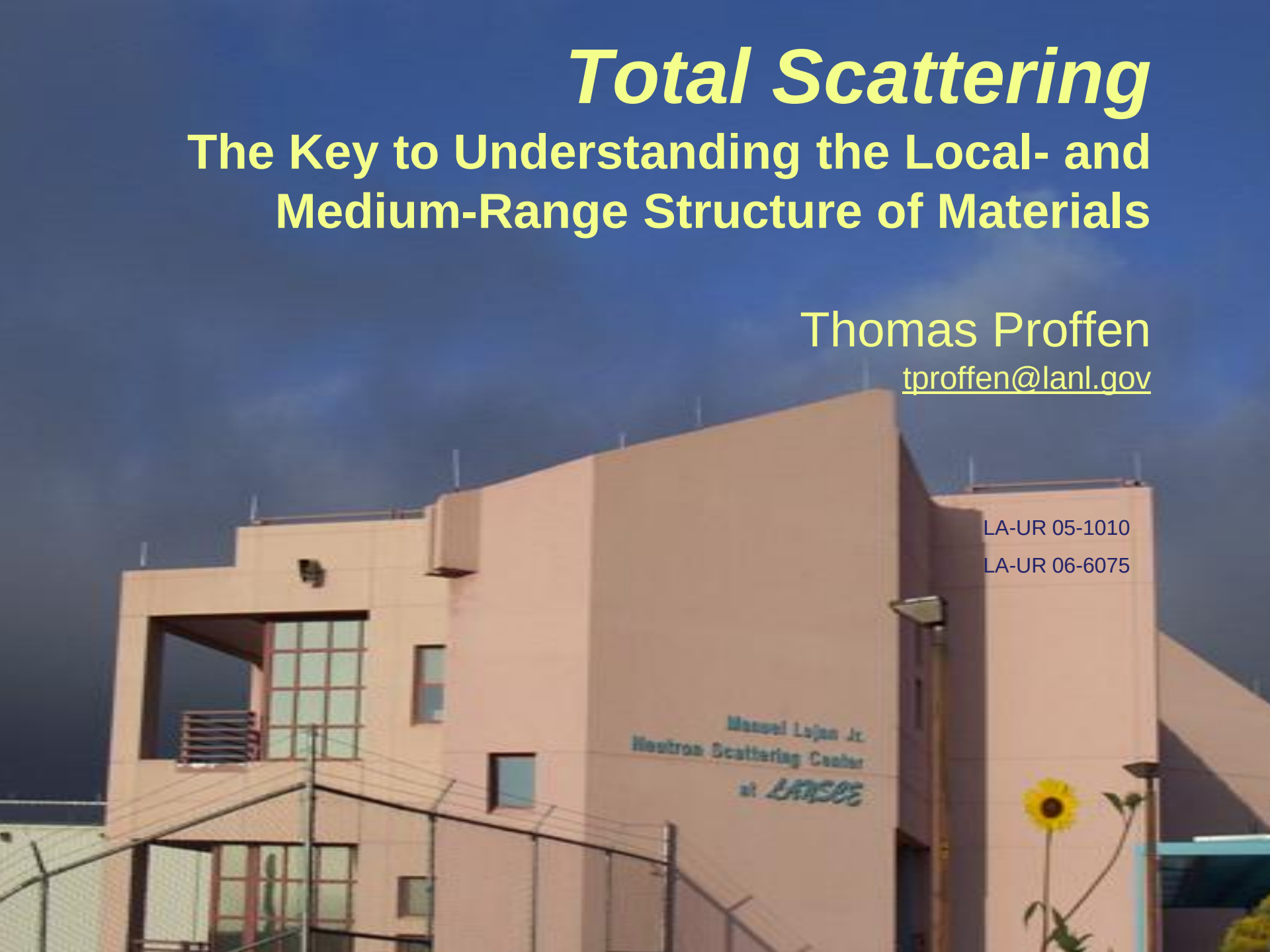
Total Scattering

The Key to Understanding the Local- and Medium-Range Structure of Materials

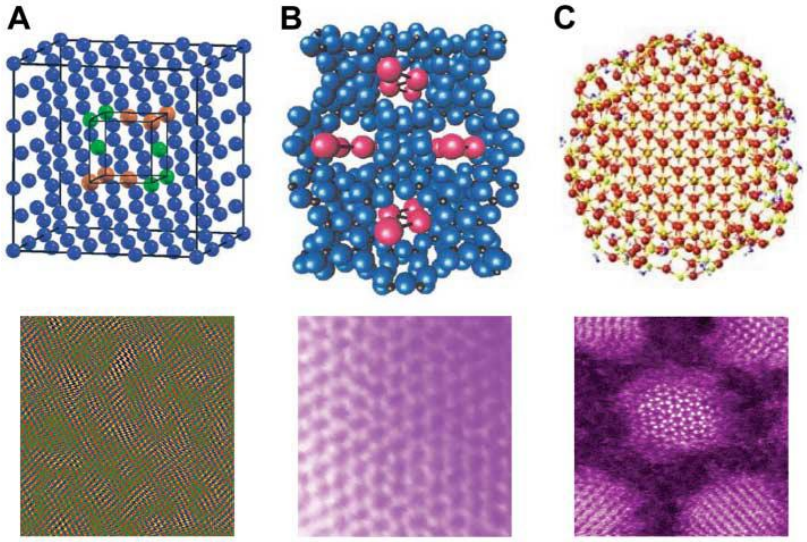
Thomas Proffen
tproffen@lanl.gov

LA-UR 05-1010
LA-UR 06-6075



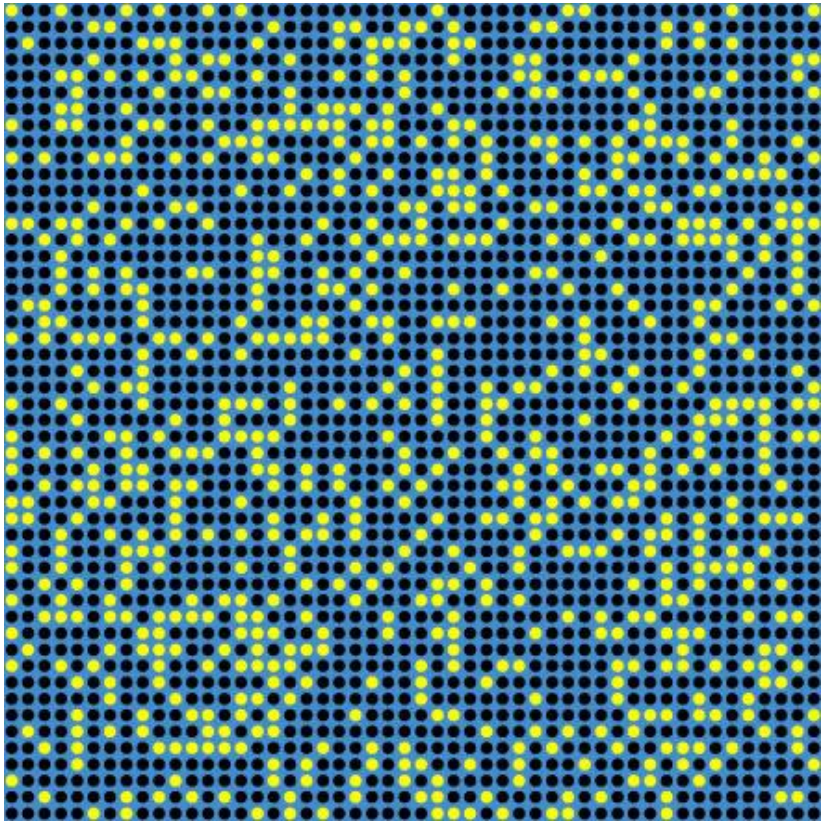
The challenge : Knowing the local structure

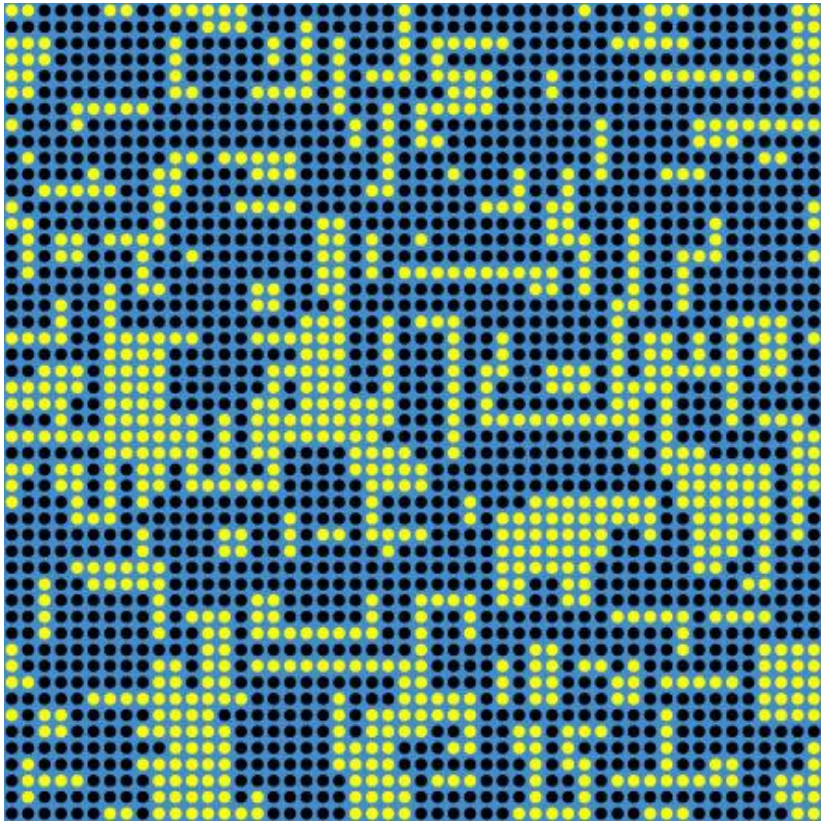
- Traditional crystallographic approach to structure determination is insufficient or fails for
  - **Non crystalline materials**
  - **Disordered materials**: The interesting properties are often governed by the defects or local structure !
  - **Nanostructures**: Well defined local structure, but long-range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

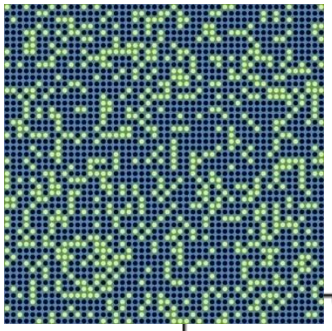




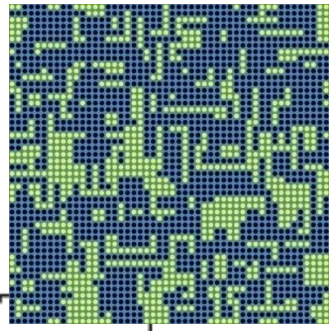
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

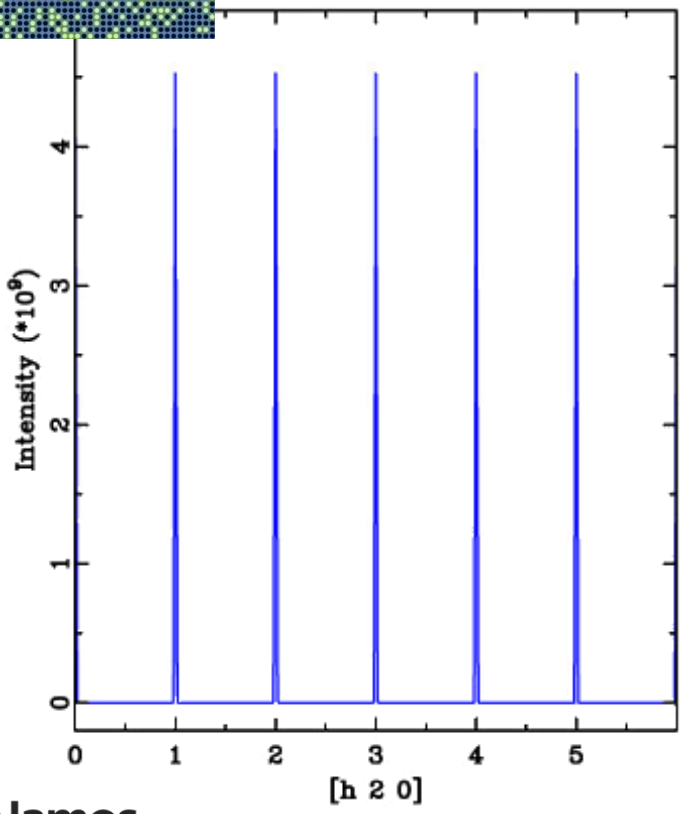
Properties might depend on vacancy ordering !!

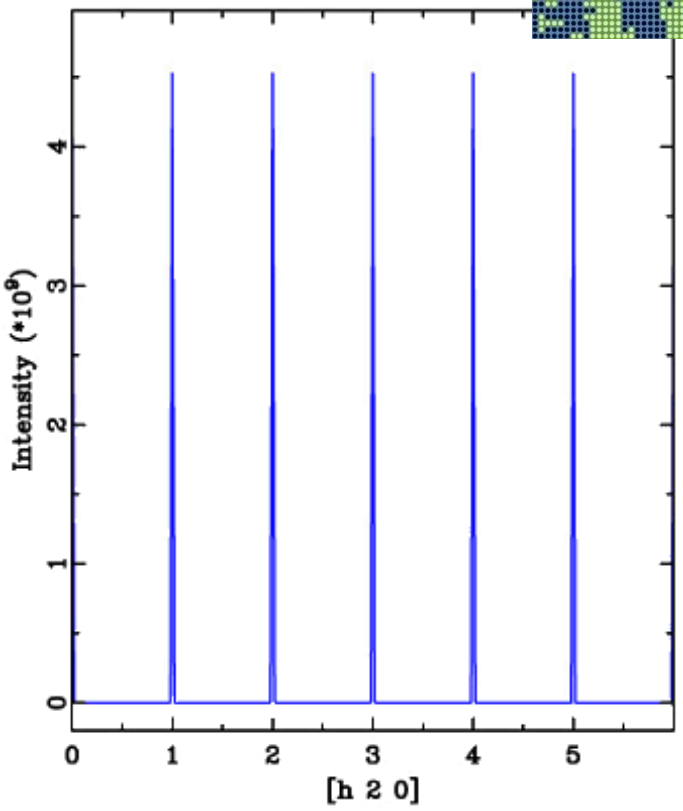
Bragg peaks are blind ..



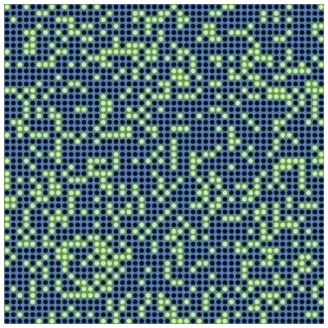
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.



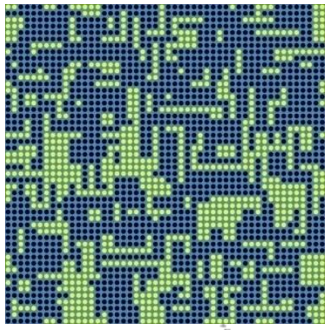


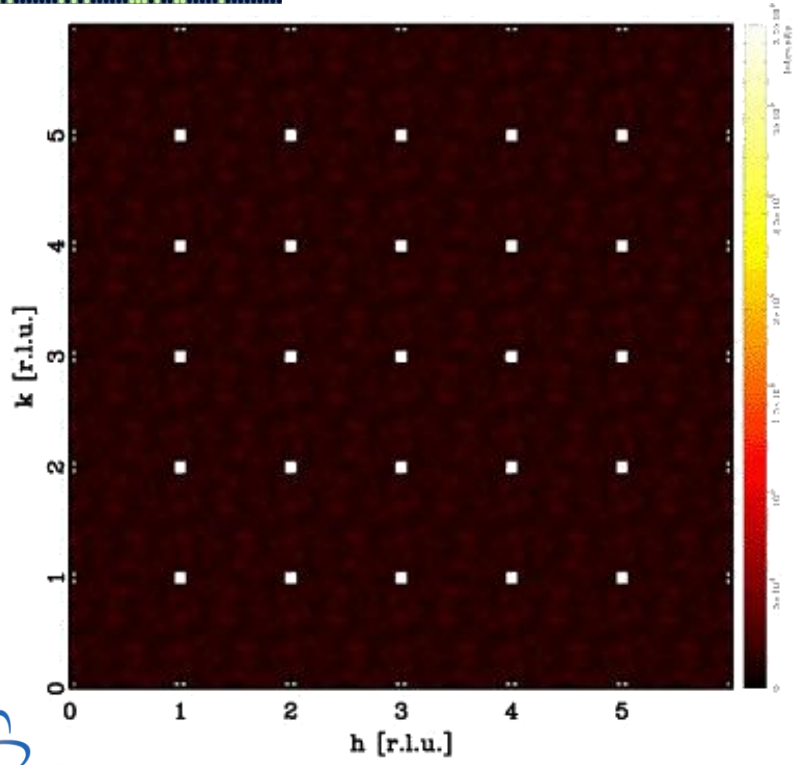


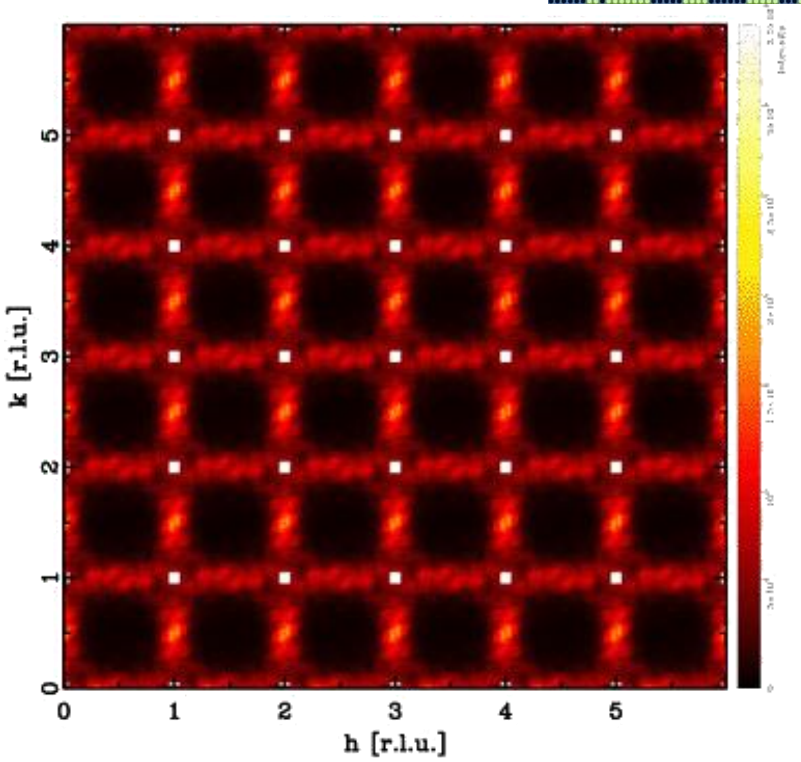
Diffuse scattering to the rescue ..



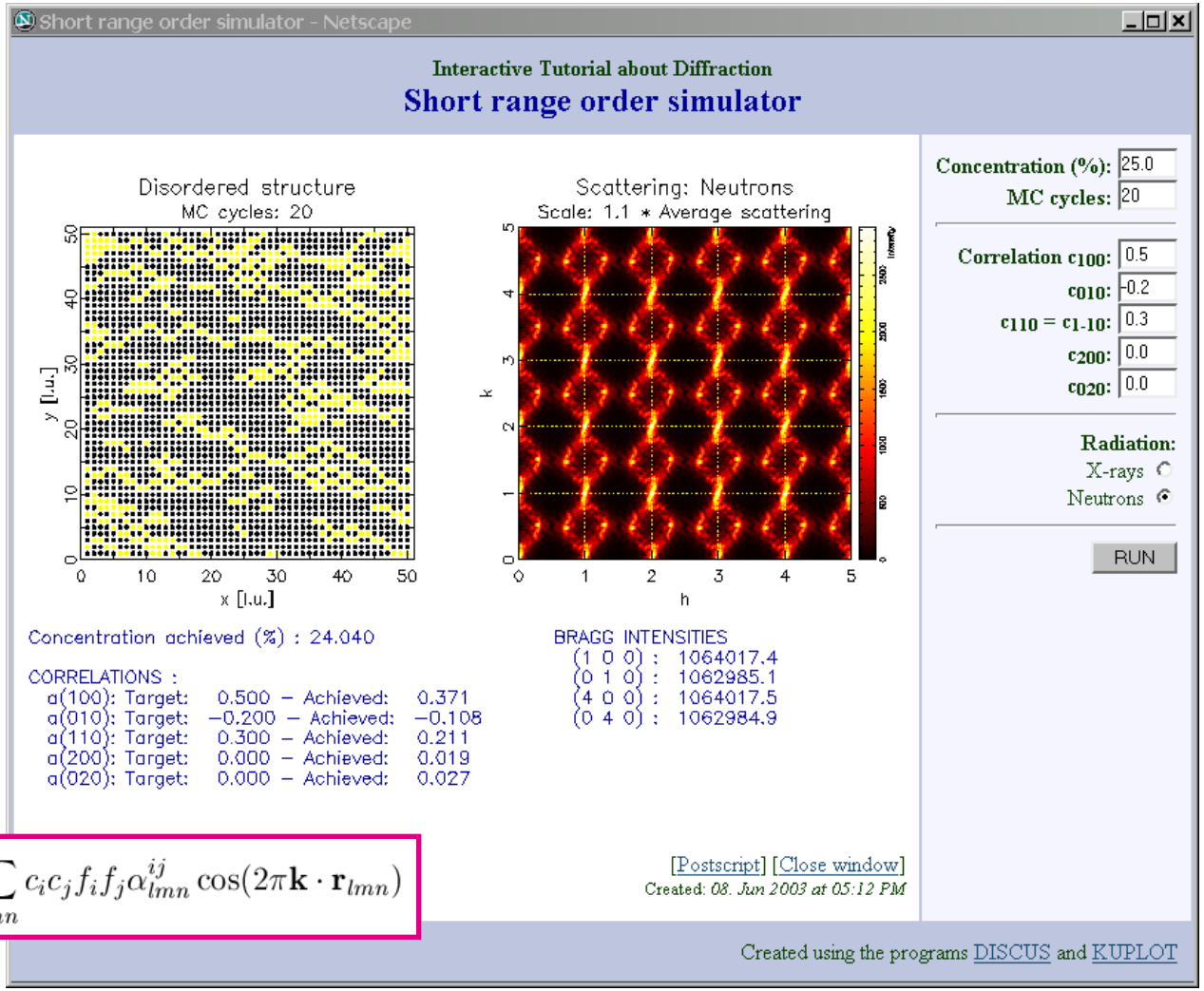
Diffuse scattering: Information about *two-body correlations*, *i.e.* chemical short-range order or local distortions.







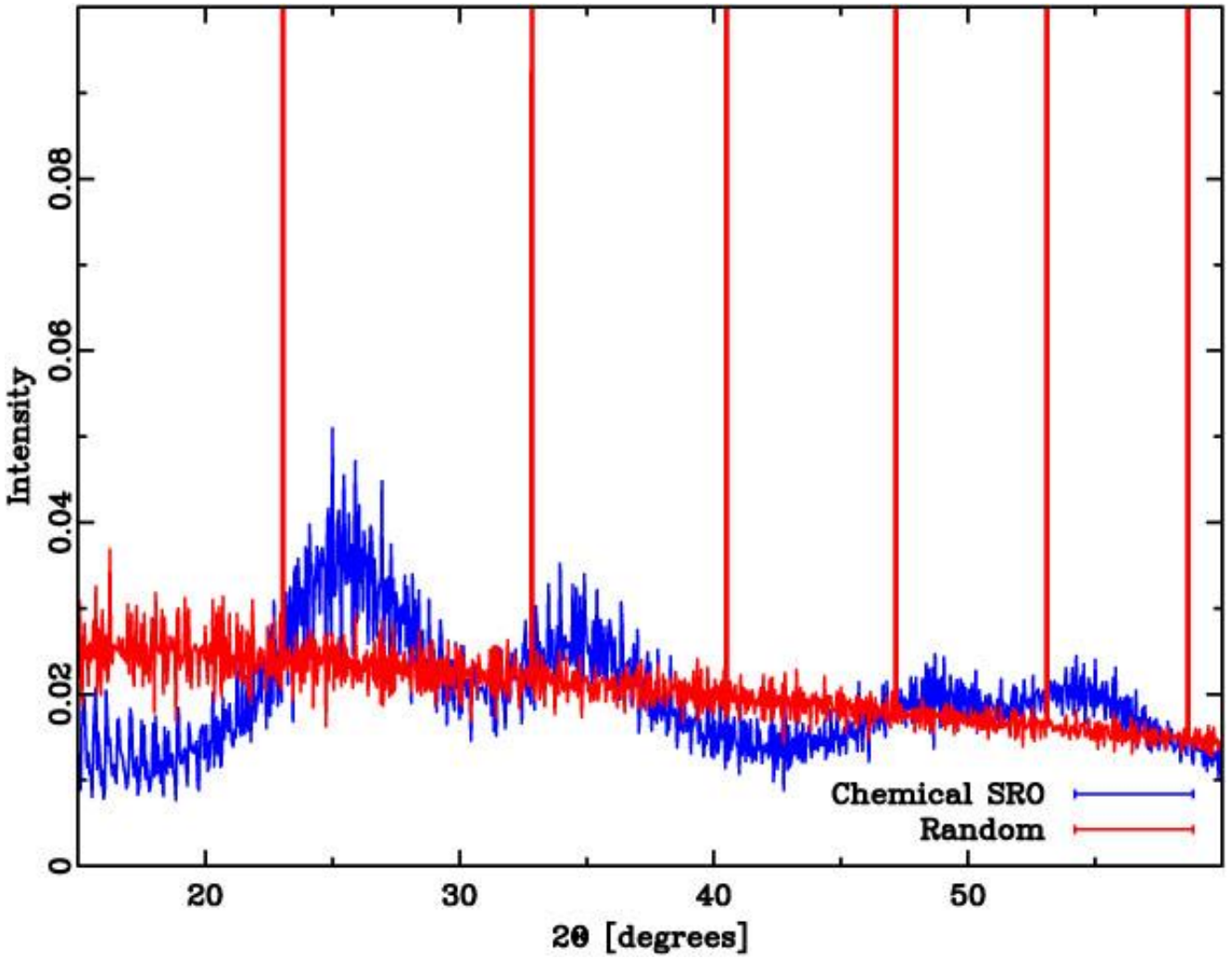
See http://www.totalscattering.org/teaching/



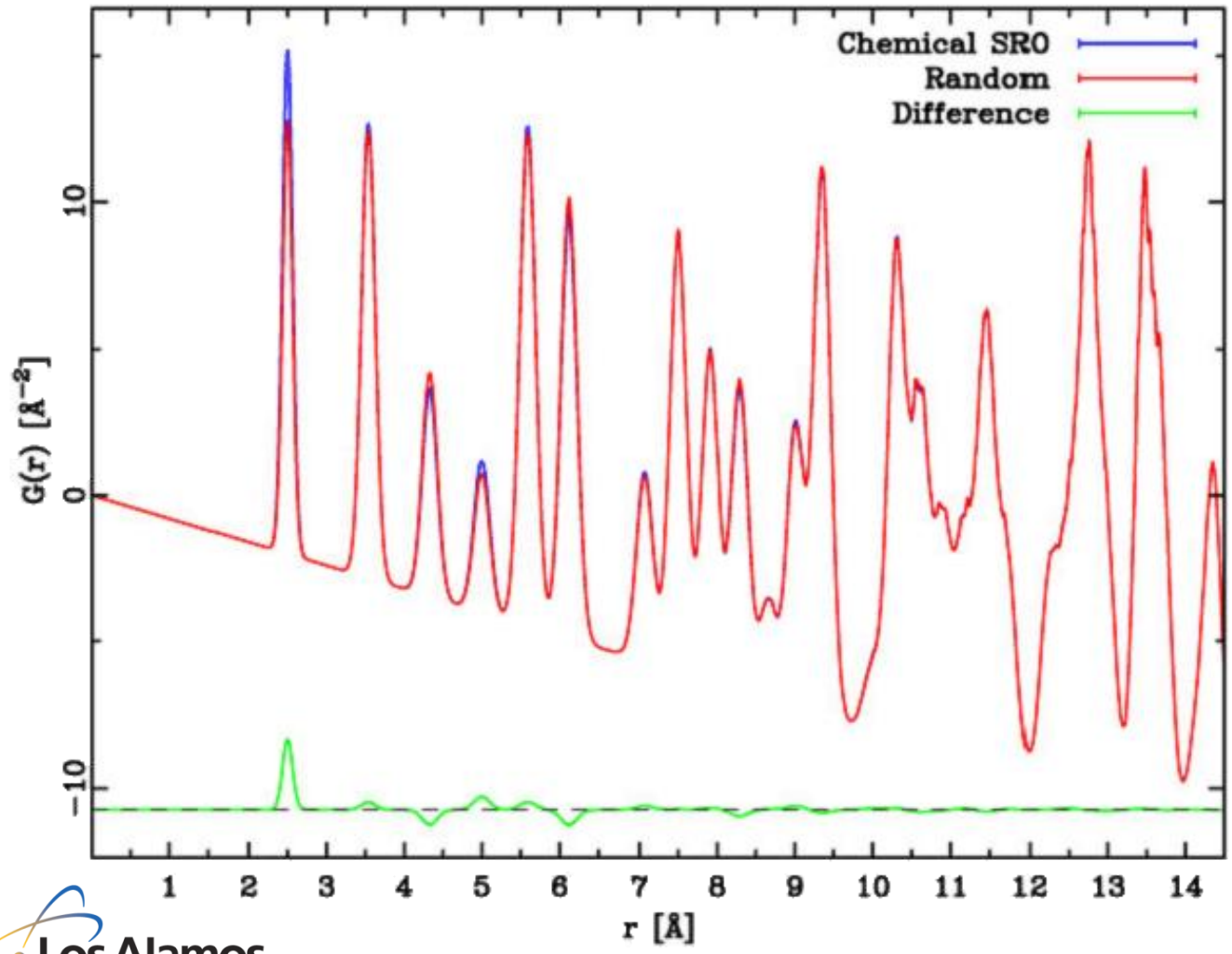
$$I_{\mathrm{sro}} = -\sum_{ij}\sum_{lmn} c_i c_j f_i f_j \alpha_{lmn}^{ij} \cos(2\pi \mathbf{k}\cdot\mathbf{r}_{lmn})$$

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

How about powder diffraction ?



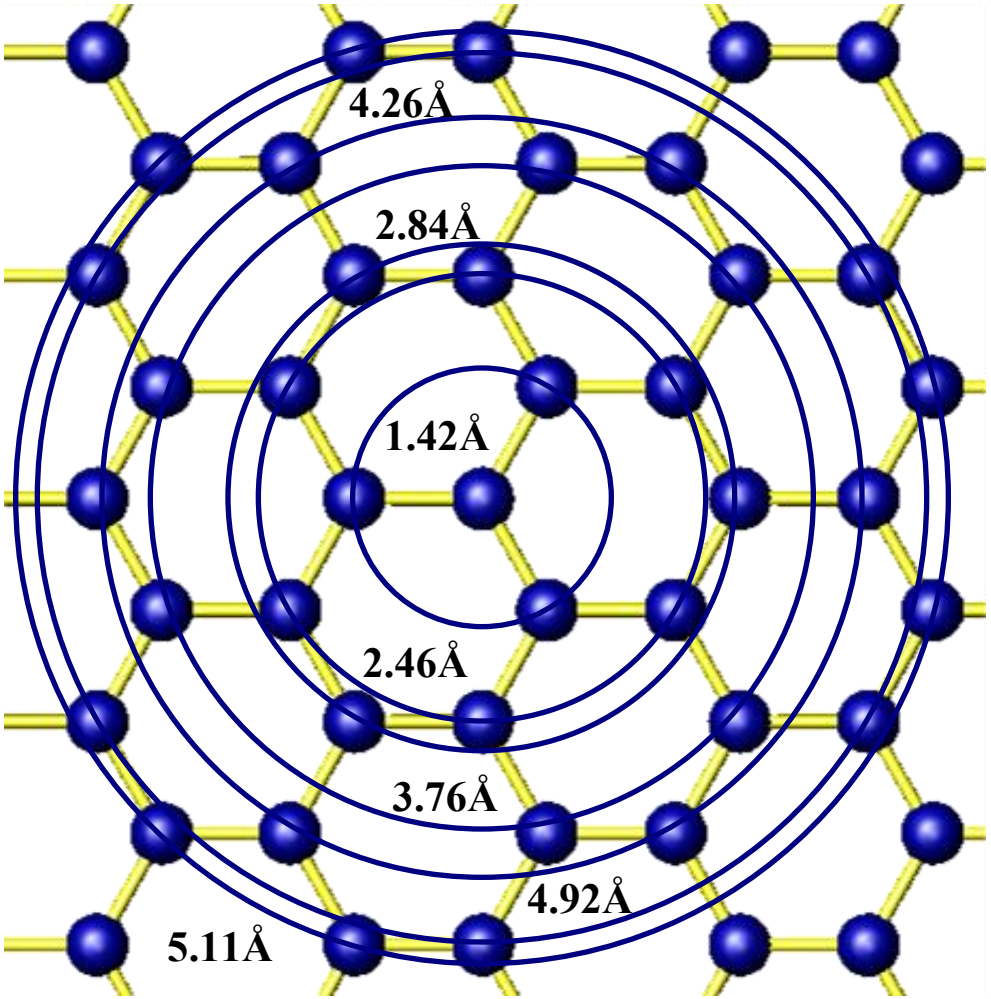
Finally the Pair Distribution Function (PDF)



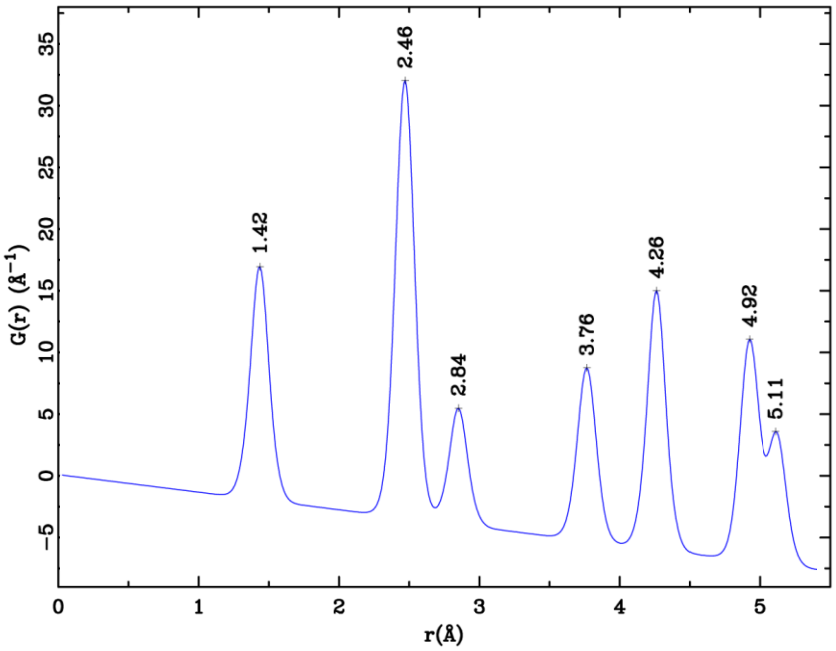
The PDF is the Fourier transform of the total scattering diffraction pattern !

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

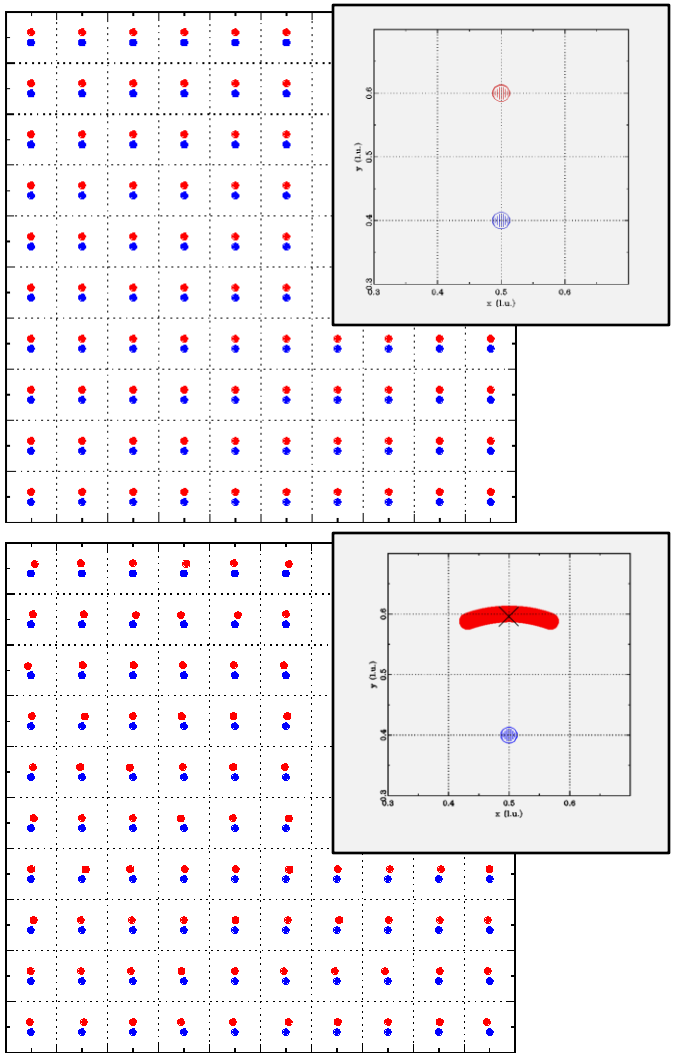
What is a PDF?

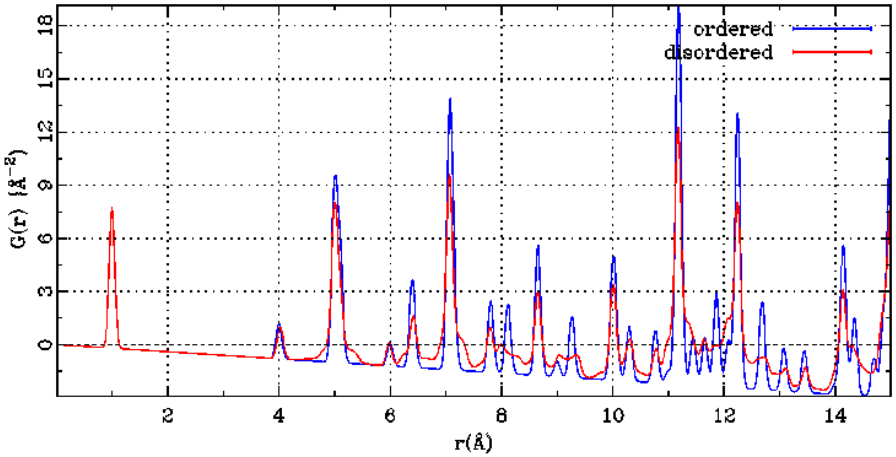


Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.



PDF allows r-dependent refinements





In both cases:
'Real' NN distance = 1.0Å

Average structure:
Ordered: NN distance = 1.00Å
Disordered: NN distance = 0.98Å

Instruments
and
Software

What is required to obtain high quality PDFs ?

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

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

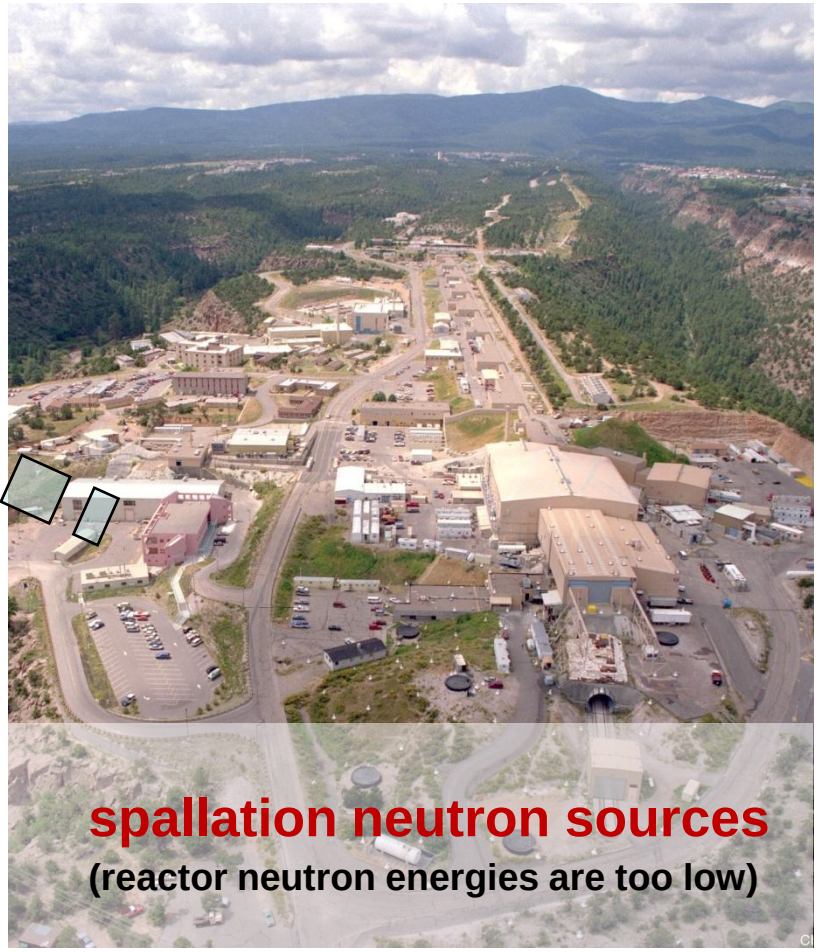
Requirements to obtain 'good' PDF:

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

Where ?

Synchrotron sources
(high energy X-rays)

or

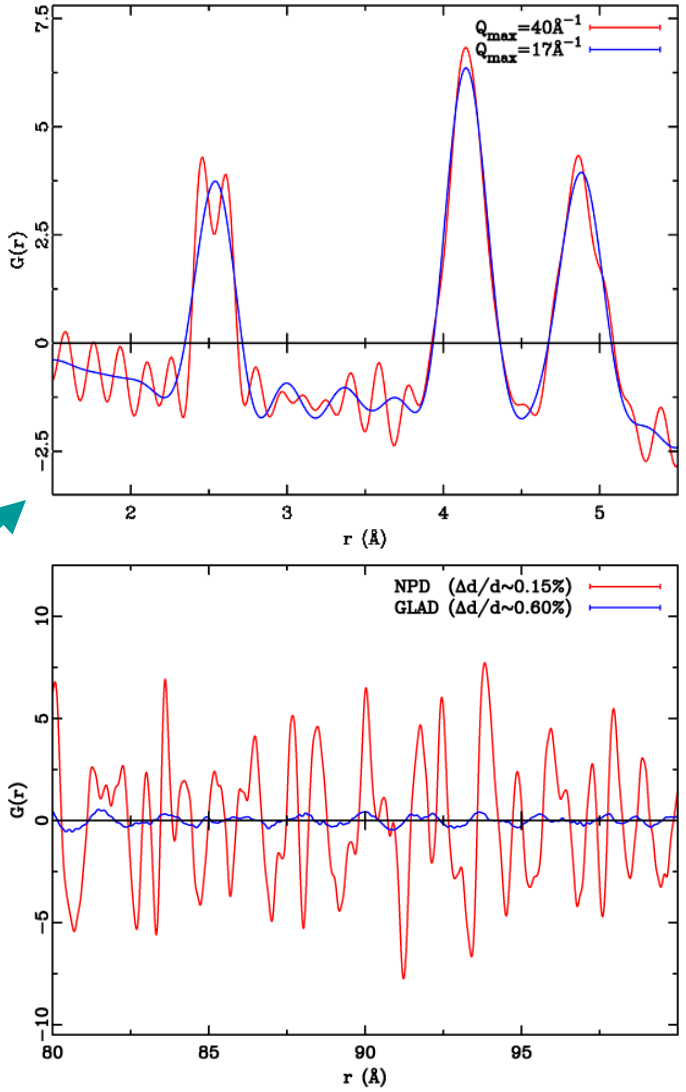


spallation neutron sources
(reactor neutron energies are too low)

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):

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

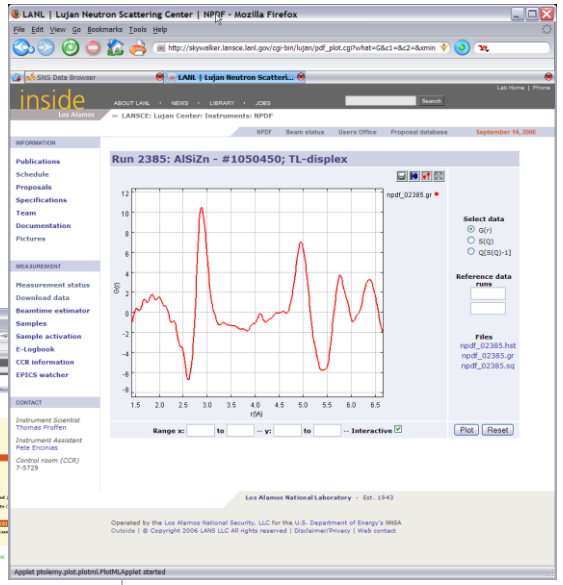


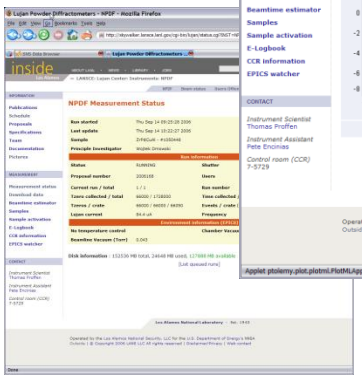
Requirements to obtain 'good' PDF:

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

NPDF: Overview

- Specifications
  - Upgrade finished Sep. 2002
  - L1: 32m, Q_{max}=50Å^{-1}, Δd/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





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

X-ray PDF: The fast way

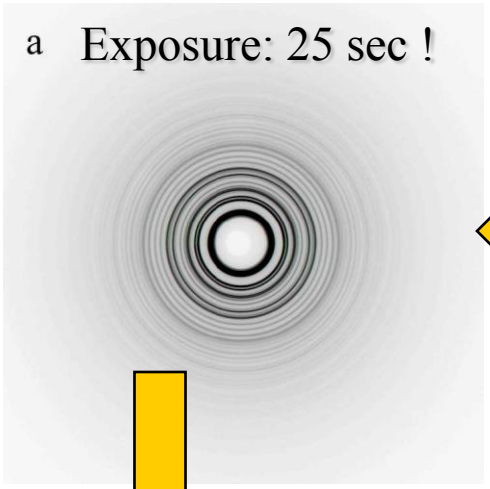
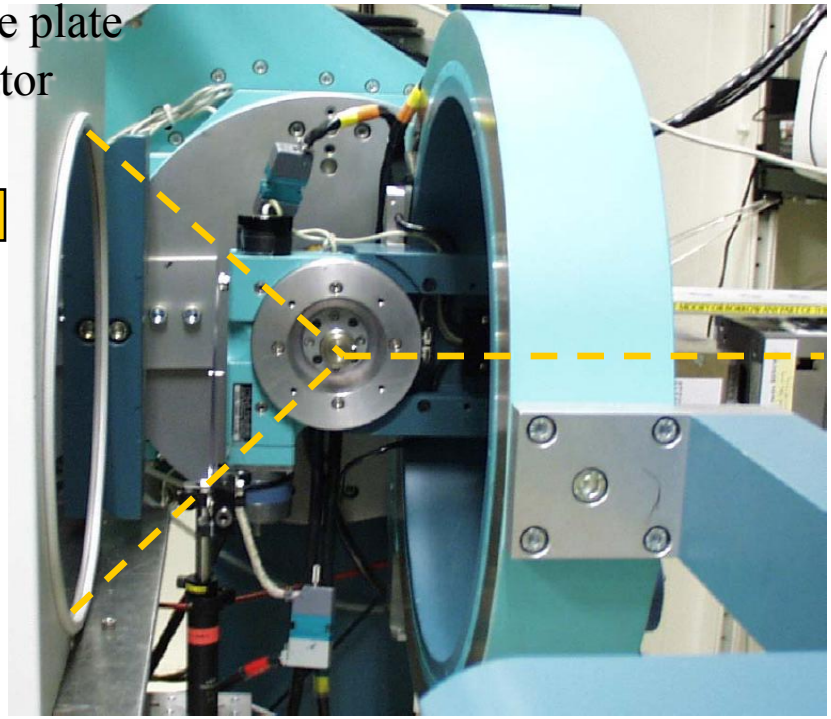
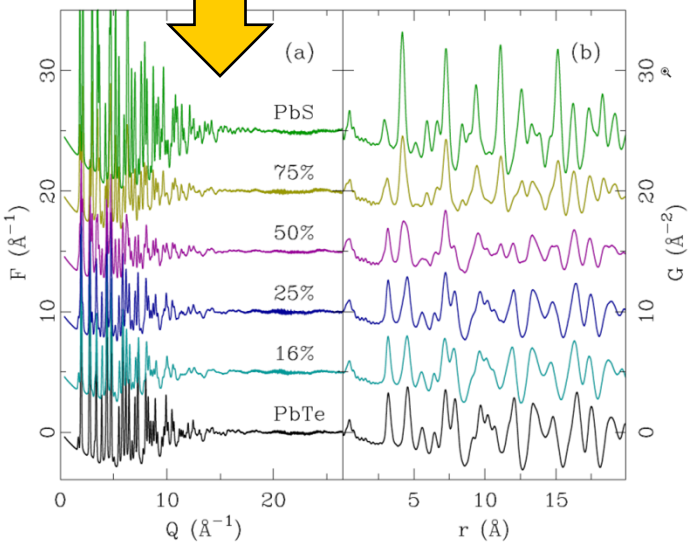


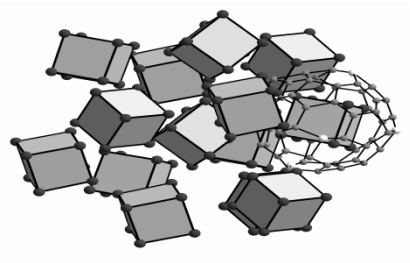
Image plate detector



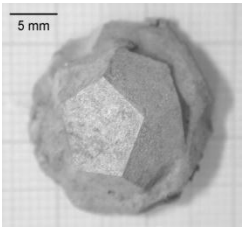


P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, **Rapid-acquisition pair distribution function (RA-PDF) analysis**, *J. Appl. Cryst.* **36**, 1342-1347 (2003).

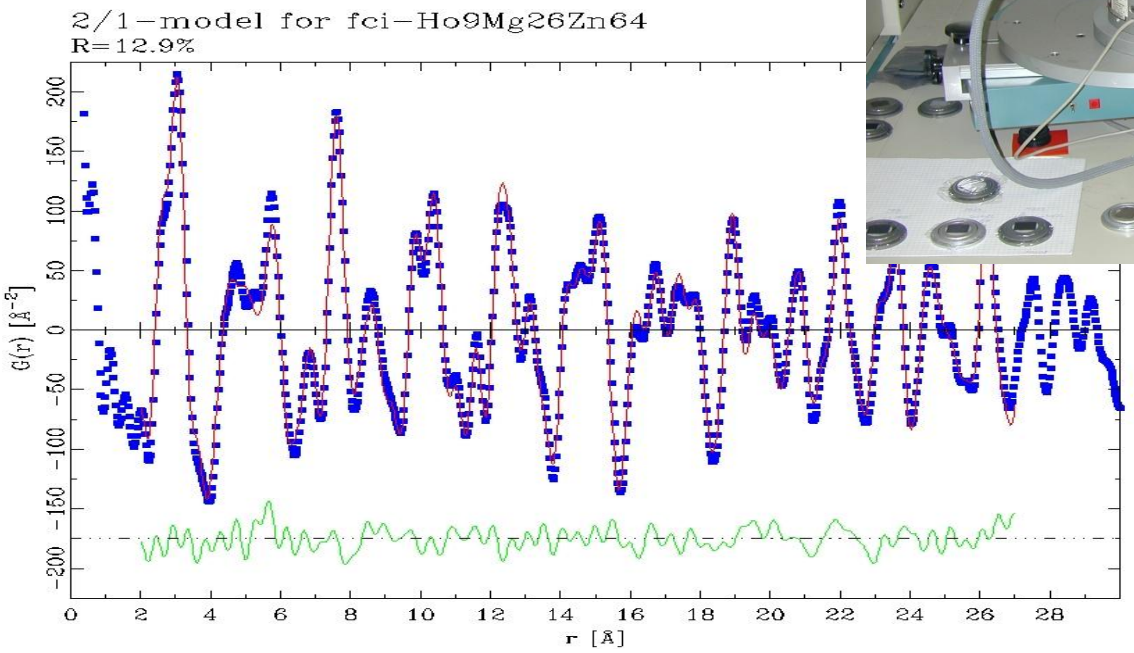
X-ray PDF: In house measurements



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



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

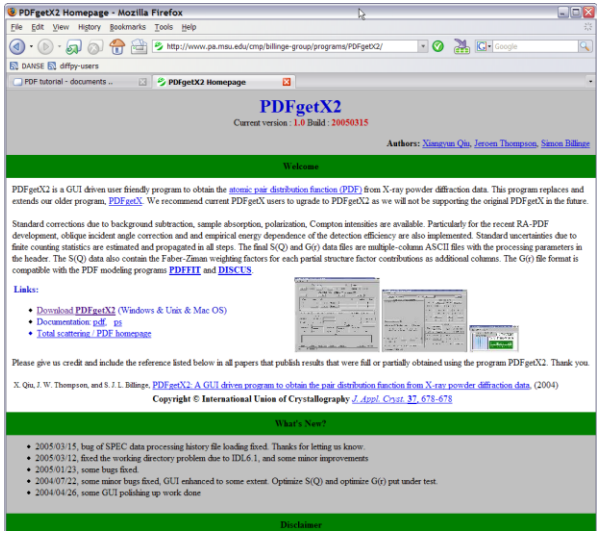


Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

Software: Data reduction

X-rays

- IDL based.
- Laboratory and synchrotron data
- http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/



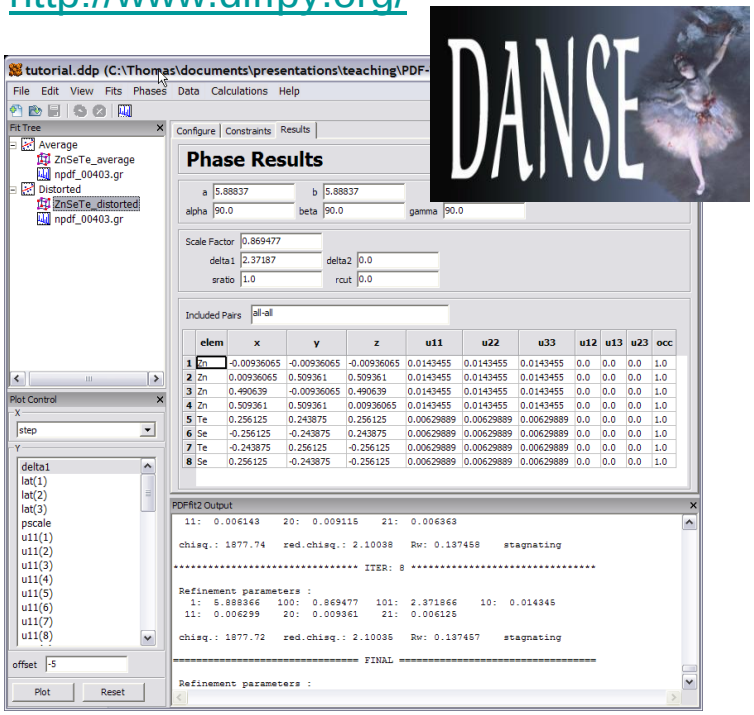
Neutrons

- GLASS package / Perl/TK frontend
- Automatic data reduction on NPDF
- http://pdfgetn.sourceforge.net/

Software: Data modeling

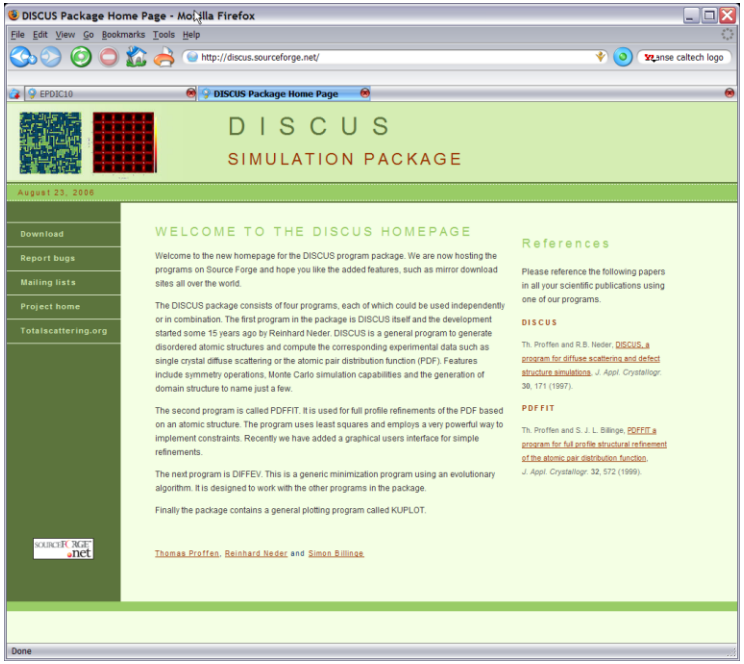
PDFgui

- Part of DANSE project.
- PDF refinement of ‘small’ models.
- http://www.diffpy.org/



DISCUS

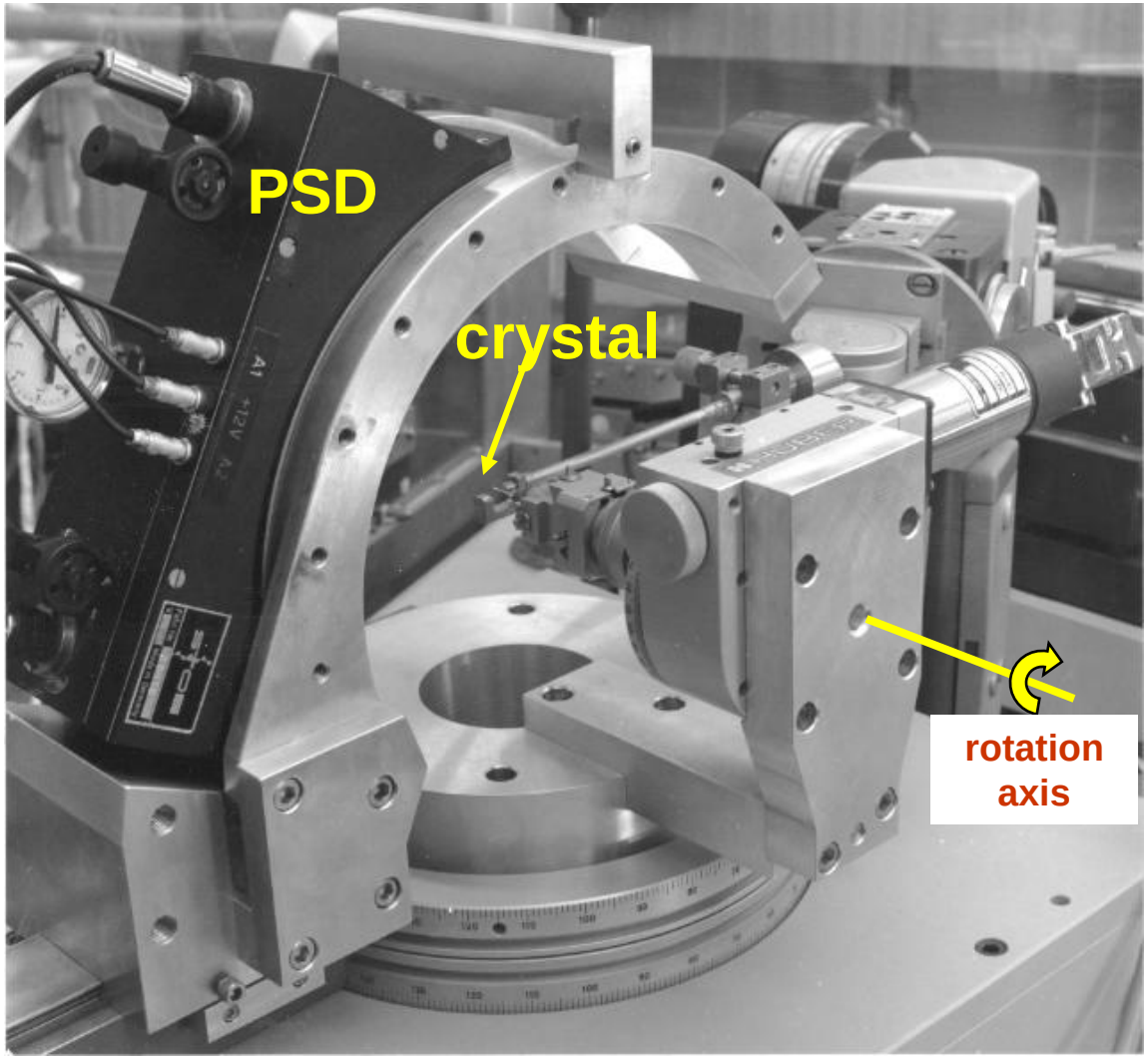
- Disordered materials simulations
- Refinement via DIFFEV / RMC
- http://discus.sourceforge.net/



Disorder in $Fe_3(CO)_{12}$

Richard Welberry
Thomas Proffen (LANL)

Diffuse scattering single crystal diffractometer



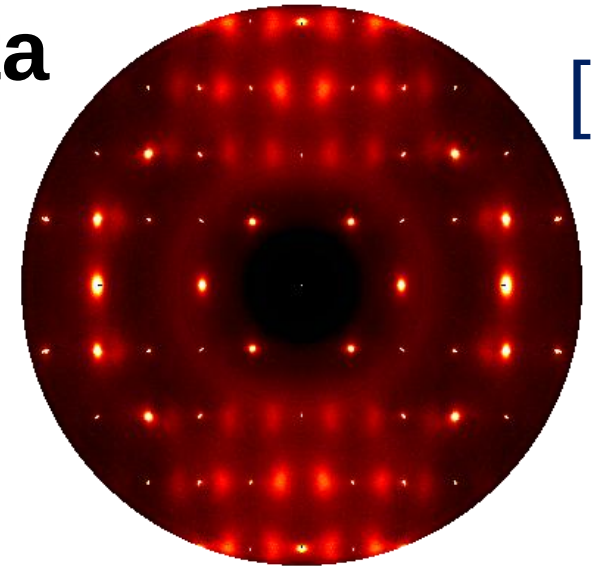
Los Alamos NATIONAL LABORATORY EST.1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA
NNSA
Lujancenter

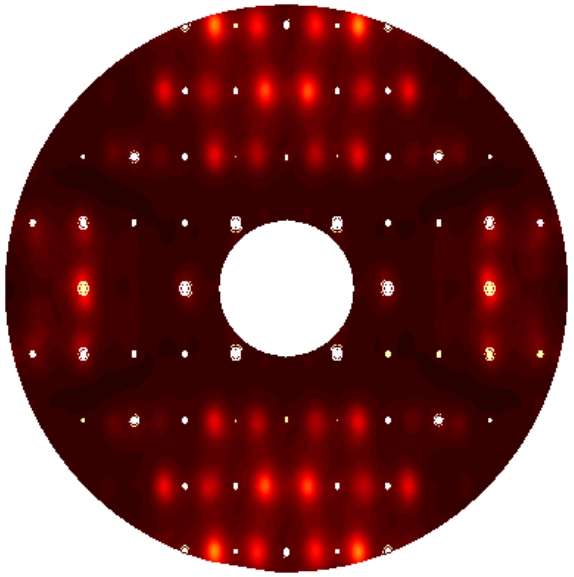
$Fe_3(CO)_{12}$: AMC refinement

Data

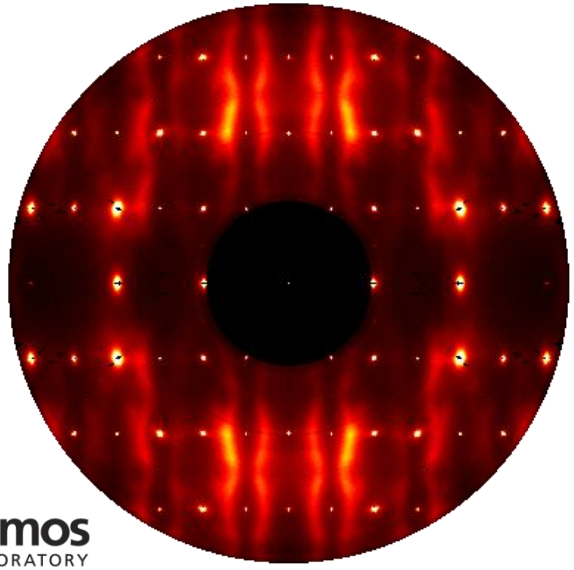
Model

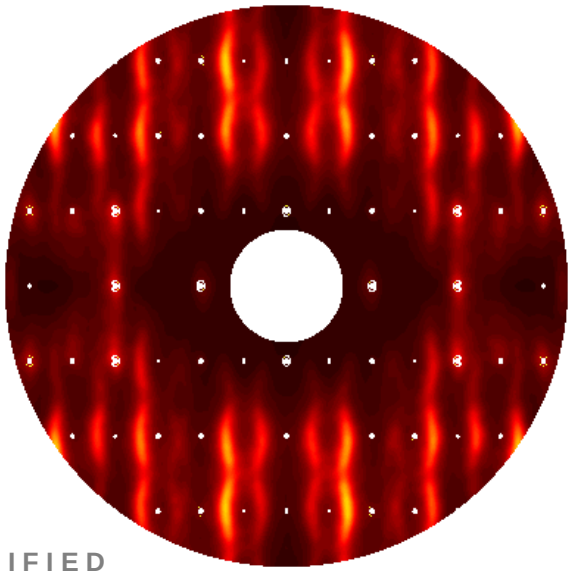
[100]





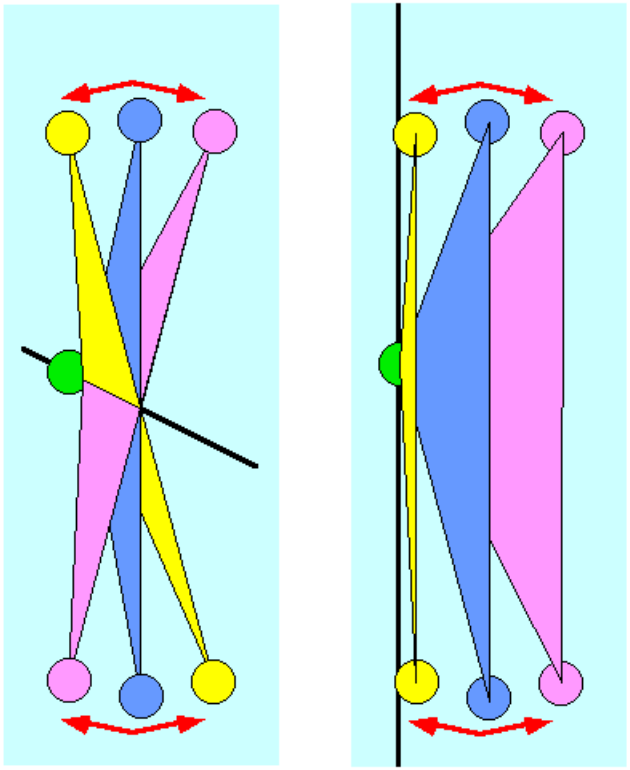
[101]

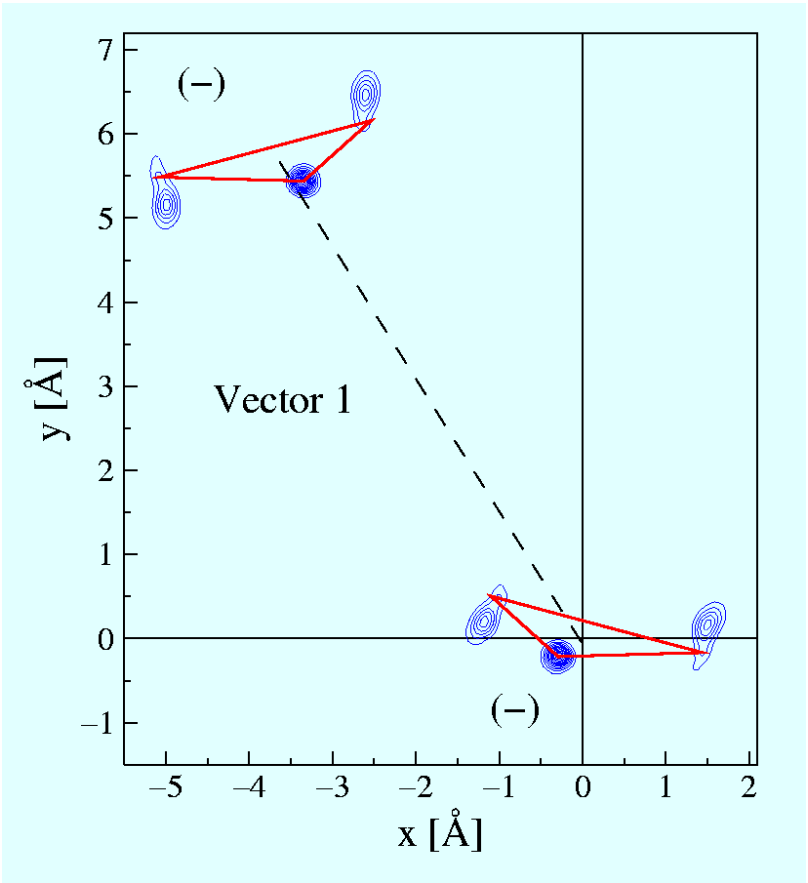




$Fe_3(CO)_{12}$: Resulting structure

Positions of Fe averaged over unit cells containing either (+ +) or (- -) combinations on nearest-neighbor vector 1.





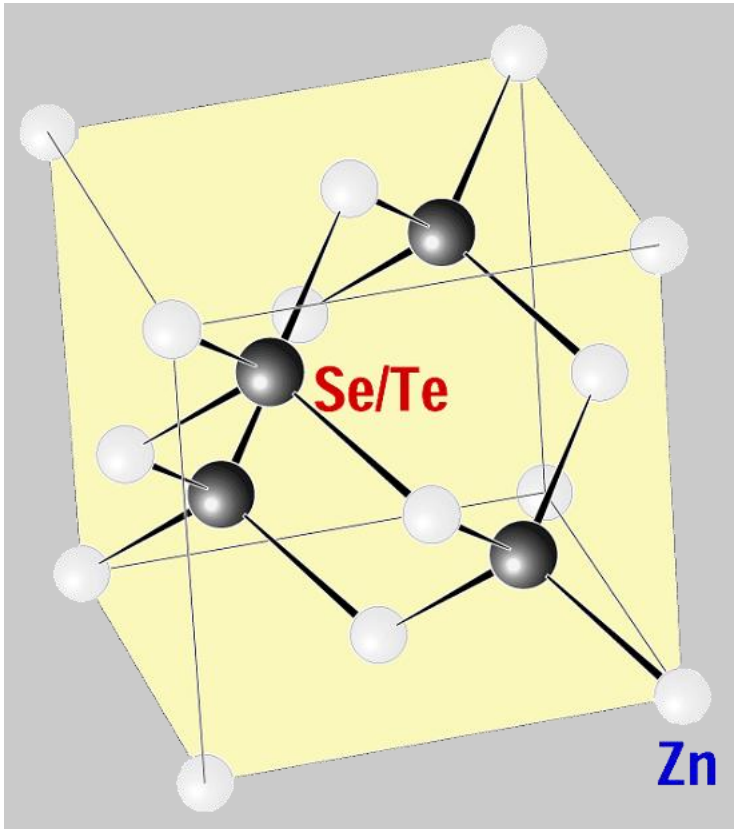
Two modes of libration not distinguished by Bragg scattering

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

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

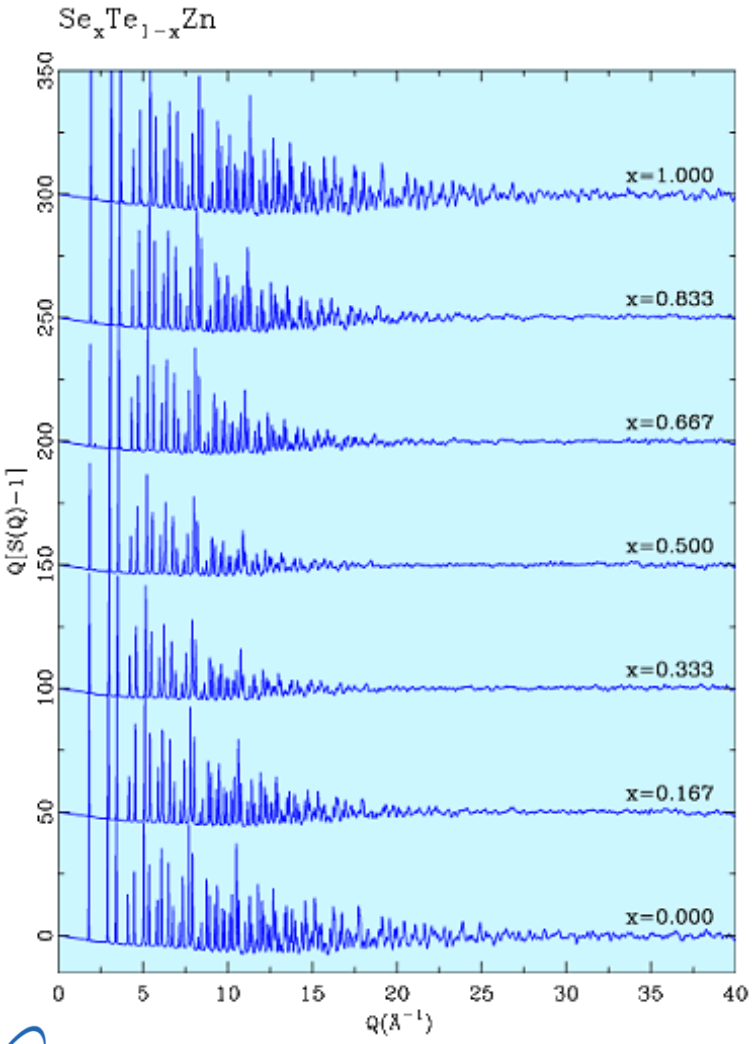
$ZnSe_{1-x}Te_x$: Structure

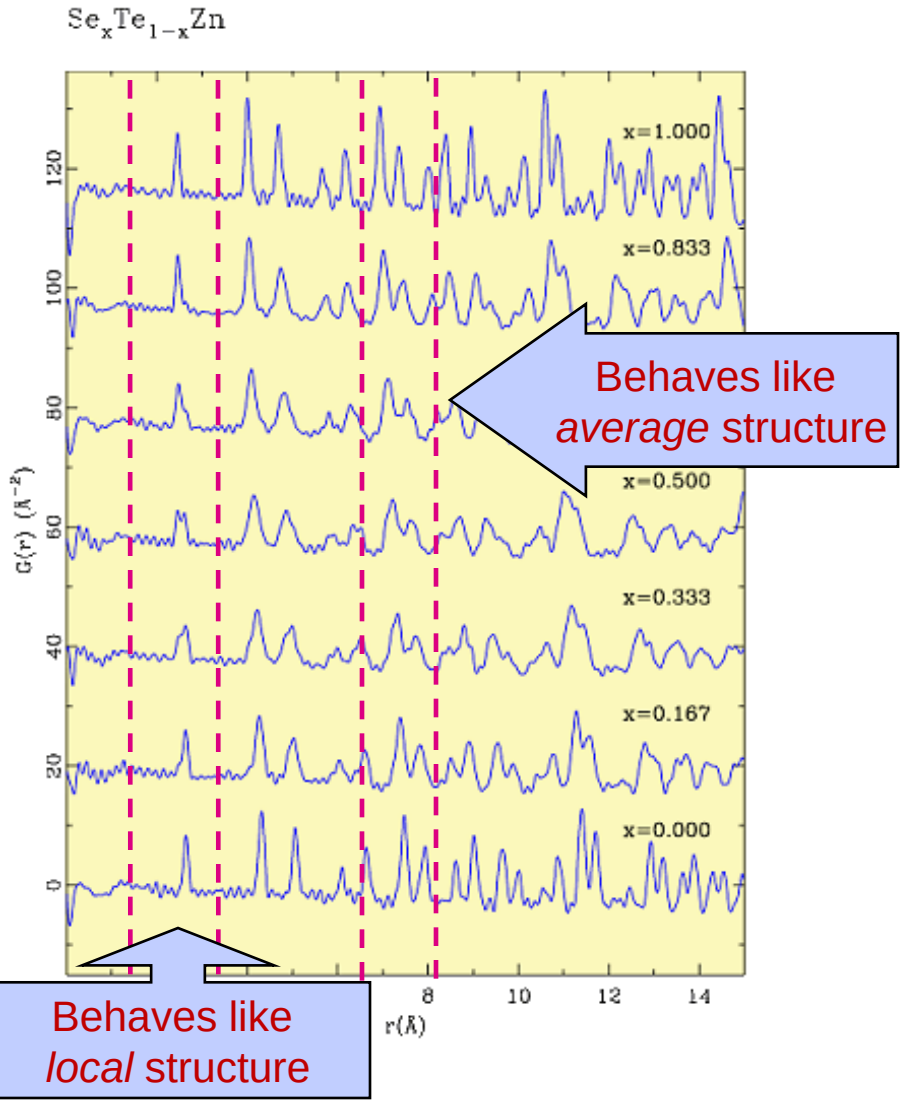
- Zinc blend structure (F43m)
- Technological important : Electronic band gap can be tuned by the composition *x*.
- Bond length difference *Zn-Se* and *Zn-Te* ⇒ strain.
- Local structural probe required !



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

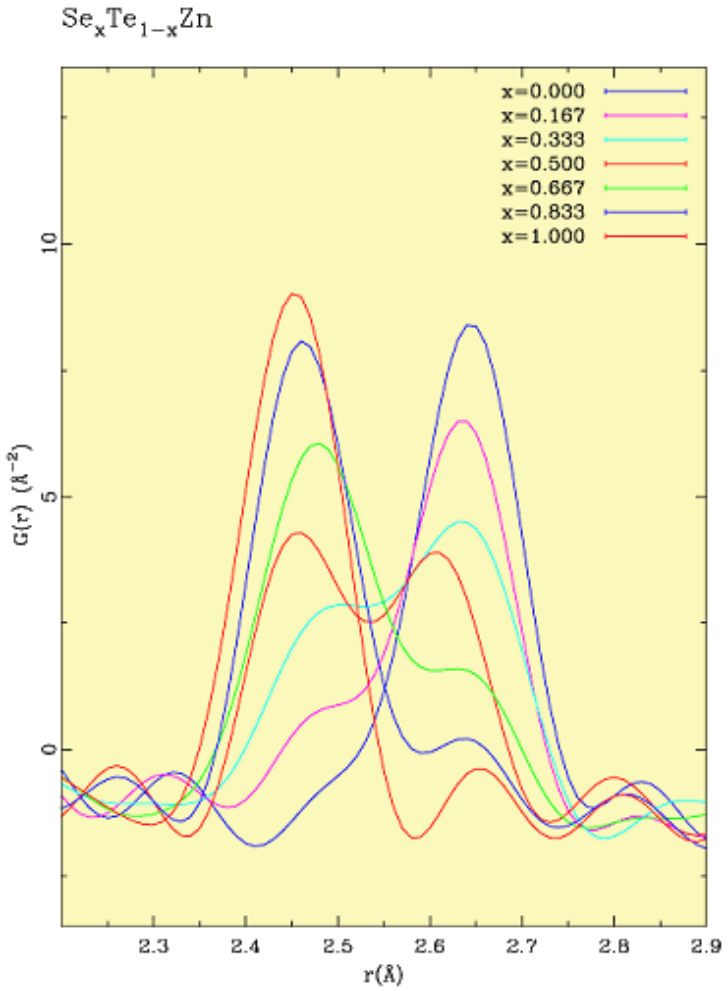
Peterson et al., *Phys. Rev.* B**63,** 165211 (2001)

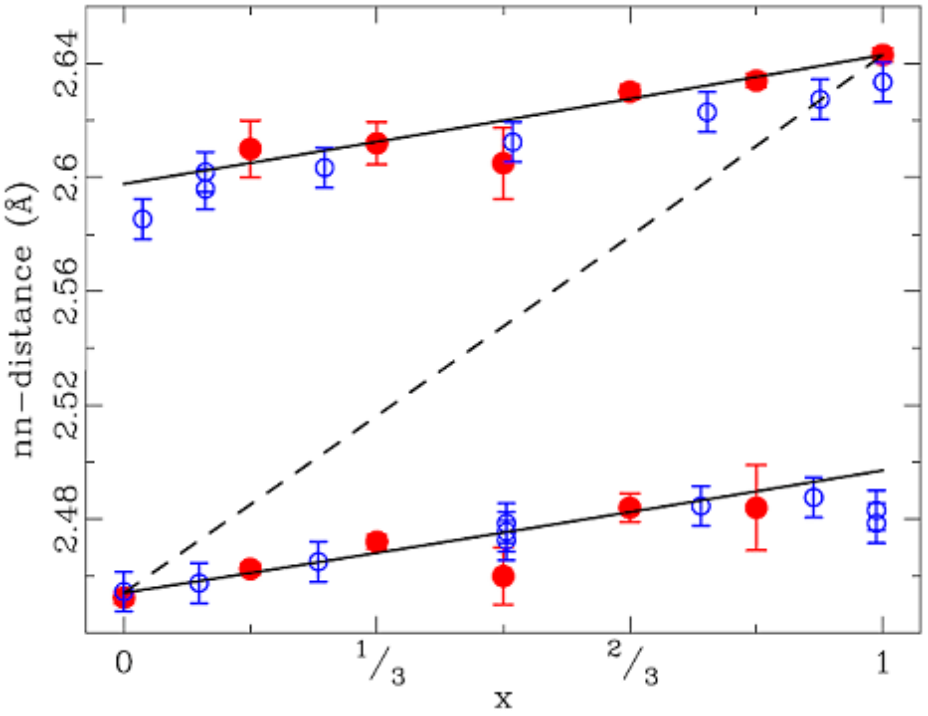




Los Alamos NATIONAL LABORATORY EST.1943
Operated by the Los Alamos National Security, LLC for the DOE/NNSA
NNSA Lujancenter

$ZnSe_{1-x}Te_x$: Nearest neighbors and Z-plots ..





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

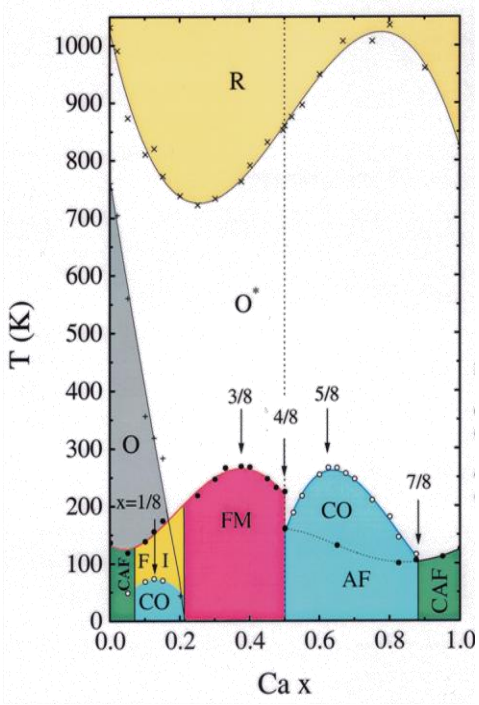
Example:

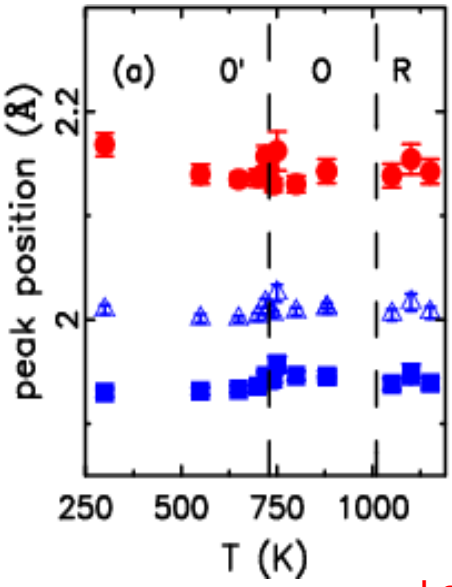
Local structure in $La_xCa_{1-x}MnO_3$

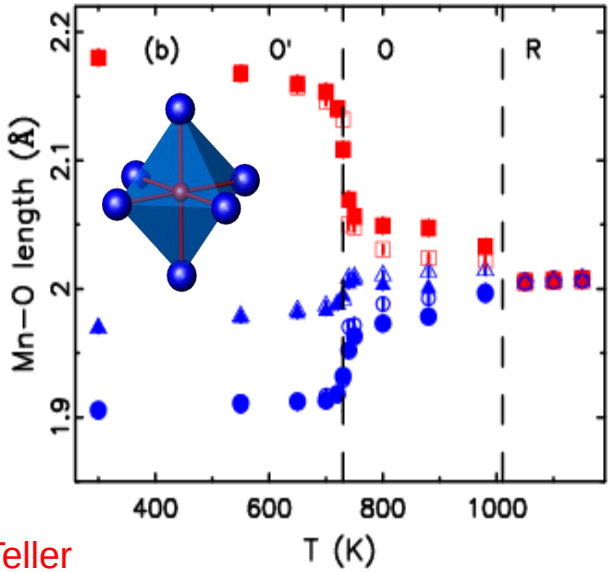
Simon Billinge
Emil Bozin
Xiangyn Qiu

Thomas Proffen

$LaMnO_3$: Jahn-Teller distortion







Jahn Teller
Long Mn-O bond

Local structure

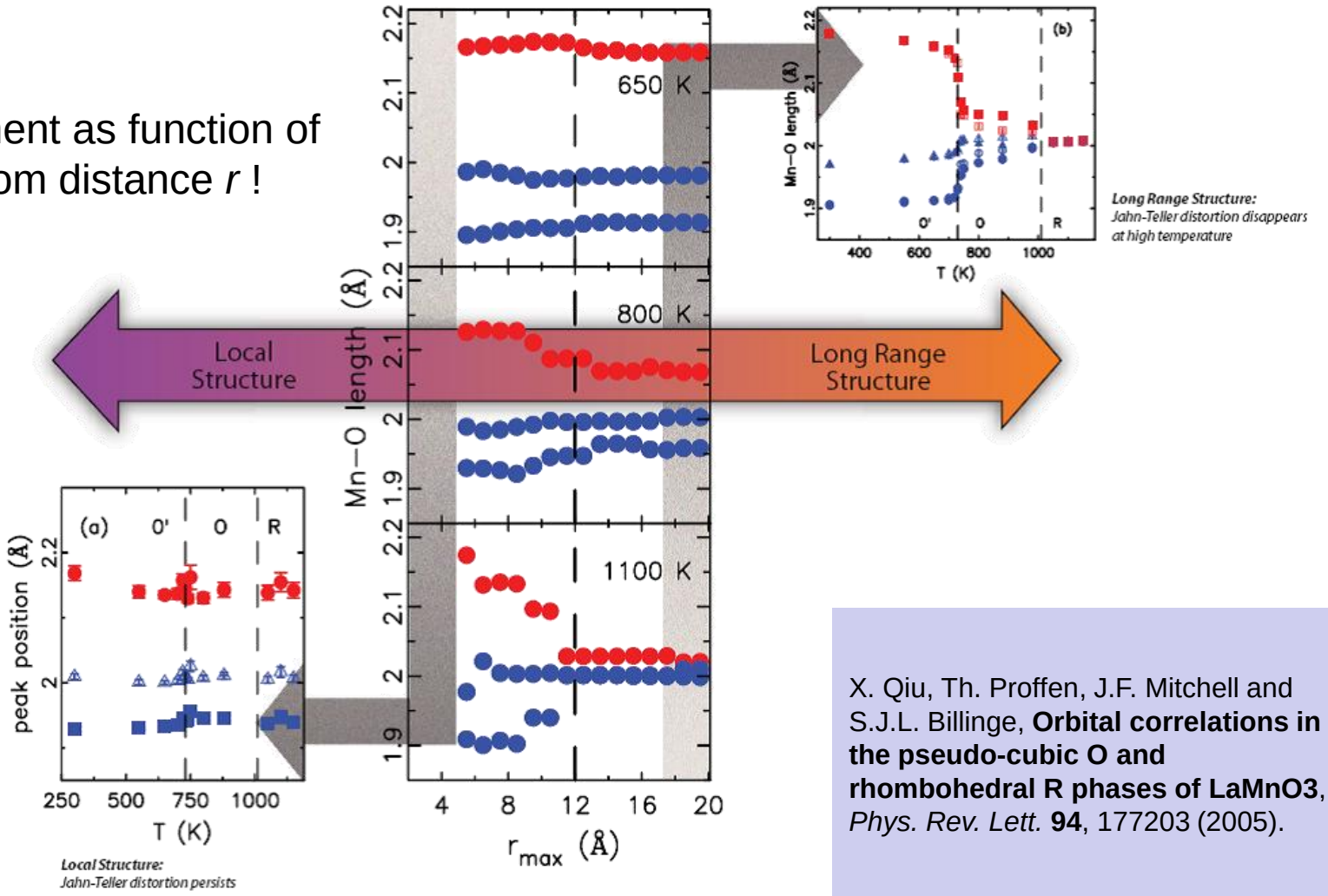
Average structure

- 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?

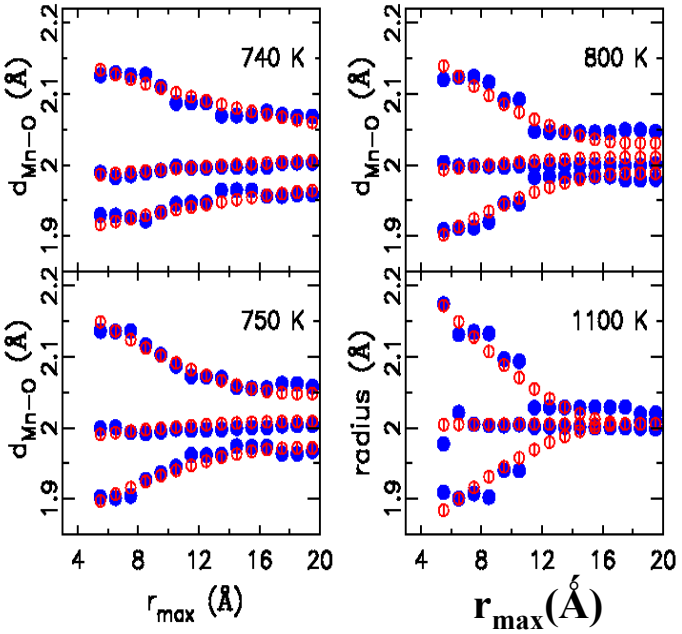
Study of the Jahn-Teller distortion in $LaMnO_3$

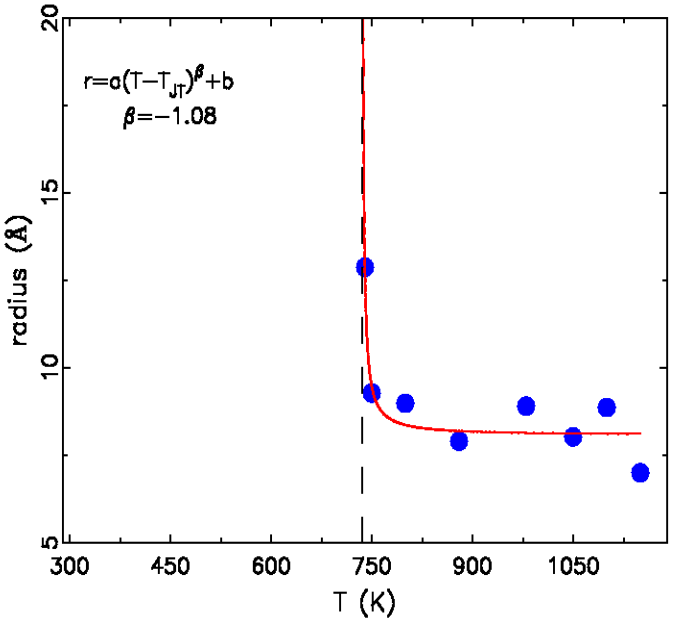
Refinement as function of atom-atom distance *r* !



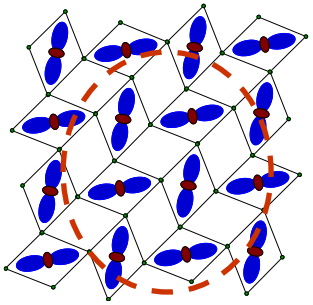
X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of LaMnO3**, *Phys. Rev. Lett.* **94**, 177203 (2005).

$LaMnO_3$: T-dependence of orbital clusters from PDF



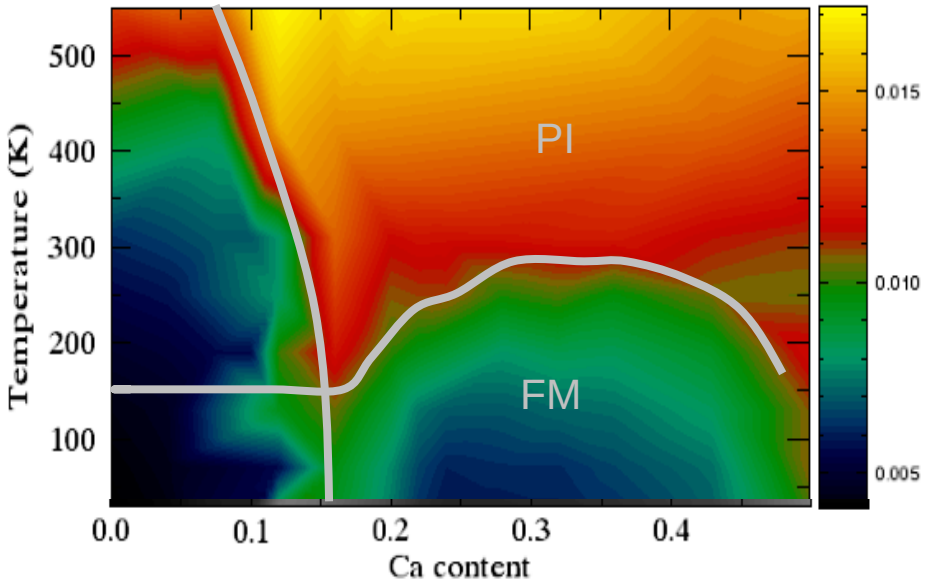


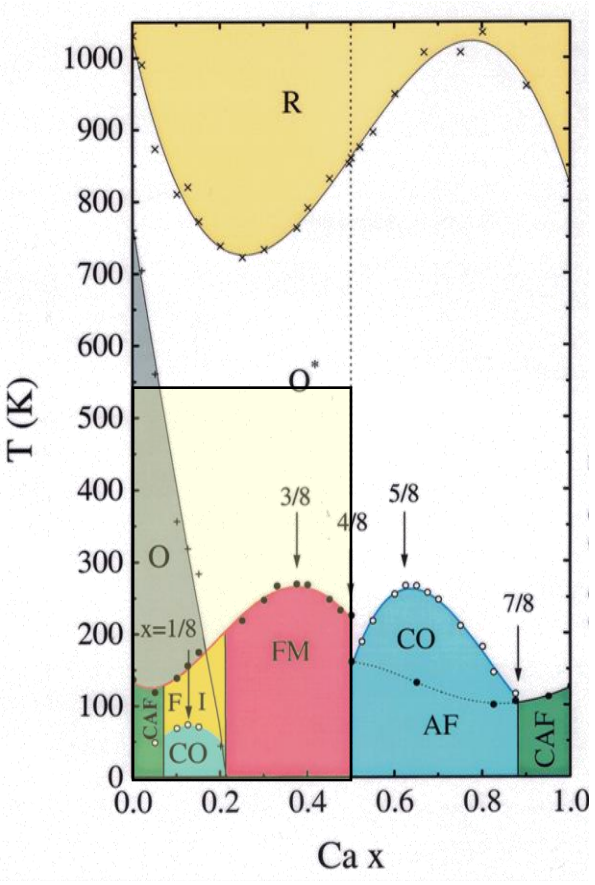
- Diameter of orbitally ordered domains above T_{JT} is 16Å
- Appears to diverge close to T_{JT}
- Red lines are a guide to the eye (don't take the fits too seriously!)



$La_{1-x}Ca_xMnO_3$: Structural phase diagram

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



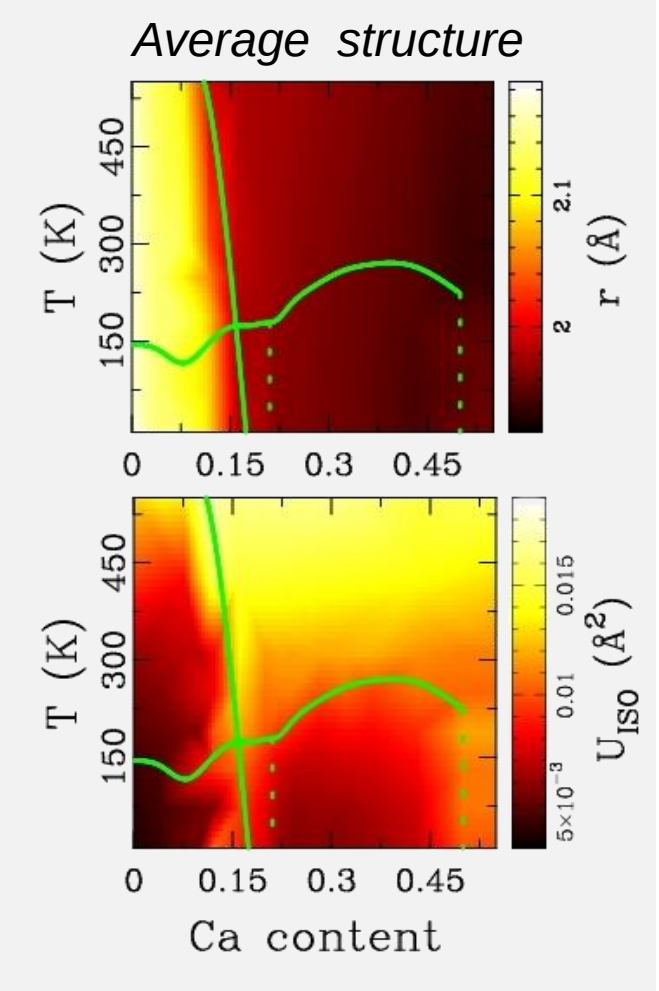


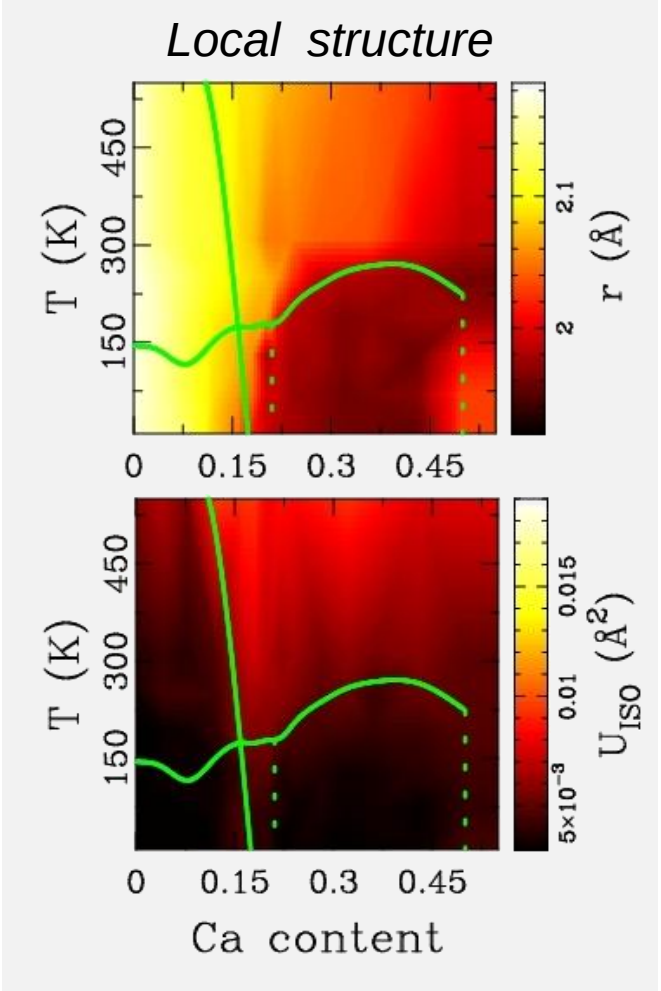
- Phase diagram draws itself from the parameters.
- Unexpected detail emerges and demands interpretation.

$La_{1-x}Ca_xMnO_3$: Structural phase diagram

Mn-O long bond

ADP Oxygen





Example:
"Complete" structure of Gold Nanoparticless

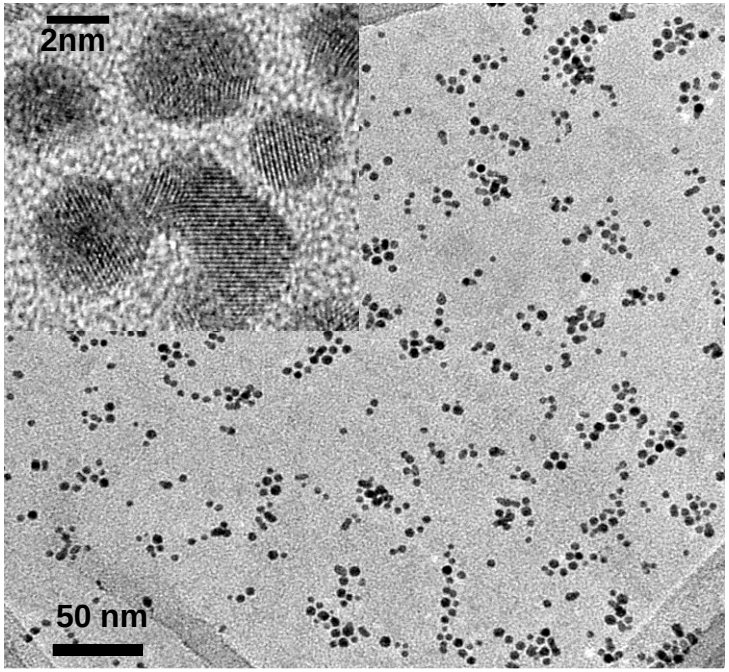
Katharine Page
Ram Seshadri
Tony Cheetham

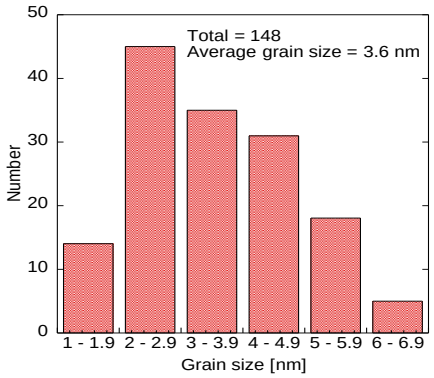
Thomas Proffen

Gold nanoparticles

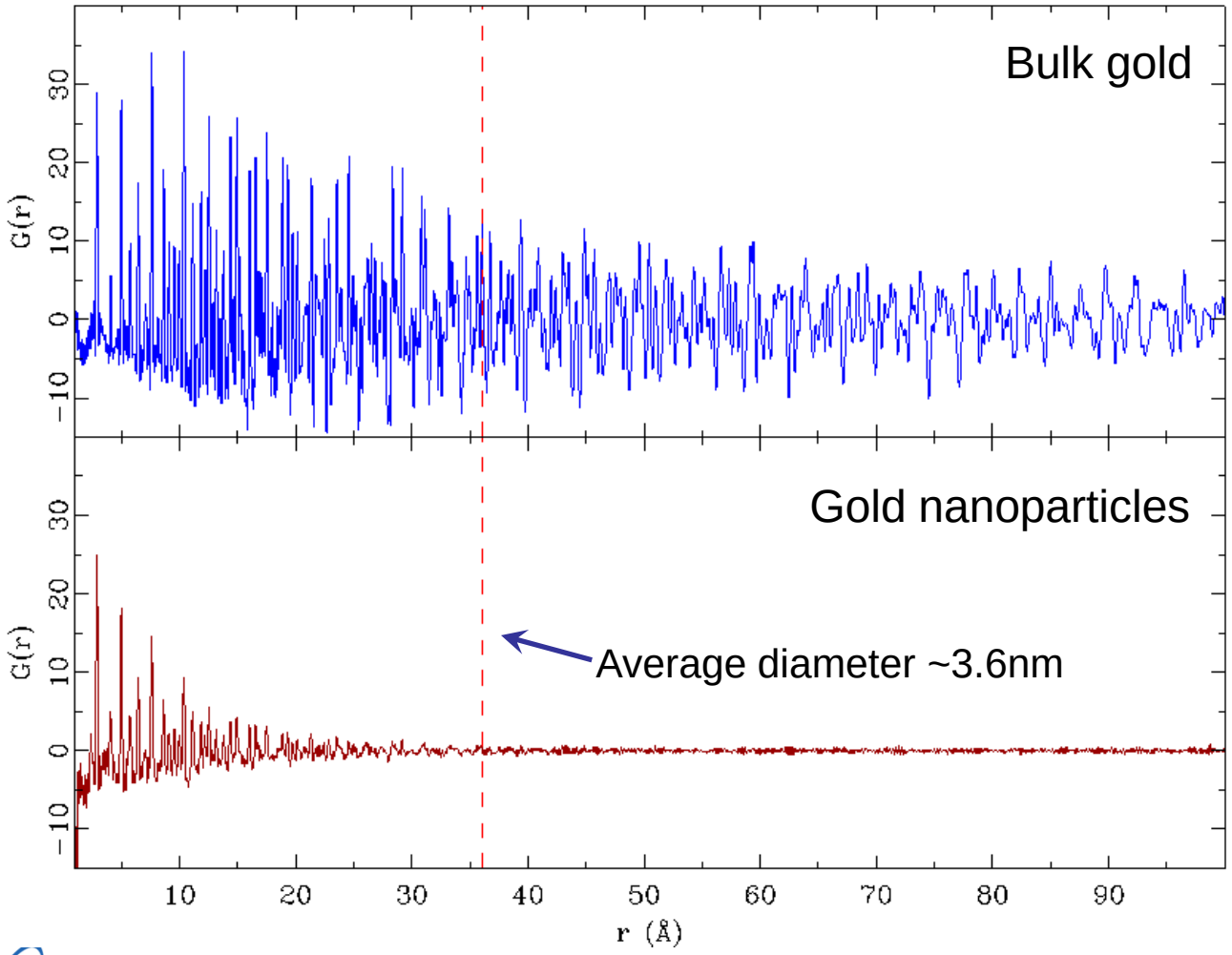
- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.

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



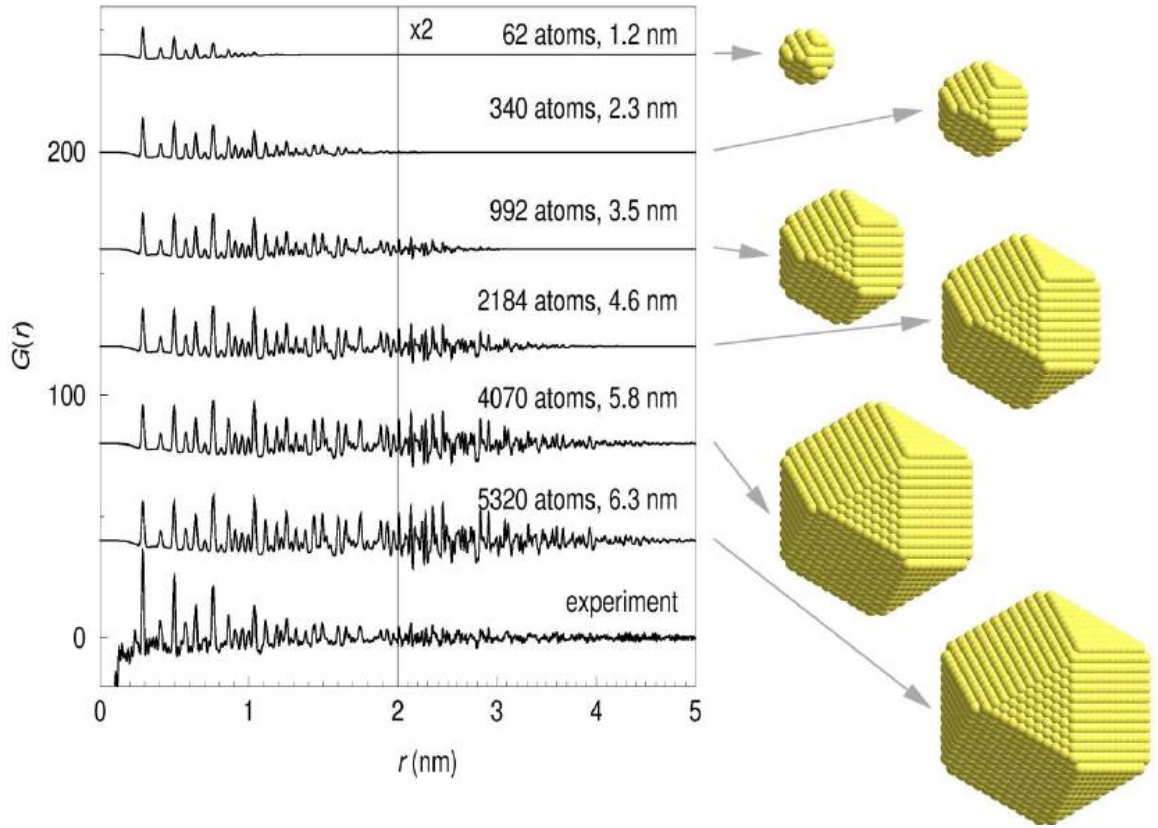


Gold nanoparticles: First NPDF data



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).

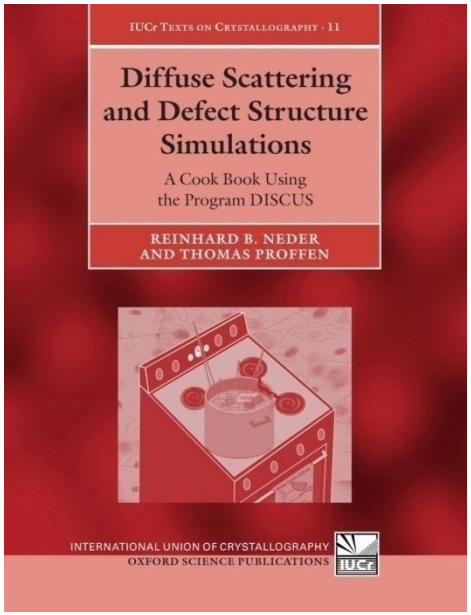
Au nanoparticles: Particle size

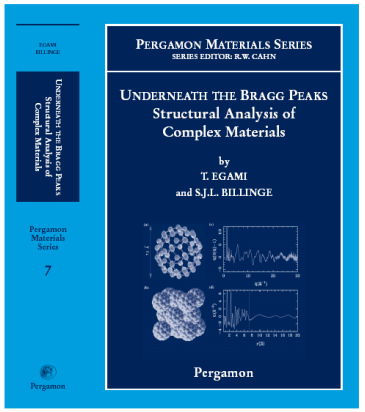


We're dealing with a length scale that can be simulated on an atom by atom basis, perhaps opening the door to extremely detailed refinements.

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
- Fast powder measurements allow systematic exploration of local structure as function of *T*, *x*, *P*





http://www.totalscattering.org

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

Thank you
LANSCE