Atomic Pair Distribution Function (PDF) Analysis

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Atomic Pair Distribution Function (PDF) Analysis

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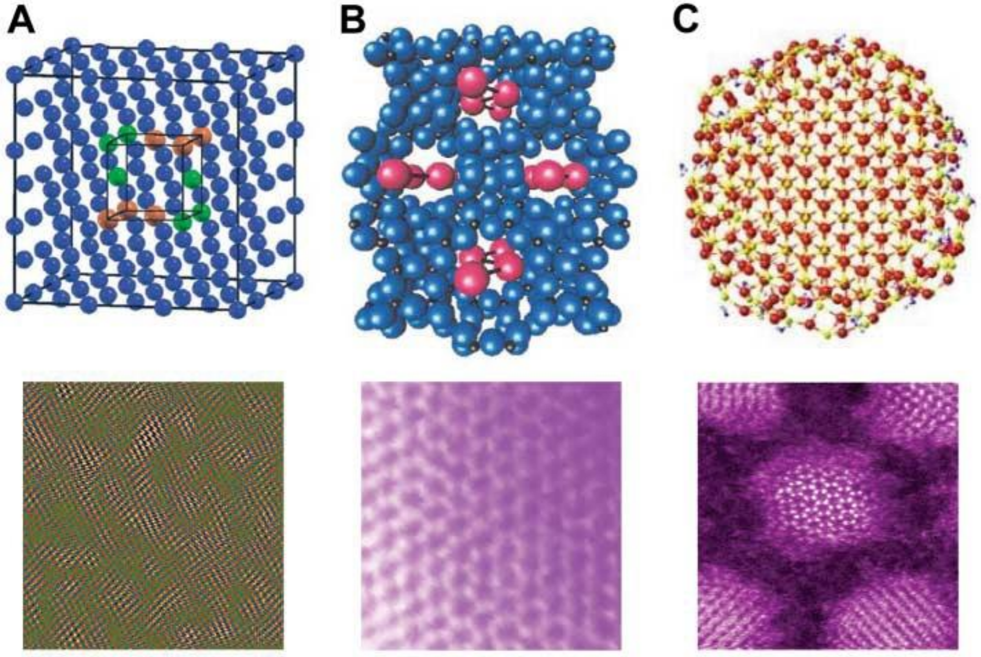
Outline

- Local Structure and Total Scattering
- The Pair Distribution Function (PDF)
- Applications
  - Local Distortions
  - Chemical Short-Range Order
  - Nanomaterial Structure
  - Amorphous Structures
- Experimental Considerations
- Modeling a PDF
- Emerging Areas

What is a *local structure*?

- **Disordered materials**: The interesting properties are often governed by the defects or local structure
- **Non crystalline materials:** Amorphous solids, liquids, glasses and polymers
- **Nanostructures**: Well defined local structure, but long-range order limited to nanometers lengthscales (poorly defined Bragg peaks)

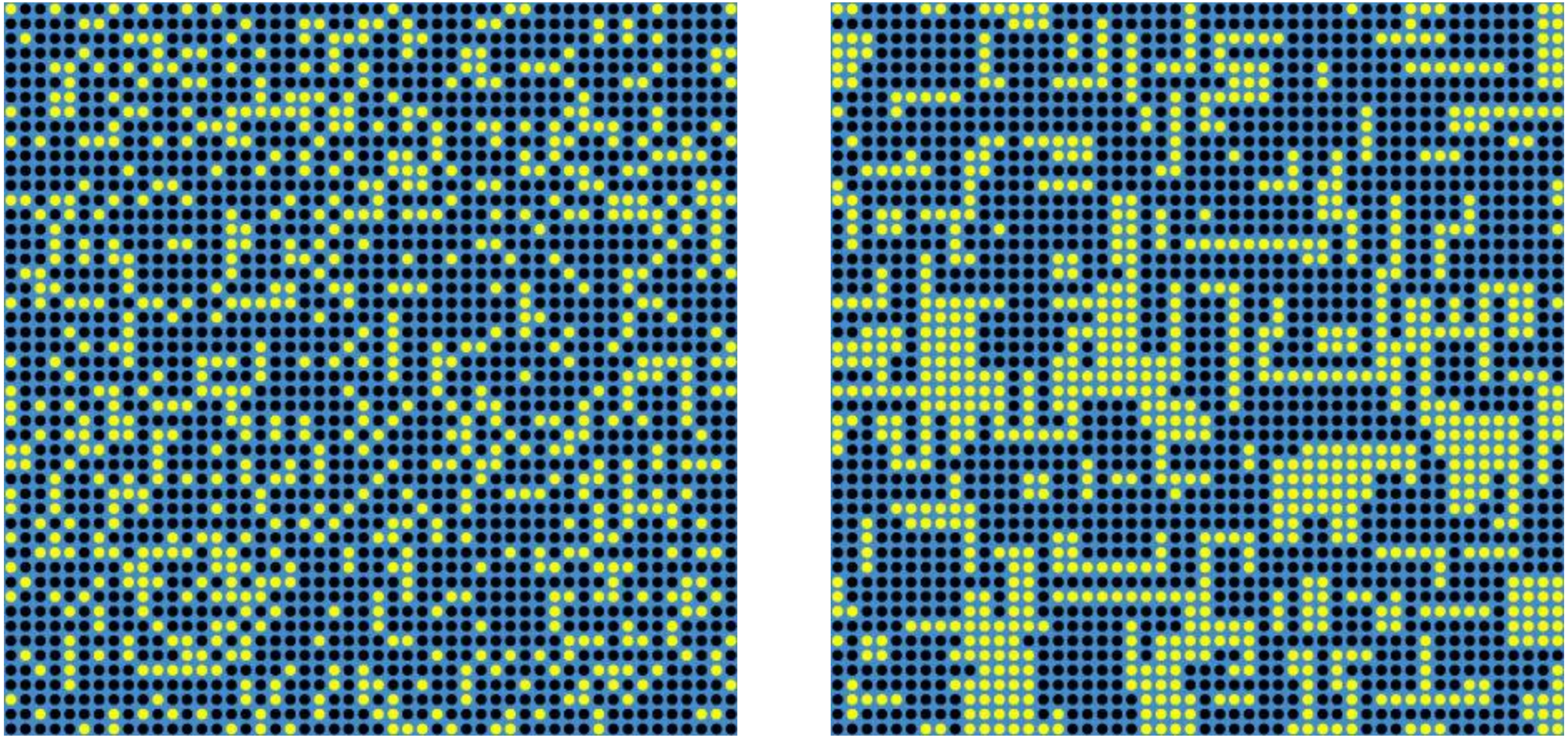


S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

D. A. Keen and A. L. Goodwin, **The crystallography of correlated disorder**, *Nature* 521, 303–309 (2015).

What is *total* scattering?

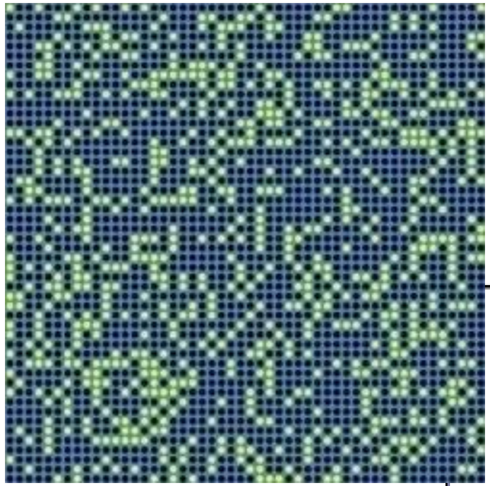
Courtesy of Thomas Proffen



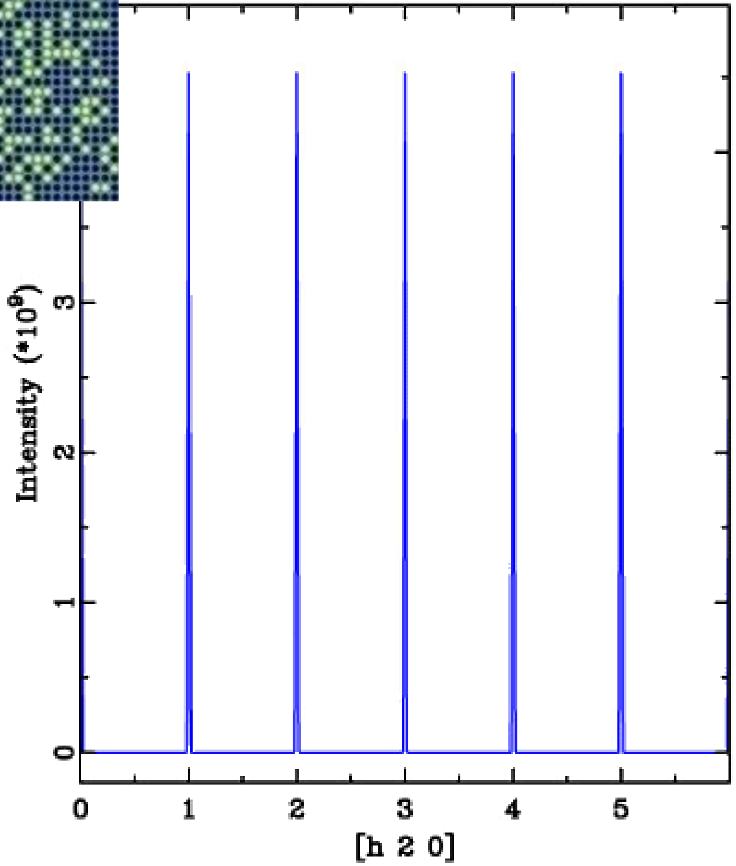
Cross section of 50x50x50 unit cell model crystal consisting of 70% blue atoms and 30% *vacancies*.

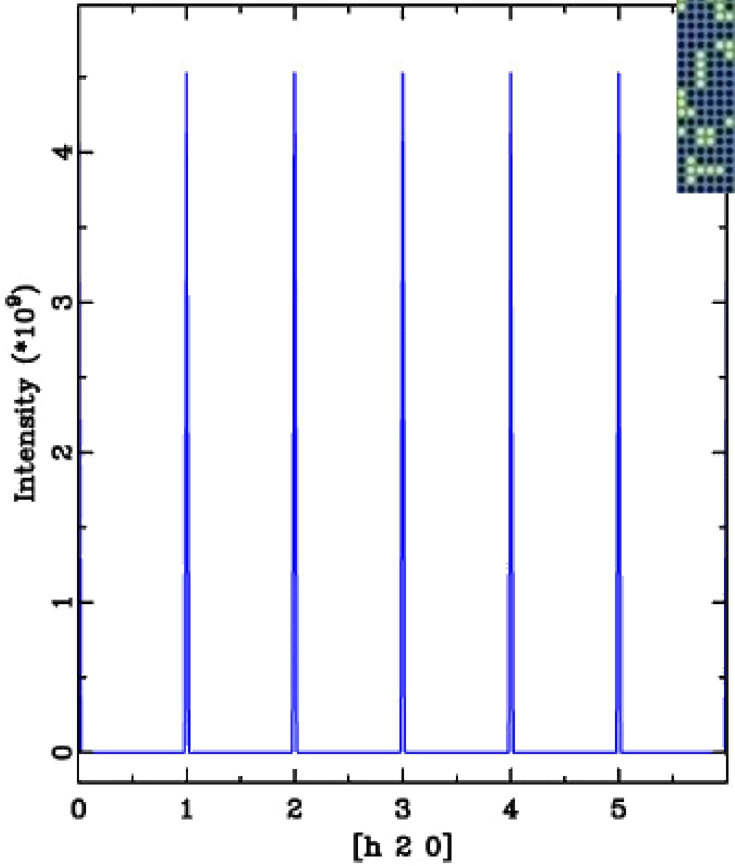
Properties might depend on vacancy ordering!

Bragg peaks are “blind”



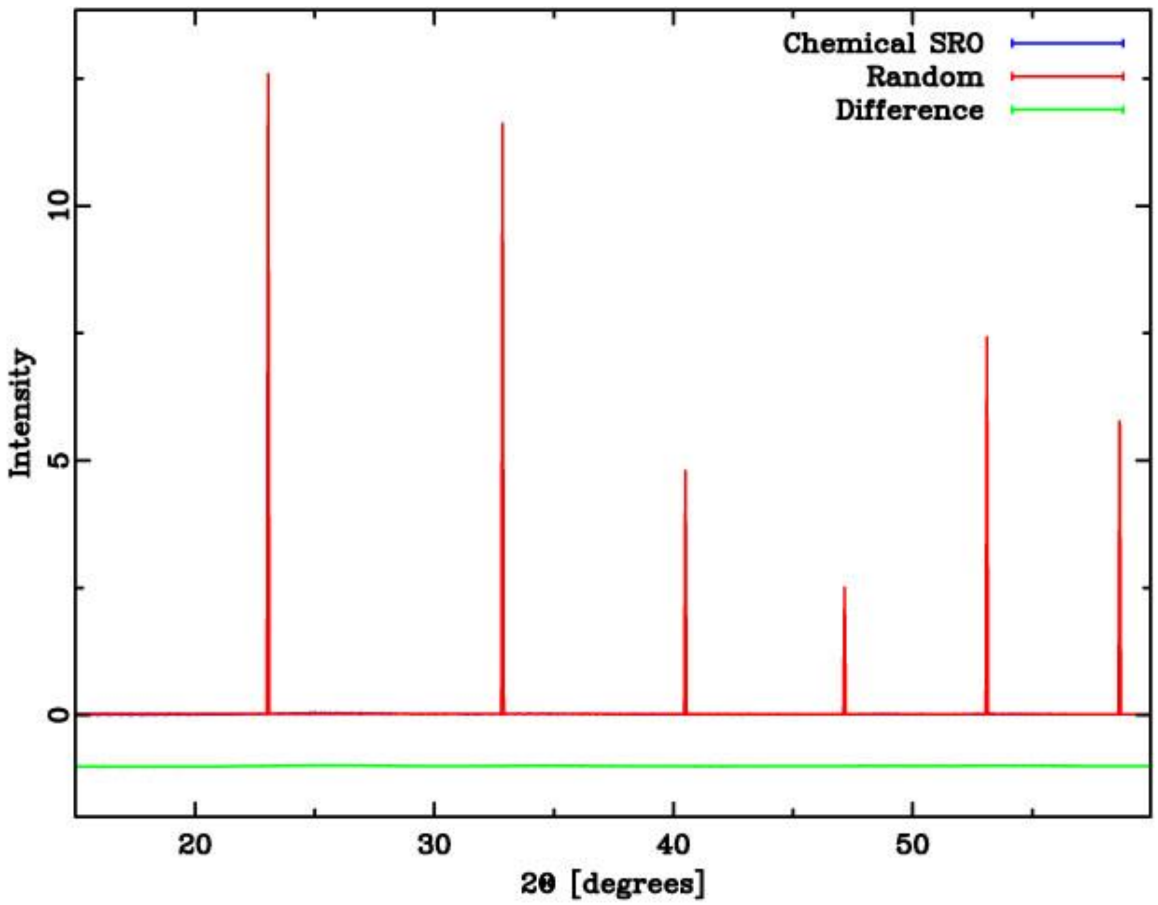
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.

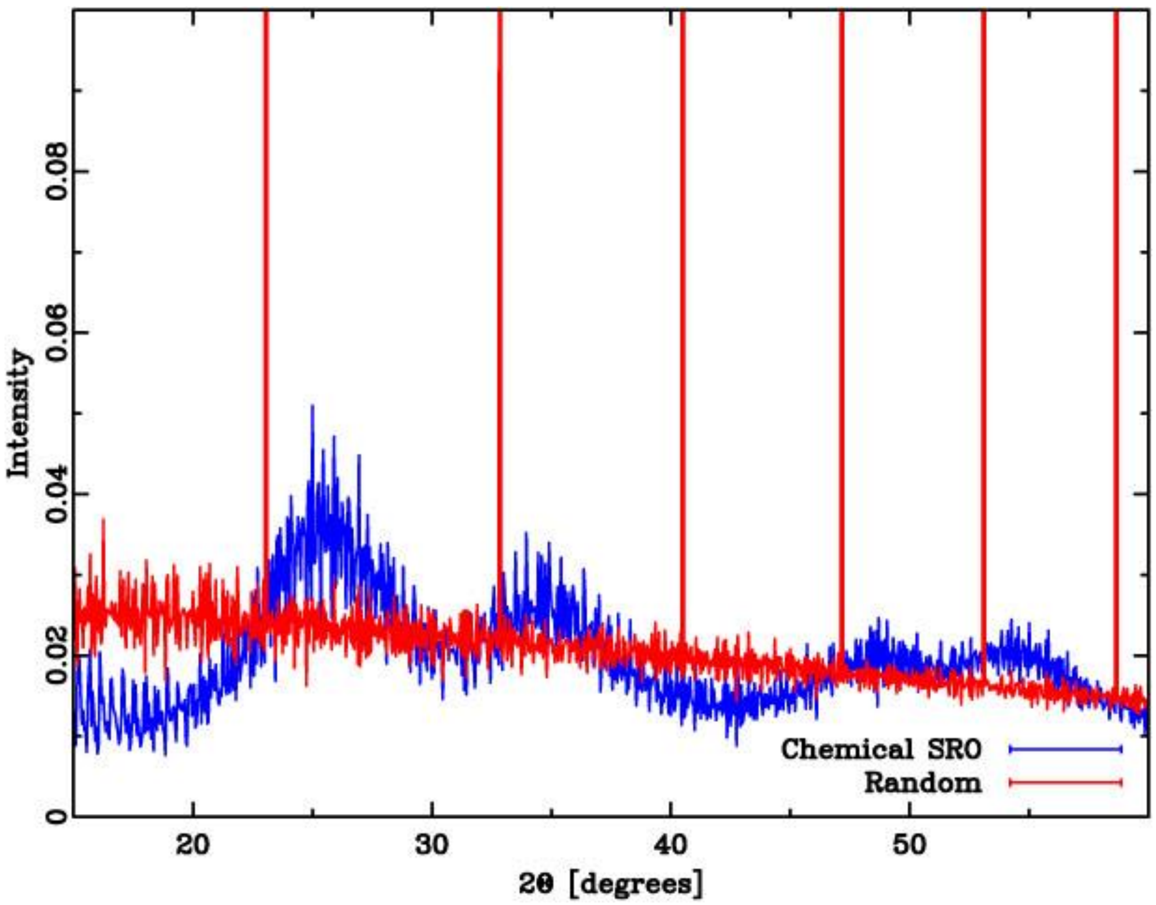




Courtesy of Thomas Proffen

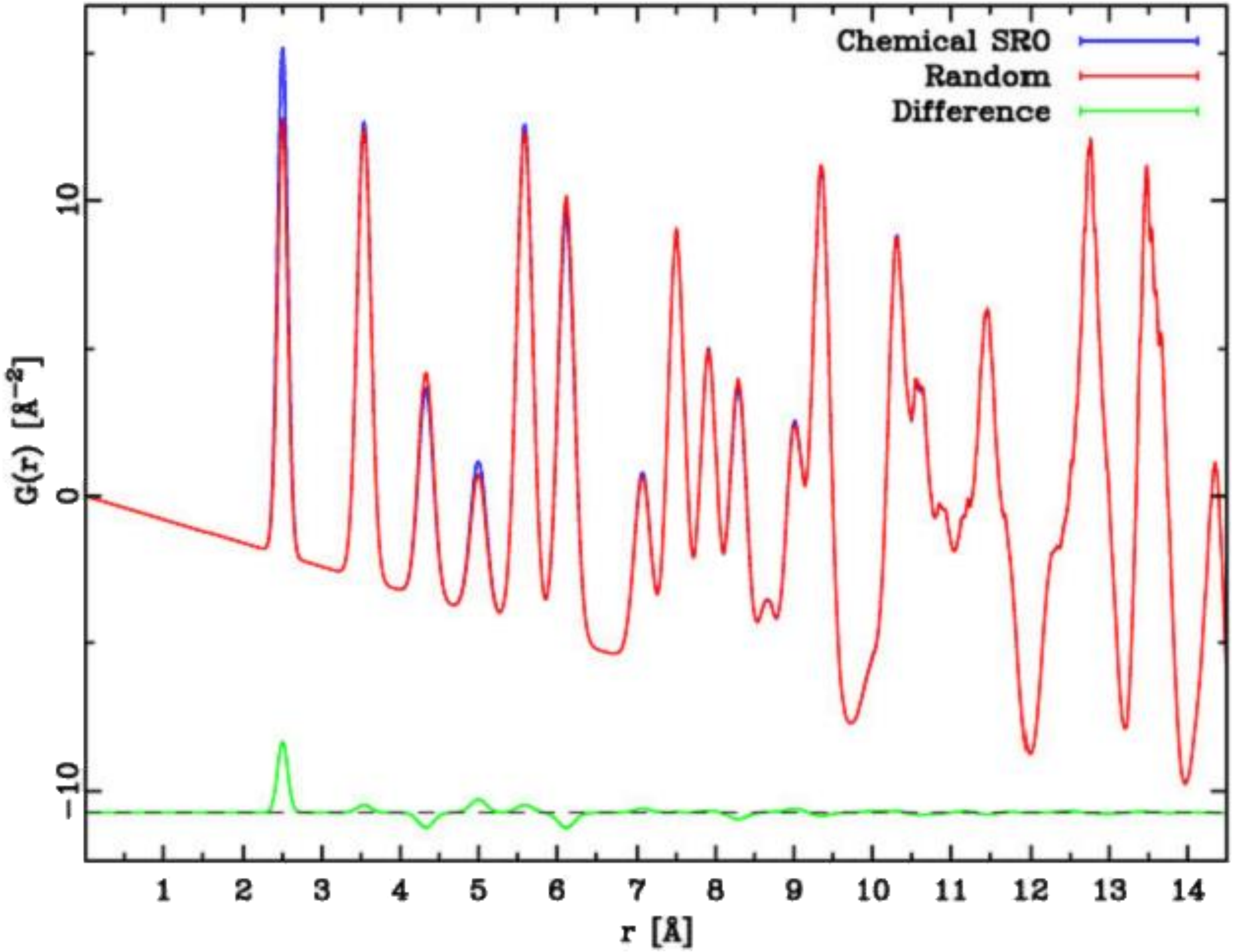
How about powder diffraction?





Courtesy of Thomas Proffen

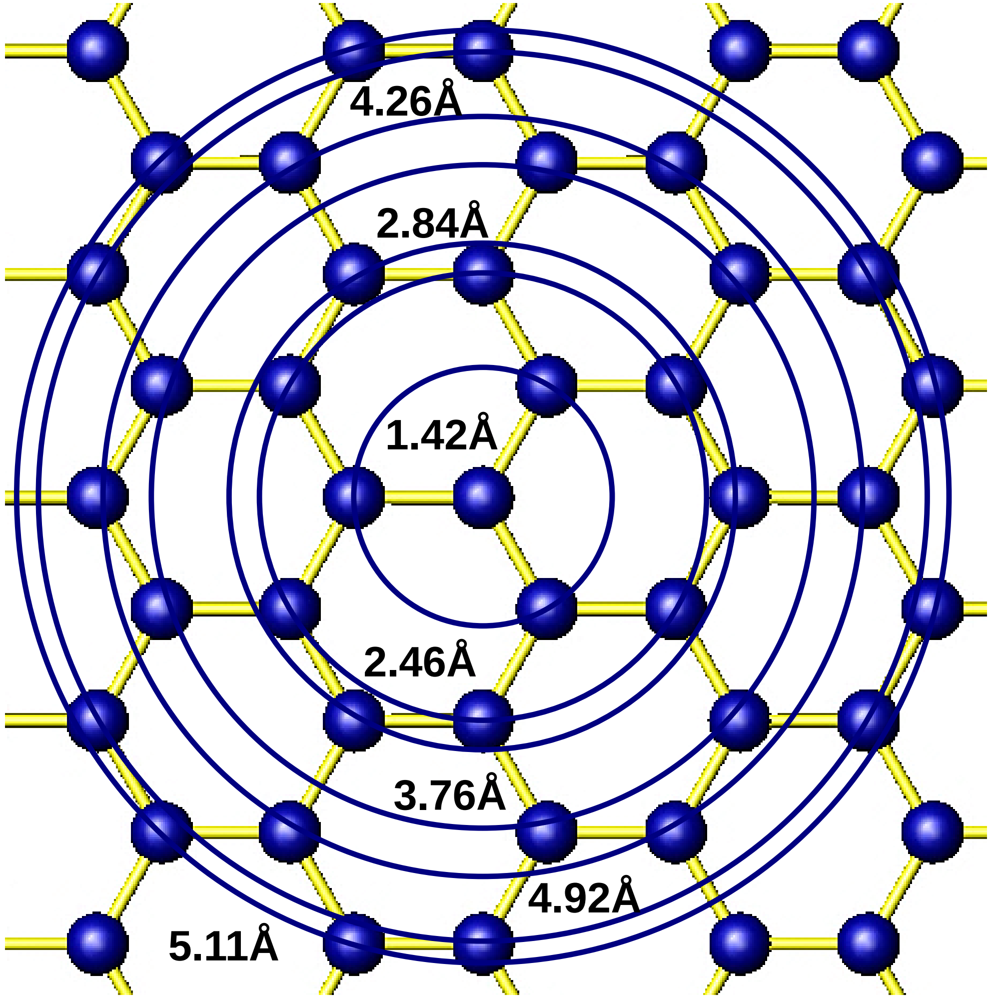
The Pair Distribution Function



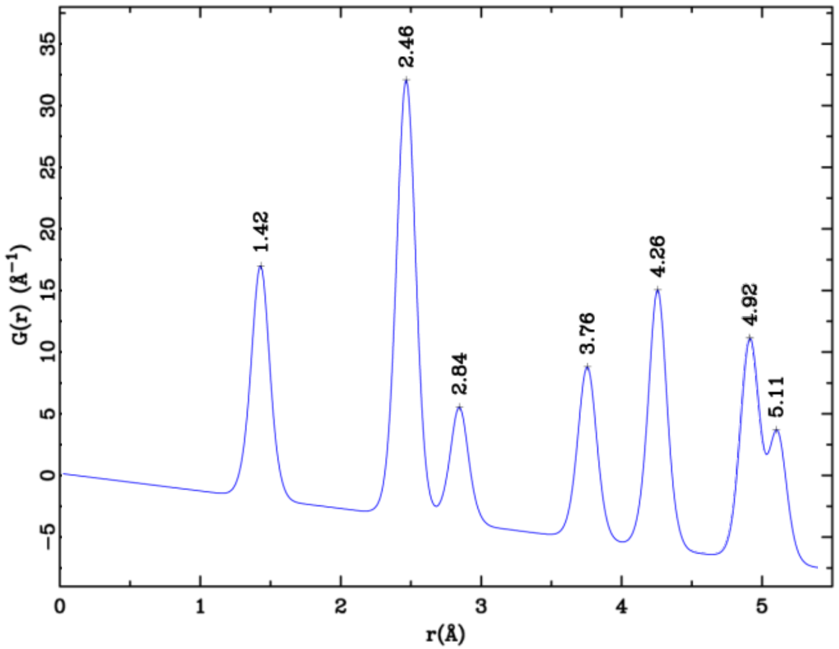
The PDF is the **Sine-Fourier transform** of the **total scattering** (Bragg and diffuse) diffraction pattern

Th. Proffen, Analysis of occupational and displacive disorder using the atomic pair distribution function: a systematic investigation, *Z. Krist*, **215**, 661 (2000).

What is a PDF?



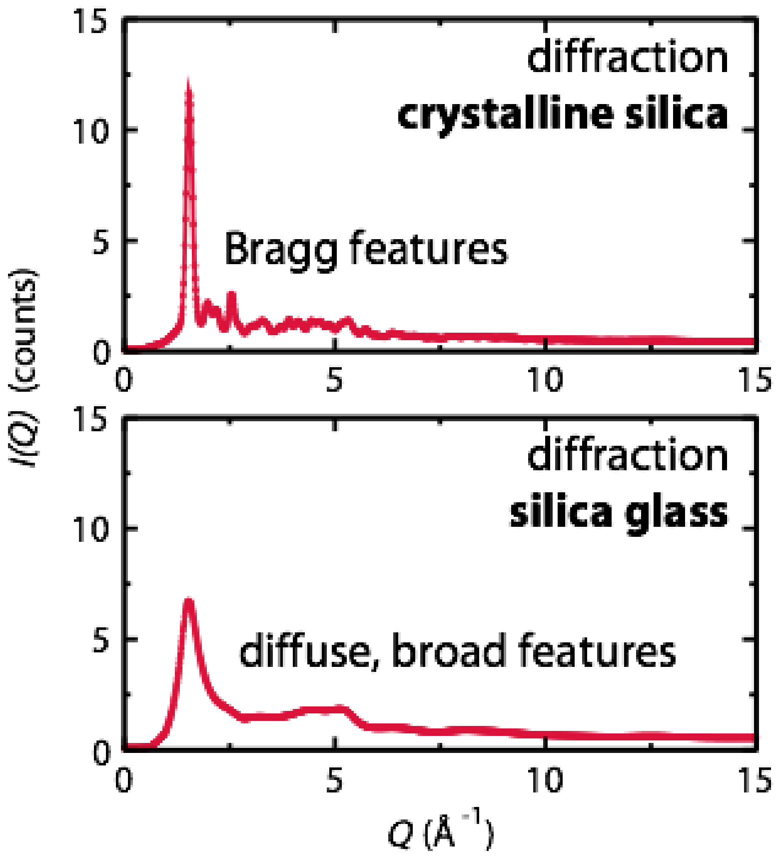
The **Pair Distribution Function (PDF)** gives the probability of finding an atom at a distance "r" from a given atom.

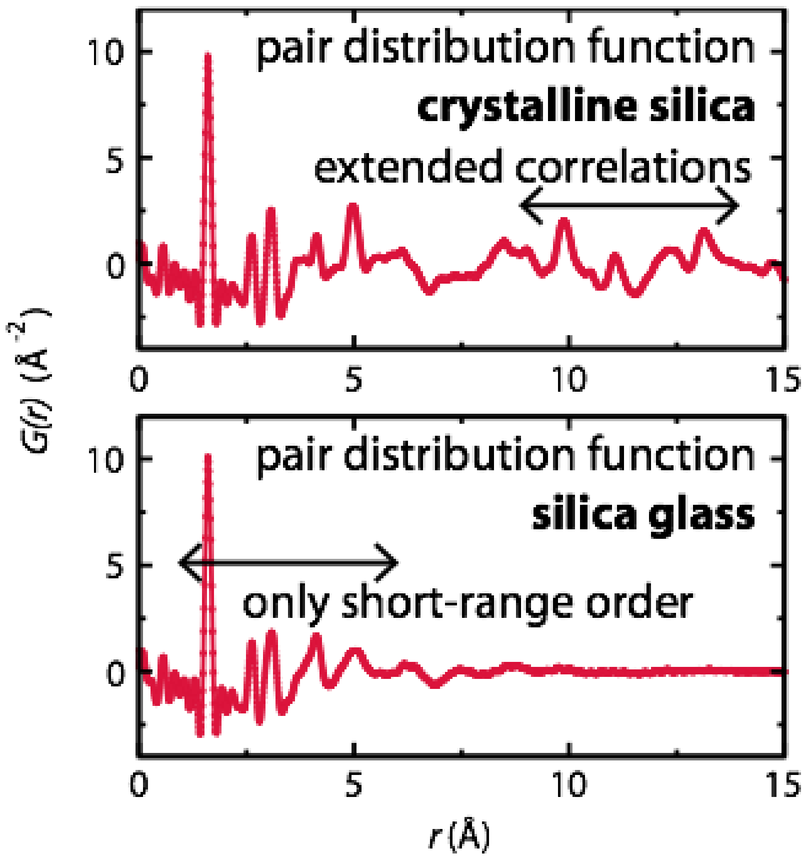


Pair Distribution Function

Sine-Fourier transform of **all** scattered neutron/X-ray intensity (crystalline and amorphous)

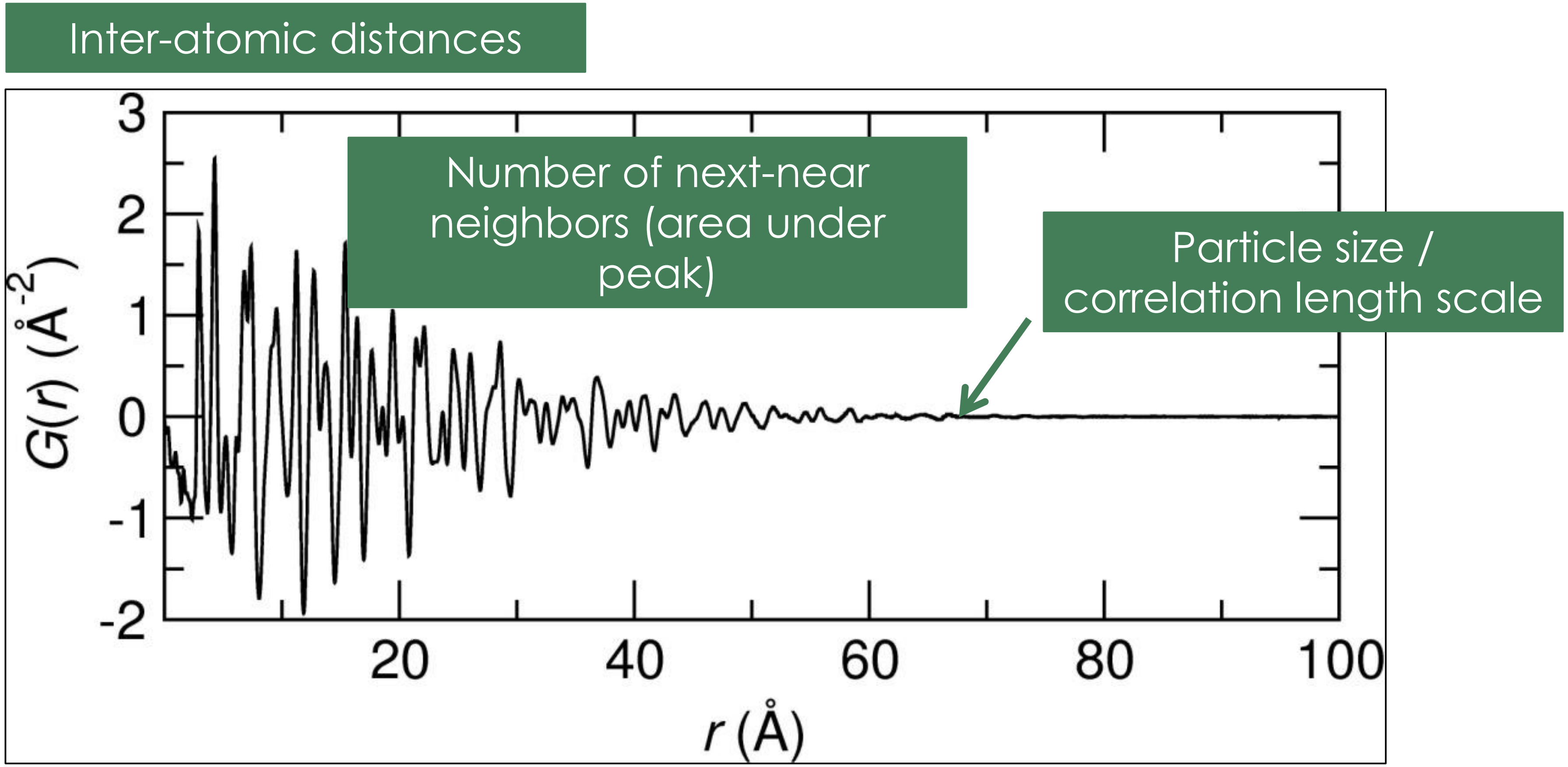
→*Experimental, ensemble, real-space, atom-atom histogram*





Pair Distribution Function

PDF analysis → Local atomic structure for disordered crystalline materials, nanomaterials, and amorphous materials



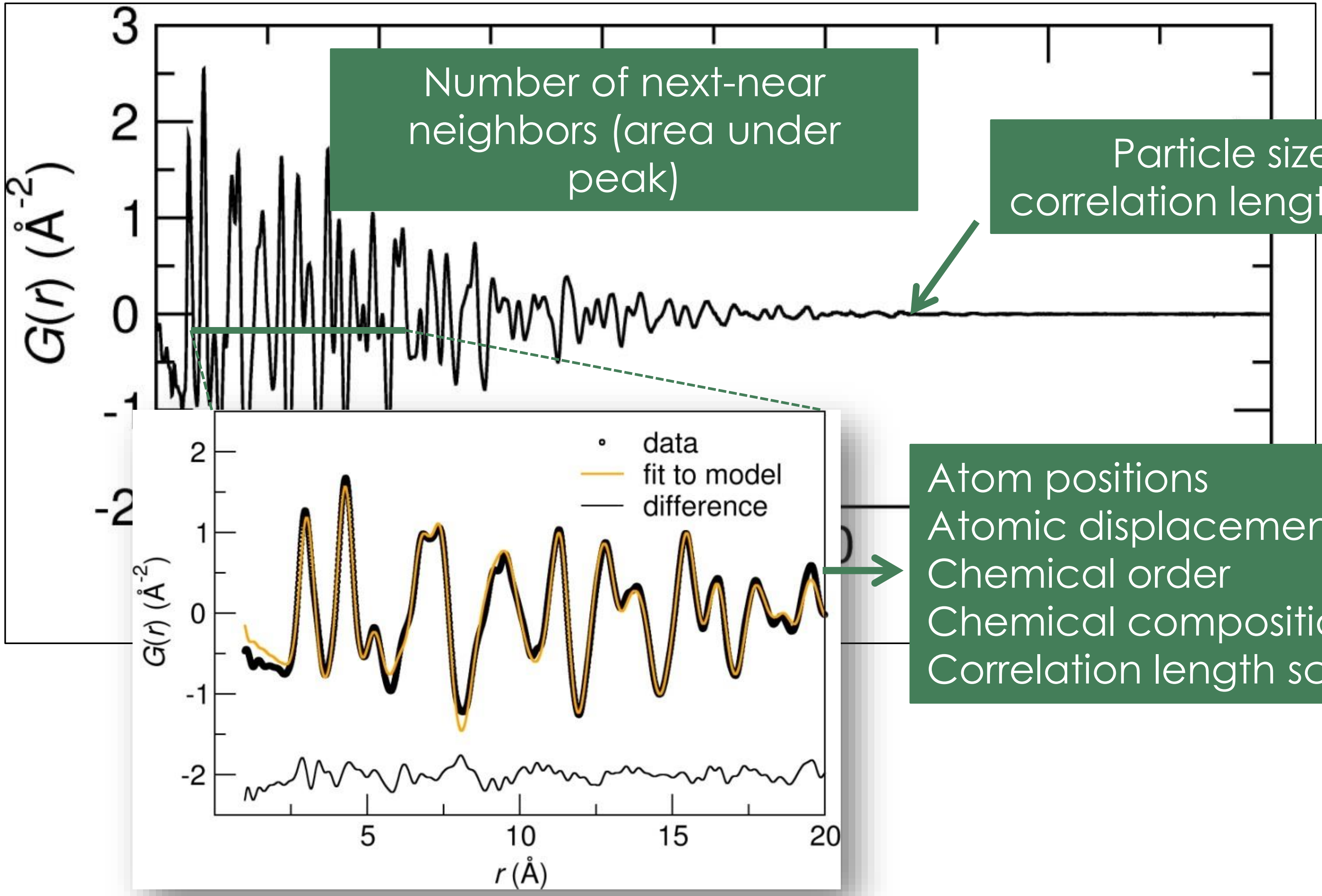
Pair Distribution Function

Quantitative analysis→ fitting a model to the data over specific ranges

Inter-atomic distances

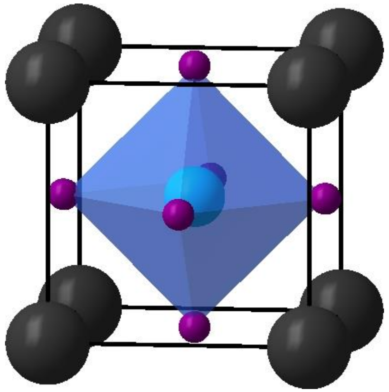
Number of next-near neighbors (area under peak)

Particle size / correlation length scale



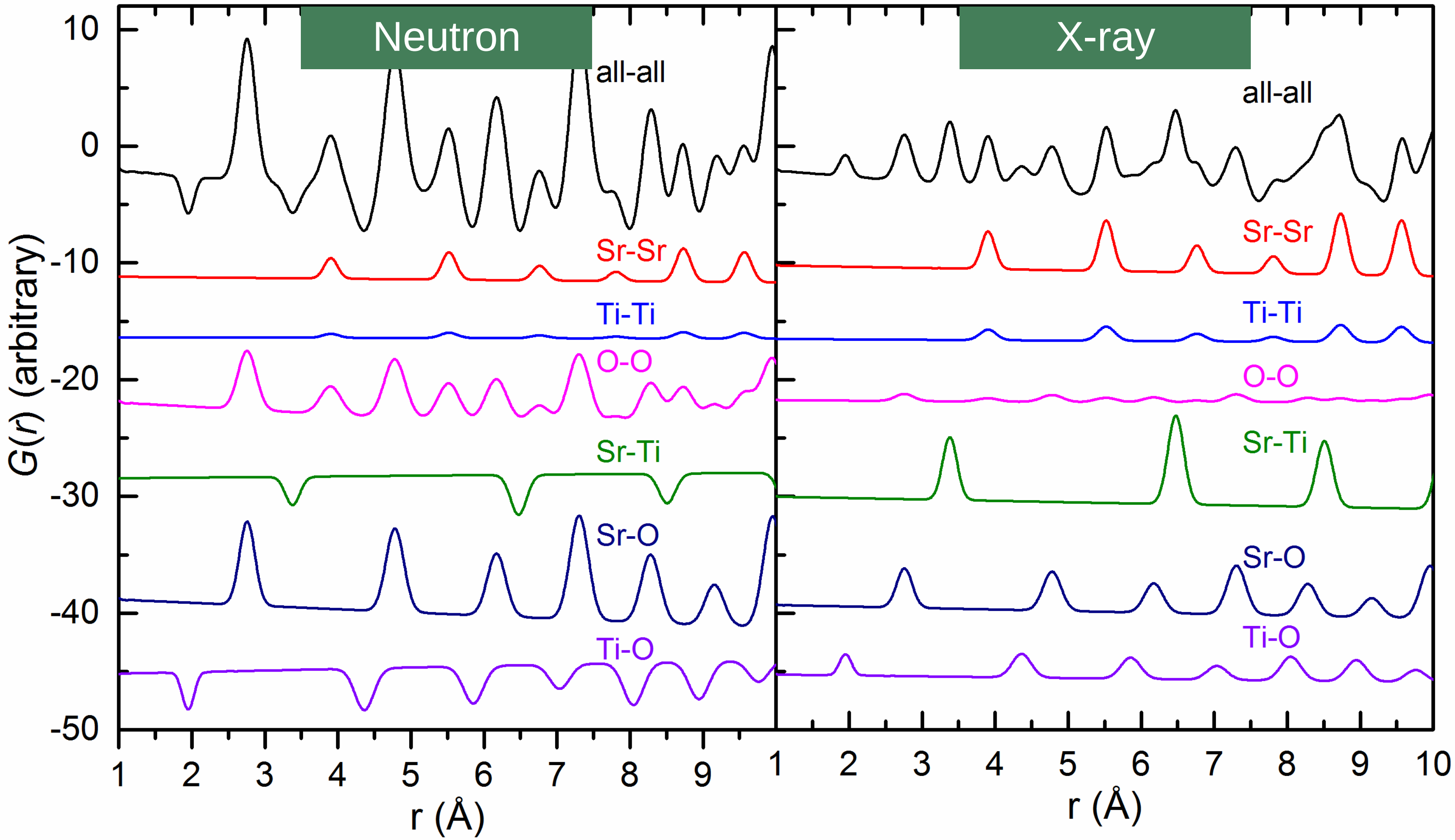
Atom positions
Atomic displacements
Chemical order
Chemical composition
Correlation length scale

Partial PDFs



$SrTiO_3$

s*(*s*+1)/2** partial structure factors characterize a system containing ***s species



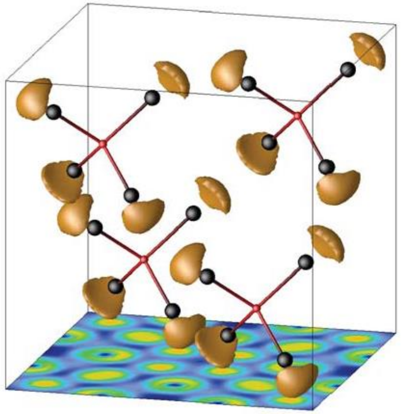
Neutron and x-ray PDFs are often highly complementary.

What types of studies can be done with the PDF technique?

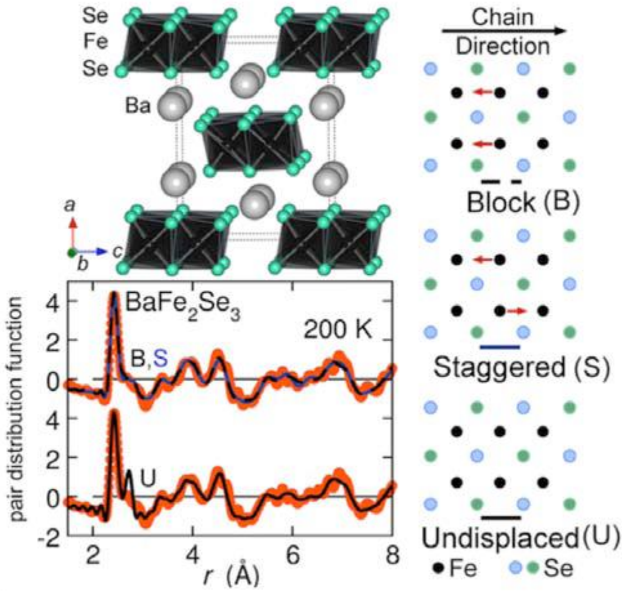
- Local Distortions
- Chemical Short Range Ordering
- Nanostructures
- Amorphous Structures

Local distortions *via* PDF

- Local dipoles
- Local Jahn-Teller distortions
- Frustrated lattices
- Orbital ordering
- *etc.*

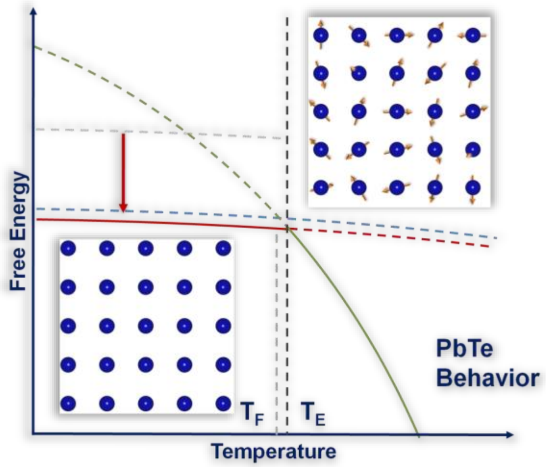


D. P. Shoemaker, *et al.*, Reverse Monte Carlo neutron scattering study of the 'ordered-ice' oxide pyrochlore $Pb_2Ru_2O_{6.5}$, *J. Phys.: Condens. Matter* **23** (2011).



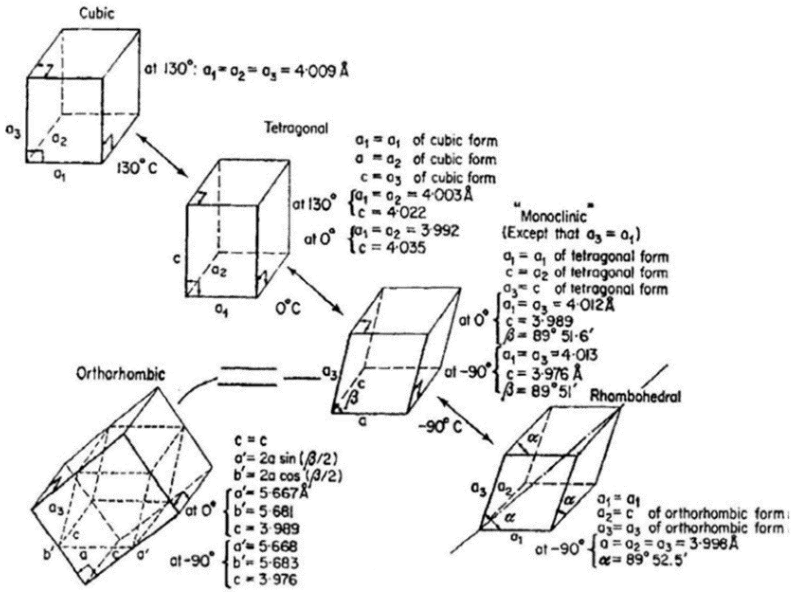
D. Louca, *et al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).

E. Bozin, *et al.*, Entropically Stabilized Local Dipole Formation in Lead Chalcogenides, *Science* **330**, 1660 (2010).



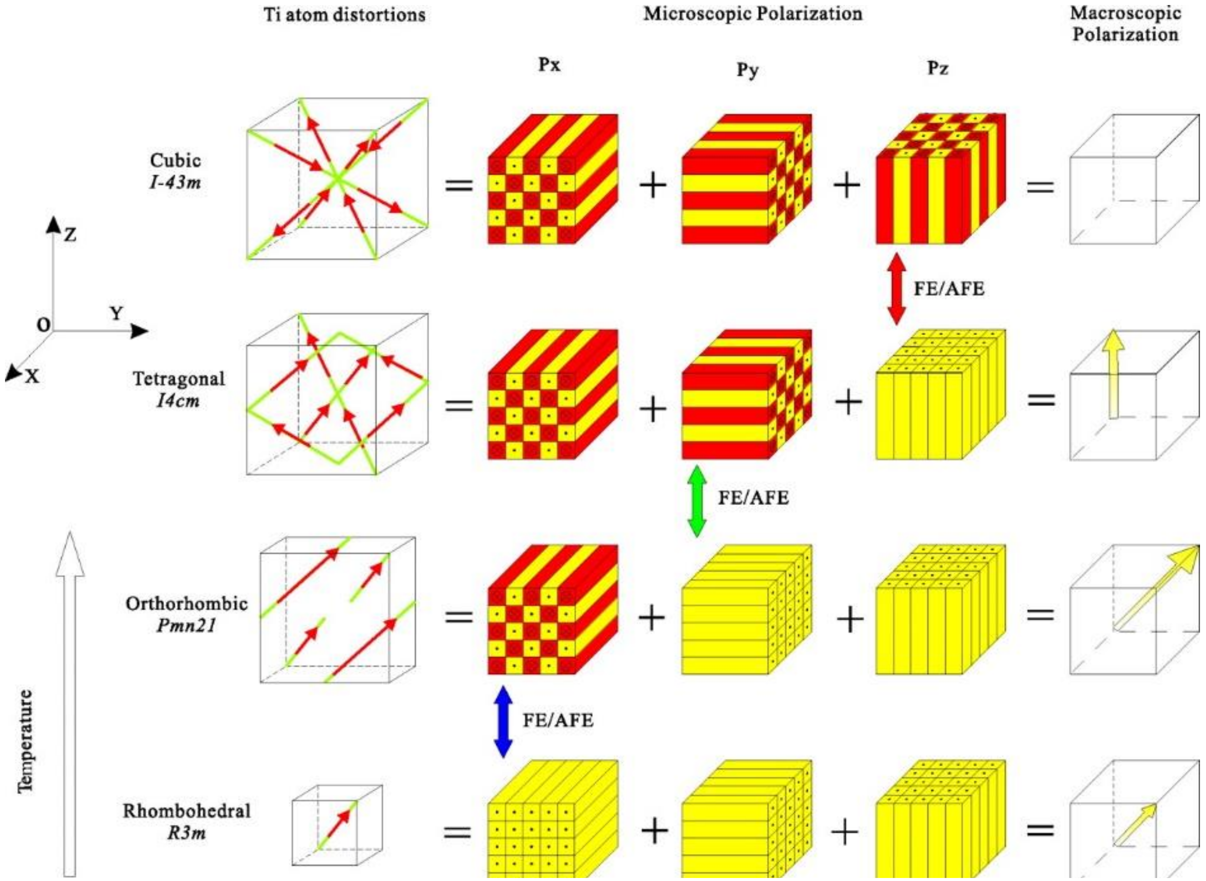
Example: Local structure in $BaTiO_3$

Crystallographic Phase Transitions



Jaffe, Cook, and Jaffe, *Piezoelectric ceramics*, Academic Press, 1971.

Long-range: cubic → tetragonal → orthorhombic → rhombohedral

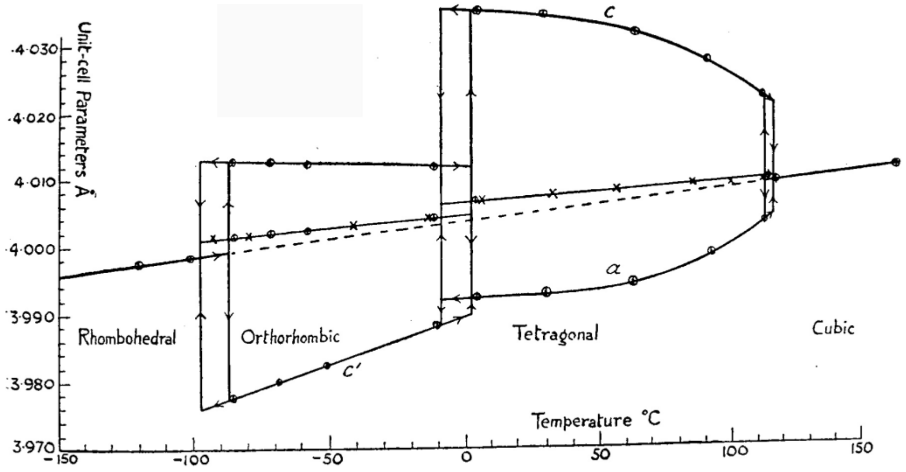


Locally, Ti^{4+} displacements are always along [111] directions (octahedral faces) → Results in 3 short and 3 long Ti-O bonds

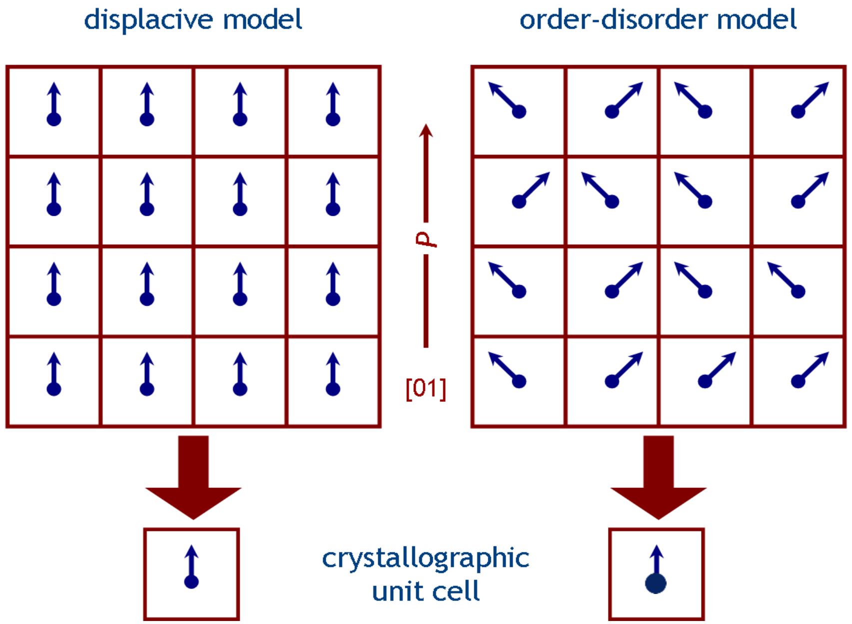
Zhang, Cagin, and Goddard, The ferroelectric and cubic phases in $BaTiO_3$ferroelectrics are also antiferroelectric, *PNAS*, **103**, 14695-14700 (2006).

Example: Local structure in $BaTiO_3$

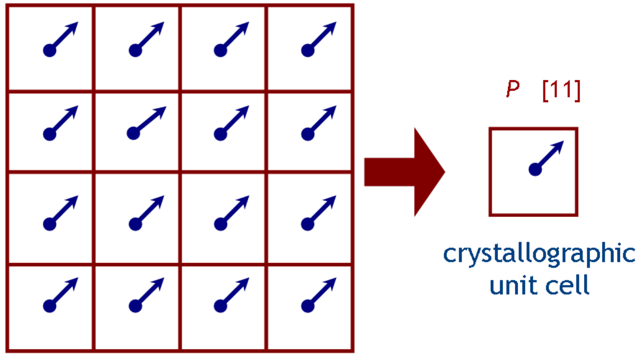
$BaTiO_3$: Ferroelectric oxide, a rhombohedral (*R3m*) ground state and a room temperature tetragonal (*P4mm*) structure



2D models with distinct local motifs but similar "average" motifs



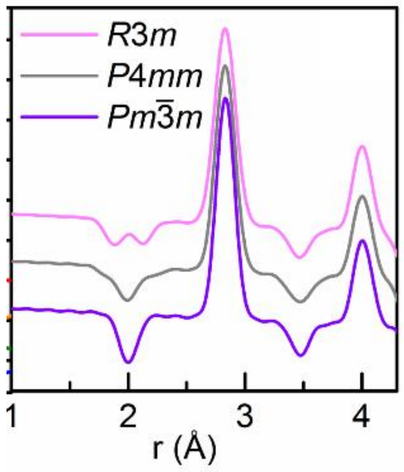
A 2D model where local and average motifs are the same

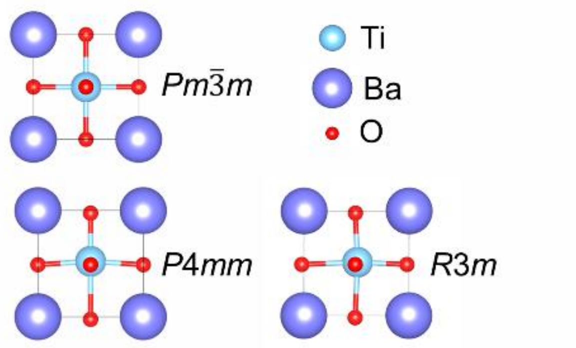


$BaTiO_3$ displays order-disorder phenomena: room temperature local structure known to have rhombohedral-like pair-pair correlations

Neutron PDF for bulk/nano $BaTiO_3$

Calculated $BaTiO_3$ PDFs



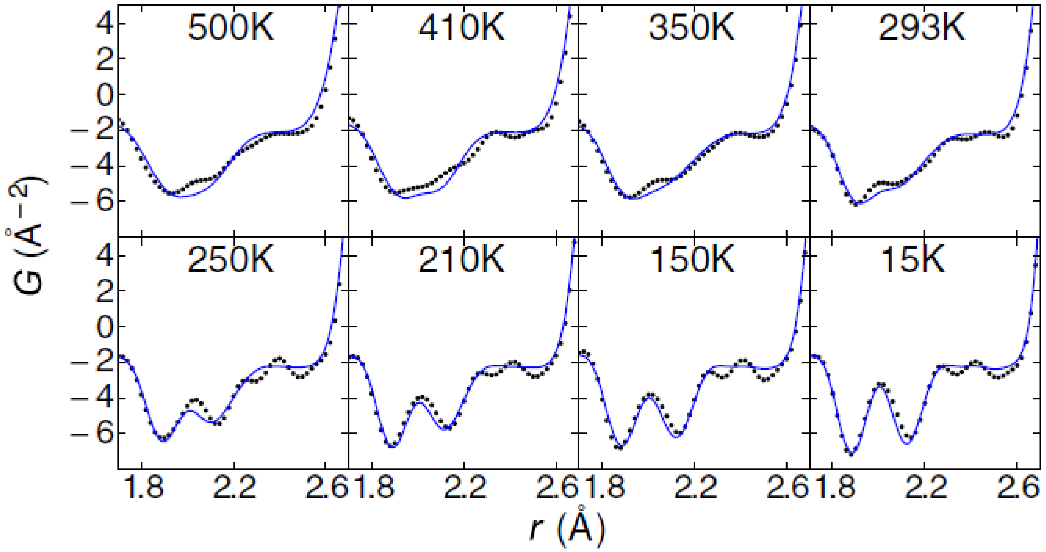


Usher et al., *J. Appl. Phys*. **120**, 184102 (2016).

- Neutron PDF is sensitive to Ti-O correlations
- At room temperature, $BaTiO_3$ locally has a split (*R3m* like) first Ti-O peak, displaying classic order-disorder behavior

Experimental $BaTiO_3$ PDFs

M. S. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac, and A. L. Goodwin, **Emergence of Long-Range Order in $BaTiO_3$ from Local Symmetry-Breaking Distortions**, *Phys. Rev. Lett*. **116**, 207602 (2016).

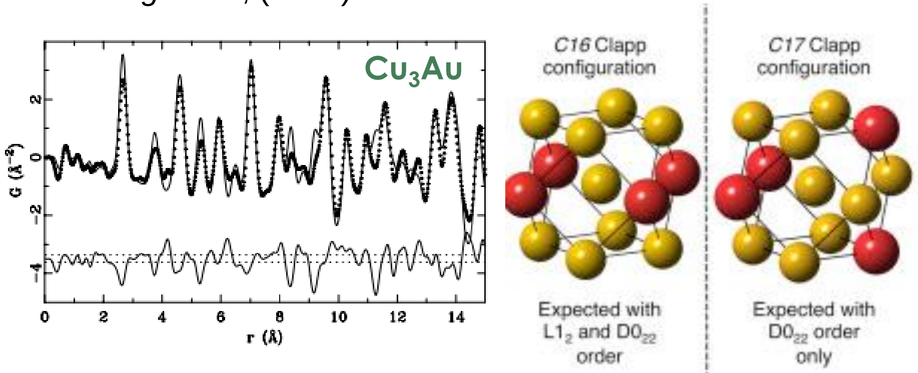


K. Page *et al.*, *Chem. Mater*. **22**, 4386–4391 (2010).
K. Page, *et al.*, *Phys. Rev. Lett*. **101**, 205502 (2008).

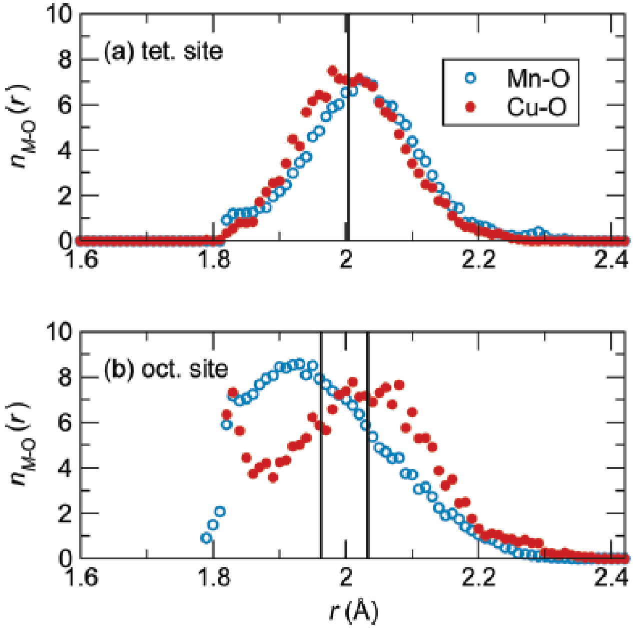
Chemical Short-Range order *via* PDF

- Substitution effects
- Chemical clustering
- Ion-specific local environments
- Vacancy ordering

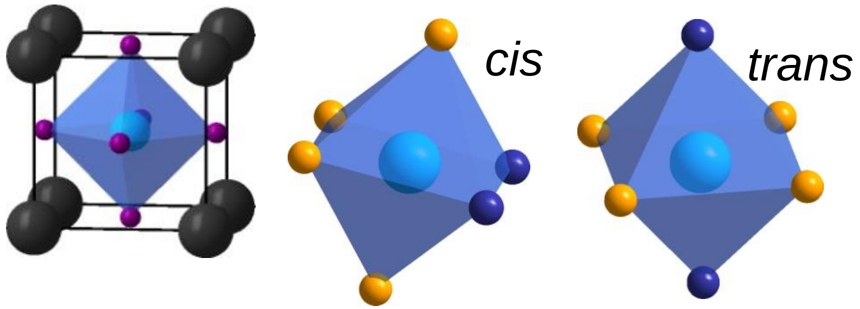
Th. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt, Chemical short range order obtained from the atomic pair distribution function, *Z. Kristallogr*. **217**, (2002) 47–50.



L.R. Owen, H.Y. Playford, H.J. Stone and M.G. Tucker, Analysis of short-range order in Cu_3Au using X-ray pair distribution functions. *Acta Materialia* (2017) 125, 15-26.



D. P. Shoemaker, J. Li, and R. Seshadri, Unraveling Atomic Positions in an Oxide Spinel with Two Jahn-Teller Ions: Local Structure Investigation of $CuMn_2O_4$, *J. Am. Chem. Soc.* **131,** 11450 (2009).



K. Page, *et al*., Local atomic ordering in $BaTaO_2N$ studied by neutron pair distribution function analysis and density functional theory, *Chem. Mater.* **19** (2007) 4037-4042.

Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

High operating voltage (~4.7 V versus Li^+/Li) and facile three-dimensional lithium ionic conductivity
Zhong *et al.*, 1997; Ohzuku *et al.*, 1999

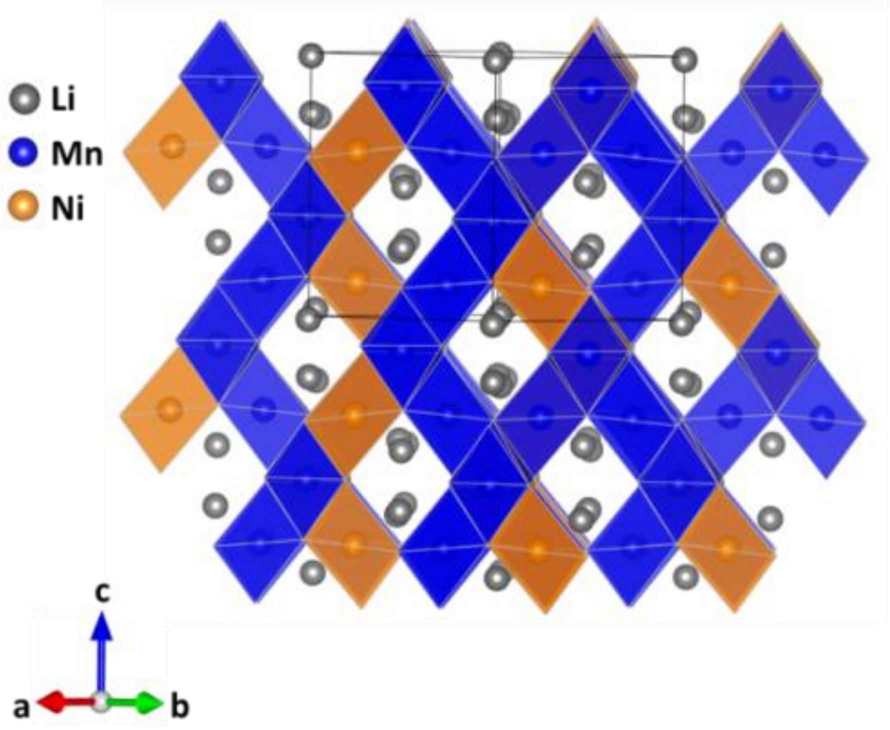
Two distinct polymorphs are known: Ni/Mn cation ordering strongly impacts electrochemical performance   Idemoto *et al*., 2003; Zhong *et al*., 1997

(1) Disordered phase (S.G. *Fd-3m*), where Ni/Mn are randomly distributed at the 16d site via high temperature solid state reaction

(2) Long-range cation ordered phase (S.G. $P4_332$ or $P4_132$) via extended post-annealing at 700 °C to 600 °C

Kunduraci & Amatucci, 2006; Kunduraci *et al*., 2006; Kim *et al*., 2004; Ma *et al*., 2010; Moorhead-Rosenberg *et al*., 2015

We studied the nature and length-scale of local cation ordering in this system and related it to electrochemical performance



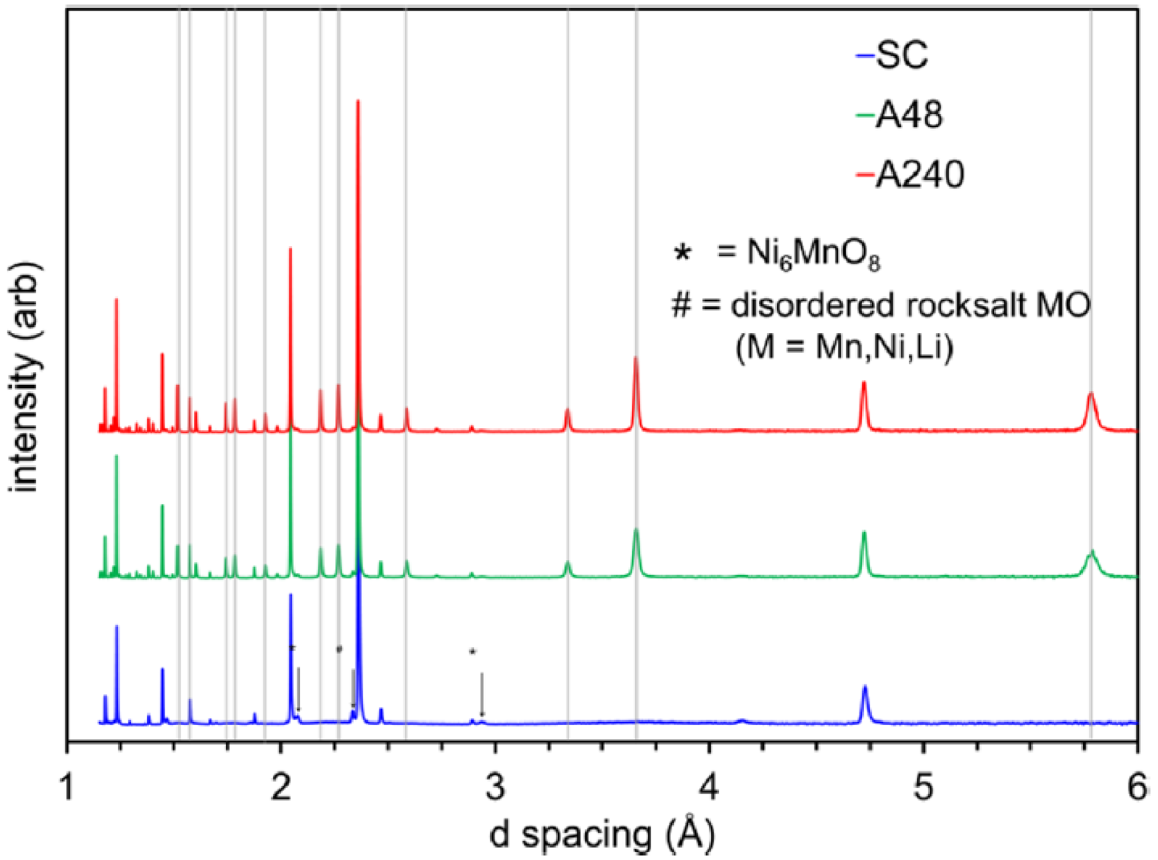
Example: High Voltage Spinel Cathode $^7LiNi_{0.5}Mn_{1.5}O_4$

Slow Cooled (SC): 8 hours at 900°C, 1.5°C/min cooling

Fast Cooled (FC): 8 hours at 900°C, 5°C/min cooling

Annealed (A48): 48 hours at 700°C

Annealed (A240): 240 hours at 700°C



Cation ordering examined at the POWGEN Beamline, SNS: large nuclear scattering length contrast between nickel (*b* = 10.3 fm) and manganese (*b* = -3.73 fm)

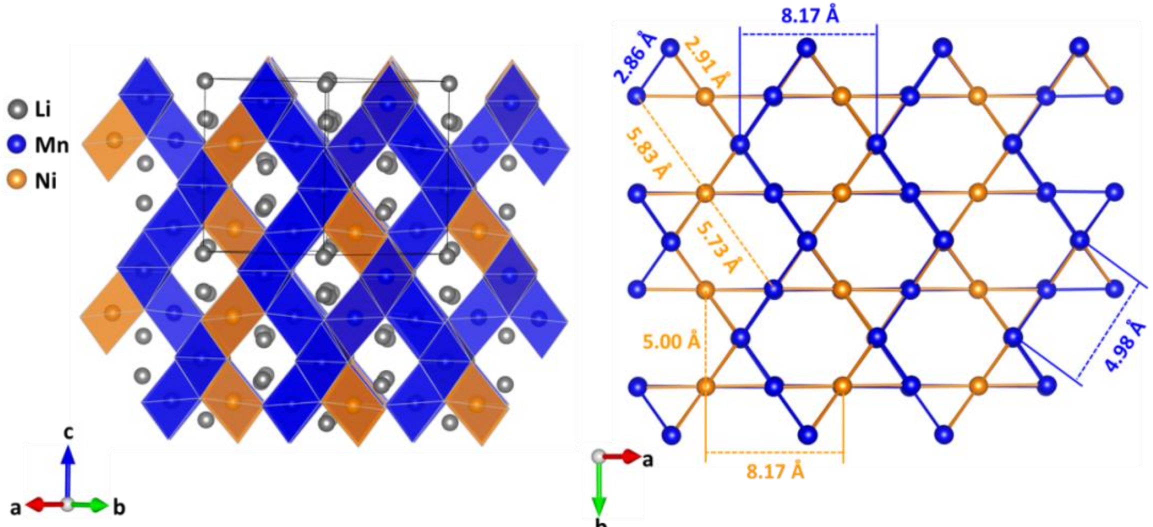
Z. Moorhead-Rosenberg, A. Huq, J. B. Goodenough, & A. Manthiram, *Chem. Mater.* (2015) **27**, 6934-6945.

Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

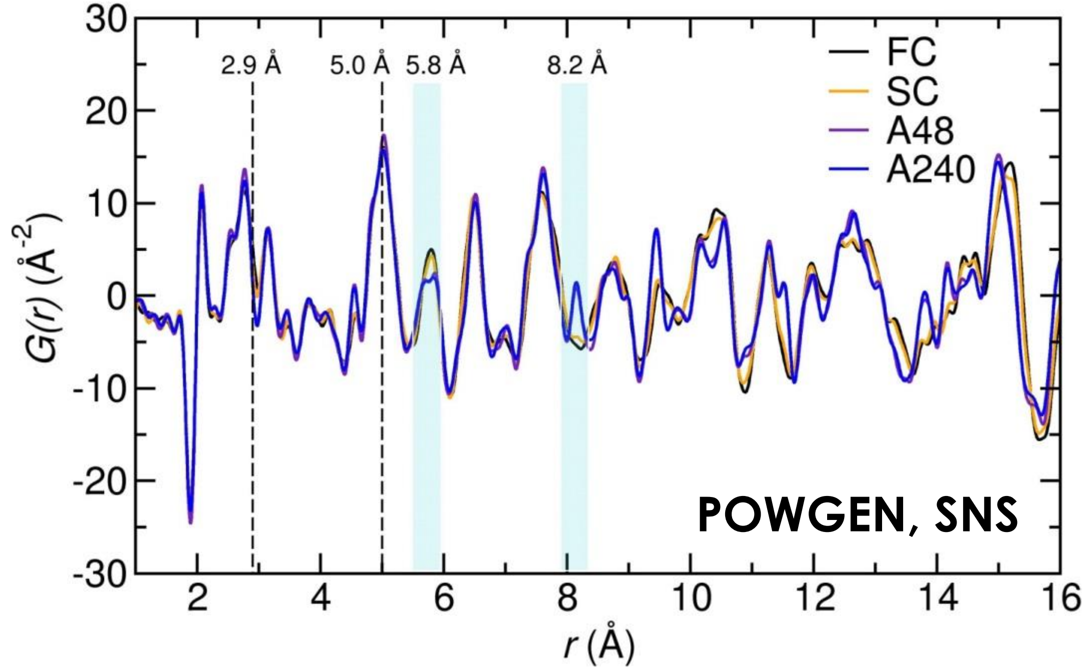
A lot can be observed by looking at the PDFs:

- Local atomic structures almost identical up to 5 Å (two nearest B-site neighbors)
- Sample structures diverge after that
- Annealed samples: two distinguishable sets of Ni/Mn pairs at third nearest Ni/Mn neighbor distance
- By fourth nearest Ni/Mn neighbor the samples are distinct

Liu J., Huq A., Moorhead-Rosenberg Z., Manthiram A., Page K., **Nanoscale Ni/Mn Ordering in the High Voltage Spinel Cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials,* 28, (2016) 6817–6821.



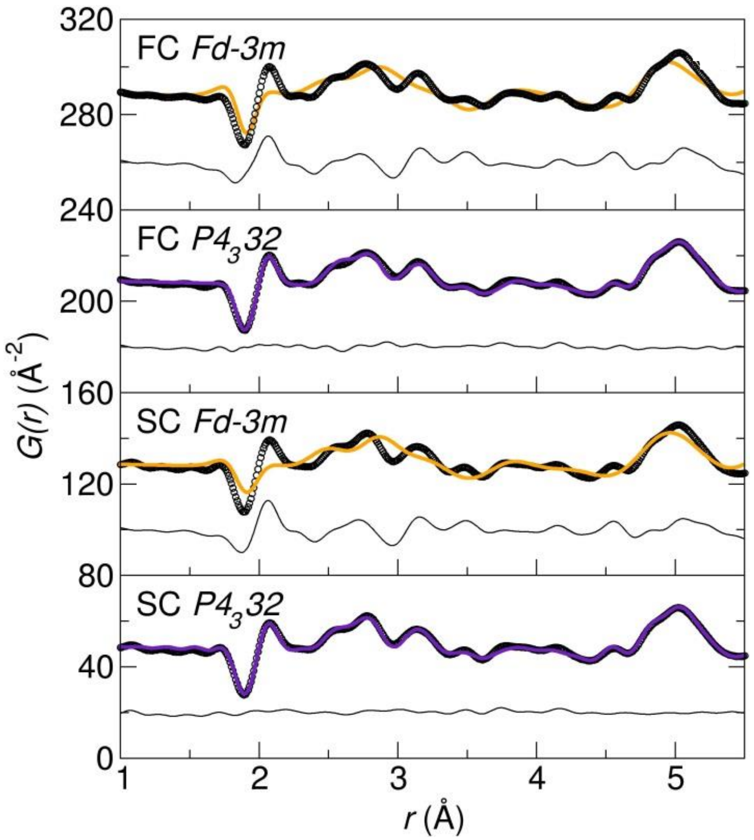
ordered $LiNi_{0.5}Mn_{1.5}O_4$ (S.G. *$P4_332$*)



Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

Additional information from modeling the local structure

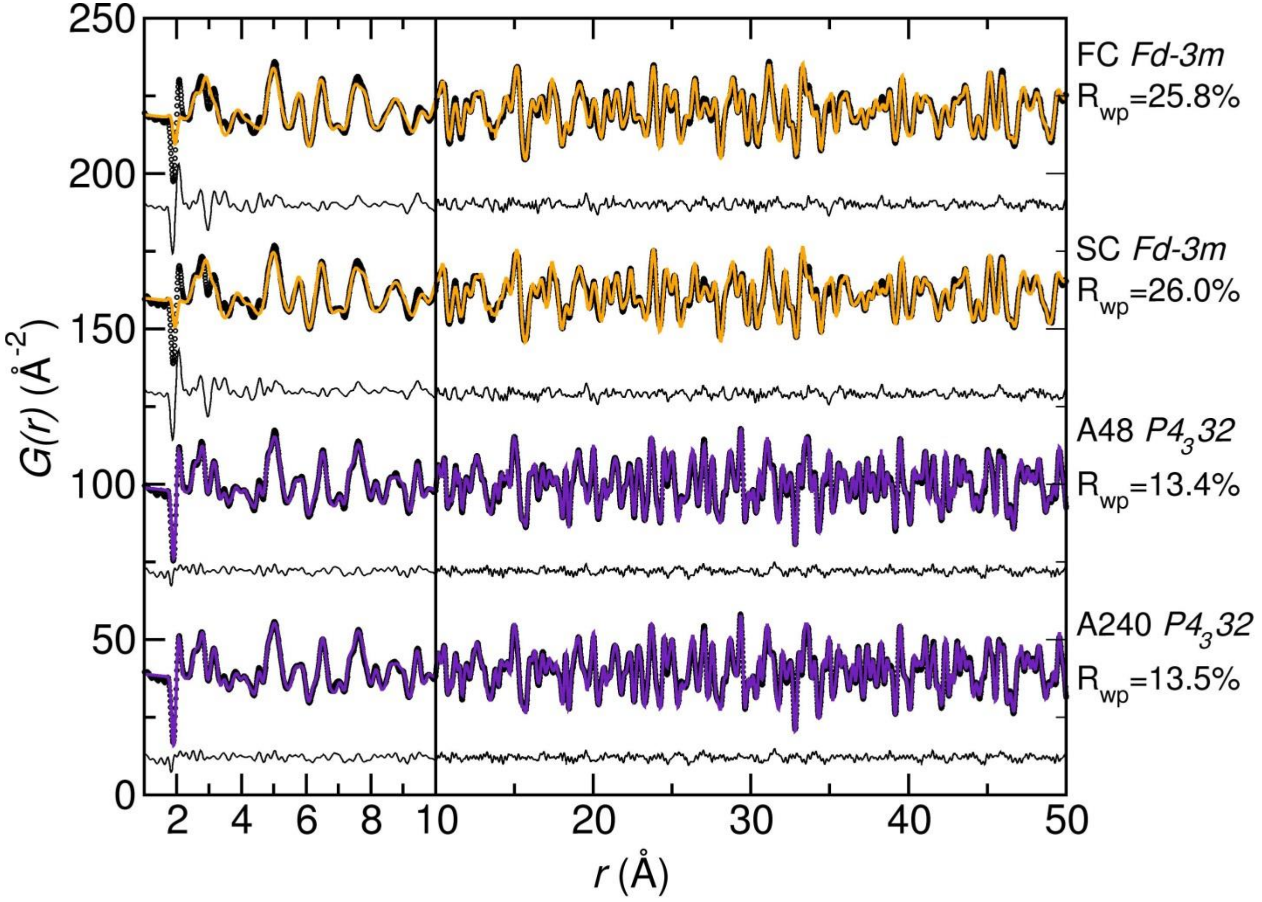
- Least squares refinements of the ordered structure model (*P4₃32*) were carried out in a manner that *4b* site (Ni site) and *12d* site (Mn site) occupancies are allowed to refine simultaneously but with site multiplicity constraints
- Over 1 to 5 Å range the ordered models (*P4₃32*) with Mn/Ni site mixing provide much better fits for local PDF profiles
- **Ni/Mn are locally well-ordered in the long-range "disordered" samples**
- **But up to what length scale?**

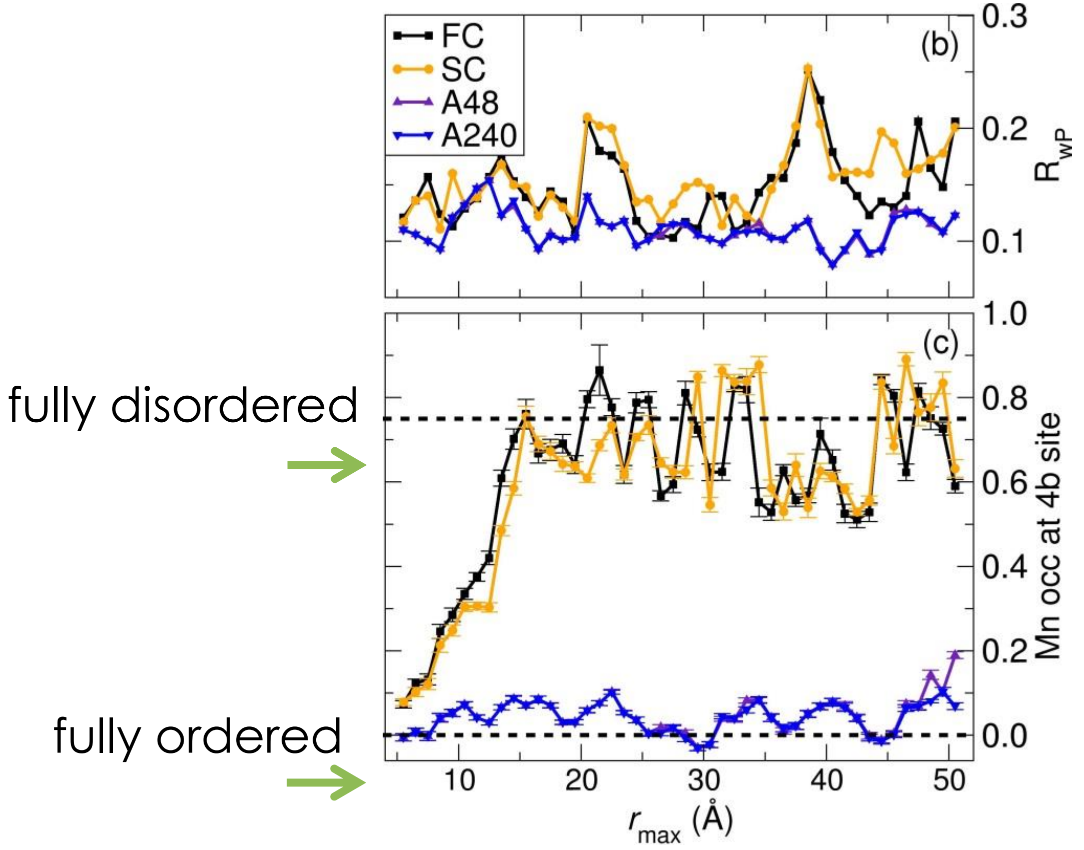


J. Liu, A. Huq, Z. Moorhead-Rosenberg, A. Manthiram, and K. Page, **Nanoscale Ni/Mn ordering in the high voltage spinel cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials*, 28, 19, 6817–6821, 2016.

Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

15 Å correlation length scale for SRO

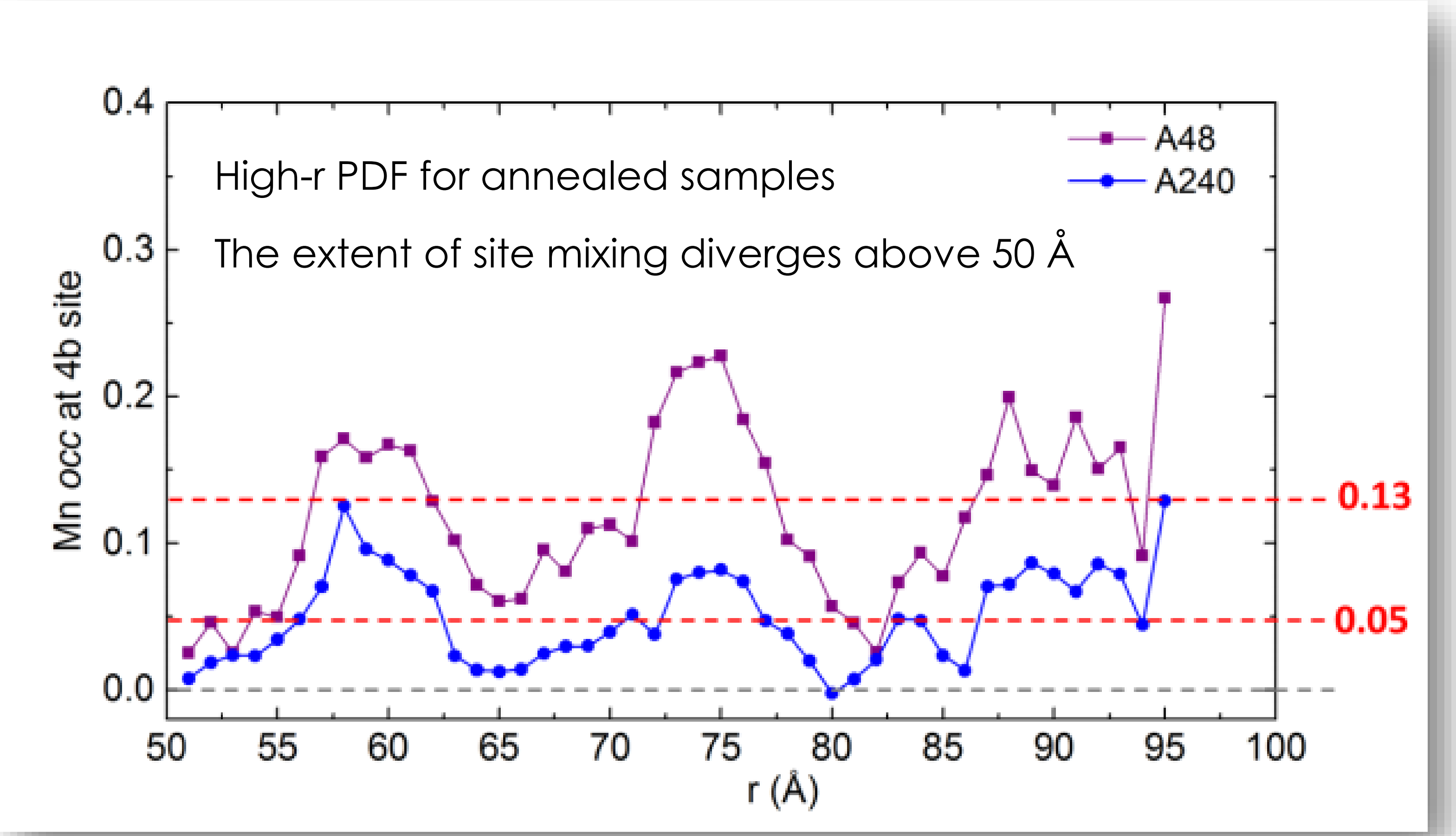




- 5% site mixing in the A48 and A240 patterns throughout the entire range
- FC and SC samples are nearly fully disordered at pair distances beyond 15.5 Å

Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

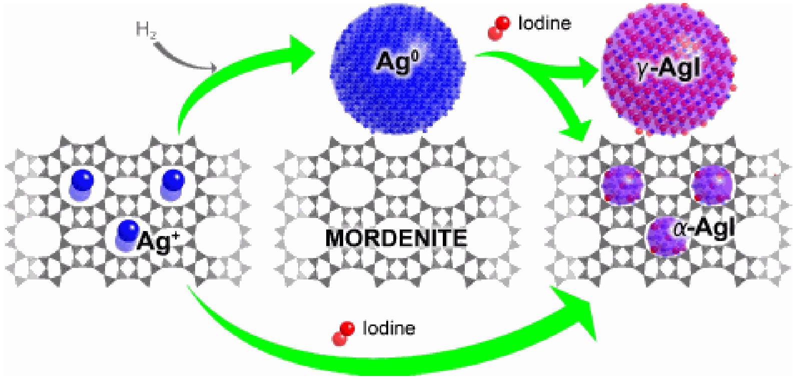
Fit the PDFs within a 4.5 Å "box" in 1 Å steps (a "box-car" refinement)



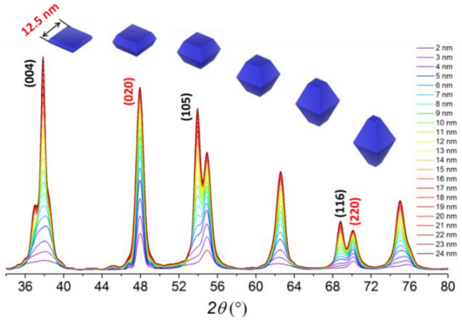
Spinel cathode materials are distinguished by their unique correlation length scales for chemical short range ordering

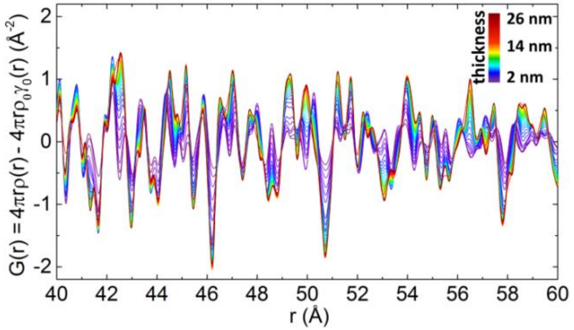
Nanomaterial structure *via* PDF

- Finite size/shape effects
- Surface/Interface structure
- Nanostructure polymorphs
- Growth and transformation

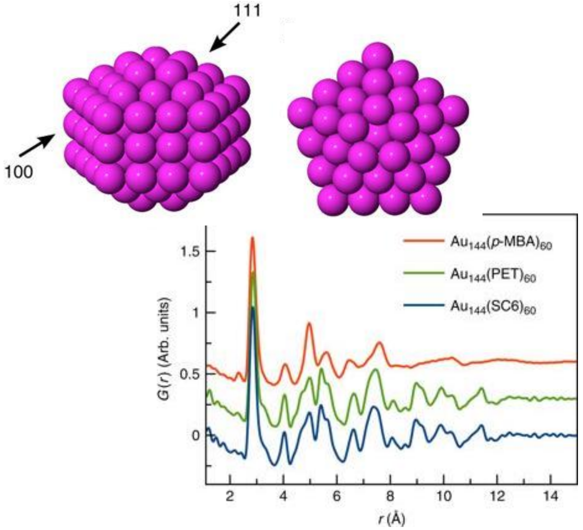


K. W. Chapman, P. J. Chupas, and T. M. Nenoff, **Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation**, *J. Am. Chem. Soc.* 132, 8897 (2010).





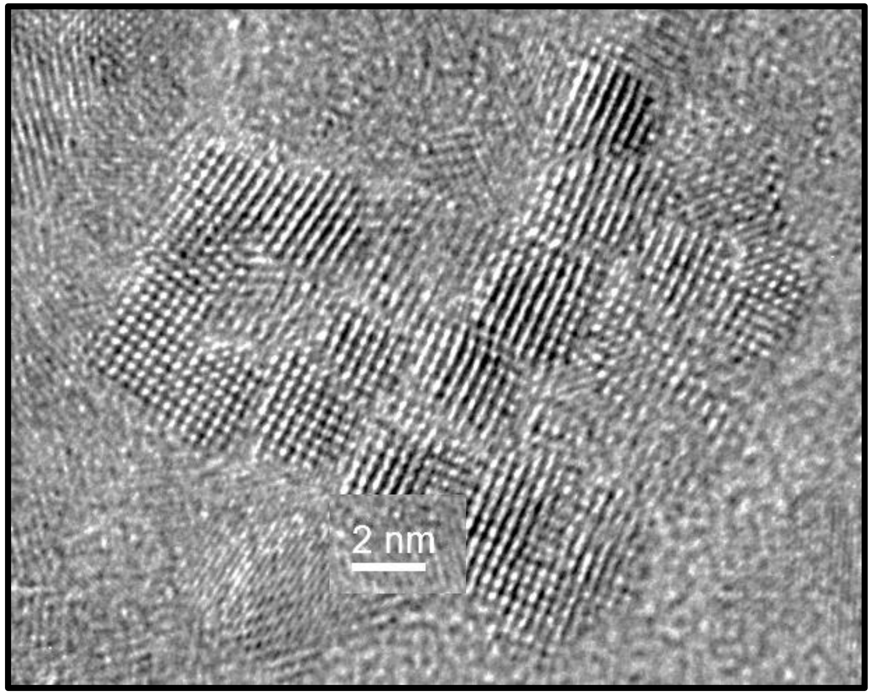
J. Liu, D. Olds, R. Peng, L. Yu, G. S. Foo, S. Qian, J. Keum, B. S. Guiton, Z. Wu, and K. Page, **Quantitative analysis of the morphology of {101} and {001} faceted anatase TiO_2 nanocrystals**, *Chem. Mater.* 29, 5591–5604 (2017).

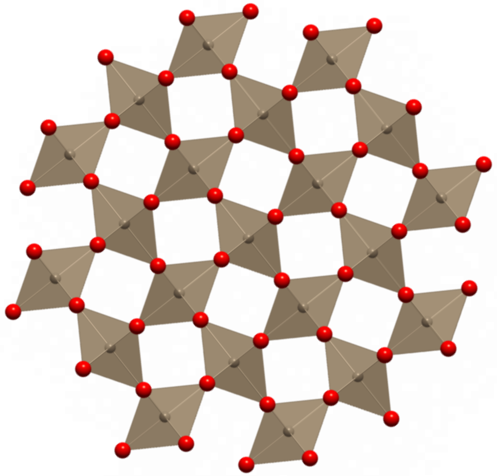


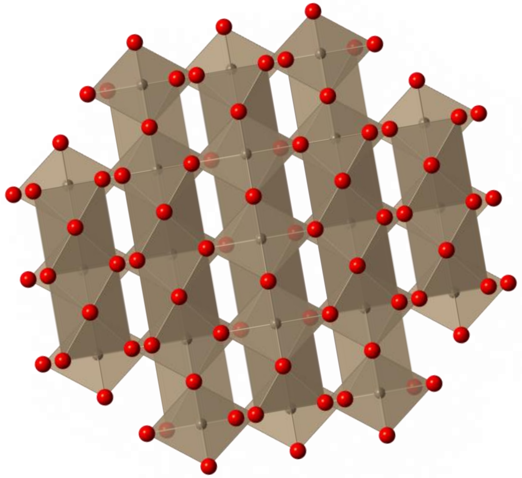
K. M. O. Jensen, P. Juhas, M. A. Tofanelli, C. L Heinecke, G. Vaughan, and C. J. Ackerson, **Polymorphism in magic-sized $Au_{144}(SR)_{60}$ clusters**, *Nature Communications* 7, 11859 (2016).

Example: SnO_2 Nanocrystals

~2 nm SnO_2 (cassiterite) nanocrystals capped with H_2O/OH or D_2O/OD groups







H.-W. Wang, D. J. Wesolowski, T. Proffen, L. Vlcek, W. Wang, L. F. Allard, A. I. Kolesnikov, M. Feygenson, L. M. Anovitz, and R. L. Paul, **Structure and stability of SnO_2 nanocrystals and surface-bound water species**, *J. Am. Chem. Soc.*, 135, 6885-6895, 2013.

TGA suggests 2 steps dehydration.

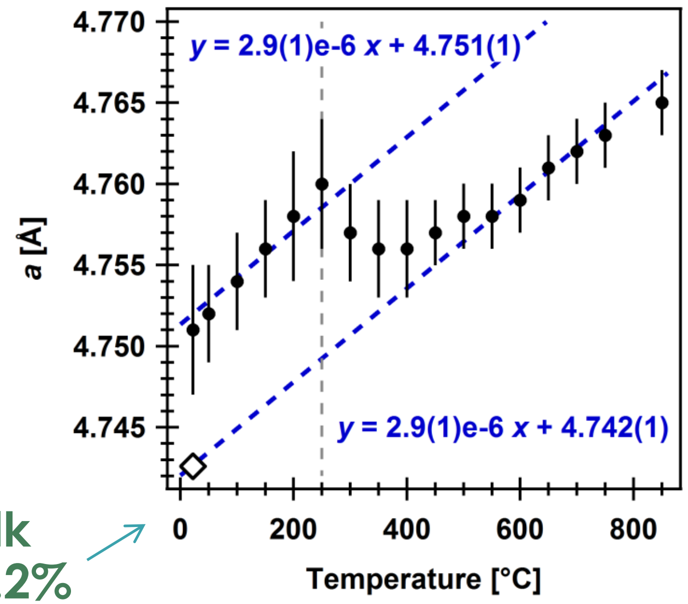
How many layers of water are at the surface?

How is water bonded to surfaces?

What are the dynamics of dehydration?

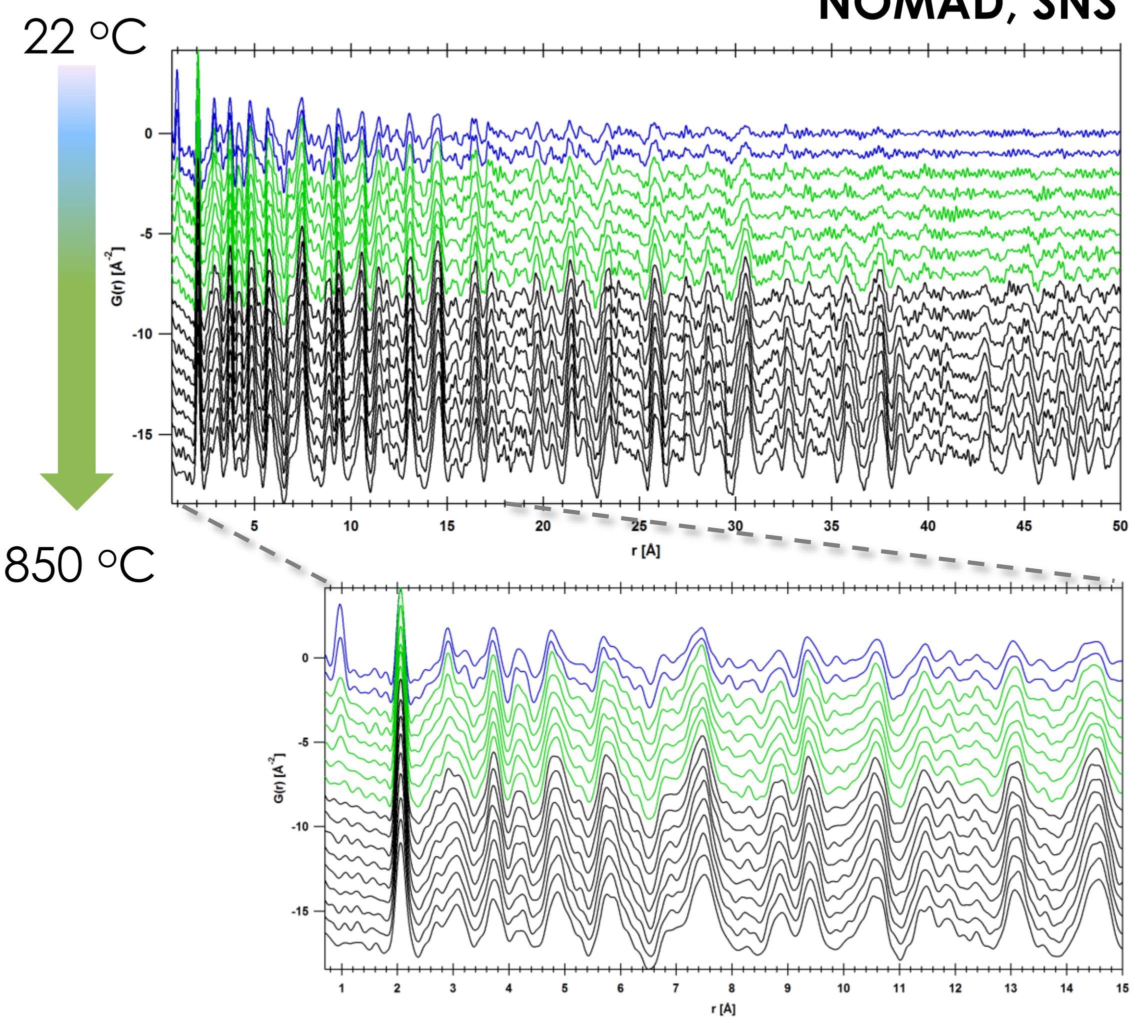
Example: SnO_2 Nanocrystals

- 22 to 50 °C: $L_1 + L_2 + L_3$,
- 50 to 350 °C: $L_1 + L_2$
- 400 to 850 °C: SnO_2 grain growth



Bulk ~0.2% smaller

NOMAD, SNS

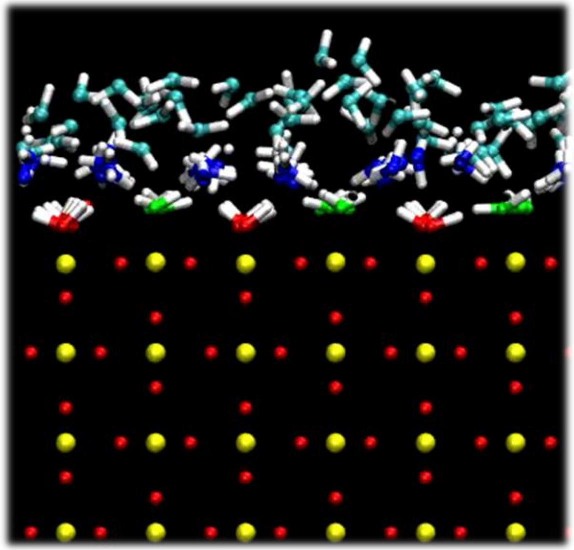


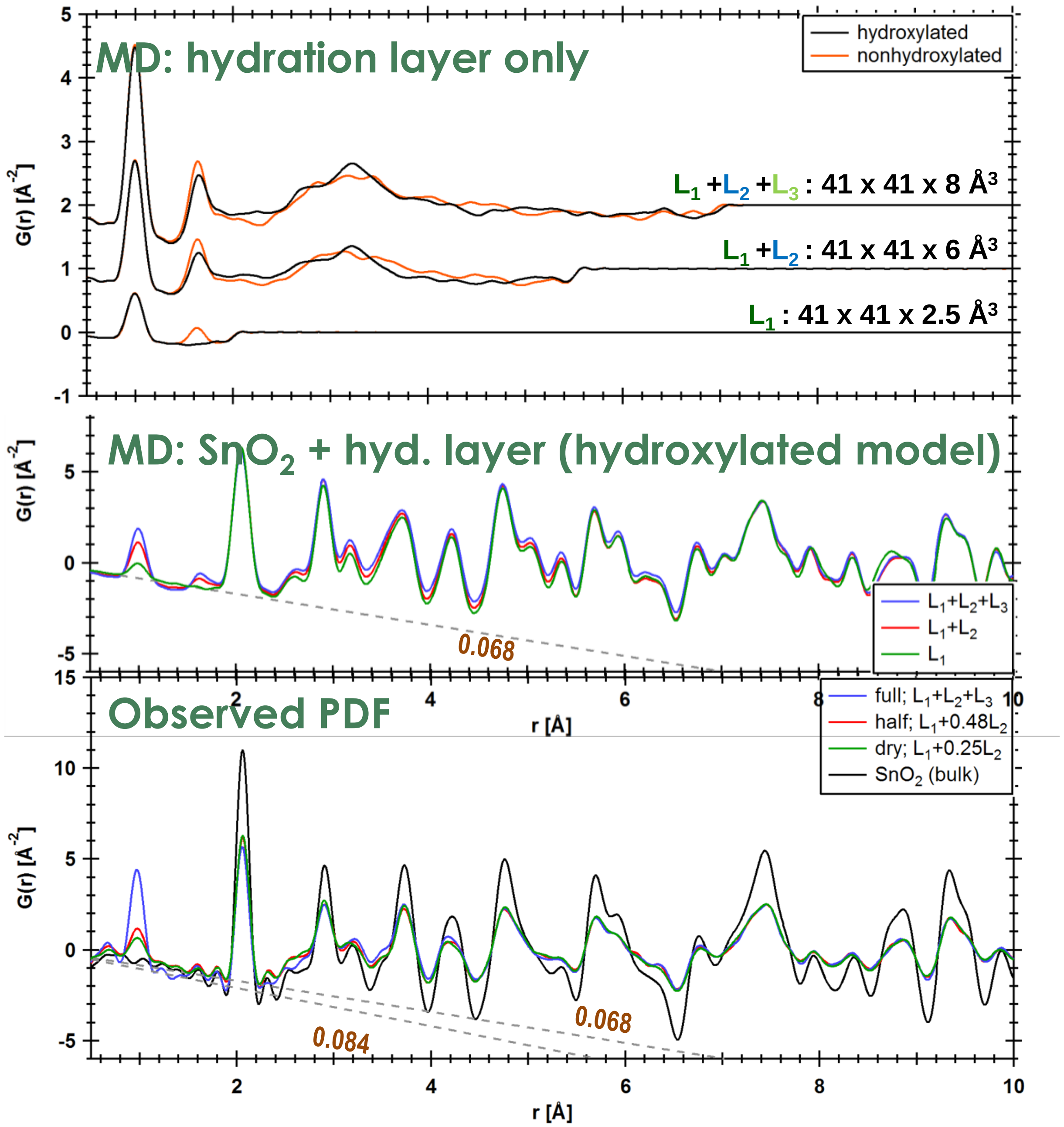
In situ dehydration answers these questions and indicates that water plays a key role in stabilizing the nanocrystals.

MD and PDF

Data is compared to Molecular Dynamics Simulation PDFs for nonhydroxylated and hydroxylated models:

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





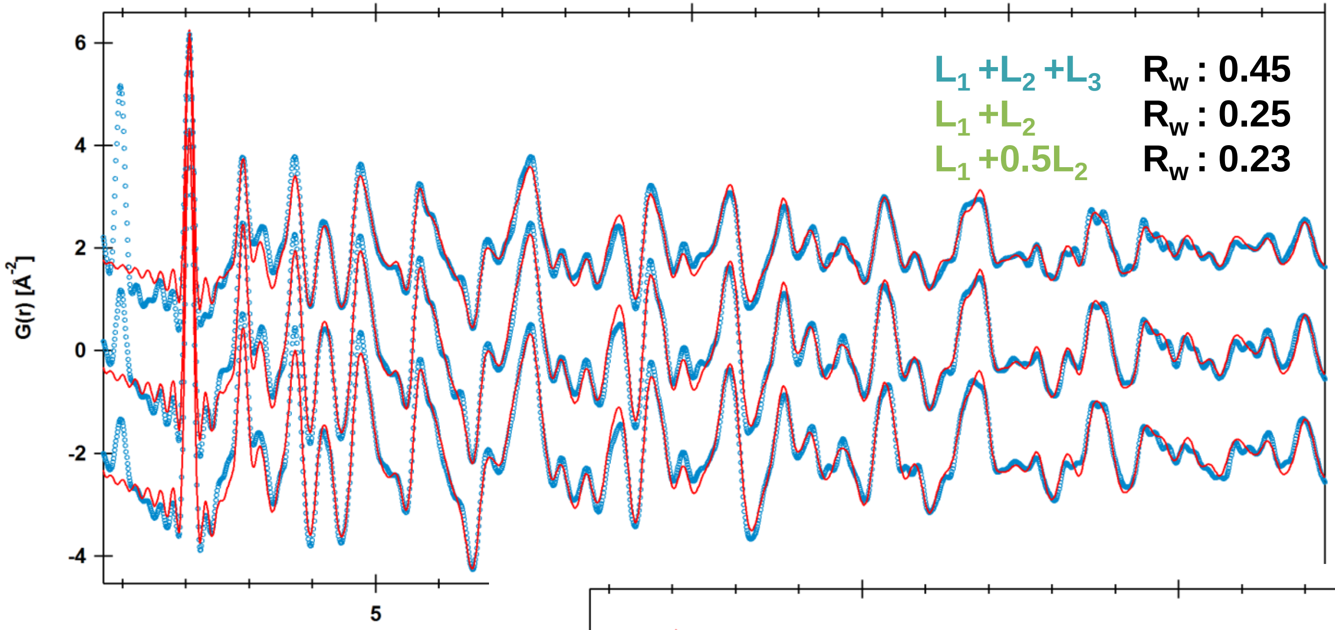
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

size = ~47 Å

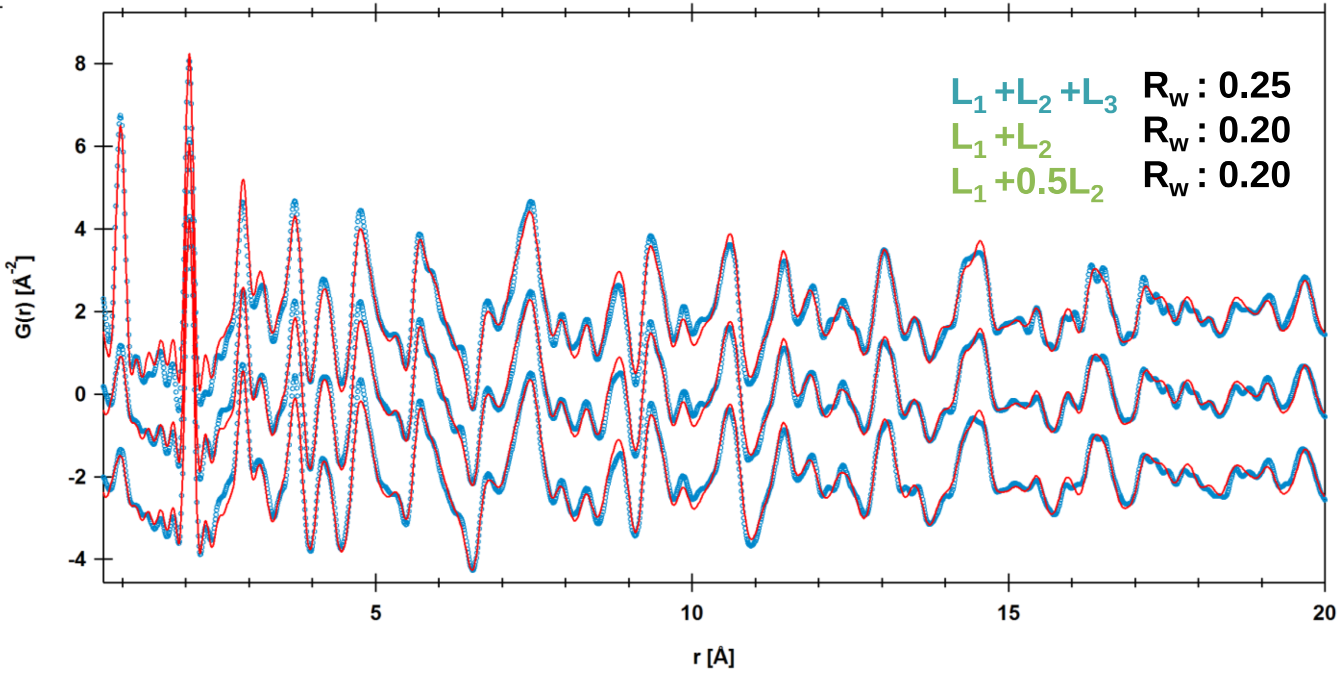


Two phase model:

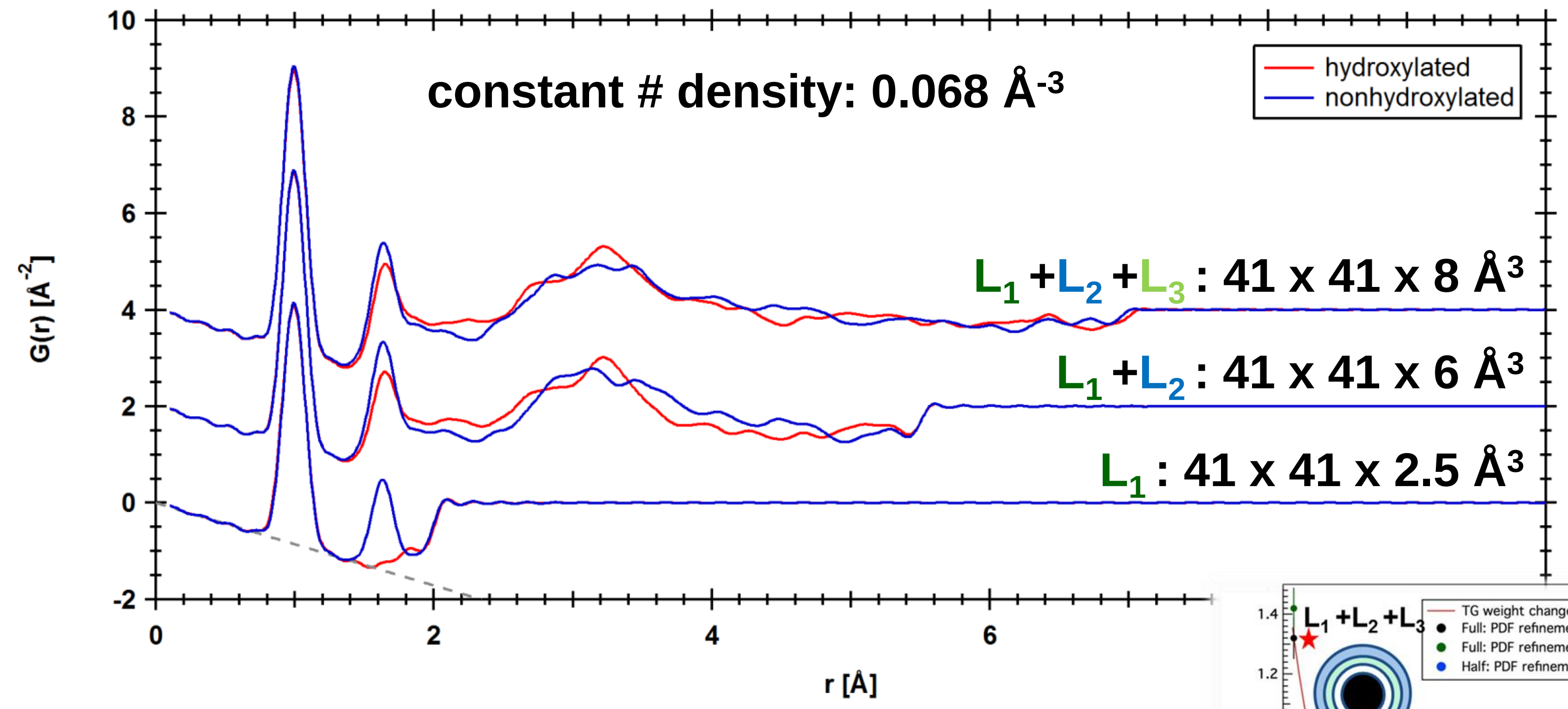
SnO_2 bulk +

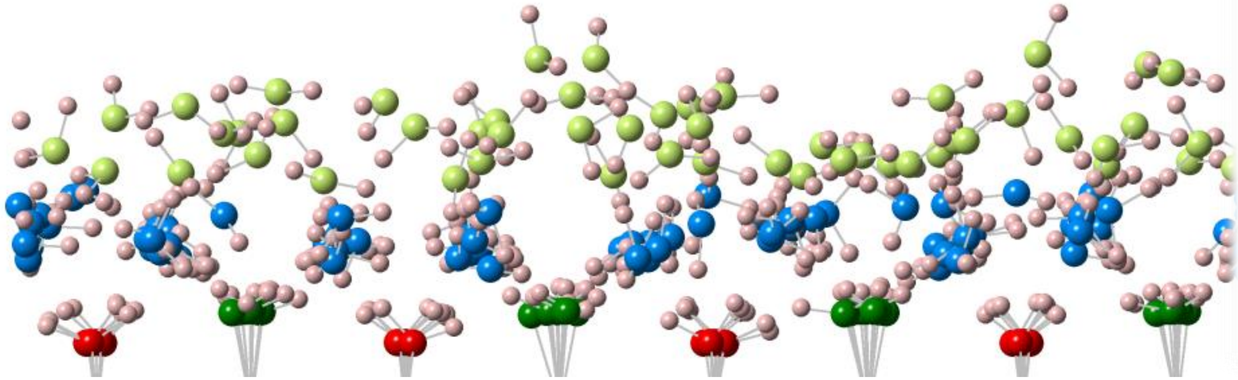
layered MD

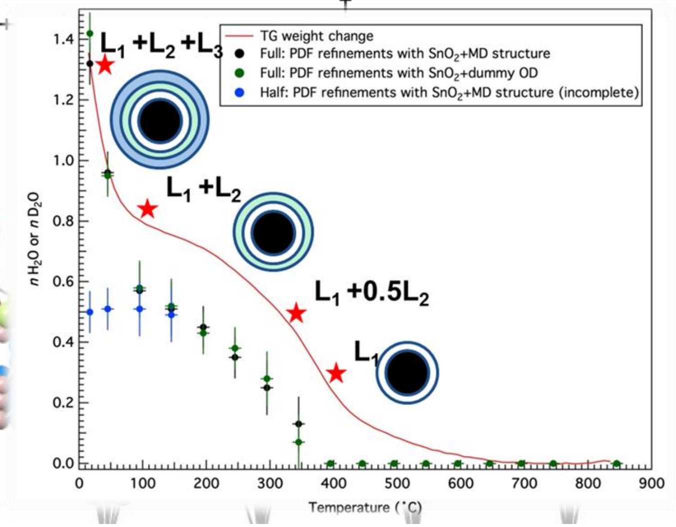
water structure



Example: SnO_2 Nanocrystals



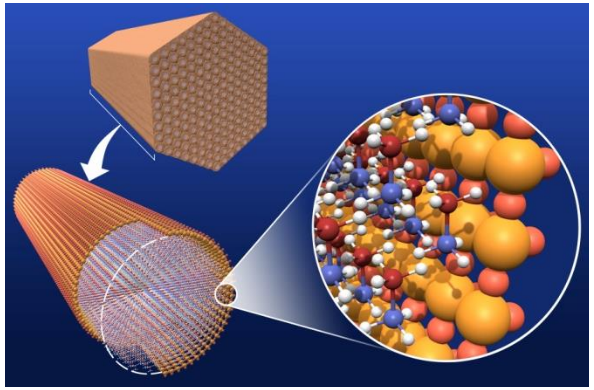




H.-W. Wang, D. J. Wesolowski, T. Proffen, L. Vlcek, W. Wang, L. F. Allard, A. I. Kolesnikov, M. Feygenson, L. M. Anovitz, and R. L. Paul, **Structure and stability of SnO_2 nanocrystals and surface-bound water species**, *J. Am. Chem. Soc.*, 135, 6885-6895, 2013.

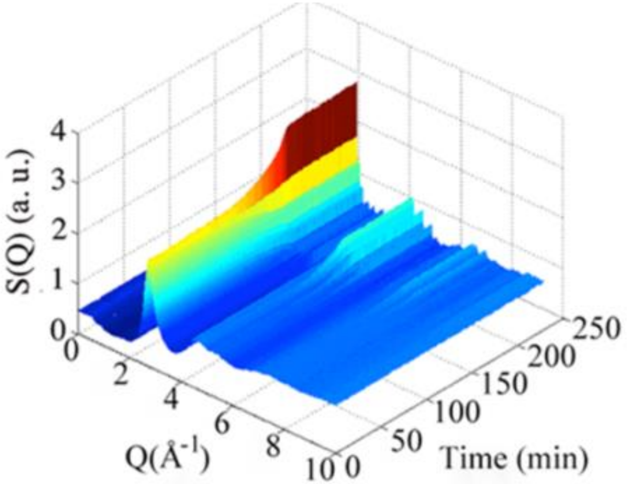
Amorphous structures *via* PDF

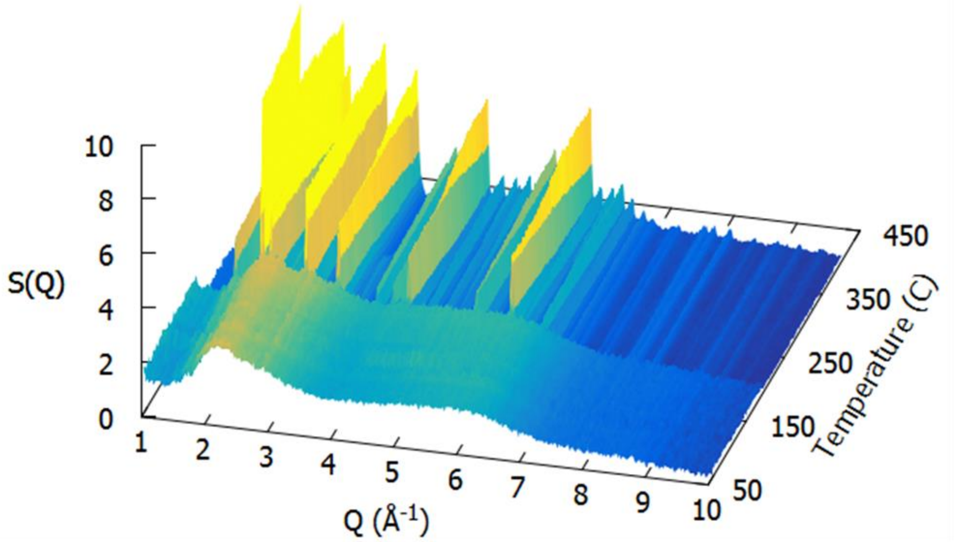
- Glasses
- Liquids
- Concretes
- Adsorbed/absorbed gases
- *etc.*



H. Kim, T. Proffen, P. J. Chupas, A. Karkamkar, N. J. Hess, and T. Autrey, **Determination of structure and phase transition of light element nanocomposites in mesoporous silica: case study of NH_3BH_3 in MCM-41**, *J. Am. Chem. Soc. 131*, 13749-13755 (2009).

S. Lan, X.. Wei, J. Zhou, Z. Lu, X. Wu, M. Feygenson, J. Neuefeind, X. Wang, **In situ study of crystallization kinetics in ternary bulk metallic glass alloys with different glass forming abilities**, *Applied Physics Letters*, 105, 201906 (2014).

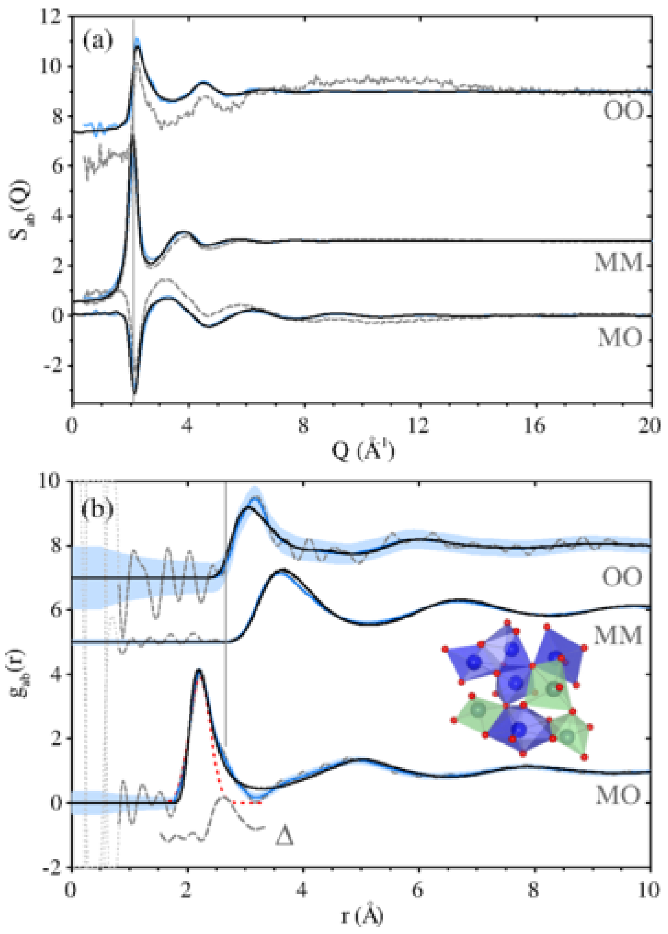




H.-W. Wang; L. L. Daemen, M. C. Cheshire, M. K. Kidder, A. G. Stack, L. F. Allard, J. Neuefeind, D. Olds, J. Liu, and K. Page, **Synthesis and structure of synthetically pure and deuterated amorphous (basic) calcium carbonates**, *Chem. Commun*., 53, 2942-2945 (2017).

Example: Molten Rare Earth Oxides

Understanding of oxide liquids is essential in nuclear meltdown scenarios, evolution of planetary bodies, glass formation and crystal nucleation.



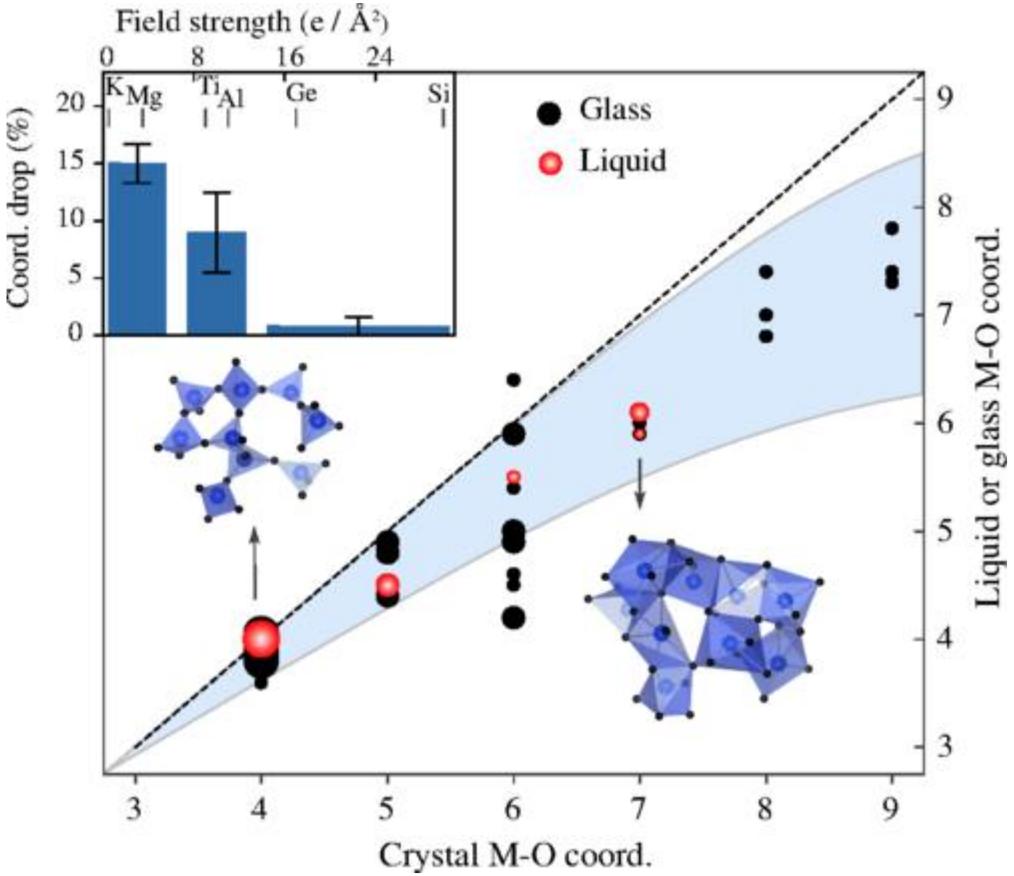
NOMAD, SNS / 11-ID-C, APS

- Partial pair distribution functions for molten M_2O_3 (M= Y or Ho) at 2870 K
- Aerodynamic levitation and laser heating in conjunction with neutron and high energy X-ray diffraction
- Complete set of partial pair distribution functions obtained for the first time for a high temperature oxide melt

Skinner L.B., Benmore C.J., Weber J.K.R., Du J., Neuefeind J., Tumber S.K., and Parise, J.B., **Low Cation Coordination in Oxide Melts**, *Physical Review Letters*, 112, 157801, (2014).

University of North Texas Argonne National Laboratory MDI Instruments for Innovation® Stony Brook University

Example: Molten Rare Earth Oxides



- Metal oxygen first shell coordination number is significantly lower than in the corresponding crystal
- Trend persists in other oxide melts
- Reduction in coordination number is correlated with the ionic field strength of the constituting metal ion

A Few Experimental Considerations

- Measurements and corrections
- Resolution and range effects
- Instruments

Total Scattering Structure Function

Structure function, determined from the scattering intensity/differential cross section:

coherent scattering intensity (corrected)

scattering length (neutrons) or atomic form factor (x-rays)

$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{\left|\sum c_i b_i\right|^2} + 1 \qquad Q = \frac{4\pi \sin\theta}{\lambda}$$

Corrected for: Container & background scattering, self-absorption, *etc.*

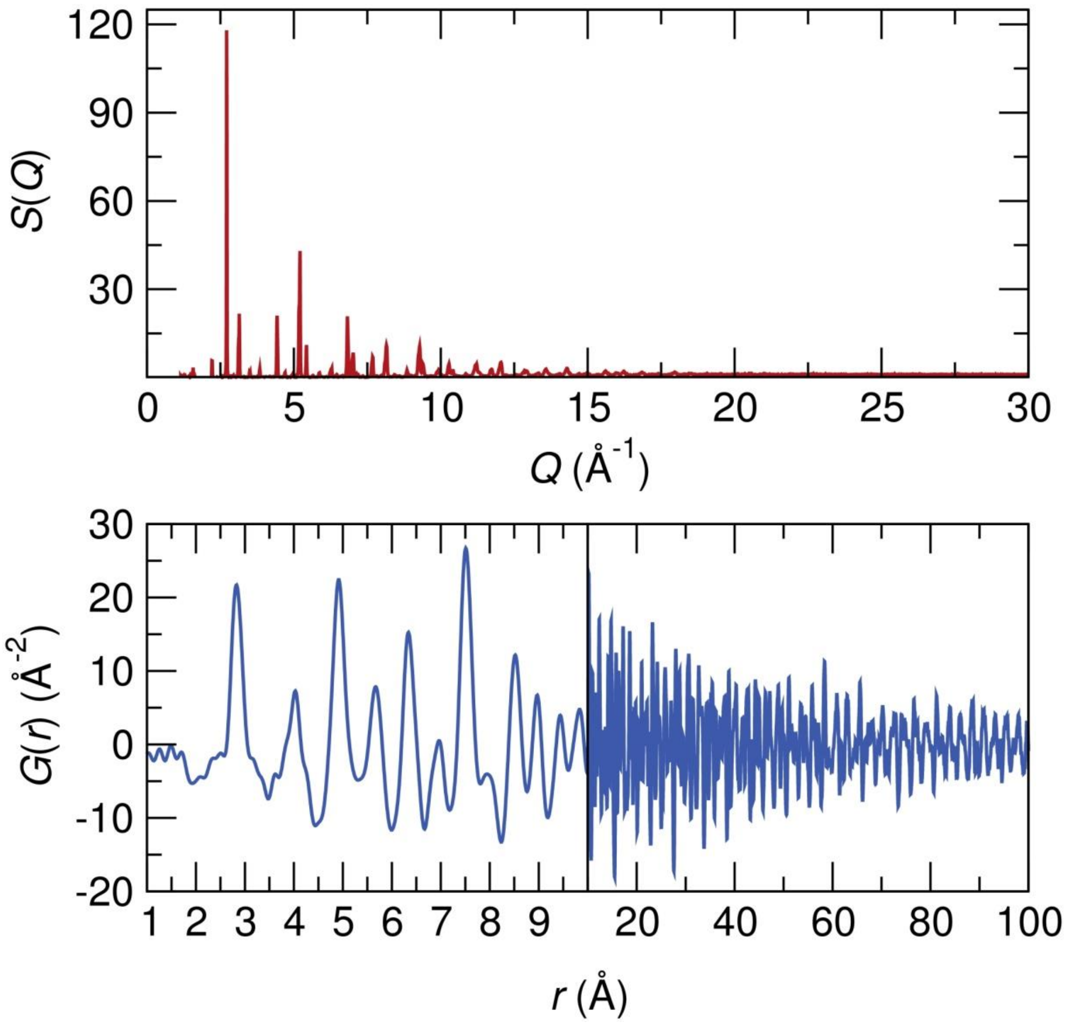
Normalized by: Incident flux, number of atoms, square of the scattering length/form factor

For unambiguous derivation of this derivation and relationship to other forms:

C. Farrow and S. J. L. Billinge, *Acta Cryst.* (2009) A65, 232–239.
D. A. Keen, *J. Appl. Cryst*. 34 (2001) 172-177.

The Experimental PDF

The Sine Fourier transform of the total (Bragg and diffuse) scattering



The total scattering structure factor: $S(Q)$

$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{\left|\sum c_i b_i\right|^2} + 1$$

Sine Fourier transform

The Pair Distribution Function (PDF): $G(r)$

$$G(r) = \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} Q[S(Q)-1]\sin(Qr)\,dQ$$

Obtaining High Quality PDFs

(1) High maximum momentum transfer (Q_{max})

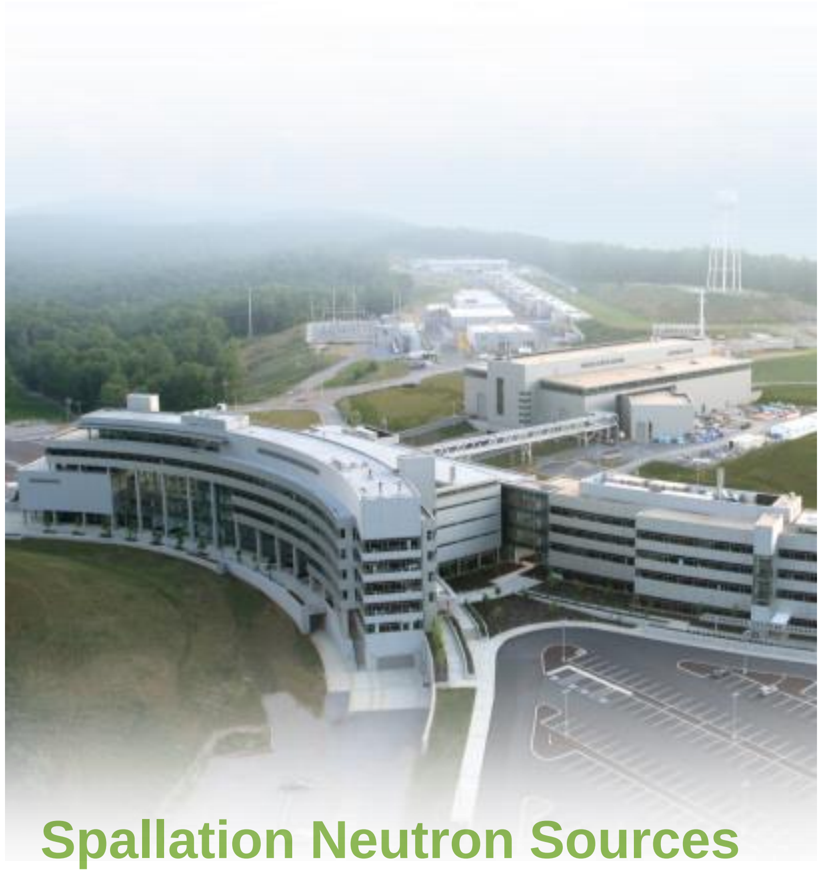
(2) Good Q-resolution, dQ

(3) Good counting statistics

(4) Low (and stable) instrument background

An ideal measurement would have no contribution from the instrument resolution

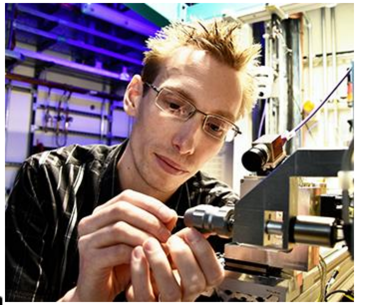
For PDF: a wide Q range and high flux is balanced with resolution



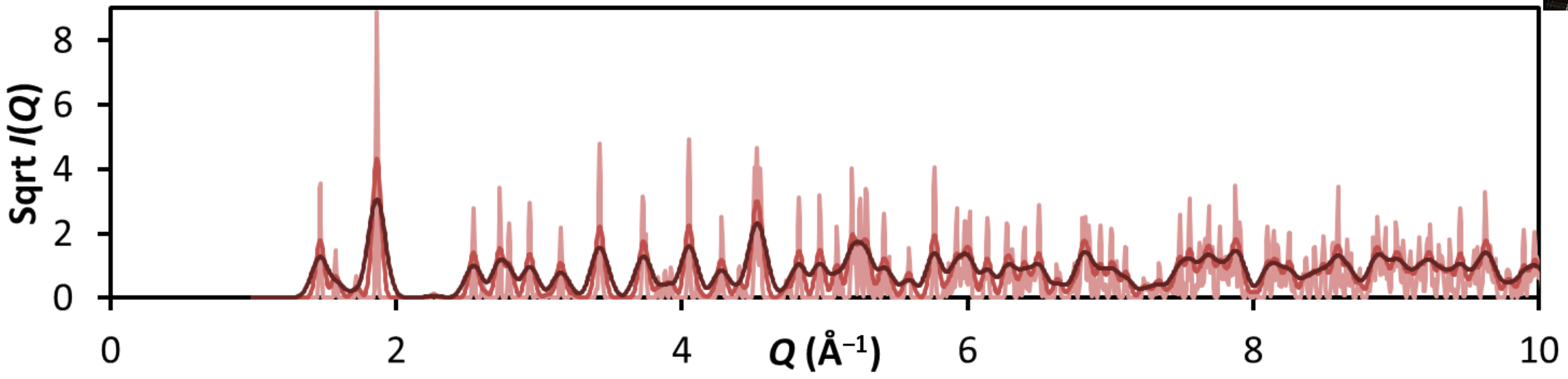
Synchrotron sources **(high energy X-rays)** **or** **Spallation Neutron Sources** **(reactor neutron energies are too low)**

Resolution Effect

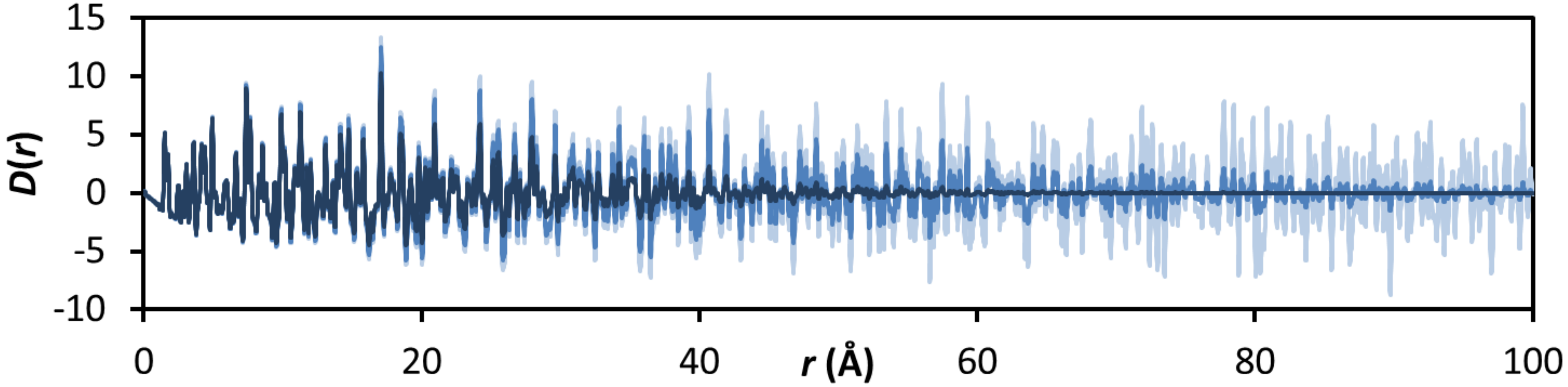
Courtesy of Phil Chater, Diamond Light Source



Reciprocal space: Peak width, *dQ*



Real space: Damping with *r*



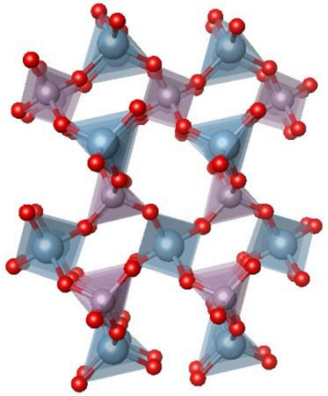
Q_{max} Effect

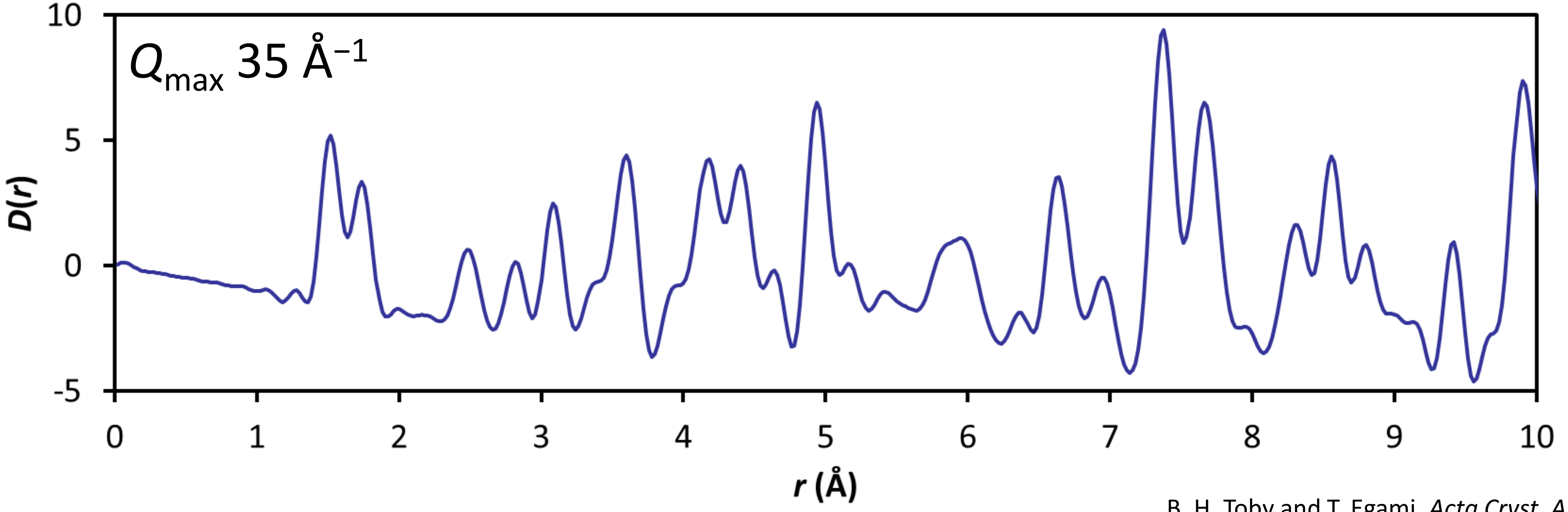
Courtesy of Phil Chater, Diamond Light Source

Δr resolution of a PDF is dominated by Q_{max}

- $Q = 2\pi/d = 4\pi\sin\theta/\lambda$
- $\Delta r \approx 2\pi/Q_{max}$

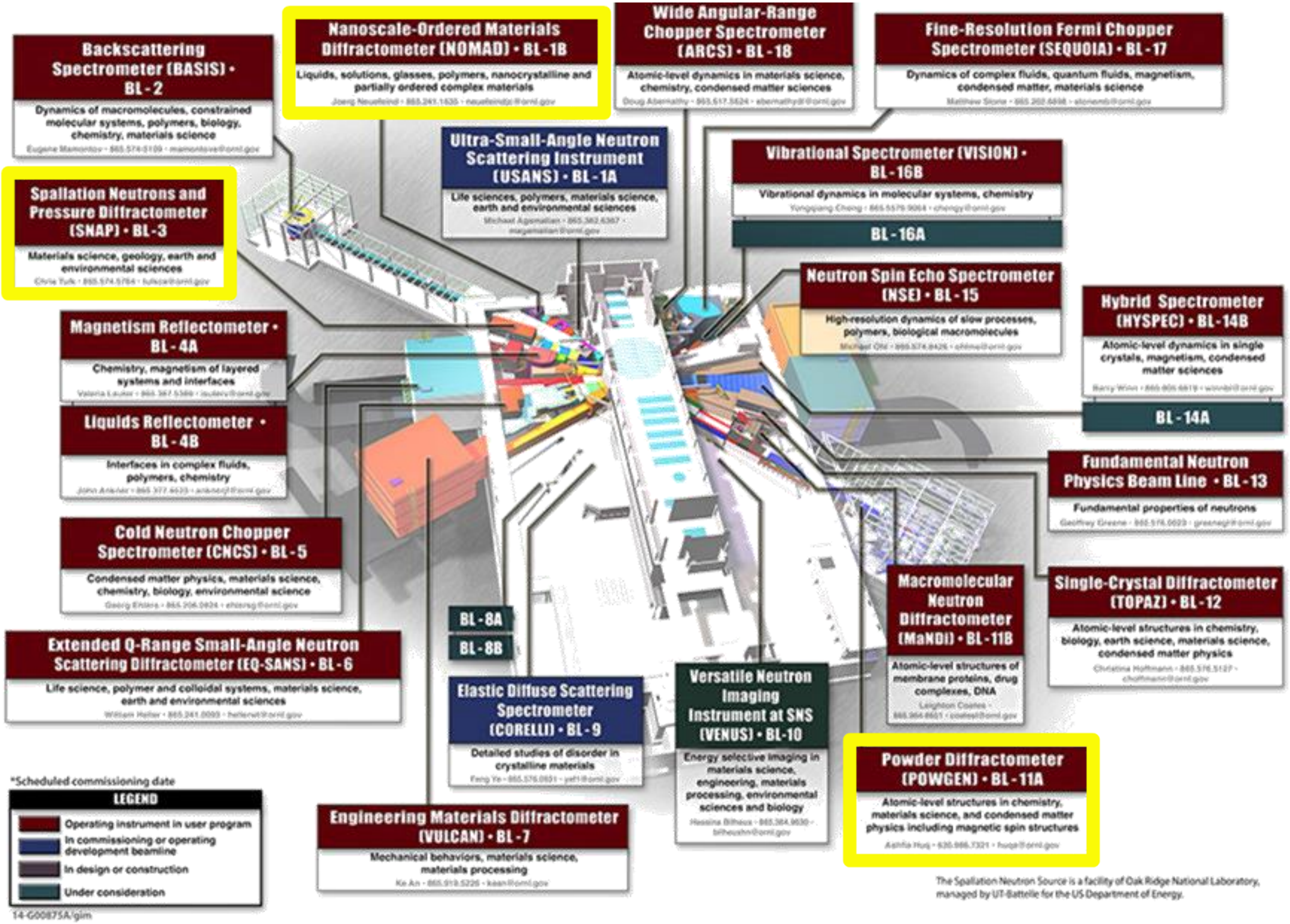
$AlPO_4$





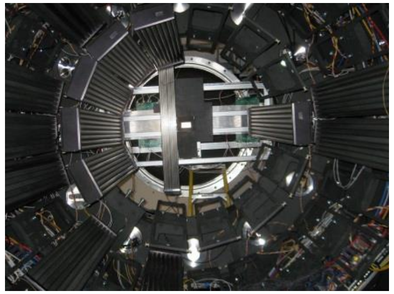
B. H. Toby and T. Egami, *Acta Cryst. A*, **48** 336 (1992).

Instruments at SNS for PDF studies



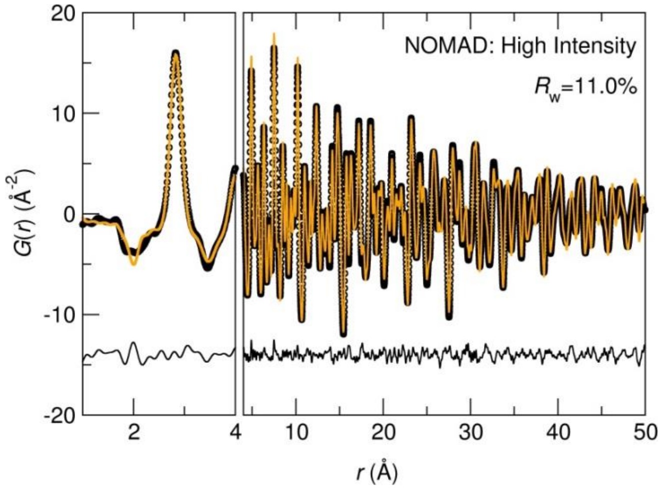
TOF Diffraction and Total Scattering at SNS

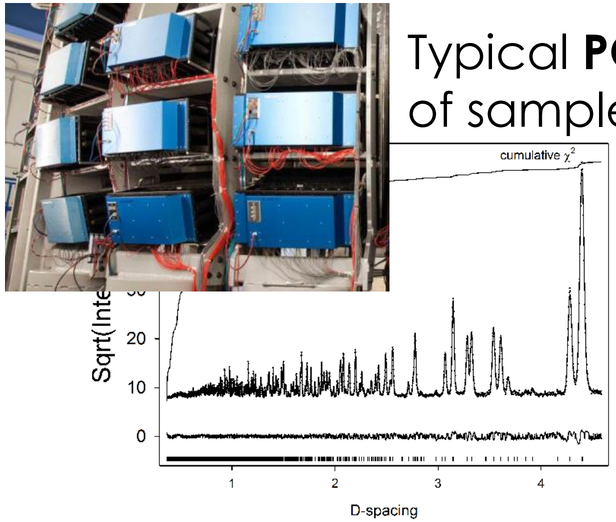
Pair Distribution Function (PDF) methods follow local atomic bonding configurations, intermediate structure, and correlation length scale- *regardless of a material's long-range structure*



Typical **NOMAD** data can be collected for **30 - 100 mg** of sample in a 3 mm quartz capillary in ~**1 hour**

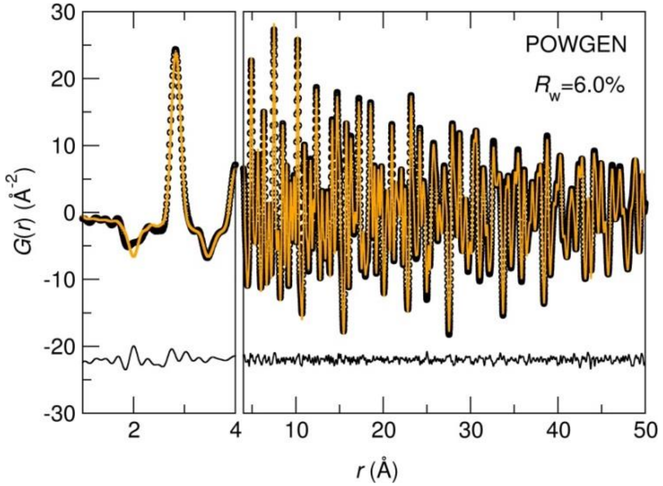
high intensity *diffraction and PDF for small samples and in situ studies on amorphous, nanostructured, and crystalline materials*





Typical **POWGEN** data can be collected for ~**3** - **10 g** of sample in a 6 mm vanadium canister in ~**3 hours**

high resolution *diffraction and PDF of crystalline materials*



feature articles

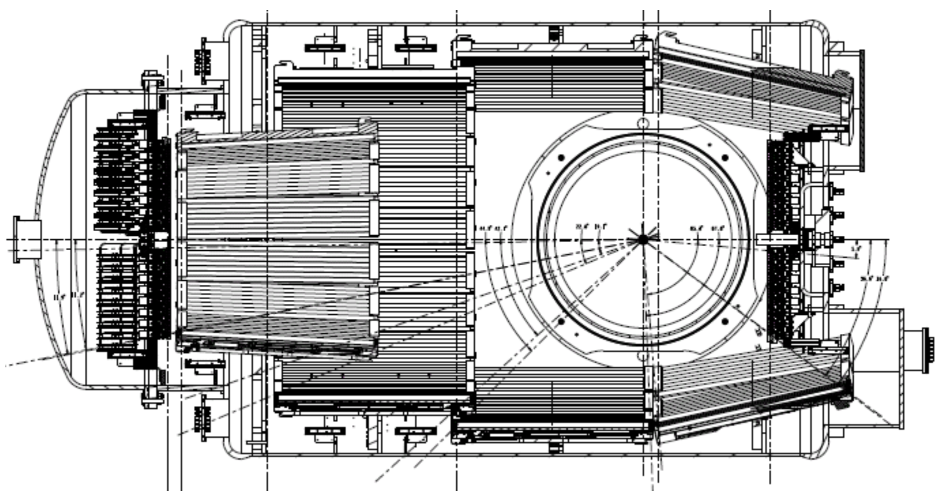
FOUNDATIONS ADVANCES

ISSN 2053-2733

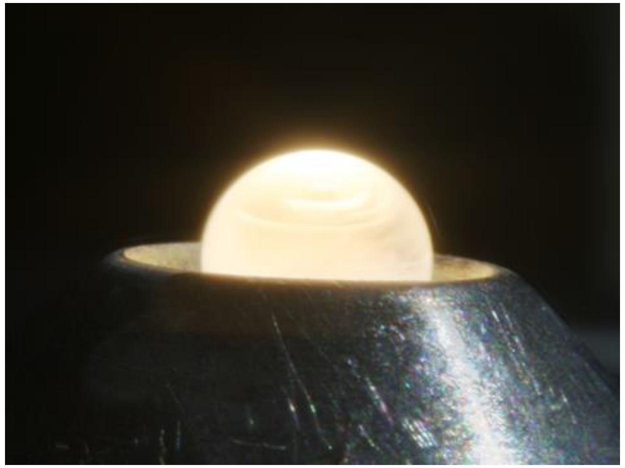
Precise implications for real-space pair distribution function modeling of effects intrinsic to modern time-of-flight neutron diffractometers

Daniel Olds,[a]* Claire N. Saunders,[b] Megan Peters,[c] Thomas Proffen,[a] Joerg Neuefeind[a] and Katharine Page[a]*

Nanoscale-Ordered Materials Diffractometer (NOMAD)



Neuefeind J., Feygenson M., Carruth J., Hoffmann R., Chipley K., **The Nanoscale Ordered MAterials Diffractometer NOMAD at the Spallation Neutron Source SNS**, *Nuclear Instruments and Methods B*, 287, 68-75, (2012).



- Large bandwidth of neutron energies
- Extensive detector coverage
- Count rates exceed comparable instruments by one to two orders of magnitude
- Routine Q-range of 0.2 to 40 Å^{-1}

Sample Environments

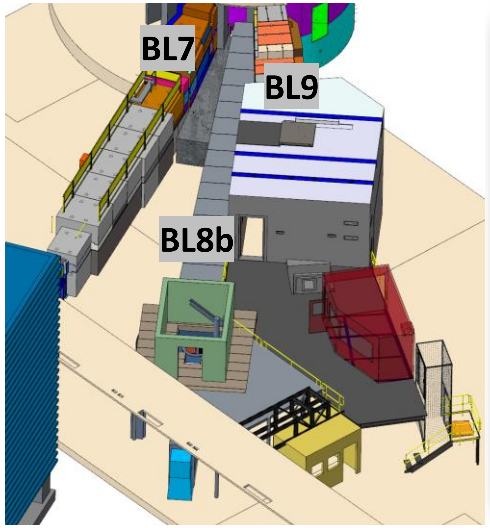
- Sample translation stage (80K- 500K)
- Orange cryostat (2K- 300K)
- ILL furnace (300K- 1400K)
- Aerodynamic levitator (800K- 3500K)
- High precision gas flow cell (RT-800K)
- High voltage set-up (10kV)

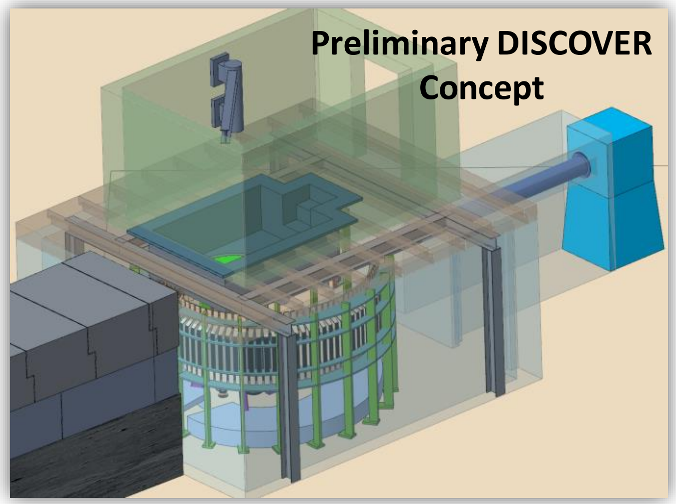
DISCOVER: An SNS Diffractometer for Materials Discovery

Proposed Instrument for Diffraction and PDF, BL-8b, SNS

Atomic and intermediate range order (and heterogeneity) need to be understood simultaneously and as they evolve to enable materials discovery and design

- What is the connection between global symmetry (i.e. that found over long length-scales) and local symmetry (i.e. that found at the atomic scale)?
- How does order evolve from the atomic to macroscale?
- How can we control it?



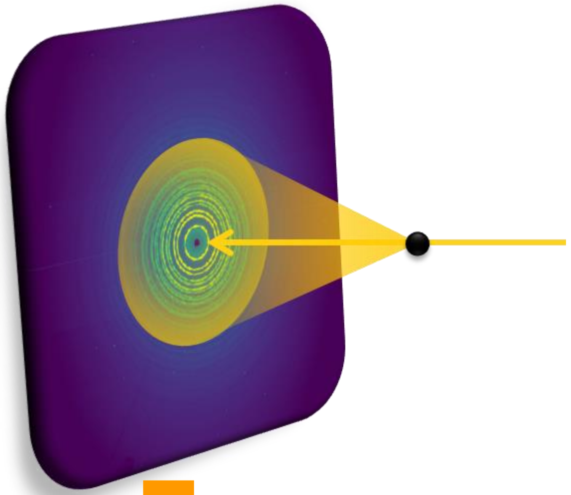


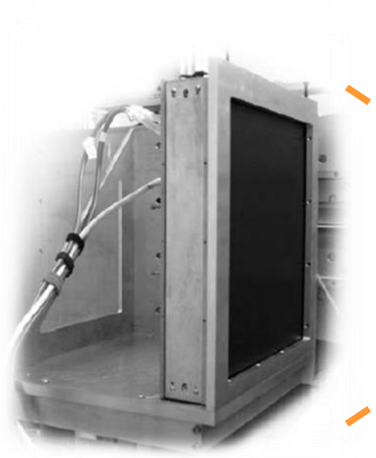
Day 1 New Capabilities

Simultaneous average (diffraction) and local structure (PDF) determination to follow the evolution of order from atomic to macroscales *in real time* (minutes)

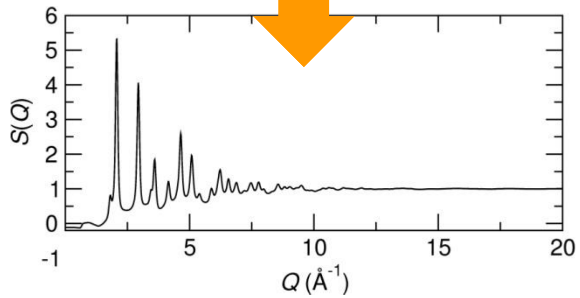
Ability to study hydrogenous materials (particularly ubiquitous in synthesis and catalysis science) with neutrons by separating static from dynamic contributions

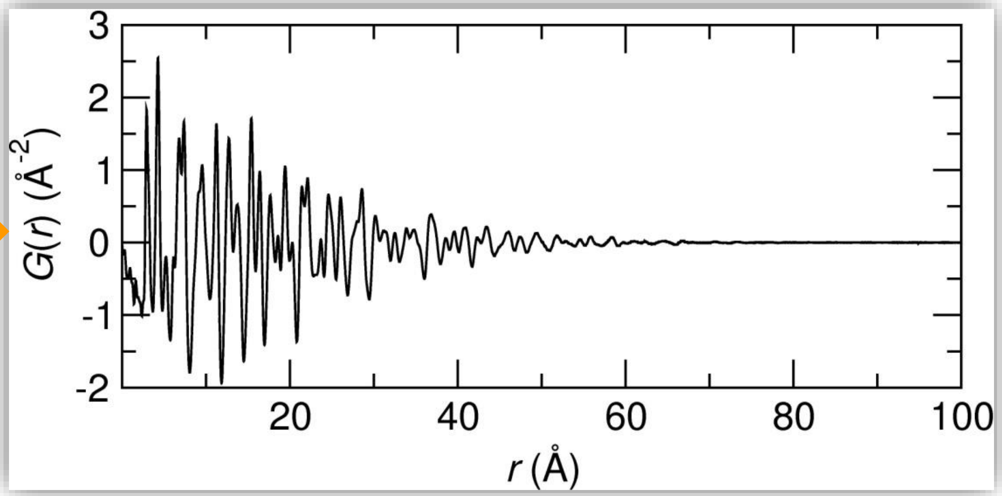
Synchrotron Total Scattering: 2D Amorphous Si Detector





In the US:
11-ID-B, APS
PDF, NSLS-II





P. J. Chupas, K. W. Chapman, P. L. Lee, **Applications of an amorphous silicon-based area detector for high resolution, high sensitivity and fast time-resolved pair distribution function measurements**, *J. Appl. Crystallogr*. 40, 463, 2007. http://dx.doi.org/10.1107/S0021889807007856

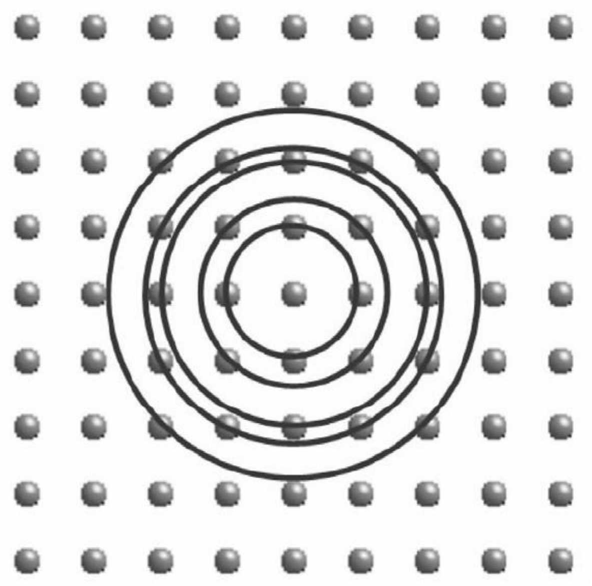
Modeling a PDF

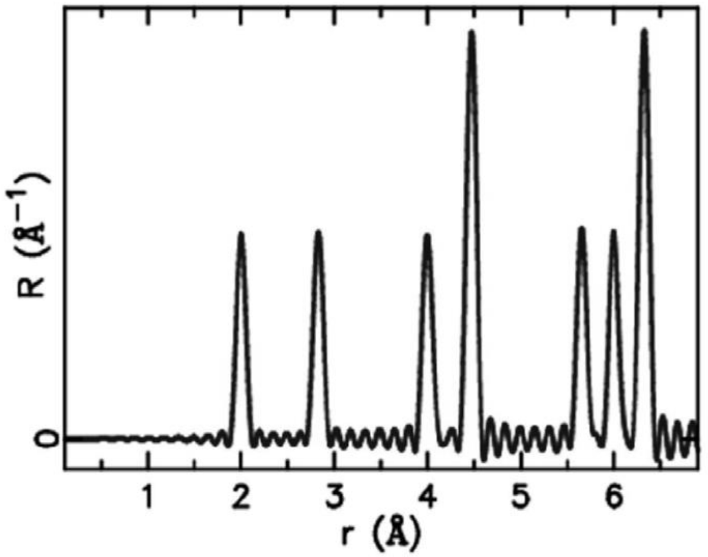
- Calculating a PDF from a model
- Available software
- Nanoparticle shape effects

Pair Distribution Function

Based on the *radial distribution function* (RDF):

S.J.L Billinge, *Z. Kristallogr. Suppl.*,26,17 (2007)





Atomic PDF (PDFFIT notation):

$$G(r) = 4\pi r[\rho(r) - \rho_0]$$

atomic form factors
(Z for x-rays, b for neutrons)

distance between i and j atoms

$$G(r) = \sum_{ij}\left[\frac{b_i b_j}{\langle b \rangle^2}\delta(r - r_{ij})\right] - 4\pi r \rho_0$$

average density

sum over all atoms

Calculating a PDF from a Model

Calculating a PDF from an atomistic model:

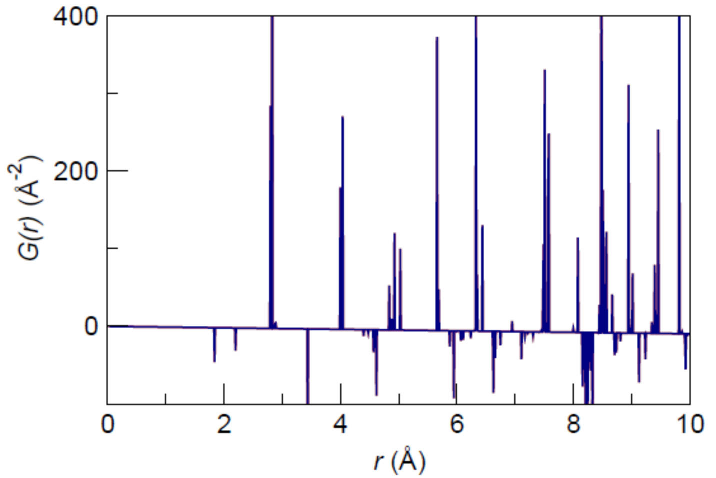
$$G(r) = \sum_{ij} \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

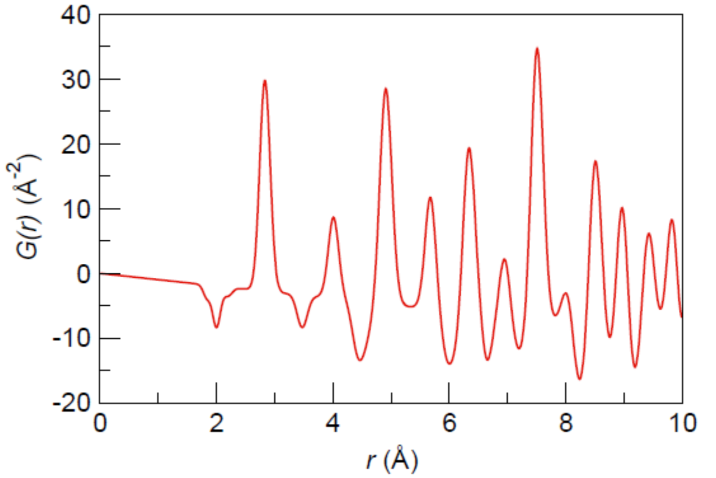
Peak Width

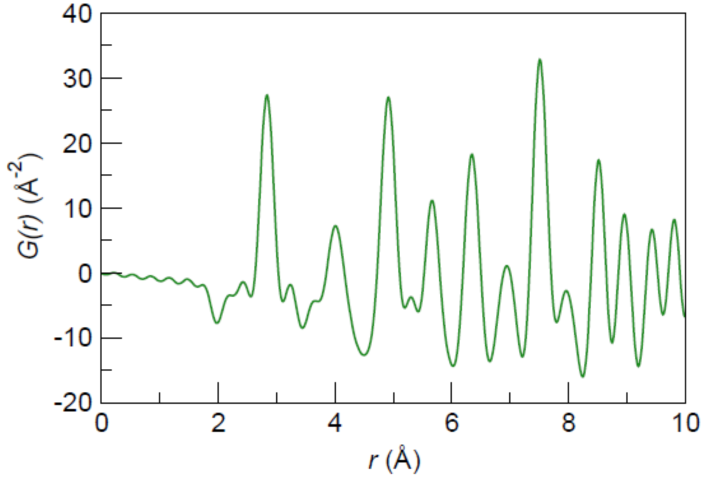
- Small model: convolution of $\delta(r-r_{ij})$ with distribution function (*PDFgui* & *TOPAS v6*)
- Large model: ensemble average of actual displacements (*RMCprofile*)

Termination ripples + instrumental dampening

- Multiplication with step function in reciprocal space gives convolution with $\sin(Q_{max}r)/r$ in real space
- …







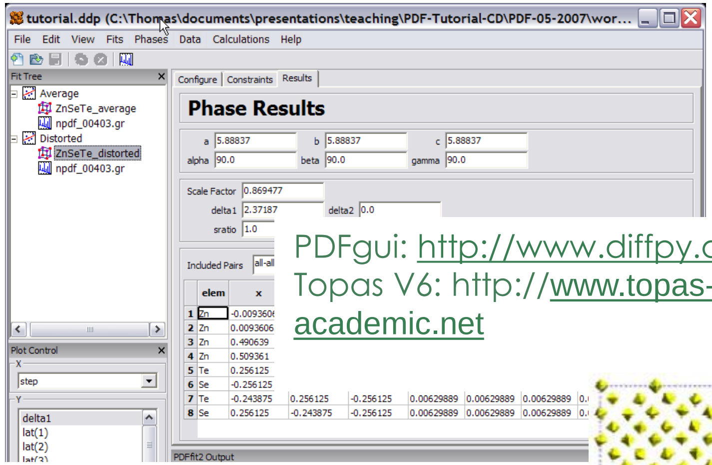
Atomic PDF Modeling

Small Models: Least Squares Refinement
Up to several hundred atoms
'Rietveld'-type parameters: *lattice parameters, atomic positions, displacement parameters, etc.*
Refinements as function of *r*-range

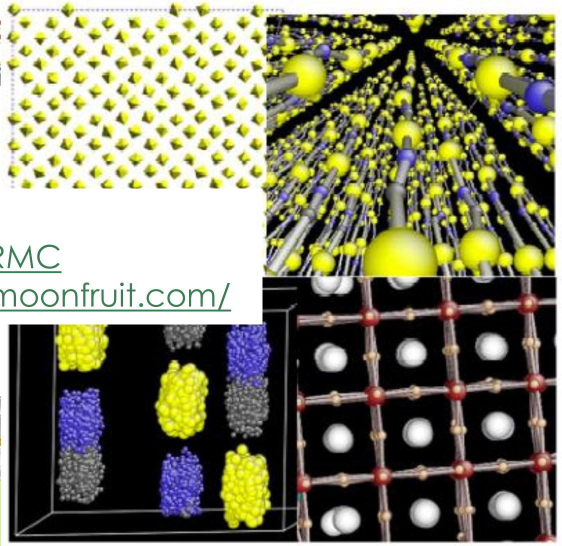
Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q)*, *G(r)* , Bragg profile
Constraints utilized
Static 3-D model of the structure (a snap-shot)

Multi-level / Complex Modeling
Refine higher level parameters (not each atom)
Example nanoparticle: *diameter, layer spacing, stacking fault probability*
Choose minimization scheme

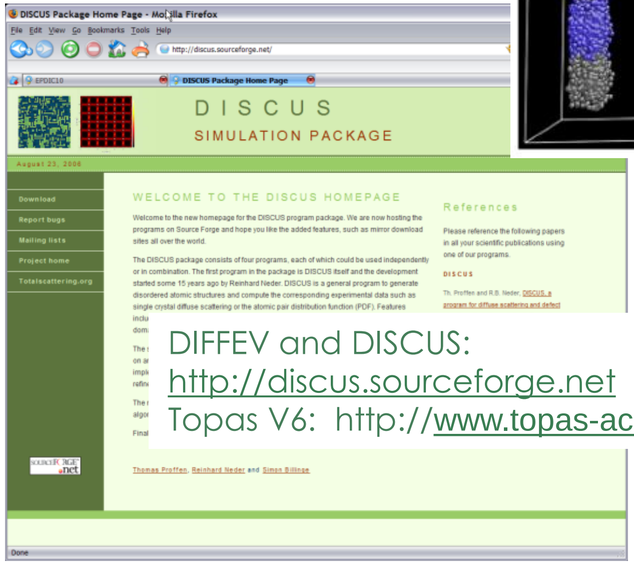
***ab initio* and force-field based approaches**
Density Functional Theory
Molecular Dynamics



PDFgui: http://www.diffpy.org/
Topas V6: http://www.topas-academic.net

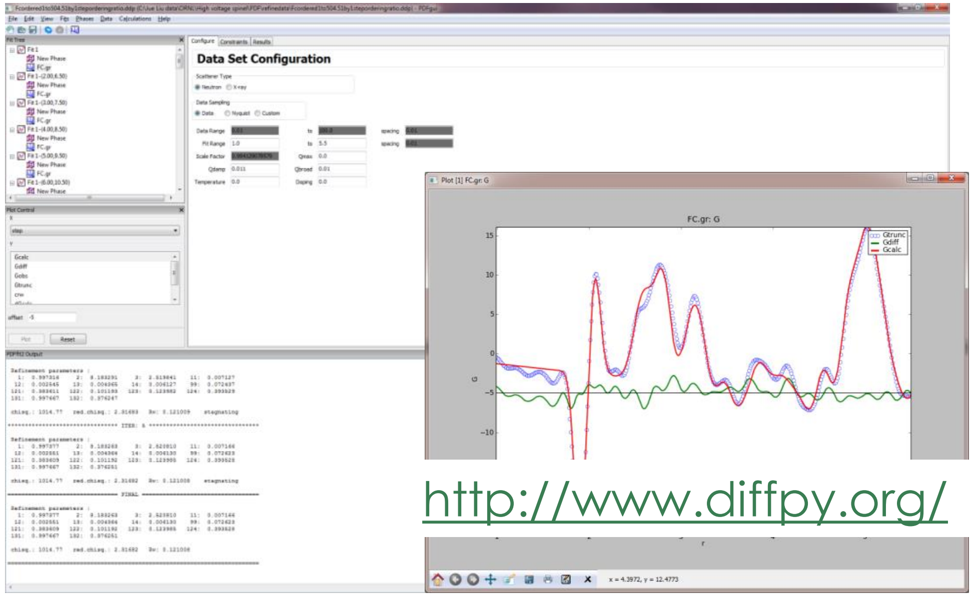


RMCprofile: http://www.isis.rl.ac.uk/RMC
EPSR: http://disordmat.moonfruit.com/



DIFFEV and DISCUS: http://discus.sourceforge.net
Topas V6: http://www.topas-academic.net

Small Box: Software Comparison



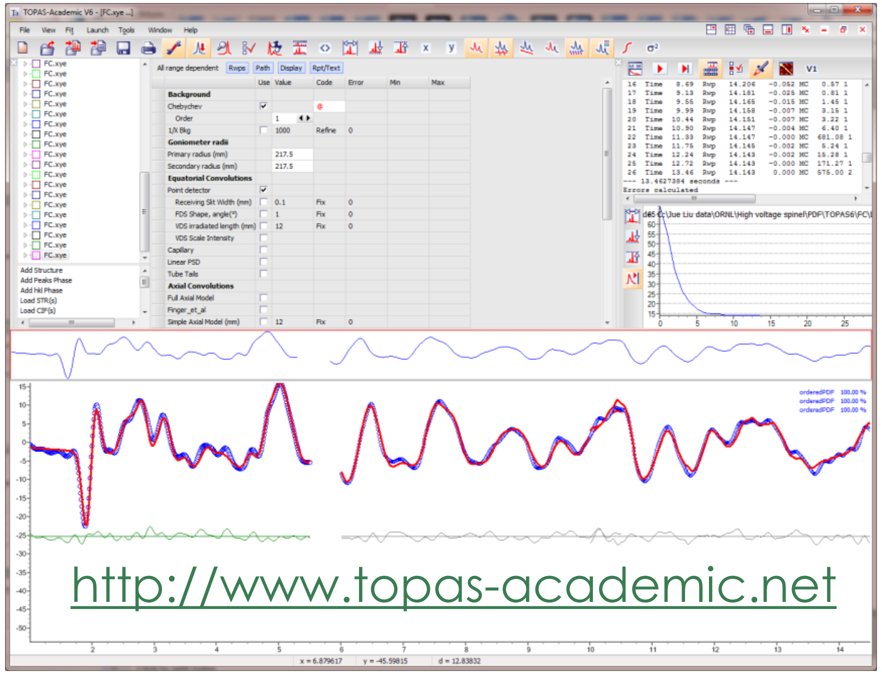
http://www.diffpy.org/

PDFgui

+ Open Source and Free
+ GUI is Simple and User-friendly
- Slow refinement, especially for high-*r*

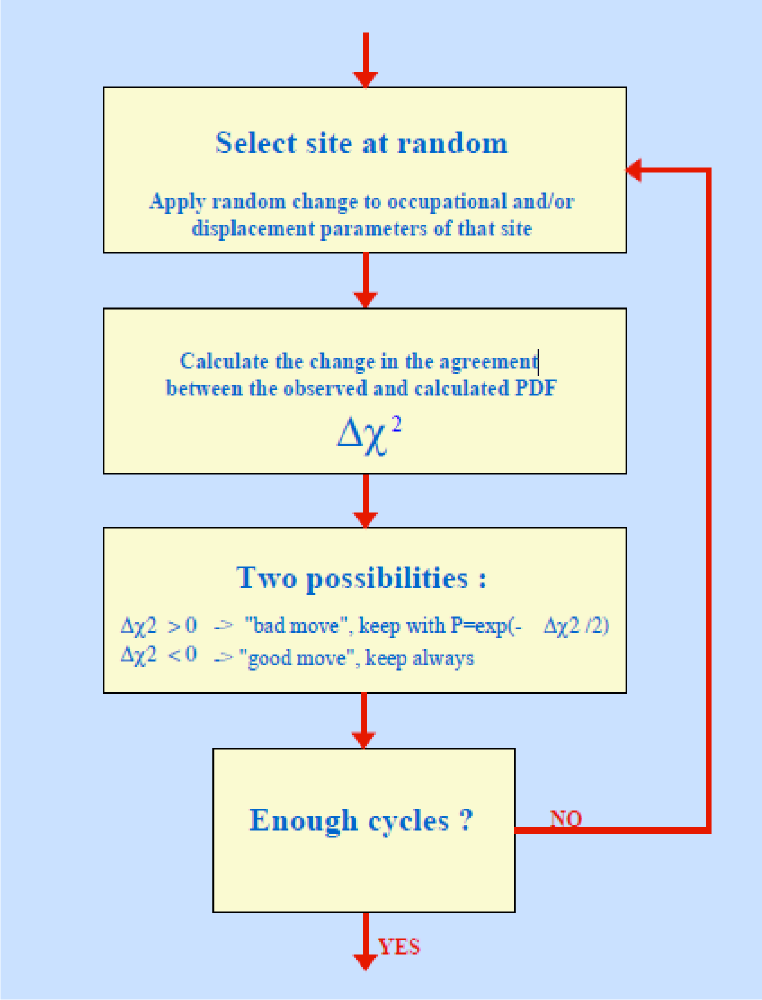
TOPAS PDF

+ Super Fast
+ Flexible
+ Fit Bragg and PDF together
- Steeper learning curve
- Have to write your own macro



http://www.topas-academic.net

Large Box: Reverse Monte Carlo



RMCprofile

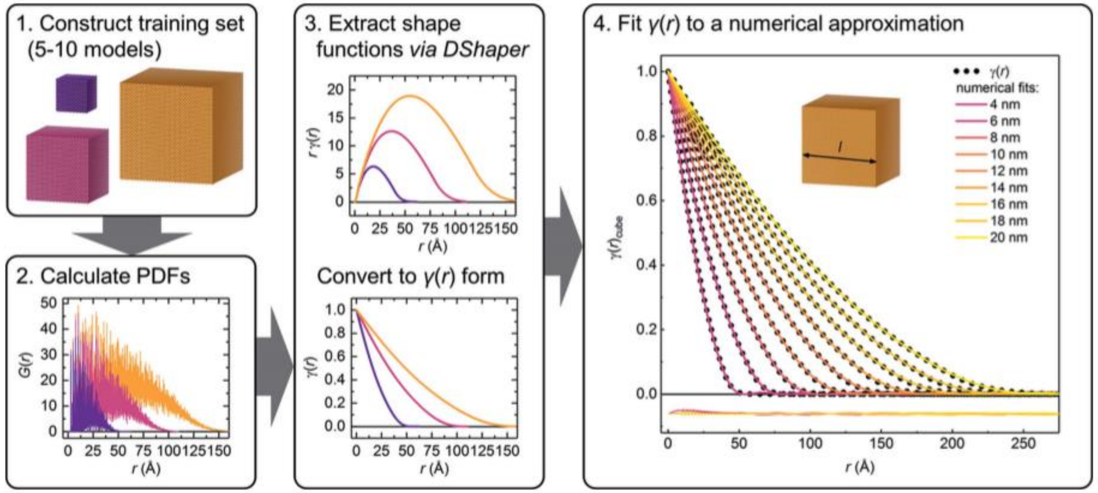
- Atomic configurations ~600 to 20000+ atoms
- Fit both X-ray and neutron F(Q)
- Fit G(r)
- Fit Bragg profile (GSAS ToF 1-3)
- Polyhedral restraints
- Coordination constraints
- Closest approach constraints

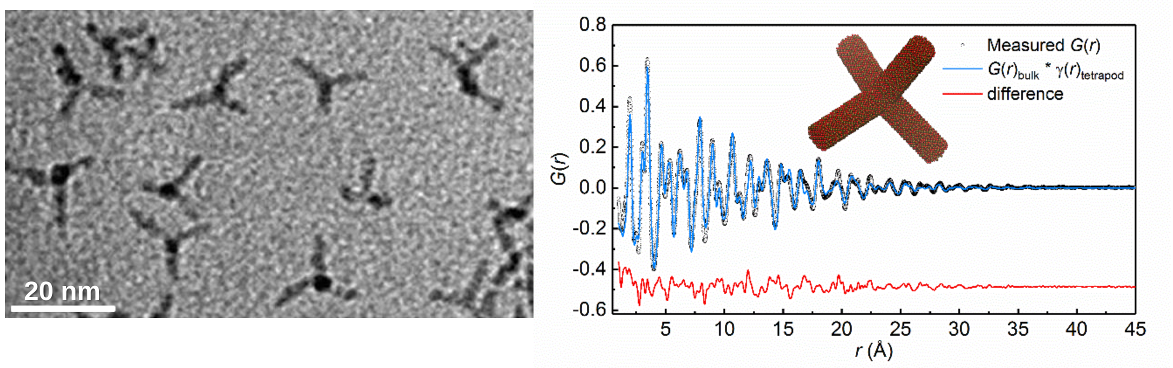
- **Produce a static 3-D model of the structure (a snap-shot in time)**

http://www.isis.rl.ac.uk/RMC

Modeling nanoscale morphology in real space

$$G(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} Q[S(Q)-1]\sin(Qr)\,dQ = 4\pi r[\rho(r) - \rho_0\gamma_0(r)]$$





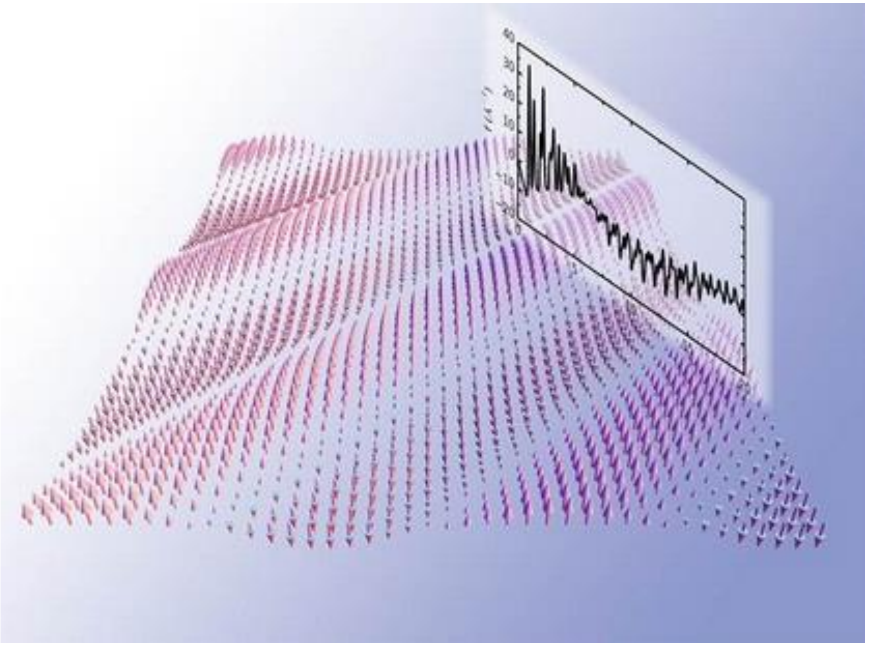
- $\gamma_0(r)$ is the particle shape function, it varies significantly from unity for nanomaterials and should be implemented as an *r*-dependent function
- Can fit physically-relevant shape parameters, such as a nanocube edge length, nanorod length and diameter, or arm length, width, and arm tip-to-arm tip distance in Fe_2O_3 tetrapods (left)
- Options exist in DISCUS, Topas-v6, and Diffpy

For use with Debye scattering approach: D. Olds, H.-W. Wang and K. Page, *J. Appl. Cryst.* ***48***, 1651-1659 (2015).
For use in small-box modeling approach: T.-M. Usher, D. Olds, J. Liu, K. Page, *Acta Cryst. A74* (2018).

A Few Emerging Areas

- Magnetic PDF
- Field-dependent PDF
- Dynamic PDF
- 3D PDF
- Thin-Film PDF

Magnetic PDF: mPDF



CrossMark advances

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Magnetic pair distribution function analysis of local magnetic correlations

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- Being developed to provide direct access to long-range and short-range magnetic correlations in real space

- **Spin order in diluted magnetic semiconductors, spin-stripe correlations in cuprate superconductors, spin fluctuations in frustrated magnetic systems, etc.**

ARTICLE

Received 14 Jul 2016 | Accepted 4 Nov 2016 | Published 20 Dec 2016 DOI: 10.1038/ncomms13842 OPEN

Emergent order in the kagome Ising magnet $Dy_3Mg_2Sb_3O_{14}$

Joseph A.M. Paddison[1,2], Harapan S. Ong[1], James O. Hamp[1], Paromita Mukherjee[1], Xiaojian Bai[2], Matthew G. Tucker[3,4], Nicholas P. Butch[5], Claudio Castelnovo[1], Martin Mourigal[2] & S.E. Dutton[1]

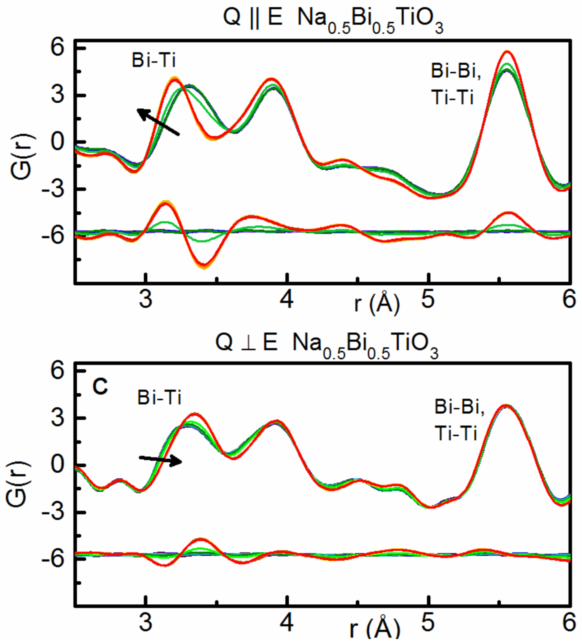
PRL **116,** 197204 (2016) PHYSICAL REVIEW LETTERS week ending 13 MAY 2016

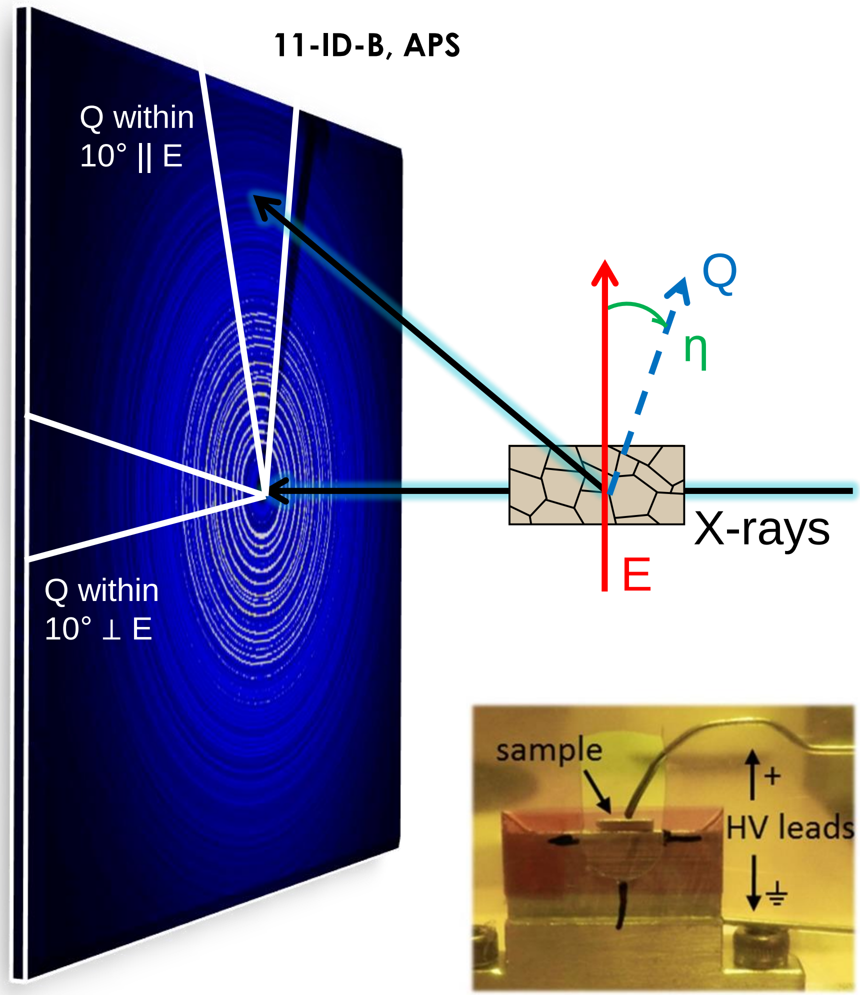
Verification of Anderson Superexchange in MnO via Magnetic Pair Distribution Function Analysis and *ab initio* Theory

Benjamin A. Frandsen,[1] Michela Brunelli,[2] Katharine Page,[3] Yasutomo J. Uemura,[1] Julie B. Staunton,[4] and Simon J. L. Billinge[5,6,*]

Field-Dependent PDF

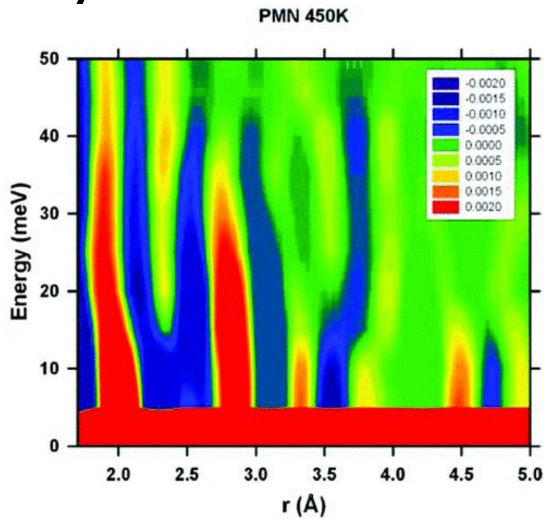
- X-ray total scattering measured while static electric fields (0 to ~4 kV/mm) are applied to $Na_{1/2}Bi_{1/2}TiO_3$ polycrystalline ceramic samples
- Bi^{3+} reorientation observed at high electric field





T.-M. Usher, I. Levin, J.E. Daniels, and J.L. Jones, *Scientific Reports* 5, 14678 (2015).
A. J. Goetzee-Barral et al., Phys. Rev. B 96, 014118 (2017).

Dynamic PDF: DyPDF



T. Egami and W. Dmowski, **Dynamic pair-density function method for neutron and X-ray inelastic scattering**, *Z. Kristallogr.* 227, 233–237 (2012).

W. Dmowski, S. B. Vakhrushev, I.-K. Jeong, M. P. Hehlen, F. Trouw, T. Egami, **Local Lattice Dynamics and the Origin of the Relaxor Ferroelectric Behavior**, *Phys. Rev. Lett.* 100, 137602 (2008).

$Pb(Mg_{1/3}Nb_{2/3})O_3$

ARTICLE

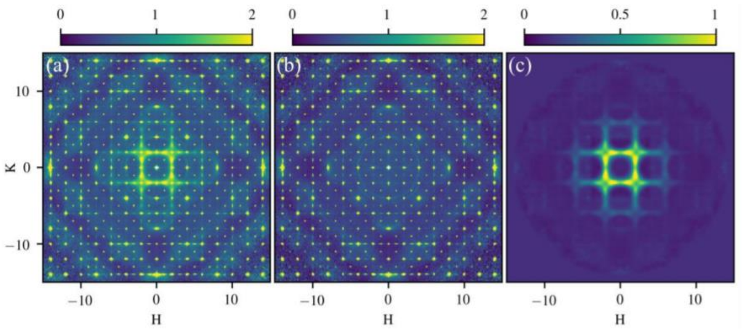
Received 28 Jun 2016 | Accepted 17 Mar 2017 | Published 4 May 2017 DOI: 10.1038/ncomms15294 OPEN

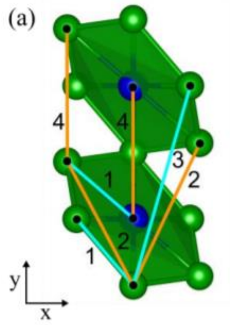
Observation of dynamic atom-atom correlation in liquid helium in real space

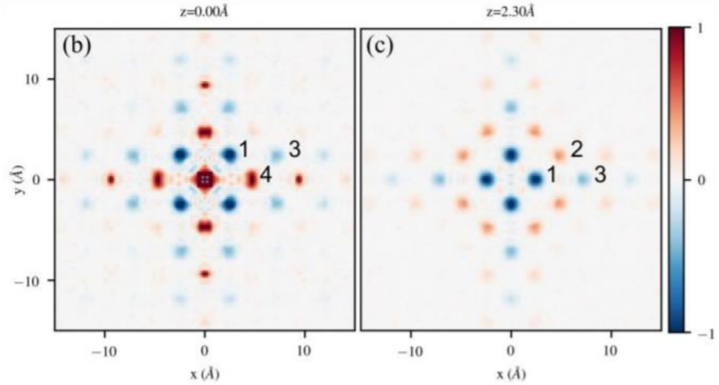
W. Dmowski[1,2], S.O. Diallo[3], K. Lokshin[1,2], G. Ehlers[3], G. Ferré[4], J. Boronat[4] & T. Egami[1,2,3,5]

3D - PDF

T. Weber and A. Simonov, **The three-dimensional pair distribution function analysis of disordered single crystals: basic concepts**, Z Krystallogr. 227, 238-247 (2012).





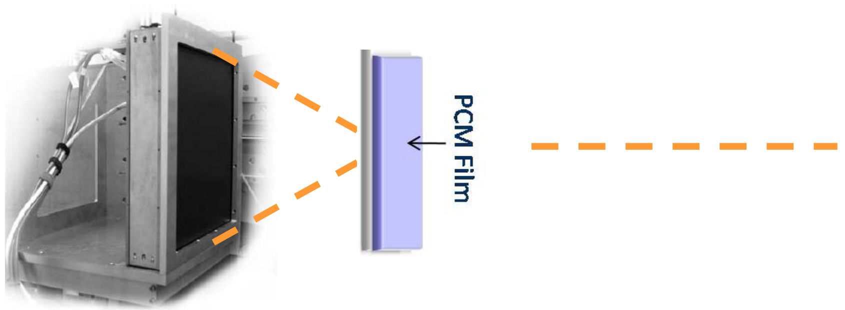


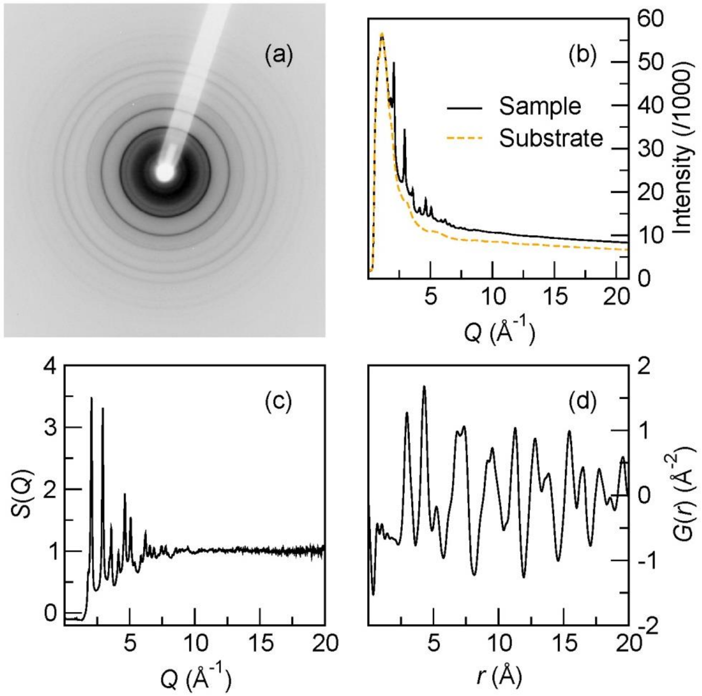
$(Mn_{1-x}Fe_x)_2O_3$

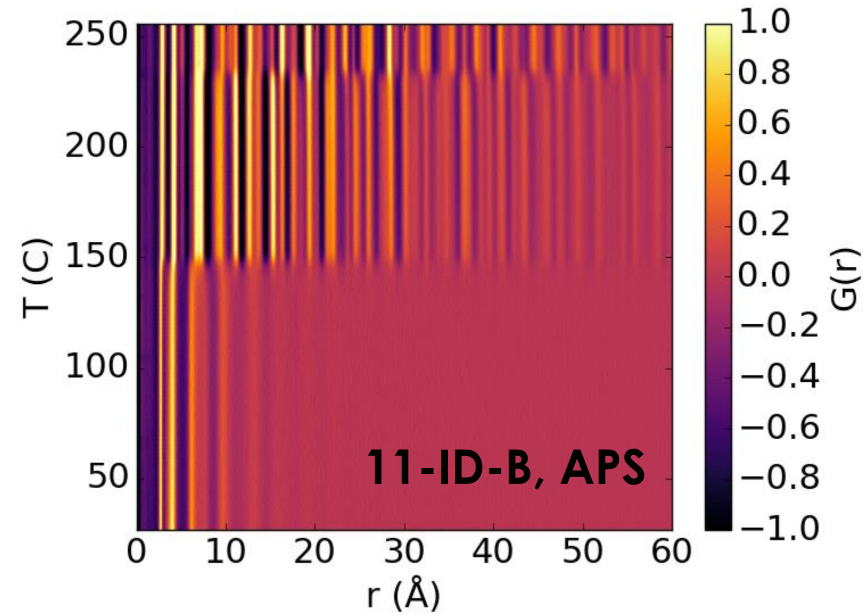
N. Roth, A. F. May, F. Ye, B. C. Chakoumakos, and B. B. Iversen, **Model-free reconstruction of magnetic correlations in frustrated magnets**, IUCrJ, 5, 410-416 (2018).

Thin Film PDF(tfPDF)

K. M. Ø. Jensen, A. B. Blichfeld, S. R. Bauers, S. R. Wood, E. Dooryhée, D. C. Johnson, B. B. Iversen, and S. J. L. Billingea, **Demonstration of thin film pair distribution function analysis (tfPDF) for the study of local structure in amorphous and crystalline thin films**, *IUCrJ*, 2 (2015) 481-489.







Data collected for 1 μm films deposited **on kapton**, thermally annealed in situ under flowing He to 155˚C and measured at ~60 keV in transmission

K. Page, J. K. Baldwin, Th. Proffen, unpublished.

When Should You Pursue PDF Studies of a Crystalline Material?

- ✓ You have modeled everything you can in reciprocal space
- ✓ You suspect the local structure may differ from the long-range structure

Why Would You Suspect a Distinct Local Structure?

Maybe…

- You find signatures of disorder through complementary methods
- An average structure model fails to explain observed material properties
- A theoretical study proposes an alternate structure to the one globally observed
- Lots of experience with a materials family or structural archetype

Some Resources and Programs

Data Collection

- Neutron: http://neutronsources.org
- X-ray: http://www.lightsources.org

Data Extraction

- PDFgetN: http://pdfgetn.sourceforge.net
- PDFgetX2/X3: http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/ http://www.diffpy.org/products/pdfgetx3.html
- Gudrun: http://disordmat.moonfruit.com/
- ADDIE: ADvanced DIffraction Environment: coming soon from ORNL!

Data Modeling

- PDFgui: http://www.diffpy.org/
- Topas Academic: http://www.topas-academic.net
- RMCprofile: http://www.isis.rl.ac.uk/RMC
- DISCUS/DIFFEV: http://discus.sourceforge.net
- EPSR: http://disordmat.moonfruit.com/

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D. A. Keen and A. L. Goodwin, The crystallography of correlated disorder, Nature 521, 303–309, 2015. http://dx.doi.org/10.1038/nature14453

H. Y. Playford, L. R. Owen, I. Levin, and M. G. Tucker, New insights into complex materials using Reverse Monte Carlo modeling, Annual Review of Materials Research, 44, 429-449, 2014. http://dx.doi.org/10.1146/annurev-matsci-071312-121712

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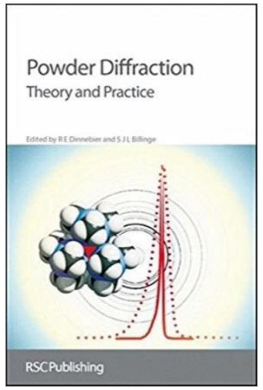
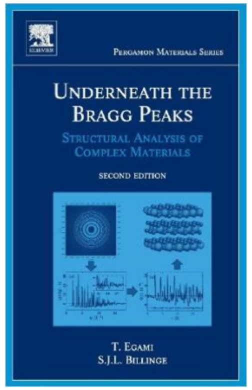
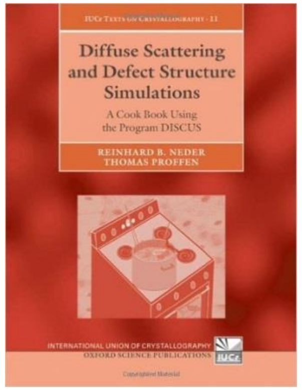






Summary

Atomic PDF from total (Bragg and diffuse) scattering data gives access to:

- Amorphous and nanomaterial structure

- Departure from long range (average structure)
  - Displacements
  - Chemical short-range order
  - Interstitials/vacancies

- Correlation length scale of features (size)

- Structure ⇔ property relationships

Use multiple data sets (e.g. x-ray and neutron data, diffraction and PDF) to characterize complex materials

High-resolution instruments open the door to medium-range order investigations

Programs/Partnerships for Users

Open Proposal Call for 2020 Cycle A

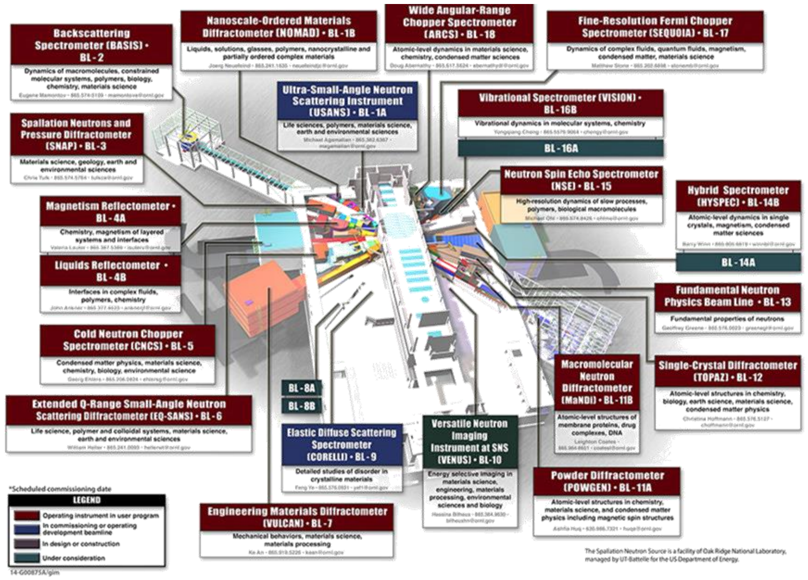
- SNS or HFIR's User Program Instruments (diffraction, small angle, reflectometry, spectroscopy, neutron imaging…)
- Next Proposal deadline: ***September 2019***

Mail-in Programs (NOMAD and POWGEN)

- Up to five samples or temperatures (in standard mode)
- Opportunities on most weeks during the run cycle: ***Submit Any Time***

Complimentary x-ray PDF and x-ray Diffraction access

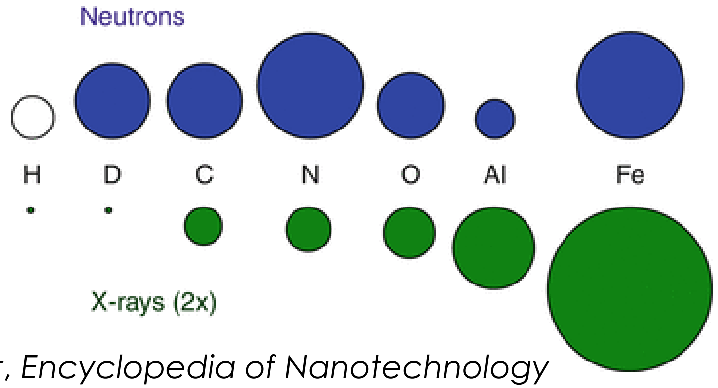
- Measure samples ~3 times per year, and provide reduced data



http://neutrons.sns.gov

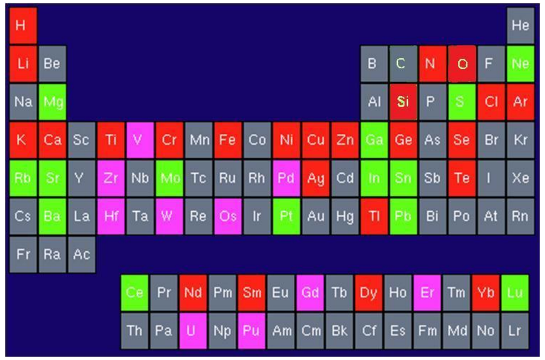
Neutron Total Scattering

Light Atom and Neighboring Atom Species



M. Laver, *Encyclopedia of Nanotechnology* (2012), 2437-2450.

Isotope Substitution



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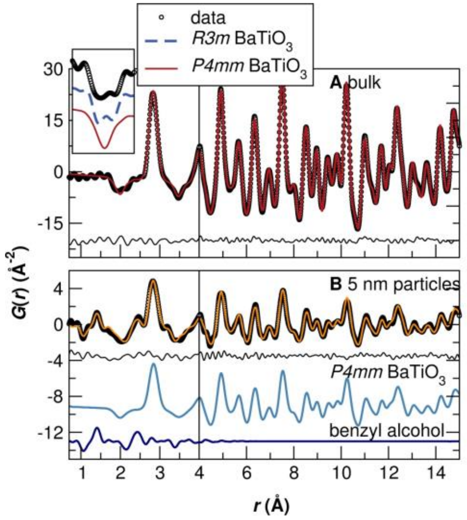
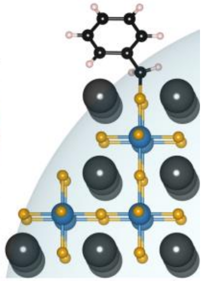
Surface Species of Nanomaterials





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Magnetic Structure

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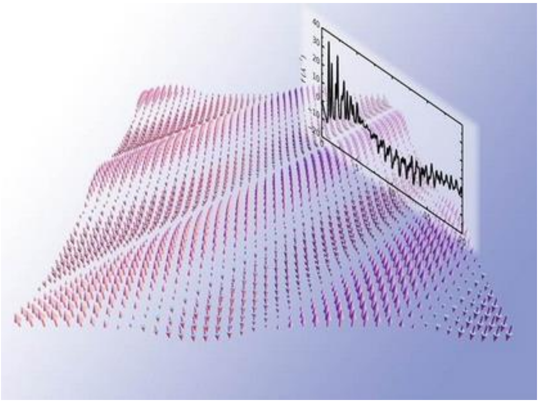

Nondestructive

Penetration of Sample Environments

Questions?

pagekl@ornl.gov