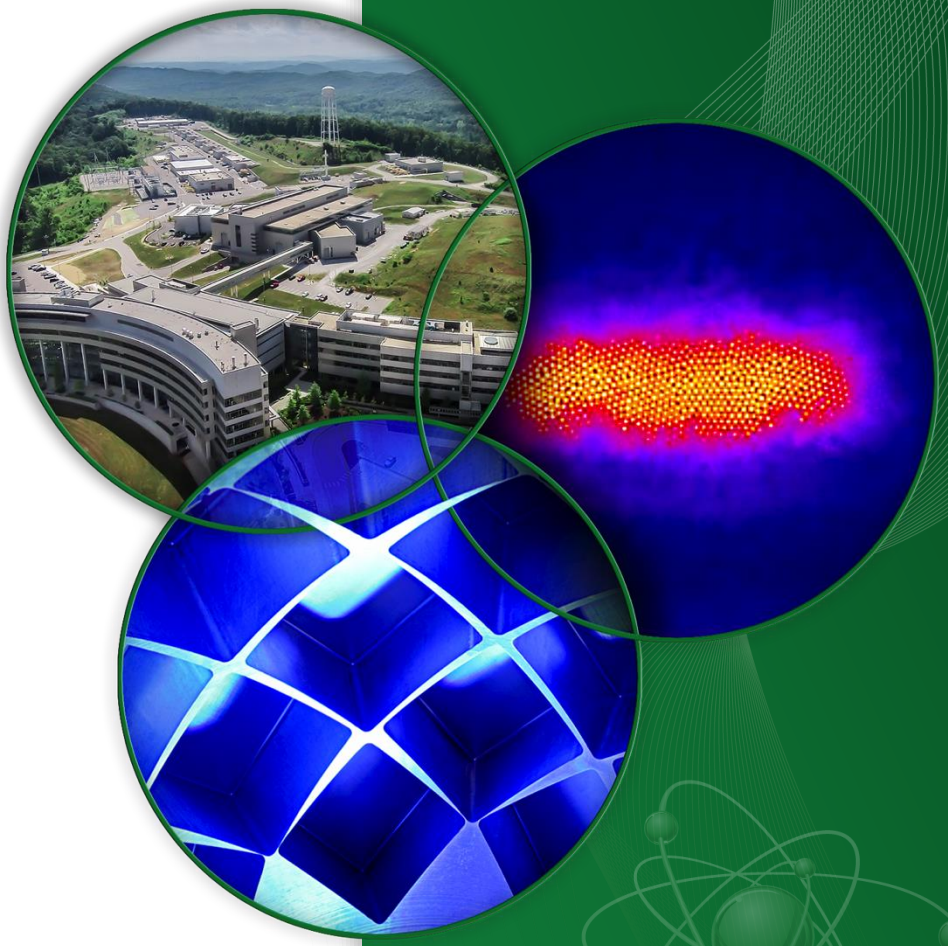
Atomic Pair Distribution Function (PDF) Analysis



2018 Neutron and X-ray Scattering School

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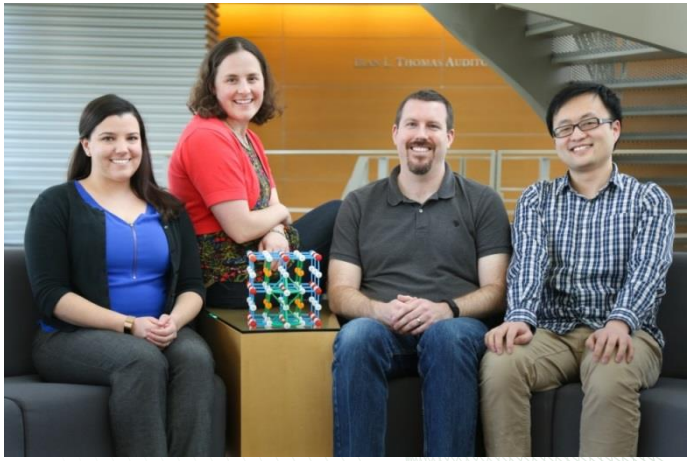
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Diffraction Group, ORNL

Diffraction Group
Group Leader: Matthew Tucker

About Me (an Instrument Scientist)

- 2004: BS in Chemical Engineering University of Maine
- 2008: PhD in Materials, UC Santa Barbara
- 2009/2010: Director's Postdoctoral Fellow; 2011-2014: Scientist, Lujan Neutron Scattering Center, Los Alamos National Laboratory (LANL)
- 2014-Present: Scientist, Neutron Scattering Division, Oak Ridge National Laboratory (ORNL)



Dr. Liu, his wife (Dr. Luo), and baby boy on the way

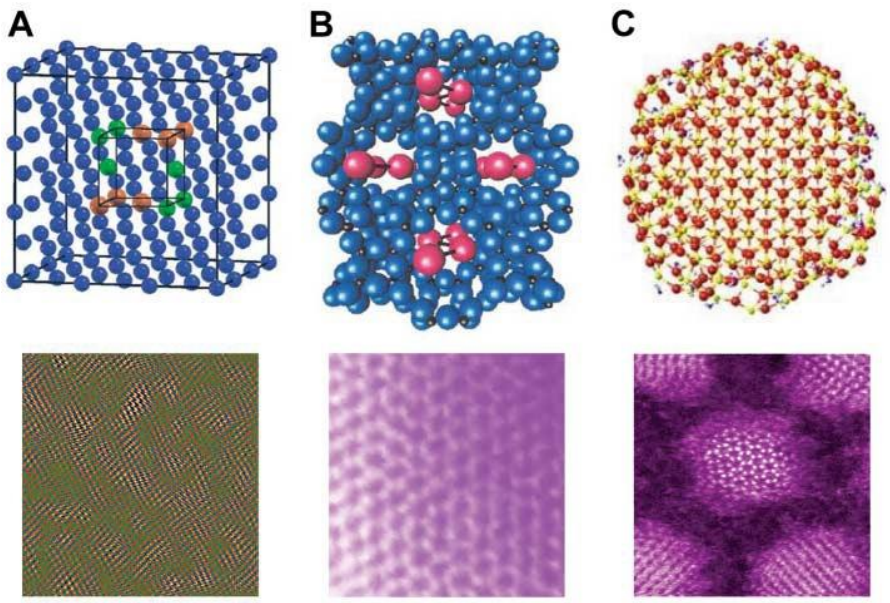
Dr. Olds, AJ, and Max

Dr. Usher-Ditzian and Ellie

Dr. Page, Wriston, and Abbie

What is a *local structure*?

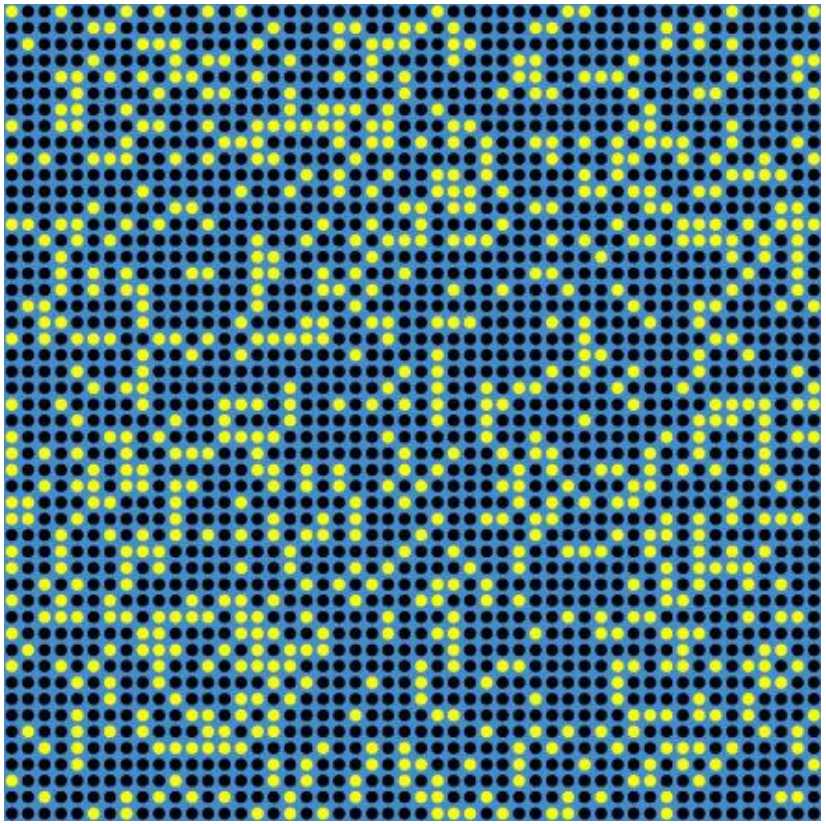
- **Disordered materials**: The interesting properties are often governed by the defects or local structure
- **Non crystalline materials:** Amorphous solids and polymers
- **Nanostructures**: Well defined local structure, but long-range order limited to few nanometers (poorly defined Bragg peaks)

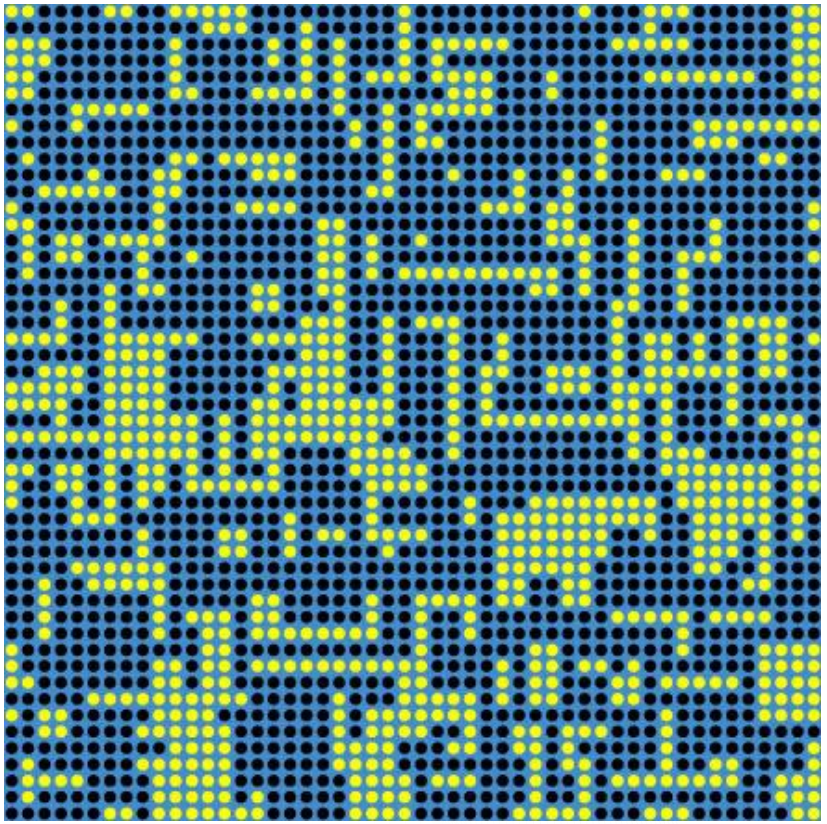


S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

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

What is *total* scattering?



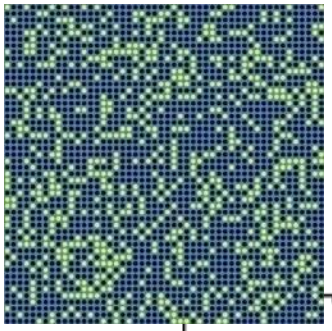


Cross section of 50x50x50 unit cell model crystal consisting of 70% blue atoms and 30% *vacancies.*

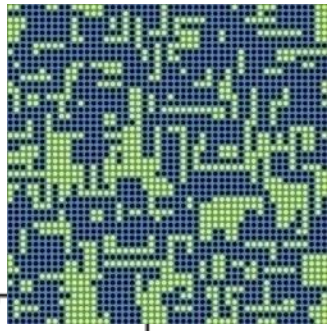
Properties might depend on vacancy ordering!

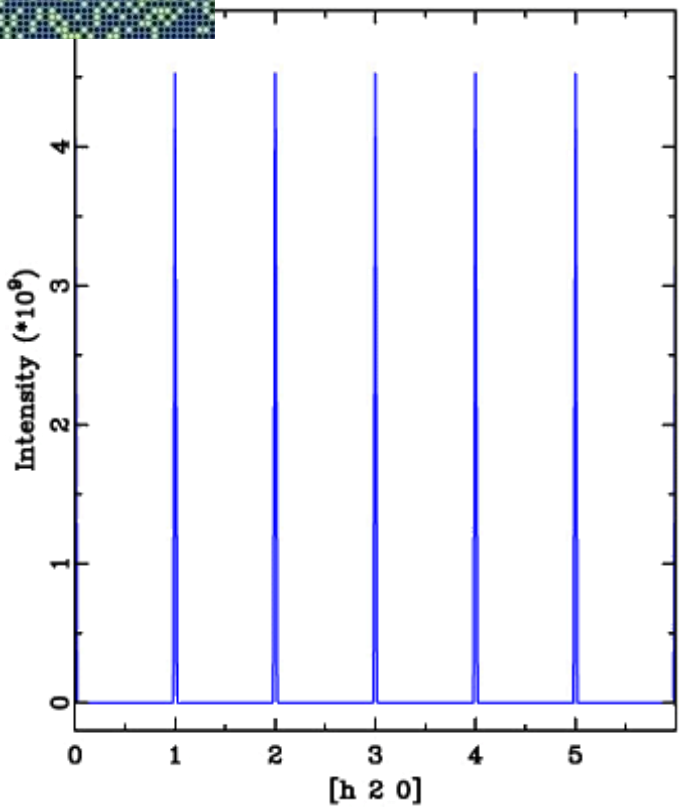
Courtesy of Thomas Proffen

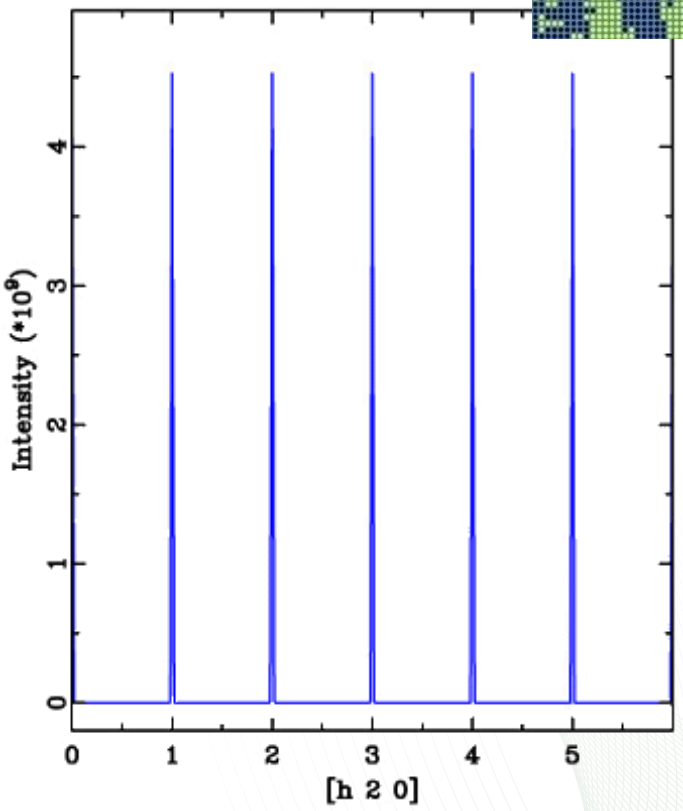
Bragg peaks are “blind”



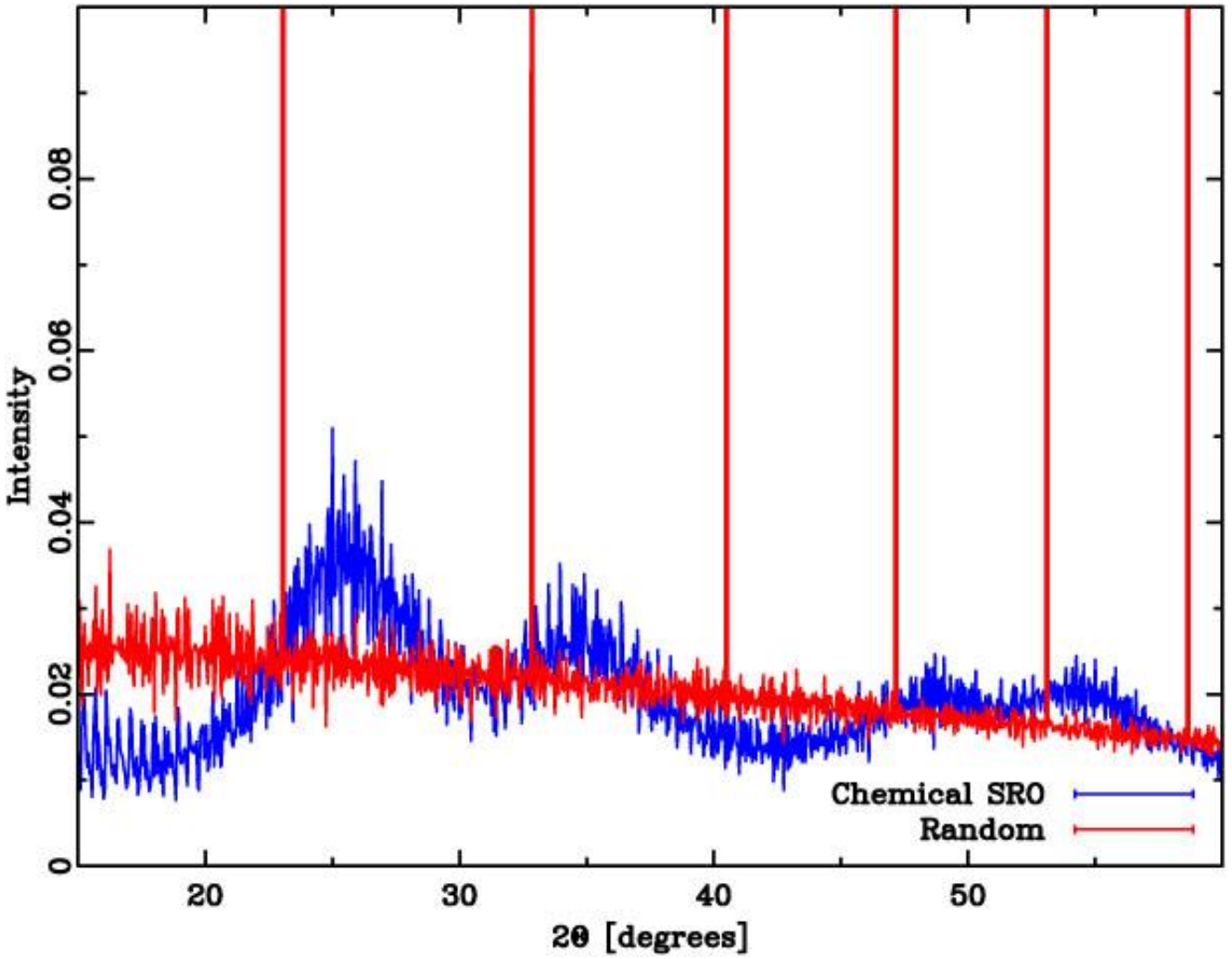
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.





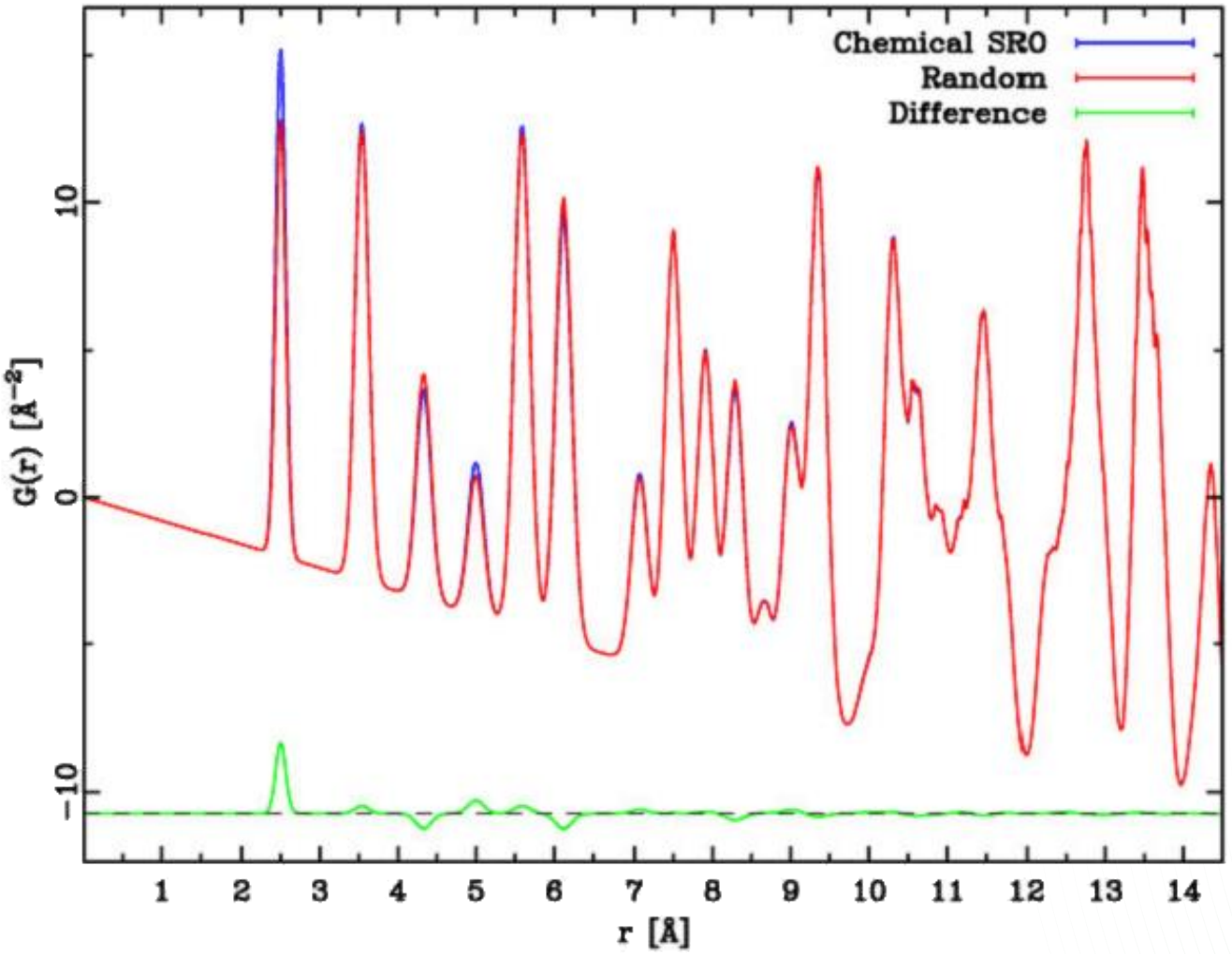


How about powder diffraction?



Courtesy of Thomas Proffen

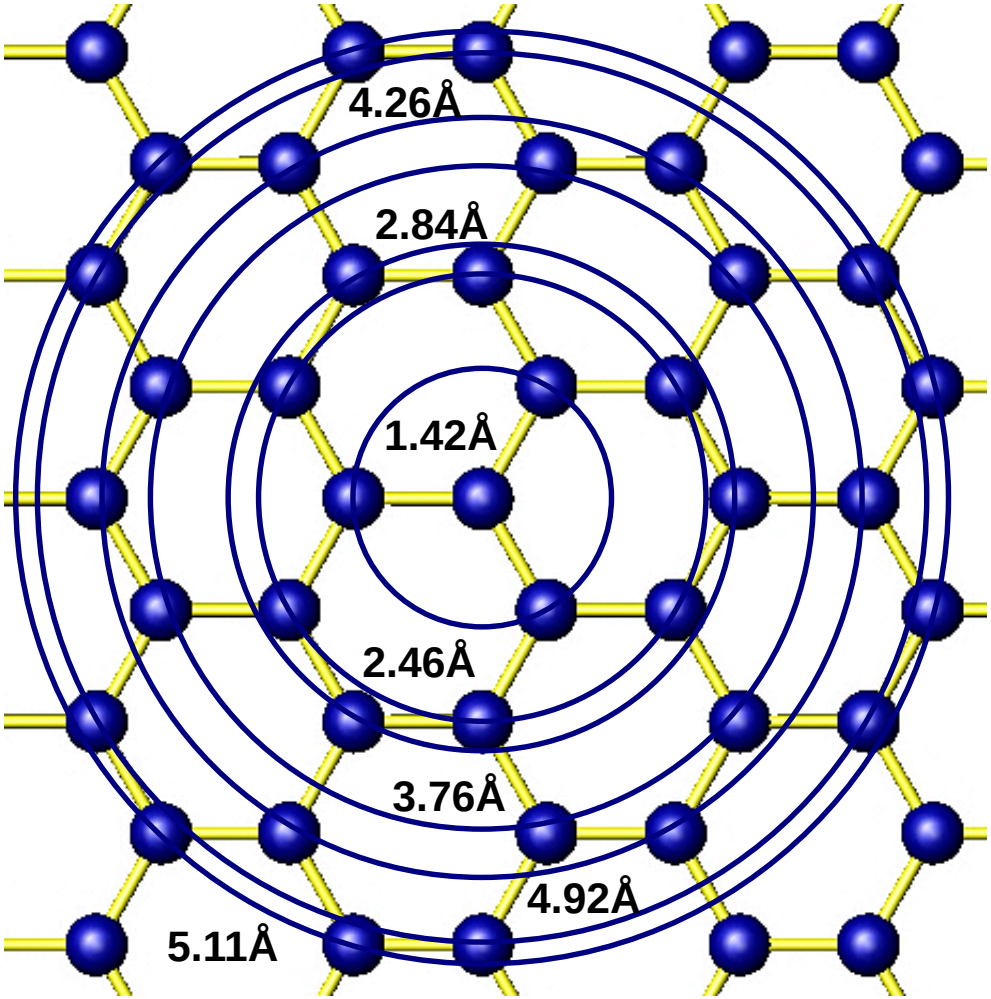
The Pair Distribution Function



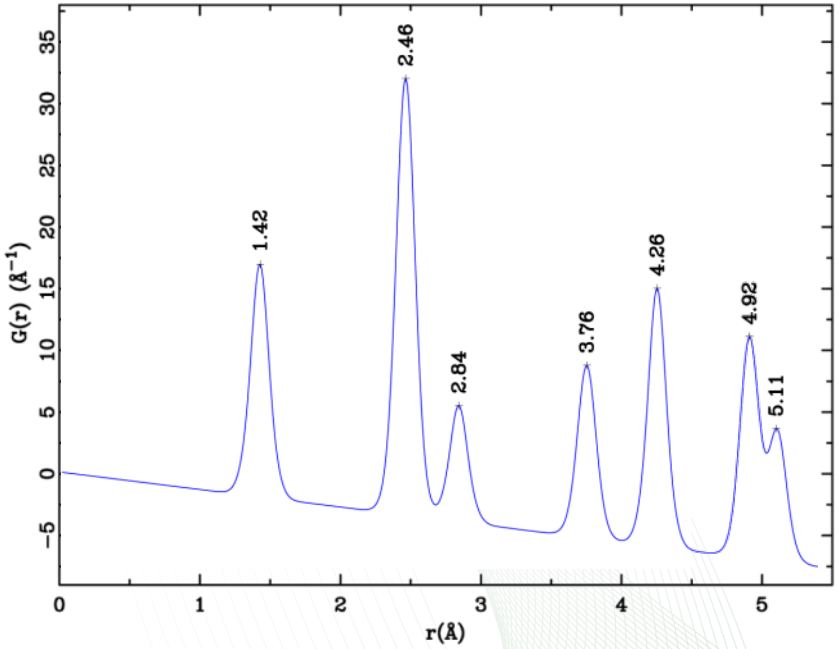
The PDF is the Sine-Fourier transform of the total scattering (Bragg and diffuse) diffraction pattern

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?



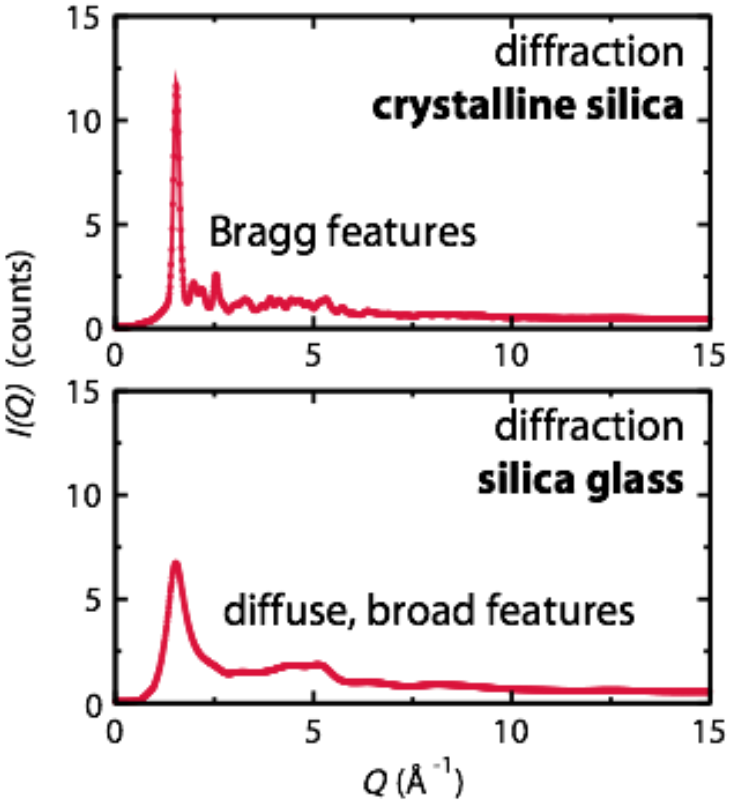
The Pair Distribution Function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.

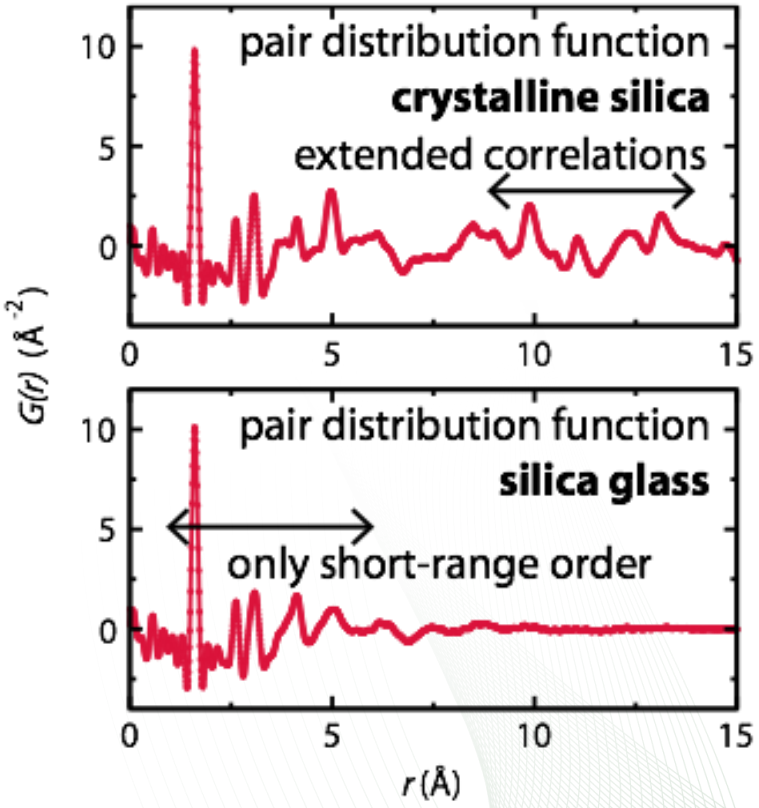


Pair Distribution Function

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

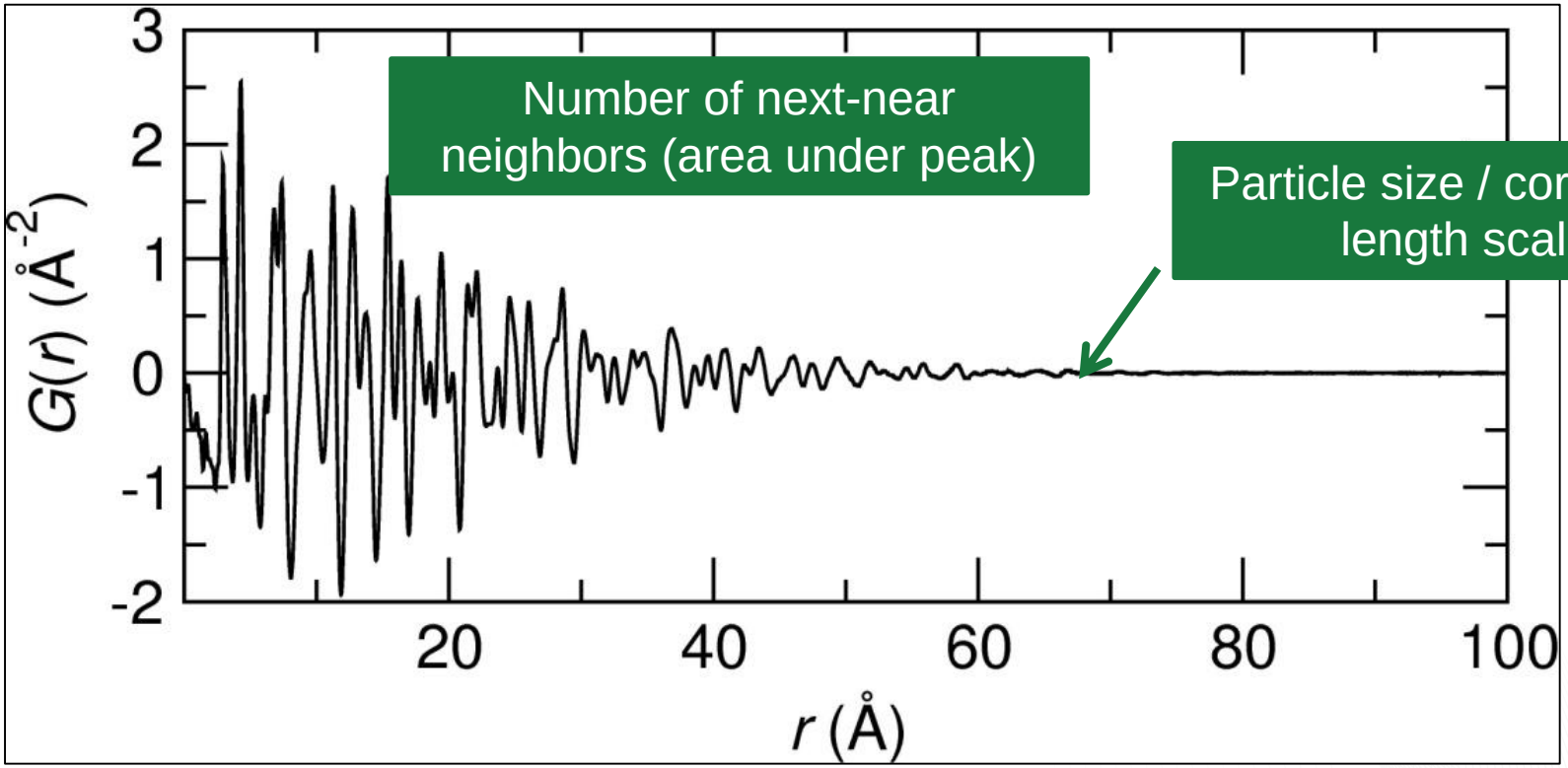
→*Experimental, ensemble, real-space, atom-atom histogram*





Pair Distribution Function

Inter-atomic distances

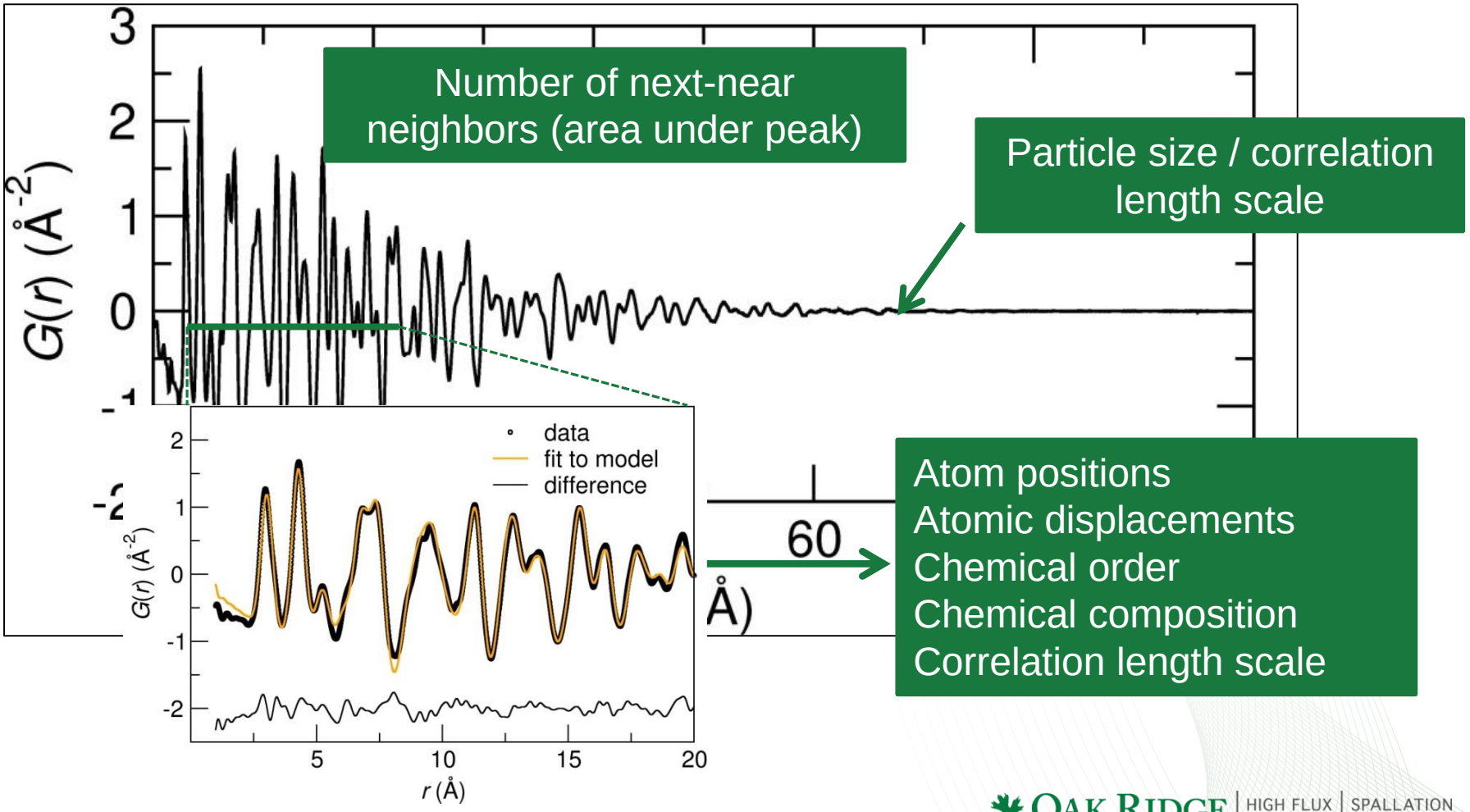


PDF analysis → Average and short-range structure for disordered crystalline materials, nanomaterials, and amorphous materials

Pair Distribution Function

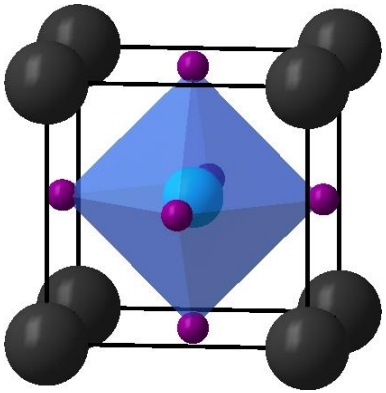
Quantitative analysis: fitting a model to the data over specific ranges

Inter-atomic distances



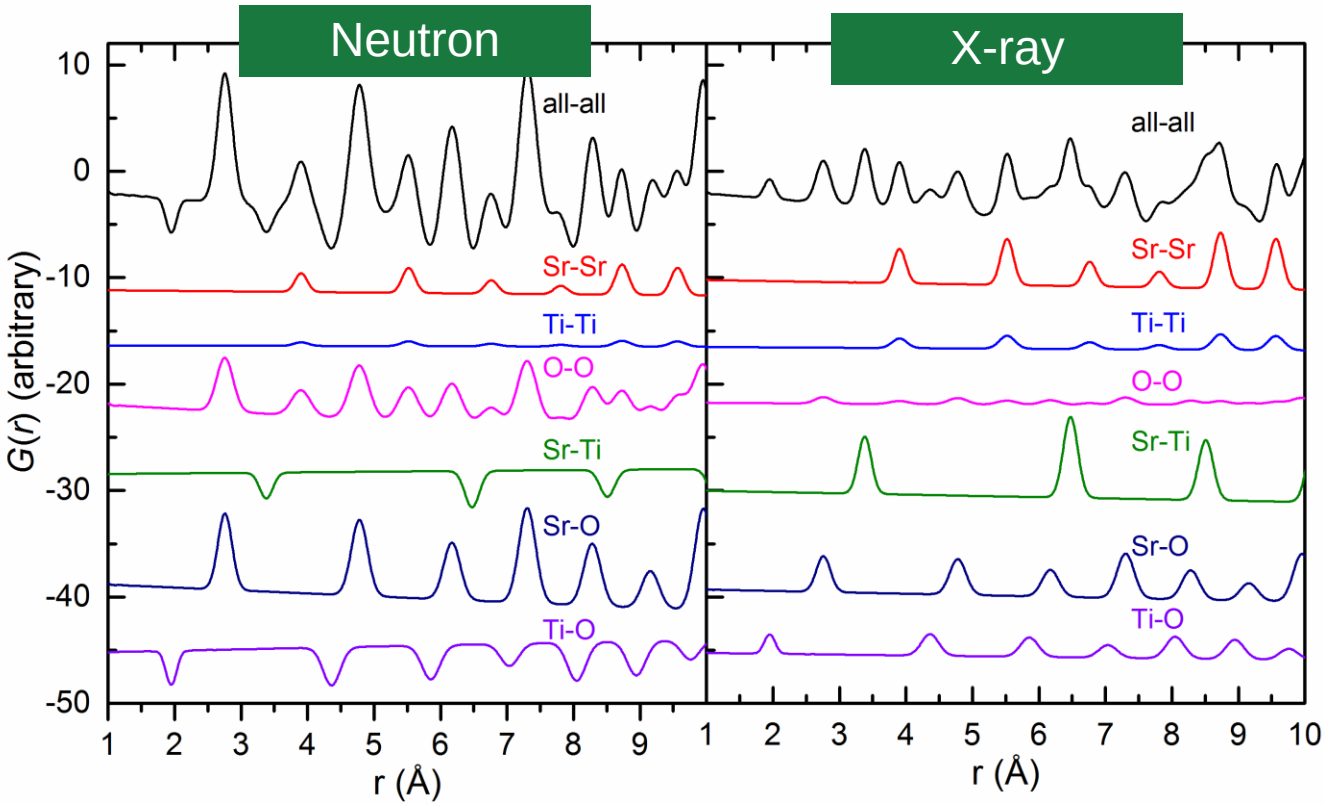
Atom positions
Atomic displacements
Chemical order
Chemical composition
Correlation length scale

Partial PDFs



$SrTiO_3$

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

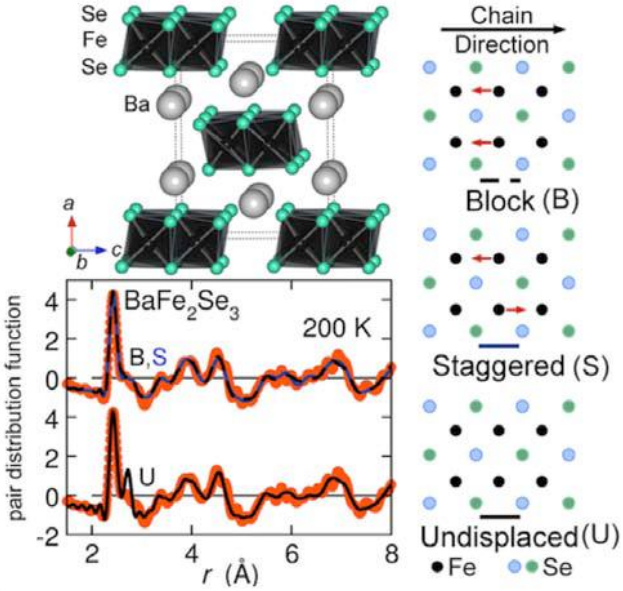


Neutron and x-ray PDFs are often highly complementary!

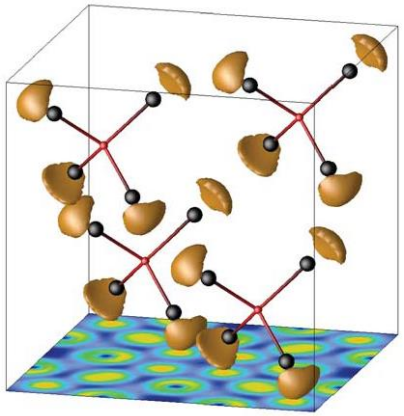
What types of studies can be done with the PDF technique?

Local distortions *via* PDF

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

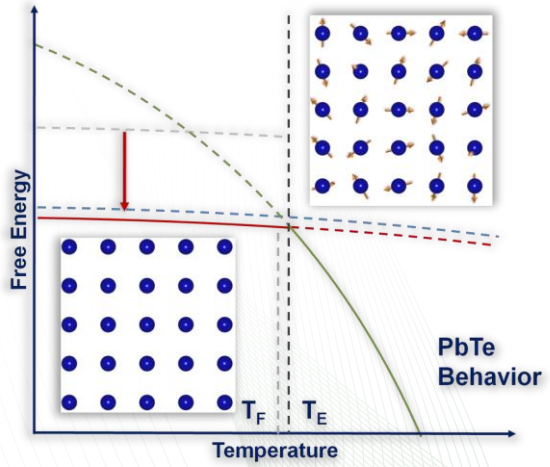


D. Louca, *et al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).



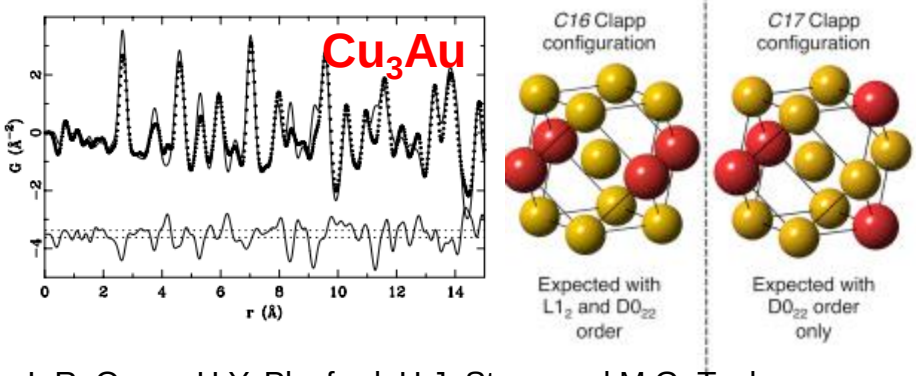
D. P. Shoemaker, *et al.*, Reverse Monte Carlo neutron scattering study of the 'ordered-ice' oxide pyrochlore $Pb_2Ru_2O_{6.5}$, *J. Phys.: Condens. Matter* **23** (2011).

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



Chemical Short Range order *via* PDF

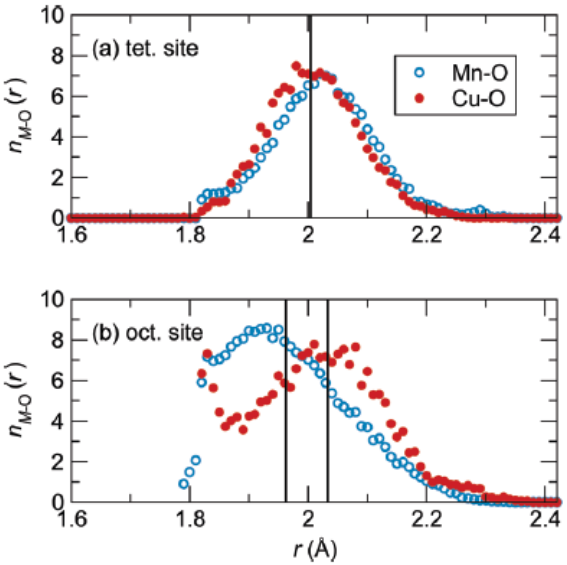
Th. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt, Chemical short range order obtained from the atomic pair distribution function, *Z. Kristallogr*. **217**, (2002) 47–50.

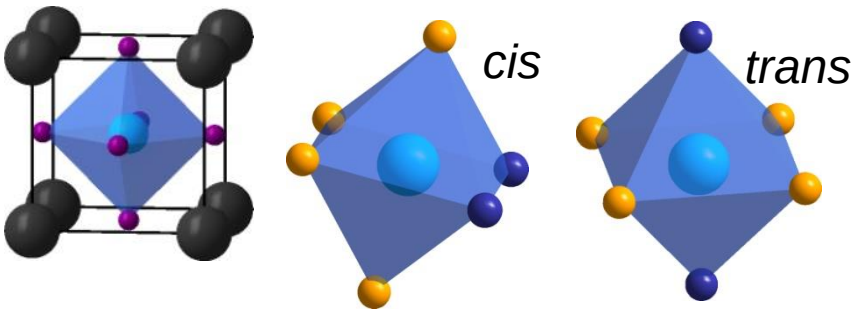


L.R. Owen, H.Y. Playford, H.J. Stone and M.G. Tucker, Analysis of short-range order in Cu_3Au using X-ray pair distribution functions. *Acta Materialia* (2017) 125, 15-26.

Substitution effects
Chemical clustering
Ion-specific local environments
Vacancy ordering

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).



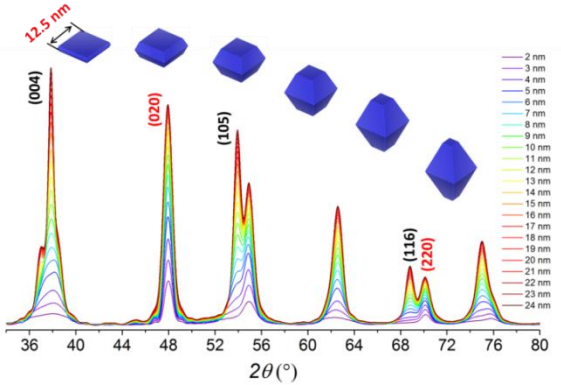


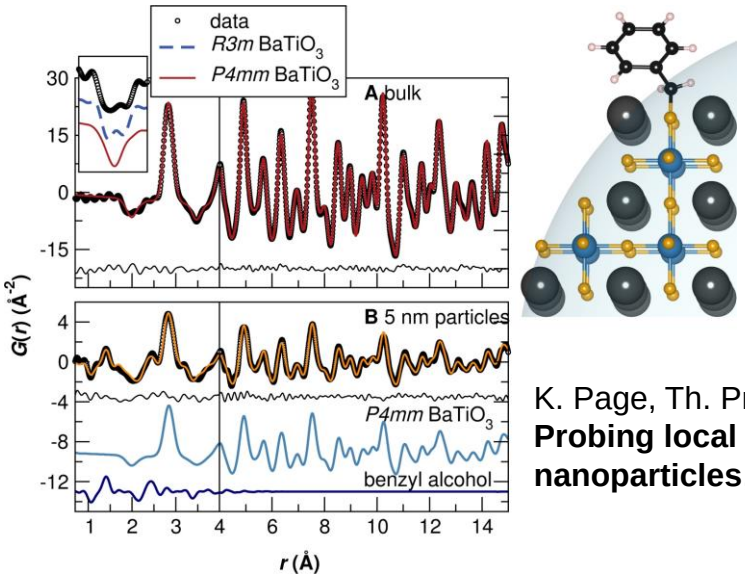
K. Page, *et al*., Local atomic ordering in $BaTaO_2N$ studied by neutron pair distribution function analysis and density functional theory, *Chem. Mater.* **19** (2007) 4037-4042.

Nanomaterial structure *via* PDF

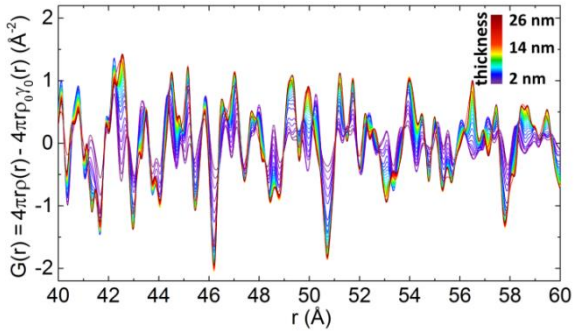
K. W. Chapman, P. J. Chupas, and T. M. Nenoff, **Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation**, *J. Am. Chem. Soc.* 132, 8897 (2010).

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





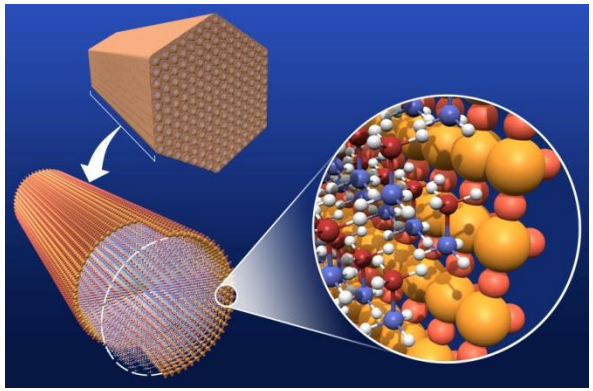
J. Liu et al, **Quantitative analysis of the morphology of {101} and {001} faceted anatase TiO_2 nanocrystals**, *Chem. Mater.* 29, 5591–5604 (2017).



K. Page, Th. Proffen, M. Niederberger, and R. Seshadri, **Probing local dipoles and ligand structure in $BaTiO_3$ nanoparticles**, *Chem. Mater*. 22 (2010), 43864391.

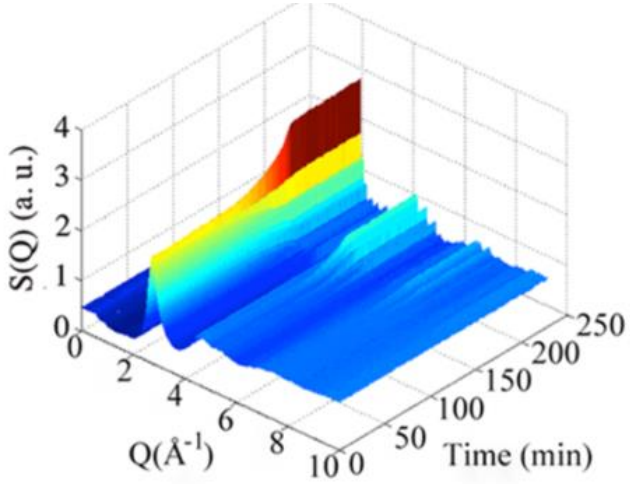
Amorphous structures *via* PDF

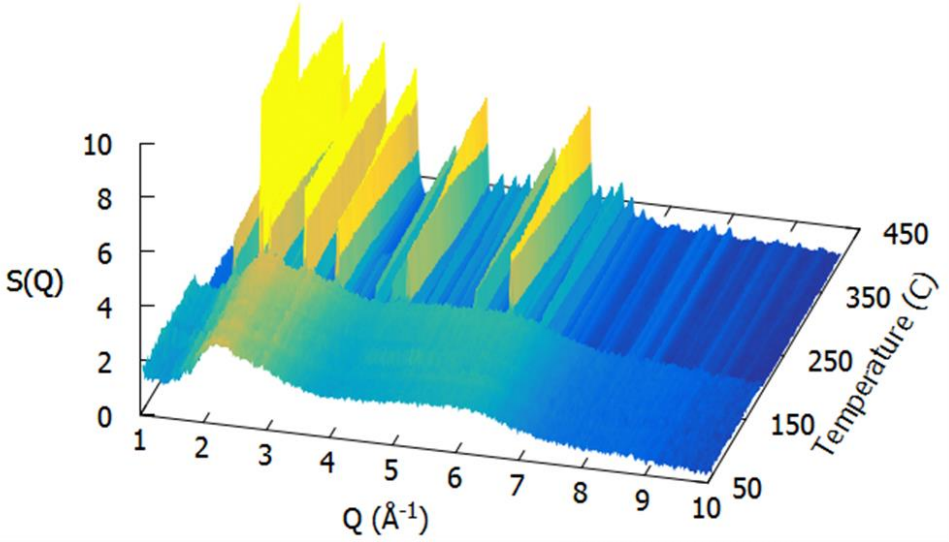
Glasses
Liquids
Concretes
Adsorbed gases
etc.



Kim, H.; Proffen, T.; Chupas, P. J.; Karkamkar, A.; Hess, N. J.; Autrey, T., **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.* **2009,** *131(38)* 13749-13755.

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 (2014) 201906.

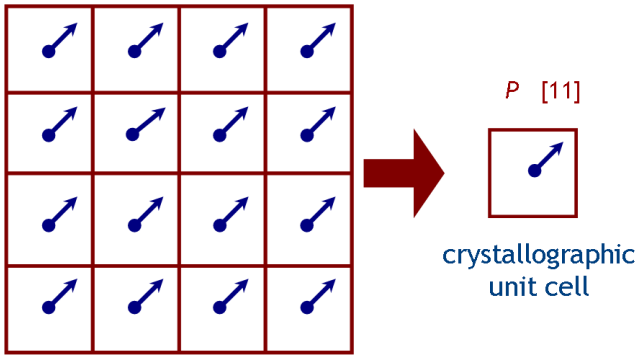


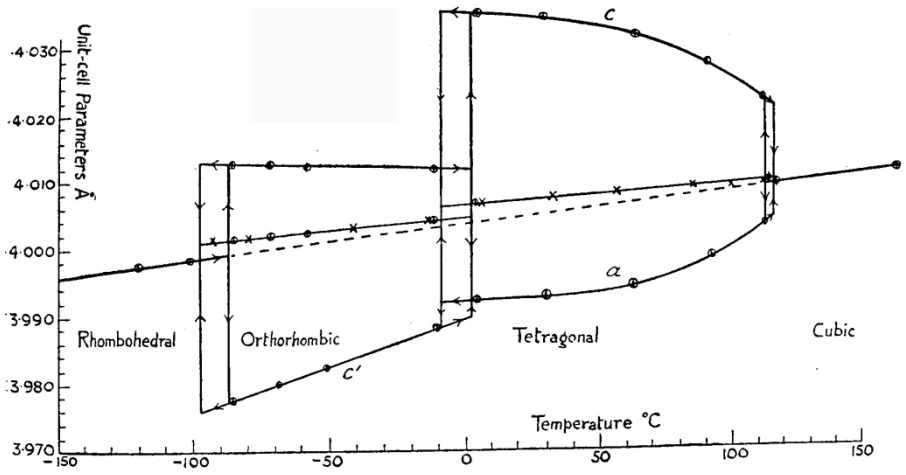


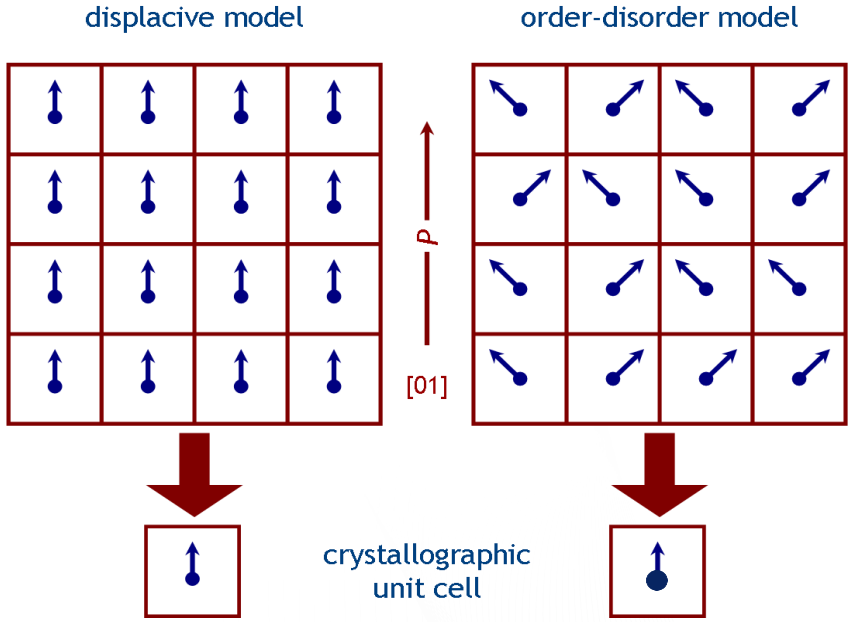
H.-W. Wang; L. L. Daemen, M. C. Cheshire, M. K. Kidder, A. G. Stack, L. F. Allard, J. Neuefeind, D. Olds, J. Liu, and K. Page, **Synthesis and structure of synthetically pure and deuterated amorphous (basic) calcium carbonates**, *Chem. Commun*., 53, 2942-2945 (2017).

Example: Local structure in $BaTiO_3$

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



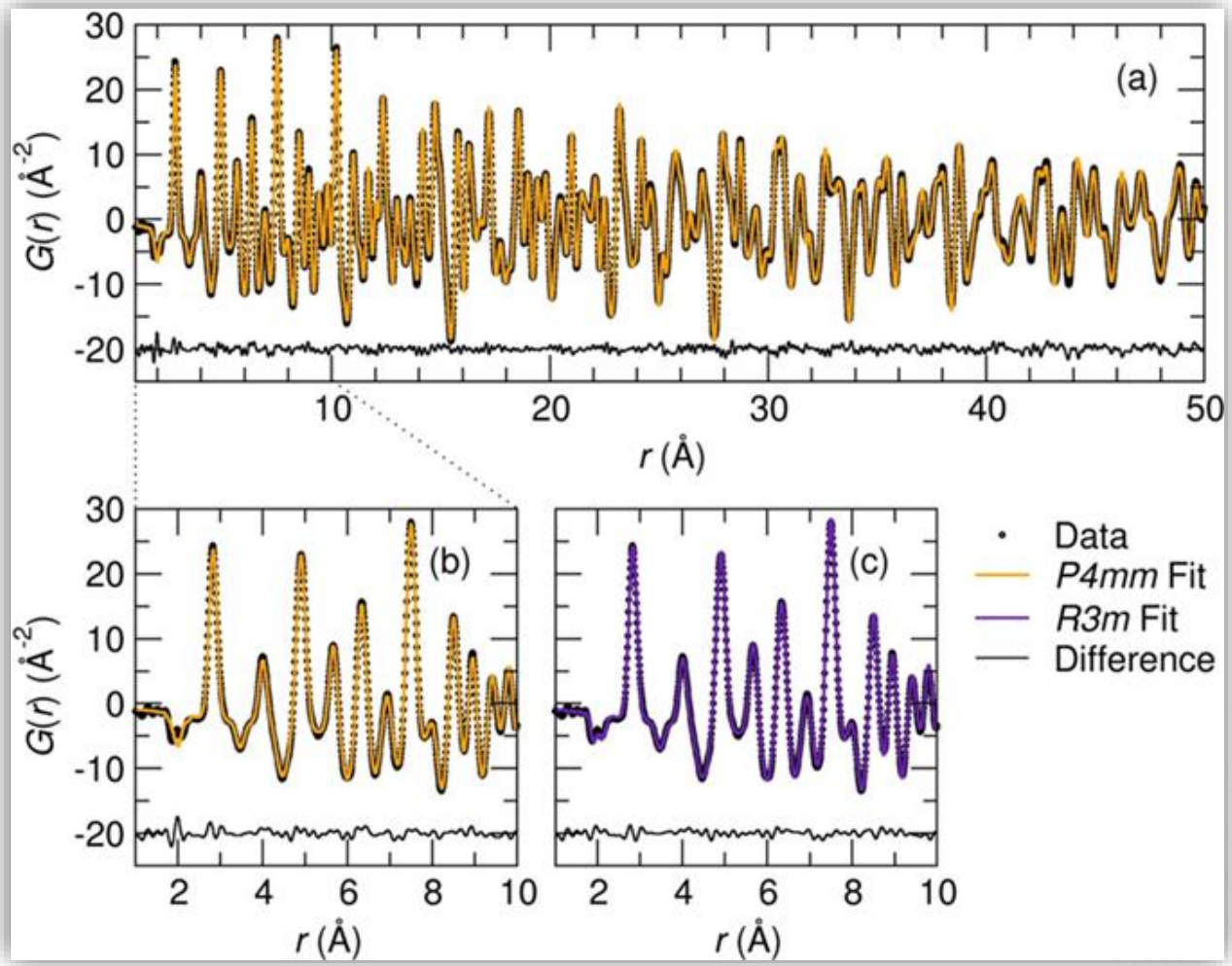


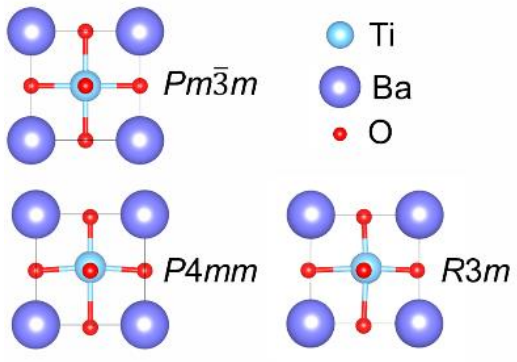


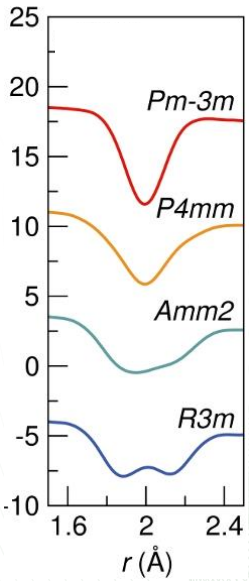
Displays order-disorder phenomena: room temperature local structure known to have rhombohedral pair-pair correlations

Example: Local structure in $BaTiO_3$

$BaTiO_3$: At room temperature, locally has a split (*R3m*) first Ti-O peak, displaying classic order-disorder behavior







K. Page, T. Kolodiazhnyi, T. Proffen, A. K. Cheetham, and R. Seshadri,, *Phys. Rev. Lett.* **101**, 205502 (2008).

Usher *et al.*, J. Appl. Phys. **120**, 184102 (2016)
Senn *et al.*, Phys. Rev. Lett. **116**, 207602 (2016)

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

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

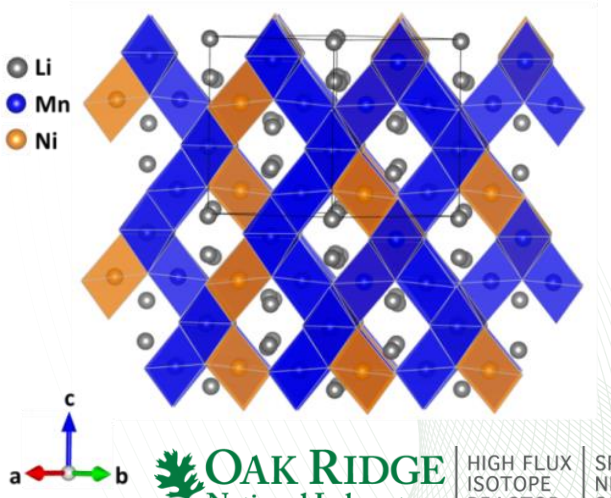
Two distinct polymorphs are known: Ni/Mn cation ordering strongly impacts electrochemical performance Idemoto *et al*., 2003; Zhong *et al*., 1997

(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

Nature of the cation ordering and detailed mechanisms are still debated

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



Example: High Voltage Spinel Cathode

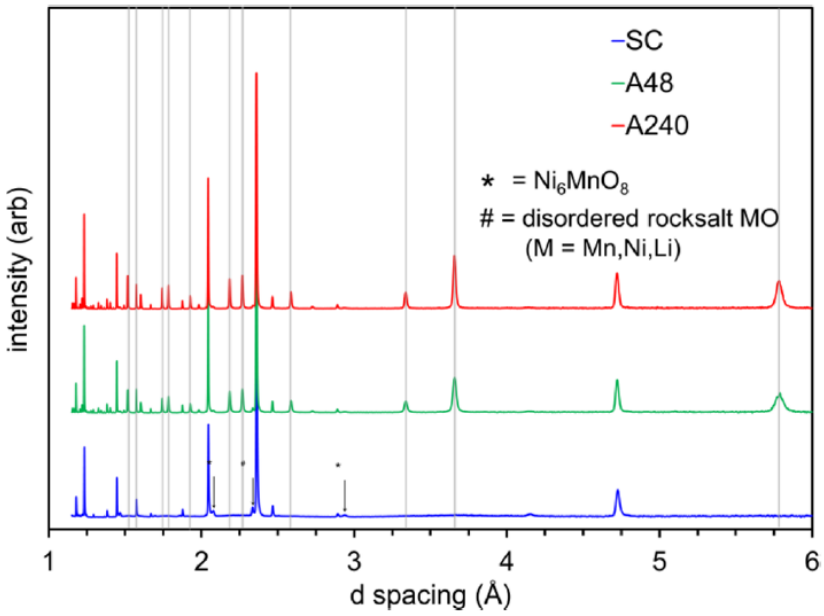
Cation ordering examined at the POWGEN Beamline, SNS

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



Ni/Mn ordering: large nuclear scattering length contrast between nickel (*b* = 10.3 fm) and manganese (*b* = -3.73 fm).

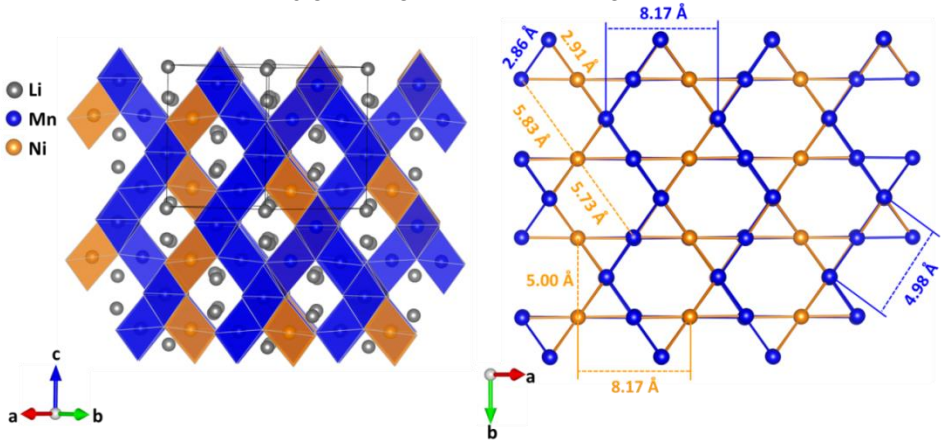
Moorhead-Rosenberg, Z., Huq, A., Goodenough, J. B. & Manthiram, A. **Electronic and Electrochemical Properties of Li1–xMn1.5Ni0.5O4 Spinel Cathodes As a Function of Lithium Content and Cation Ordering**, *Chem. Mater.* 27, 6934-6945, 2015.

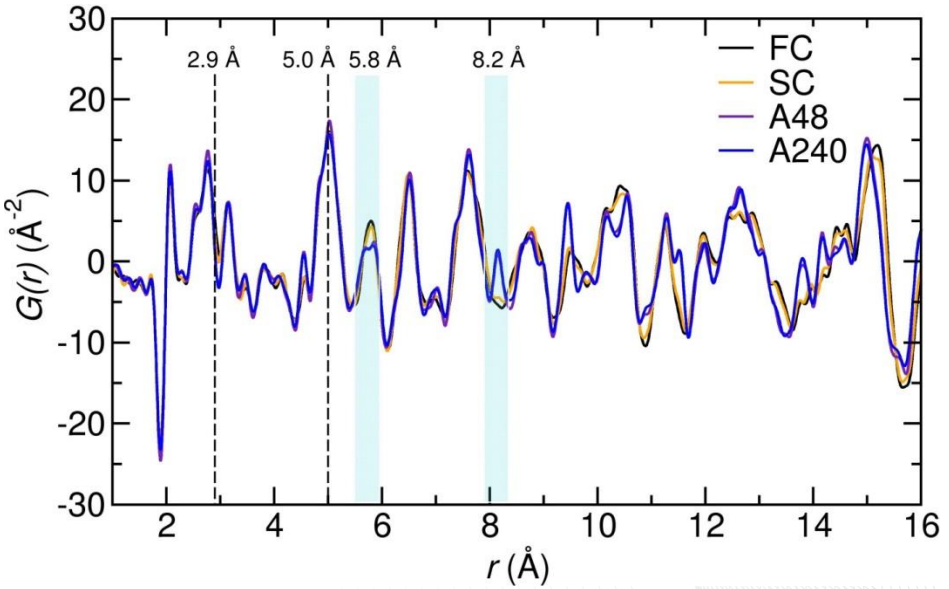
We can tell a lot by *looking* at PDF data

- 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 samples are very distinct

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.

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

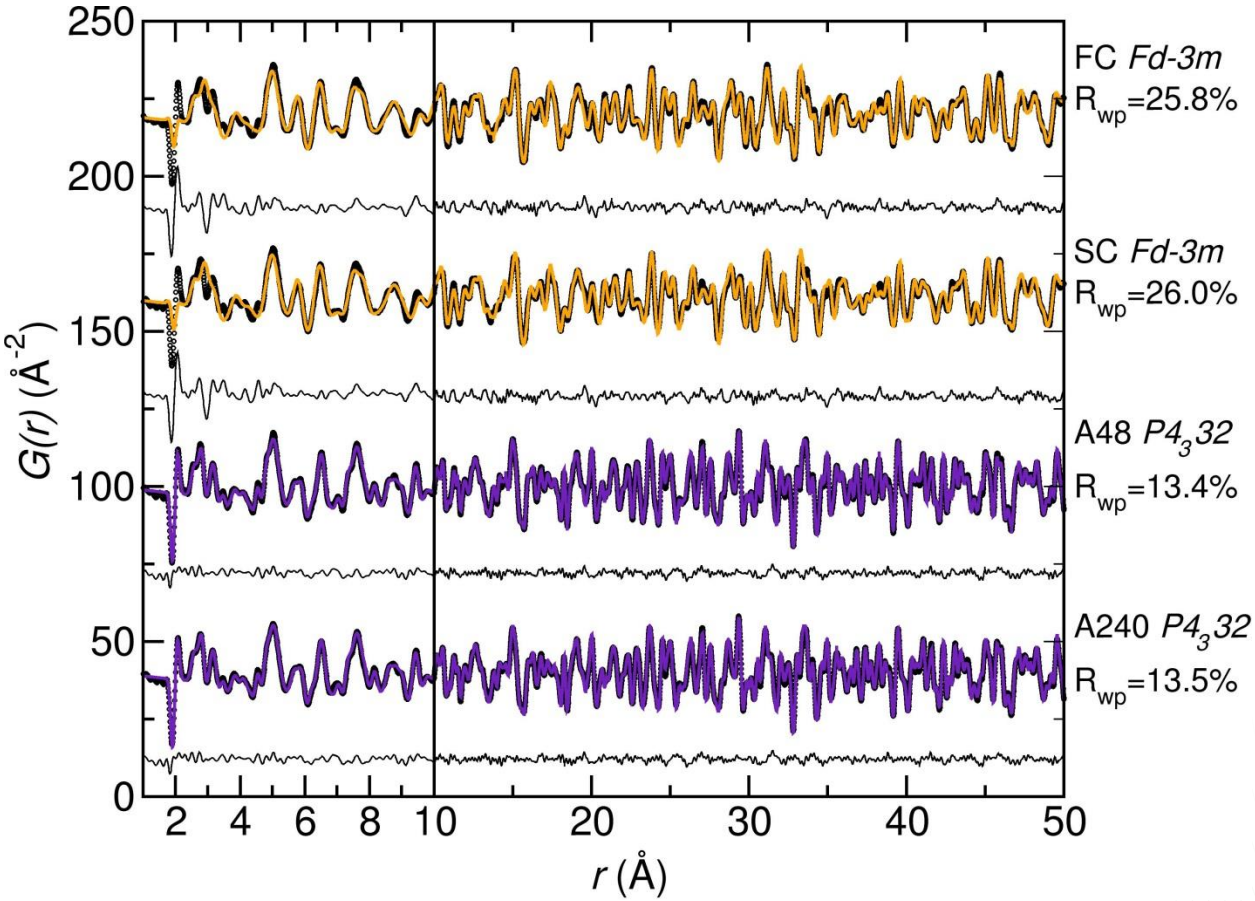




POWGEN: 3 hours per frame, *Q*-range: 1 – 30 $Å^{-1}$

Example: High Voltage Spinel Cathode

Modeling the local structure with average structure models determined from Rietveld refinement

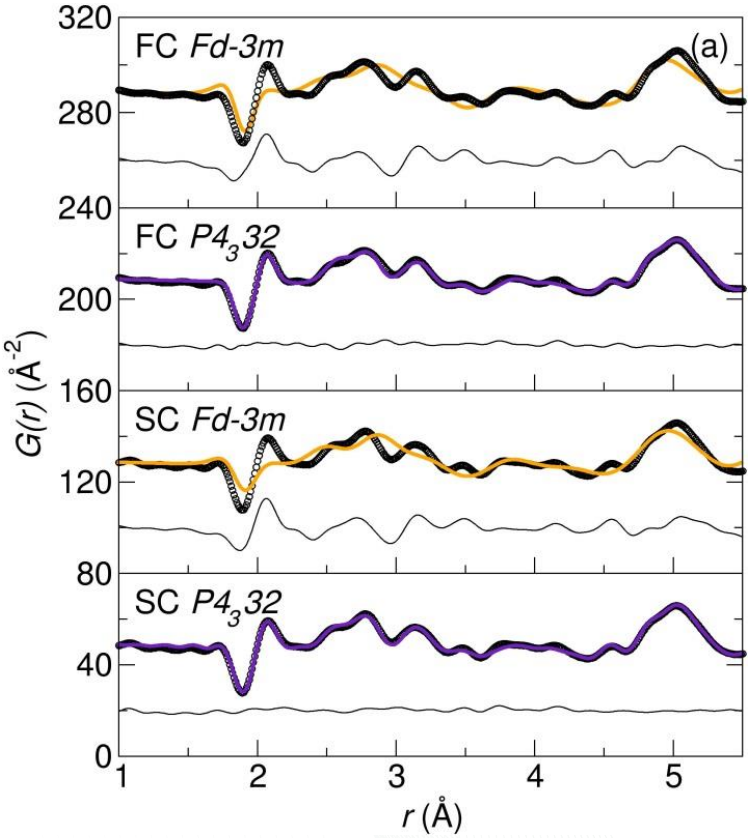


- First 10 Å of non-annealed sample data (FC and SC) differ *strongly* from long-range crystallographic structures
- Local atomic structure of annealed samples (A48 and A240) are well-described by the long-range crystallographic structures

Example: High Voltage Spinel Cathode

Modeling the local structure with alternate models

- Least squares refinements of the ordered structure model ($P4_332$) 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 ($P4_332$) 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?**



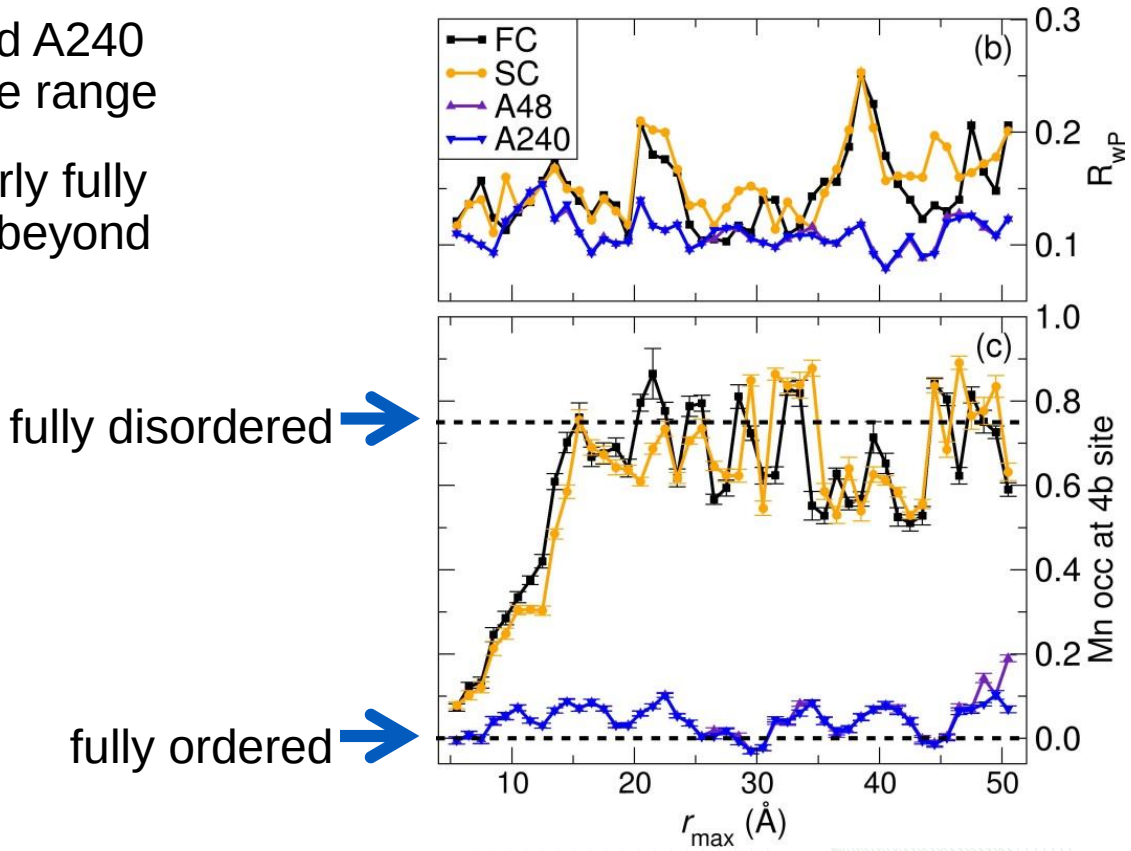
J. Liu, A. Huq, Z. Moorhead-Rosenberg, A. Manthiram, and K. Page, **Nanoscale Ni/Mn ordering in the high voltage spinel cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials*, 28, 19, 6817–6821, 2016.

Example: High Voltage Spinel Cathode

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

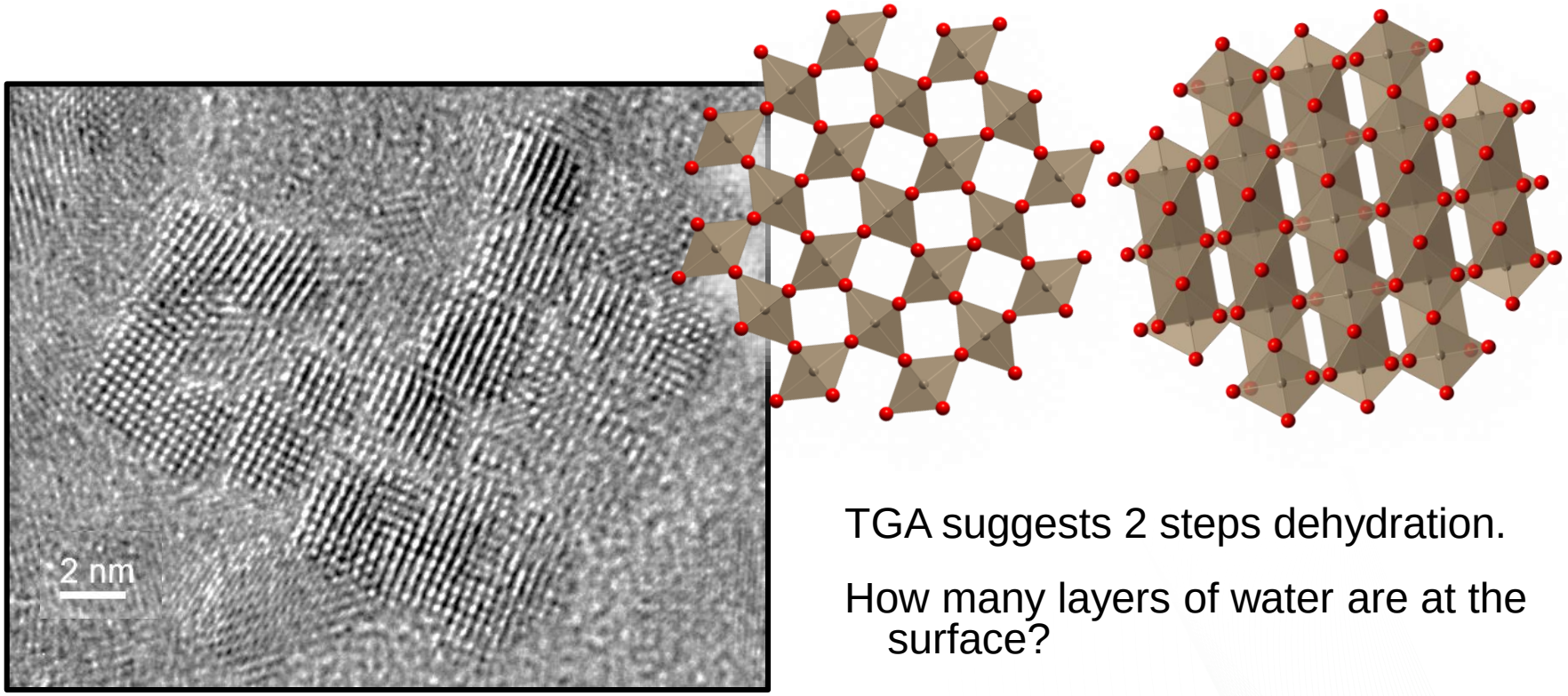
- 5% site mixing in the A48 and A240 patterns throughout the entire range
- FC and SC samples are nearly fully disordered at pair distances beyond 15.5 Å

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



Example: SnO_2 Nanocrystals

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



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?

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.

Example: SnO_2 Nanocrystals

In situ Dehydration at NOMAD, SNS

Starting with full coverage

- Blue lines:

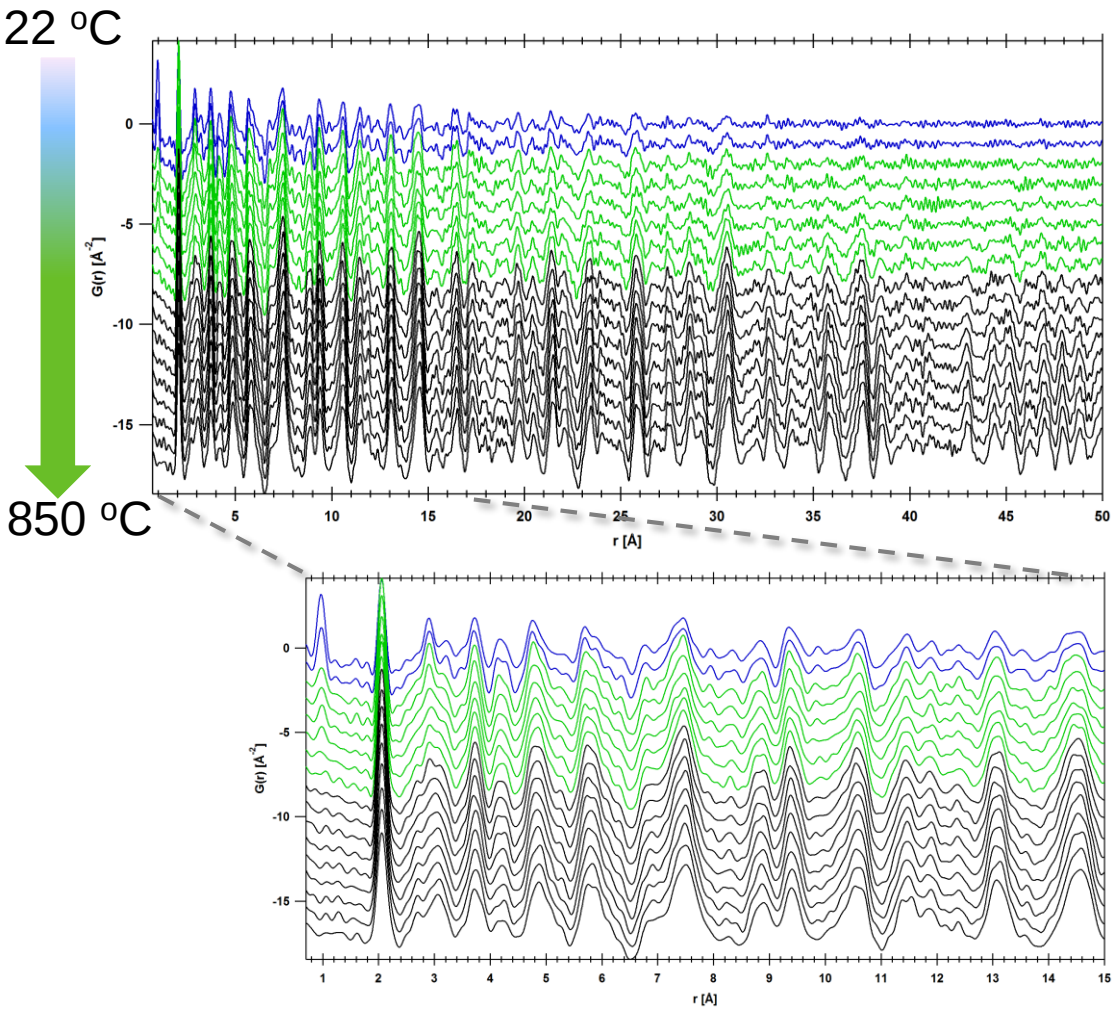
  22 and 50 ºC - $L_1 + L_2 + L_3$

- Green lines:

  50 to 350 ºC (with 50 ºC increments) - $L_1 + L_2$

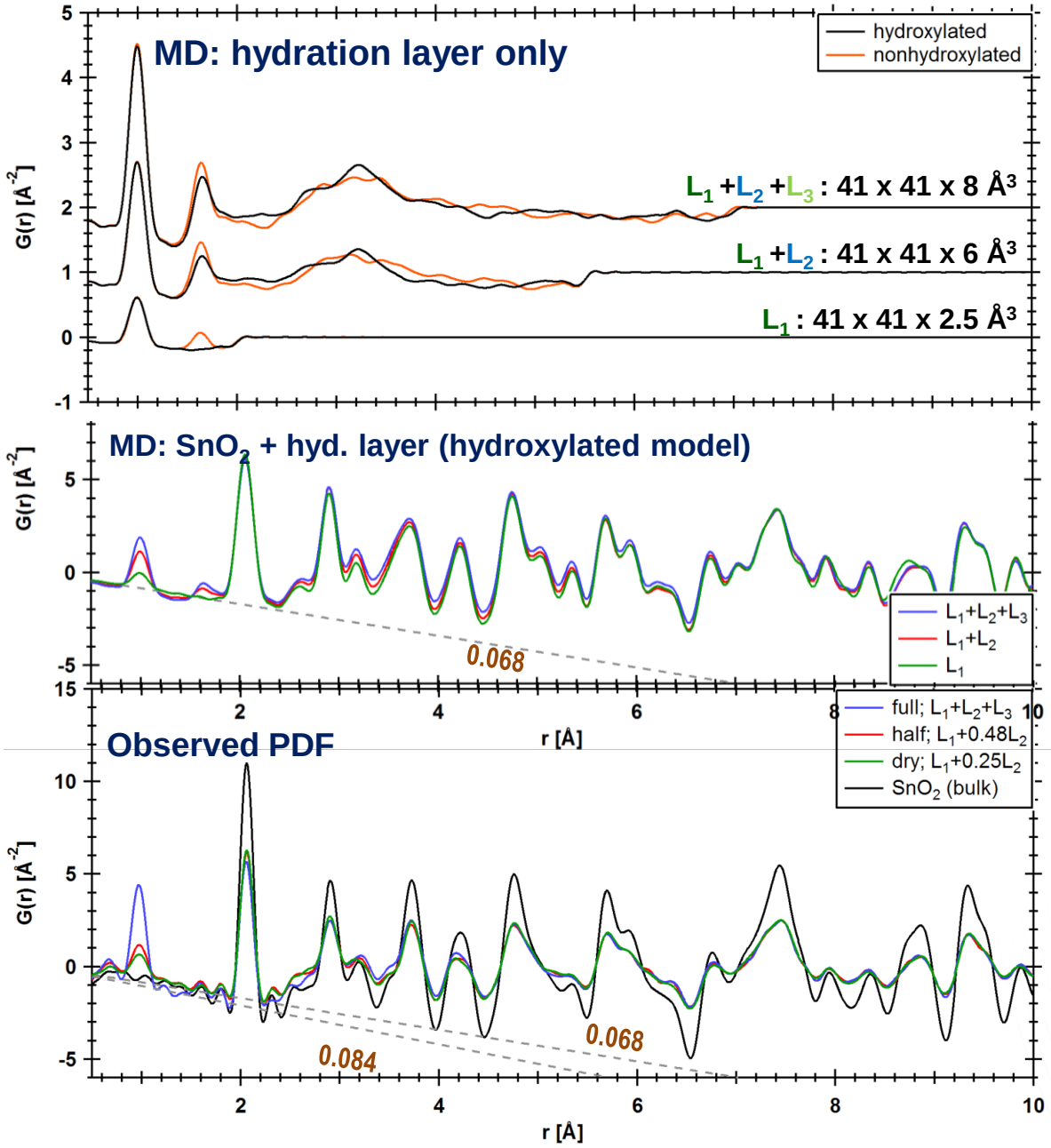
- Black lines:

  400 to 850 ºC (with 50 ºC increments) – SnO_2 grain growth



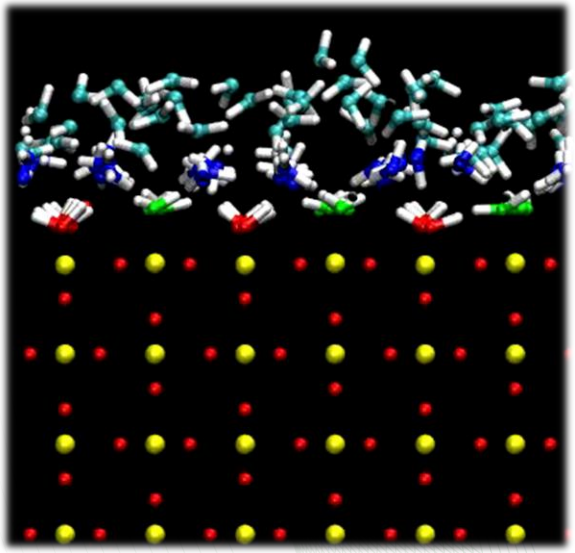
H.W. Wang, et al, *J. Am. Chem. Soc.*, 2013, 135 , 6885–6895.

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



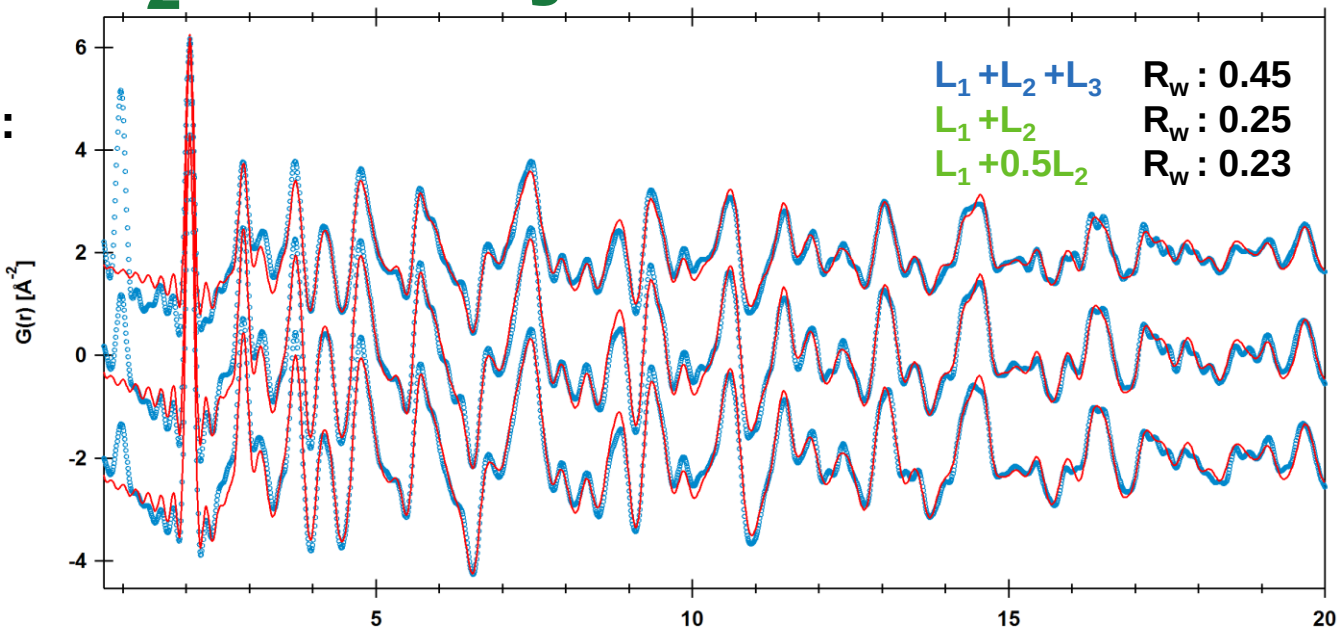
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

size = ~47 Å

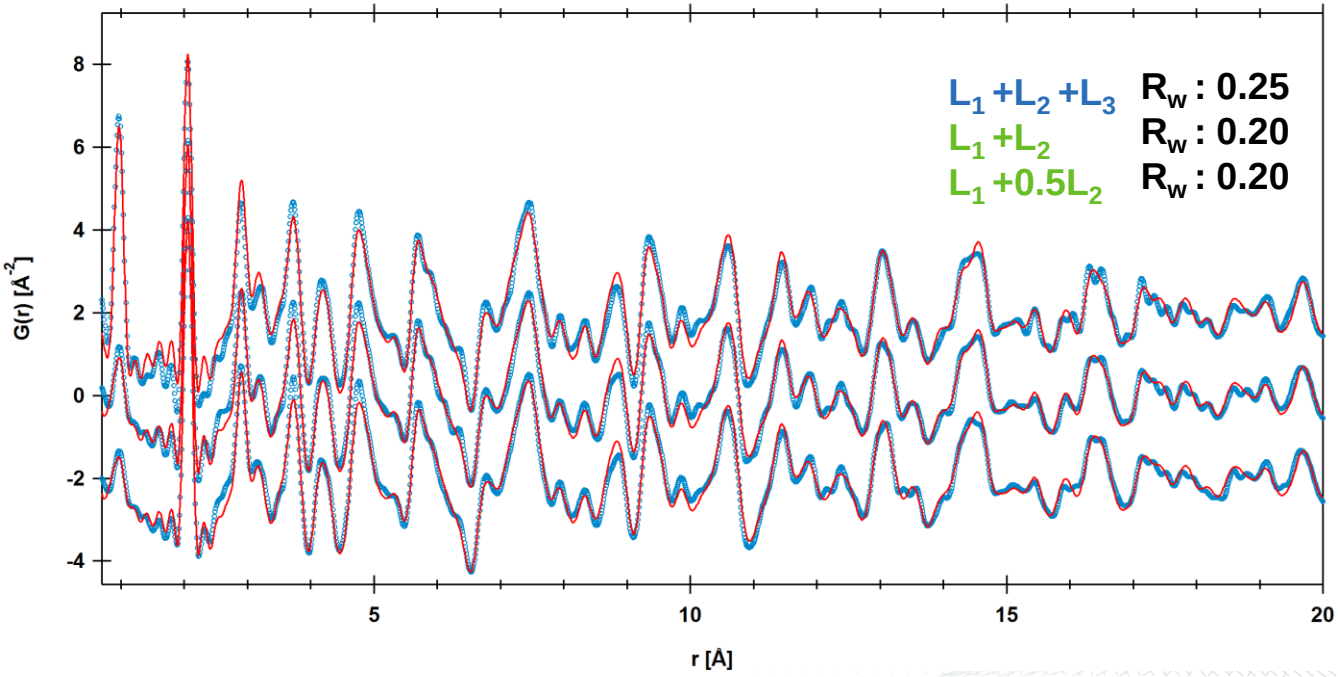


Two phase model:

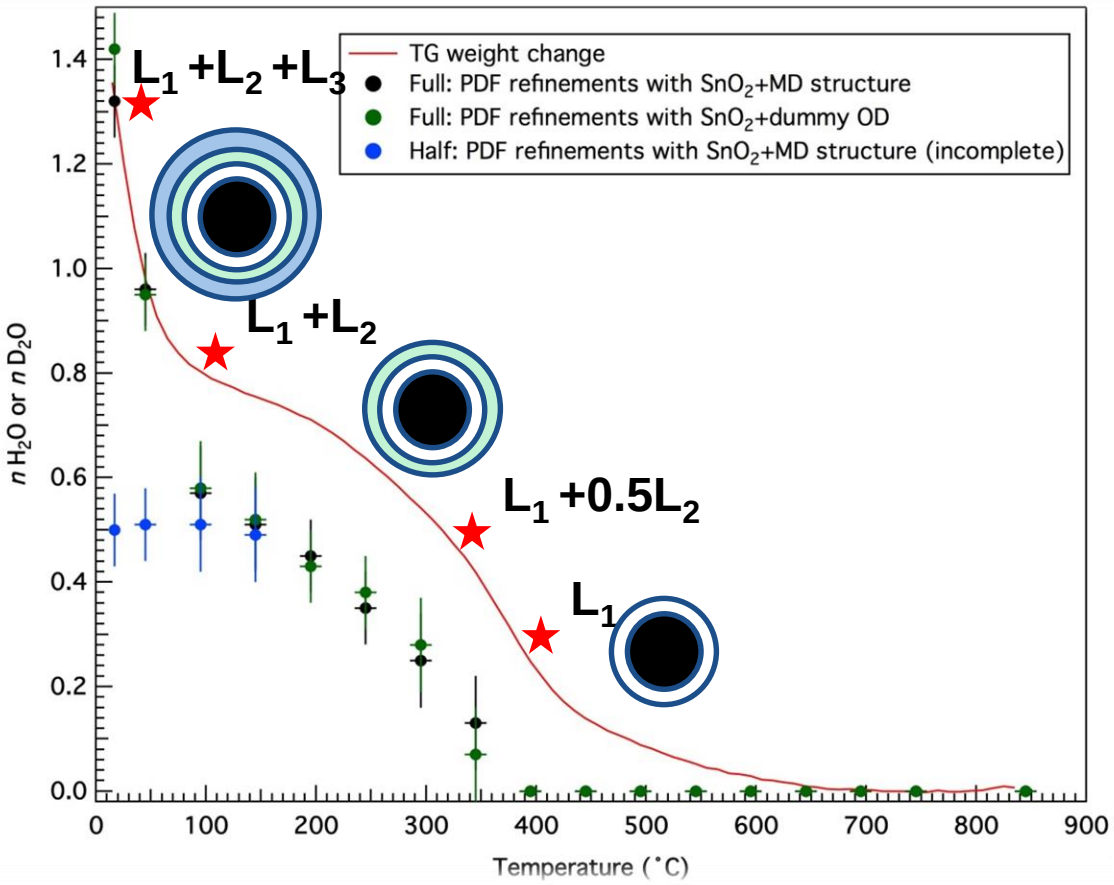
SnO_2 bulk +

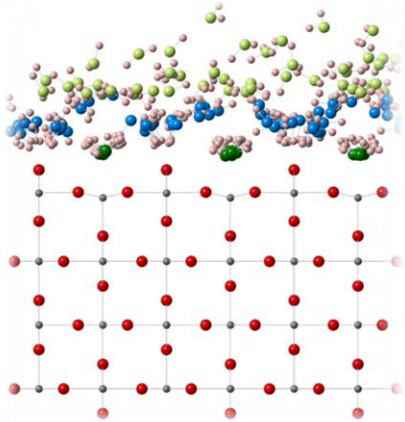
layered MD water

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.

A Few Experimental Considerations

OAK RIDGE National Laboratory

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)

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

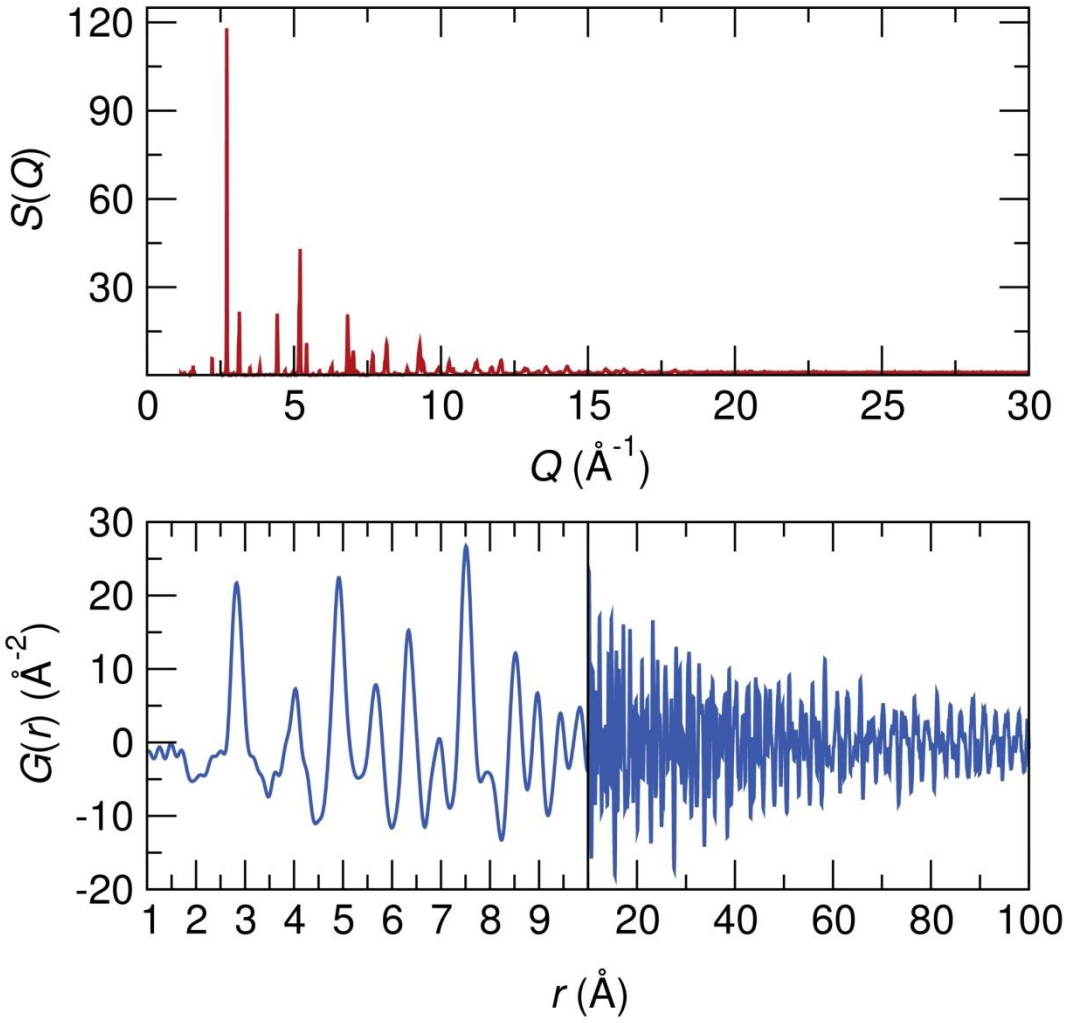
Corrected for: Container & background scattering, self-absorption, *etc.*
Normalized by: Incident flux, number of atoms, square of the scattering length/form factor

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: $S(Q)$

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

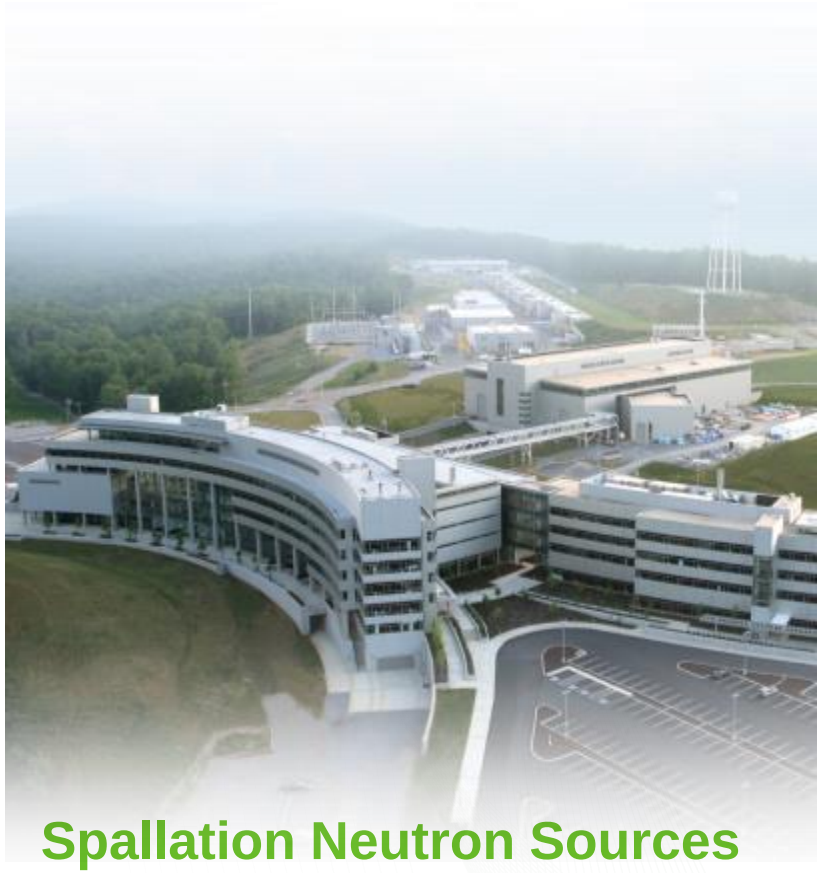
(4) Low (and stable) instrument background

An ideal measurement would have no contribution from the instrument resolution

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

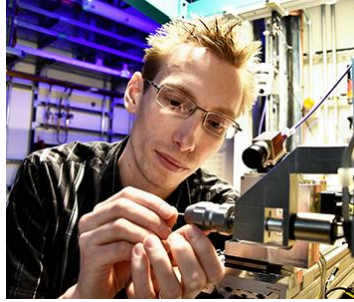
Synchrotron sources
(high energy X-rays)

or



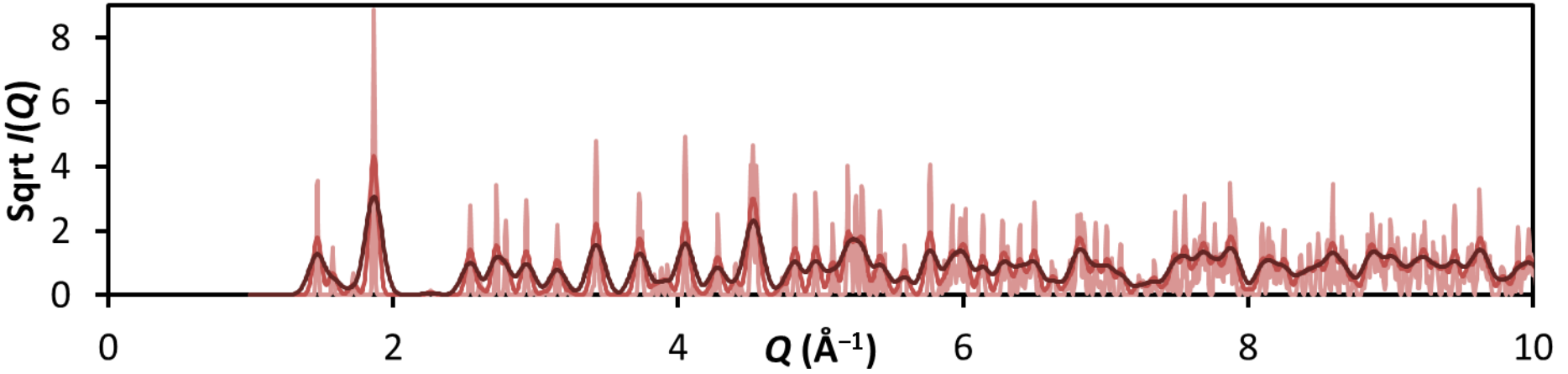
Spallation Neutron Sources
(reactor neutron energies are too low)

Resolution Effect

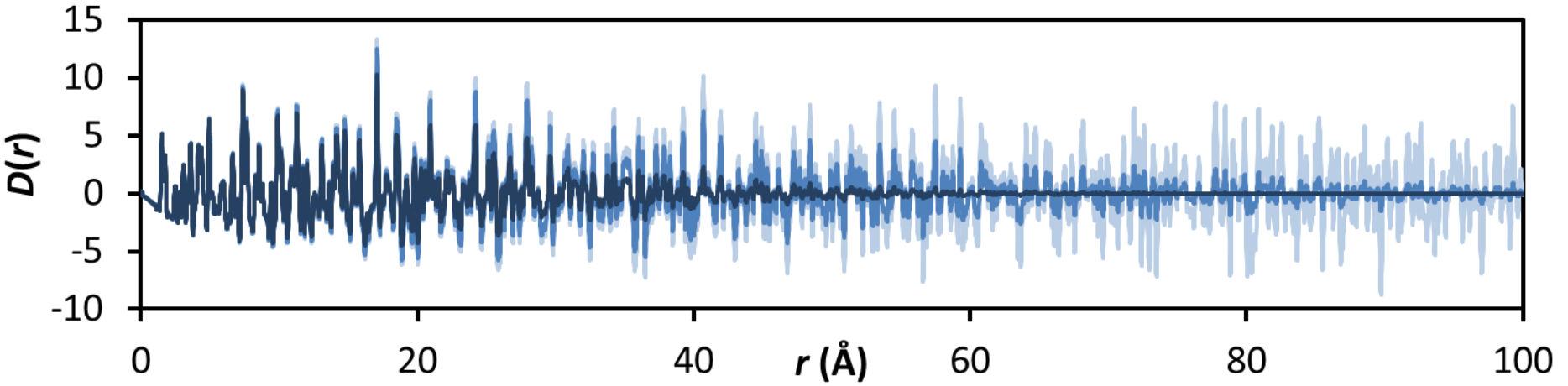


Courtesy of Phil Chater, Diamond Light Source

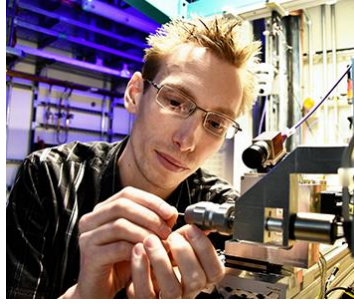
Reciprocal space: Peak width, *dQ*



Real space: Damping with *r*



Q_{max} Effect

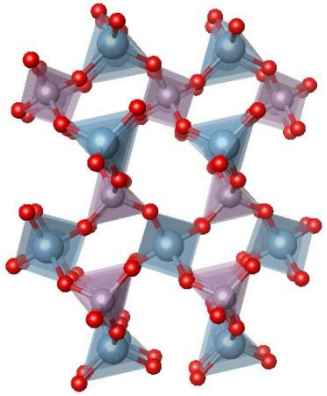


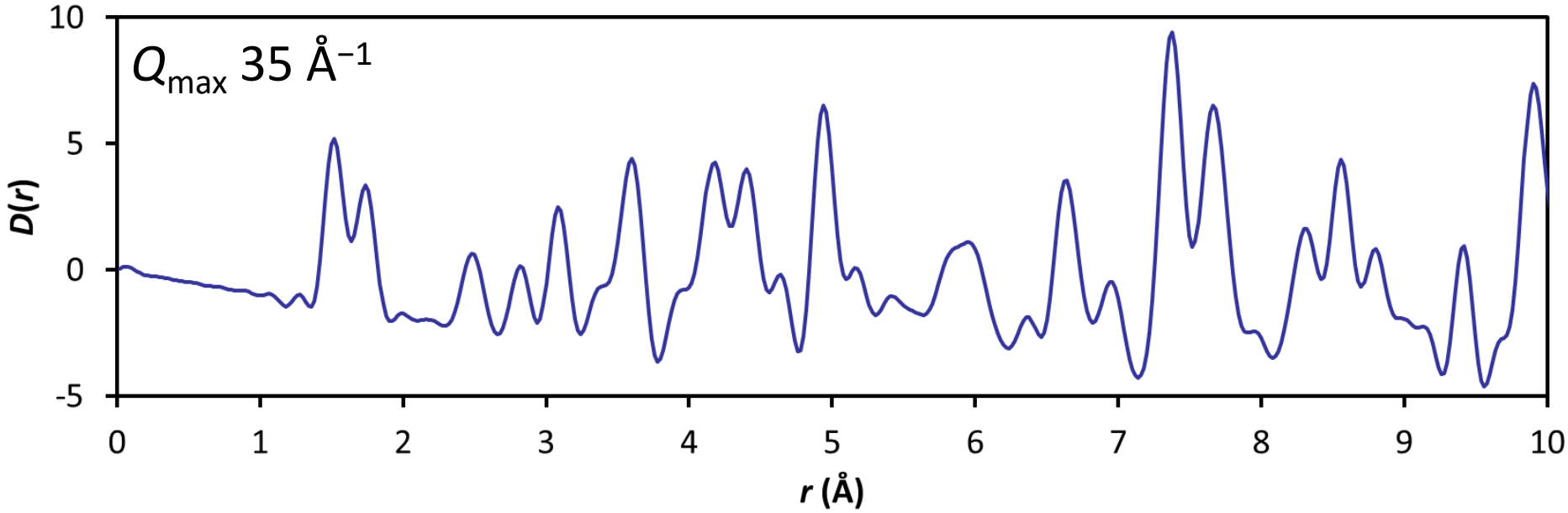
Courtesy of Phil Chater, Diamond Light Source

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

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

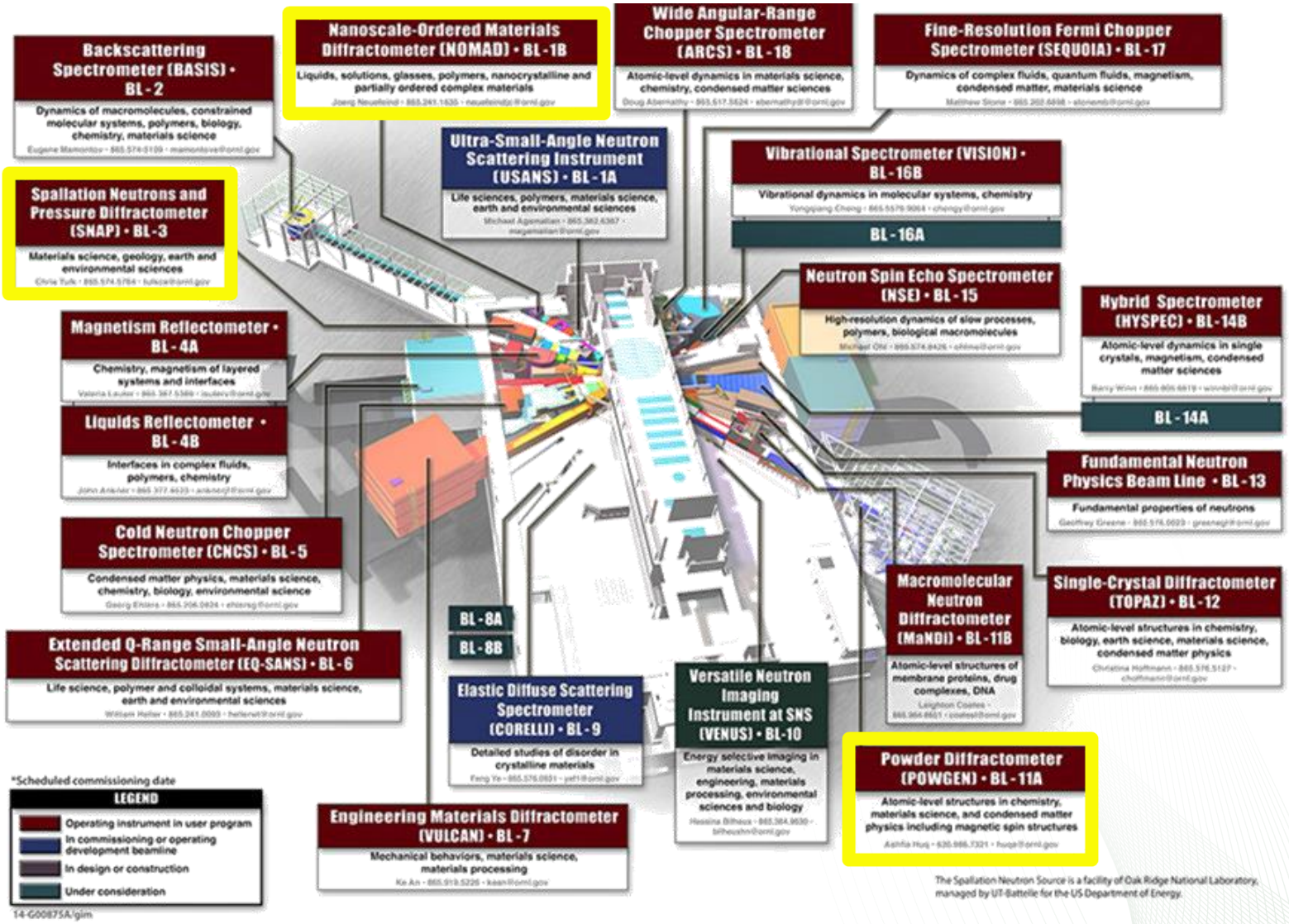
$AlPO_4$





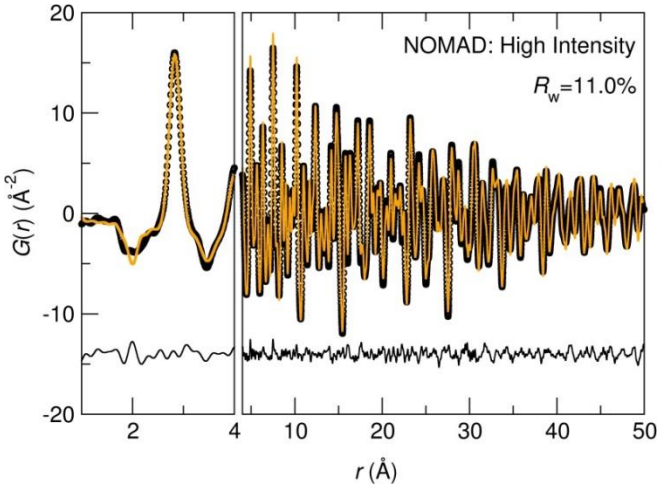
B. H. Toby and T. Egami, *Acta Cryst. A*, **48** (1992) 336

Instruments at SNS for PDF studies

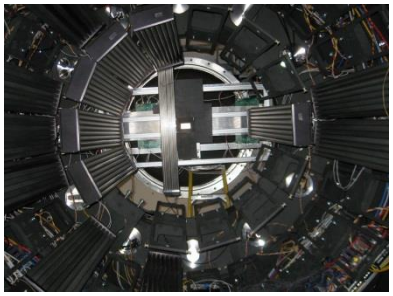


Total Scattering at the SNS

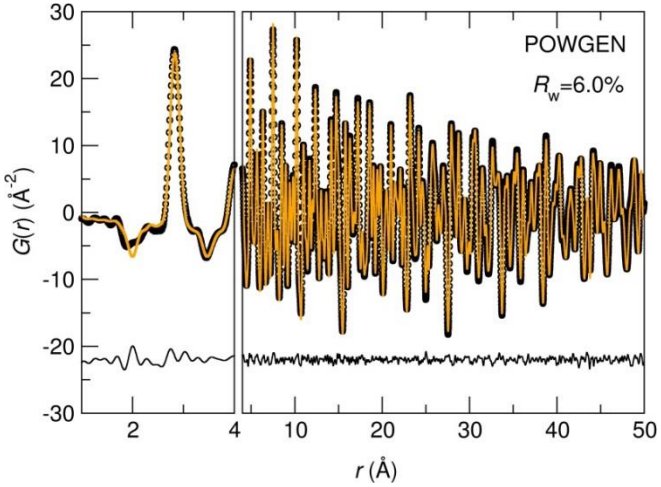
Pair Distribution Function (PDF) methods follow local atomic bonding configurations, intermediate structure, and correlation length scale- *regardless of a material's long range structure*



NOMAD data collected on **100 mg** of sample in a 3 mm quartz capillary in **3 hours**.



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



POWGEN data collected on **10 g** of sample in a 10 mm vanadium canister in **12 hours**.

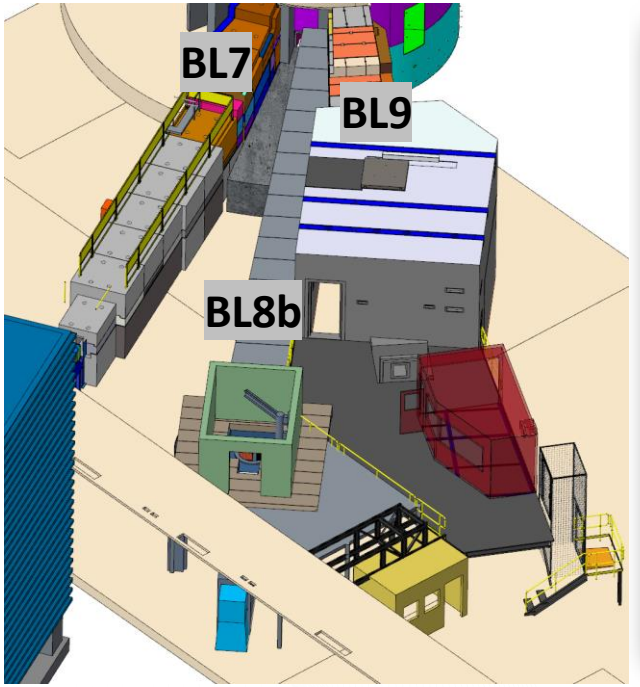
high resolution *diffraction and PDF of crystalline materials*

DISCOVER: Proposed Instrument for Diffraction and PDF, BL-8b

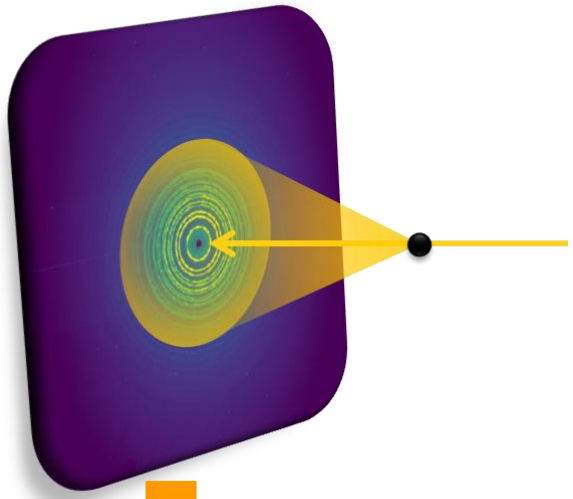
Materials Discovery

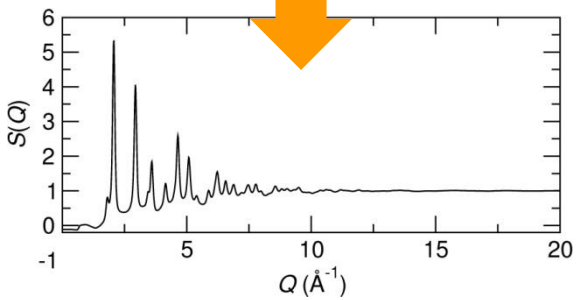
Understand the critical roles of heterogeneity, interfaces, and disorder

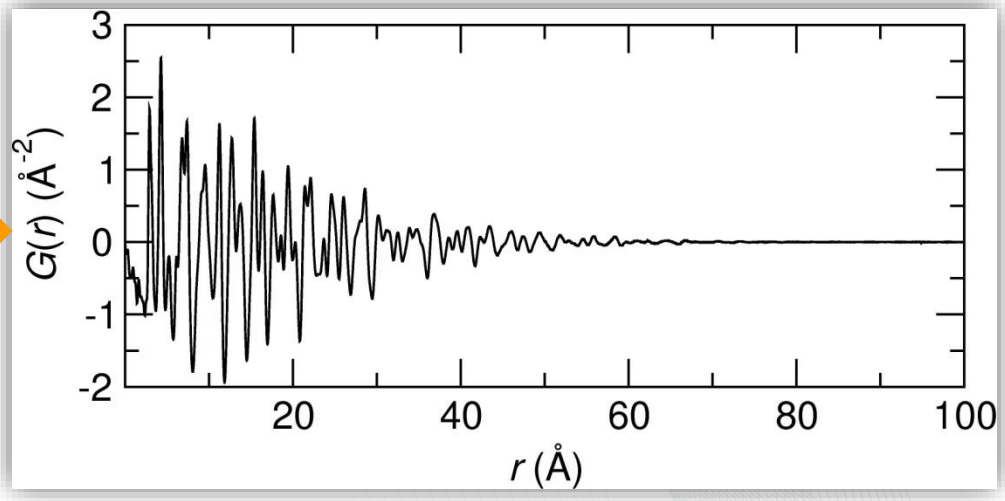
- What is the connection between global symmetry (i.e. that found over long length-scales) and local symmetry (i.e. that found at the atomic scale)?
- How does order evolve from the atomic to macroscale?
- Why does order evolve, and how can we control it?



Synchrotron Total Scattering: 2D Amorphous Si Detector





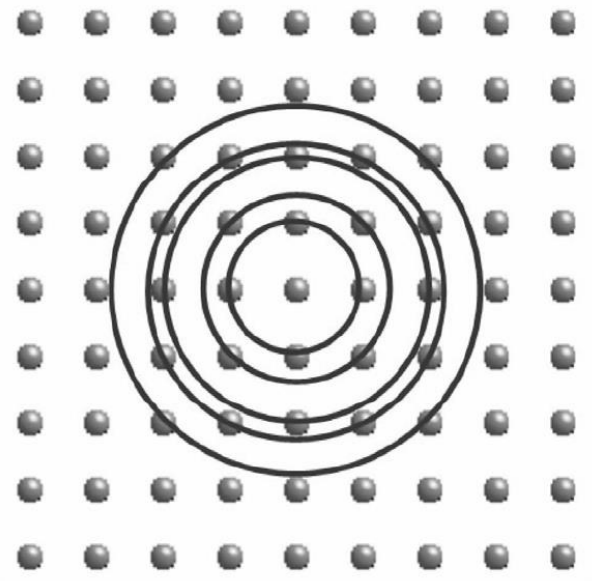


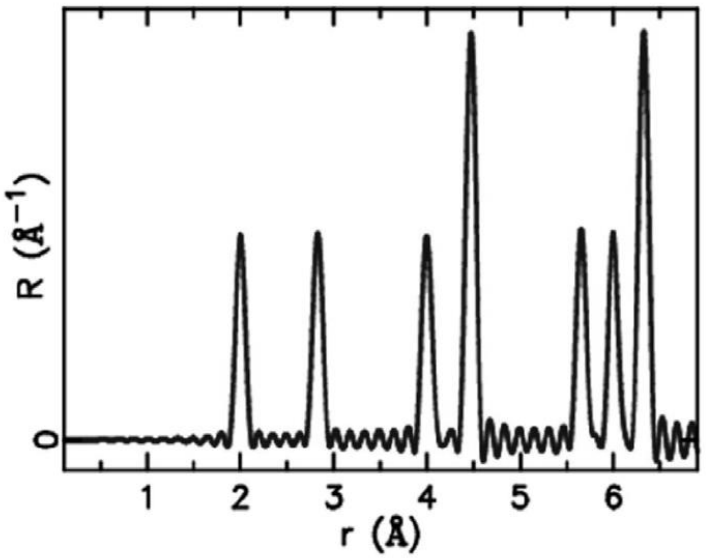
P. J. Chupas, K. W. Chapman, P. L. Lee, **Applications of an amorphous silicon-based area detector for high resolution, high sensitivity and fast time-resolved pair distribution function measurements**, *J. Appl. Crystallogr*. 40, 463, 2007. http://dx.doi.org/10.1107/S0021889807007856

Modeling a PDF

Pair Distribution Function

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





Atomic PDF (PDFFIT notation):

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

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

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

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

distance between i and j atoms

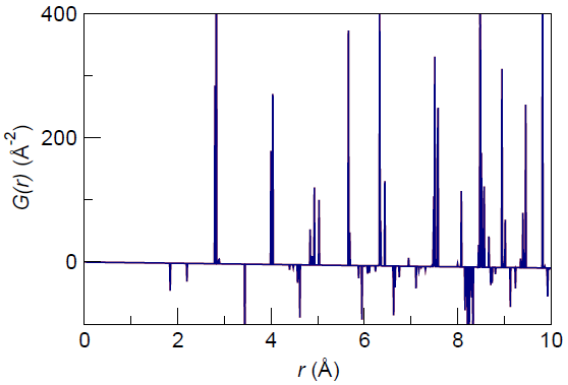
average density

sum over all atoms

Calculating a PDF from a Model

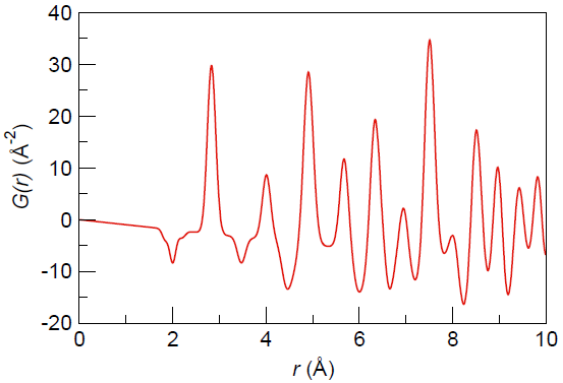
Calculating a PDF from an atomistic model:

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



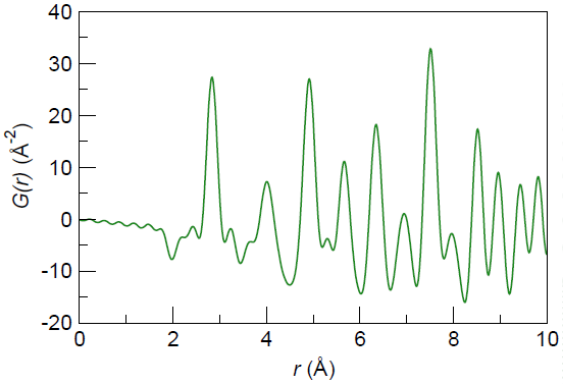
Peak Width

- 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
- …



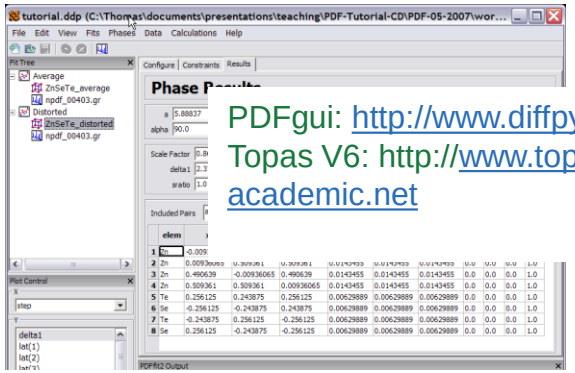
Atomic PDF Modeling

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

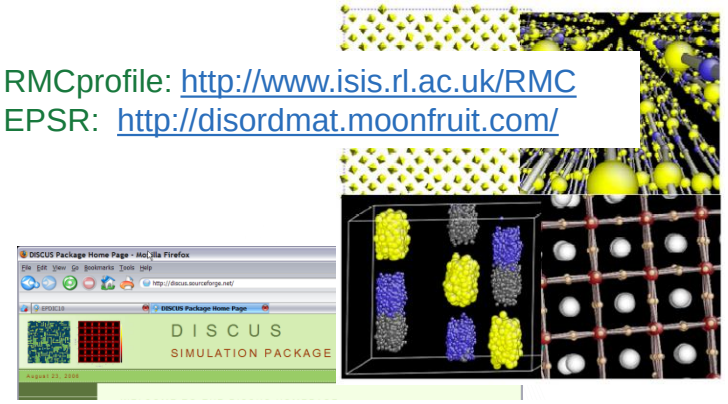
Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q), G(r)* , Bragg profile
Constraints utilized
Static 3-D model of the structure (a snap-shot)

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

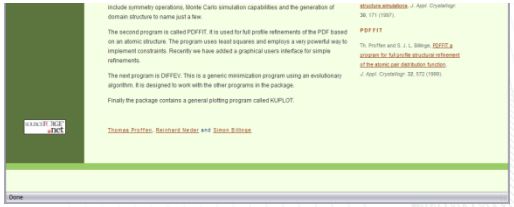


PDFgui: http://www.diffpy.org/
Topas V6: http://www.topas-academic.net

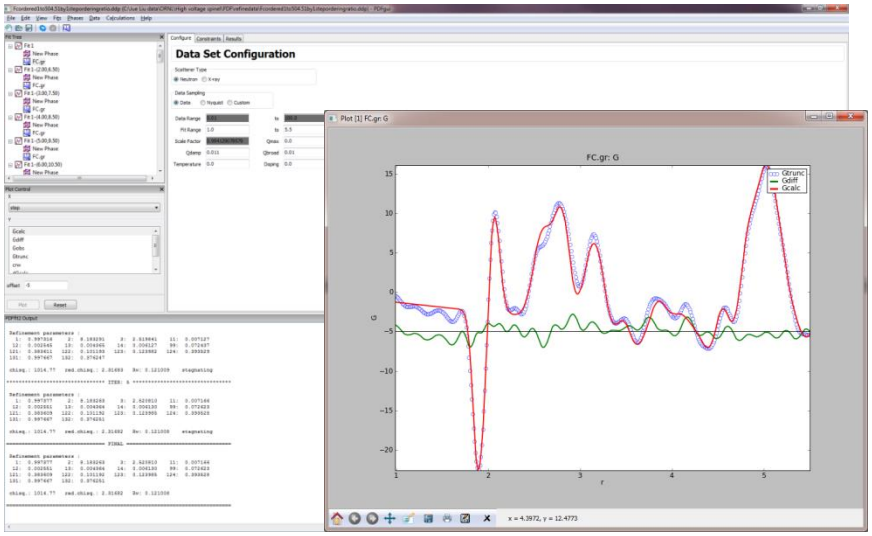


RMCprofile: http://www.isis.rl.ac.uk/RMC
EPSR: http://disordmat.moonfruit.com/

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



Small Box: Software Comparison

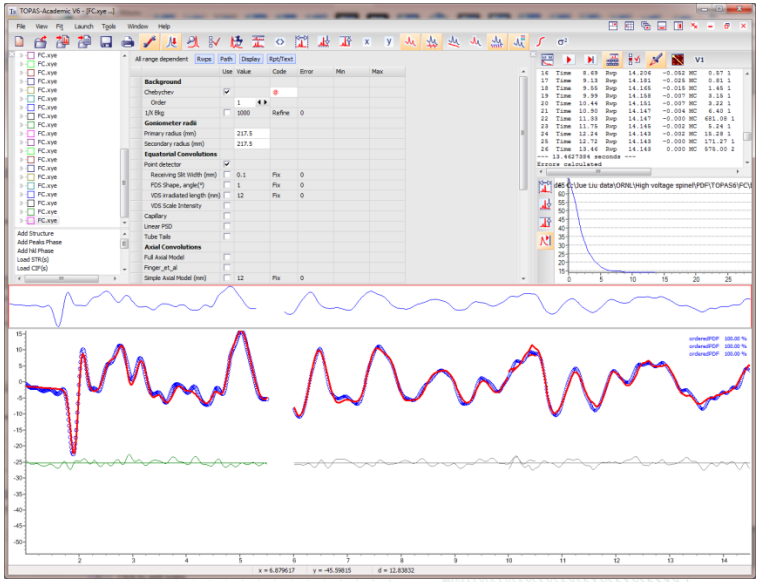


PDFgui http://www.diffpy.org/

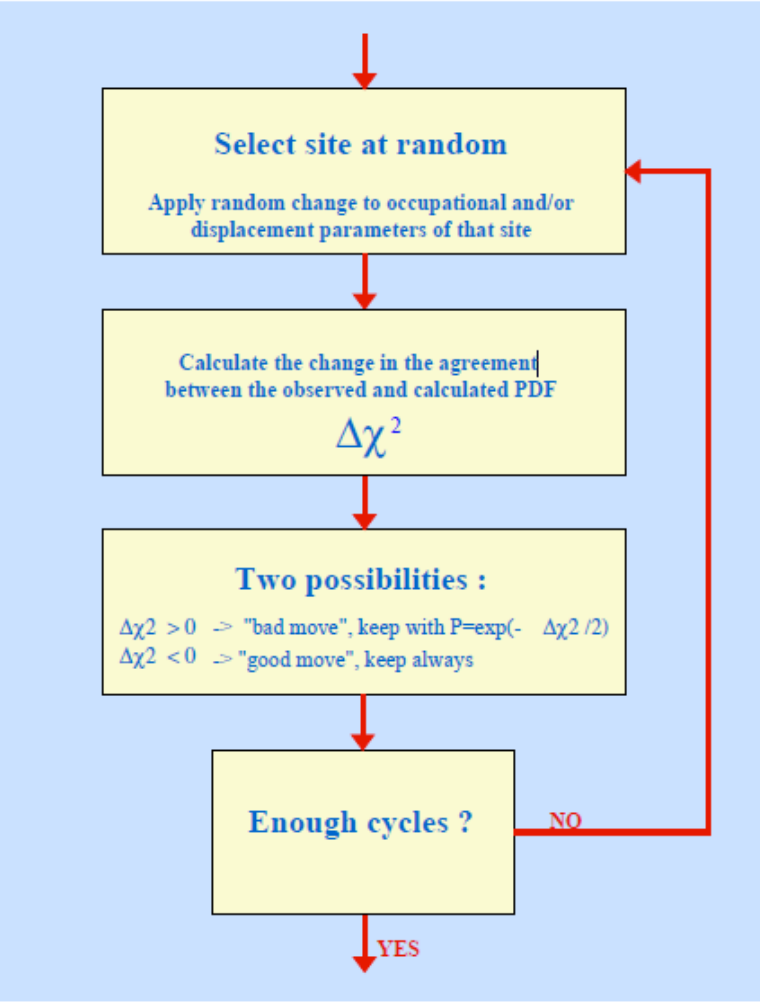
+ Open Source and Free
+ GUI is Simple and User-friendly
- Slow refinement, especially for high-*r*
- No longer actively developed

TOPAS PDF http://www.topas-academic.net

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



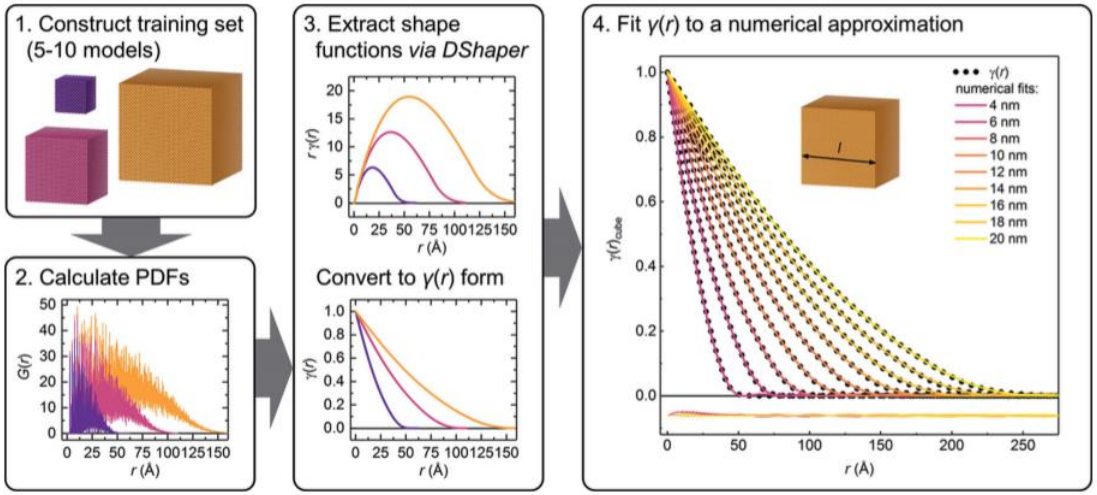
Large Box: Reverse Monte Carlo

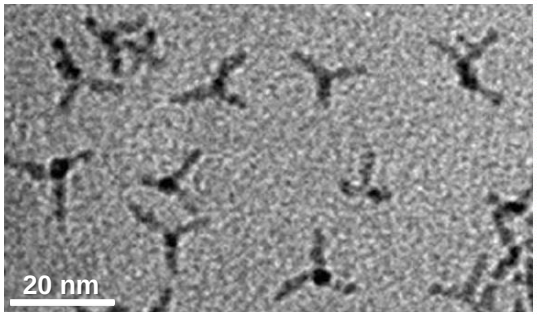


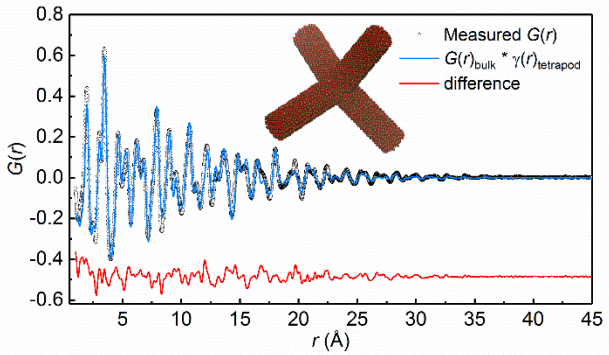
- **RMCprofile**
  - Atomic configurations ~600 to 20000+ atoms
  - Fit both X-ray and neutron F(Q)
  - Fit G(r)
  - Fit Bragg profile (GSAS ToF 1-3)
  - Polyhedral restraints
  - Coordination constraints
  - Closest approach constraints
- **Produce a static 3-D model of the structure (a snap-shot in time)**
- **Link**: http://www.isis.rl.ac.uk/RMC

Modeling nanoscale morphology in real space

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







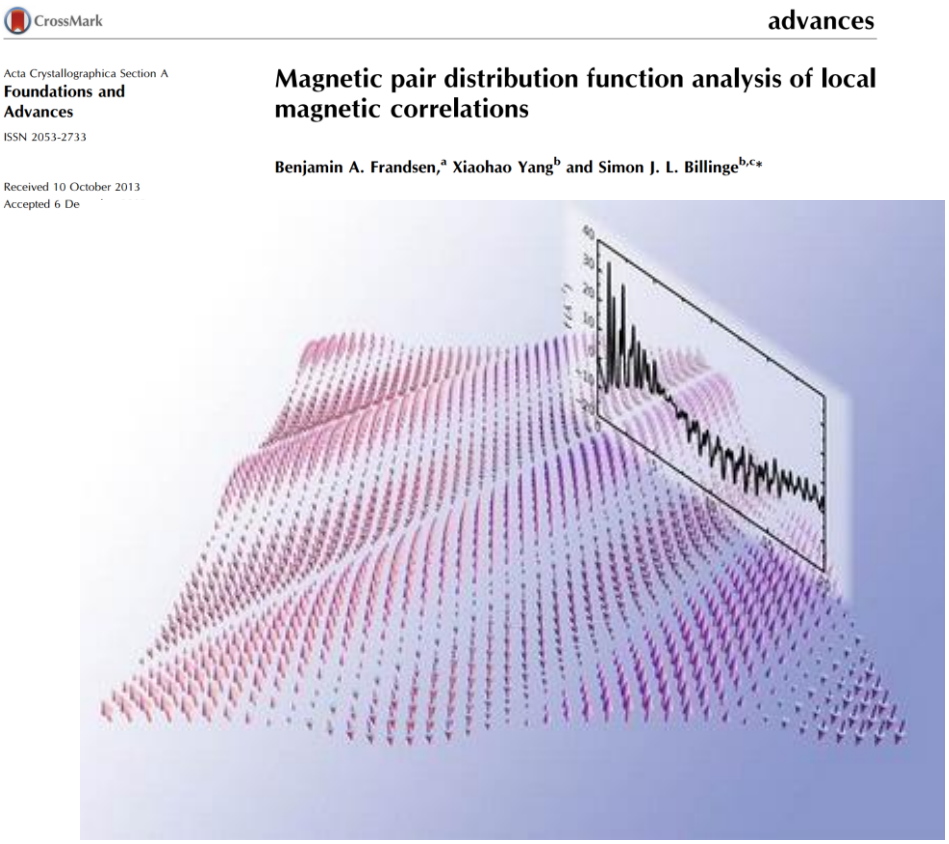
- $\gamma_0(r)$ is the particle shape function, it varies significantly from unity for nanomaterials and should be implemented as an *r*-dependent function
- Can fit physically-relevant shape parameters, such as a nanocube edge length, nanorod length and diameter, or arm length, width, and arm tip-to-arm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

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

OAK RIDGE National Laboratory

Magnetic PDF: mPDF



- 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
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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]

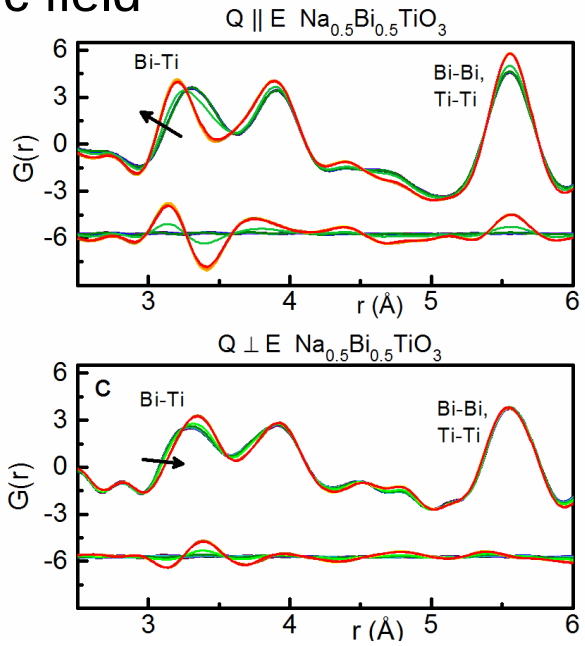
PRL 116, 197204 (2016) PHYSICAL REVIEW LETTERS week ending 13 MAY 2016

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 $Na_{½}Bi_{½}TiO_3$ polycrystalline ceramic samples
- Bi^{3+} reorientation observed at high electric field



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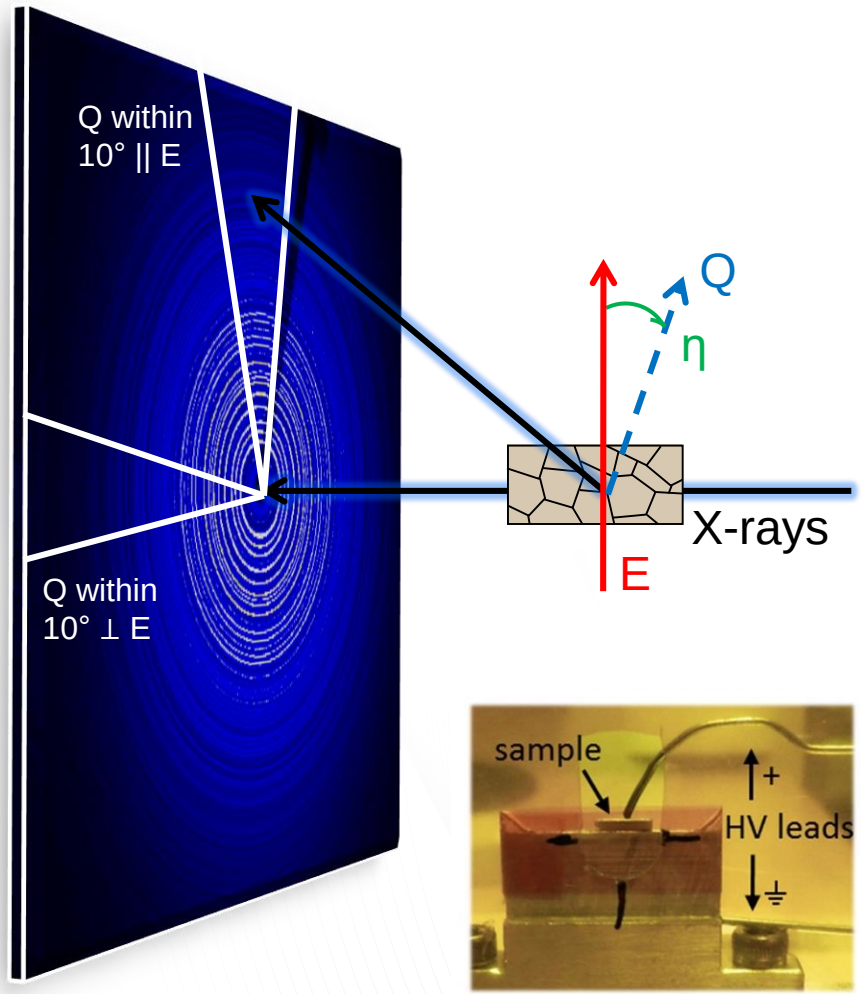

T.-M. Usher, I. Levin, J.E. Daniels, and J.L. Jones, *Scientific Reports* 5, 14678 (2015).
A. J. Goetzee-Barral et al., Phys. Rev. B 96,, 014118 (2017).

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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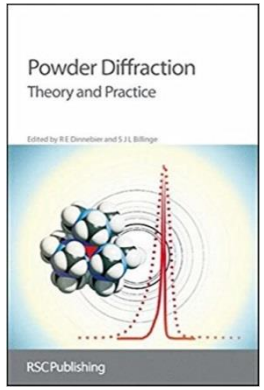

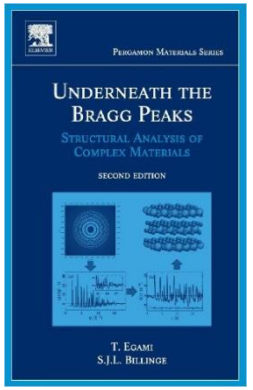

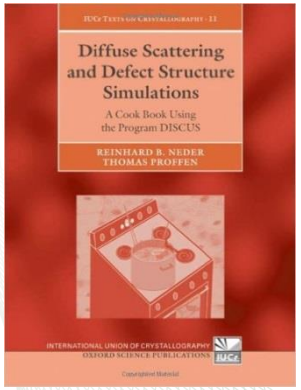

Summary

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

Questions?

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