Total Scattering

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

Thomas Proffen

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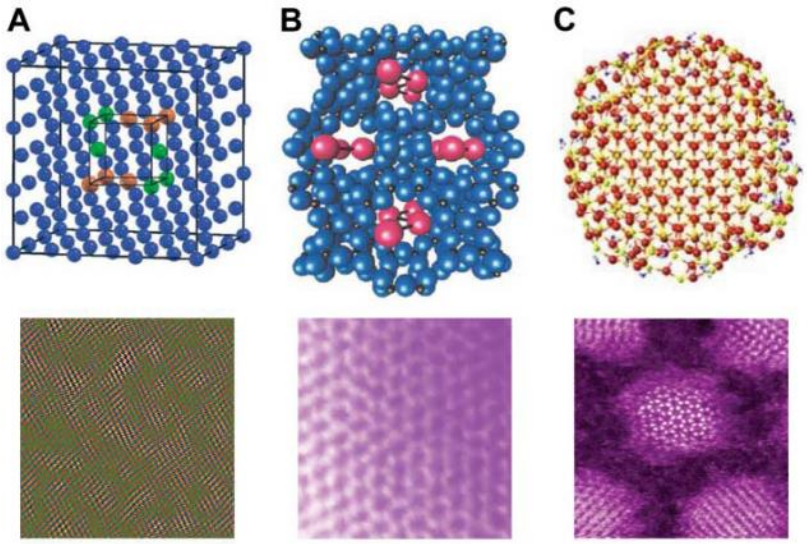
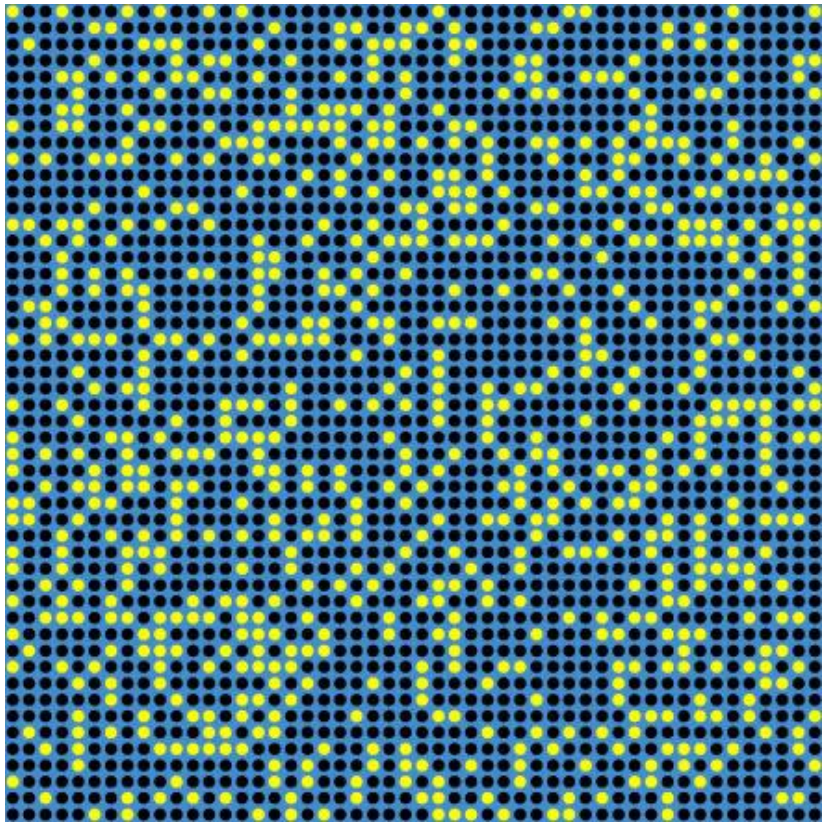
The challenge : Knowing the local structure

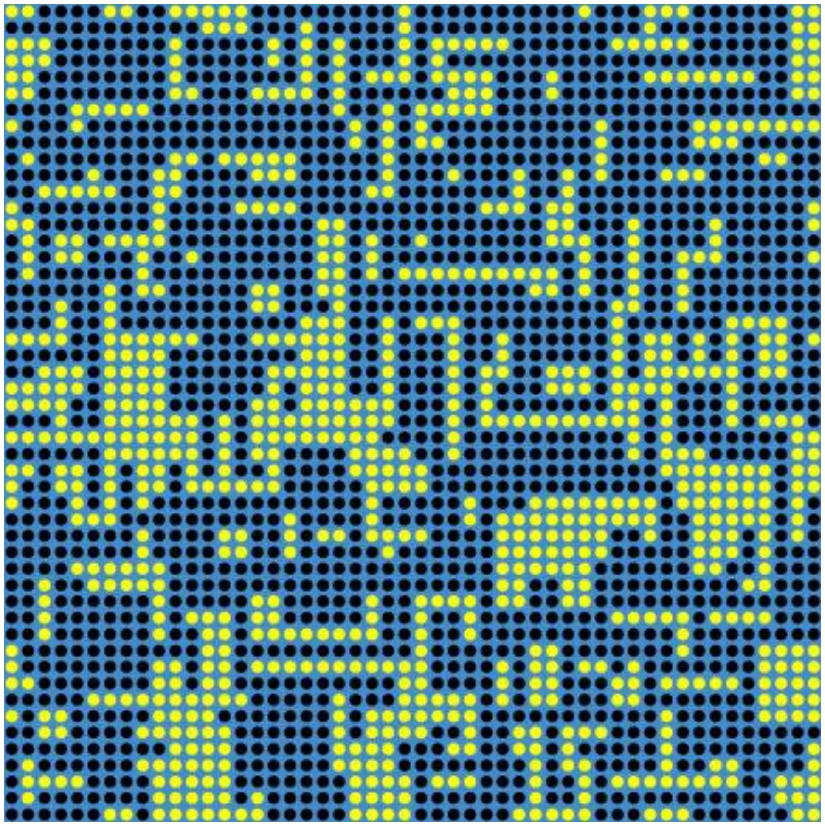
- Traditional crystallographic approach to structure determination is insufficient or fails for
  - **Non crystalline materials**
  - **Disordered materials**: The interesting properties are often governed by the defects or local structure !
  - **Nanostructures**: Well defined local structure, but long-range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

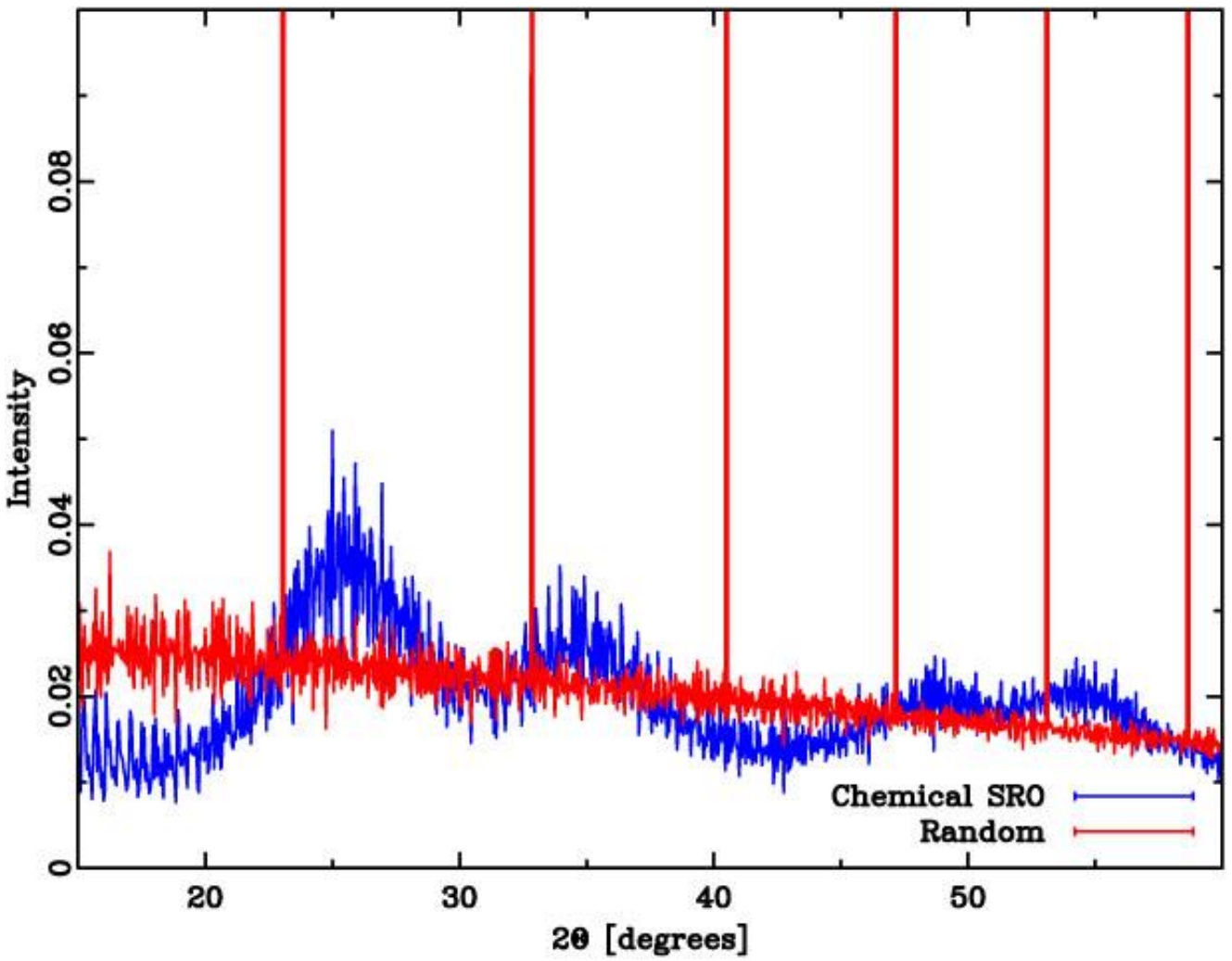




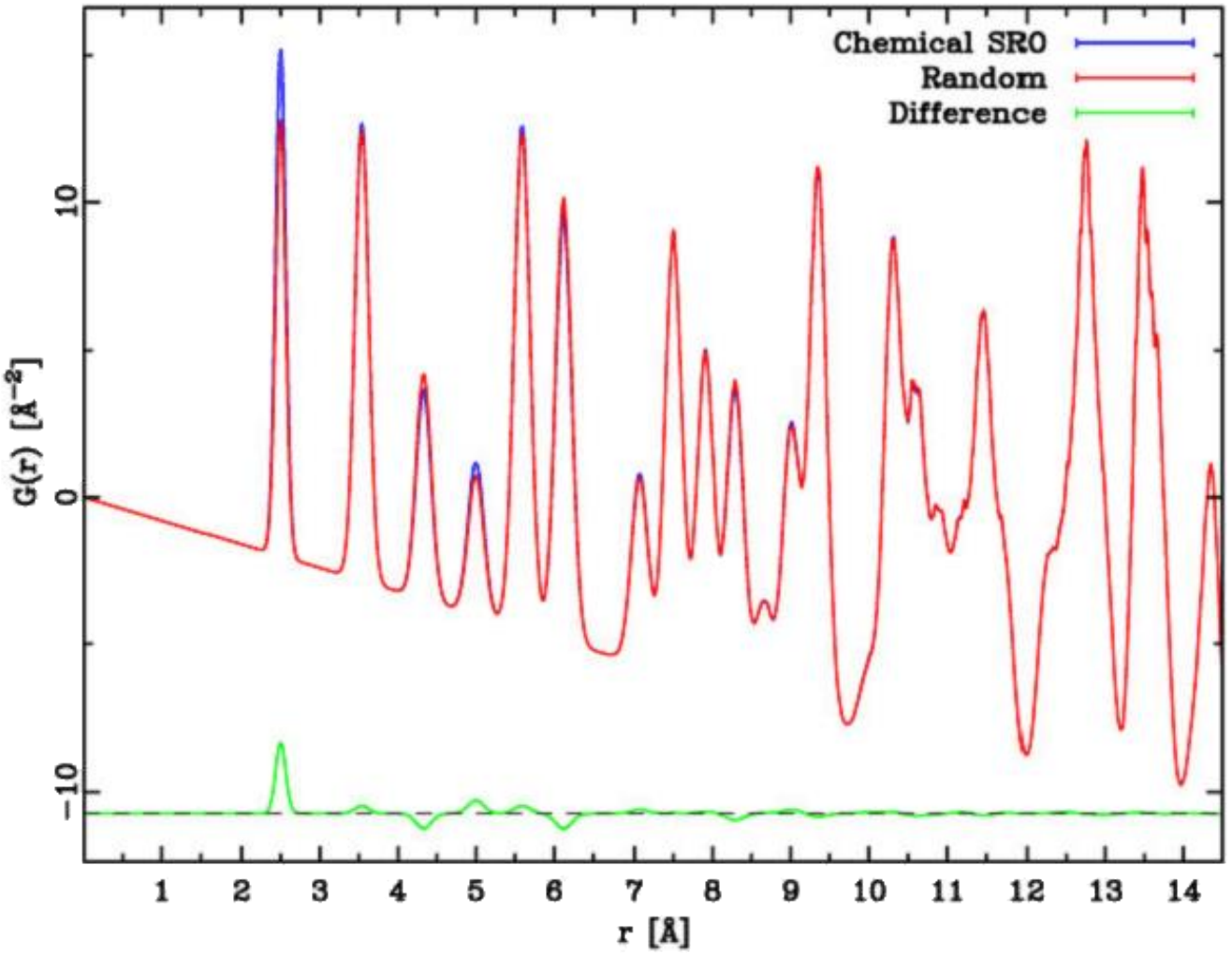
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

Properties might depend on vacancy ordering !!

How about powder diffraction ?



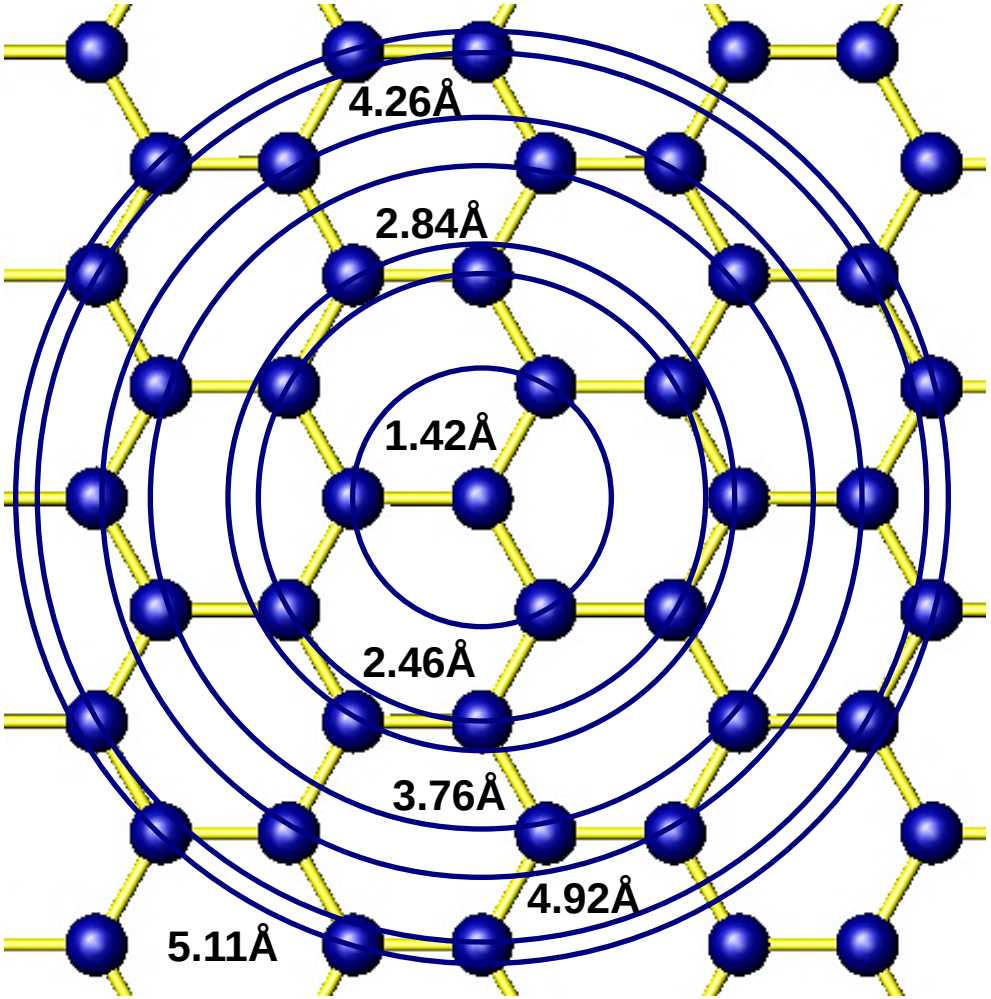
Finally the Pair Distribution Function



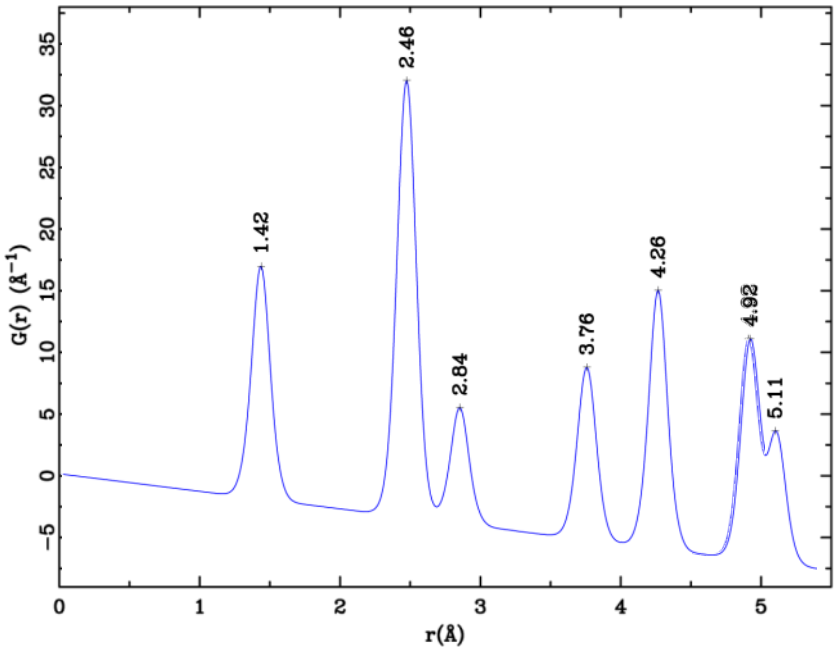
The PDF is the Fourier transform of the total scattering diffraction pattern !

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

What is a PDF?



Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.

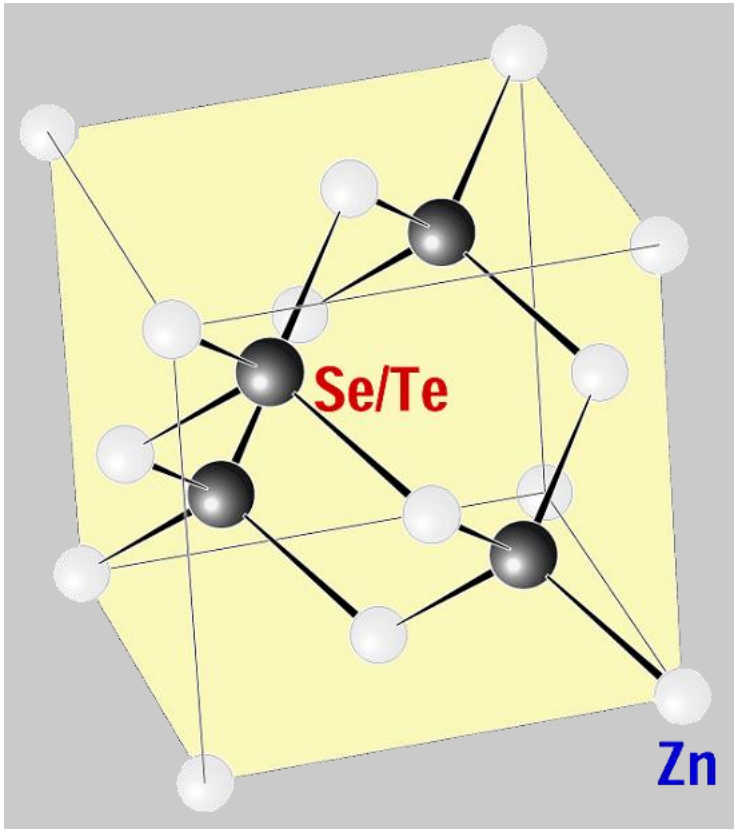


Example:
Local atomic strain in $ZnSe_{1-x}Te_x$

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

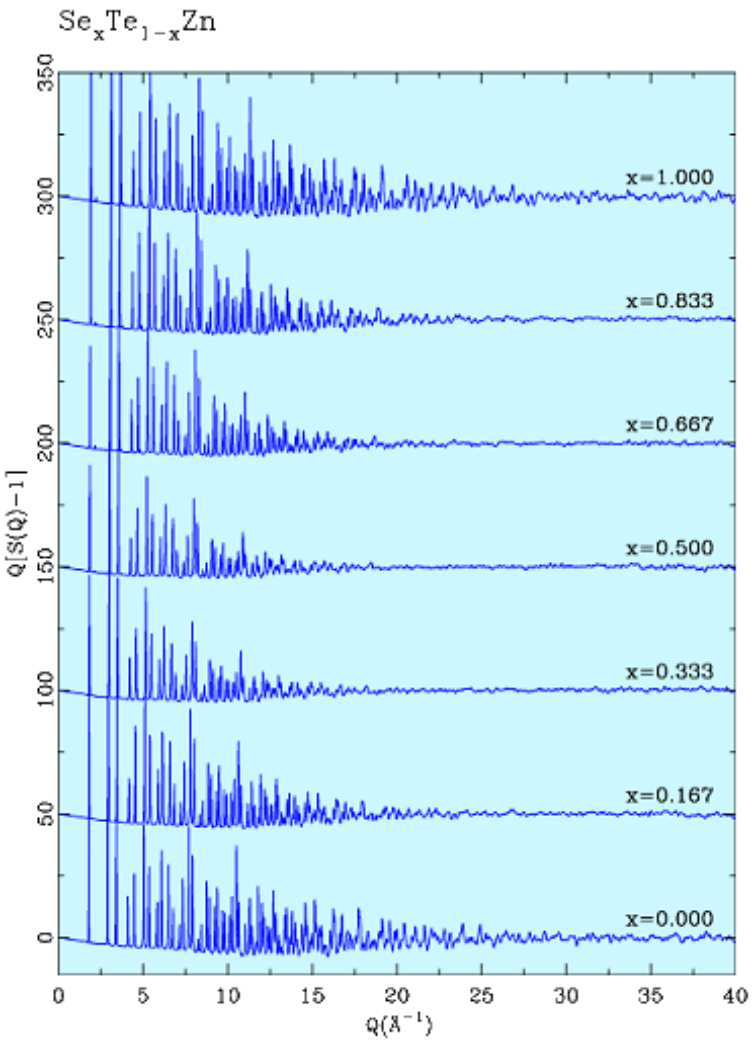
$ZnSe_{1-x}Te_x$: Structure

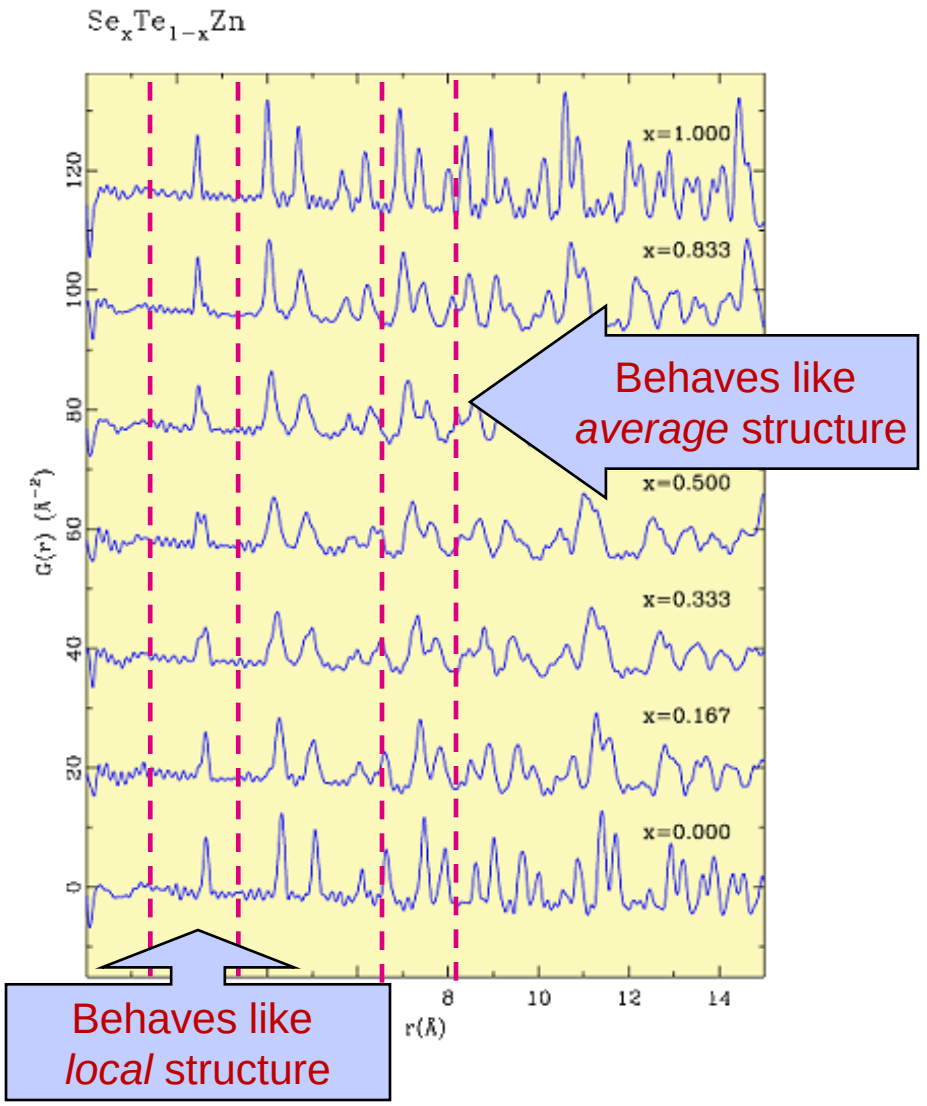
- Zinc blend structure (F43m)
- Technological important : Electronic band gap can be tuned by the composition *x*.
- Bond length difference *Zn-Se* and *Zn-Te* $\Rightarrow$ strain.
- Local structural probe required !



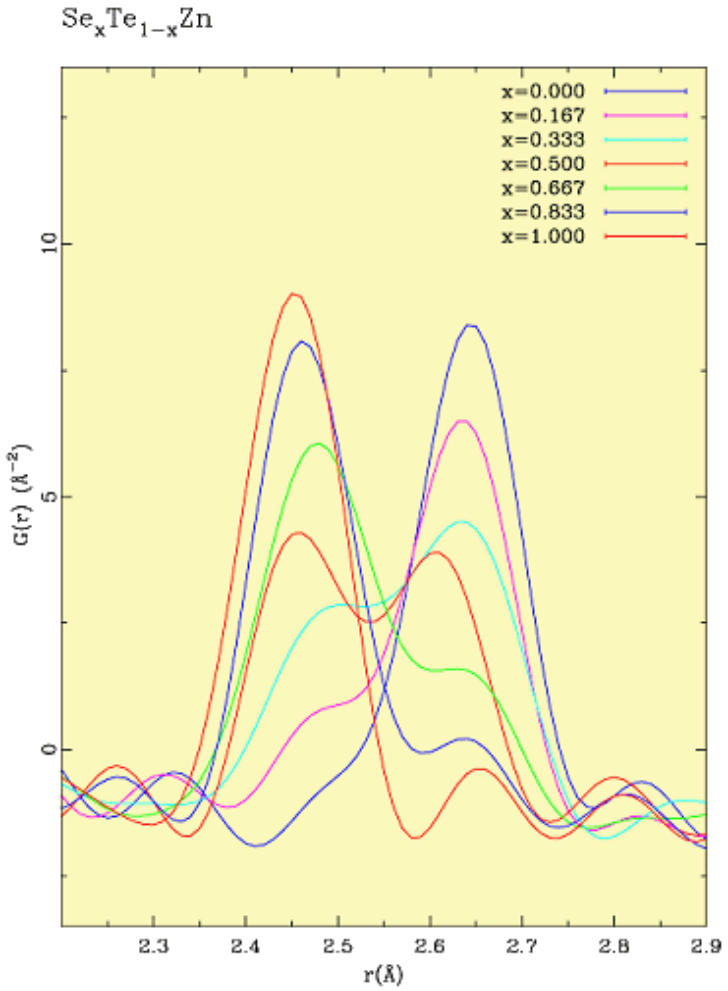
$ZnSe_{1-x}Te_x$: Total scattering

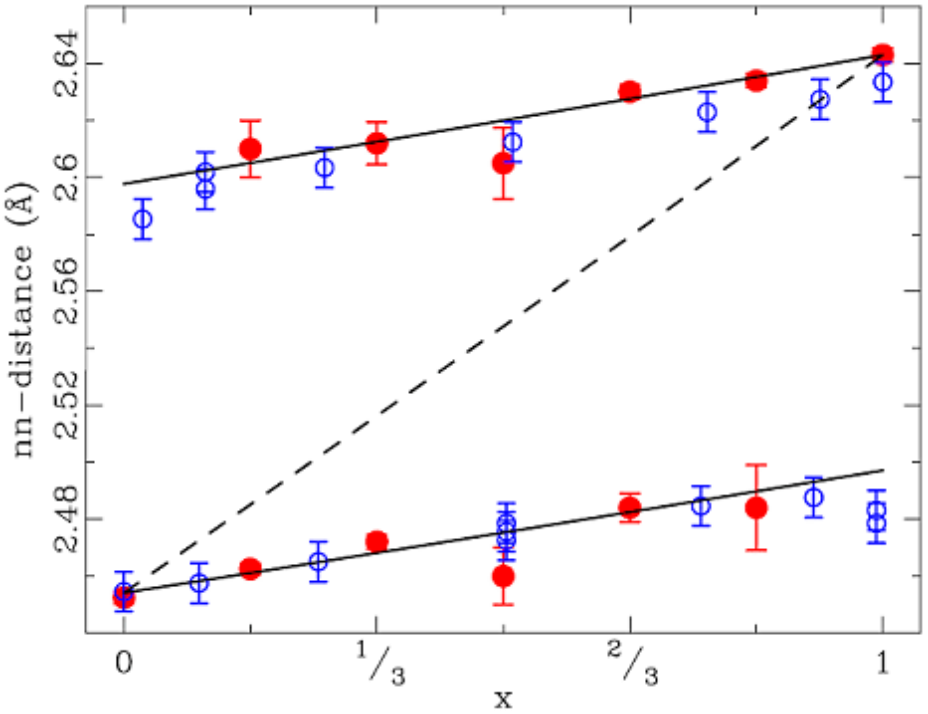
Peterson et al., *Phys. Rev.* B**63,** 165211 (2001)





$ZnSe_{1-x}Te_x$: 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

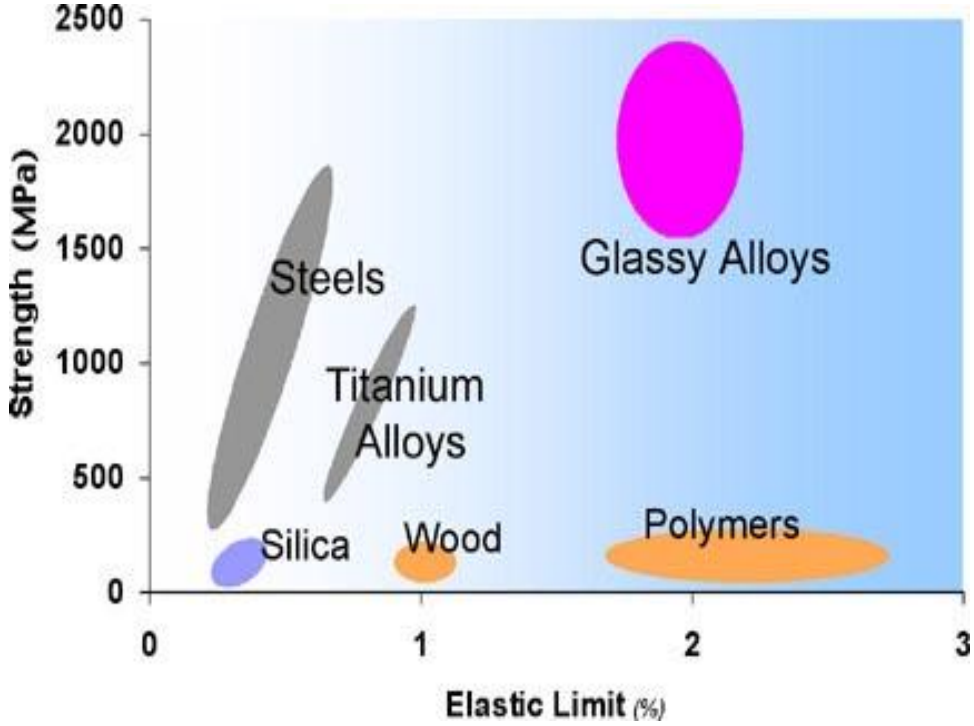
Facilities: Lujan
Funding: DOE, NSF

BMG : Properties

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

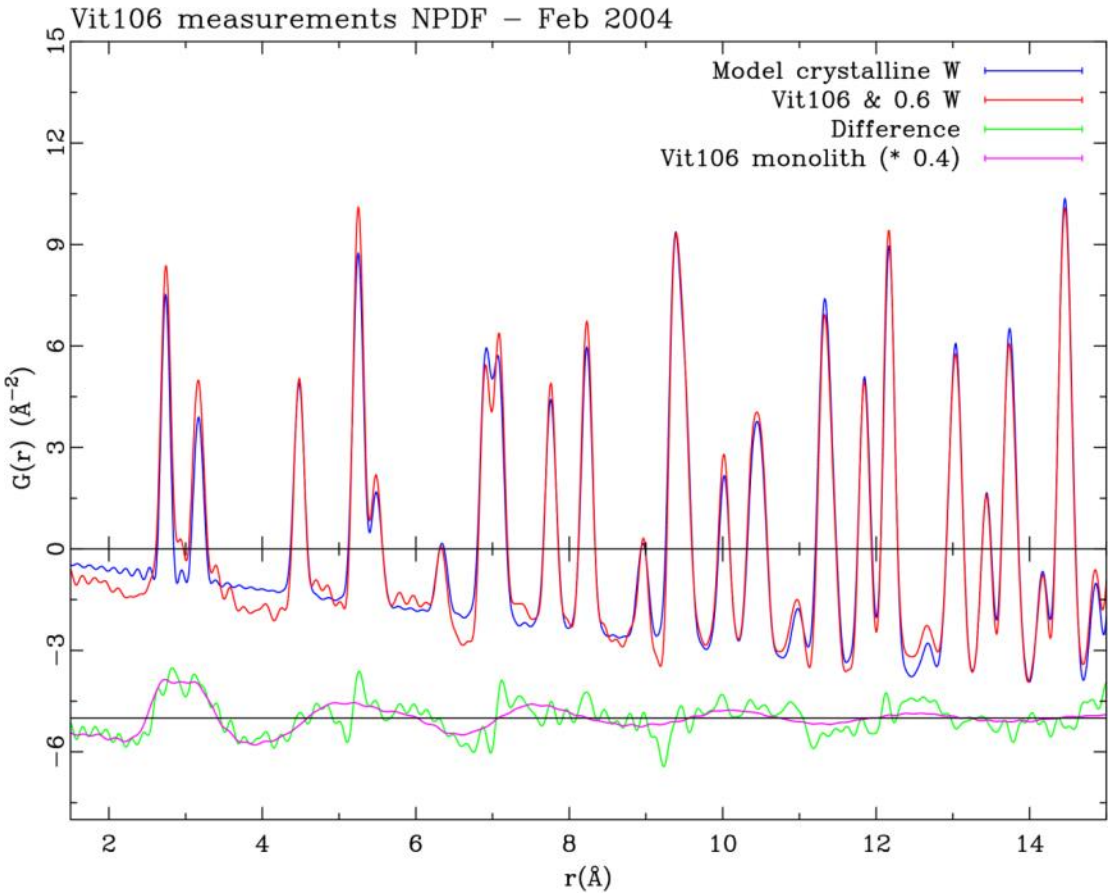
- BMG's are prone to catastrophic failure during unconstrained loading due to the formation of macroscopic shear bands

- *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

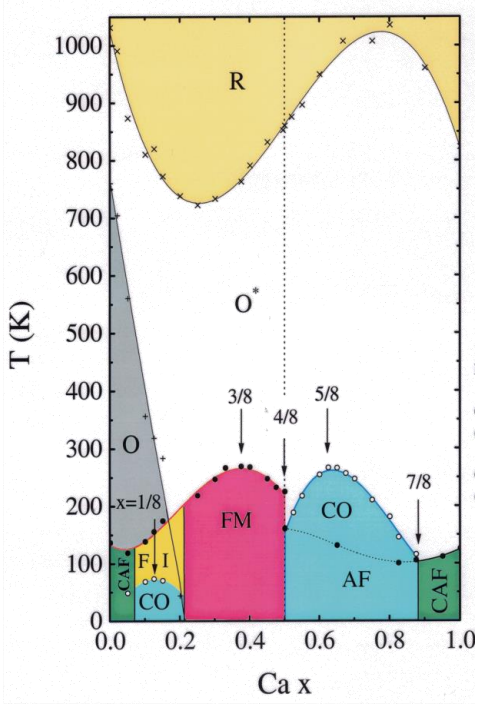
Example:
Local structure in $La_xCa_{1-x}MnO_3$

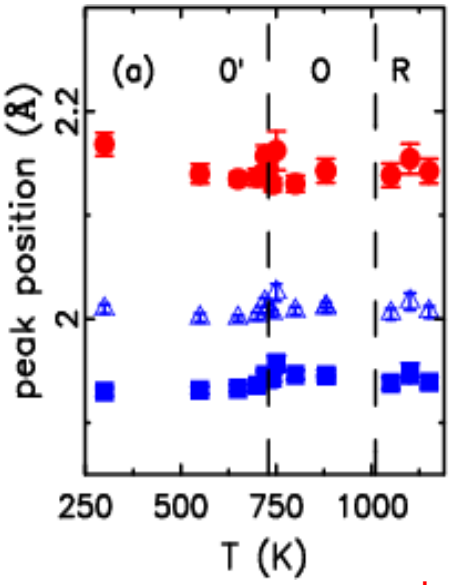
MICHIGAN STATE UNIVERSITY

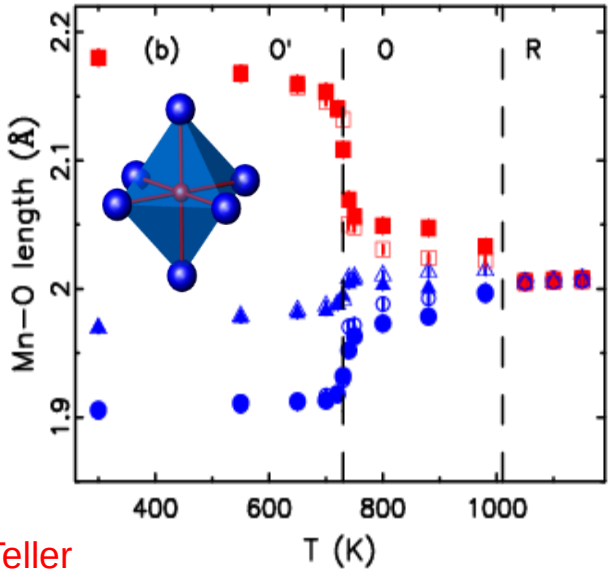
Simon Billinge
Emil Bozin
Xiangyn Qiu

Thomas Proffen

$LaMnO_3$: Jahn-Teller distortion







Jahn Teller
Long Mn-O bond

Local structure

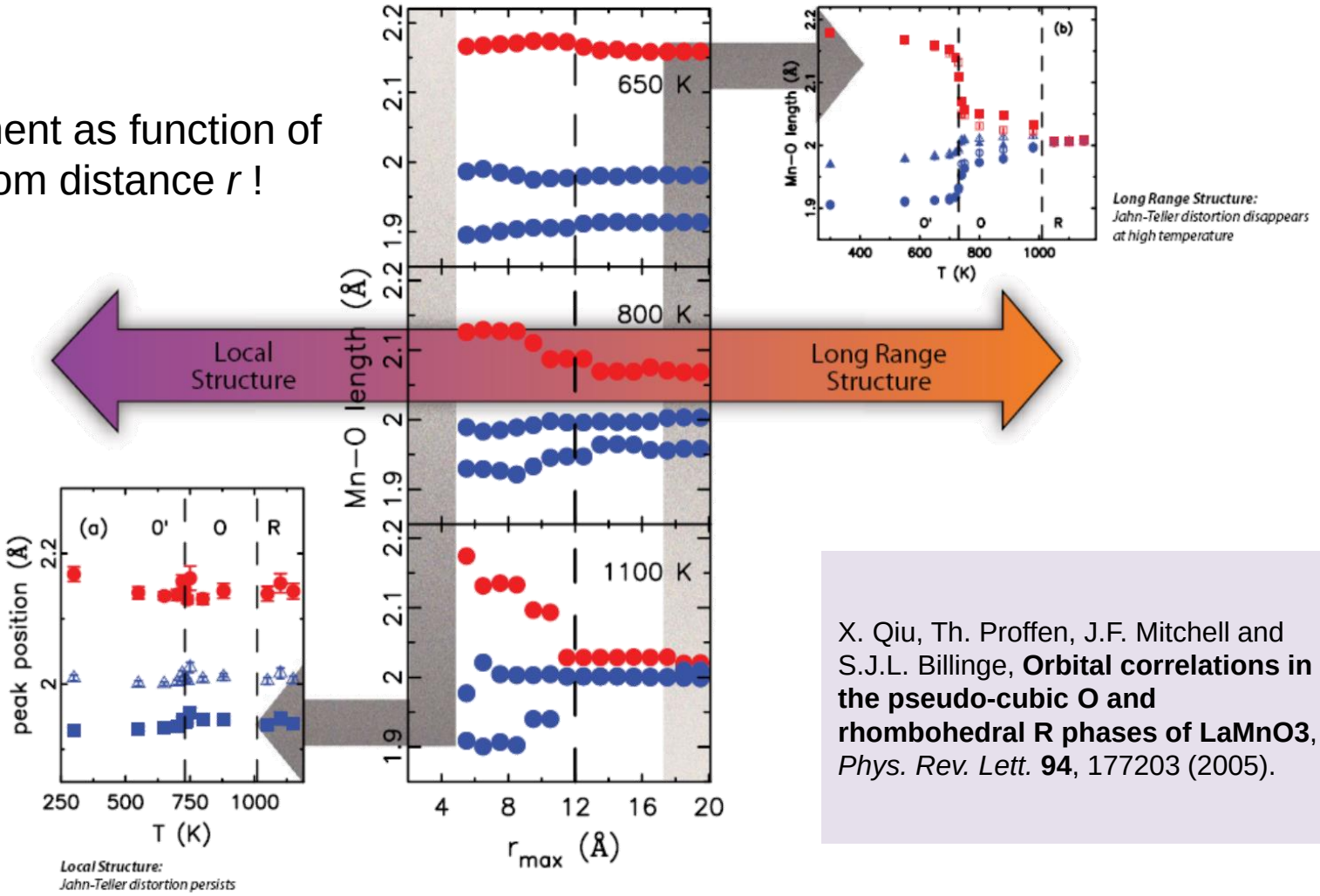
Average structure

- 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?

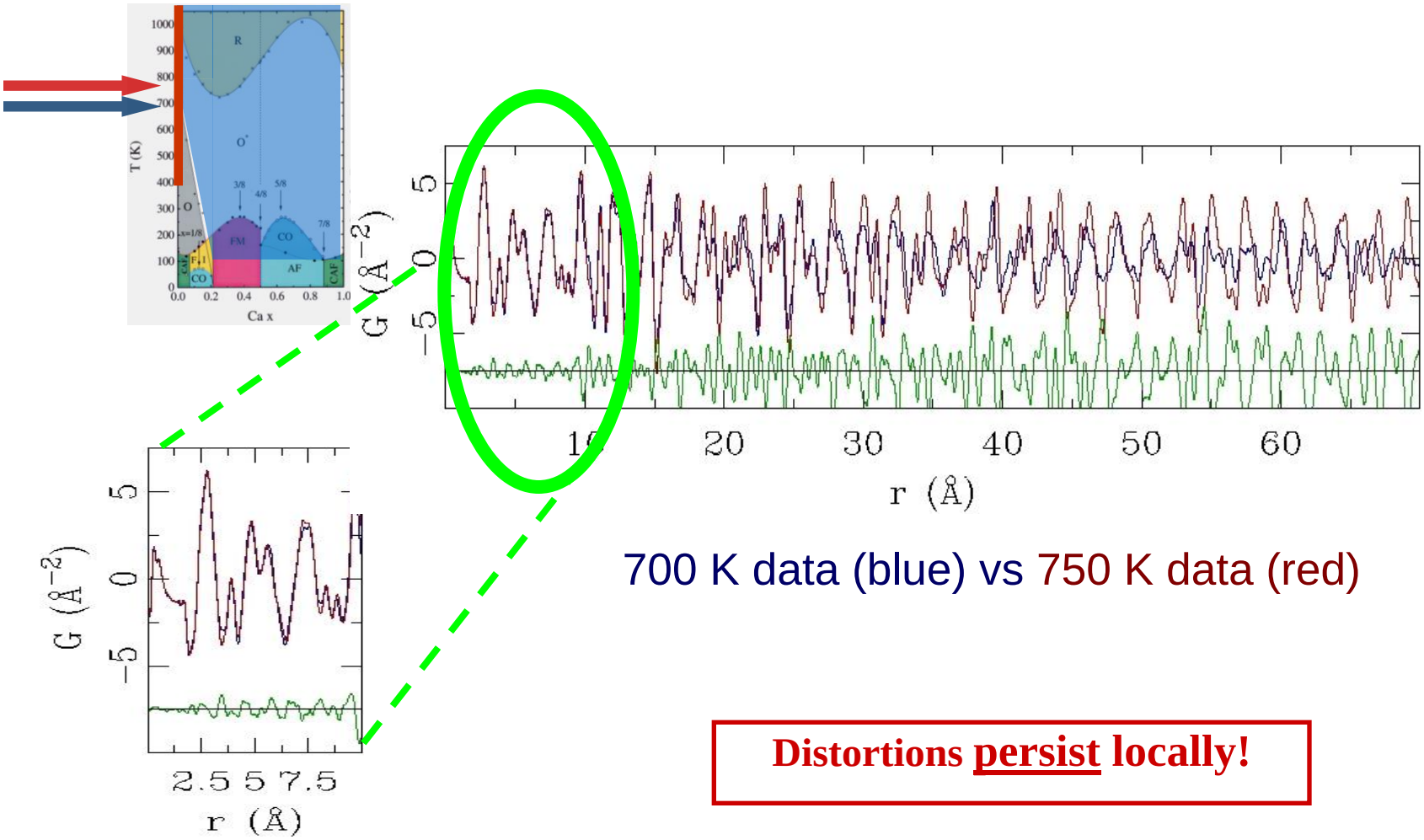
Study of the Jahn-Teller distortion in $LaMnO_3$

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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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.

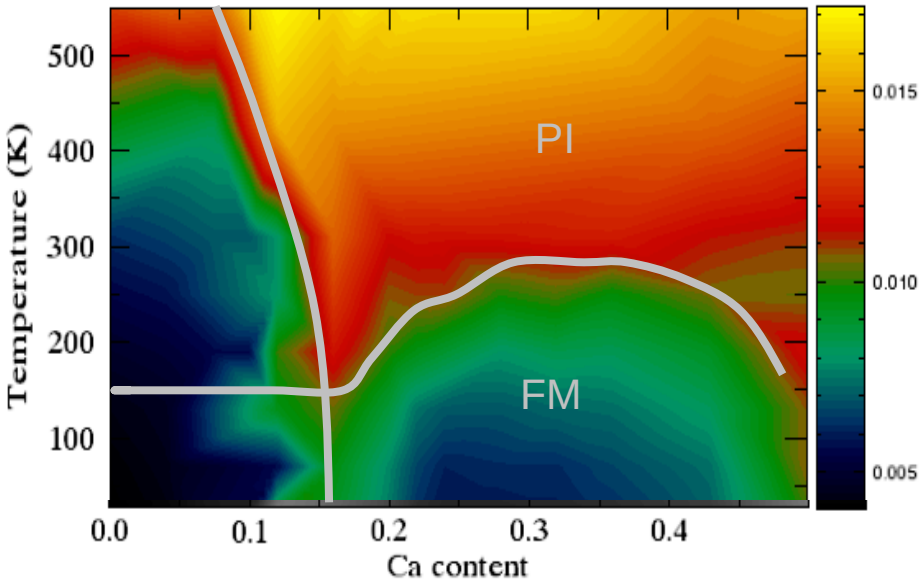
Tutorials

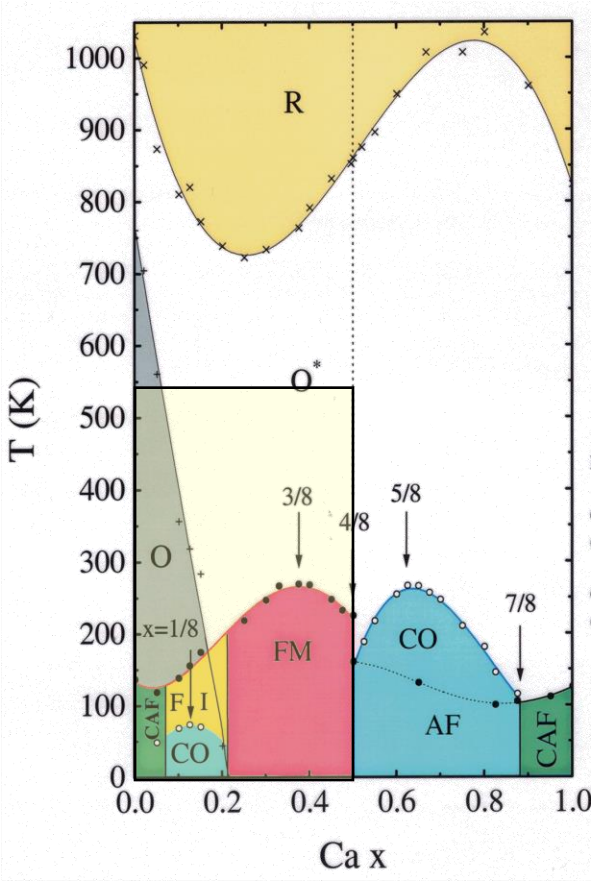
Make your own nanoparticles. Cartoons shown on this website were created by **Julie Coxe**, a talented artist and former summer student of the total scattering group.

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

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

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



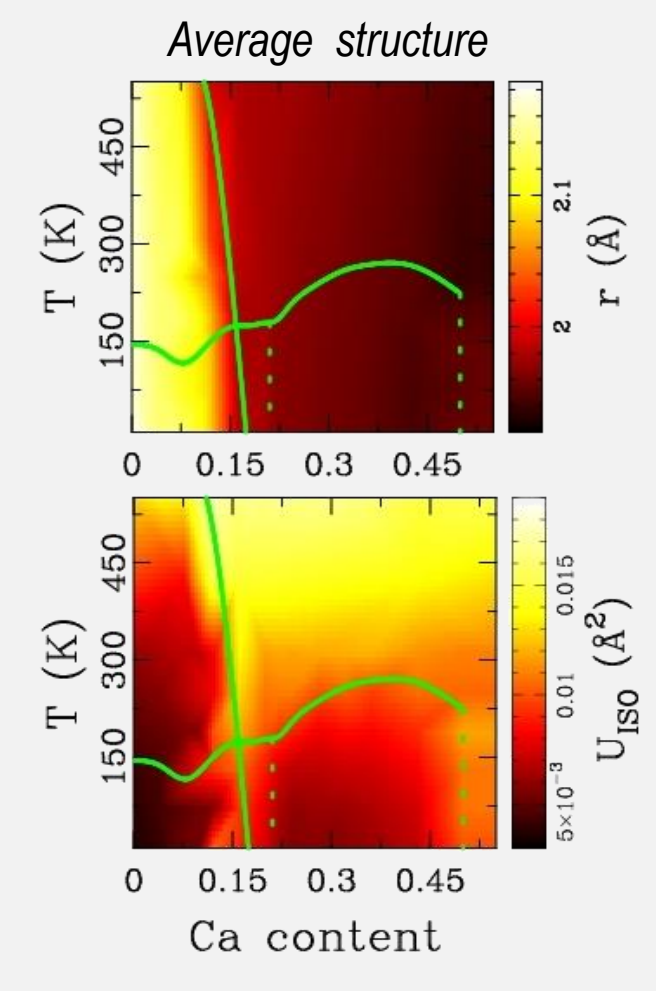


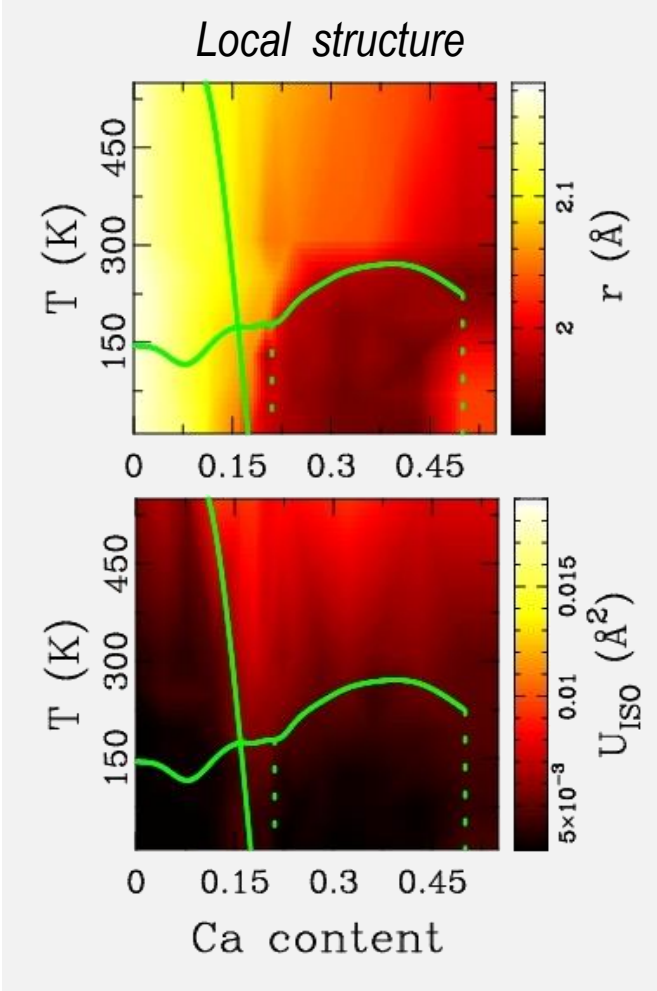
- Phase diagram draws itself from the parameters.
- Unexpected detail emerges and demands interpretation.

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

Mn-O long bond

ADP Oxygen





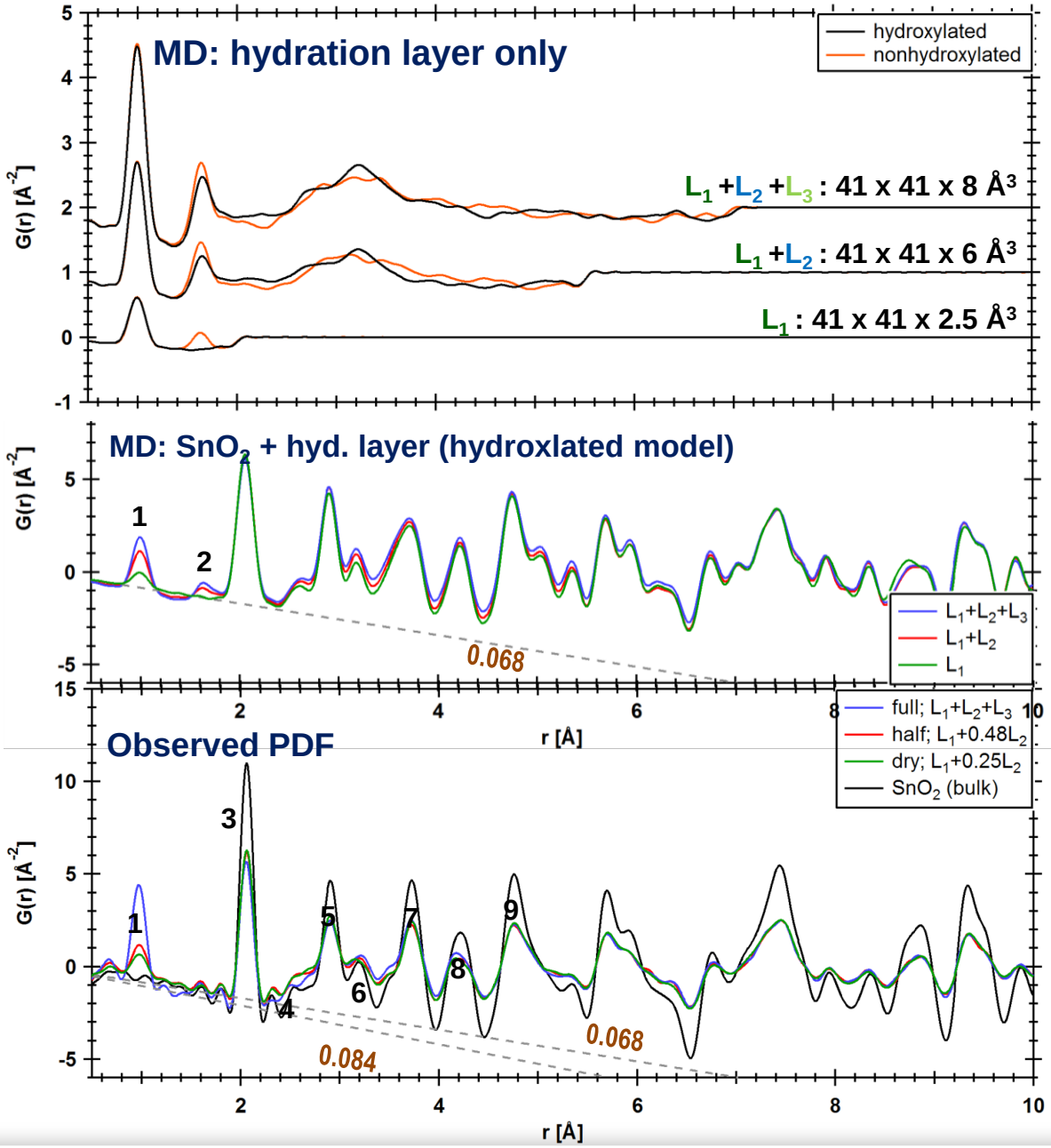
Example

Investigation of the structure and stability of SnO_2 nanocrystal and its surface-bound water

H.-W. Wang[1], D. J. Wesolowski[1], T. E. Proffen[2], A. I. Kolesnikov[2], L. Vlcek[1], W. Wang[3], M. Feygenson[2], J. O. Sofo[4], L. F. Allard Jr.[5], and L. M. Anovitz[1]

BES/Geosciences Program-Geochemical Equilibria and Reaction Dynamics: Atomic- to Pore-Scale Processes (ERKCC72)

MD and PDF

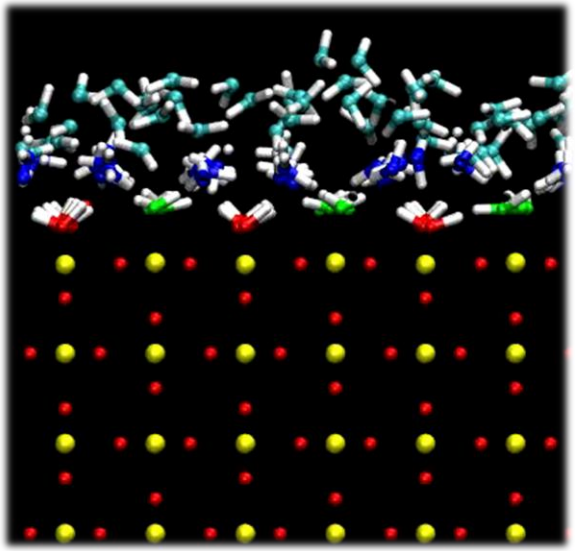


PDF for nonhydroxylated and hydroxylated models:

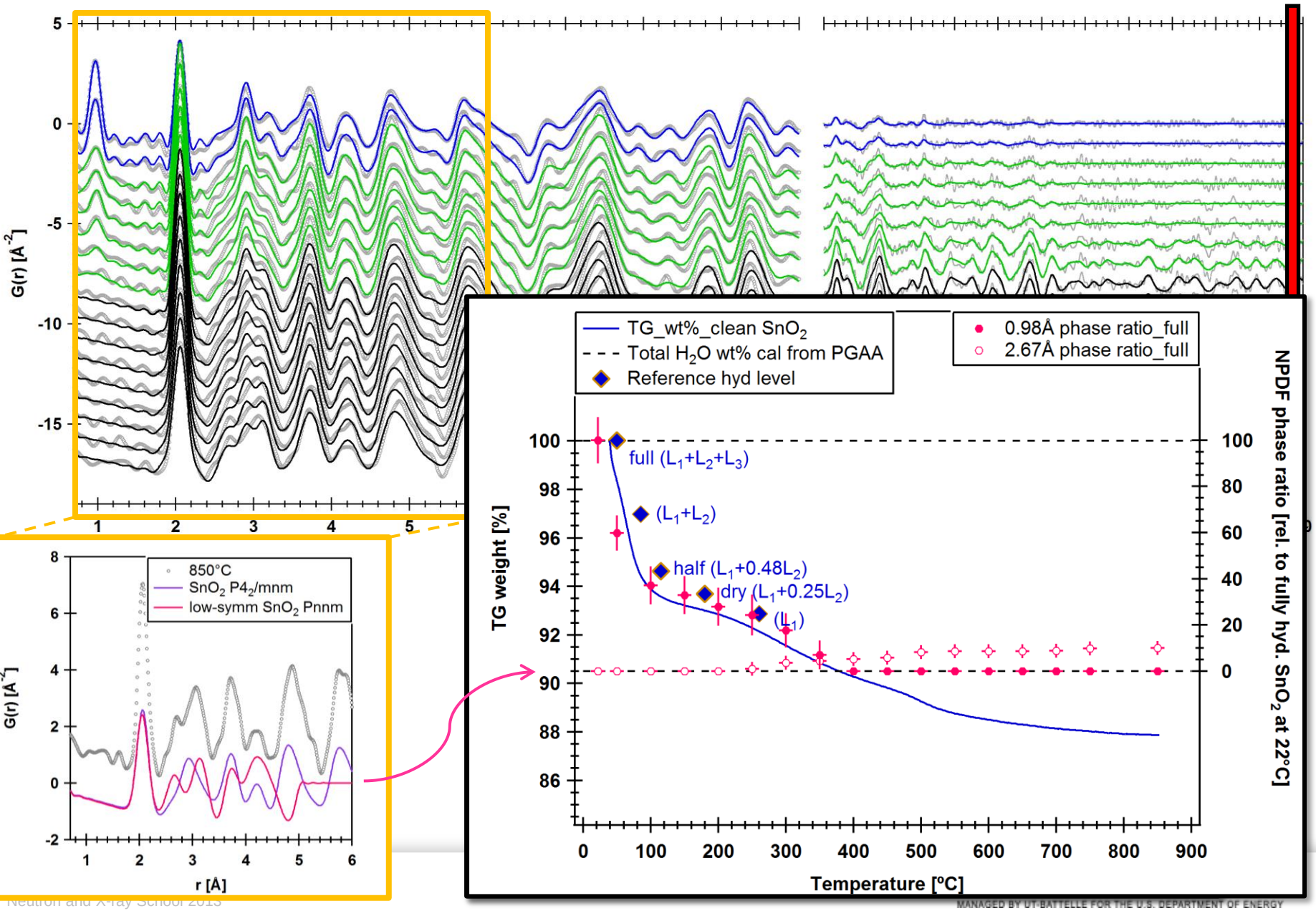
Box size: 41 x 41 x 23 Å^3 ; 2592 atoms; # density = 0.068 Å^{-3}; U_{iso} = 0.003 Å^2;

1st coord. shell - 1:O-D; 2:D-D; 3:Sn-O; 4/5/6:O-O and Sn-Sn (*c* axis);

2nd coord. shell - 7/8:Sn-Sn, Sn-O, and O-O; 9: Sn-Sn (*a* and *b* axes)



PDF *in-situ* dehydration (cont.)



Example:
"Complete" structure of Gold Nanoparticles

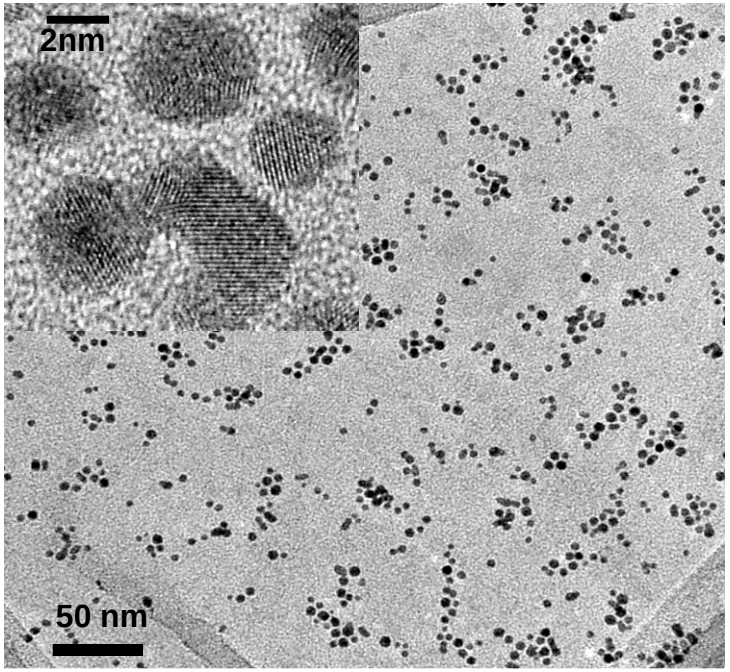
Katharine Page
Ram Seshadri
Tony Cheetham

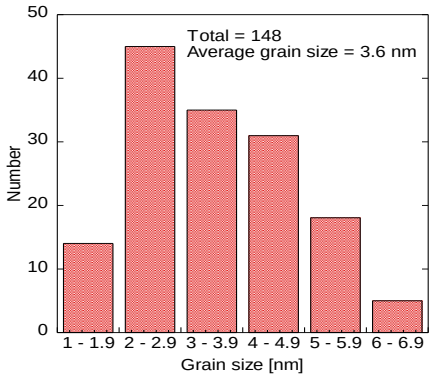
Thomas Proffen

Gold nanoparticles

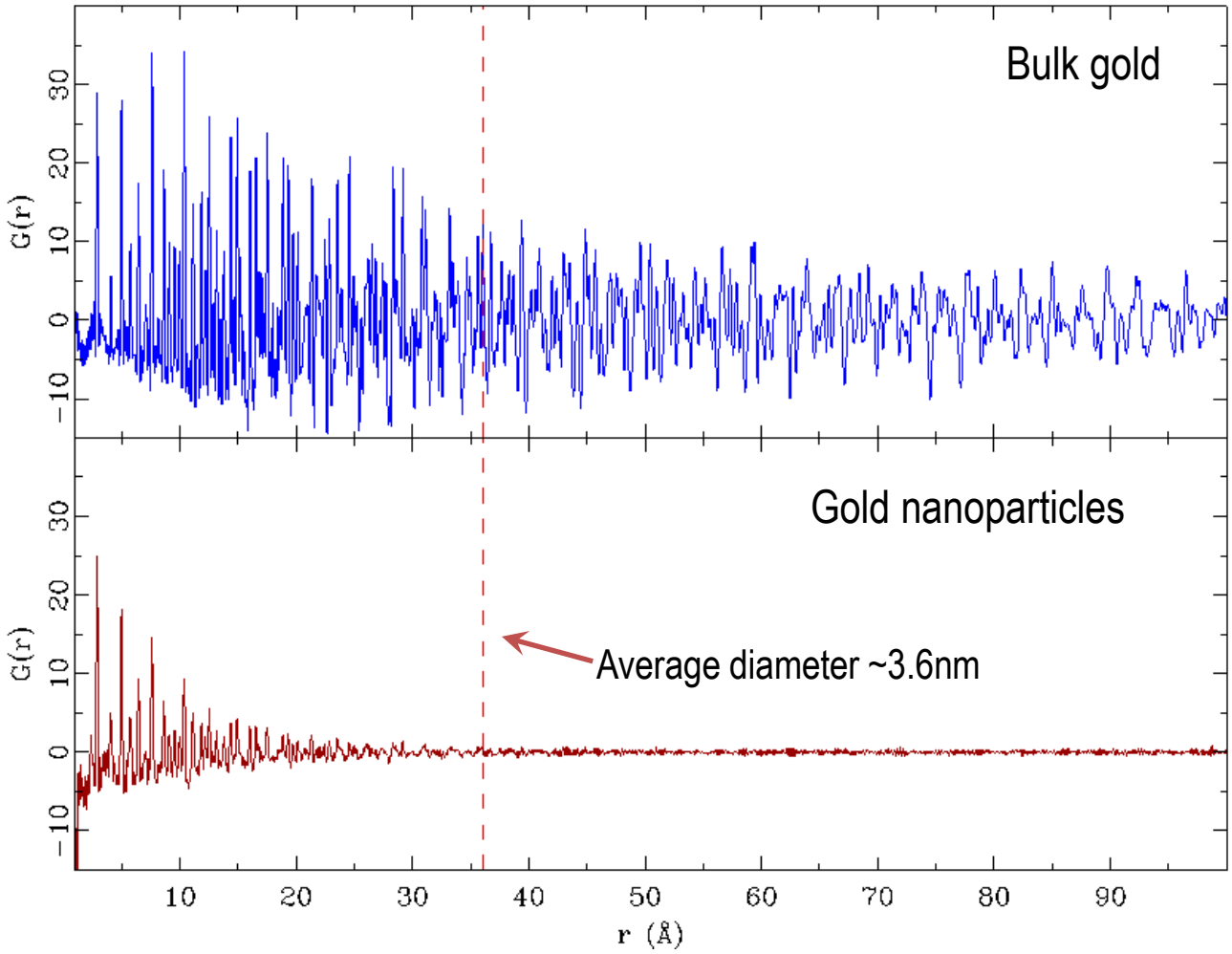
- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.

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



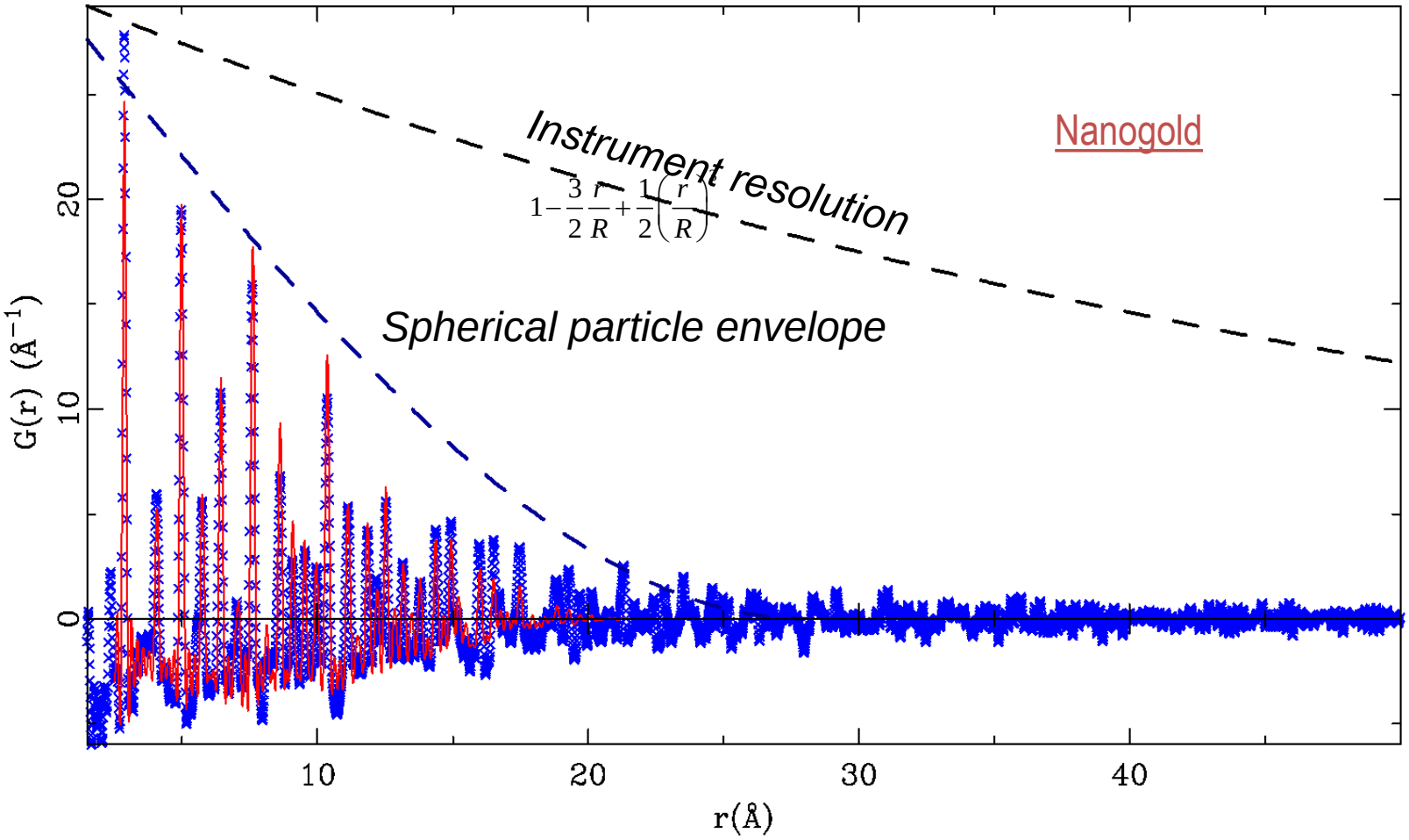


Gold nanoparticles: First NPDF data

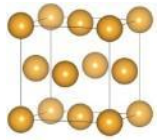


K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

Nanoparticles: Particle size



Modeling Au structure only

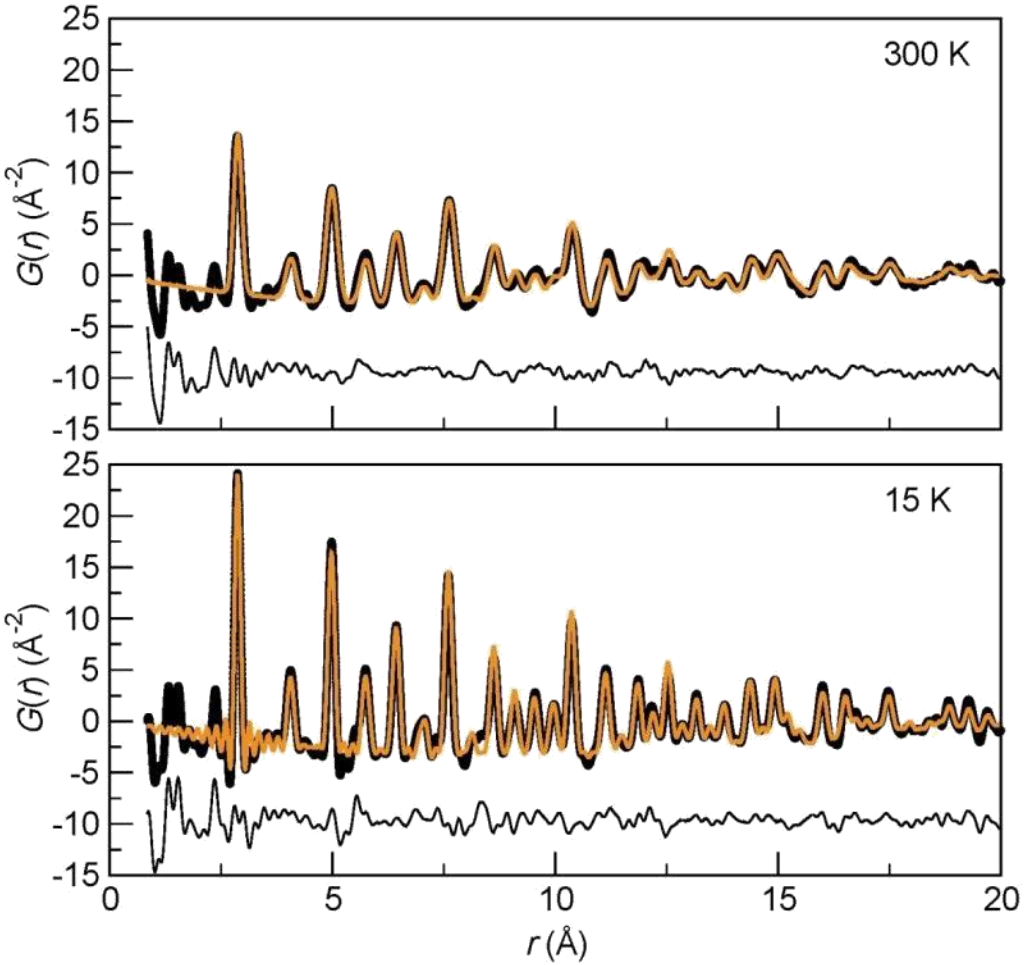


300 K: R_w = 33.8 %

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

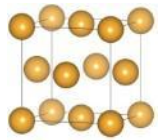
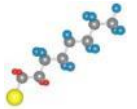
15 K: R_w = 27.8 %

- 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


+


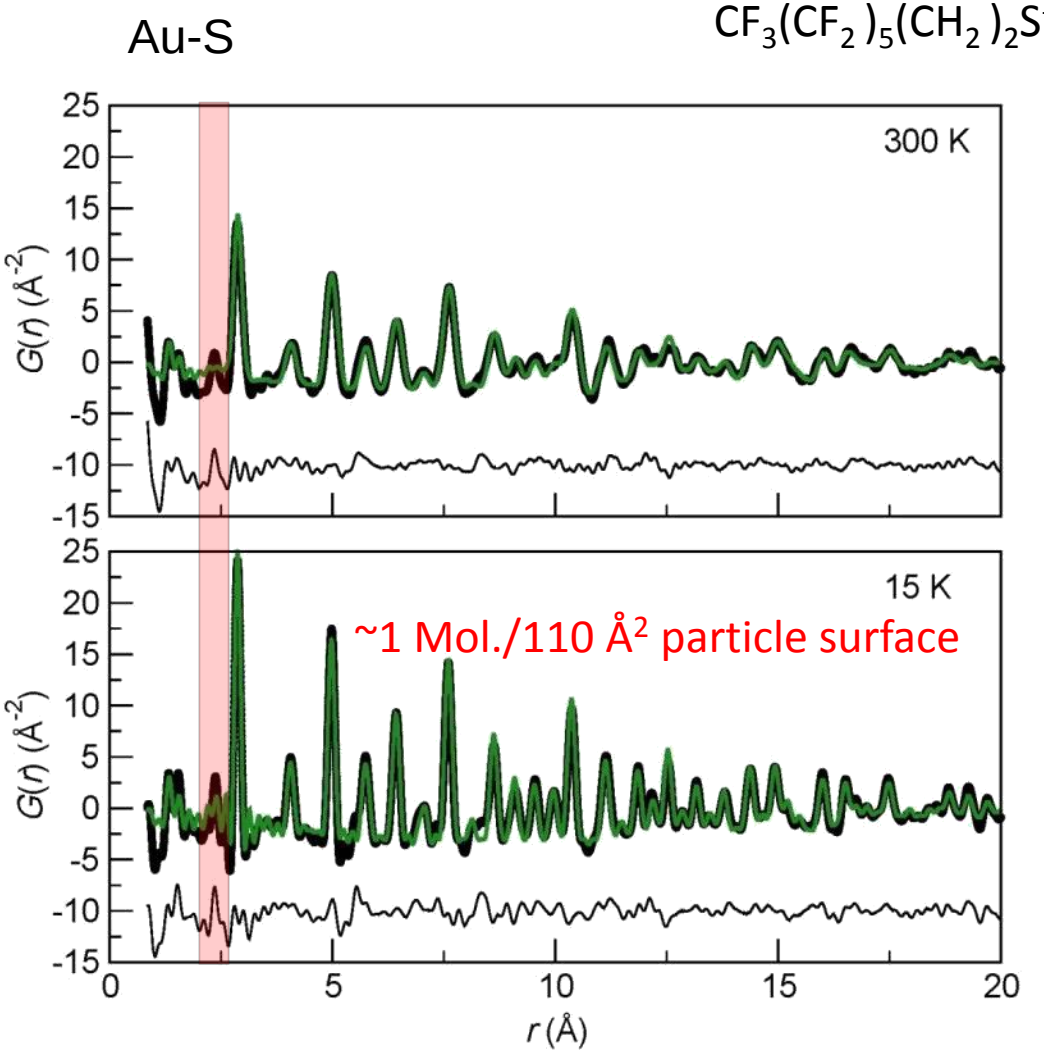
$CF_3(CF_2)_5(CH_2)_2S^-$

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 %

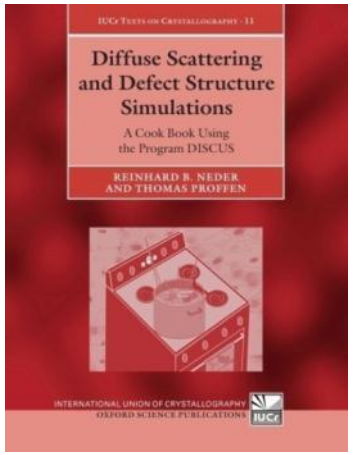
- scale (Au) = 0.2054(4)
- scale (molecule) = 0.0604(6)
- a (Au) = 4.06500(5)
- a(molecule) = 49.23(2)
- u_{iso}(Au/molec) = 0.00433(2)
- δ1 (Au) = 2.256(6)
- srat (molecule)= 0.03(14)



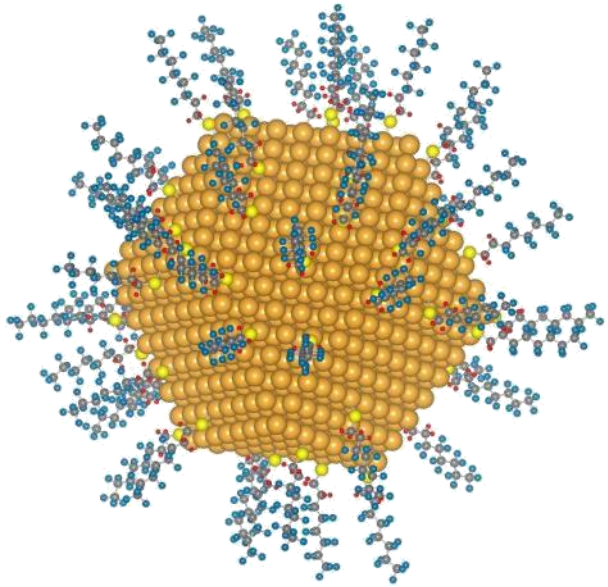
Modeling of nanoparticle data - future !

Using DISCUS/DIFFEV

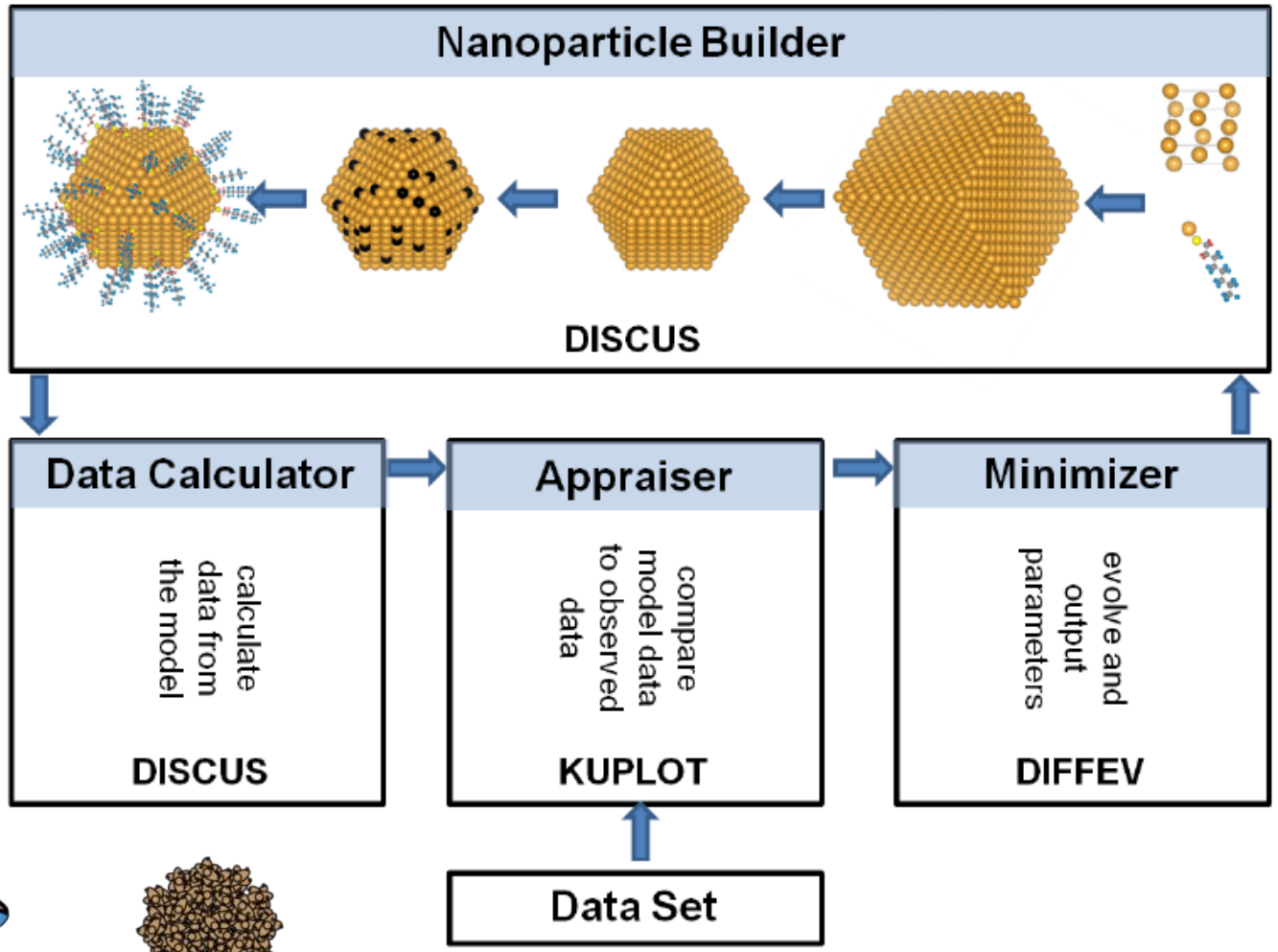
Oxford University Press, October 2009



- 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).

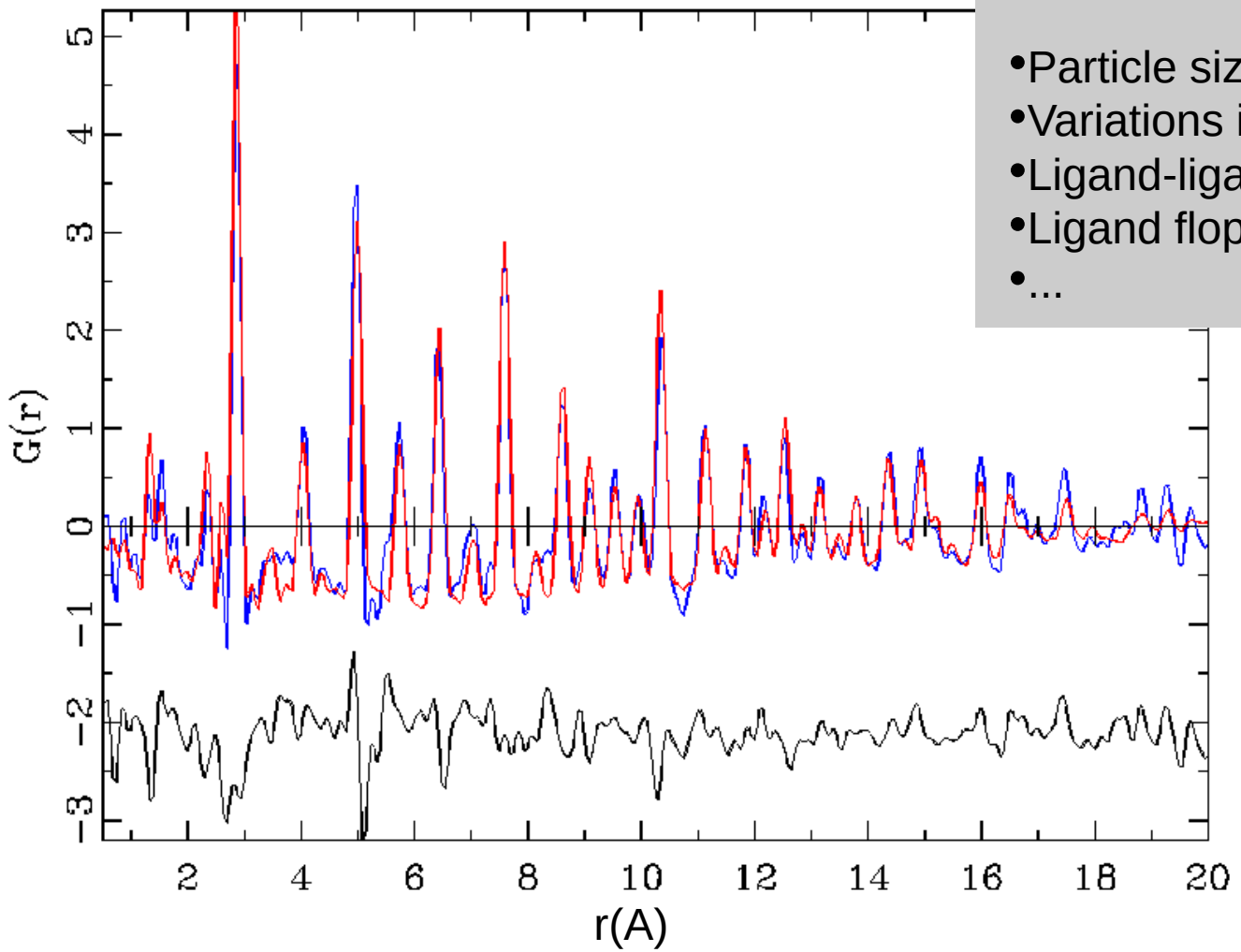


Nanoparticle builder



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):

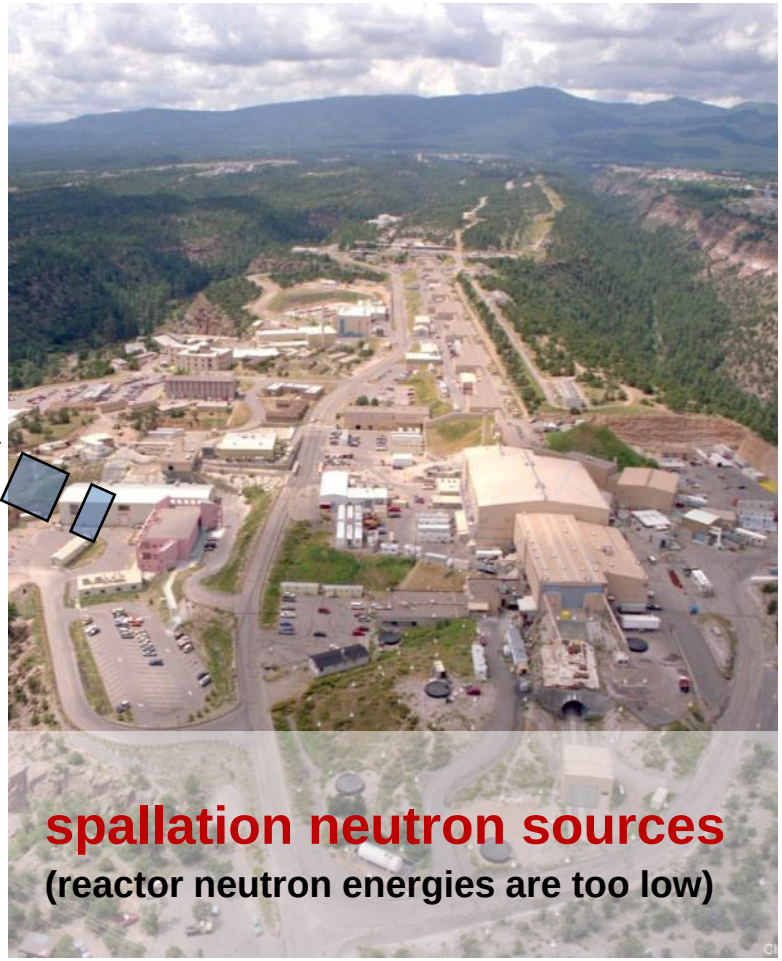
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

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**
(high energy X-rays)



spallation neutron sources
(reactor neutron energies are too low)

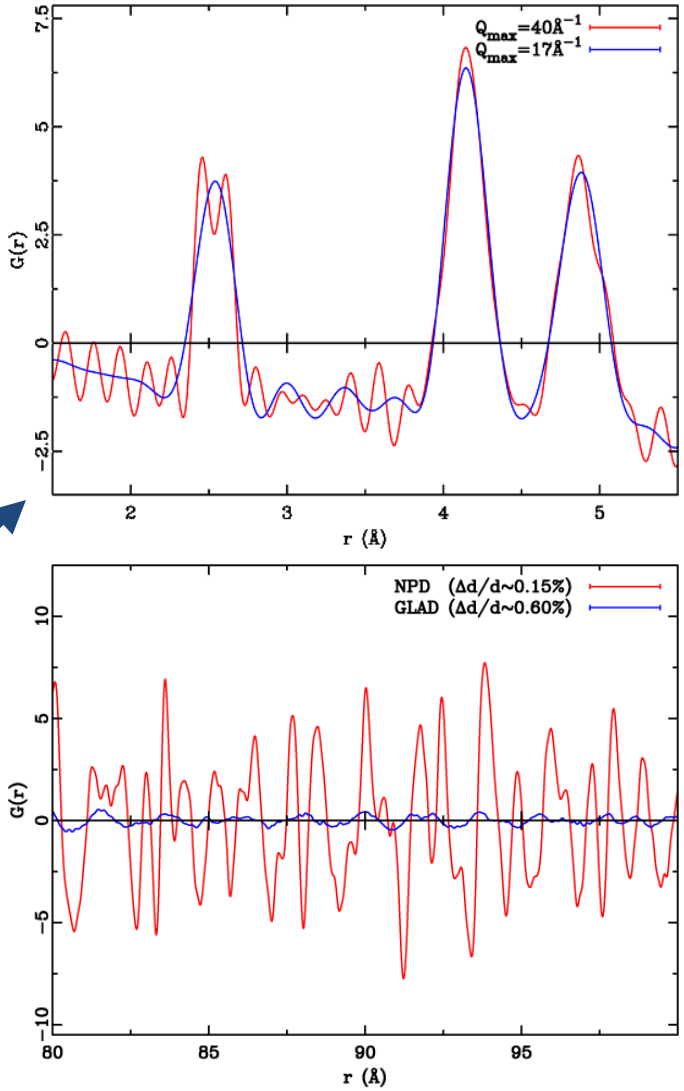
NPDF: the key to high quality, high r PDFs

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

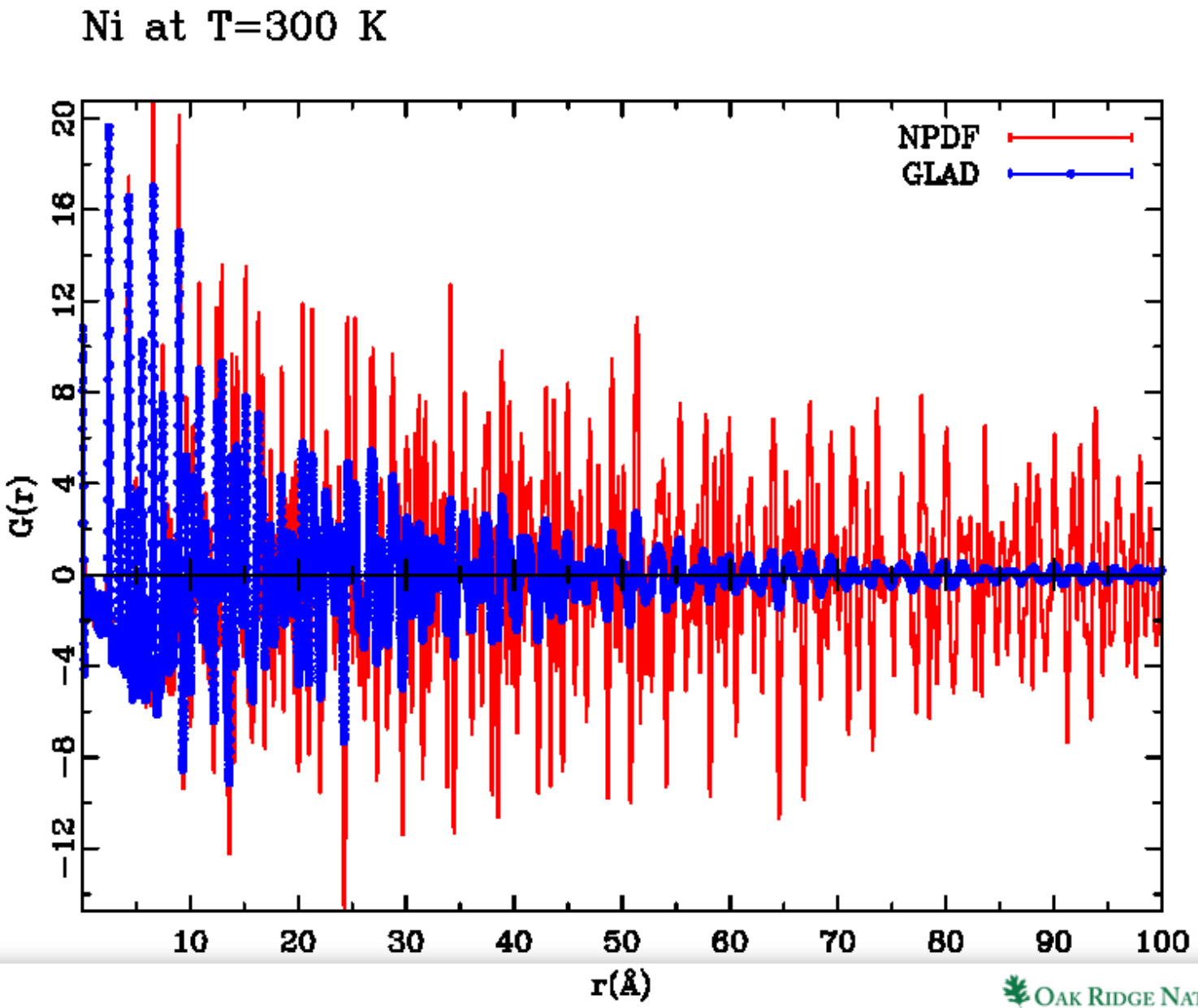
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

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

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

contact

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Mikhail Feygenson
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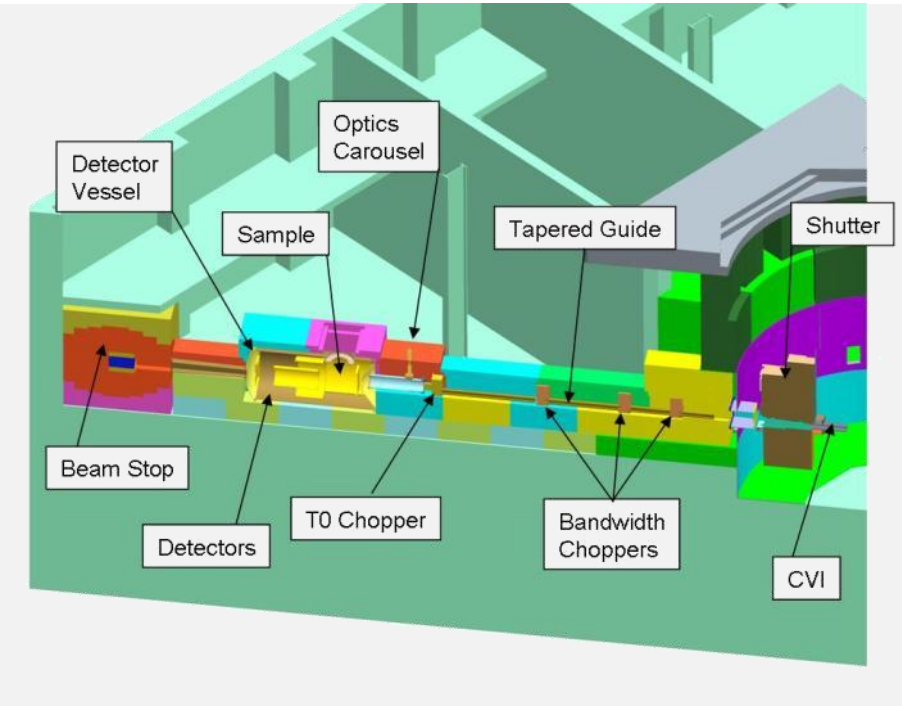
SPECIFICATIONS

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}



X-ray PDF: The fast way

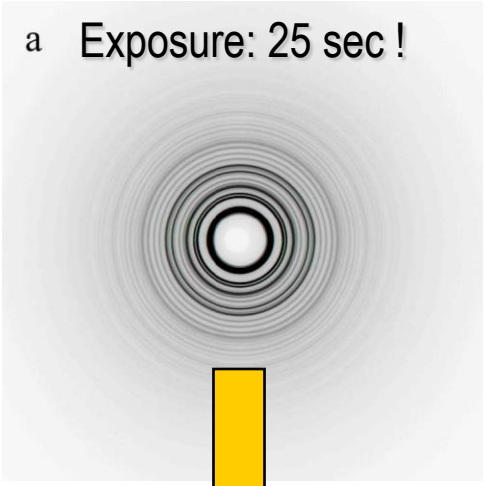
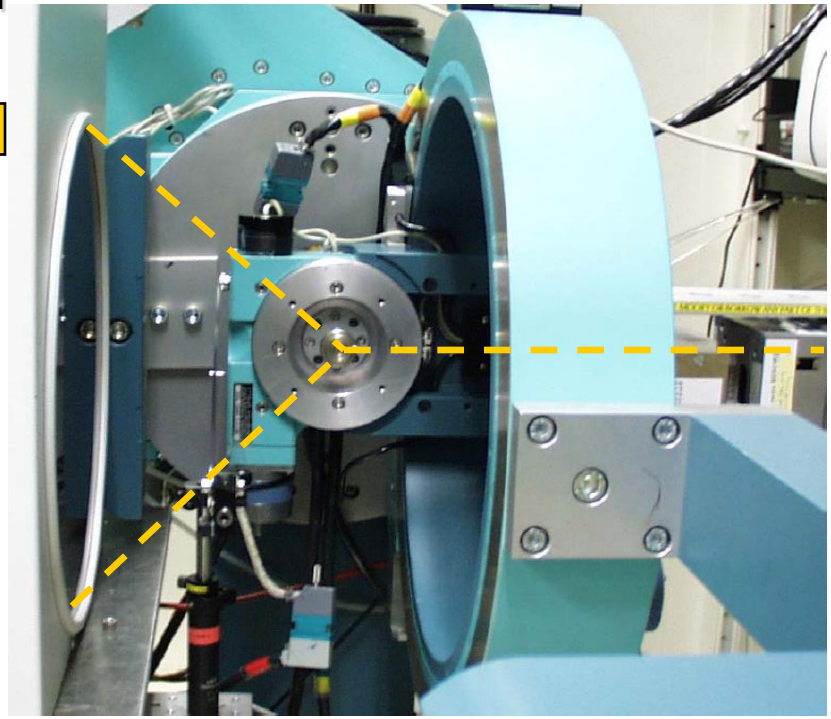
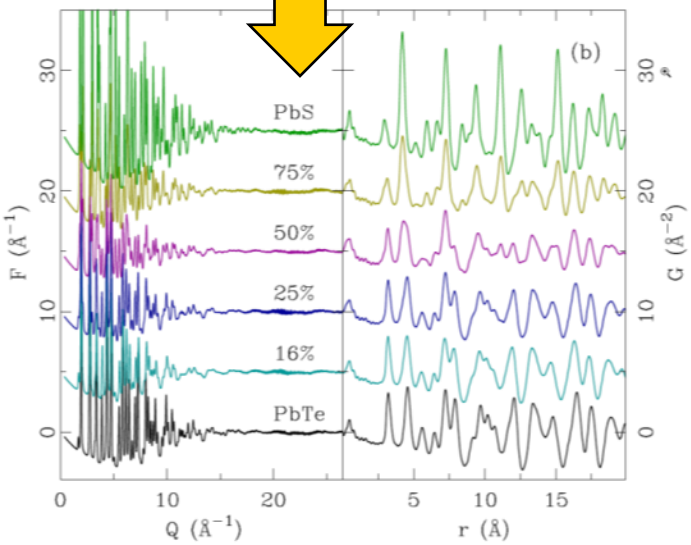


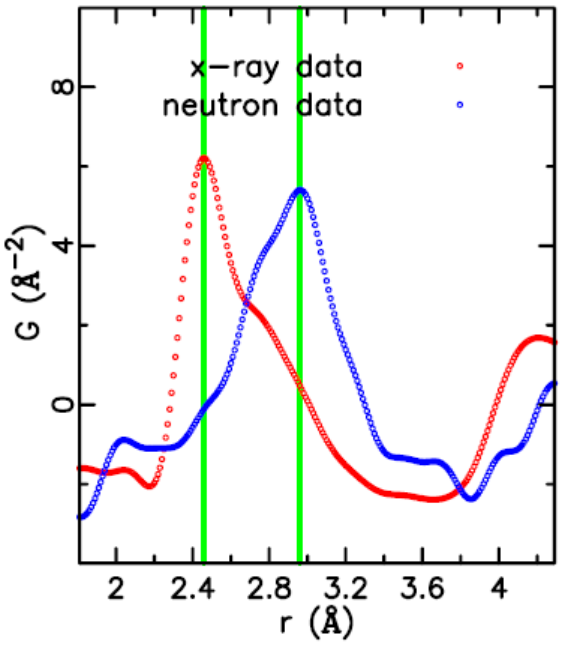
Image plate detector





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).

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



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

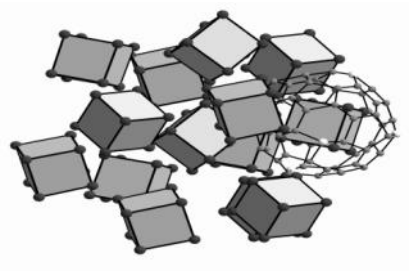
where b_i is the scattering length of the i^{th} atom.

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

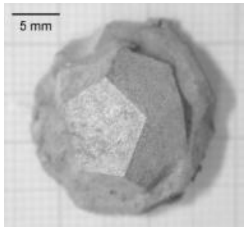
$b_m b_n$	Mg-Mg	Mg-Co	Co-Co
x-ray	144	324	729
neutron	13.18	2.83	0.607

NOMAD users have access to x-ray PDF measurements through ORNL-APS partner proposal.

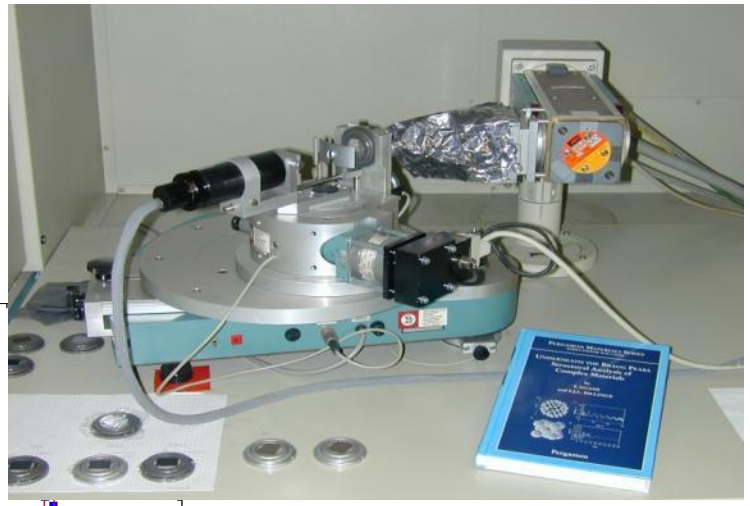
X-ray PDF: In house measurements

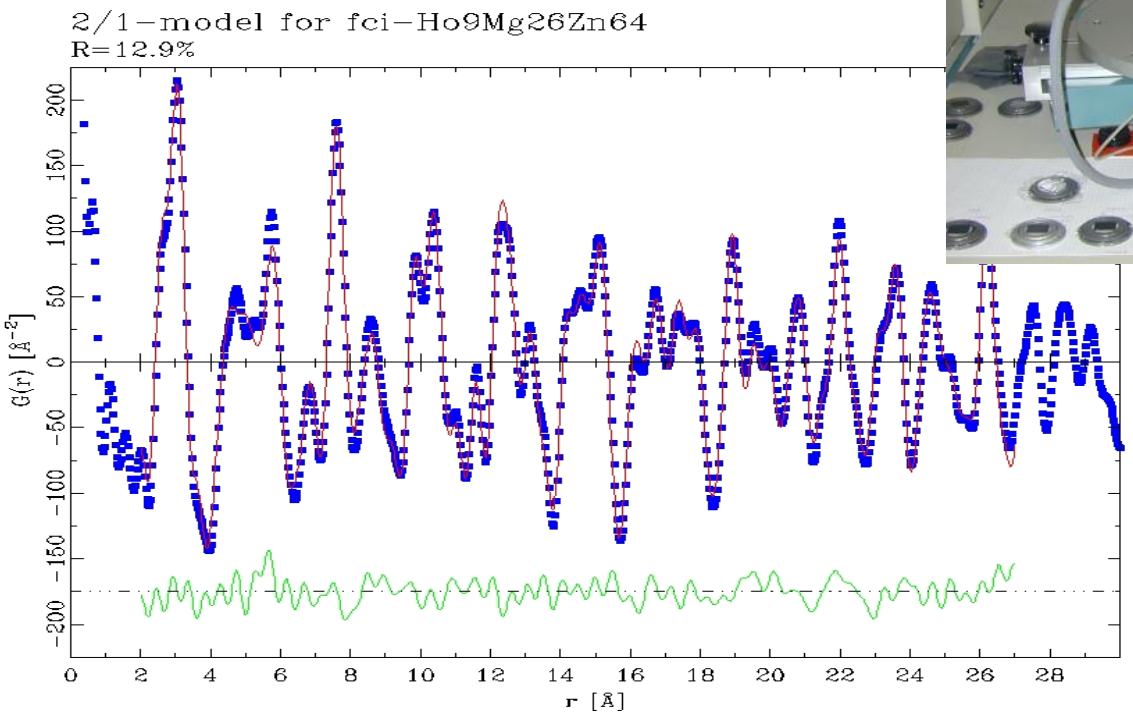


***fci*-Ho-Mg-Zn**



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





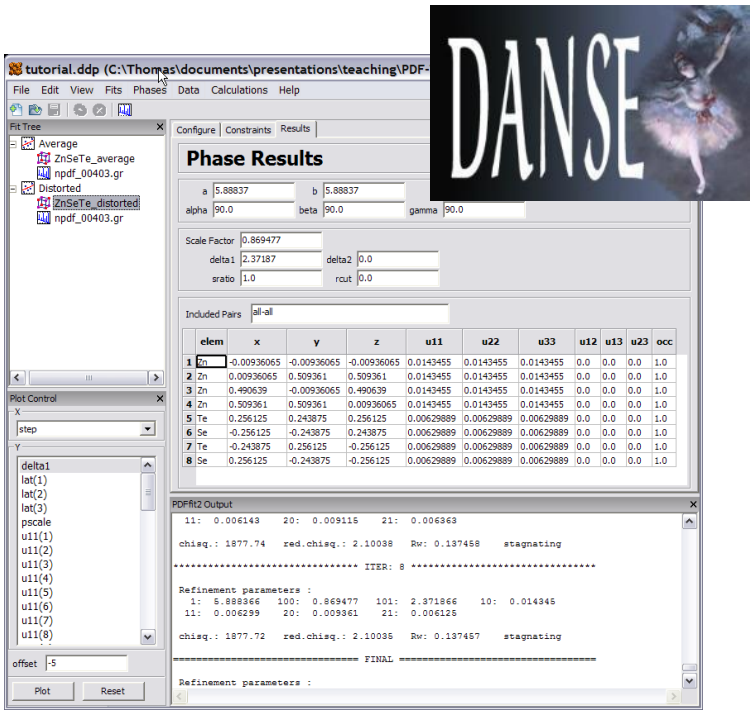
Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

Software

Software: Data modeling

PDFgui

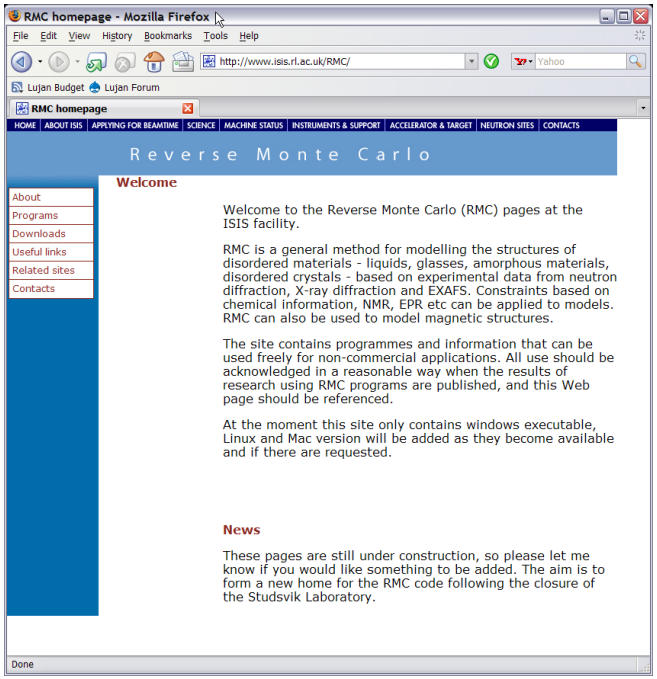
- Part of DANSE project.
- http://www.diffpy.org/



- 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.

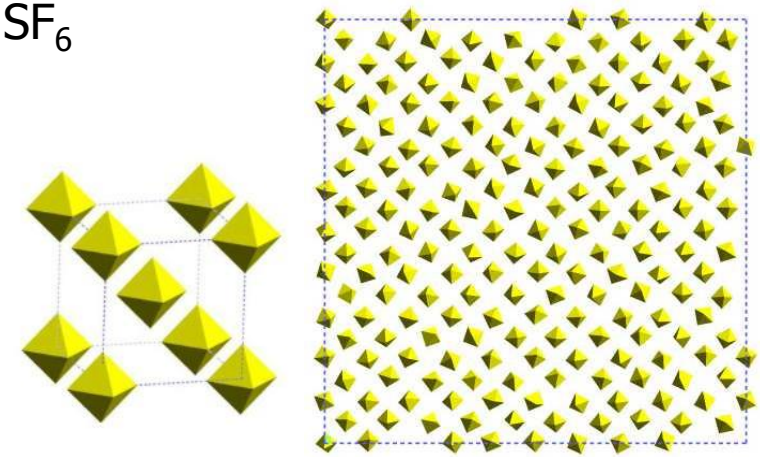
Software: RMCprofile

- 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

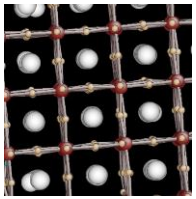


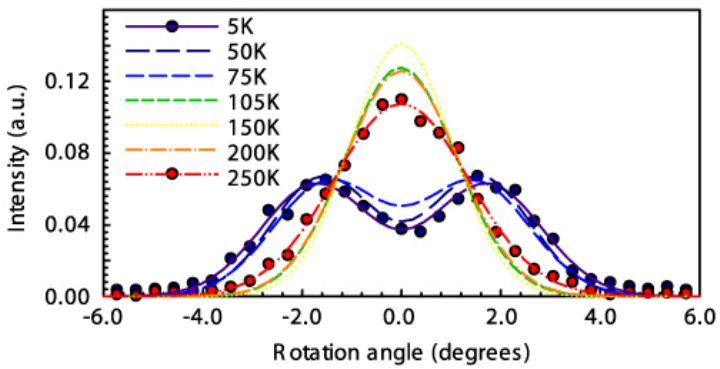
RMC: Examples

SF_6

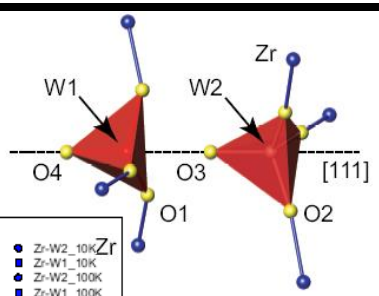


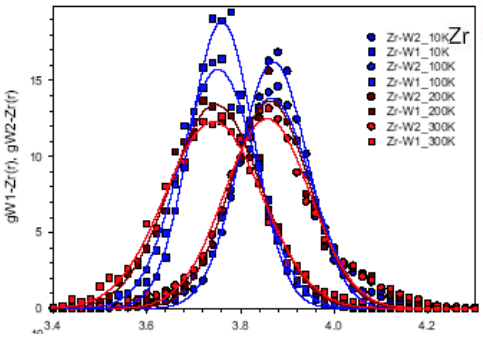
$SrTiO_3$



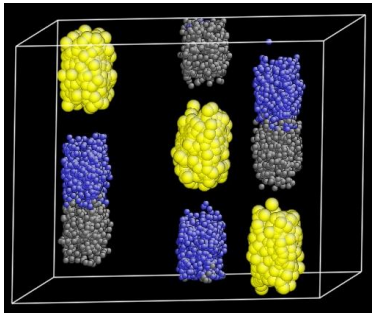


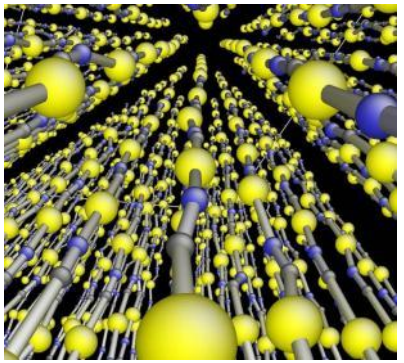
ZrW_2O_8





AuCN

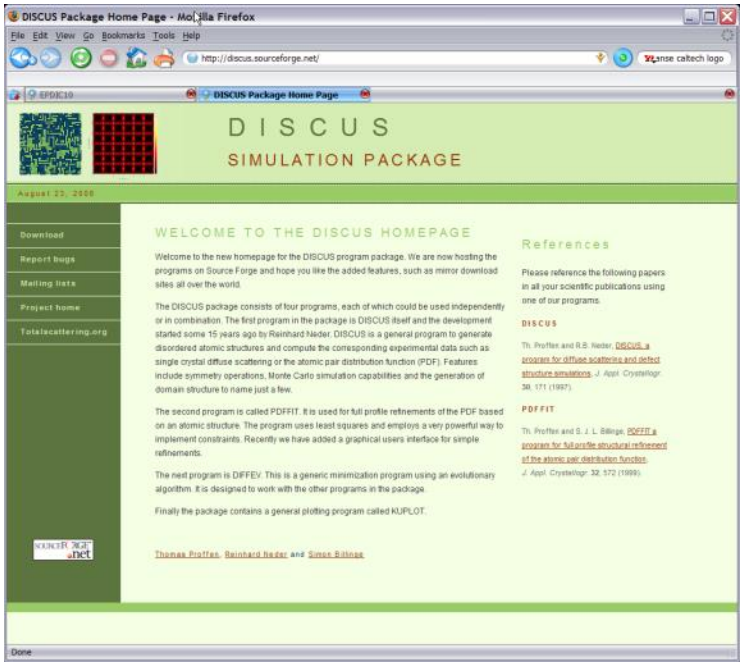


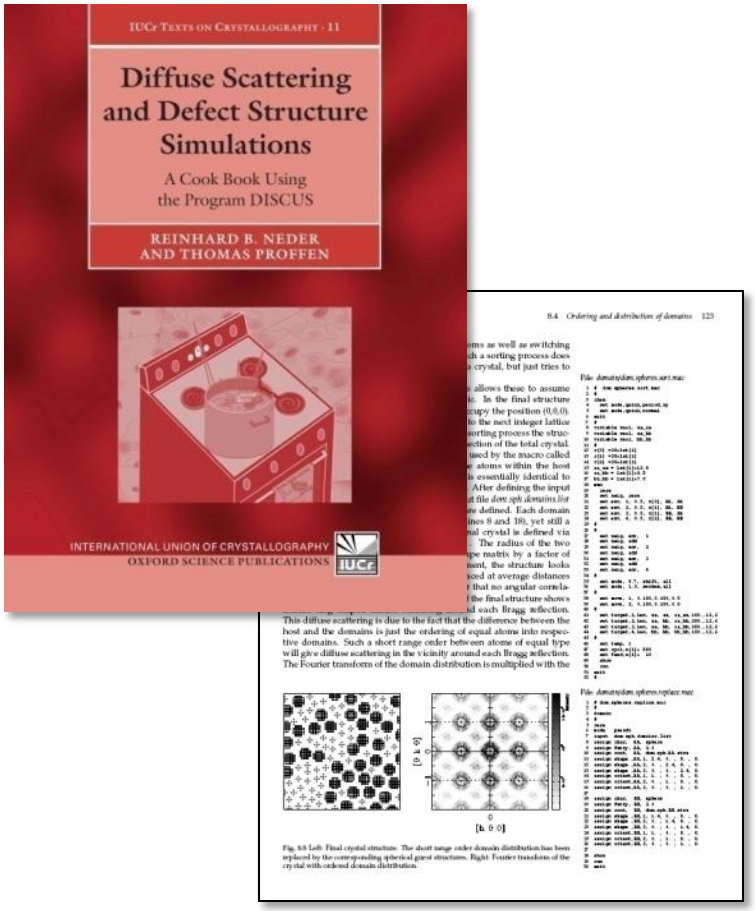


Software: Data modeling

DISCUS

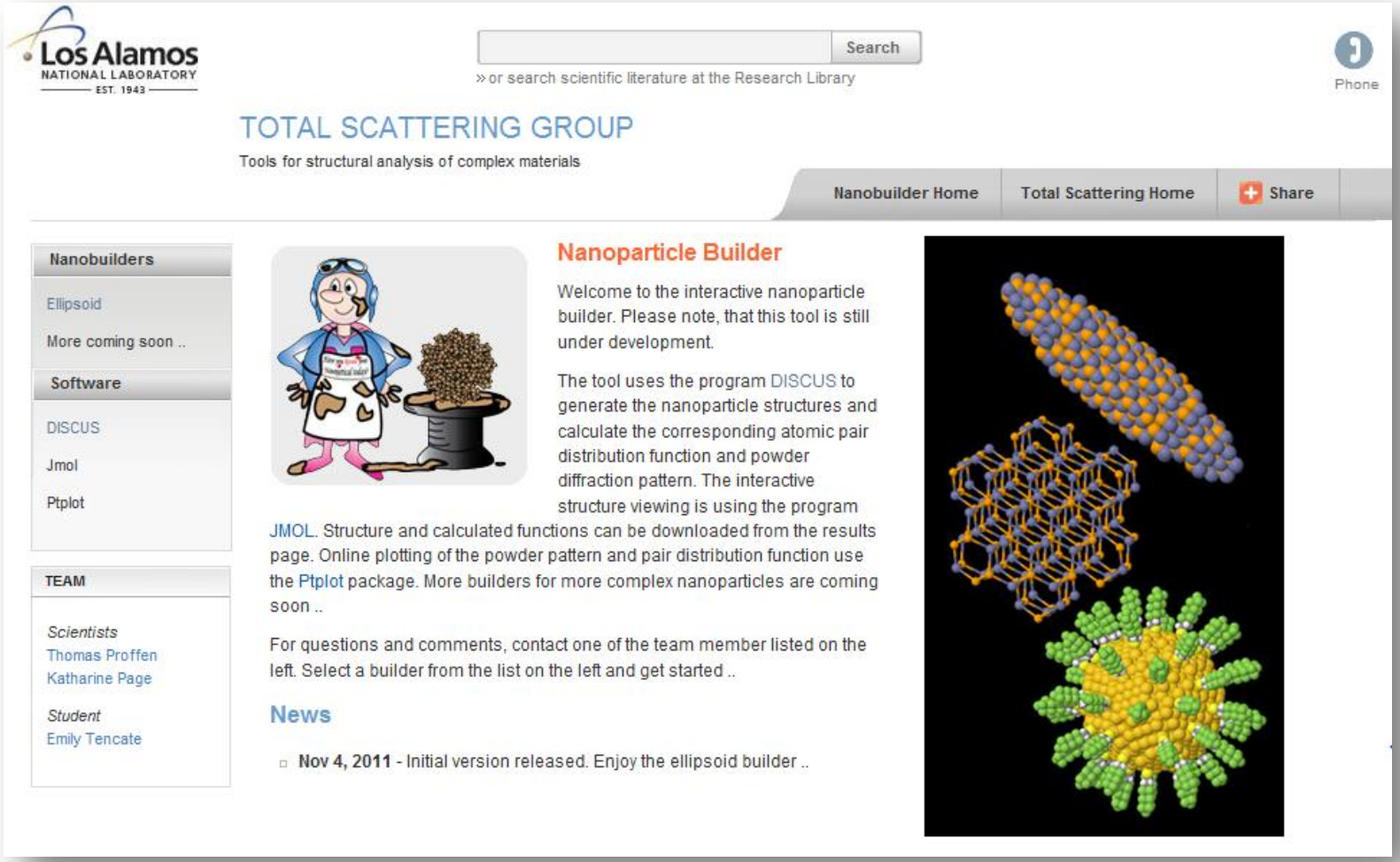
- Disordered materials simulations
- Refinement via DIFFEV / RMC
- http://discus.sourceforge.net/





Oxford University Press, October 2008

Nanoparticle builder



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

http://totalscattering.lanl.gov