Recent developments in atomic pair distribution function analysis applied to amorphous and nanocrystalline materials

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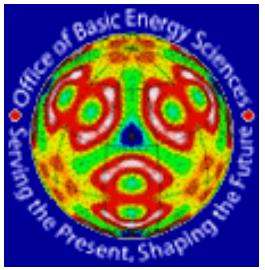
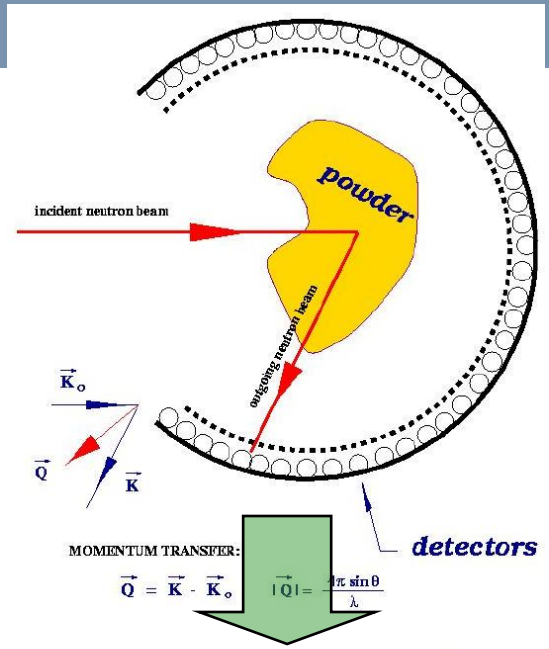
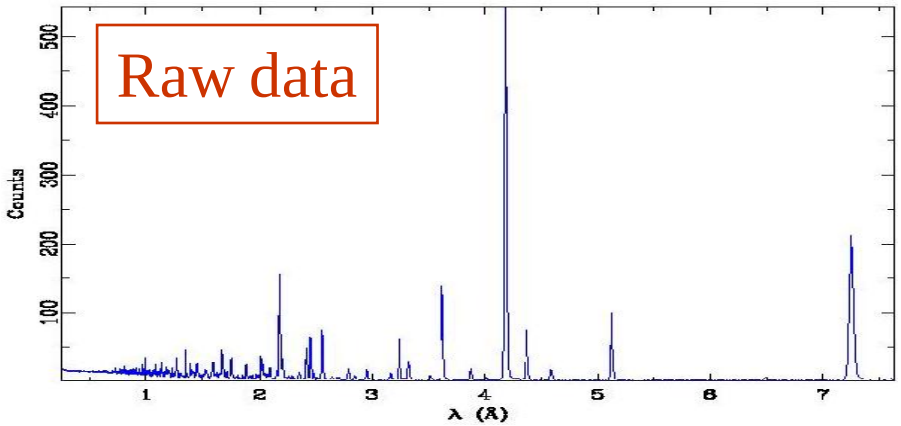


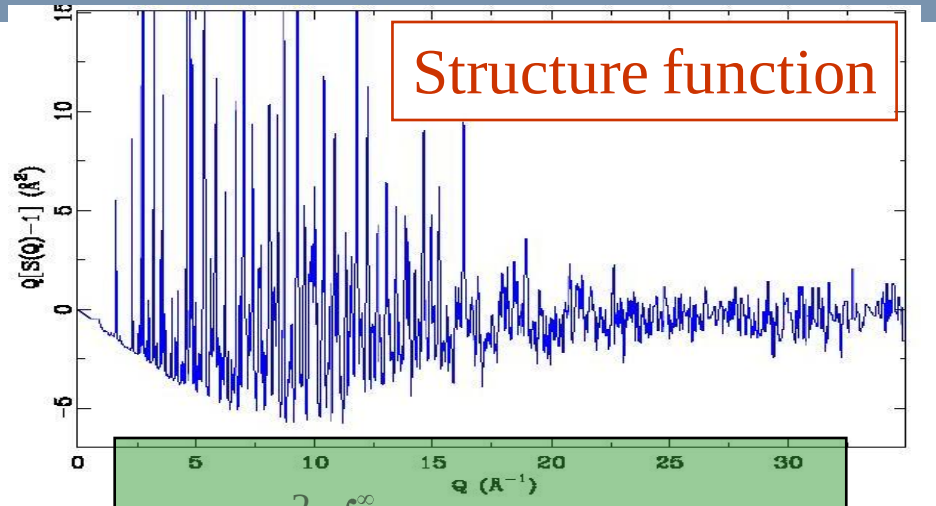
Atomic scale structure

- A knowledge of atomic-scale structure is a prerequisite to understanding and controlling material properties
- Crystallography provides robust, quantitative structure solutions for crystals but fails for non-crystalline materials
- Diffraction methods still provide useful information

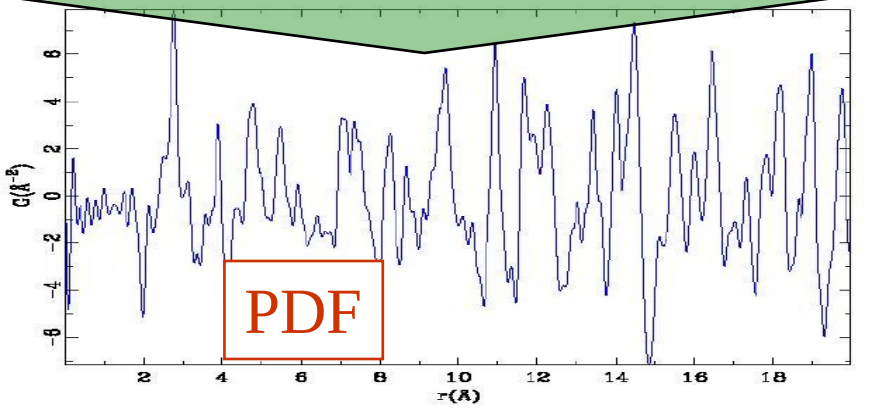
Obtaining the PDF



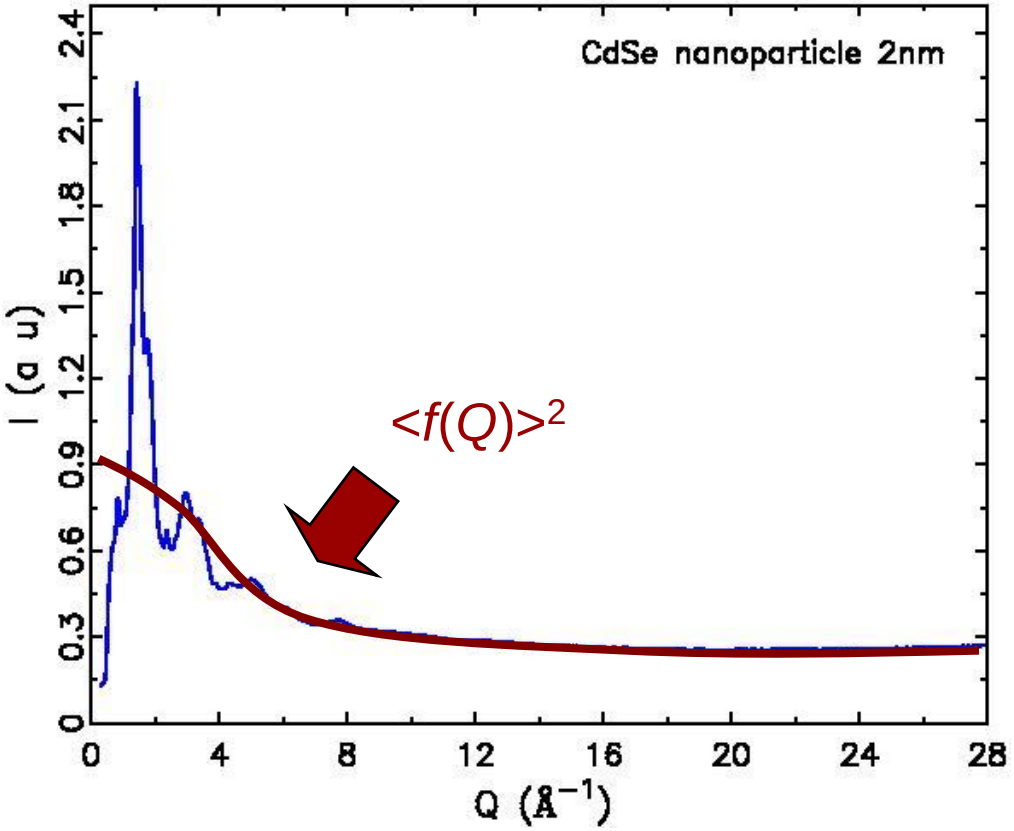


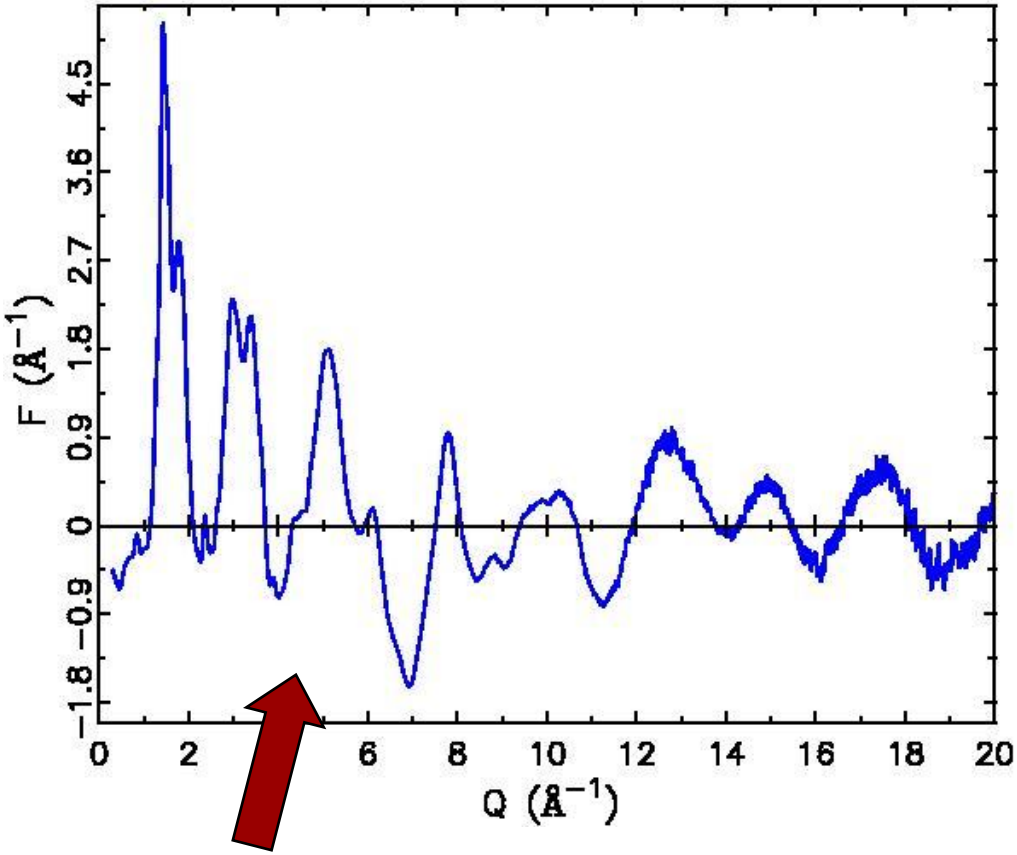


$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q)-1]\sin QrdQ$$



But there is no information at high-Q…?

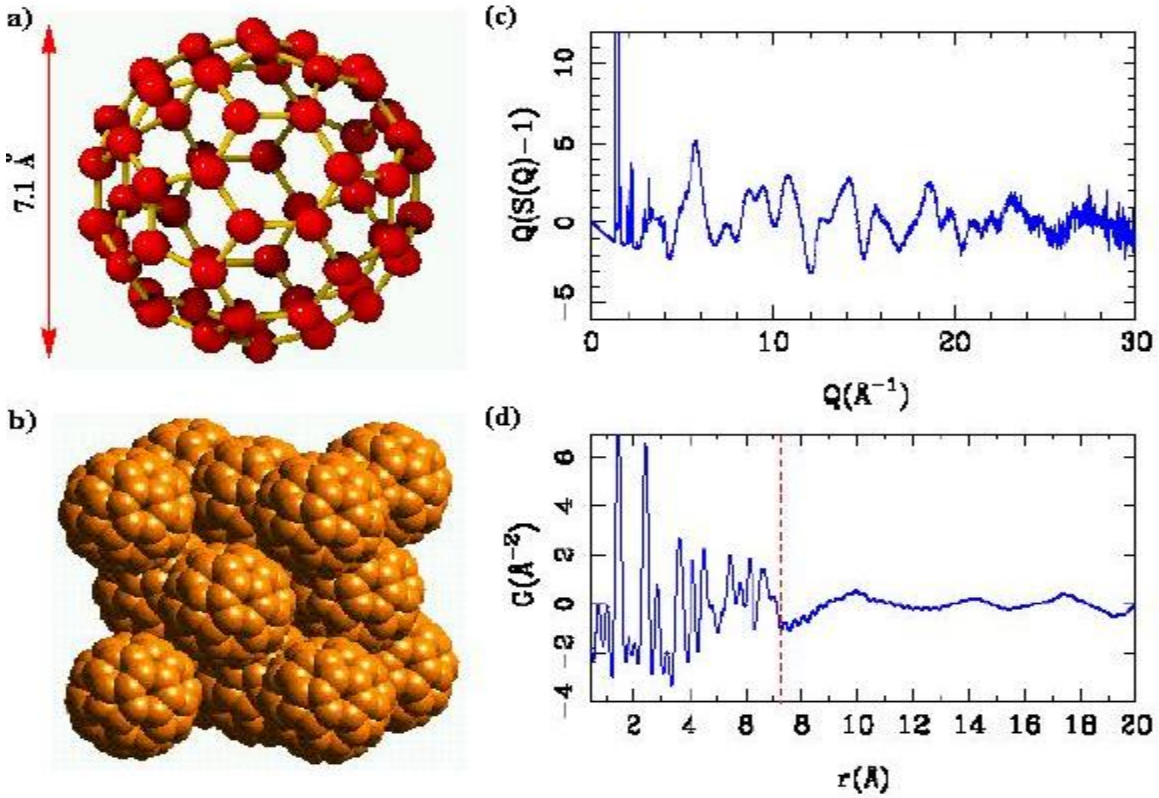




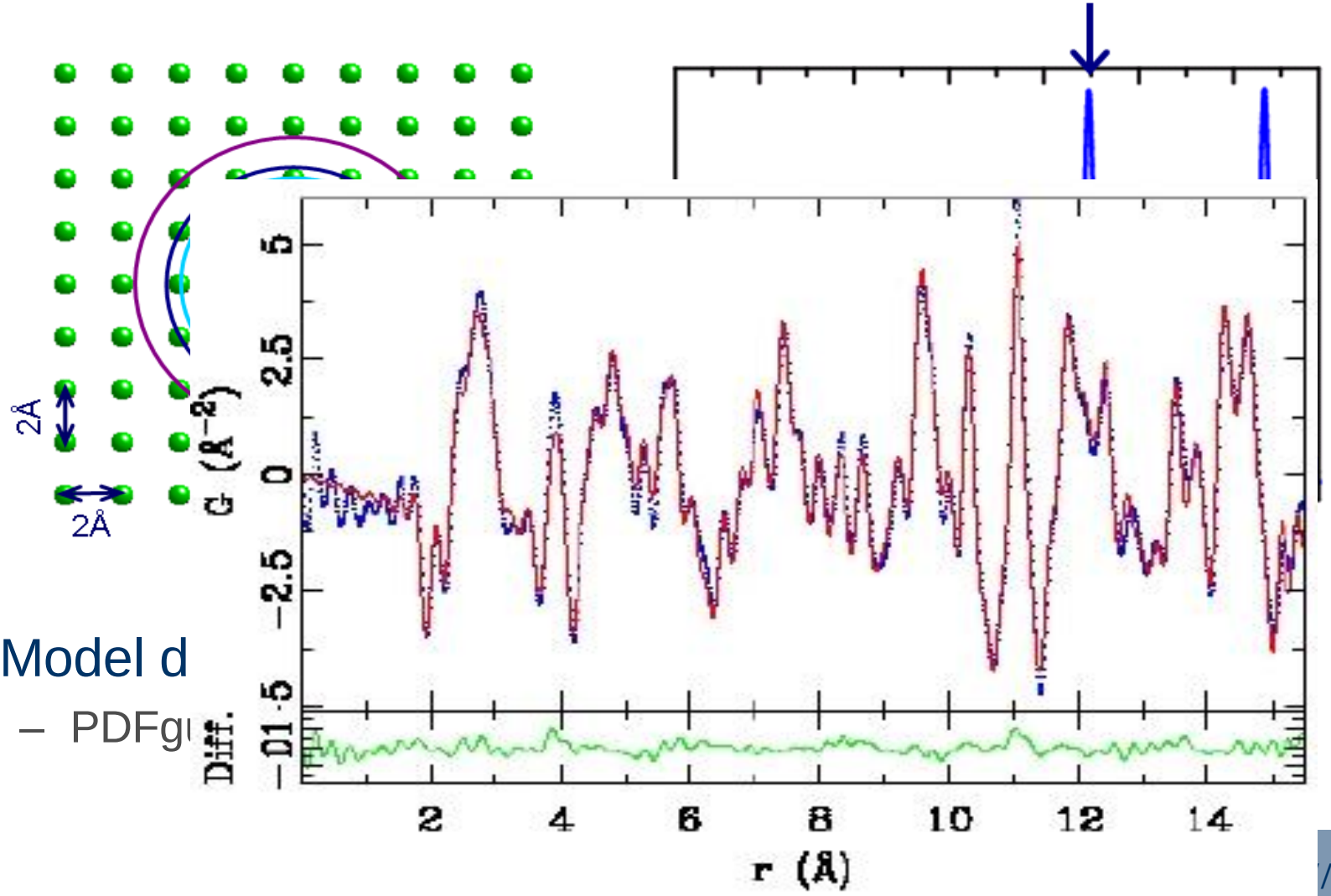
$$G(r) = \frac{2}{\pi}\int_0^\infty \boxed{Q[S(Q)-1]}\sin Qr\,\mathrm{d}Q$$

What is the PDF?

- Sit on an atom and look at your neighborhood
- *G(r)* gives the probability of finding a neighbor at a distance *r*
- PDF is experimentally accessible
- PDF gives the local structure

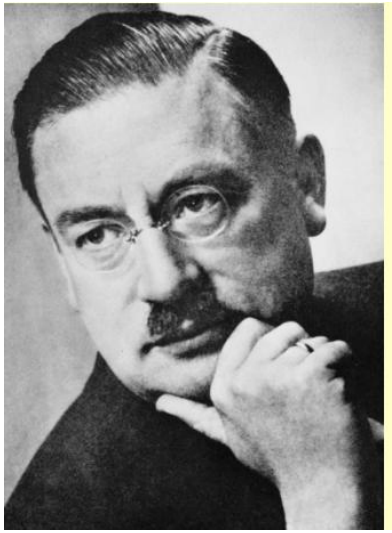


Modeling the PDF



- Model d
  - PDFg

Computational issues: A Brief History of PDF



- Pieter Debye, 1912:

$$I = \sum_n \sum_m f_m f_n^* \frac{\sin qr_{mn}}{qr_{mn}}$$

- Fritz Zernike and Jon Prins, 1927:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi} \int_0^\infty qi(q) \sin qr dq$$

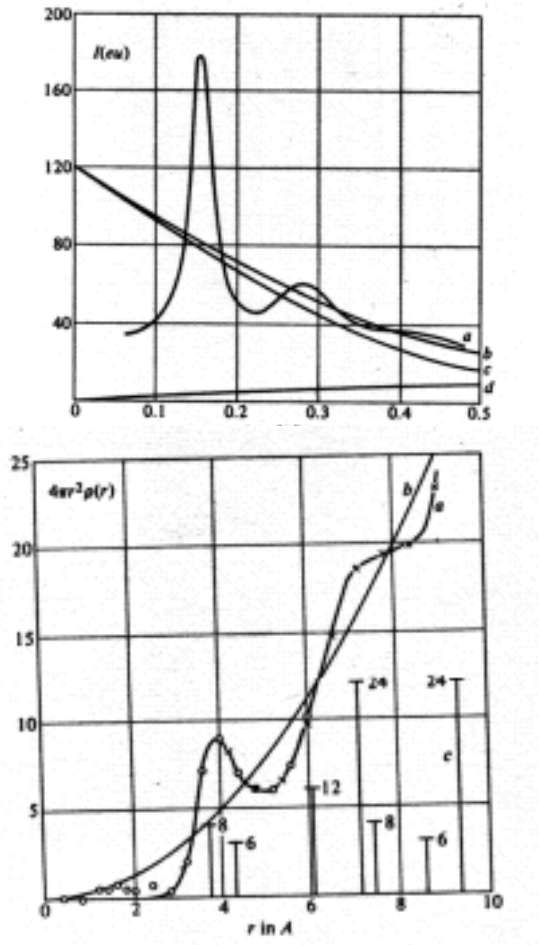
History

Debye and Menke, Z. Phys. (1930)

PDFs of mercury

Tarasov, L. P., and Warren, B. E., (1936) *J. Chem. Phys*., **4**, 236.

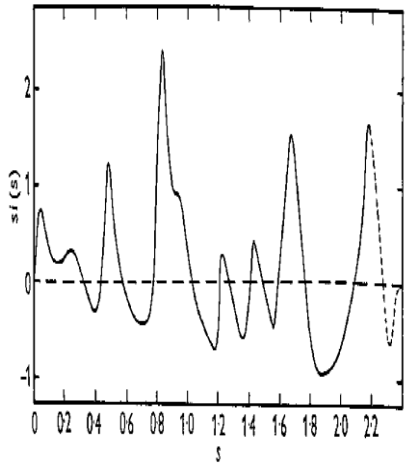
X-ray PDFs of molten sodium

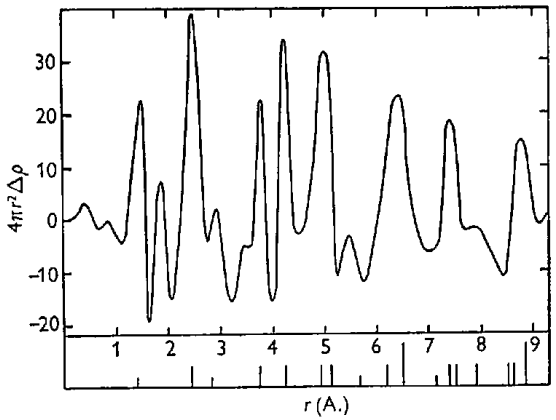


History of PDF

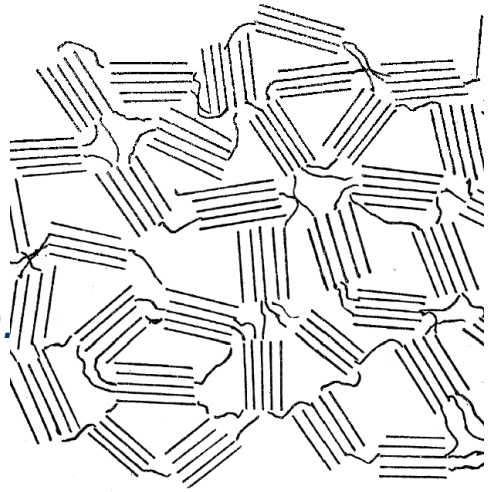
- Early 1930's
  - Computer: slide rule
  - Time to Fourier transform: few days
  - Time to paper: 6 months

History





Disordered Carbon



Warren, B. E., (1934) *J. Chem. Phys.* **2**, 551.

Franklin R. E. (1950) *Acta Crystallogr*. **3**, 107

Franklin R. E. (1951) *Proc. R. Soc. London A*,. **209**, 196

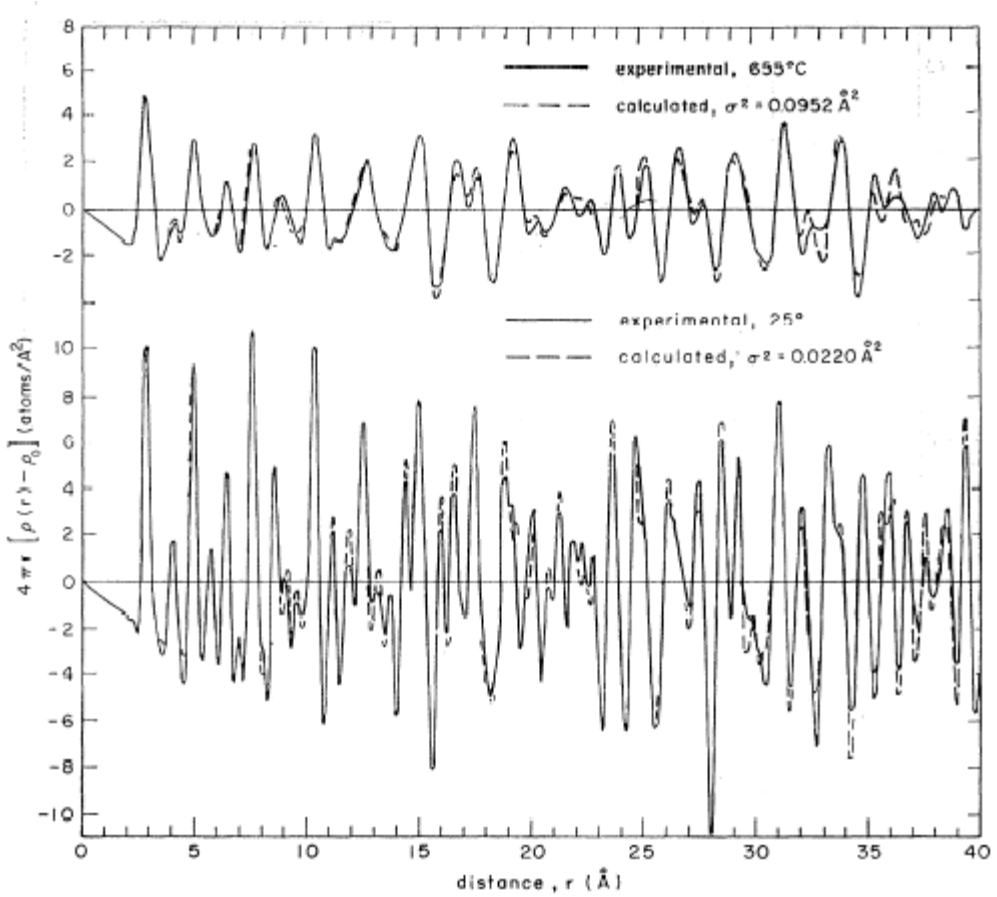
History of PDF

- 1930's
  - Computer: slide rule
  - Time to Fourier transform: few days
  - Time to paper: 6 months
- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months

Beevers Lipson strips

Gould BCA newsletter

History



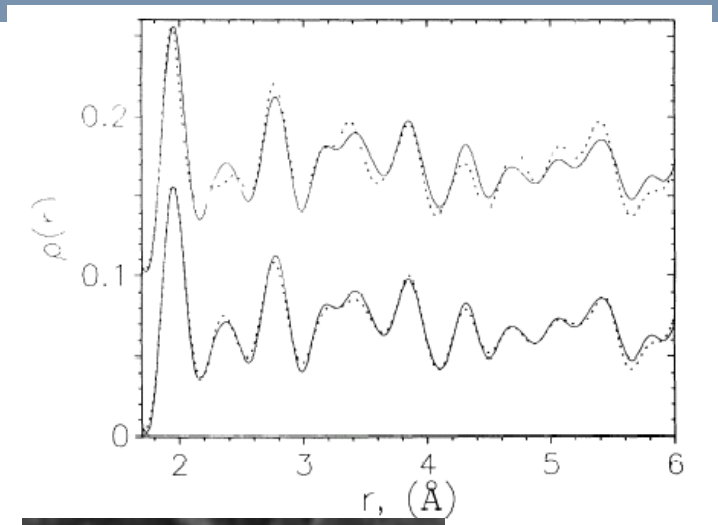
PDFs from crystalline Aluminum

R. R. Fessler, Roy Kaplow and B. L. Averbach, *Phys. Rev.* **150**, 34 (1966).

First use of Reverse-Monte-Carlo refinement

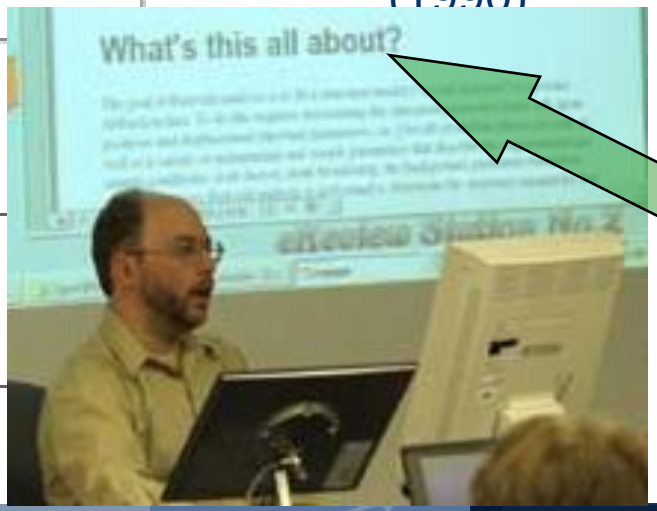
Kaplow R, Rowe, T. A. and Averbach, B. L. (1968), *Phys. Rev*. **168**, 1068.

20 years later…



Combine Monte-Carlo modelling with crystalline PDFs to get real, quantitative, local structural information: the first such paper was on Tl high-Tc superconductors

B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, *Phys. Rev. Lett*. **64**, 2414-2417 (1990)



And yet 20 years on Brian's still confused about the subject

History of PDF

- 1930's
  - Computer: slide rule
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- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months
- 1980's
  - Computer: DEC microvax
  - Time to Fourier transform: ~15 mins.
  - Time to paper: 6 months

PDF of crystals: the early days

- Microvax: 16Mb memory, 100Mb hard drive
- PDFvax: 6 students, 2 postdocs, no crashes
- Picture credit: Tom Carlson
  Location: Williamsburg, VA
- Well, my employer was re-modeling the basement and they were going to **throw it out**! Look at it! Would you let them just toss it! I think not. (And to think, they kept the AS/400! What were they thinking?) So I somehow wedged both towers into my Volkswagen and went to pick up my wife at her work. I could tell you what she said, but I like schools to be able to link to here.

History of PDF

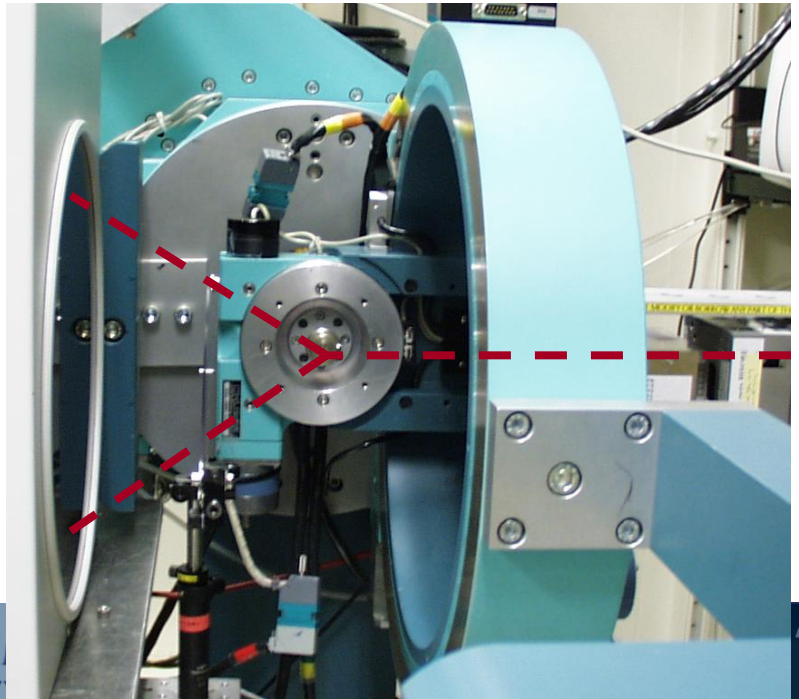
- 1930's
  - Computer: slide rule
  - Time to Fourier transform: few days
  - Time to paper: 6 months
- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months
- 1980's
  - Computer: DEC microvax
  - Time to Fourier transform: ~15 mins.
  - Time to paper: 6 months
- 2000's
  - Computer: 3 GHz Pentium PC
  - Time to Fourier transform: <1 second
  - Time to paper: 6 months

Recent Developments

- Modern experimental methods
  - X-rays
  - Neutrons
- High sensitivity
- High resolution
- High throughput – Special environments
- Nanostructured materials
- Advanced Modeling

The Atomic Pair Distribution Function (PDF) Method

- Use modern high intensity x-ray and neutron sources to collect unprecedentedly precise data
- Utilize all the information: Bragg and diffuse scattering
- Use modern computing capabilities to analyze, model and visualize the data

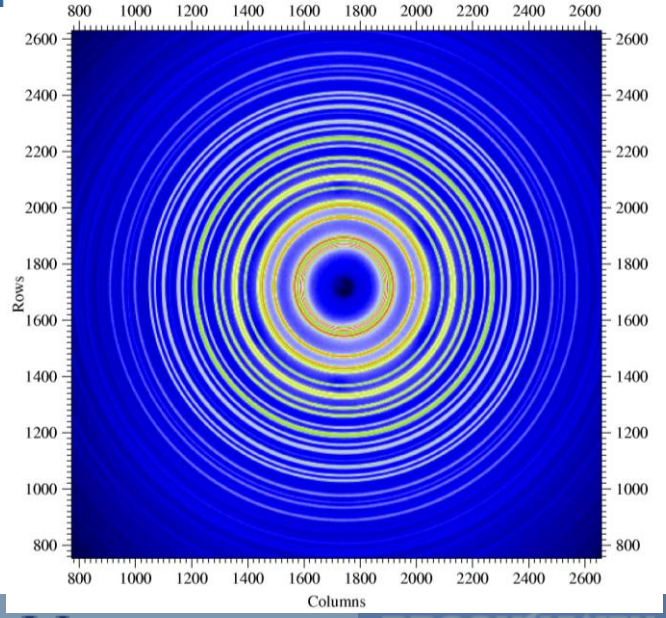


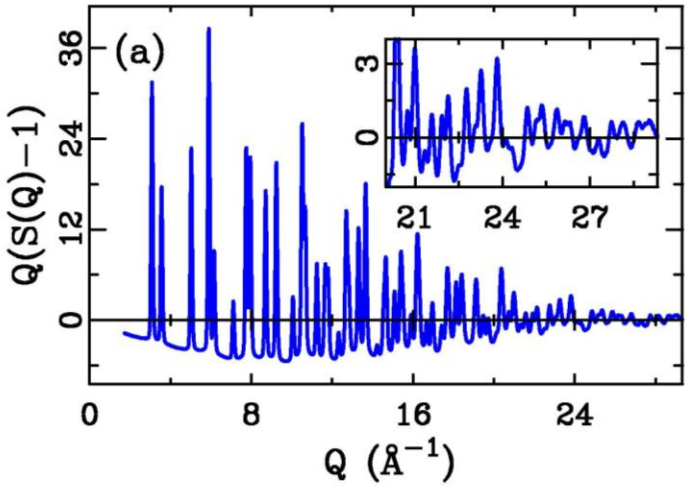
- Chupas SJB et al., J. Appl. Crystallogr. (2003)
- Billinge-group, BNL, SUNY-SB, APS collaboration

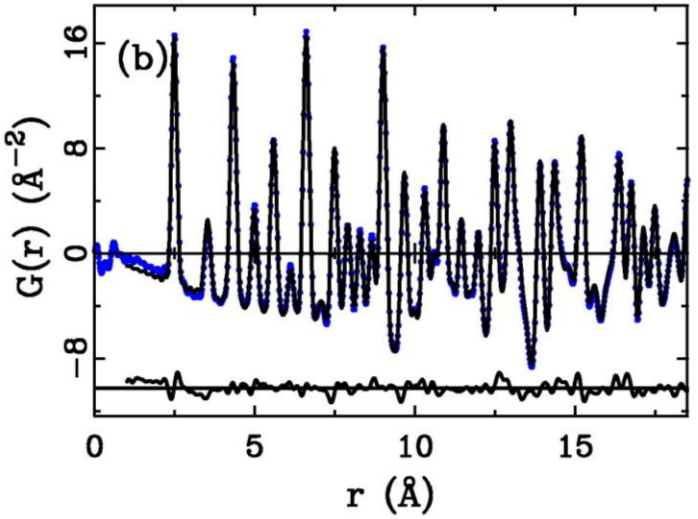
Rapid Acquisition PDFs

Fast x-ray PDFs

- Four orders of magnitude decrease in data collection time!
- Nickel data, 1s collection time, Q_{max} 28 $Å^{-1}$
- Developed in collaboration with Xiangyun Qiu, Pete Chupas, Jon Hanson, Peter Lee and Clare Grey

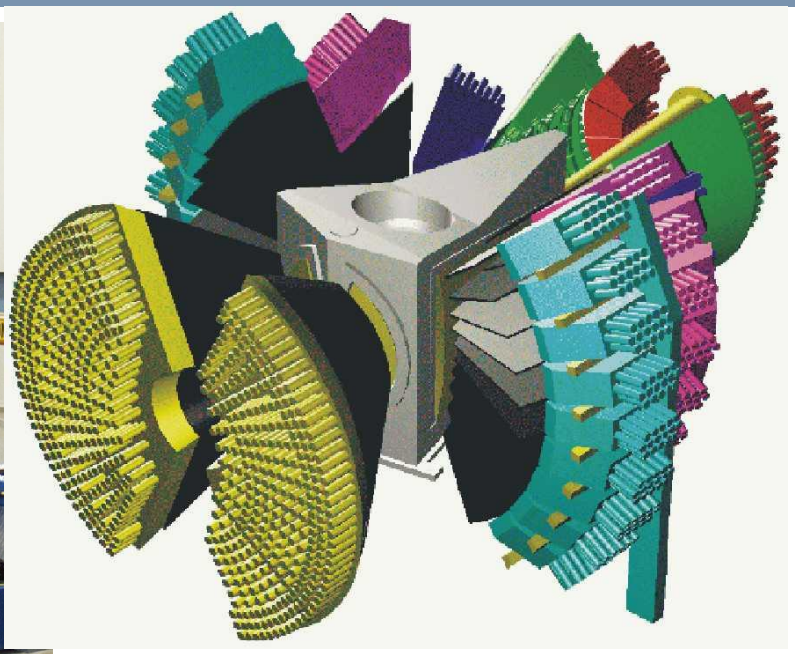






RAPDF with Neutrons

NPDF at LANSE

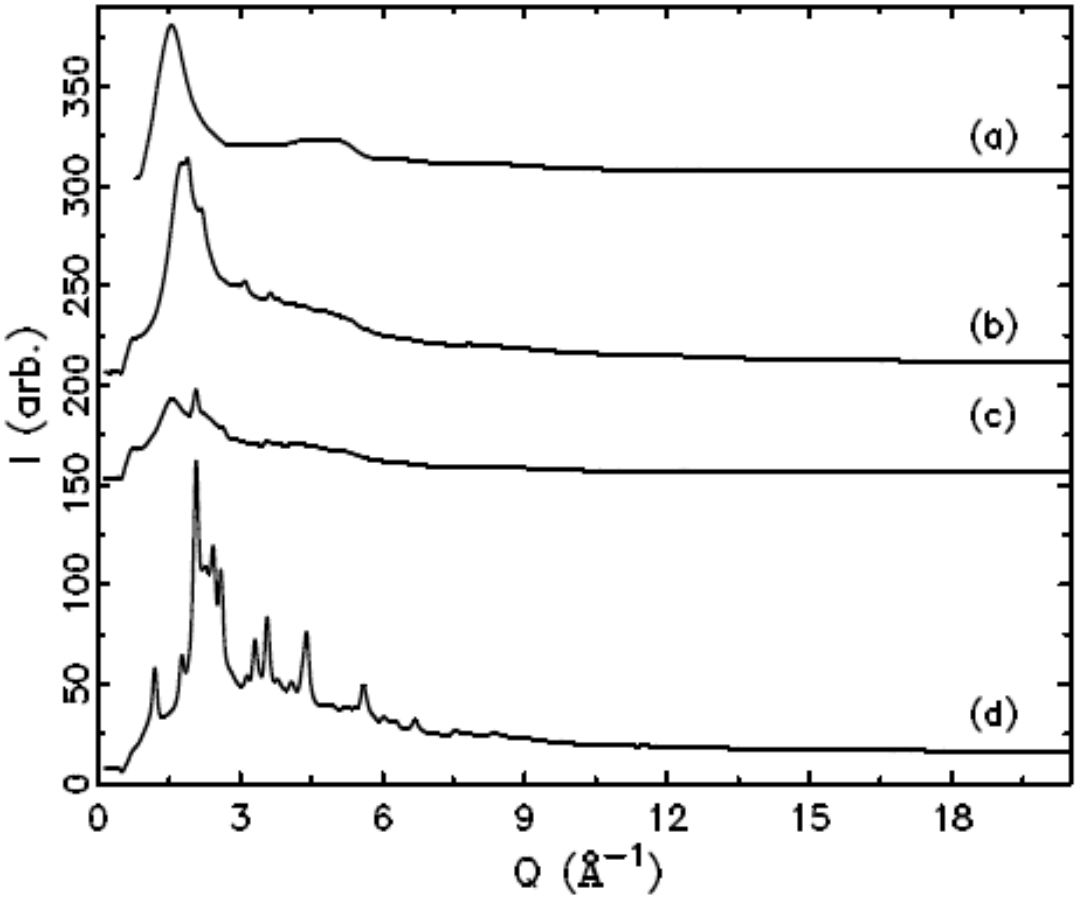


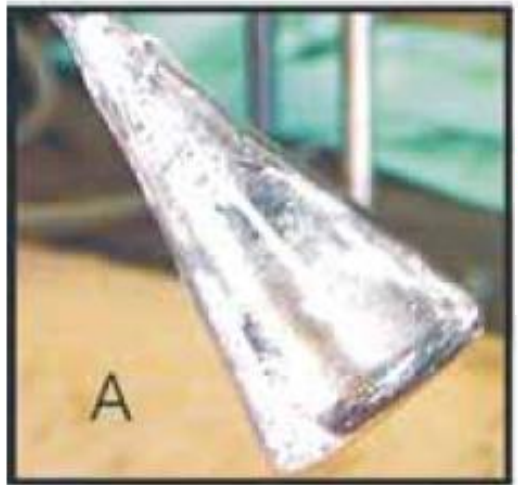
GEM at ISIS

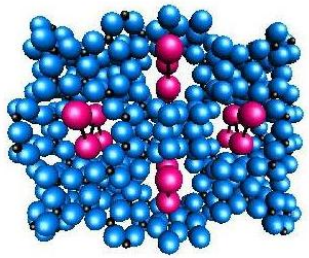
POWGEN3 &
NOMAD at SNS

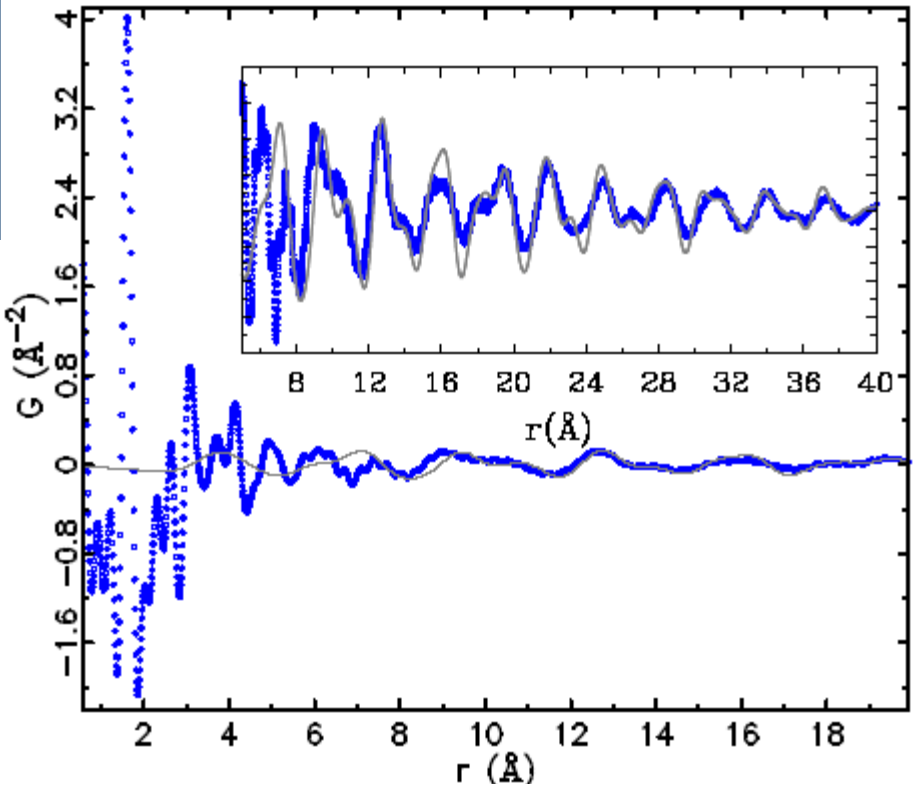
High Sensitivity

Nanoporous Materials: novel reducing agent









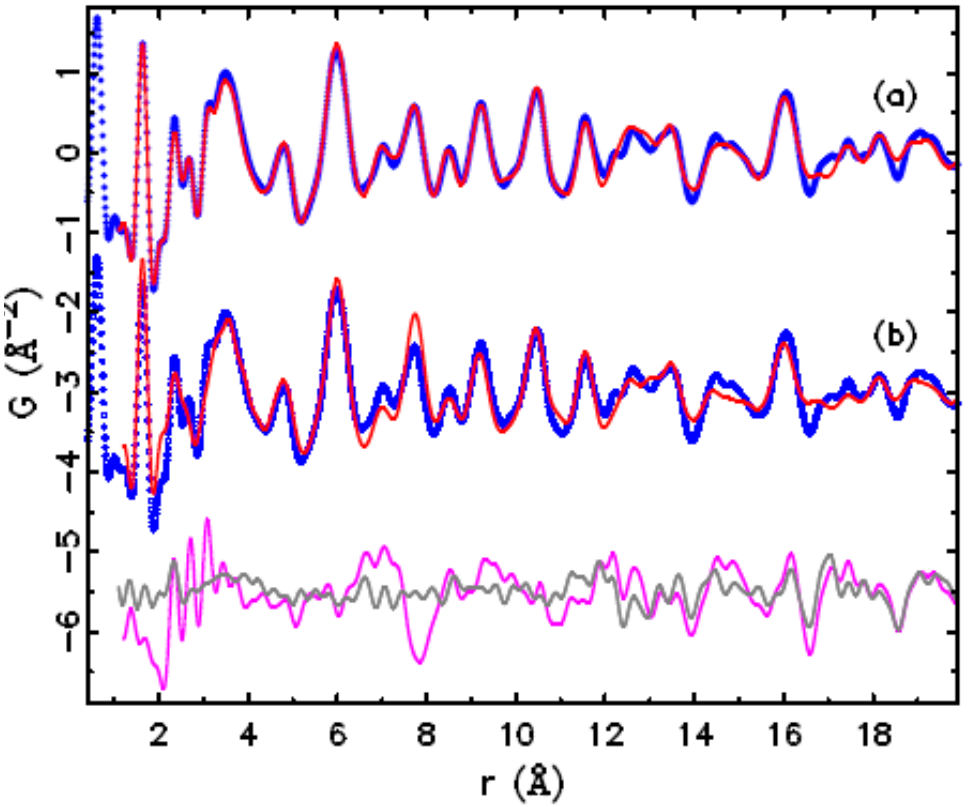


TABLE I: Refined dual-phase structure of the Na-SGII material.

Na_2SiO_3

$a(Å) = 10.43$, $b(Å) = 6.11$, $c(Å) = 4.93$

Atom	x	y	z	U(Å ^{2})
Na($8b$)	0.165	0.347	0.00	0.015
Si($4a$)	0.00	0.118	0.481	0.068
O1($4a$)	0.000	0.113	0.811	0.041
O2($8b$)	0.123	0.281	0.5	0.024

NaSi

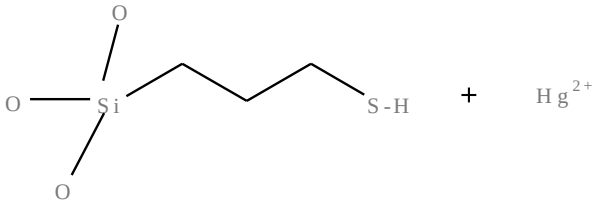
$a = 12.72Å$ $b = 7.25Å$ $c = 10.56Å$

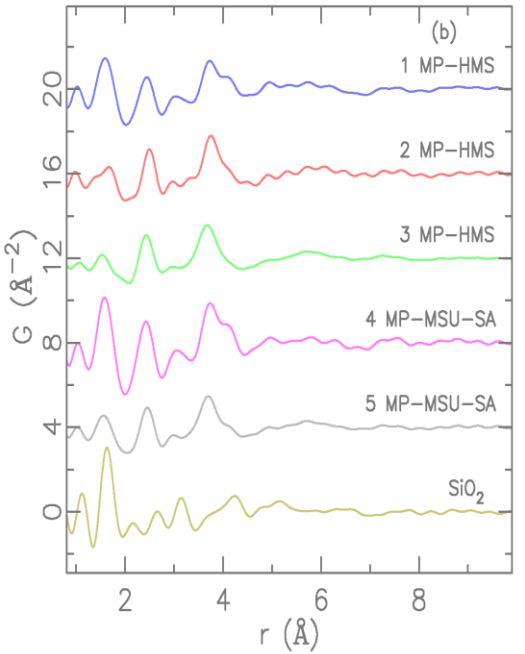
Atom	x	y	z	U(Å ^{2})
Na1($8f$)	0.292	0.732	0.353	0.009
Na2($8f$)	0.678	0.0458	0.513	0.011
Si1($8f$)	0.447	0.252	0.323	0.011
Si2($8f$)	0.624	0.553	0.359	0.031

M. S. Shatnawi *et al.* submitted, (2006)

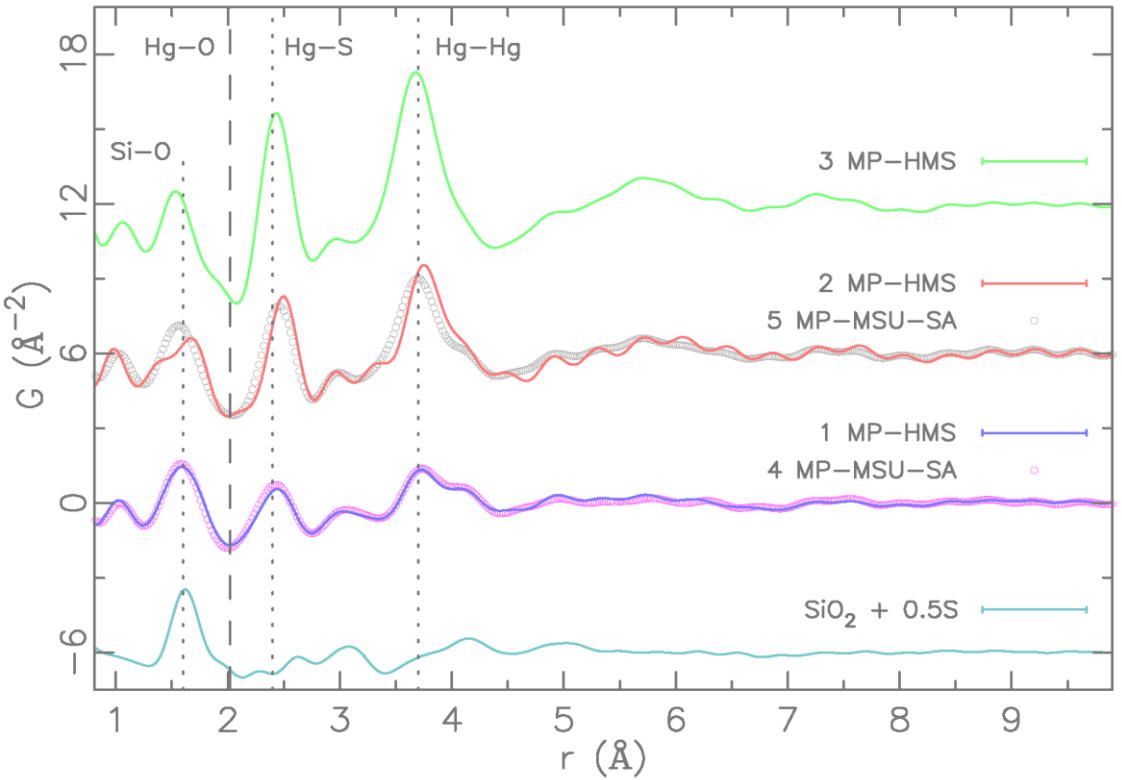
Sequestering mercury in nanoporous silica

- Mouath Shatnawi, HyunJeong kim, Collaboration with Tom Pinnavaia and Emily McKimmy,
- Functionalize the nanoporous silica with mercaptan
- Sucks up mercury like a sponge
- What is the nature of the binding in the pores?
- Pores are disordered within an atomically disordered silica framework. Can we make any progress?
- PDF data collected at APS sector 6 (MuCAT) and sector 11





Isolating the Hg signal from the PDF



6.33 mmol Hg/g

4.16/4.85 mmol Hg/g

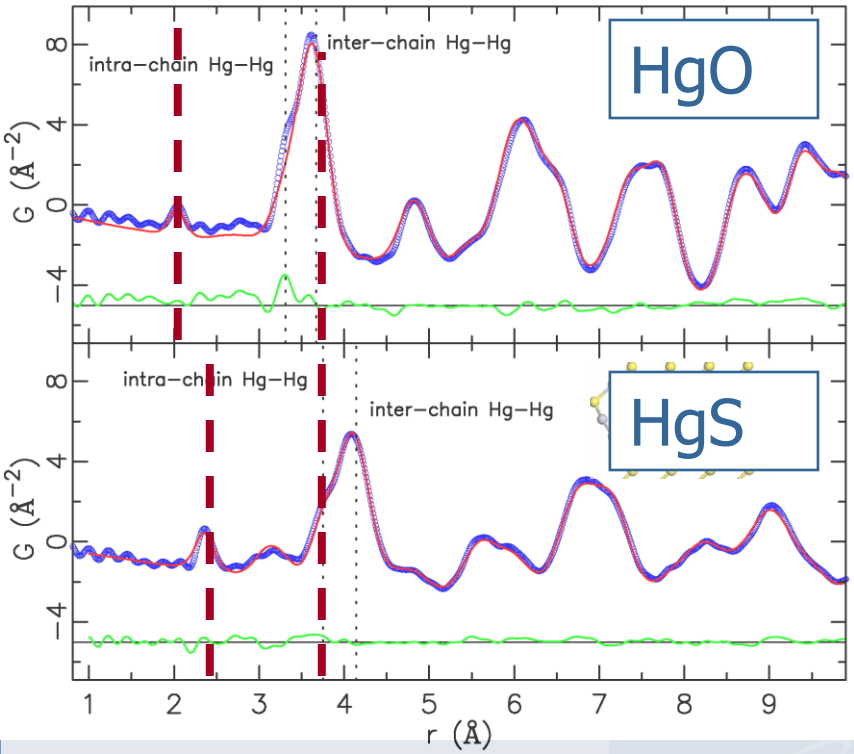
2.52/2.99 mmol Hg/g

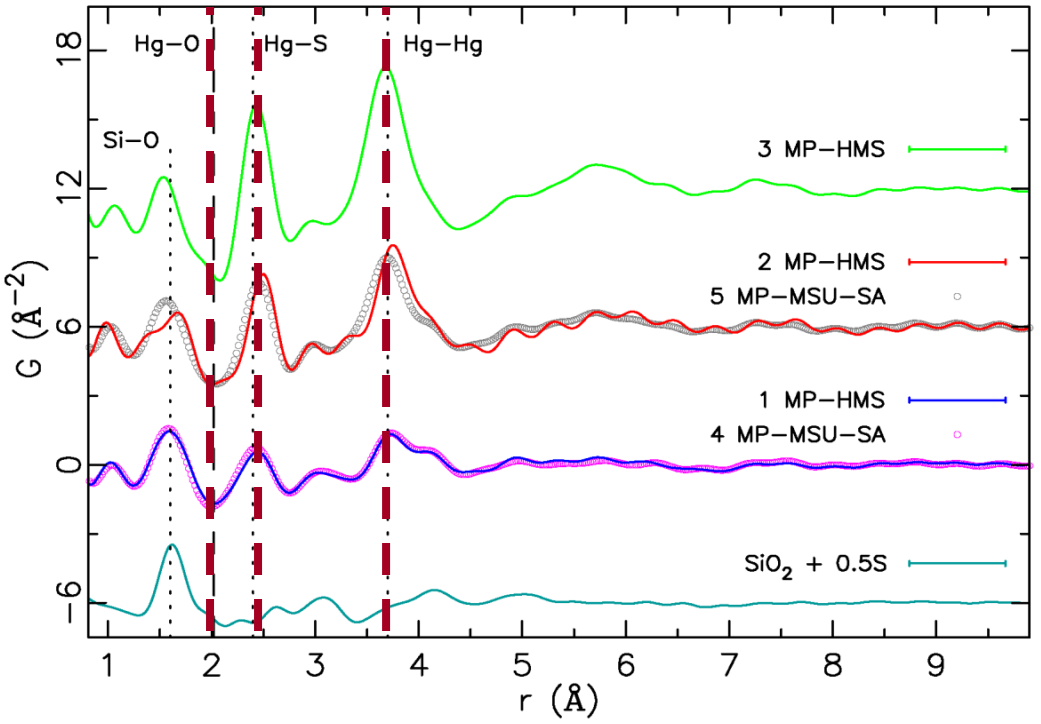
0 mmol Hg/g

- Data renormalized to the silica peak (r=1.61 Å)
- Peaks appear and grow at 2.35 Å and 3.75 Å. These originate from the Hg in the pores. What can we learn from them?

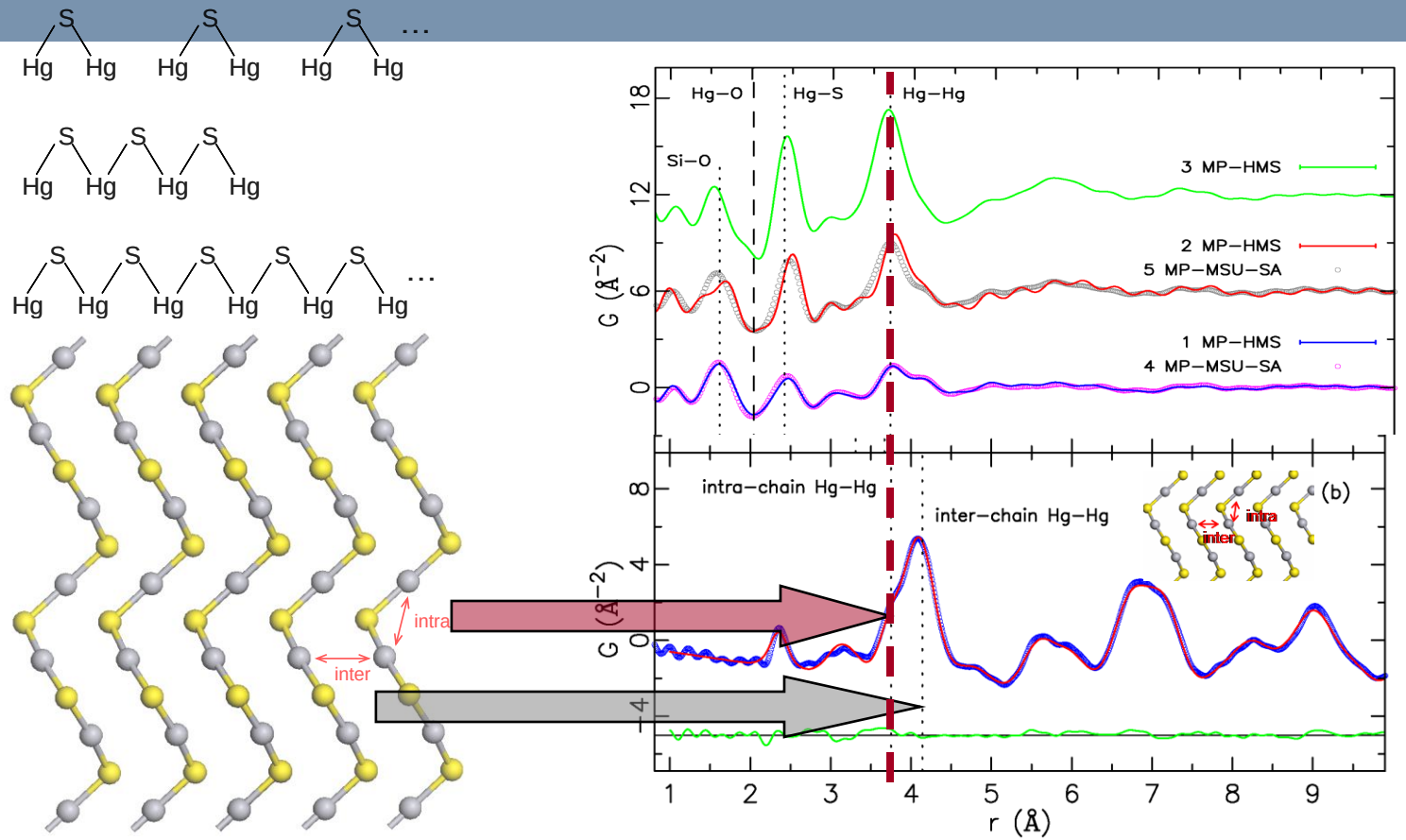
What can we learn I

- Hg is bonded to sulphur only (contradicts an earlier XAFS result, Chen, C.-C et al., *Environmental Science and Technology* **2004**, *38*, 4758-4762 that indicated 50% of Hg bonded to Oxygen)





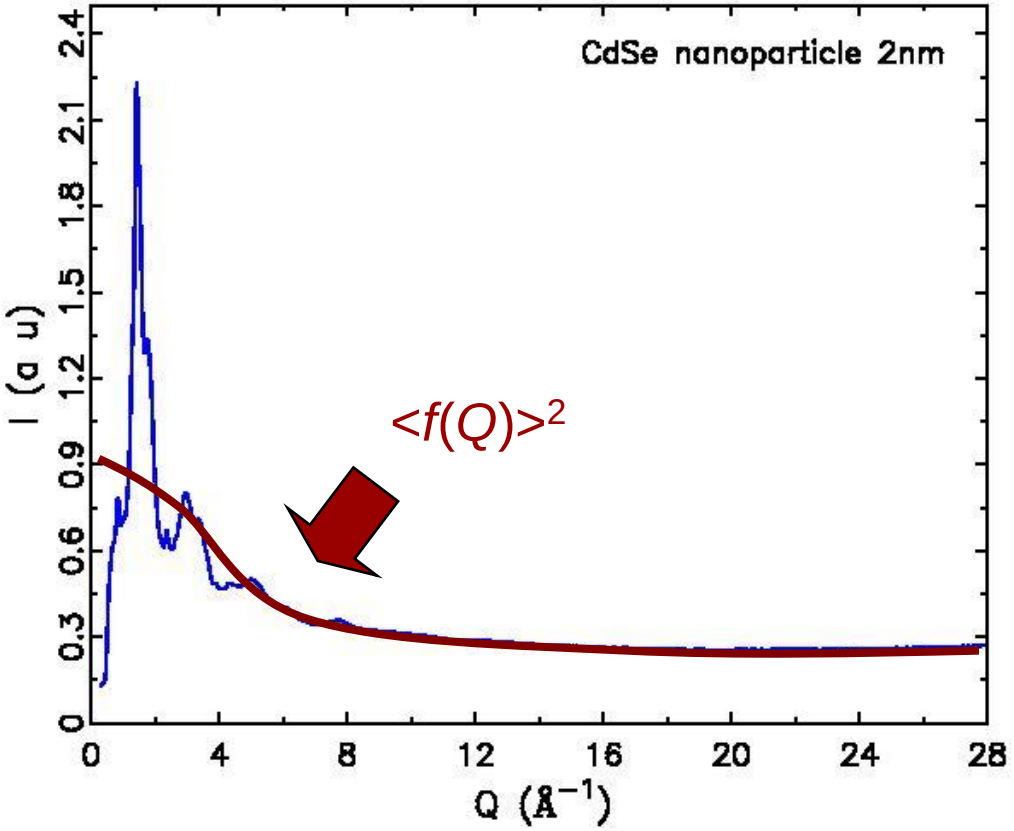
Hg-S chains form inside the nanopores

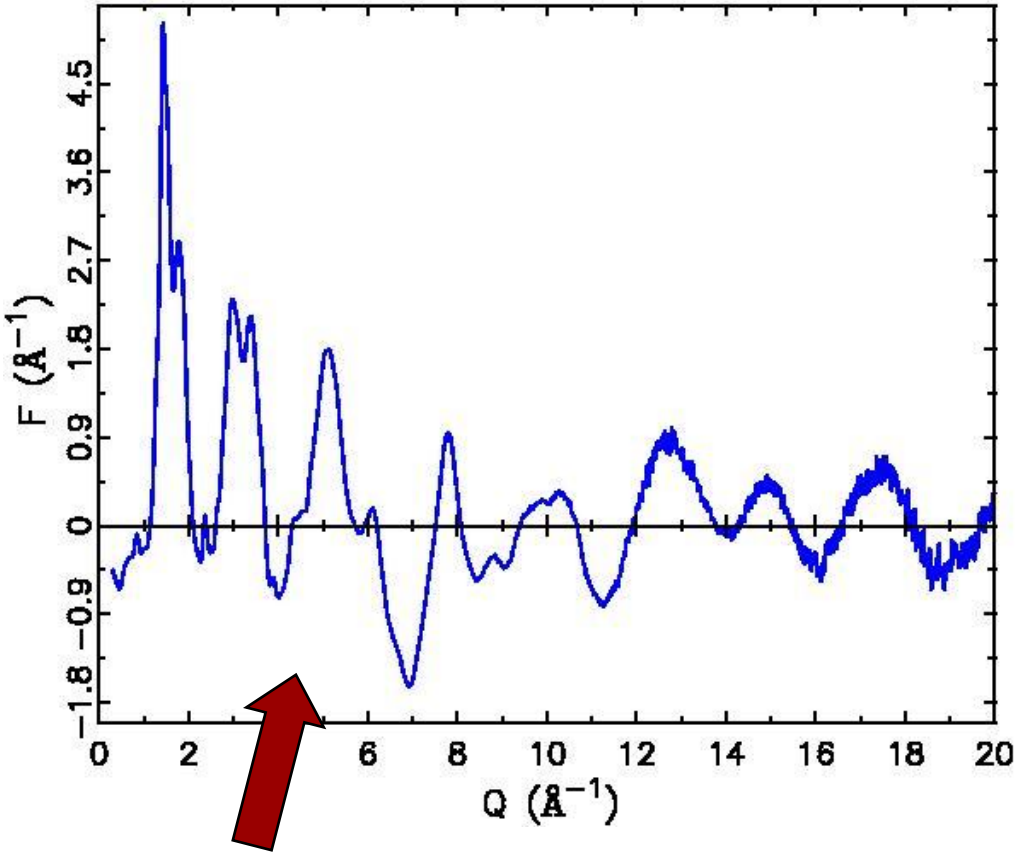


- Intra-chain Hg-Hg distance is seen in the Hg-loaded nanoporous silicas, but no evidence for the inter-chain distance
- Rigid [-Hg-S-Hg-] linkages present but chain-chain packing is absent or disordered

High Resolution

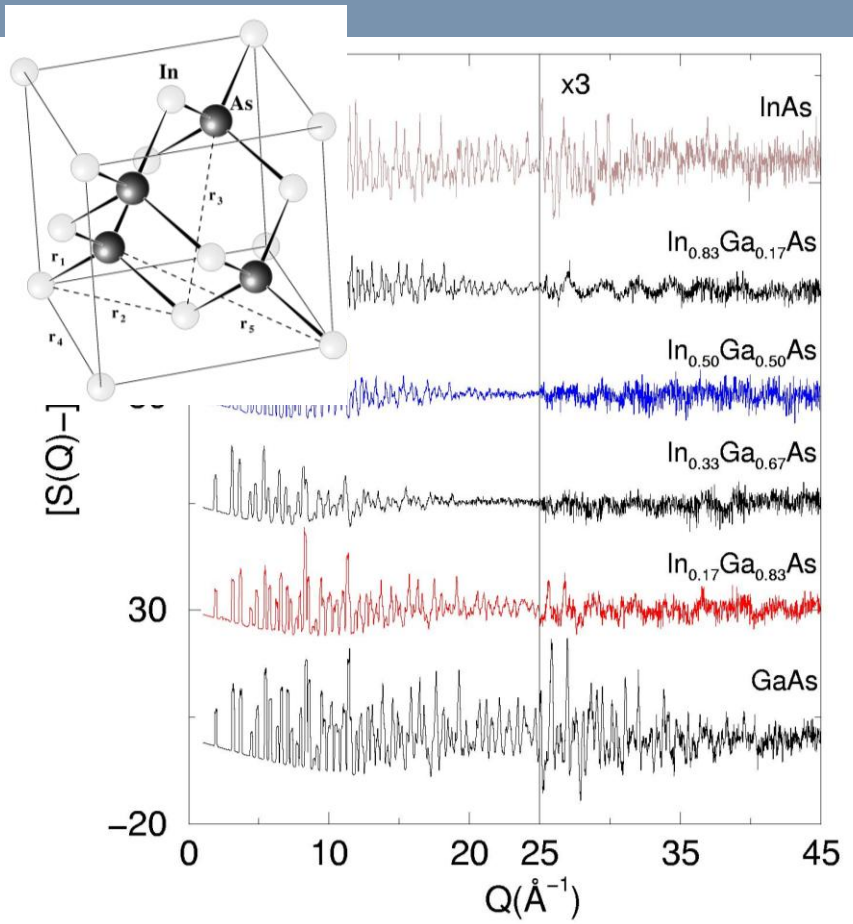
But there is no information at high-Q…?





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

Total scattering from $In_{1-x}Ga_xAs$



Petkov et al., *Phys. Rev. Lett*. **83**, 4089 (1999);
Jeong *et al. Phys. Rev. B* **63**, 205202 (2001)

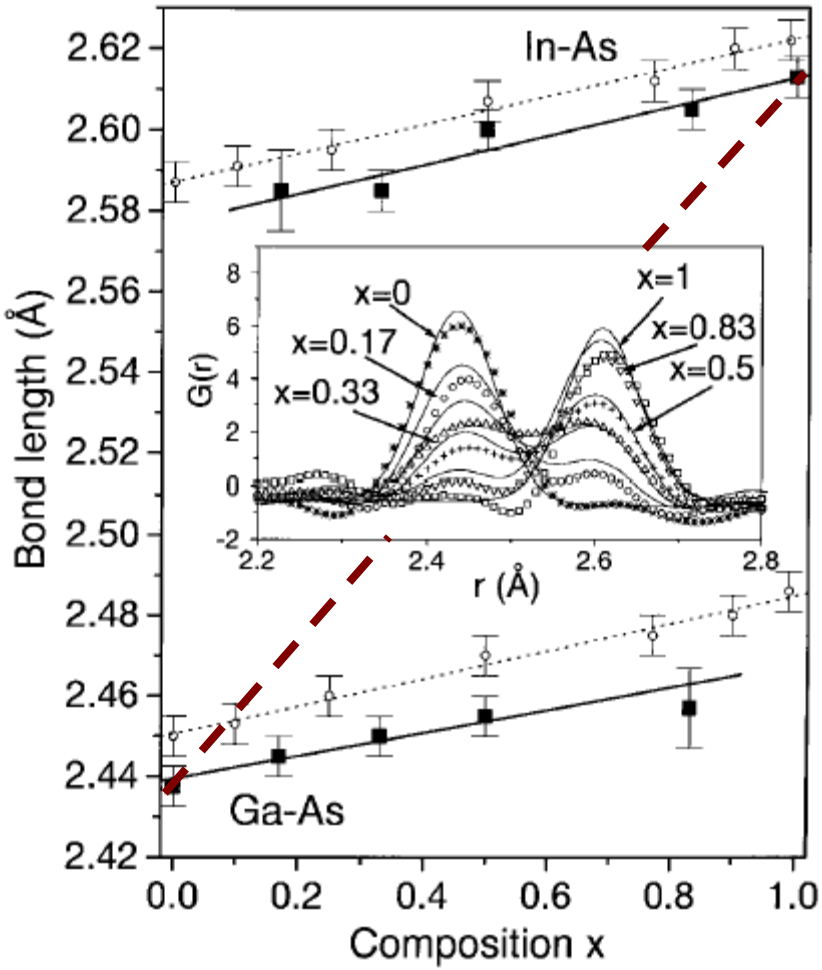
- Semiconductor alloys such as $In_{1-x}Ga_xAs$ are technologically important because band gap and lattice parameter can be engineered
- No full solution of the local structure (including strain) existed
- X-ray powder diffraction data from CHESS
- 60keV incident energy
- Data collected at 10K

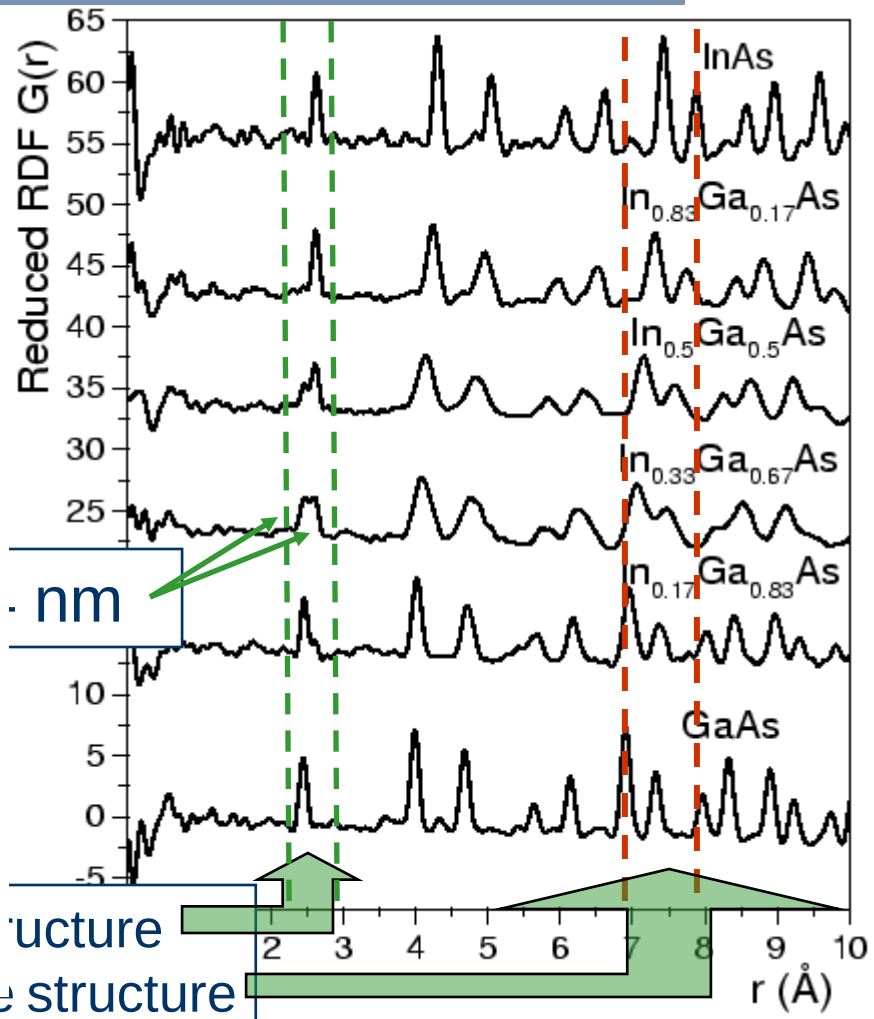
Local vs. long-range structure: semiconductor alloy $In_{1-x}Ga_xAs$

$In_{0.}$

$In_{0.50}$

Averag
distribu
concen





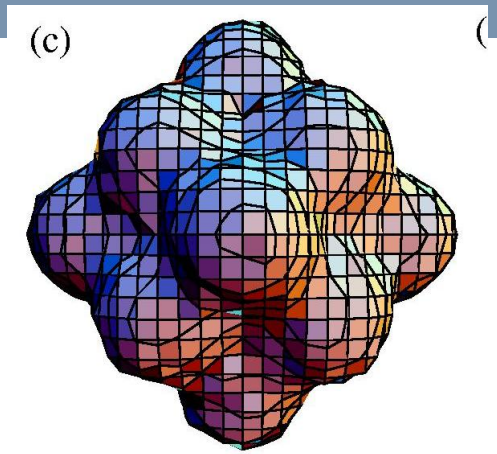
nm

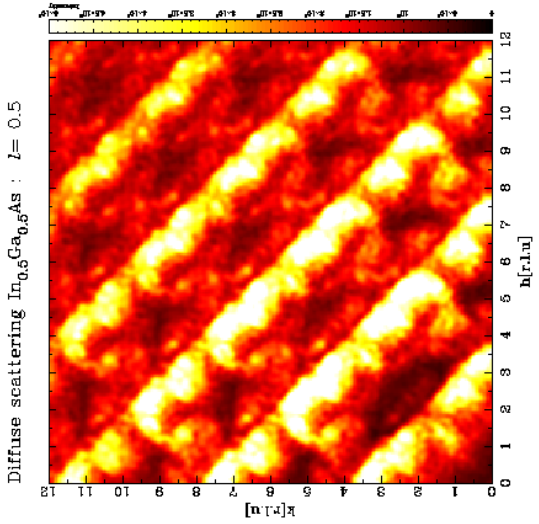
ucture

average structure

[Petkov et al., *PRL*. **83**, 4089 (1999); Jeong et al., PRB (2001)]

Correlations Nota Bene

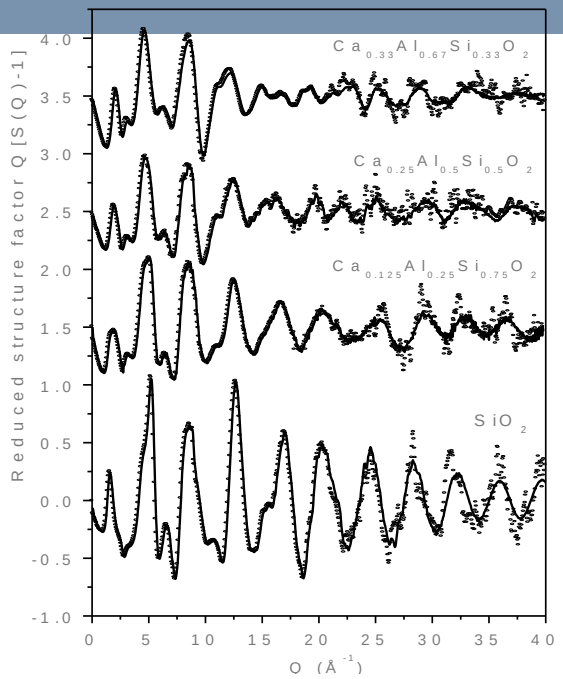


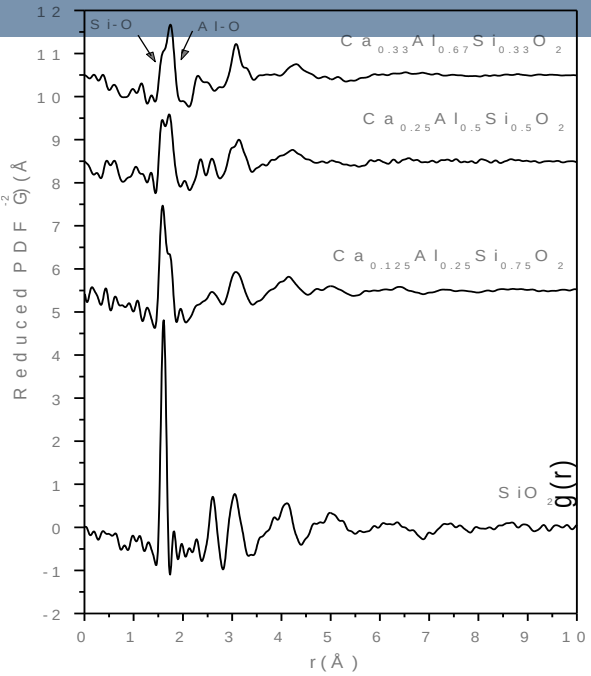


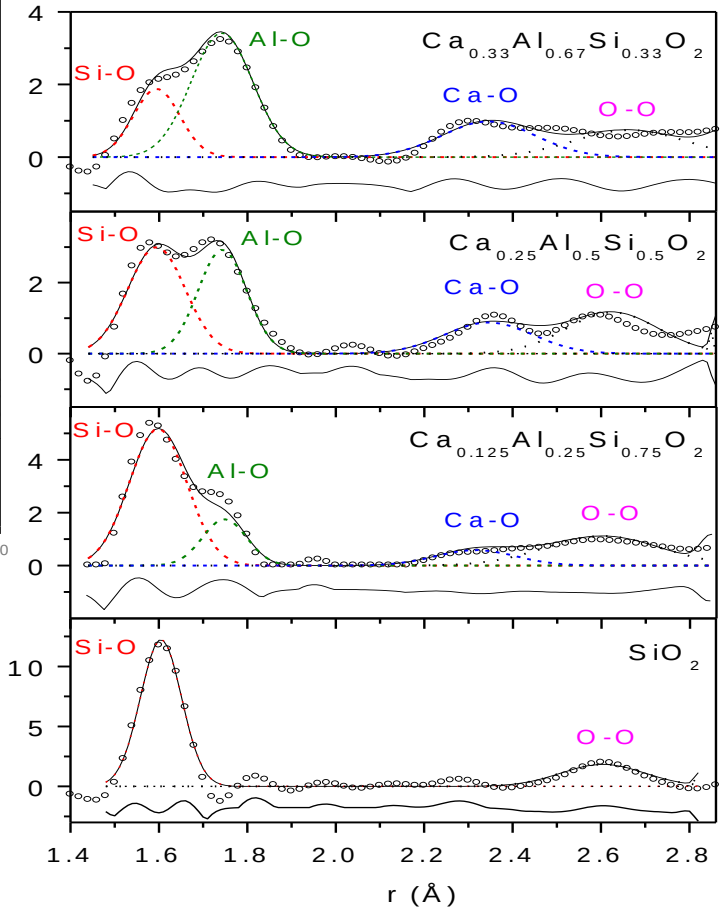
- PDF shows that atomic displacements are along [100] and [111] directions
- Diffuse scattering (observed and theoretical) shows streaks along [110] directions
- The displacements are along [100] and [111] but they are correlated along [110]!
- Crystal is stiffest along [110] direction (see 5th peak in the PDF)!

Jeong *et al. Phys. Rev. B* **63**, 205202 (2001)

Alumino-silicates





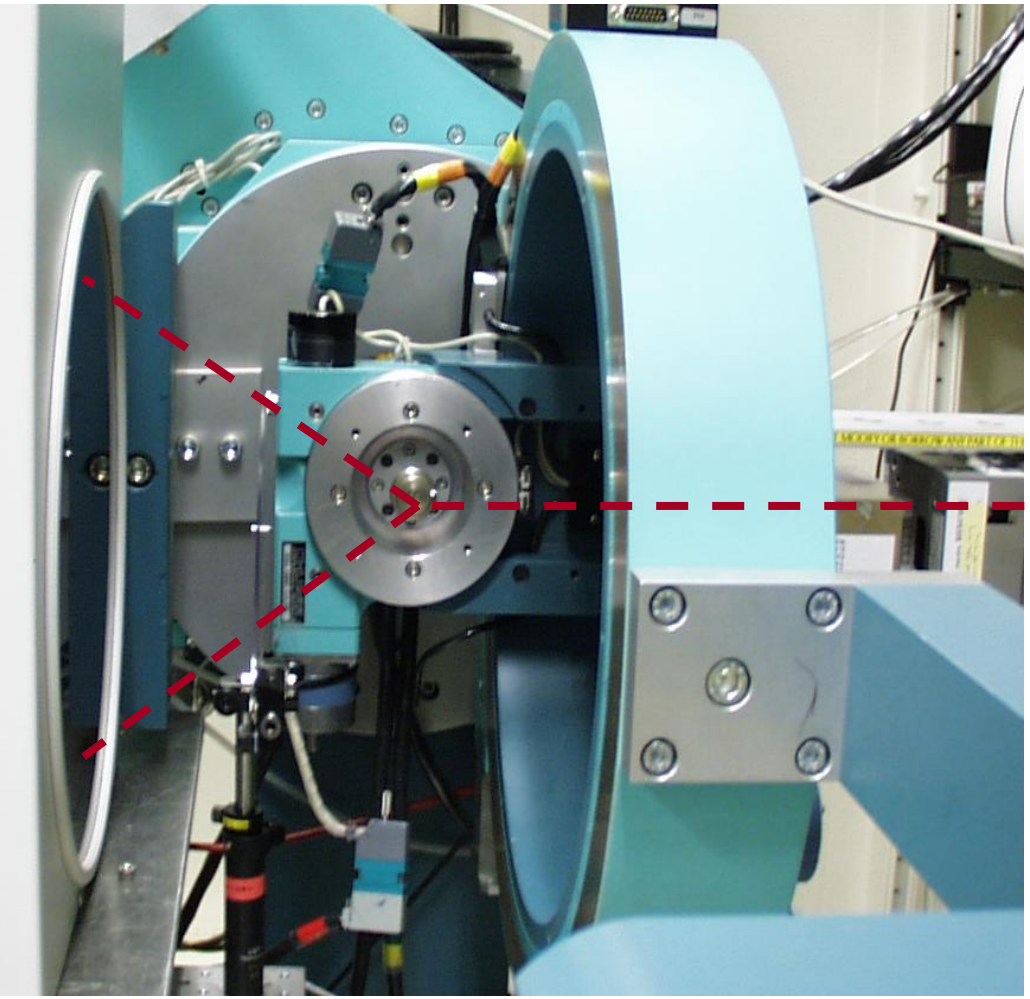


- $(Si,Al)O_4$ tetrahedral networks
- Important catalysts: zeolites, microporous materials
- Cannot study AlO_4 and SiO_4 separately (Si and Al have similar x-ray and neutron scattering lengths)
- R_{Si} = 1.61A, R_{Al} = 1.75A, ΔR = 0.14A
- x-ray data from Advanced Photon Source

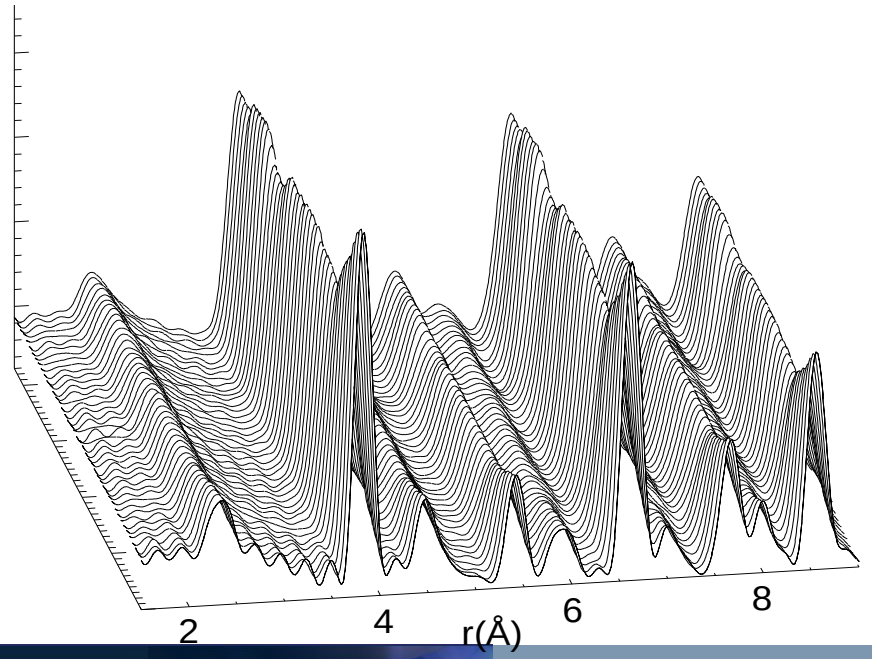
V. Petkov *et al.*, *Phys. Rev. Lett.*, **85**, 3436 (2000)

High Throughput - Special Environments

Rapid throughput nanostructure studies



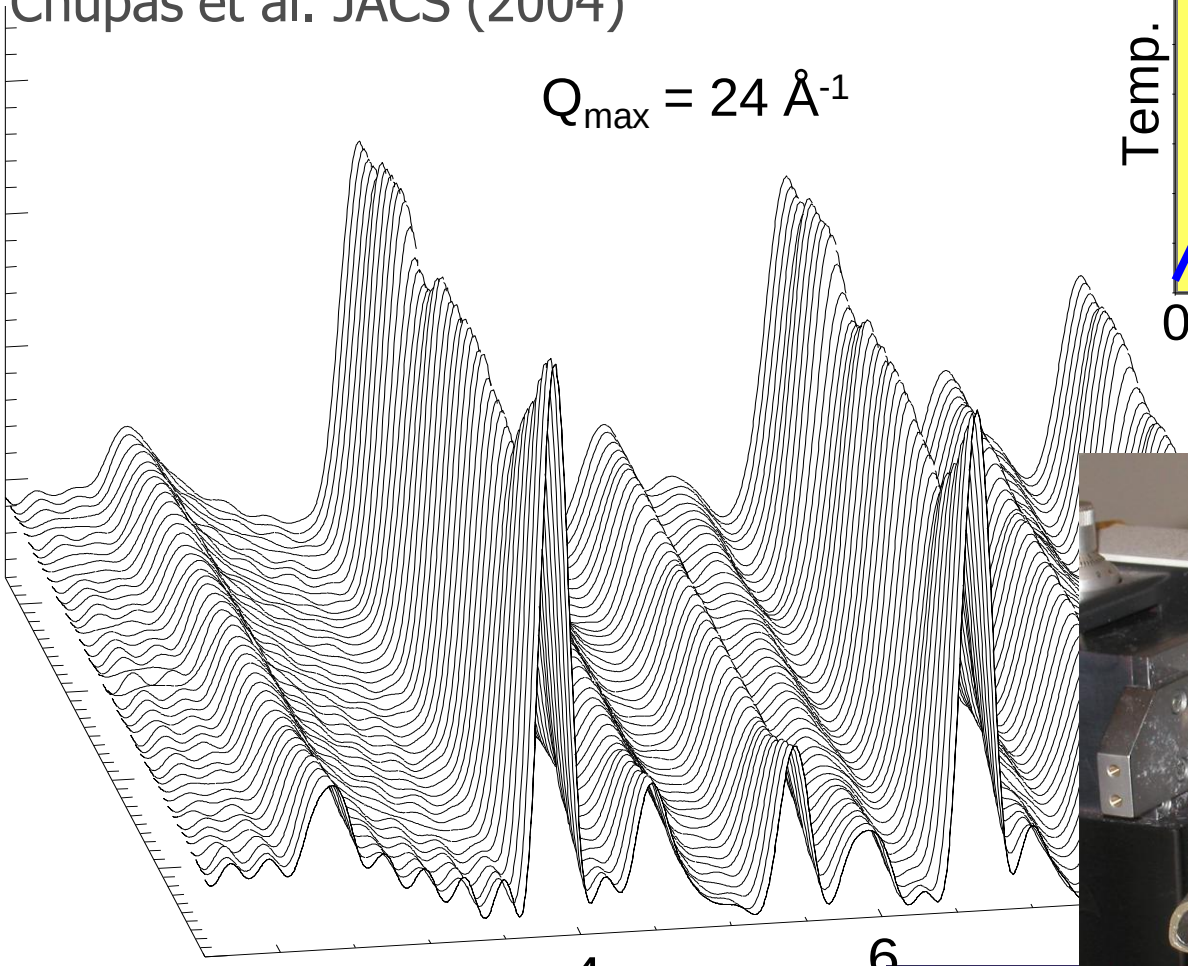
- Data shown below are rapid throughput data of Pete Chupas on nano-ceria

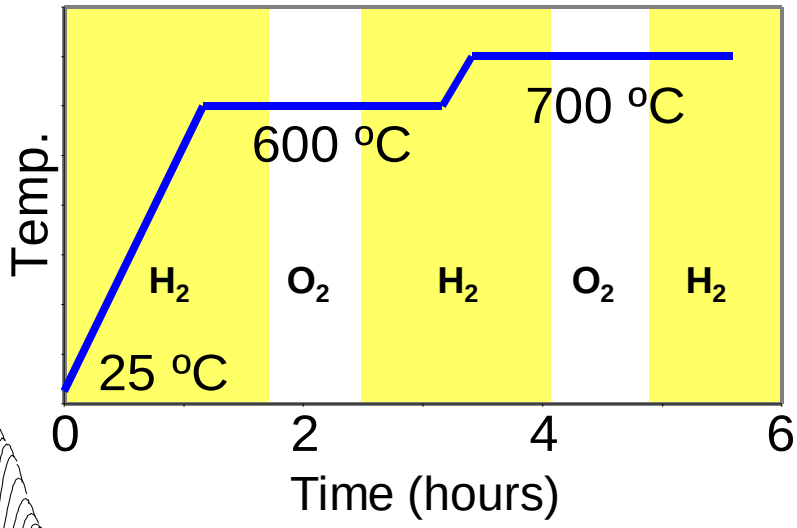


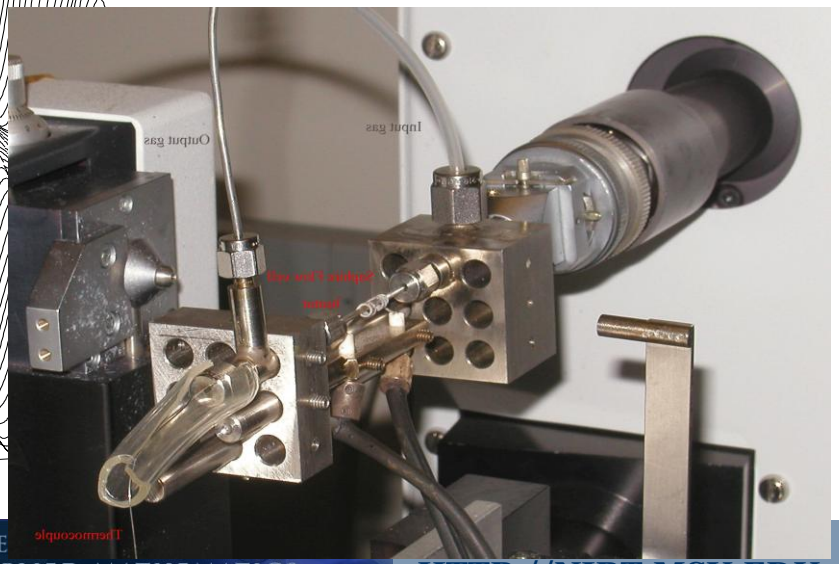
In-Situ Reduction and Oxidation

Study of nano-ceria demonstrated by Pete Chupas, Clare Grey and Jon Hanson

Chupas et al. JACS (2004)

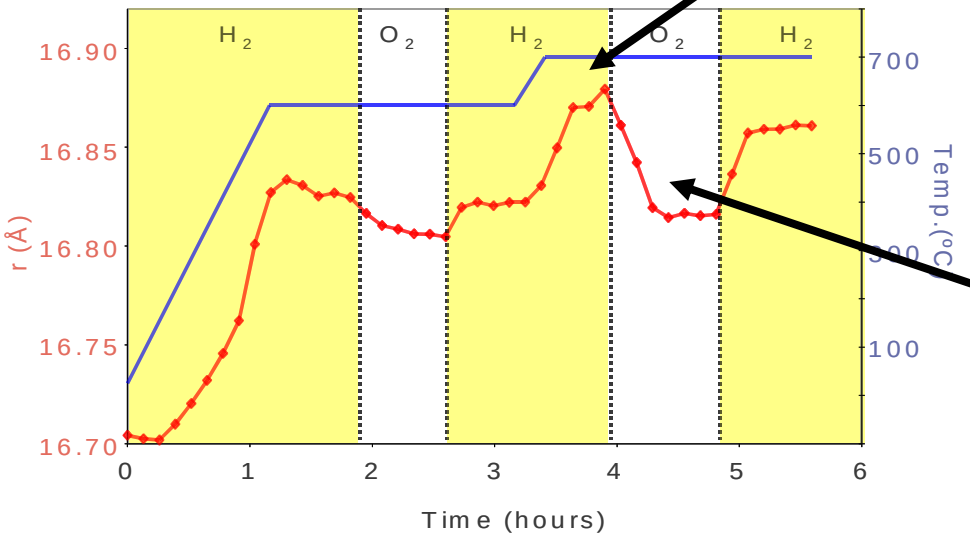


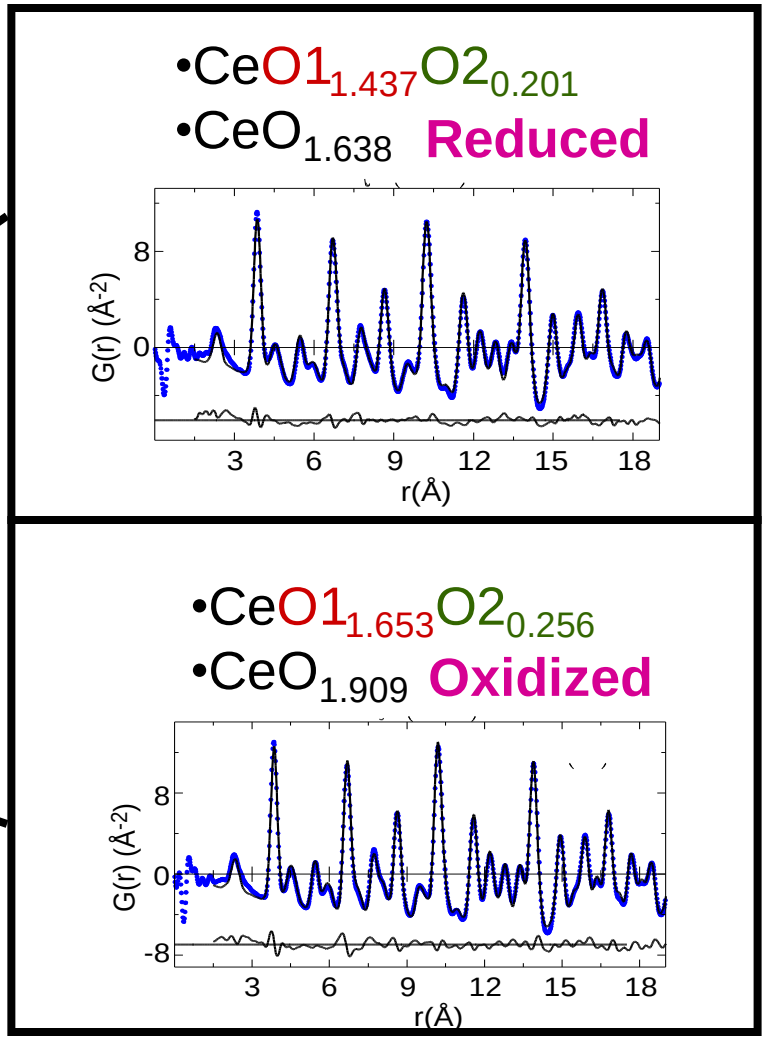




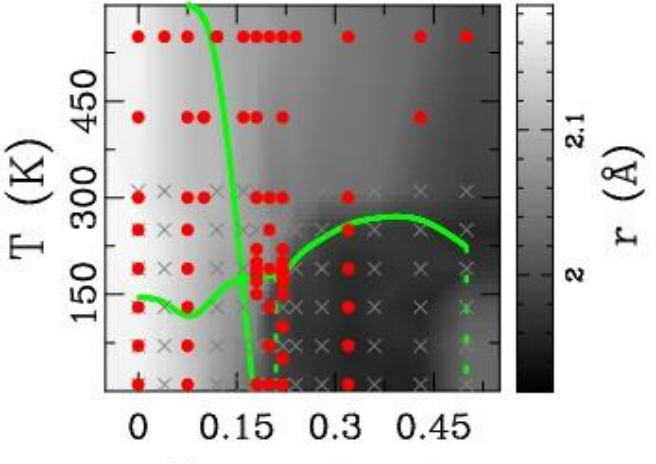
Reduced vs. Oxidized Structure

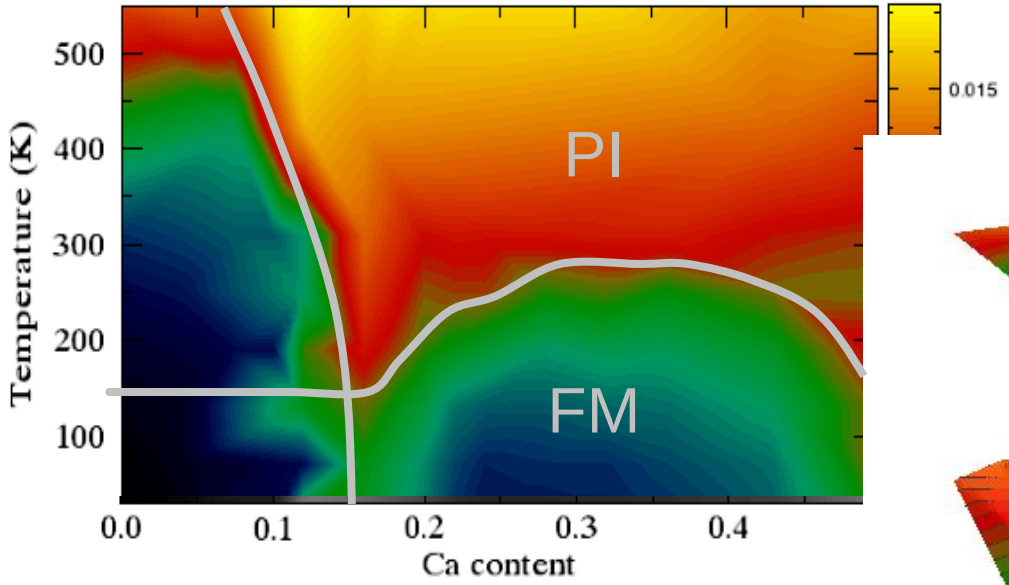
- It is possible to see oxygen move in and out of the structure
- Are there cooperative effects between the defect site and tetrahedral O site?
- Chupas et al JACS 2004

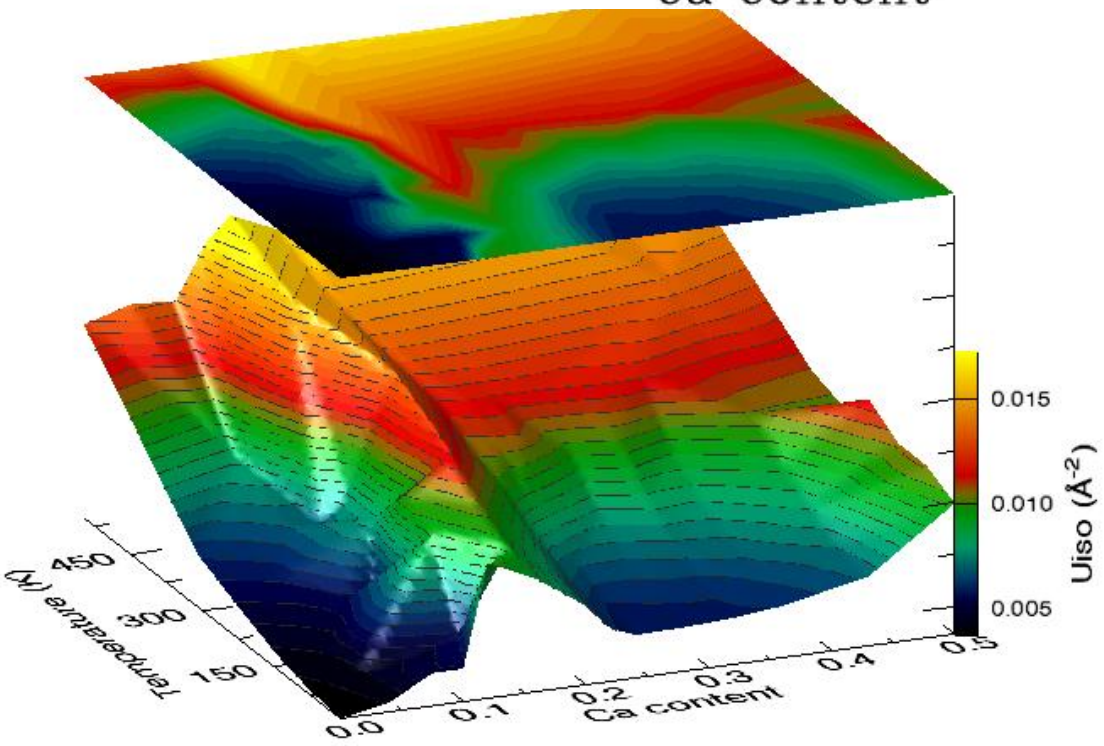




Scientific power of high throughput studies:





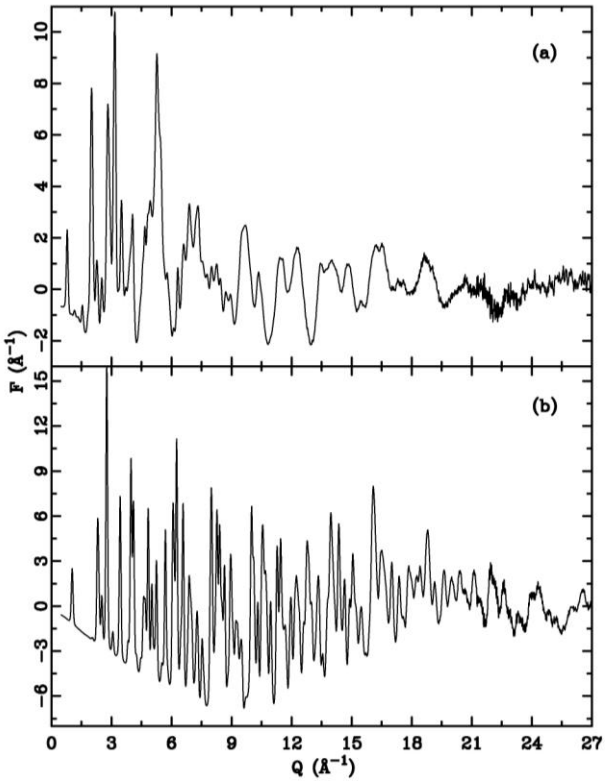


- Phase diagram draws itself from refined parameters
- System: Ca doped lanthanum manganites

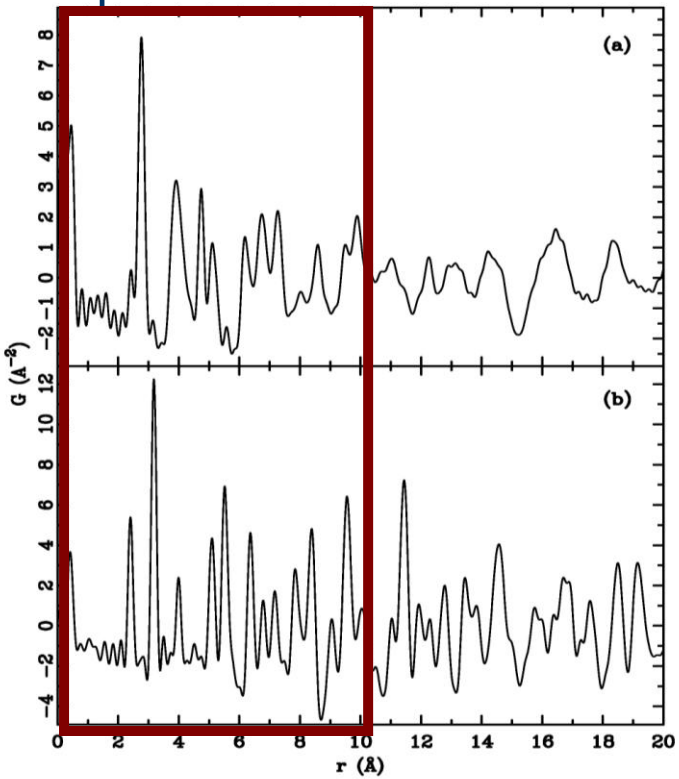
Nanostructured Materials

$Mo_6S_xI_{10-x}$ nanowires

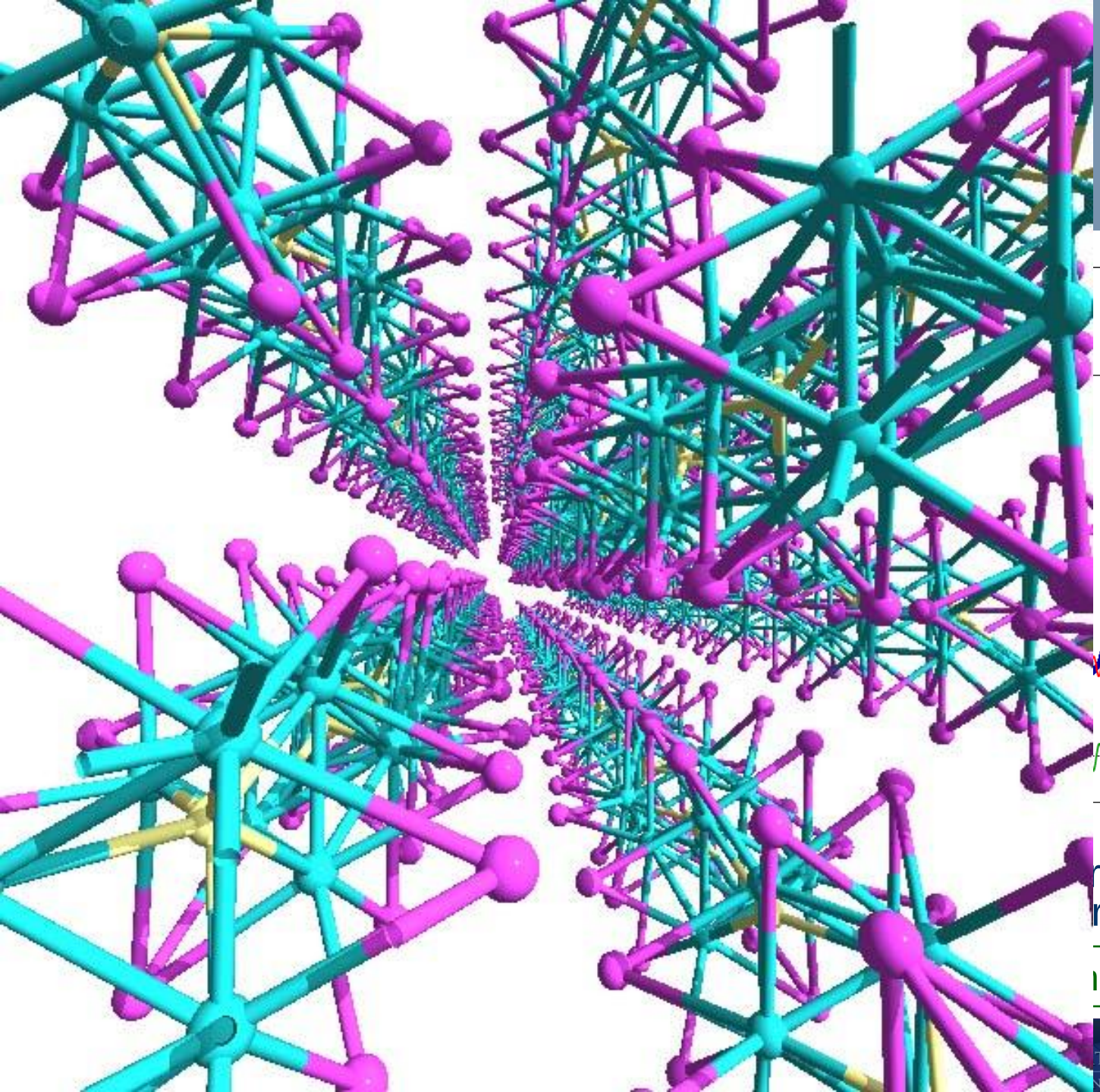
Total scattering

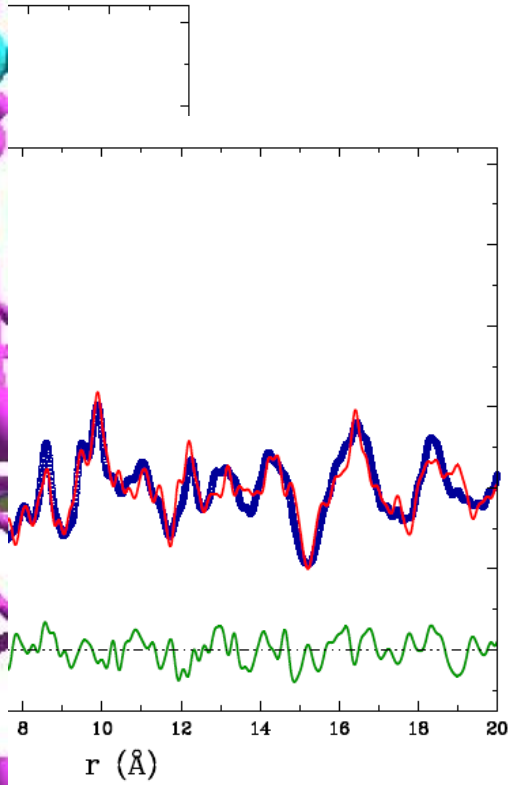


pair distribution function



- Things are better in real-space using the atomic Pair Distribution Function (PDF) method (peaks are sharp in both cases).
- Structure models can be differentiated and refined



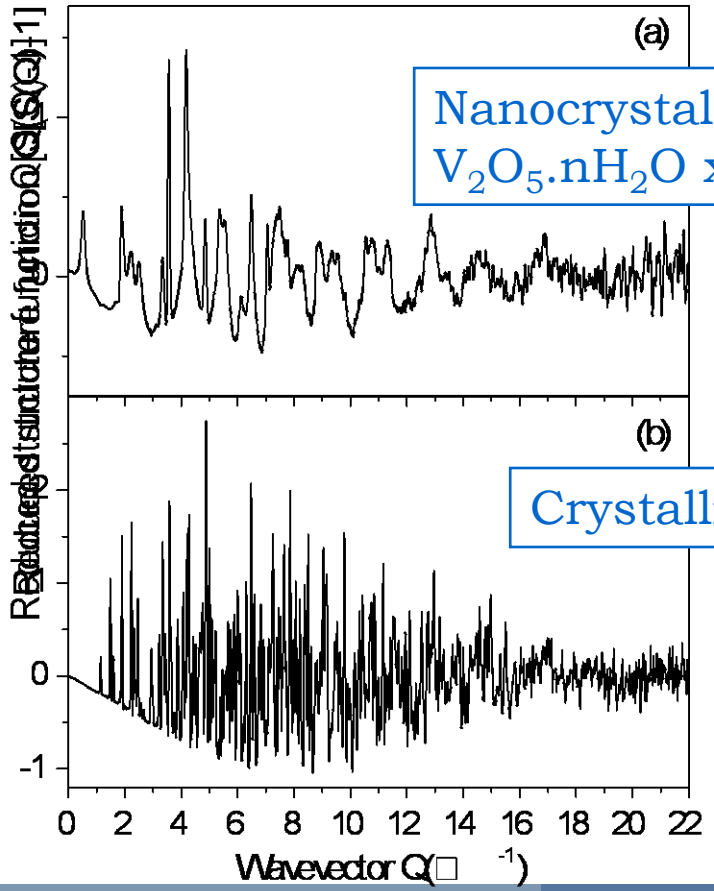


re rather than a tube,
r and Iodine outside

em. Mater., (2006)

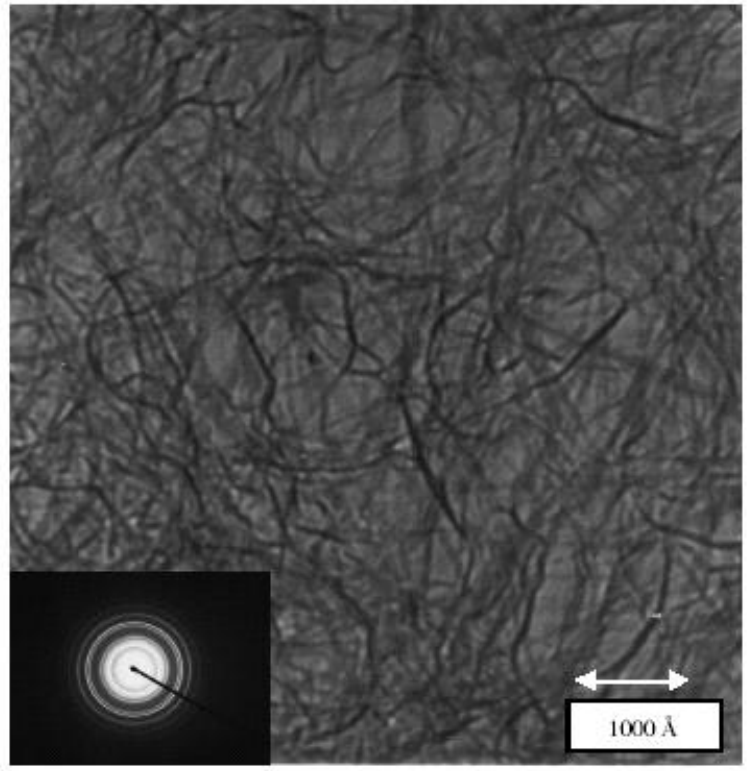
Beyond Crystallography

- Crystallography fails in nanocrystalline materials:



Nanocrystalline $V_2O_5.nH_2O$ xerogel

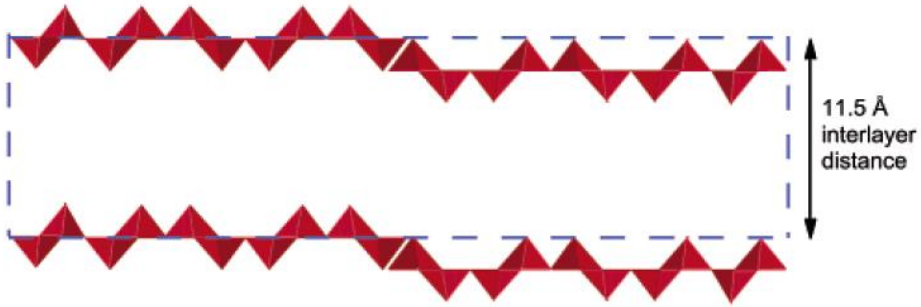
Crystalline V_2O_5



V. Petkov, SJB et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

Nanostructure solution by trial and error: Comparison of 3 distinct models

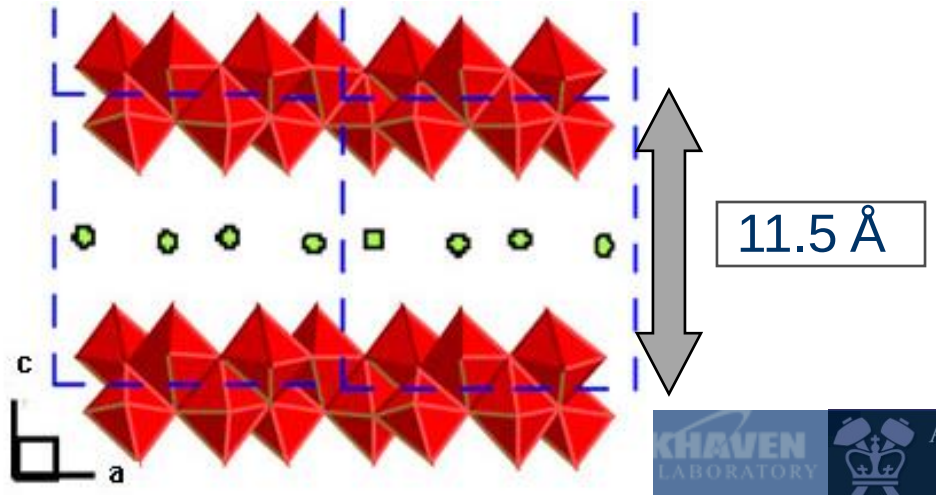
(a)

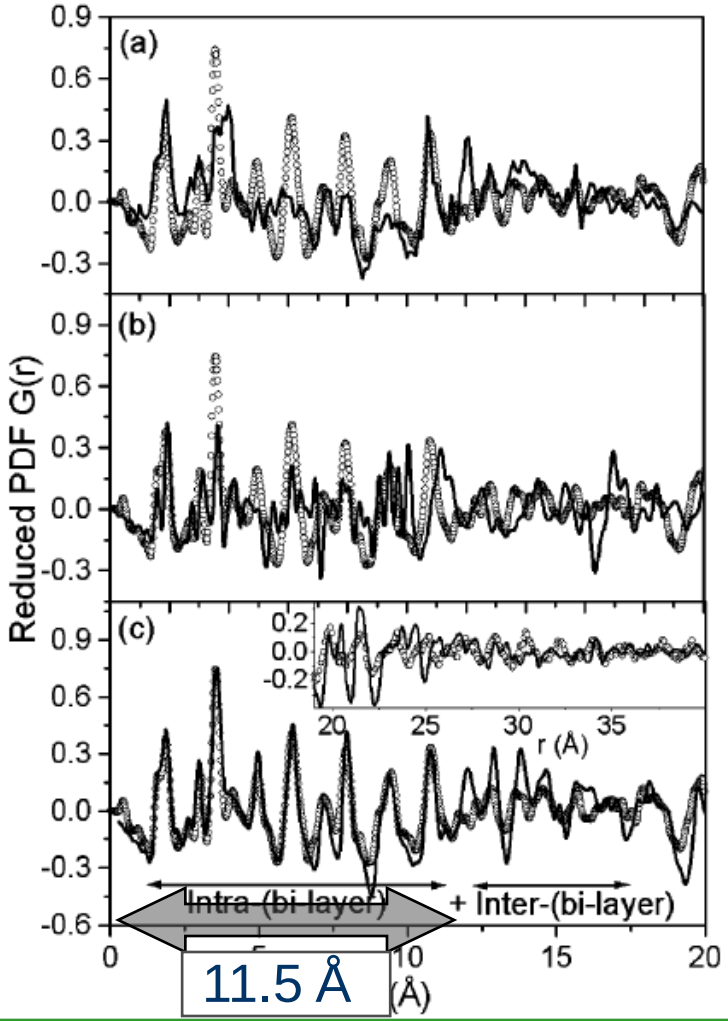


Structure proposed by

- Livage et al. J. Chem Mater. 1991
- Petkov et al. J. Appl. Crystallogr. 1998
- Oka et al. J. Mater. Chem. 1992

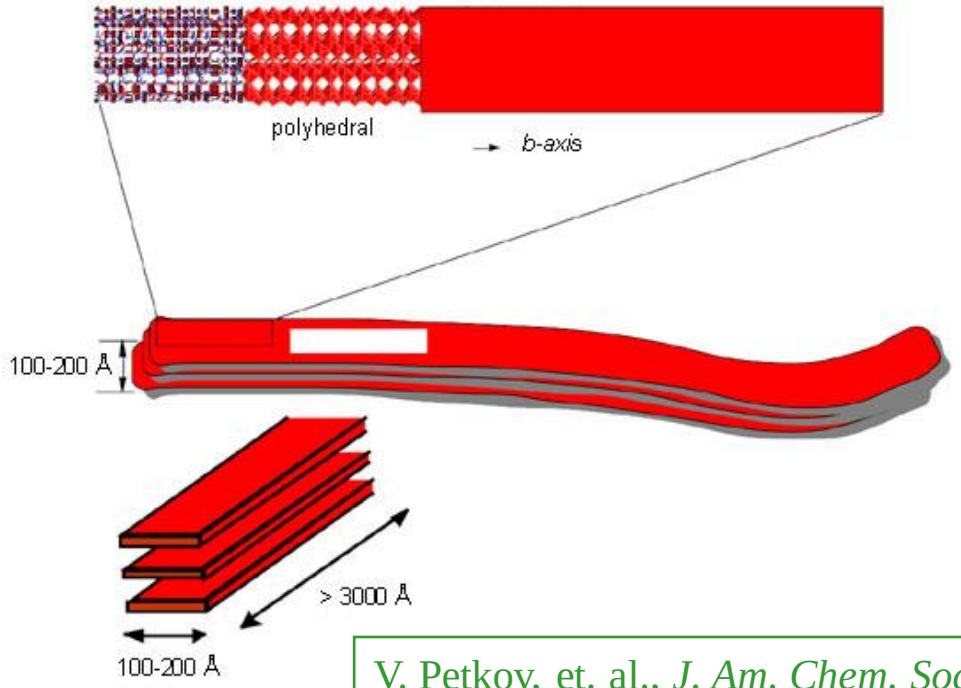
(c)



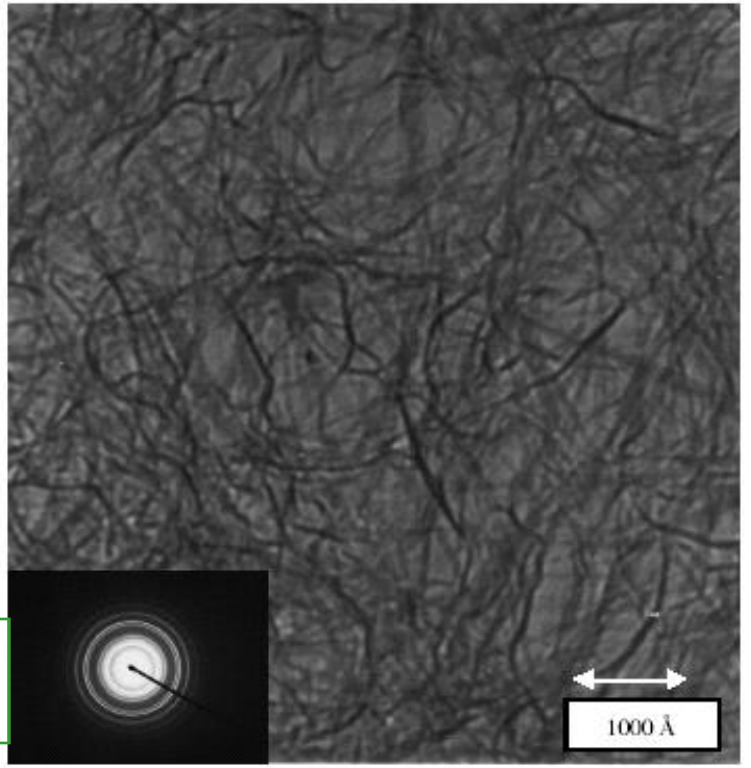


V. Petkov, SJB et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

“Nanostructure” in the xerogel

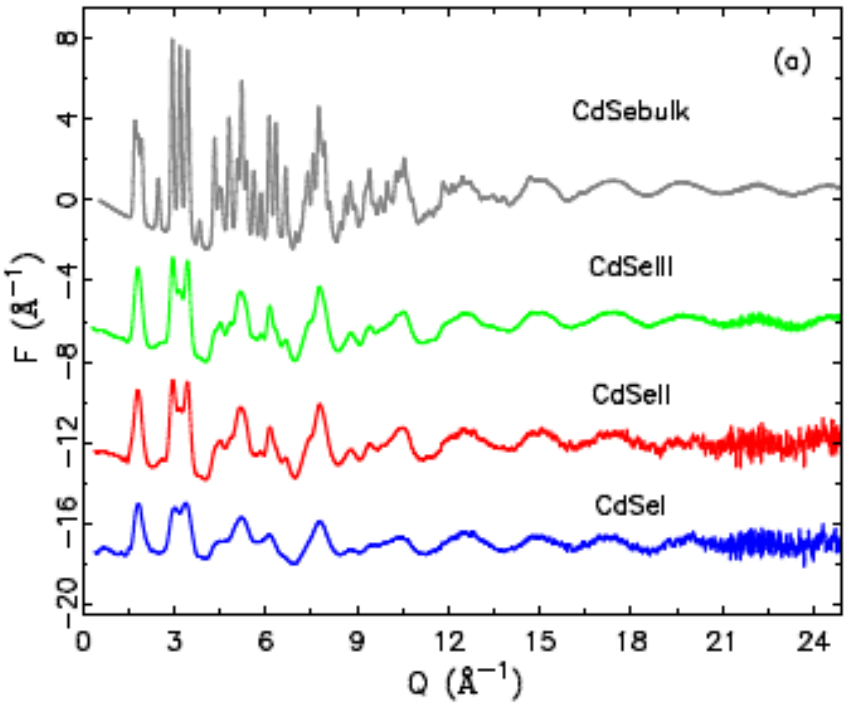


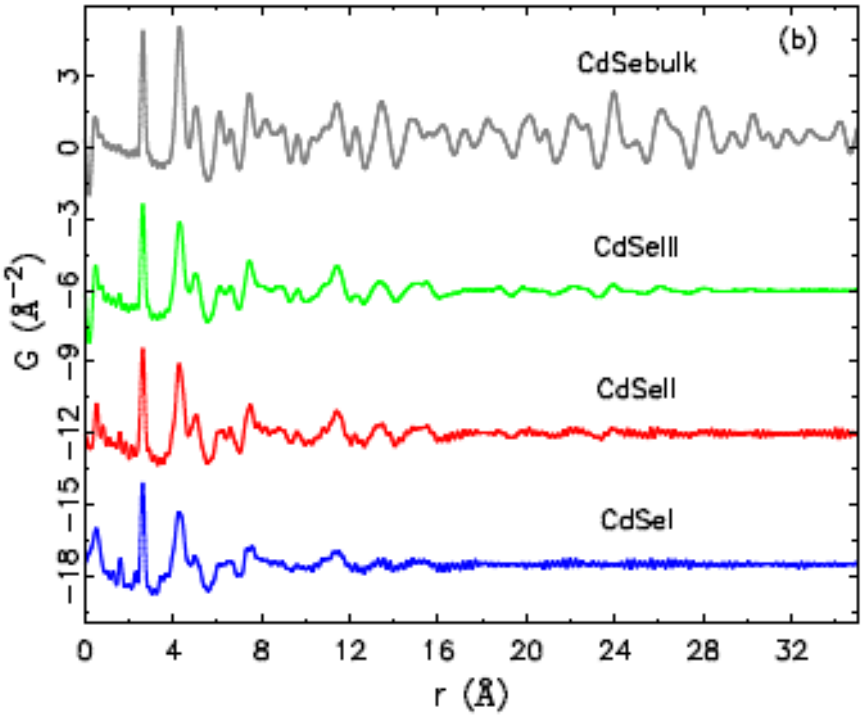
V. Petkov, et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).



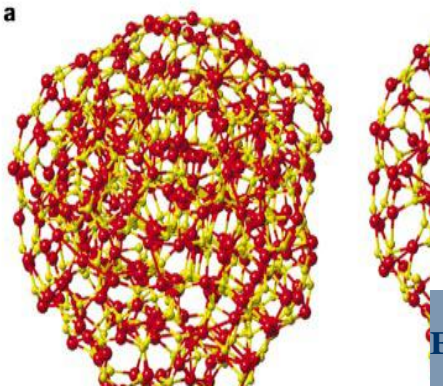
- Turbostratic disorder seen in the PDF consistent with bent and tangled fibres

CdSe quantum dots

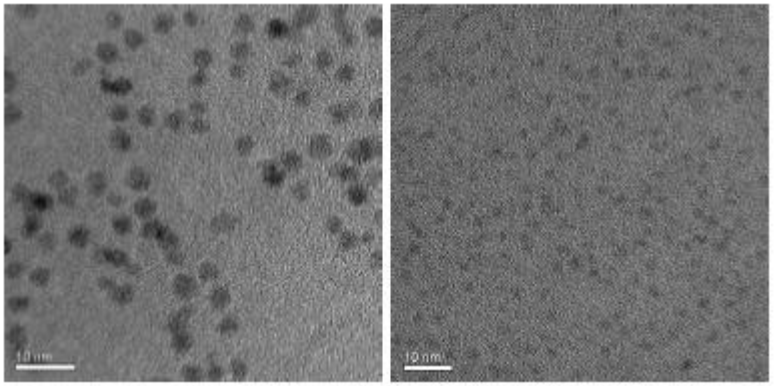


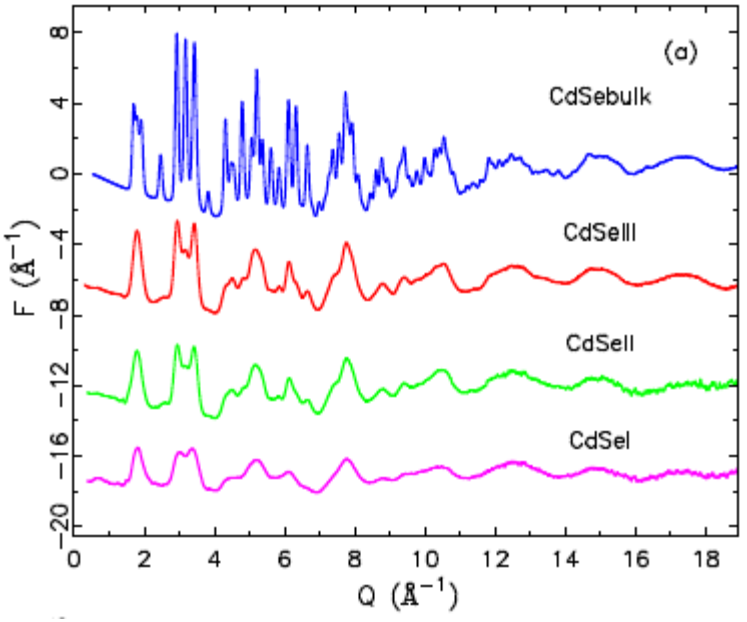


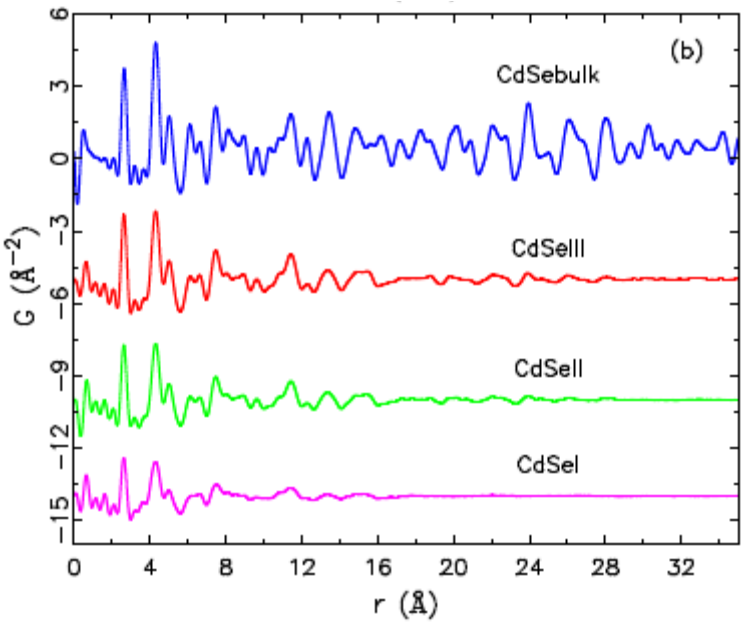
- RAPDF experiments at APS, Sector 6
- Work of grad student Ahmad Masadeh
- Masadeh et al. PRB 2007



CdSe nanoparticles

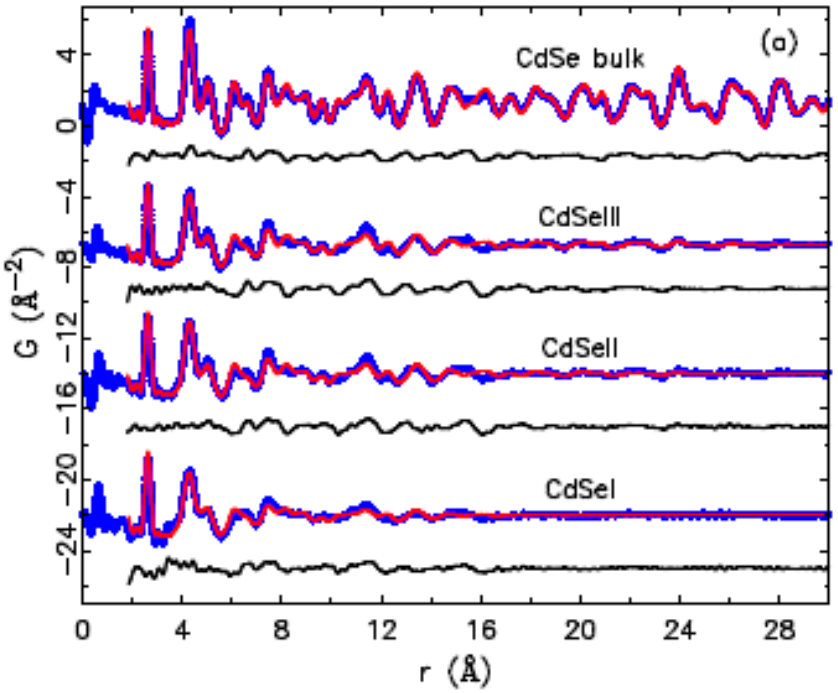


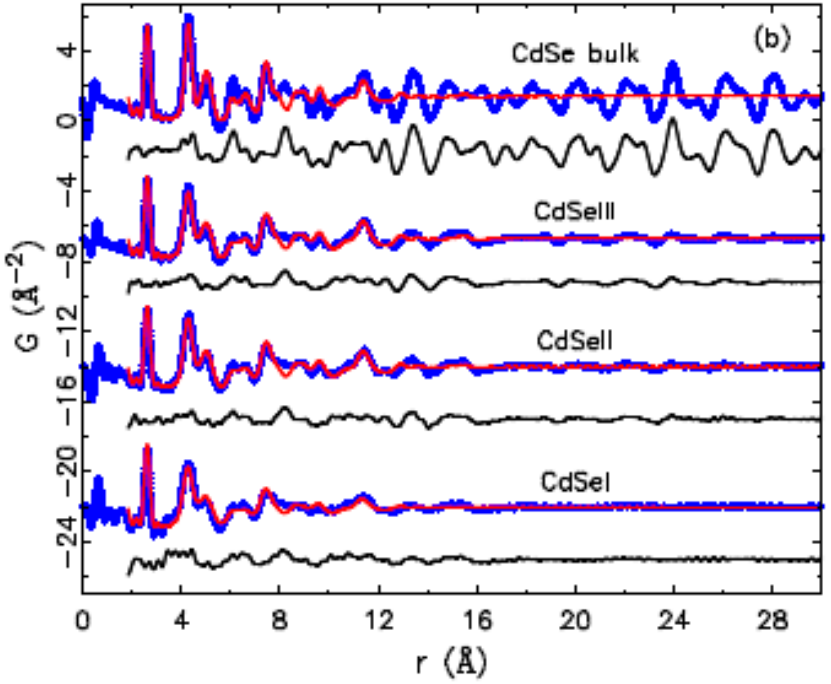




- Size effects do not broaden peaks in real-space, but do decrease amplitude of features at high-*r*
- Accurately measure local bond lengths, vibrational amplitudes, strain, structure, size

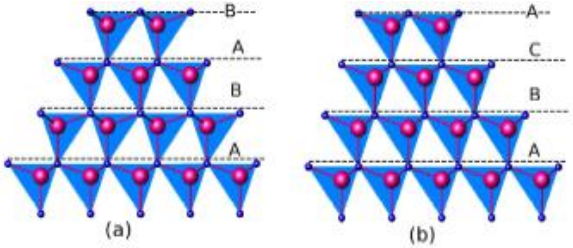
Structure of the CdSe core

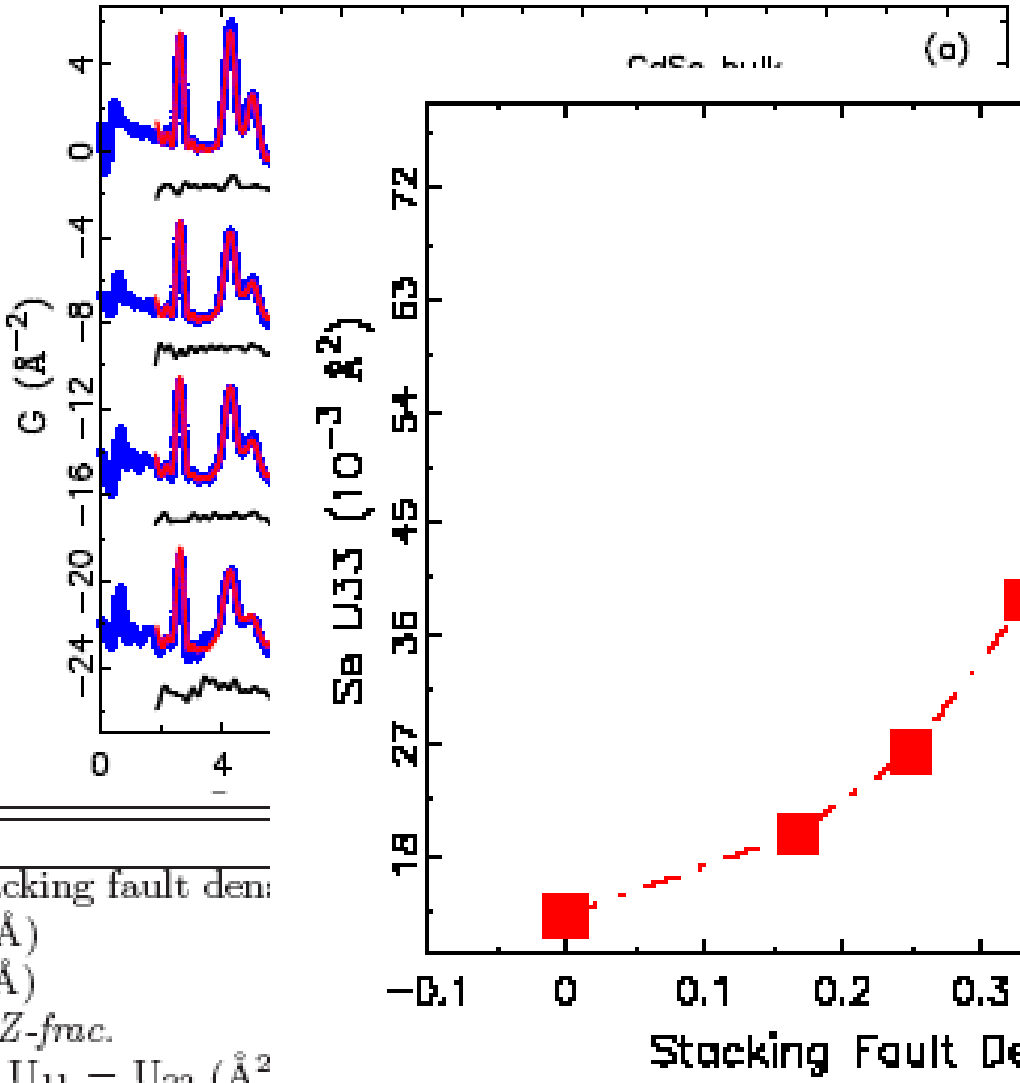




- Wurtzite structure

- Zinc blende structure





th
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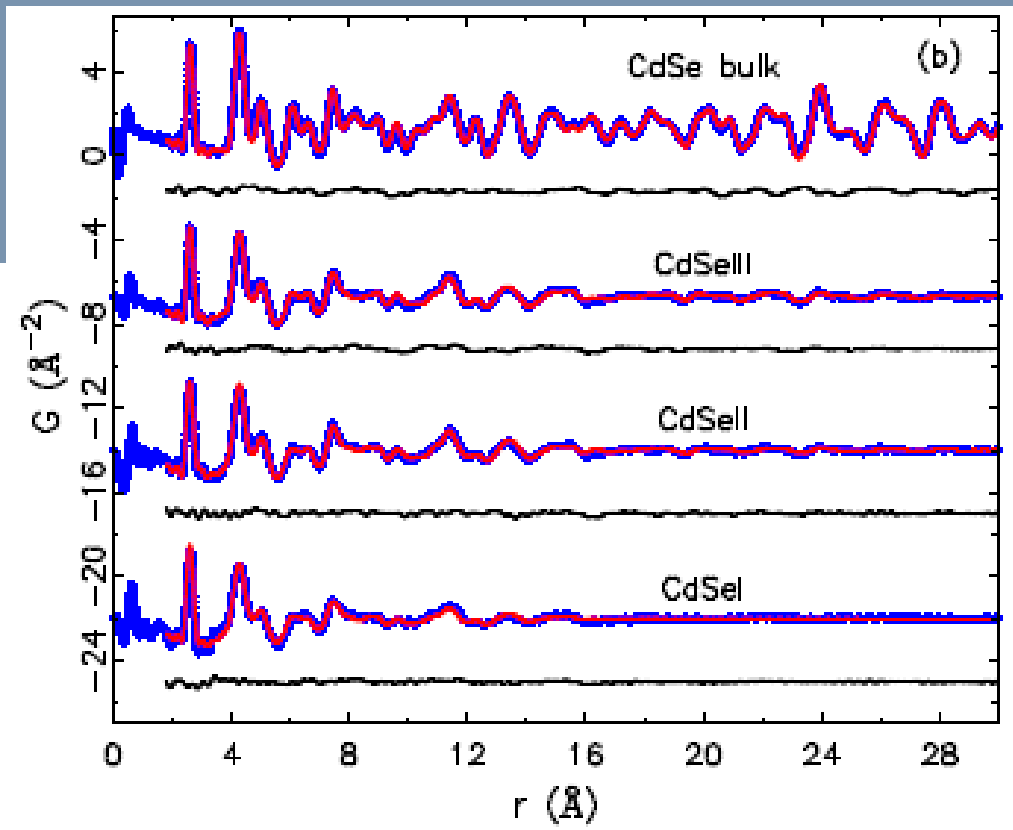
..but huge

f turbostratic

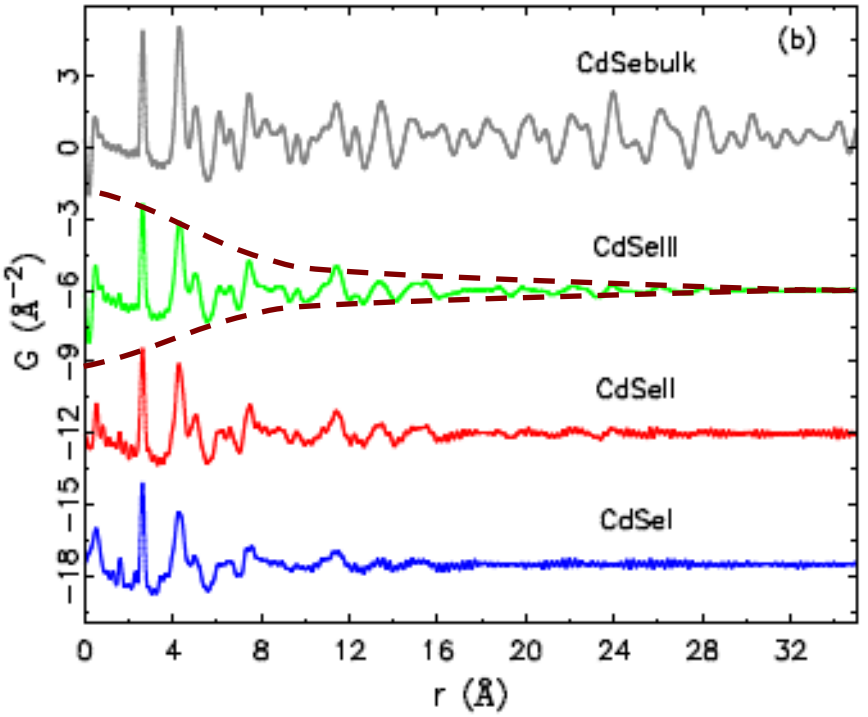
							CdSeI	
Stacking fault den:							0.0	50.0
a (Å)							4.2930(9)	4.2930(8)
c (Å)							6.9405(9)	6.9405(7)
Se *Z-frac.*							0.3685(9)	0.3694(9)
Cd $U_{11} = U_{22}$ (Å^2							0.0237(9)	0.0213(8)
U_{33} (Å^2)							0.0261(9)	0.0281(9)
Se $U_{11} = U_{22}$ (Å^2)	0.0109(9)	0.0102(9)	0.0077(7)	0.0138(7)	0.0083(7)	0.0121(7)	0.0110(9)	0.0191(9)
U_{33} (Å^2)	0.0462(9)	0.0115(9)	0.1501(9)	0.02301(9)	0.1628(9)	0.0265(9)	0.1765(9)	0.0311(9)
NP[a] diameter (nm)	∞	∞	3.7(1)	3.7(1)	3.1(1)	3.1(1)	2.4(2)	2.2(2)
R_w	0.12	0.09	0.20	0.14	0.18	0.15	0.27	0.21

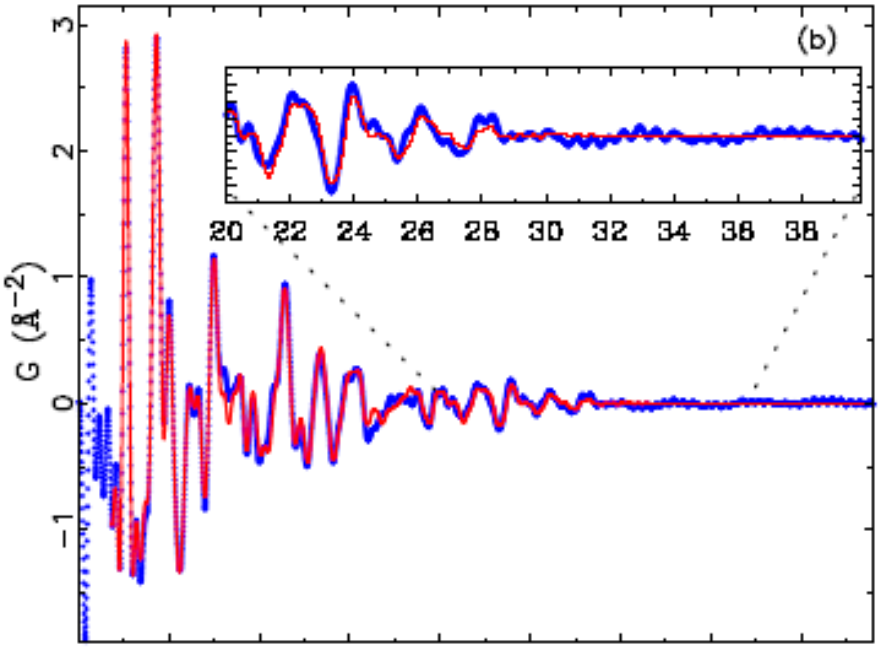


- Masadeh et al. PRB 2007
- Thanks to Reinhard Neder for help with stacking fault models

	CdSe-bulk		CdSeIII		CdSeII		CdSeI	
Stacking fault density (%)	0.0	33.0	0.0	50.0	0.0	50.0	0.0	50.0
a (Å)	4.3014(4)	4.3012(4)	4.2997(9)	4.2987(9)	4.3028(9)	4.3015(9)	4.2930(9)	4.2930(8)
c (Å)	7.0146(9)	7.0123(9)	7.0145(4)	7.0123(4)	6.9987(9)	6.9975(9)	6.9405(9)	6.9405(7)
Se *Z-frac.*	0.3774(3)	0.3771(3)	0.3761(9)	0.3759(9)	0.3751(6)	0.3747(6)	0.3685(9)	0.3694(9)
Cd $U_{11} = U_{22}$ (Å^2)	0.0108(2)	0.0102(2)	0.0146(7)	0.0149(7)	0.0149(6)	0.0112(5)	0.0237(9)	0.0213(8)
U_{33} (Å^2)	0.0113(3)	0.0112(3)	0.0262(9)	0.0241(9)	0.0274(9)	0.0271(9)	0.0261(9)	0.0281(9)
Se $U_{11} = U_{22}$ (Å^2)	0.0109(9)	0.0102(9)	0.0077(7)	0.0138(7)	0.0083(7)	0.0121(7)	0.0110(9)	0.0191(9)
U_{33} (Å^2)	0.0462(9)	0.0115(9)	0.1501(9)	0.02301(9)	0.1628(9)	0.0265(9)	0.1765(9)	0.0311(9)
NP[a] diameter (nm)	∞	∞	3.7(1)	3.7(1)	3.1(1)	3.1(1)	2.4(2)	2.2(2)
R_w	0.12	0.09	0.20	0.14	0.18	0.15	0.27	0.21

Size of the structural core





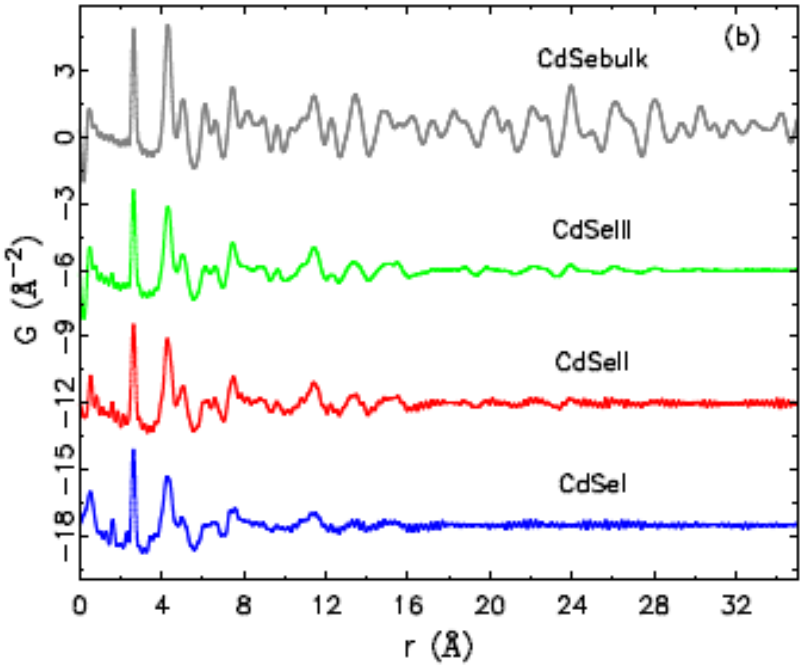
$$f\,(r,d) = \left[1 - \frac{3r}{2d} + \frac{1}{2}\left(\frac{r}{d}\right)^3\right]\Theta(d-r),$$

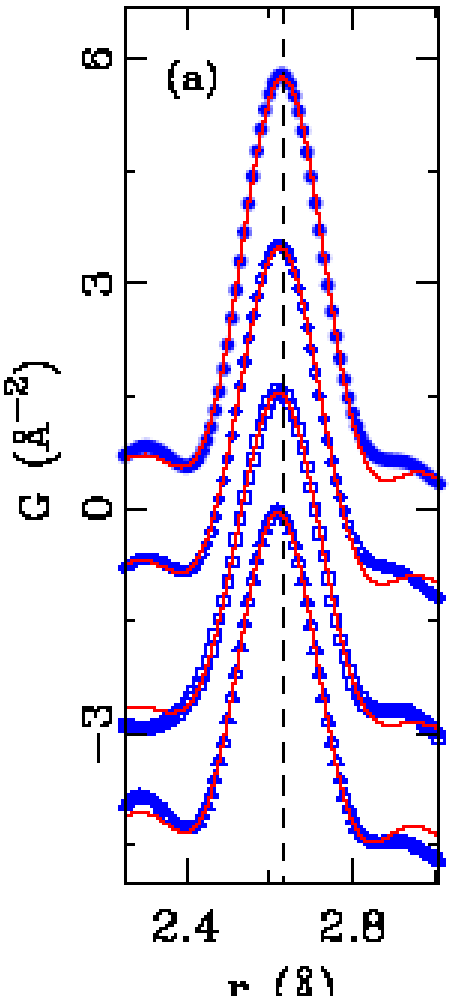
TABLE I: CdSe nanoparticle diameter as determined using various methods.

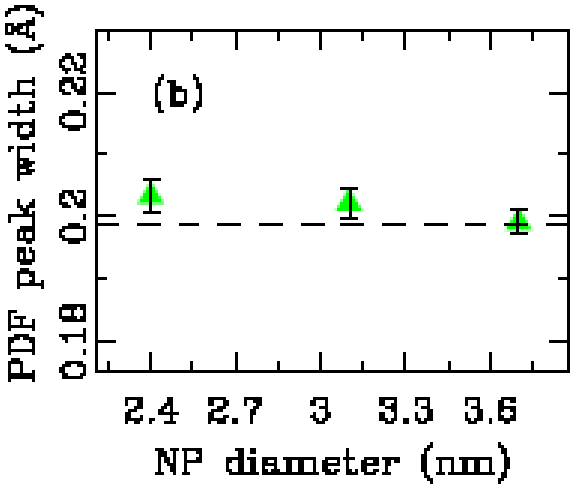
	CdSeIII	CdSeII	CdSeI
Nucleation time (s)	1200	630	15
Diameter (nm)			
TEM	3.5(2)	2.7(2)	2.0(2)
UV-vis	3.5(4)	2.9(3)	≤ 1.90
PL	3.6(4)	2.9(3)	≤ 2.1
PDF	3.7(1)	3.1(1)	2.2(2)

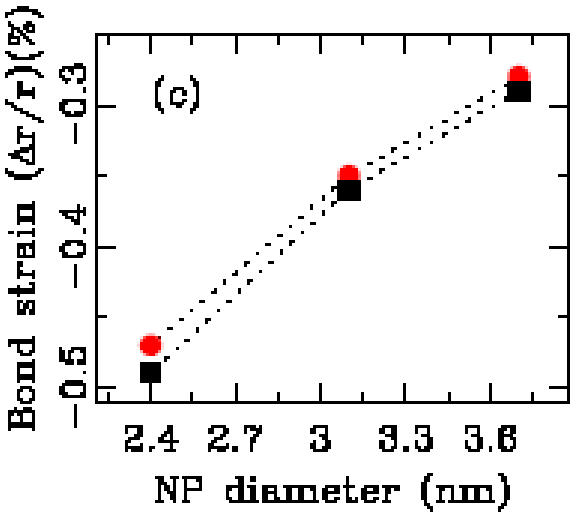
- Also see Shamoto paper, JAC 2007

Homogeneous and inhomogeneous strain in the nanoparticle







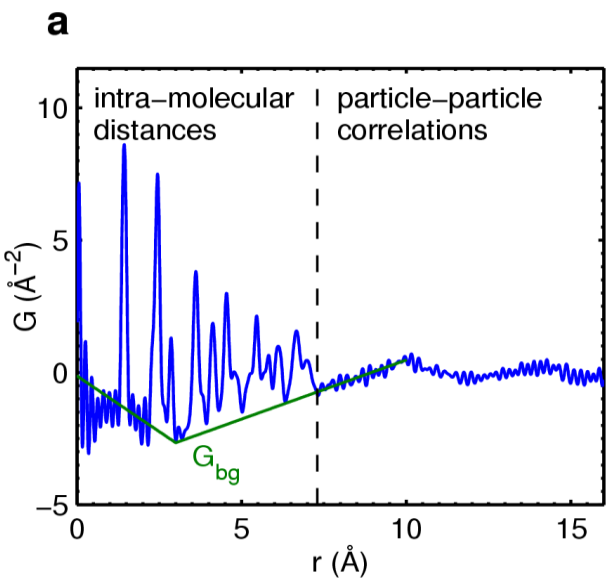


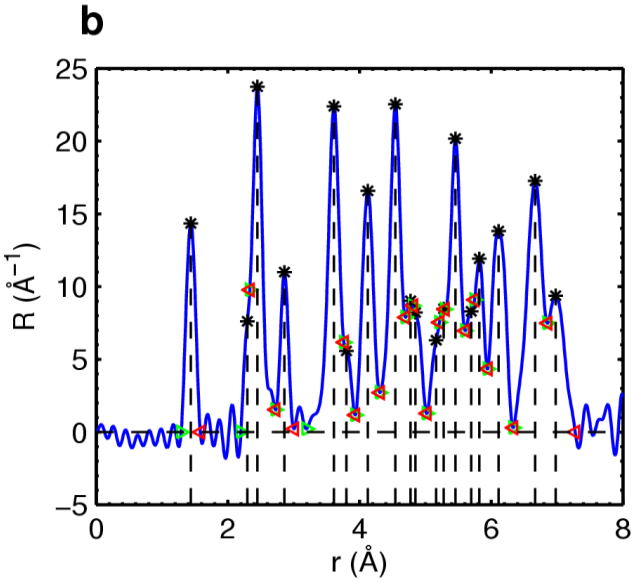
- Homogeneous strain from the PDF peak positions
- Inhomogeneous strain from the widths
- Masadeh et al, PRB 2007

Is there enough information for an ab-initio structure solution?

Example: C60

- 60 atoms => n(n-1)/2 = 1770 pair-vectors
- We know the lengths (not the directions) of ~18 unique distances
- We have an imperfect measure of the multiplicities of those distances
- We don't have any symmetry information to help us





Is the problem well conditioned or ill conditioned?

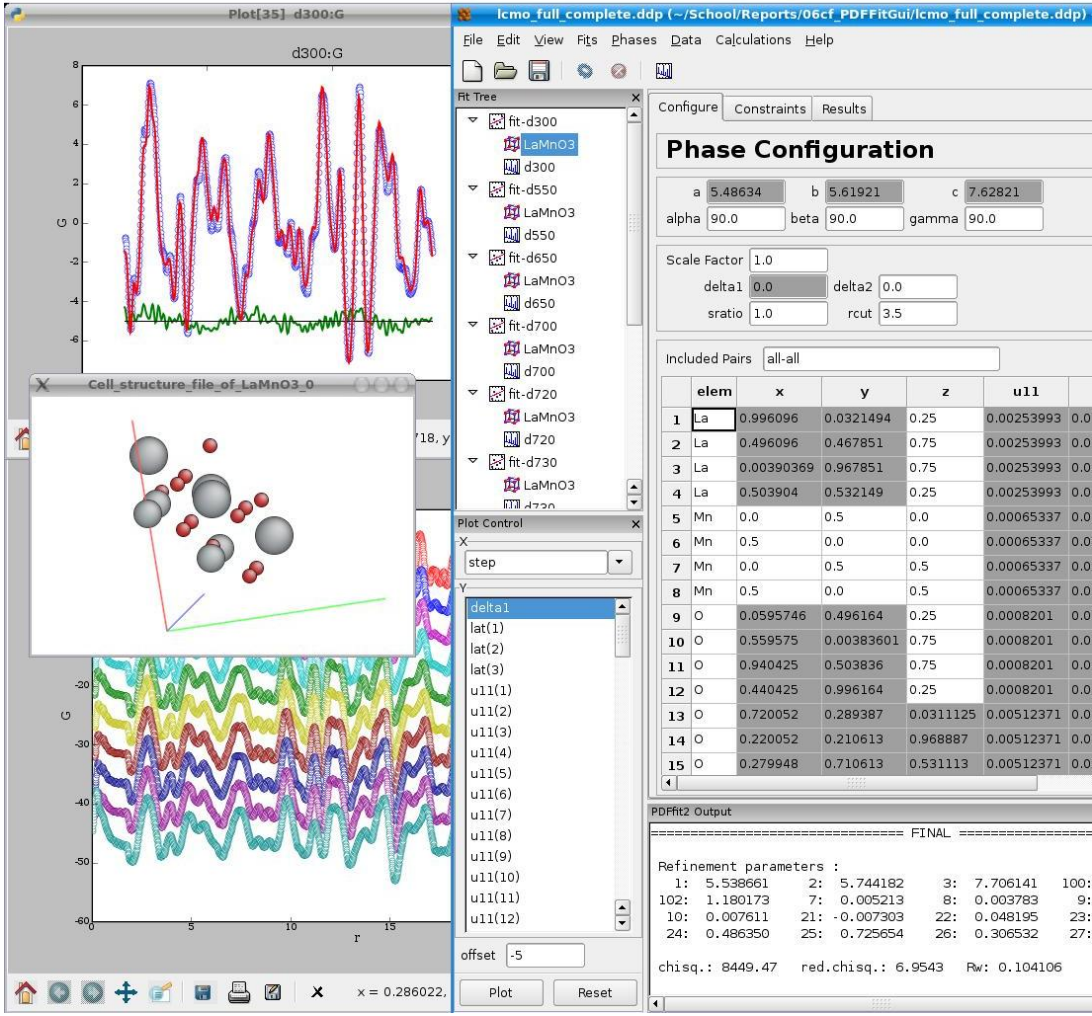
Is there a unique solution?

Advanced Modelling

Progress: PDFgui v1.0beta: www.diffpy.org

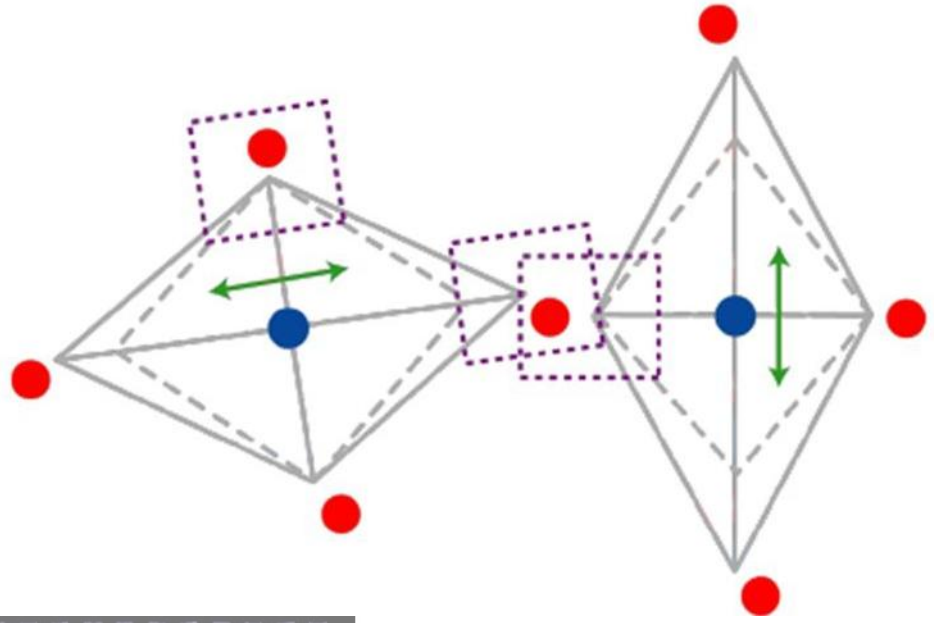
Full featured, gui-driven program replaces PDFfit

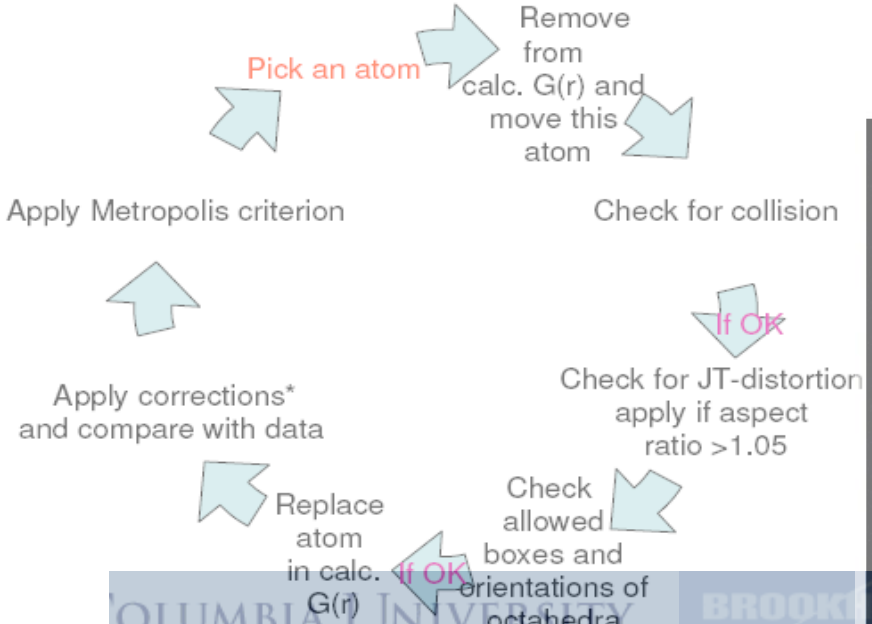
- New features:
  - Dynamic memory allocation
  - Supports space-groups
  - Supercell expansion
  - Spherical nanoparticle form-factor implemented
  - Supports xyz, CIF, PDB file formats (expanded from discus)
  - Automatically generates
    - Symmetry constraints
    - Analytic derivatives of user and symmetry constraint equations
  - Live plotting
  - Structure visualization
  - Parametric plotting
  - Macro language for T-series, doping-series, r-series
  - Smart extraction of meta-data from files and file-names
  - User requested usability features such as fit summary and automated updating of inputs
  - Built-in bug-reporting

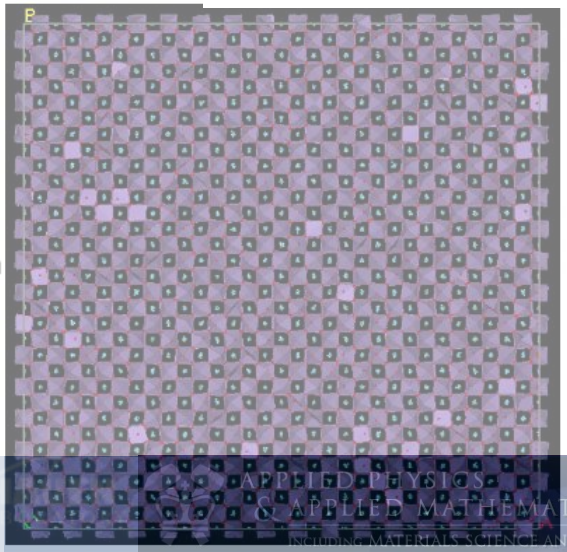


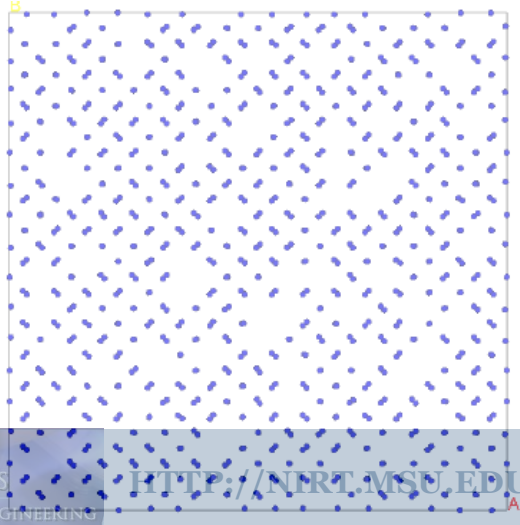
Intermediate range structure: Big box Monte Carlo modeling: Geometric Refinement

- Geometrically constrained Big-Box refinement
- Find intermediate range structure
- Collaboration with Mike Thorpe, Stephen Wells and Asel Sartbaeva

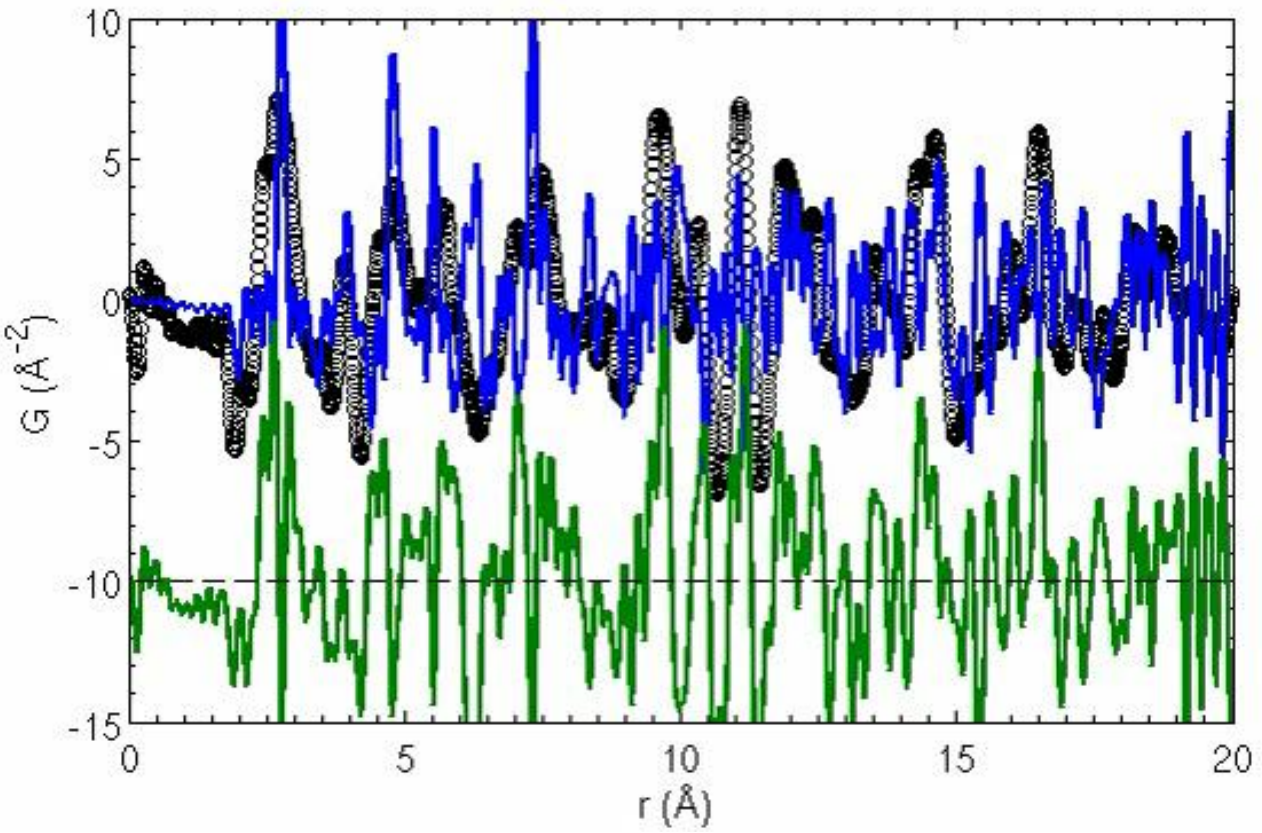






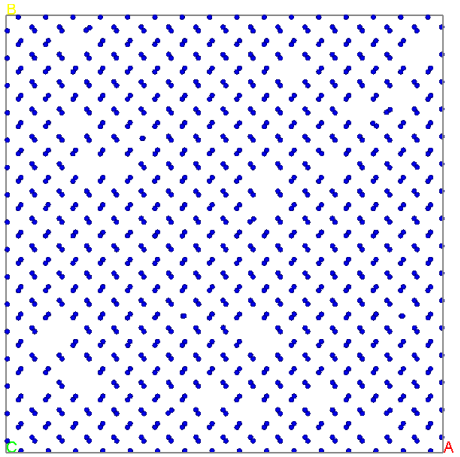


Strength: good convergence

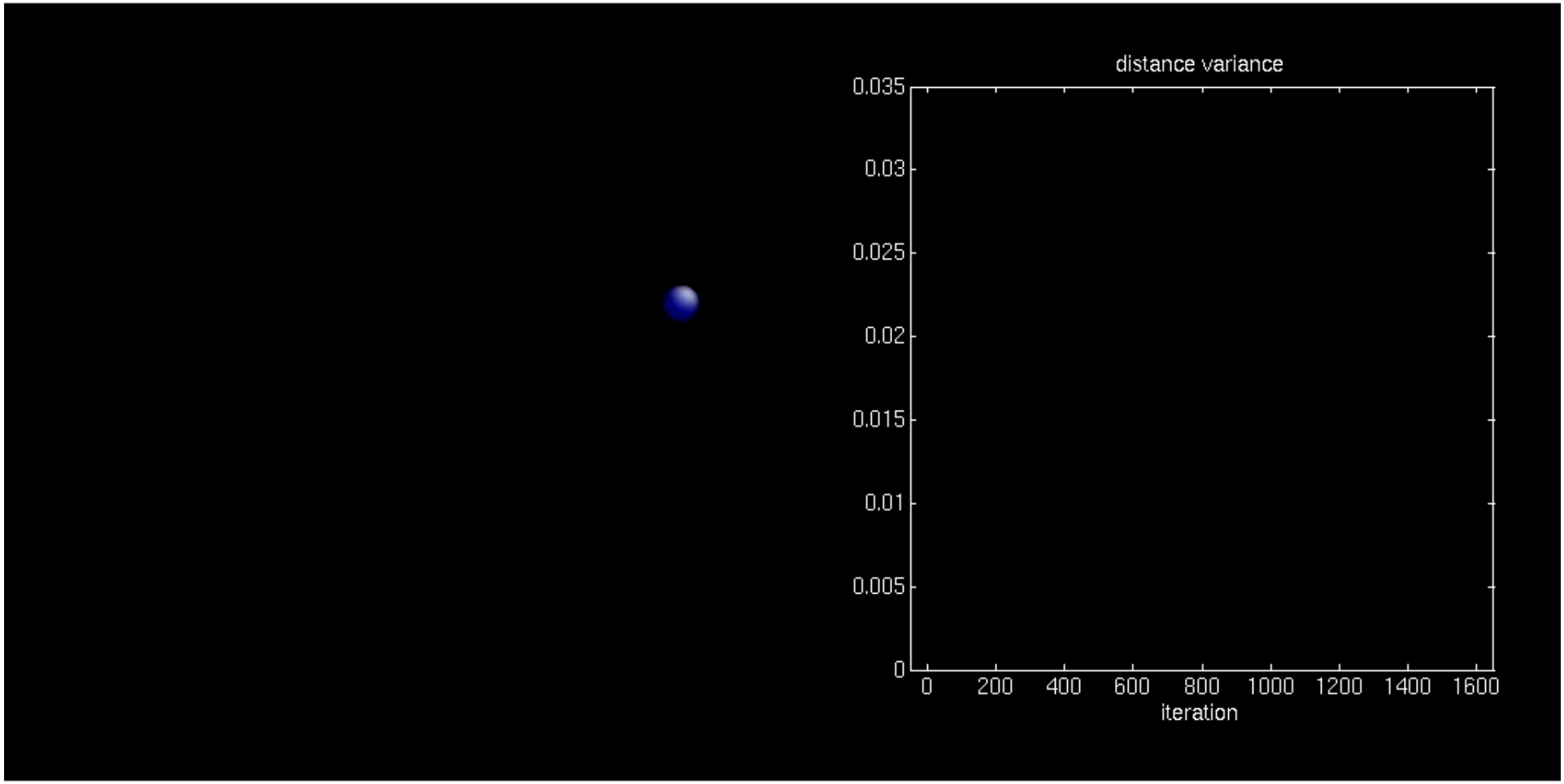


Sartbaeva et al. PRL 2007

- Starting point: cubic manganite, all Mn-O-Mn bonds 180^{o}
- Initial structure far from correct solution with no JT distortions
- Final structure:



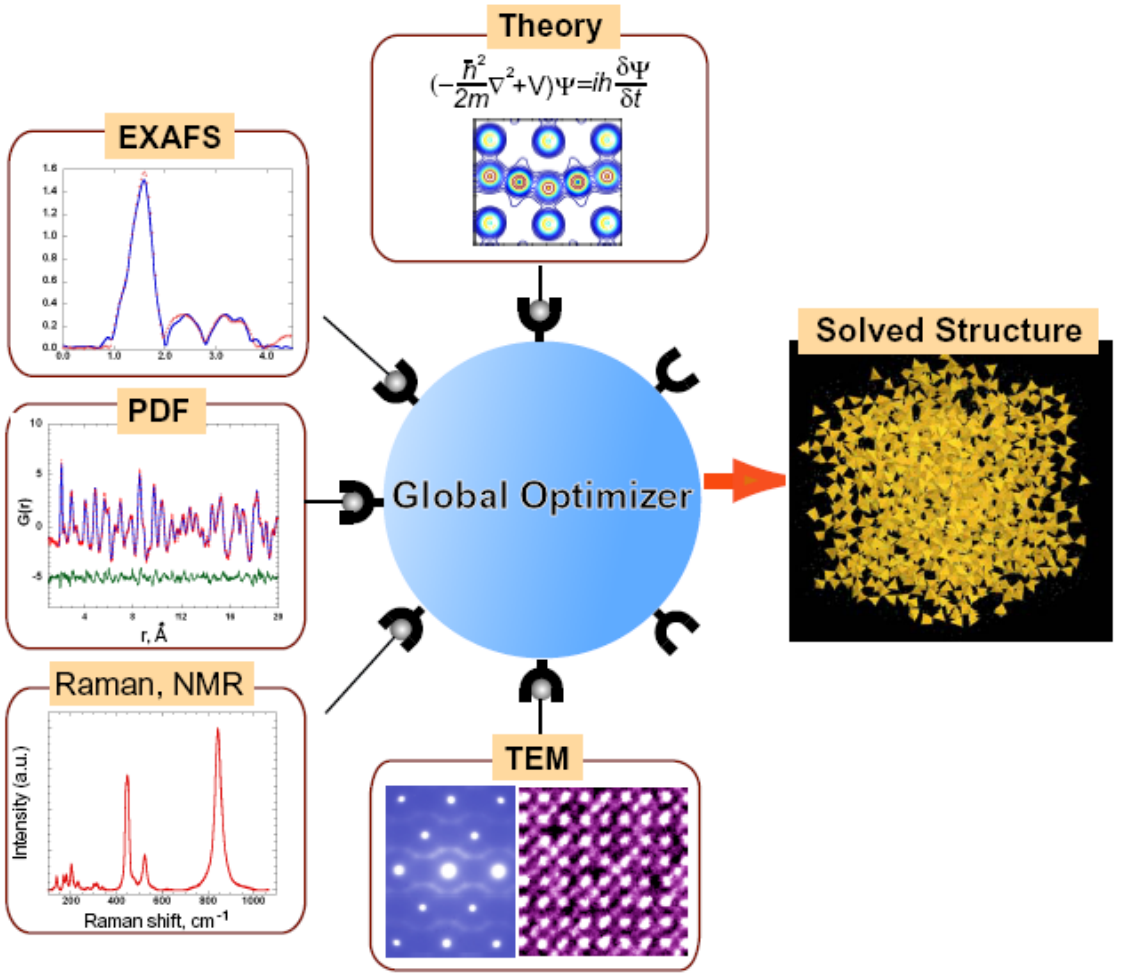
ab-initio structure solution directly from PDF data



1. Make the problem well-conditioned: Complex modeling

- c = a + ib – complex number mixes real and imaginary parts
- m = e + it – complex modeling mixes experiment and theory in a coherent computational framework

- Billinge and Levin, Science 2007



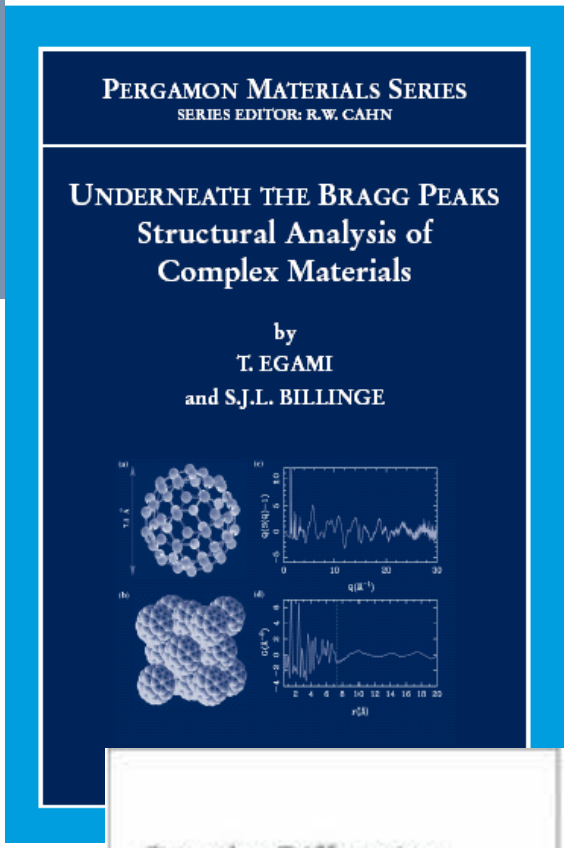
How do we get the PDF?

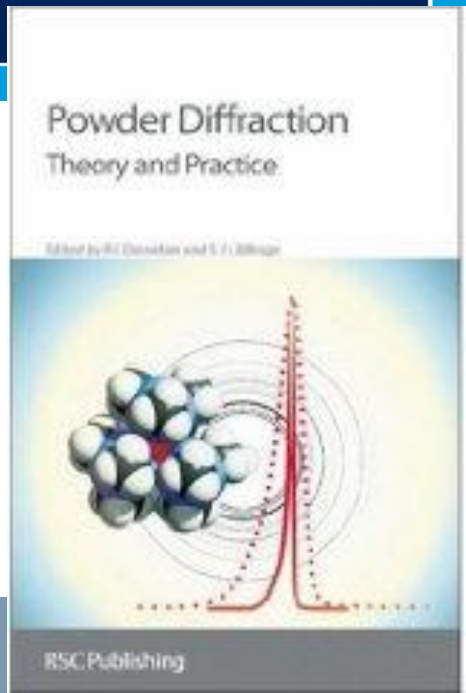
- Collect data
  - X-ray synchrotron
    - X17A NSLS, NSLS-II, Brookhaven, New York
    - 11IDB APS, Argonne, Chicago
    - Spring8, Japan
    - ESRF, France
  - Neutron source
    - NPDF@Los Alamos, New Mexico
    - SNS@Oak Ridge, Tennessee
    - ISIS@Rutherford Lab, UK

Summary

- PDF and total scattering are powerful tools for nanostructure determination and refinement for ensembles of disordered nanoparticles
  - There are many real-world examples: Catalysis, energy materials, minerals, nanoparticles
  - Complexing complementary information sources will
- PDF and total scattering are useful complements for disorder and local structure in crystalline materials
  - Surprising number of applications…many systems warrant a relook
- Rapid throughput and special environments: Materials Science and chemistry at the local scale
  - Time resolved and in-situ measurements => phase diagrams and *in operando* measurements of local structure

http://groups.google.com/group/totalscattering





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- APS, CHESS, NSLS (and people therein)
- MLNSC, ISIS, IPNS (and people therein)

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