Understanding Short- and Medium Range Order in Materials Using Total Scattering

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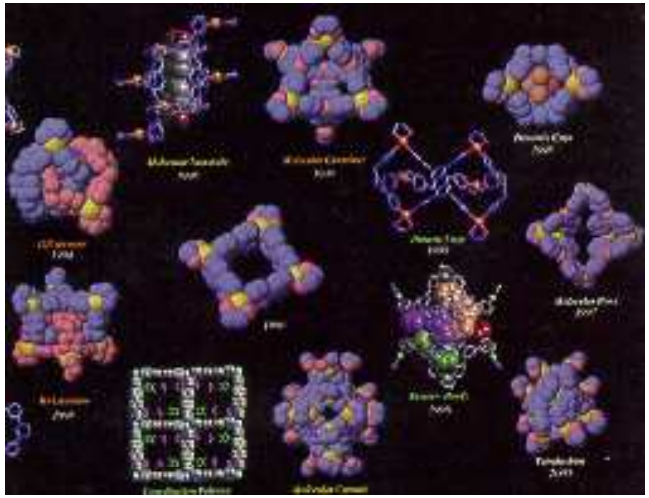
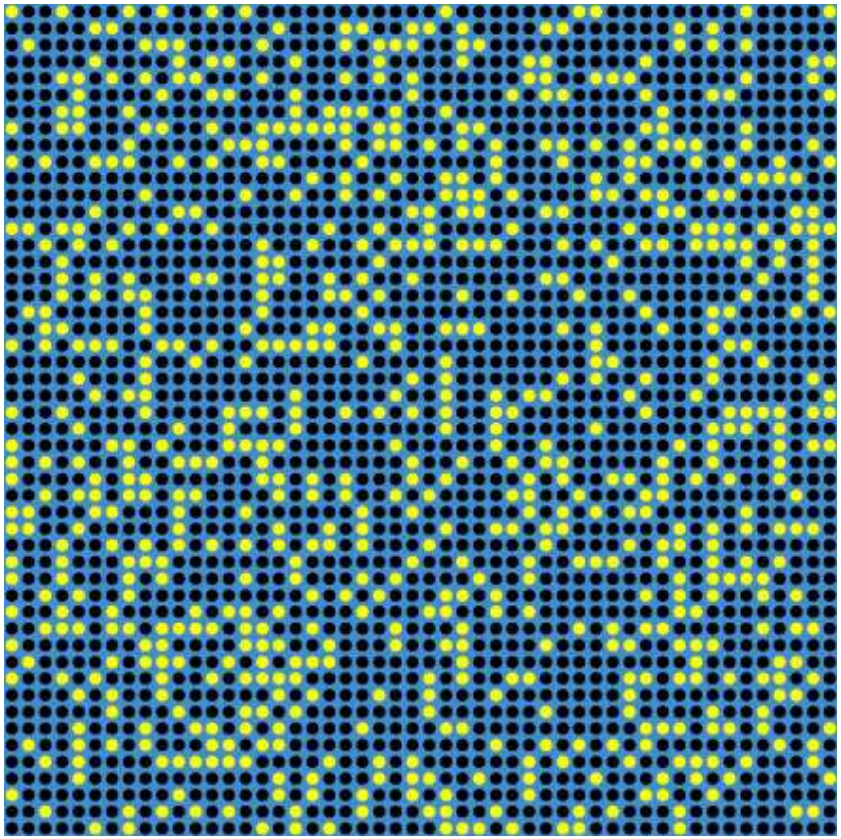
The challenge of *real* materials

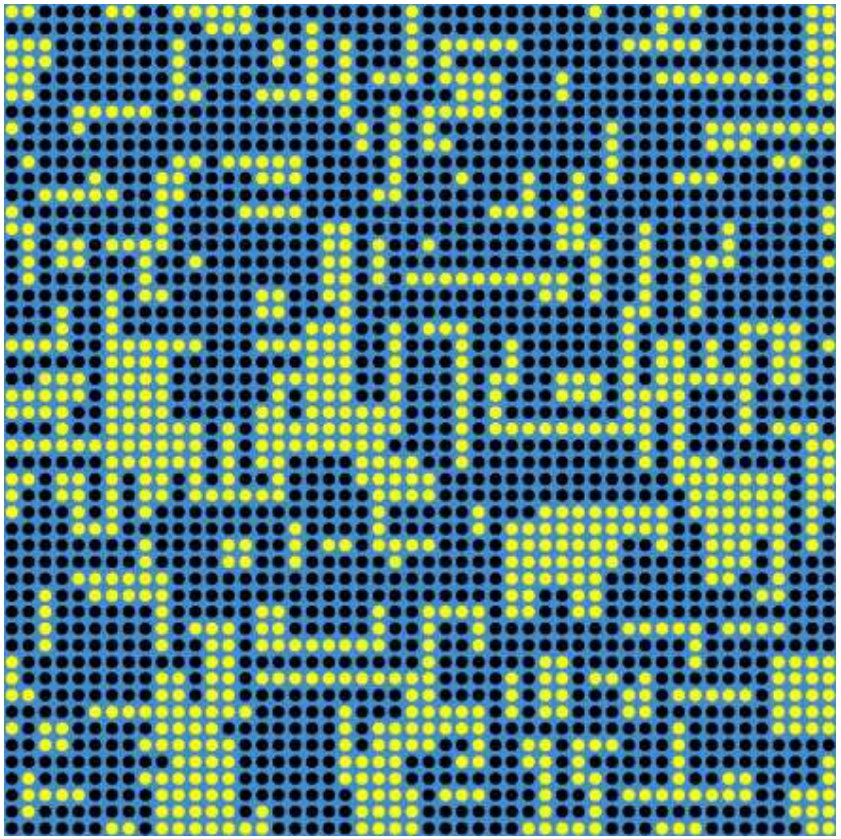
- Traditional crystallographic approach to structure determination is insufficient or fails for
  - Non crystalline materials
  - Disordered materials: The interesting properties are often governed by the defects or local structure !
  - Nanostructures: Well defined local structure, but long-range order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

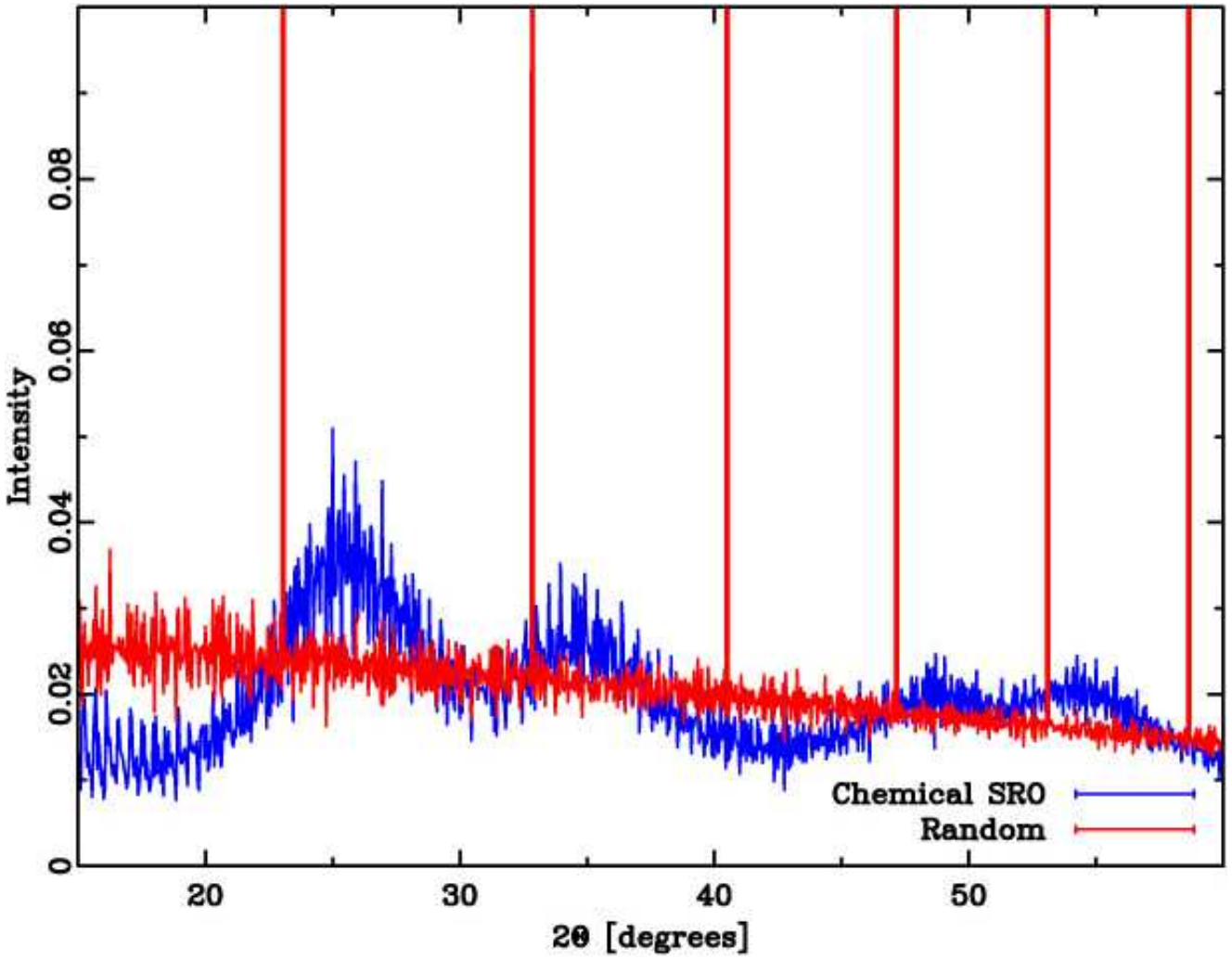




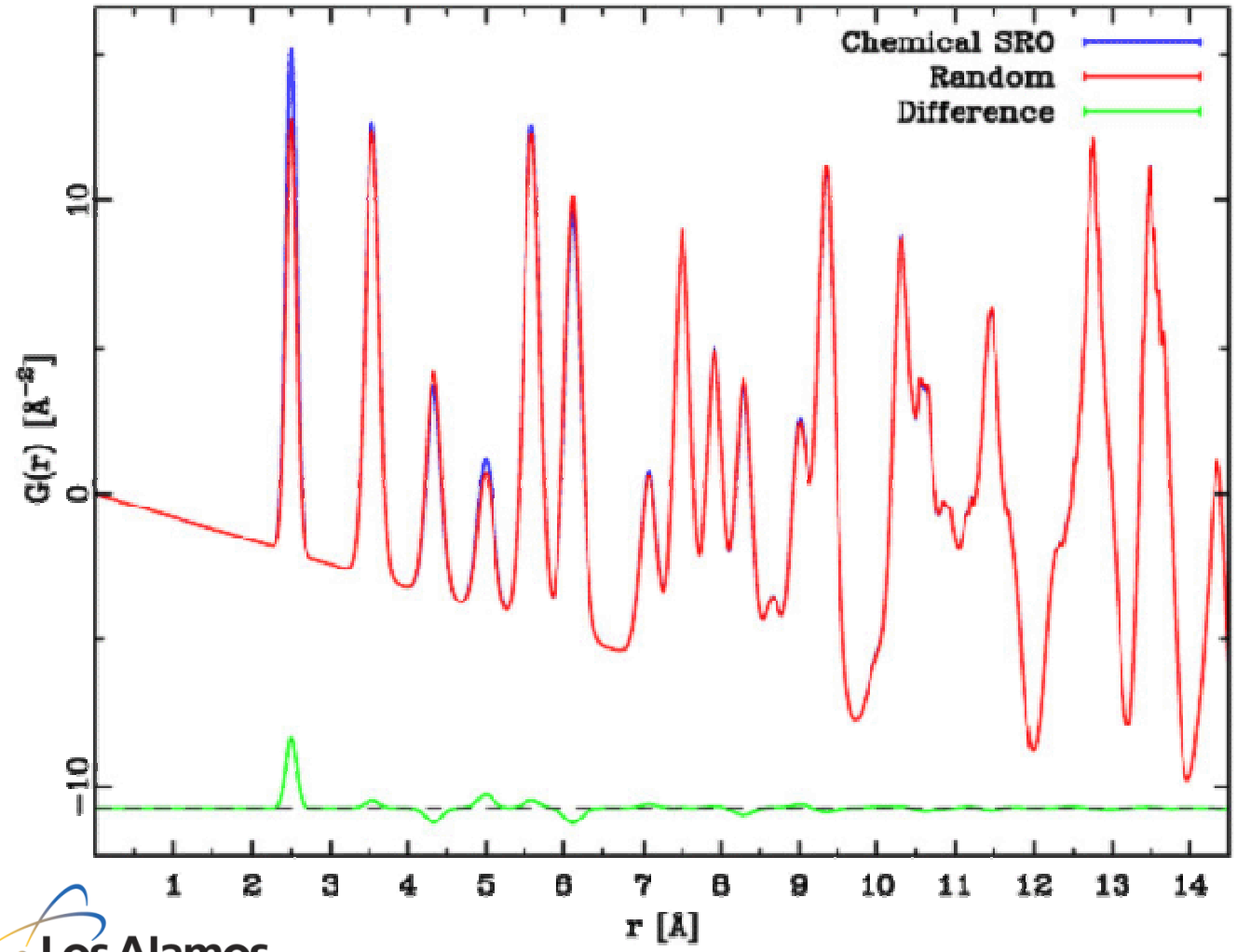
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

Properties might depend on vacancy ordering !!

How about powder diffraction ?



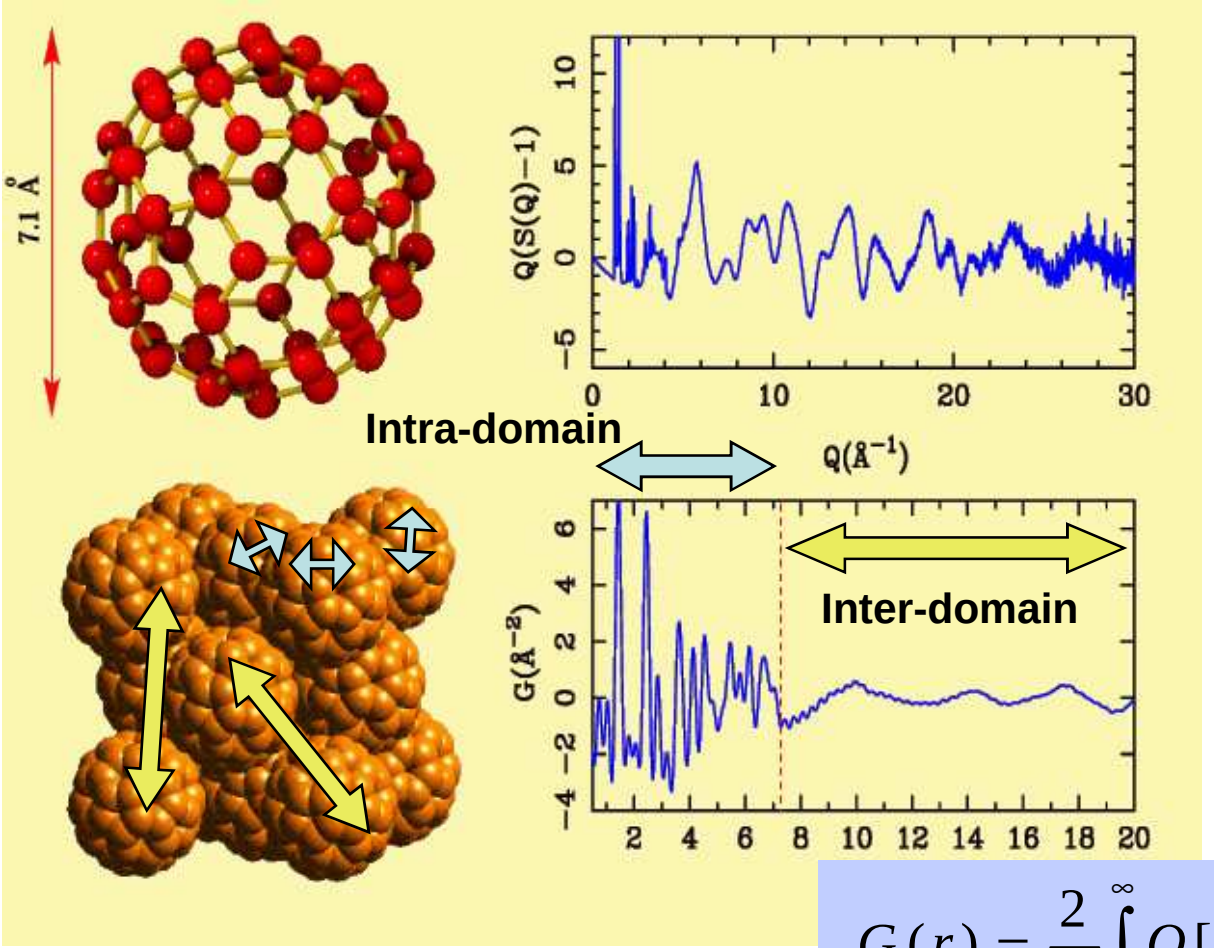
Finally the Pair Distribution Function (PDF)



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

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):

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

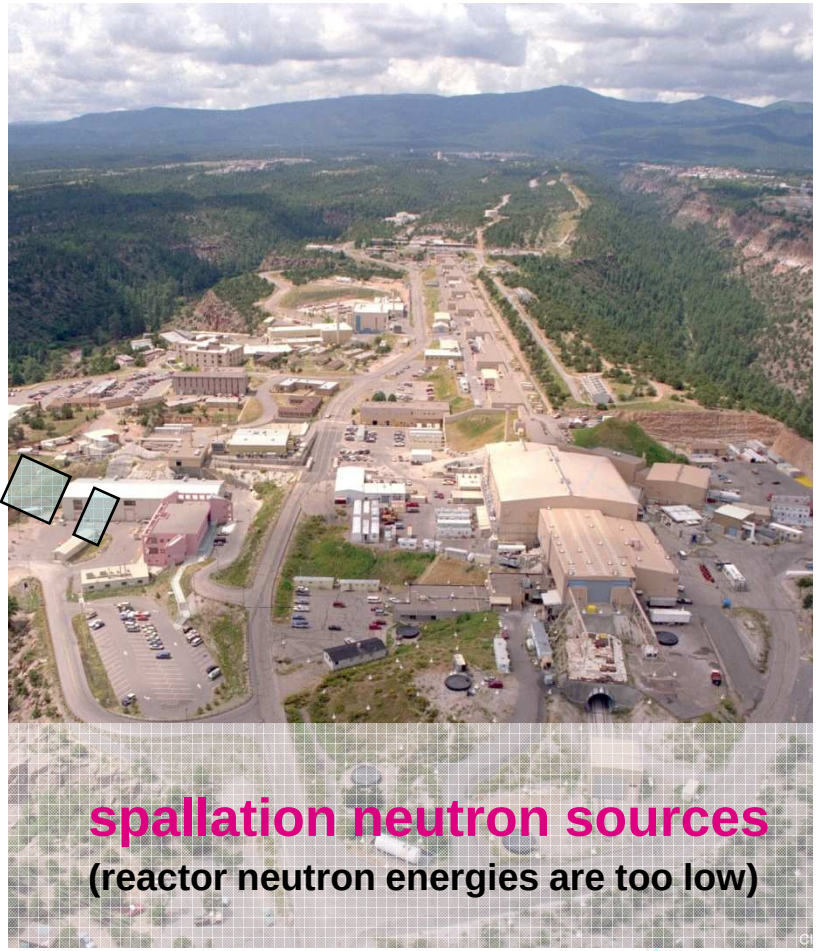
Requirements to obtain 'good' PDF:

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

Where ?

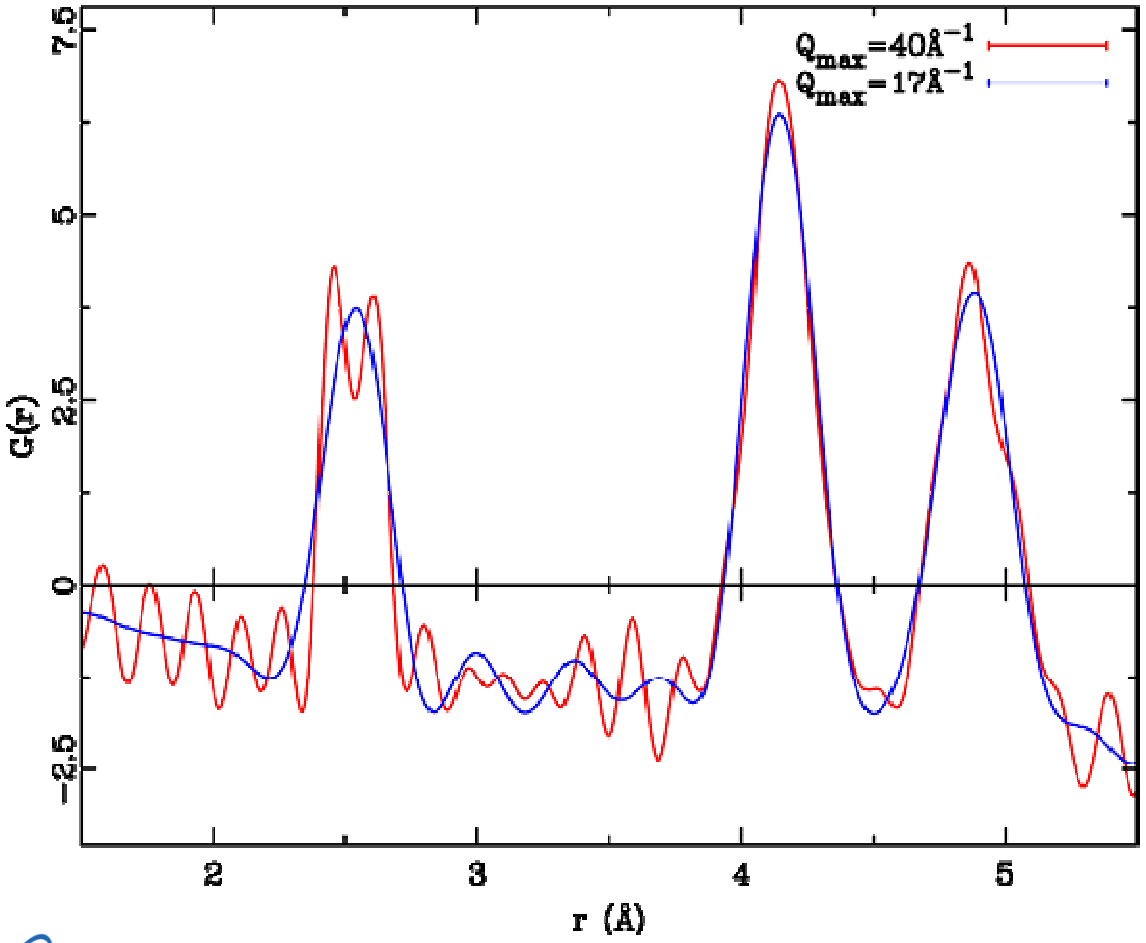
Synchrotron sources
(high energy X-rays)

or



spallation neutron sources
(reactor neutron energies are too low)

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



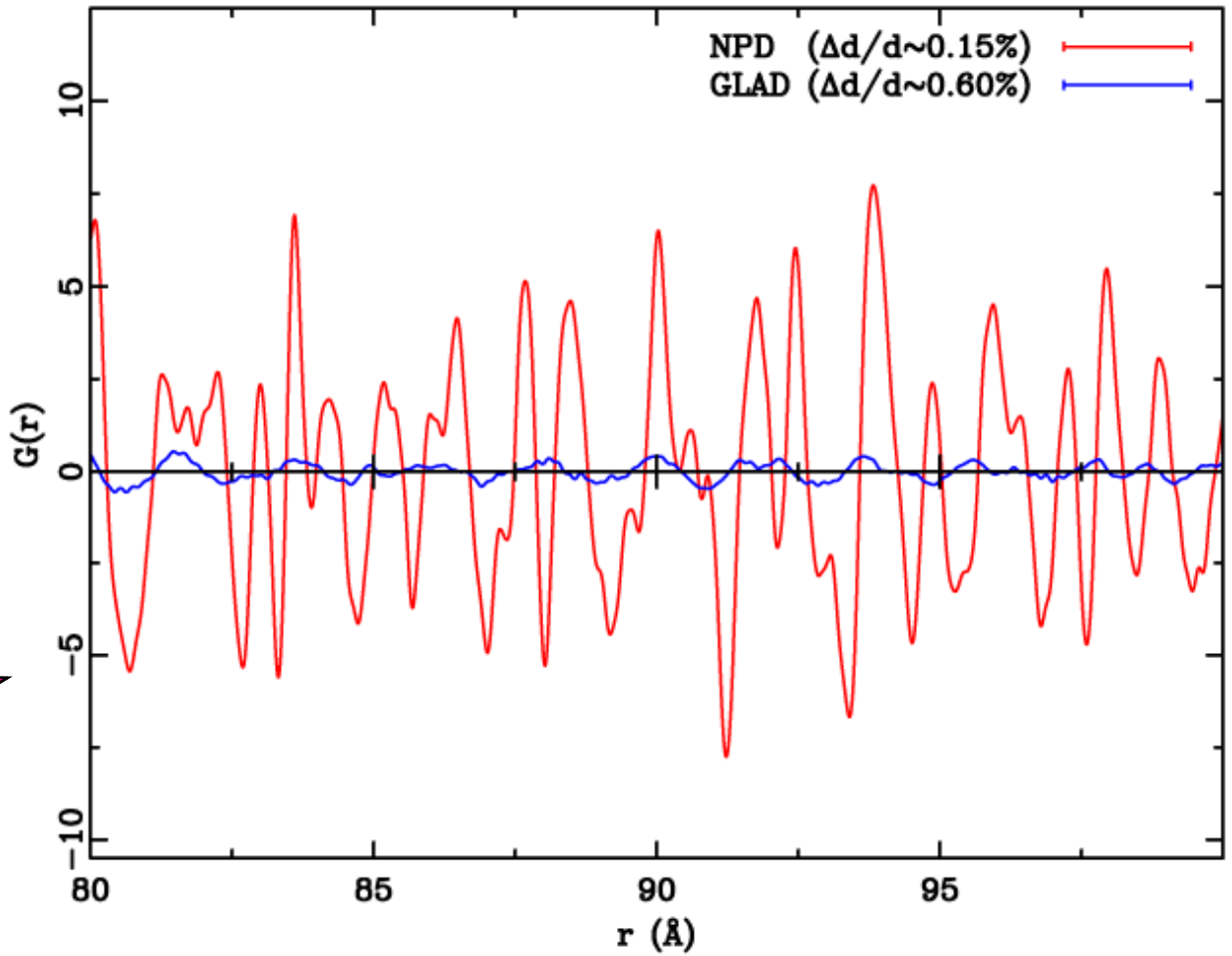
Termination of integral at Q_{max} results in convolution of G(r) with $\sin(Q_{max}\, r)/r$.

$ZnSe_{0.5}Te_{0.5}$ 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.

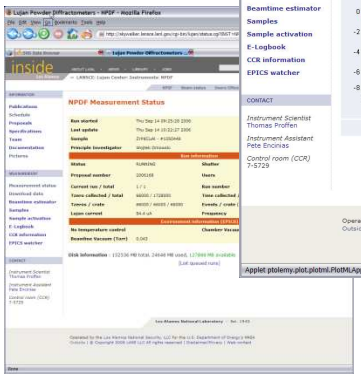


PDF goes "Nano"

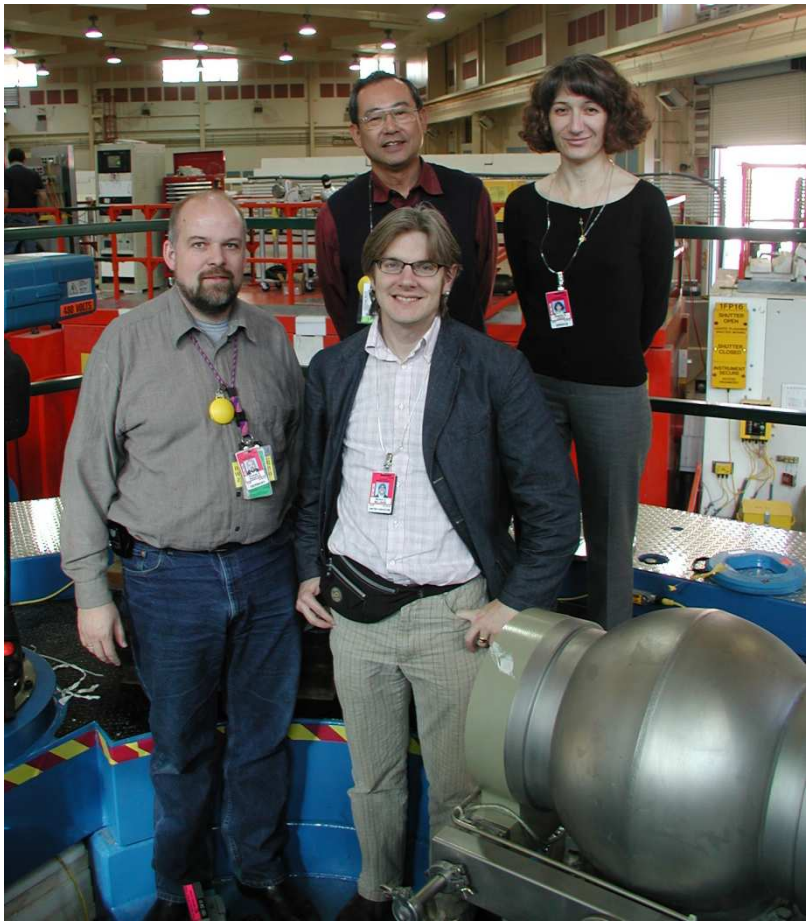
High Q resolution: Large *r* range (PDF dampened by *exp -(rΔQ)²/2)*)

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)



Upgrade project NPDF (PI: Takeshi Egami)



X-ray PDF: The fast way

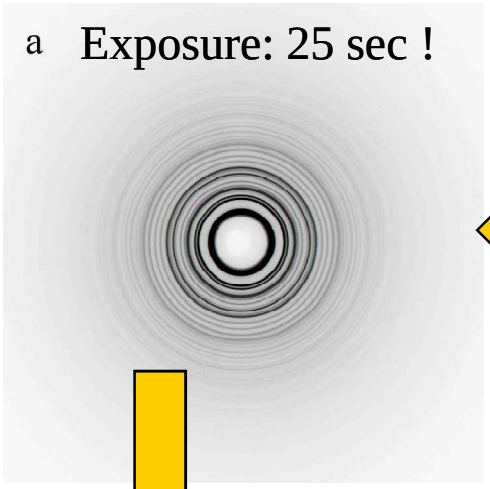
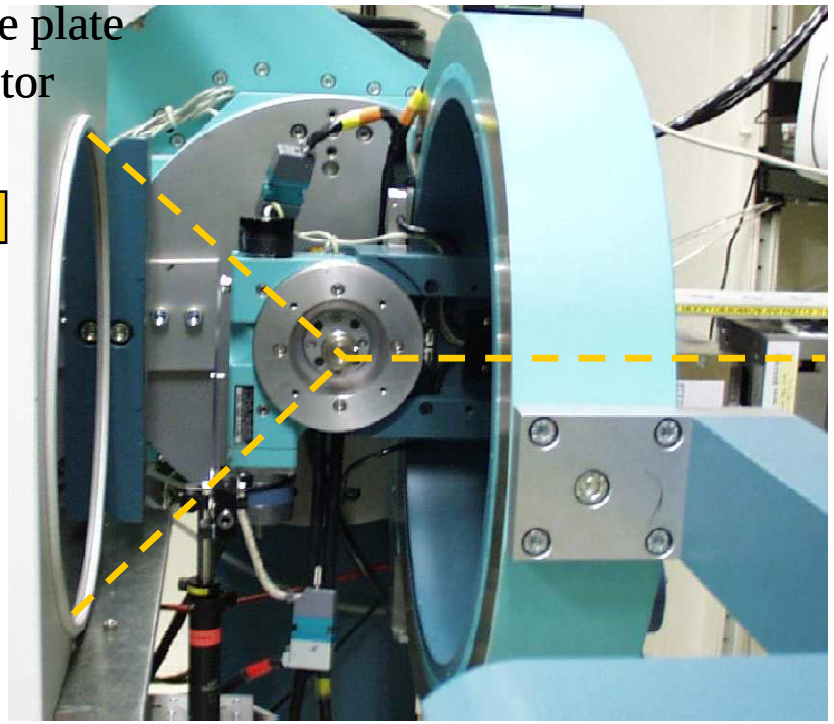
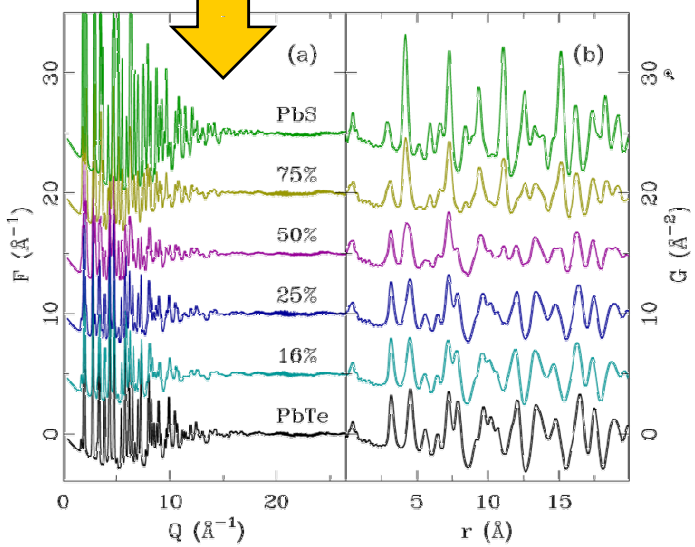


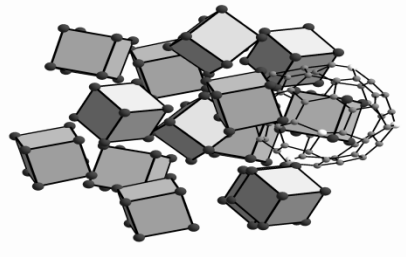
Image plate detector



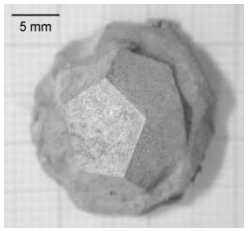


P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, **Rapid-acquisition pair distribution function (RA-PDF) analysis**, *J. Appl. Cryst.* **36**, 1342-1347 (2003).

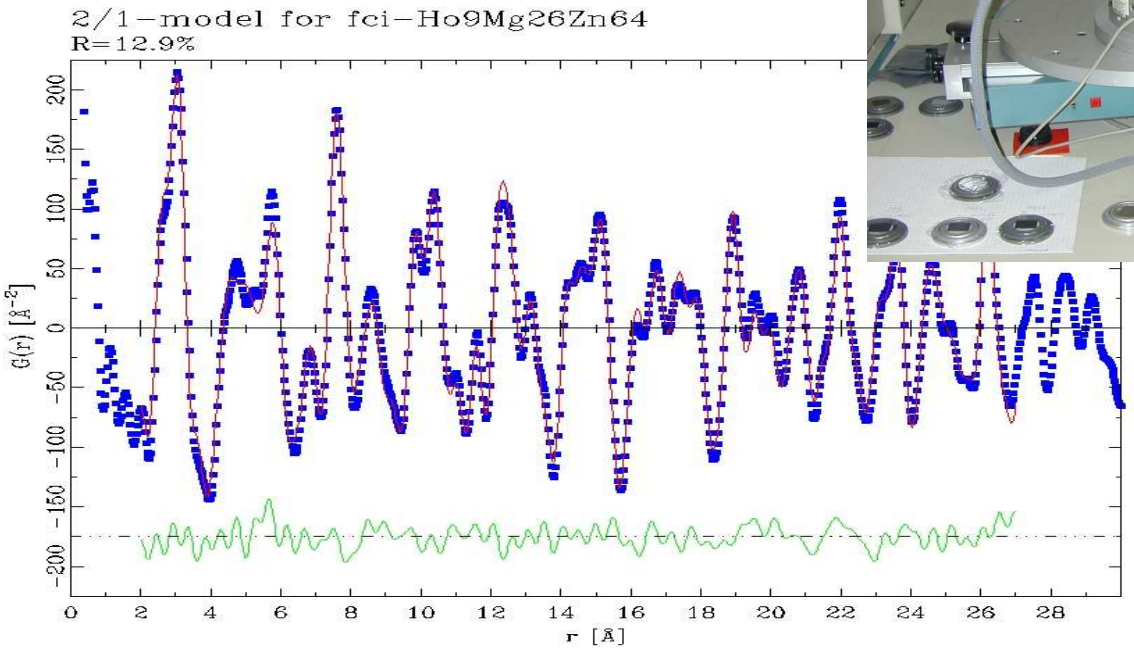
X-ray PDF: In house measurements



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



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



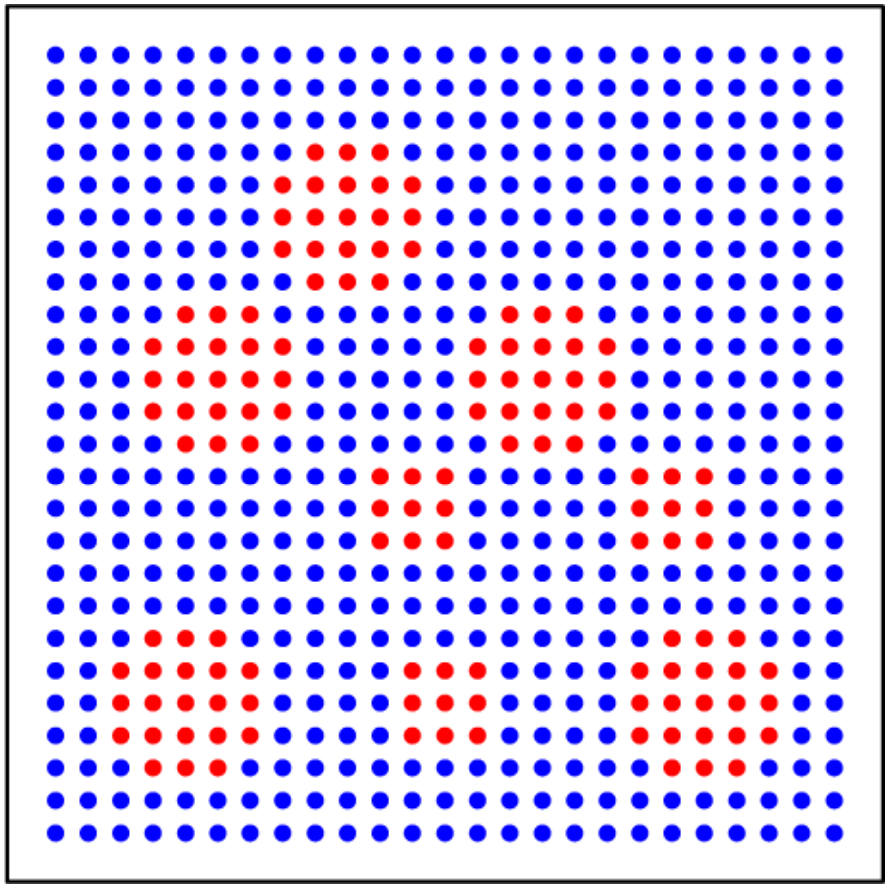
Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

Modeling
and
Software

Outline

- What to do with your PDF ?
- Give it to your favorite theorist.
- Try ‘experimentalists’ modeling on a structural model
  - A new parameter – *r*
  - Small models: Least square refinements
  - Large models: Reverse Monte Carlo
  - Any model: Evolutionary Algorithms

Refinement range – length scales in structure

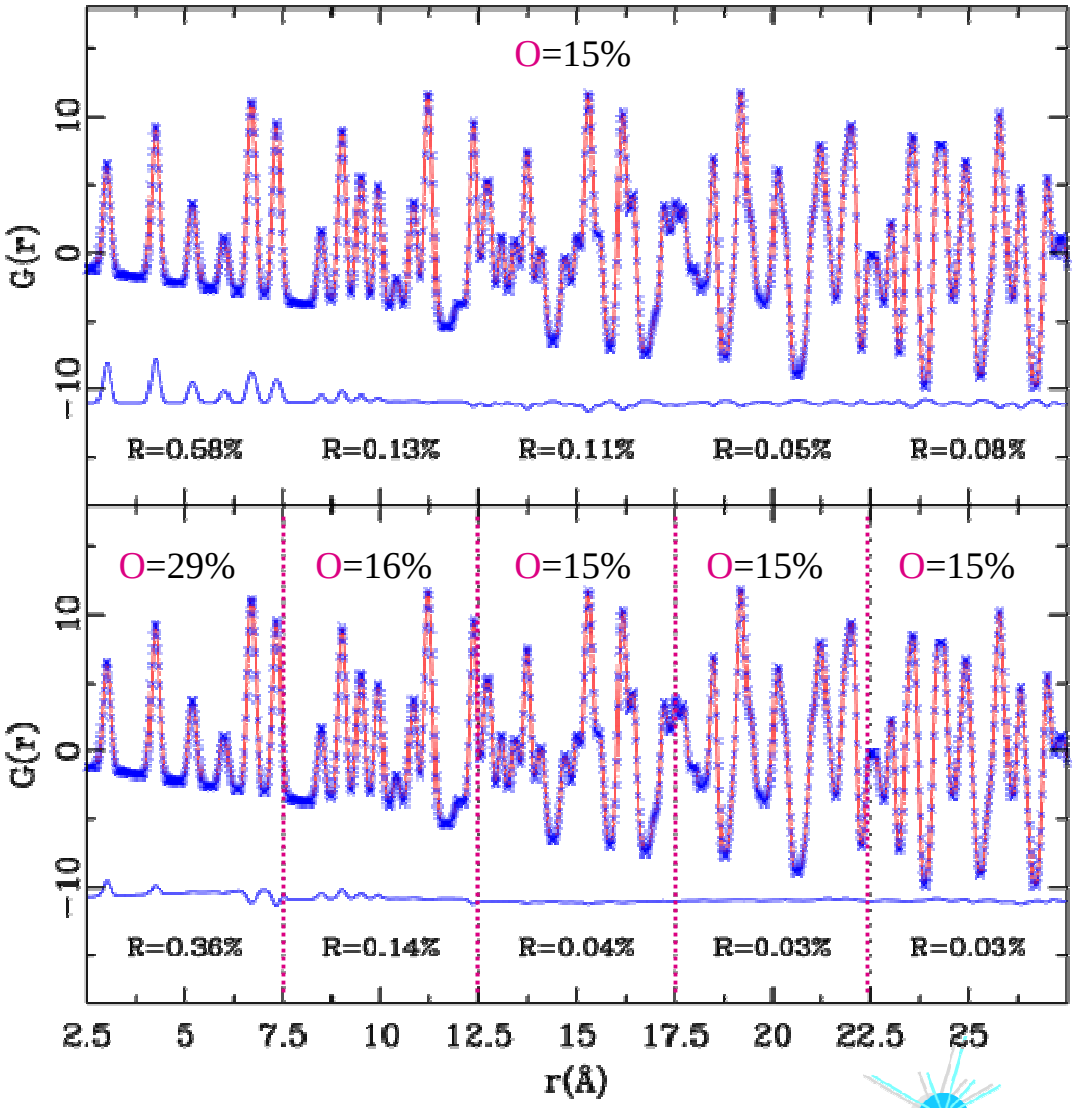


- Simulated structure of 20x20x20 unit cells.
- Matrix (M): blue atoms
- Domains (D): red atoms, spherical shape, d=15Å.
- Simulated using DISCUS.

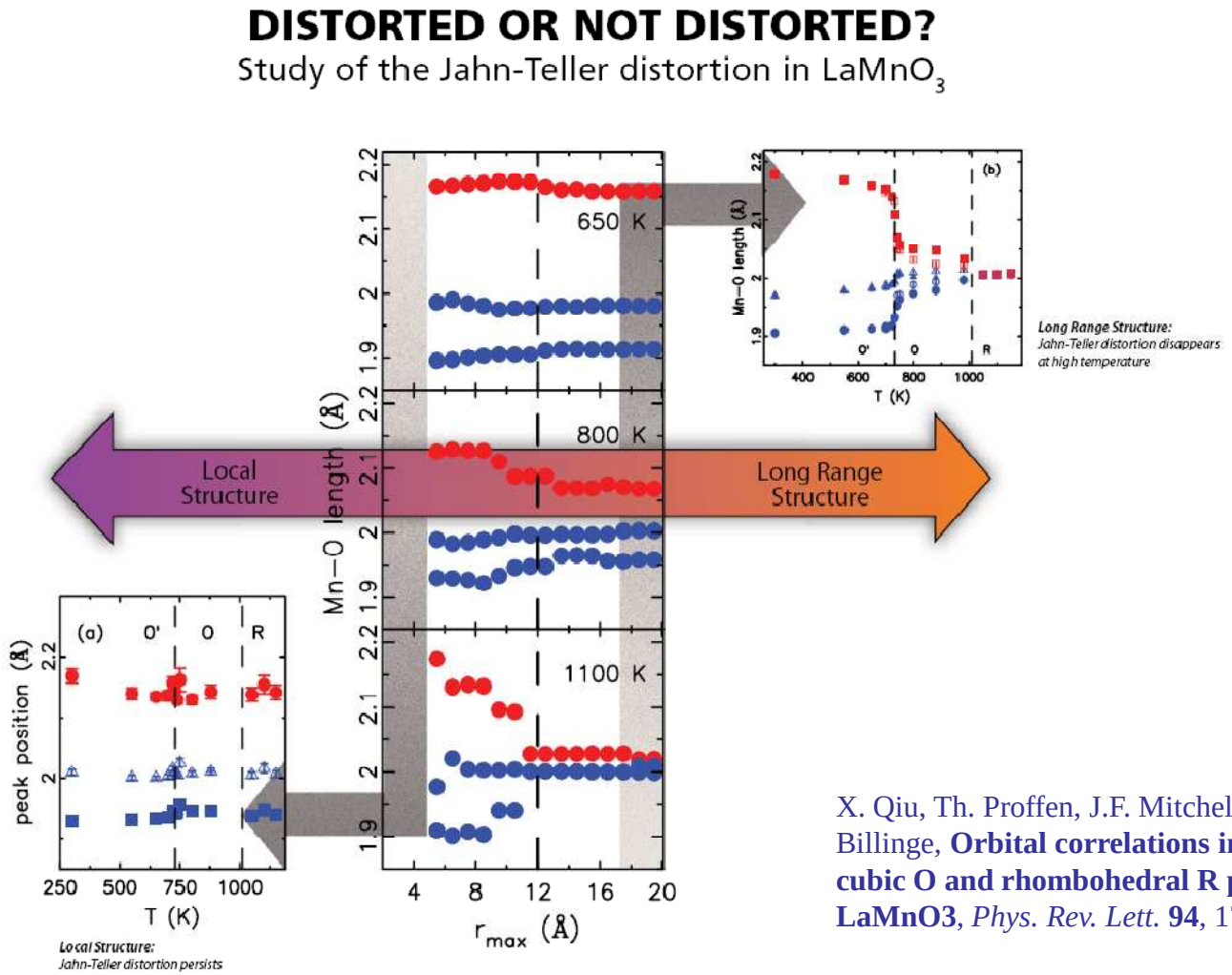
Th. Proffen and K.L. Page, **Obtaining Structural Information from the Atomic Pair Distribution Function**, *Z. Krist.* **219**, 130-135 (2004).

Refinement range – length scales in structure

- *Top*: Single-phase model with blue/red fractional occupancies (O).
- *Bottom*: Refinement of same model for 5Å wide sections.
- Extensions:
  - Multi phase models
  - Modeling of boundary
  - R-dependent refinable mixing parameters



Refinement range – the mystery of $LaMnO_3$



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).

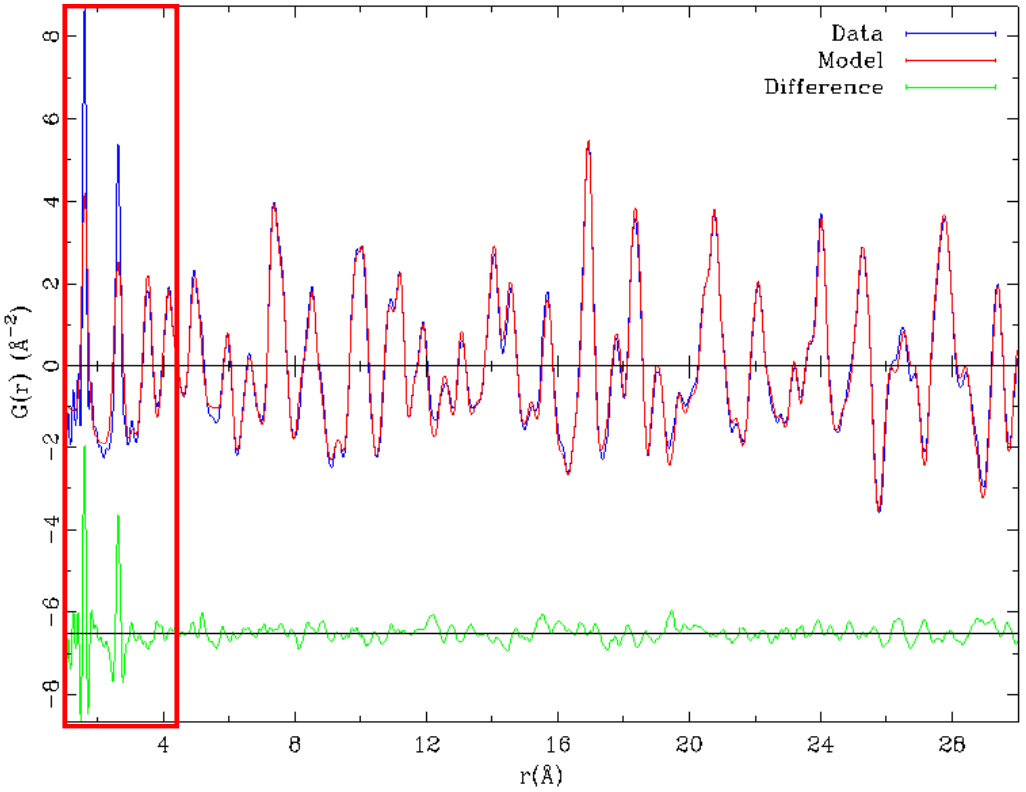
PDFfit

Refining a small structural model to the PDF

PDFfit: Refinement of a small structural model

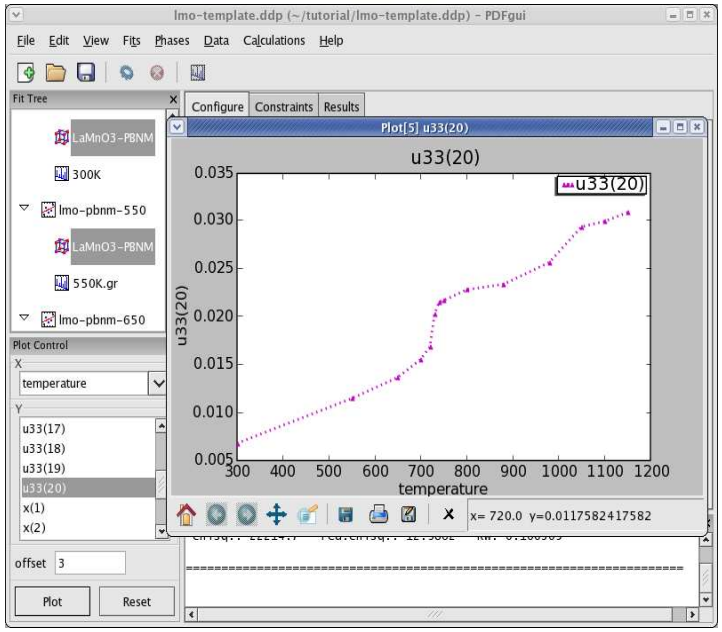
- "Real space Rietveld"
- Refinement of structural parameters: *lattice parameters, atom positions, occupancies, adp's, ..*
- Small models (<200 atoms).
- Corrections for Q_{max}, *instrument resolution, correlated motion.*
- Software: *PDFfit, PDFfit2 and PDFGui.*

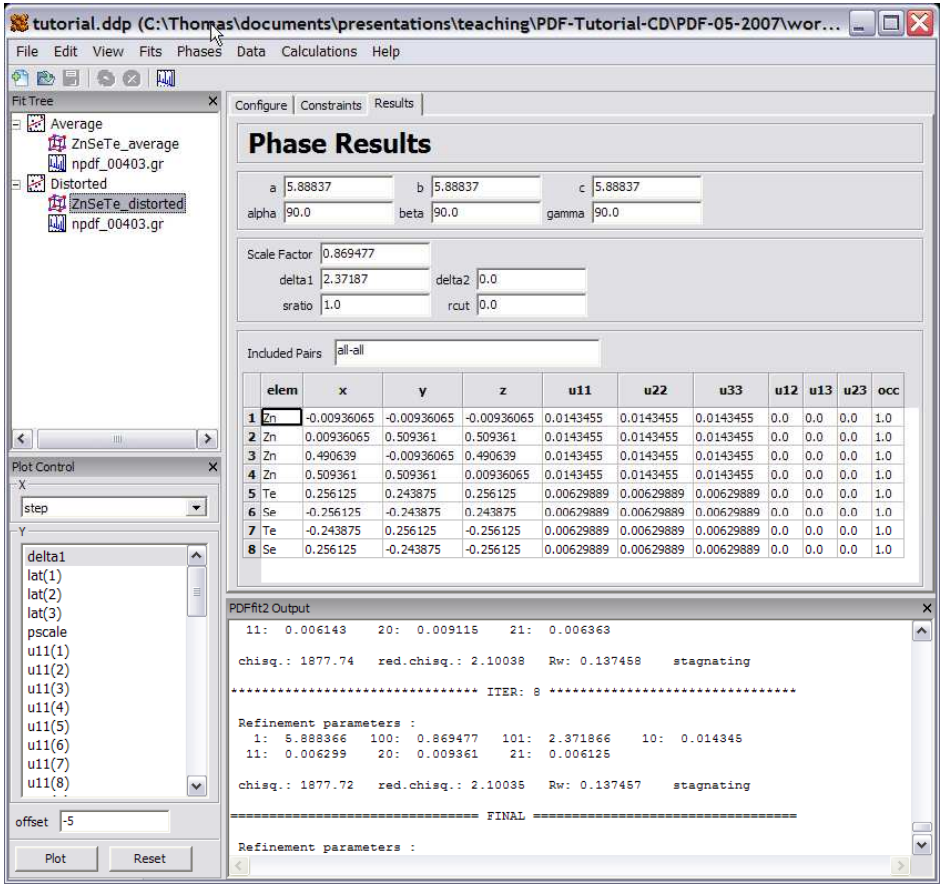
Example: Is sandstone simply quartz ?



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 ?**, *Geophys. Res. Lett.* **31**, L24606 (2004).

PDFgui – looks cool ..





http://www.diffpy.org

RMC

Shaking a big box of atoms.

Courtesy of M. Tucker, ISIS

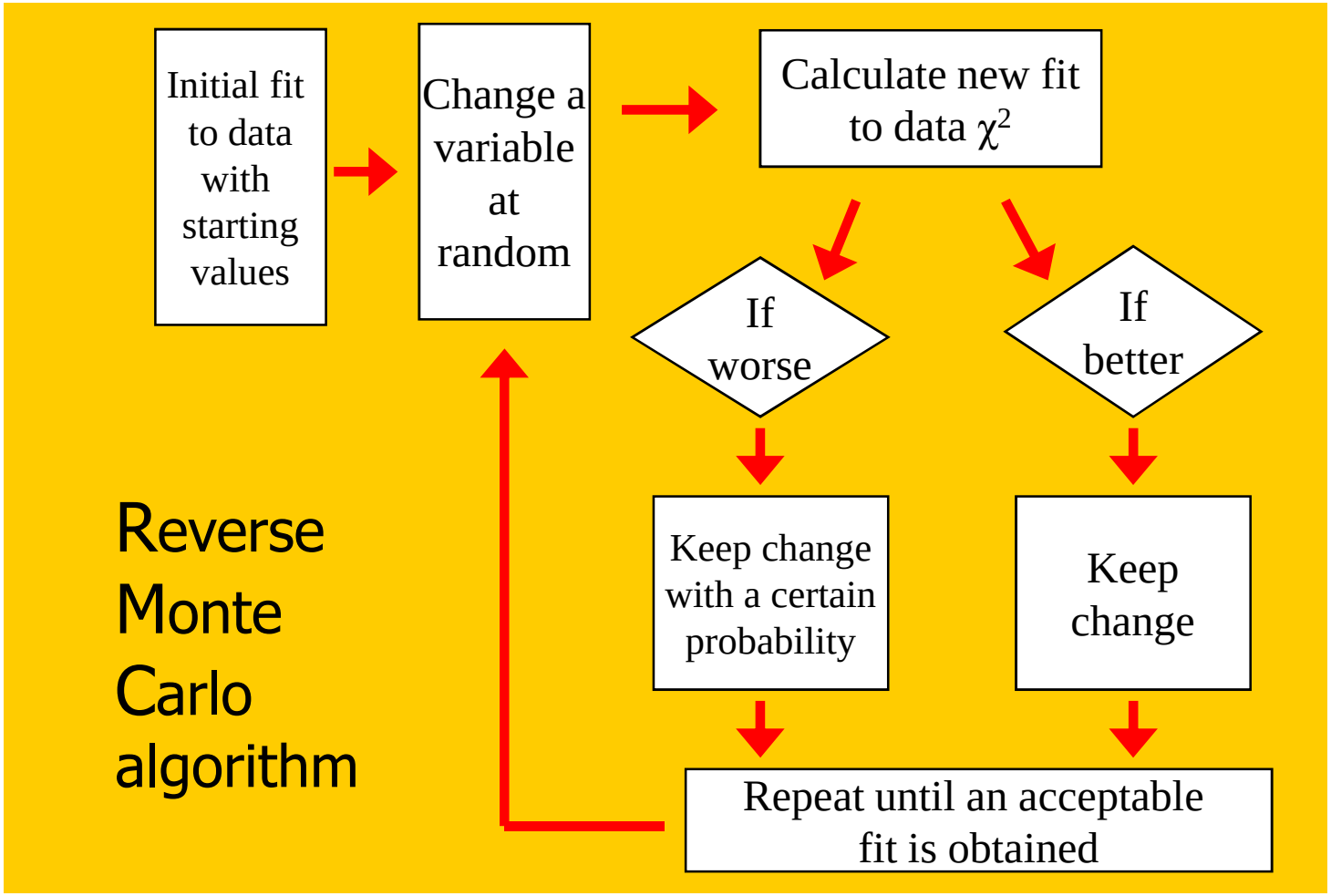
Reverse Monte Carlo

- Commonly used to model glasses and liquids (no long range order).
- Recently applied to disordered crystalline materials.
- Large model structures.
- Importance of constrains.
- Uniqueness of solution ?

R.L. McGreevy and L. Pusztai, **Reverse Monte Carlo Simulation: a New Technique for the Determination of Disordered Structures** , *Mol. Simul.* **1**, 359-367 (1988).

M.G. Tucker, M.T. Dove and D.A. Keen, **Application of the Reverse Monte Carlo Method to Crystalline Materials** , *J. Appl. Cryst.* **34**, 630-638 (2001).

RMC: How does it work ?

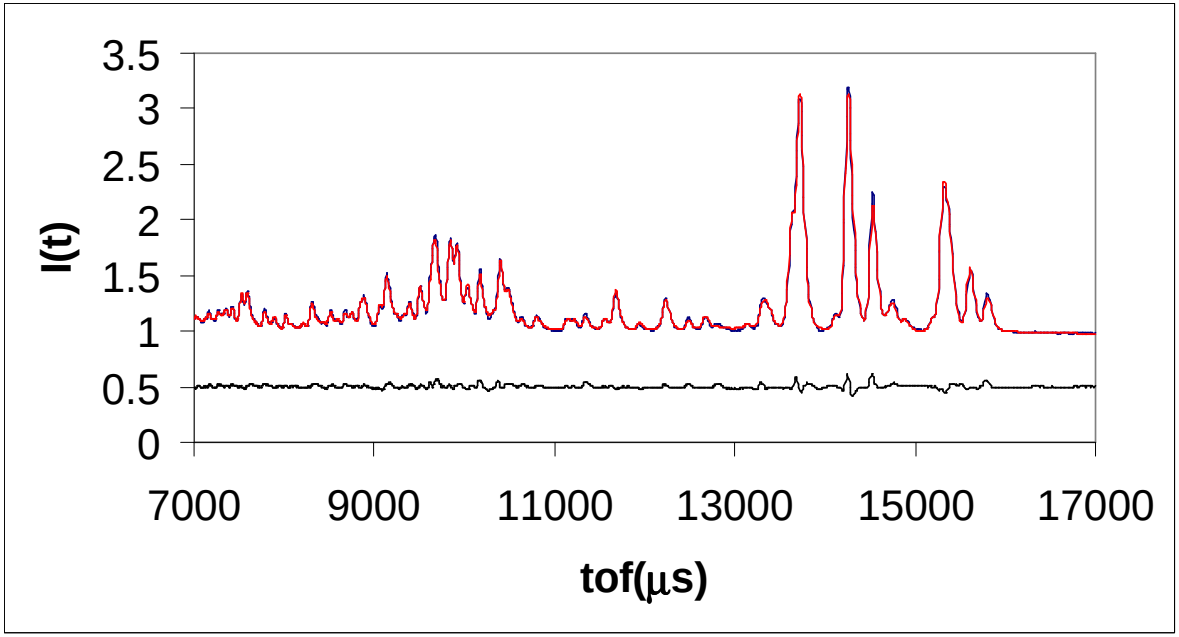


Include Bragg intensities ..

Use GSAS to fit :
Peak shape
Background
Lattice parameters

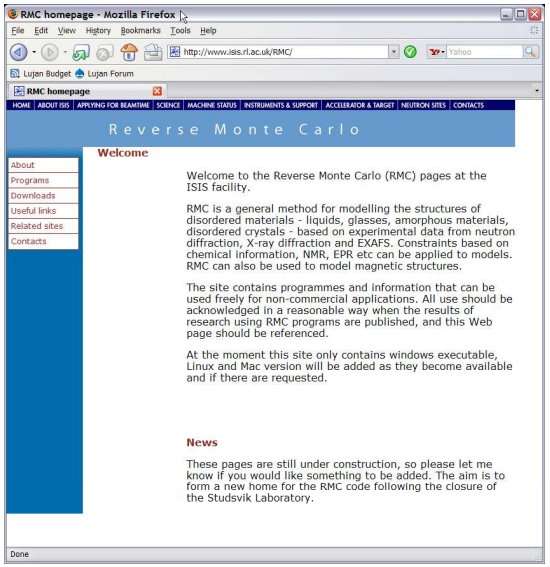
RMCProfile calculates the intensities and then produces the profile.

$$+\sum_j | I_{\text{expt}}(t_j) - sI_{\text{calc}}(t_j) |^2 / \sigma^2_{I(t_j)}$$



Software: RMCprofile and DISCUS

- 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



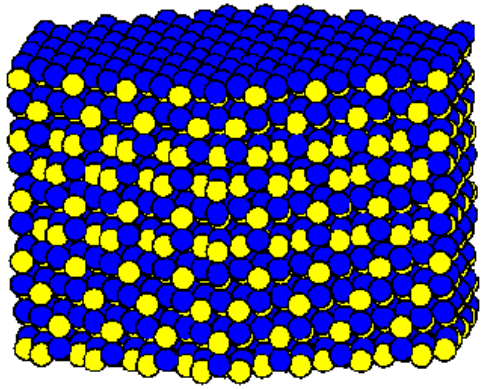
DIFFEV

Refining parameters of a disordered particle/crystal

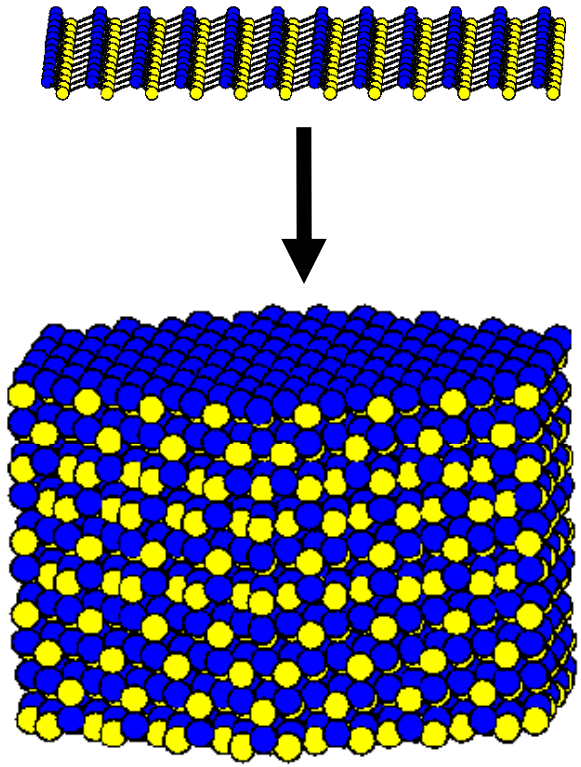
Courtesy of R.B. Neder,
U Würzburg

DIFFEV: Refining model parameters

- PDFfit and RMC
  - Refine structure directly in terms of atom coordinates etc ..
  - Difficult for complex systems
- Alternative
  - Refine parameters of a structural model and not each atom.
  - Example nanoparticle: *diameter, atom spacing, stacking fault probability, …*
  - Choose minimization – here DIFFEV



Example: ZnSe nanoparticles - Model



{110} and {001}

create a large single Wurtzite layer A/B

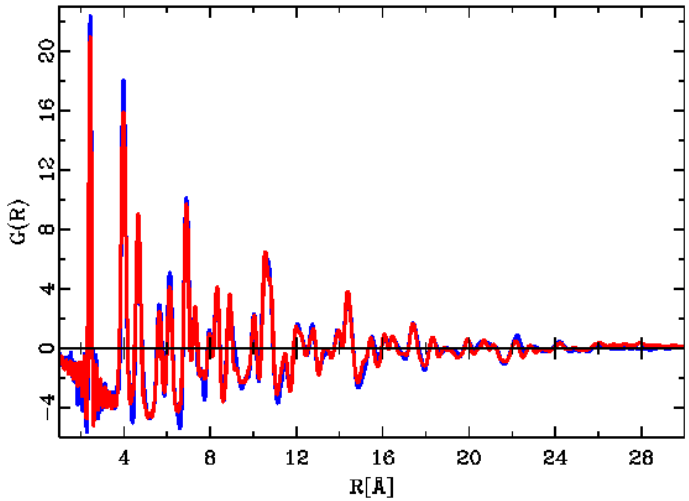
- Stack along c (with faults)
- Cut to proper size
- Calculate PDF / powder pattern

Repeat and average

Repeat with new set of parameter
using a Differential Evolutionary Scheme

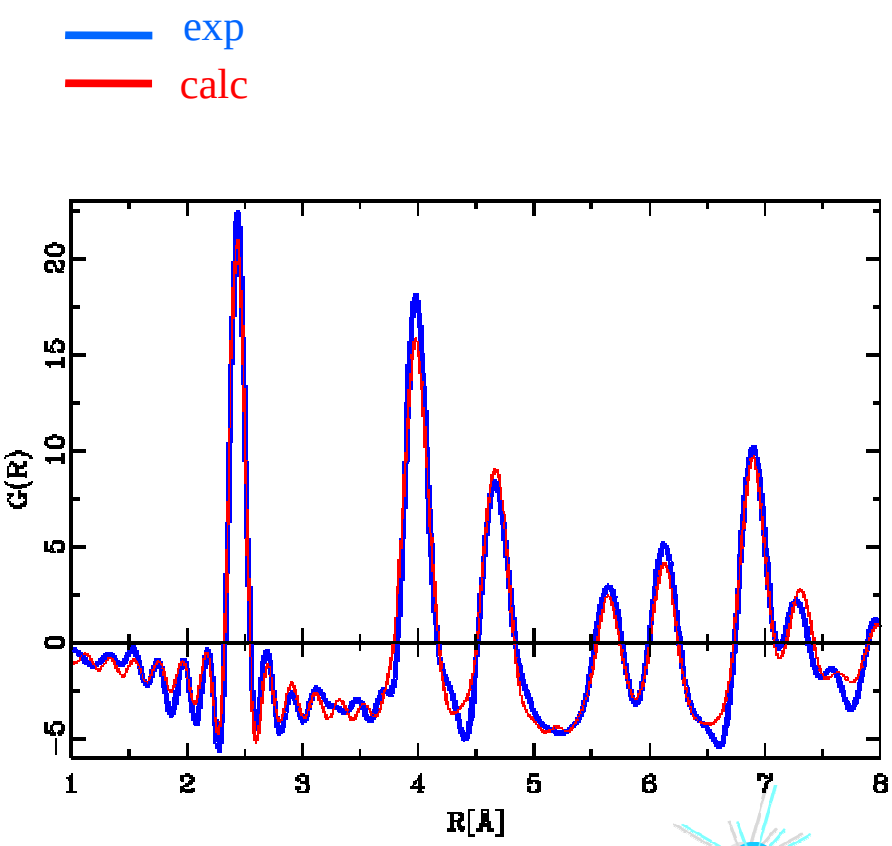
Software: DISCUS and DIFFEV

Example: ZnSe nanoparticles - Results



C. Kumpf, R.B. Neder et al., **Structure determination of CdS and ZnS nanoparticles: Direct modeling of synchrotron-radiation diffraction data**, *J. Chem. Phys.* **123**, 224707 (2005).

- Results:
  - a=3.973Å, c=6.494Å
  - Diameter ~26Å
  - Stacking fault prob. 70%

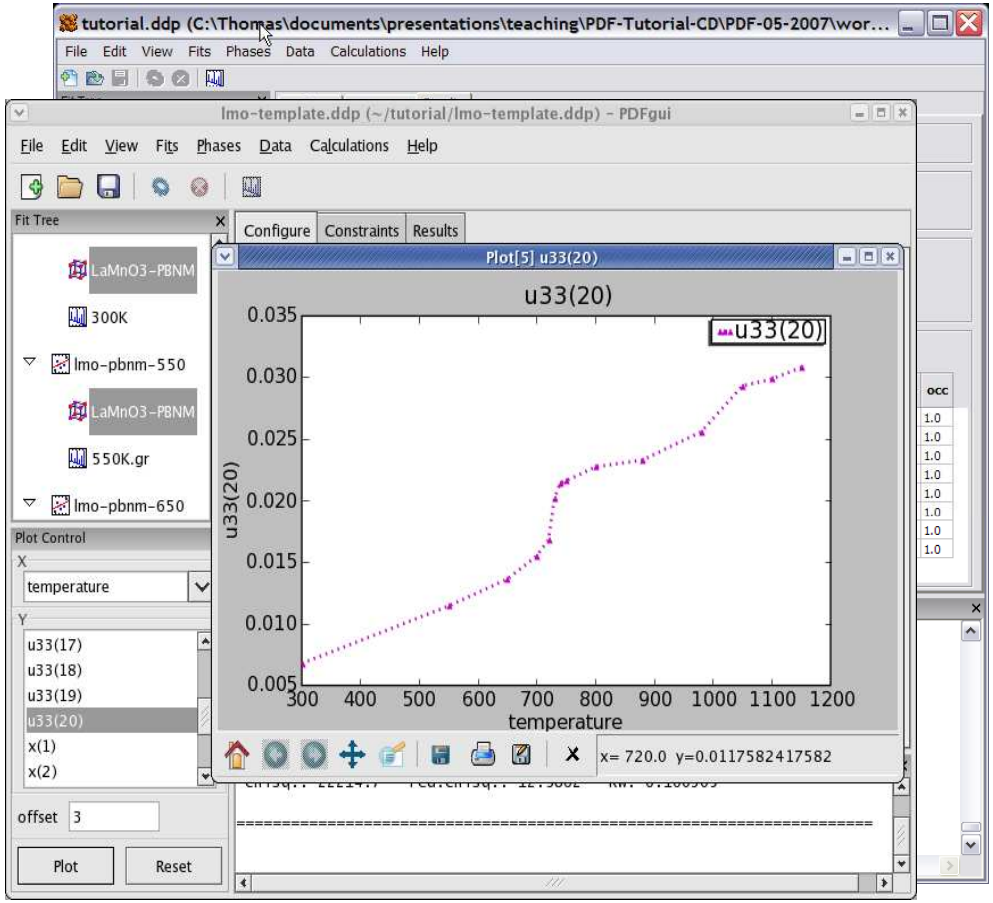


How to model PDF data ?

- 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 ..

Challenge software – exciting developments ..

- PDFFIT2 and PDFgui
- Part of the DANSE project.
- Diffraction headed by Simon Billinge (MSU)
- NSF award of ~$12M.



http://www.diffpy.org

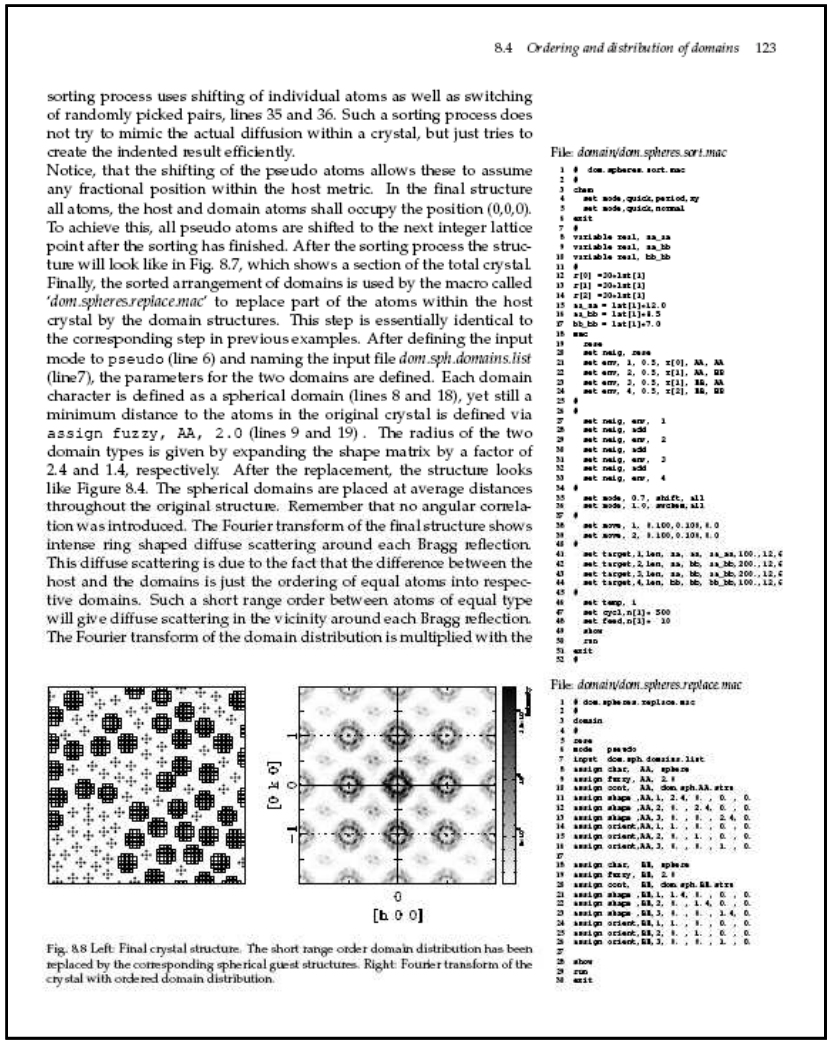
Downloads

http://discus.sourceforge.net

http://pdfgetn.sourceforge.net

The DISCUS cook book – coming soon !

- To be published by Oxford University Press as IUCr text.
- Includes CDROM with many examples.
- Summer 2008



8.4 *Ordering and distribution of domains* 123

sorting process uses shifting of individual atoms as well as switching of randomly picked pairs, lines 35 and 36. Such a sorting process does not try to mimic the actual diffusion within a crystal, but just tries to create the indented result efficiently.
Notice, that the shifting of the pseudo atoms allows these to assume any fractional position within the host metric. In the final structure all atoms, the host and domain atoms shall occupy the position (0,0,0). To achieve this, all pseudo atoms are shifted to the next integer lattice point after the sorting has finished. After the sorting process the structure will look like in Fig. 8.7, which shows a section of the total crystal. Finally, the sorted arrangement of domains is used by the macro called *'dom.spheres.replace.mac'* to replace part of the atoms within the host crystal by the domain structures. This step is essentially identical to the corresponding step in previous examples. After defining the input mode to `pseudo` (line 6) and naming the input file *dom.sph.domains.list* (line7), the parameters for the two domains are defined. Each domain character is defined as a spherical domain (lines 8 and 18), yet still a minimum distance to the atoms in the original crystal is defined via `assign fuzzy, AA, 2.0` (lines 9 and 19). The radius of the two domain types is given by expanding the shape matrix by a factor of 2.4 and 1.4, respectively. After the replacement, the structure looks like Figure 8.4. The spherical domains are placed at average distances throughout the original structure. Remember that no angular correlation was introduced. The Fourier transform of the final structure shows intense ring shaped diffuse scattering around each Bragg reflection. This diffuse scattering is due to the fact that the difference between the host and the domains is just the ordering of equal atoms into respective domains. Such a short range order between atoms of equal type will give diffuse scattering in the vicinity around each Bragg reflection. The Fourier transform of the domain distribution is multiplied with the

File: *domain/dom.spheres.sort.mac*

```
1  # dom.spheres.sort.mac
2  #
3  chan
4    set mode,quick,period,xy
5    set mode,quick,normal
6  exit
7  #
8  variable real, aa_aa
9  variable real, aa_bb
10 variable real, bb_bb
11 #
12 r[0] =20*lat[1]
13 r[1] =20*lat[2]
14 r[2] =20*lat[3]
15 aa_aa = lat[1]*12.0
16 aa_bb = lat[1]*8.5
17 bb_bb = lat[1]*7.0
18 mac
19   zero
20   set neig, zero
21   set anv, 1, 0.5, r[0], AA, AA
22   set anv, 2, 0.5, r[1], AA, BB
23   set anv, 3, 0.5, r[1], BB, AA
24   set anv, 4, 0.5, r[2], BB, BB
25 #
26 #
27   set neig, anv,  1
28   set neig, add
29   set neig, anv,  2
30   set neig, add
31   set neig, anv,  3
32   set neig, add
33   set neig, anv,  4
34 #
35   set mode, 0.7, shift, all
36   set mode, 1.0, sweden, all
37 #
38   set anvw, 1, 8.100,0.100, 8.0
39   set anvw, 2, 8.100,0.100, 8.0
40 #
41   set target,1,len, aa, aa, aa_aa,100.,12,6
42   set target,2,len, aa, bb, aa_bb,200.,12,6
43   set target,3,len, aa, bb, aa_bb,200.,12,6
44   set target,4,len, bb, bb, bb_bb,100.,12,6
45 #
46   set temp, 1
47   set cyc1,n[1]* 500
48   set feed,n[1]* 10
49   show
50   run
51 exit
52 #
```

File: *domain/dom.spheres.replace.mac*

```
1  # dom.spheres.replace.mac
2  #
3  domain
4  #
5  zero
6  mode  pseudo
7  inpst  dom.sph.domains.list
8  assign char,  AA, sphere
9  assign fuzzy, AA, 2.0
10 assign cont,  AA, dom.sph.AA.strx
11 assign shape ,AA,1, 2.4, 0. , 0. , 0.
12 assign shape ,AA,2, 0. , 2.4, 0. , 0.
13 assign shape ,AA,3, 0. , 0. , 2.4, 0.
14 assign orient,AA,1, 1. , 0. , 0. , 0.
15 assign orient,AA,2, 0. , 1. , 0. , 0.
16 assign orient,AA,3, 0. , 0. , 1. , 0.
17
18 assign char,  BB, sphere
19 assign fuzzy, BB, 2.0
20 assign cont,  BB, dom.sph.BB.strx
21 assign shape ,BB,1, 1.4, 0. , 0. , 0.
22 assign shape ,BB,2, 0. , 1.4, 0. , 0.
23 assign shape ,BB,3, 0. , 0. , 1.4, 0.
24 assign orient,BB,1, 1. , 0. , 0. , 0.
25 assign orient,BB,2, 0. , 1. , 0. , 0.
26 assign orient,BB,3, 0. , 0. , 1. , 0.
27
28 show
29 run
30 exit
```


Fig. 8.8 Left: Final crystal structure. The short range order domain distribution has been replaced by the corresponding spherical guest structures. Right: Fourier transform of the crystal with ordered domain distribution.

Examples

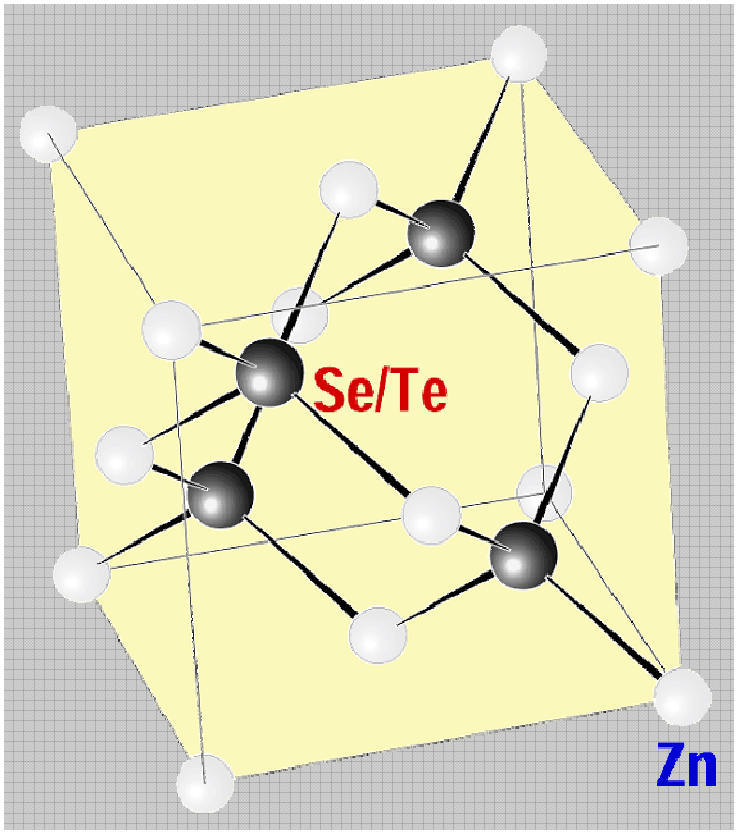
Local atomic strain in $ZnSe_{1-x}Te_x$

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

Facilities: IPNS, Lujan
Funding: DOE, NSF

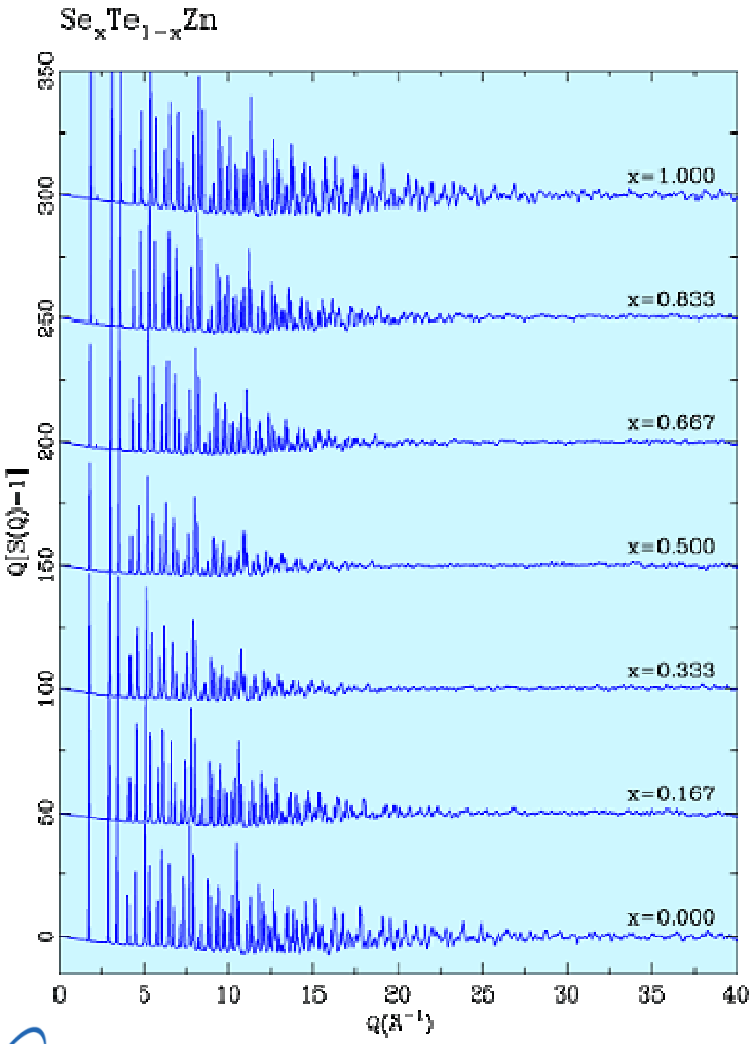
$ZnSe_{1-x}Te_x$: Structure

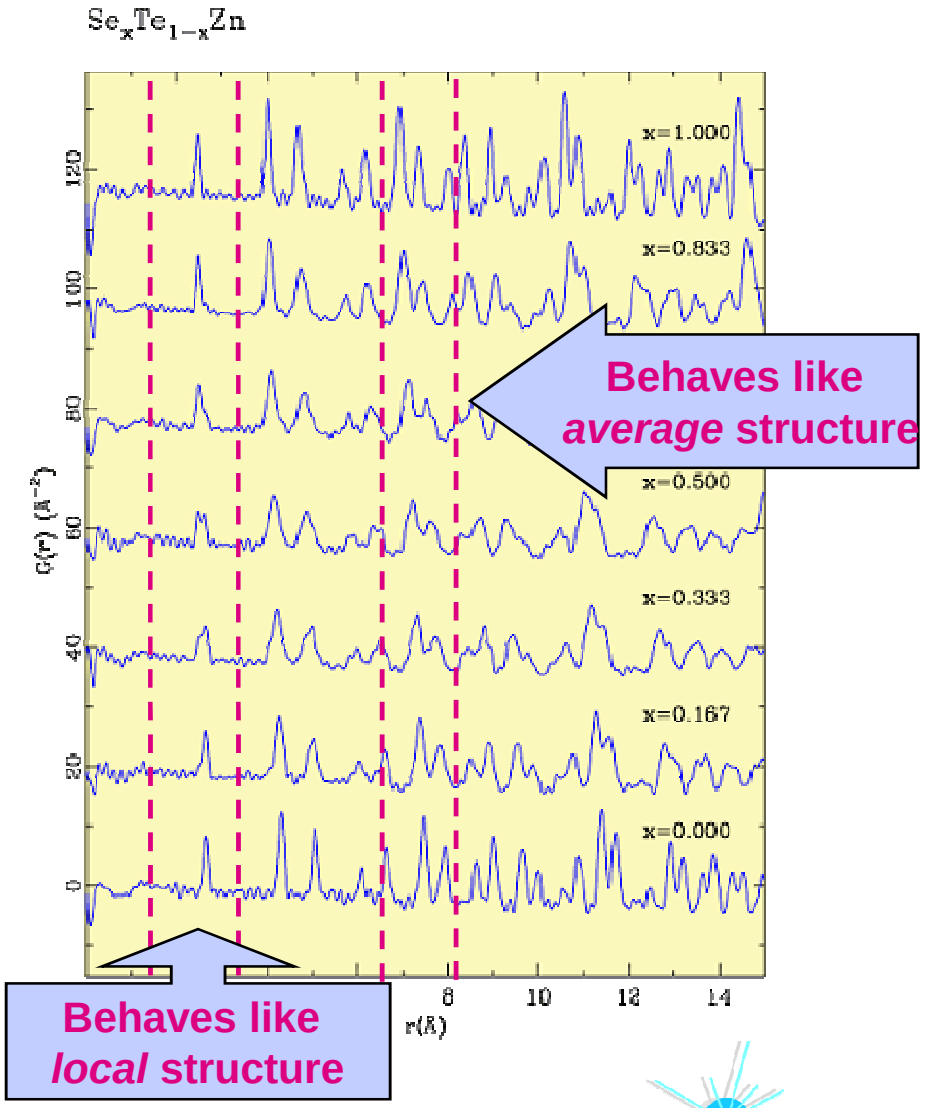
- Zinc blend structure (F43m)
- Technological important : Electronic band gap can be tuned by the composition *x*.
- Bond length difference *Zn-Se* and *Zn-Te* $\Rightarrow$ strain.
- Local structural probe required !



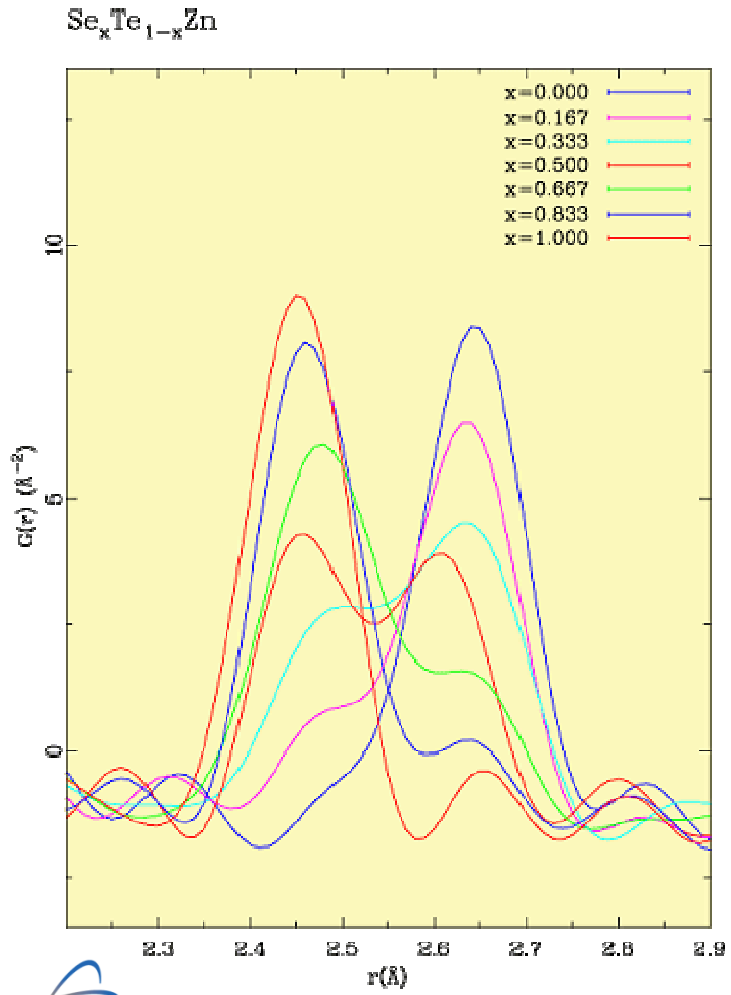
$ZnSe_{1-x}Te_x$: Total scattering

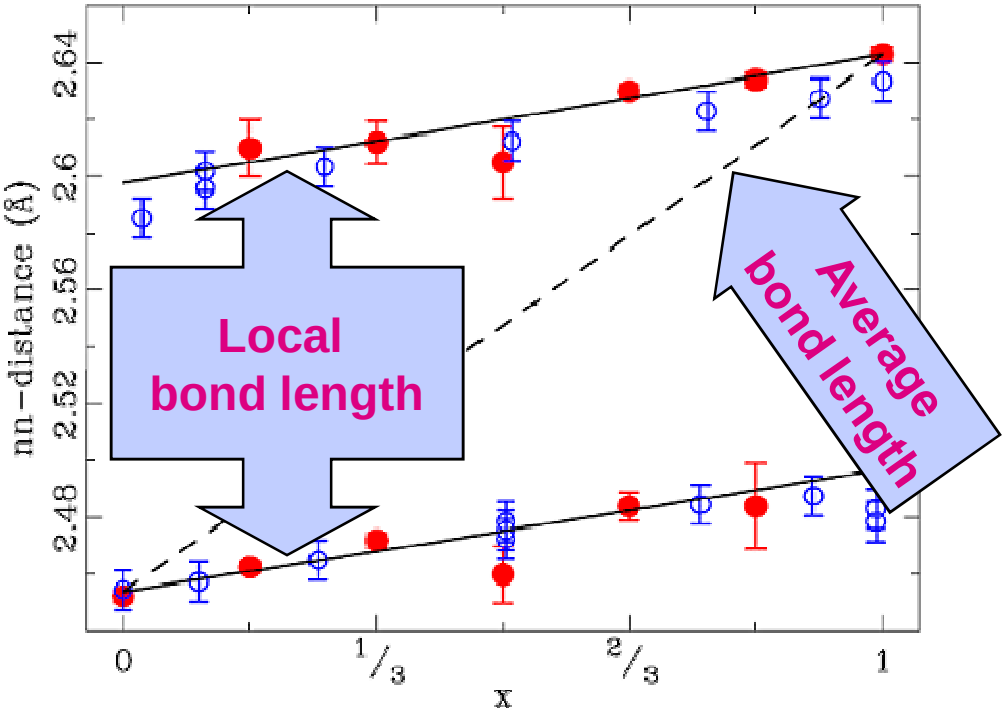
Peterson et al., *Phys. Rev.* B**63,** 165211 (2001)





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





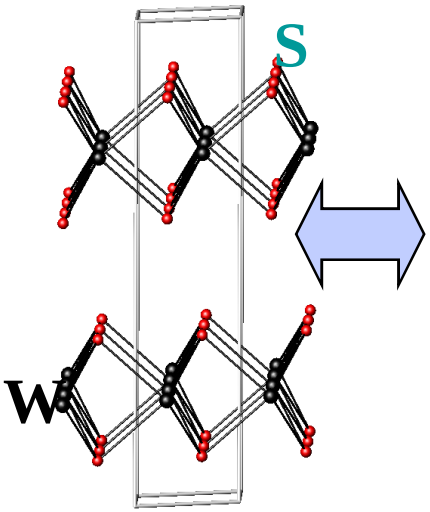
BLUE: XAFS from Boyce et al., *J. Cryst. Growth.* **98**, 37 (1989); RED: PDF results.

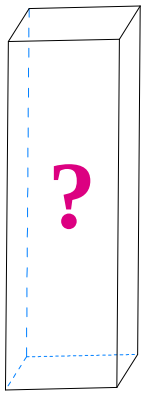
Local structure of WS_2

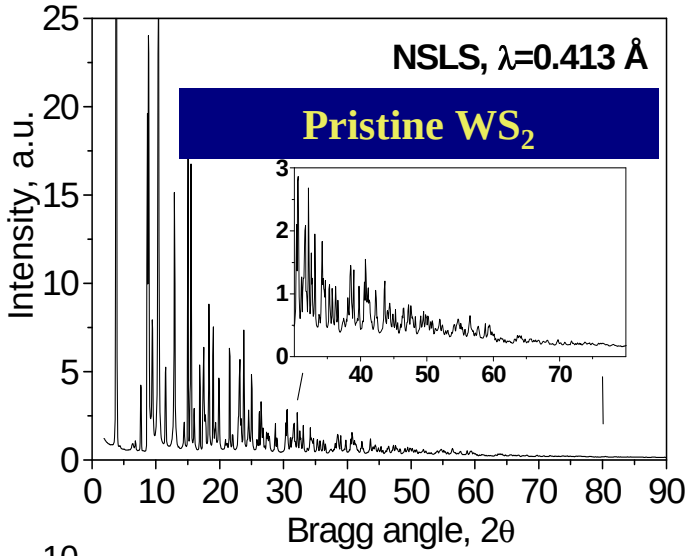
Simon Billinge
Thomas Proffen (LANL)
Peter Peterson (SNS)
Valeri Petkov (CMU)

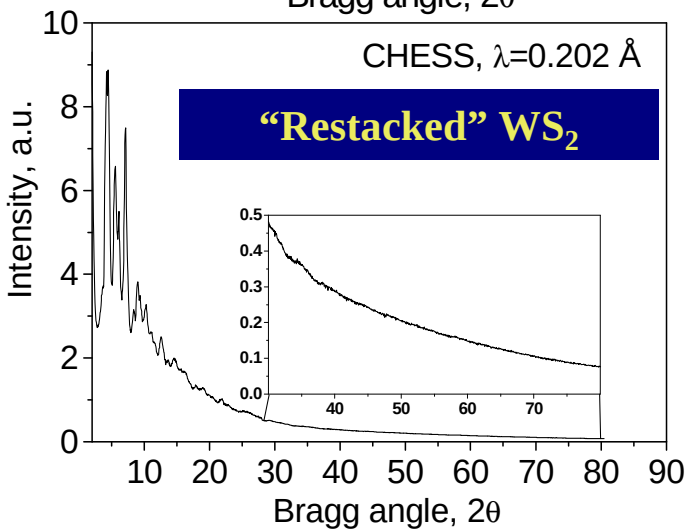
Facilities: Chess
Funding: DOE, NSF

WS_2 : Structure of the "restacked" material



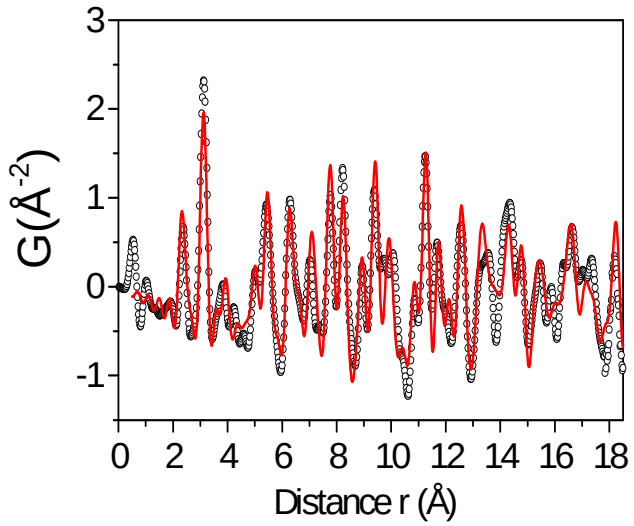






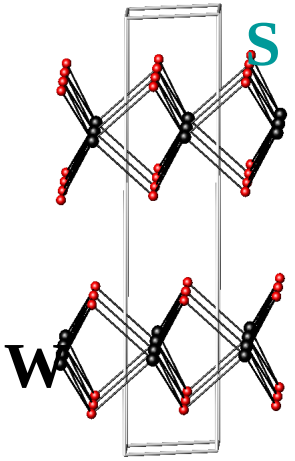
- WS_2 useful as a lubricant, catalyst, solid-state electrolyte.
- Exfoliated and restacked WS_2 has a metastable disordered structure. Disorder precluded a full structural solution.

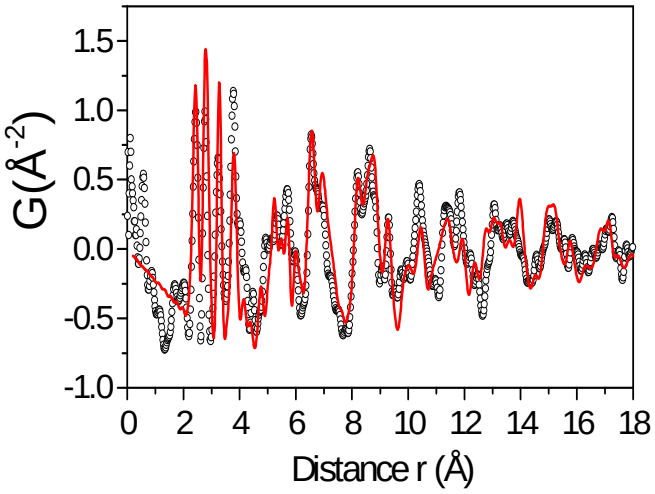
WS_2 : PDF to the rescue



Pristine WS_2:

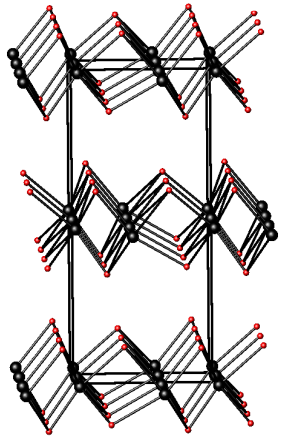
Hexagonal
$P6_3/mmc$





"Restacked" WS_2:

Monoclinic
$P112_1$
(disordered derivative of WTe_2)



Petkov et al., *J. Am. Chem. Soc.* **122,** 11571 (2001)

Jahn Teller Distortion in $LaMnO_3$

Simon Billinge
Emil Bozin
Xiangyn Qiu

MICHIGAN STATE UNIVERSITY

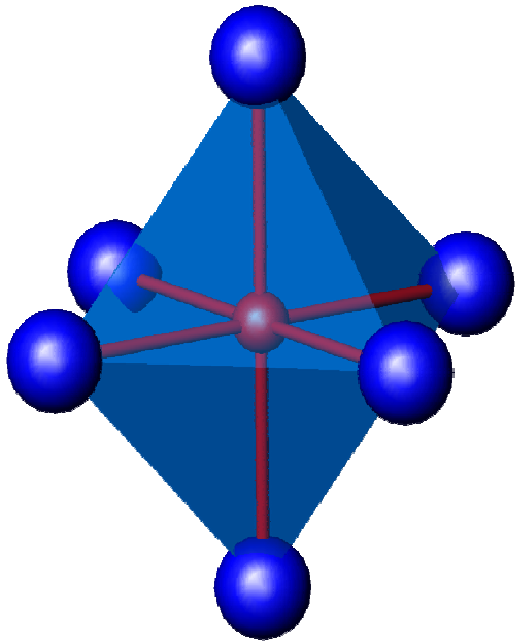
Thomas Proffen

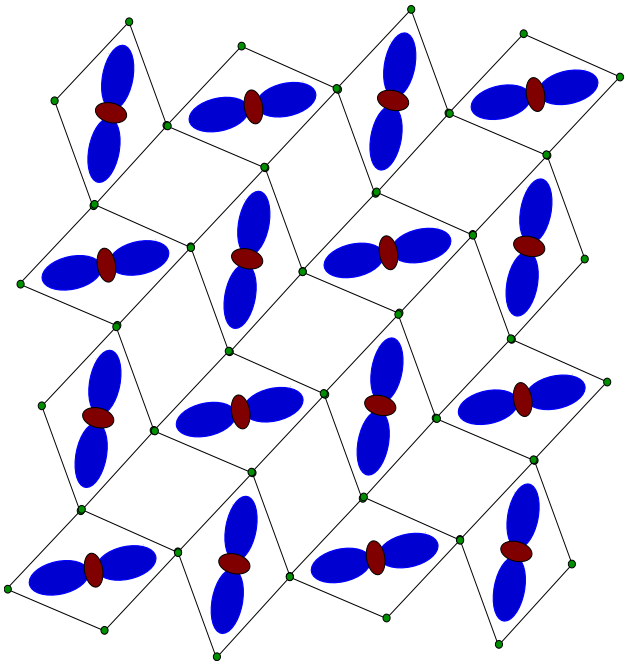
Los Alamos

Facilities: Lujan
Funding: DOE, NSF

$LaMnO_3$: Local structure *vs*. electronic state

- JT orbitals are ordered at low-temperature in a checker-board pattern:





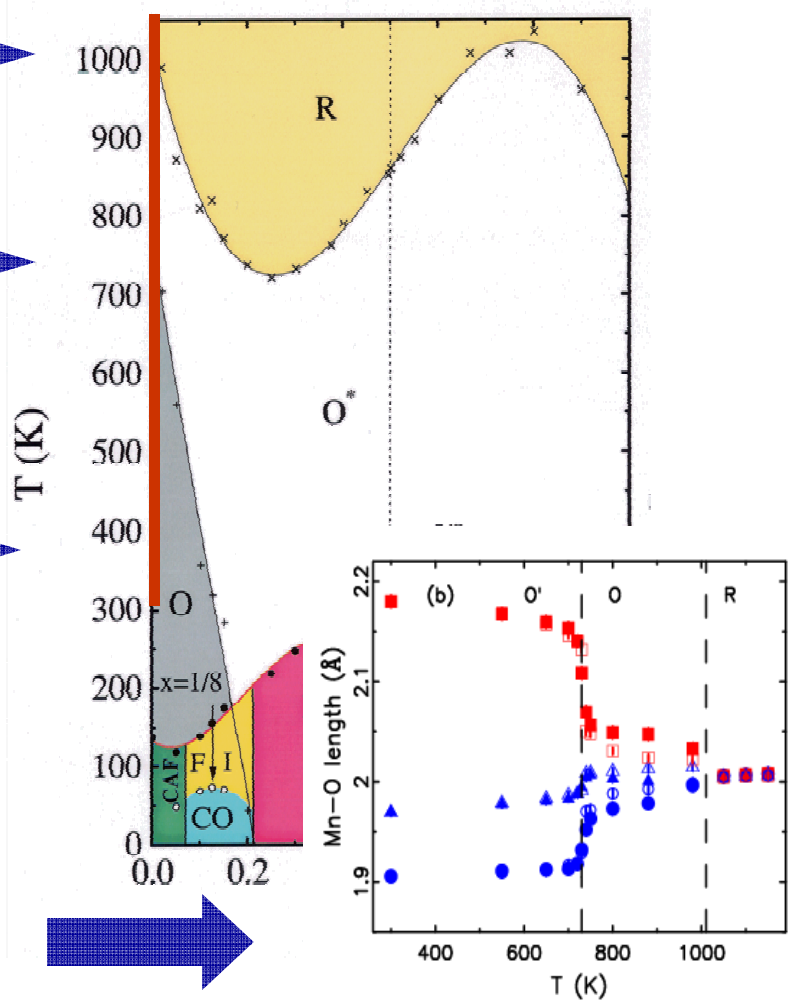
$LaMnO_3$: Crystallography

Rhombohedral
No JT distortion

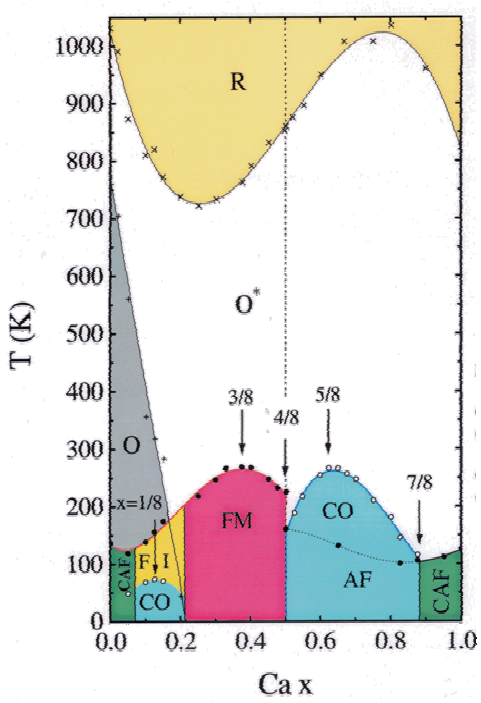
Less-Orthorhombic-O‘
Virtually no JT distortion

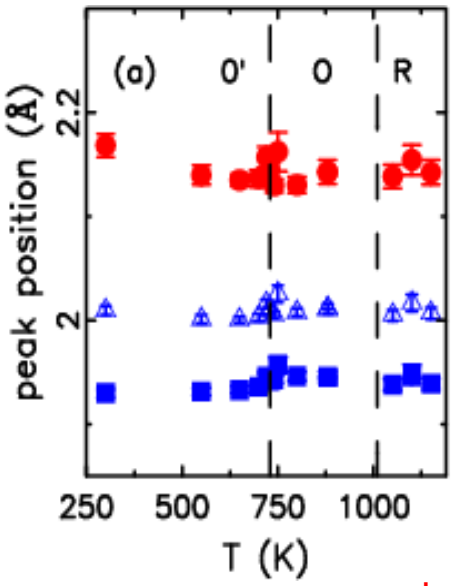
Orthorhombic-O
Large JT distortion

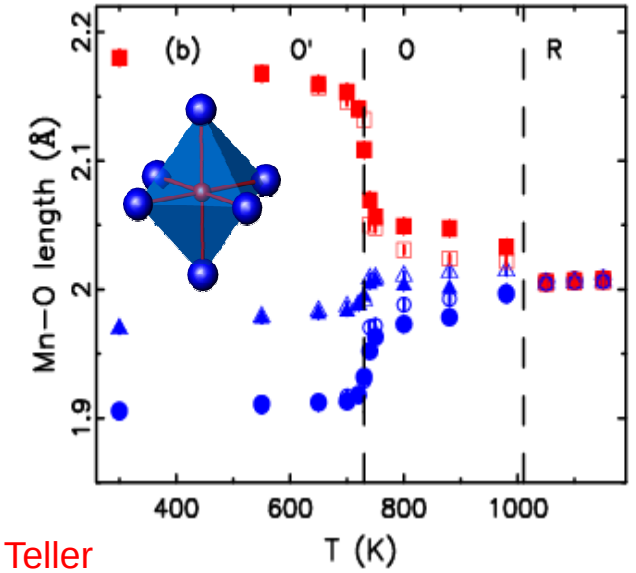
JT distortion disappears at the O-O’ transition



$LaMnO_3$: Jahn-Teller distortion







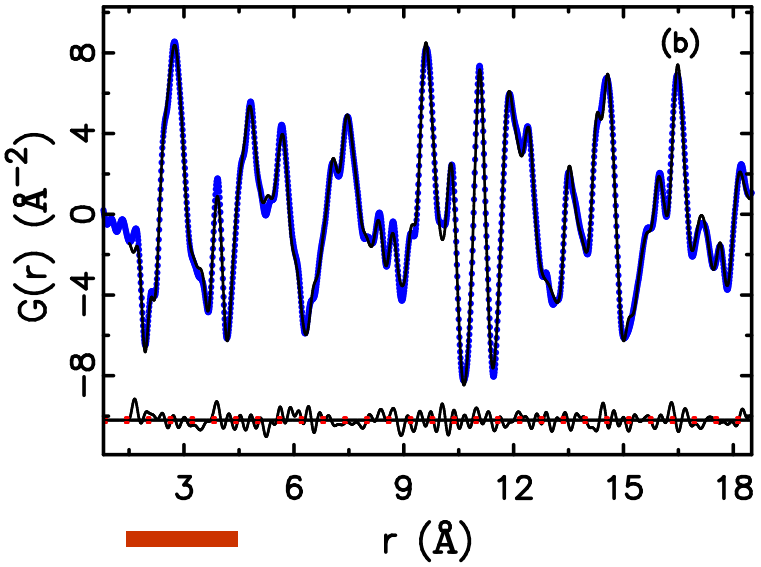
Jahn Teller
Long Mn-O bond

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).

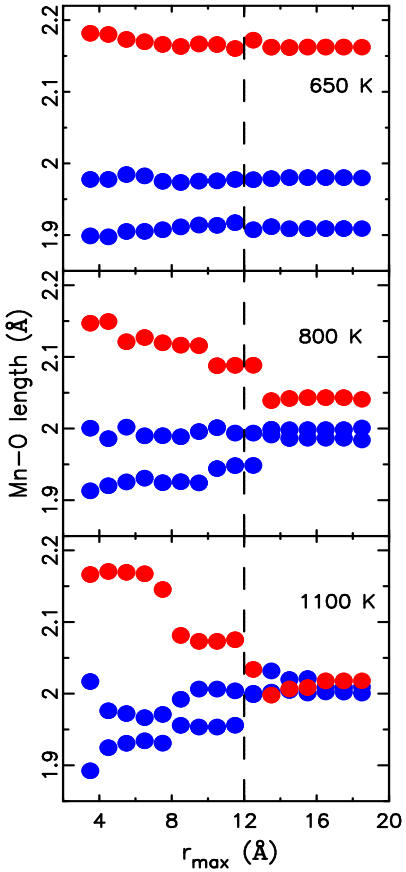
$LaMnO_3$: Jahn-Teller distortion



Local

Average

Intermediate ?



Mn-O bonds

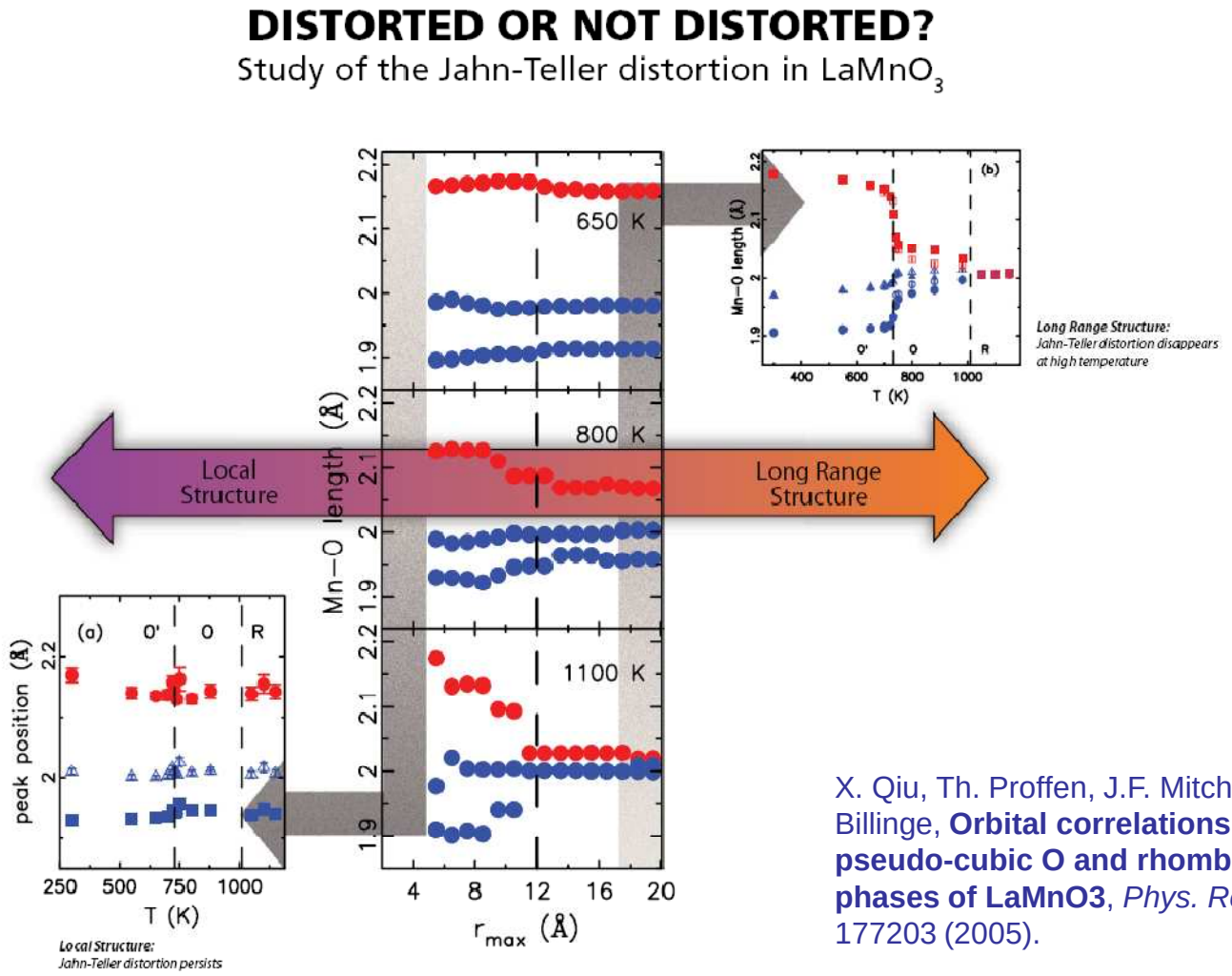
O

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).

Refinement range – the mystery of $LaMnO_3$



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

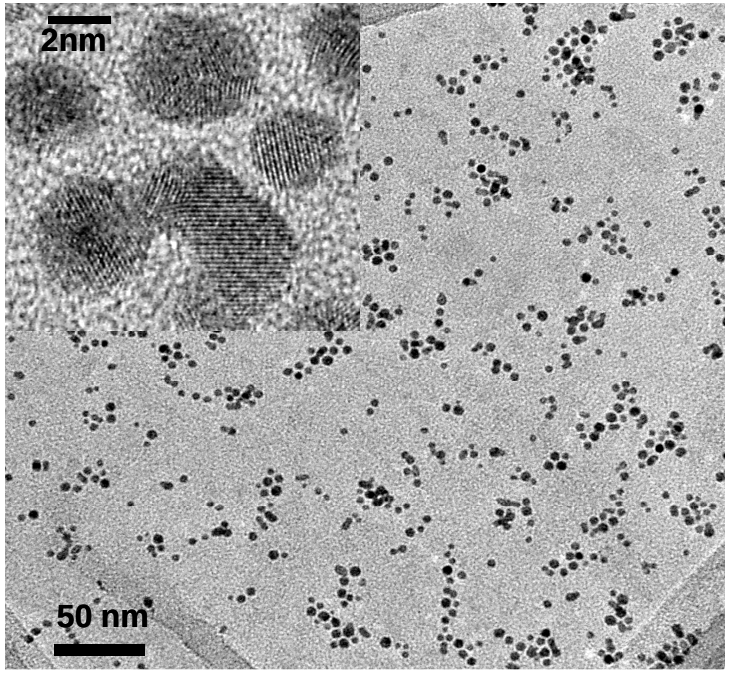
Ram Seshadri
Tony Cheetham

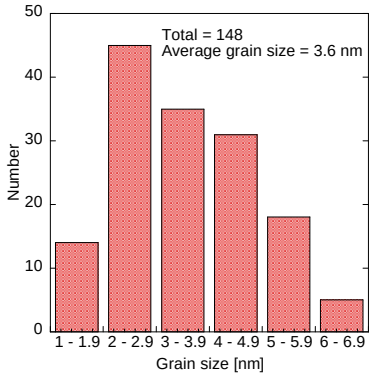
Facilities: Lujan
Funding: DOE, NASA

Example: Gold nanoparticles

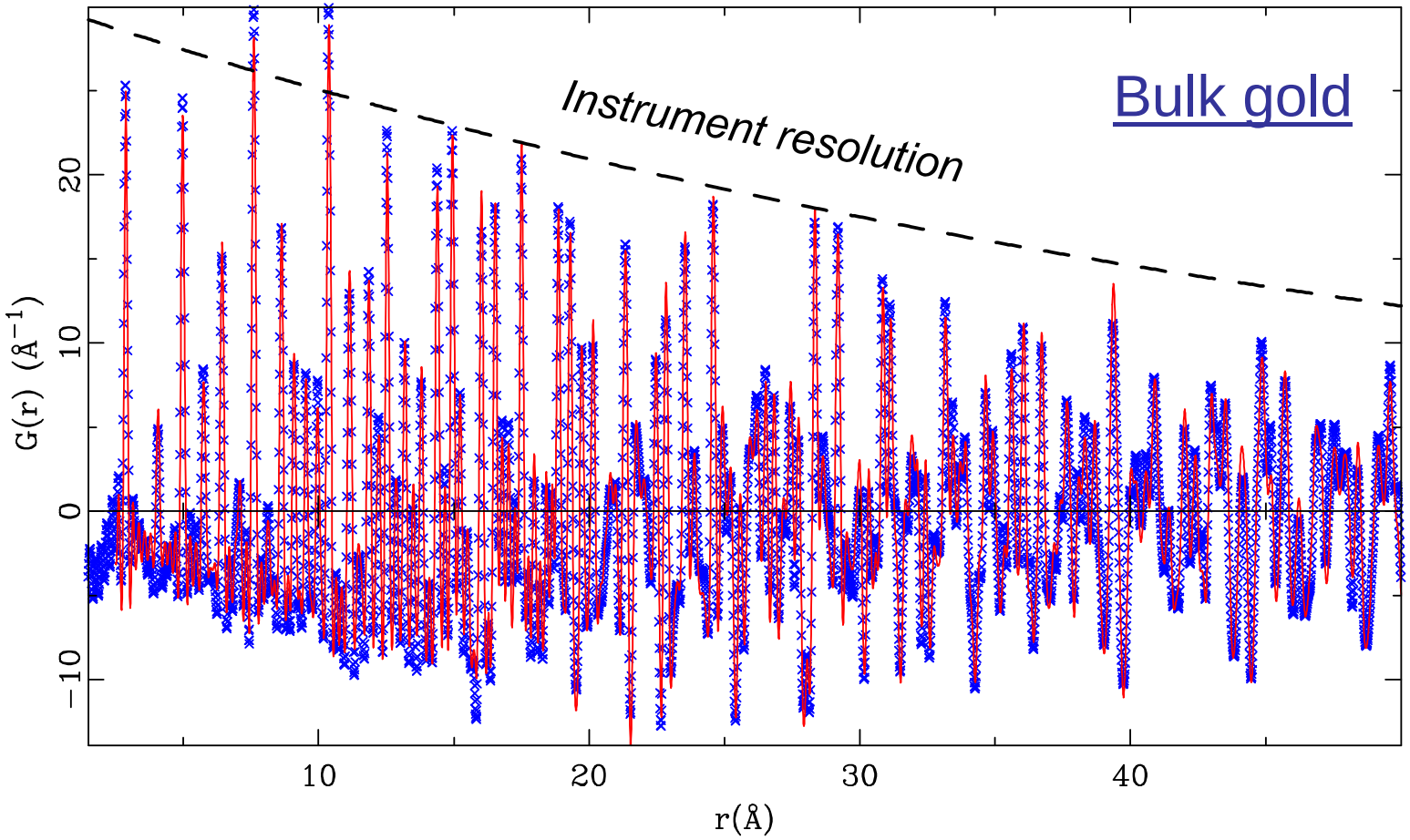
- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.

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

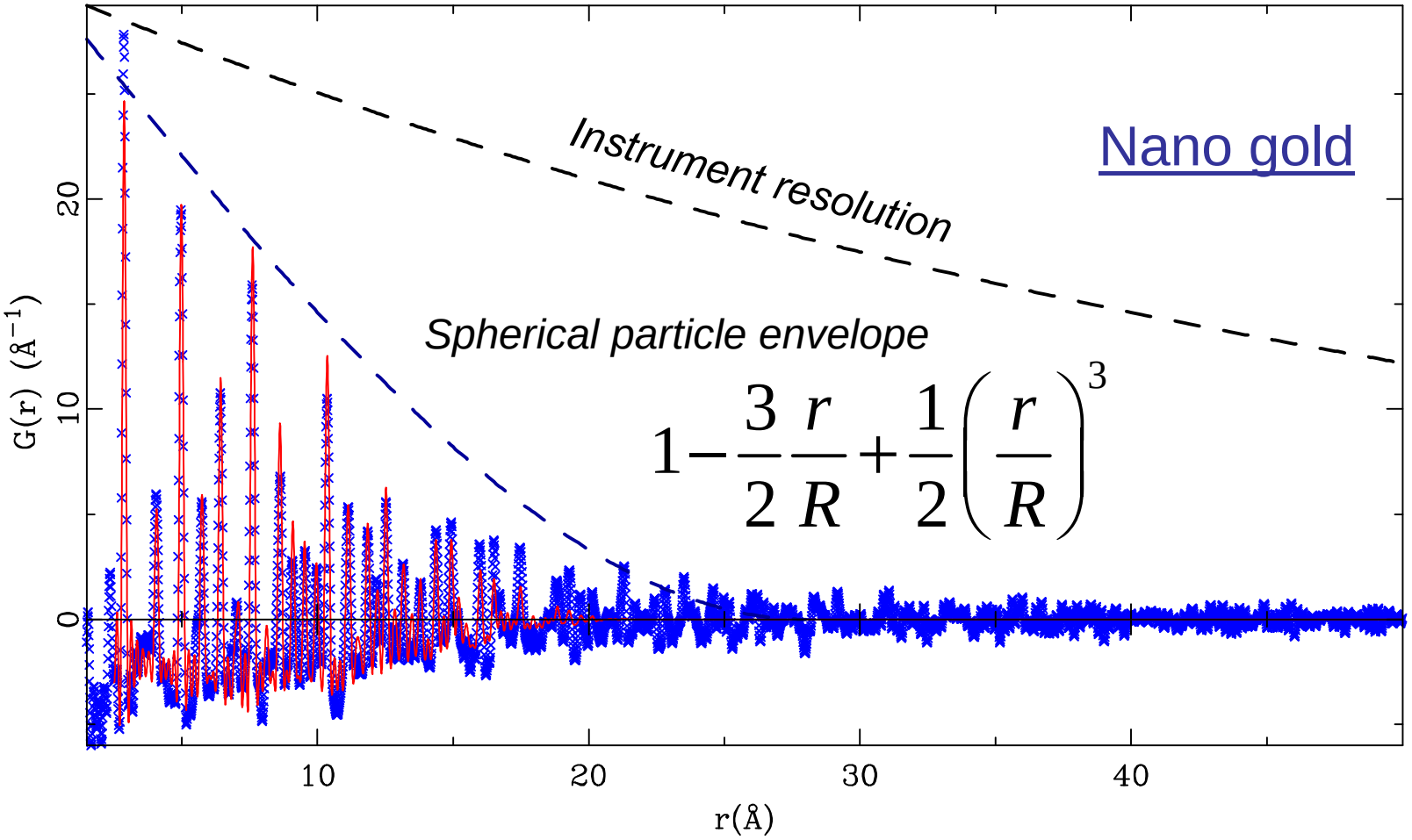




Au nanoparticles: Particle size



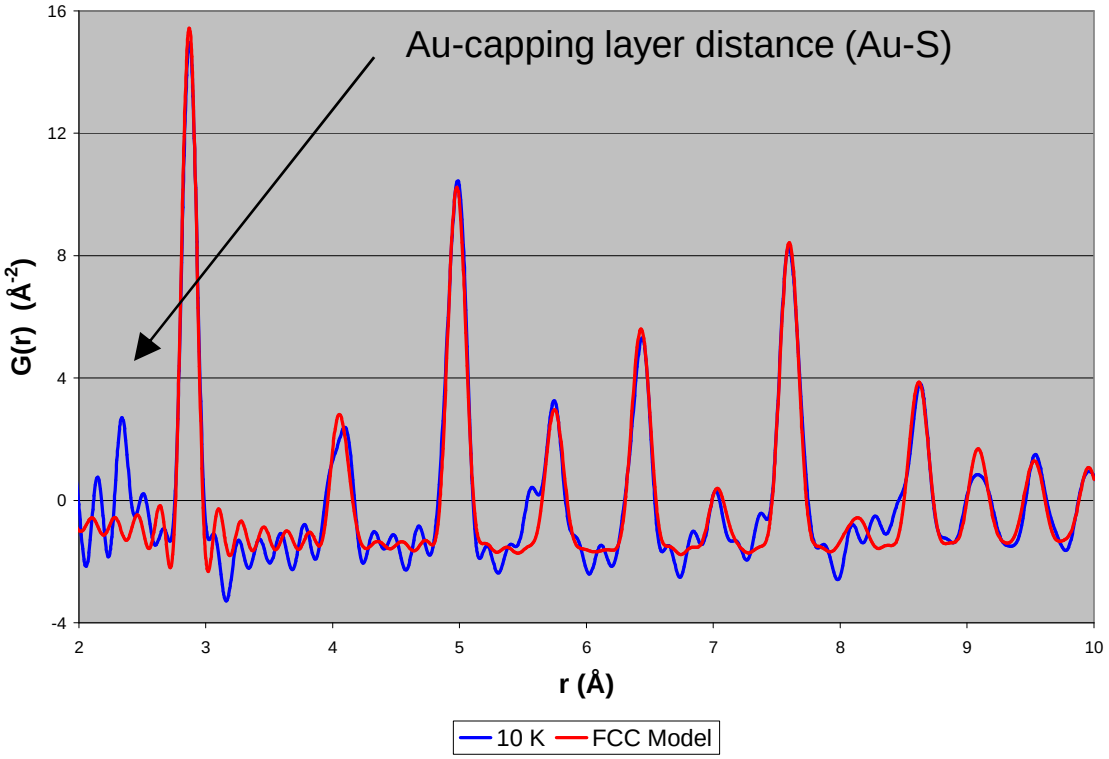
Au nanoparticles: Particle size



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).

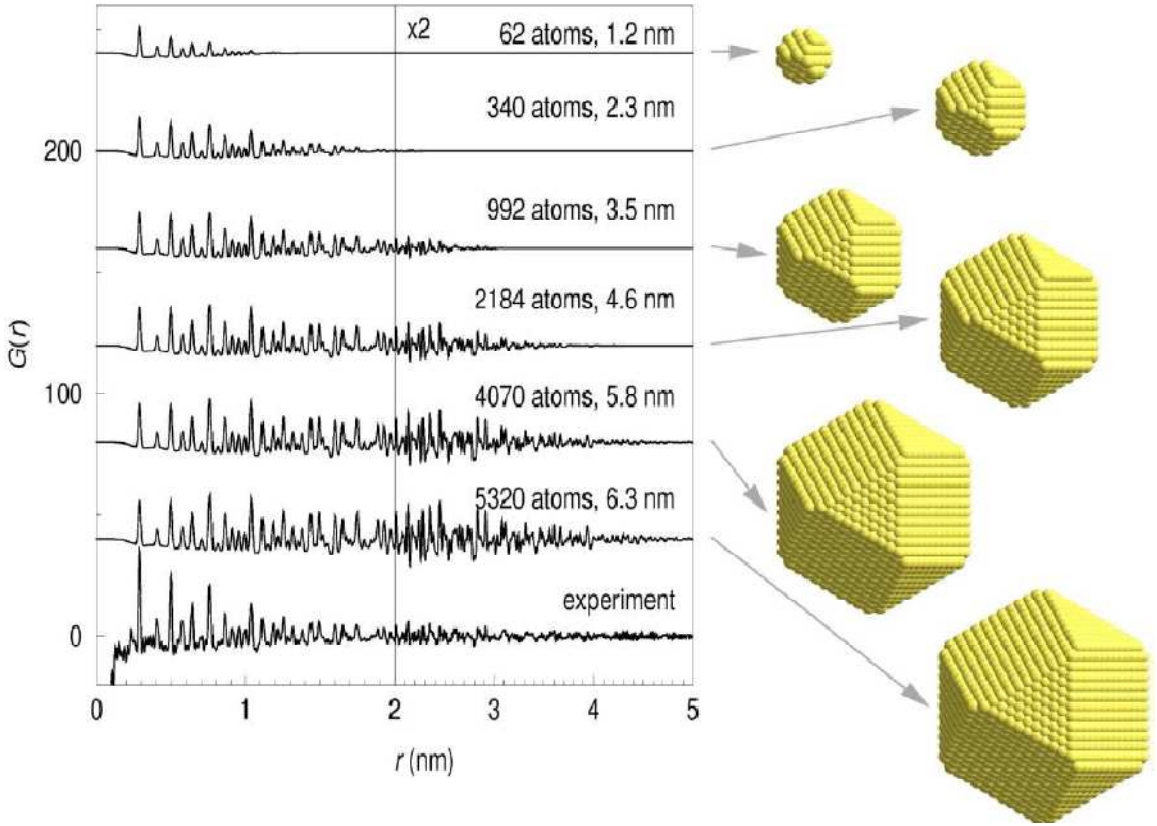
Au nanoparticles : Structural refinements

- 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.

Nano-structured transition metal carbides

Katharine Page
(PhD work)

UCSB

Ram Seshadri
Tony Cheetham

Thomas Proffen

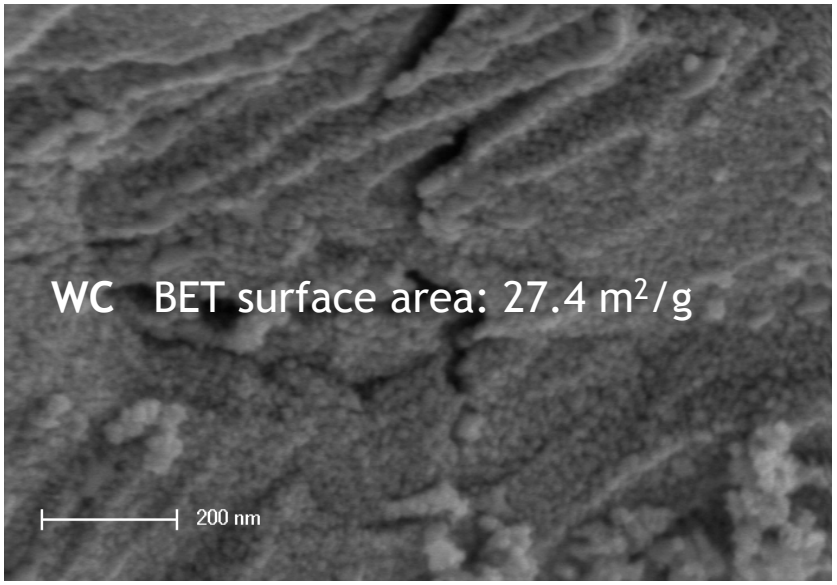
Los Alamos

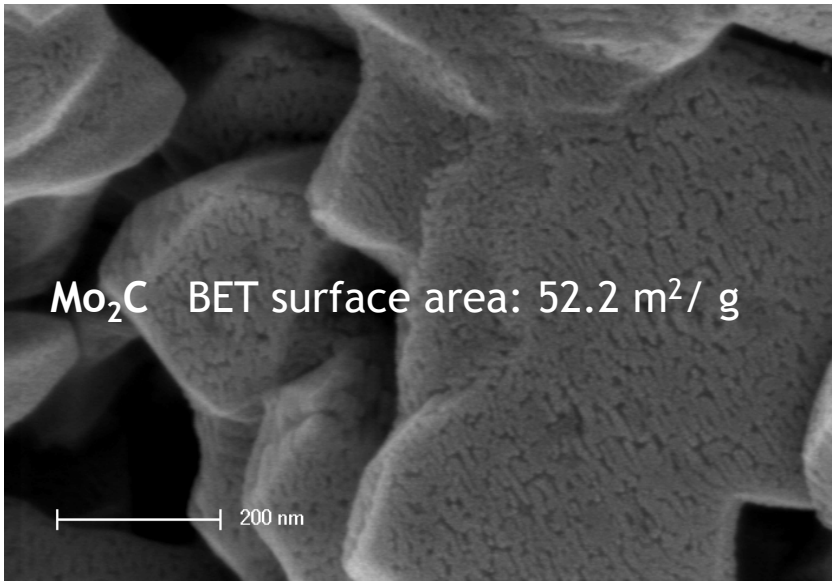
Facilities: Lujan

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.

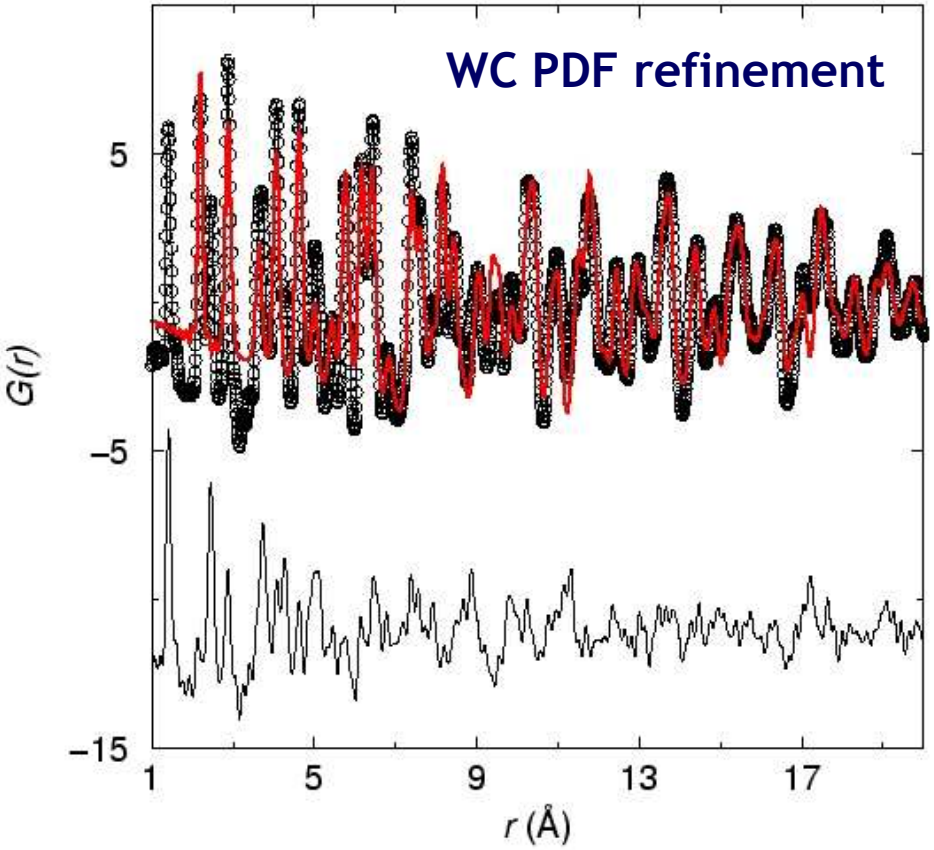


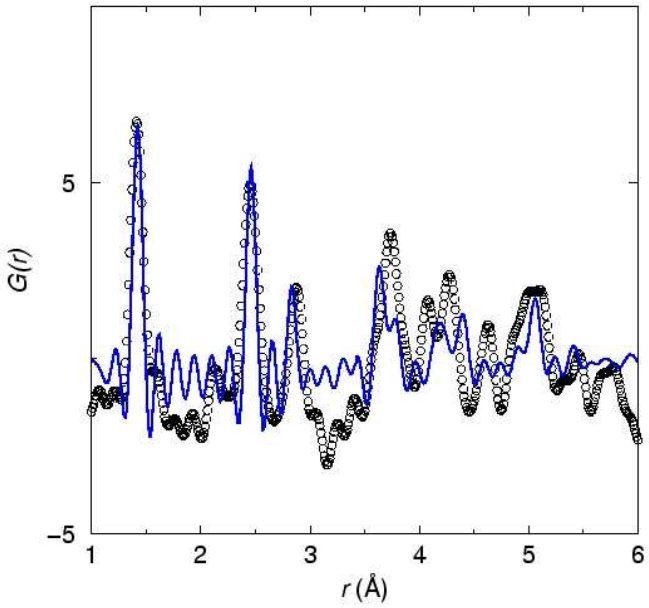


Prepared by treating molybdtates/tungstates in a quartz tube with flowing 50%-H_2/CH_4 at 10 mL/min at elevated temperatures.

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.

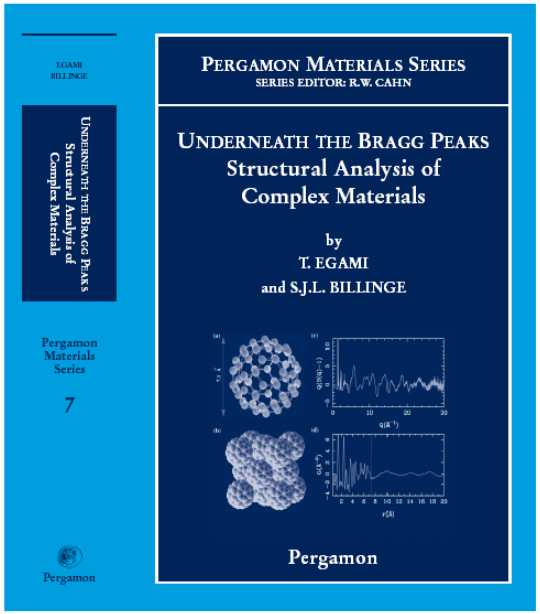




The difference curve, fit with the graphite structure.

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


Thank you