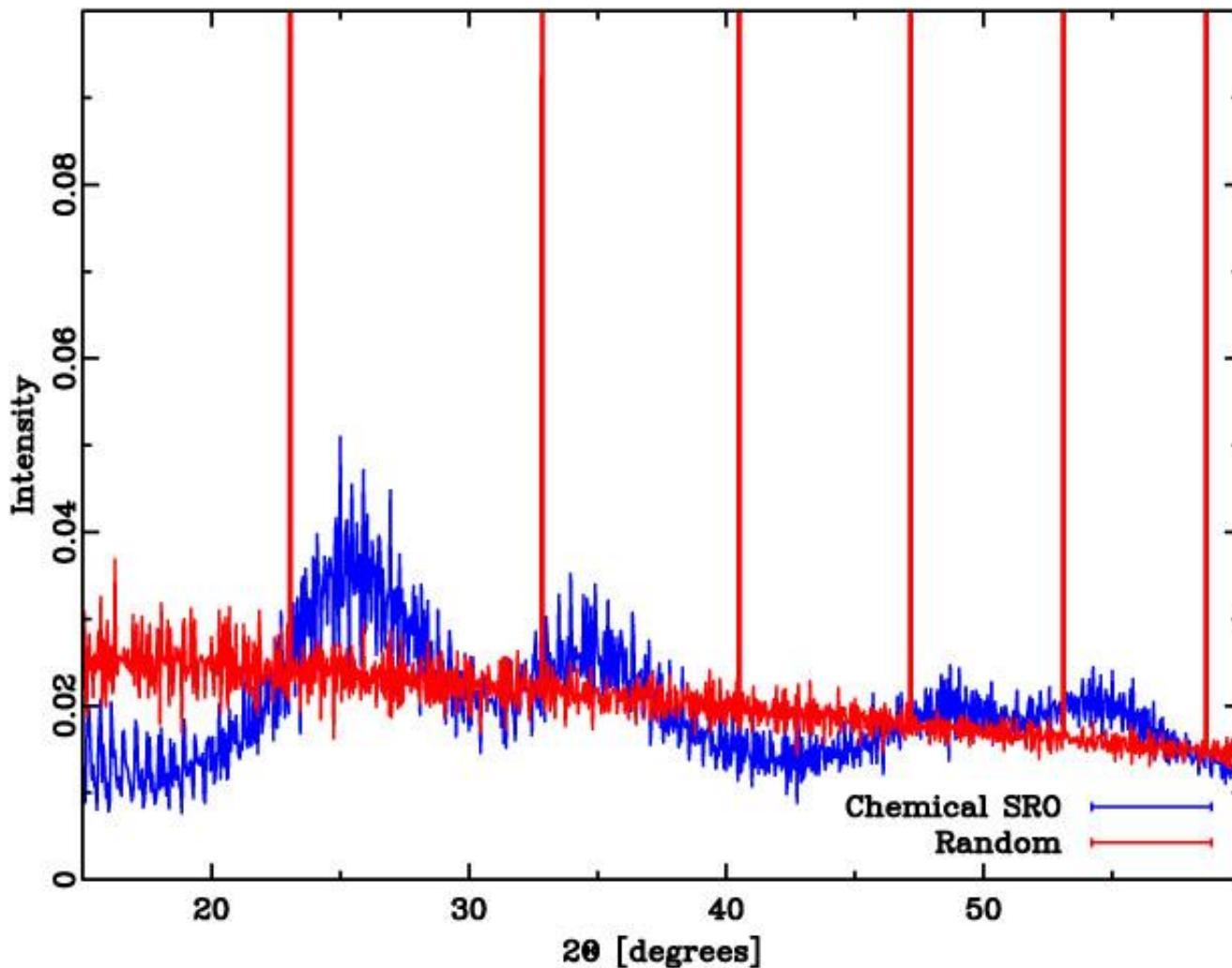
UNCLASSIFIED

Total scattering ?



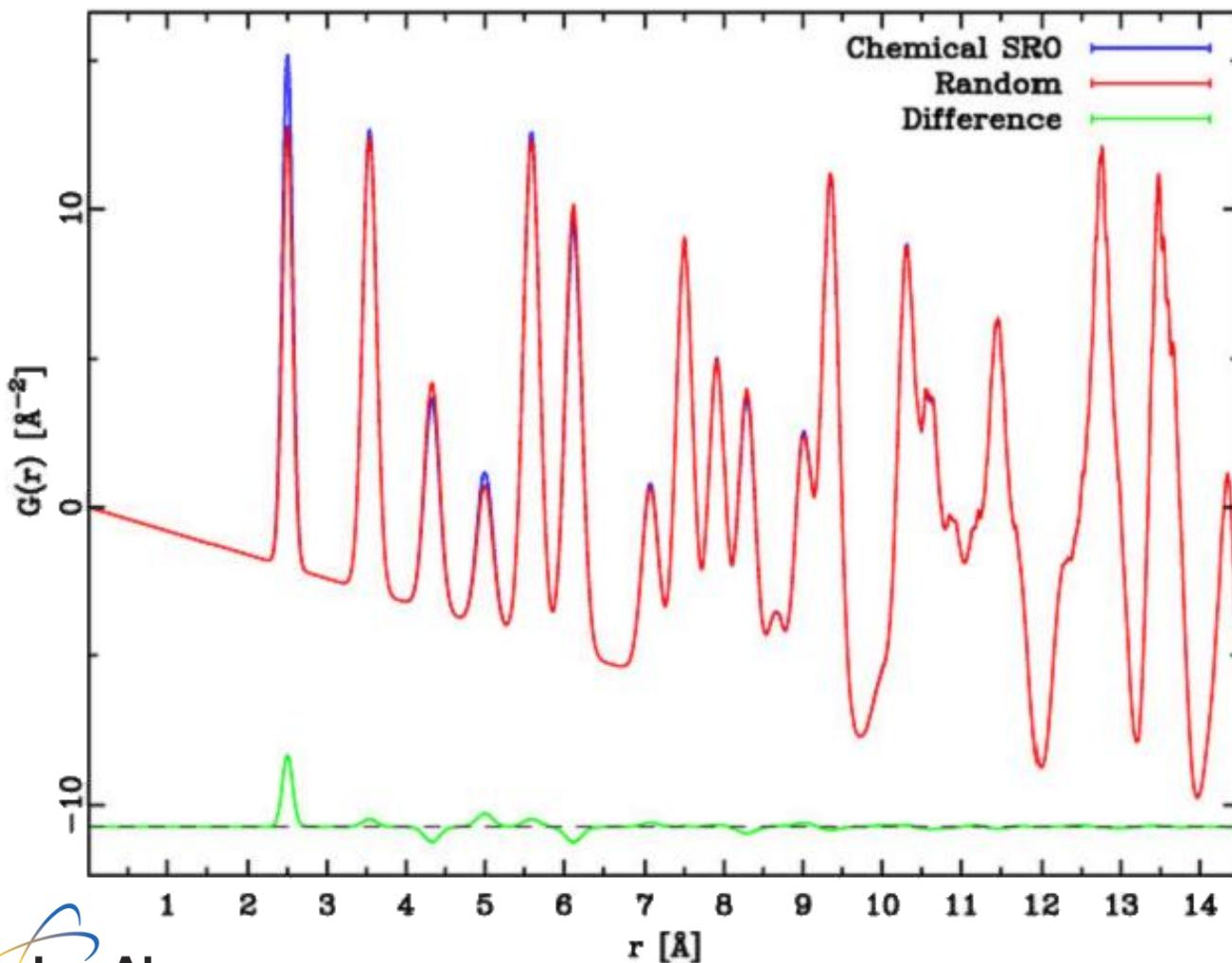
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% vacancies !
Properties might depend on vacancy ordering !!

How about powder diffraction ?



<http://totalscattering.lanl.gov>

Finally the Pair Distribution Function (PDF)



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

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

Experimental Considerations

<http://totalscattering.lanl.gov>



EST. 1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA

UNCLASSIFIED



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 ?

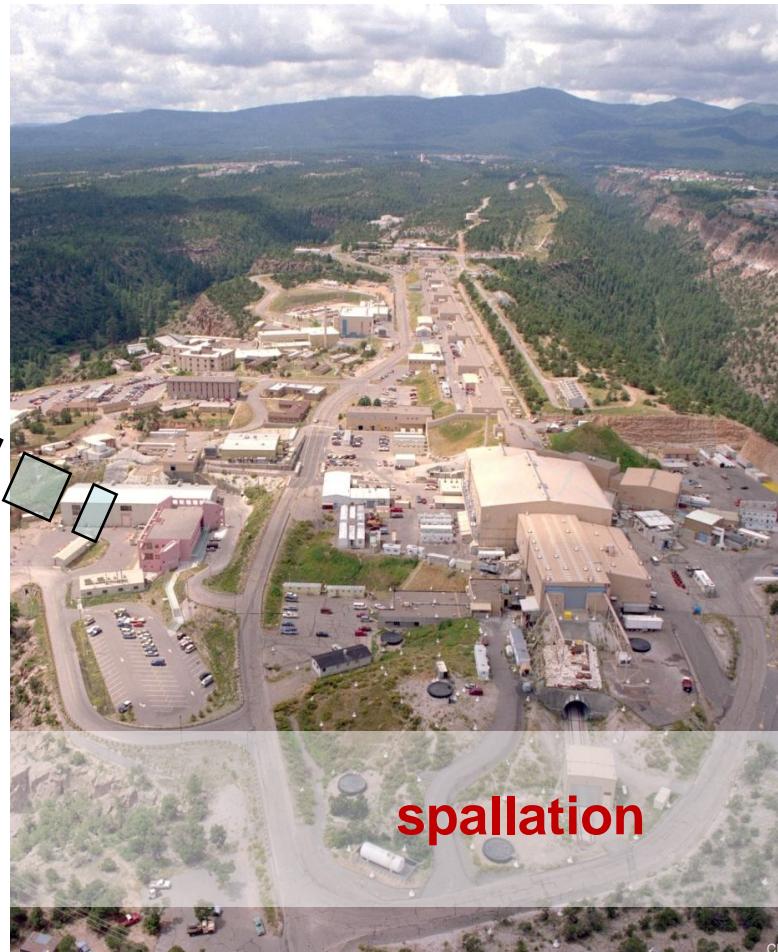
Synchrotron sources

or

neutron sources

(high energy X-rays)

(reactor neutron energies are too low)



NPDF: Overview

- **Specifications**

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



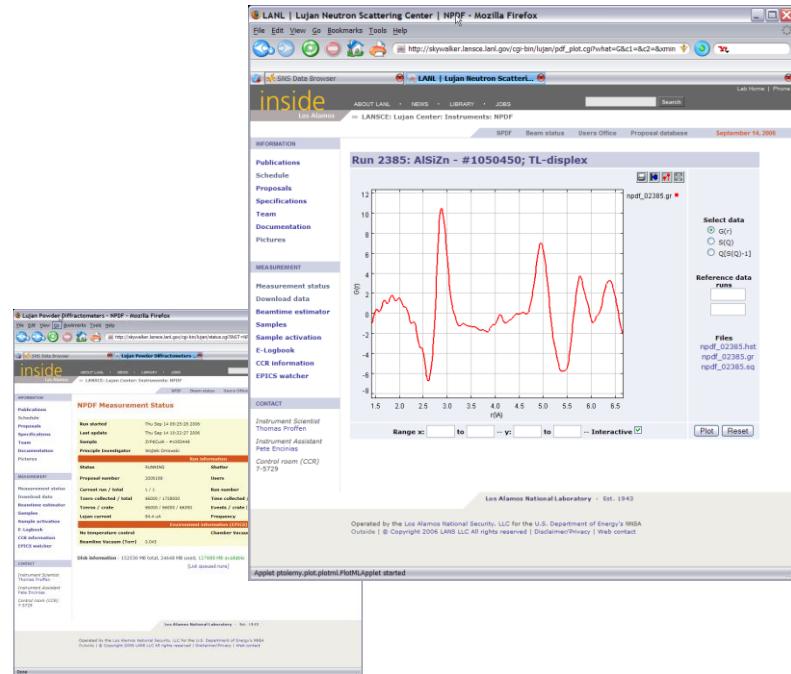
- **Science**

- 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)

- <http://www.lansce.lanl.gov>



<http://totalscattering.lanl.gov>

X-ray PDF: The fast way

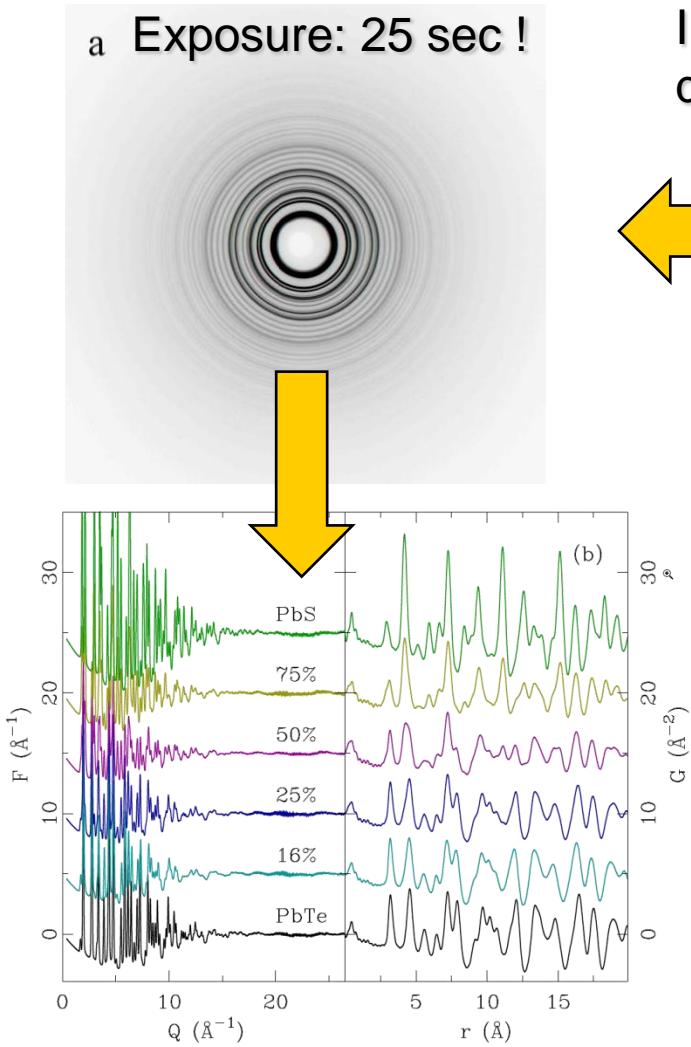
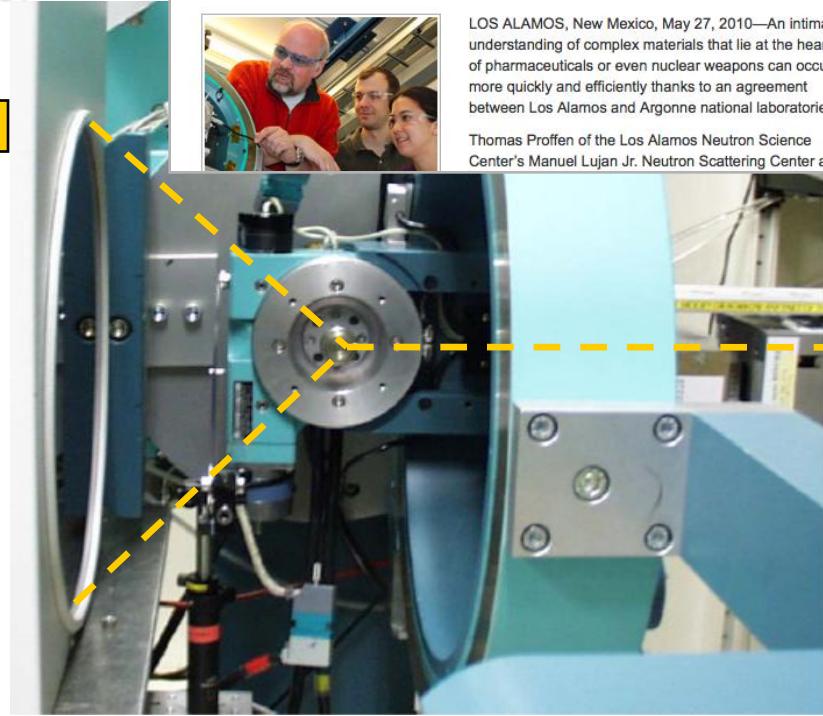
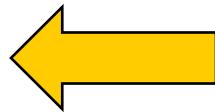


Image plate
detector



News Release

All: News > News Releases >

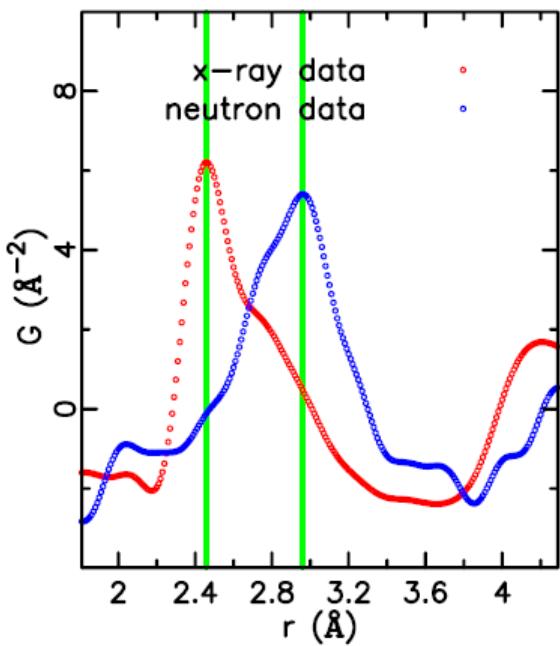
Los Alamos-Argonne partnership will aid understanding of complex materials

LOS ALAMOS, New Mexico, May 27, 2010—An intimate understanding of complex materials that lie at the heart of pharmaceuticals or even nuclear weapons can occur more quickly and efficiently thanks to an agreement between Los Alamos and Argonne national laboratories.

Thomas Proffen of the Los Alamos Neutron Science Center's Manuel Lujan Jr. Neutron Scattering Center and

<http://totalscattering.lanl.gov>

MgCo – the power of combining neutrons and x-rays



$$\text{PDF peak intensity} \propto \sum_{mn} \frac{b_m b_n}{\langle b \rangle^2} \delta(r - r_{mn})$$

where b_i is the scattering length of the i^{th} atom.

	b_i for x-ray	b_i for neutron
Mg	12	3.631
Co	27	0.779

$b_m b_n$	Mg-Mg	Mg-Co	Co-Co
x-ray	144	324	729
neutron	13.18	2.83	0.607

Some recent examples ..

<http://totalscattering.lanl.gov>

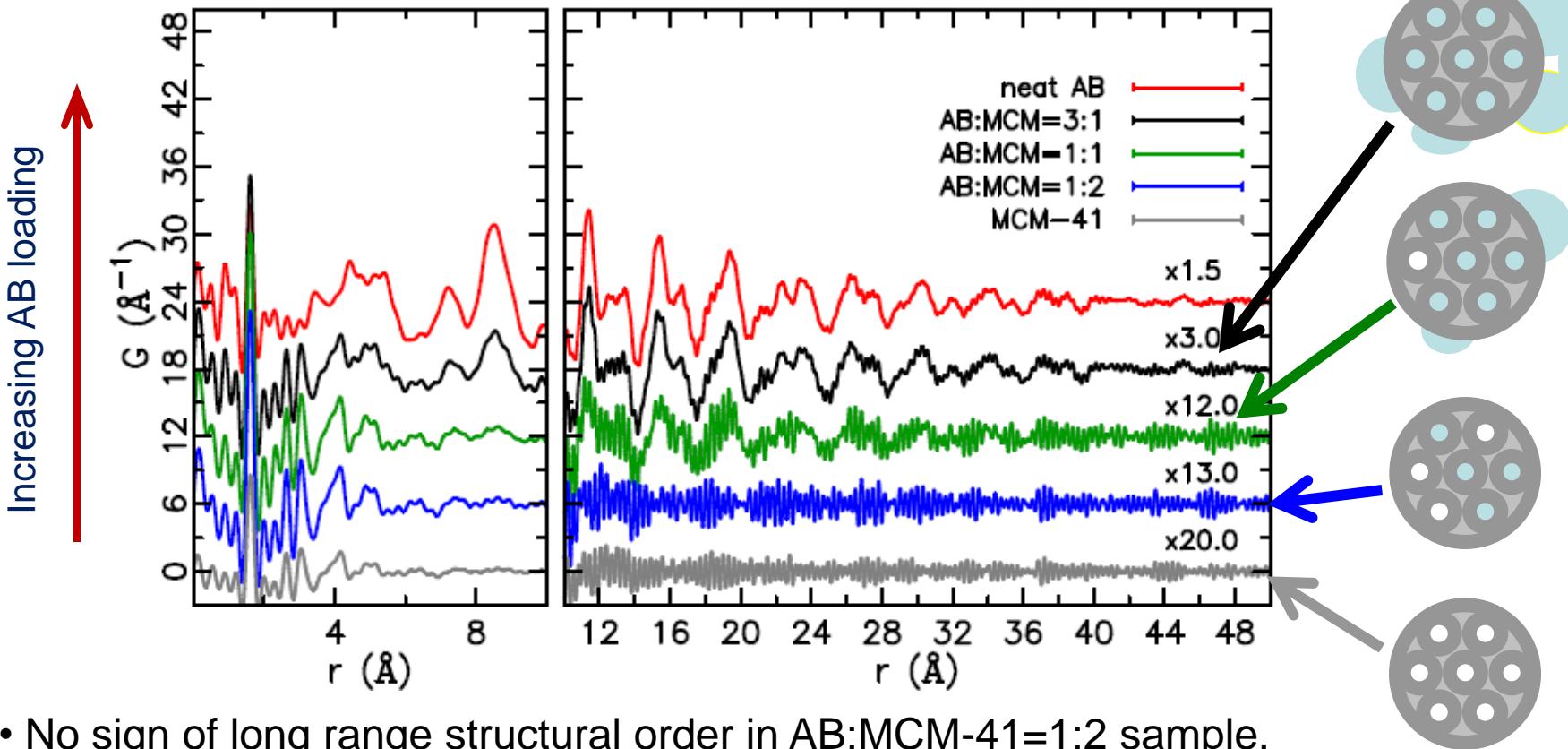


EST. 1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA

UNCLASSIFIED



AB in MCM41 – X-ray study



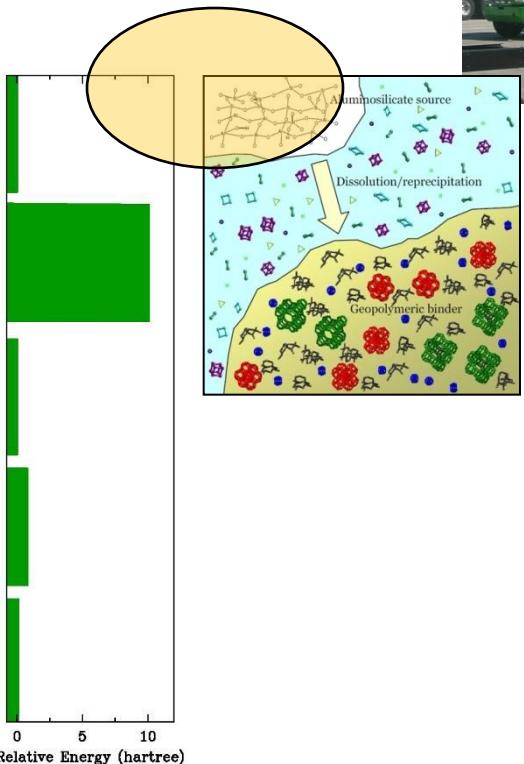
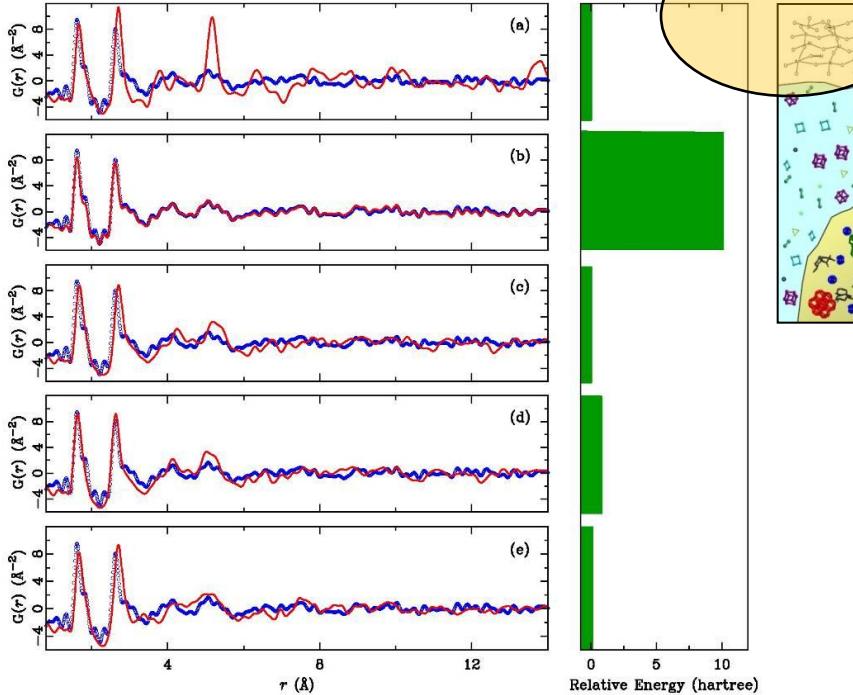
- No sign of long range structural order in AB:MCM-41=1:2 sample.
- AB **inside** pores might be disordered at RT.
- **Long range order** in high AB loading due to **AB aggregates**.

H. Kim, A. Karkamkar, T. Autrey, P. Chupas and Th. Proffen, **Determination of structure and phase transition of light element nanocomposites in mesoporous silica: case study of NH₃BH₃ in MCM-41**, *J. Am. Chem. Soc.* **131**, 13749-13755 (2009).

UNCLASSIFIED

Towards green concrete ..

Cement production accounts for 5 - 8% of global man-made CO₂ emissions! Geopolymer concrete is a viable alternative (80 – 90% less CO₂ emitted)



Approach

Use of Density Functional Theory (DFT) and PDF to solve the structure.

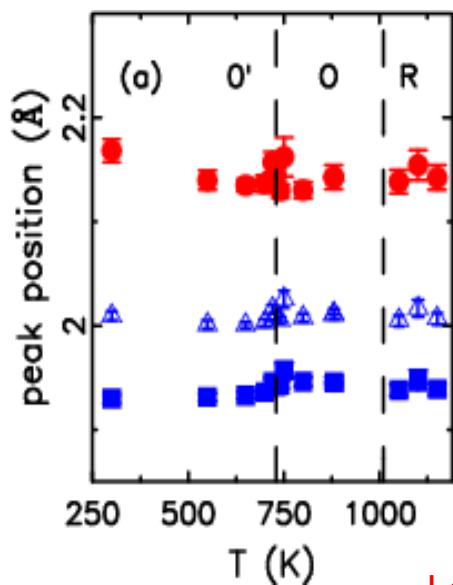
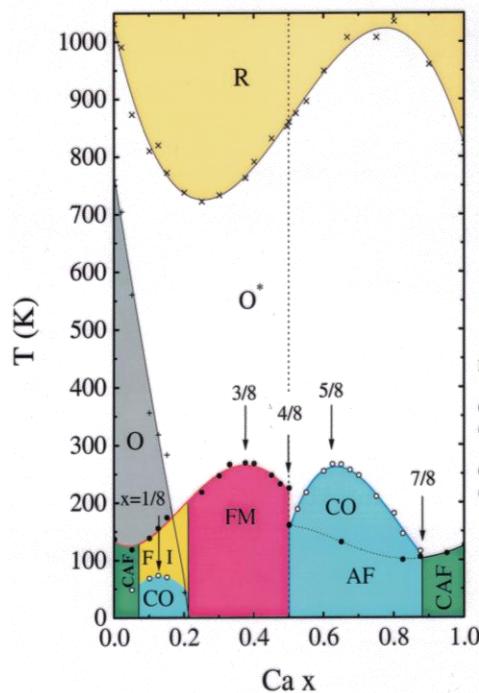
Bond lengths comparable to parent material (kaolinite)

Bond angle distributions are broader than kaolinite.

Evidence for 3 coordinated aluminum.

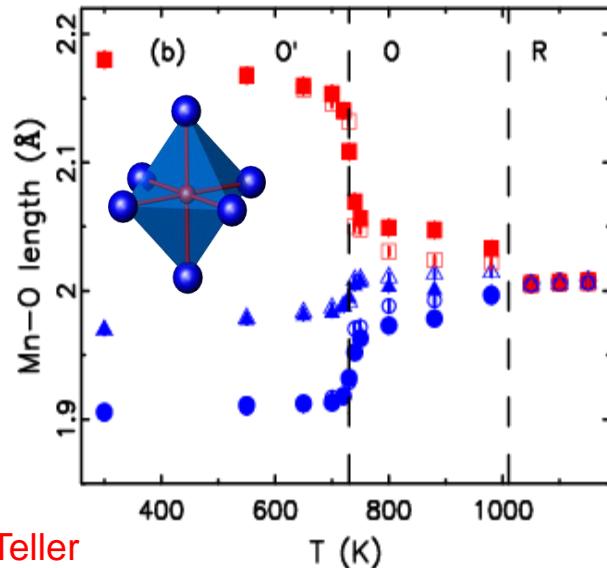
Goal: Understanding of the complete (and complex) system of geopolymer concrete.

LaMnO₃: Jahn-Teller distortion



Local structure

Jahn Teller
Long Mn-O bond



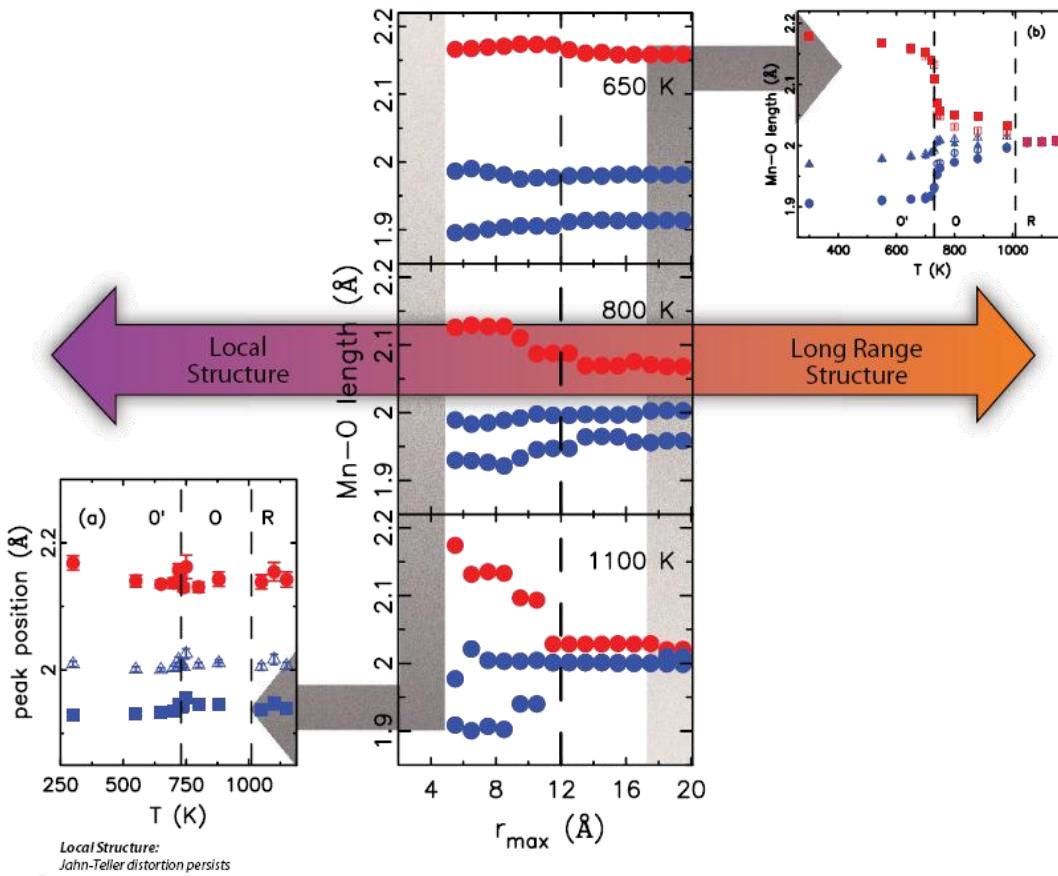
Average structure

- 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).

NPDF unravels the local structure in LaMnO_3

DISTORTED OR NOT DISTORTED?

Study of the Jahn-Teller distortion in LaMnO_3



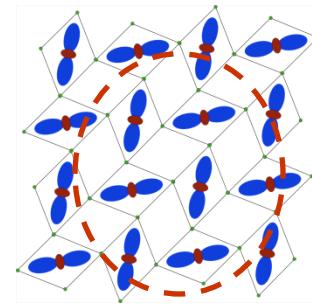
PDF Probes the Structure as a Function of Length Scale

Manganites are among the many complex materials used in applications all around us. Understanding their properties allows us to engineer materials with even superior properties, but requires detailed knowledge of the atomic level structure.

Here, NPDF experiments revealed local atomic distortions and their distribution in a particular manganite, LaMnO_3 , leading to a better understanding of its electronic and magnetic properties.

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_3** , *Phys. Rev. Lett.* **94**, 177203 (2005).

UNCLASSIFIED



PDF for nano particles

<http://totalscattering.lanl.gov>

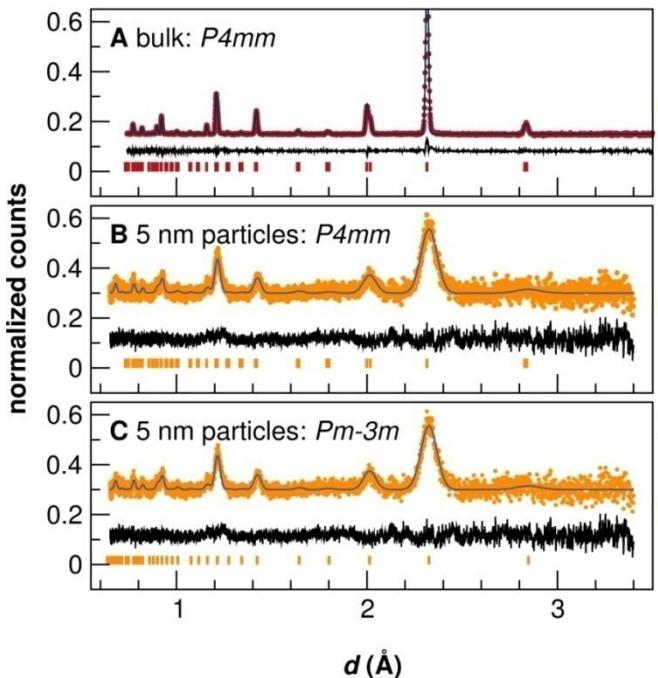


EST. 1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA

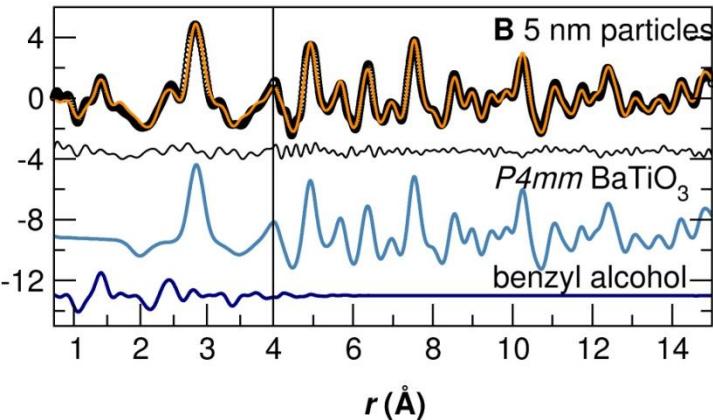
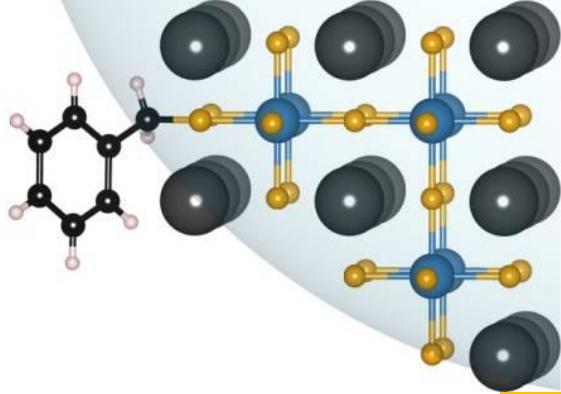
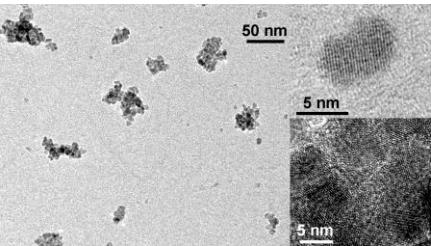
UNCLASSIFIED



Enhanced local dipoles in 5nm BaTiO₃



Rietveld analysis for ferroelectric bulk BaTiO₃ unambiguously supports tetragonal (polar) symmetry. For the nanoparticle data, tetragonal ($P4mm$) and cubic ($Pm\text{-}3m$) perovskite models are indistinguishable. **Are small BaTiO₃ particles polar?**



Total scattering clearly supports local polar symmetry ($P4mm$) symmetry. In addition the ligand structure can be readily observed.

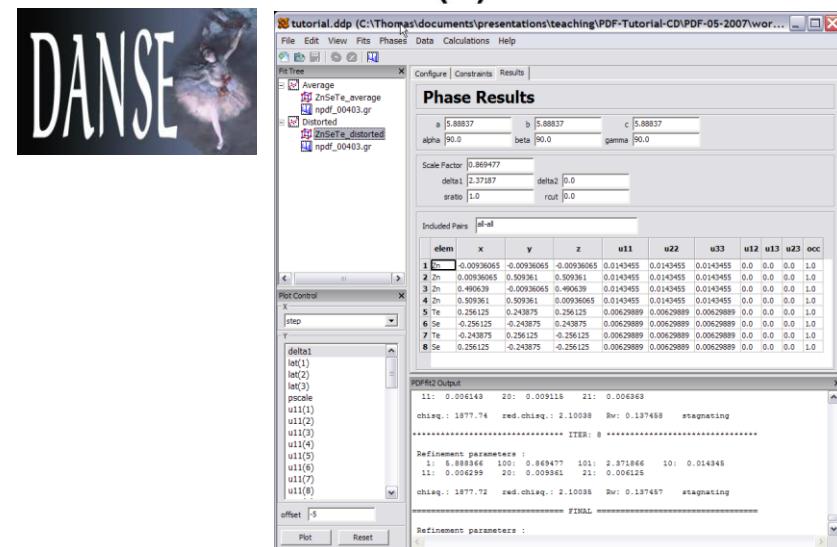
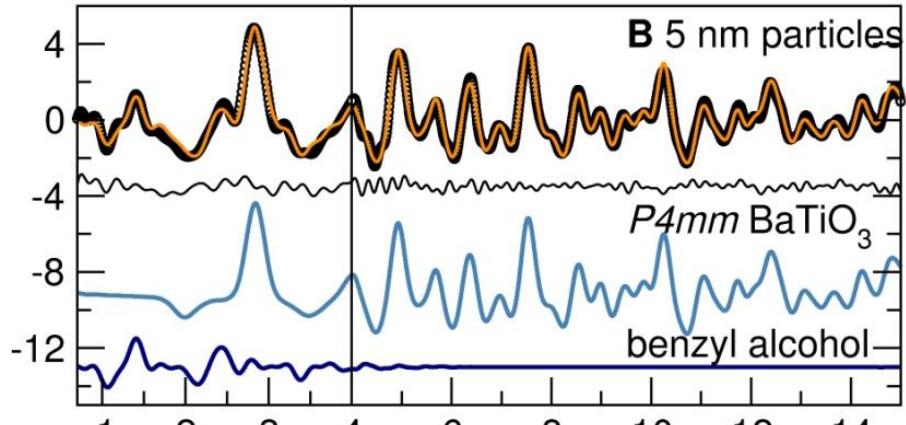
K. Page, T. Proffen, M. Niederberger, and R. Seshadri, **Enhanced local dipoles in BaTiO₃ nanoparticles**, *Chem Mater.*, in press

UNCLASSIFIED

Challenge: Modeling of nanoparticle data / current

Using PDFgui

- ❖ Calculation and refinement of small model system (< 1000 atoms)
- ❖ ‘Rietveld’ type parameters: *lattice parameters, atomic positions, displacement parameters, ..*
- ❖ New possibilities: *Refinements as function of r range !*
- ❖ <http://www.diffpy.org/>

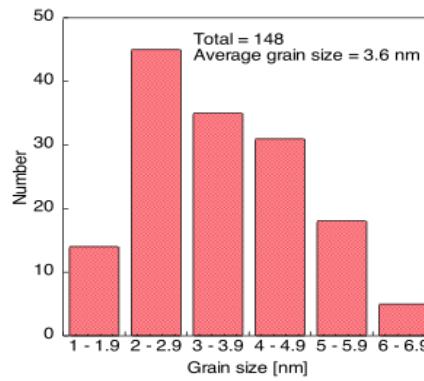
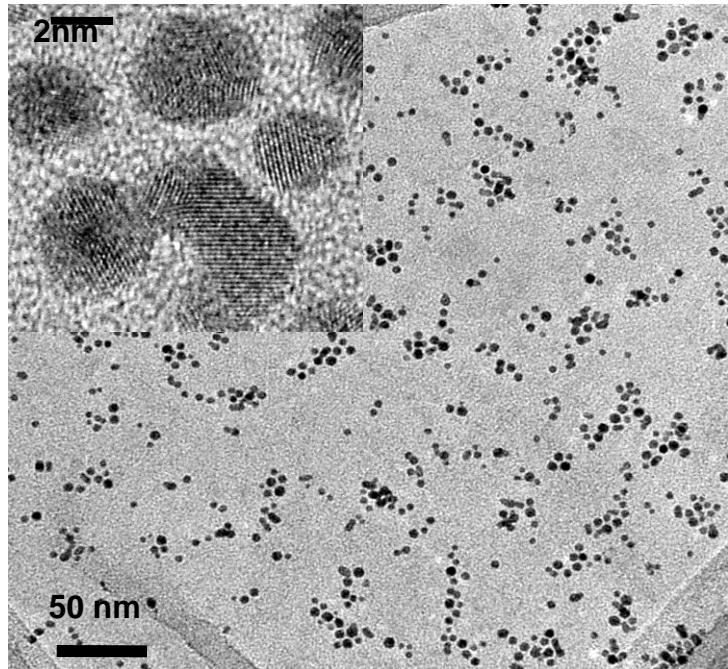


Nanoparticle case

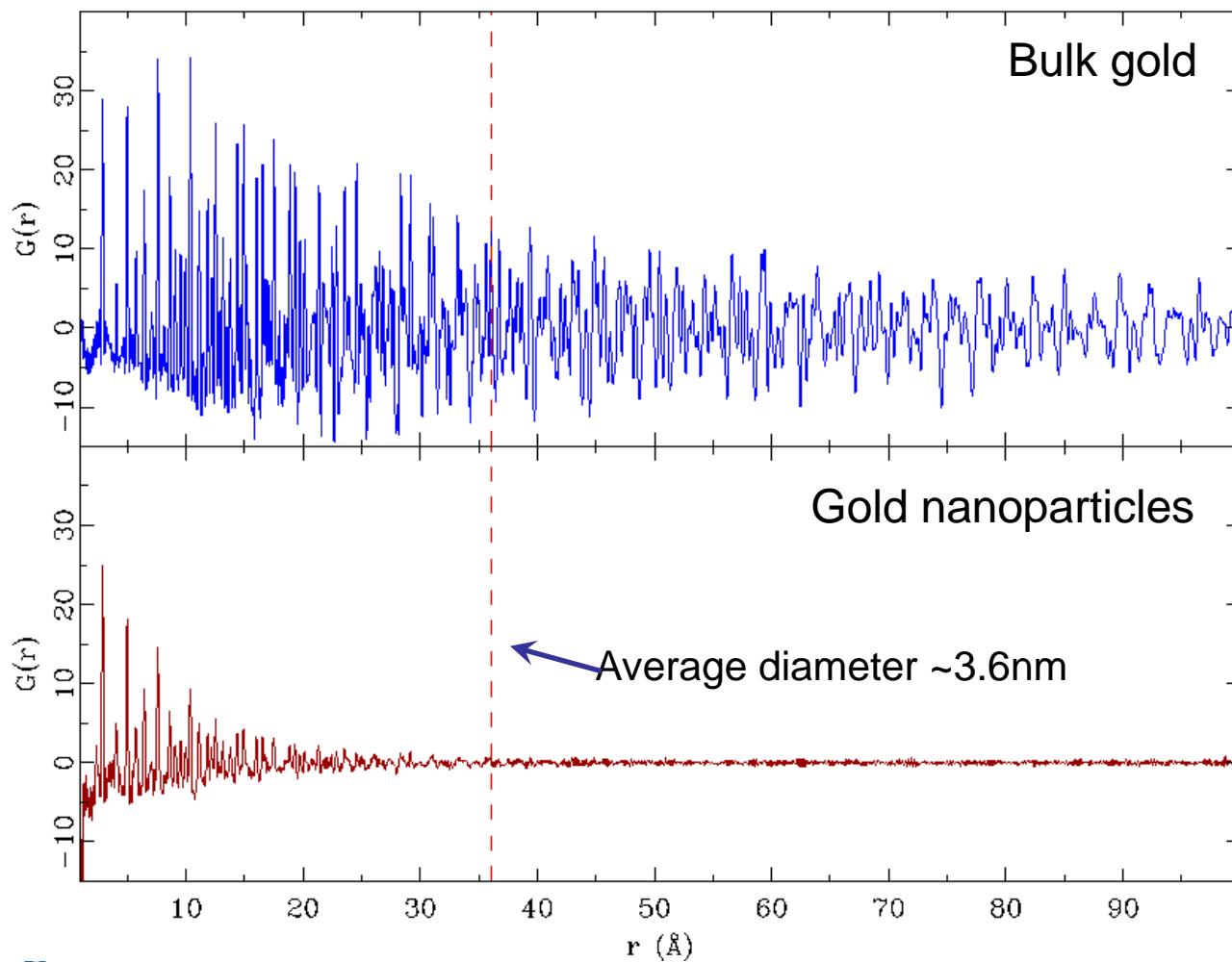
- ❖ Nanoparticle is modeled as **bulk** with a formfactor for the limited shape.
- ❖ Ligands are modeled as single molecules in box and **no** particle/ligand correlations are included.

Gold nanoparticles (revisited)

- 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



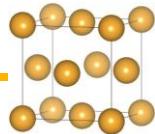
Gold nanoparticles: First NPDF data



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).

<http://totalscattering.lanl.gov>

Modeling Au structure only

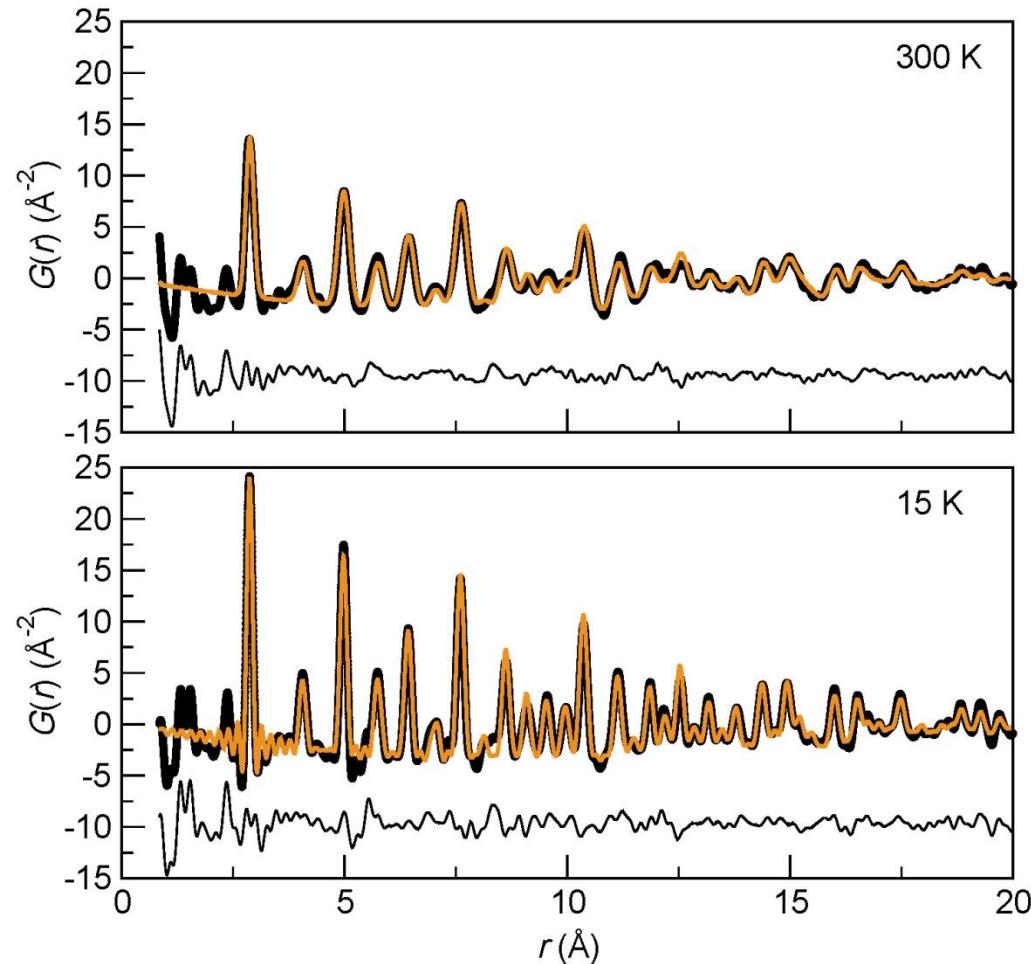


300 K: $R_w = 33.8\%$

- scale = 0.2121(5)
- a = 4.0753(1)
- $u_{iso}(\text{Au})$ = 0.01267(6)
- δ_1 = 1.980(7)
- d = 26.13(7) Å

15 K: $R_w = 27.8\%$

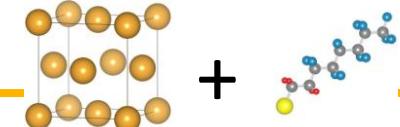
- scale = 0.2070(4)
- a = 4.06515(5)
- $u_{iso}(\text{Au})$ = 0.0044(2)
- δ_1 = 2.257(5)
- d = 25.54(4) Å



This is the conventional PDF nanoparticle approach... no ligand modeling.

UNCLASSIFIED

Modeling Au structure & ligand

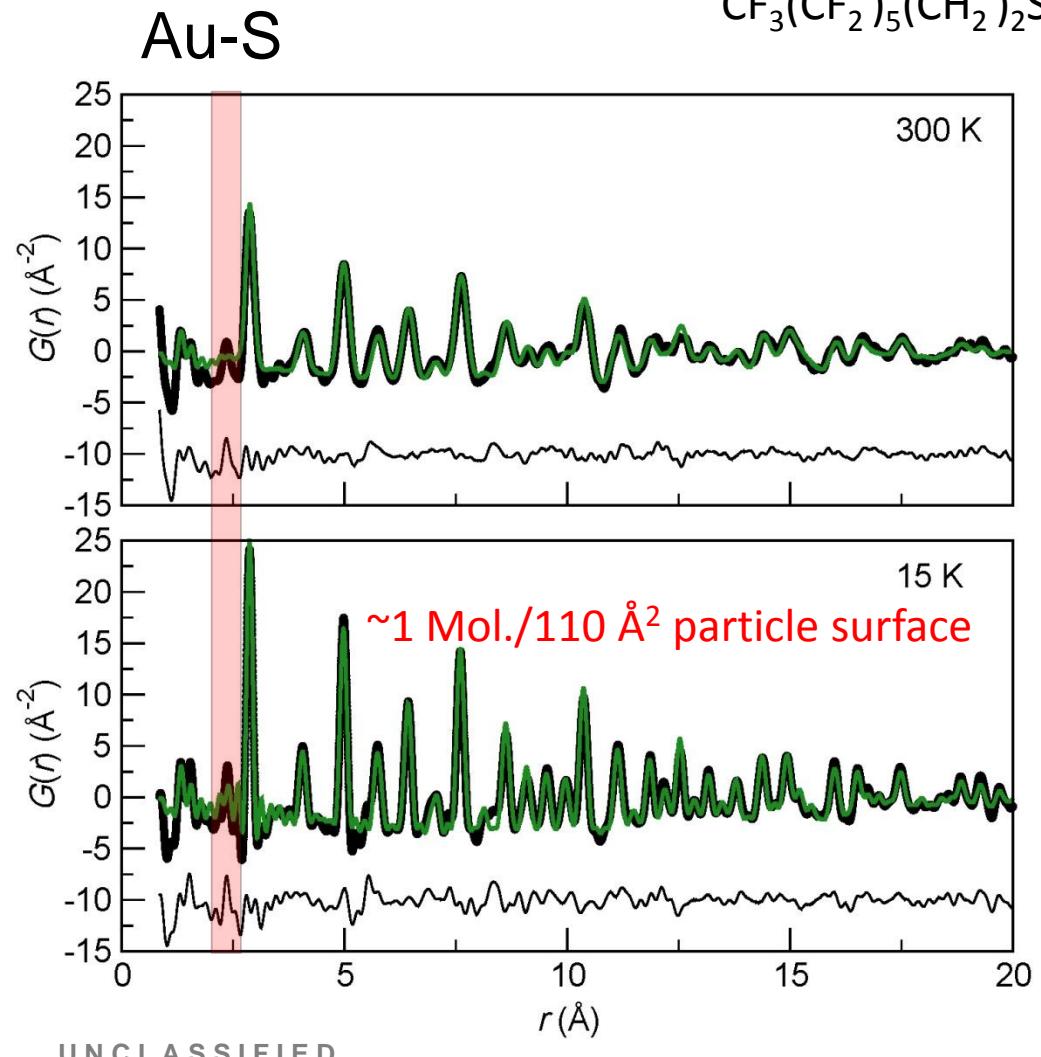


300 K: $R_w = 31.4\%$

- scale (Au) = 0.2082(5)
- scale (molecule) = 0.0485(6)
- a (Au) = 4.0755(1)
- a(molecule) = 49.40(3)
- u_{iso} (Au/molec) = 0.01227(5)
- δ_1 (Au) = 1.953(7)
- srat (molecule)= 0.02(3)

15 K: $R_w = 24.7\%$

- scale (Au) = 0.2054(4)
- scale (molecule) = 0.0604(6)
- a (Au) = 4.06500(5)
- a(molecule) = 49.23(2)
- u_{iso} (Au/molec) = 0.00433(2)
- δ_1 (Au) = 2.256(6)
- srat (molecule)= 0.03(14)

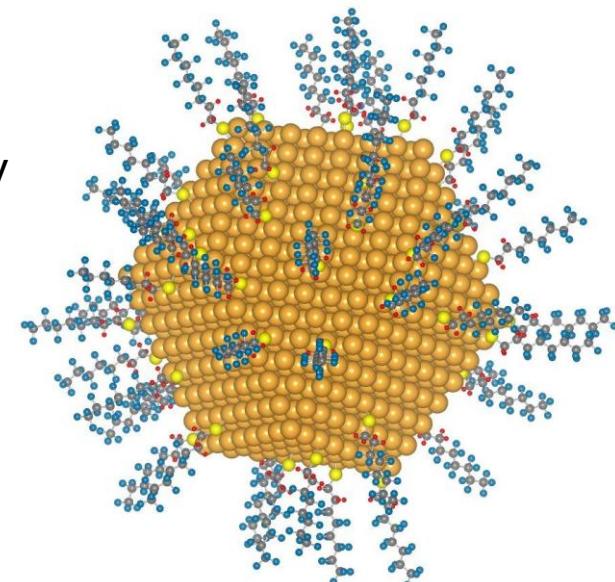
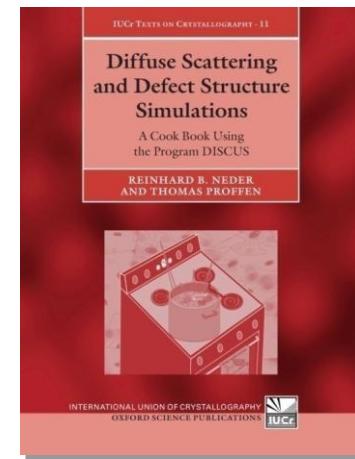


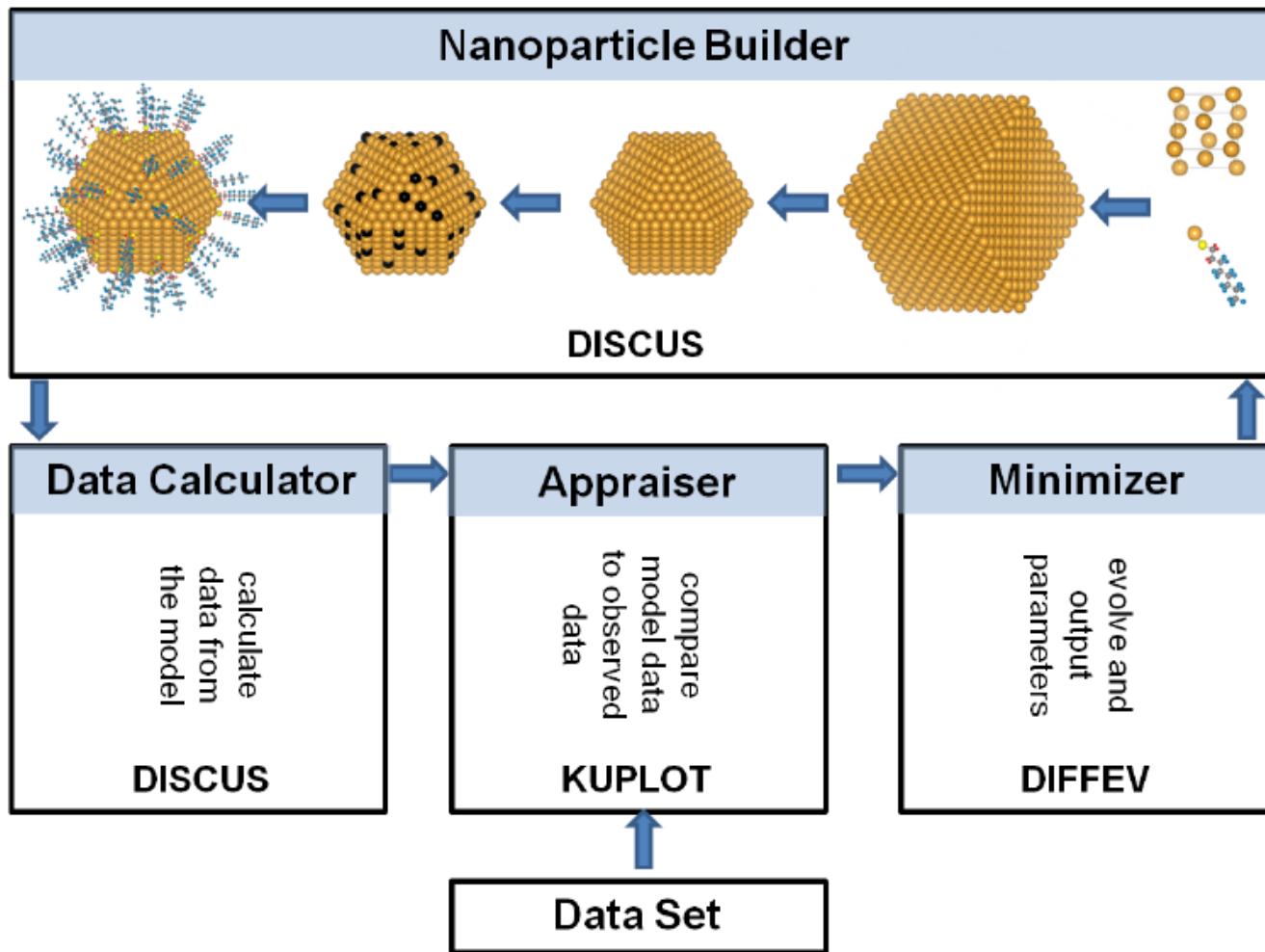
Challenge: Modeling of nanoparticle data - the future !

Using DISCUS/DIFFEV

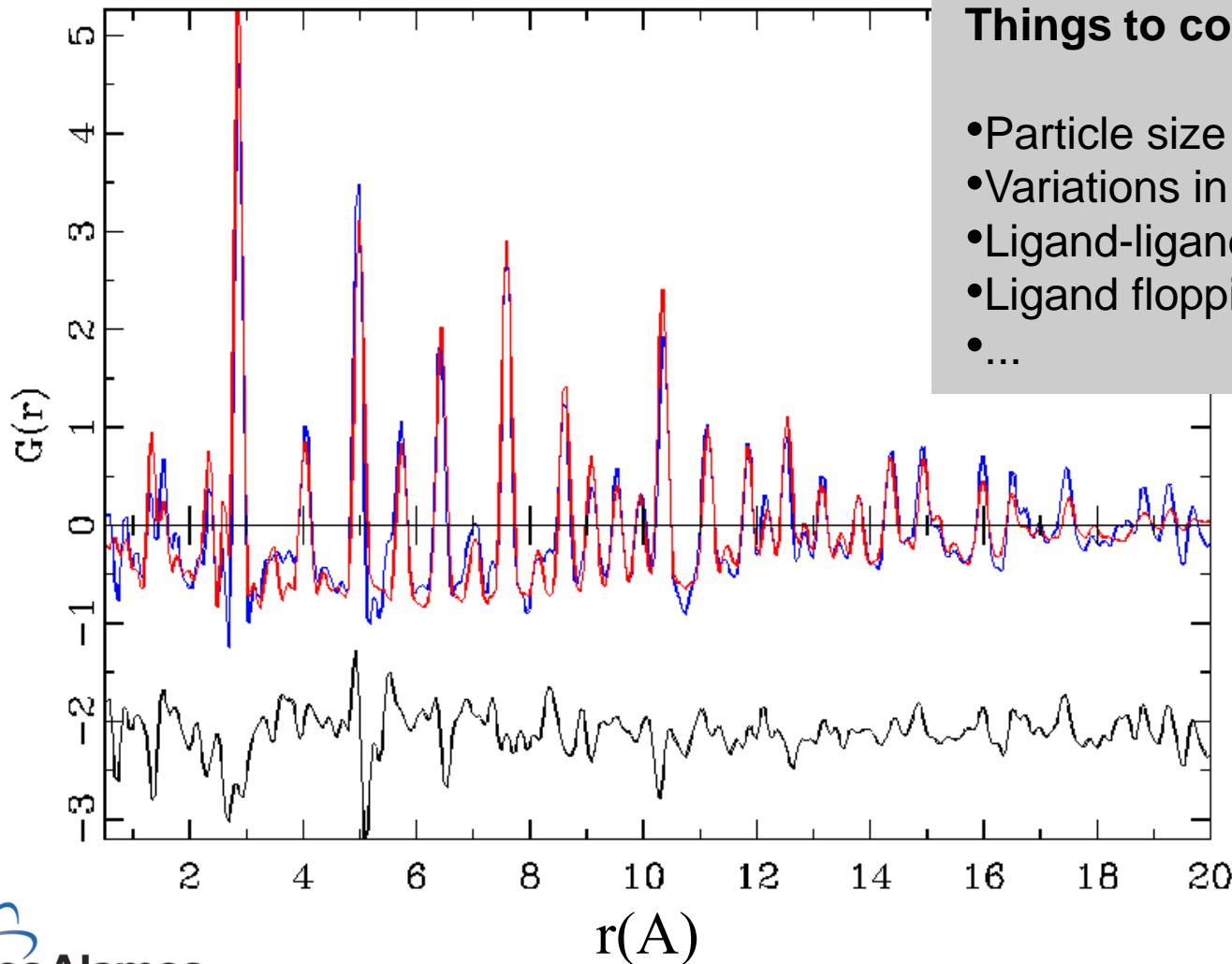
- ❖ <http://discus.sourceforge.net/>
- ❖ Approach: The particle is modeled as a whole.
- ❖ Current work on gold nanoparticles: An *fcc* Au particle is constructed in DISCUS, we select a cuboctahedron.
- ❖ Ligands (with 'internal' structure as constructed with DFT minimization) are located randomly at the particle surface with a defined surface density and defined Au-S distance, orientated out from the particle center.
- ❖ Evolutionary algorithm is used to refine model parameters above (CPU intensive).

Oxford University
Press, October 2009





First results ..



Things to consider

- Particle size distribution
- Variations in ligands
- Ligand-ligand interactions ?
- Ligand floppiness
- ...

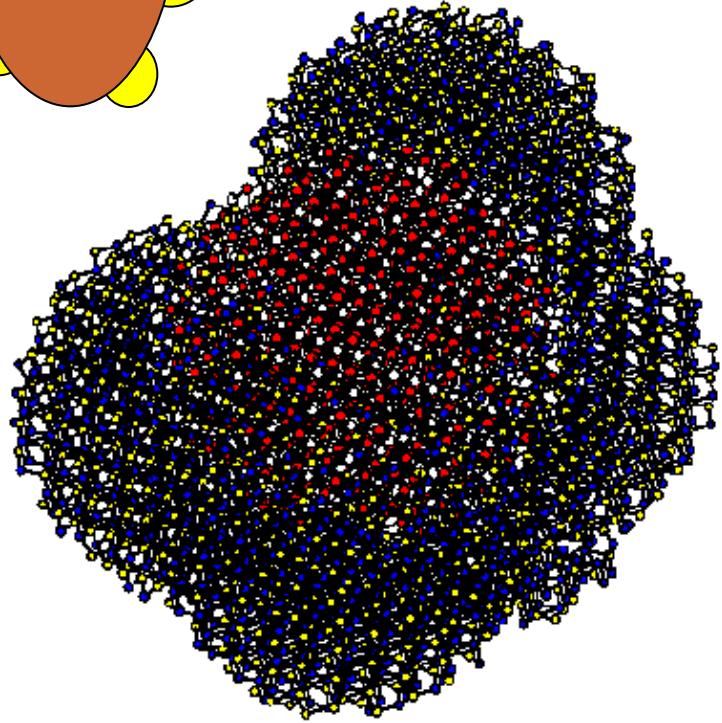
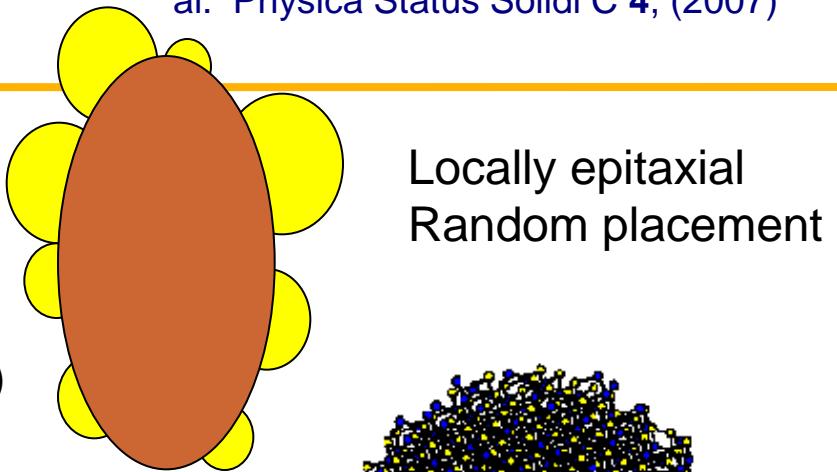
3.5 day DISCUS Workshops

- May 2011 U New York at Stony Brook (USA)
- Spring 2012 U Erlangen (Germany)



What is next ??

- Systematic studies (*samples* !)
- Extensions
 - Anisotropic shapes
 - Complex architectures (core-shell)
- Software
 - Nanoparticle Builder
 - Other refinement strategies
 - Using more complementary data
 - <http://discus.sourceforge.net>



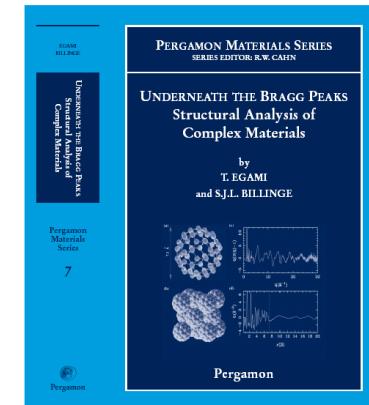
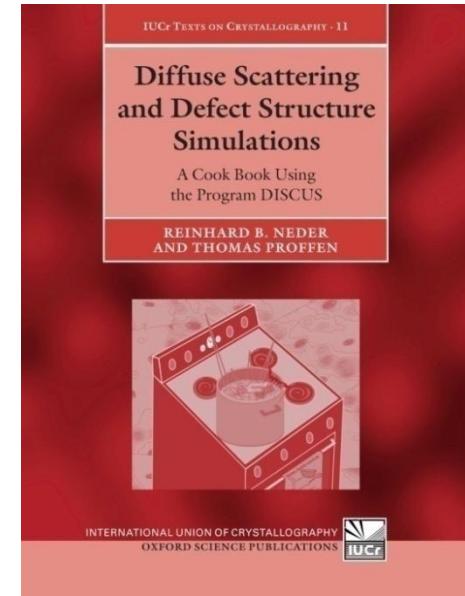
CdSe - ZnS core-shell
(R. Neder, U Erlangen)



Summary

- Analysis of total scattering gives valuable insight in **structure TM properties relationship**
- **High-resolution instruments** open the door to medium-range order investigations
- Obtain structural information from disordered crystalline, amorphous or composite materials
- Use multiple data sets (e.g. x-ray and neutron data) to characterize complex materials.
- **PDF approach well suited for nano-materials**
- **Better modeling approaches are needed ..**

<http://totalscattering.lanl.gov>



Thank you



LANSCE