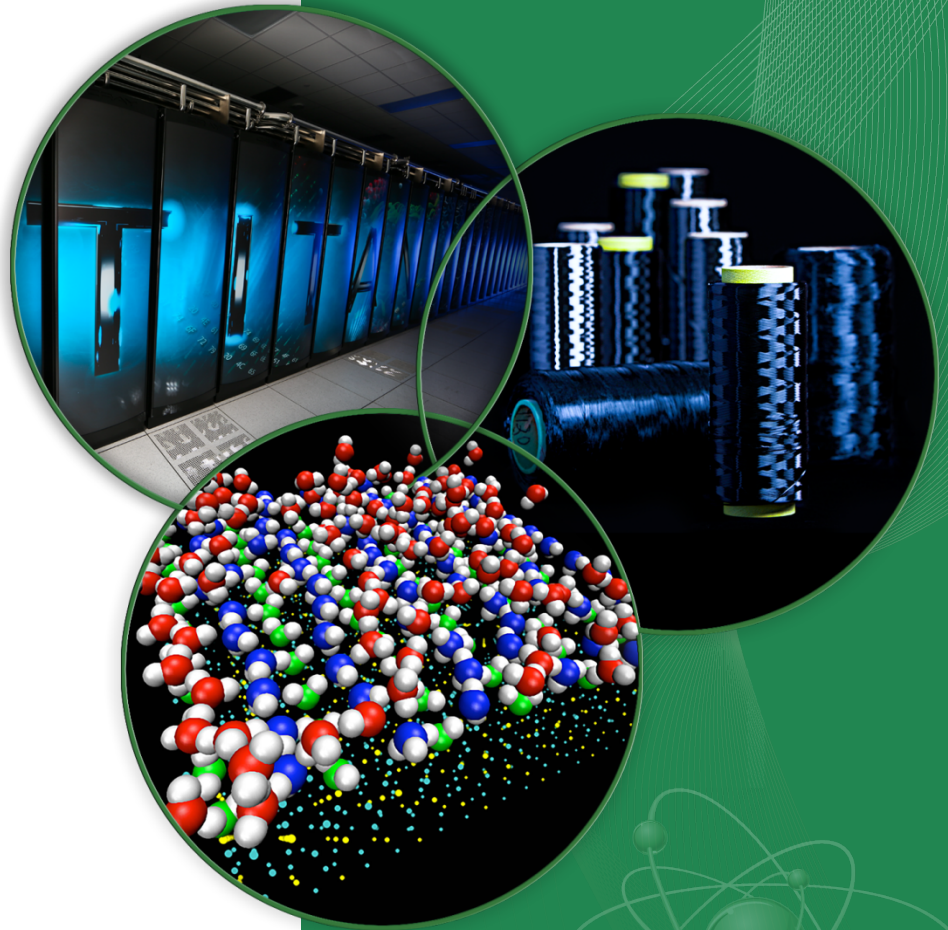


# Total Scattering

The Key to  
Understanding  
disordered, nano-  
crystalline and  
amorphous materials.

Thomas Proffen

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

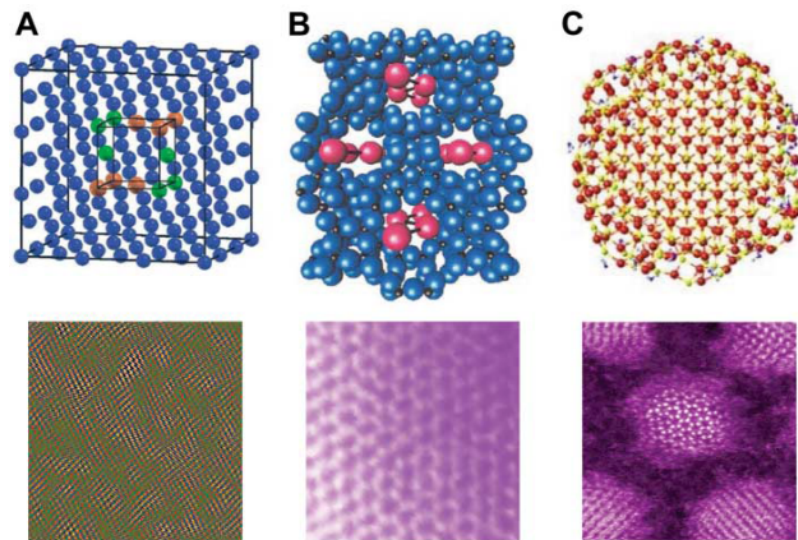


# The challenge : Knowing the local structure

❖ Traditional crystallographic approach to structure determination is insufficient or fails for

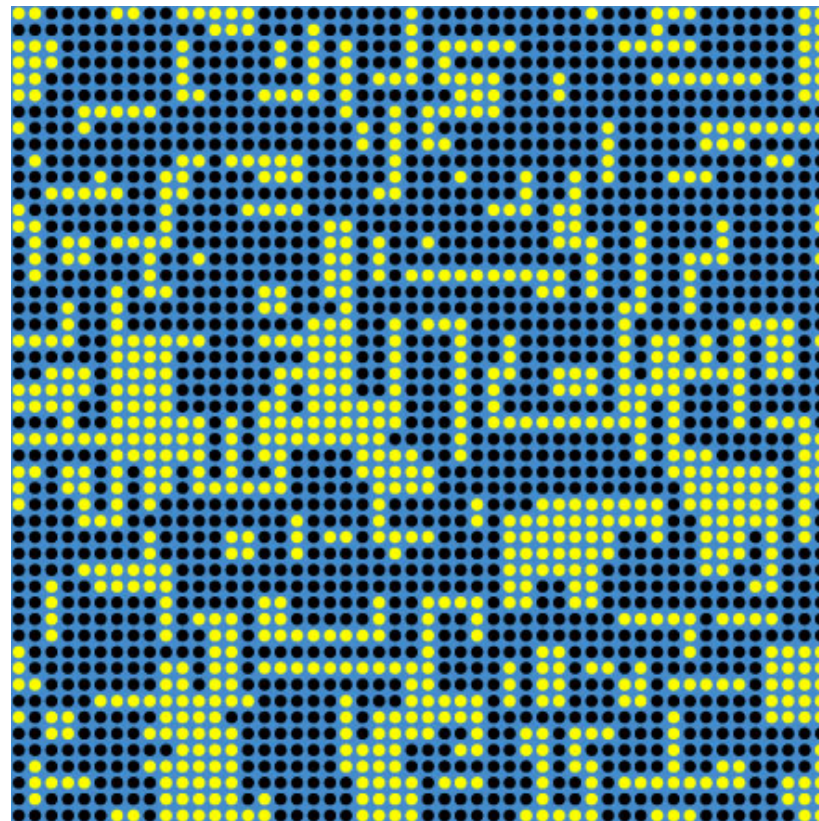
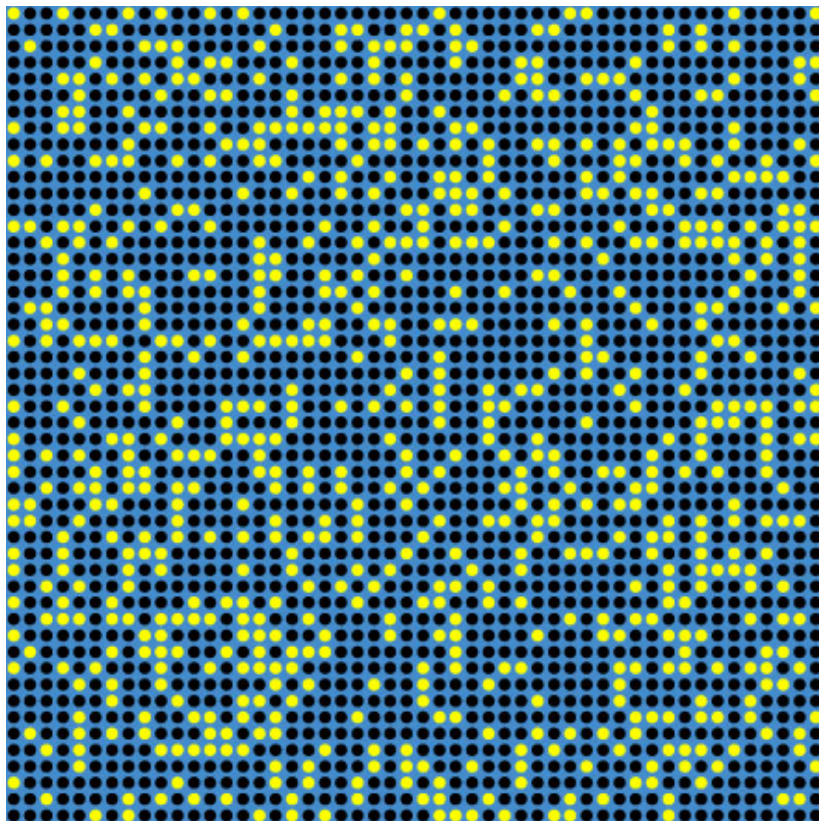
- ❖ **Non crystalline materials**
- ❖ **Disordered materials**: The interesting properties are often governed by the defects or local structure !
- ❖ **Nanostructures**: Well defined local structure, but long-range order limited to few nanometers (-> poorly defined Bragg peaks)

❖ A new approach to determine **local** and **nano-scale** structures is needed.



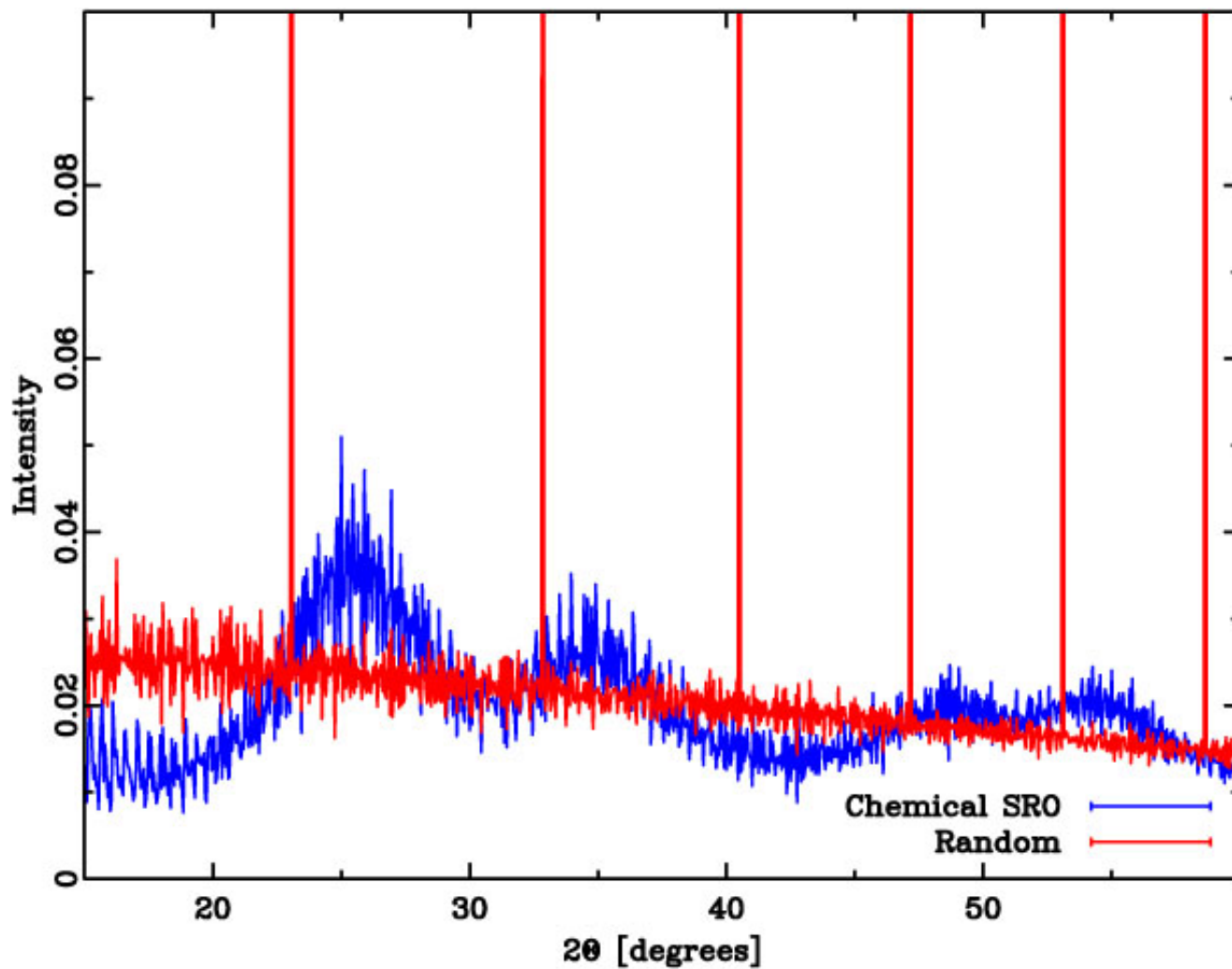
S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

# Total scattering ?

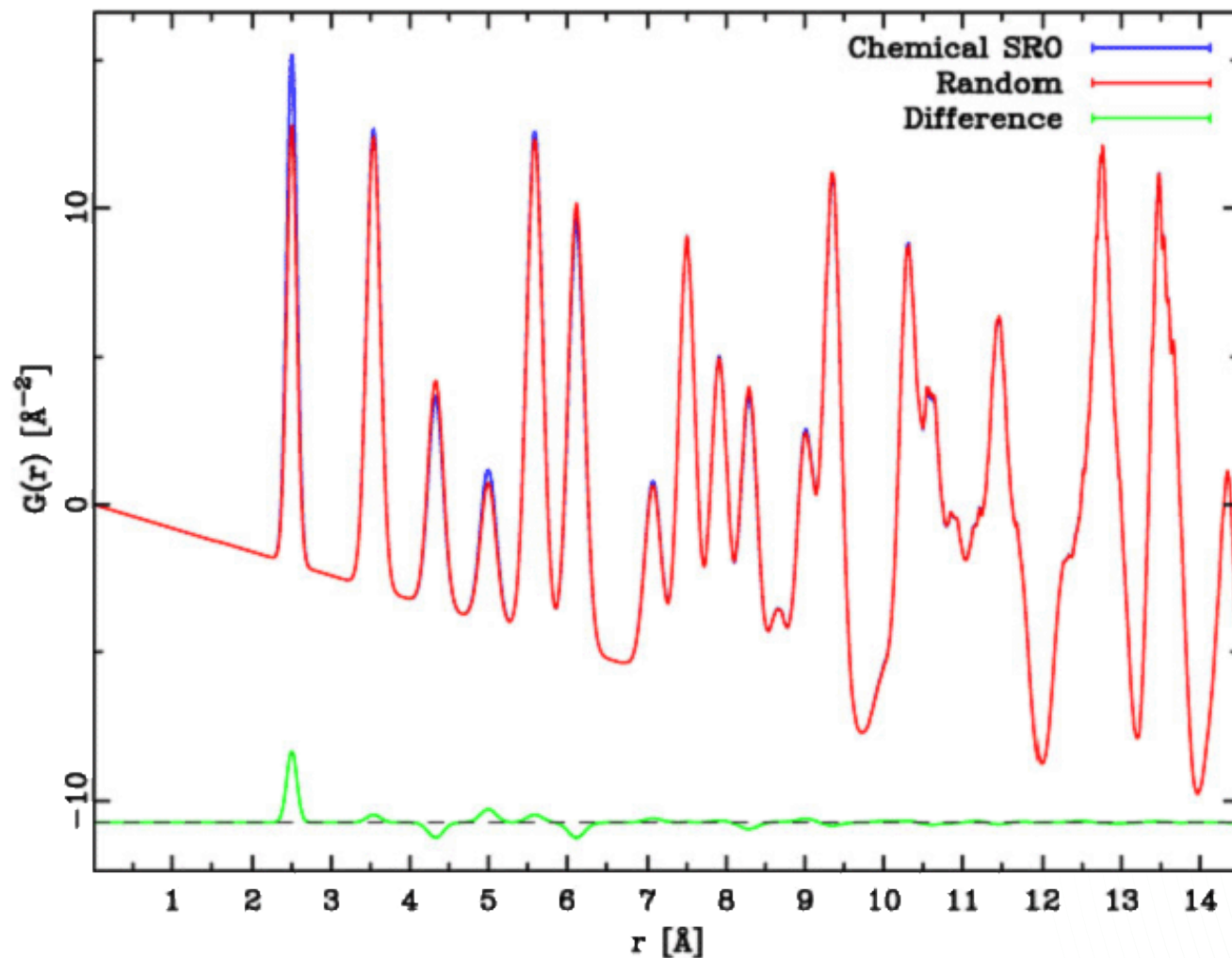


Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !  
**Properties might depend on vacancy ordering !!**

# How about powder diffraction ?



# Finally the Pair Distribution Function



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

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

# Example:

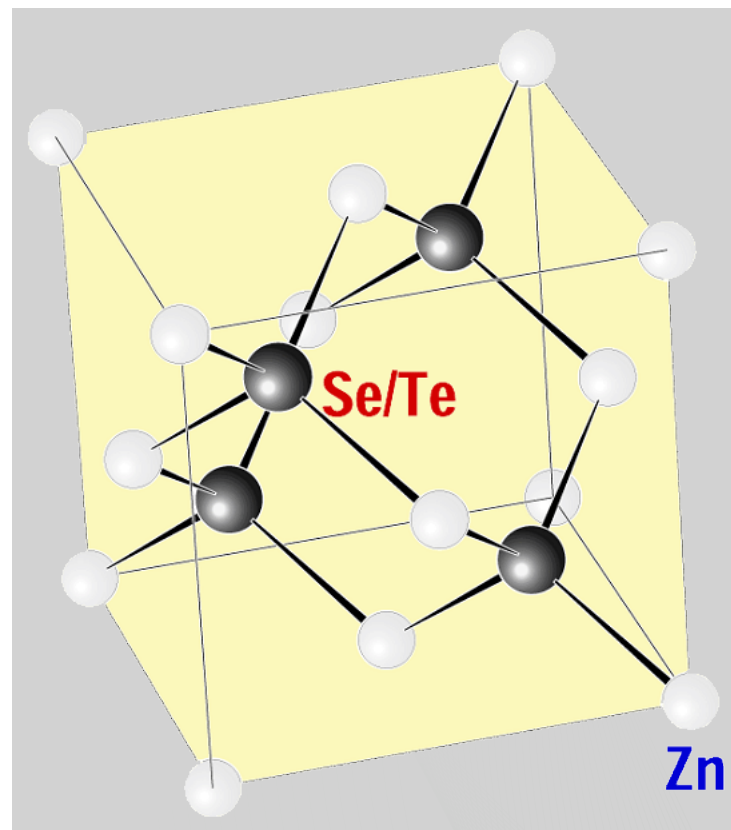
## Local atomic strain in $\text{ZnSe}_{1-x}\text{Te}_x$



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

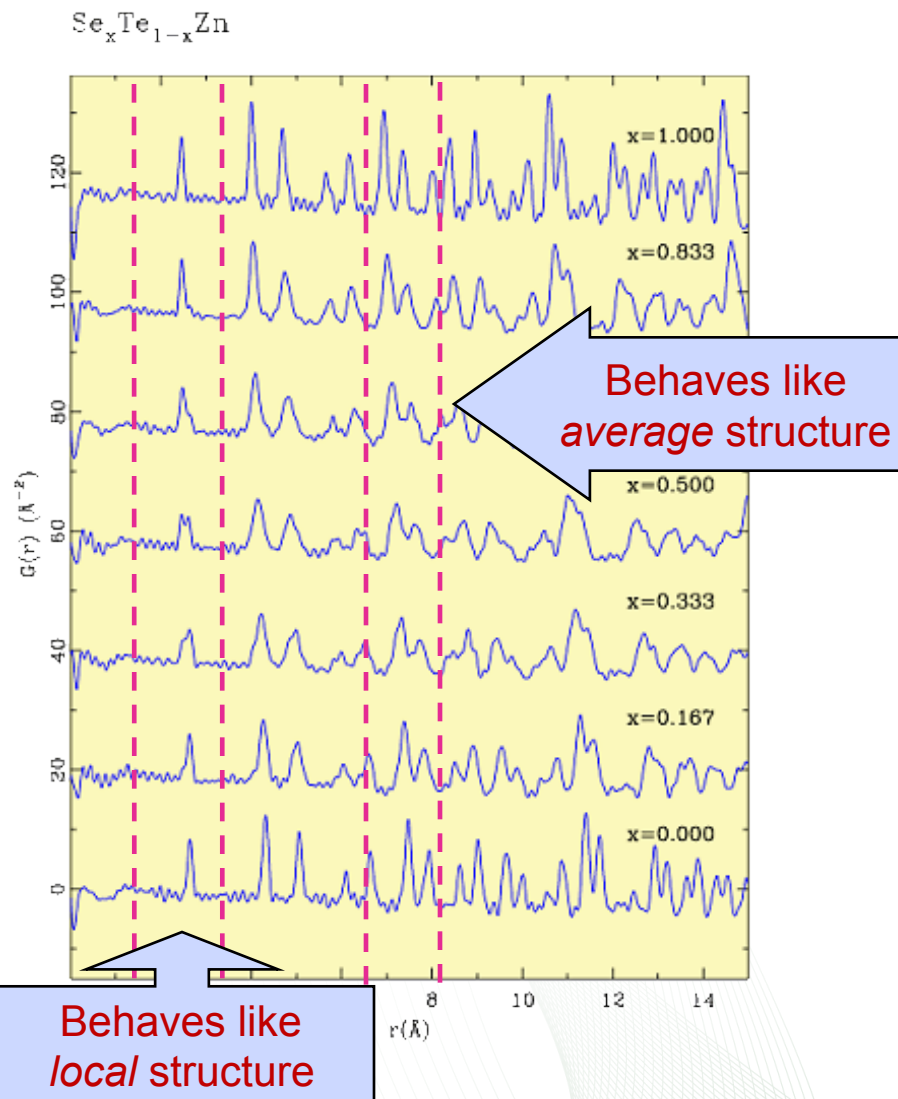
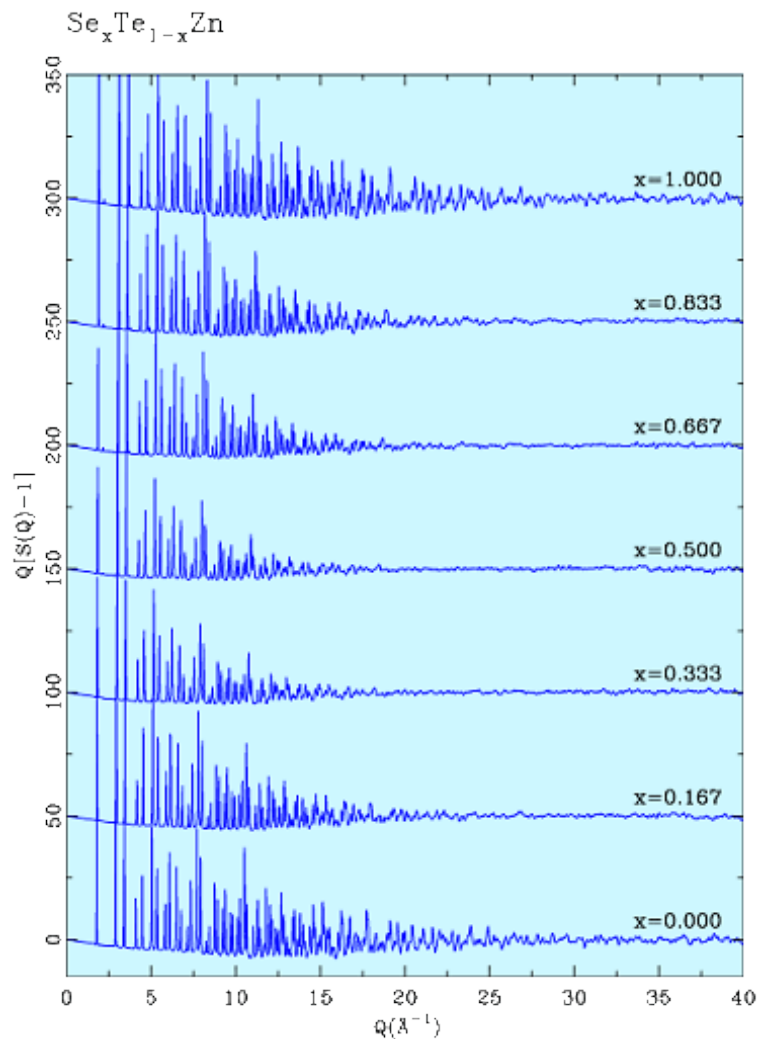
# $\text{ZnSe}_{1-x}\text{Te}_x$ : Structure

- ❖ Zinc blend structure (F43m)
- ❖ **Technological important** :  
Electronic band gap can be tuned by the composition  $x$ .
- ❖ Bond length difference  $\text{Zn-Se}$  and  $\text{Zn-Te} \Rightarrow$  **strain**.
- ❖ Local structural probe required !

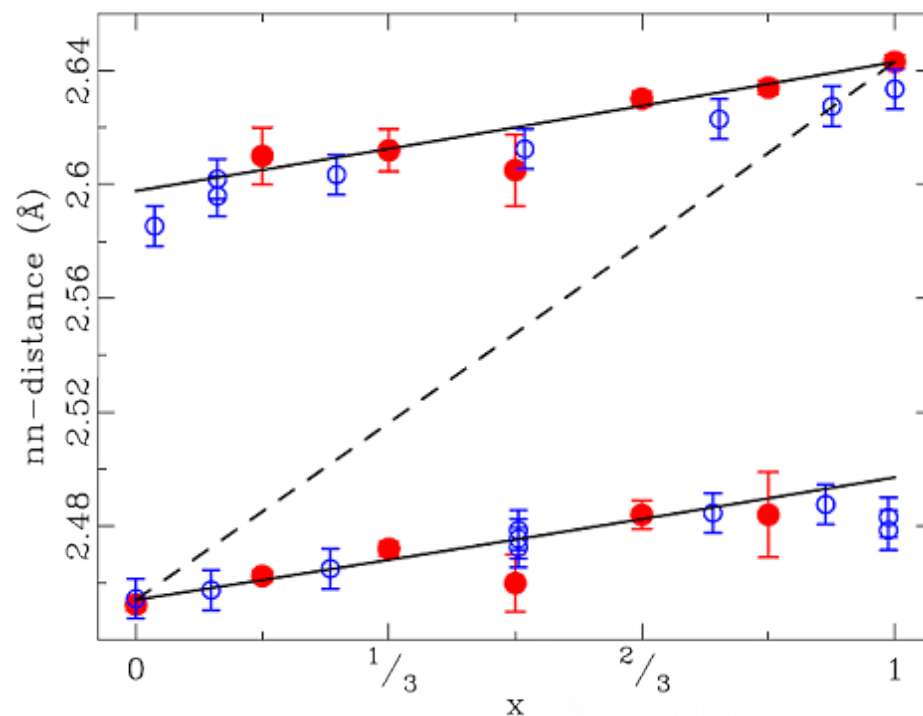
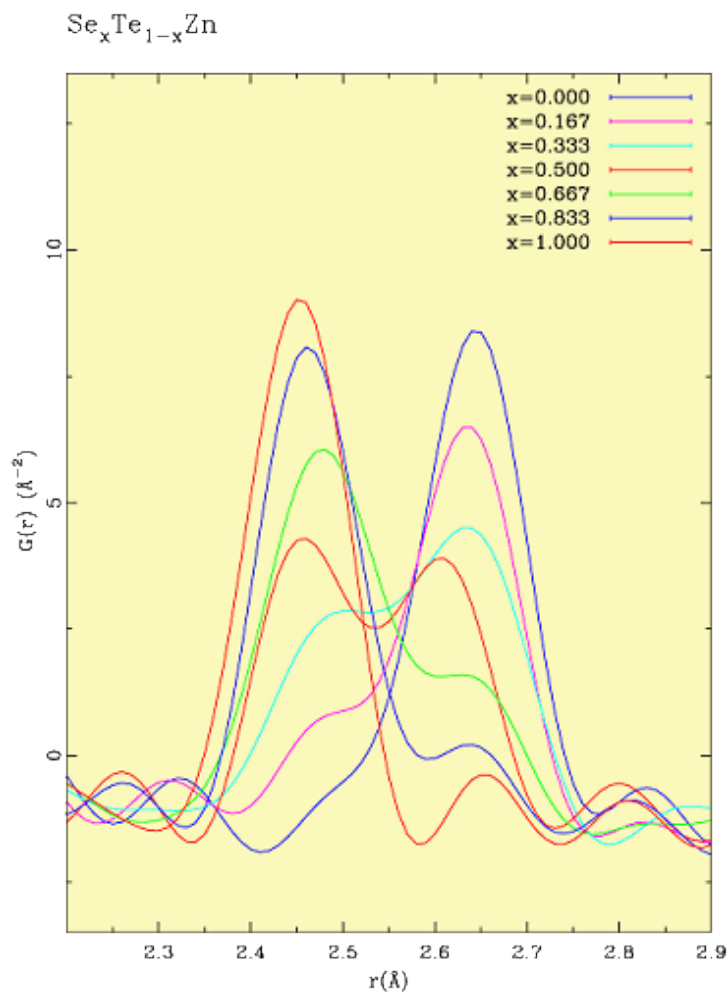


# ZnSe<sub>1-x</sub>Te<sub>x</sub> : Total scattering

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



# ZnSe<sub>1-x</sub>Te<sub>x</sub> : Nearest neighbors



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

# Example:

## Elastic properties of bulk metallic glasses

**Katharine Page**



**Thomas Proffen  
Bjorn Clausen**



**Ersan Ustundag  
Seung-Yub Lee**

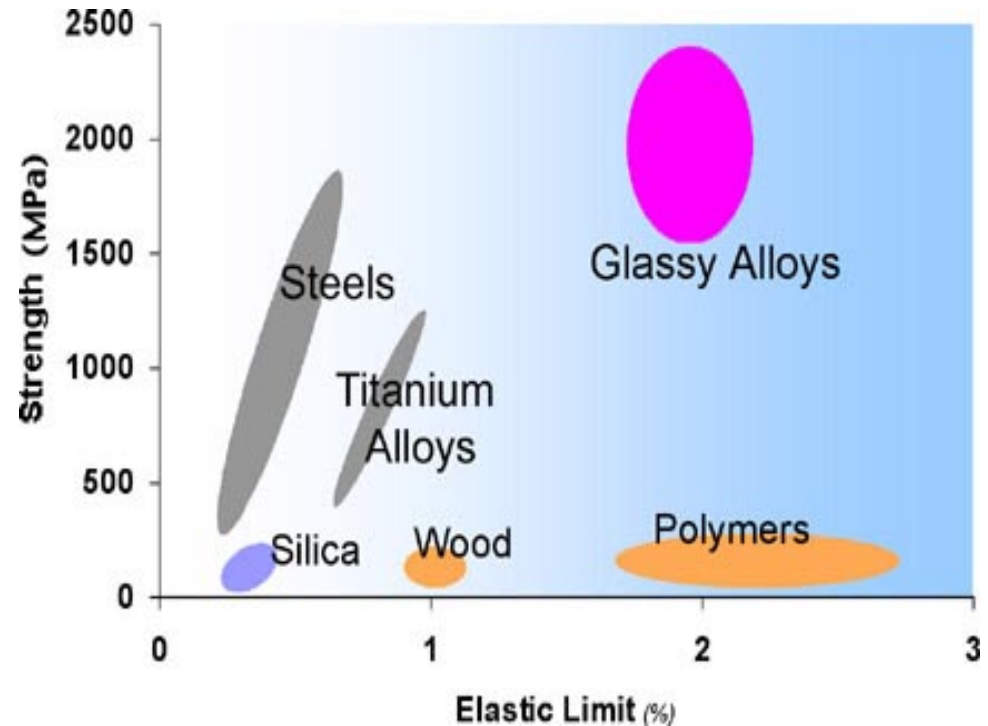


**Facilities:** Lujan  
**Funding:** DOE, NSF



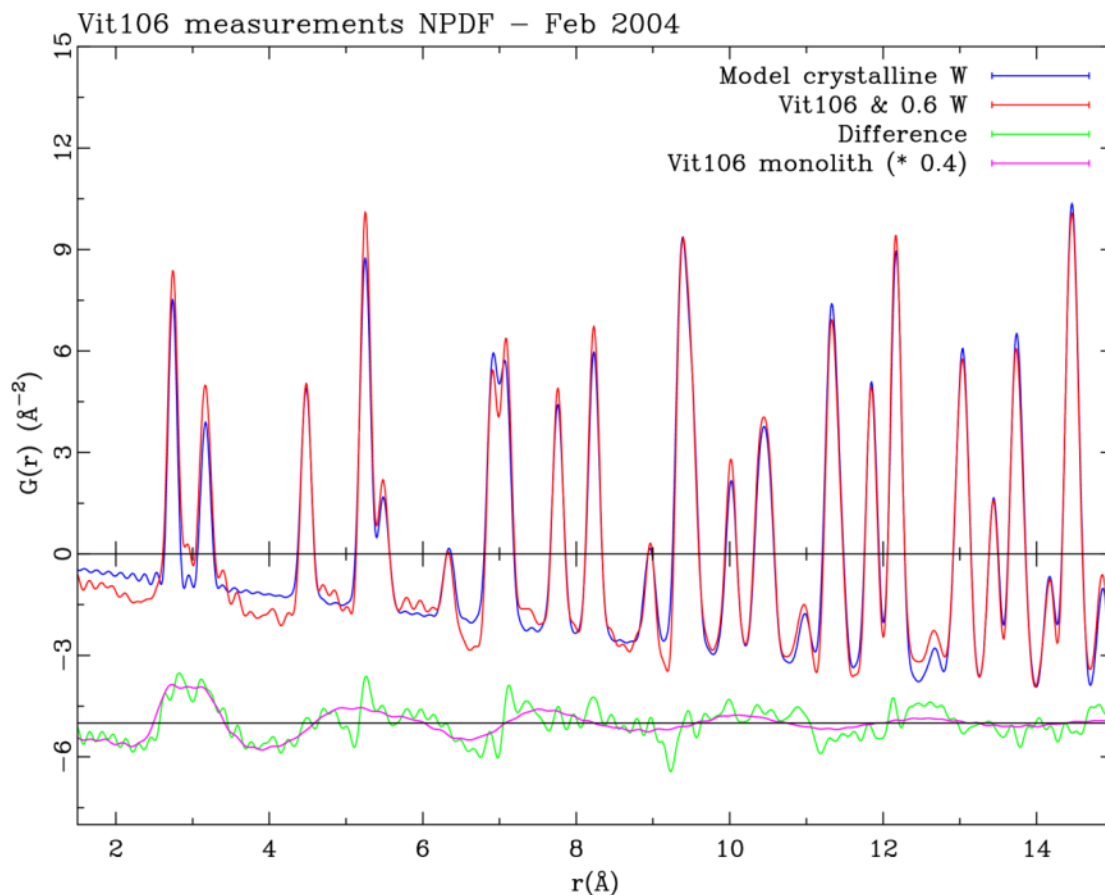
# BMG : Properties

- ❖ High Specific Strength
- ❖ Light Weight
- ❖ High Elastic Strain
- ❖ High Hardness
- ❖ Excellent Wear Resistance
- ❖ Excellent Corrosion Resistance
- ❖ BMG's are prone to catastrophic failure during unconstrained loading due to the formation of macroscopic shear bands
- ❖ *Crystalline reinforcements to suppress the formation of macroscopic shear bands*



[http://www.its.caltech.edu/~matsci/wlj/wlj\\_research.html](http://www.its.caltech.edu/~matsci/wlj/wlj_research.html)

# BMG: Phases in composite sample



- Ability to distinguish between phases - Difference between measured composite PDF and calculated Tungsten PDF agrees well with measured BMG PDF

# Example:

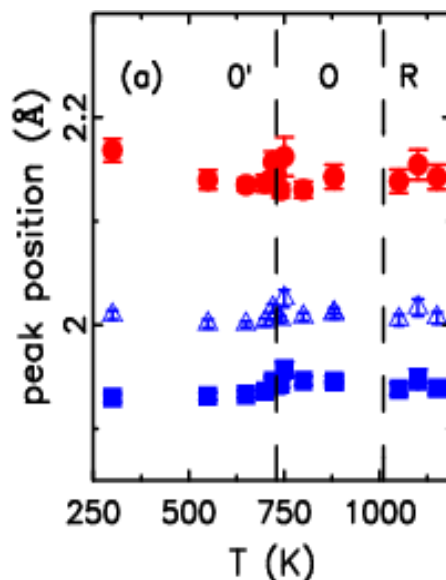
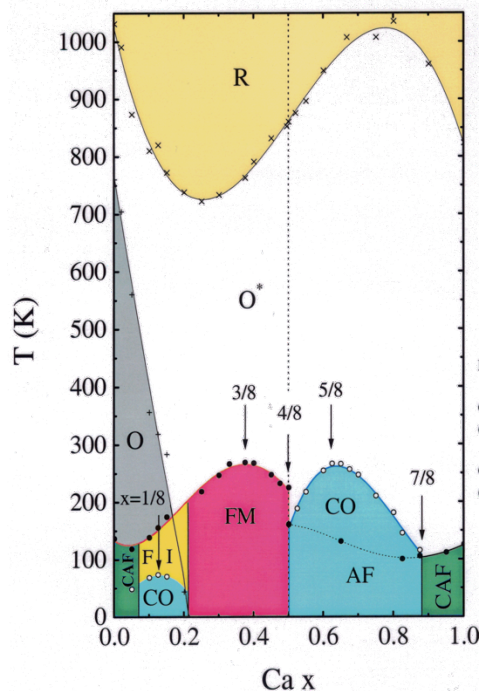
## Local structure in $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$



Simon Billinge  
Emil Bozin  
Xiangyn Qiu

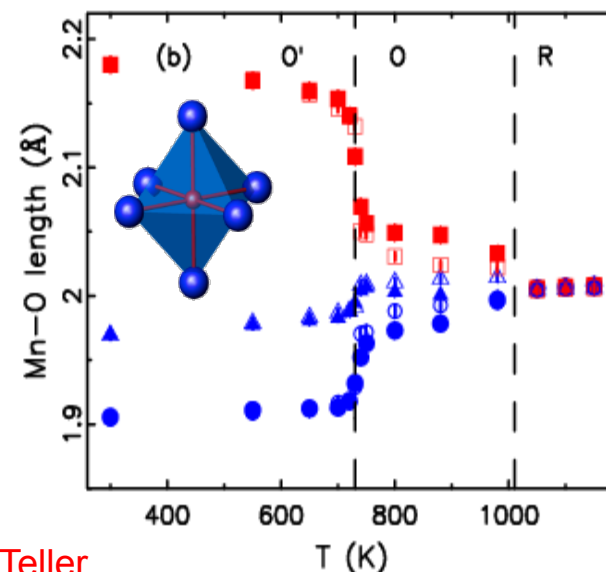
Thomas Proffen

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



Local structure

Jahn Teller  
Long Mn-O bond



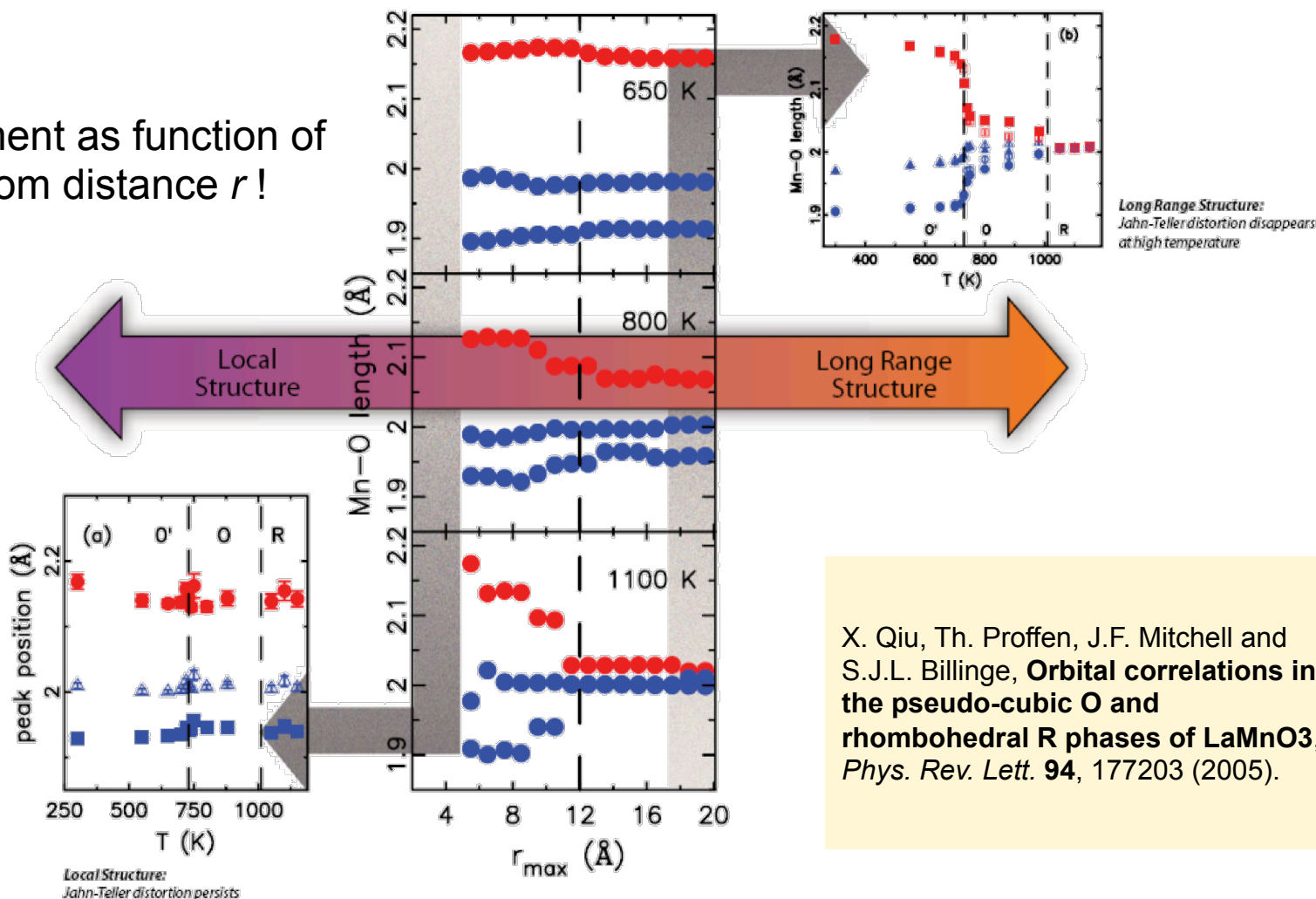
Average structure

- 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).

# DISTORTED OR NOT DISTORTED?

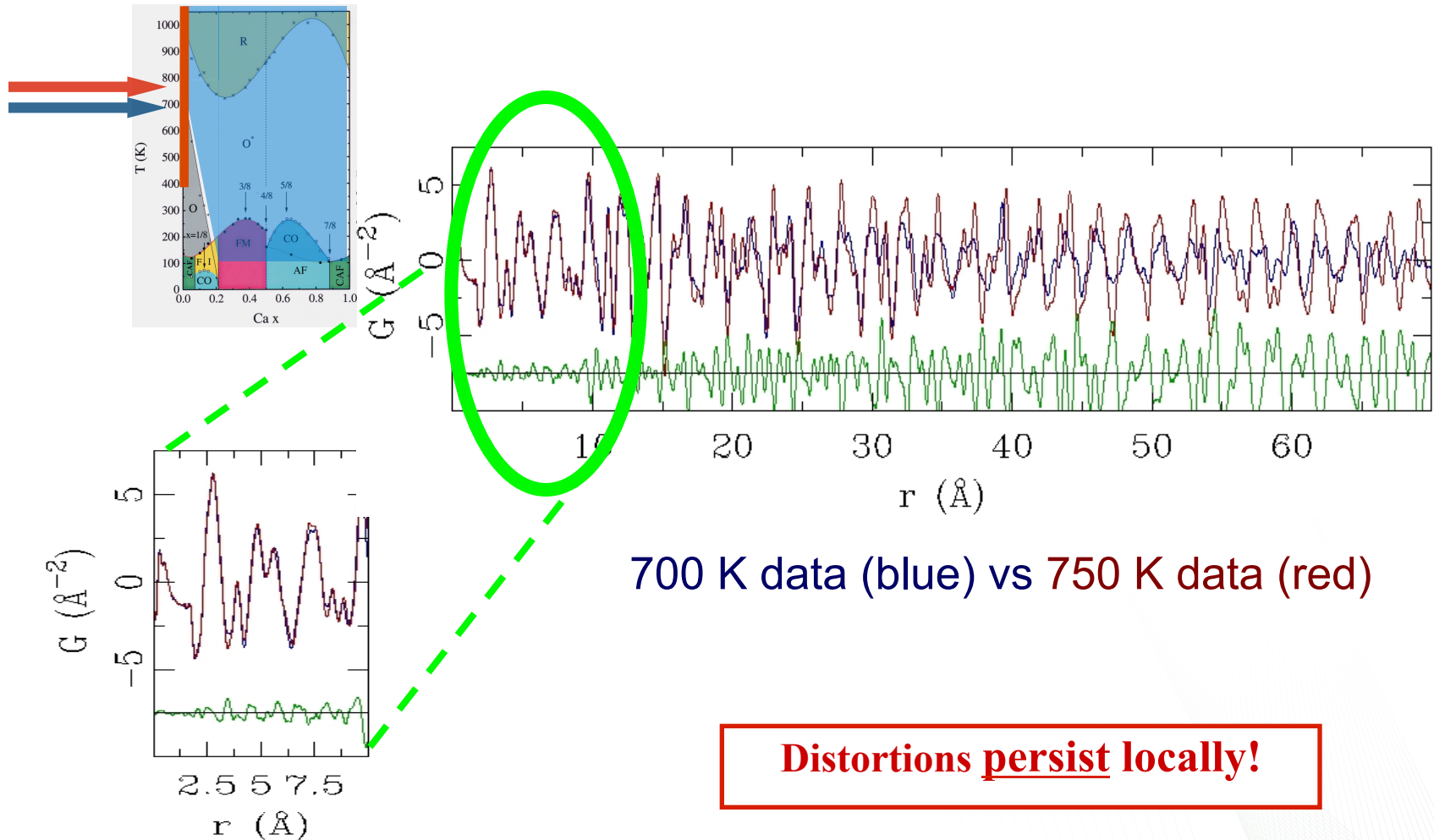
Study of the Jahn-Teller distortion in  $\text{LaMnO}_3$

Refinement as function of atom-atom distance  $r$  !



X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of  $\text{LaMnO}_3$** , *Phys. Rev. Lett.* **94**, 177203 (2005).

# LaMnO<sub>3</sub>: Simplicity of the PDF approach



## TOTAL SCATTERING GROUP

Tools for structural analysis of complex materials

Home

About Us

Share

### Total Scattering

Highlights

About us

On the road

### RESOURCES

Facilities

Publications

Software

Tutorials

For kids

Links

## Tutorials

### Total scattering

- [LANSCE Neutron School - NPDF practical](#)  
This is the tutorial used for NPDF at the [LANSCE Neutron School](#). It illustrates the use of [PDFgui](#) using  $\text{LaMnO}_3$  data collected on NPDF.
- [PDF Tutorial](#)  
This tutorial gives an introduction to neutron data reduction using [PDFgetN](#) and simple refinements of the local structure using [PDFgui](#). The material is adapted from a tutorial CDROM developed by *Thomas Proffen* and *Simon Billinge*.

### Rietveld

- [Powder Diffraction Crystallography Resources](#)  
This is an extensive collection of talks and tutorials related to powder diffraction hosted at the [Advanced Photon Source](#).

### Other

- [Interactive Tutorial about Diffraction](#)  
This tutorial gives a basic interactive introduction into diffraction and diffuse scattering. The interactive examples are generated using [DISCUS](#).
- [Kevin Cowtan's Book of Fourier](#)  
This is a book of pictorial 2-d Fourier Transforms. These are particularly relevant to the field of crystallography.

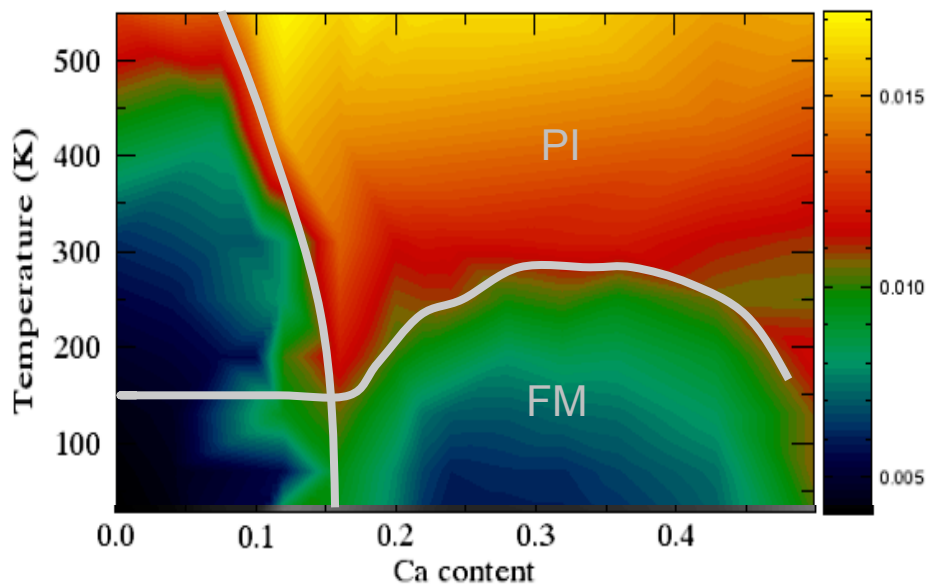


## Tutorials

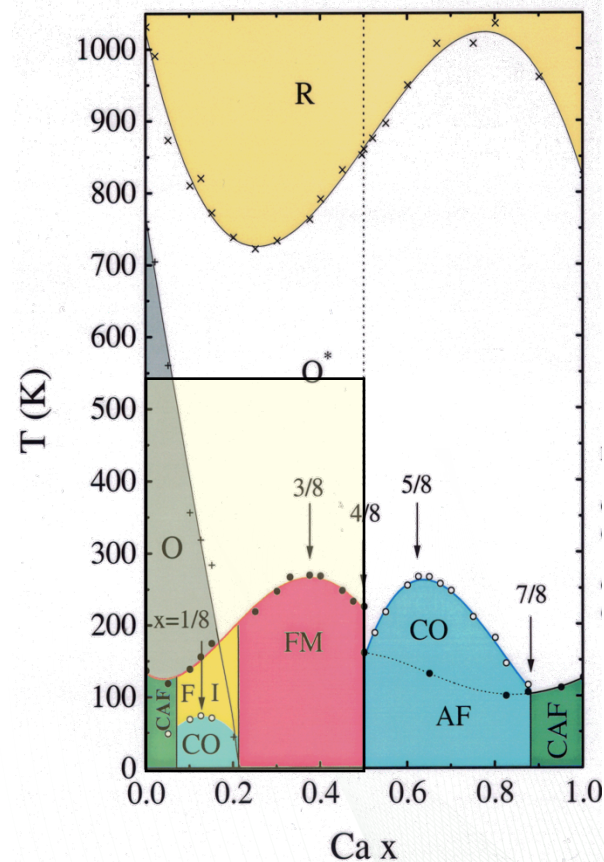
Make your own nanoparticles. Cartoons shown on this website were created by **Julie Coxe**, a talented artist and former summer student of the total scattering group.

# $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ : Phase diagram

**Atomic displacement parameter (ADP) for Oxygen**  
(measure for thermal and static deviations from site)



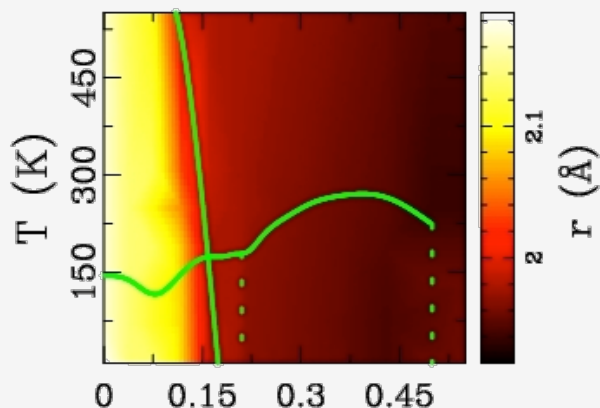
- Phase diagram draws itself from the parameters.
- Unexpected detail emerges and demands interpretation.



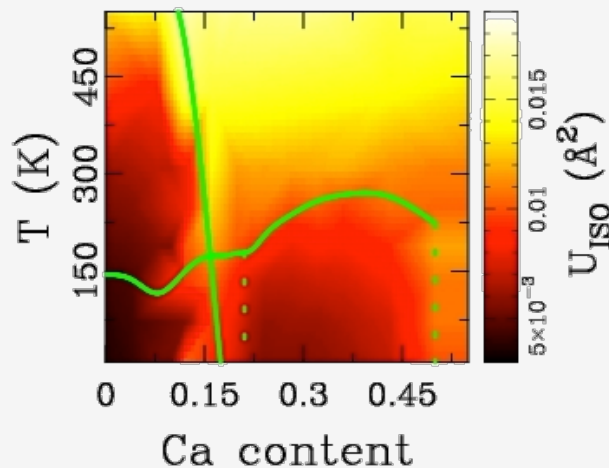
# $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ : Phase diagram

Mn-O  
long  
bond

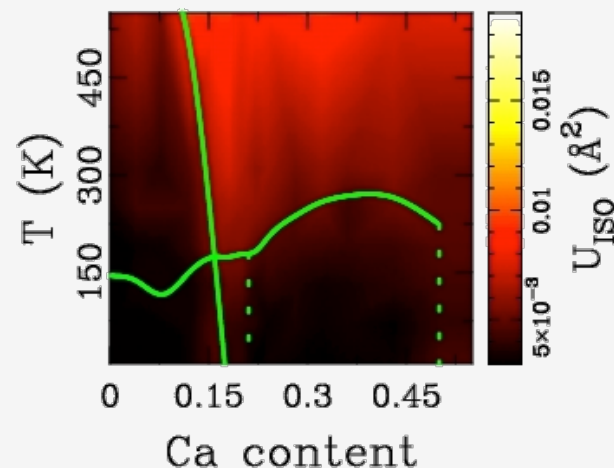
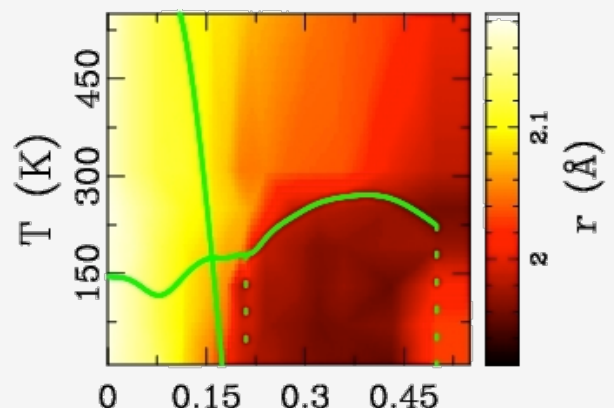
*Average structure*



ADP  
Oxygen



*Local structure*



# Example:

## “Complete” structure of Gold Nanoparticles

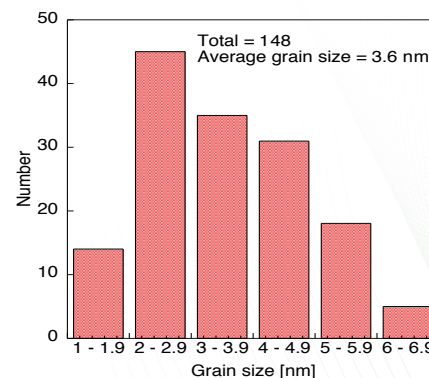
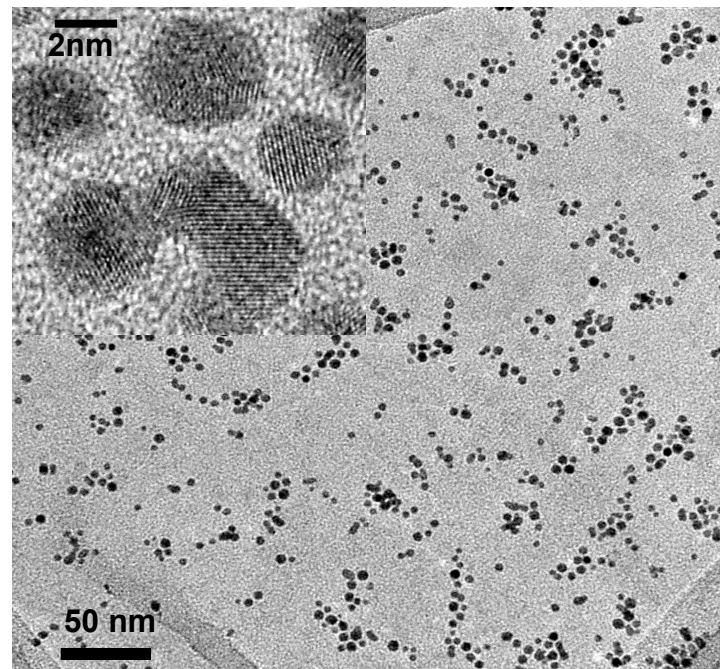


Katharine Page  
Ram Seshadri  
Tony Cheetham

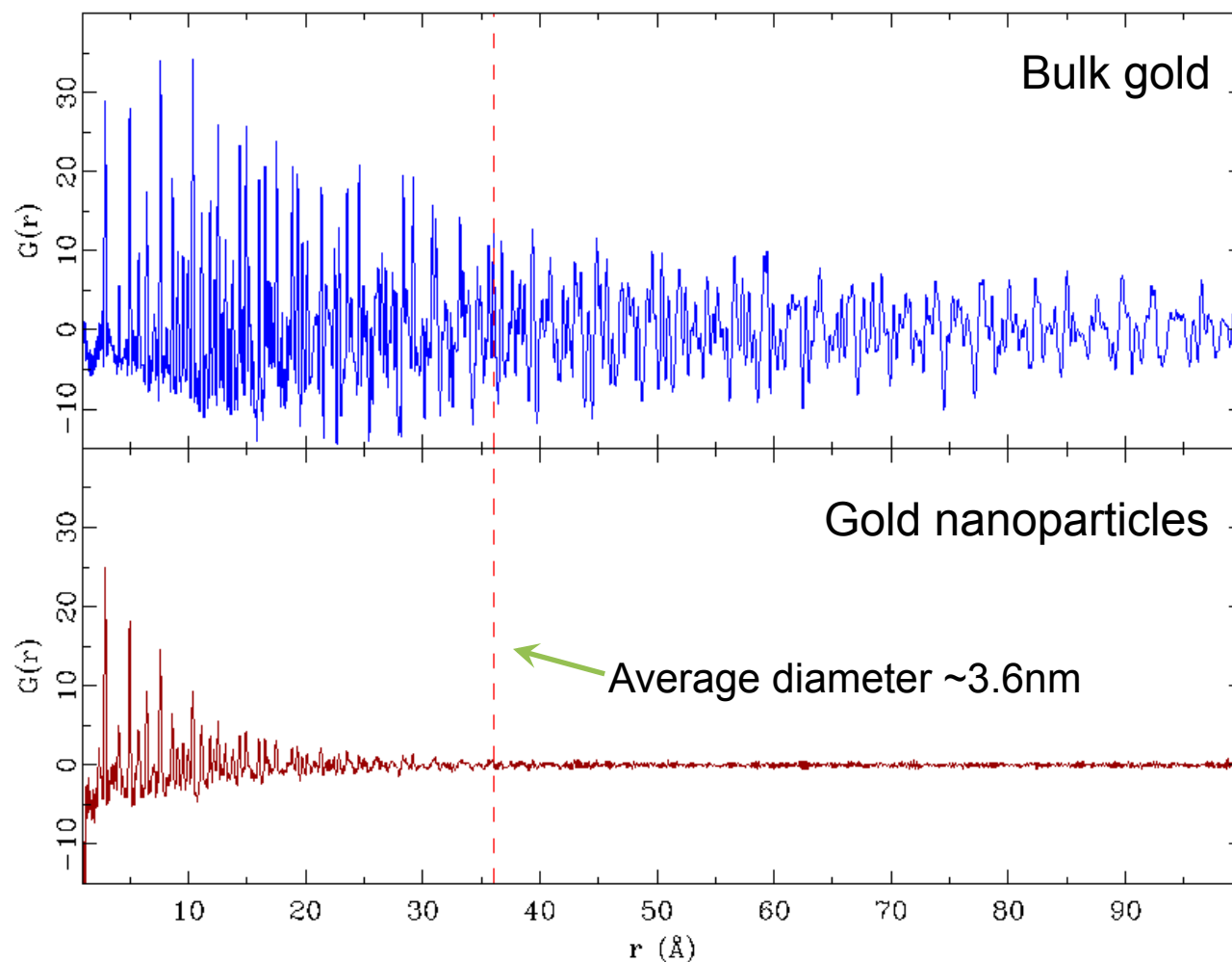
Thomas Proffen

# 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

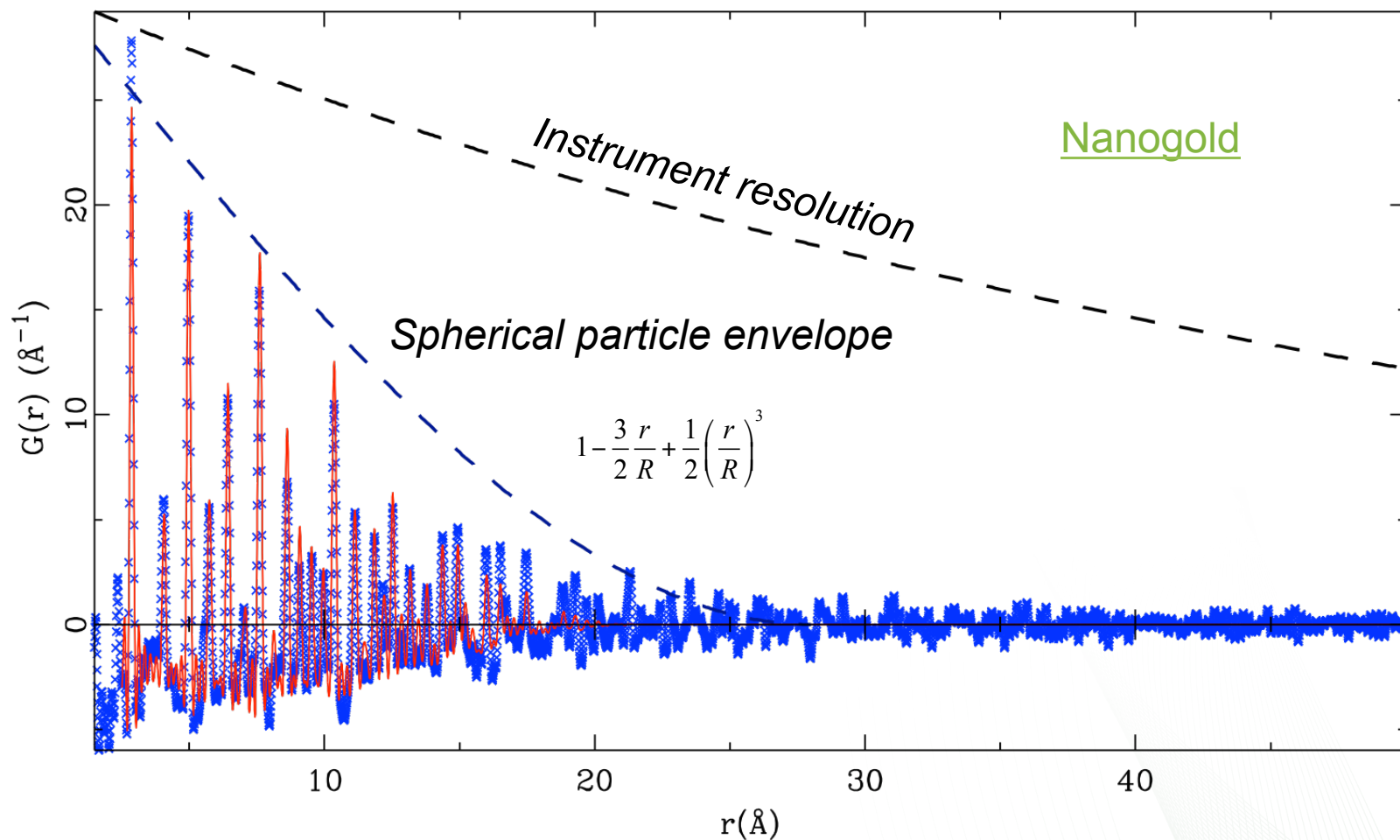


# Gold nanoparticles: First NPDF data

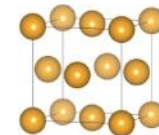


K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

# Nanoparticles: Particle size



# Modeling Au structure only

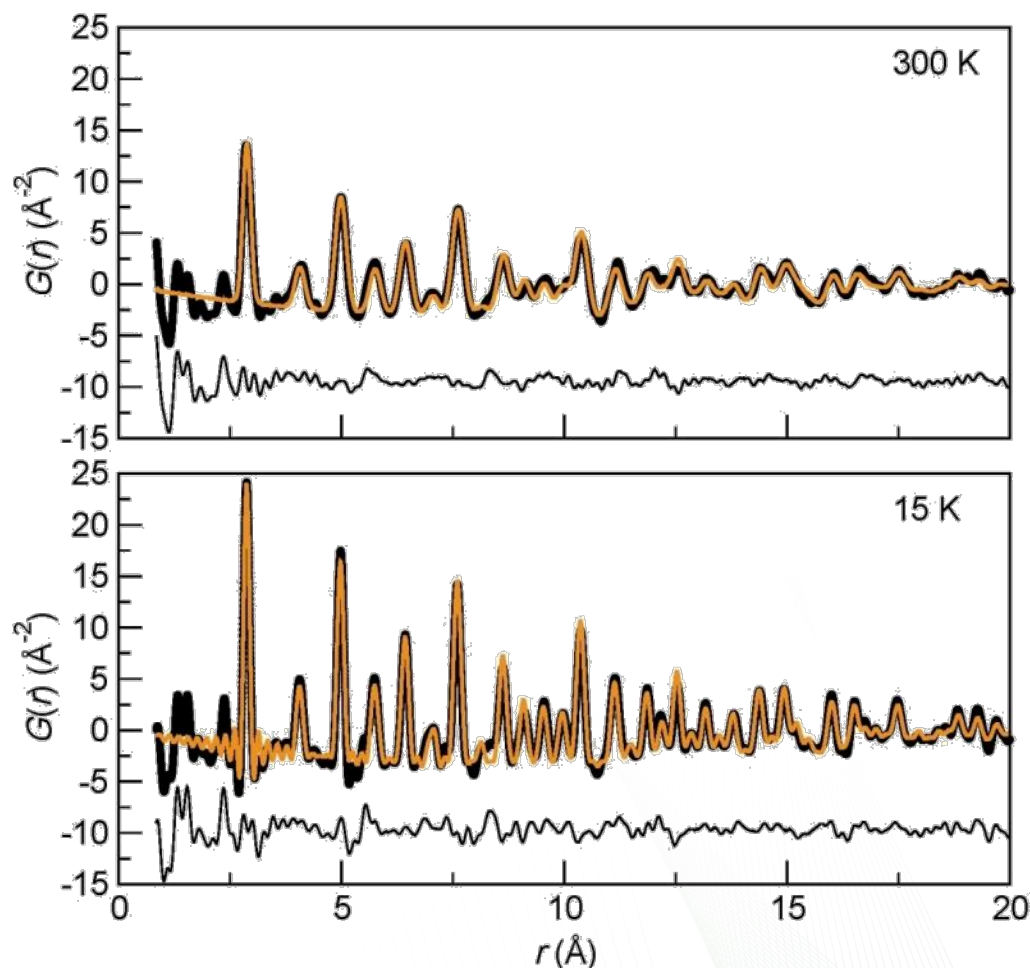


300 K:  $R_w = 33.8 \%$

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

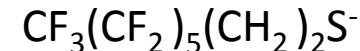
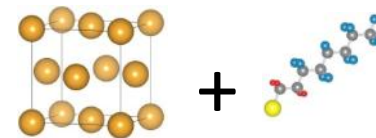
15 K:  $R_w = 27.8 \%$

- scale = 0.2070(4)
- a = 4.06515(5)
- $u_{iso}(\text{Au}) = 0.0044(2)$
- $\delta 1 = 2.257(5)$
- d = 25.54(4) Å



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

# Modeling Au structure & ligand

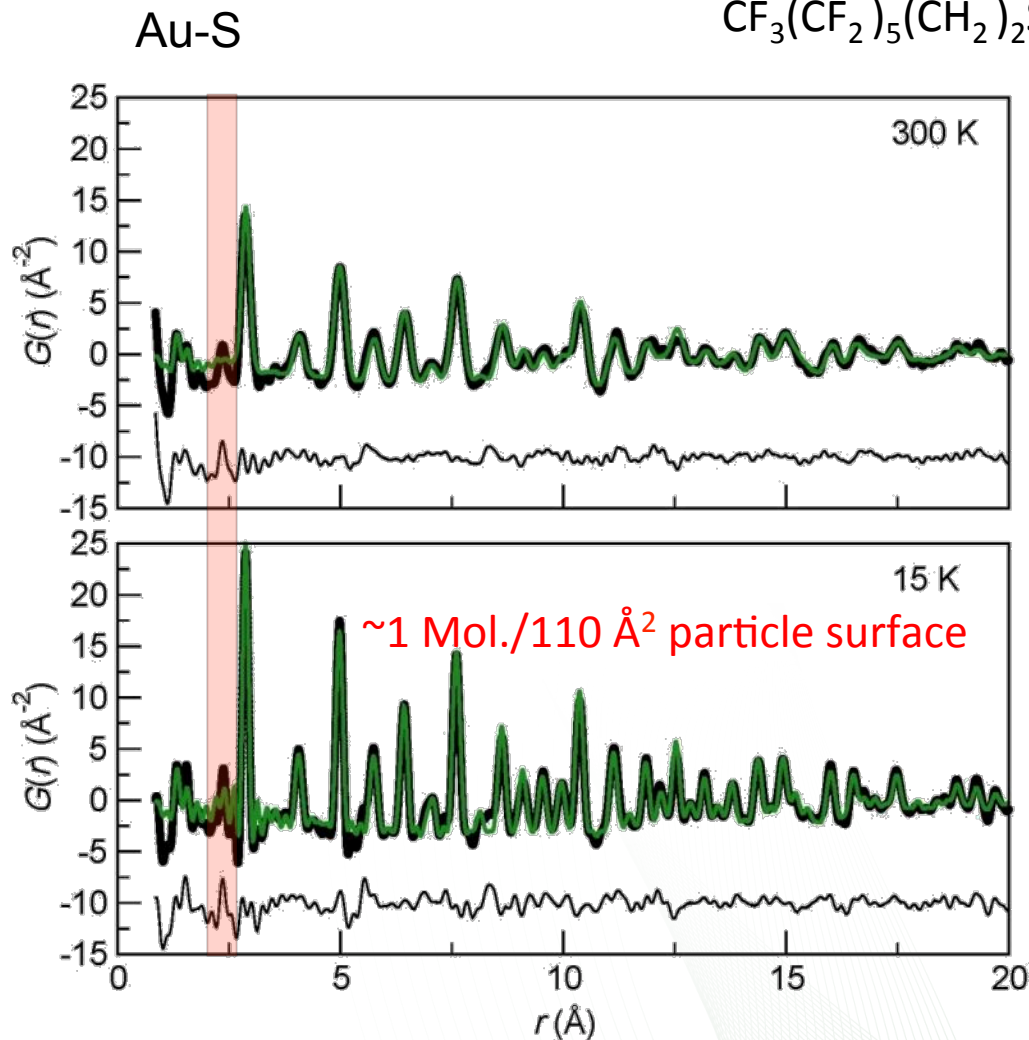


300 K:  $R_w = 31.4 \%$

- scale (Au) = 0.2082(5)
- scale (molecule) = 0.0485(6)
- a (Au) = 4.0755(1)
- a(molecule) = 49.40(3)
- $u_{\text{iso}}$ (Au/molec) = 0.01227(5)
- $\delta 1$  (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)
- $u_{\text{iso}}$ (Au/molec) = 0.00433(2)
- $\delta 1$  (Au) = 2.256(6)
- srat (molecule)= 0.03(14)

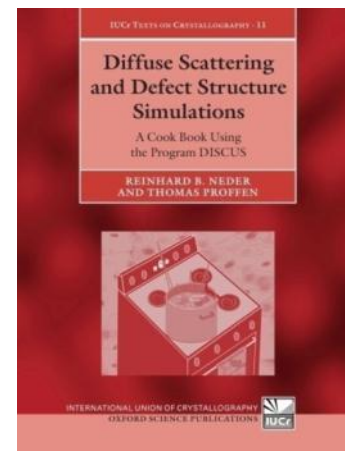


UNCLASSIFIED

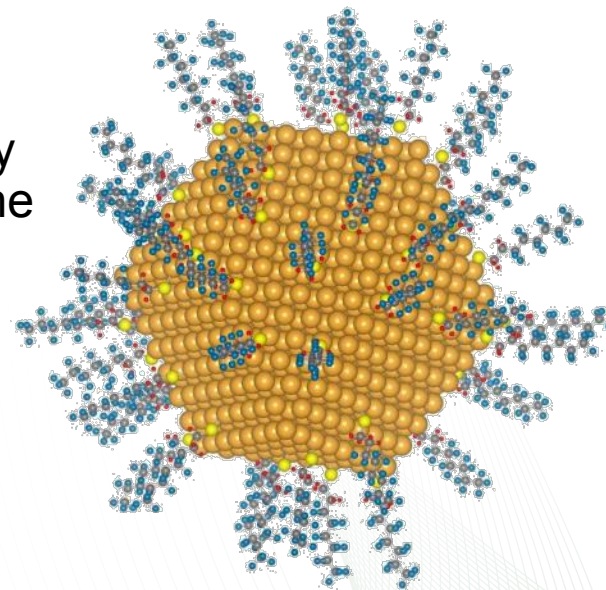
# Modeling of nanoparticle data - future !

## Using DISCUS/DIFFEV

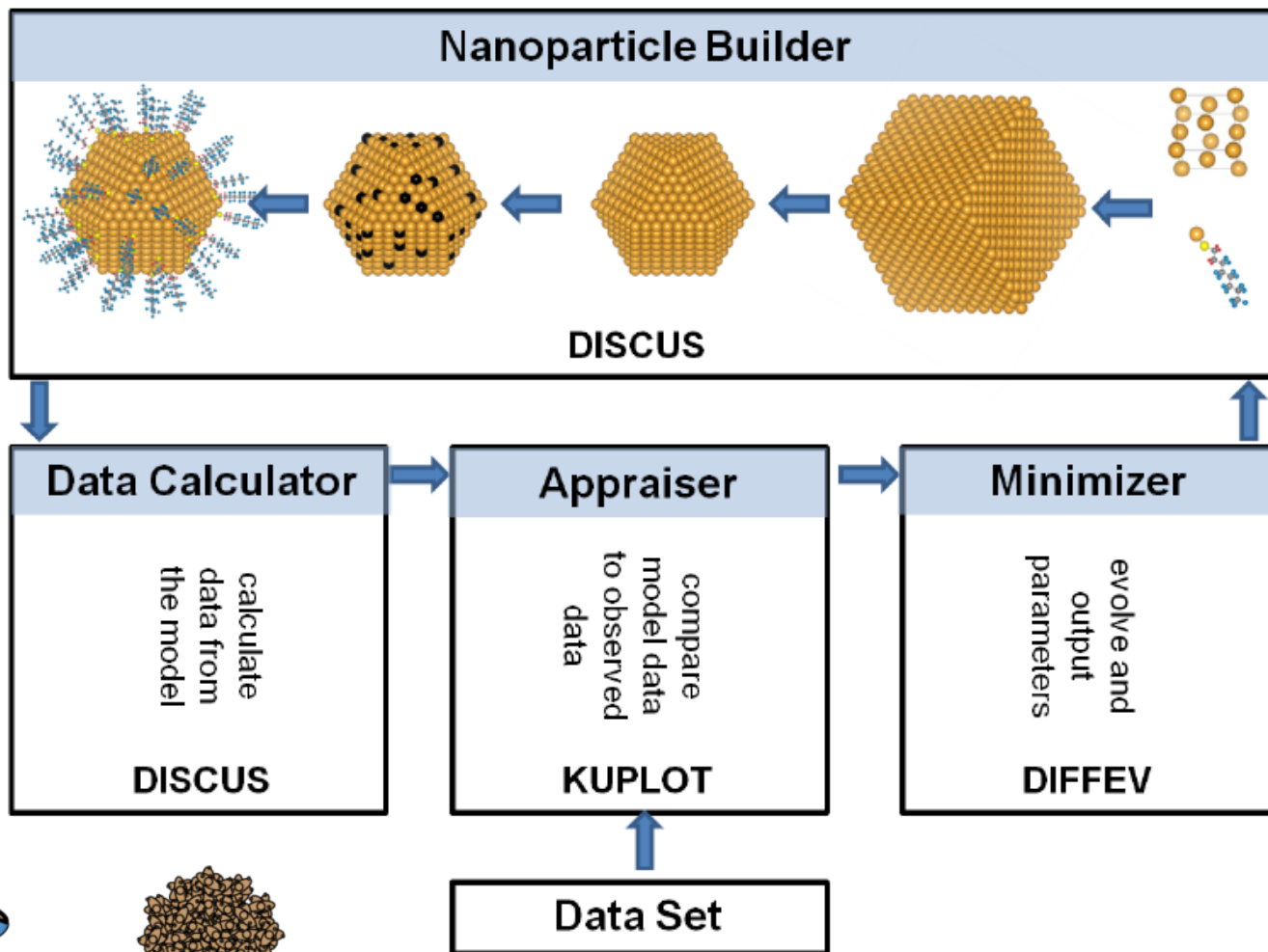
Oxford University  
Press, October 2009



- ❖ <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).



# Nanoparticle builder

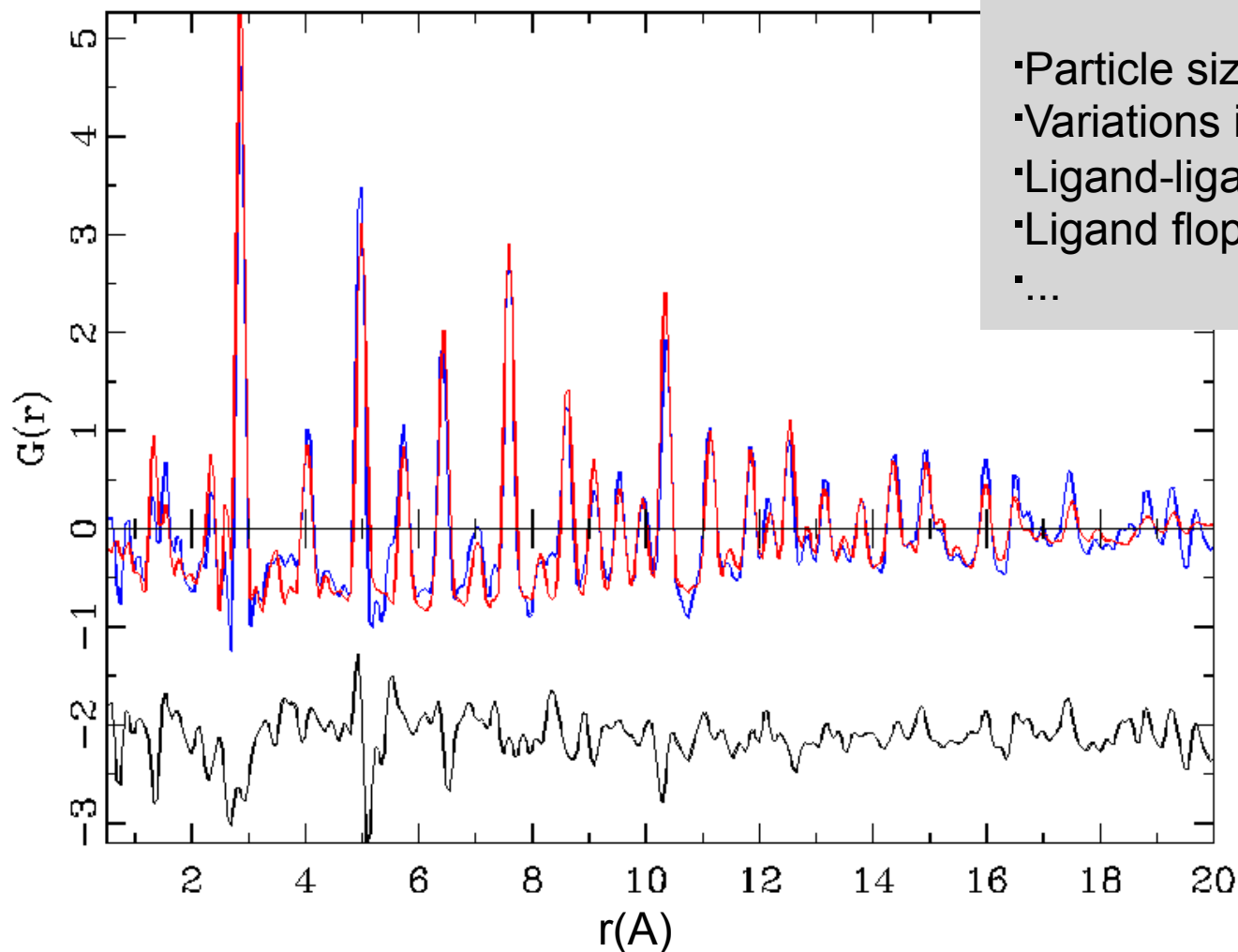


Page, K., Hood, TC, Proffen, T, Neder, RB,  
*J. Appl. Cryst.*, **44** (2), 327 - 336 (2011)

# First results (in progress ..)

## Things to consider

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



# **Experimental Considerations**

# How 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:**

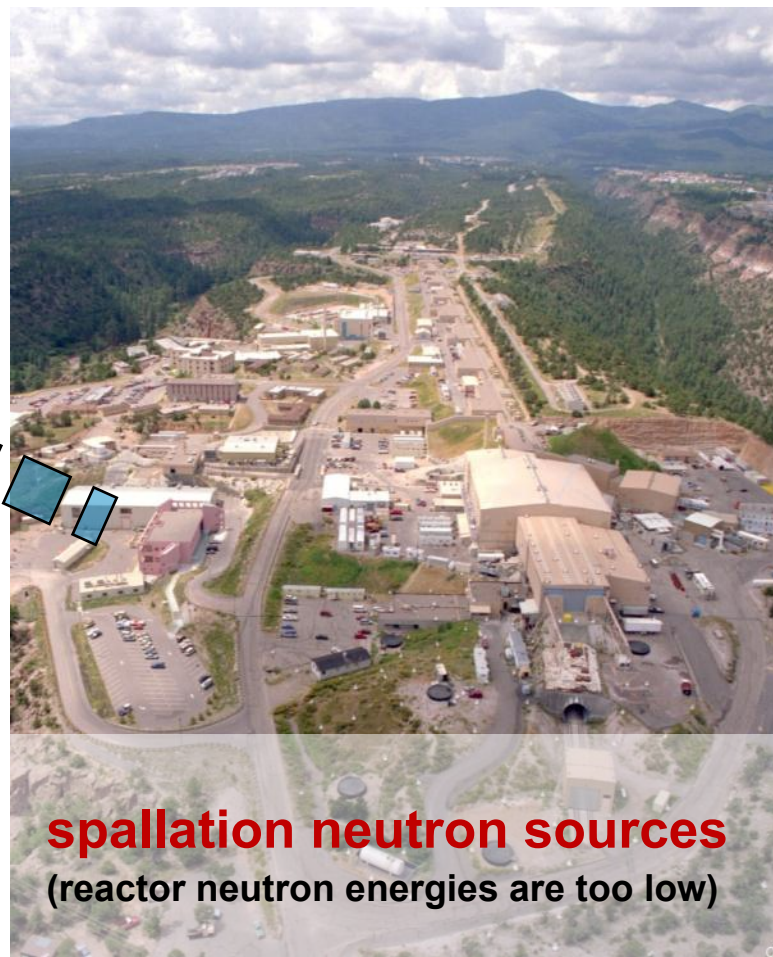
- High maximum momentum transfer,  $Q_{\max}$ .
- High Q-resolution.
- Good counting statistics @ high Q.
- Low instrument background

**Where ?**

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

or

**spallation neutron sources**  
(reactor neutron energies are too low)



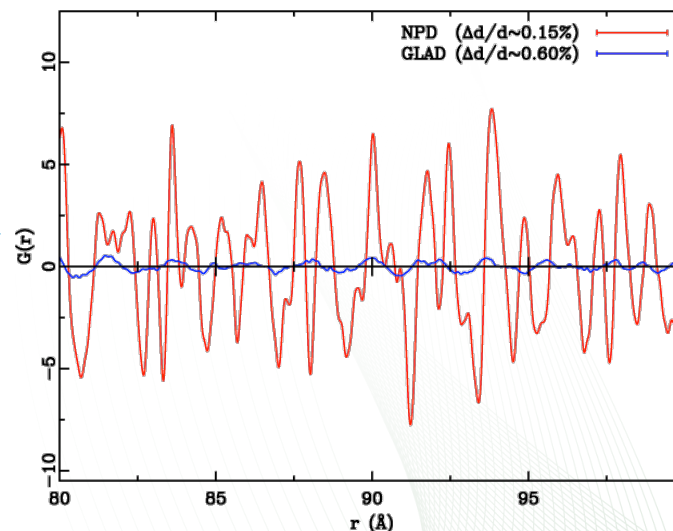
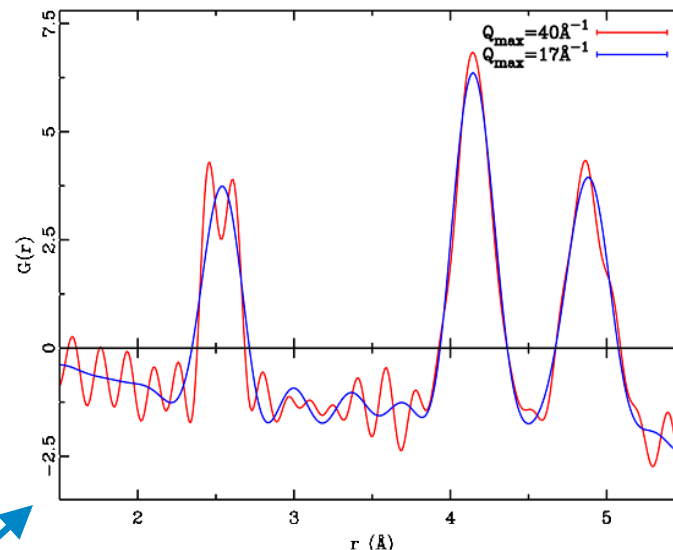
# NPDPF: the key to high quality, high r PDFs

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

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

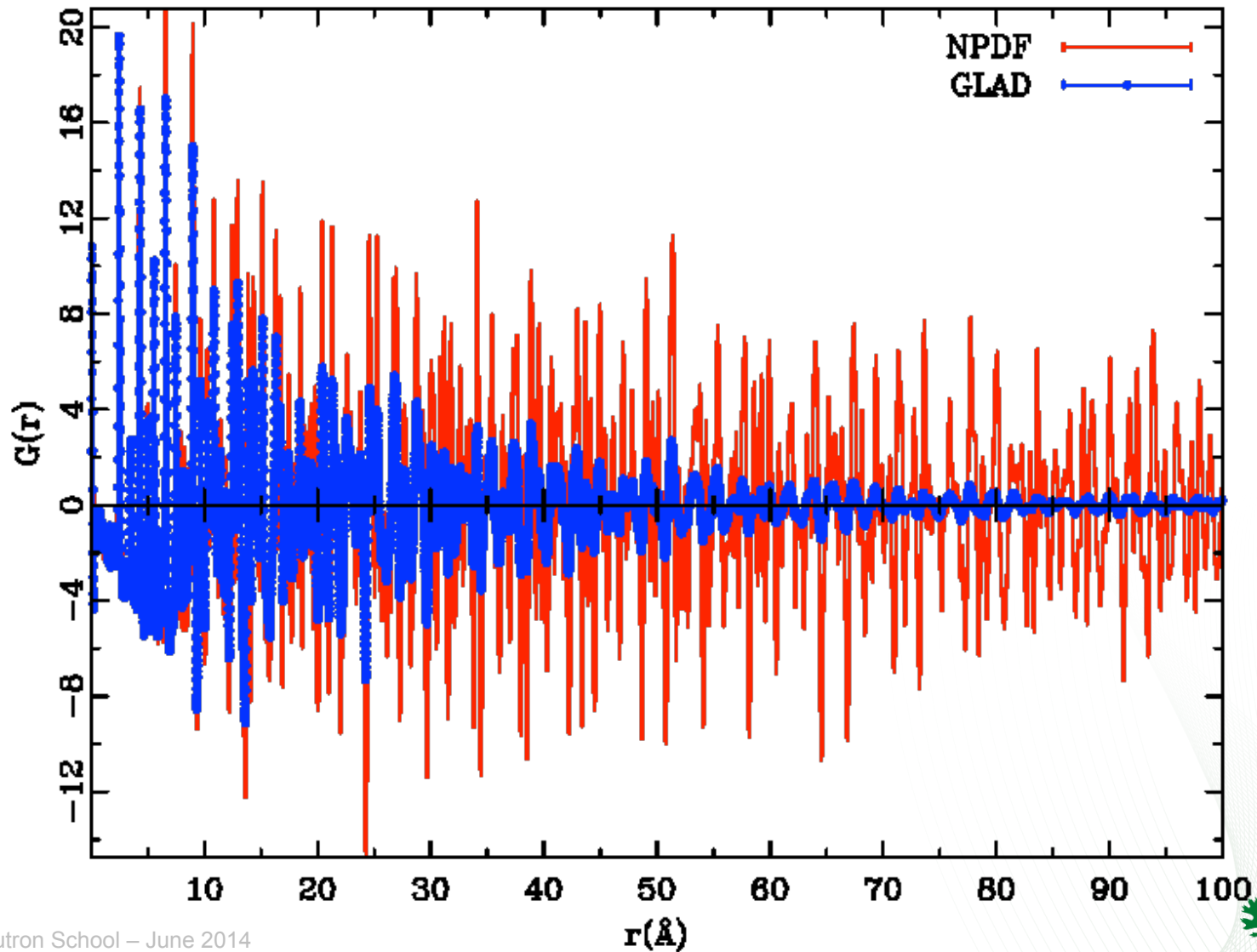
*Requirements to obtain 'good' PDF:*

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



# Q resolution ..

Ni at  $T=300$  K



# NOMAD

## SPECIFICATIONS

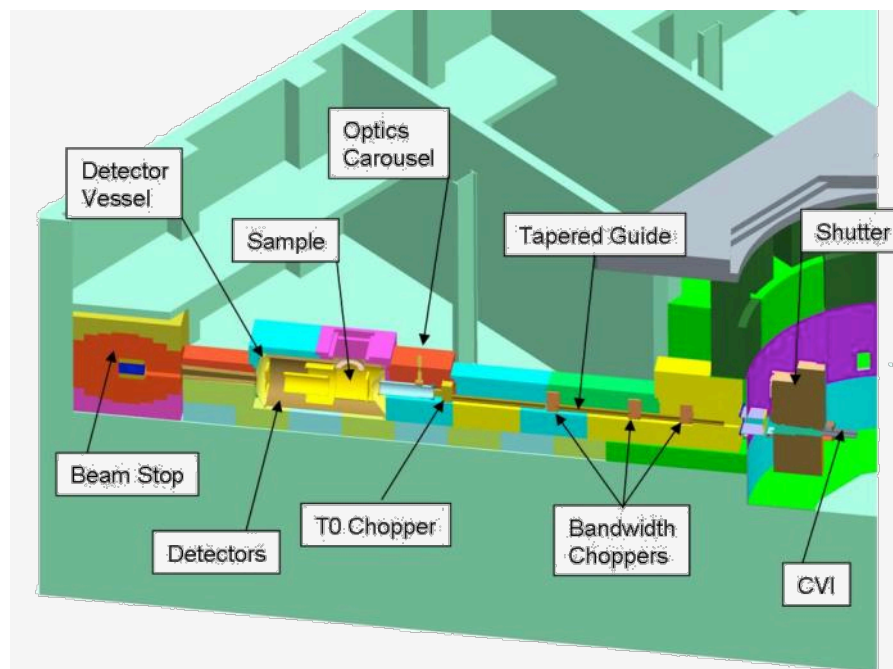
Moderator	Decoupled poisoned supercritical hydrogen
Moderator-to-sample distance	19.5 m
Sample-to-detector distance	0.5–3 m
Wavelength range	0.1–3 Å
Detector angular range	3–175° scattering angle
Initial coverage	4.0 sr
Full detector complement	8.2 sr
Flux on sample	$\sim 1 \times 10^8$ neutrons cm <sup>-2</sup> sec <sup>-1</sup>

- Total scattering instrument
- Science of disordered materials, glasses and nano-materials
- Commissioning – partial user program

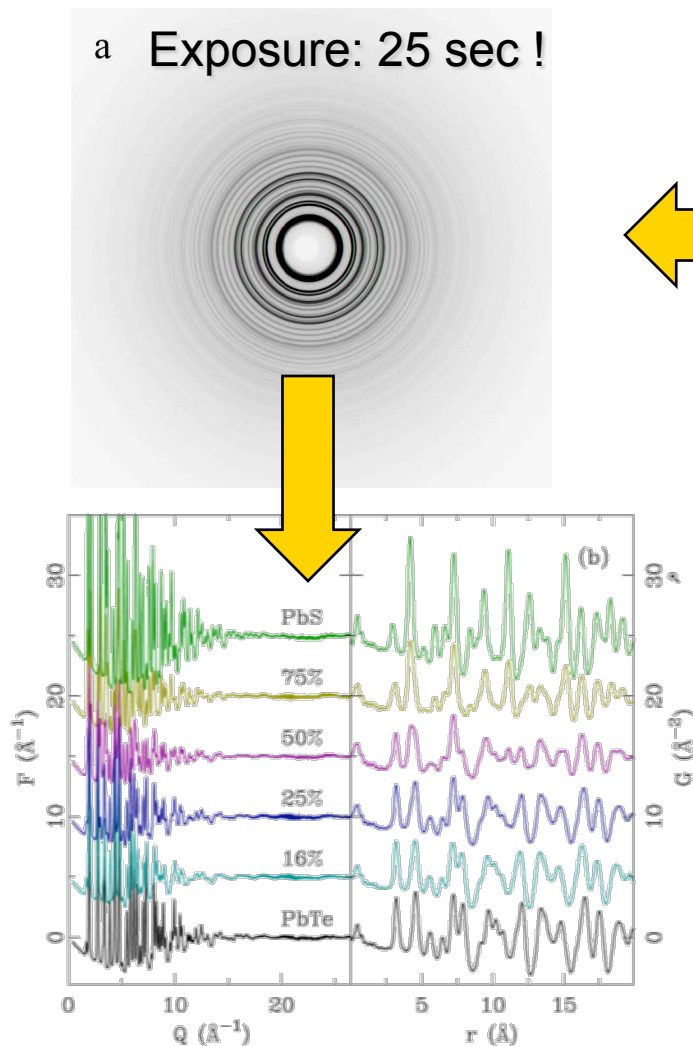
**contact**

**Jorg Neufeind**  
[neufeindjc@ornl.gov](mailto:neufeindjc@ornl.gov)

**Mikhail Feygenson**  
[feygensonm@ornl.gov](mailto:feygensonm@ornl.gov)

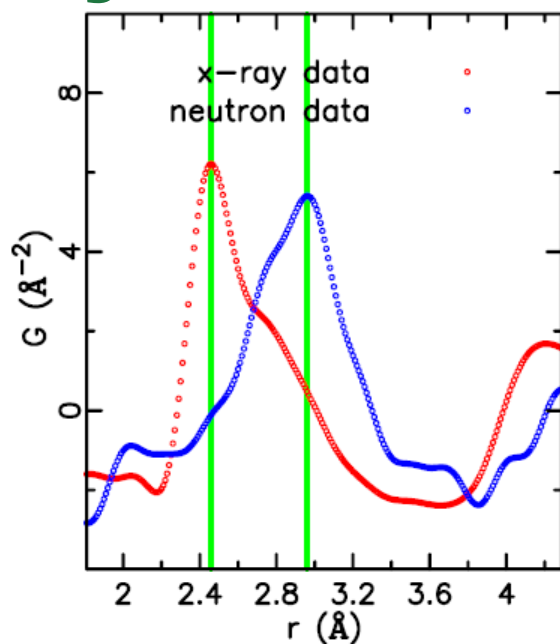


# X-ray PDF: The fast way



P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, **Rapid-acquisition pair distribution function (RA-PDF) analysis**, *J. Appl. Cryst.* **36**, 1342-1347 (2003).

# MgCo – the power of neutrons *and* x-rays



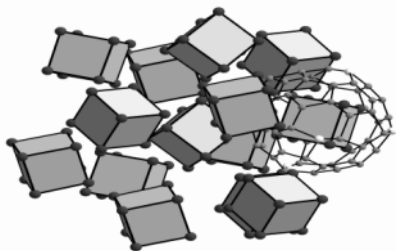
PDF peak intensity  $\propto \sum_{mn} \frac{b_m b_n}{\langle b \rangle^2} \delta(r - r_{mn})$

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

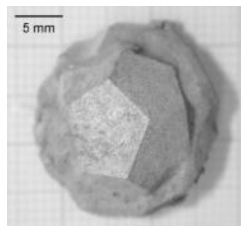
	$b_i$ for x-ray	$b_i$ for neutron
Mg	12	3.631
Co	27	0.779

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

# X-ray PDF: In house measurements

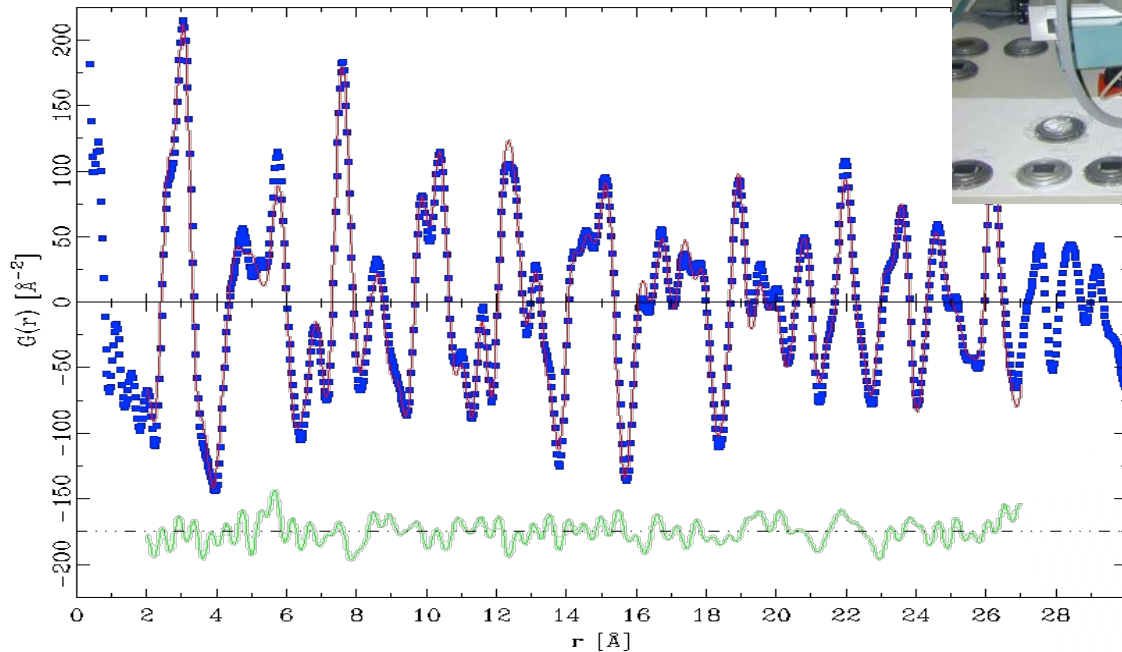


*fci-Ho-Mg-Zn*



Huber Guinier diffractometer  
 $Q_{\max} = 13.5 \text{ \AA}^{-1}$

2/1-model for fci-Ho<sub>9</sub>Mg<sub>26</sub>Zn<sub>64</sub>  
R=12.9%



Brühne et al., *Z. Kristallogr.*  
**219** (2004) 245-258

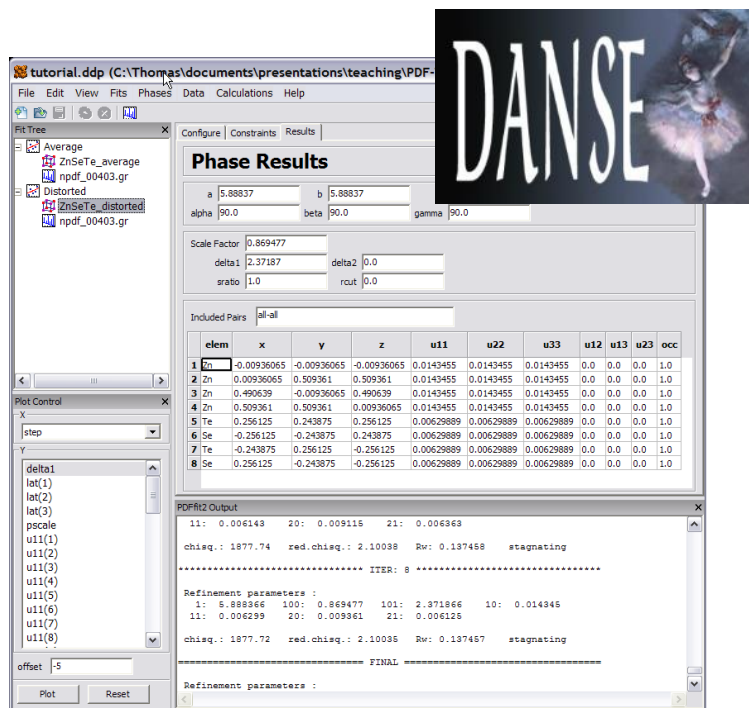
# Software



# Software: Data modeling

## PDFgui

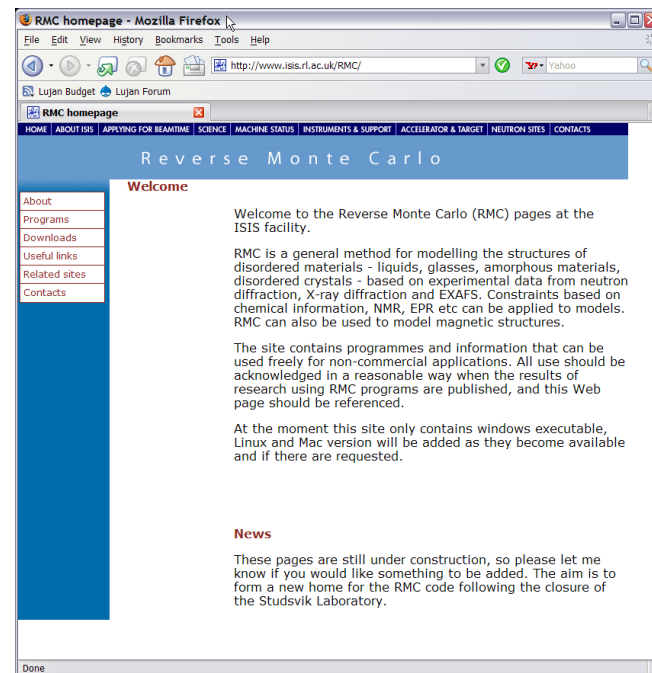
- ❖ Part of DANSE project.
- ❖ <http://www.diffpy.org/>



- ❖ 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 !*
- ❖ Automatic refinement of multiple datasets as function of *T* or *x*.
- ❖ Intuitive GUI.
- ❖ Engine *pdfit2* can also be used in command mode.

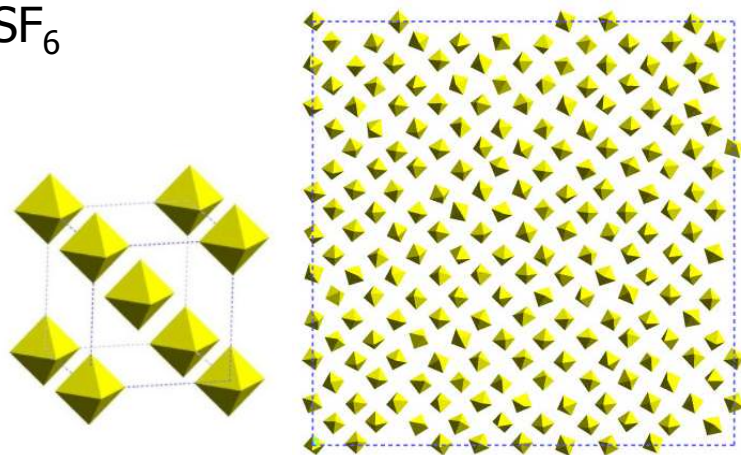
# Software: RMCprofile

- RMCprofile
  - Configurations ~600 to 20000+ atoms
  - Fit both X-ray and neutron  $F(Q)$
  - Fit  $G(r)$
  - Fit Bragg profile
  - Polyhedral restraints
  - Coordination constraints
  - Closest approach constraints
- Produce a static 3-D model of the structure (a snap-shot in time)
- Link: <http://www.isis.rl.ac.uk/RMC>

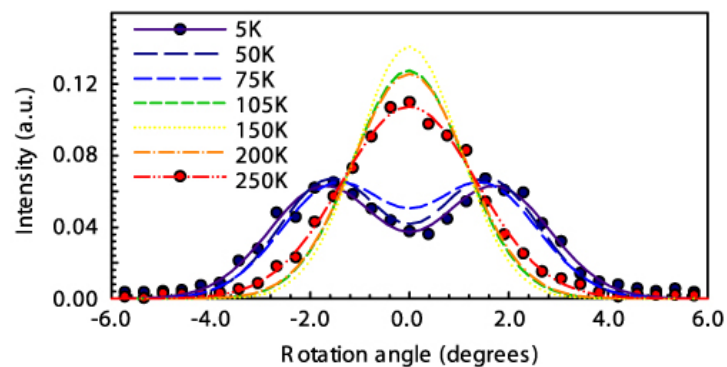
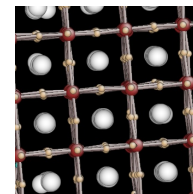


# RMC: Examples

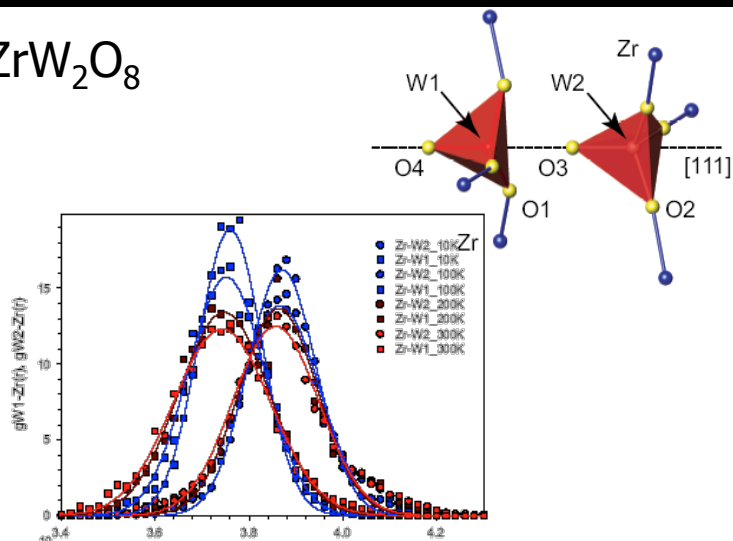
$\text{SF}_6$



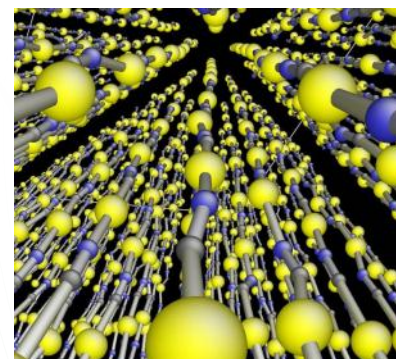
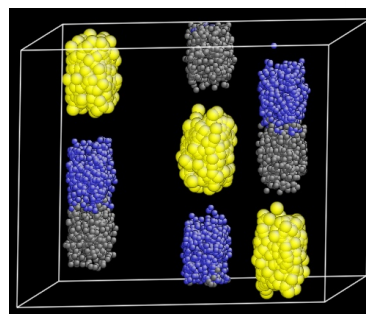
$\text{SrTiO}_3$



$\text{ZrW}_2\text{O}_8$



$\text{AuCN}$



# Software: Data modeling


## DISCUS

- ❖ Disordered materials simulations
- ❖ Refinement via DIFFEV / RMC
- ❖ <http://discus.sourceforge.net/>



Oxford University  
Press, October 2008

# Nanoparticle builder



» or search scientific literature at the Research Library

Phone

TOTAL SCATTERING GROUP

Tools for structural analysis of complex materials

Nanobuilder HomeTotal Scattering HomeShare

Nanobuilders

Ellipsoid

More coming soon ..

Software

DISCUS

Jmol

Ptplot

TEAM


Scientists

Thomas Proffen

Katharine Page

Student

Emily Tencate



### Nanoparticle Builder

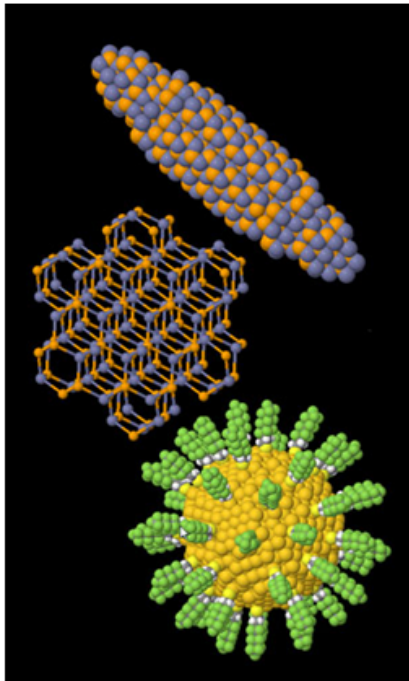
Welcome to the interactive nanoparticle builder. Please note, that this tool is still under development.

The tool uses the program **DISCUS** to generate the nanoparticle structures and calculate the corresponding atomic pair distribution function and powder diffraction pattern. The interactive structure viewing is using the program **JMOL**. Structure and calculated functions can be downloaded from the results page. Online plotting of the powder pattern and pair distribution function use the **Ptplot** package. More builders for more complex nanoparticles are coming soon ..

For questions and comments, contact one of the team member listed on the left. Select a builder from the list on the left and get started ..

### News

- Nov 4, 2011 - Initial version released. Enjoy the ellipsoid builder ..



<http://totalscattering.lanl.gov/nano/>

# Summary

- 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
- Use multiple data sets (e.g. x-ray and neutron data) to characterize complex materials

**<http://totalscattering.lanl.gov>**