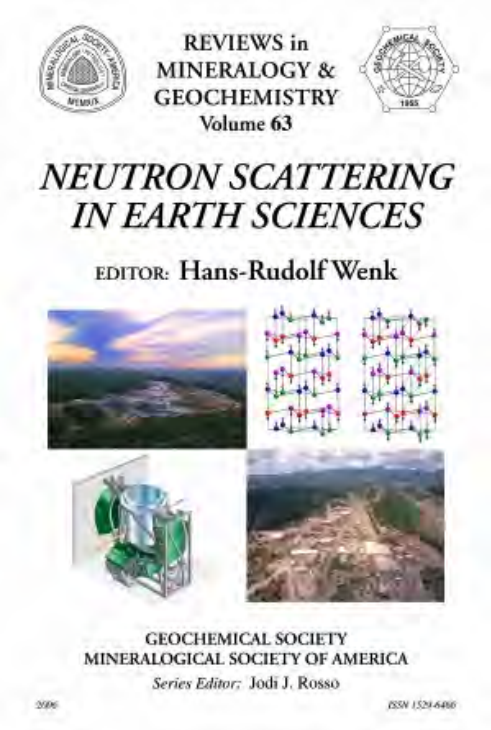
Analysis of Disordered Materials Using Total Scattering and the Atomic Pair Distribution Function



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Los Alamos NATIONAL LABORATORY EST.1943

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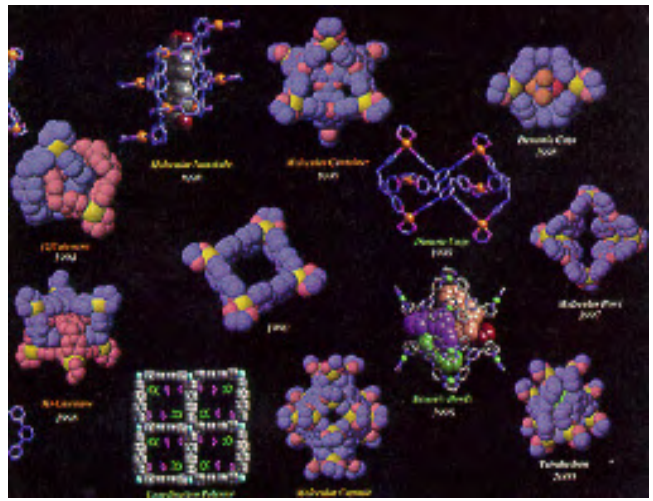
NNSA

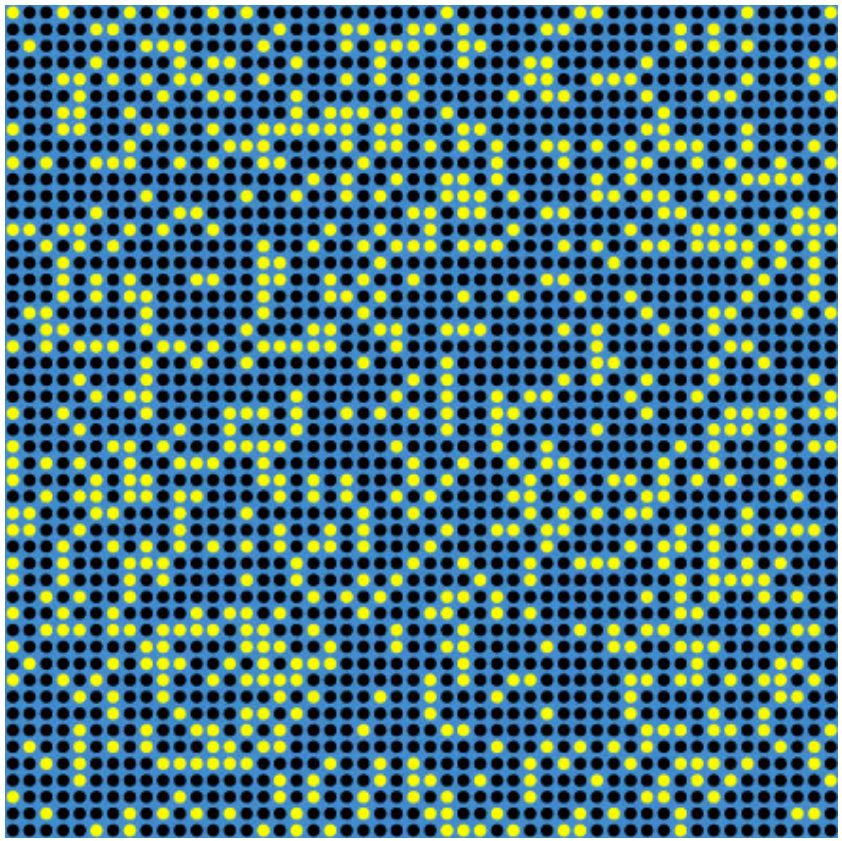
The challenge of *real* materials

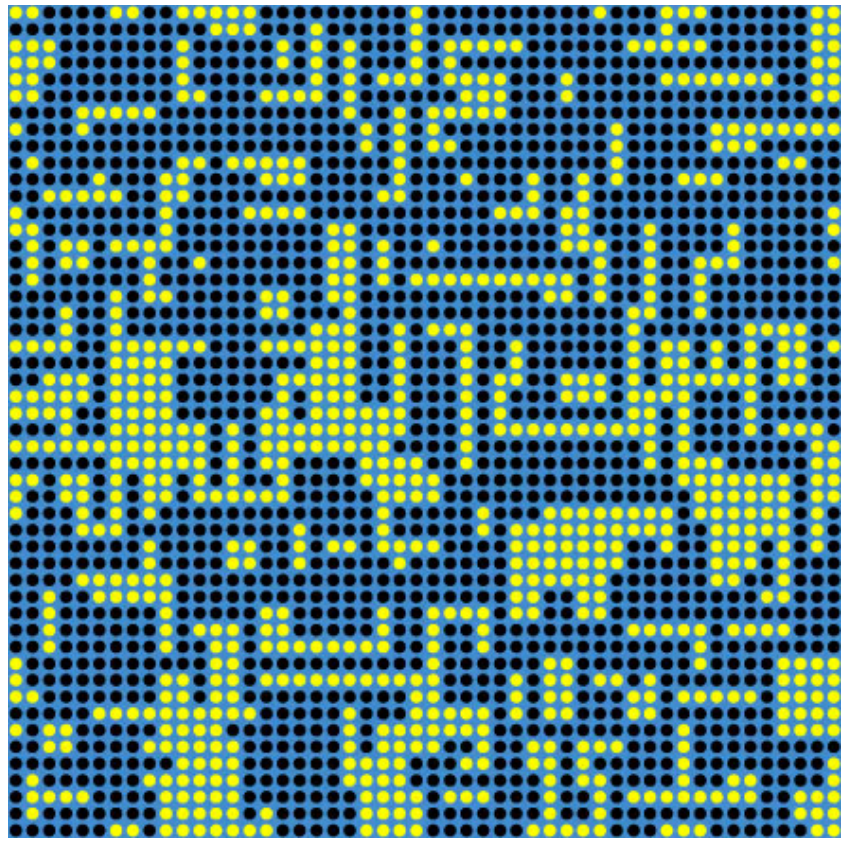
- Traditional crystallographic approach to structure determination is insufficient or fails for
  - Non crystalline materials
  - Disordered materials: The interesting properties are often governed by the defects or local structure !
  - Nanostructures: Well defined local structure, but long-range order limited to few nanometers (-> badly defined Bragg peaks)
- An approach to determine local and nano-scale structures is needed.



Nanostructures: *Science (290) 2000*

Total scattering ?

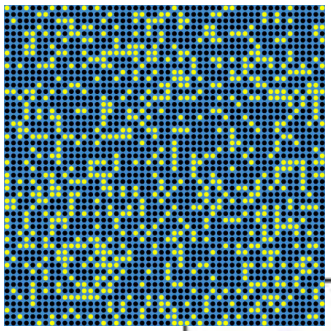




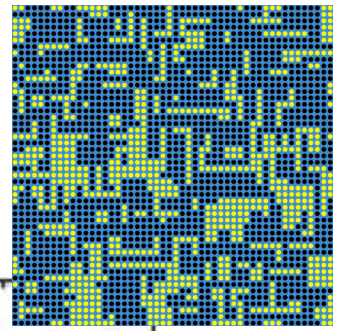
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

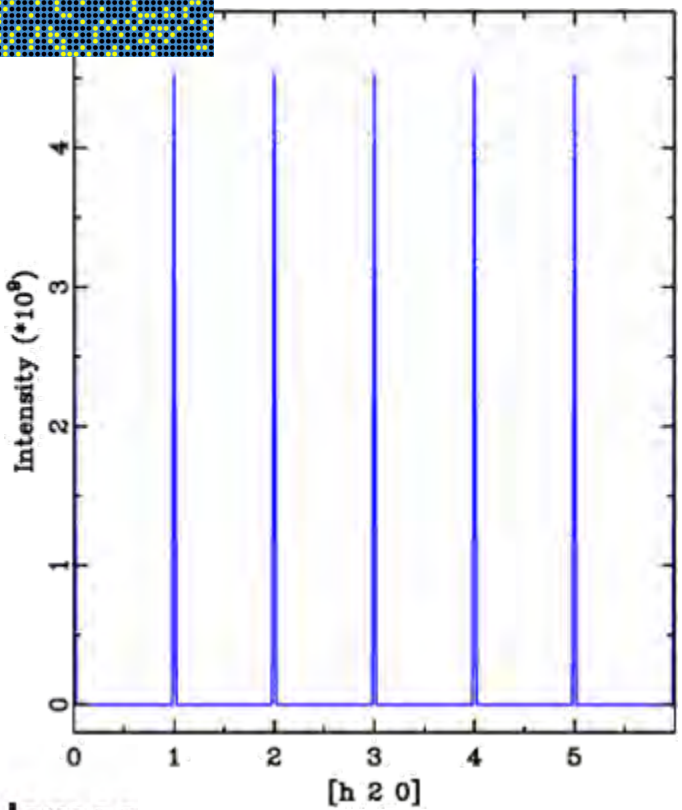
Properties might depend on vacancy ordering !!

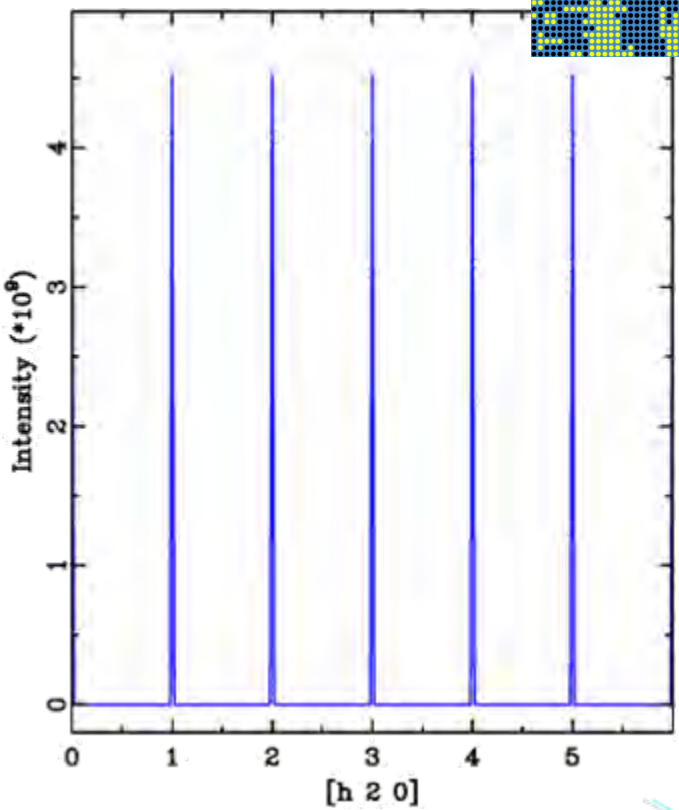
Bragg peaks are blind ..



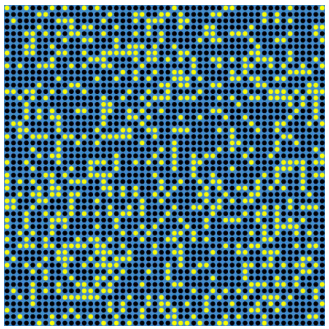
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.



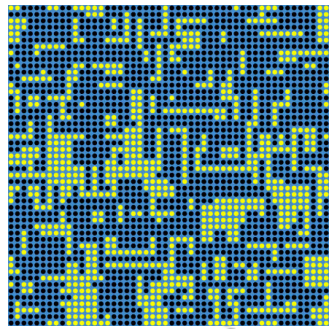


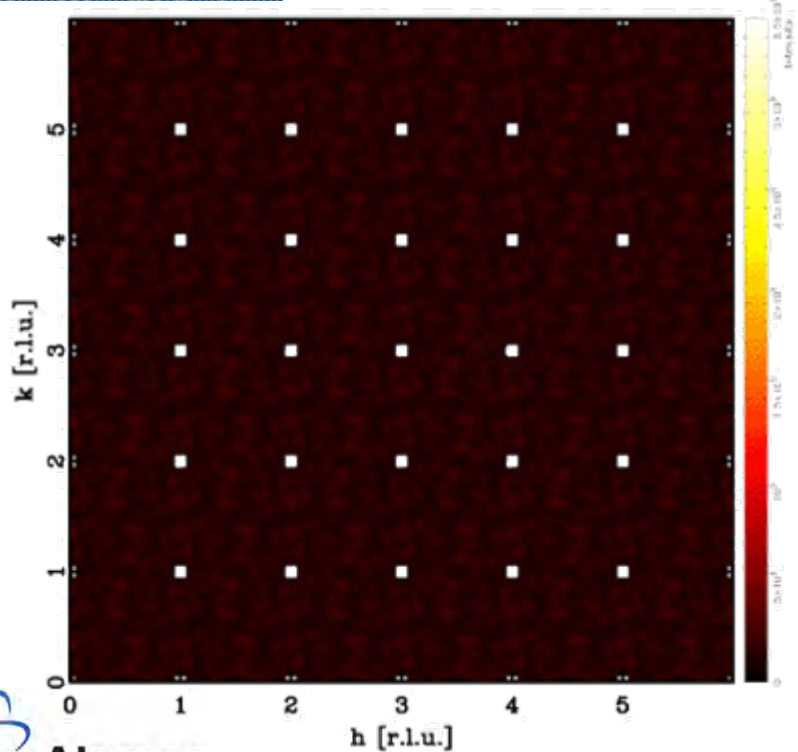


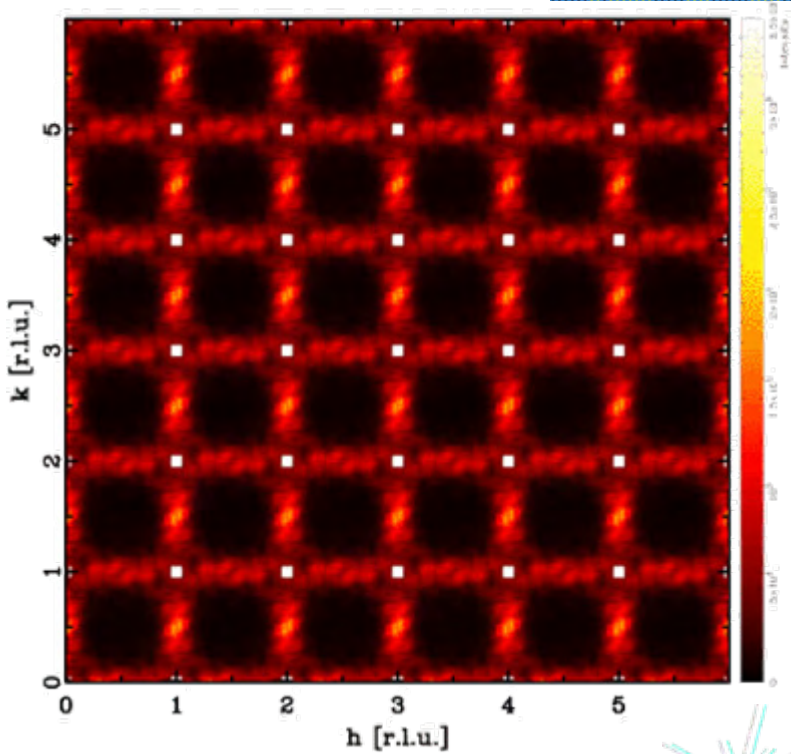
Diffuse scattering to the rescue ..



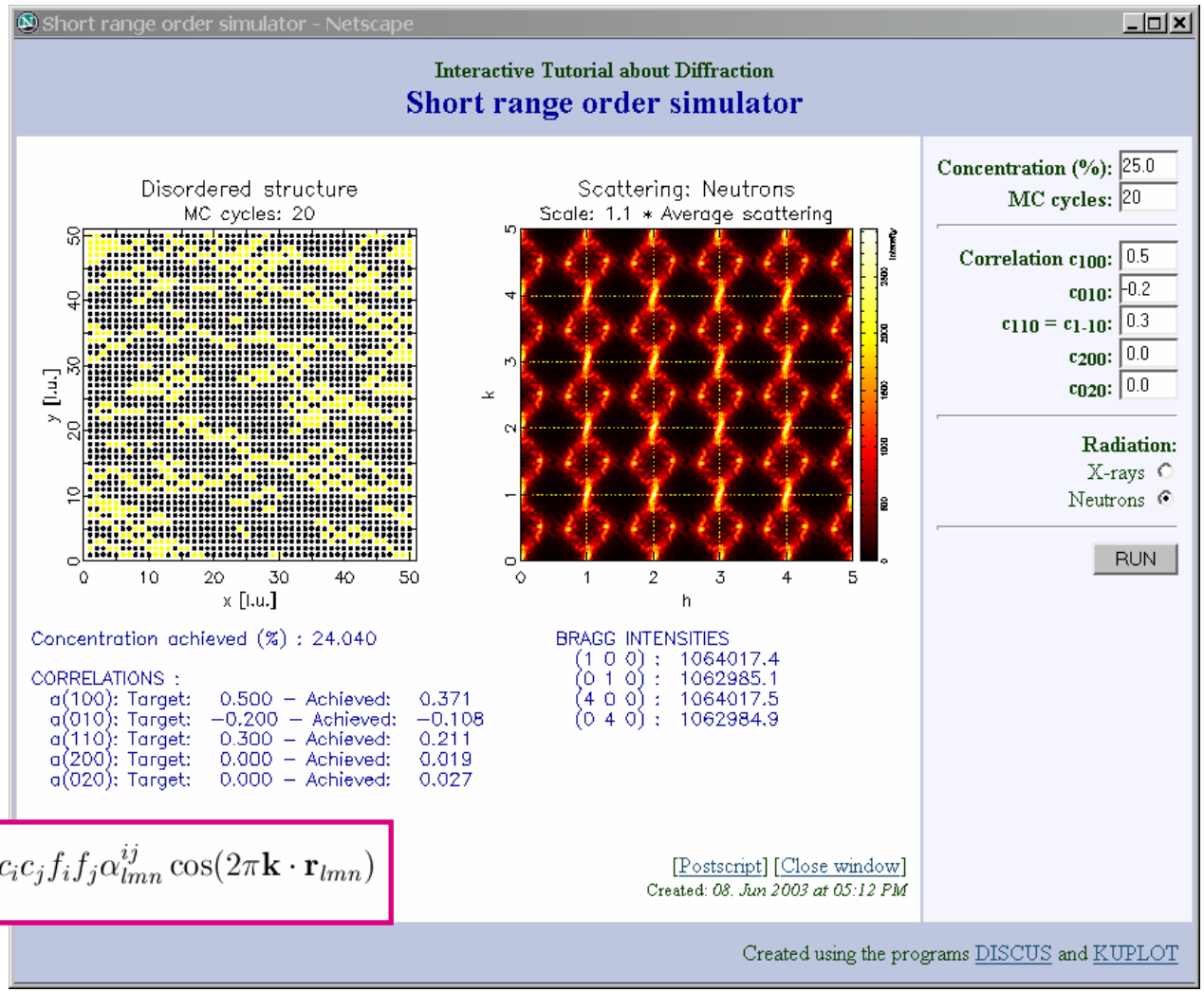
Diffuse scattering: Information about *two-body correlations*, *i.e.* chemical short-range order or local distortions.





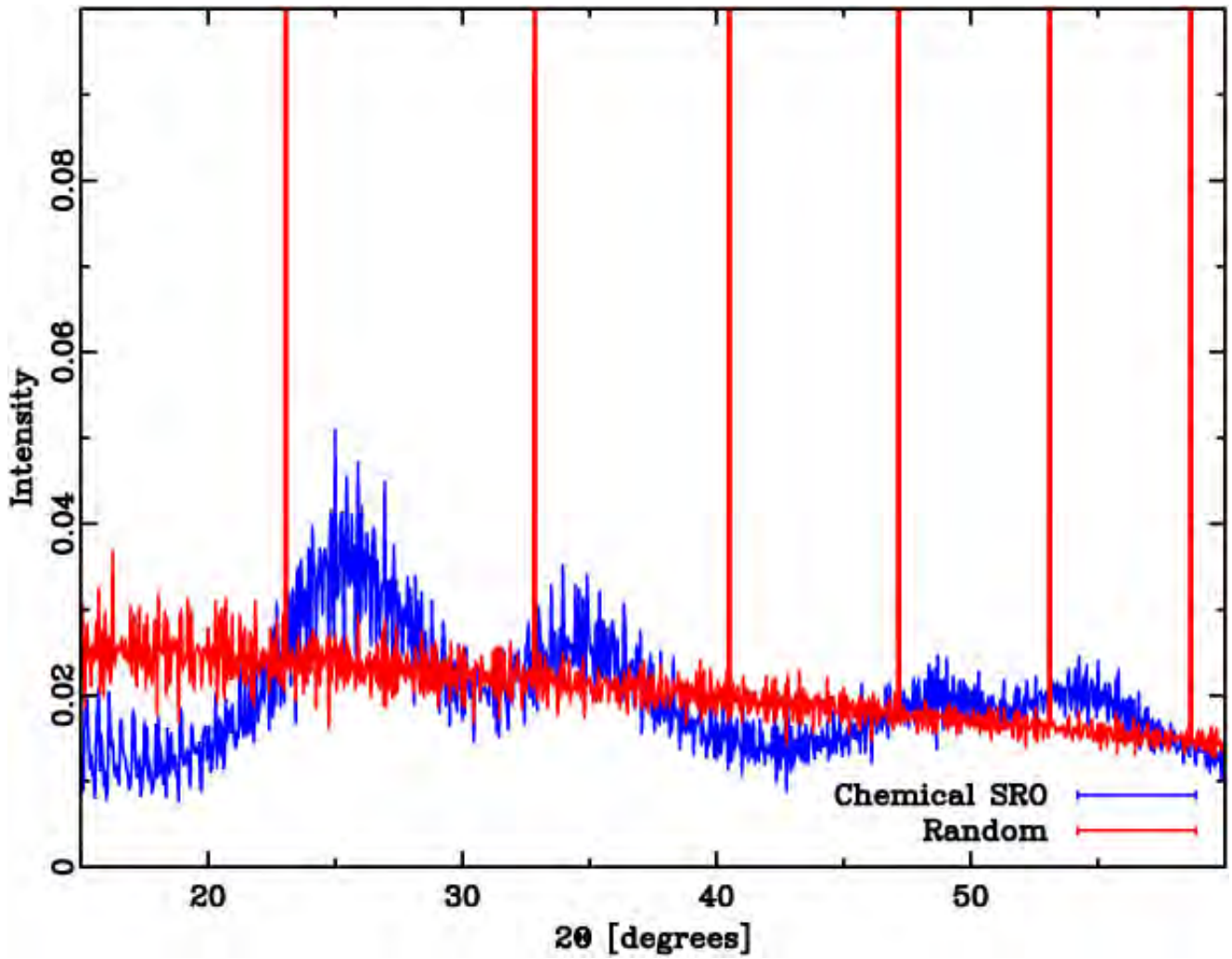


See http://www.totalscattering.org/teaching/

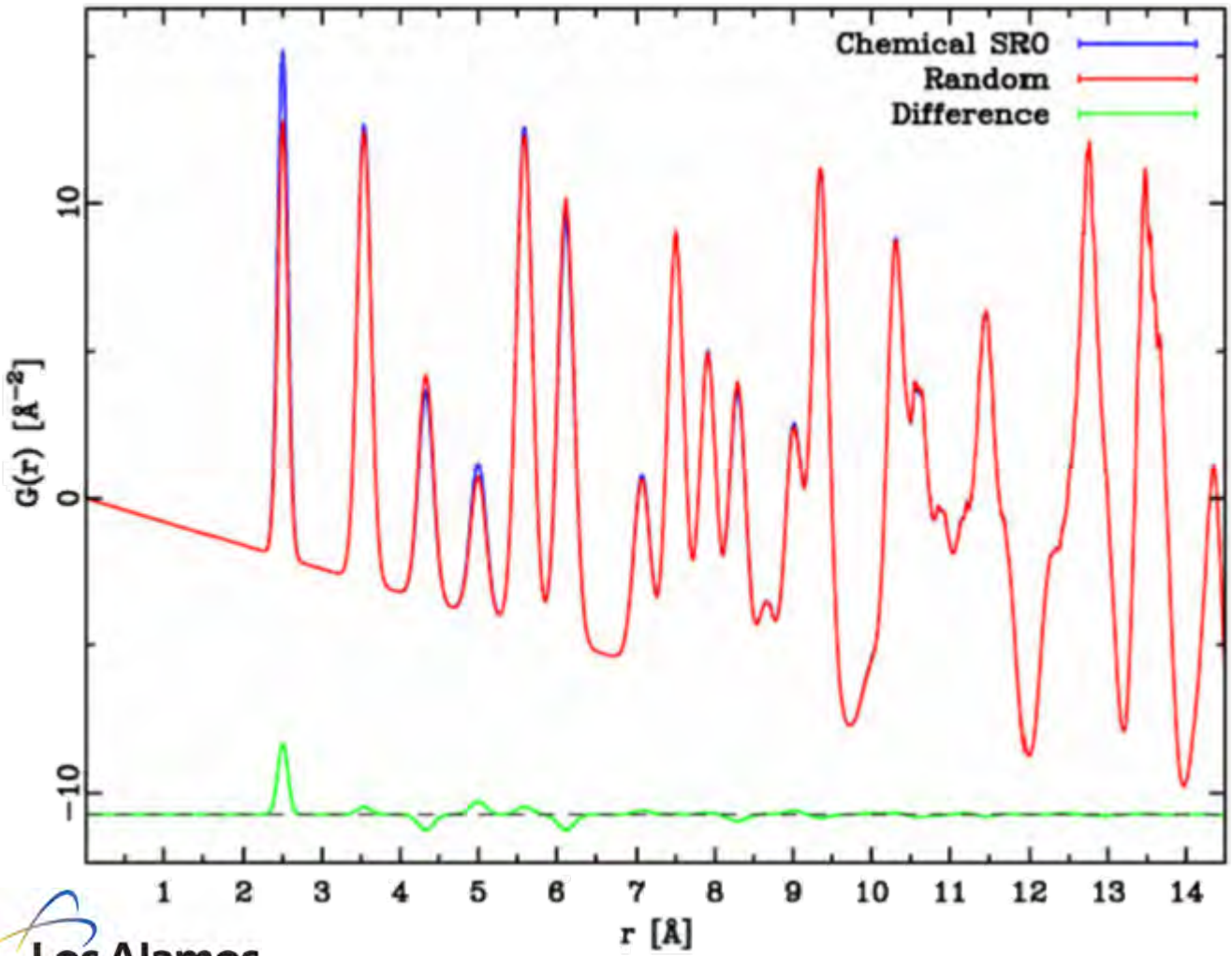


$$I_{\mathrm{sro}} = -\sum_{ij}\sum_{lmn} c_i c_j f_i f_j \alpha_{lmn}^{ij} \cos(2\pi \mathbf{k}\cdot\mathbf{r}_{lmn})$$

How about powder diffraction ?



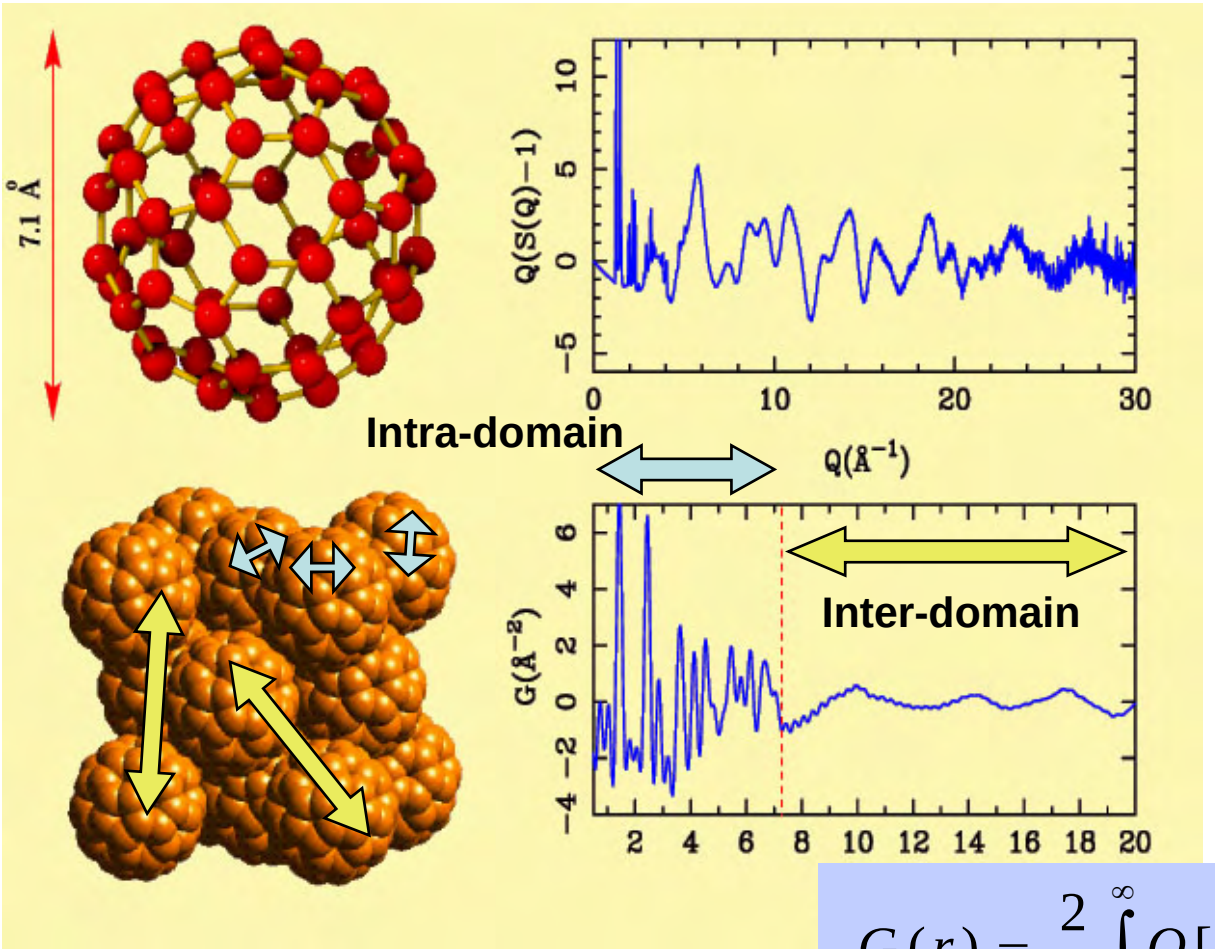
Finally the Pair Distribution Function (PDF)



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

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

What is a PDF?



Example:
C_{60} - 'Bucky balls'

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

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

$$Q = 4\pi\sin\theta/\lambda$$

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):

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

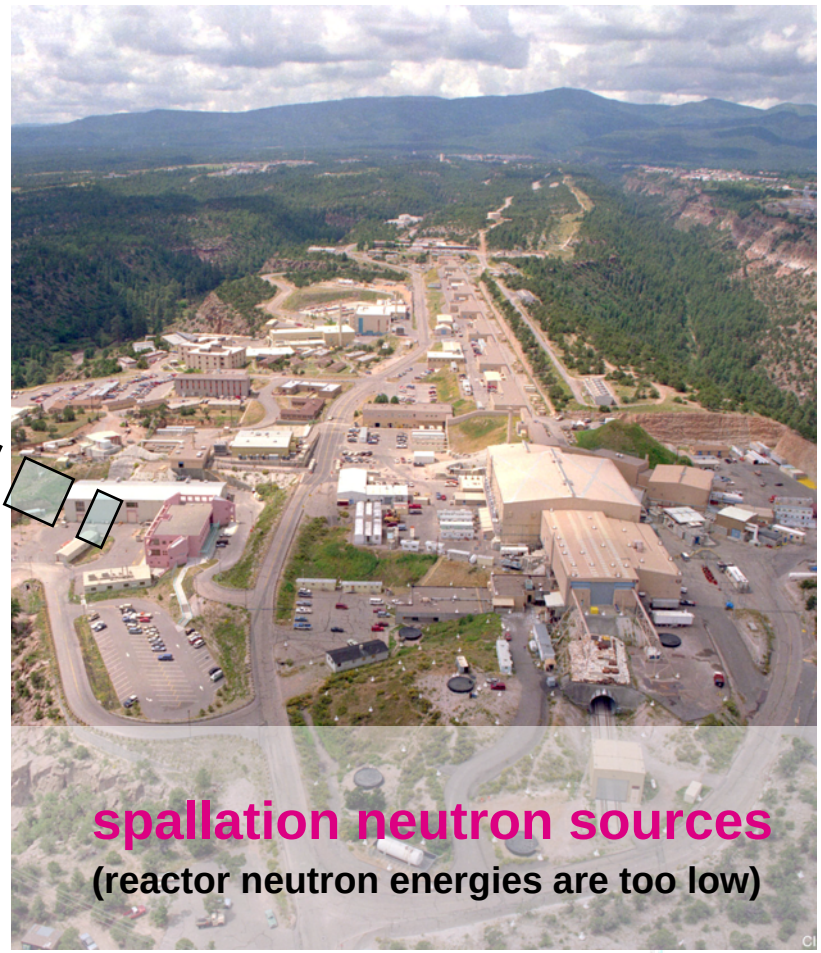
Requirements to obtain 'good' PDF:

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

Where ?

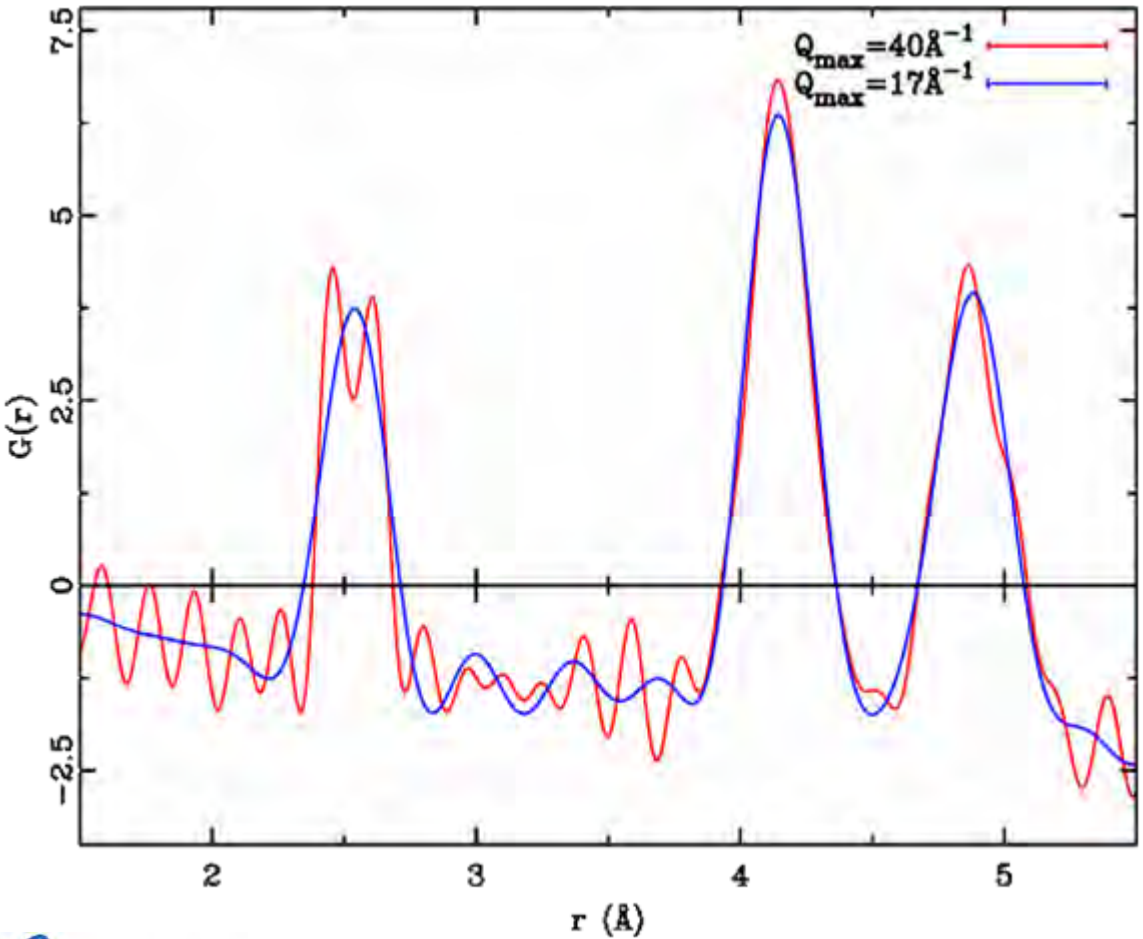
Synchrotron sources
(high energy X-rays)

or



spallation neutron sources
(reactor neutron energies are too low)

What makes a good PDF: Influence of Q_{max} …



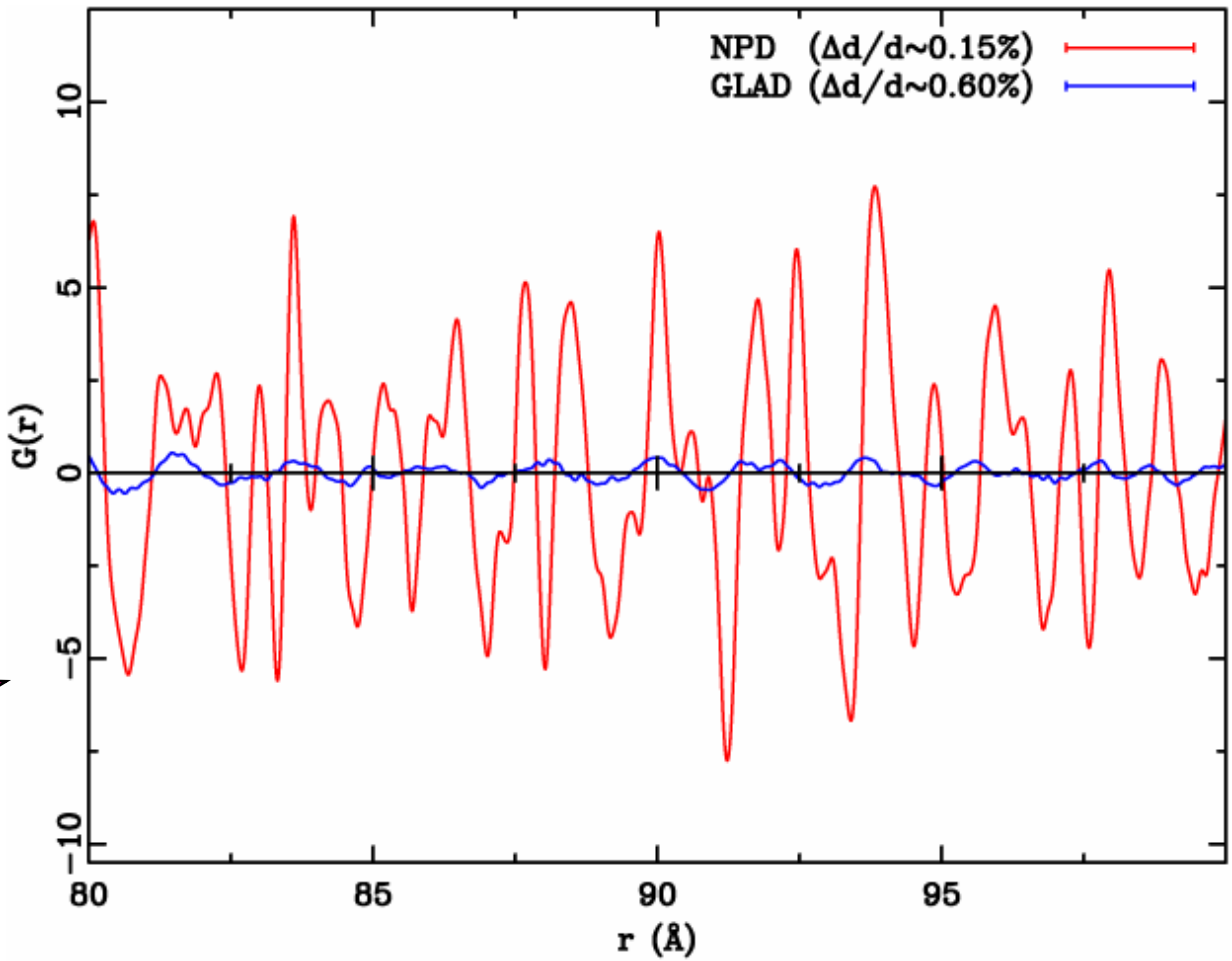
Termination of integral at Q_{max} results in convolution of G(r) with $\sin(Q_{max} r)/r$.

$ZnSe_{0.5}Te_{0.5}$ data collected on GEM terminated at 40 Å^{-1} and 17 Å^{-1}

NN split unresolved at 17 Å^{-1} !

What makes a good PDF: Influence of Q resolution …

Comparison of measurements of Nickel powder on instruments GLAD at IPNS and NPD at MLNSC.

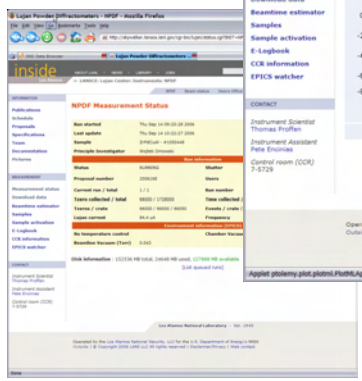


PDF goes "Nano"

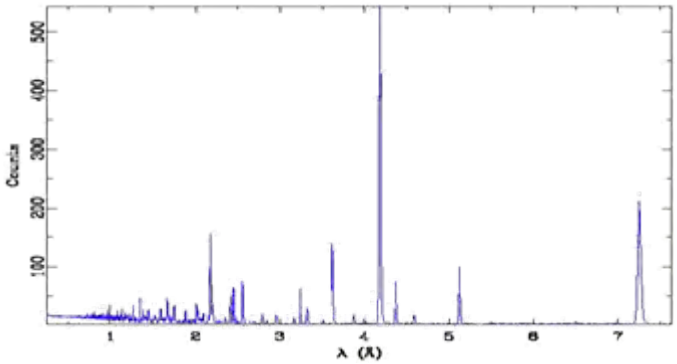
High Q resolution: Large *r* range (PDF dampened by *exp -(rΔQ)²/2)*)

NPDF: Overview

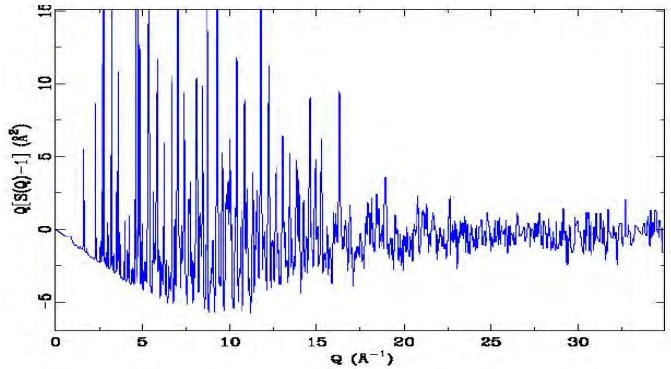
- Specifications
  - Upgrade finished Sep. 2002
  - L1: 32m, Q_{max}=50Å^{-1}, $\Delta d/d$=0.15%
  - Typical PDF measurement 1 - 4 hrs
  - Sample amounts down to 200 mg
  - Ancillary: 10K-1500K, soon: 0.5K, 11T
- Science
  - 95% PDF studies, hard matter
  - Many users *new* to PDF
  - Oversubscription in 2006: ~1.6
- Software
  - Web based instrument interface
  - Automatic creation of PDF
  - Integration in SNS data portal (soon)



Neutron data processing

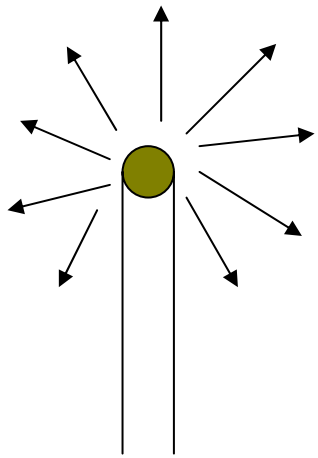


Corrections, Normalization, ..



Cylindrical Time-Of-Flight geometry (energy dispersive)

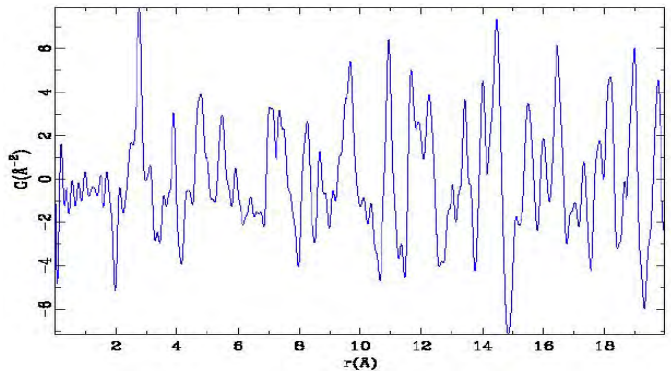
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin QrdQ$$



Typical characterization runs

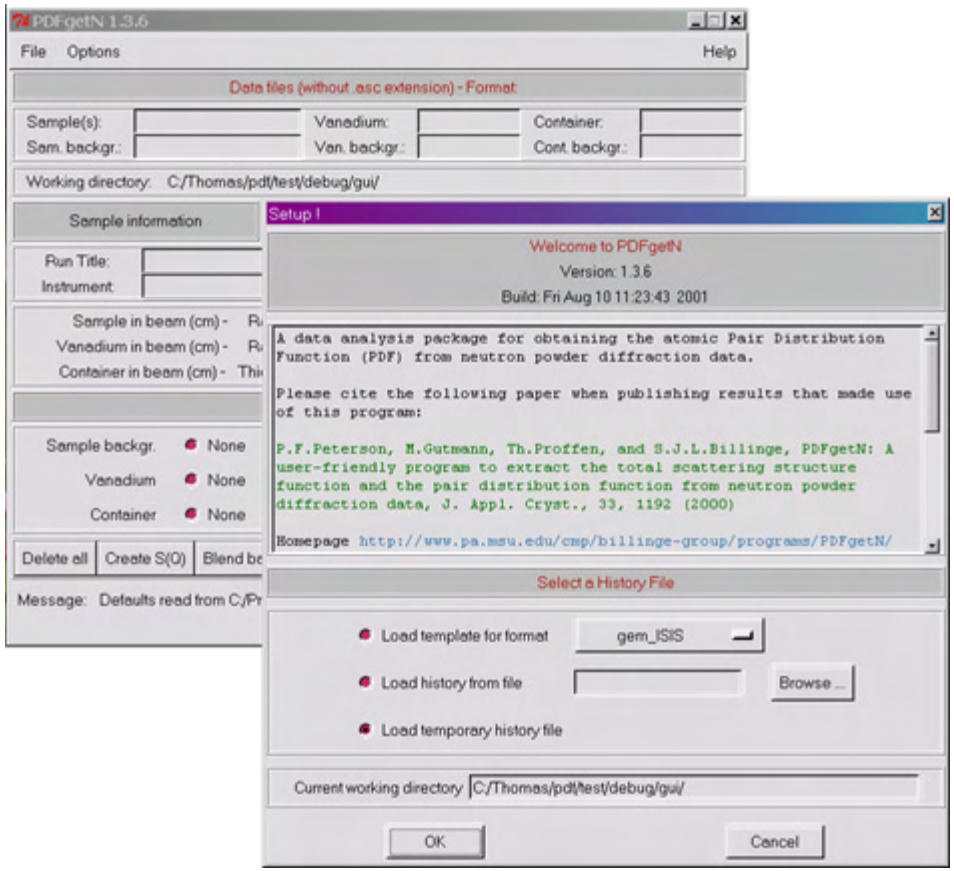
- Empty instrument (B)
- Empty Container (C)
- Empty Container background (CB)
- Vanadium (V)
- Vanadium background (VB)
- Sample (S)

$S_{corr}=[(S-SB)-\alpha(C-CB)]/[V-VB]$



PDFgetN

- Based on GLASS package.
- Graphical users interface & integrated plotting.
- Supports most TOF neutron powder file formats.
- Records all processing parameters as part of output files G(r) and S(Q).
- Runs on Windows 95/98/NT/2000 and UNIX



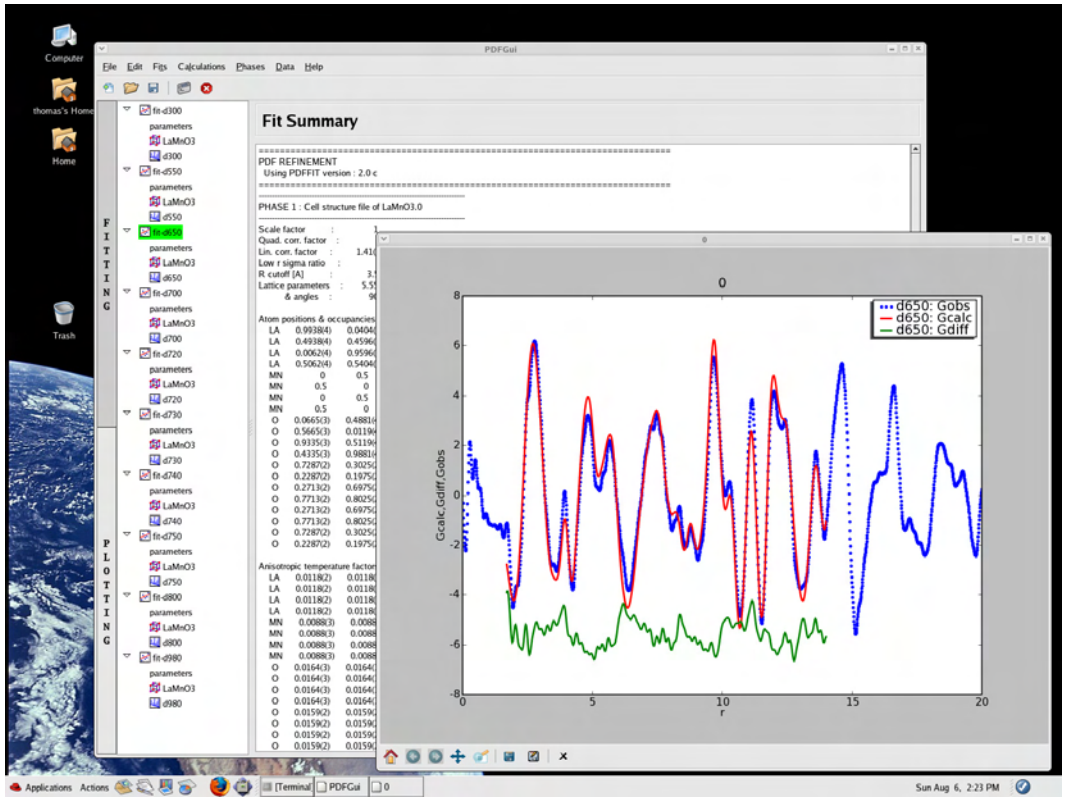
Peterson et al., *J. Appl. Cryst.* **33**, 1192 (2000)

How to model PDF data ?

- Single peak fitting
  - PDF peak position / widths as function of T,x,P,..
  - PDF peak widths as function of r $\Rightarrow$ correlated motion, ..
- Modeling based on structural model
  - Comparison to average crystal structure
  - **DISCUS:** Large model systems, using e.g. RMC
  - ***PDFFIT:*** 'Real space Rietveld' (few unit cells)
- Compare to theoretical predictions
  - let the theorist do the work ..

Next generation PDFFIT (under development)

- PDFFIT2 and PDFgui
- Part of the DANSE project.
- NSF award of ~$12M.

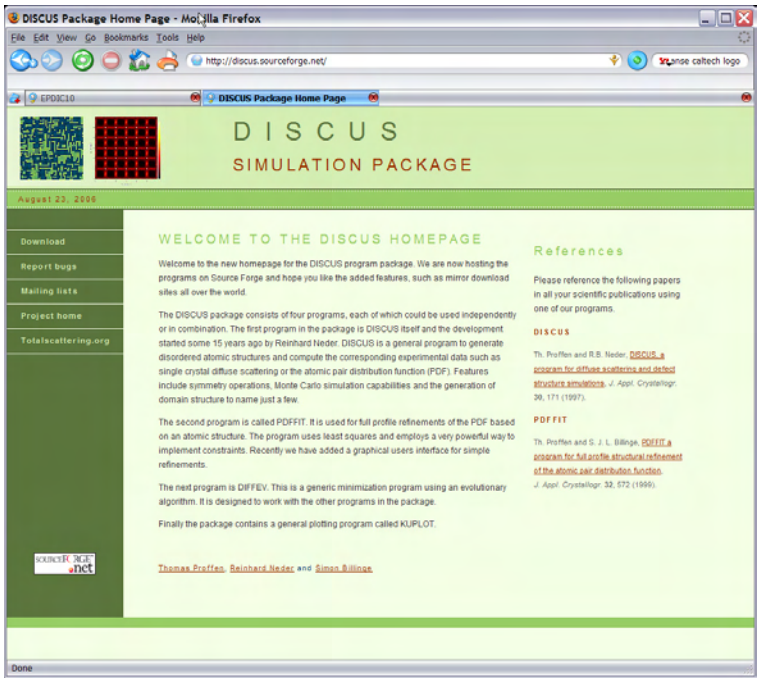


http://wiki.cacr.caltech.edu/danse/index.php/Main_Page

Downloads

http://discus.sourceforge.net

http://pdfgetn.sourceforge.net



Examples

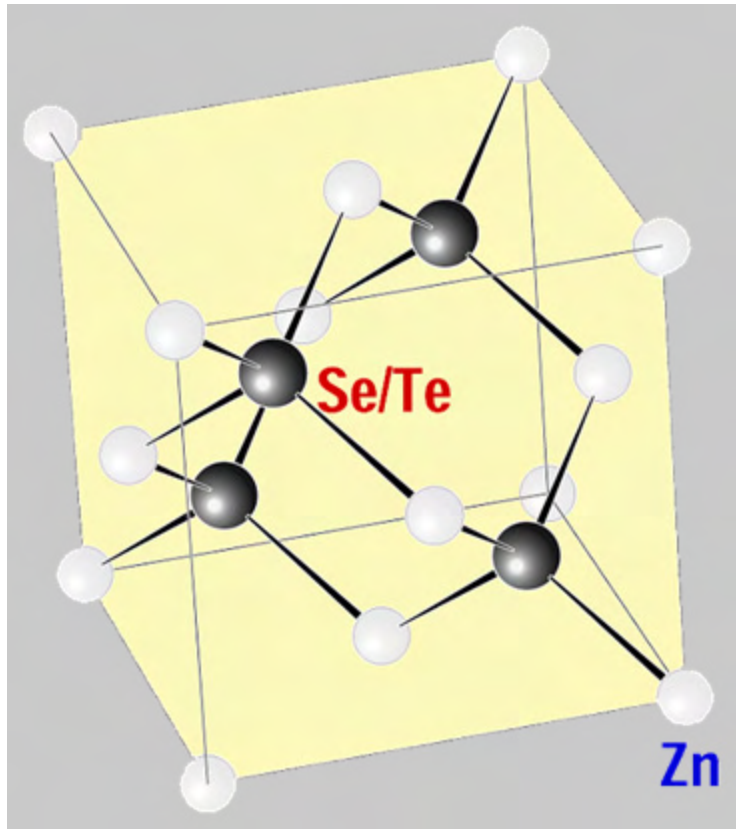
Local atomic strain in $ZnSe_{1-x}Te_x$

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

Facilities: IPNS, Lujan
Funding: DOE, NSF

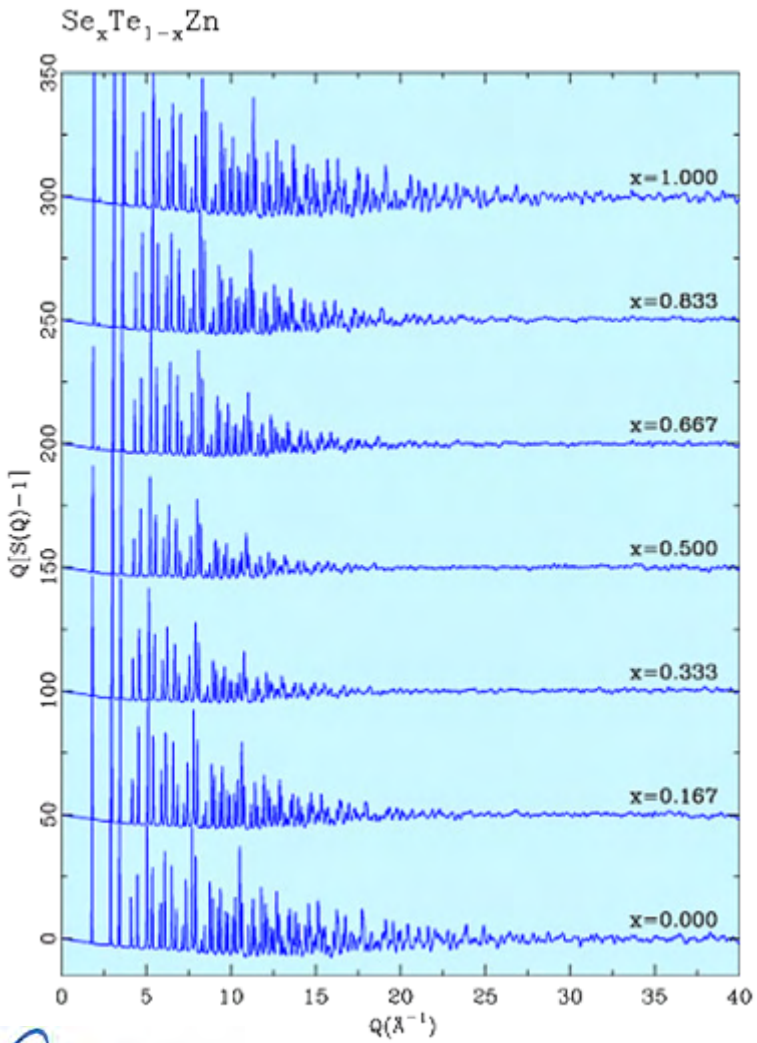
$ZnSe_{1-x}Te_x$: Structure

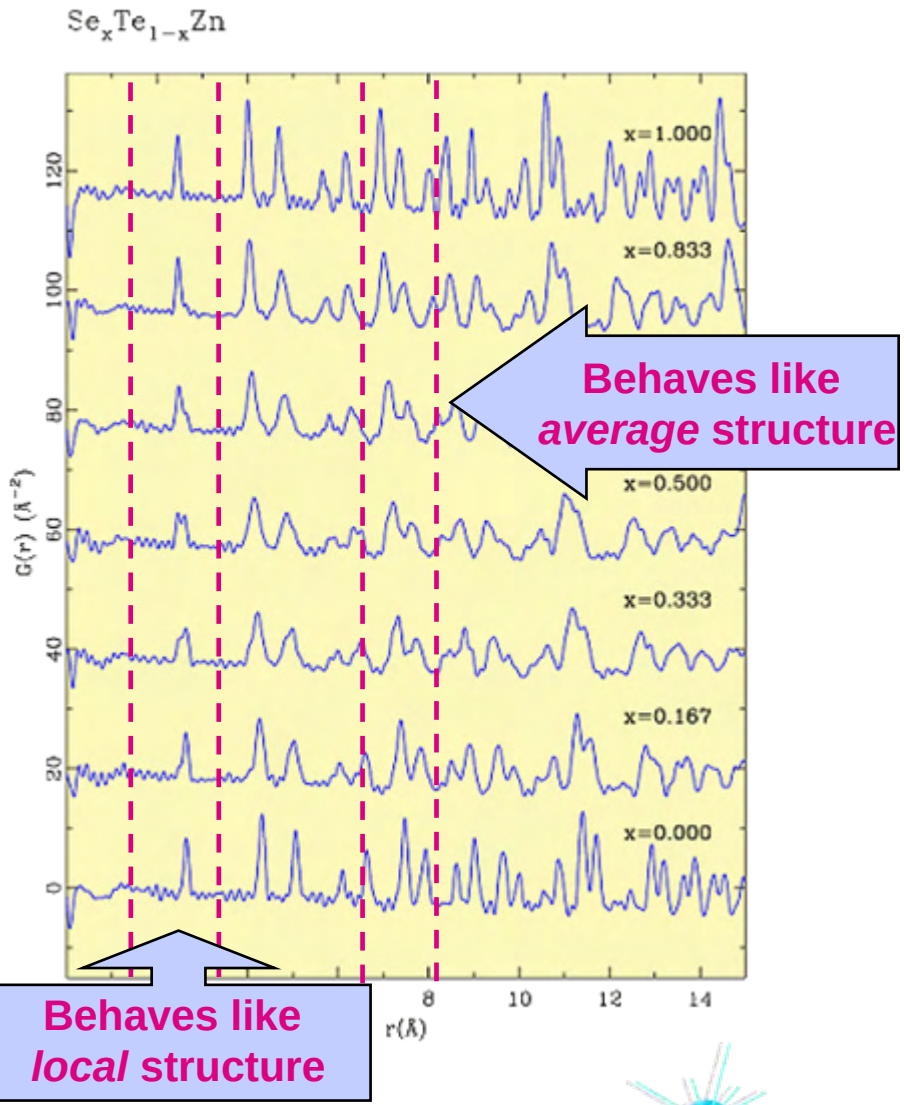
- Zinc blend structure (F43m)
- Technological important : Electronic band gap can be tuned by the composition *x*.
- Bond length difference *Zn-Se* and *Zn-Te* $\Rightarrow$ strain.
- Local structural probe required !



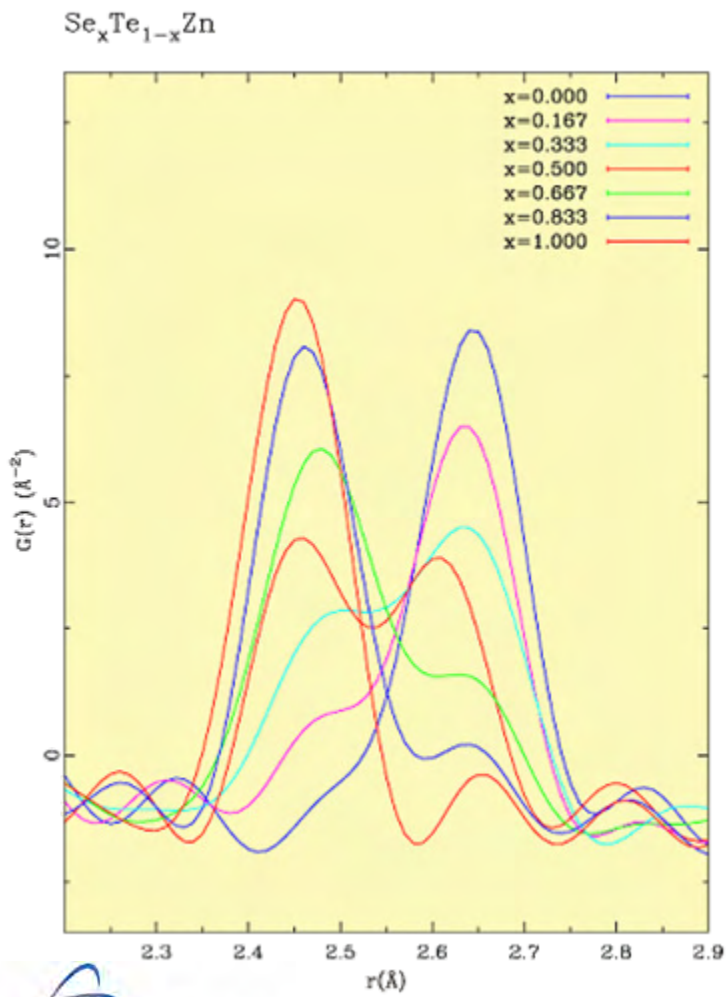
$ZnSe_{1-x}Te_x$: Total scattering

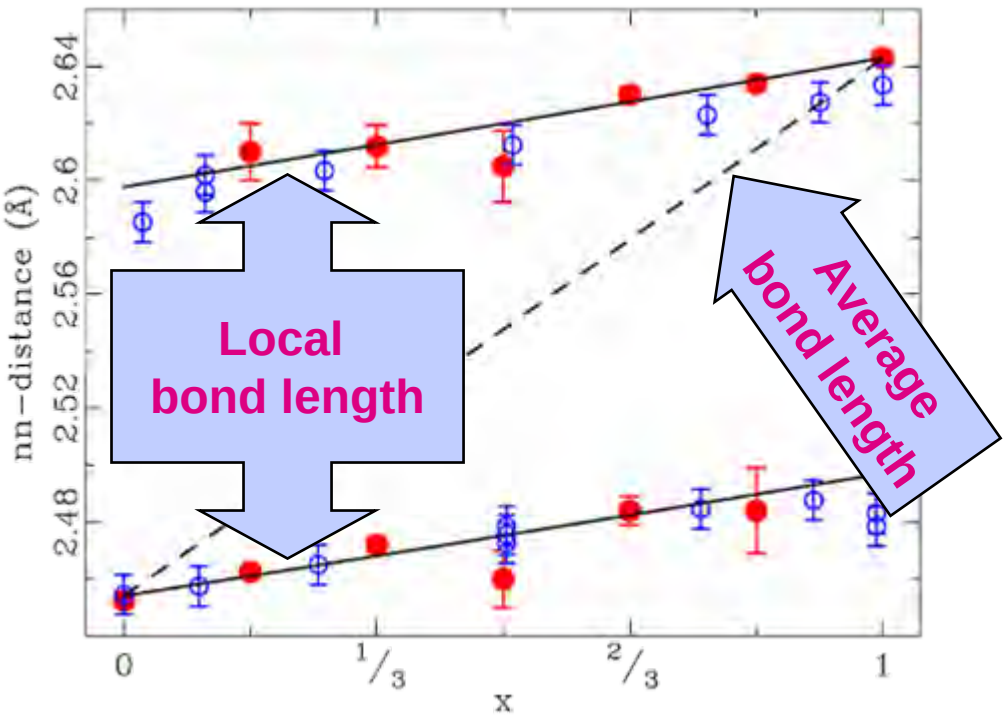
Peterson et al., *Phys. Rev.* B**63,** 165211 (2001)





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





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

Jahn Teller Distortion in $LaMnO_3$

Simon Billinge
Emil Bozin
Xiangyn Qiu

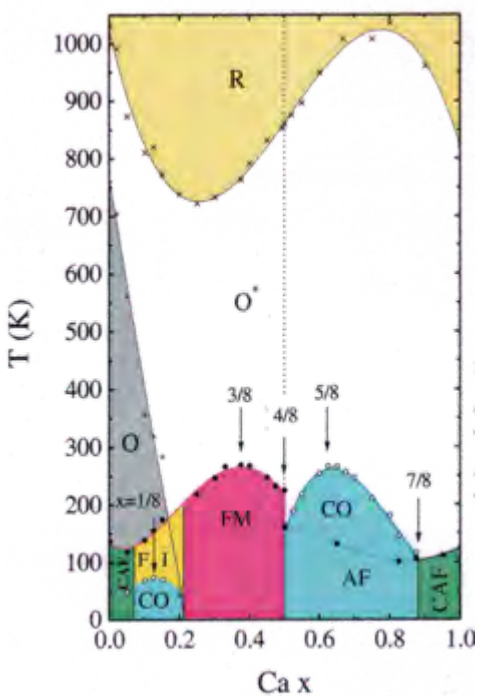
MICHIGAN STATE UNIVERSITY

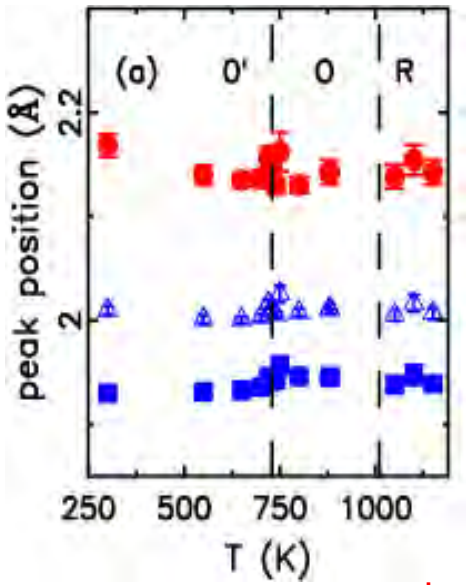
Thomas Proffen

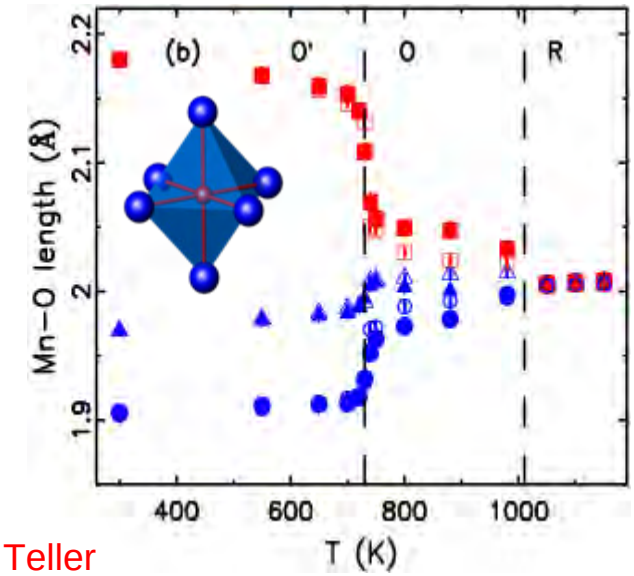
Los Alamos

Facilities: Lujan
Funding: DOE, NSF

$LaMnO_3$: Jahn-Teller distortion







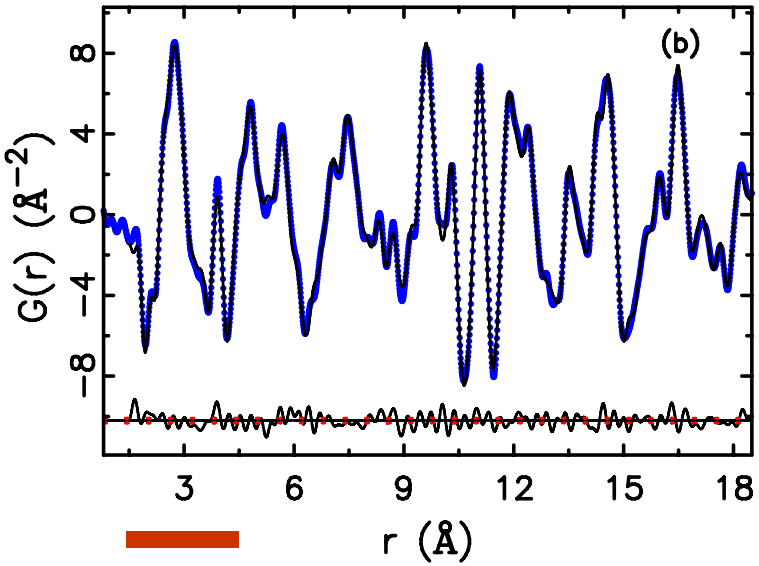
Jahn Teller
Long Mn-O bond

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).

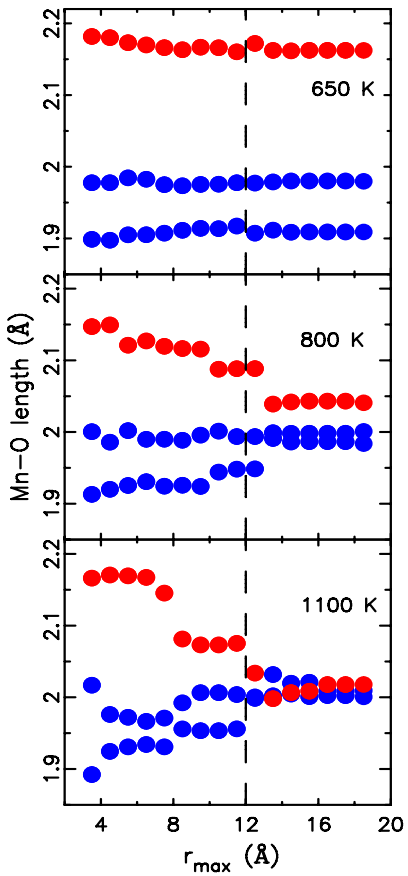
$LaMnO_3$: Jahn-Teller distortion



Local

Average

Intermediate ?



Mn-O bonds

O

O'

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).

“Complete” Structure of Gold Nanoparticles

Katharine Page

Thomas Proffen

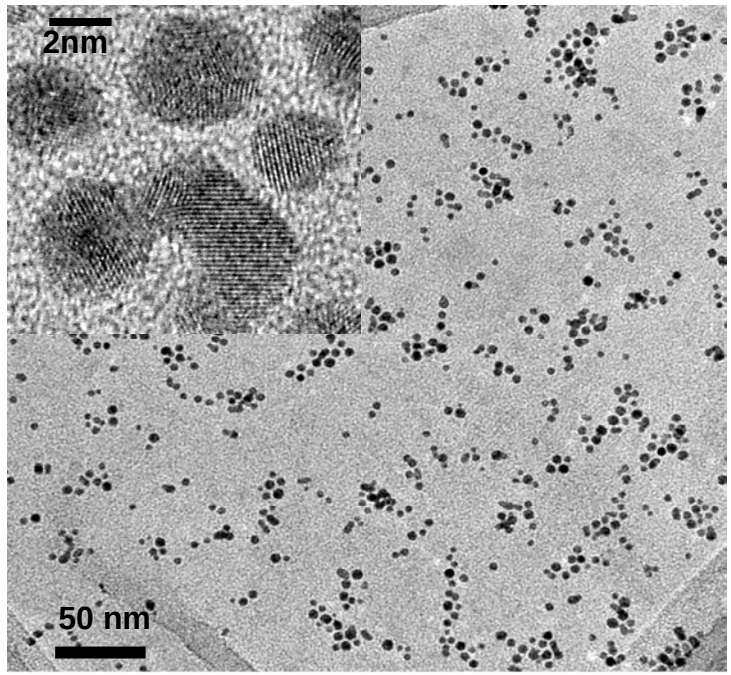
Ram Seshadri
Tony Cheetham

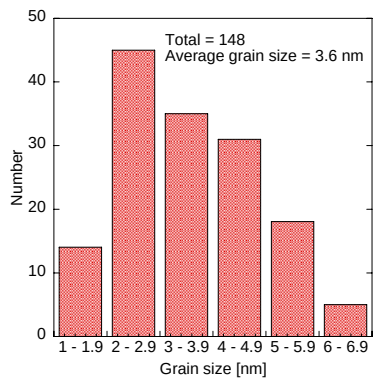
Facilities: Lujan
Funding: DOE, NASA

Example: Gold nanoparticles

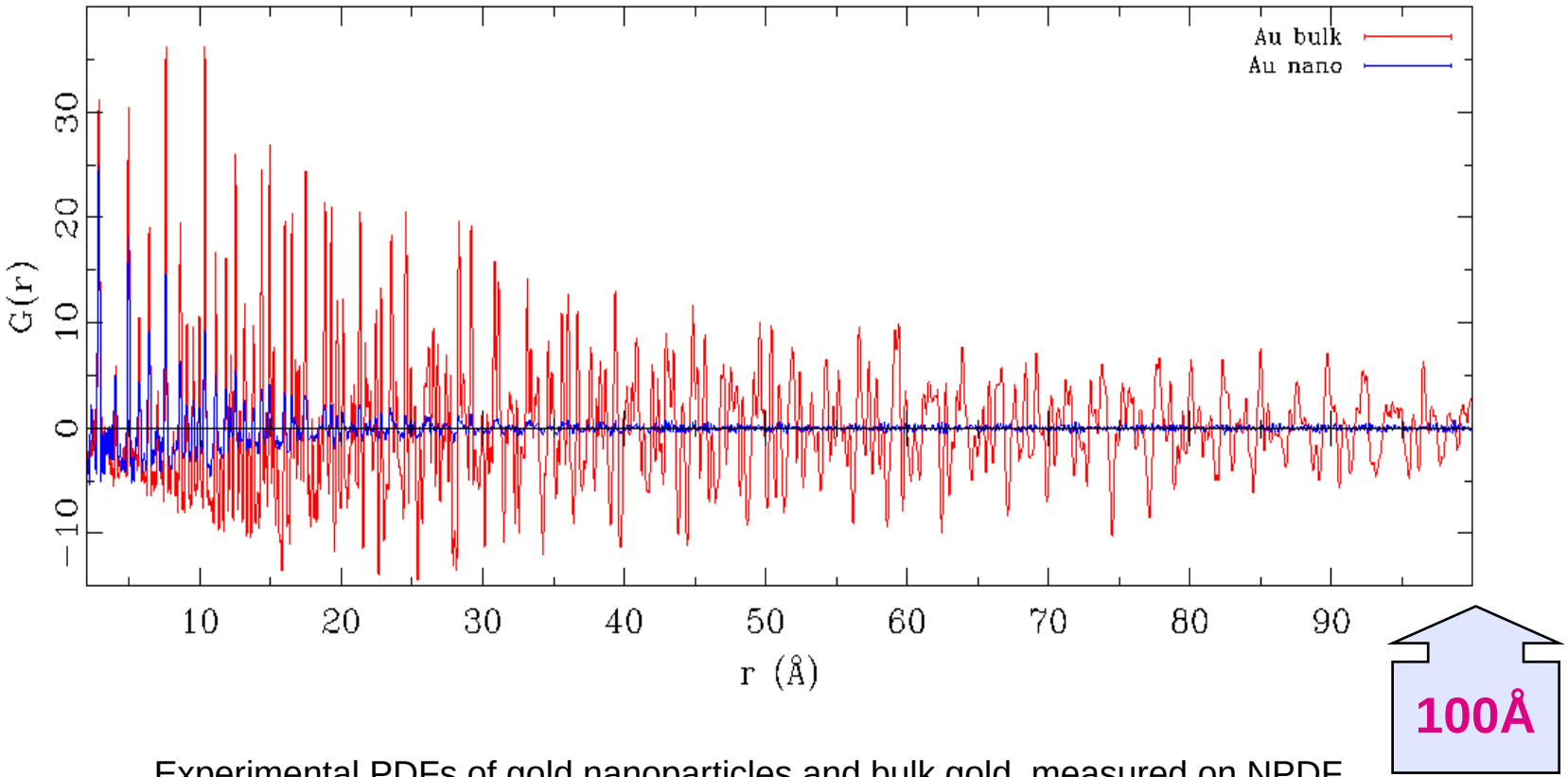
- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.

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





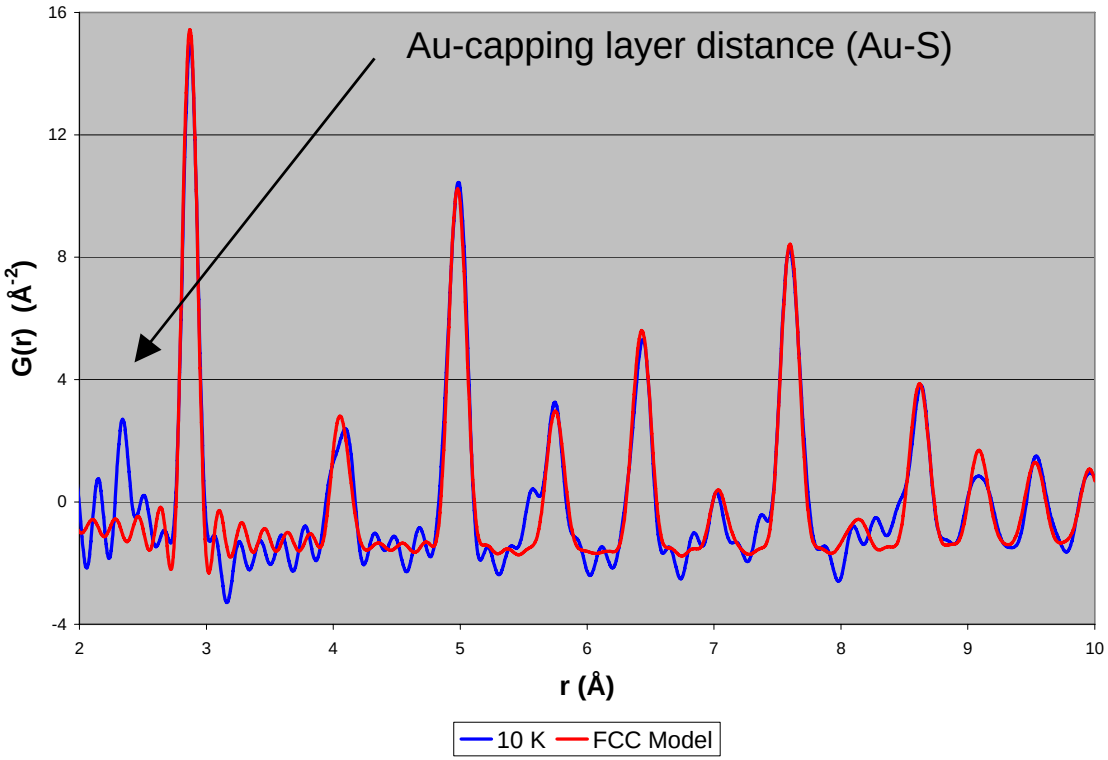
Au nanoparticles : Nano *vs*. bulk



Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF.

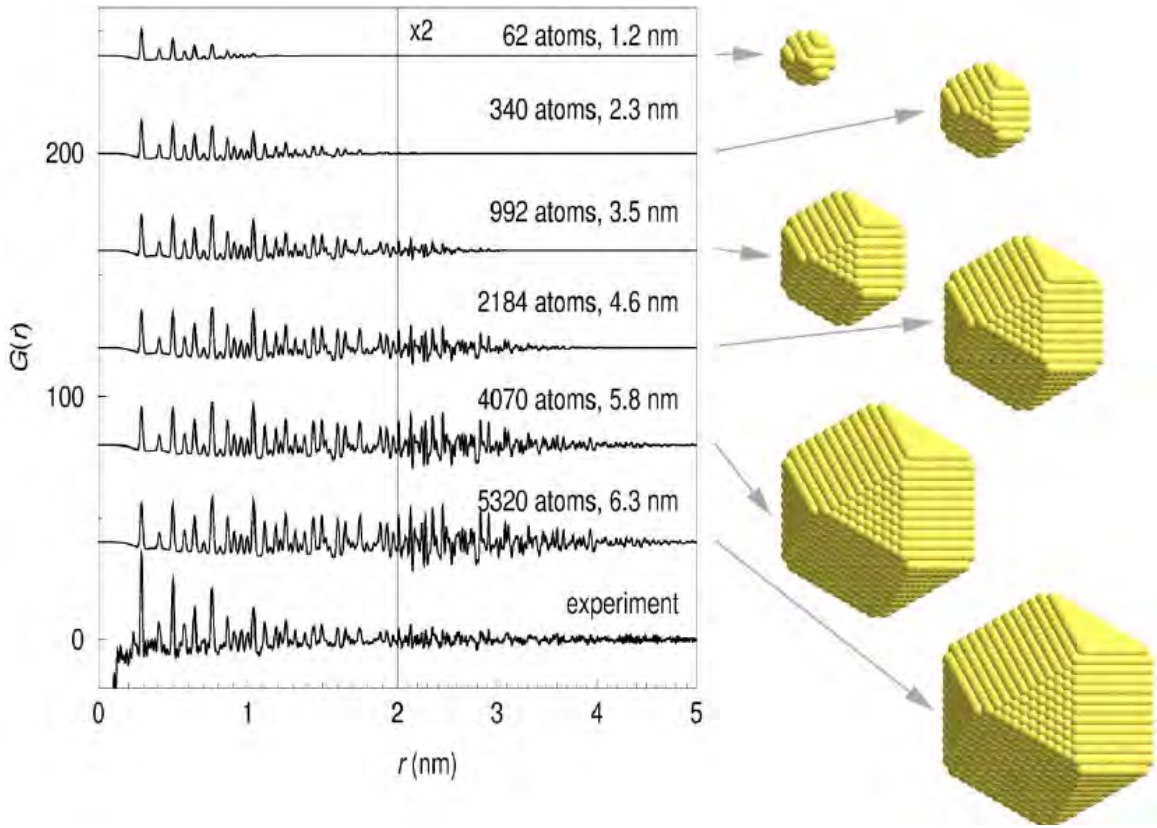
Au nanoparticles : Structural refinements

- PDF from nano- and bulk gold refined using PDFFIT.
- Nanoparticles show “normal” gold structure.
- No indication of surface relaxations.
- $a_{bulk} < a_{nano}$
- Indication of Au-cap distances



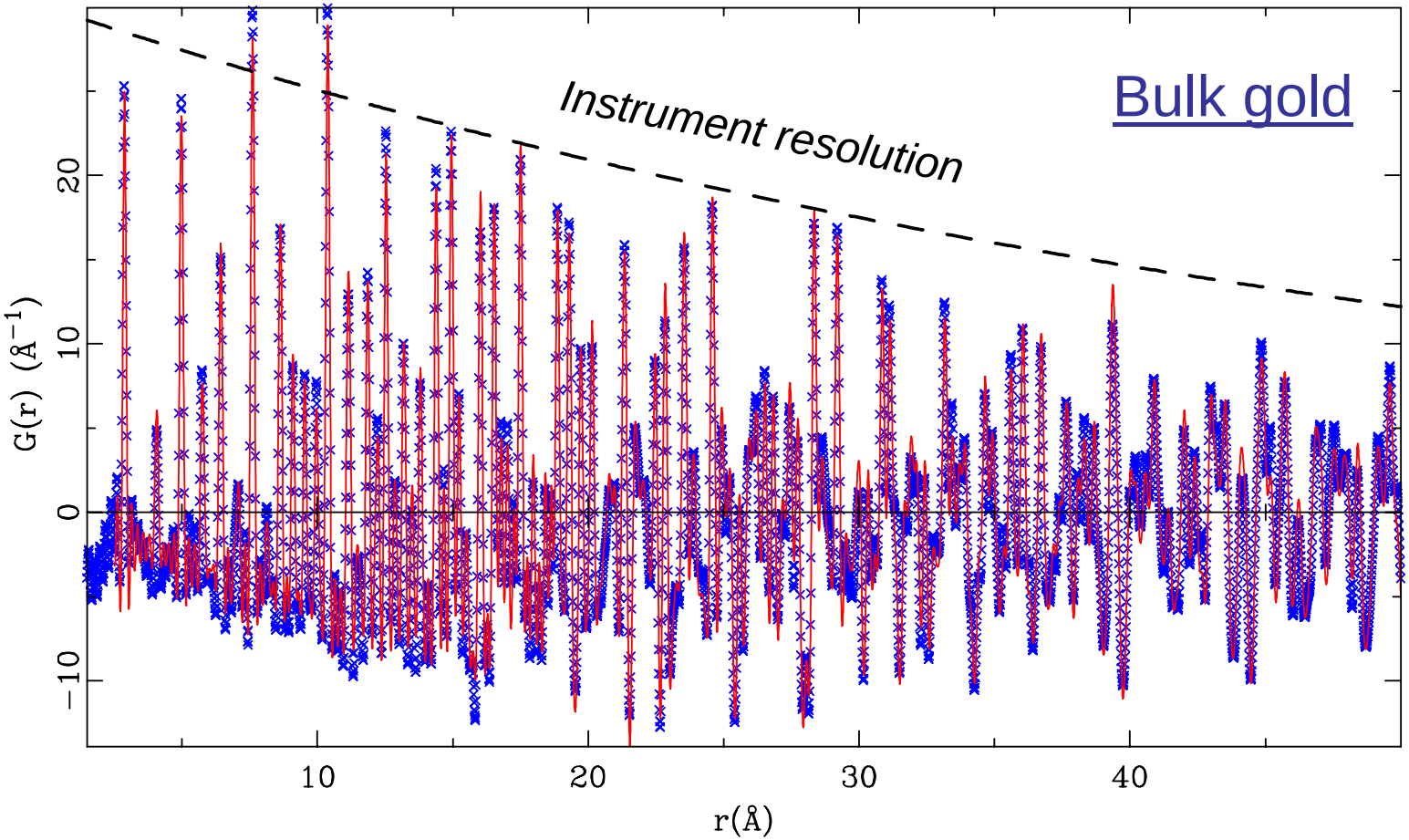
K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

Au nanoparticles: Particle size

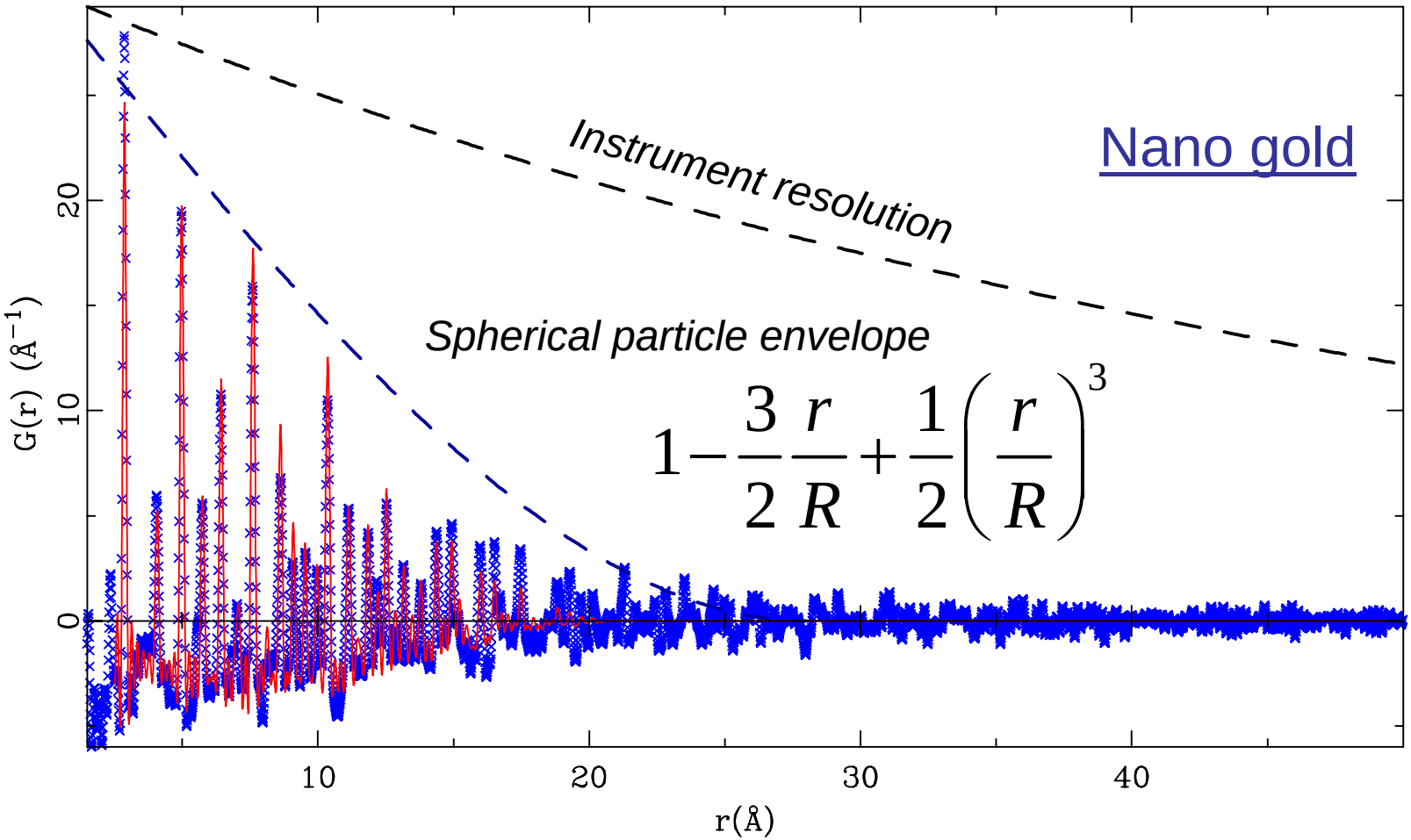


We're dealing with a length scale that can be simulated on an atom by atom basis, perhaps opening the door to extremely detailed refinements.

Au nanoparticles: Particle size



Au nanoparticles: Particle size



R.C. Howell, Th. Proffen and S.D. Conradson, **The pair distribution function and structure factor of spherical particles**, *Phys. Rev. B* **73**, 094107 (2006).

Local structure in sandstone

Katharine Page
Christina Herrera

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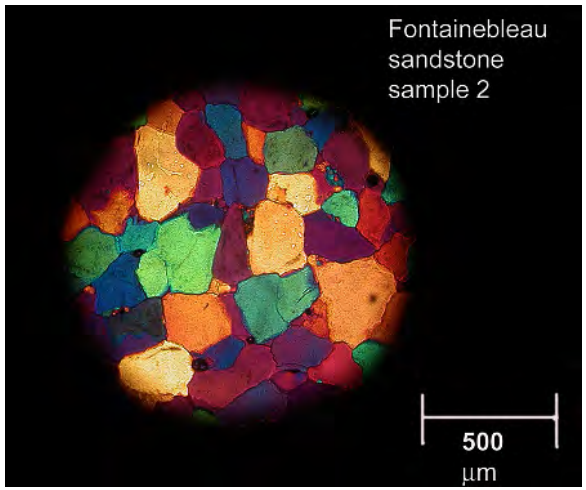
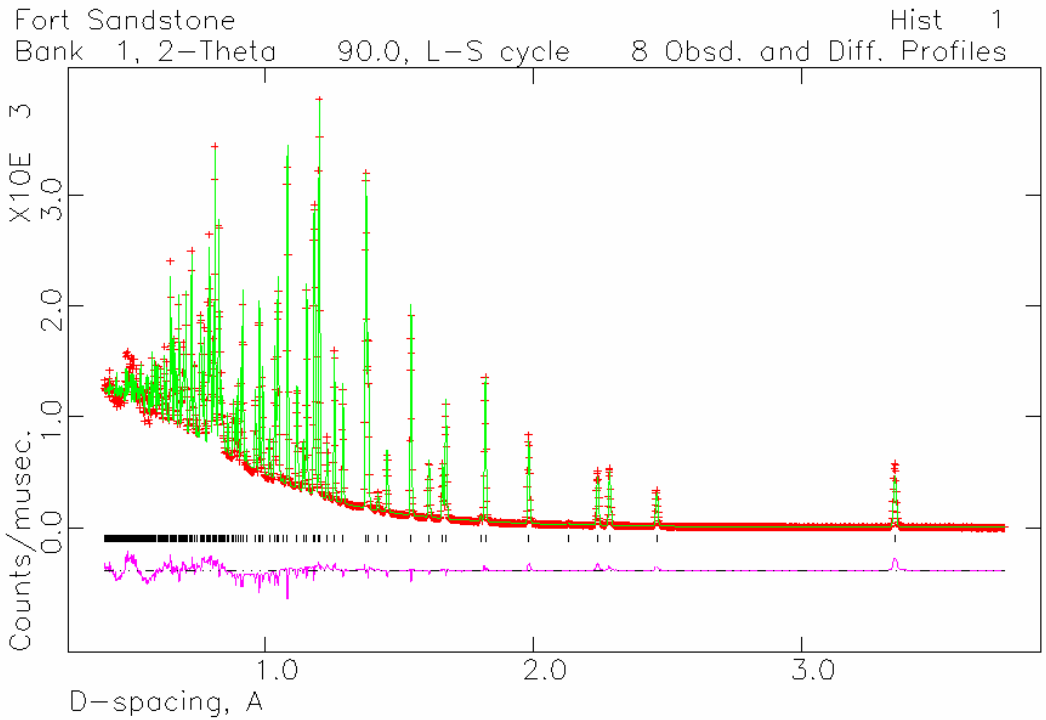
Facilities: Lujan
Funding: DOE, NSF

Sandstone: Crystalline quartz ?

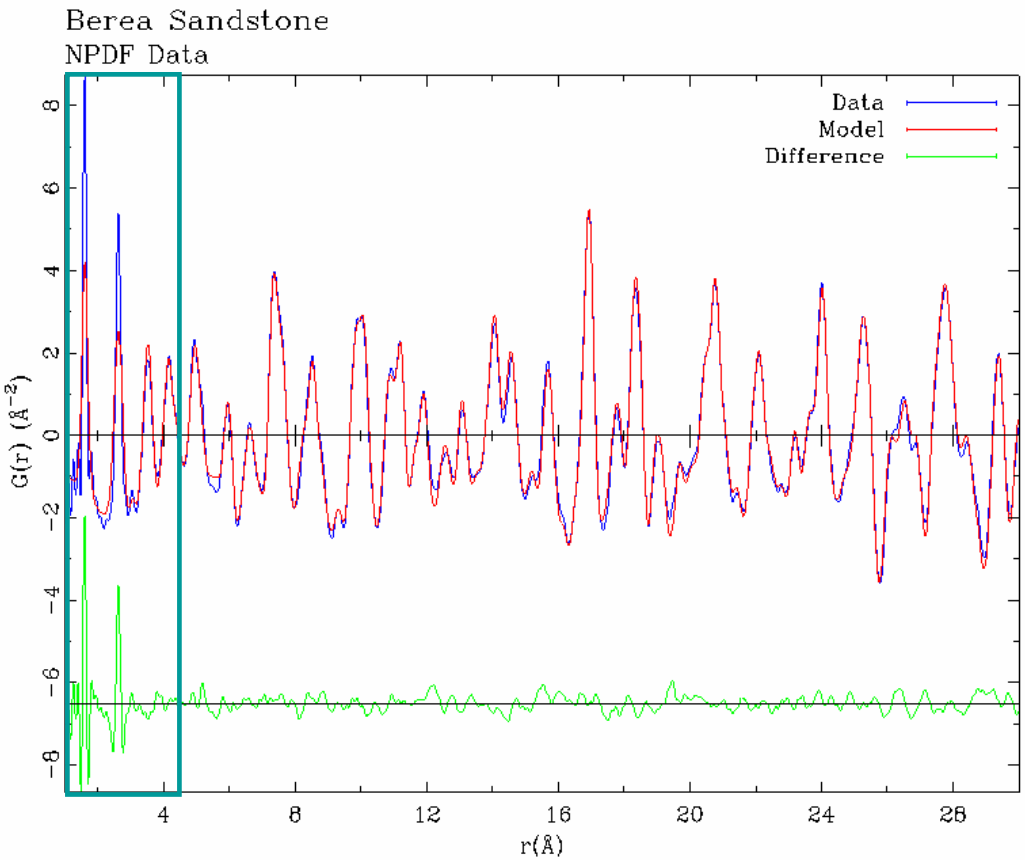




- Measured on NPDF
- High statistics data (24 hrs)
- Solid rock sample
- Ambient conditions – sealed to avoid taking up of water
- Motivation: Structural explanation for non-linear acoustic properties

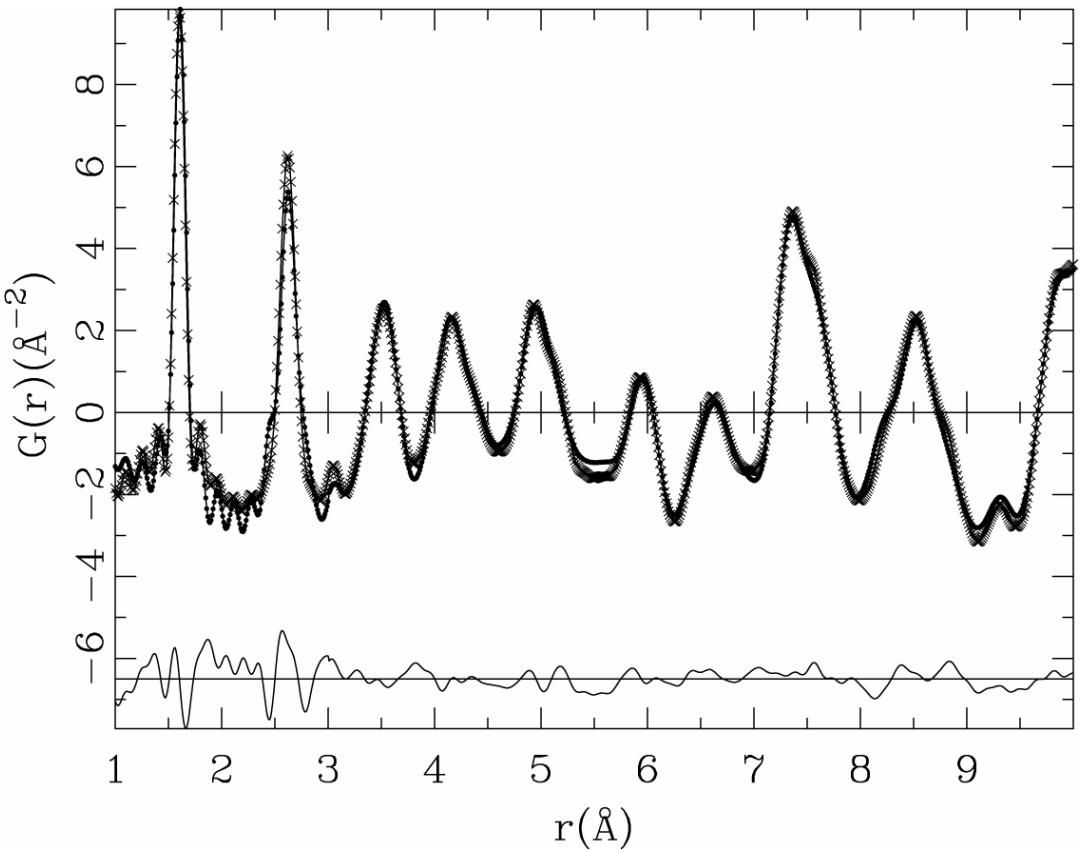
Sandstone: Local structure

- Refinement of single phase quartz model.
- Good agreement above r > 3Å.
- Missing “intensity” in first two PDF peaks corresponding to Si-O and O-O NN distances.



Sandstone: Local structure

- Refinement of two phases :
  - Crystalline quartz
  - “Amorphous” quartz up to 3Å
- Good agreement over complete range
- Amorphous regions “stress formed” by point like contacts at grain contacts ?



K.L. Page, Th. Proffen, S.E. McLain, T.W. Darling and J.A. TenCate, **Local Atomic Structure of Fontainebleau Sandstone: Evidence for an Amorphous Phase ?**, *Geophysical Research Lett.* **31**, L24606 (2004)

Nano-structured transition metal carbides

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(PhD work)

Ram Seshadri
Tony Cheetham

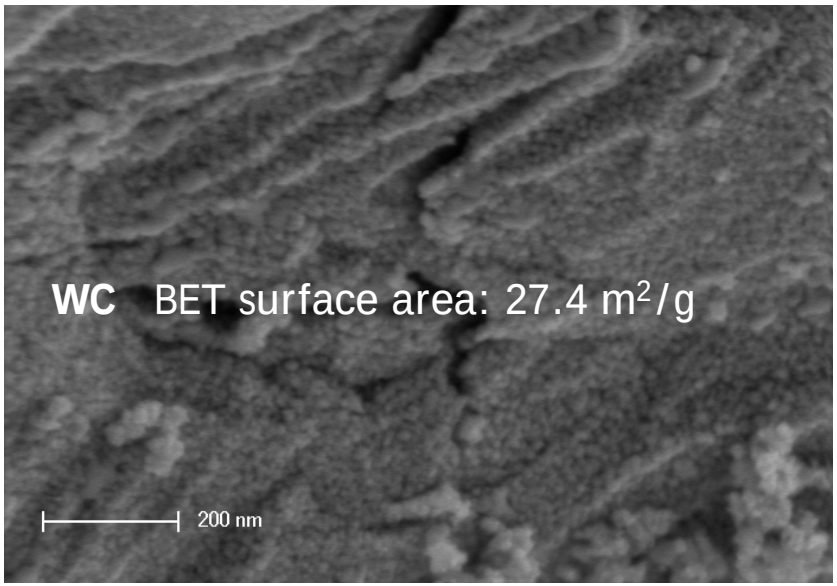
Thomas Proffen

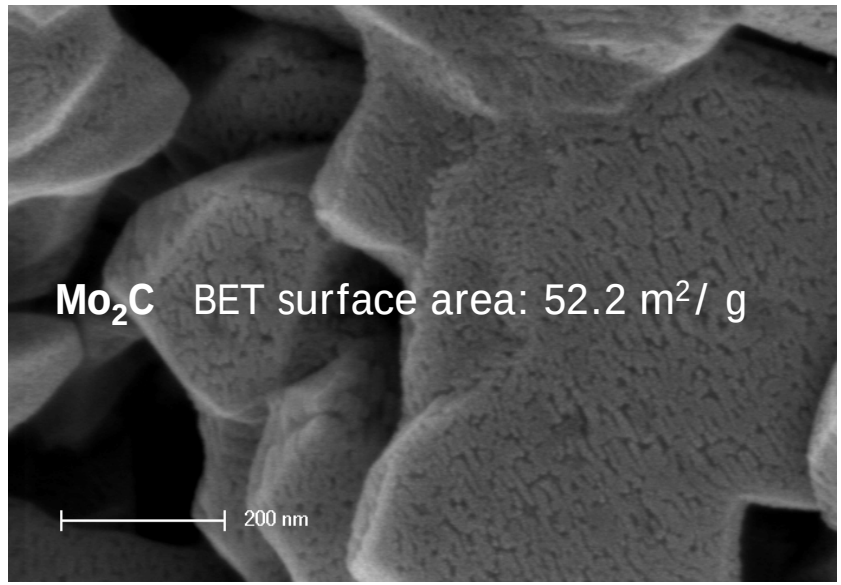
Facilities: Lujan

Nanostructures transition metal carbides

Catalytic activity of platinum group metals with greater thermal stability and resistance to poisoning.

Nanostructured Mo and W carbide will provide higher surface area than traditionally prepared materials.

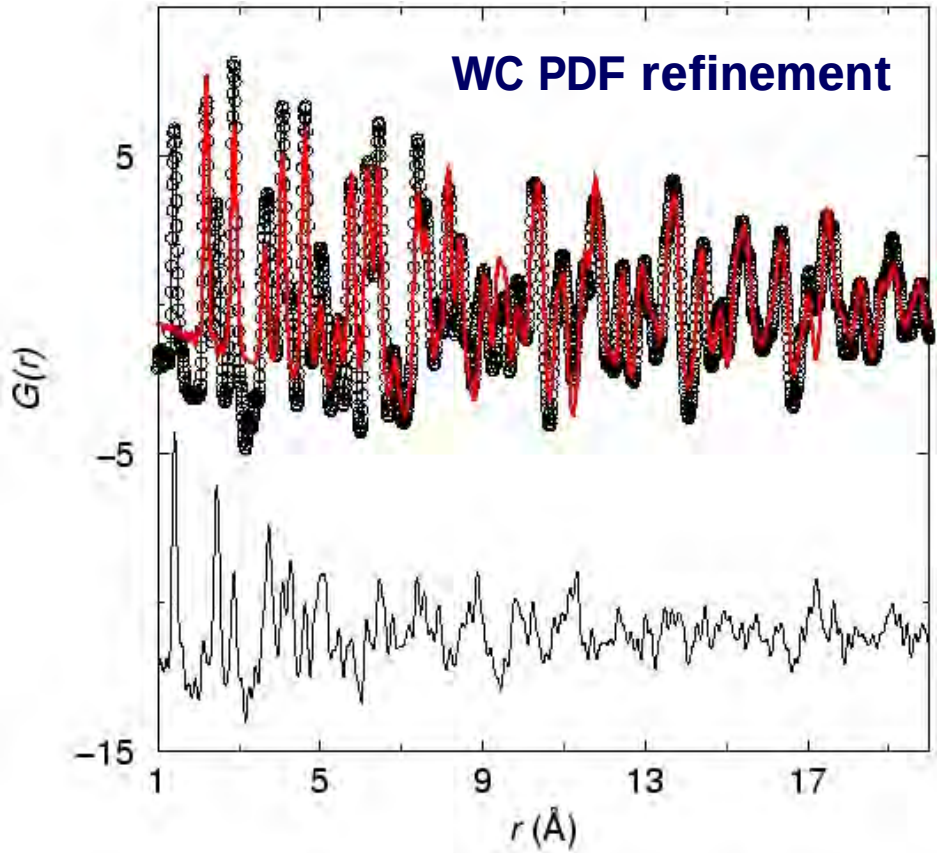


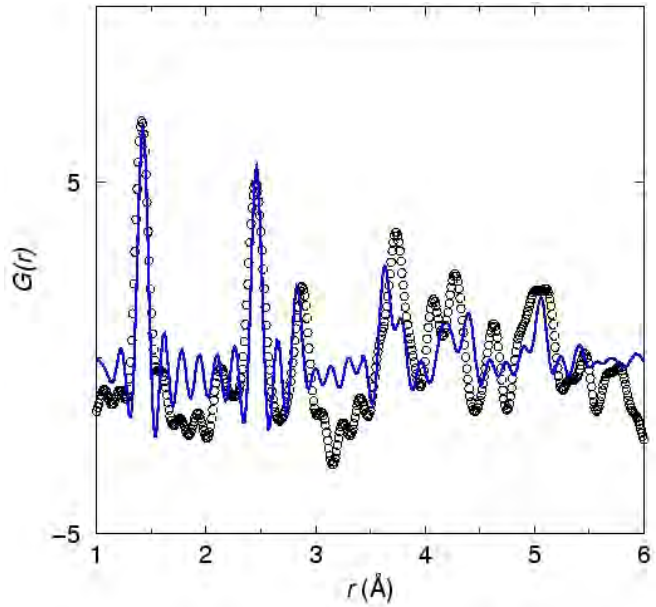


Prepared by treating molybdtates/tungstates in a quartz tube with flowing 50%-H_2/CH_4 at 10 mL/min at elevated temperatures.

NPDF measurements

XPS studies suggest there is a significant contribution of non-carbide carbon.
It is known that graphitic carbon can block almost all of the active surface.

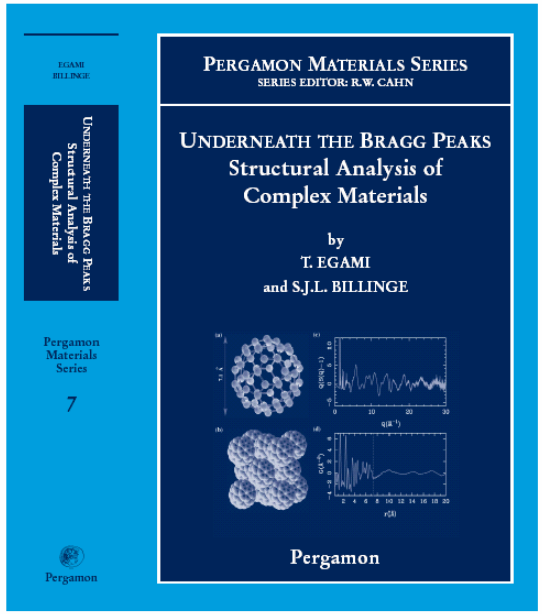




The difference curve, fit with the graphite structure.

Summary and more information

- 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