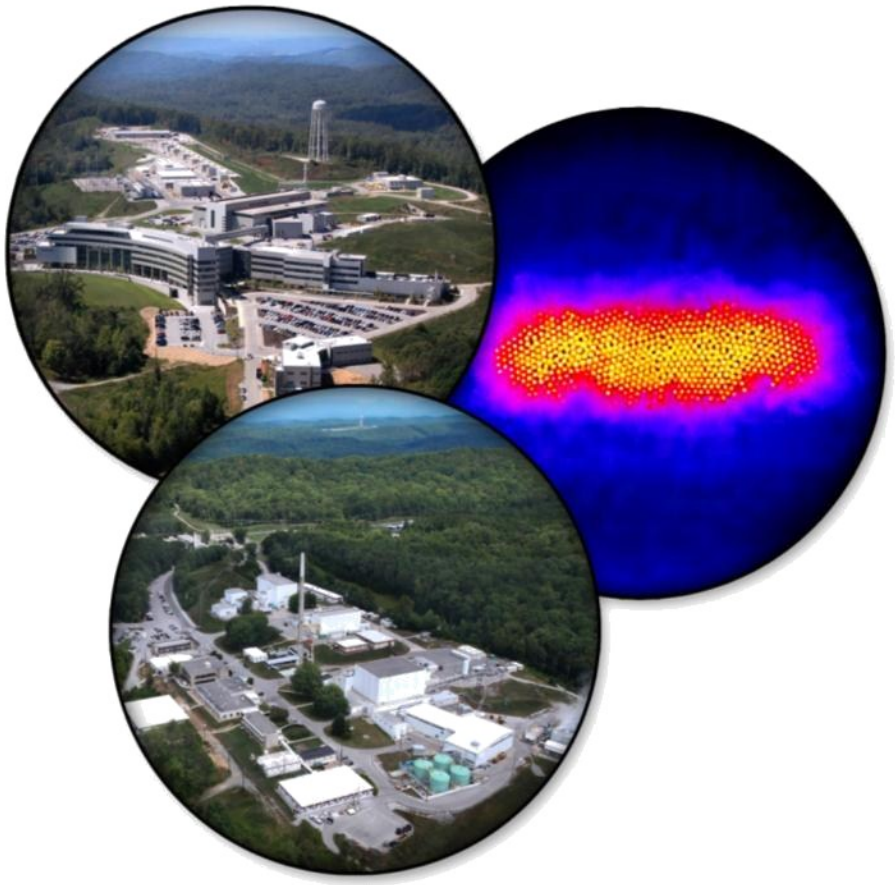
Total Scattering

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



Thomas Proffen
Diffraction Group Leader
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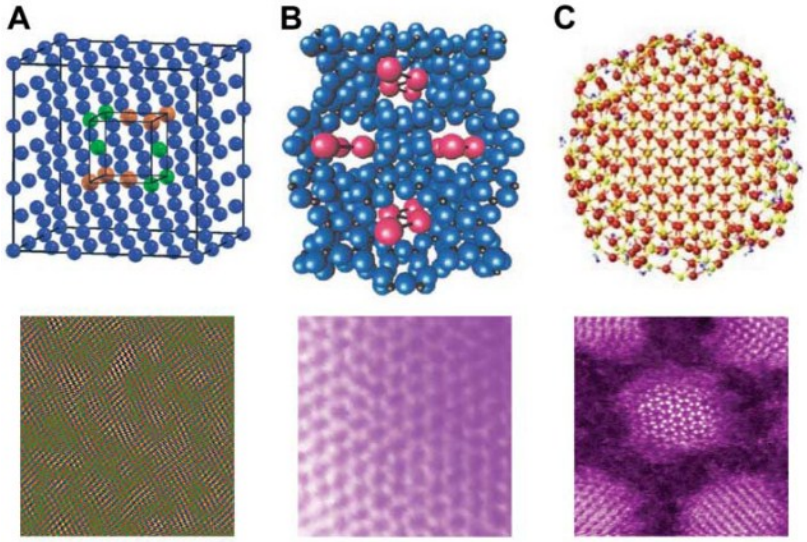
U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

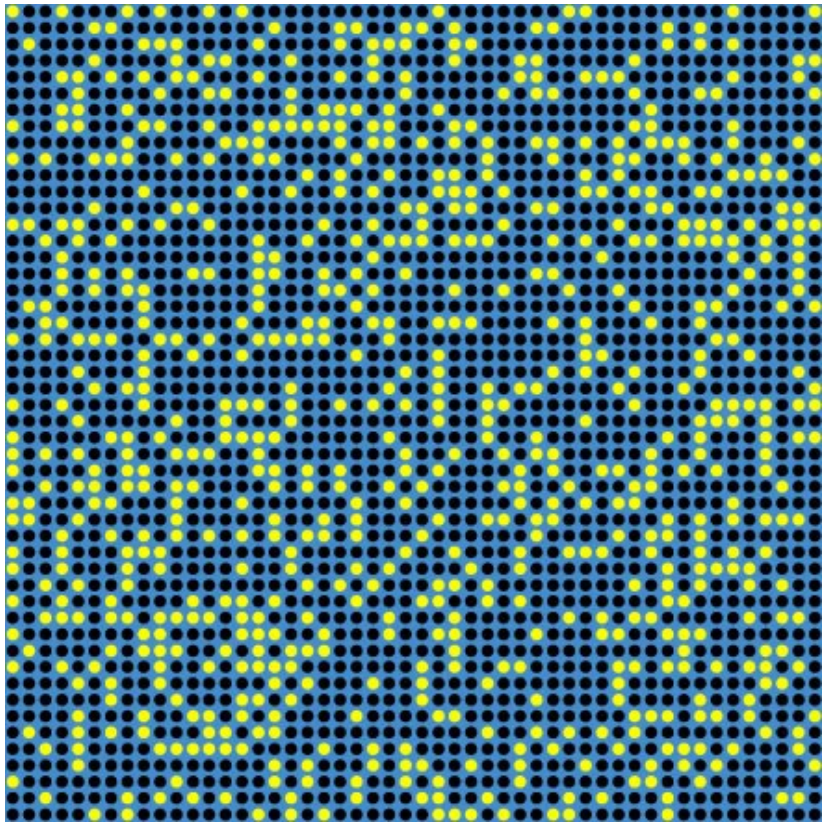
The challenge : Knowing the local structure

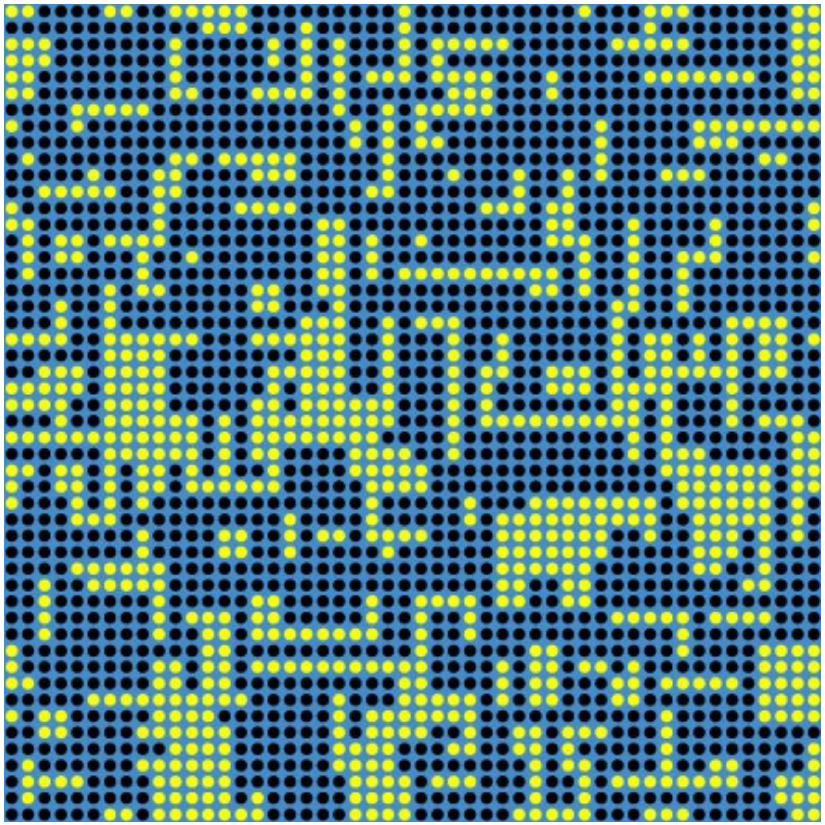
- Traditional crystallographic approach to structure determination is insufficient or fails for
  - Non crystalline materials
  - Disordered materials: The interesting properties are often governed by the defects or local structure !
  - Nanostructures: Well defined local structure, but long-range order 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 ?

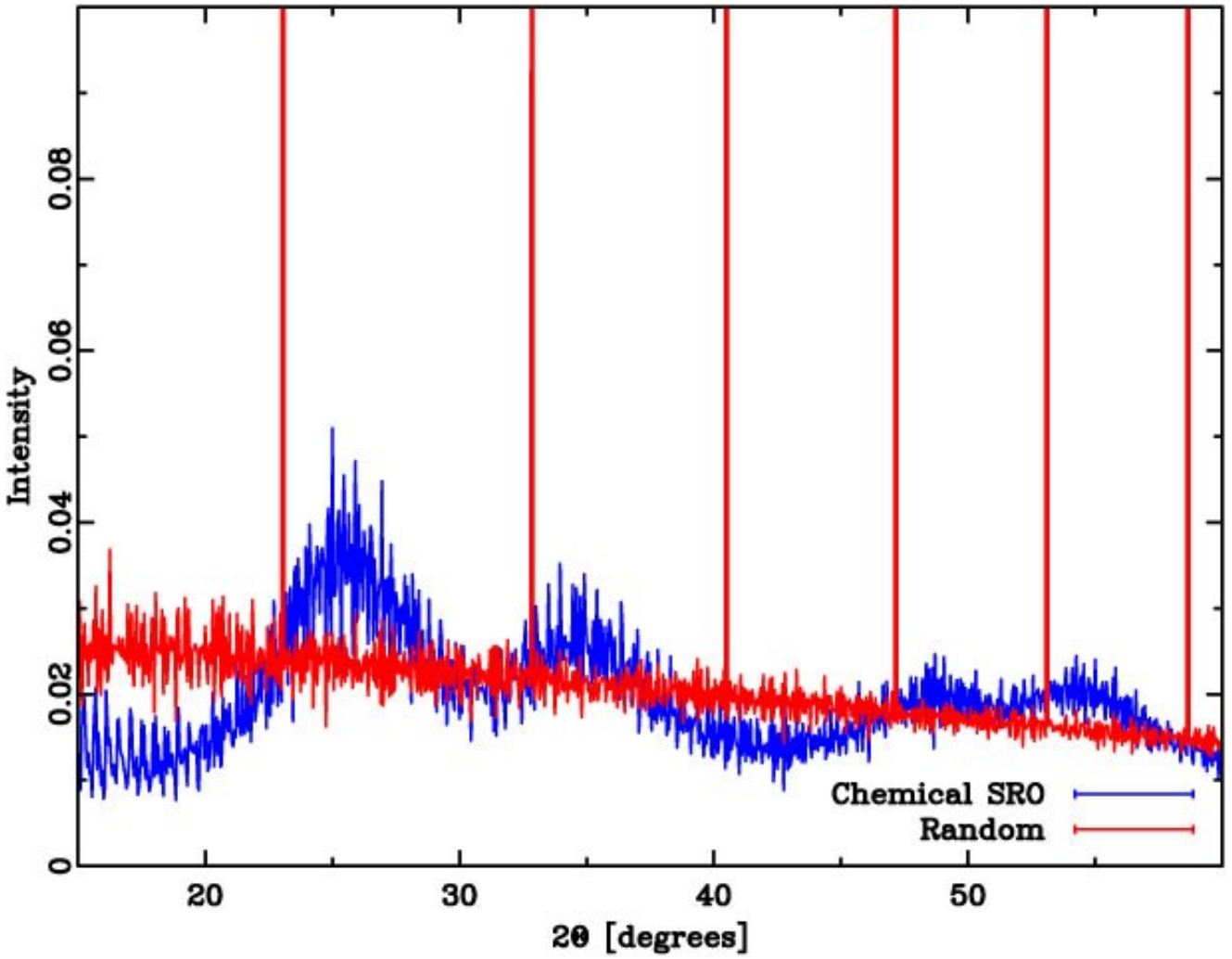




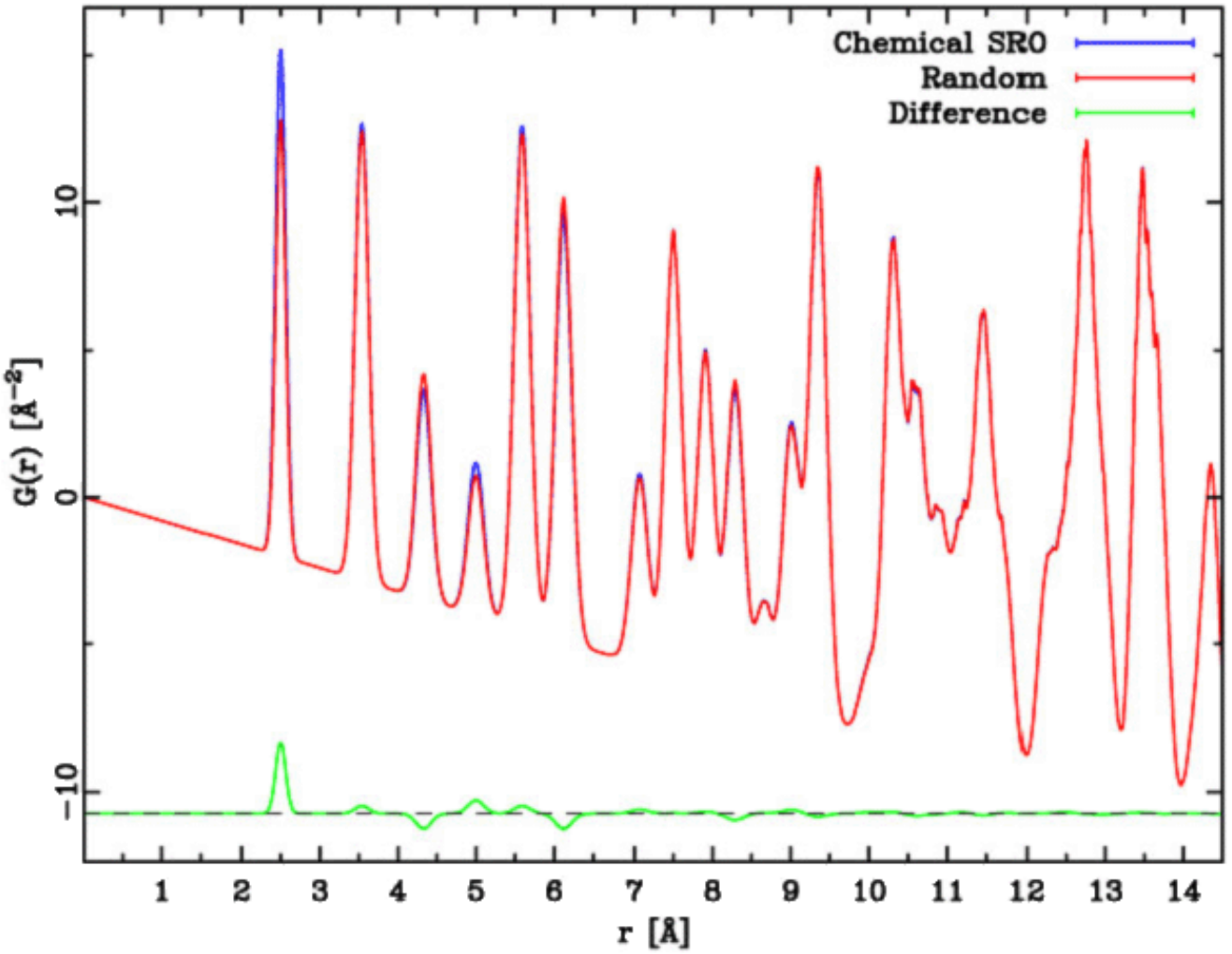
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

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 !

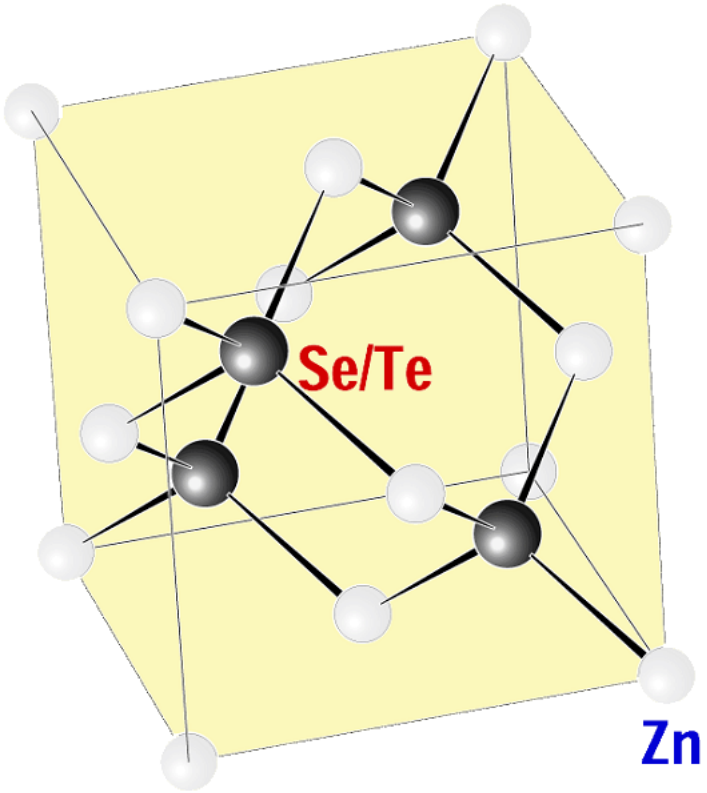
Proffen, *Z. Krist*, **215**, 661 (2000)

Example:
Local atomic strain in $ZnSe_{1-x}Te_x$

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

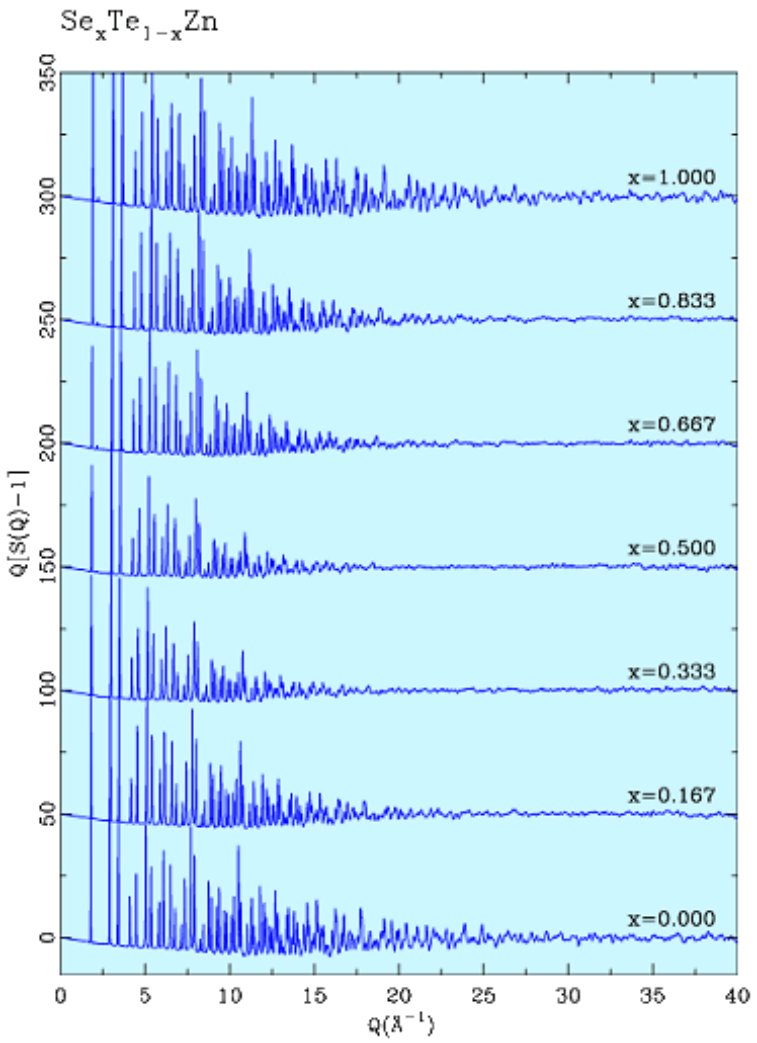
$ZnSe_{1-x}Te_x$: Structure

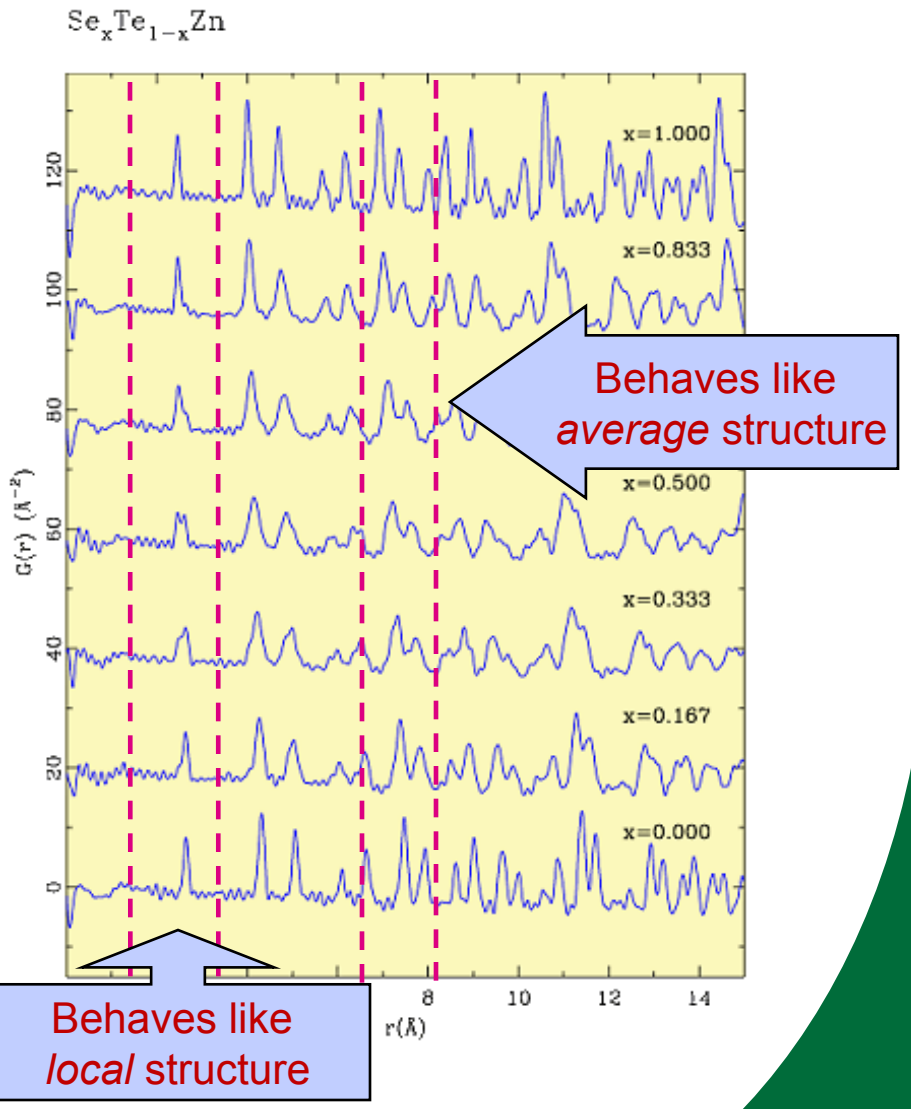
- Zinc blend structure (F43m)
- **Technological important** :
  Electronic band gap can be tuned by the composition *x*.
- Bond length difference *Zn-Se* and *Zn-Te* ⇒ **strain**.
- Local structural probe required !



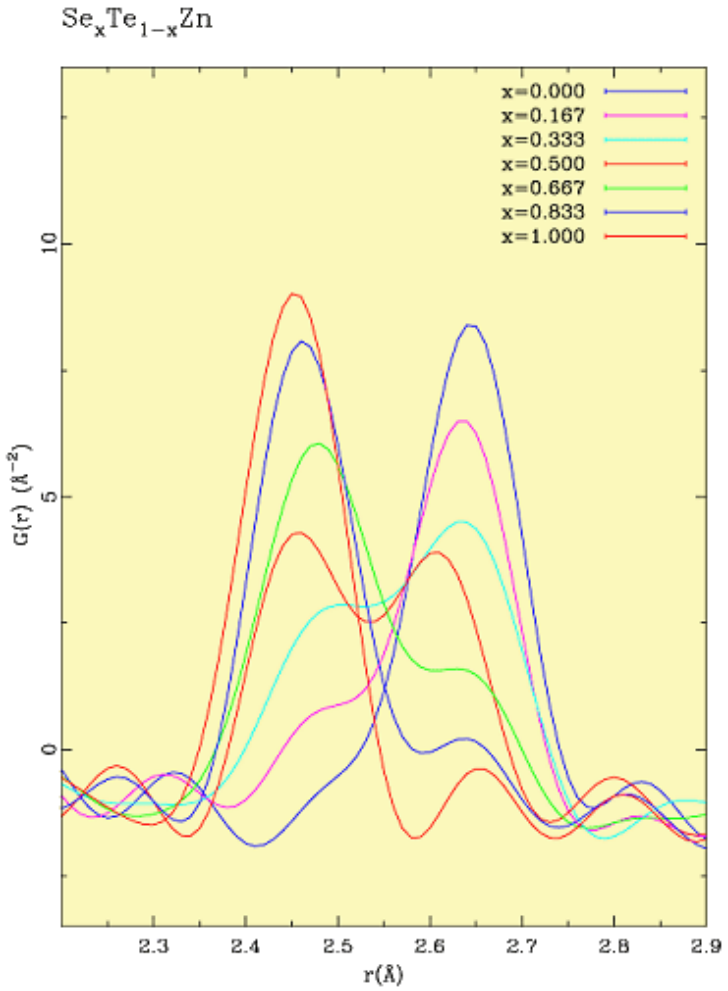
$ZnSe_{1-x}Te_x$: Total scattering

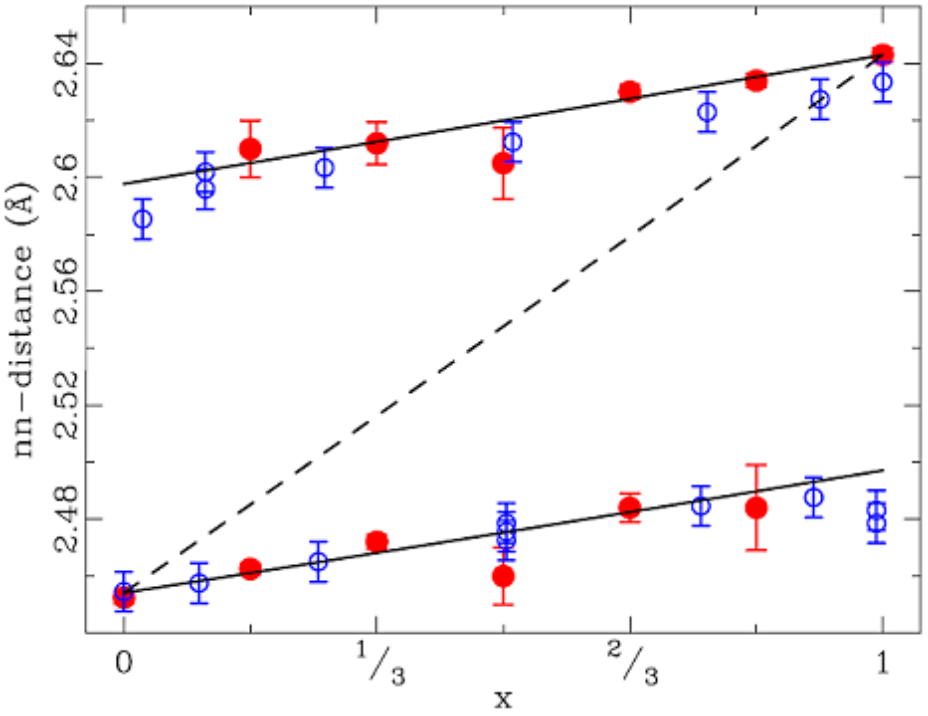
Peterson et al., *Phys. Rev.* B**63,** 165211 (2001)





$ZnSe_{1-x}Te_x$: 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

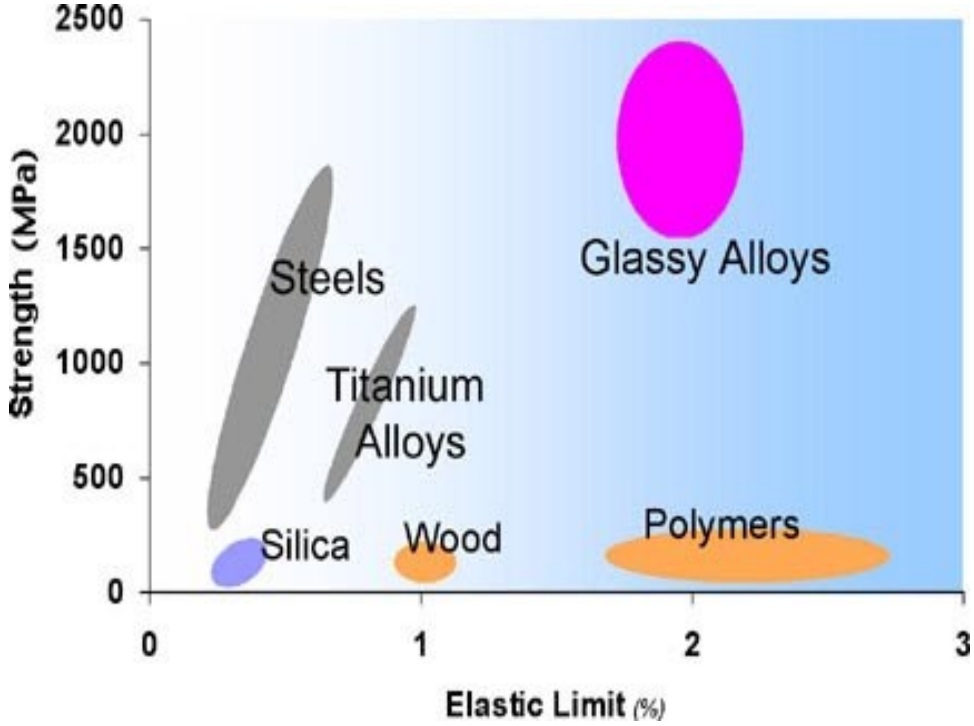
Facilities: Lujan
Funding: DOE, NSF

BMG : Properties

- High Specific Strength
- Light Weight
- High Elastic Strain
- High Hardness
- Excellent Wear Resistance
- Excellent Corrosion Resistance

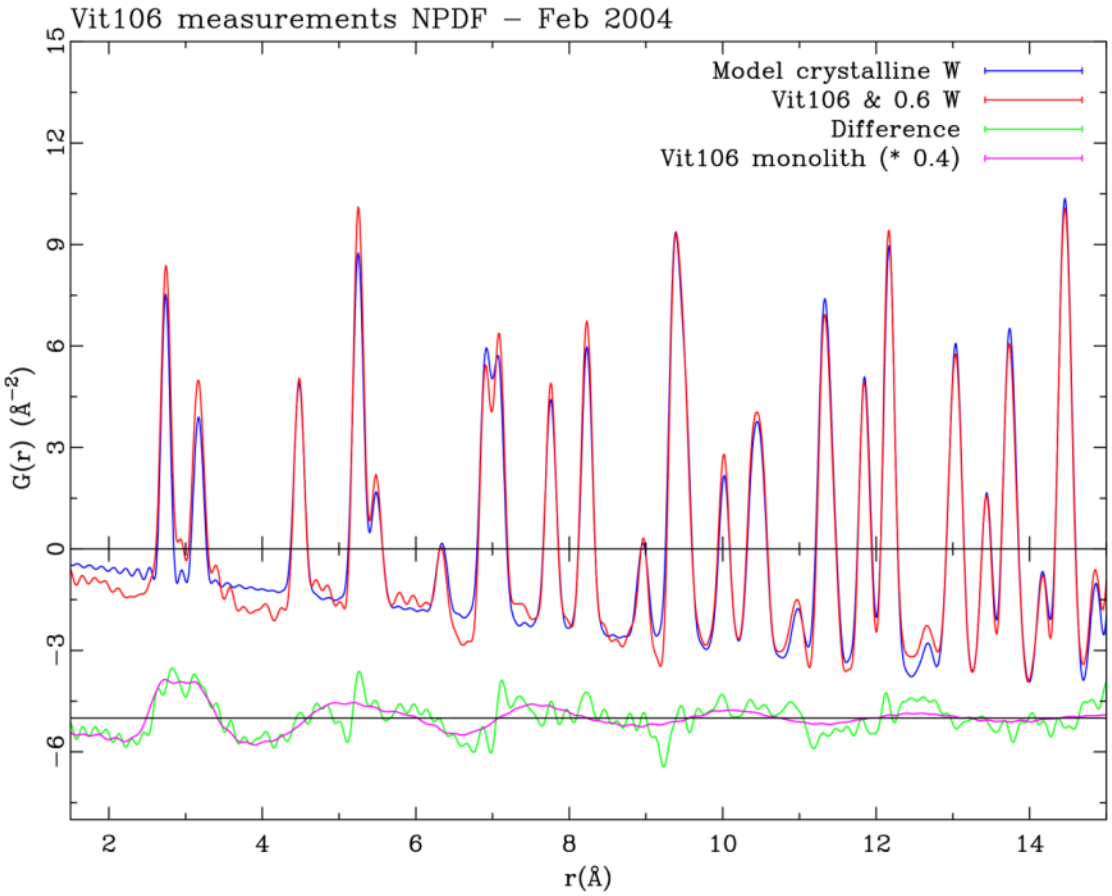
- BMG's are prone to catastrophic failure during unconstrained loading due to the formation of macroscopic shear bands

- *Crystalline reinforcements to suppress the formation of macroscopic shear bands*



http://www.its.caltech.edu/~matsci/wlj/wlj_research.html

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**

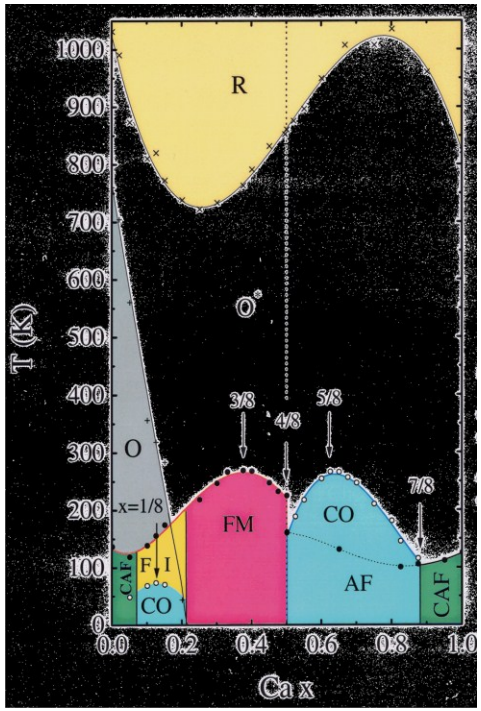
Example:
Local structure in $La_xCa_{1-x}MnO_3$

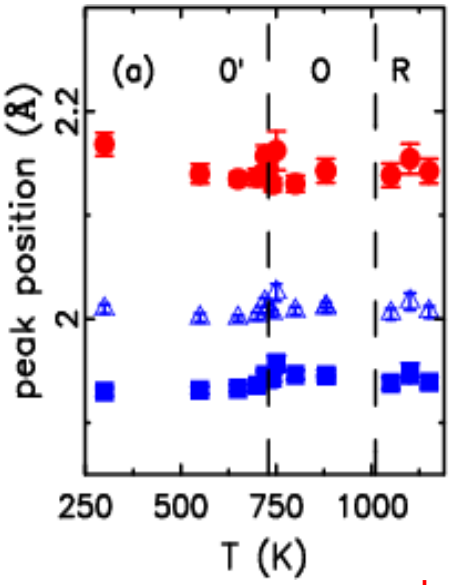
MICHIGAN STATE UNIVERSITY

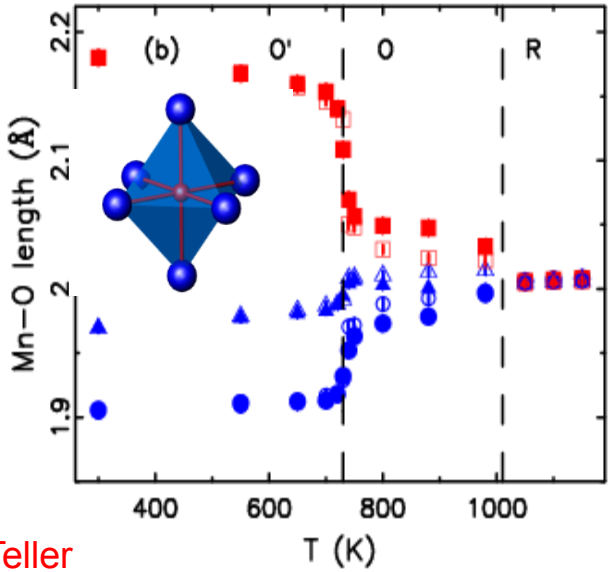
Simon Billinge
Emil Bozin
Xiangyn Qiu

Thomas Proffen

$LaMnO_3$: Jahn-Teller distortion







Jahn Teller
Long Mn-O bond

Local structure

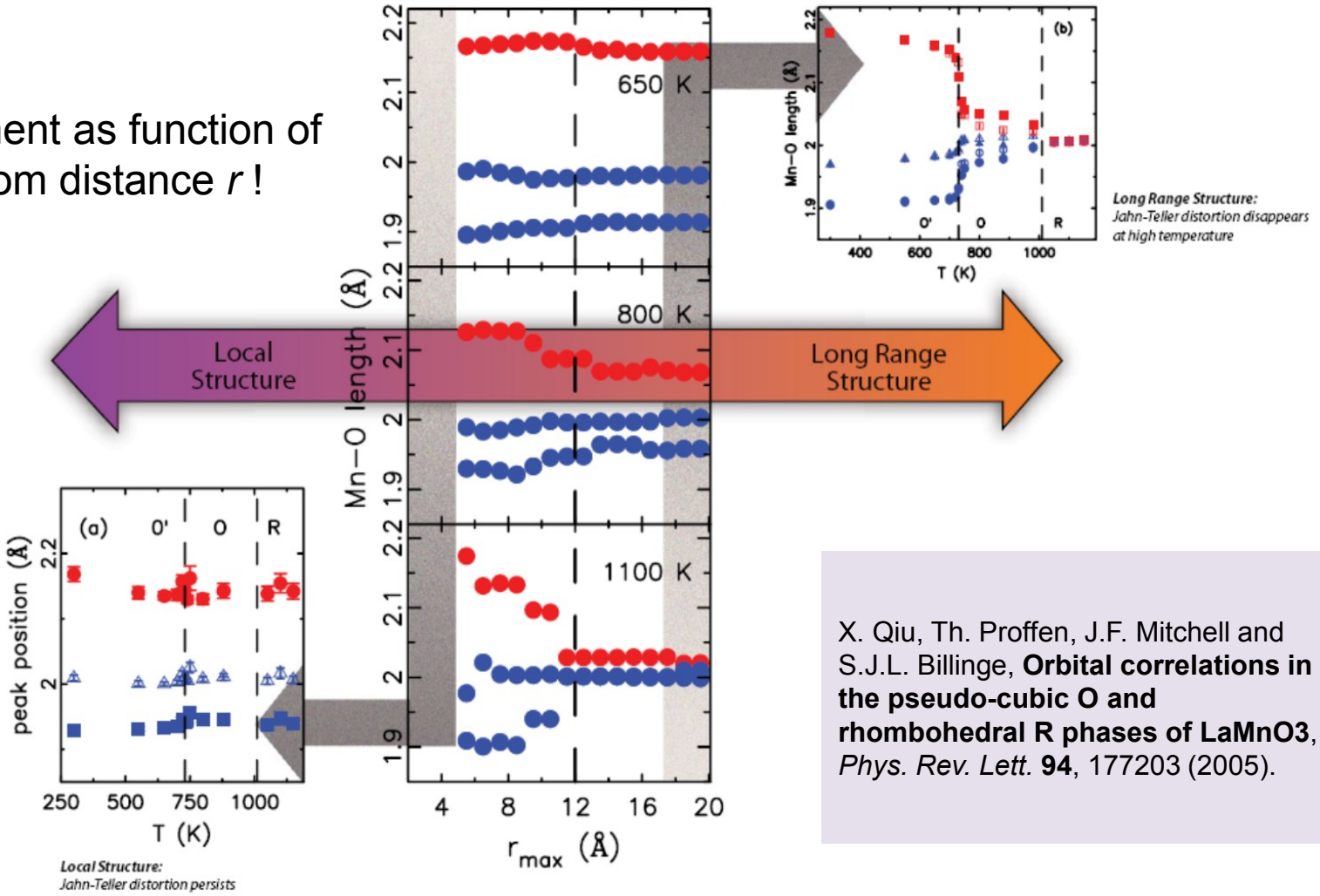
Average structure

- 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?

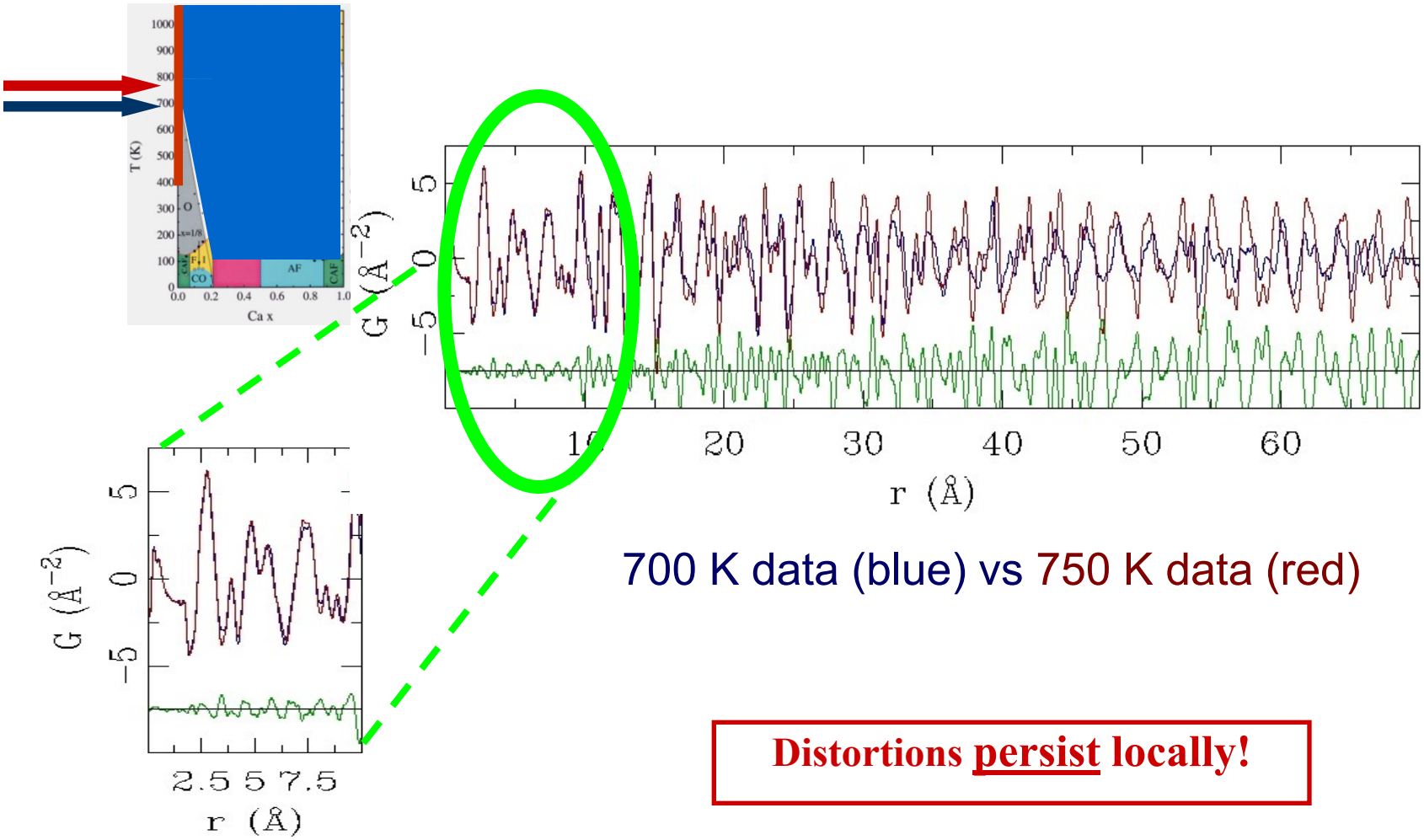
Study of the Jahn-Teller distortion in $LaMnO_3$

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 LaMnO3**, *Phys. Rev. Lett.* **94**, 177203 (2005).

$LaMnO_3$: Simplicity of the PDF approach



Distortions <u>persist</u> locally!

Los Alamos NATIONAL LABORATORY EST. 1943

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Tools for structural analysis of complex materials

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RESOURCES

- Facilities
- Publications
- Software
- Tutorials
- For kids
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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 $LaMnO_3$ 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

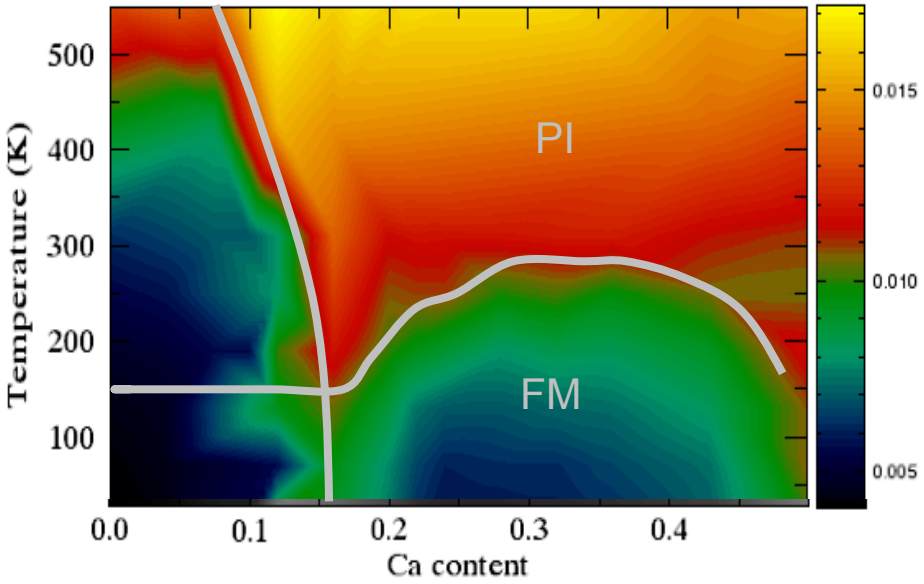
- Interactive Tutorial about Diffraction
  This tutorial gives a basic interactive introduction into diffraction and diffuse scattering. The interactive examples are generated using DISCUS.
- Kevin Cowtan's Book of Fourier
  This is a book of pictorial 2-d Fourier Transforms. These are particularly relevant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

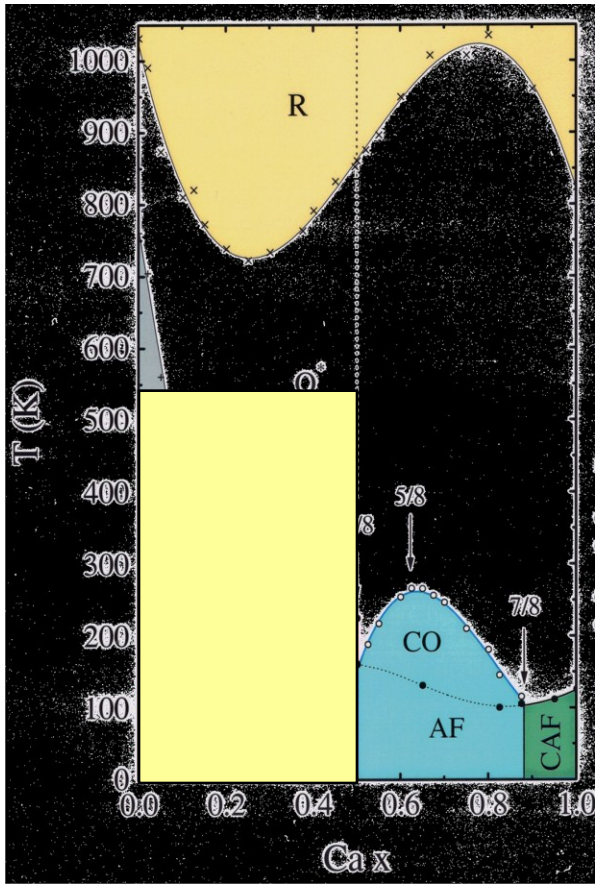
Tutorials

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.

$La_{1-x}Ca_xMnO_3$: Phase diagram

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



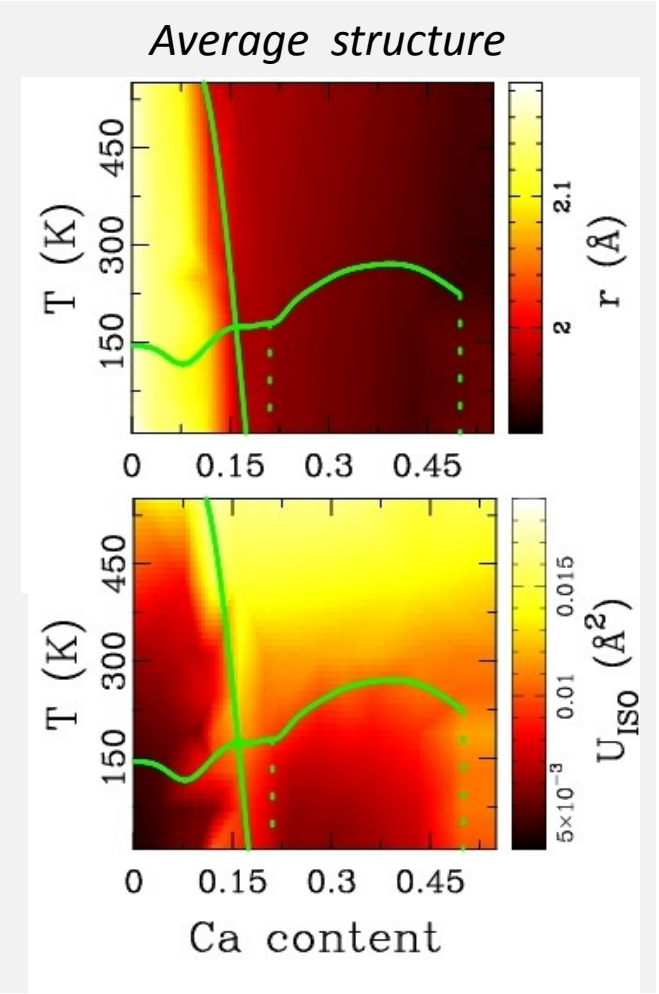


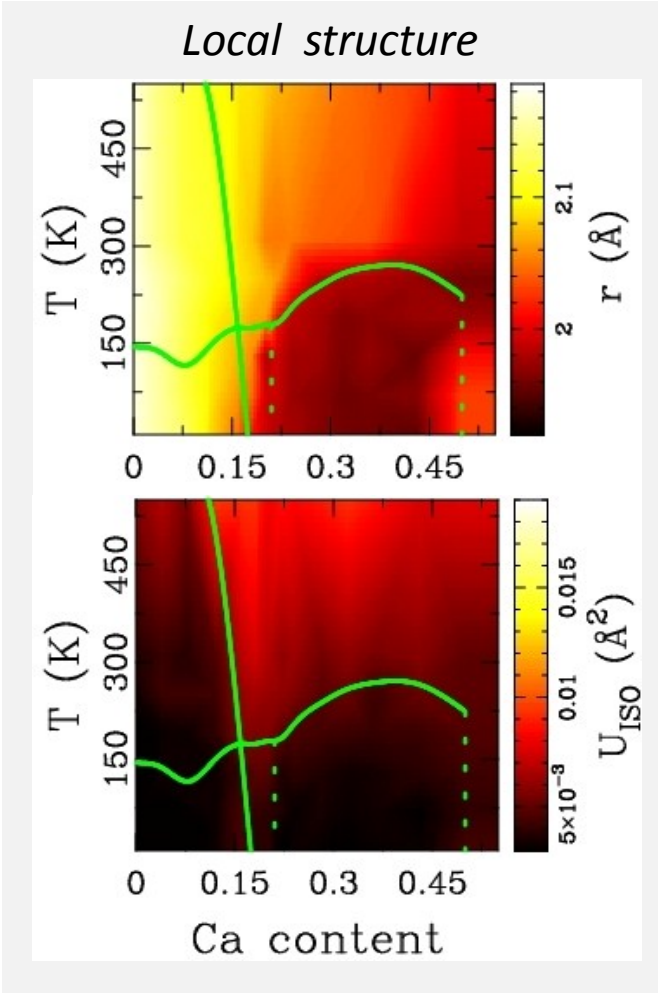
- **Phase diagram draws itself from the parameters.**
- **Unexpected detail emerges and demands interpretation.**

$La_{1-x}Ca_xMnO_3$: Phase diagram

Mn-O long bond

ADP Oxygen





Example:
"Complete" structure of Gold Nanoparticles

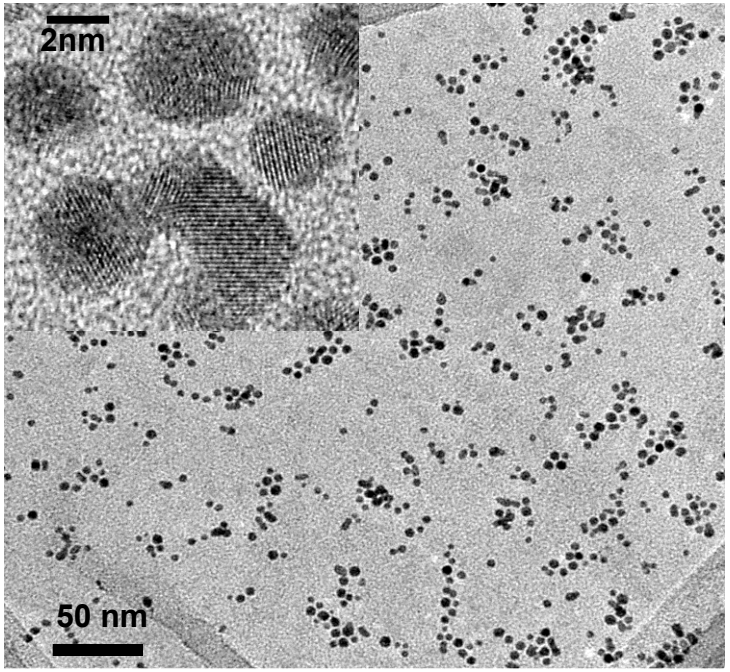
Katharine Page
Ram Seshadri
Tony Cheetham

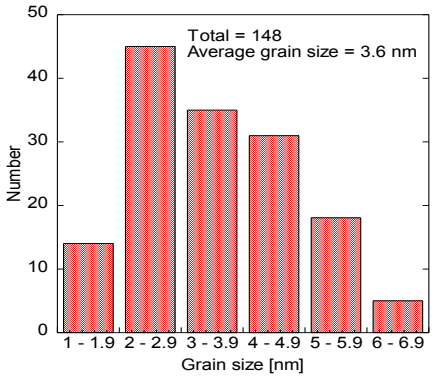
Thomas Proffen

Gold nanoparticles

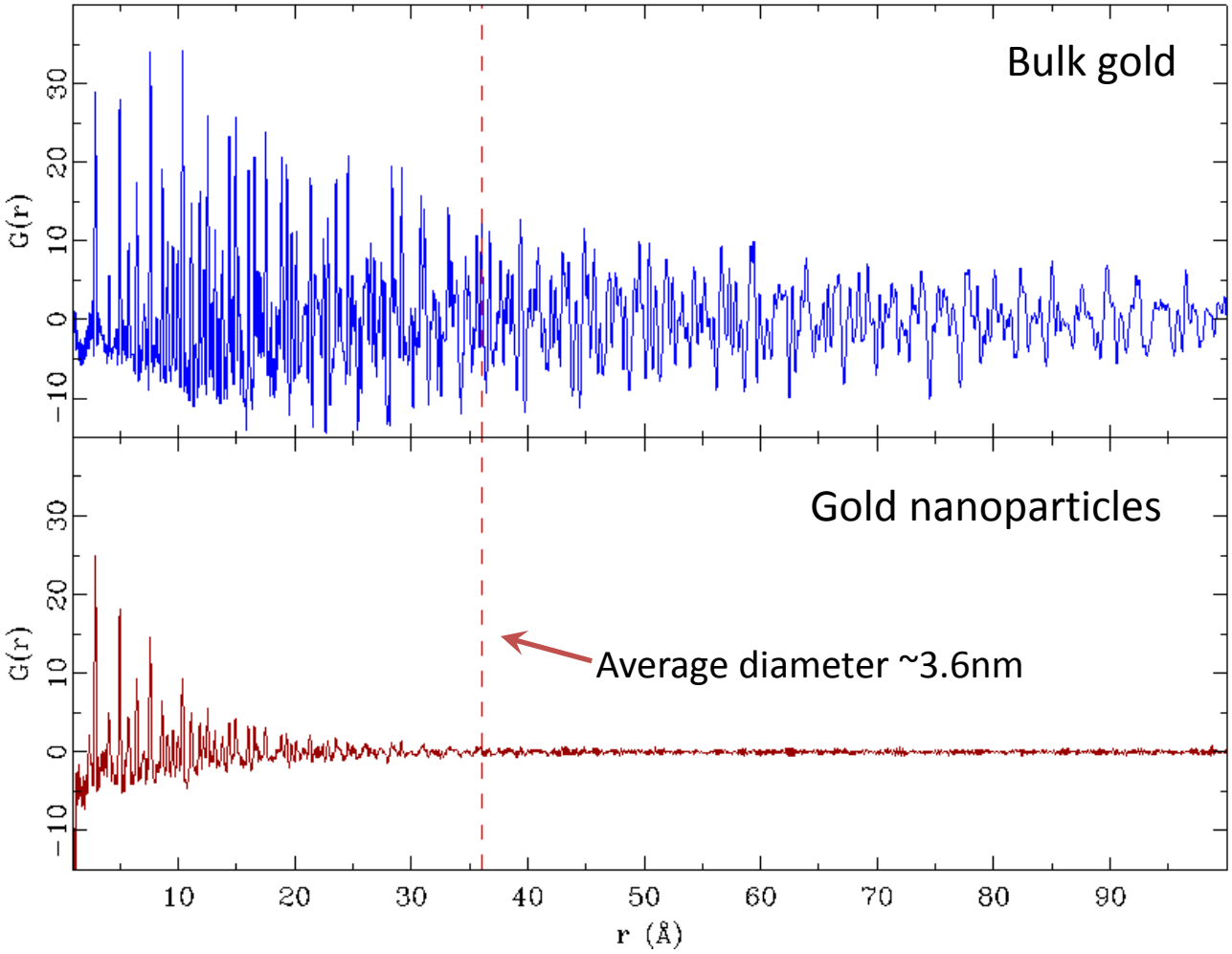
- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.

- This study:
  - 5nm monodisperse Au nanoparticles
  - 1.5 grams of material
  - Neutron measurements on NPDF



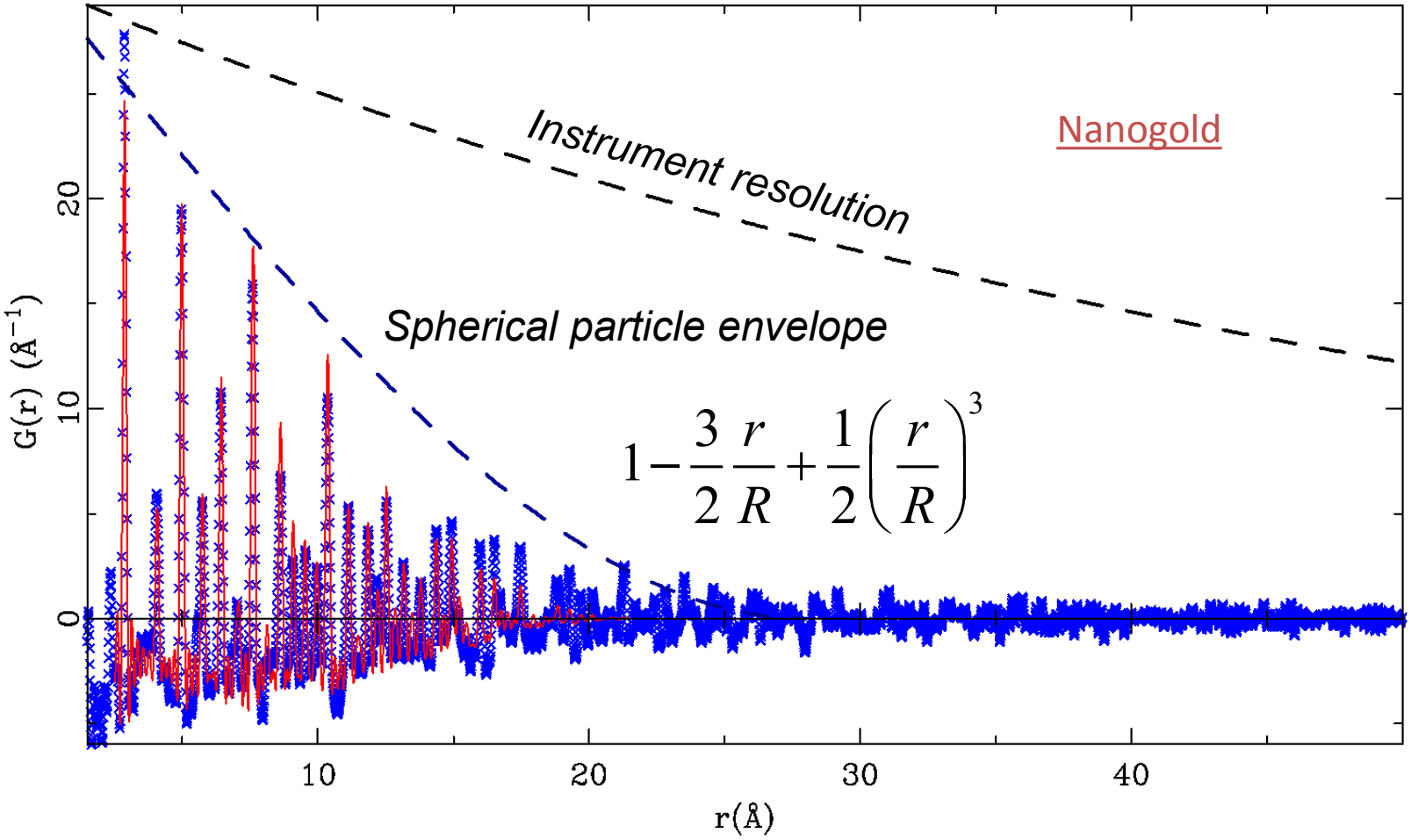


Gold nanoparticles: First NPDF data

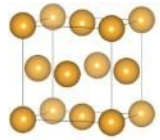


K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

Nanoparticles: Particle size



Modeling Au structure only

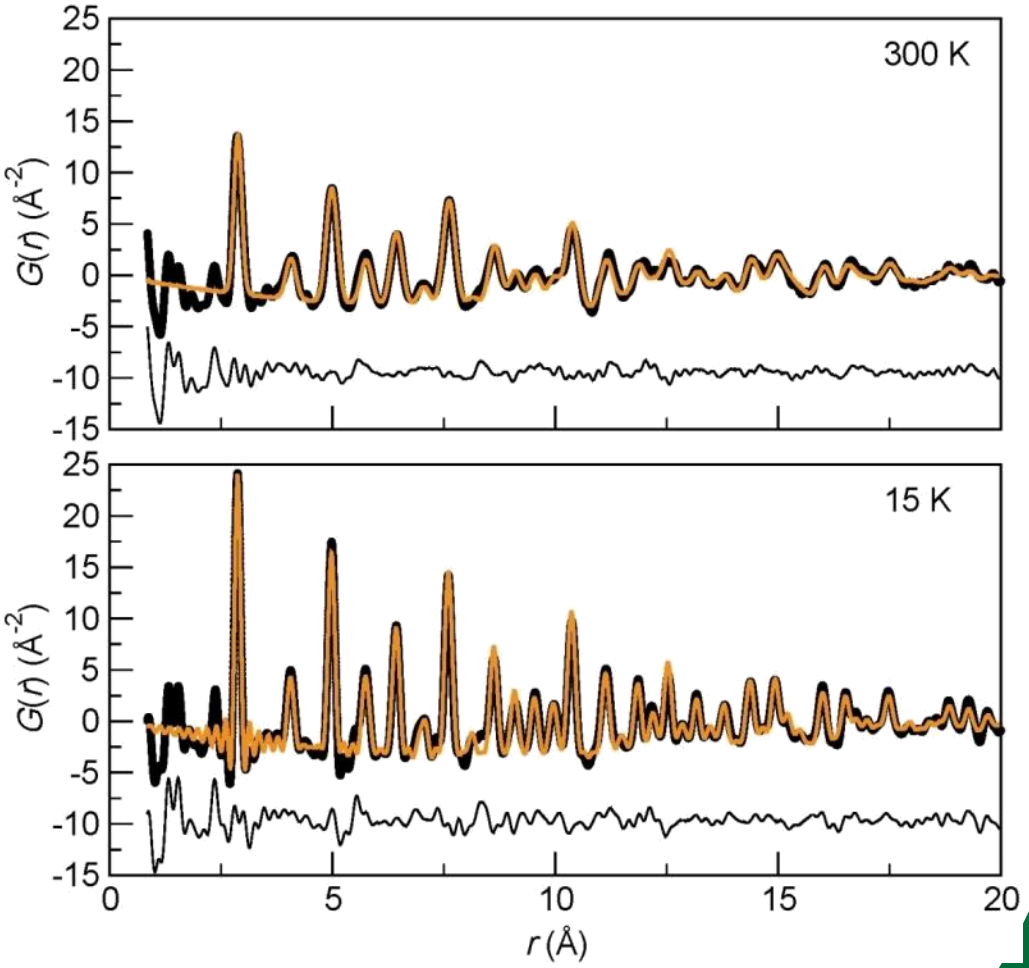


300 K: R_w = 33.8 %

- scale = 0.2121(5)
- a = 4.0753(1)
- u_{iso}(Au) = 0.01267(6)
- δ1 = 1.980(7)
- d = 26.13(7) Å

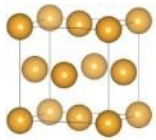
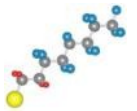
15 K: R_w = 27.8 %

- scale = 0.2070(4)
- a = 4.06515(5)
- u_{iso}(Au) = 0.0044(2)
- δ1 = 2.257(5)
- d = 25.54(4) Å



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

Modeling Au structure & ligand


+


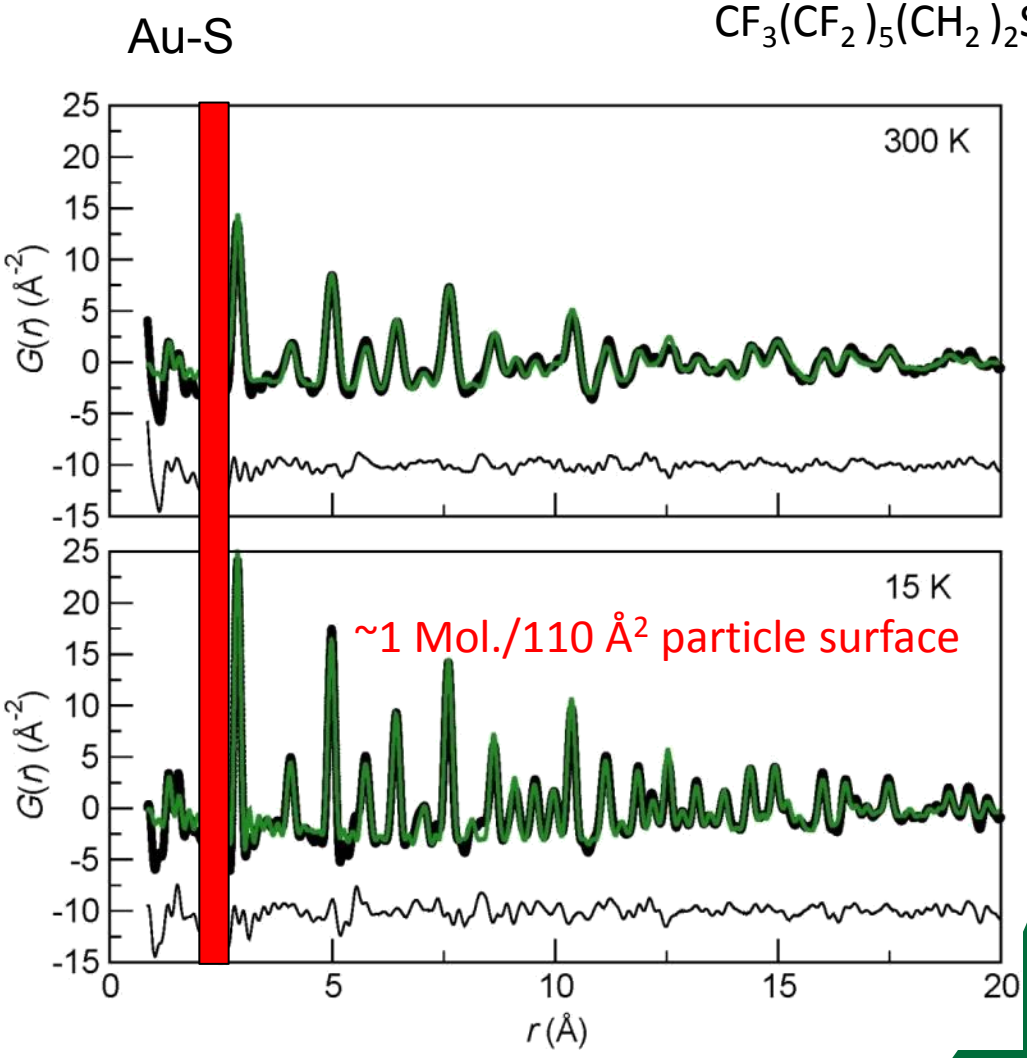
$CF_3(CF_2)_5(CH_2)_2S^-$

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)
- δ1 (Au) = 1.953(7)
- srat (molecule)= 0.02(3)

15 K: R_w = 24.7 %

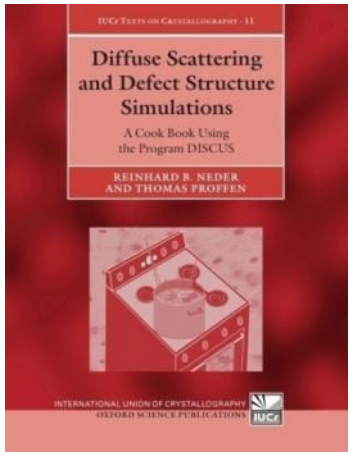
- scale (Au) = 0.2054(4)
- scale (molecule) = 0.0604(6)
- a (Au) = 4.06500(5)
- a(molecule) = 49.23(2)
- u_{iso}(Au/molec) = 0.00433(2)
- δ1 (Au) = 2.256(6)
- srat (molecule)= 0.03(14)



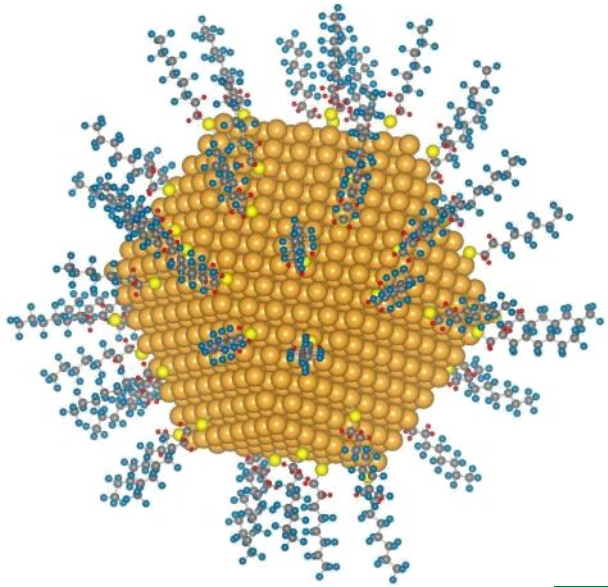
Modeling of nanoparticle data - future !

Using DISCUS/DIFFEV

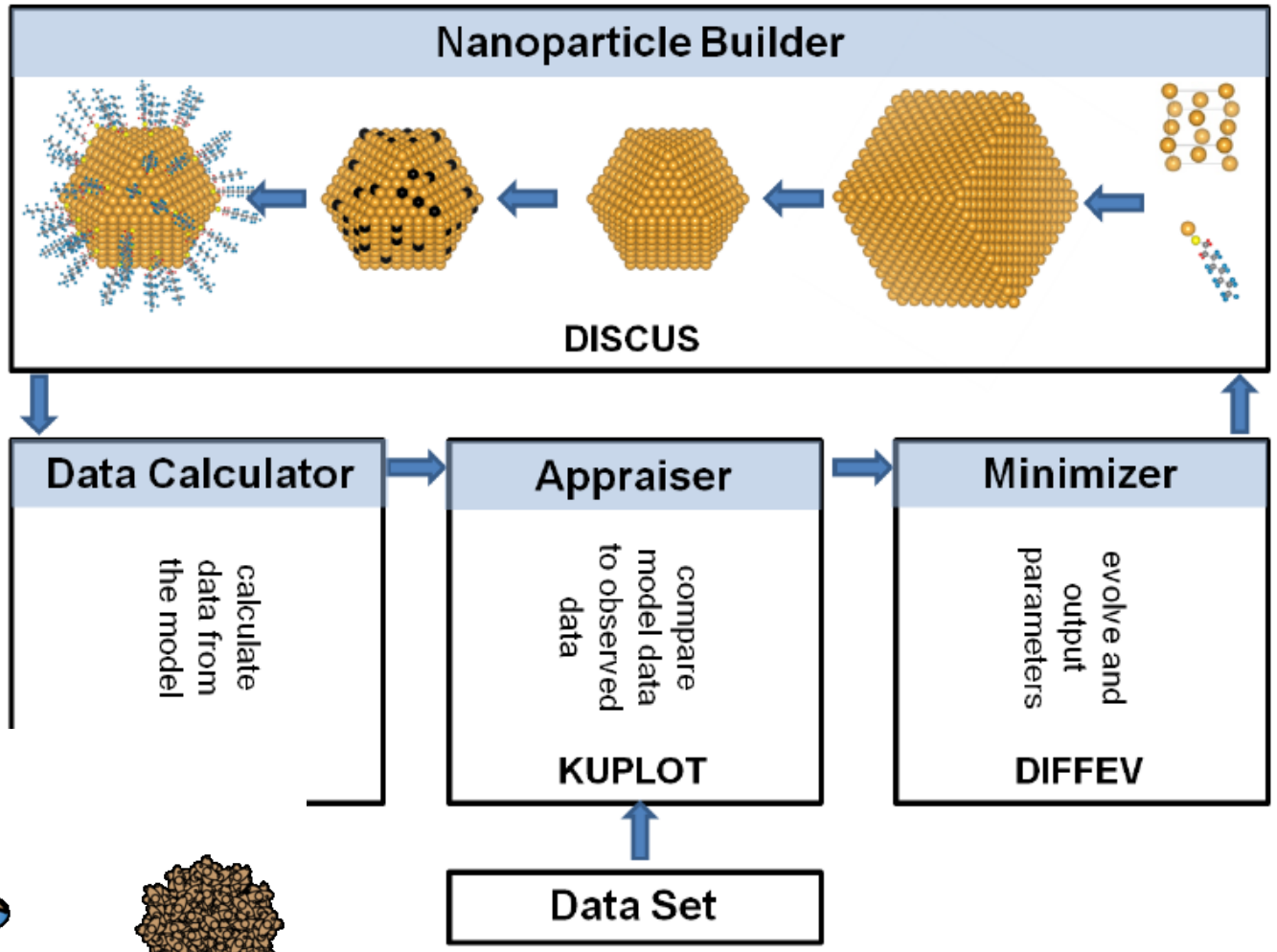
Oxford University Press, October 2009



- 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).

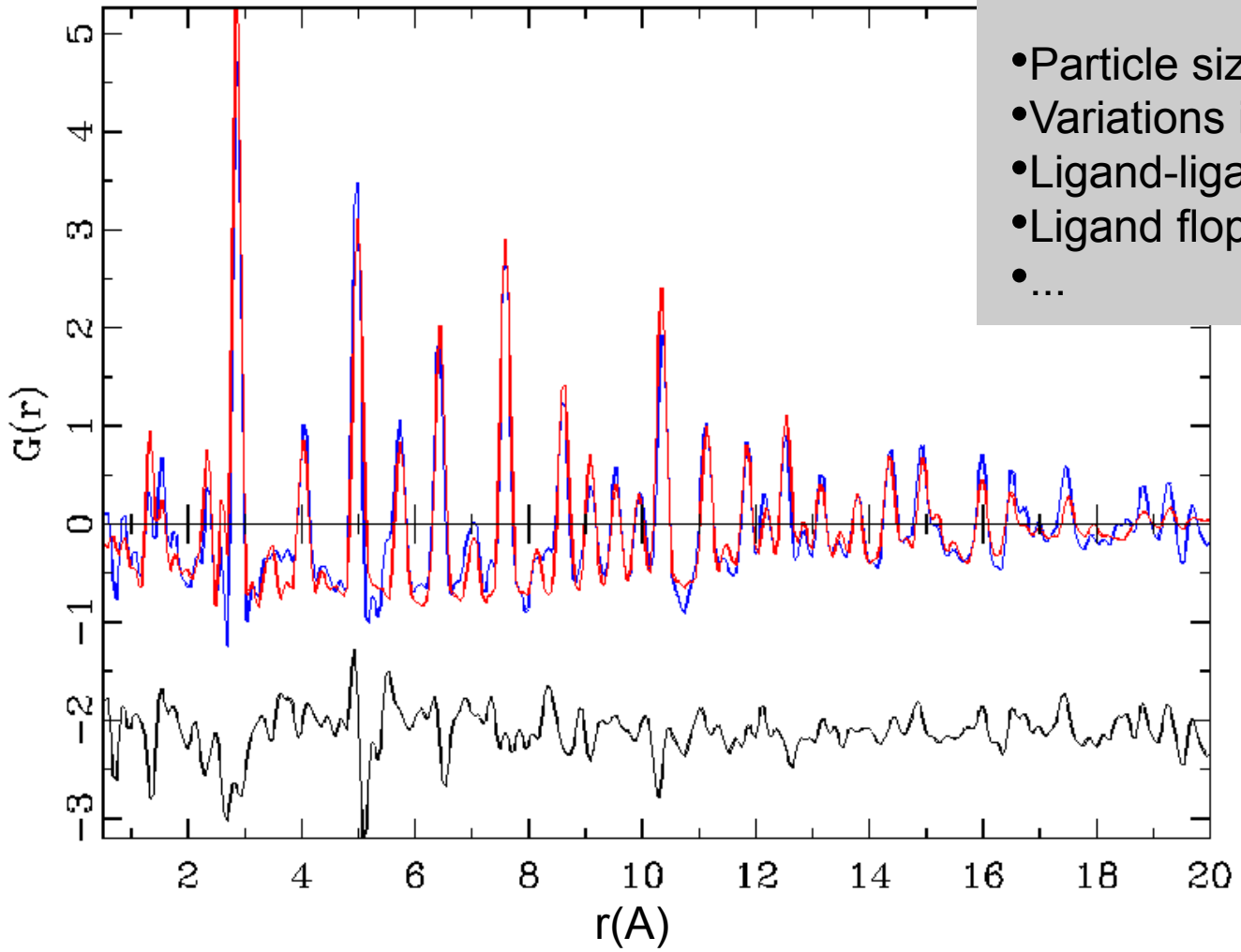


Nanoparticle builder



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 **or** **spallation neutron sources**

(high energy X-rays) **(reactor neutron energies are too low)**

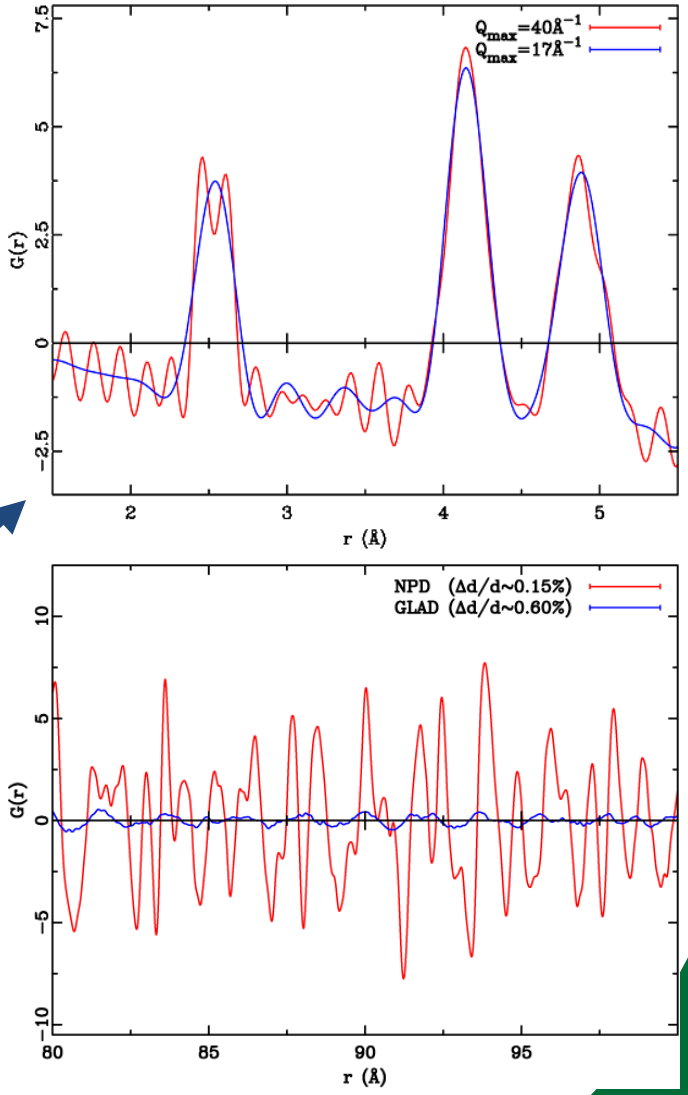
NPDF: the key to high quality, high r PDFs

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

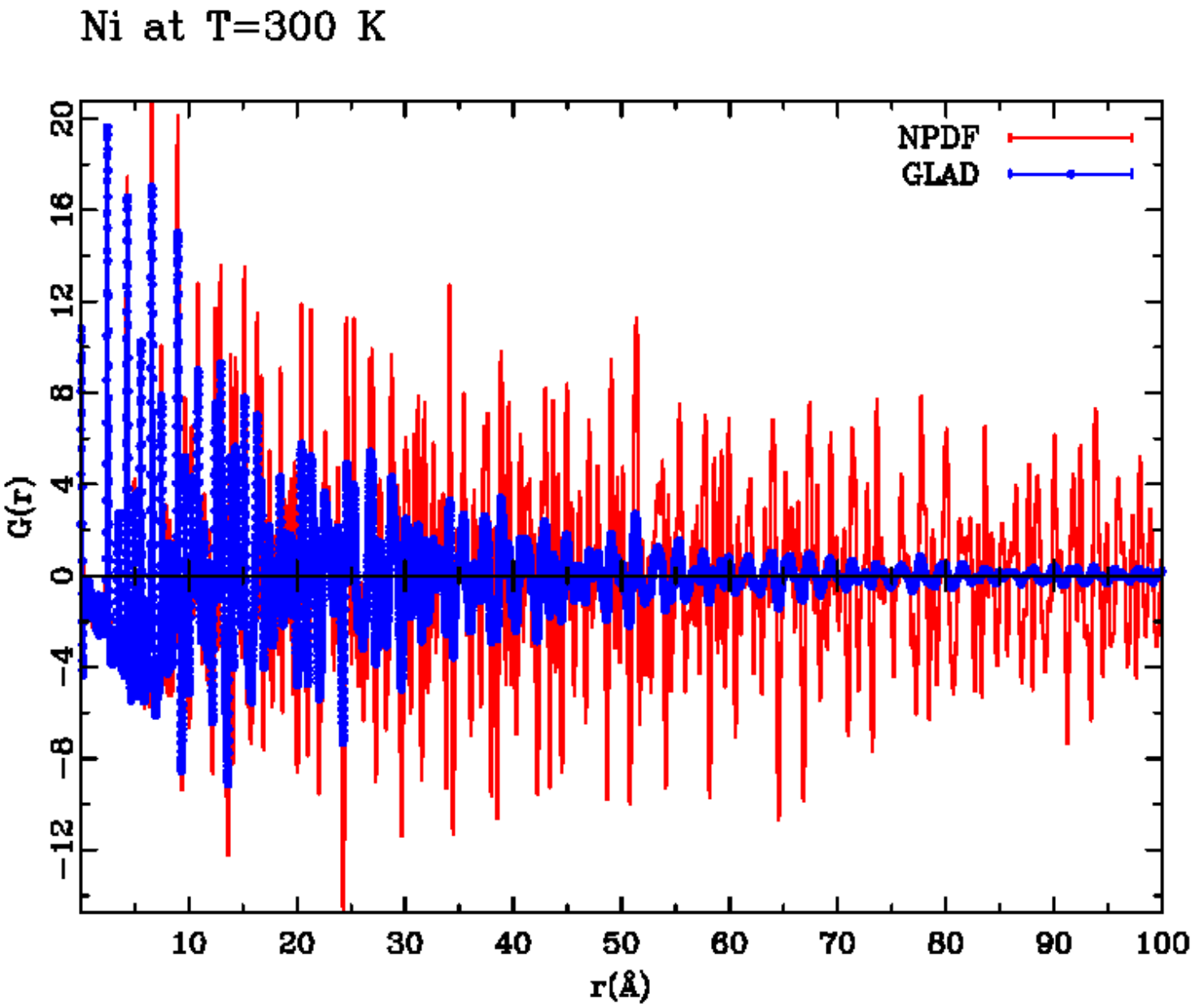
$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q)-1]\sin(Qr)dQ$$

Requirements to obtain 'good' PDF:

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



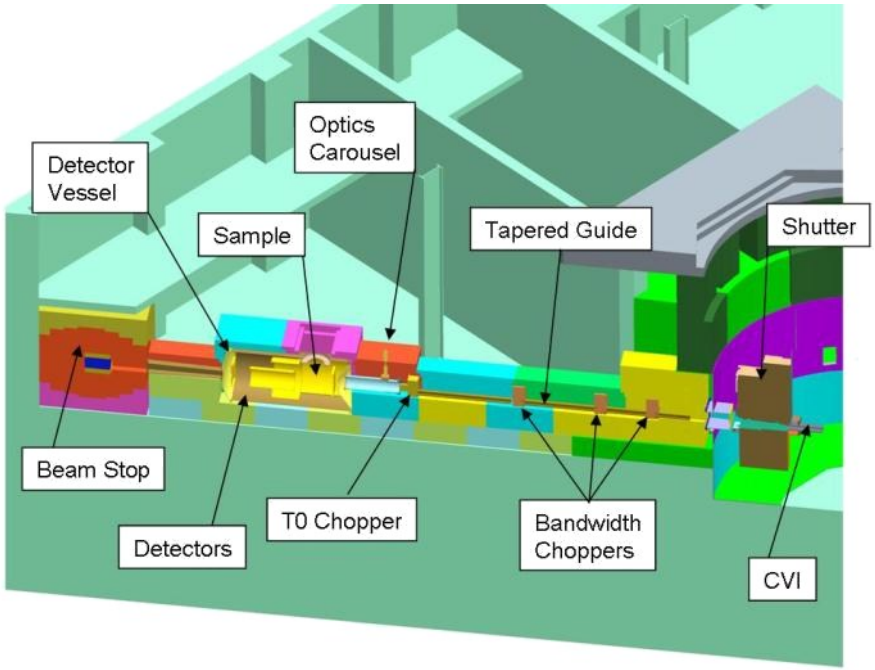
Q resolution ..



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	~1 x 10^8 neutrons cm^{-2} sec^{-1}

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



contact

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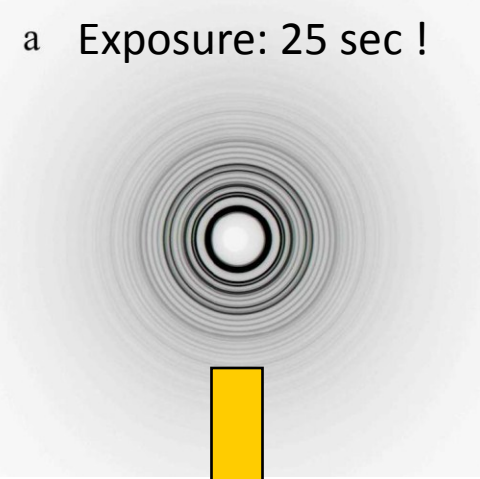
Mikhail Feygenson
feygensonm@ornl.gov

X-ray PDF: The fast way



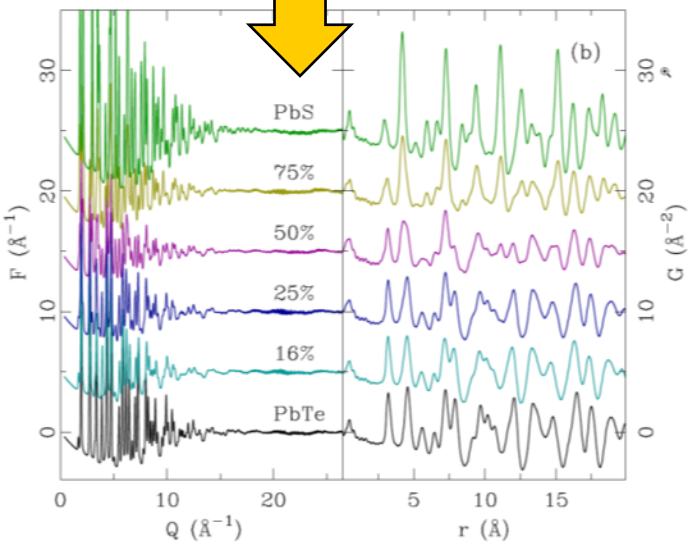
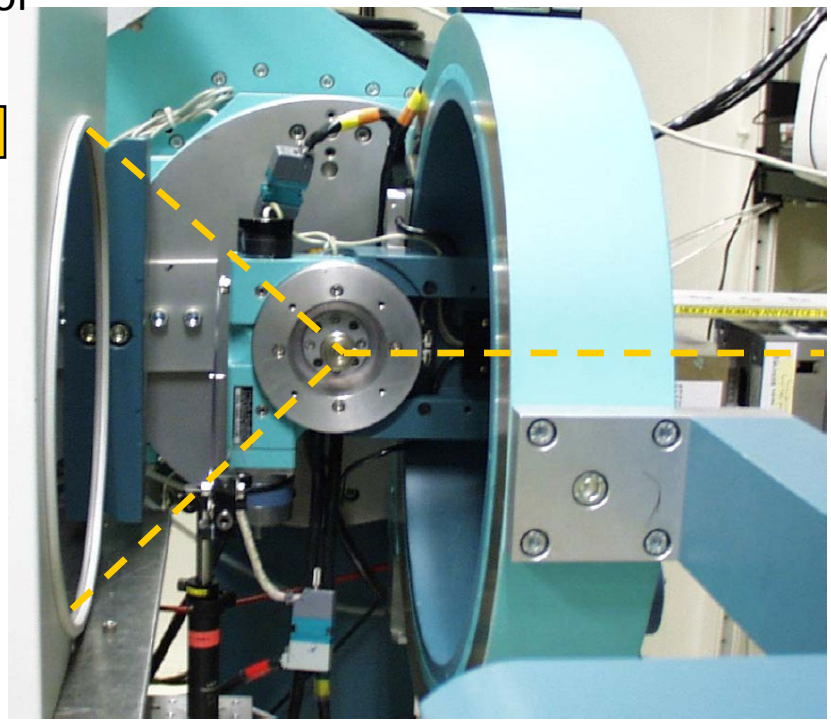


Image plate detector



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).

Agreement between LANL and ANL ..

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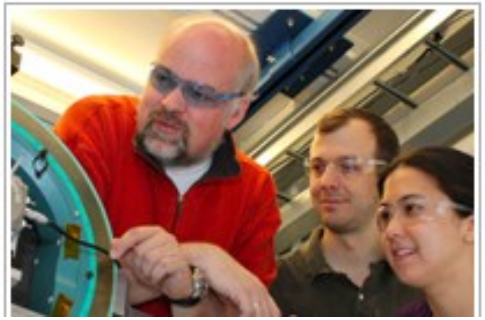
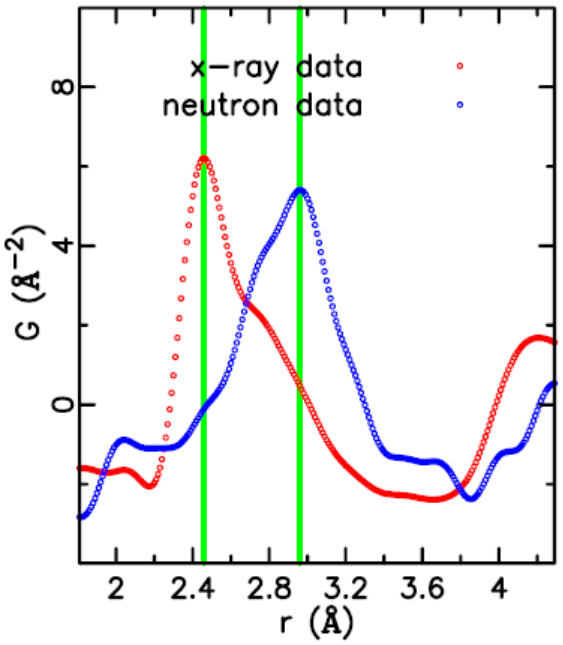
Los Alamos-Argonne partnership will aid understanding of complex materials



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

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



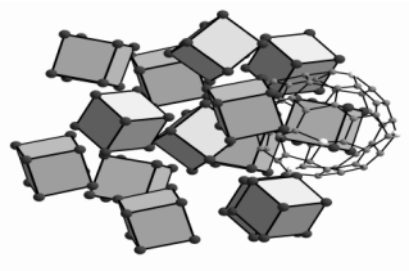
PDF peak intensity $\propto$ $$\sum_{mn} \frac{b_m b_n}{\langle b \rangle^2} \delta(r - r_{mn})$$

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

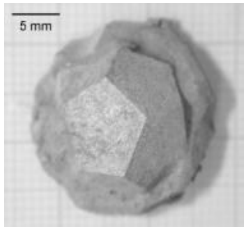
	b_i for x-ray	b_i for neutron
Mg	12	3.631
Co	27	0.779

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

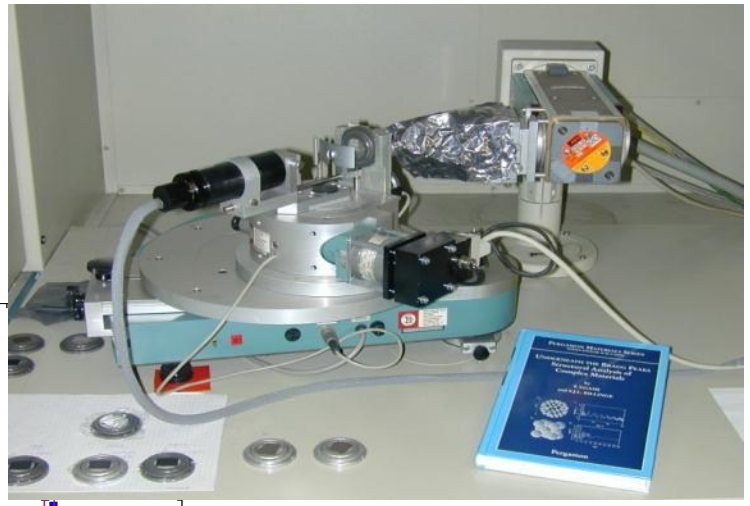
X-ray PDF: In house measurements

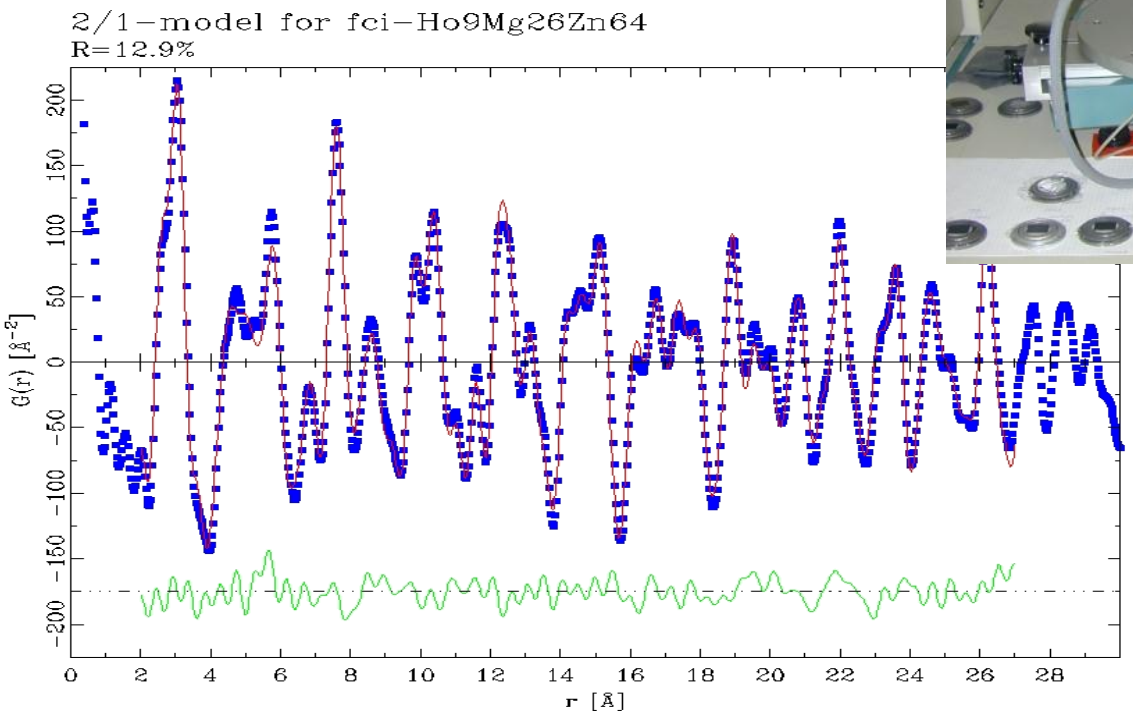


***fci*-Ho-Mg-Zn**



Huber Gunier diffractometer
Q_{max} = 13.5Å^{-1}





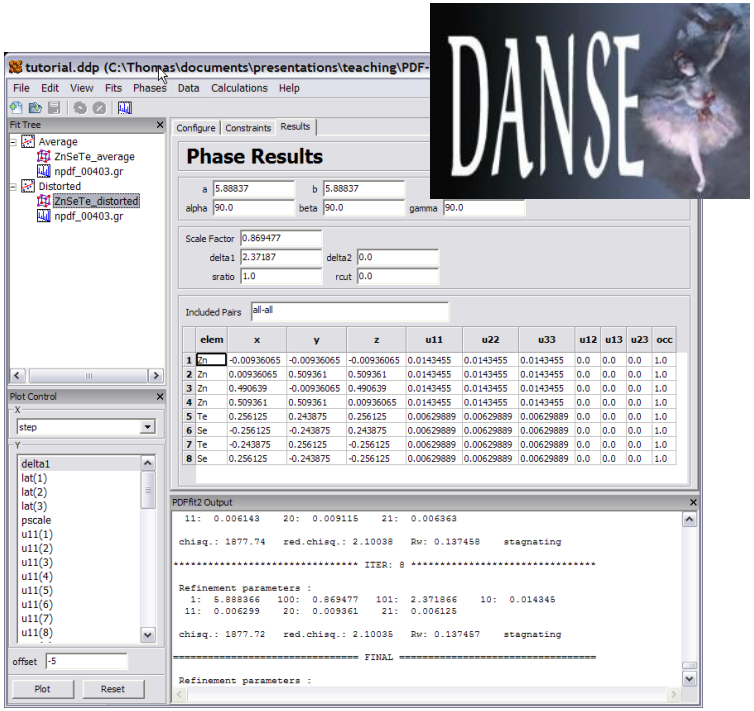
Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

Software

Software: Data modeling

PDFgui

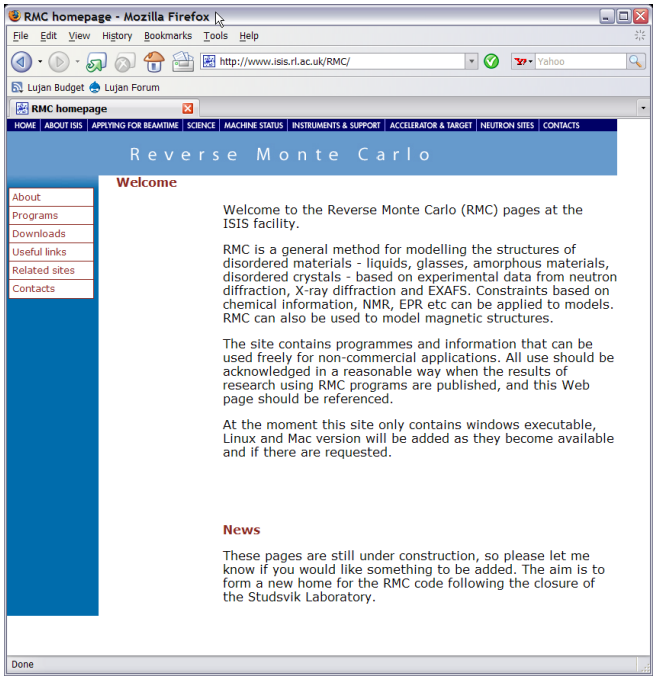
- **Part of DANSE project.**
- http://www.diffpy.org/



- 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 *pdffit2* can also be used in command mode.

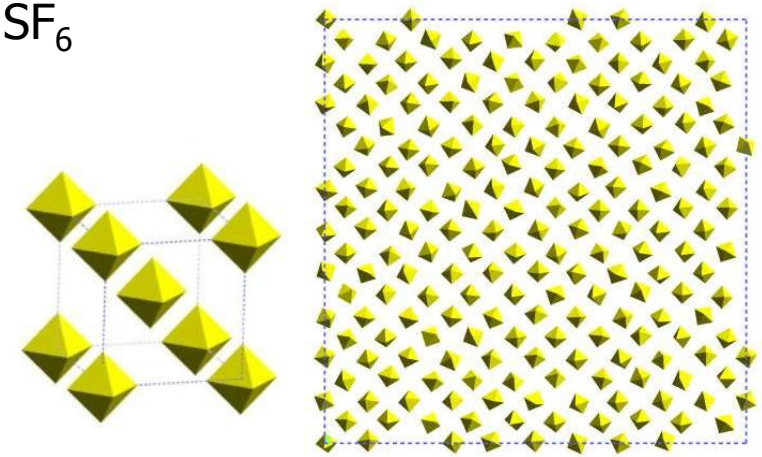
Software: RMCprofile

- **RMCprofile**
  - Atomic configurations ~600 to 20000+ atoms
  - Fit both X-ray and neutron F(Q)
  - Fit G(r)
  - Fit Bragg profile (GSAS tof 1,2 & 3)
  - 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

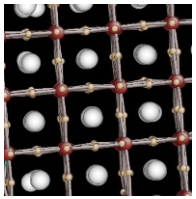


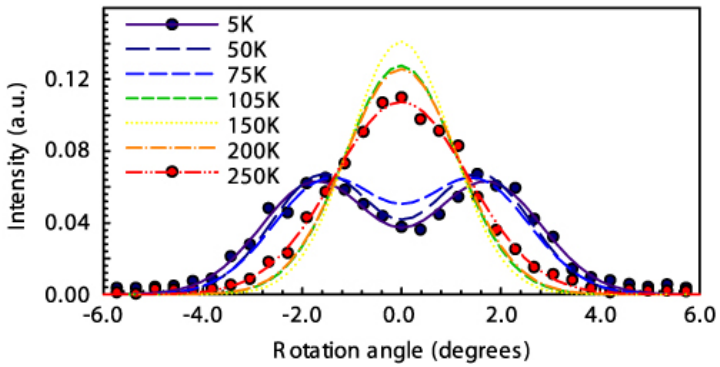
RMC: Examples

SF_6

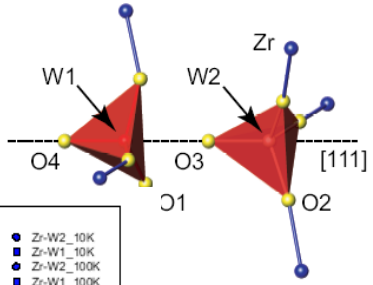


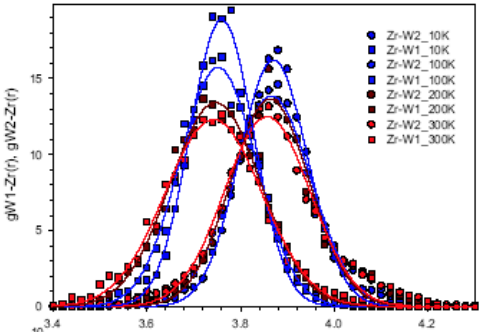
$SrTiO_3$



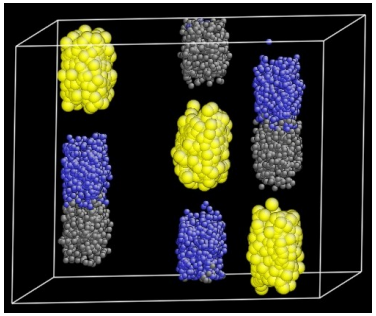


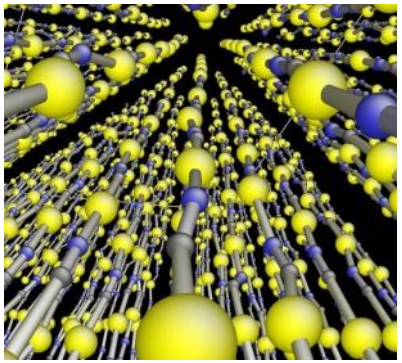
ZrW_2O_8





AuCN

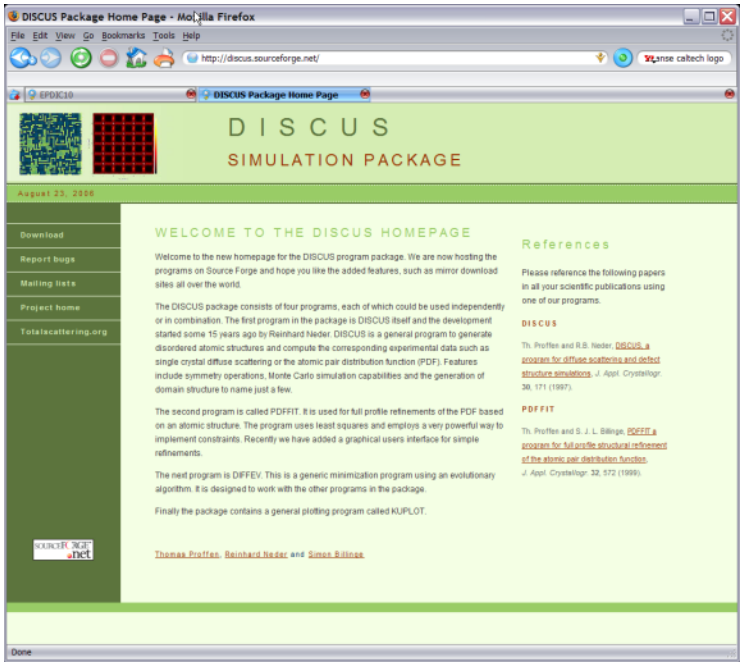


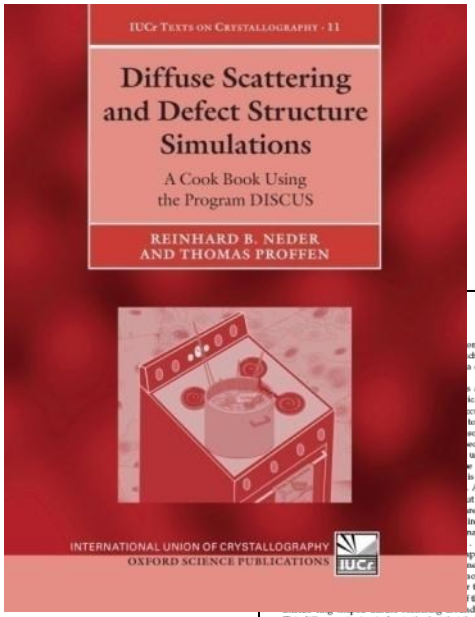


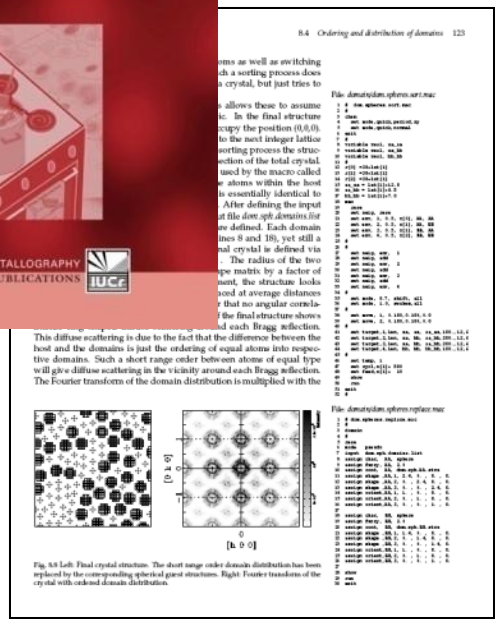
Software: Data modeling

DISCUS

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







Oxford University Press, October 2008

Nanoparticle builder

Los Alamos NATIONAL LABORATORY EST. 1943

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TOTAL SCATTERING GROUP

Tools for structural analysis of complex materials

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More coming soon ..

Software

DISCUS

Jmol

Ptplot

TEAM

Scientists

Thomas Proffen

Katharine Page

Student

Emily Tencate

Nanoparticle Builder

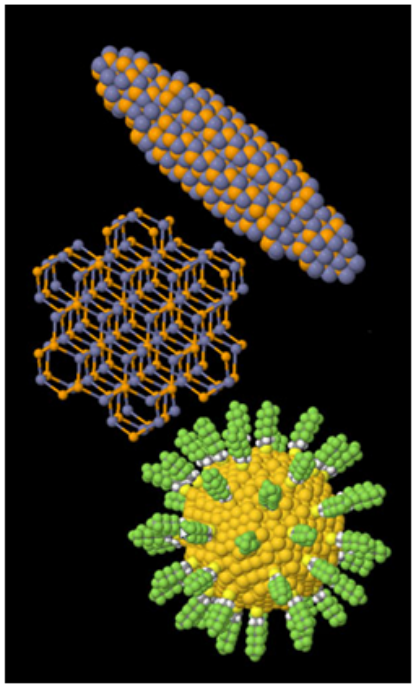
Welcome to the interactive nanoparticle builder. Please note, that this tool is still under development.

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 ⇔ properties relationship
- High-resolution instruments open the door to medium-range order investigations
- Obtain structural information from disordered crystalline, amorphous of composite materials
- Use multiple data sets (e.g. x-ray and neutron data) to characterize complex materials

Got Neutrons? – Shirts
My office – B478
$6.50

http://totalscattering.lanl.gov