Atomic Pair Distribution Function (PDF) Analysis

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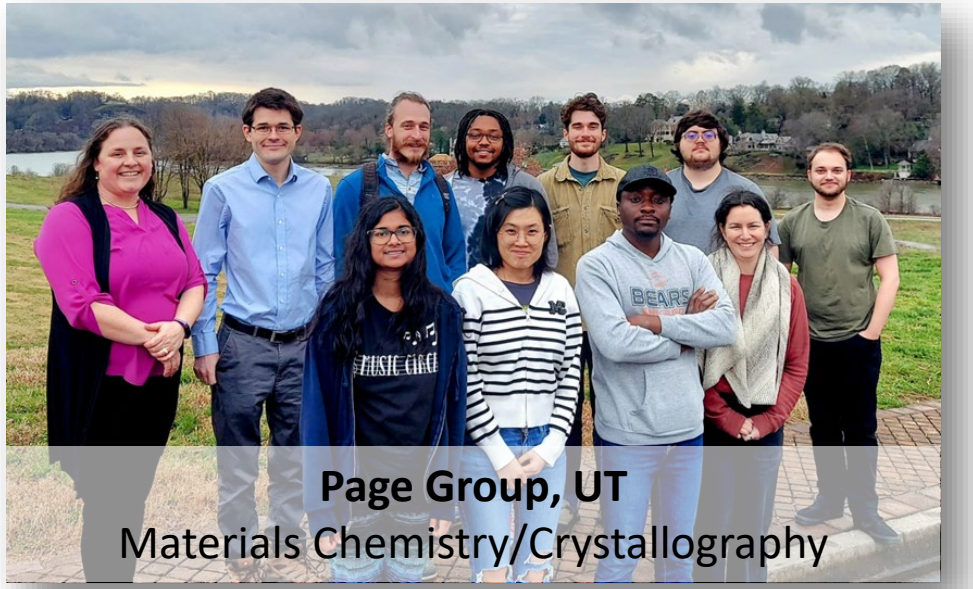
ADVANCED MATERIALS AND MANUFACTURING

MSE

OAK RIDGE National Laboratory

Shull Wollan Center
a Joint Institute for Neutron Sciences



Page Group, UT
Materials Chemistry/Crystallography

Diffraction Group, ONRL
Group Leader: Clarina de la Cruz

NSF

ACS PRF

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Oak Ridge
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DISCOVER INNOVATE ARL TRANSITION

AIR FORCE RESEARCH LABORATORY

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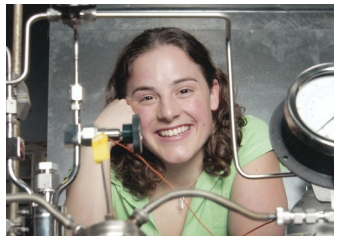
My Professional History

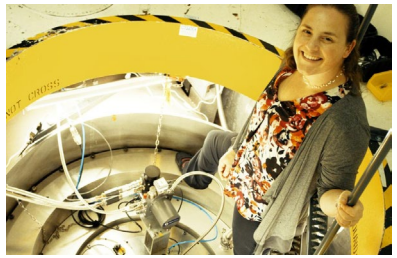


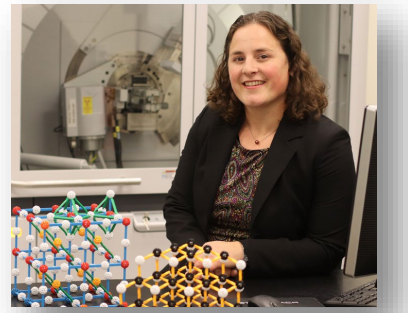
Education/Training

- 2004: BS in Chemical Engineering, University of Maine
- 2008: PhD in Materials, UC Santa Barbara
- 2009/2010: Director's Postdoctoral Fellow, Los Alamos National Laboratory

Employment

- 2011-2014: Scientist, Lujan Neutron Scattering Center, Los Alamos National Laboratory
- 2014-2019: Scientist, Neutron Scattering Division, Oak Ridge National Laboratory
- 2019-Present: Professor, Materials Science and Engineering, University of Tennessee & Joint Faculty, Oak Ridge National Laboratory ***My Dream Job!***





Outline

Part 1:

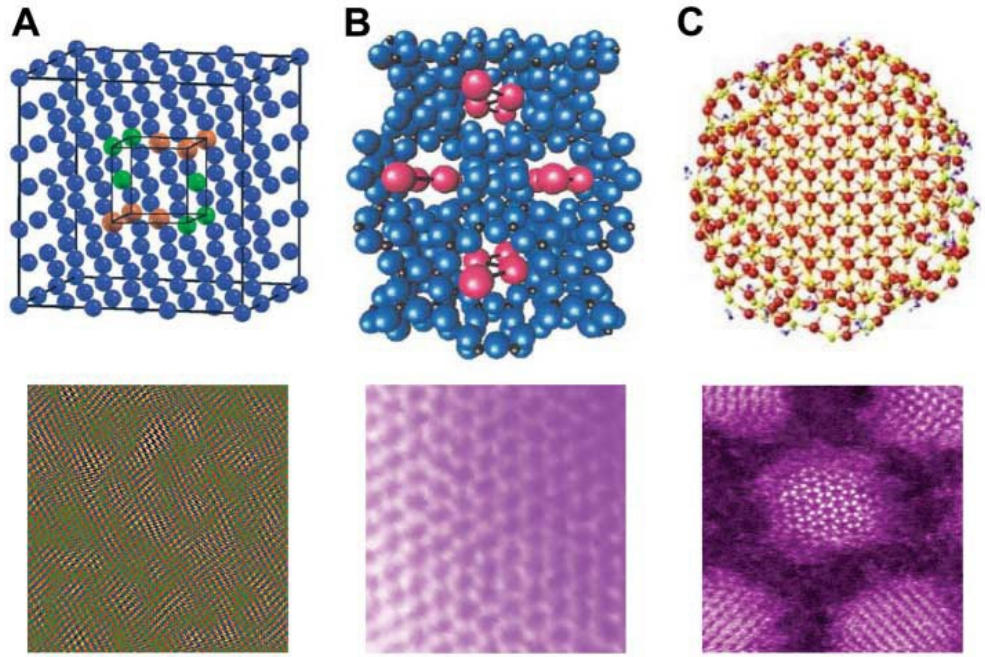
- The Pair Distribution Function (PDF)
- Applications
  - Local Distortions
  - Chemical Short-Range Order
  - Nanomaterial Structure
  - Amorphous Structure

Part 2:

- Experimental Considerations
- Modeling a PDF
- Emerging Areas

What is a *local structure*?

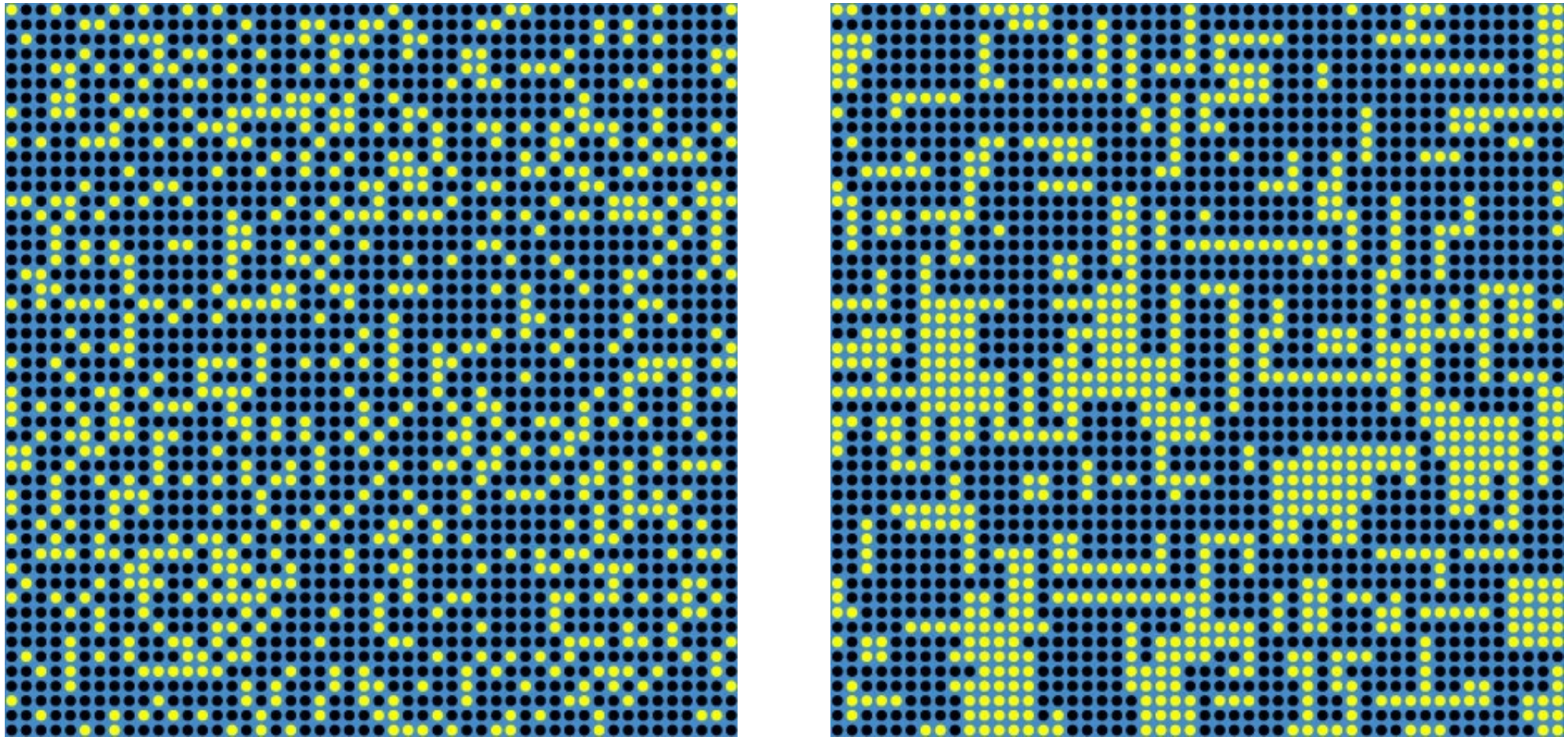
- **Disordered materials**: The interesting properties are often governed by the defects or local structure
- **Non crystalline materials:** Amorphous solids, liquids, glasses and polymers
- **Nanostructures**: Well defined local structure, but long-range order limited to nanometers lengthscales (poorly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



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

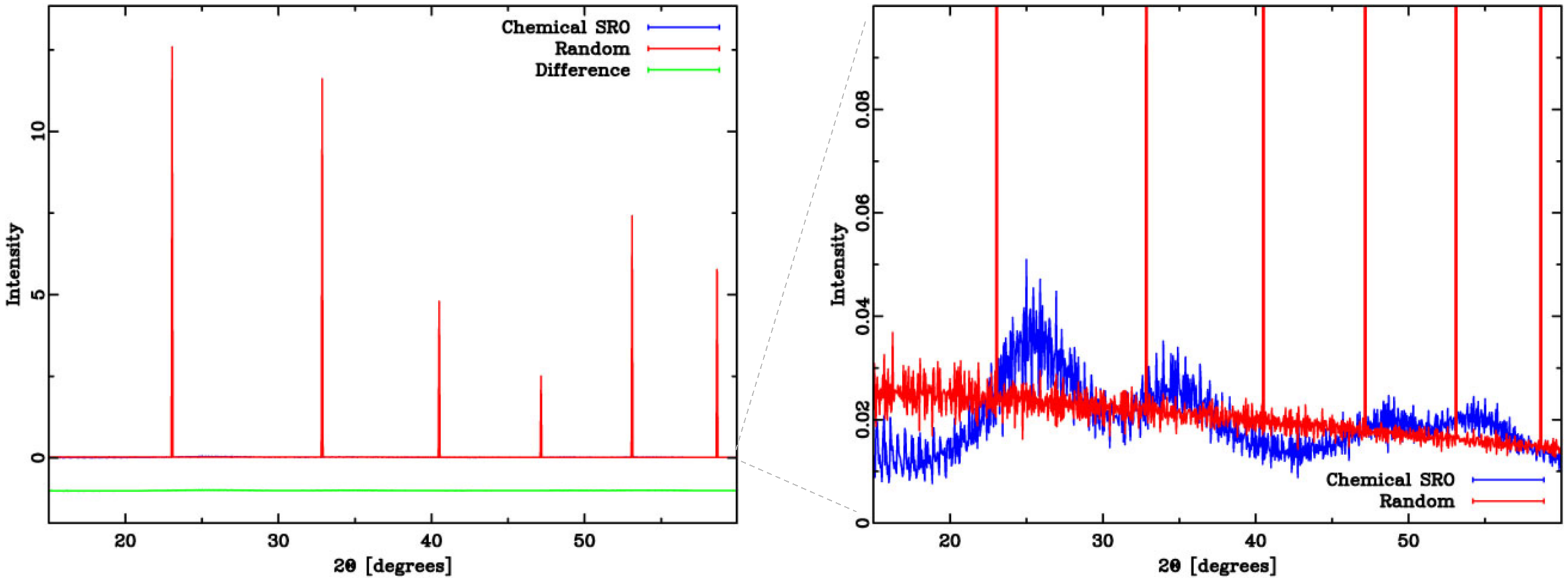
D. A. Keen and A. L. Goodwin, **The crystallography of correlated disorder**, *Nature* 521, 303–309 (2015).

What is *total* scattering?



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

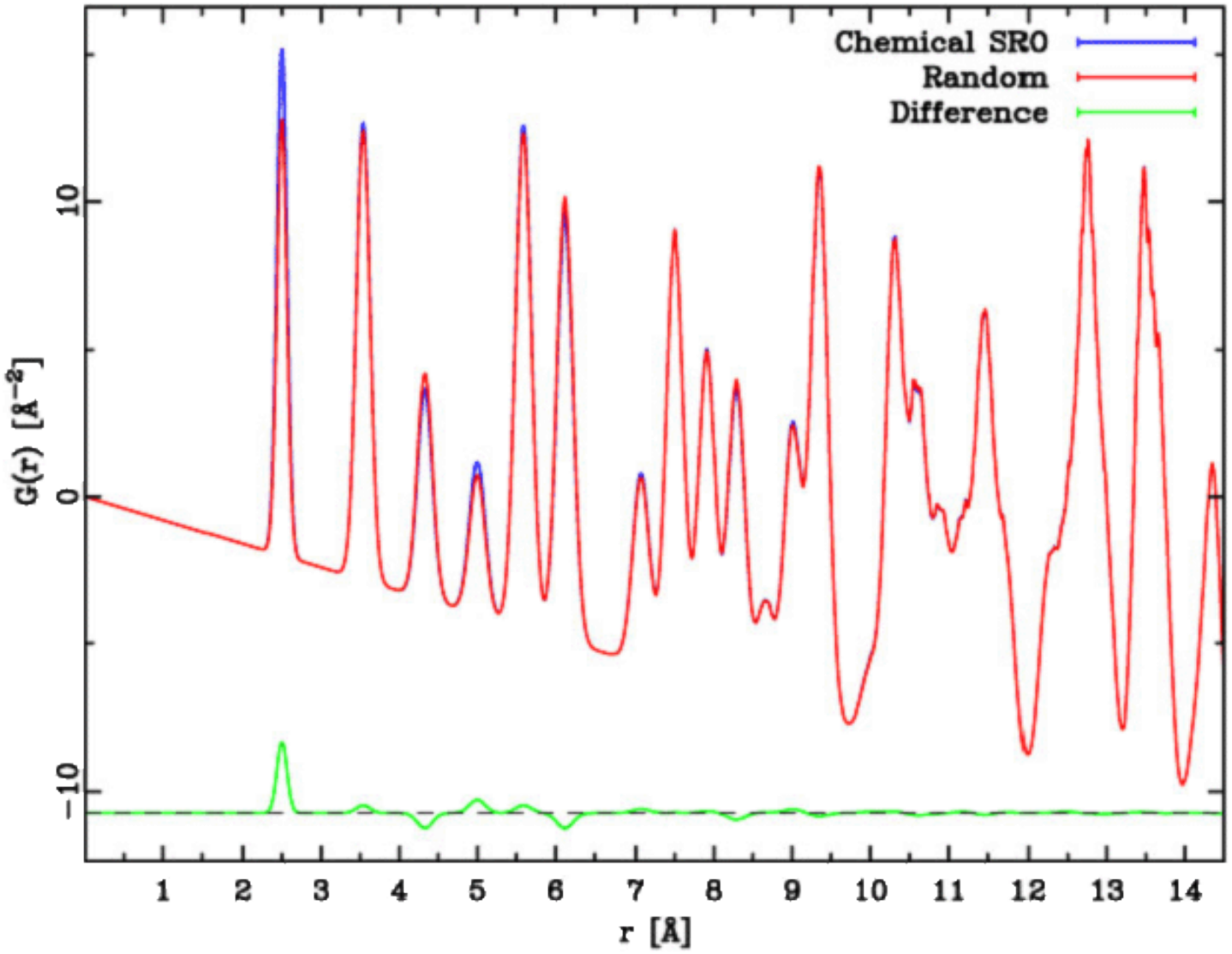
Bragg Scattering and CSRO



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

Diffuse scattering: Information "underneath the Bragg peaks," arising from disordered structure

The Pair Distribution Function



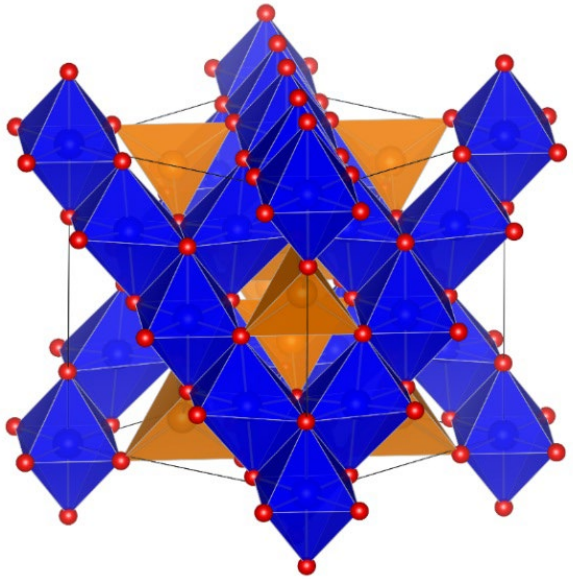
The PDF is the **Sine-Fourier transform** of the **total scattering** (Bragg and diffuse) diffraction pattern

The PDF is sensitive to the **nature** and **length-scale** of CSRO, often key to physical properties

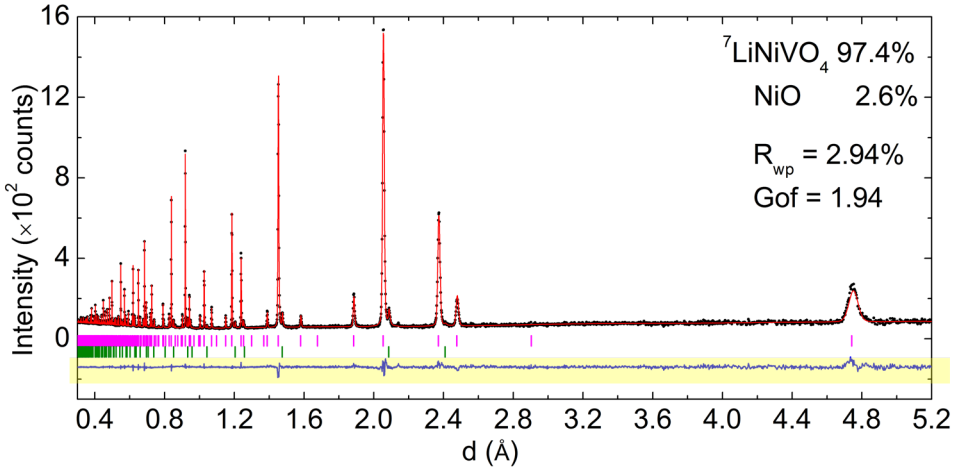
Th. Proffen, **Analysis of occupational and displacive disorder using the atomic pair distribution function: a systematic investigation**, *Z. Krist*, 215, 661 (2000). Th. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt, **Chemical short-range order obtained from the atomic pair distribution function**, Z. Kristallogr. **217** (2002) 47–50.

B-site cation ordering in inverse spinel oxides: $LiNiVO_4$

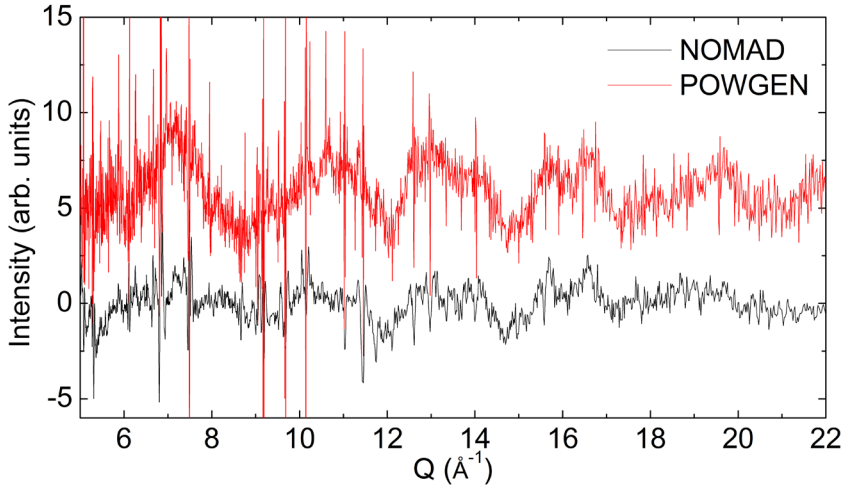
$(V)[LiNi]O_4$
S.G. *F*d-3m

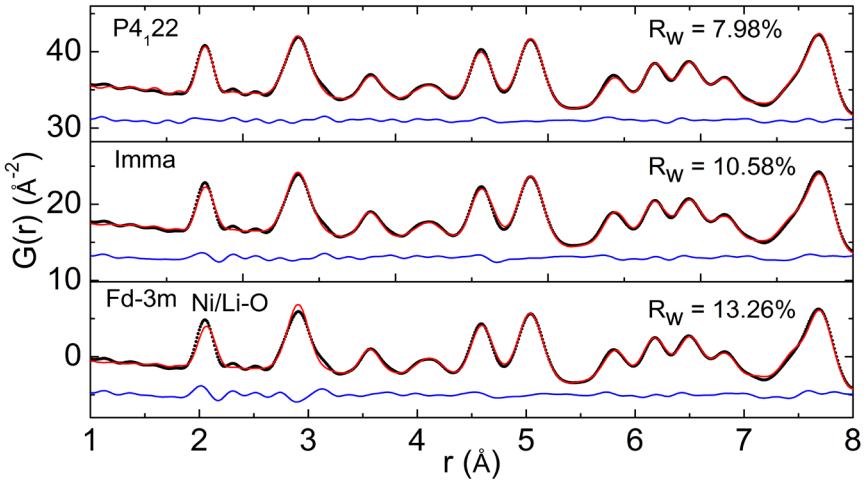


Neutron diffraction data from POWGEN, SNS



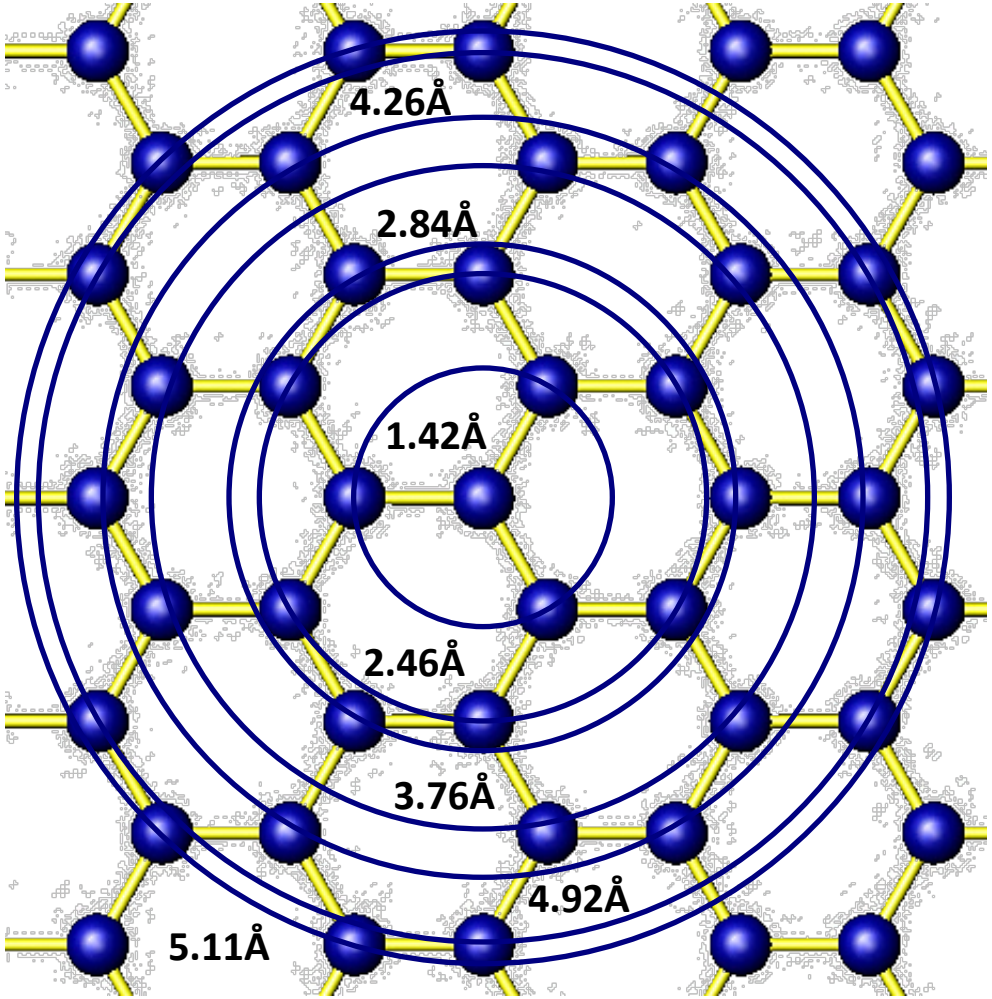
"Underneath the Bragg peaks" on *two* instruments



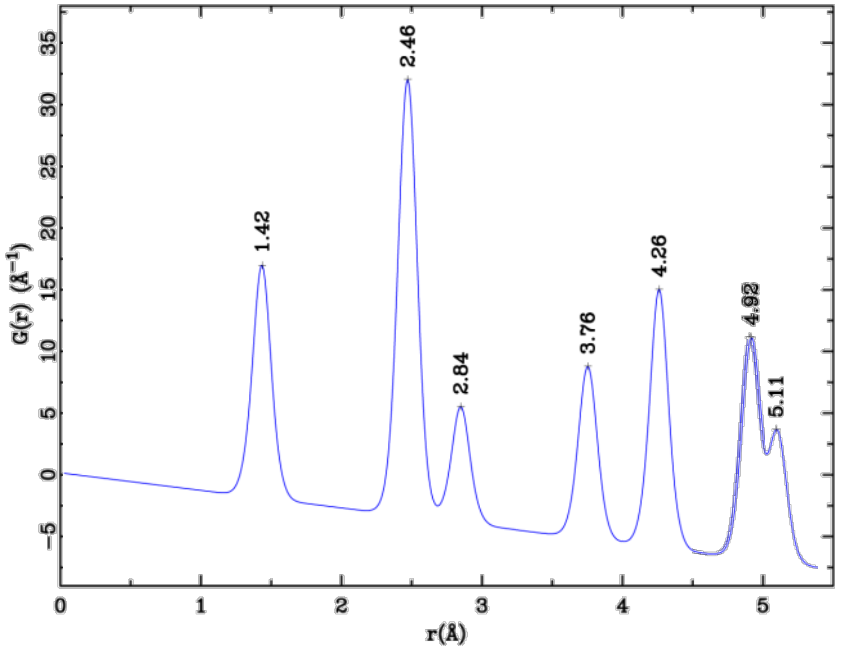


J. Liu, X. Wang, O. J. Borkiewicz, E. Hu, R. J. Xiao, L. Chen, and K. Page, **Unified view of the local cation-ordered state in inverse spinel oxides**, *Inorg. Chem.* 58 (2019) 14389-14402.

What is a PDF?



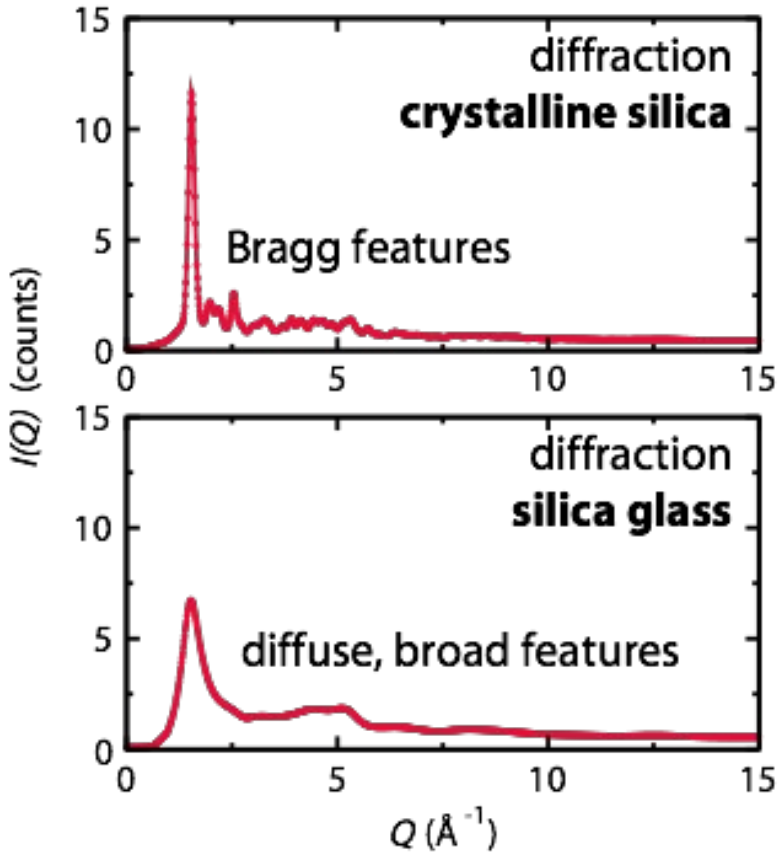
The **Pair Distribution Function (PDF)** gives the probability of finding an atom at a distance “r” from a given atom.

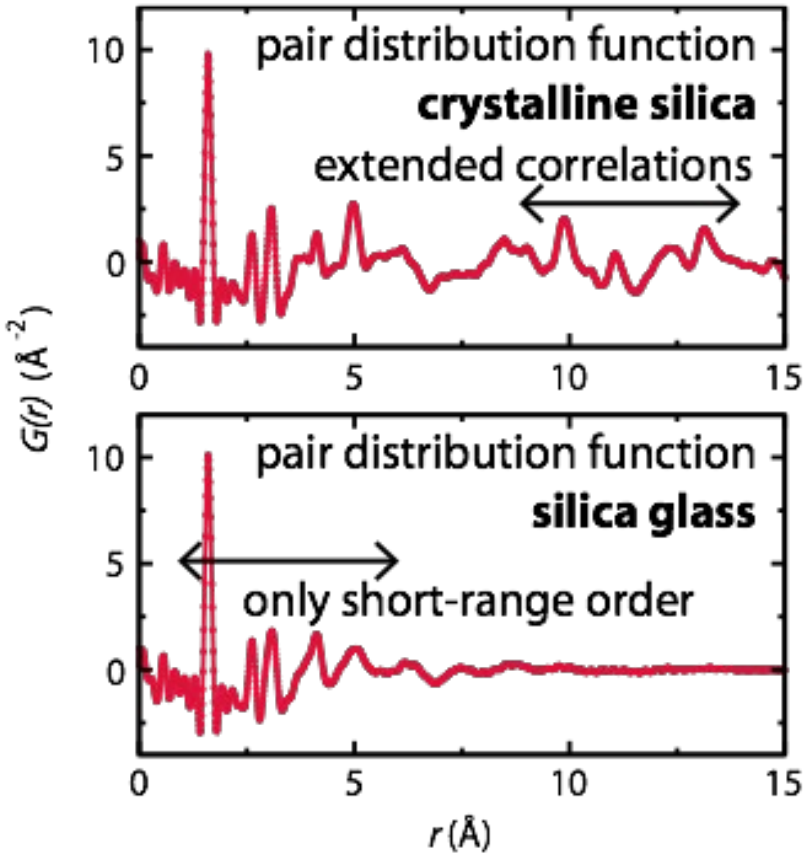


Pair Distribution Function

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

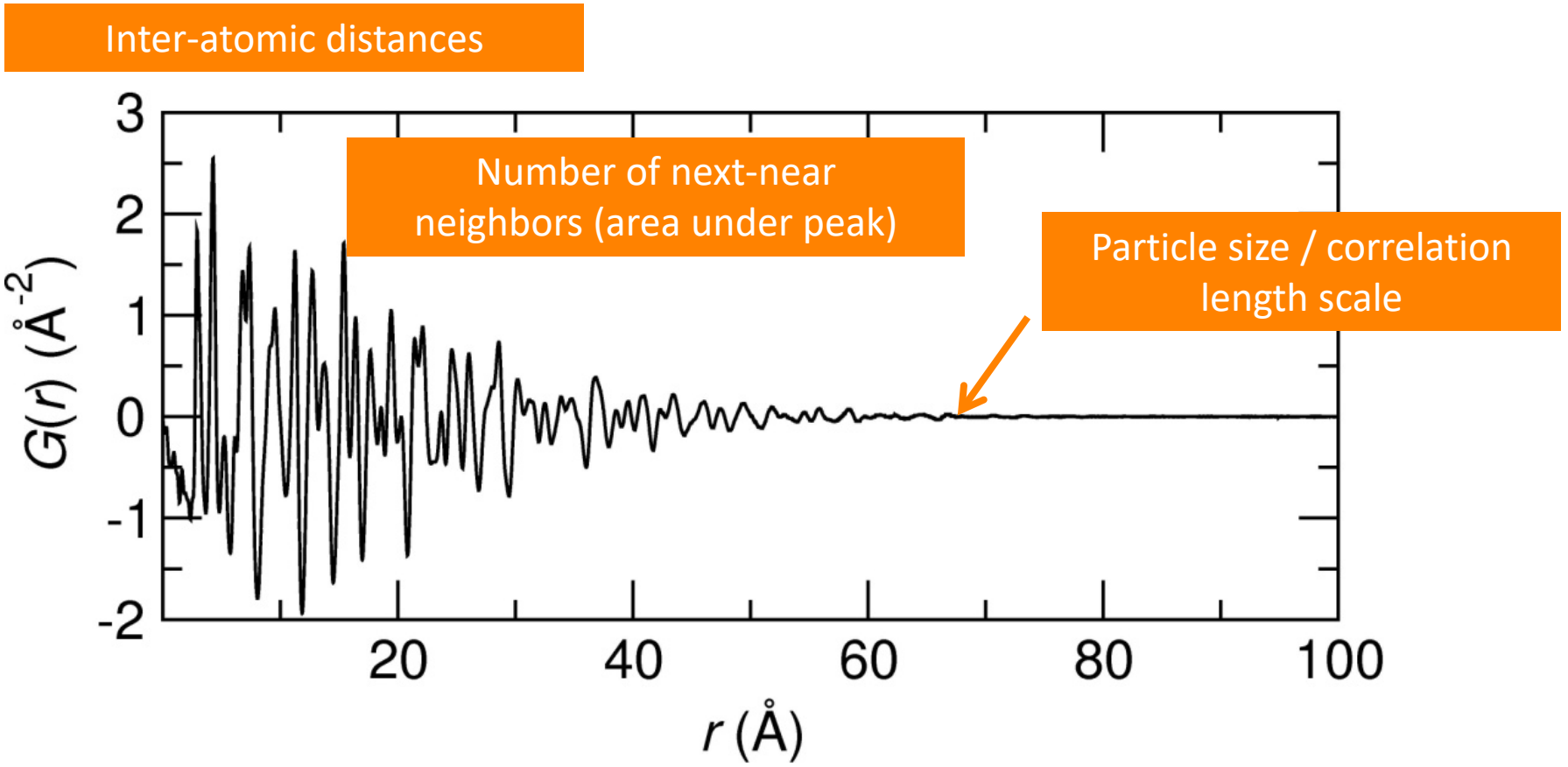
→*Experimental, ensemble, real-space, atom-atom histogram*





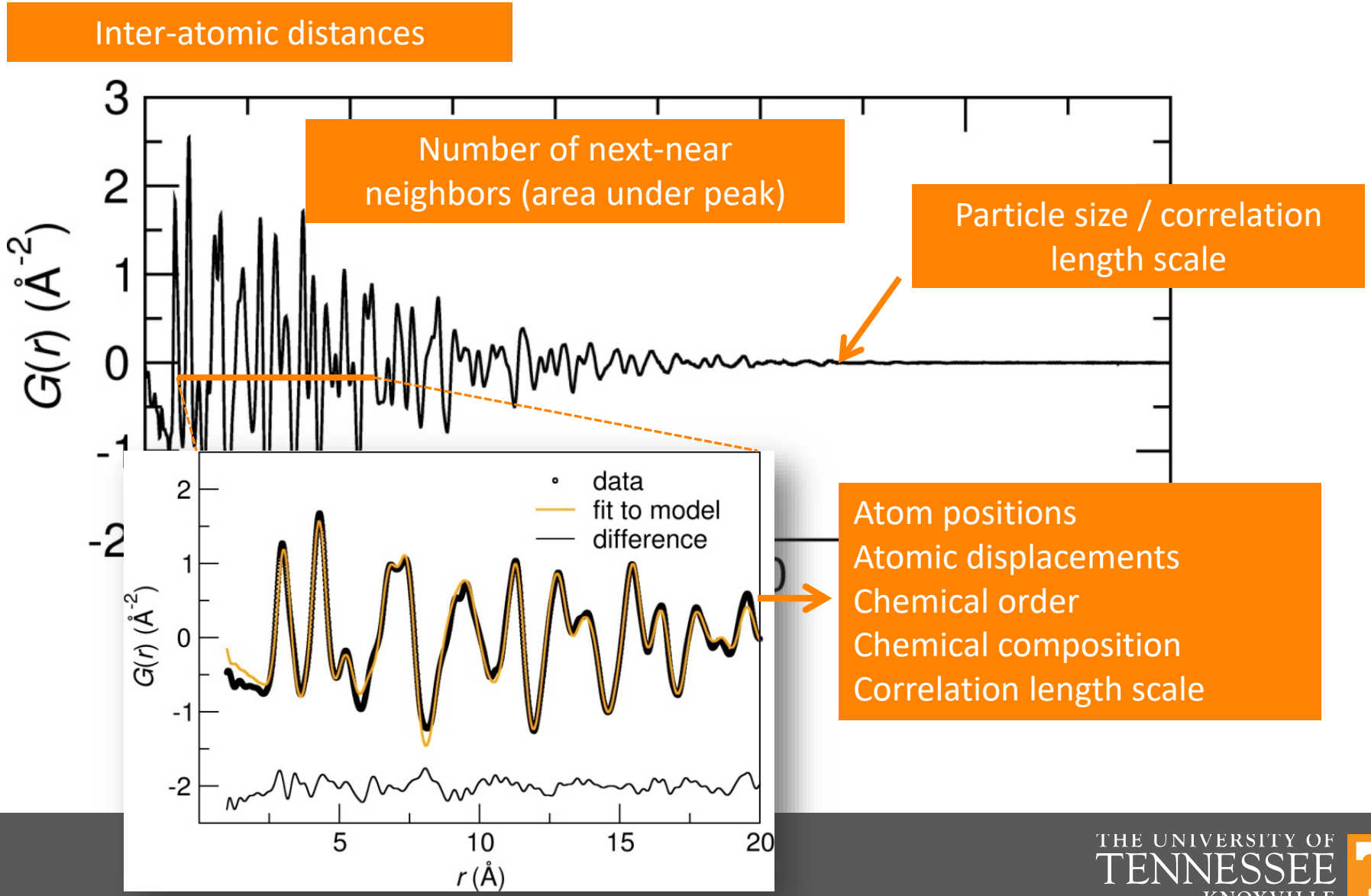
Pair Distribution Function

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

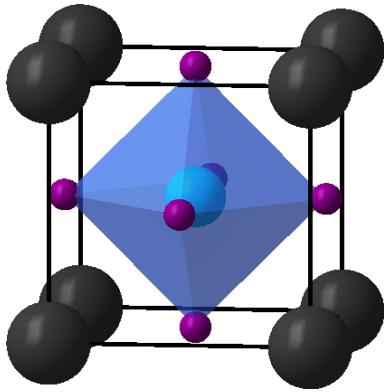


Pair Distribution Function

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

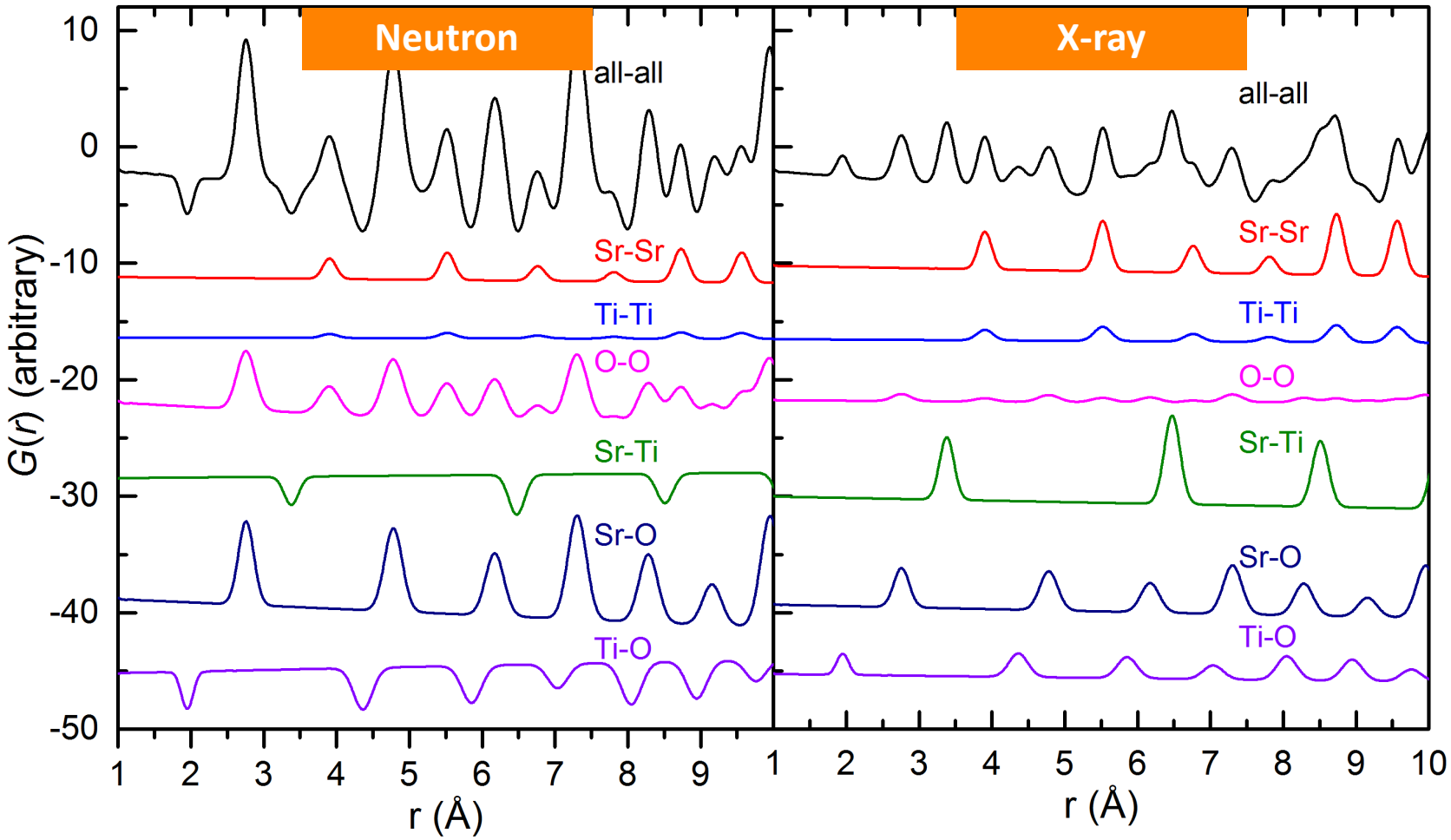


Partial PDFs



$SrTiO_3$

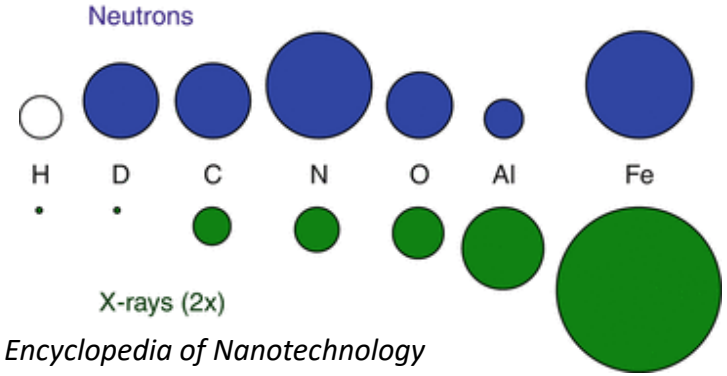
s*(*s*+1)/2** partial structure factors characterize a system containing ***s species



Neutron and x-ray PDFs are often highly complementary

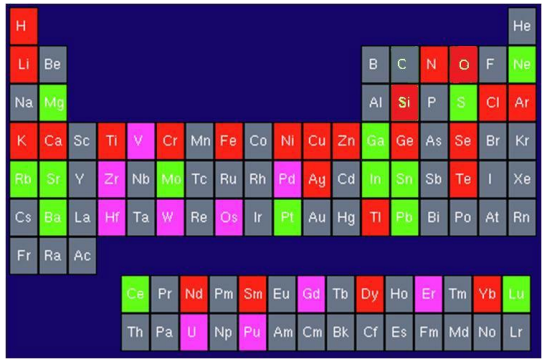
Neutron Total Scattering

Light Atom and Neighboring Atom Species



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

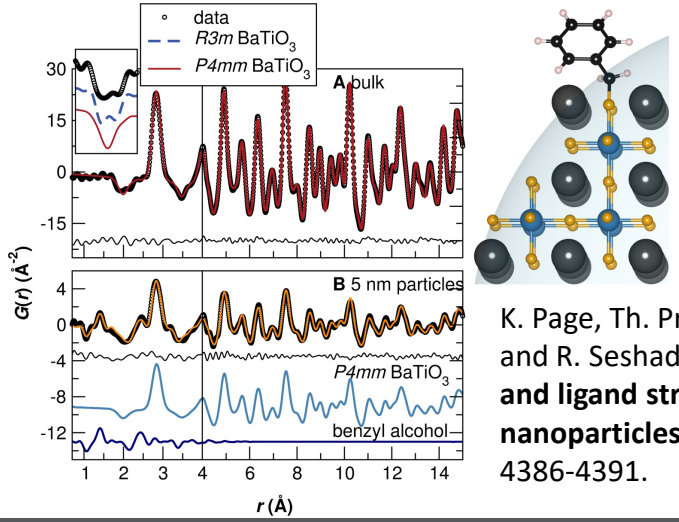
Isotope Substitution



J. E. Enderby, D.M. North, P. A. Egelstaff, **Partial structure factors of liquid Cu-Sn,** *Phil. Mag.*14 (1966) 131.

Louca, Kwei, Dabrowski, Bukowski, *Phys. Rev. B,* (1999) 60, 7558-7564.

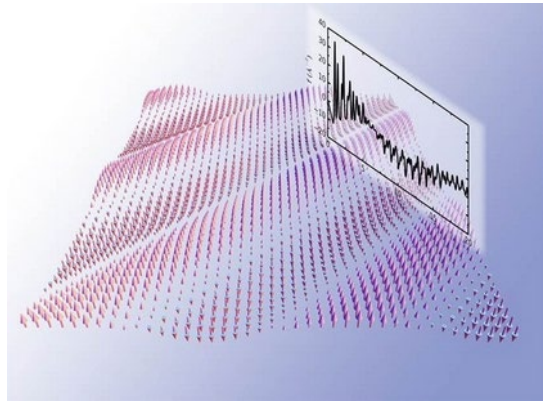
Surface Species of Nanomaterials



K. Page, Th. Proffen, M. Niederberger, and R. Seshadri, **Probing local dipoles and ligand structure in $BaTiO_3$ nanoparticles**, *Chem. Mater*. 22 (2010), 4386-4391.

Magnetic Structure

B. Frandsen, X. Yang and S. J. L. Billinge, **Magnetic pair distribution function analysis of local magnetic correlations**, *Acta Cryst*. A70 (2014), 3-11.



Nondestructive

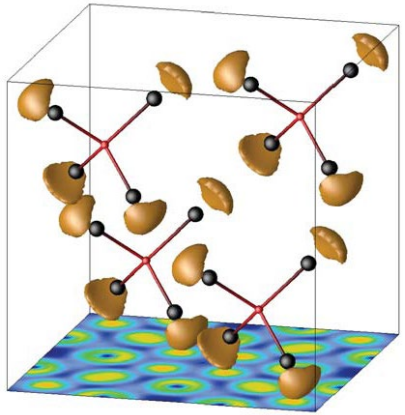
Penetration of Sample Environments

WHAT TYPES OF STUDIES CAN BE DONE WITH THE PDF TECHNIQUE?

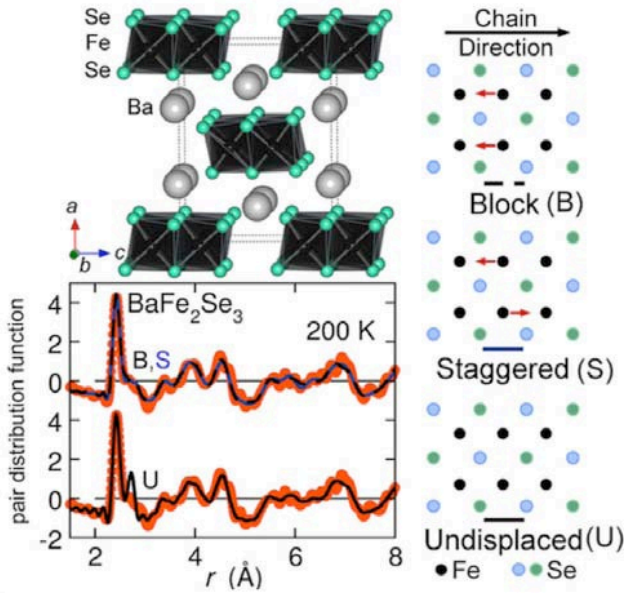
Local Distortions
Chemical Short-Range Ordering
Nanostructures
Amorphous Structures

Local distortions *via* PDF

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

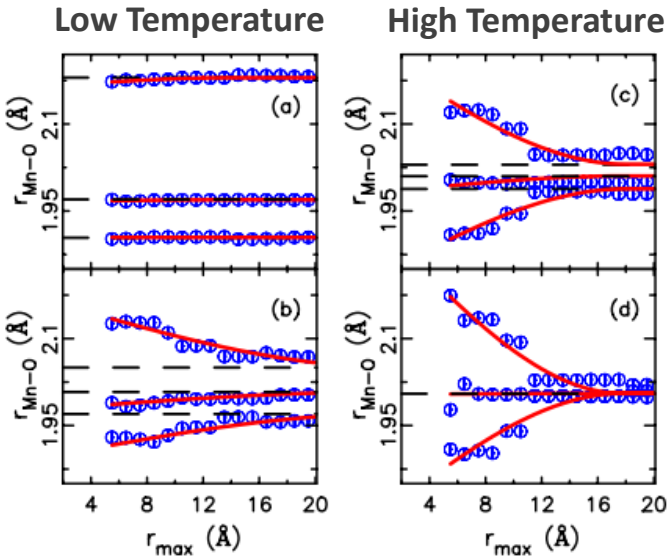


D. P. Shoemaker, *et al.*, Reverse Monte Carlo neutron scattering study of the 'ordered-ice' oxide pyrochlore $Pb_2Ru_2O_{6.5}$, *J. Phys.: Condens. Matter* **23** (2011).



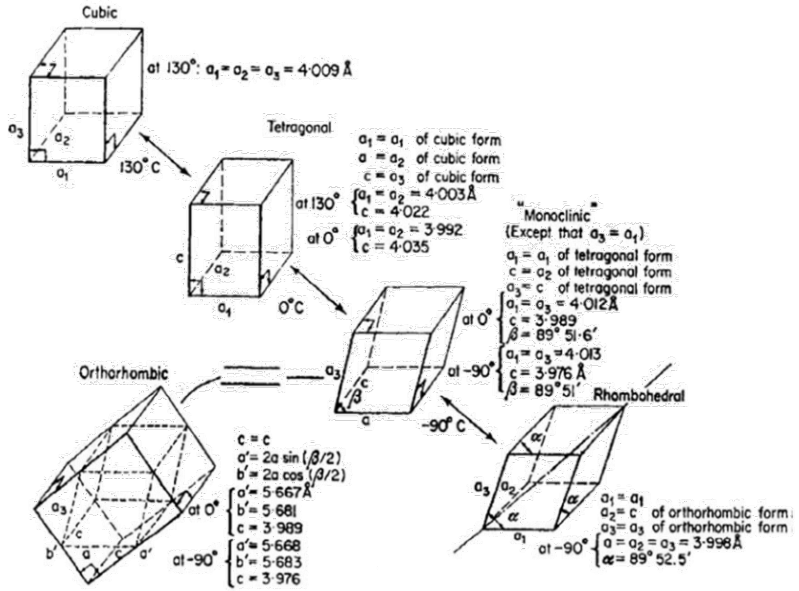
D. Louca, *et al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).

X. Qui, *et al.*, Orbital Correlatons in the Pseudocubic *O* and Rhombohedral *R* Phases of $LaMnO_3$, *Phys. Rev. Lett.* **94**, 177203 (2005).



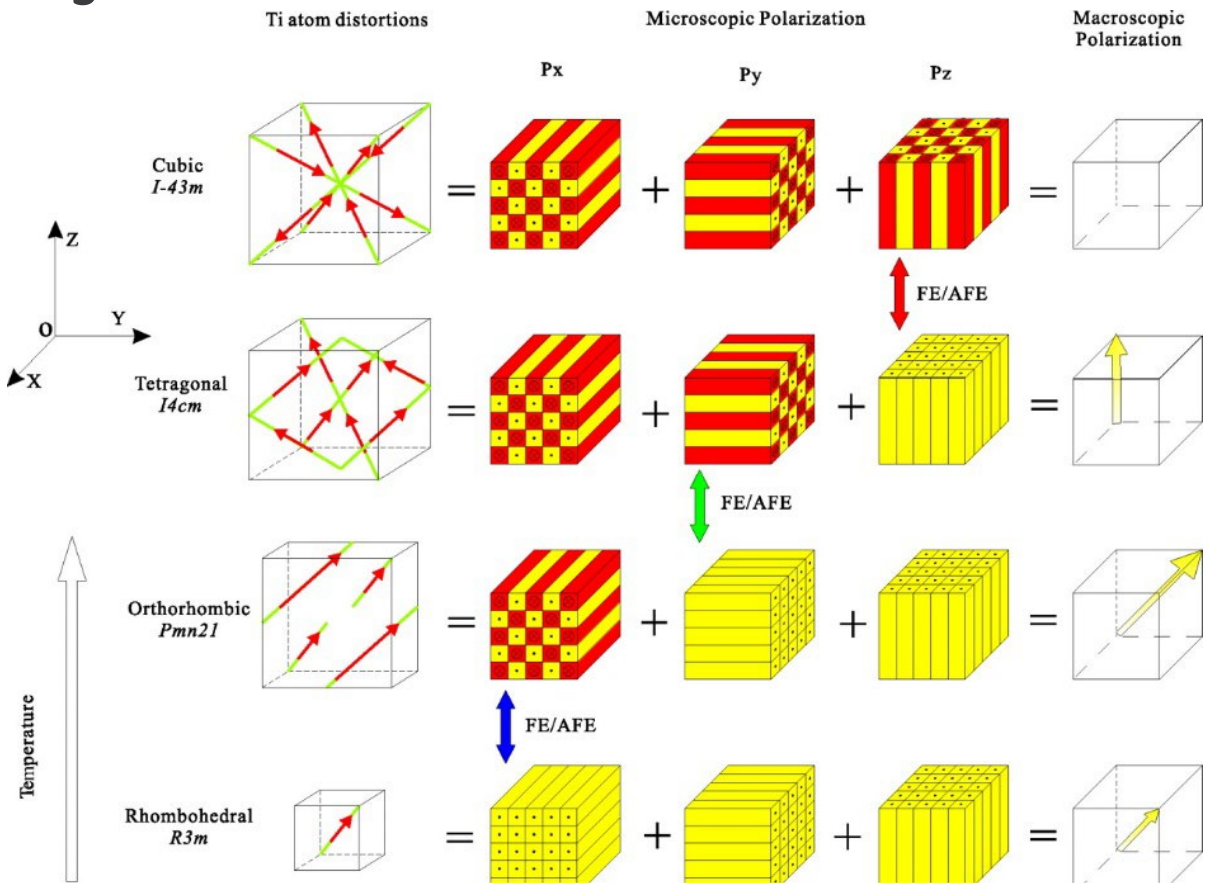
Example: Local structure in $BaTiO_3$

Crystallographic Phase Transitions



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

Long-range: cubic → tetragonal → orthorhombic → rhombohedral

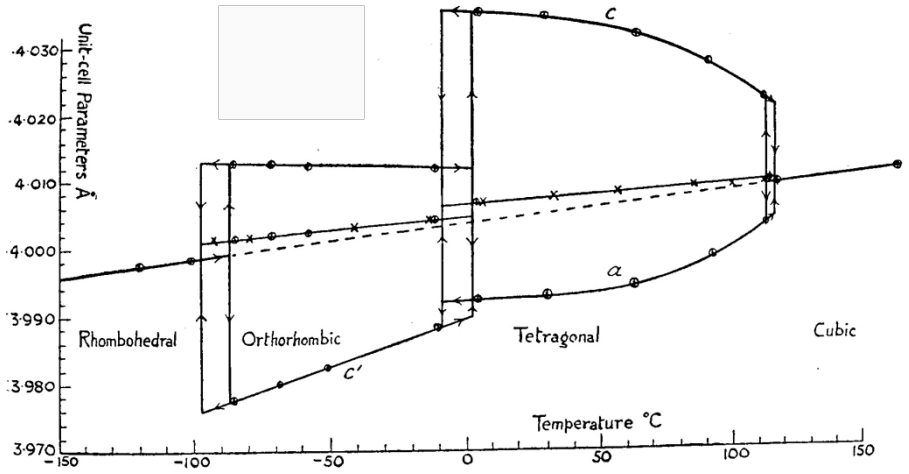


Locally, Ti^{4+} displacements are always along [111] directions (octahedral faces) → Results in 3 short and 3 long Ti-O bonds

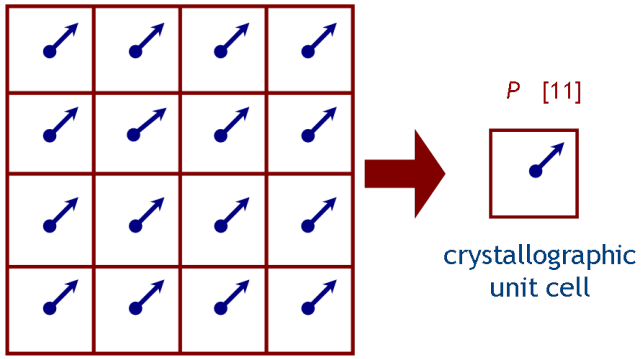
Zhang, Cagin, and Goddard, The ferroelectric and cubic phases in $BaTiO_3$ferroelectrics are also antiferroelectric, *PNAS*, **103**, 14695-14700 (2006).

Example: Local structure in $BaTiO_3$

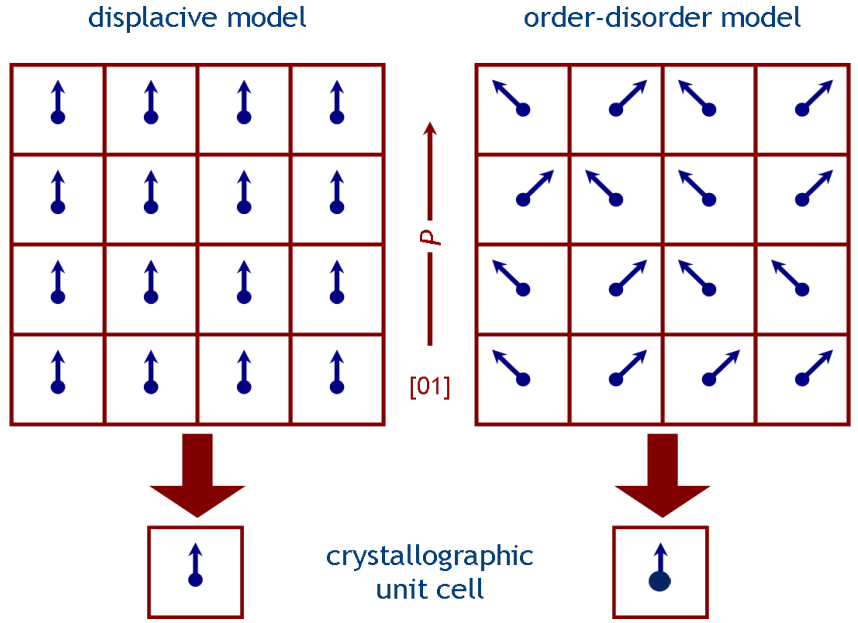
$BaTiO_3$: Ferroelectric oxide, a rhombohedral (*R3m*) ground state and a room temperature tetragonal (*P4mm*) structure



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



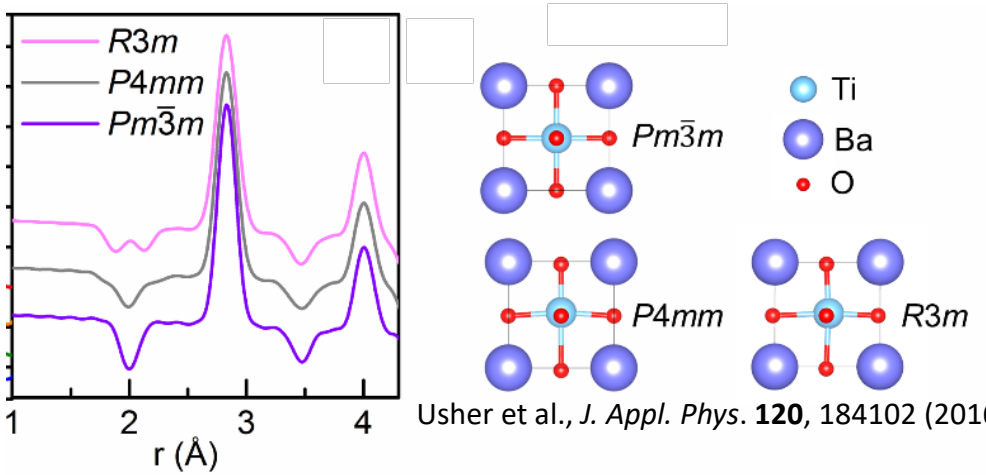
2D models with distinct local motifs but similar "average" motifs



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

Neutron PDF for $BaTiO_3$

Calculated $BaTiO_3$ PDFs



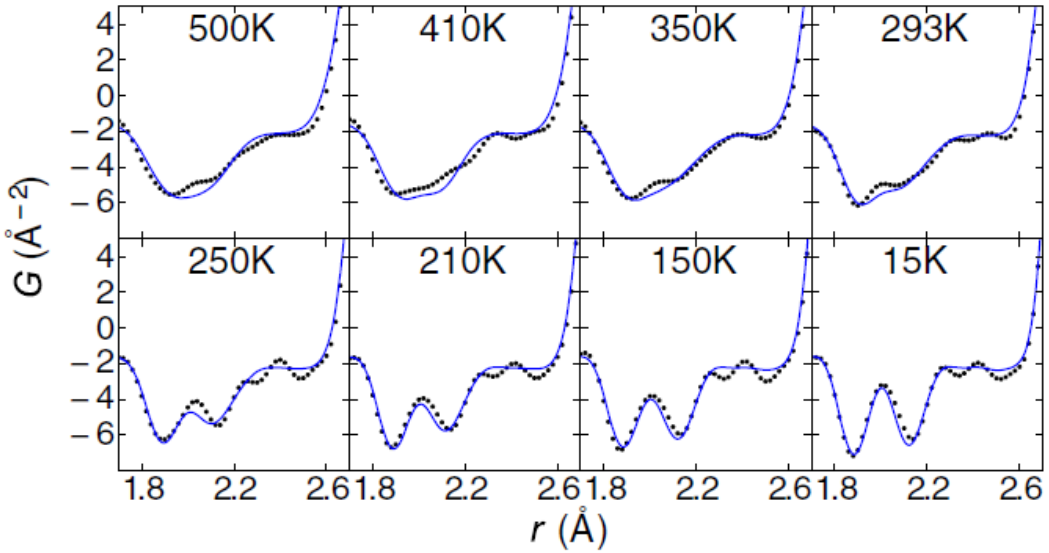
Usher et al., *J. Appl. Phys*. **120**, 184102 (2016).

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).

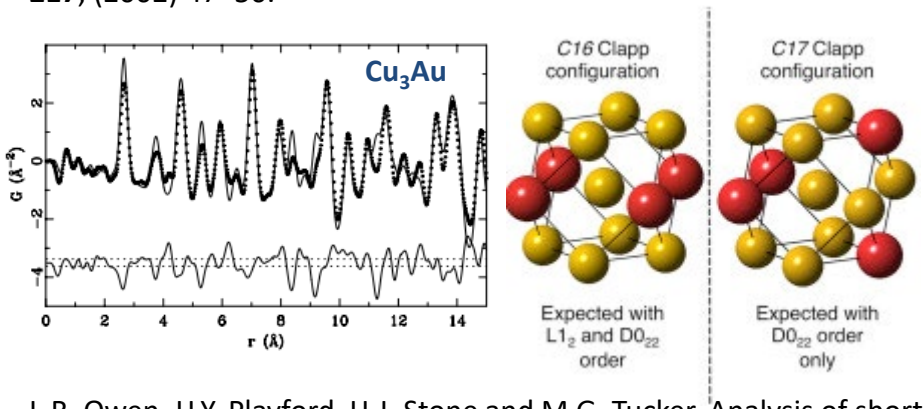
- Neutron PDF is sensitive to Ti-O correlations
- At room temperature, $BaTiO_3$ locally has a split (*R3m* like) first Ti-O peak, displaying classic order-disorder behavior



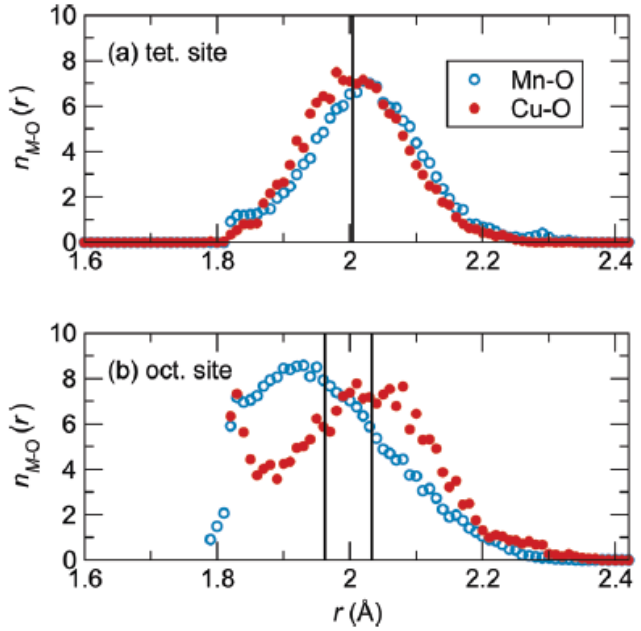
Chemical Short-Range order *via* PDF

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

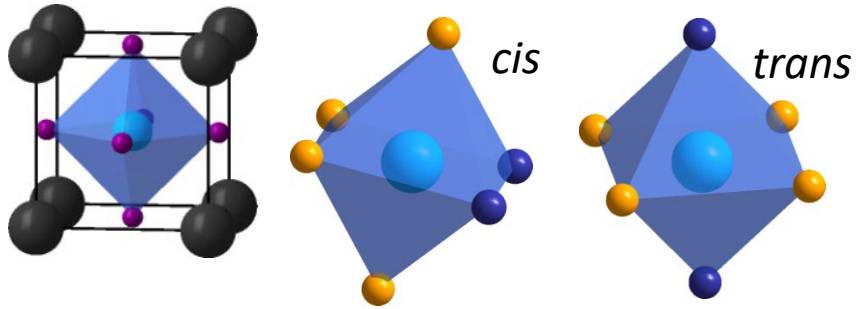
Th. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt, Chemical short range order obtained from the atomic pair distribution function, *Z. Kristallogr*. **217**, (2002) 47–50.



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

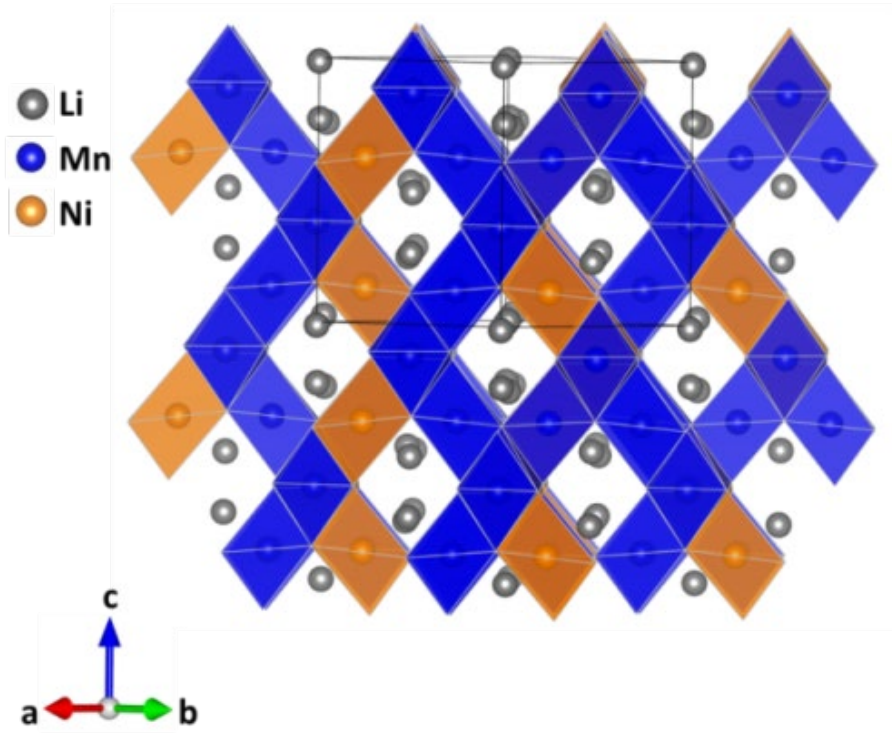
Two distinct polymorphs are known: Ni/Mn cation ordering strongly impacts electrochemical performance Idemoto *et al.*, 2003; Zhong *et al.*, 1997

(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



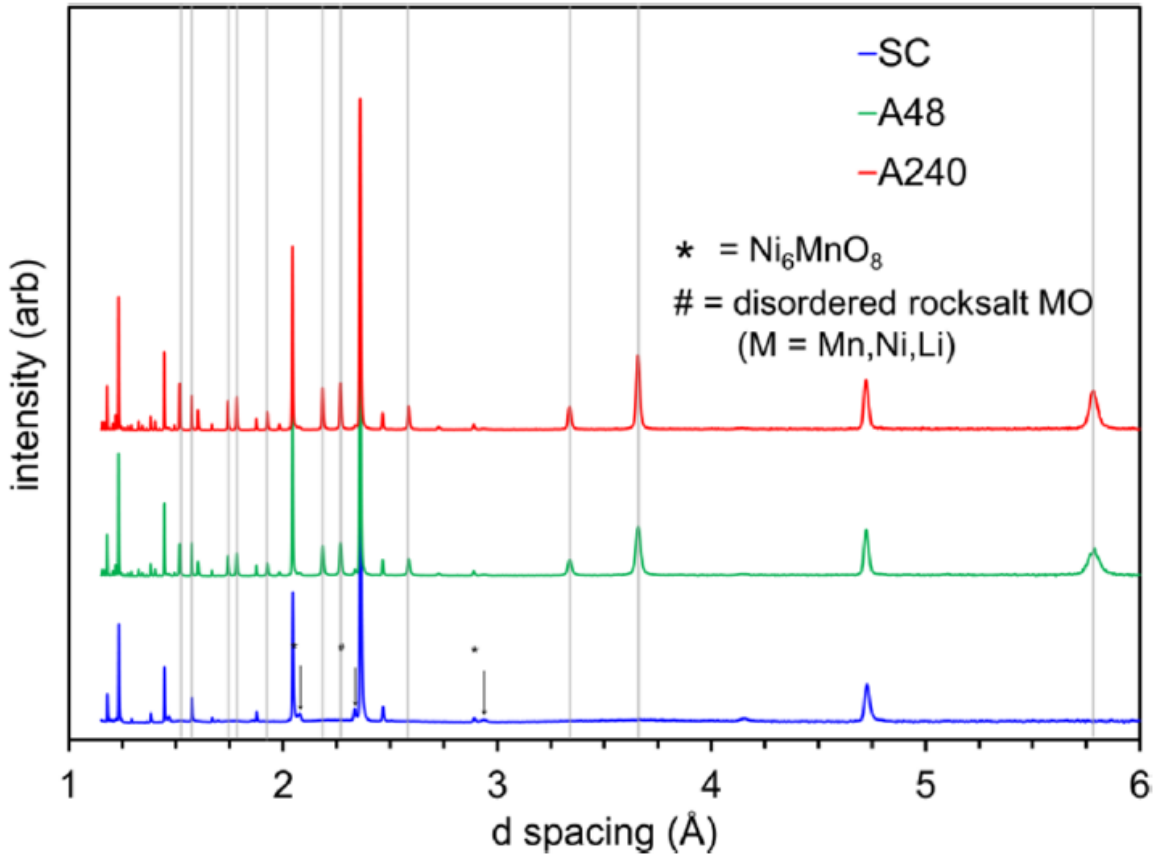
Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

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



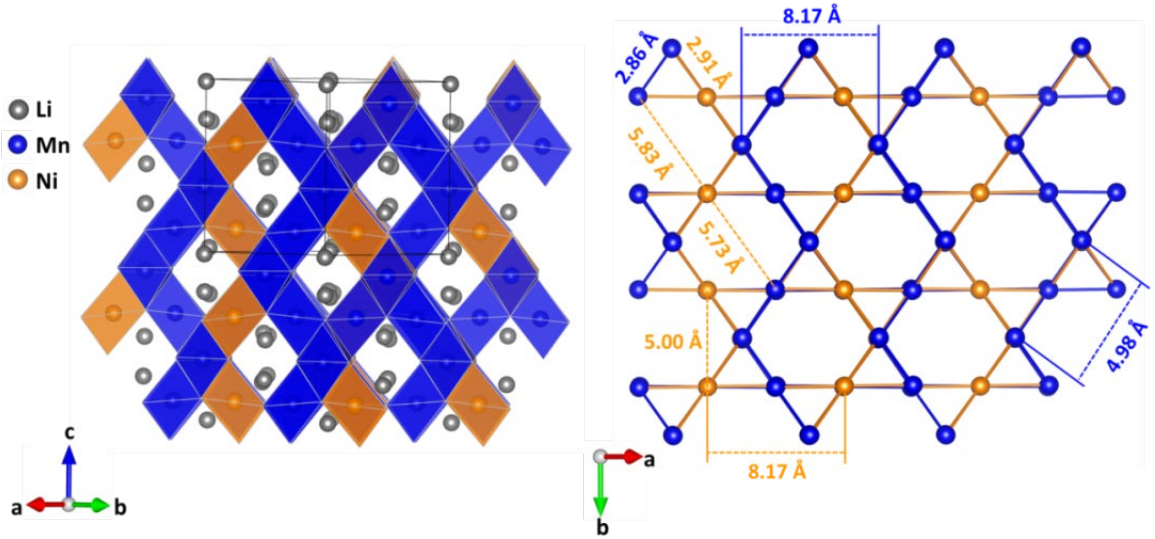
Cation ordering examined at the POWGEN Beamline, SNS: large nuclear scattering length contrast between nickel (*b* = 10.3 fm) and manganese (*b* = -3.73 fm)

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

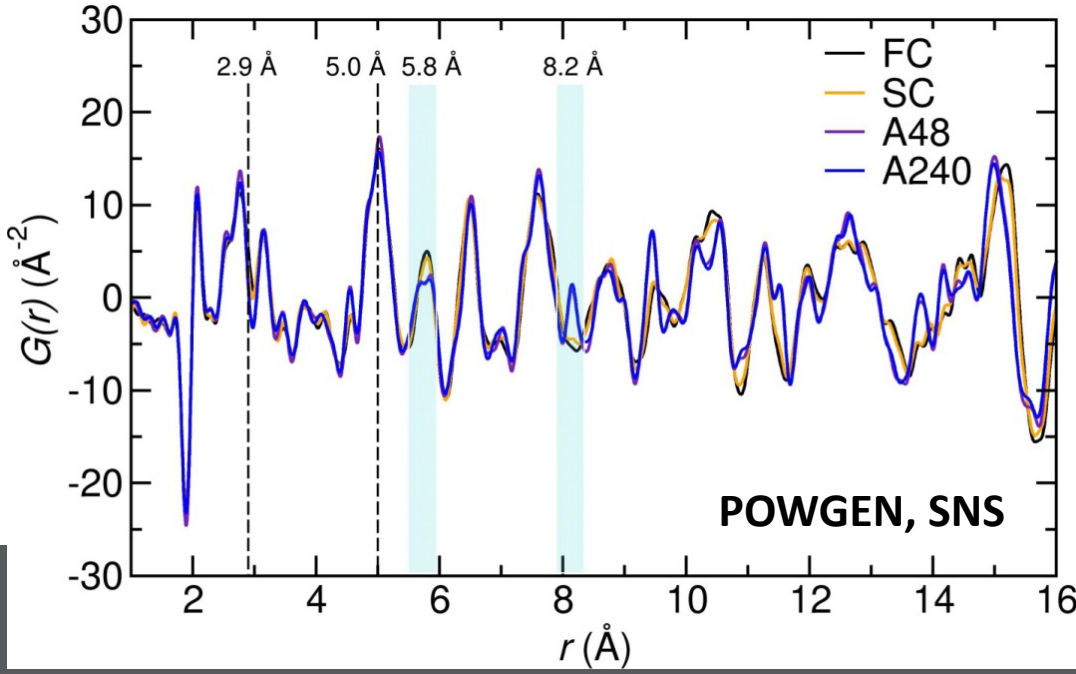
Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

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



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

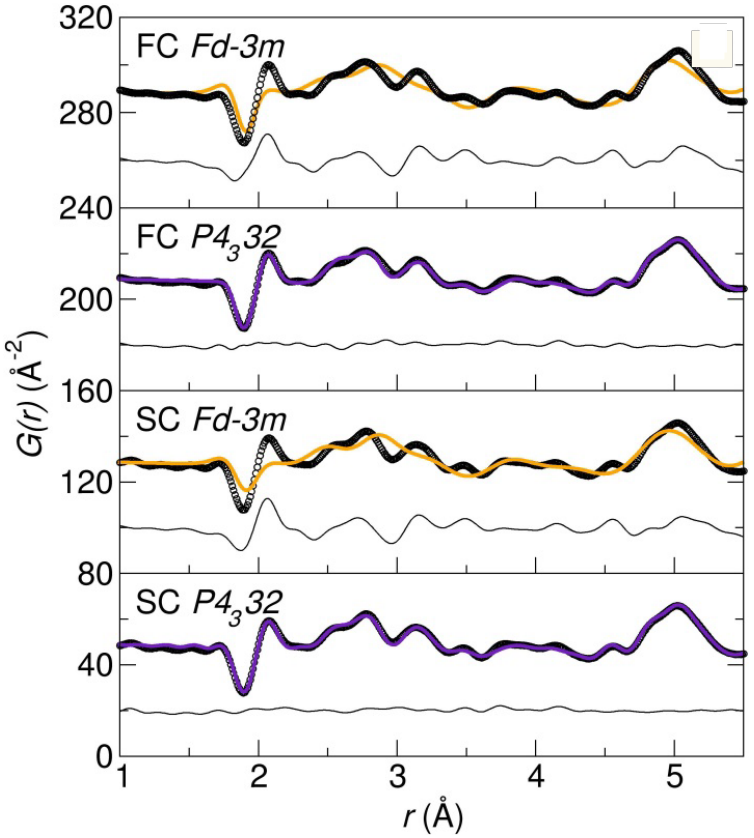


Liu J., Huq A., Moorhead-Rosenberg Z., Manthiram A., Page K., **Nanoscale Ni/Mn Ordering in the High Voltage Spinel Cathode $LiNi_{0.5}Mn_{1.5}O_4$,** *Chemistry of Materials,* 28**,** (2016) 6817–6821.

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

Additional information from modeling the local structure

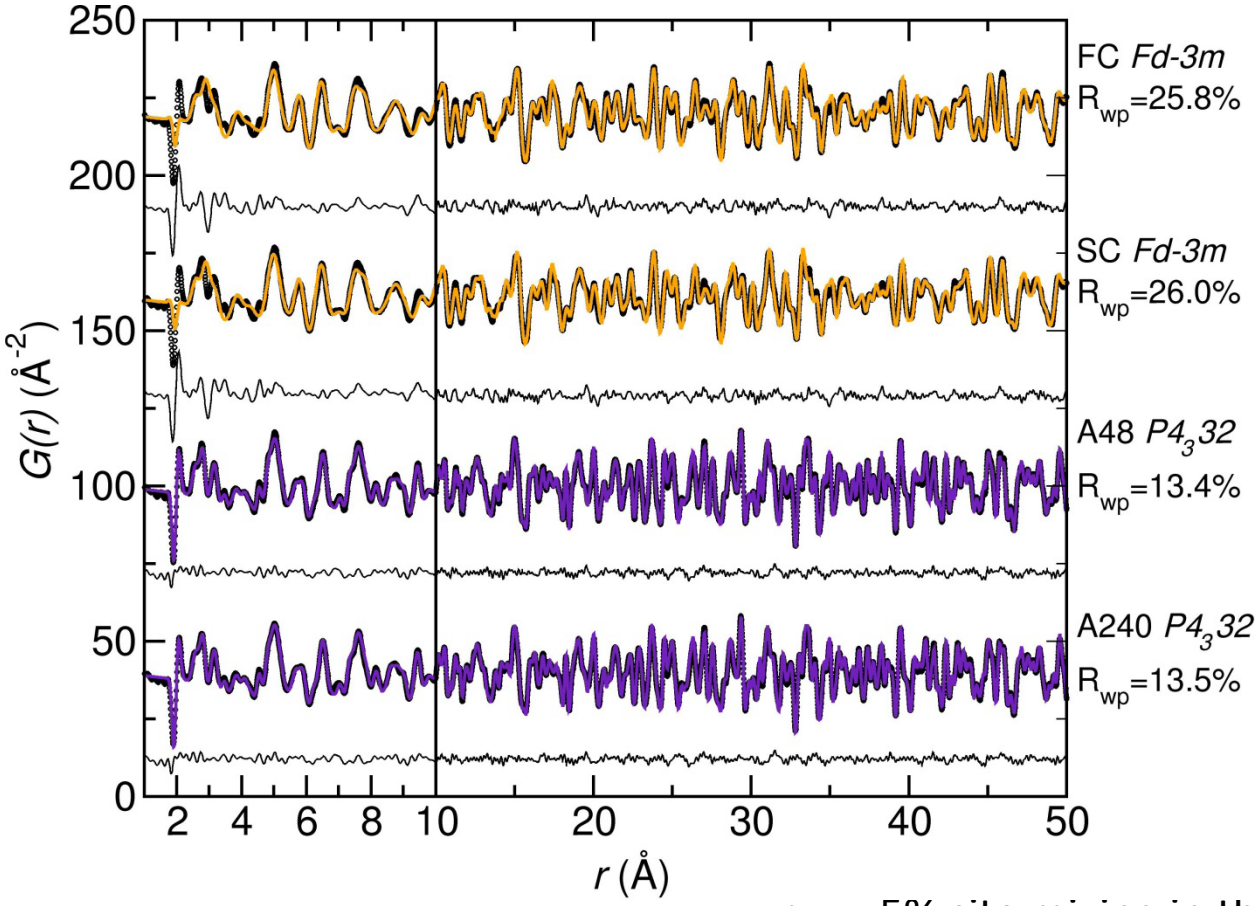
- Over 1 to 5 Å range the ordered Mn/Ni models ($P4_332$) provide much better fits for local PDF profiles in all samples
- **Ni/Mn are locally well-ordered in the long-range "disordered" samples**
- **Up to what length scale?**



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.

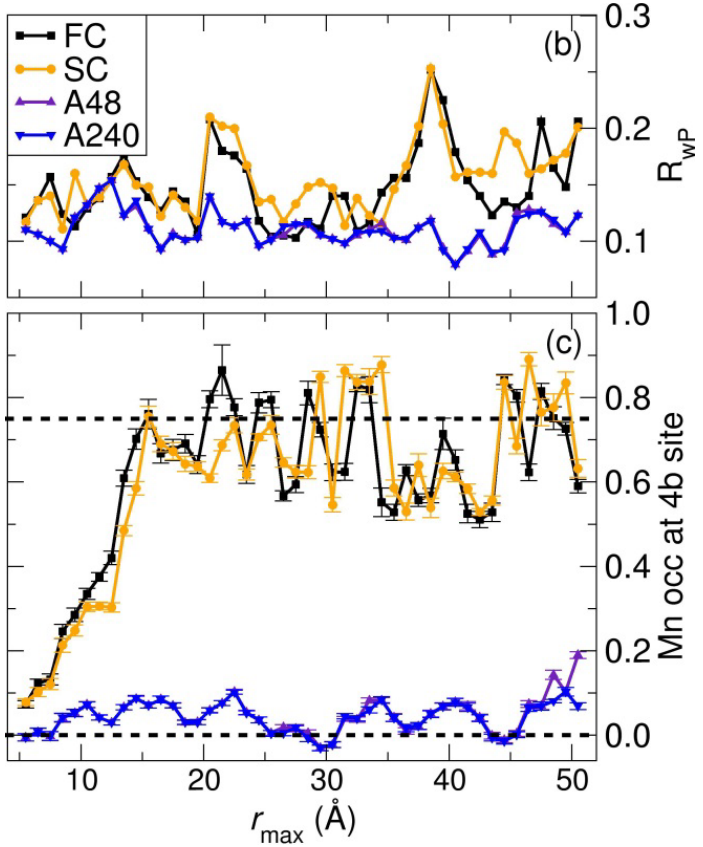
Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

15 Å correlation length scale for SRO



fully disordered

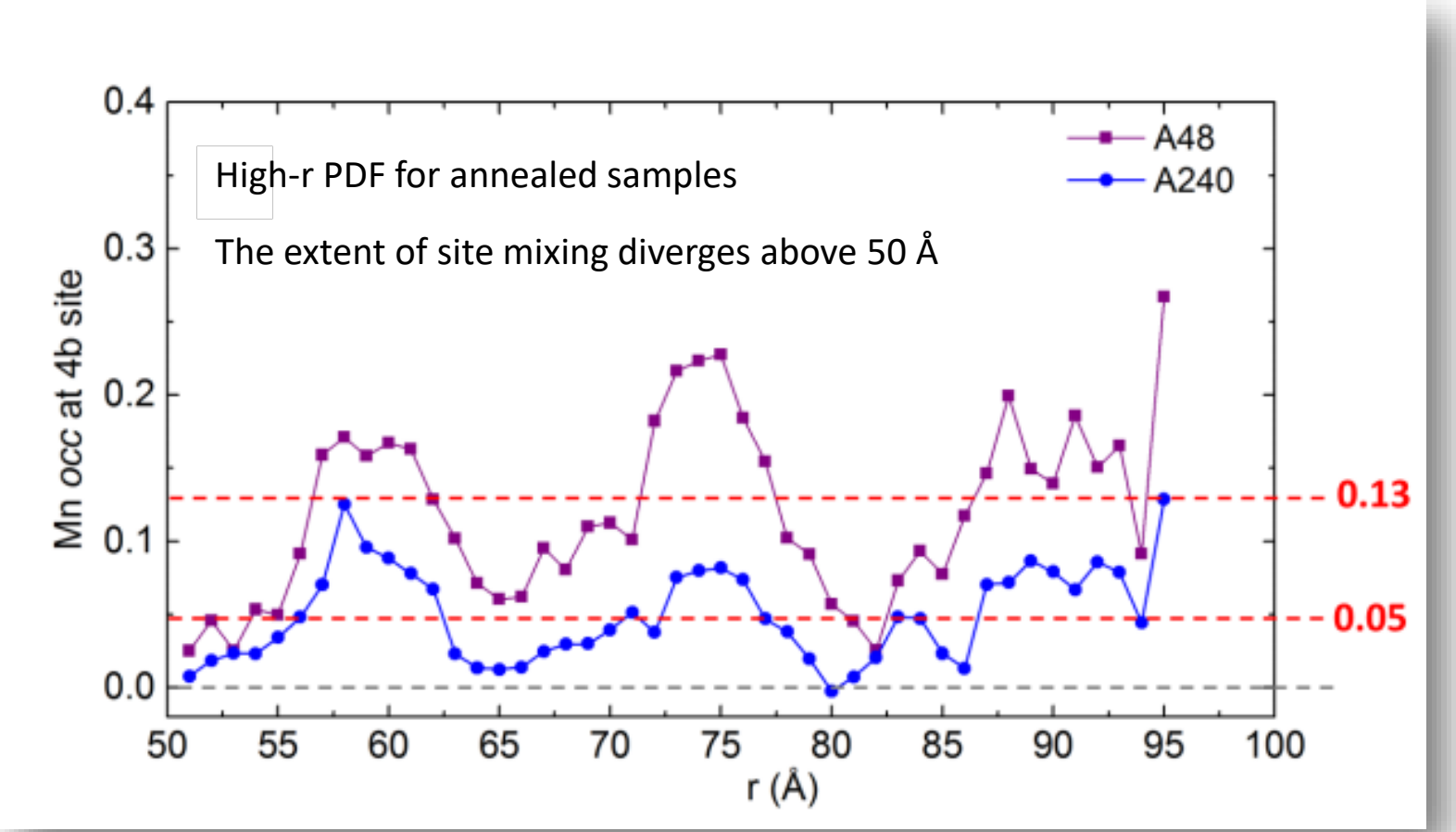
fully ordered



- 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 $^{7}LiNi_{0.5}Mn_{1.5}O_4$

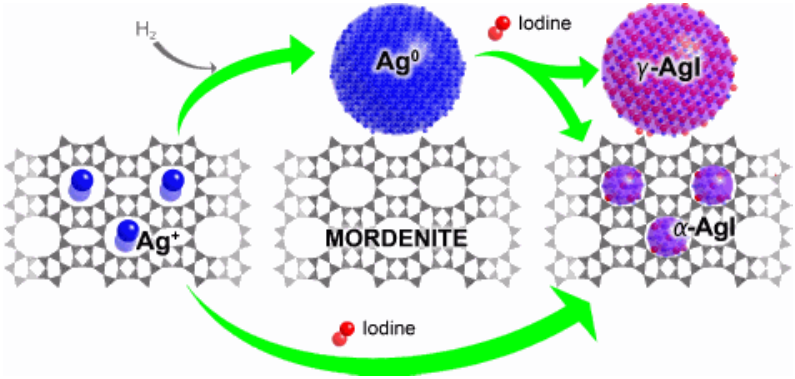
Fit the PDFs within a 4.5 Å “box” in 1 Å steps (a “box-car” refinement)



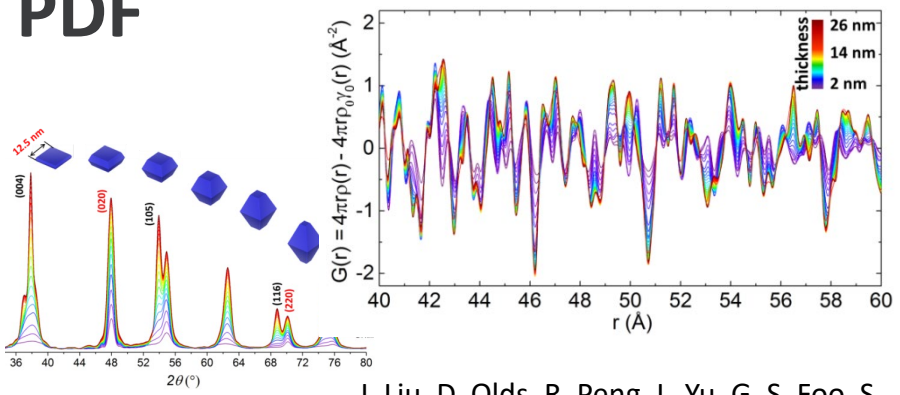
Spinel cathode materials are distinguished by their unique correlation length scales for chemical short-range ordering

Nanomaterial structure *via* PDF

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

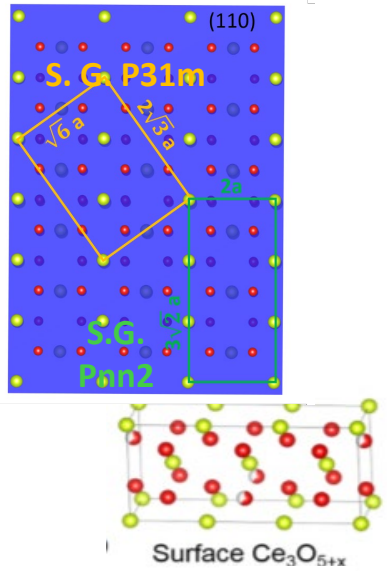


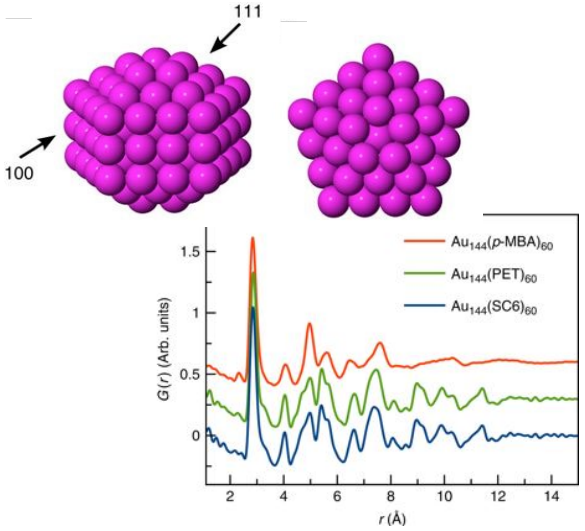
K. W. Chapman, P. J. Chupas, and T. M. Nenoff, **Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation**, *J. Am. Chem. Soc.* 132, 8897 (2010).



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).

S. Luo, M. Li, V. Fung, B. Sumpter, J. Liu… Z. Wu, and K. Page. **New Insights into the Bulk and Surface Defect Structures of Ceria Nanocrystals from Neutron Scattering Study**, *Chem. Mater.* 33, 3959–3970 (2021).

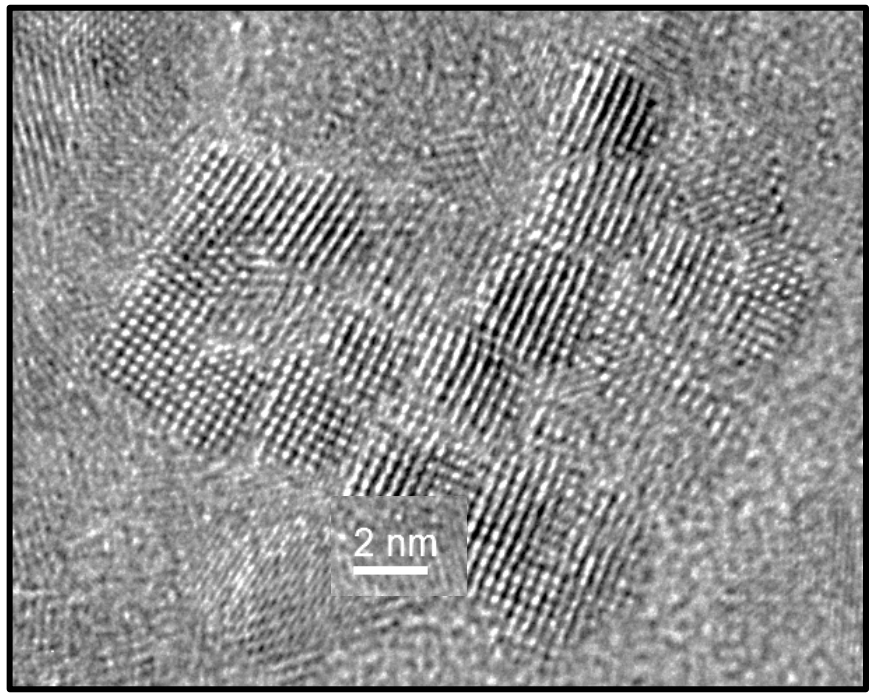


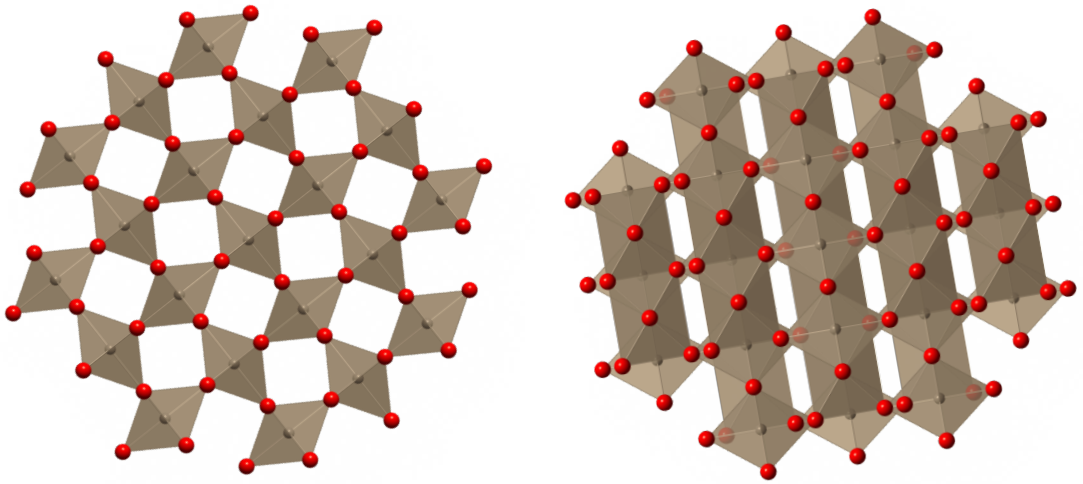


K. M. O. Jensen, P. Juhas, M. A. Tofanelli, C. L. Heinecke, G. Vaughan, and C. J. Ackerson, **Polymorphism in magic-sized $Au_{144}(SR)_{60}$clusters,** *Nature Communications* 7, 11859 (2016).

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.

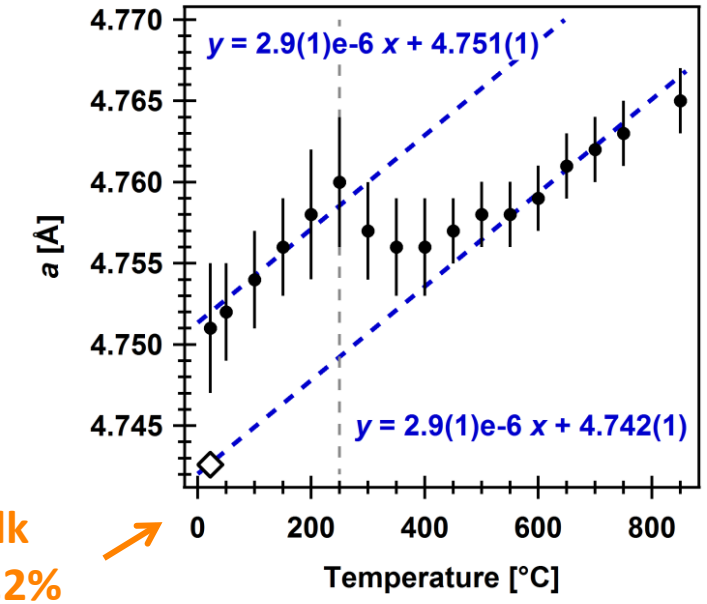
How many layers of water are at the surface?

How is water bonded to surfaces?

What are the dynamics of dehydration?

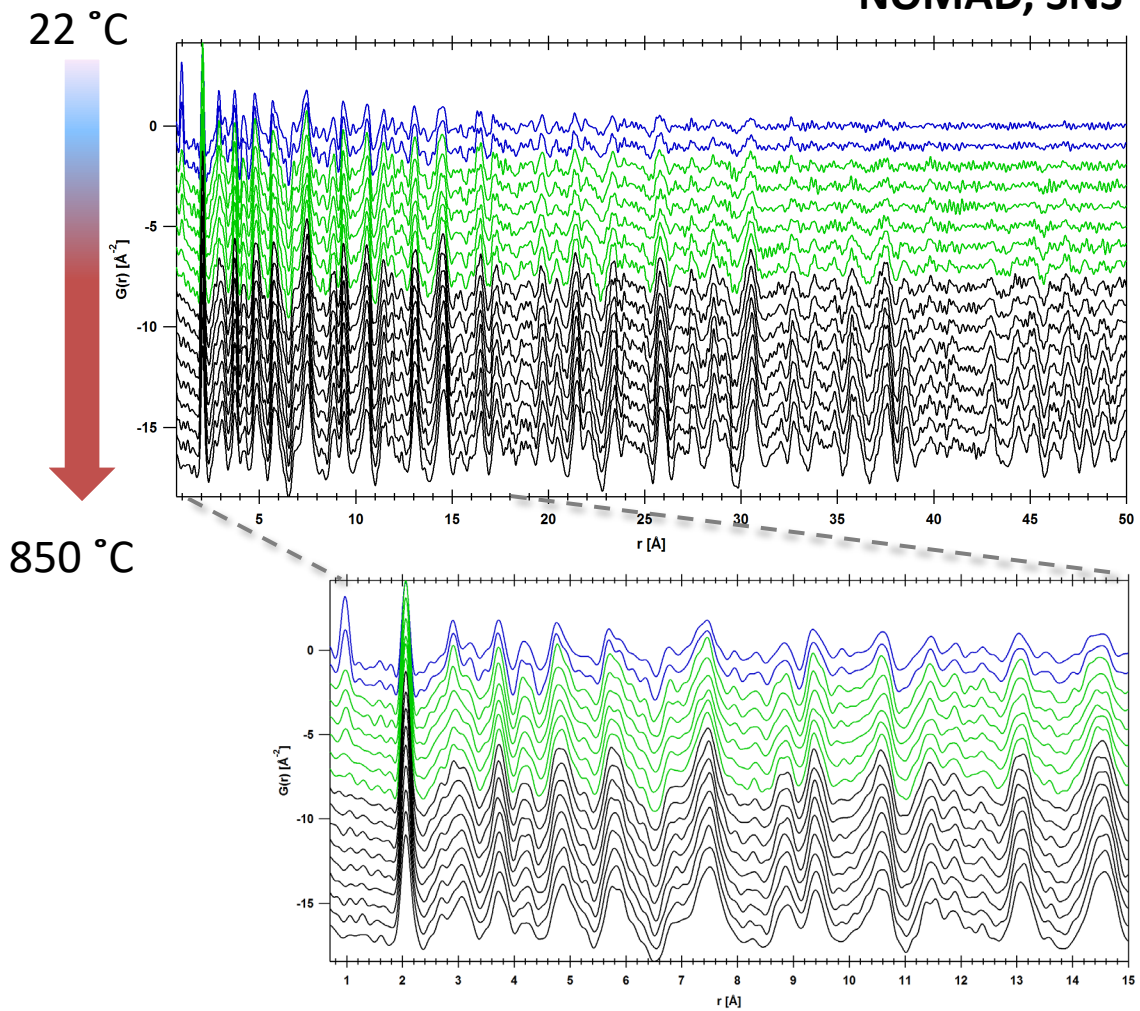
Example: SnO_2 Nanocrystals

- 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

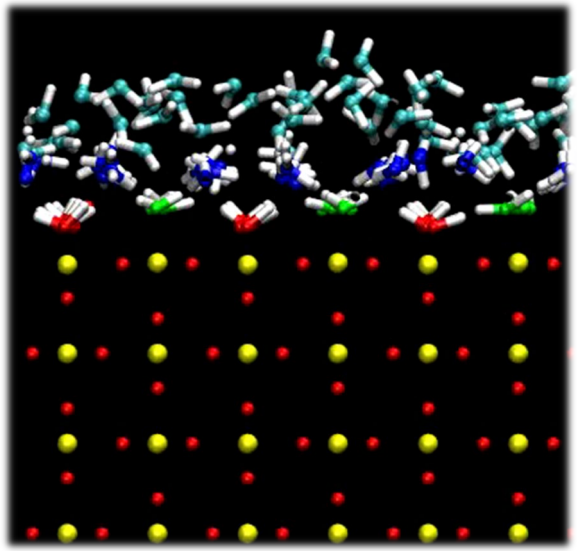


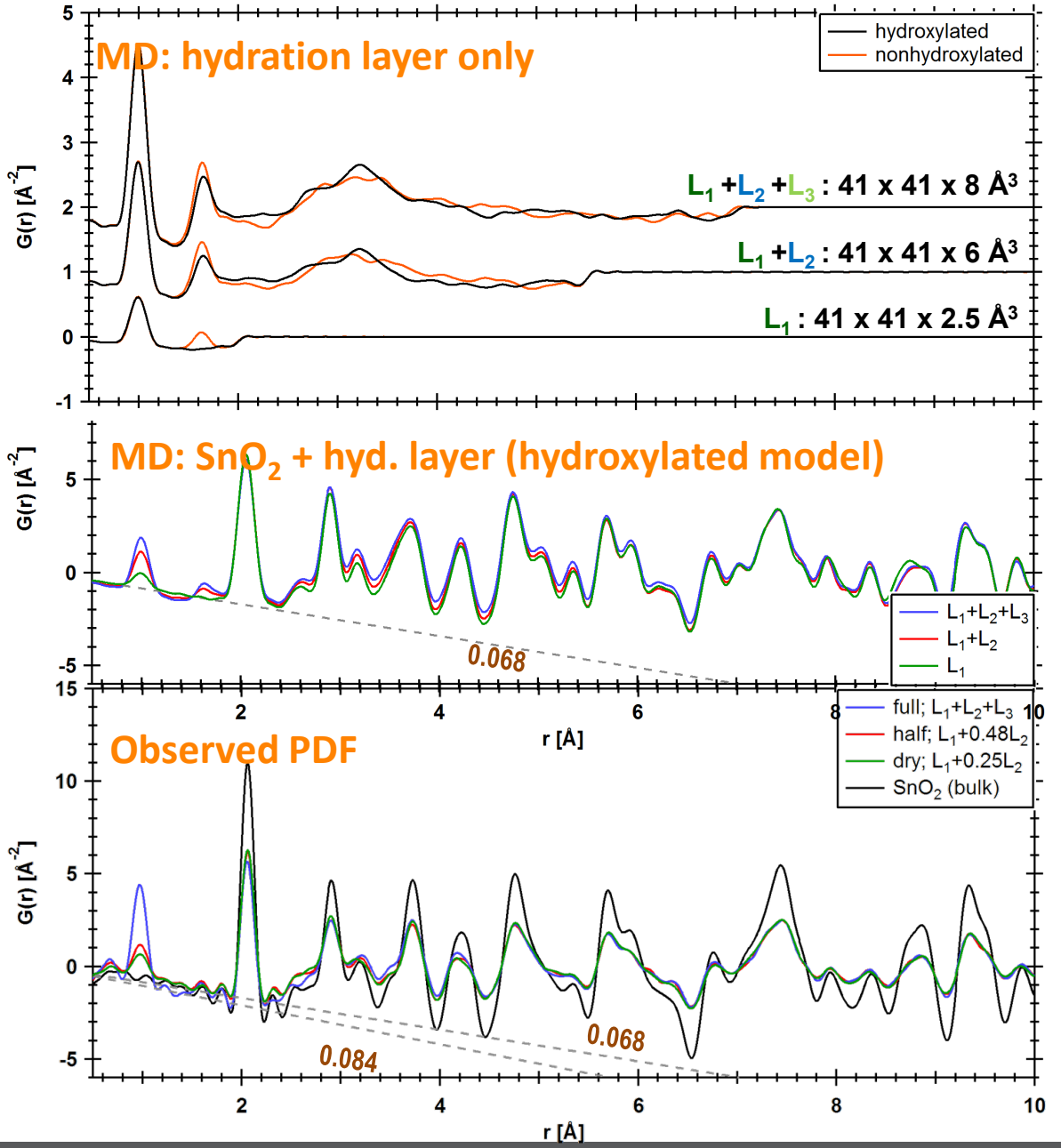
In situ dehydration answers these questions and indicates that water plays a key role in stabilizing the nanocrystals.

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 $Å^2$





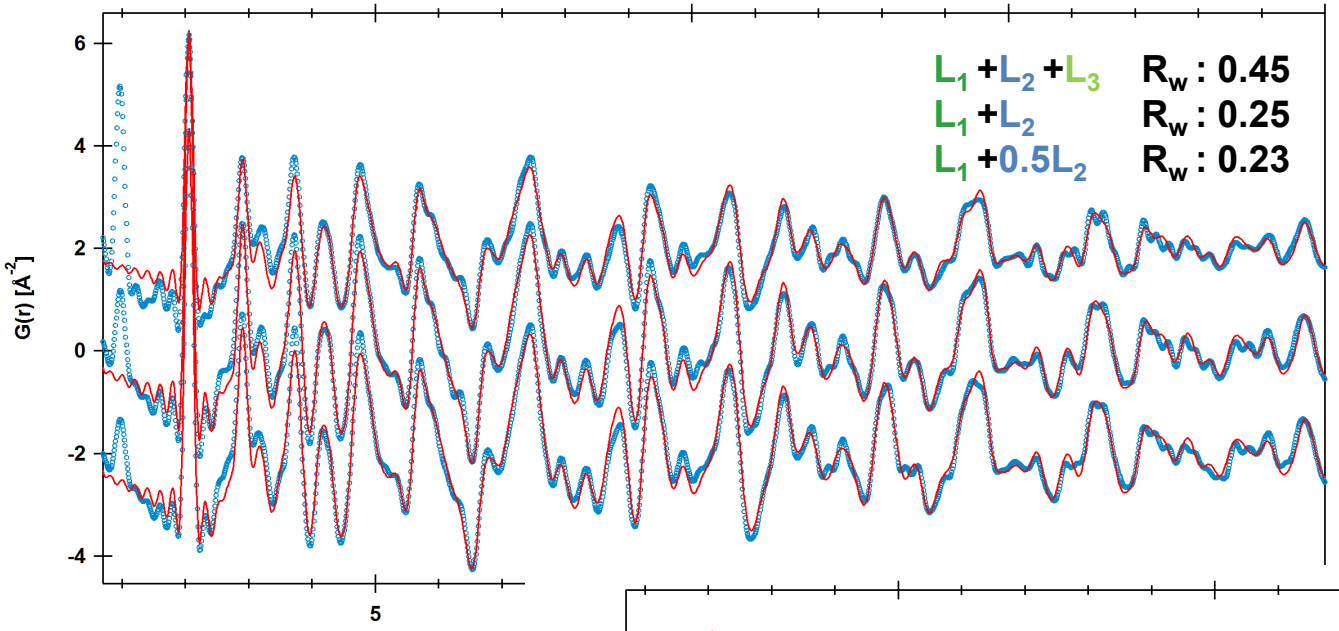
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

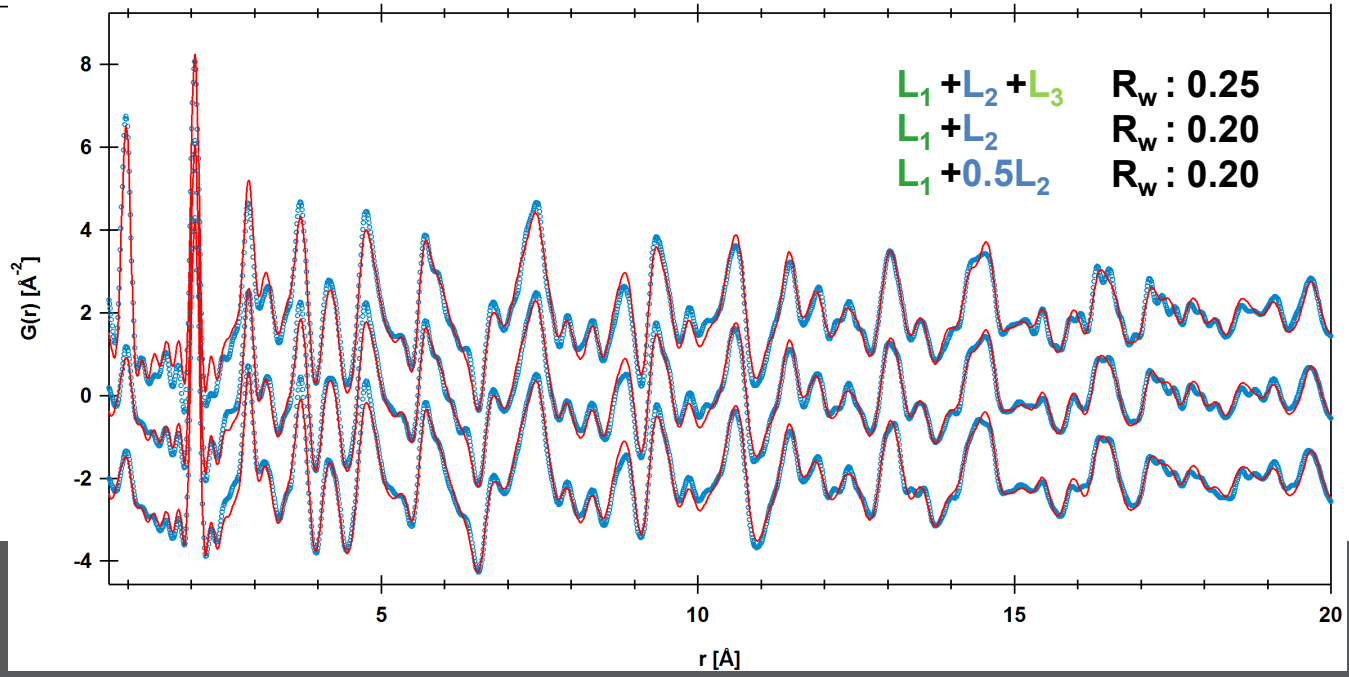
size = ~47 Å



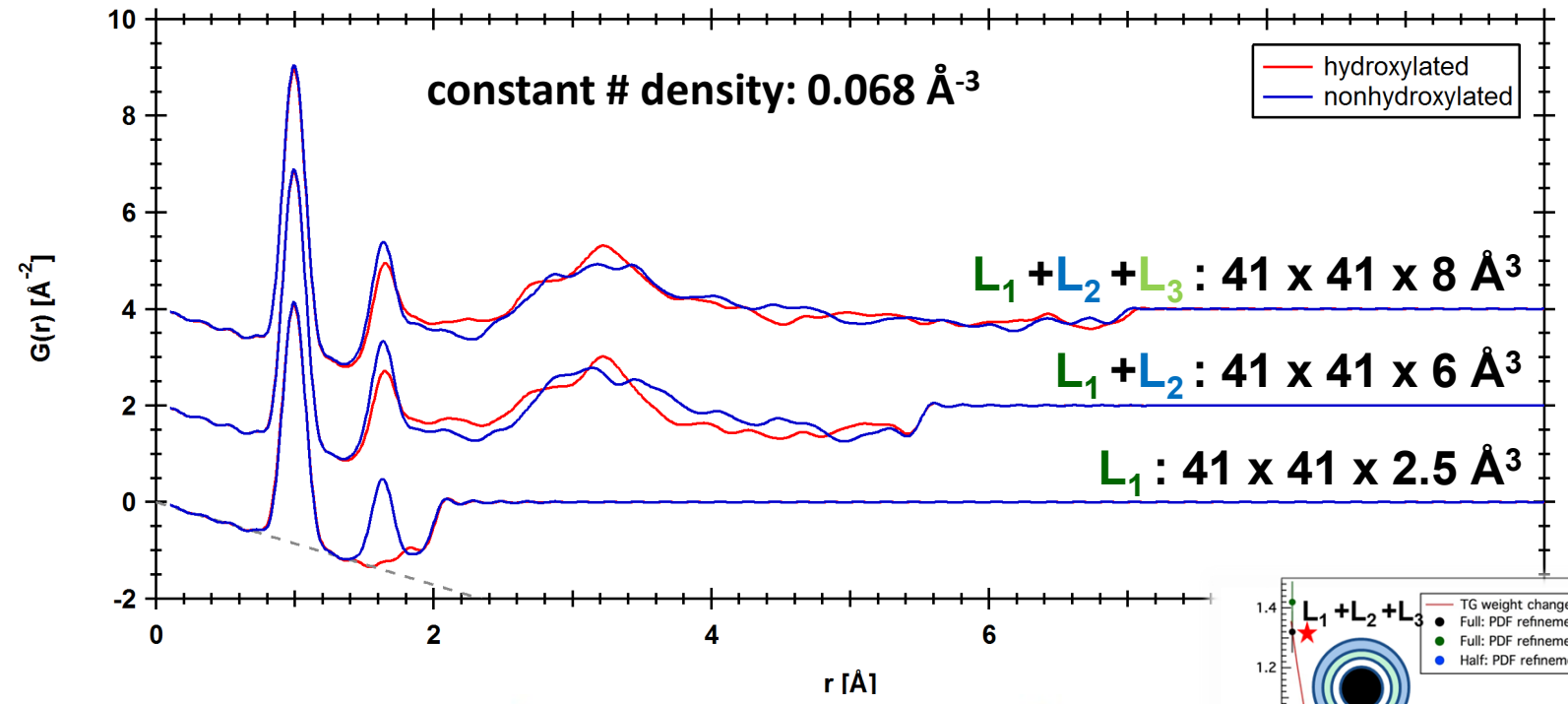
Two phase model:

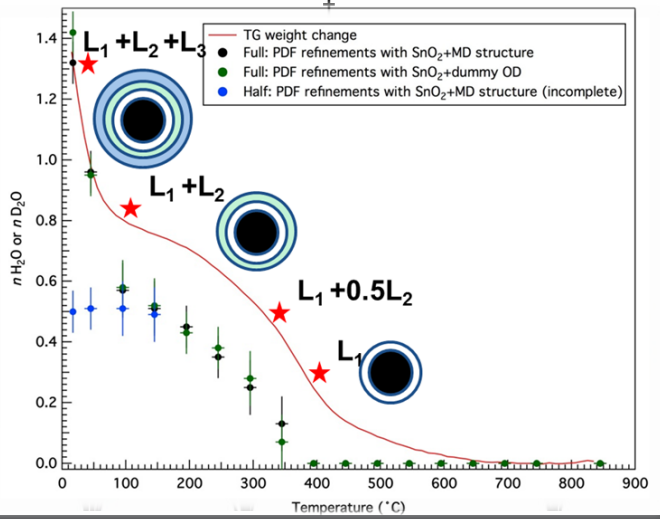
SnO_2 bulk + layered

MD water structure



Example: SnO_2 Nanocrystals

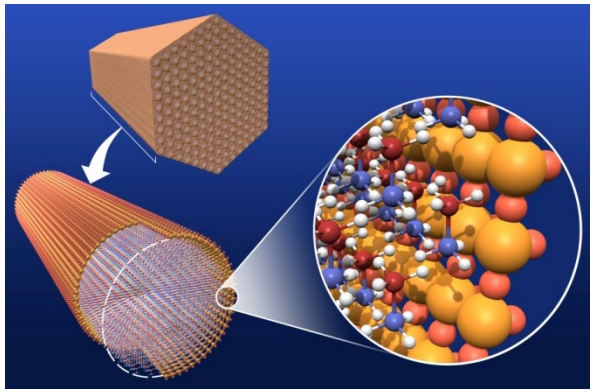




H.-W. Wang, D. J. Wesolowski, T. Proffen, L. Vlcek, W. Wang, L. F. Allard, A. I. Kolesnikov, M. Feygenson, L. M. Anovitz, and R. L. Paul, **Structure and stability of SnO_2 nanocrystals and surface-bound water species**, *J. Am. Chem. Soc.*, 135, 6885-6895, 2013.

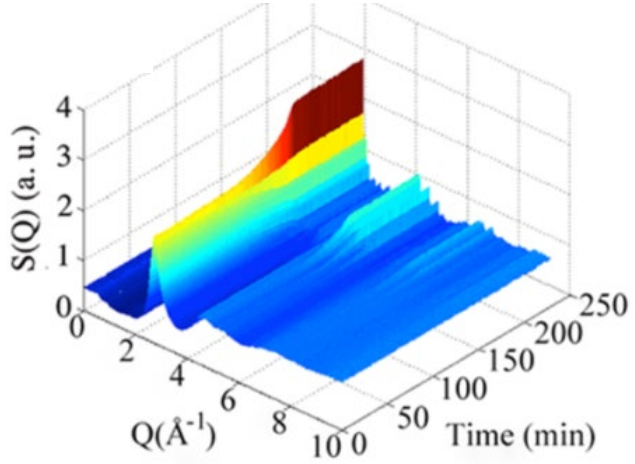
Amorphous structures *via* PDF

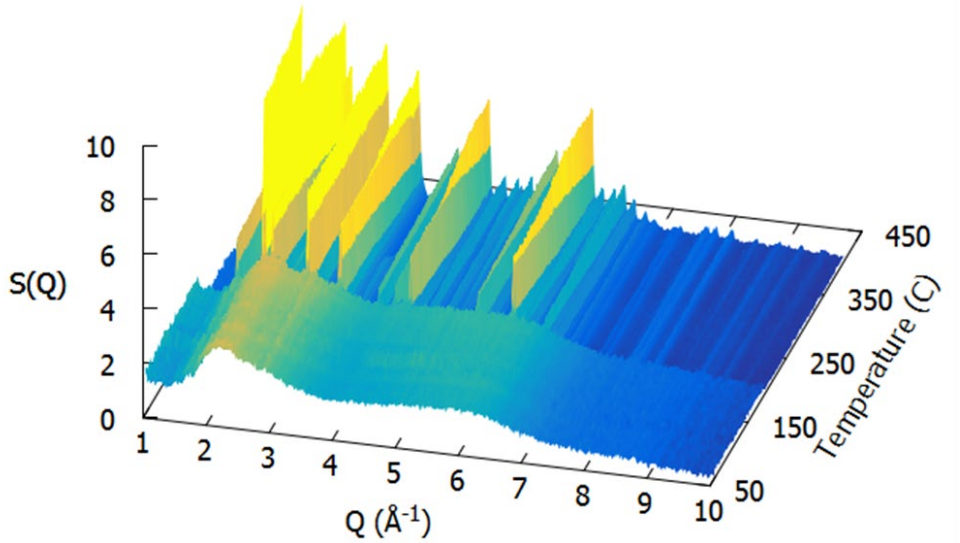
- Glasses
- Liquids
- Concretes
- Adsorbed/absorbed gases
- *etc.*



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).

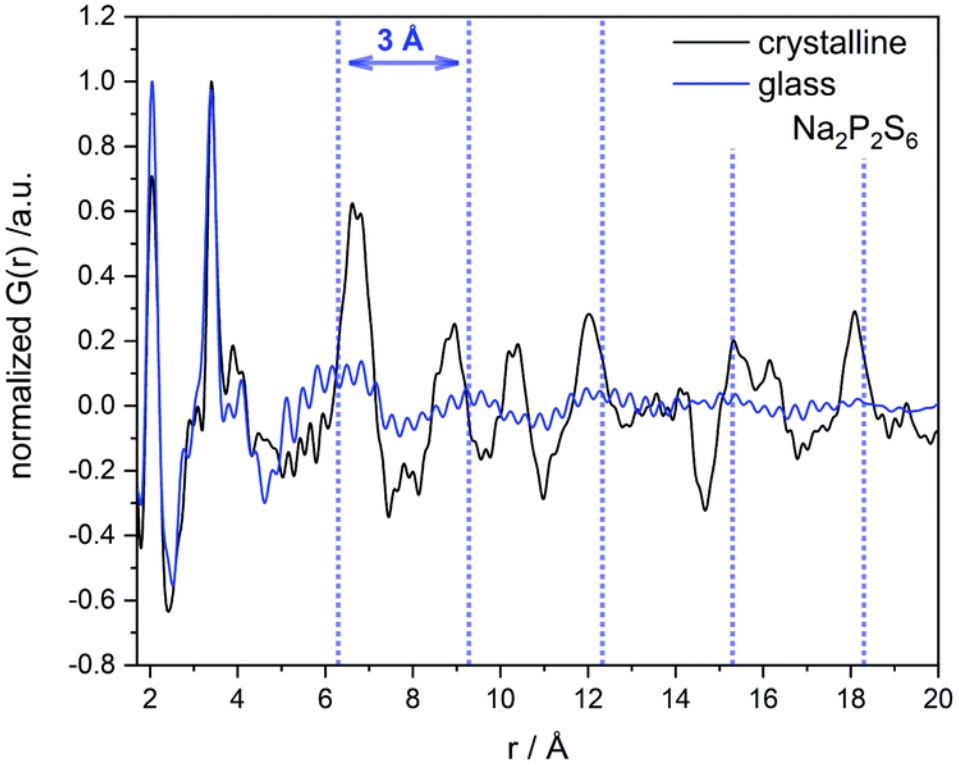




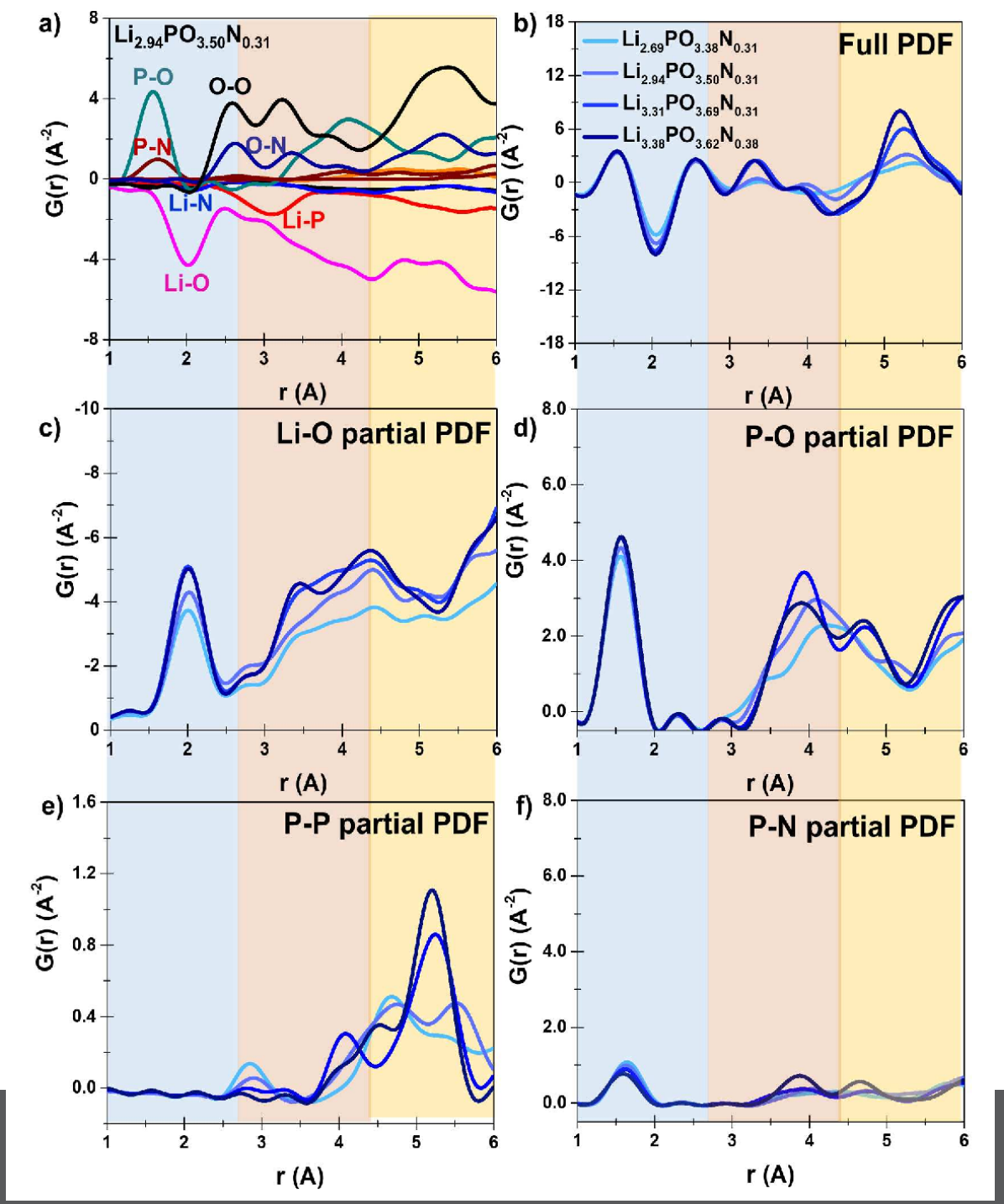
H.-W. Wang; L. L. Daemen, M. C. Cheshire, M. K. Kidder, A. G. Stack, L. F. Allard, J. Neuefeind, D. Olds, J. Liu, and K. Page, **Synthesis and structure of synthetically pure and deuterated amorphous (basic) calcium carbonates**, *Chem. Commun*., 53, 2942-2945 (2017).

Amorphous structures *via* PDF

High degree of Na disorder in amorphous $Na_2P_2S_6$ is responsible for high ionic conductivity



C. Fritsch , A.-L. Hansen, S. Indris, M. Knapp, and H. Ehrenberg, Mechanochemical synthesis of amorphous and crystalline $Na_2P_2S_6$ – elucidation of local structural changes by X-ray total scattering and NMR, *Dalton Trans.*, 2020, **49**, 1668-1673.



Questions?

U.S. DEPARTMENT OF ENERGY | Office of Science

THE UNIVERSITY OF TENNESSEE KNOXVILLE

Outline

Part 1:

- The Pair Distribution Function (PDF)
- Applications
  - Local Distortions
  - Chemical Short-Range Order
  - Nanomaterial Structure
  - Amorphous Structure

Part 2:

- Experimental Considerations
- Modeling a PDF
- Emerging Areas
- Summary

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.*

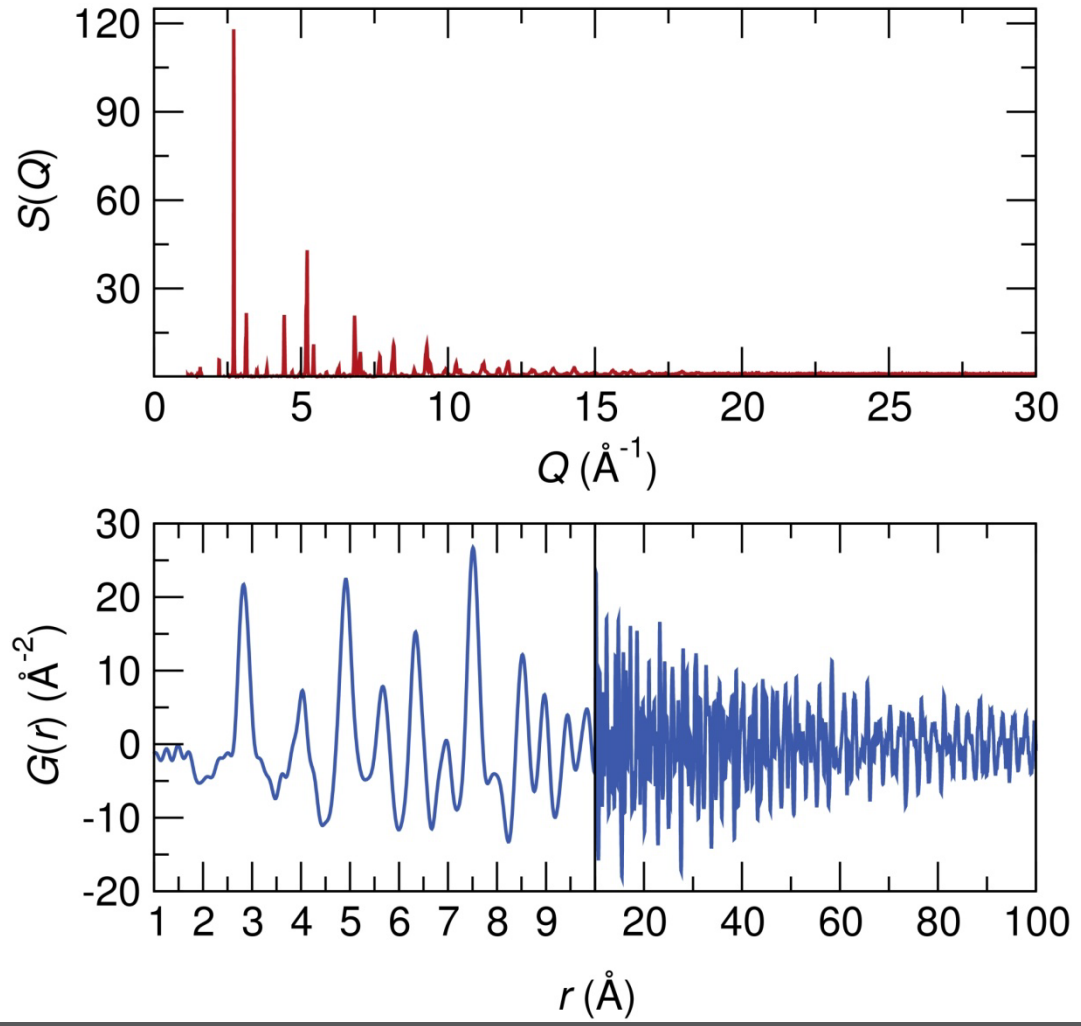
Normalized by: Incident flux, number of atoms, square of the scattering length/form factor

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

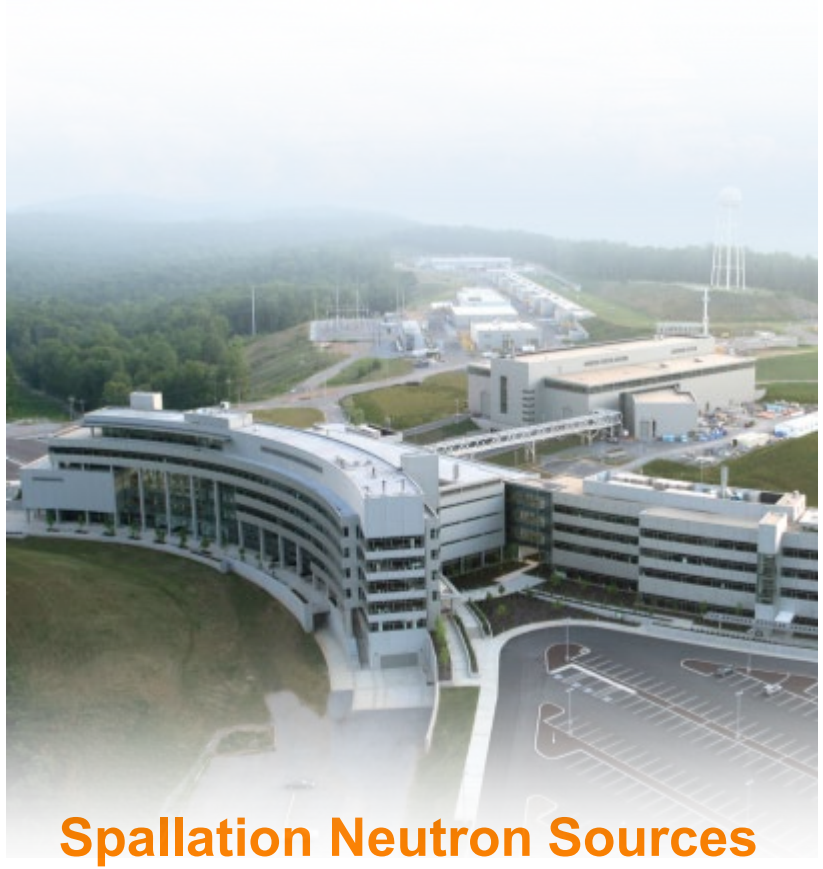
(3) Good counting statistics

(4) Low (and stable) instrument background

An ideal measurement would have no contribution from the instrument resolution

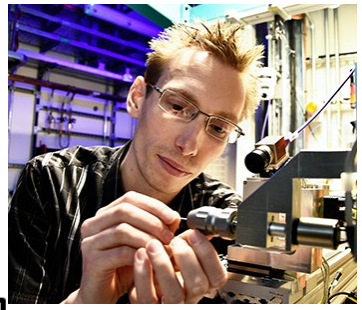
For PDF: a wide *Q* range and high flux is balanced with resolution, best done at

Synchrotron Sources **or**



Spallation Neutron Sources

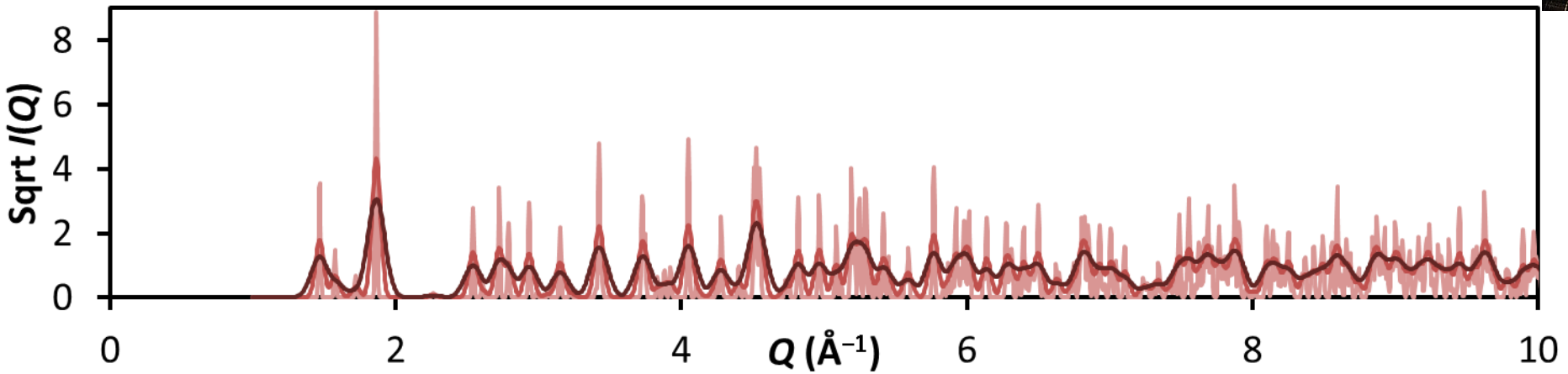
Resolution Effect

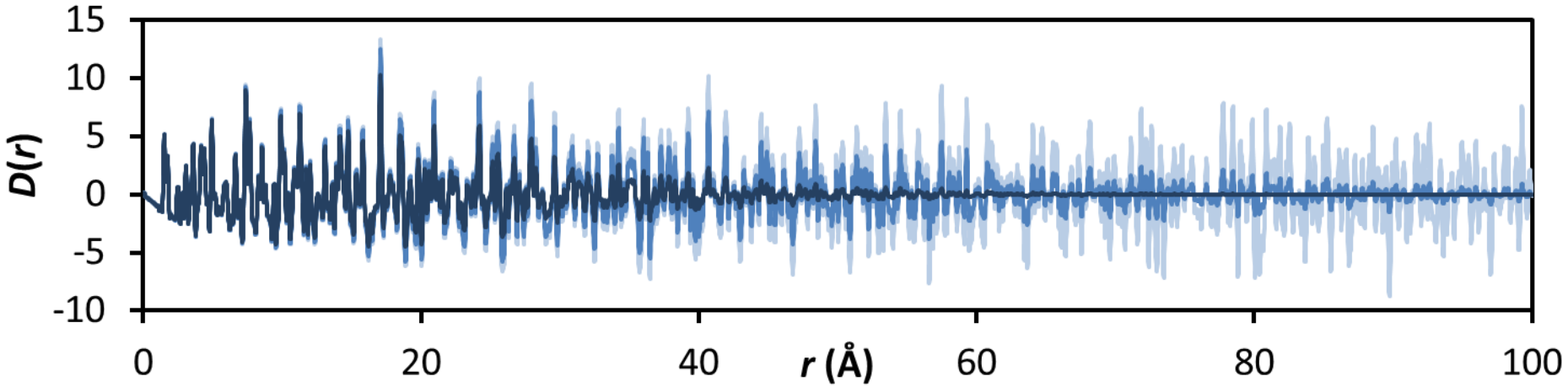


Courtesy of Phil Chater, Diamond Light Source

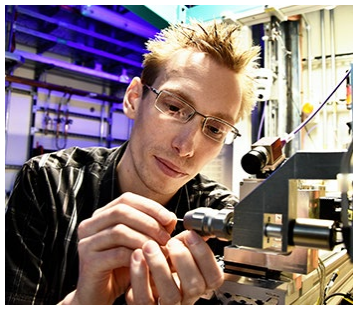
Reciprocal space: Peak width, *dQ*

Real space: D





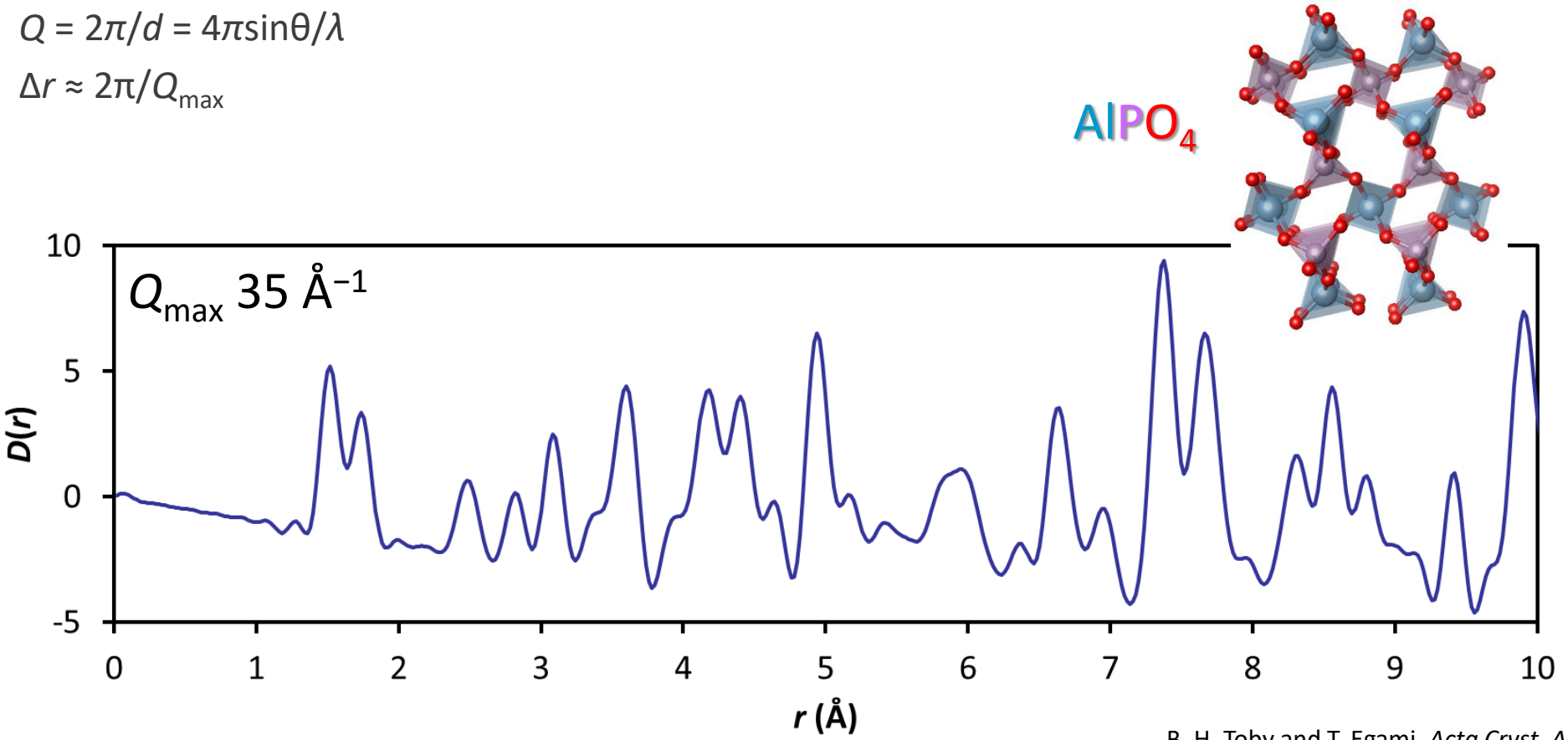
Q_{max} Effect



Courtesy of Phil Chater, Diamond Light Source

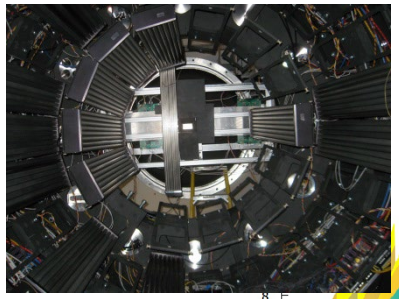
Δr resolution of a PDF is dominated by Q_{max}

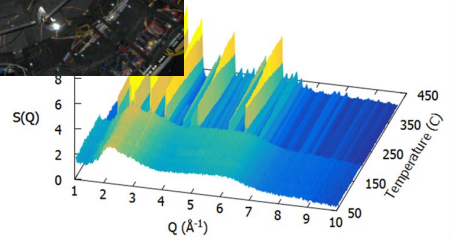
- $Q = 2\pi/d = 4\pi\sin\theta/\lambda$
- $\Delta r \approx 2\pi/Q_{max}$



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

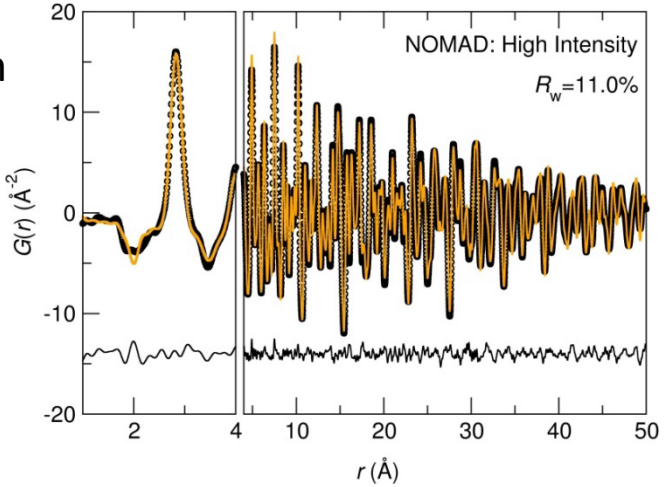
TOF Diffraction and Total Scattering at SNS

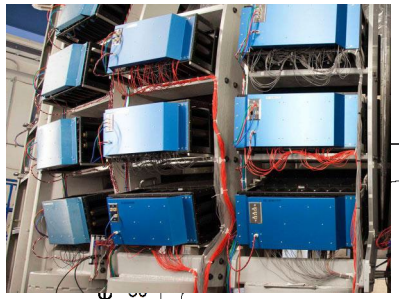


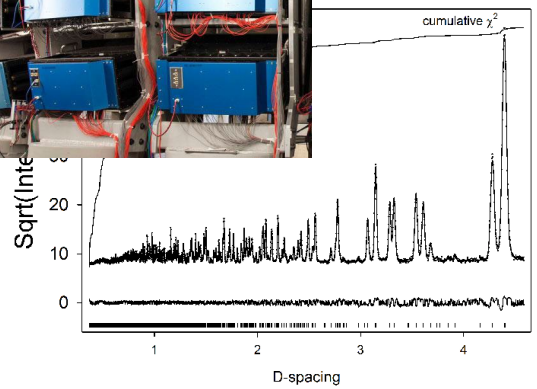


Typical **NOMAD** data can be collected for **30 - 100 mg** of sample in a 3 mm quartz capillary in **~1 hour**

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



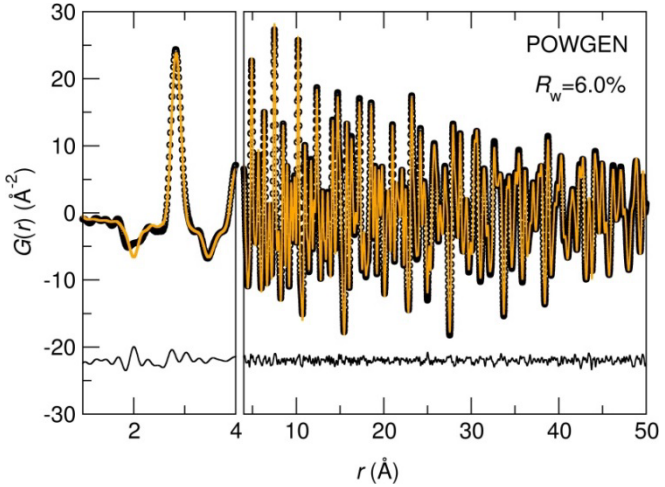




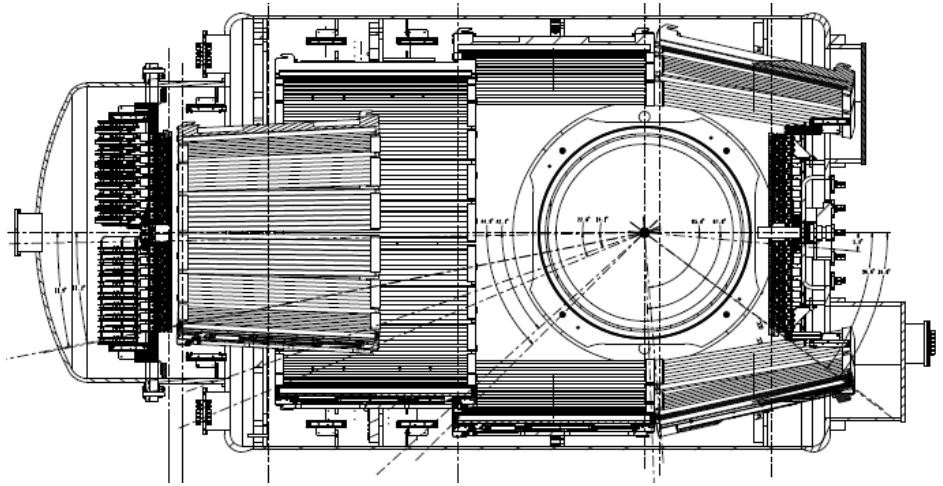
Typical **POWGEN** data can be collected for **~3 - 10 g** of sample in a 6 mm vanadium canister in **~3 hours**

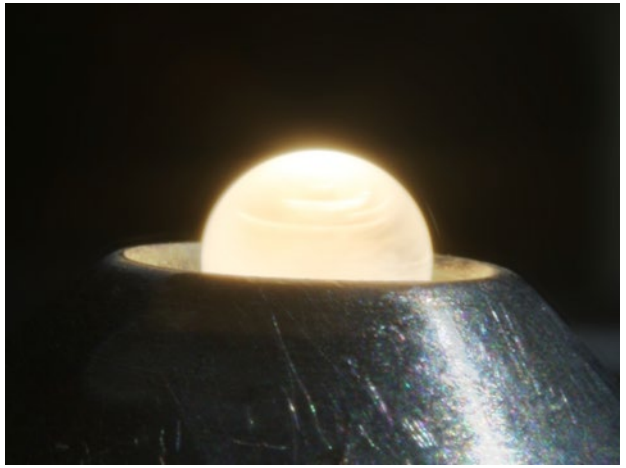
high resolution *diffraction and PDF of crystalline materials*

Mail-in programs available on both instruments



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)
- Gas flow cell (RT-800K)
- High voltage & electrochemica set-up (10kV)

MODELING A PDF

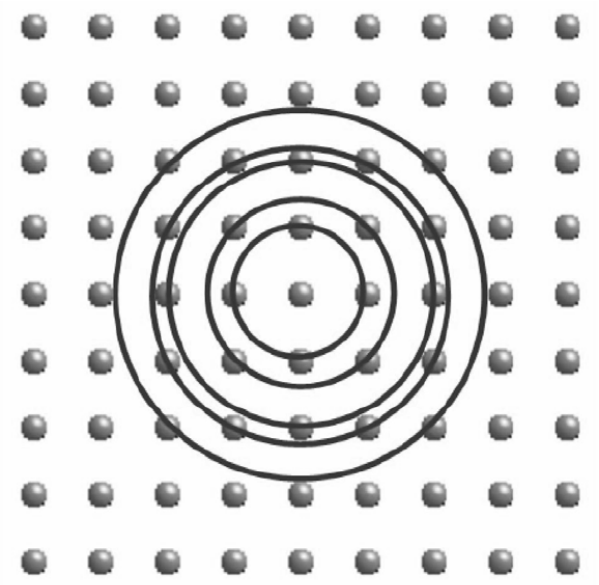
Calculating a PDF from a model

Available software

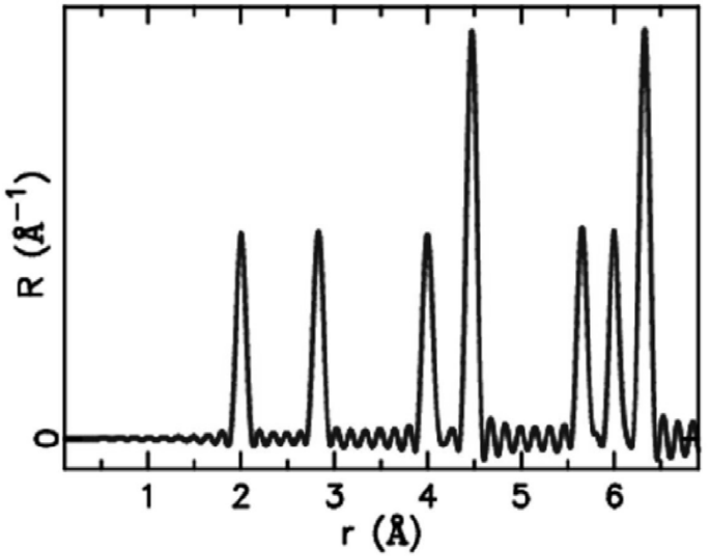
Nanoparticle shape effects

Pair Distribution Function

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



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



Atomic PDF (PDFFIT notation):

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

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

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

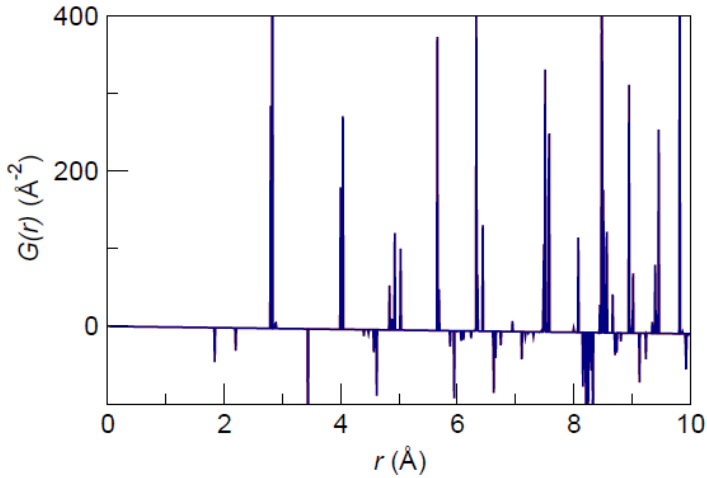
Small model: convolution of $\delta(r-r_{ij})$ with distribution function (*PDFgui & TOPAS v6*)

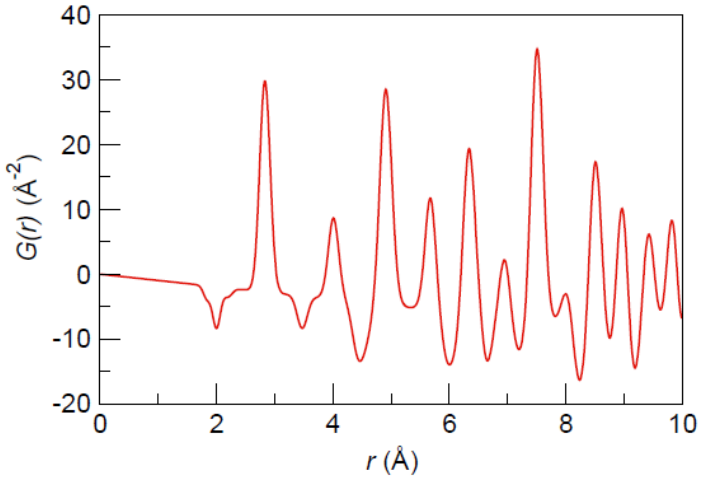
Large model: ensemble average of actual displacements (*RMCprofile*)

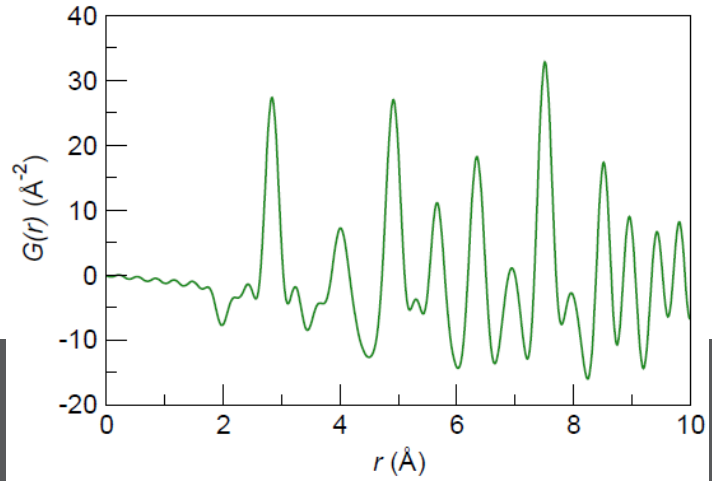
Termination ripples + instrumental dampening

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

…







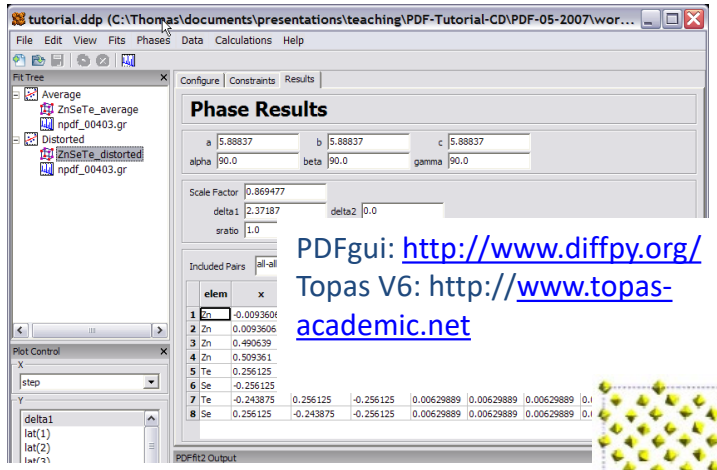
Atomic PDF Modeling

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

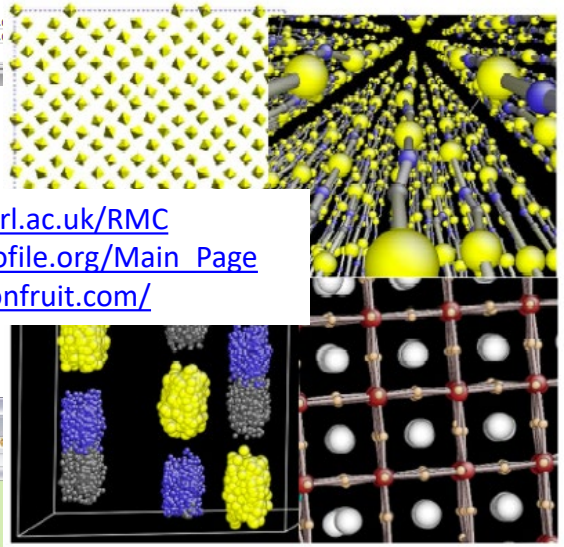
Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q), G(r),* Bragg profile, now EXAFS
Constraints utilized
Static 3-D model of the structure (a snap-shot)

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



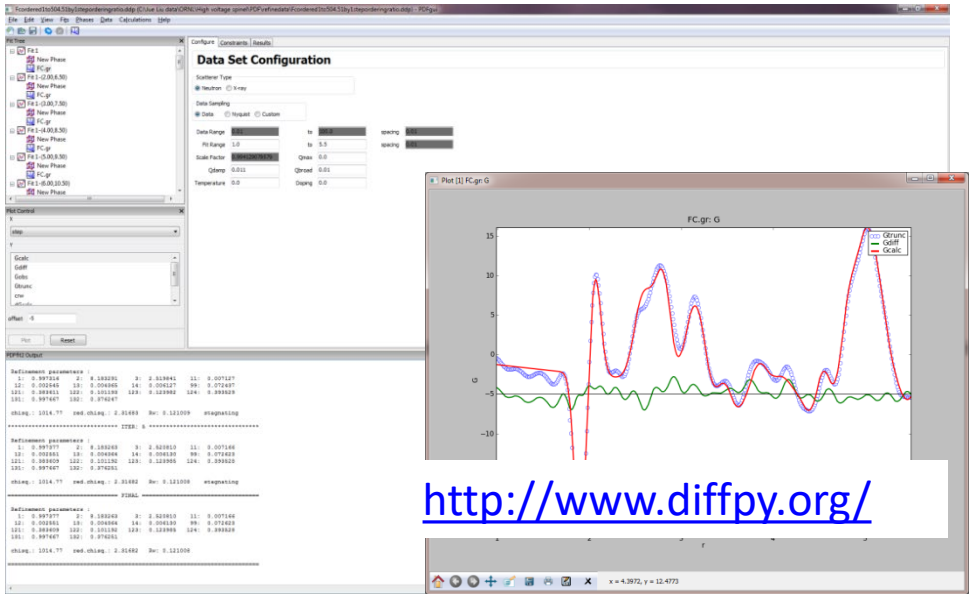
PDFgui: http://www.diffpy.org/
Topas V6: http://www.topas-academic.net



RMCprofile: http://www.isis.rl.ac.uk/RMC
FullRMC: http://www.rmcprofile.org/Main_Page
EPSR: http://disordmat.moonfruit.com/

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

Small Box: Brief Software Comparison



http://www.diffpy.org/

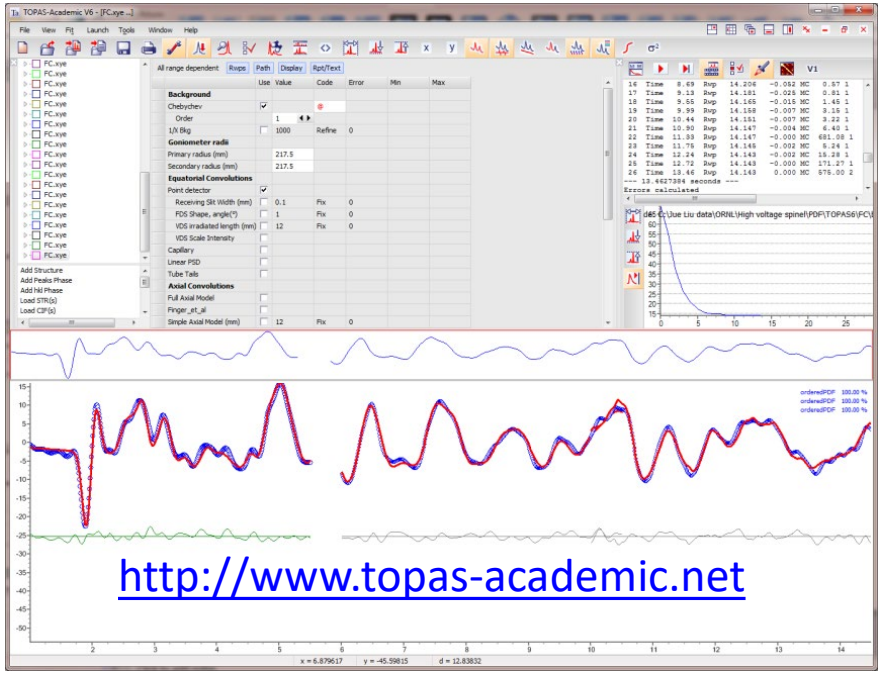
PDFgui

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

*Check out **diffpy-cmi** for a python language version*

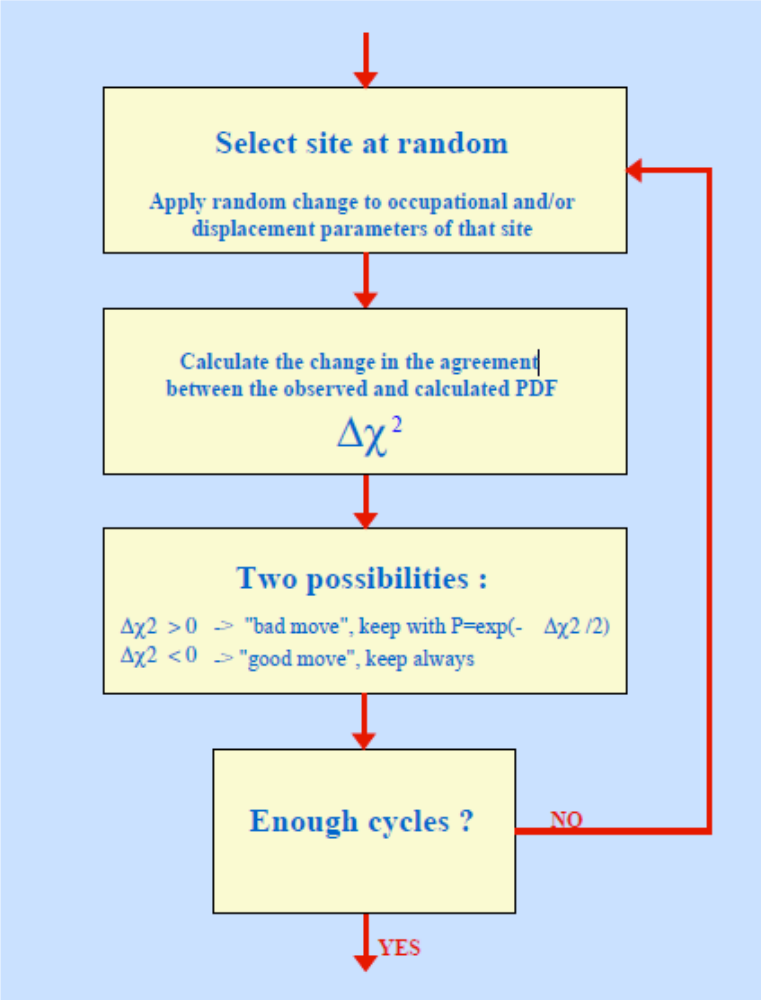
TOPAS PDF

+ Fast and 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



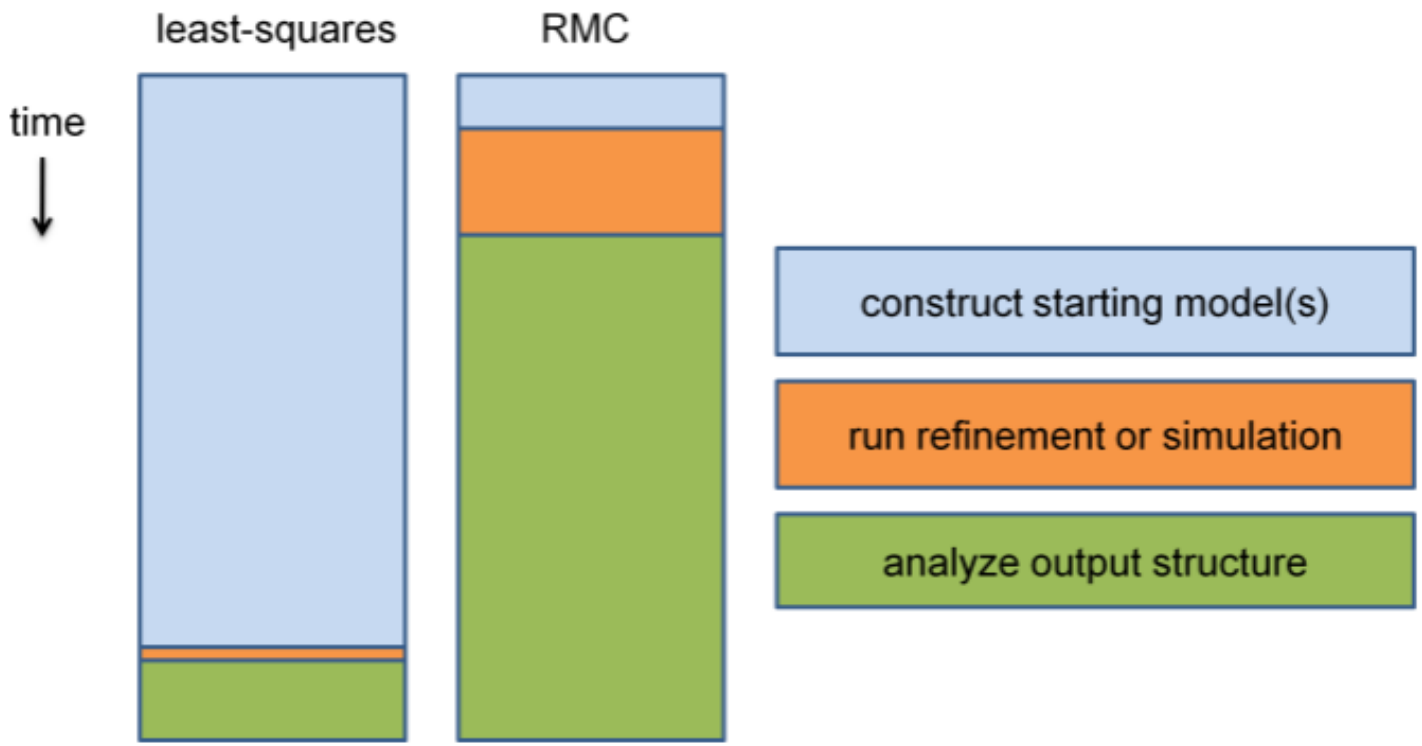
RMCprofile

- Atomic configurations ~600 to 20000+ atoms
- Fit both X-ray and neutron F(Q)
- Fit G(r)
- Fit Bragg profile
- Fit EXAFS
- Polyhedral restraints
- Coordination constraints
- Closest approach constraints
- **Produce a static 3-D model of the structure (a snap-shot in time)**
- http://www.rmcprofile.org/Main_Page

Also check out **FullRMC**

- https://bachiraoun.github.io/fullrmc/

Complexity/Investment Trade-Off?

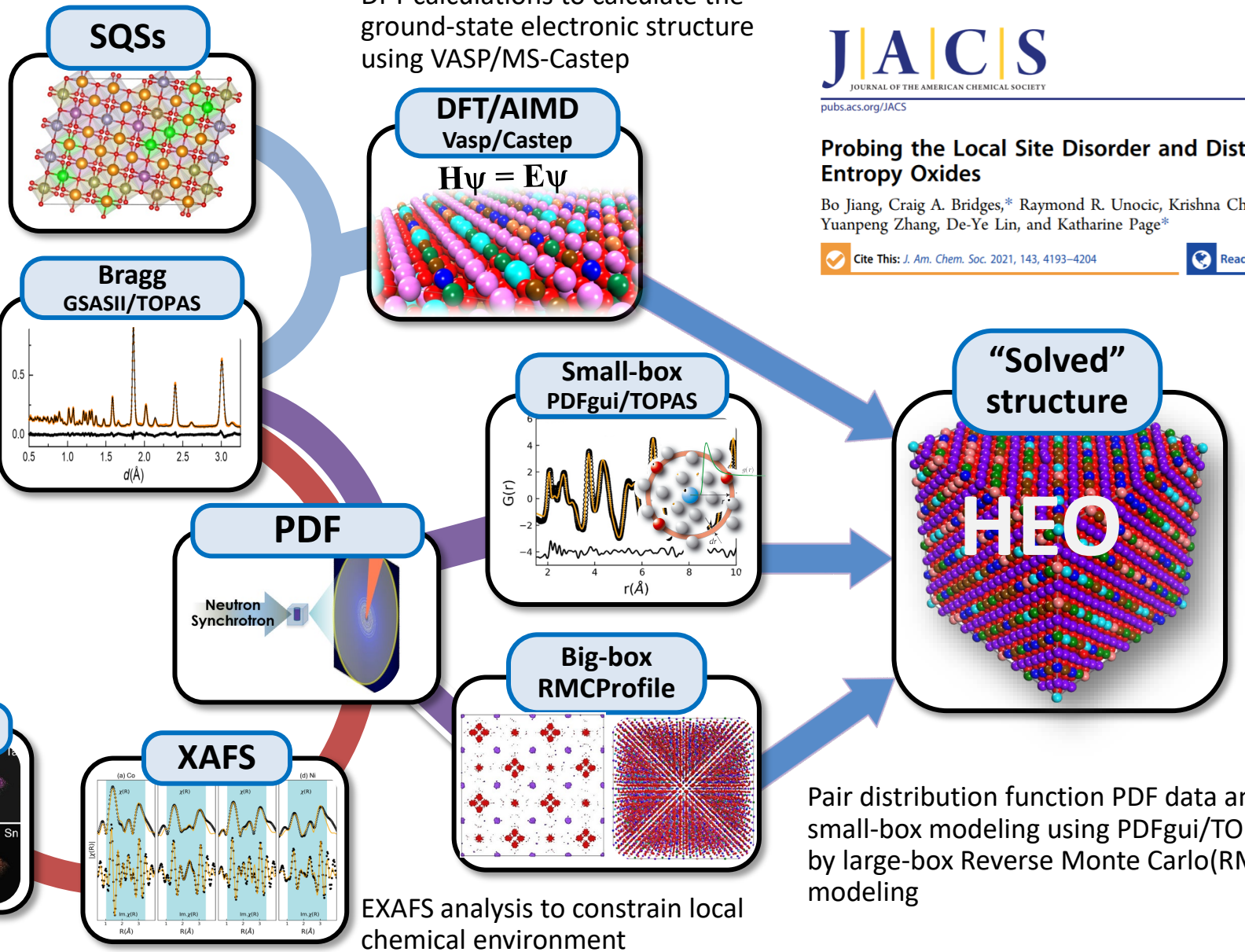


Daniel P. Shoemaker, *Understanding atomic disorder in polar and magnetic oxides* (2010).

Special quasirandom structure (SQSs) to optimize cation disorder in solid solution materials

Metropolis Monte Carlo simulations (MCS) utilized to estimate cation disorder and predict secondary phases

DFT calculations to calculate the ground-state electronic structure using VASP/MS-Castep



JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Article

Probing the Local Site Disorder and Distortion in Pyrochlore High-Entropy Oxides

Bo Jiang, Craig A. Bridges,* Raymond R. Unocic, Krishna Chaitanya Pitike, Valentino R. Cooper, Yuanpeng Zhang, De-Ye Lin, and Katharine Page*

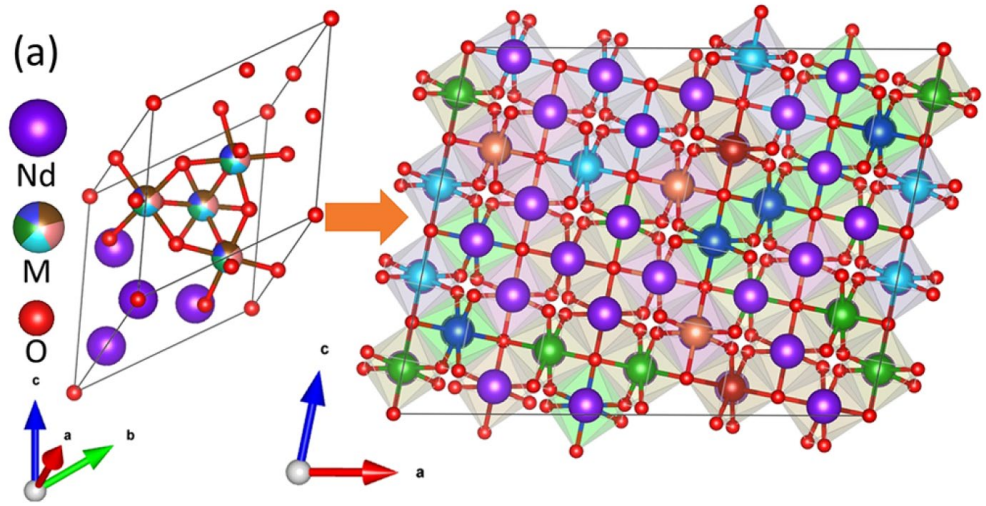
Cite This: *J. Am. Chem. Soc.* 2021, 143, 4193–4204 Read Online

EXAFS analysis to constrain local chemical environment

Pair distribution function PDF data analyzed by small-box modeling using PDFgui/TOPAS and by large-box Reverse Monte Carlo(RMC) modeling

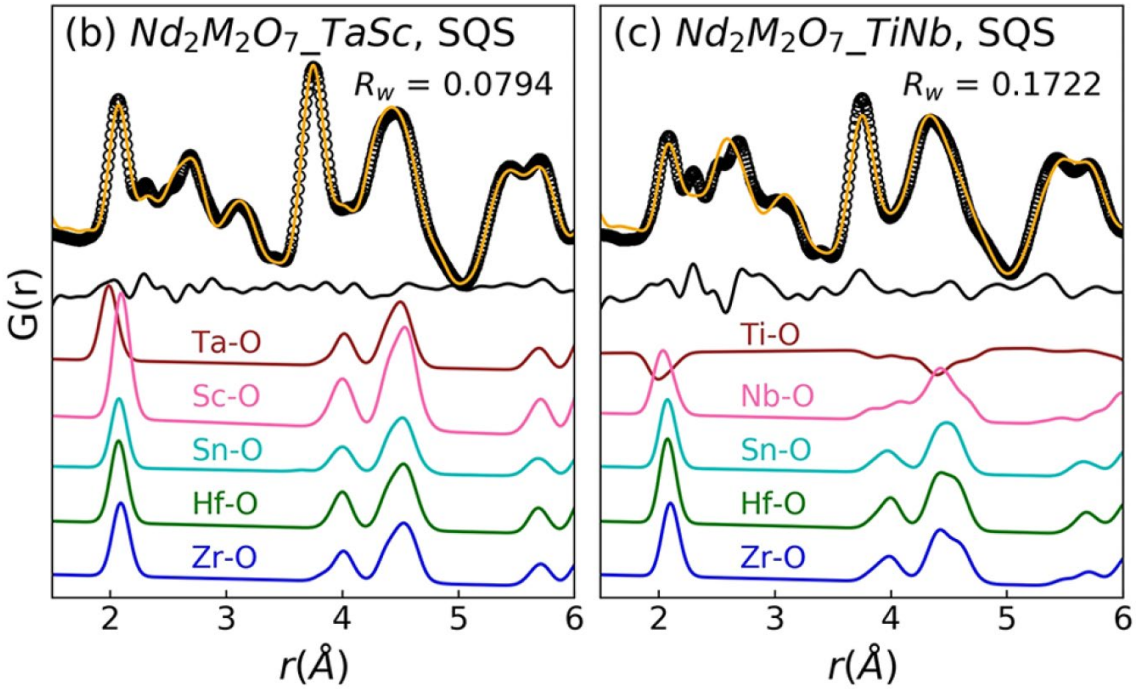
Small-box PDF fitting using DFT-relaxed SQS supercell

The Special Quasirandom Structures (SQS) approach allows one to design periodic supercells representative of a real disordered state and has been shown to successfully reproduce electronic and thermodynamic properties in disordered alloys combined with DFT calculations



Primitive unit cell and Special Quasirandom Structures (SQS) supercell

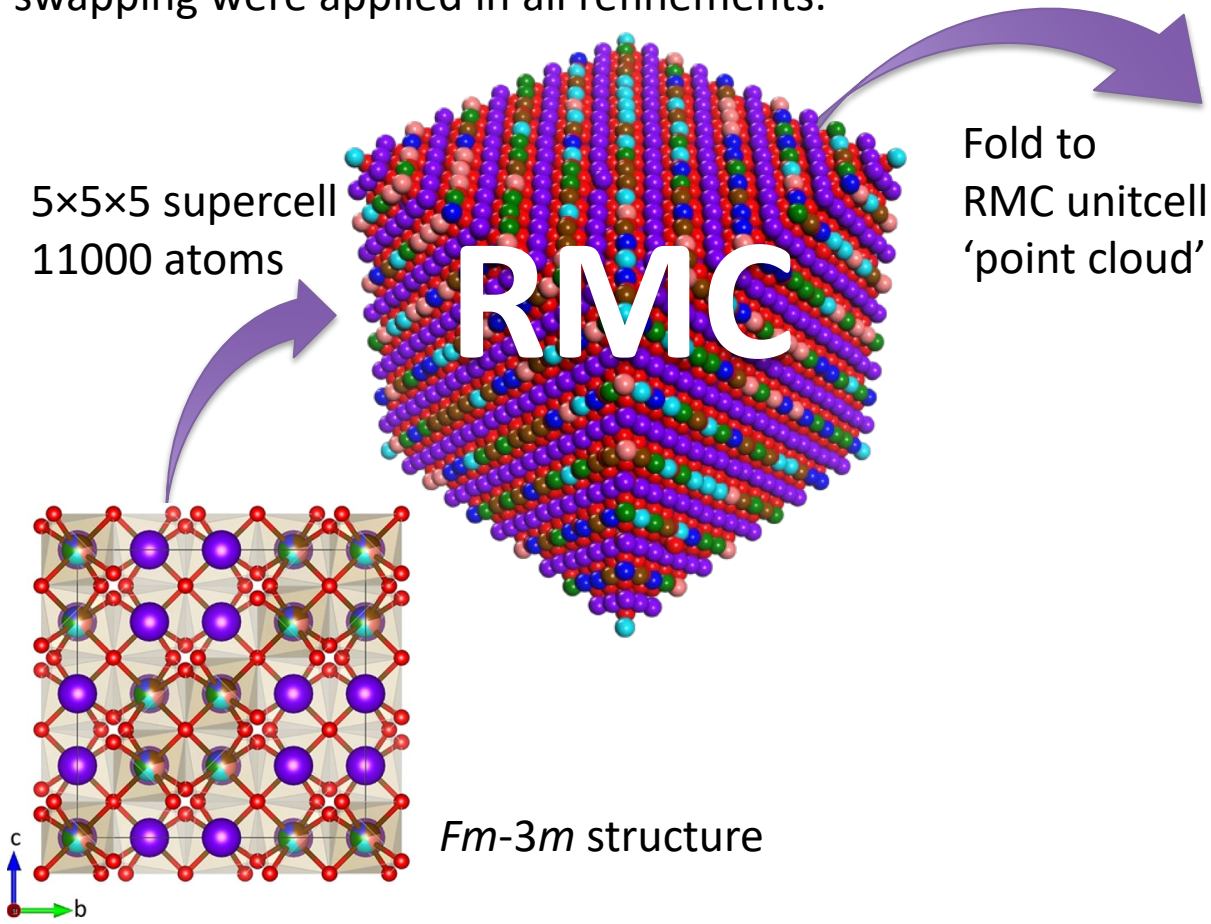
$Nd_2(Ta_{0.2}Sc_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$ $Nd_2(Ti_{0.2}Nb_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$

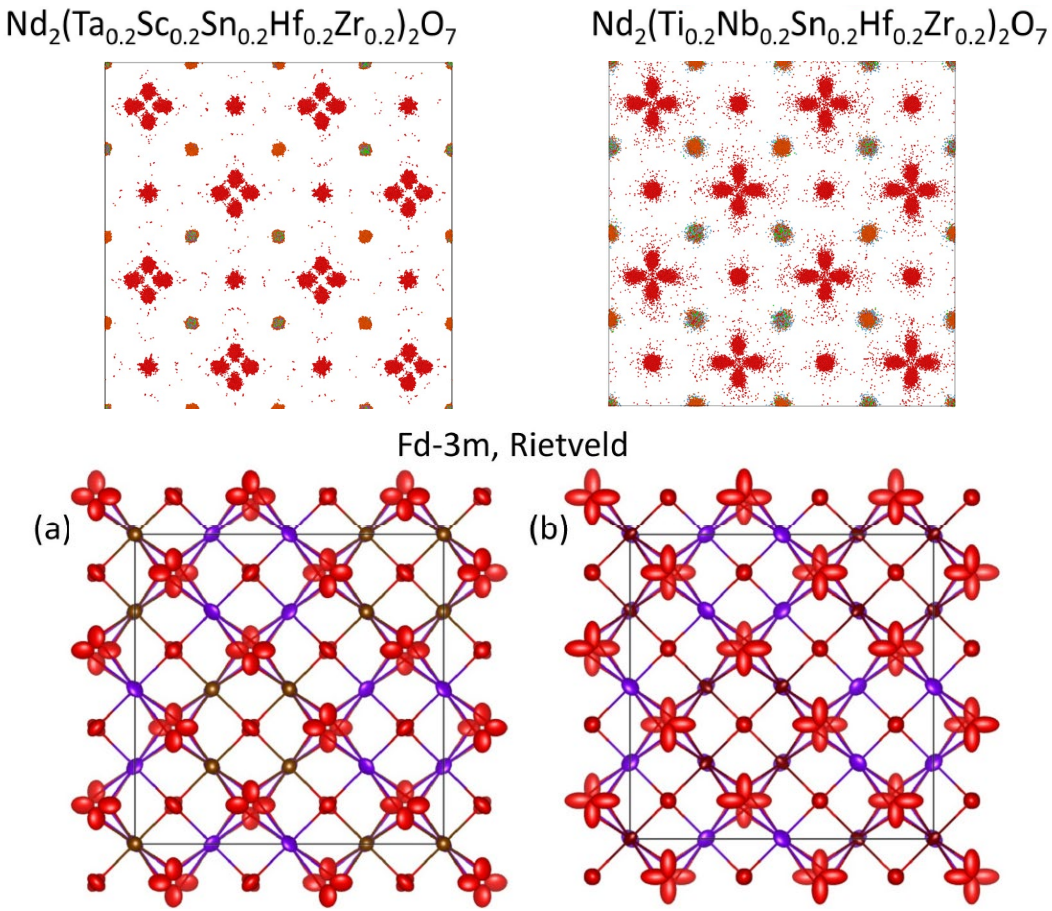


Total and decomposed partial PDFs from individual M−O pair−pair correlations

“Big-box” RMC fitting consistent with disordered M cations

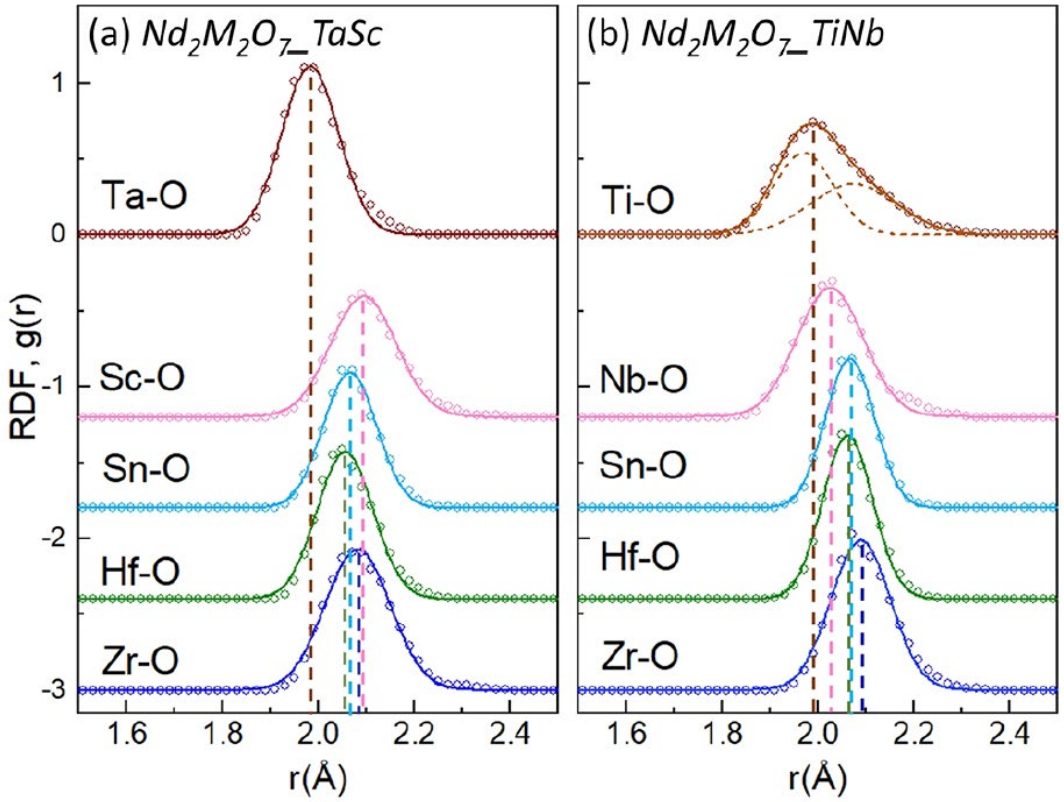
Reverse Monte Carlo (RMC) fits were performed to identify the short-range cation ordering, obtained by fitting PDF G(r), F(Q), and the neutron diffraction patterns simultaneously. Bond valence sum (BVS) restrictions and atom swapping were applied in all refinements.

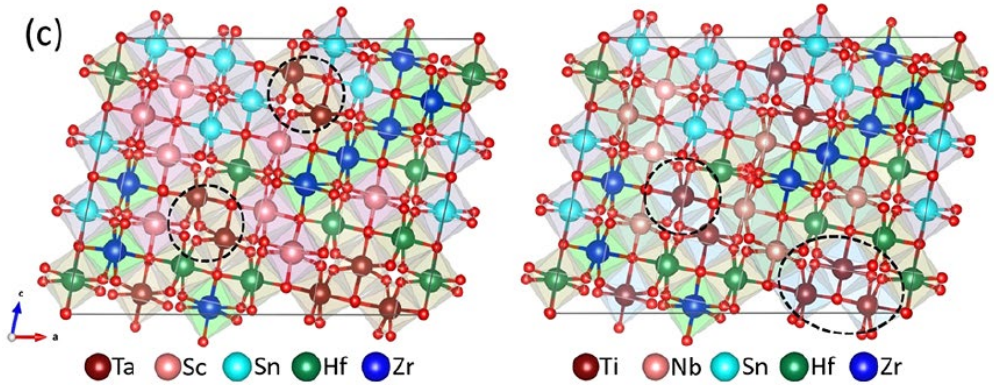




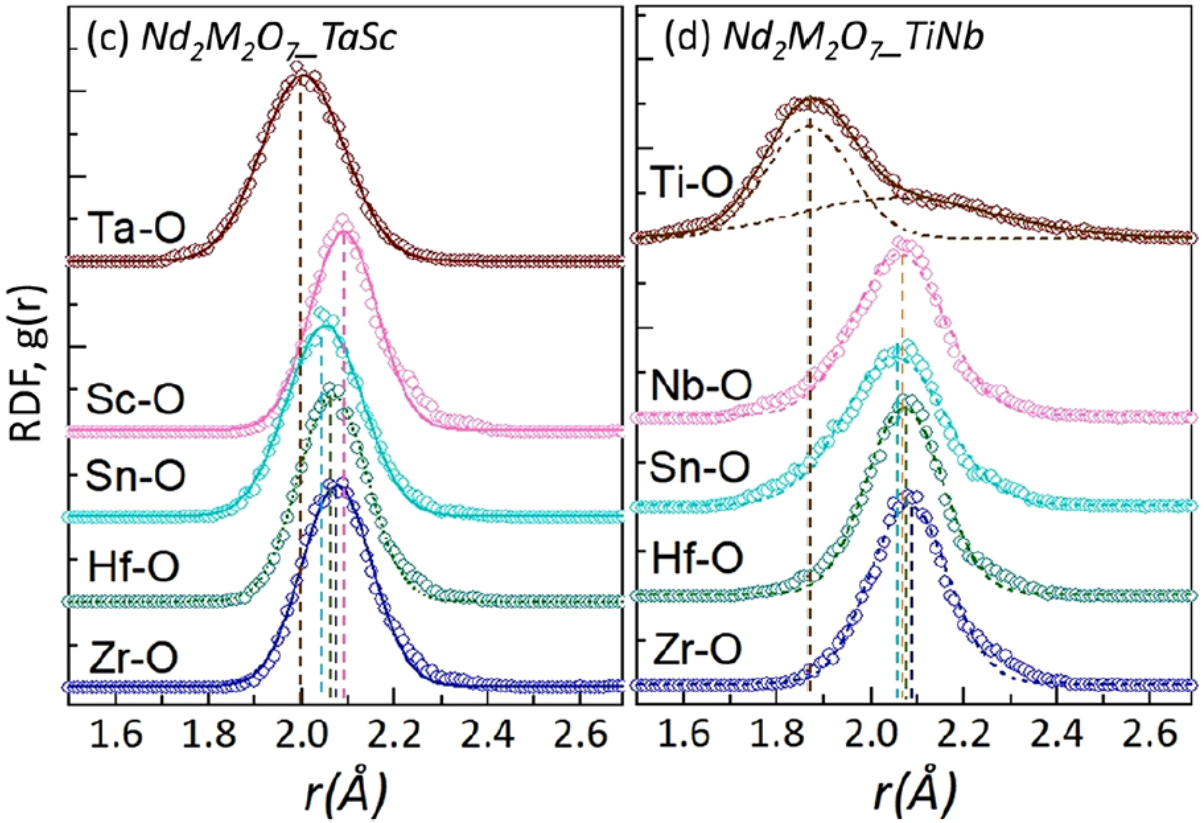
Nearest-neighbor M-O peaks

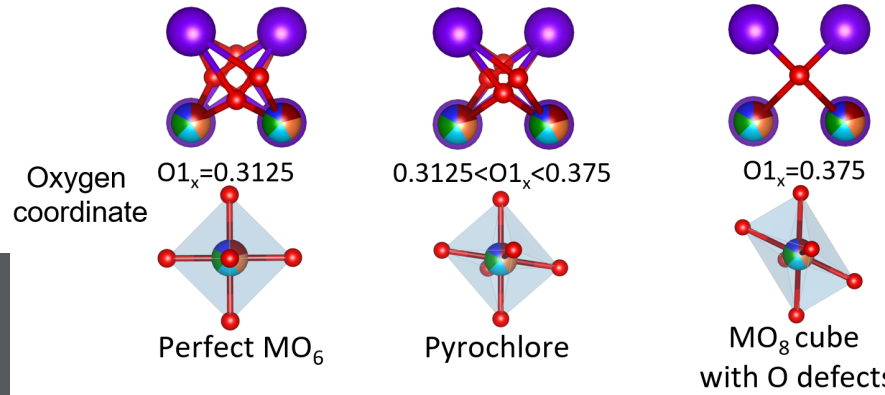
SQS





RMC

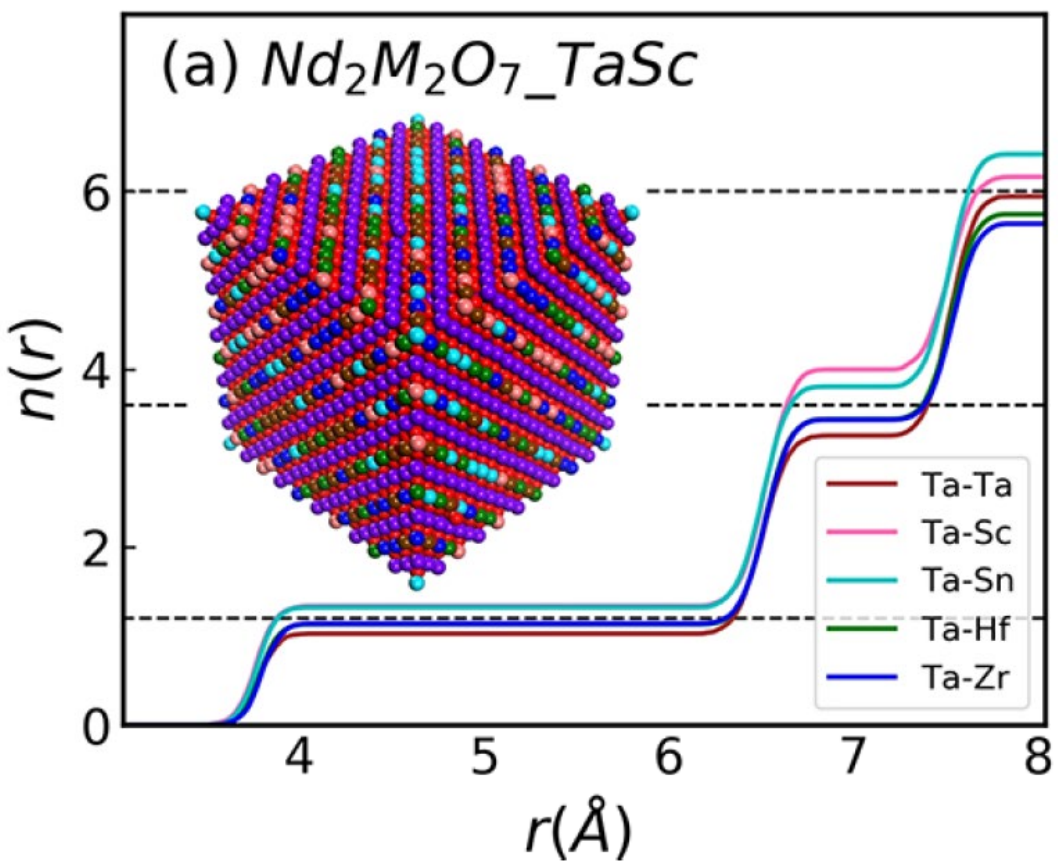


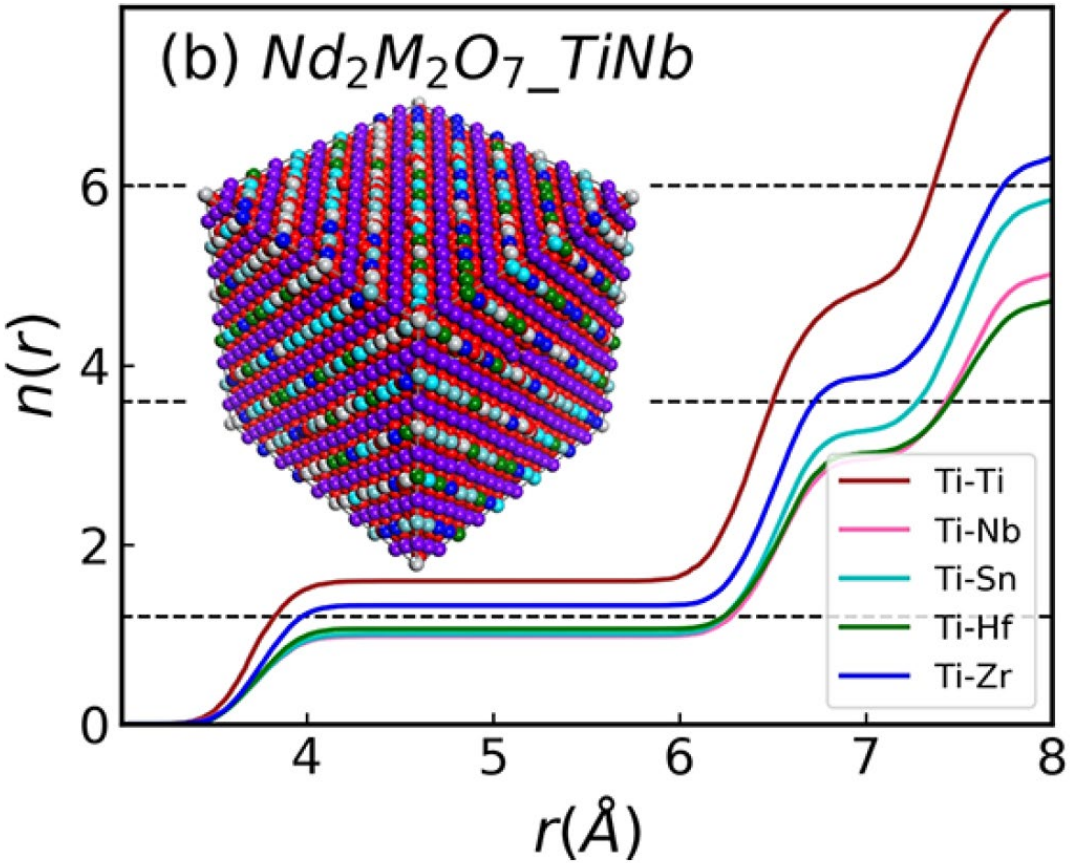


Neighbor correlations *n(r)* by RMC

The $n_{ij}(r)$ is defined as the mean number of atoms *i* surrounding a central atom *j*:

$$n_{ij}(r) = \int_{r2}^{r1} 4\pi r^2 2c_j \rho_0 g_{ij}(r) \mathrm{d}r$$



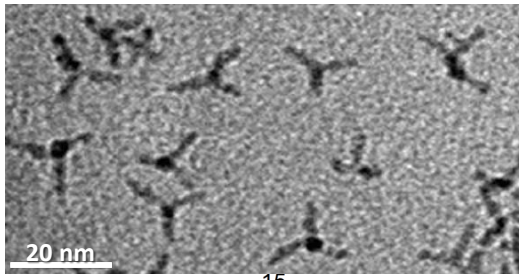


Diffraction + PDF: internal structure, interfaces, size/shape

$$4\pi r\rho(r) - 4\pi\rho_0 r\gamma_0(r) = G(r, Q_{min})$$

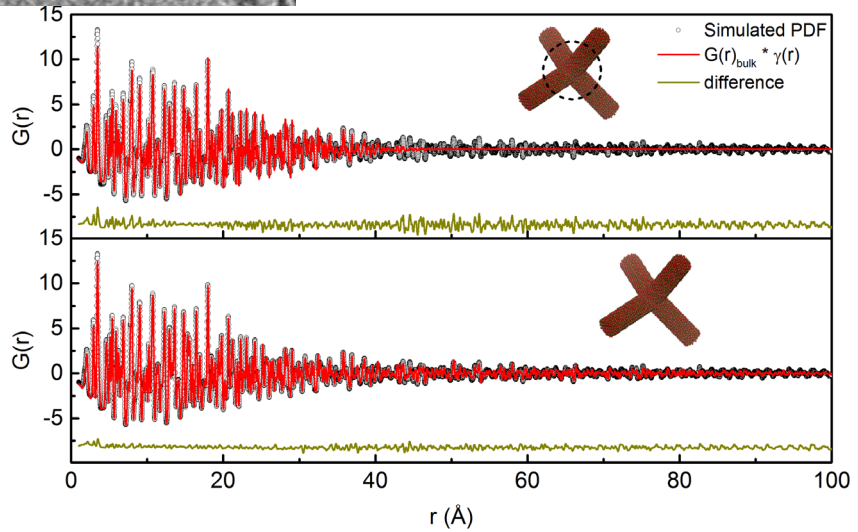
$$\rho(r) = \frac{1}{4\pi N r^2 \langle f \rangle^2} \sum_{m \neq n} f_i f_j \delta(r - r_{mn})$$

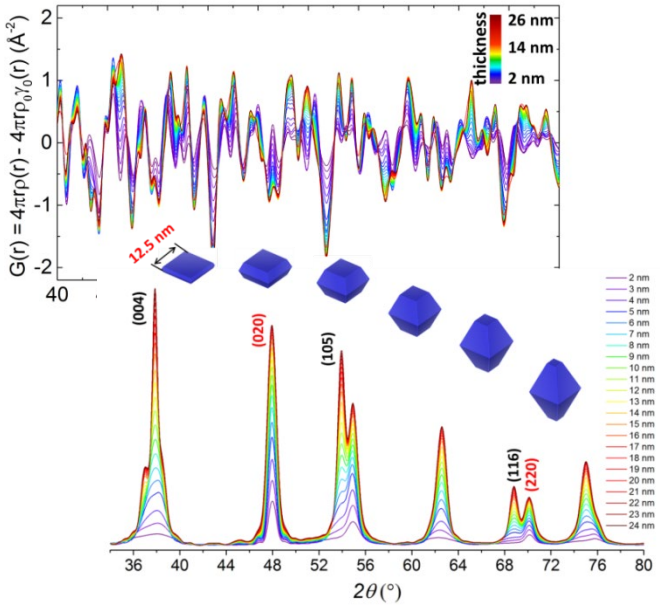
$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr)\, dQ = 4\pi r[\rho(r) - \rho_0\gamma_0(r)]$$



Cargill, G.S. III, *J. Appl. Cryst., 4, 277-283* (1971).

Farrow, C. and Billinge, S. J. L., *Acta Cryst.* A65, 232-239 (2009).



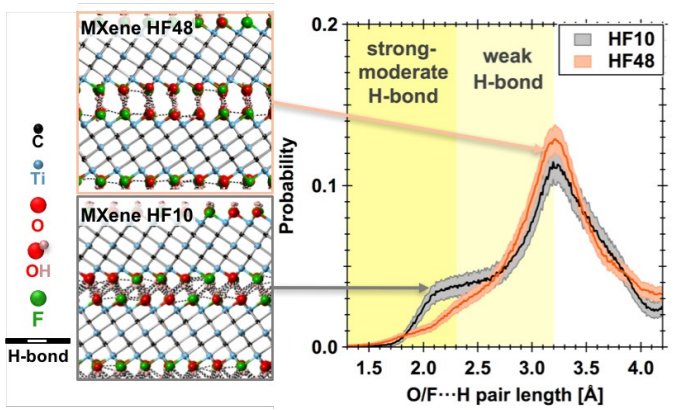


J. Liu, D. Olds, R. Peng, L. Yu, G. S. Foo, S. Qian, J. Keum, B. S. Guiton, Z. Wu, K. Page
Quantitative analysis of the morphology of {101} and {001} faceted anatase TiO_2 nanocrystals, *Chem. Mater.* 29, 5591–5604 (2017).

$$\sum_m \sum_n f_m f_n \frac{\sin(Qr_{mn})}{Qr_{mn}} = I(Q)$$

complex modeling

H.-W. Wang, M. Naguib, K, Page, D. J. Wesolowski, Y. Gogotsi, **Resolving the Structure of $Ti_3C_2T_x$ MXenes through Multi-Level Structural Modeling of the Atomic Pair Distribution Function**, *Chem. Mater*. 28, 349–359 (2016).



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).

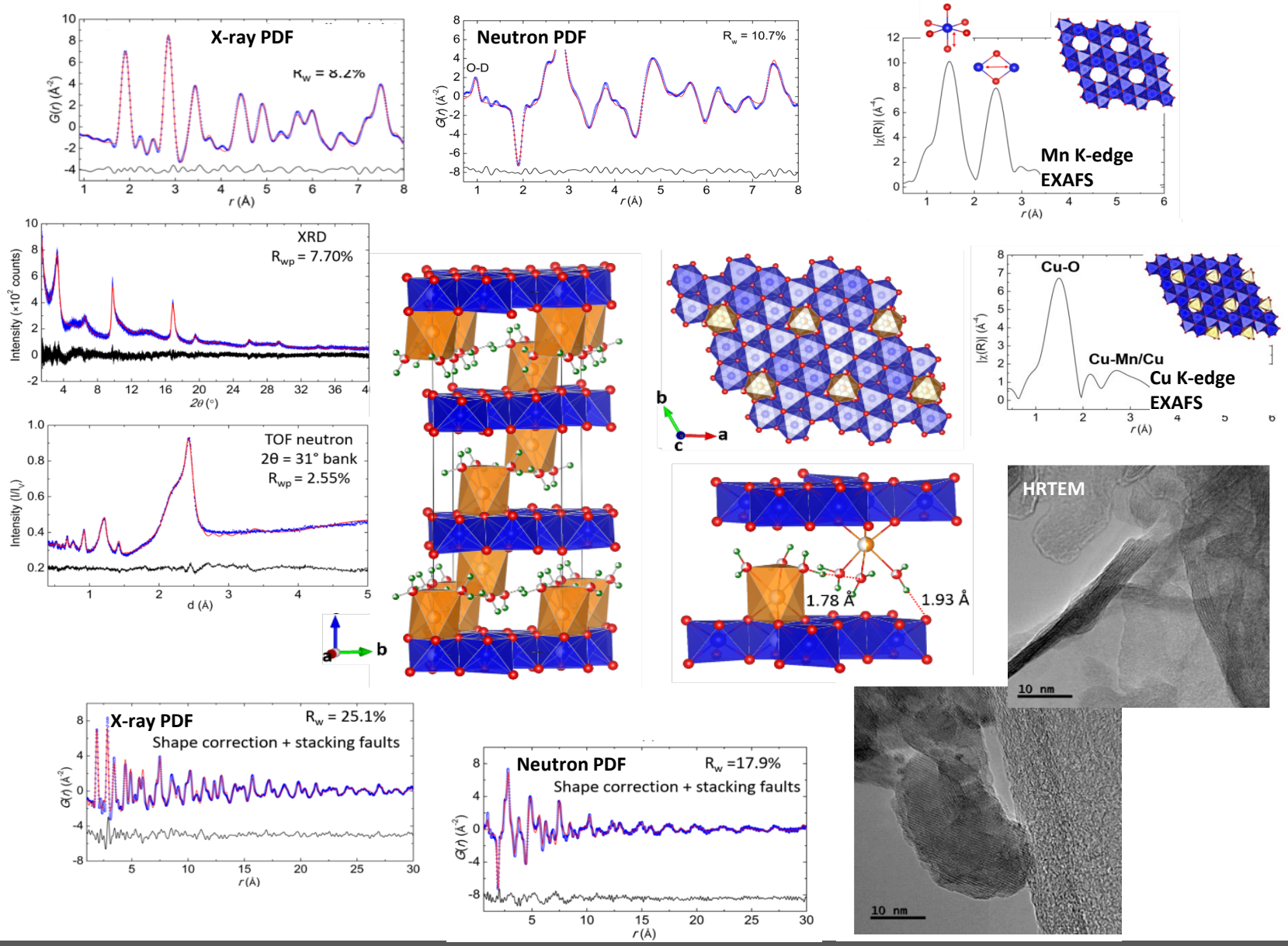
THE UNIVERSITY OF TENNESSEE KNOXVILLE

Example: δ-MnO_2

A synthetic δ-MnO2 nanoflower, comprehensive local structure investigation, and mulit-level refinement methodology:

First complete structure of the layered oxide

Coupled with electrochemical property studies



Liu J., Yu L., Hu E., Guiton B.S., Yang X.Q., Page K., **Large-Scale Synthesis and Comprehensive Structure Study of δ-MnO_2**, *Inorganic Chemistry* 57, 12, 6873-6882 (2018).

A FEW EMERGING AREAS

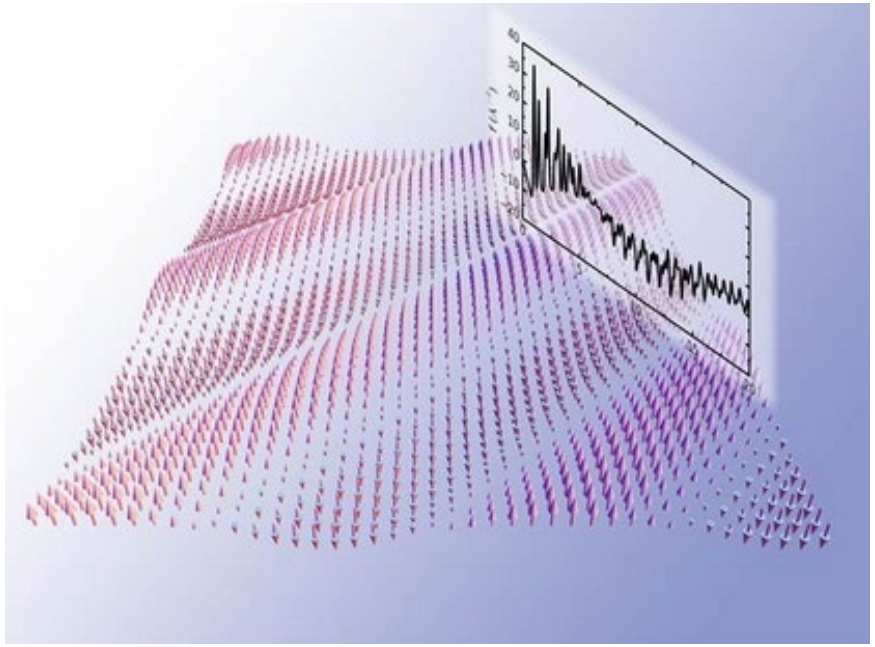
Magnetic PDF

Dynamic PDF

3D PDF

DISCOVER Beamline

Magnetic PDF: mPDF



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advances

Acta Crystallographica Section A
Foundations and Advances
ISSN 2053-2733

Received 10 October 2013
Accepted 6 December 2013

Magnetic pair distribution function analysis of local magnetic correlations

Benjamin A. Frandsen,[a] Xiaohao Yang[b] and Simon J. L. Billinge[b,c]*

[a]Department of Physics, Columbia University, New York, NY 10027, USA, [b]Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA, and [c]Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA. Correspondence e-mail: sb2896@columbia.edu

- 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 $Dy_3Mg_2Sb_3O_{14}$

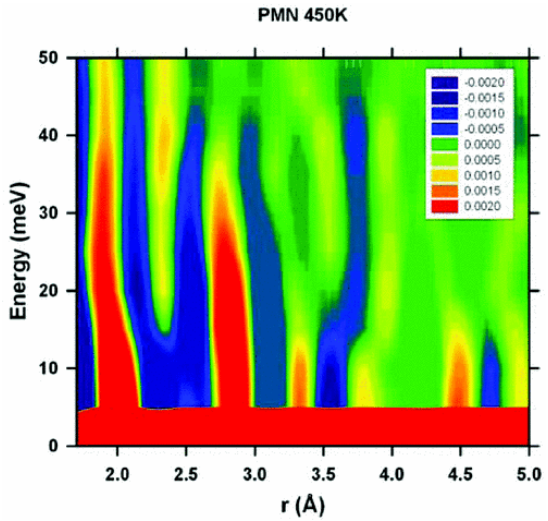
Joseph A.M. Paddison[1,2], Harapan S. Ong[1], James O. Hamp[1], Paromita Mukherjee[1], Xiaojian Bai[2], Matthew G. Tucker[3,4], Nicholas P. Butch[5], Claudio Castelnovo[1], Martin Mourigal[2] & S.E. Dutton[1]

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,*]

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

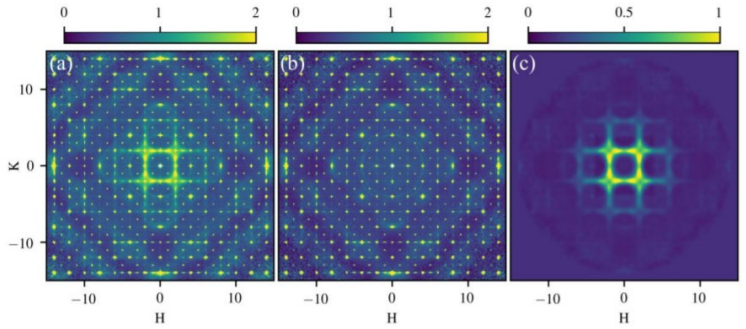
Received 28 Jun 2016 | Accepted 17 Mar 2017 | Published 4 May 2017 OPEN

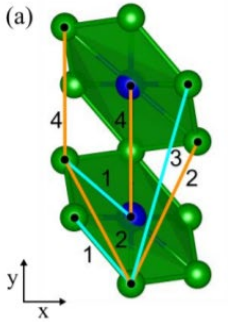
Observation of dynamic atom-atom correlation in liquid helium in real space

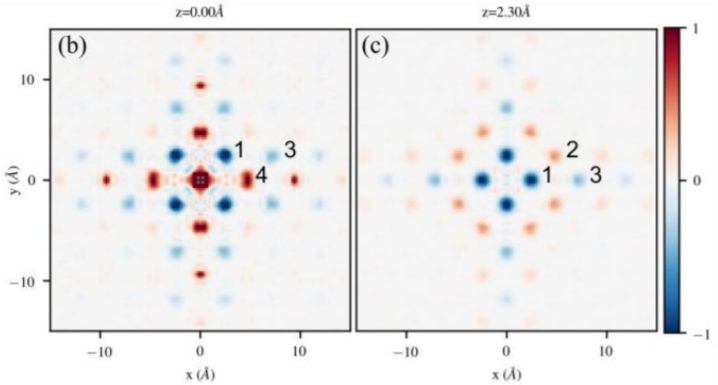
W. Dmowski[1,2], S.O. Diallo[3], K. Lokshin[1,2], G. Ehlers[3], G. Ferré[4], J. Boronat[4] & T. Egami[1,2,3,5]

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).

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, 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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R. Neder and Th. Proffen, *Diffuse Scattering and Defect Structure Simulation*, Oxford University Press, 2008.

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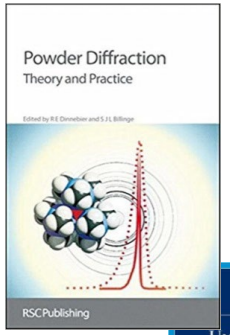

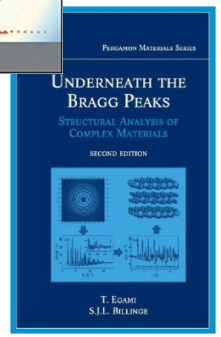

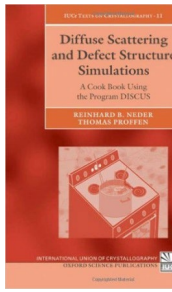

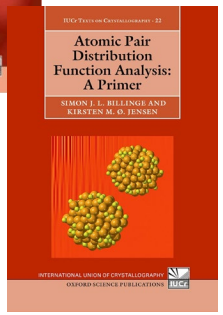

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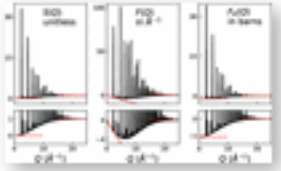

Illustrated formalisms for total scattering data: a guide for new practitioners

P. F. Peterson, D. Olds, M. T. McDonnell and K. Page

The total scattering method is the simultaneous study of both the real- and reciprocal-space representations of Rietveld refinement) provides insight into the average structure of the material, pair distribution function (PDF) Generically speaking, a PDF is generated by Fourier transforming the total measured reciprocal-space diffractio transformation employed and, by consequence, the resultant appearance and weighting of the real-space repre community continues to grow, these subtle differences in nomenclature and data representation have led to co derivation of many of these different forms of the PDF and the transformations required to bridge between ther appropriate choice of PDF in their own research are presented. This contribution aims to benefit people starting

Keywords: **total scattering**; **pair distribution function**.

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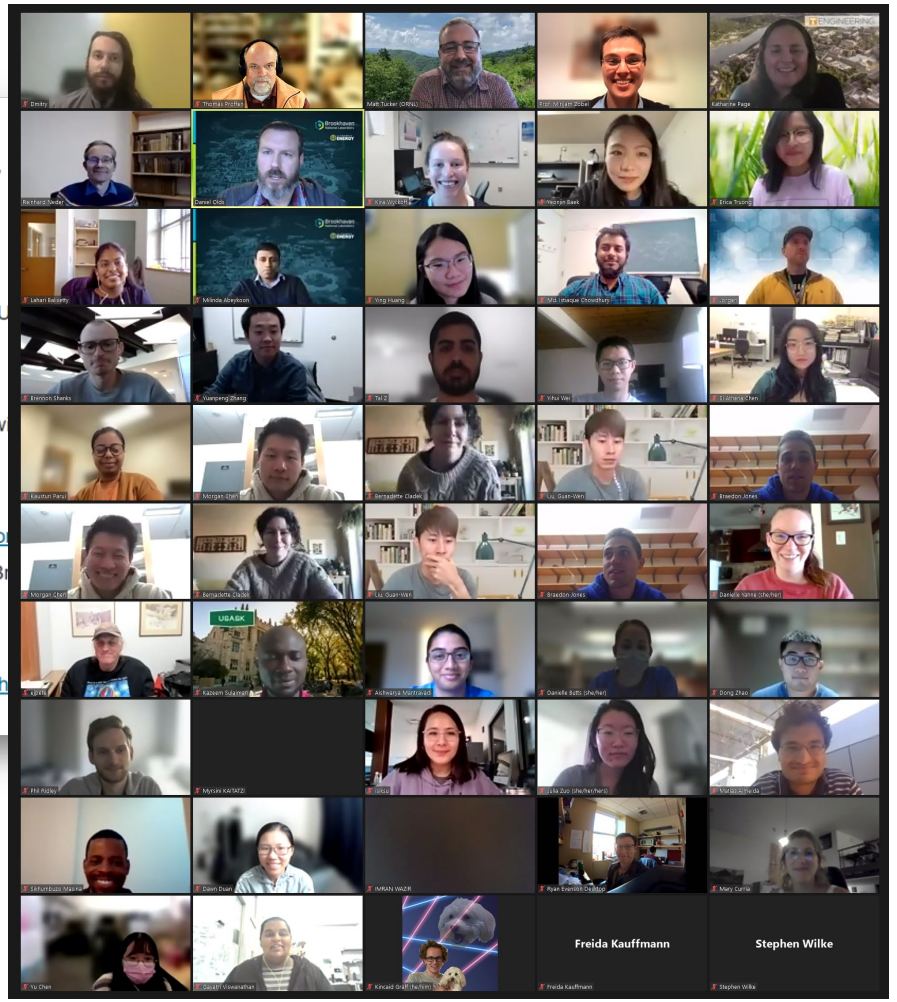


THE UNIVERSITY OF TENNESSEE KNOXVILLE

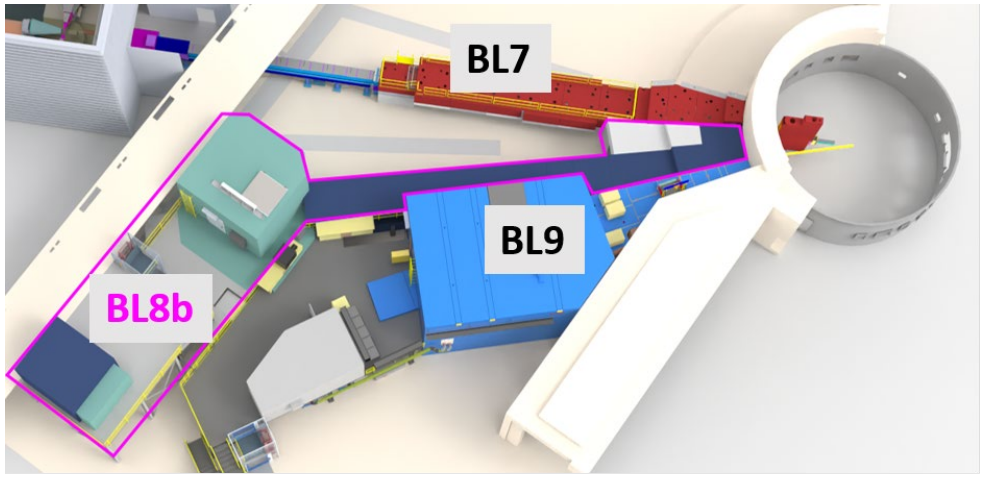
DISCOVER Beamline Concept for First Target Station, SNS

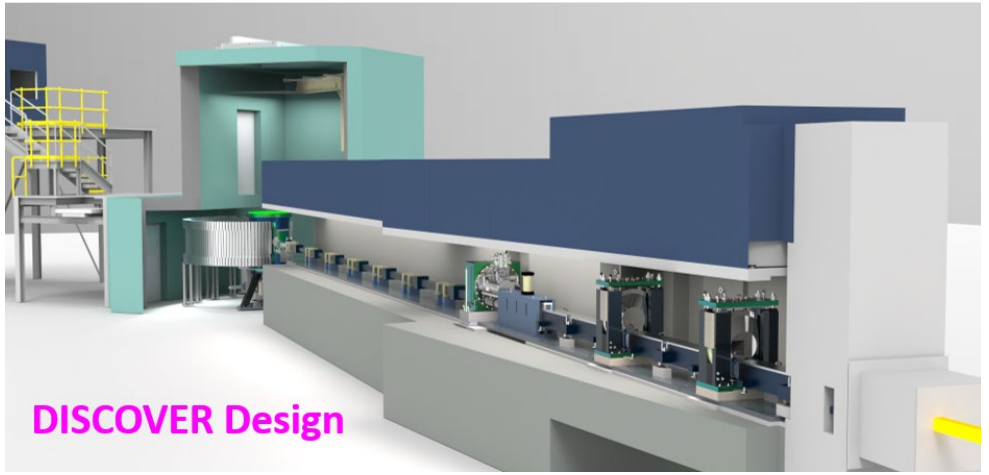
Concept: **Everything, everywhere, all at once!**

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

- Electrochemical cycling
- Mechanical loading
- Under gas flow / adsorption
- In situ synthesis
- Localized magnetic/electric fields

Page/Liaw/Tucker/Billinge: Pursuing design and funding opportunities for instrument concept jointly with team at ORNL and Columbia University





DISCOVER Beamline

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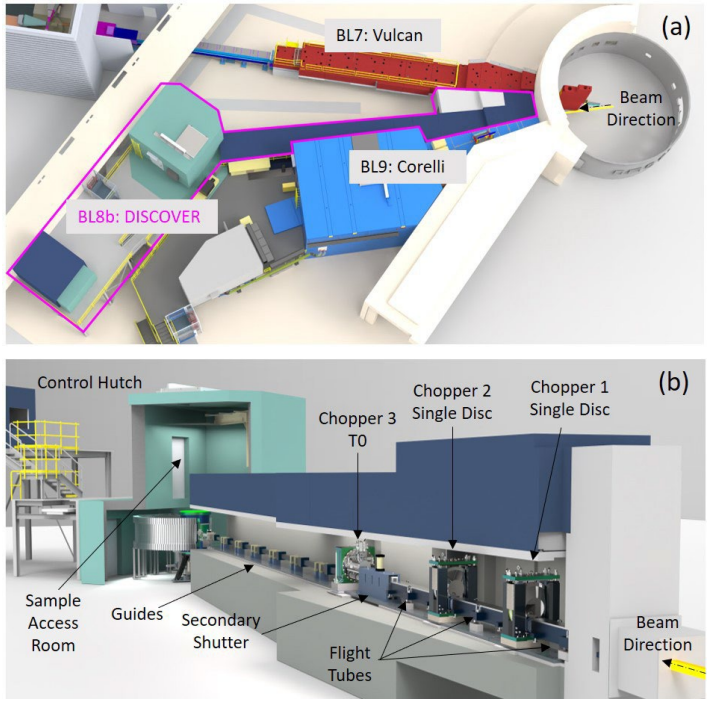

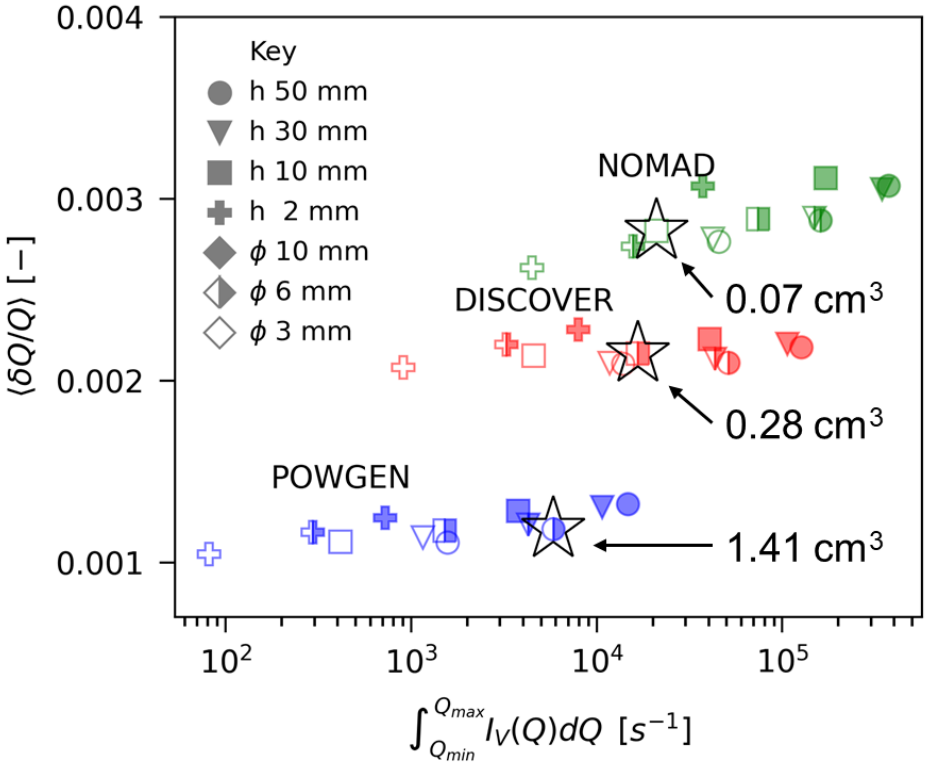

Ability to study hydrogenous materials (particularly ubiquitous in synthesis and catalysis science) with neutrons by separating static from dynamic contributions

P.C. Metz, et al. (2021) J. Appl. Cryst., 54(4) 1047–1056. DOI: 10.1107/s1600576721004787

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

Dedicated and high-resolution instruments offer many advantages

Questions?

kpage10@utk.edu
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