Atomic Pair Distribution Function (PDF) Analysis

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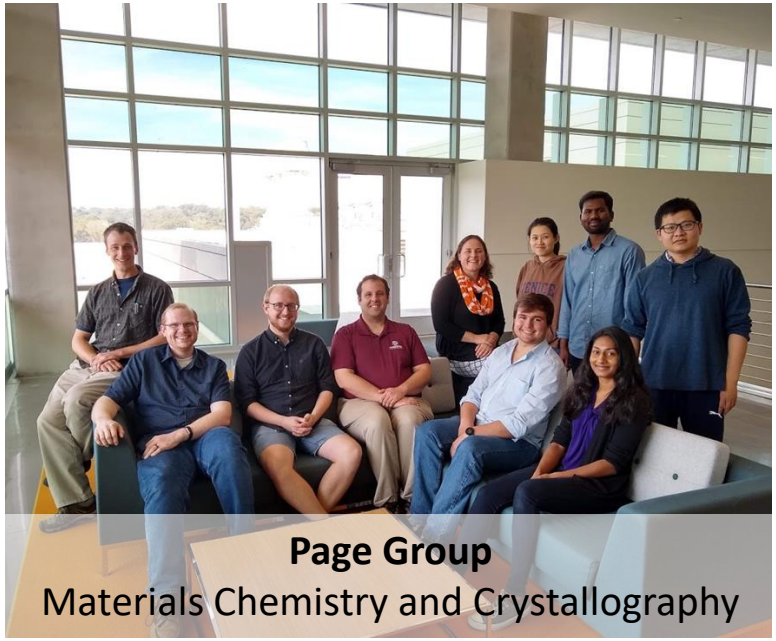

Page Group
Materials Chemistry and Crystallography

Diffraction Section
Section Leader: Matthew Tucker

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Outline

Part 1:

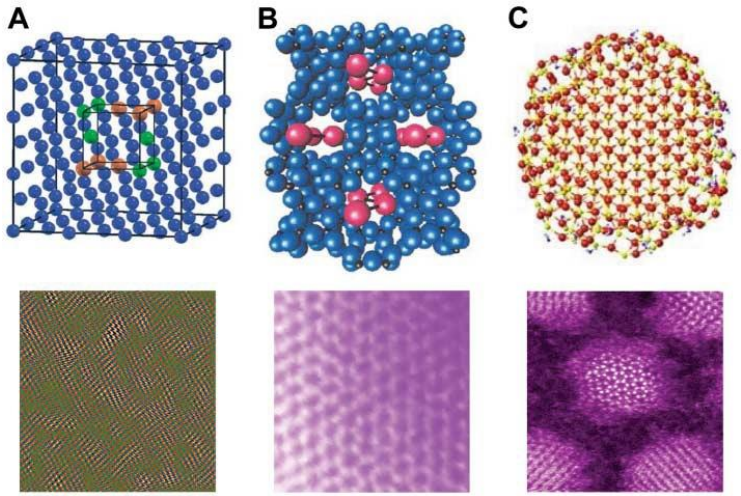
- The Pair Distribution Function (PDF)
- Applications
  - Local Distortions
  - Chemical Short-Range Order
  - Nanomaterial Structure
  - Amorphous Structure

Part 2:

- Experimental Considerations
- Modeling a PDF
- Emerging Areas

What is a *local structure*?

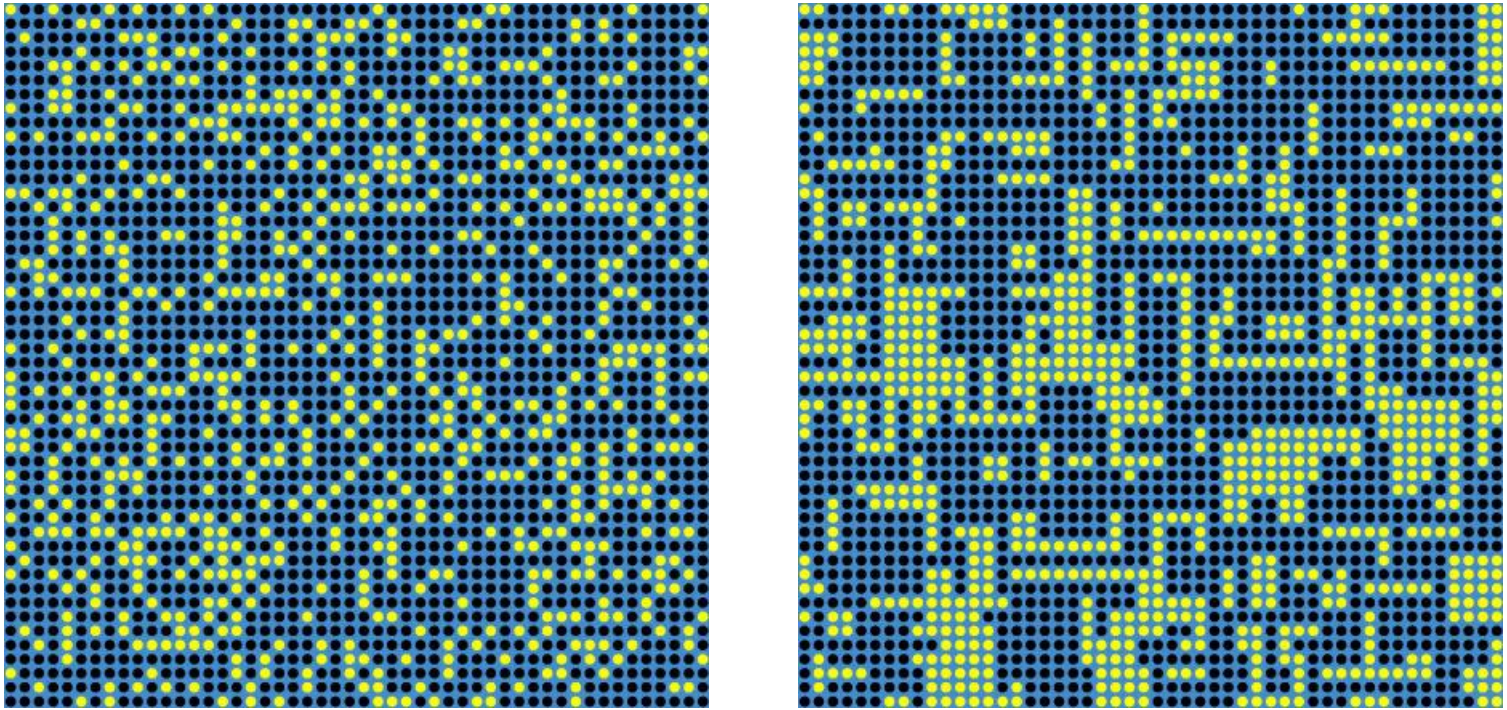
- **Disordered materials**: The interesting properties are often governed by the defects or local structure
- **Non crystalline materials:** Amorphous solids, liquids, glasses and polymers
- **Nanostructures**: Well defined local structure, but long-range order limited to nanometers lengthscales (poorly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



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

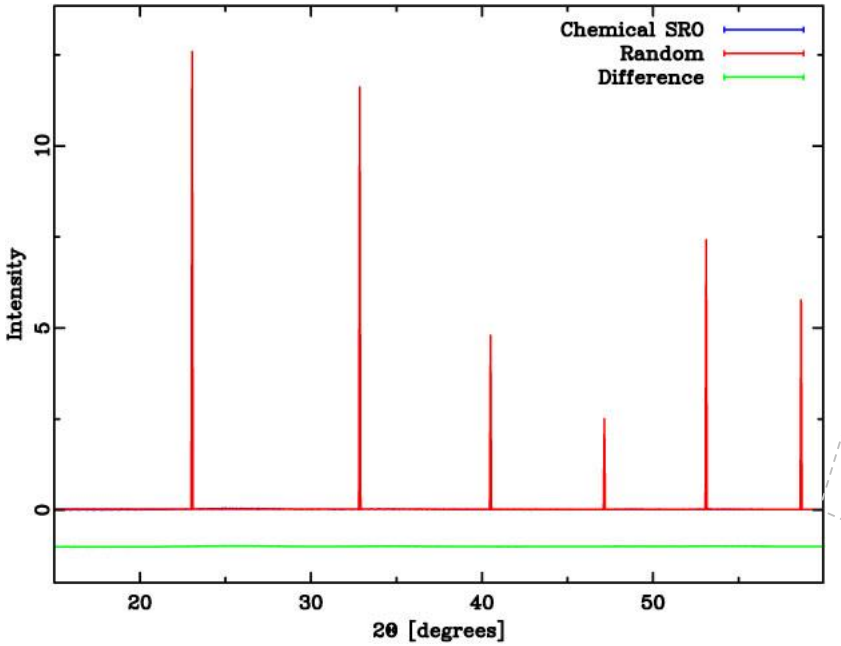
D. A. Keen and A. L. Goodwin, **The crystallography of correlated disorder**, *Nature* 521, 303–309 (2015).

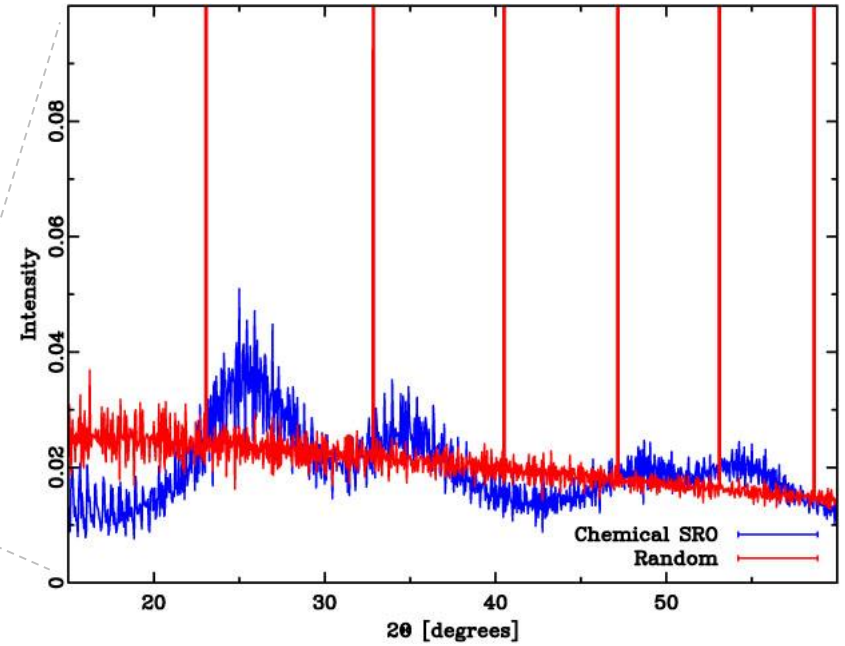
What is *total* scattering?



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

Bragg Scattering and CSRO



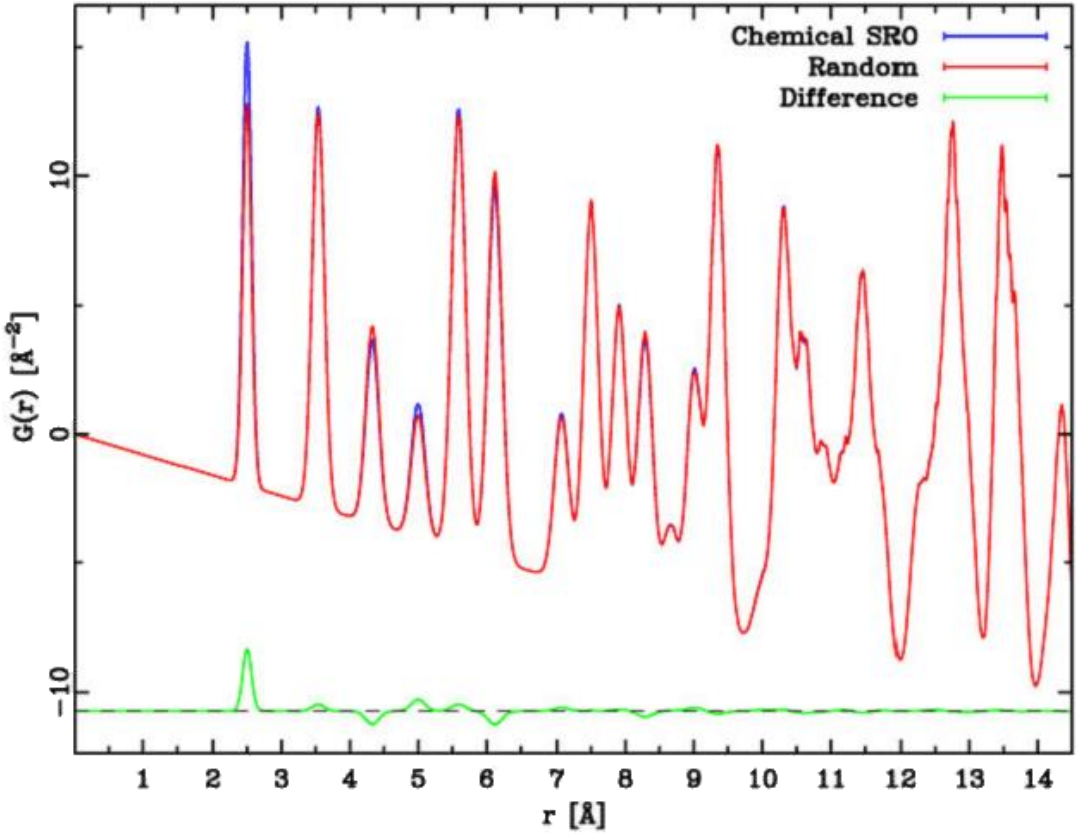


Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies

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

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

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

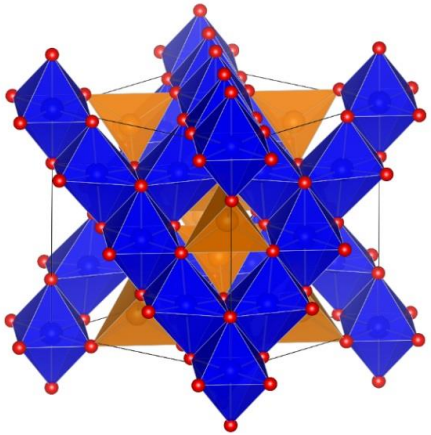
Interested in learning more?

Apply to attend the 5th Annual School on US Total Scattering Analysis
http://conference.sns.gov/e/VirtualTS-School/

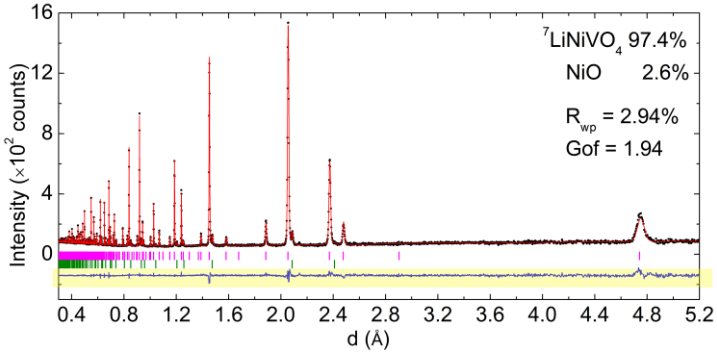
Th. Proffen, **Analysis of occupational and displacive disorder using the atomic pair distribution function: a systematic investigation**, *Z. Krist*, 215, 661 (2000). Th. Proffen, V. Petkov, S. J. L. Billinge, and T. Vogt, **Chemical short-range order obtained from the atomic pair distribution function**,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

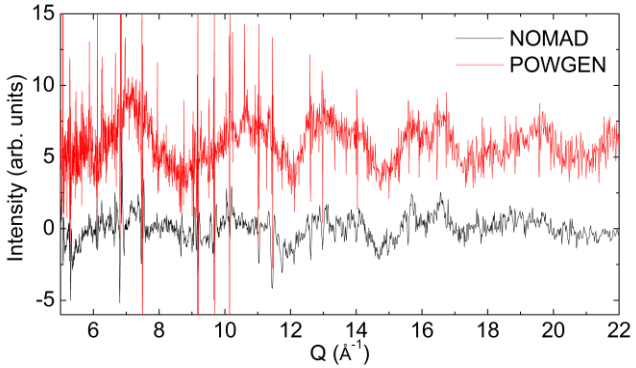
B-site cation ordering in inverse spinel oxides: $LiNiVO_4$

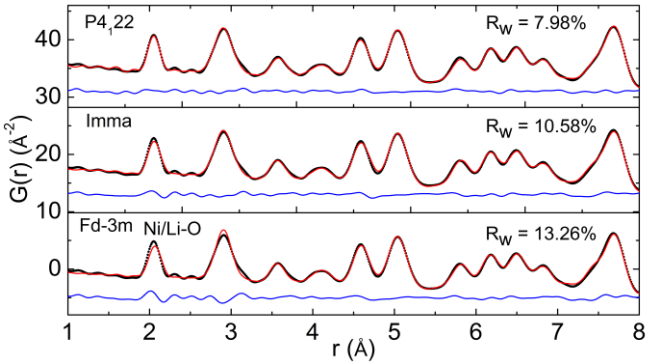
$(V)[LiNi]O_4$
S.G. *F*d-3m



Neutron diffraction data from POWGEN, SNS

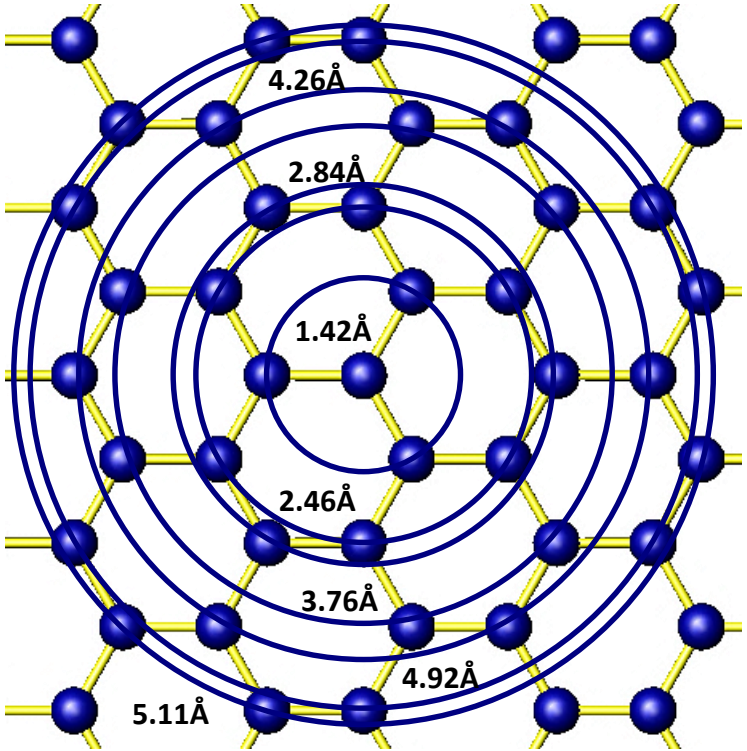




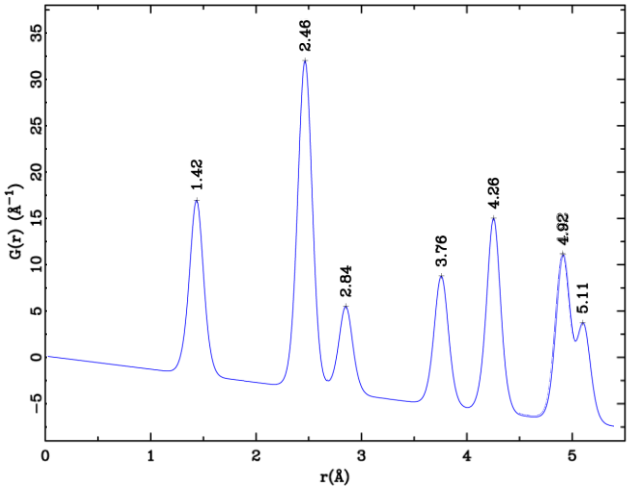


J. Liu, X. Wang, O. J. Borkiewicz, E. Hu, R. J. Xiao, L. Chen, and K. Page, **Unified view of the local cation-ordered state in inverse spinel oxides**, *Inorg. Chem.* 58 (2019) 14389-14402.

What is a PDF?



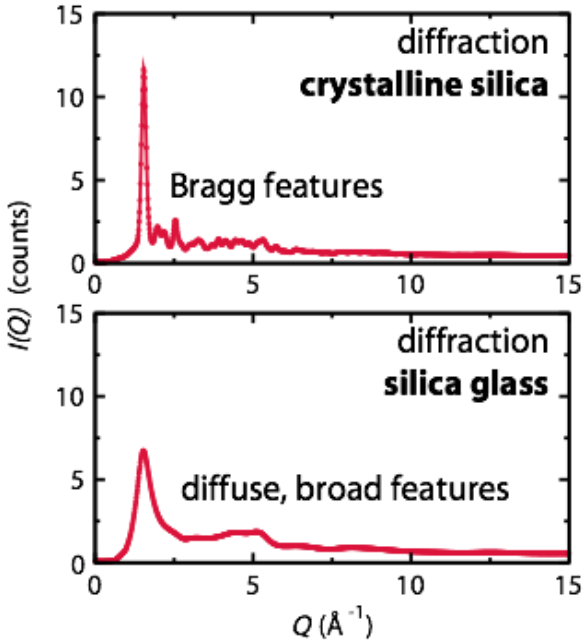
The **Pair Distribution Function (PDF)** gives the probability of finding an atom at a distance “r” from a given atom.

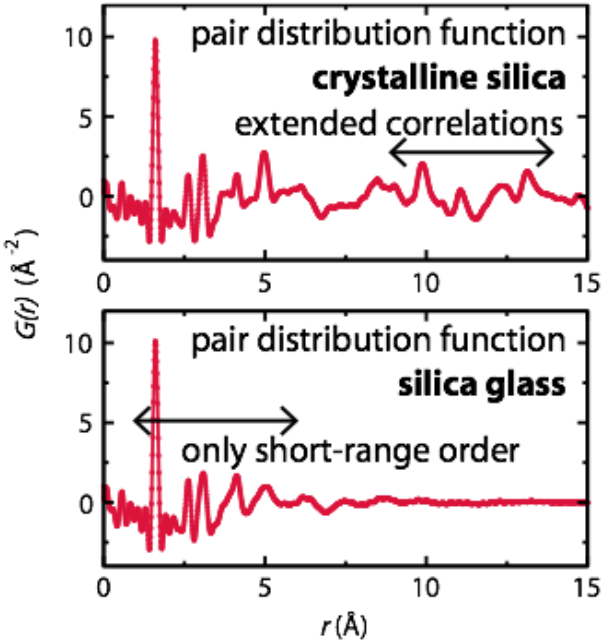


Pair Distribution Function

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

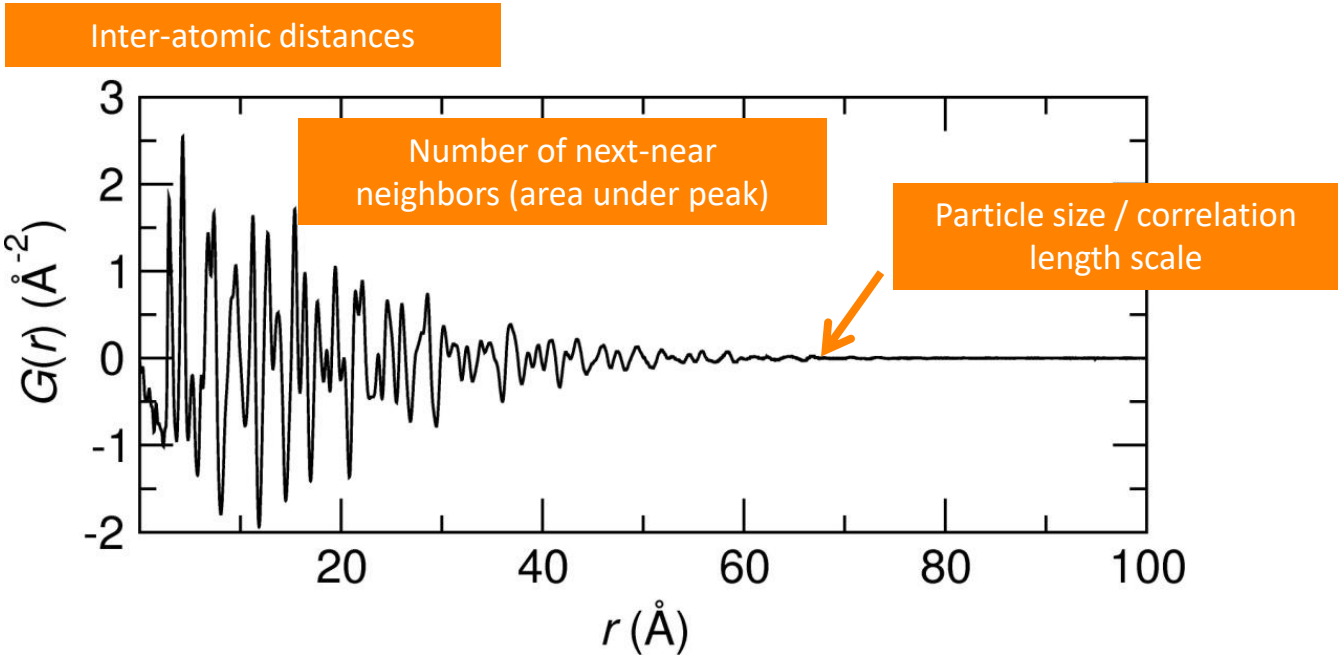
→*Experimental, ensemble, real-space, atom-atom histogram*





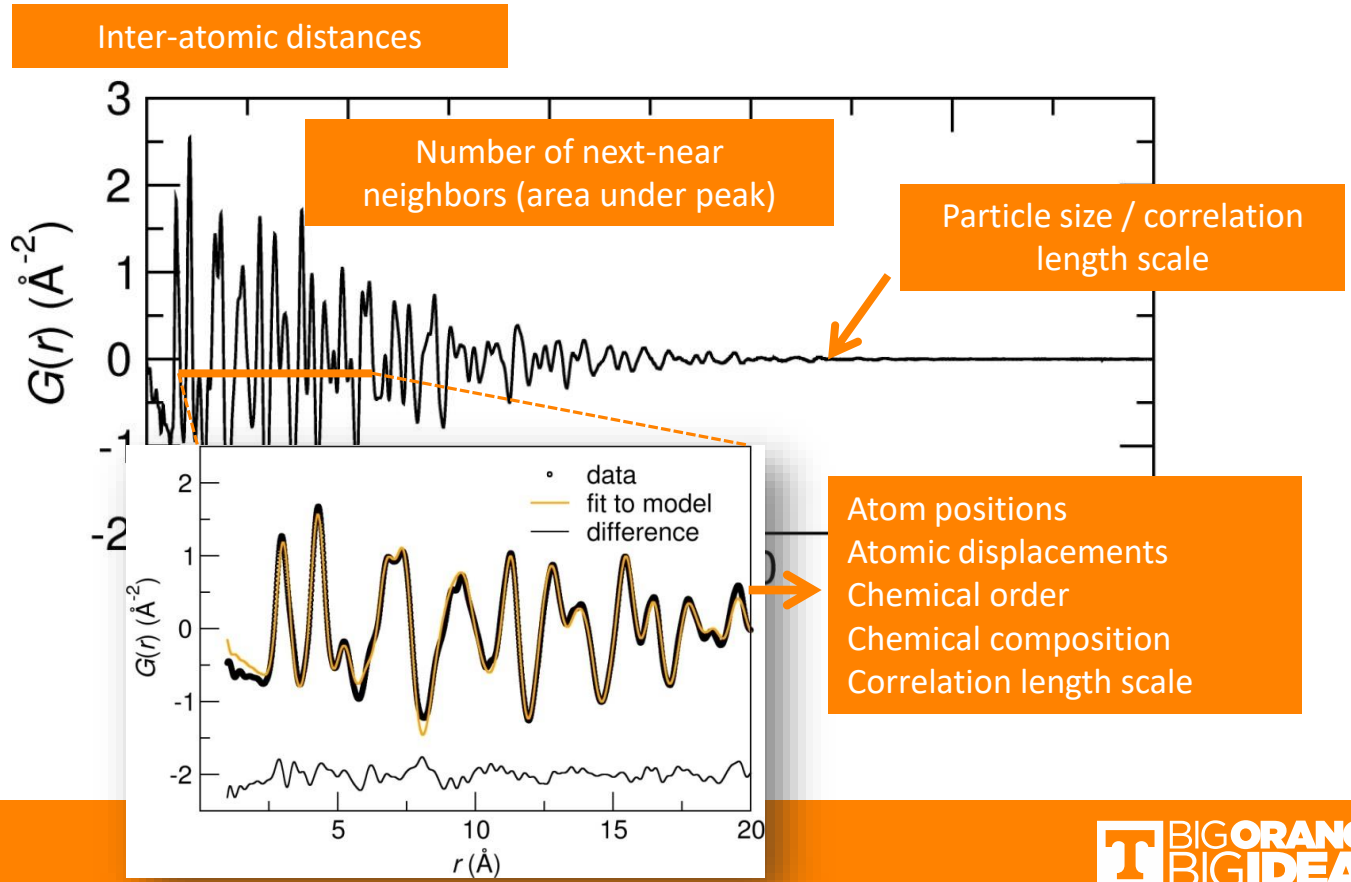
Pair Distribution Function

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

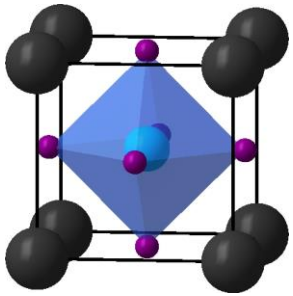


Pair Distribution Function

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

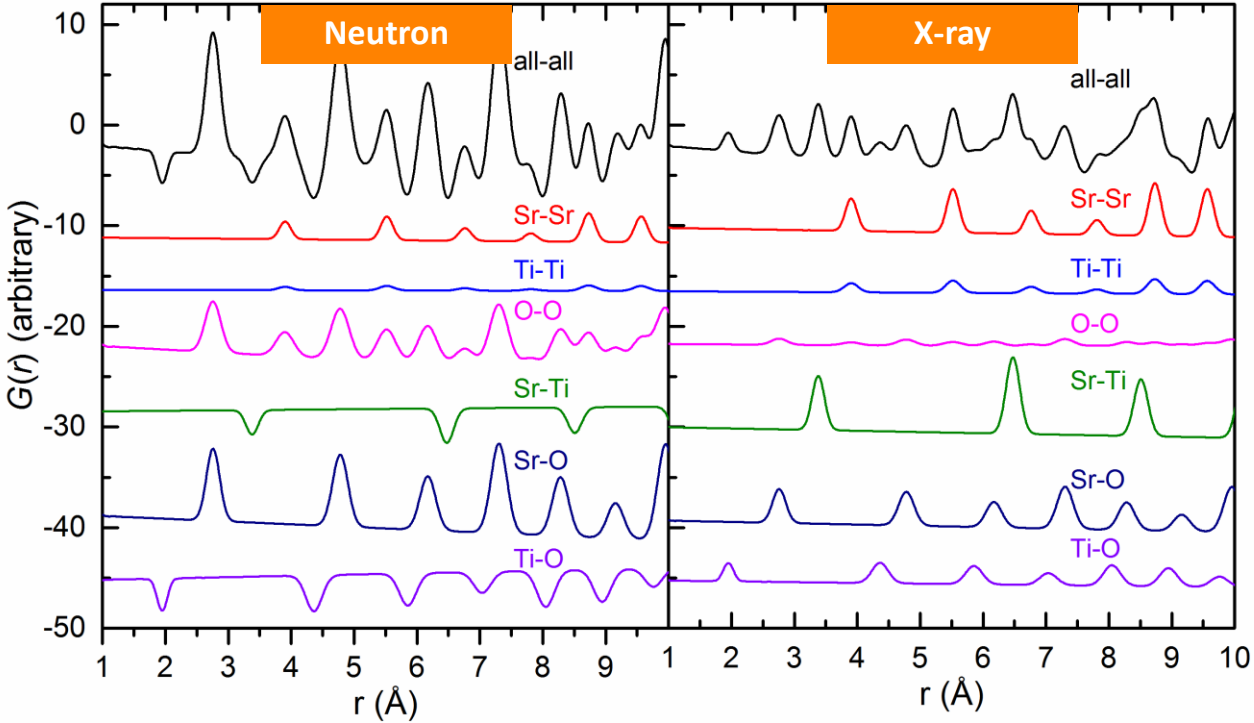


Partial PDFs



$SrTiO_3$

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



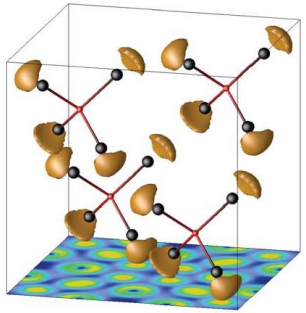
Neutron and x-ray PDFs are often highly complementary

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

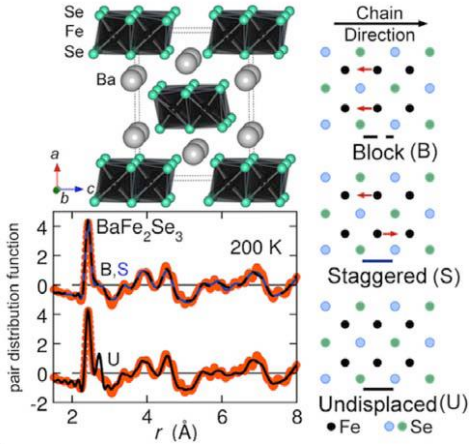
Local Distortions
Chemical Short-Range Ordering
Nanostructures
Amorphous Structures

Local distortions *via* PDF

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

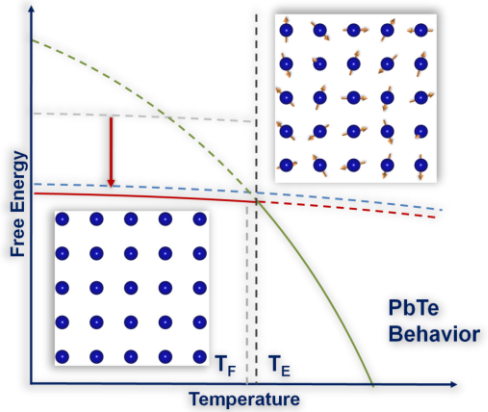


D. P. Shoemaker, *et al.,* Reverse Monte Carlo neutron scattering study of the 'ordered-ice' oxide pyrochlore $Pb_2Ru_2O_{6.5}$, *J. Phys.: Condens. Matter* **23** (2011).



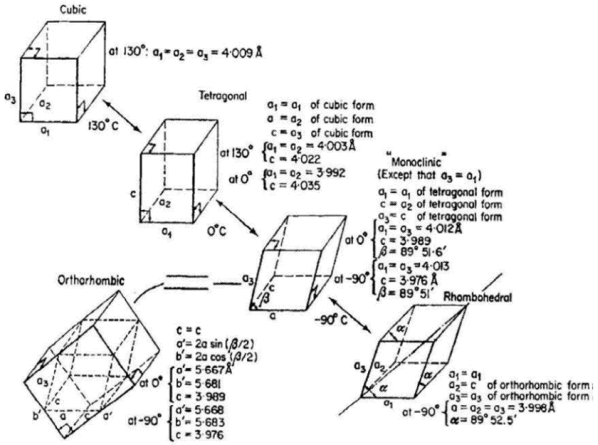
D. Louca, et *al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).

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



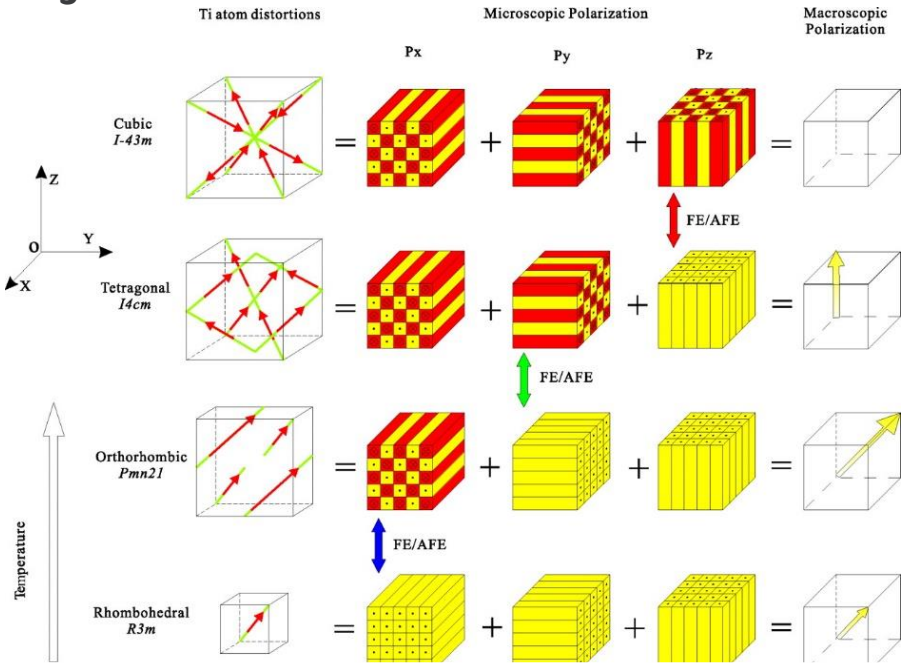
Example: Local structure in $BaTiO_3$

Crystallographic Phase Transitions



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

Long-range: cubic → tetragonal → orthorhombic → rhombohedral

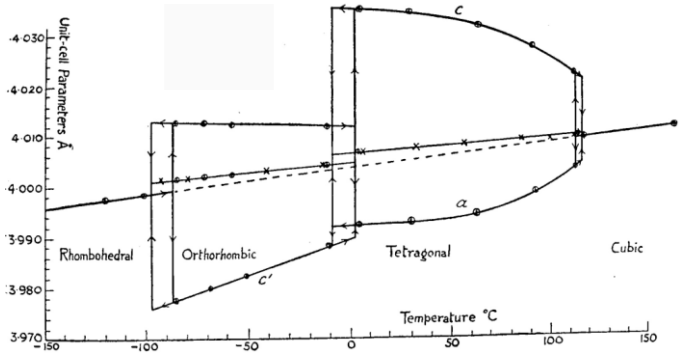


Locally, Ti^{4+} displacements are always along [111] directions (octahedral faces) → Results in 3 short and 3 long Ti-O bonds

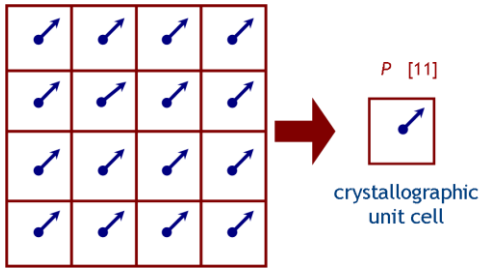
Zhang, Cagin, and Goddard, The ferroelectric and cubic phases in $BaTiO_3$ferroelectrics are also antiferroelectric, *PNAS*, **103**, 14695-14700 (2006).

Example: Local structure in $BaTiO_3$

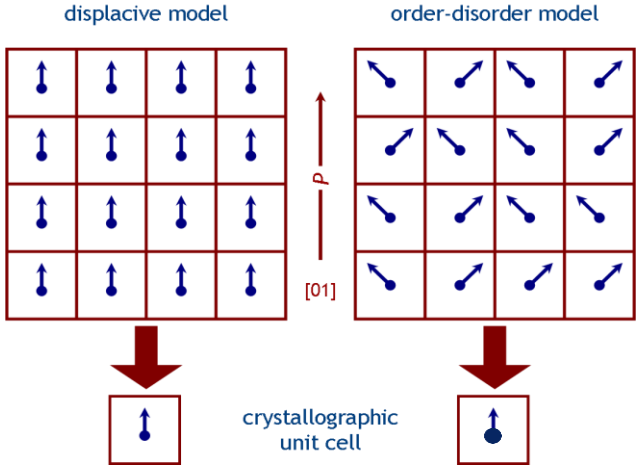
$BaTiO_3$: Ferroelectric oxide, a rhombohedral (*R3m*) ground state and a room temperature tetragonal (*P4mm*) structure



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



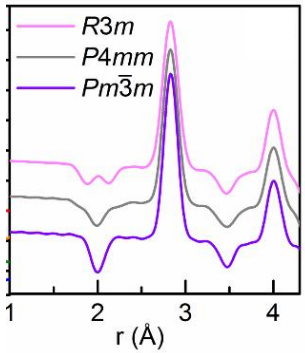
2D models with distinct local motifs but similar "average" motifs

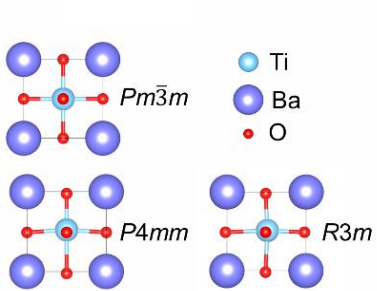


$BaTiO_3$ displays order-disorder phenomena: room temperature local structure known to have rhombohedral-like pair-pair correlations

Neutron PDF for $BaTiO_3$

Calculated $BaTiO_3$ PDFs





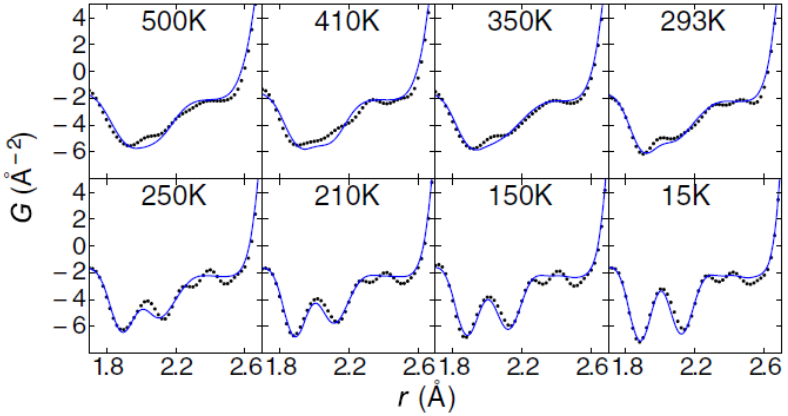
Usher et al., *J. Appl. Phys*. **120**, 184102 (2016).

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).

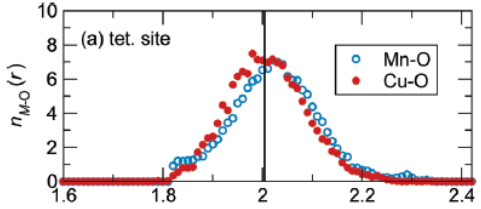
K. Page *et al.*, *Chem. Mater*. **22**, 4386–4391 (2010).
K. Page, *et al.*, *Phys. Rev. Lett.* **101**, 205502 (2008).

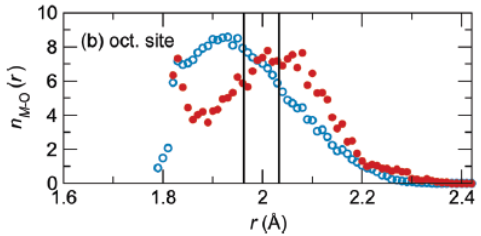
- Neutron PDF is sensitive to Ti-O correlations
- At room temperature, $BaTiO_3$ locally has a split (*R3m* like) first Ti-O peak, displaying classic order-disorder behavior



Chemical Short-Range order *via* PDF

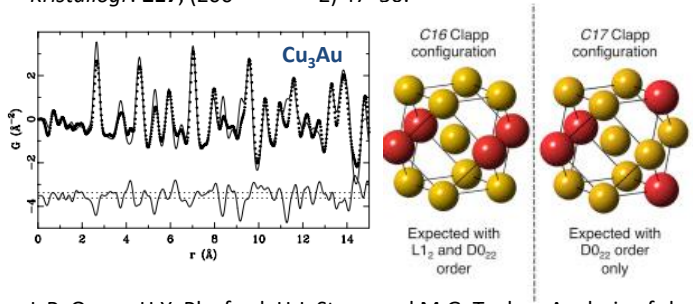
- Substitution effects
- Chemical clustering
- Ion-specific local environments
- Vacancy ordering



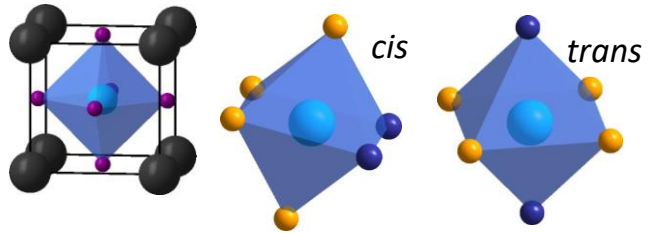


D. P. Shoemaker, J. Li, and R. Seshadri, Unraveling Atomic Positions in an Oxide Spinel with Two Jahn-Teller Ions: Local Structure Investigation of $CuMn_2O_4$, *J. Am. Chem. Soc.* **131,** 11450 (2009).

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**, (200 2) 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.



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

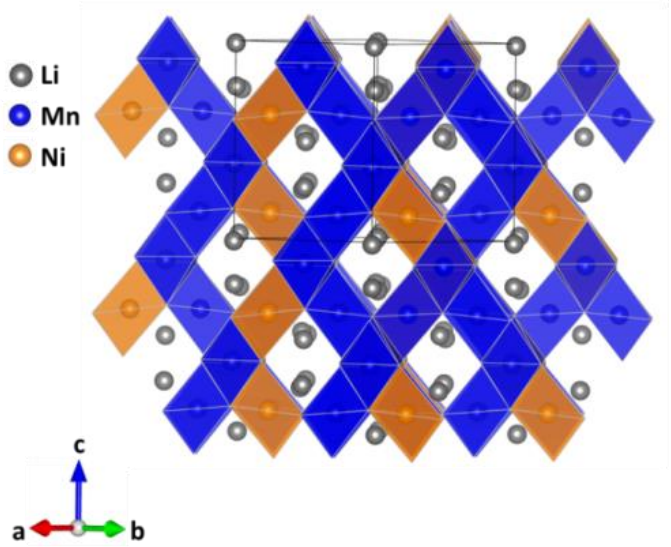
Two distinct polymorphs are known: Ni/Mn cation ordering strongly impacts electrochemical performance Idemoto *et al.*, 2003; Zhong *et al.*, 1997

(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



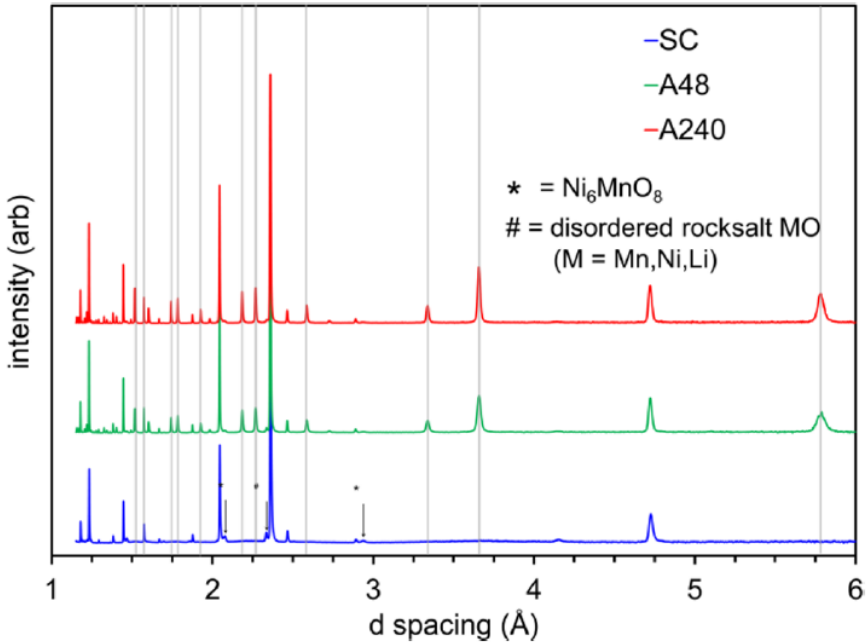
Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

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



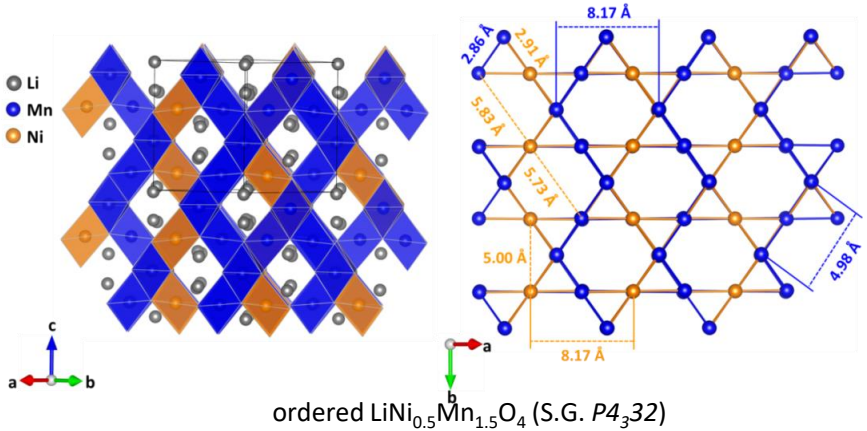
Cation ordering examined at the POWGEN Beamline, SNS: large nuclear scattering length contrast between nickel (*b* = 10.3 fm) and manganese (*b* = -3.73 fm)

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

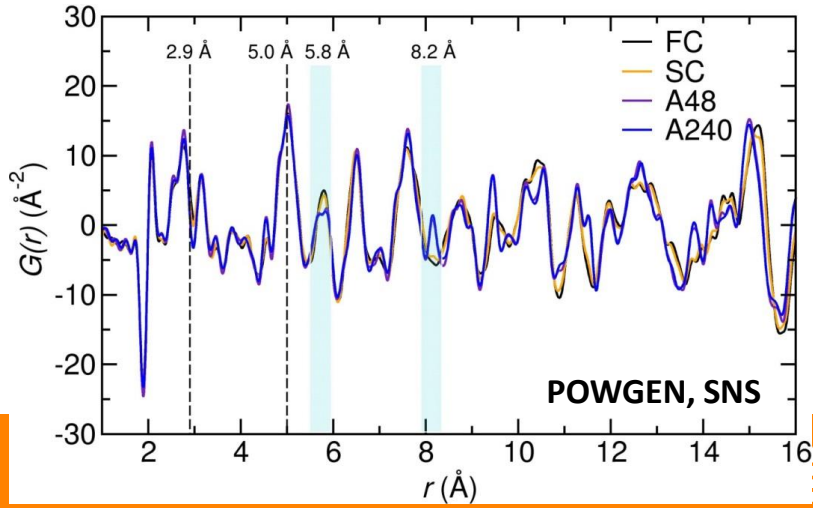
Example: High Voltage Spinel Cathode $^{7}LiNi_{0.5}Mn_{1.5}O_4$

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. *P4₃32*)

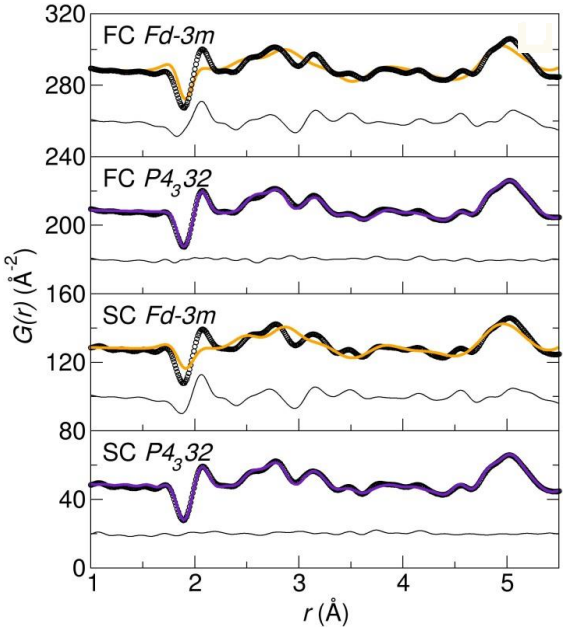


Liu J., Huq A., Moorhead-Rosenberg Z., Manthiram A., Page K., **Nanoscale Ni/Mn Ordering in the High Voltage Spinel Cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials,* 28**,** (2016) 6817–6821.

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

Additional information from modeling the local structure

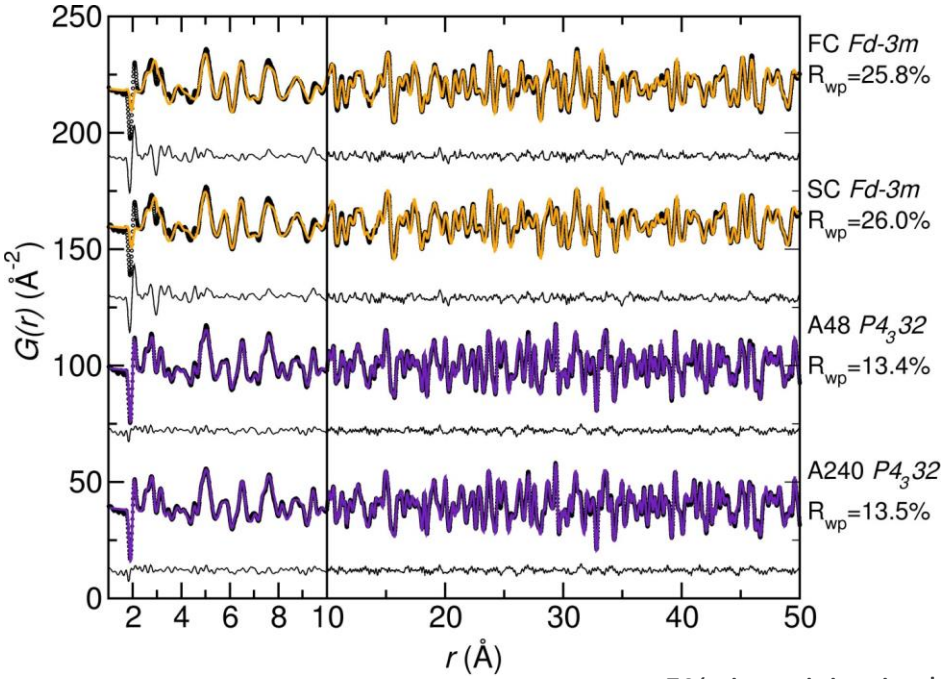
- Over 1 to 5 Å range the ordered Mn/Ni models ($P4_332$) provide much better fits for local PDF profiles in all samples
- **Ni/Mn are locally well-ordered in the long-range "disordered" samples**
- **Up to what length scale?**

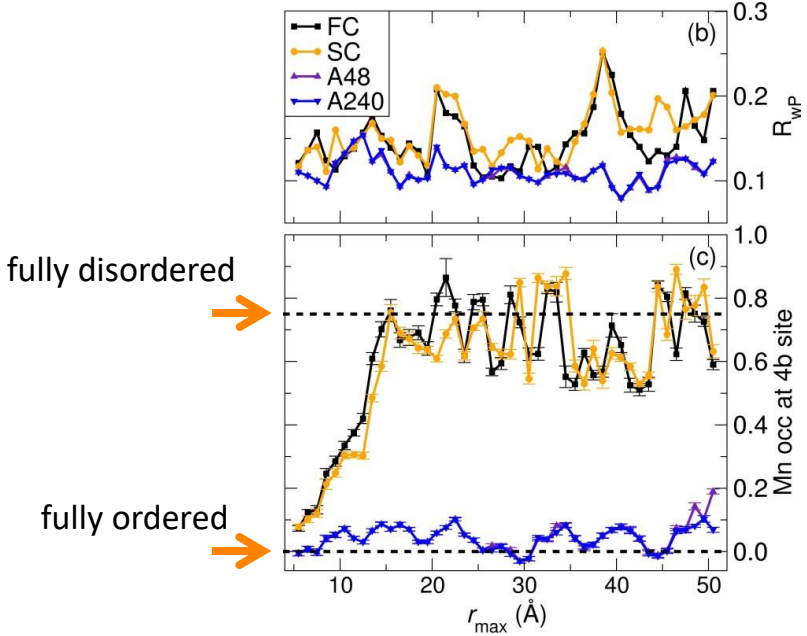


J. Liu, A. Huq, Z. Moorhead-Rosenberg, A. Manthiram, and K. Page, **Nanoscale Ni/Mn ordering in the high voltage spinel cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials*, 28, 19, 6817–6821, 2016.

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

15 Å correlation length scale for SRO





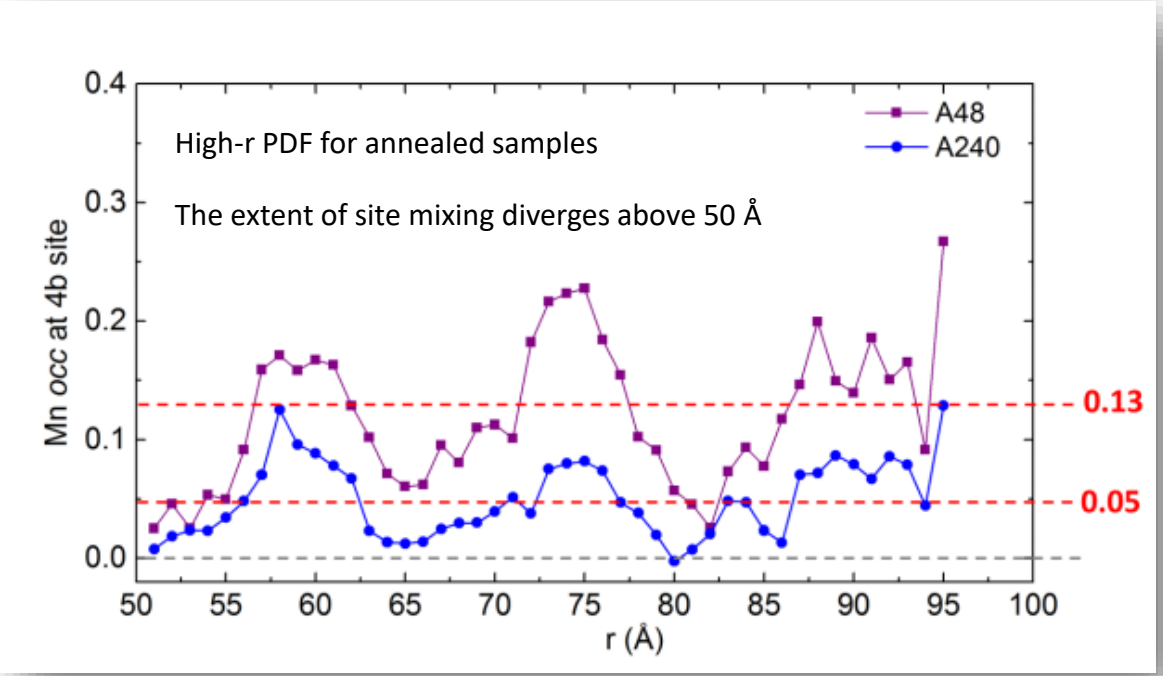
fully disordered

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

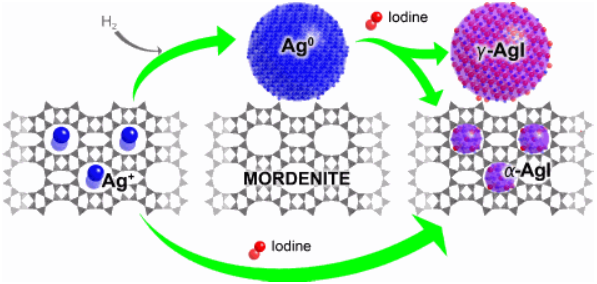
Fit the PDFs within a 4.5 Å "box" in 1 Å steps (a "box-car" refinement)



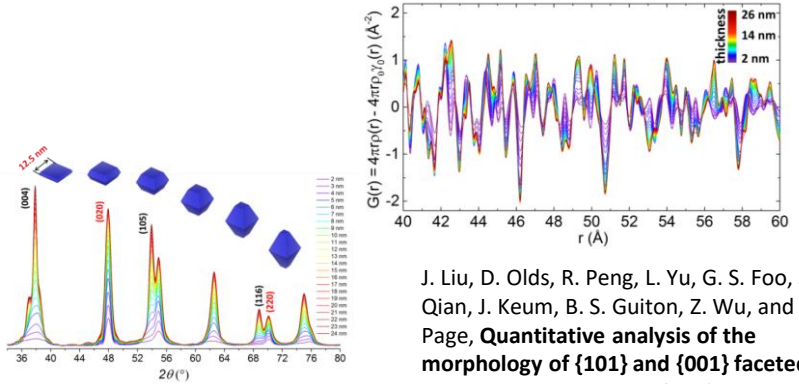
Spinel cathode materials are distinguished by their unique correlation length scales for chemical short range ordering

Nanomaterial structure *via* PDF

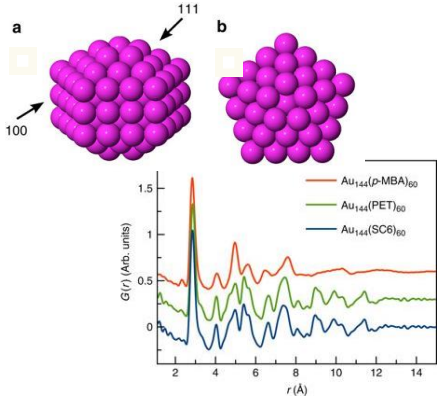
- Finite size/shape effects
- Surface/Interface structure
- Nanostructure polymorphs
- Growth and transformation



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).



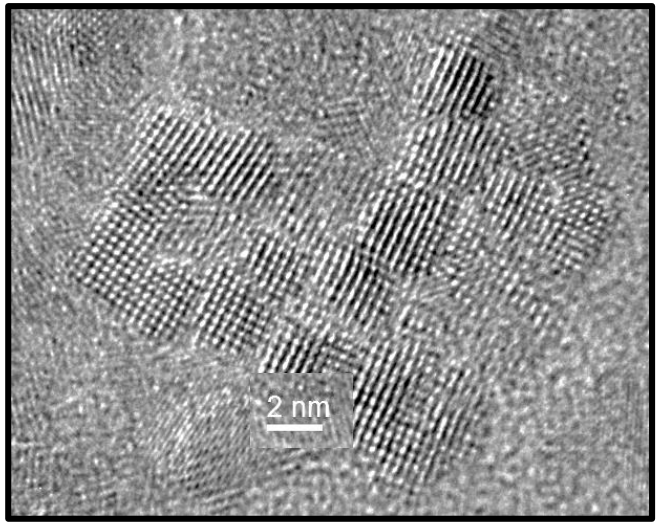
J. Liu, D. Olds, R. Peng, L. Yu, G. S. Foo, S. Qian, J. Keum, B. S. Guiton, Z. Wu, and K. Page, **Quantitative analysis of the morphology of {101} and {001} faceted anatase TiO_2 nanocrystals**, *Chem. Mater.* 29, 5591–5604 (2017).

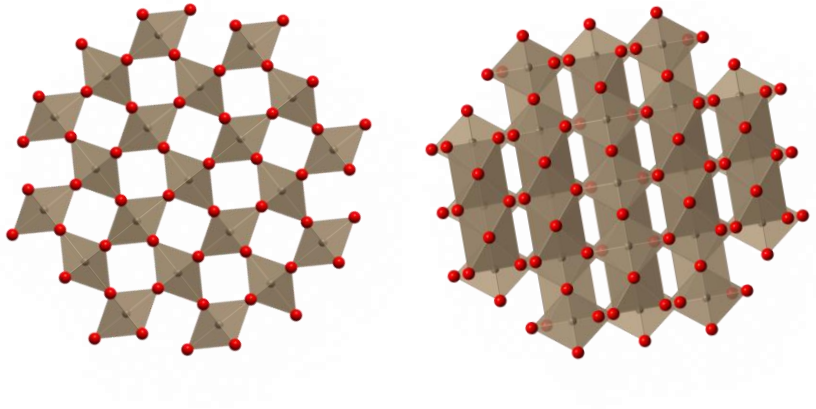


K. M. O. Jensen, P. Juhas, M. A. Tofanelli, C. L Heinecke, G. Vaughan, and C. J. Ackerson, **Polymorphism in magic-sized $Au_{144}(SR)_{60}$clusters,** *Nature Communications* 7, 11859 (2016).

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.

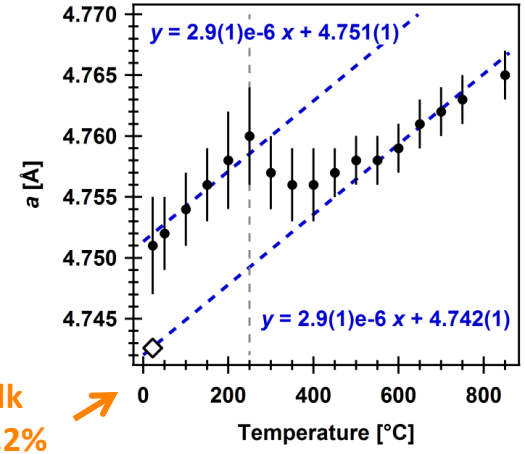
How many layers of water are at the surface?

How is water bonded to surfaces?

What are the dynamics of dehydration?

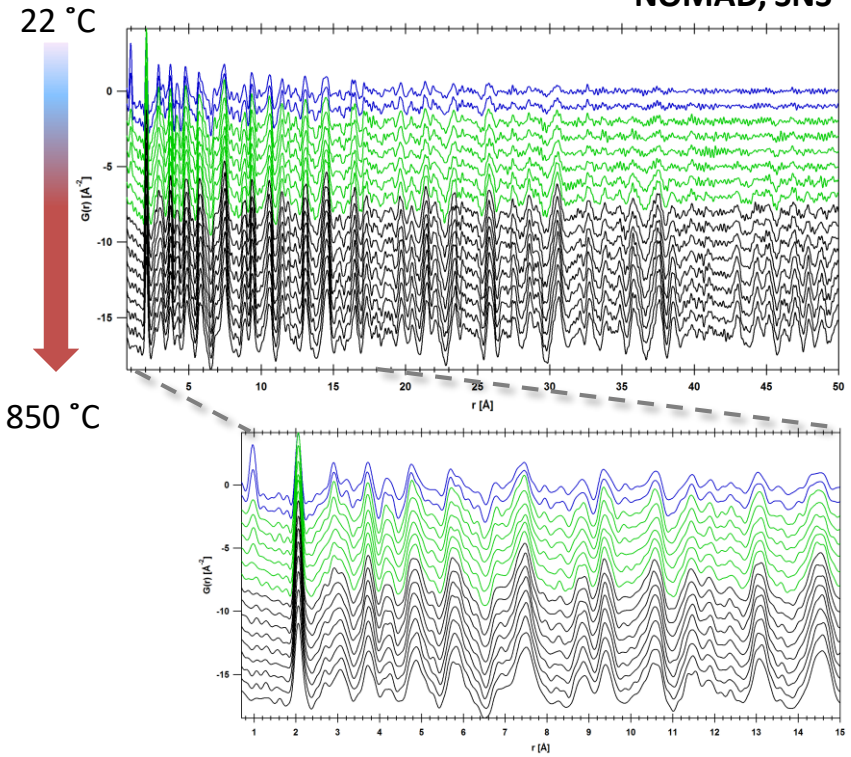
Example: SnO_2 Nanocrystals

- 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

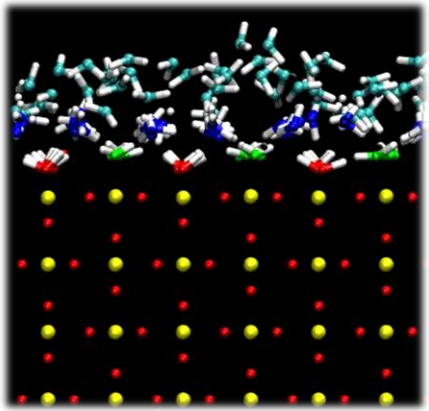


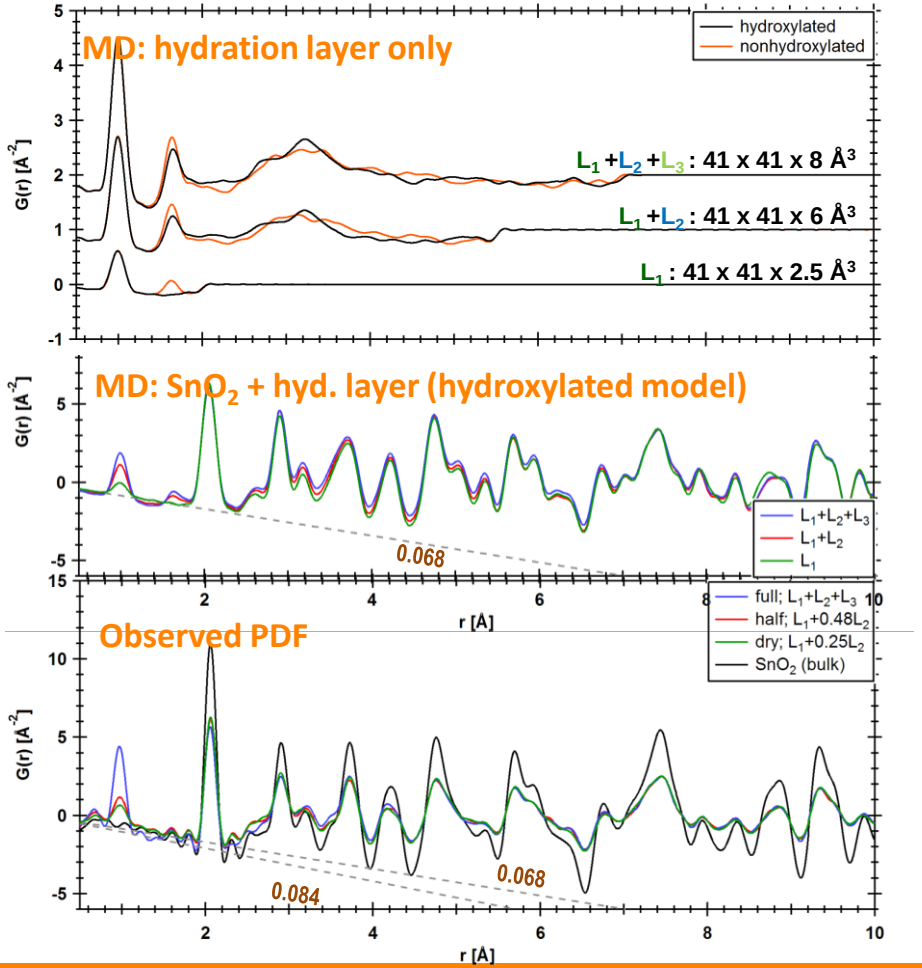
In situ dehydration answers these questions and indicates that water plays a key role in stabilizing the nanocrystals.

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





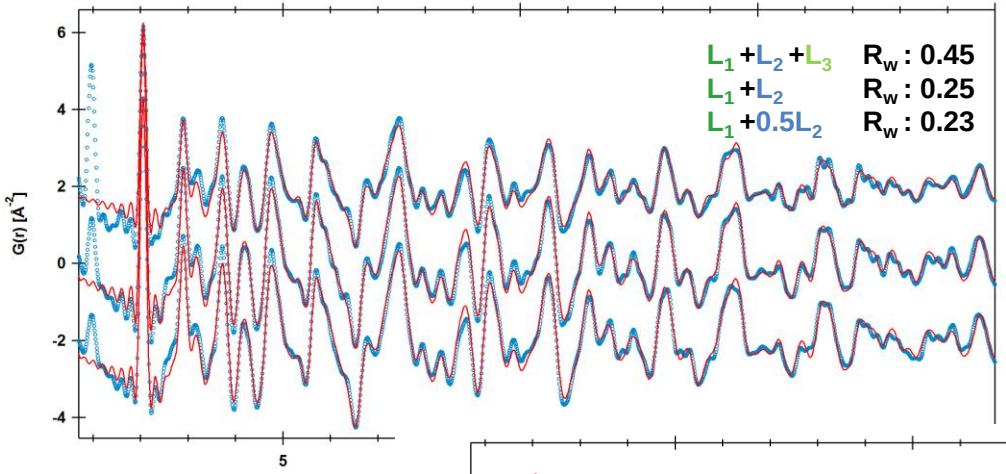
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

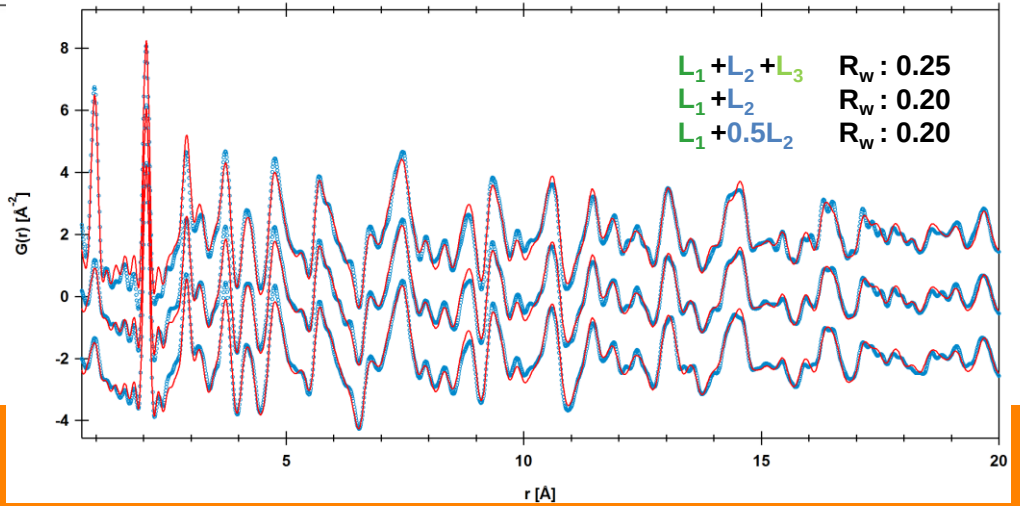
size = ~47 Å



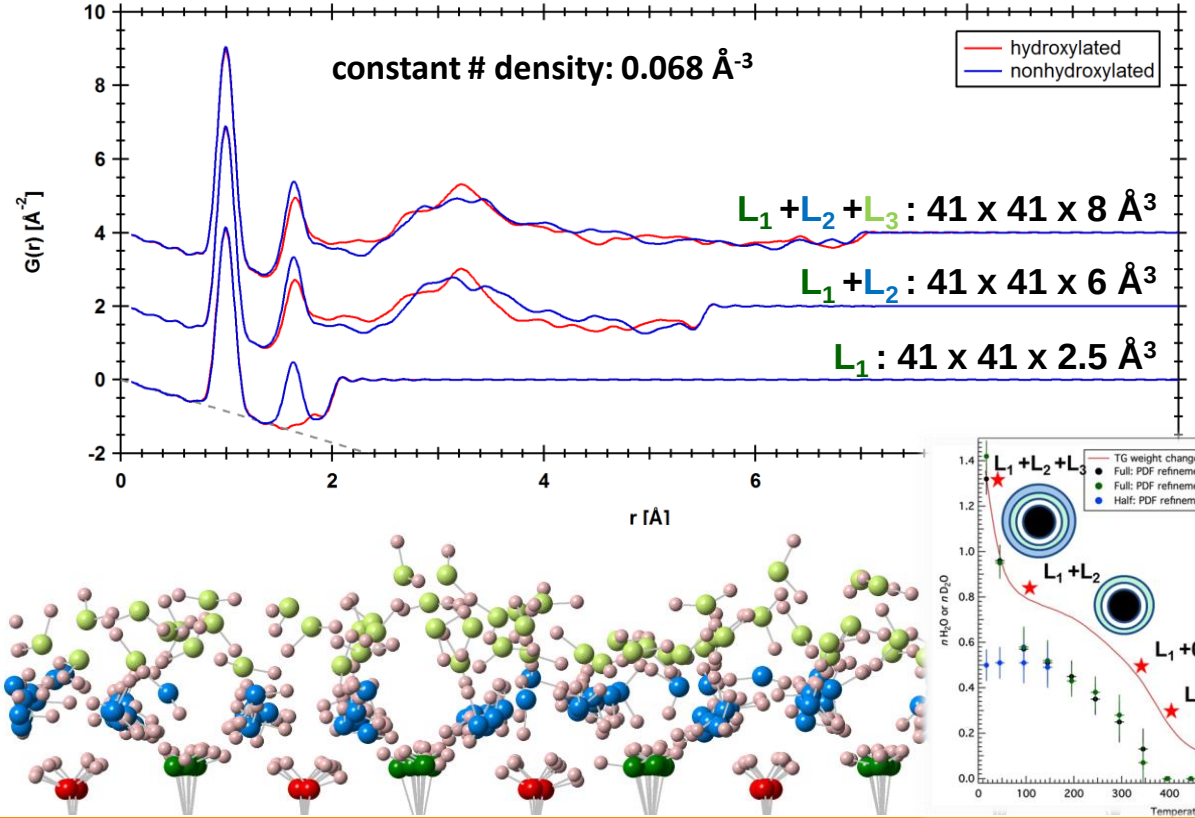
Two phase model:

SnO_2 bulk + layered

MD water structure



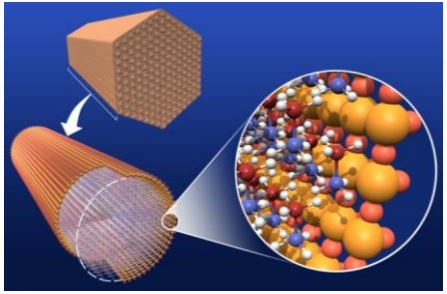
Example: SnO_2 Nanocrystals



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.

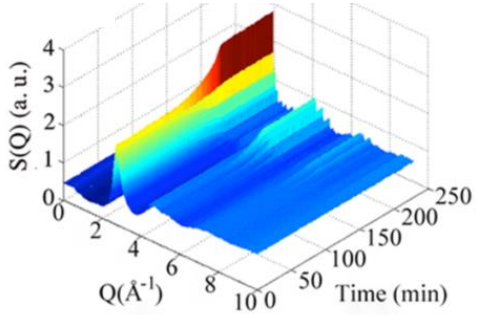
Amorphous structures *via* PDF

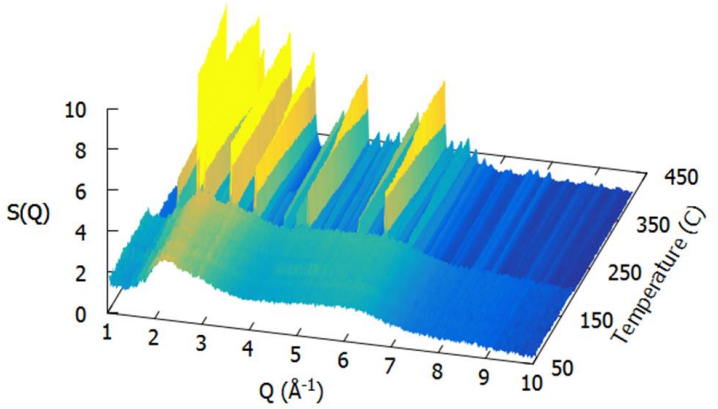
- Glasses
- Liquids
- Concretes
- Adsorbed/absorbed gases
- *etc.*



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).

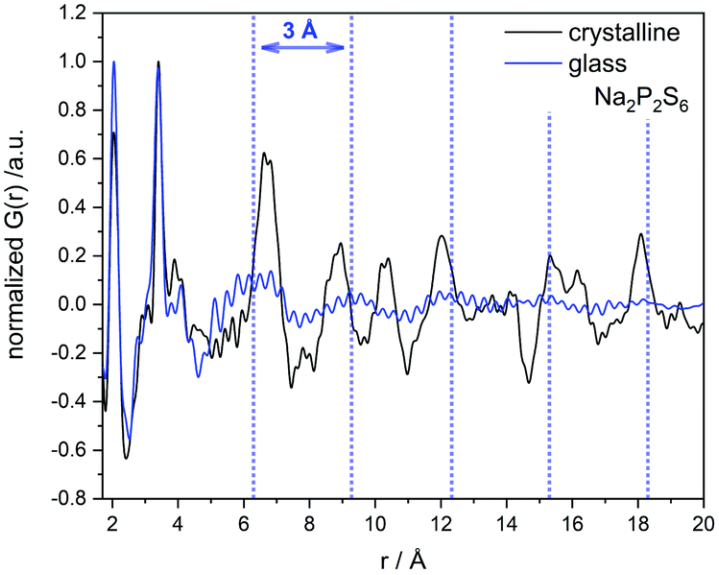




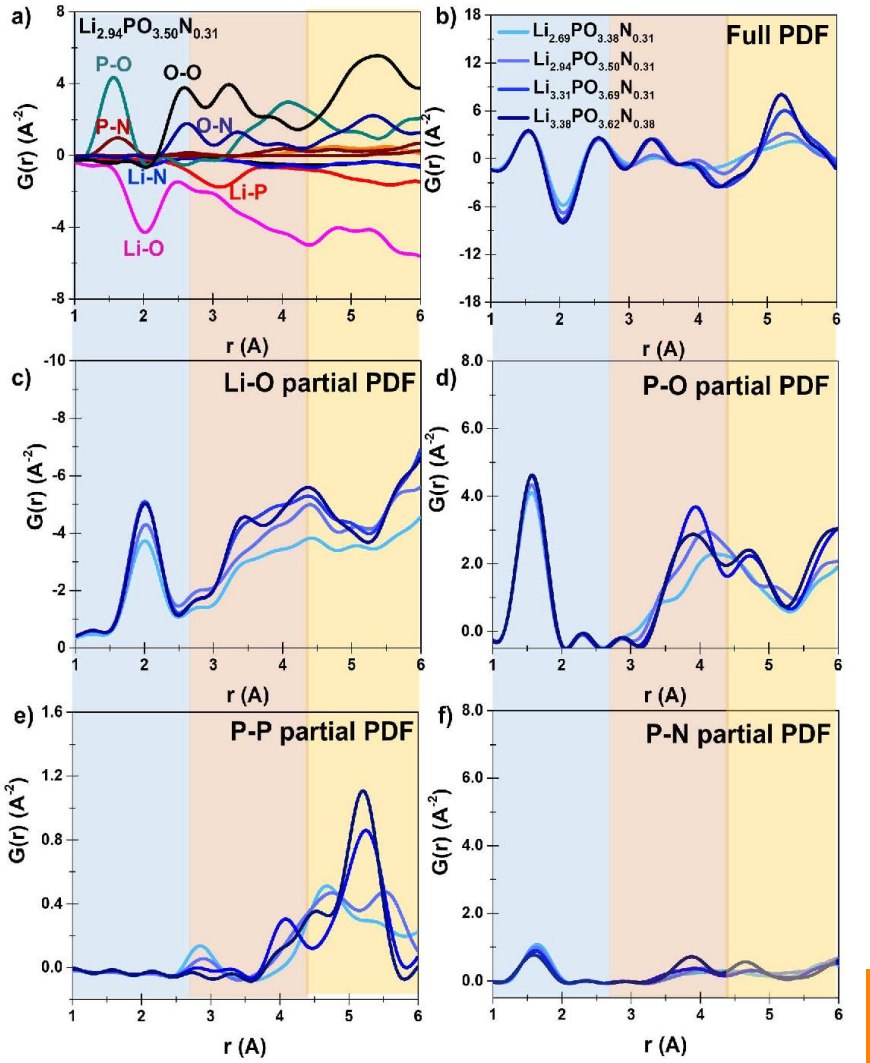
H.-W. Wang; L. L. Daemen, M. C. Cheshire, M. K. Kidder, A. G. Stack, L. F. Allard, J. Neuefeind, D. Olds, J. Liu, and K. Page, **Synthesis and structure of synthetically pure and deuterated amorphous (basic) calcium carbonates**, *Chem. Commun.*, 53, 2942-2945 (2017).

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

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.*

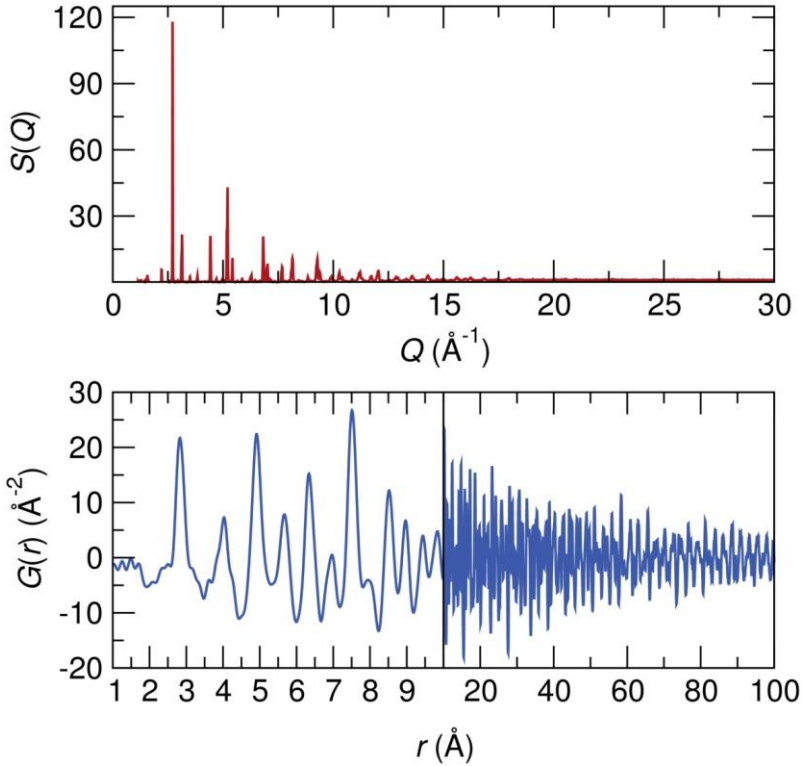
Normalized by: Incident flux, number of atoms, square of the scattering length/form factor

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

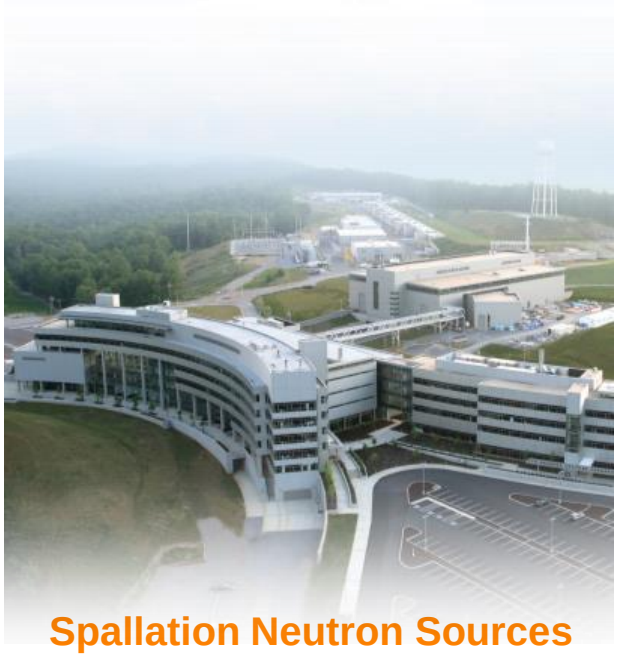
(4) Low (and stable) instrument background

An ideal measurement would have no contribution from the instrument resolution

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

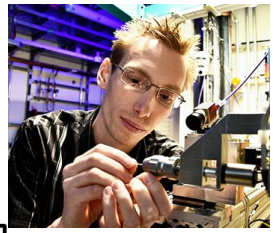
Synchrotron sources
(high energy X-rays)

or



Spallation Neutron Sources
(reactor neutron energies are too low)

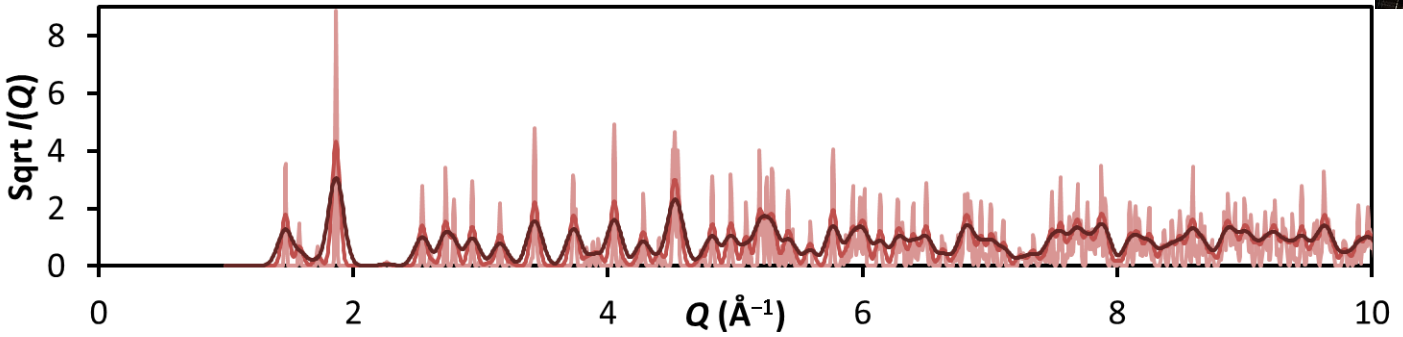
Resolution Effect

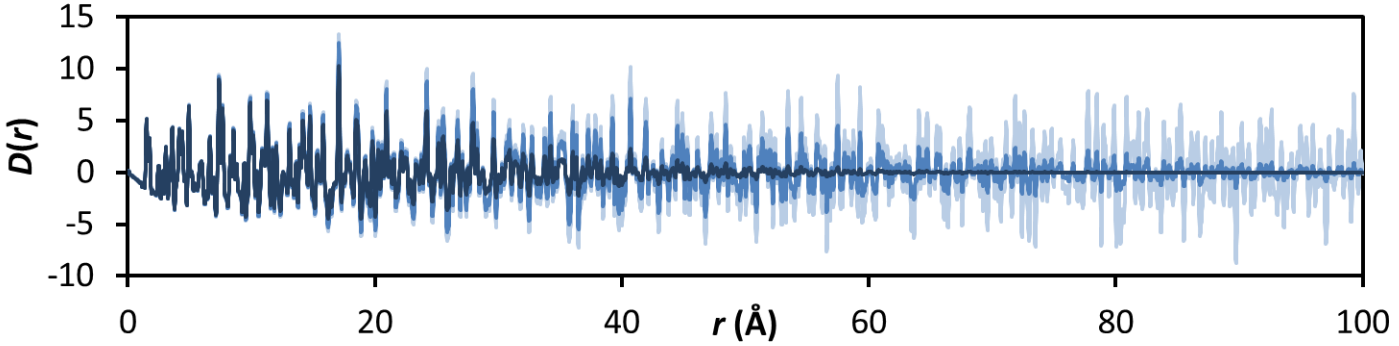


Courtesy of Phil Chater, Diamond Light Source

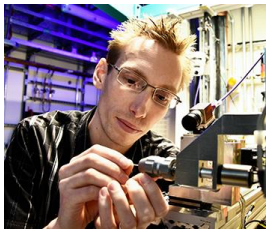
Reciprocal space: Peak width, *dQ*

Real space: D





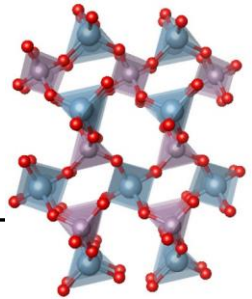
Q_{max} Effect

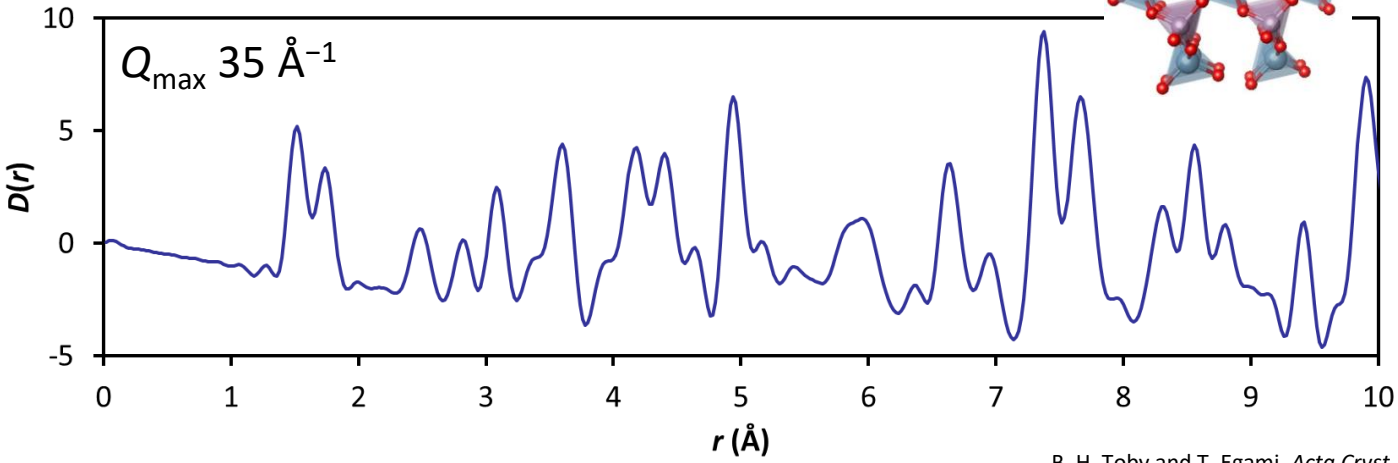


Courtesy of Phil Chater, Diamond Light Source

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

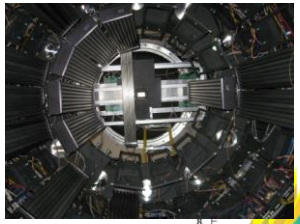
- $Q = 2\pi/d = 4\pi\sin\theta/\lambda$
- $\Delta r \approx 2\pi/Q_{max}$



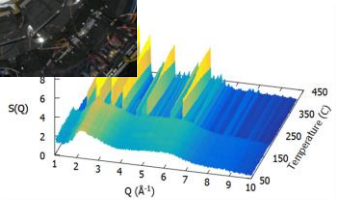


B. H. Toby and T. Egami, *Acta Cryst. A*, **48** 336 (1992).

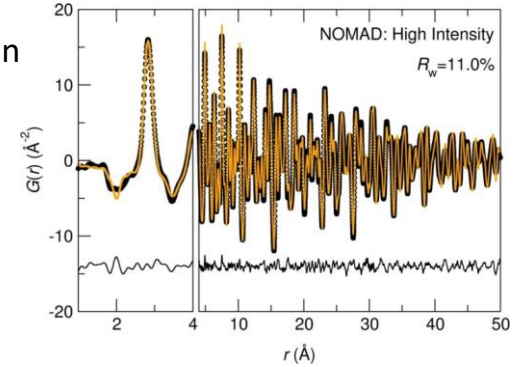
TOF Diffraction and Total Scattering at SNS



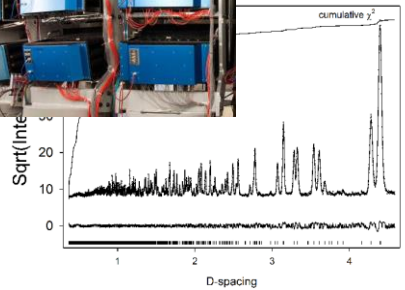
Typical **NOMAD** data can be collected for **30 - 100 mg** of sample in a 3 mm quartz capillary in **~1 hour**



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

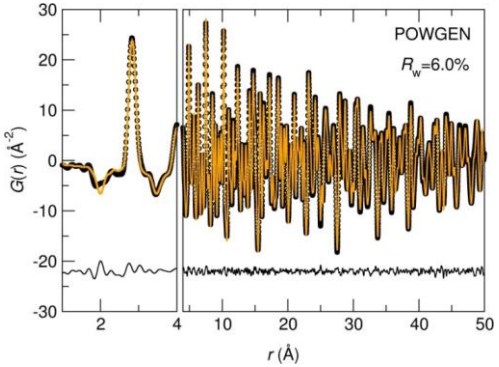


Typical **POWGEN** data can be collected for **~3 - 10 g** of sample in a 6 mm vanadium canister in **~3 hours**

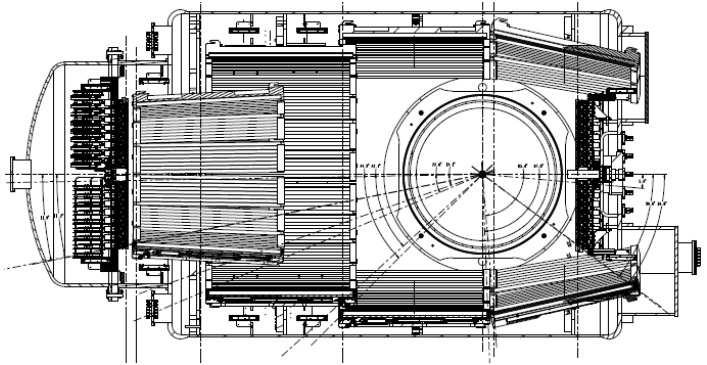


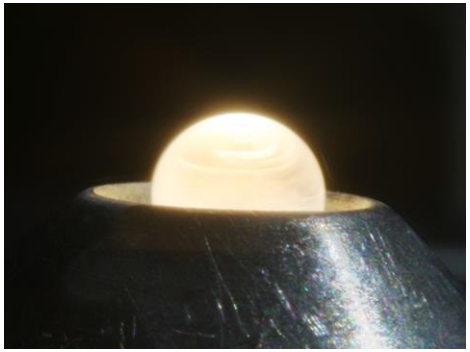
high resolution *diffraction and PDF of crystalline materials*

Mail-in programs available on both instruments



Nanoscale-Ordered Materials Diffractometer (NOMAD)





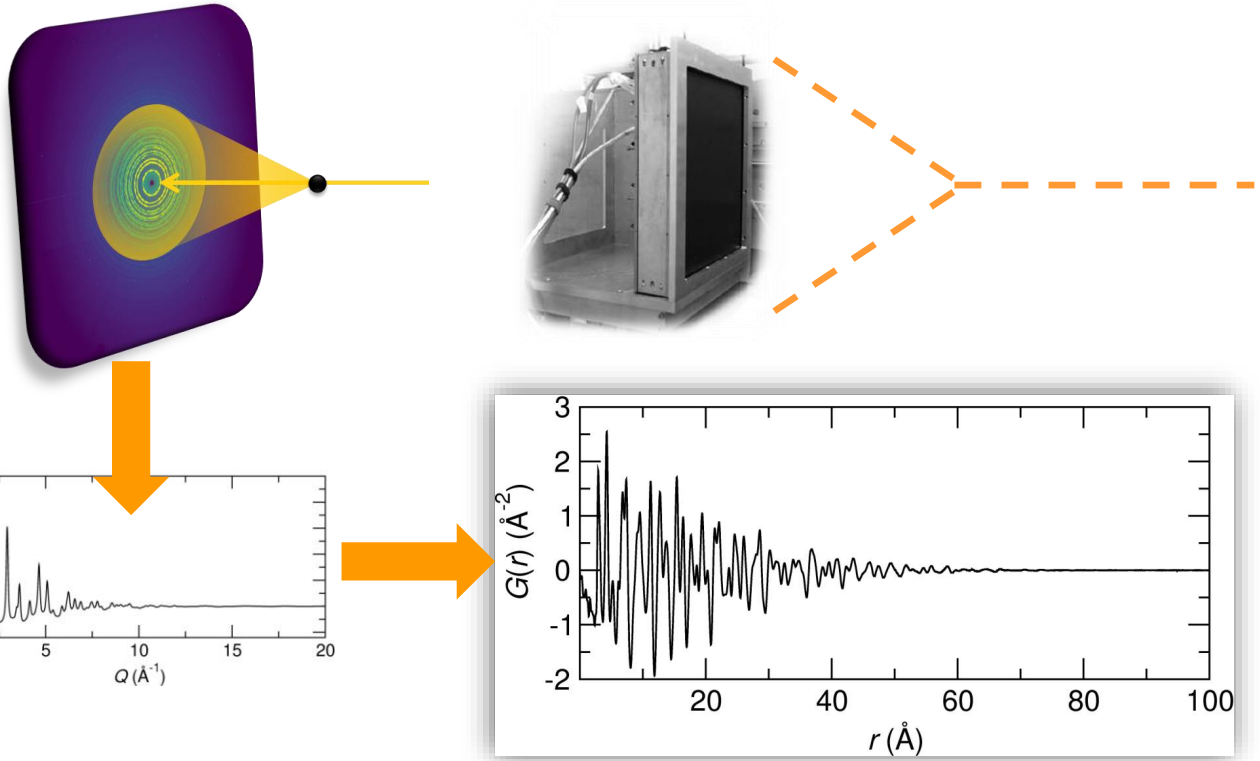
Neuefeind J., Feygenson M., Carruth J., Hoffmann R., Chipley K., **The Nanoscale Ordered MAterials Diffractometer NOMAD at the Spallation Neutron Source SNS**, *Nuclear Instruments and Methods B*, 287, 68-75, (2012).

- 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 set-up (10kV)

Synchrotron Total Scattering: 2D Amorphous Si Detector



Examples of Dedicated User Programs:

11-ID-B at APS
PDF at NSLS-II

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

MODELING A PDF

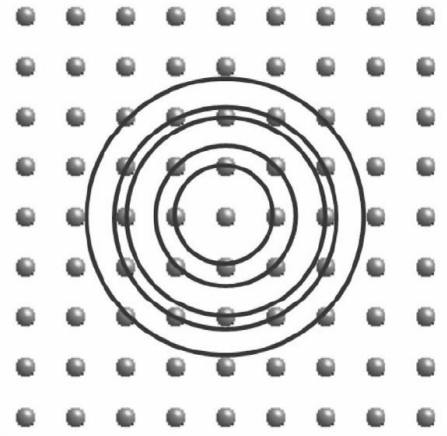
Calculating a PDF from a model

Available software

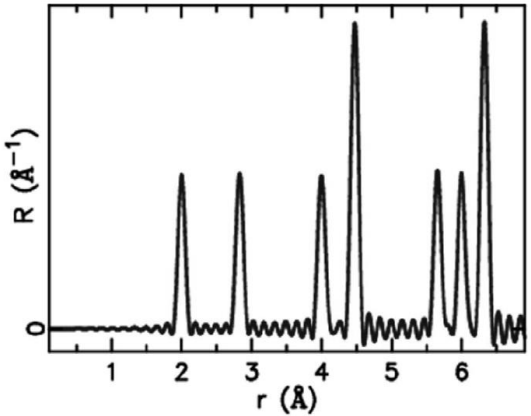
Nanoparticle shape effects

Pair Distribution Function

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



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



Atomic PDF (PDFFIT notation):

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

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

distance between i and j atoms

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

average density

sum over all atoms

Calculating a PDF from a Model

Calculating a PDF from an atomistic model

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

Peak Width

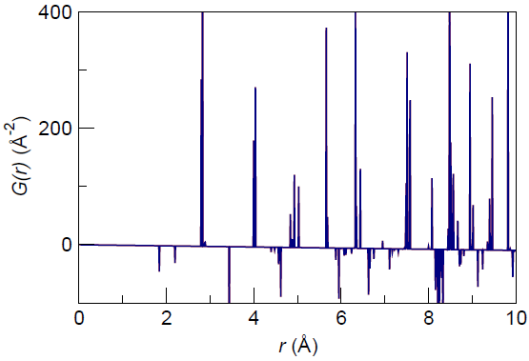
Small model: convolution of $\delta(r-r_{ij})$ with distribution function (*PDFgui & TOPAS v6*)

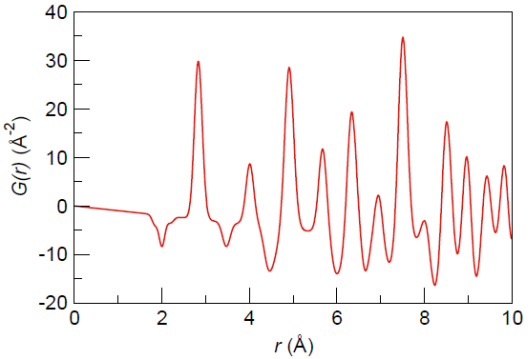
Large model: ensemble average of actual displacements (*RMCprofile*)

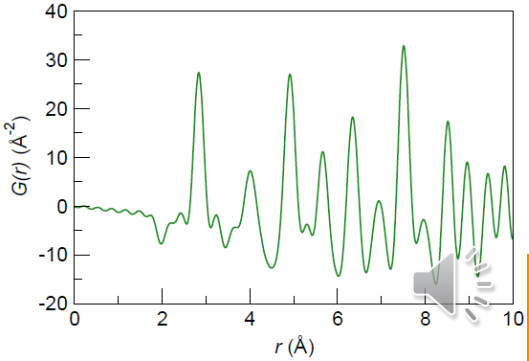
Termination ripples + instrumental dampening

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

…







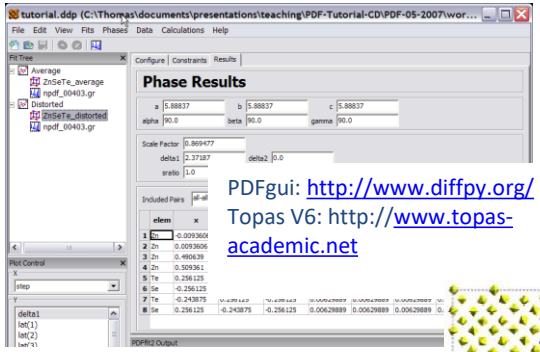
Atomic PDF Modeling

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

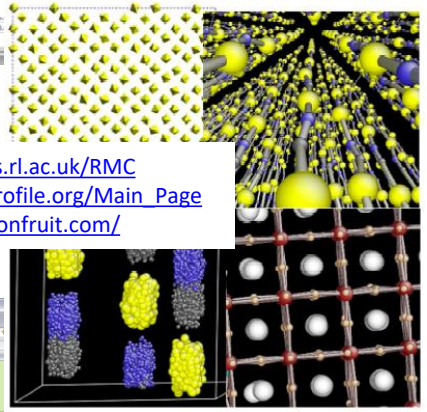
Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q), G(r),* Bragg profile, now EXAFS
Constraints utilized
Static 3-D model of the structure (a snap-shot)

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



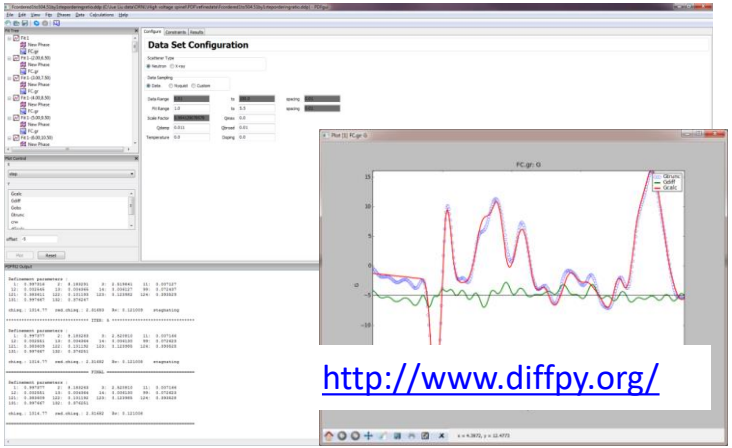
PDFgui: http://www.diffpy.org/
Topas V6: http://www.topas-academic.net



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/

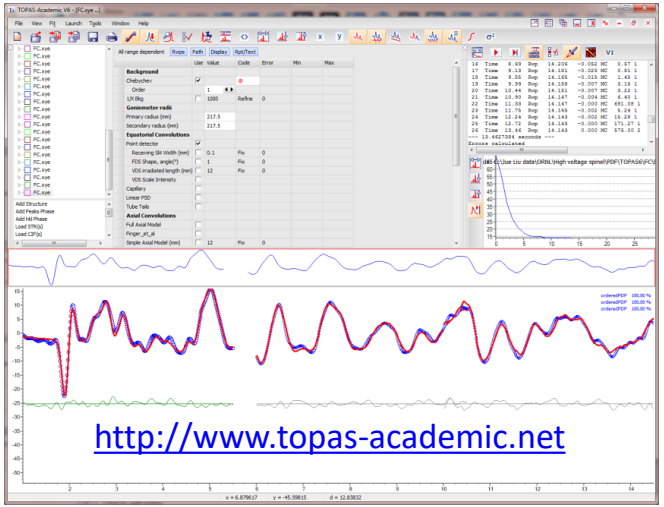
PDFgui

+ 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*

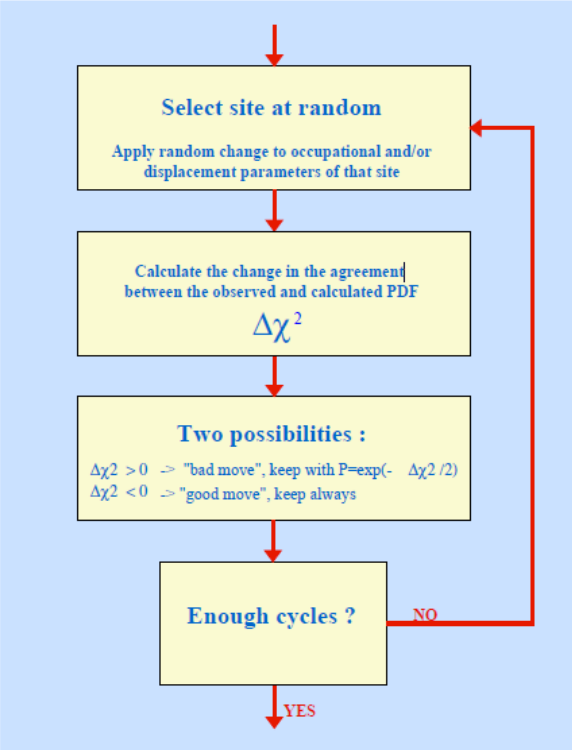
TOPAS PDF

+ 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

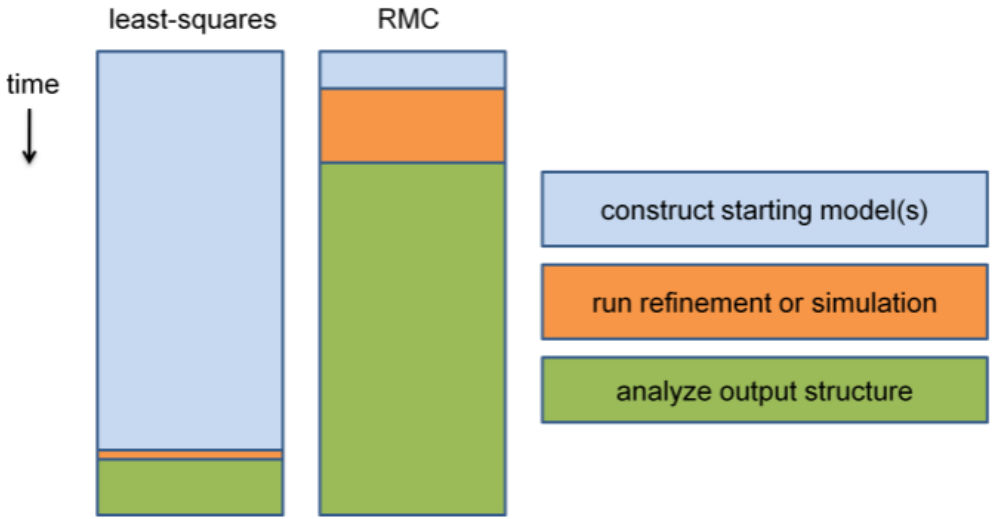


RMCprofile

- 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

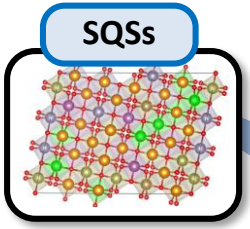
Also check out **FullRMC**

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

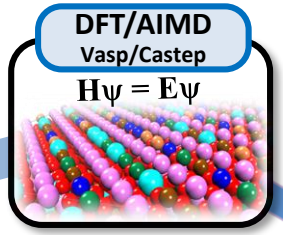


Daniel P. Shoemaker, *Understanding atomic disorder in polar and magnetic oxides* (2010).

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



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



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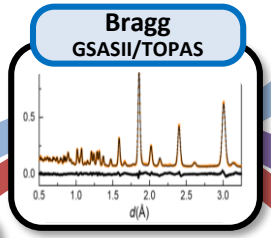
Article

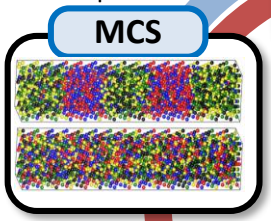
Probing the Local Site Disorder and Distortion in Pyrochlore High-Entropy Oxides

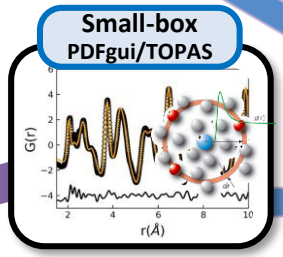
Bo Jiang, Craig A. Bridges,* Raymond R. Unocic, Krishna Chaitanya Pitike, Valentino R. Cooper, Yuanpeng Zhang, De-Ye Lin, and Katharine Page*

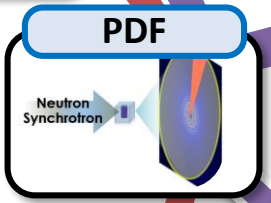
Cite This: *J. Am. Chem. Soc.* 2021, 143, 4193−4204 Read Online

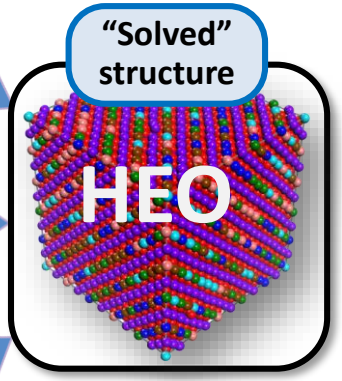
Metropolis Monte Carlo simulations (MCS) utilized to estimate cation disorder and predict secondary phases

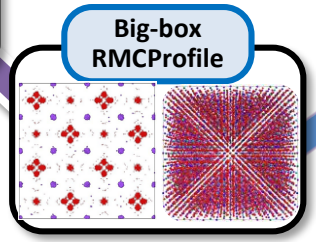


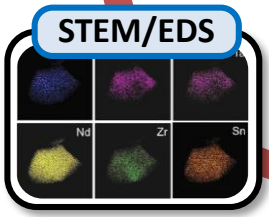


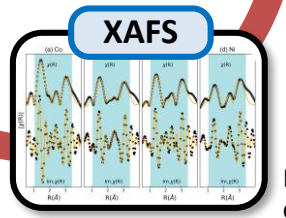










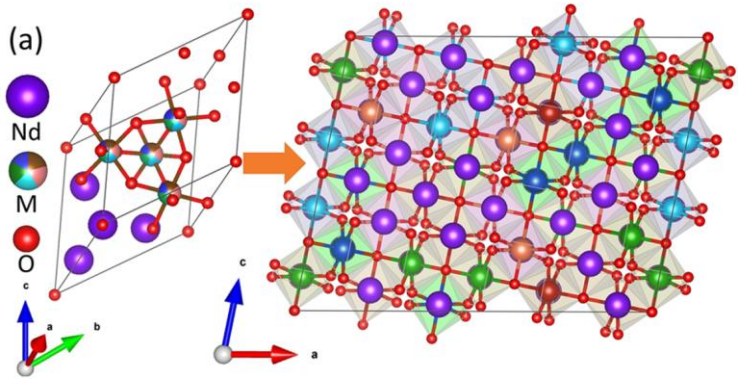


EXAFS analysis to constrain local chemical environment

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

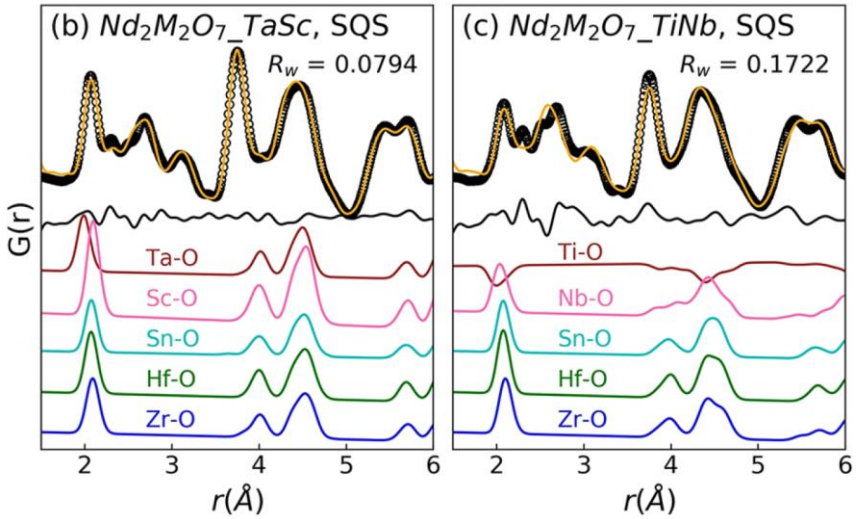
Small-box PDF fitting using DFT-relaxed SQS supercell

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

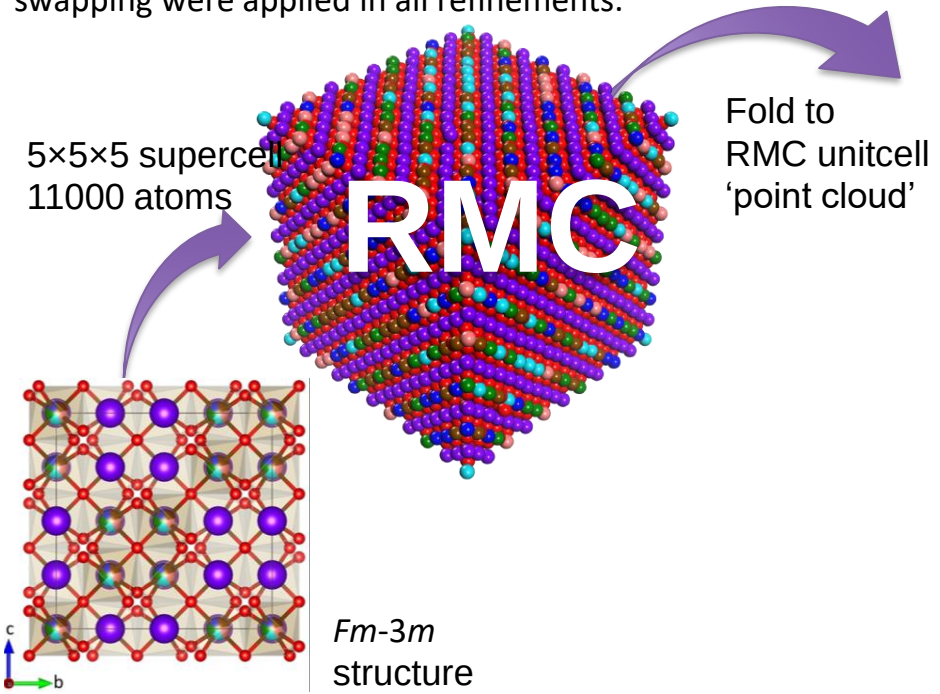
$Nd_2(Ta_{0.2}Sc_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$ $Nd_2(Ti_{0.2}Nb_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$

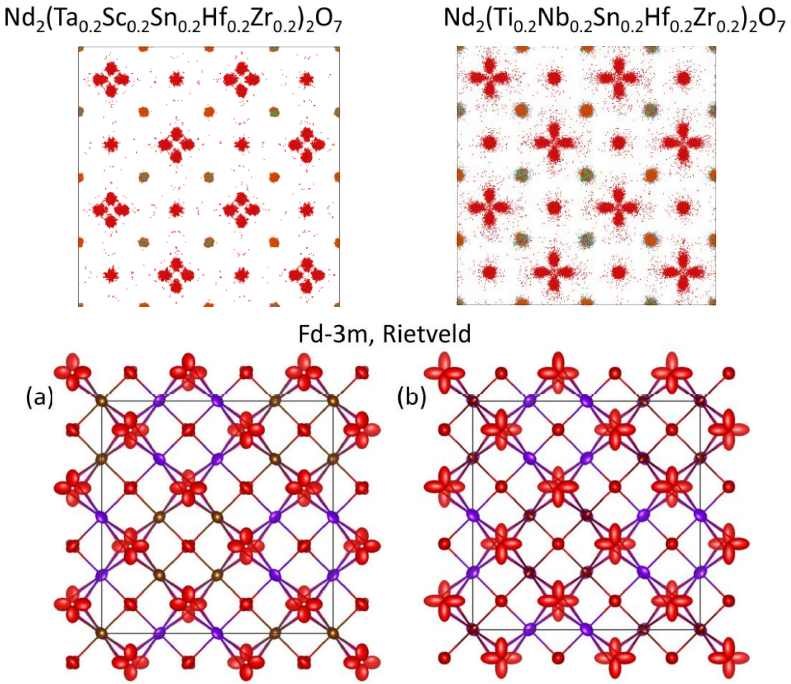


Total and decomposed partial PDFs from individual M−O pair−pair correlations

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

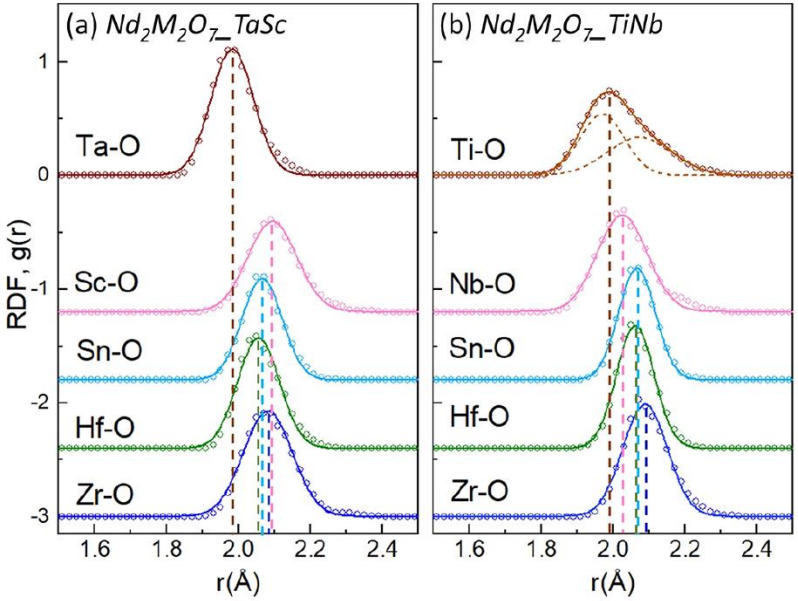
Reverse Monte Carlo (RMC) fits were performed to identify the short-range cation ordering, obtained by fitting PDF G(r), F(Q), and the neutron diffraction patterns simultaneously. Bond valence sum (BVS) restrictions and atom swapping were applied in all refinements.

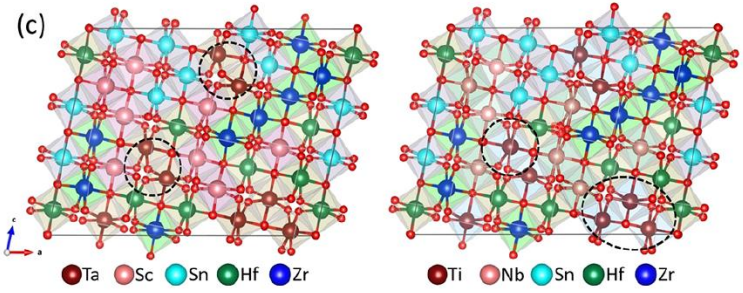




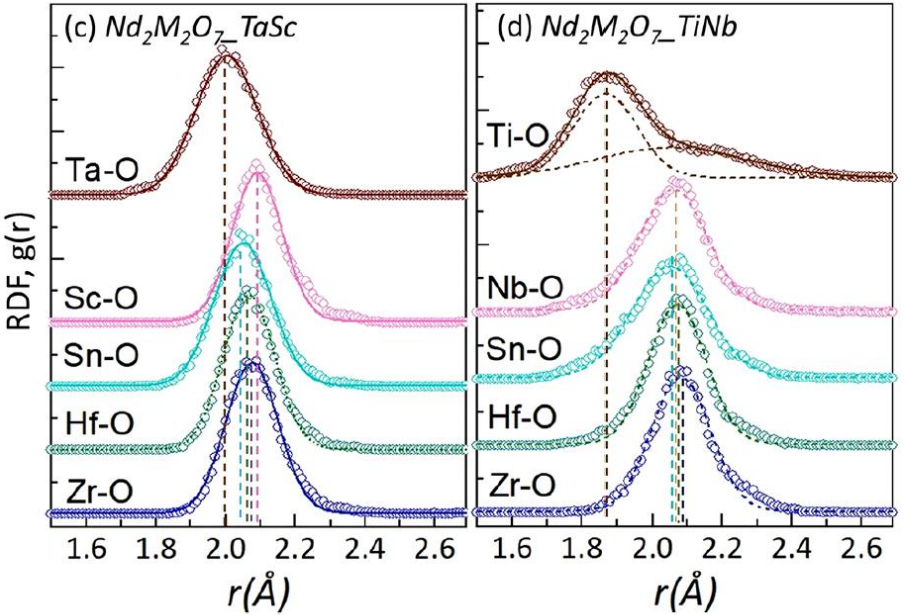
Nearest-neighbor M-O peaks

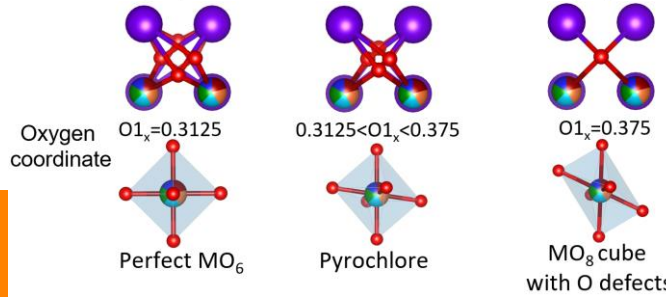
SQS





RMC

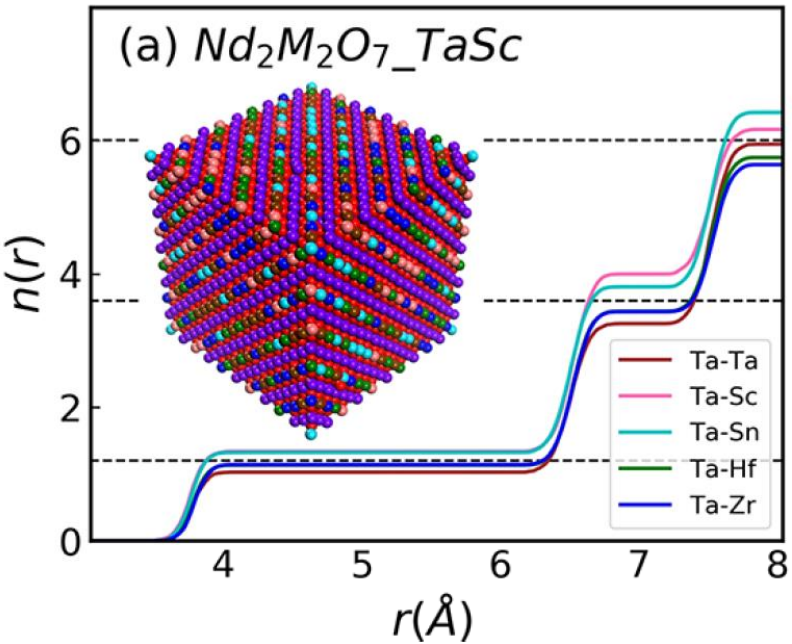


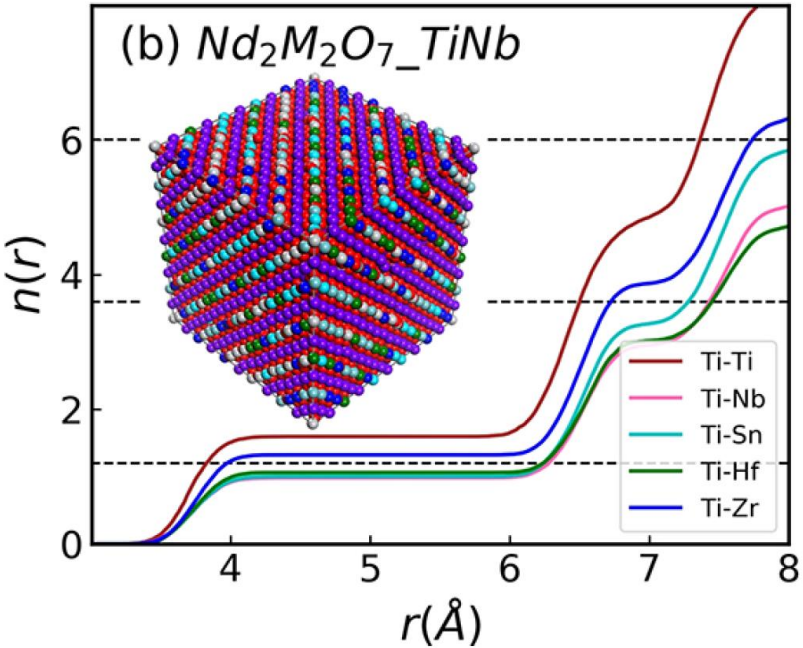


Neighbor correlations *n(r)* by RMC

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

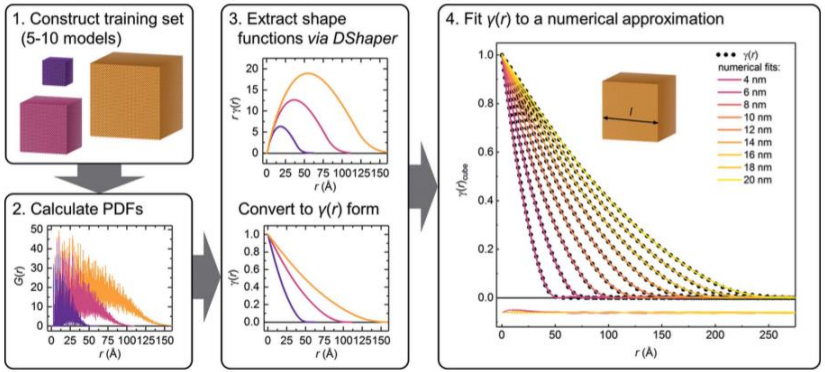
$$n_{ij}(r) = \int_{r2}^{r1} 4\pi r^2 2c_j\rho_0 g_{ij}(r)\mathrm{d}r$$

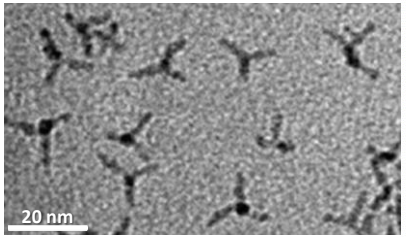


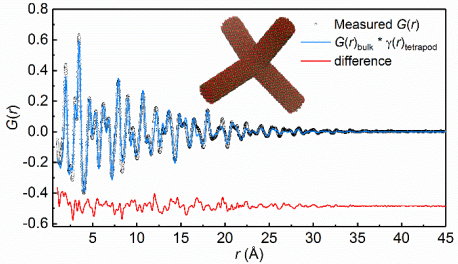


Modeling nanoscale morphology in real space

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







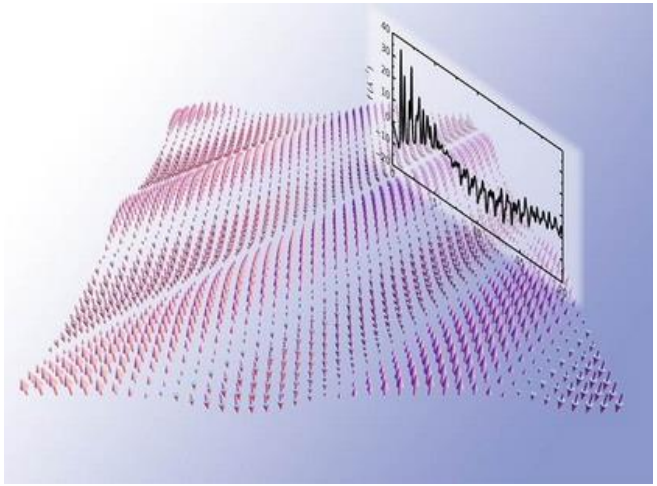
- $\gamma_0(r)$ is the particle shape function, it varies significantly from unity for nanomaterials and should be implemented as an *r*-dependent function
- Can fit physically-relevant shape parameters, such as a nanocube edge length, nanorod length and diameter, or arm length, width, and arm tip-to-arm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

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

A FEW EMERGING AREAS

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

Magnetic PDF: mPDF



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advances

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Magnetic pair distribution function analysis of local magnetic correlations

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- Being developed to provide direct access to long-range and short-range magnetic correlations in real space
- **Spin order in diluted magnetic semiconductors, spin-stripe correlations in cuprate superconductors, spin fluctuations in frustrated magnetic systems, etc.**

ARTICLE

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DOI: 10.1038/ncomms13842 OPEN

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

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

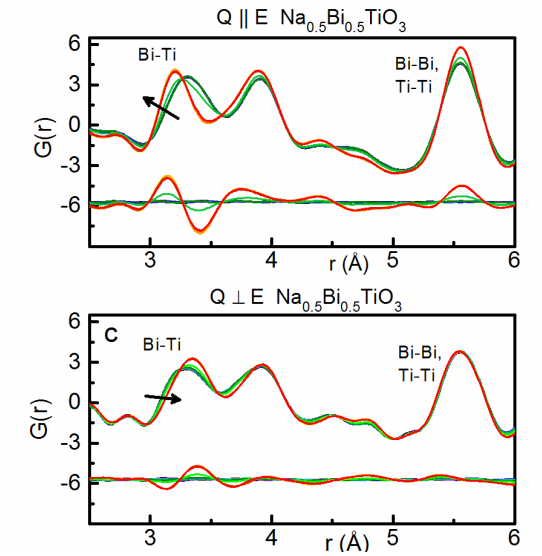
PRL 116, 197204 (2016) PHYSICAL REVIEW LETTERS week ending 13 MAY 2016

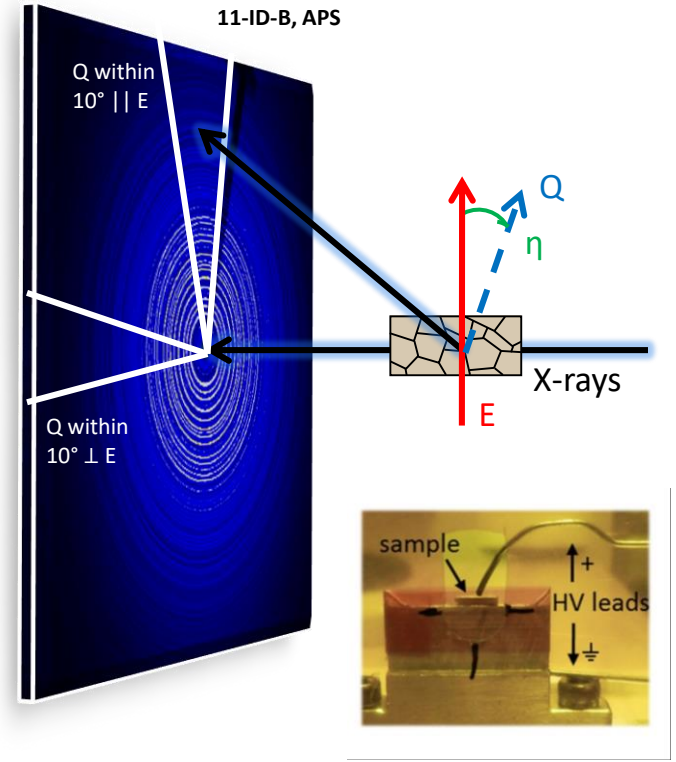
Verification of Anderson Superexchange in MnO via Magnetic Pair Distribution Function Analysis and *ab initio* Theory

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

Field-Dependent PDF

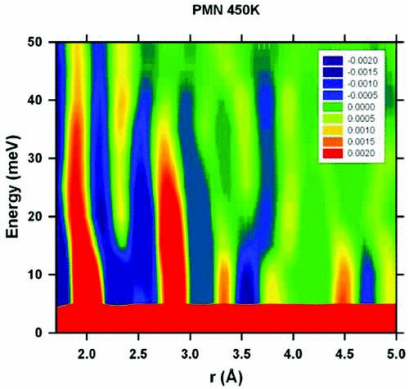
- X-ray total scattering measured while static electric fields (0 to ~4 kV/mm) are applied to $Na_{½}Bi_{½}TiO_3$ polycrystalline ceramic samples
- Bi^{3+} reorientation observed at high electric field





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

Dynamic PDF: DyPDF



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

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

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


ARTICLE

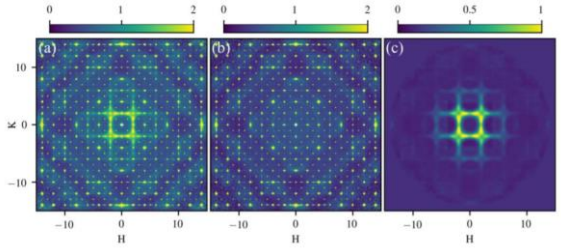
Received 28 Jun 2016 | Accepted 17 Mar 2017 | Published 4 May 2017 DOI: 10.1038/ncomms15294 OPEN

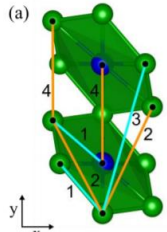
Observation of dynamic atom-atom correlation in liquid helium in real space

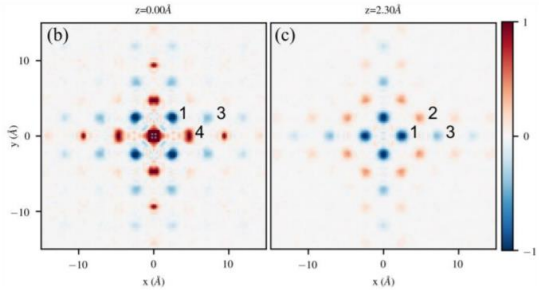
W. Dmowski[1,2], S.O. Diallo[3], K. Lokshin[1,2], G. Ehlers[3], G. Ferré[4], J. Boronat[4] & T. Egami[1,2,3,5]

3D - PDF

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





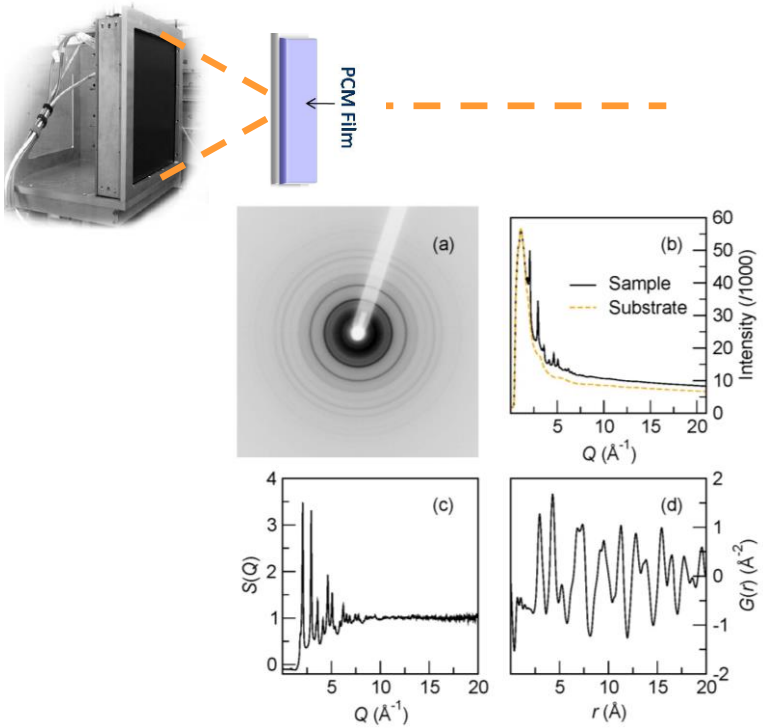


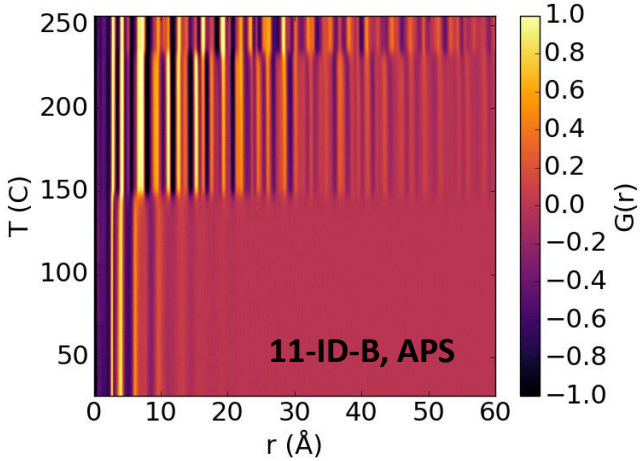
$(Mn_{1-x}Fe_x)_2O_3$

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

Thin Film PDF: tfPDF

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



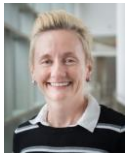


Data collected for 1 µm films deposited **on kapton**, thermally annealed in situ under flowing He to 155˚C and measured at ~60 keV in transmission

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

NOMAD Hazardous Gas Handling System (HGHS)

UNCAGE ME



CAD model of gas cabinets and exhaust line

Major Components

- 3 ventilated gas cabinets with space for 6 gas tanks
  - -Two corrosive tanks
  - -Two flammable tanks
  - -Two isotope gas lecture bottles
- 2 gas mixing manifolds with 4 mass flow controllers each
- Stainless steel/quartz/Teflon flow path compatible with acid gasses, sulfur gasses, flammables and toxics
- Gas detectors in both instrument and tank area
- 4-way switching valve for MES/SSITKA experiments
- RGA for effluent analysis
- Upgraded repeatability of sample positioning
- Software control of valves, MFC and furnace integrated with neutron data collection allowing temperature/gas composition binning

Commissioning in 2022/2023

Georgia Institute of Technology · Oak Ridge National Laboratory · Sandia National Laboratories · The University of Alabama · Lehigh University · Penn State · Washington University in St. Louis · University of Wisconsin-Madison

Previous generation gas flow:

Olds, et al. *Rev. Sci. Instrum.* **2017**, *88*, 034101.
Olds, et al. *Rev. Sci. Instrum.* **2018** *89*, 092906.

BIG ORANGE BIG IDEAS

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/

References & Reviews

S.J.L. Billinge and I. Levin, The Problem with Determining Atomic Structure at the Nanoscale, Science 316, 561 (2007). http://dx.doi.rog/10.1126/science.1135080

T. Egami and S. J. L. Billinge, Underneath the Bragg peaks: structural analysis of complex materials, Pergamon Press Elsevier, Oxford, England, 2003.

D. A. Keen, Derivation of commonly used functions for the pair distribution function technique J. Appl. Cryst. 34 (2001) 172-177. http://dx/doi.org/10.1107/S0021889800019993

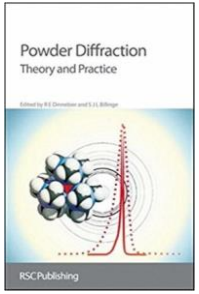
R. Neder and Th. Proffen*, Diffuse Scattering and Defect Structure Simulation*, Oxford University Press, 2008.

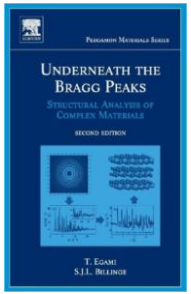
M. G. Tucker, M. T. Dove, and D. A. Keen, Application of the reverse Monte Carlo method to crystalline materials, J. Appl. Cryst. 34, 630-638 (2001). http://dx.doi.org/10.1107/S002188980100930X

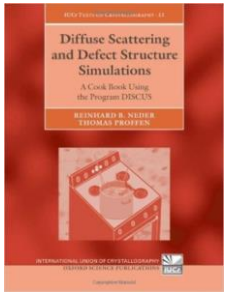
D. A. Keen and A. L. Goodwin, The crystallography of correlated disorder, Nature 521, 303–309, 2015. http://dx.doi.org/10.1038/nature14453

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

D. Olds, C. N. Saunders, M. Peters, T. Proffen, J. N. Neuefeind, and K. Page, Precise implications on real-space PDF modeling from effects intrinsic to modern time of flight neutron diffractometers, *Acta Cryst. A*74 (2018). https://doi.org/10.1107/S2053273318003224







Open Access Teaching and Education Article

JAC TEACHING AND EDUCATION

J. Appl. Cryst. (2021). **54**, 317-332
https://doi.org/10.1107/S1600576720015630
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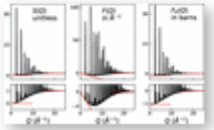


Illustrated formalisms for total scattering data: a guide for new practitioners

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**.

Read article **Similar articles**

Try Diffraction/PDF Mail-in Programs for Users!

Mail-in Neutron Program (NOMAD and POWGEN, SNS)

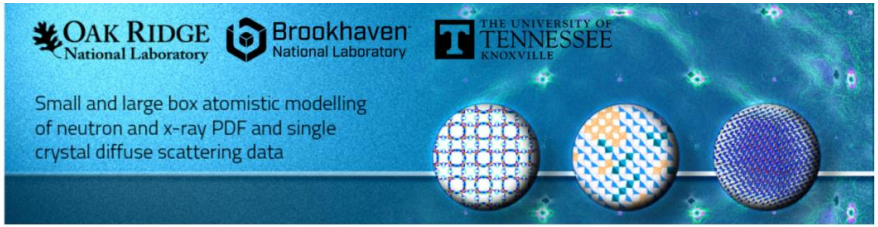
- NOMAD: Up to five samples or temperatures, ~30 - 100 mg of sample in a 3 mm quartz capillary in ~1 hour (in standard mode) https://neutrons.ornl.gov/nomad/mail-in
- POWGEN: Up to five samples or temperatures, ~3 - 10 g of sample in a 6 mm vanadium canister in ~3 hours: https://neutrons.ornl.gov/powgen/mail-in
- Opportunities on most weeks during the run cycle

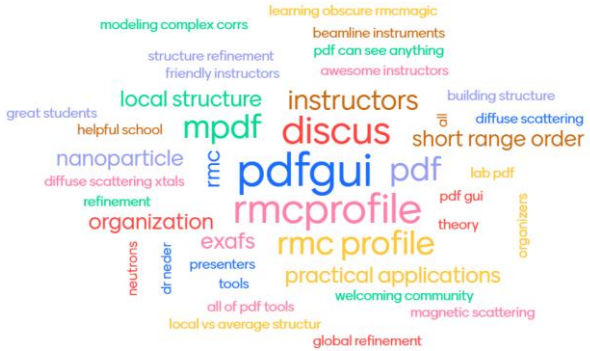
Mail-in X-ray Program (11-ID-B, APS)

- Less than a second to seconds per measurement on ~ 10 mg or sample!
- Mail-in is offered for standard measurements (powders/solids in capillaries at ambient temperatures)
- Submit rapid access mail-in proposal: https://wiki-ext.aps.anl.gov/srsmailin/index.php/SRS_mail-in

Try PDF School for Students and Postdocs!

5th US School on Total Scattering Analysis: September 12-16, 2022





Topics covered:

Introduction to Total Scattering
Modern Total Scattering Instruments and Data
Hands-on Data Analysis with:

- Small box modeling with PDFGui & Diffpy-CMI
- Large box modeling with RMCProfile & EXAFS data
- Building and refining nanoparticles with DISCUS

ORNL Organizers:

Katharine Page, Thomas Proffen and Matt Tucker

BNL Organizers:

Daniel Olds, Milinda Abeykoon, Emil Bozin and Eric Dooryhee

http://conference.sns.gov/event/346

Try Total Scattering Analysis Online Video Library!

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https://scatteringpage.utk.edu/ts-schoolvideos/

4th US School on Total Scattering Analysis: October/November 2021

October 20

Introduction to Total Scattering: Thomas Proffen, Oak Ridge National Laboratory

Big surprises from the small box- PDF endeavors in nanostructured materials: Emil Bozin, Brookhaven National Laboratory

RMCProfile as a data-fusion framework for determining nanoscale atomic order: Igor Levin, National Institute of Science and Technology

Building complex and decorated nanoparticles with DISCUS: Reinhard Neder, University Erlangen Germany

October 22

Fourier Transforms are Not Magic- How We Make Your PDF: Daniel Olds, Brookhaven National Laboratory

X-ray Total Scattering Instrumentation: Milinda Abeykoon, Brookhaven National Laboratory

X-ray Total Scattering Data Reduction: Milinda Abeykoon, Brookhaven National Laboratory

Neutron Total Scattering Instruments and Uses: Katharine Page, University of Tennessee and Oak Ridge National Laboratory

Data Reduction for Neutron Total Scattering: Yuanpeng Zhang, Oak Ridge National Laboratory

October 27

Recent and upcoming developments in PDF analysis: Simon Billinge, Brookhaven National Laboratory

October 29

Pair distribution function analysis of battery materials: Phoebe Allan, U

November 3

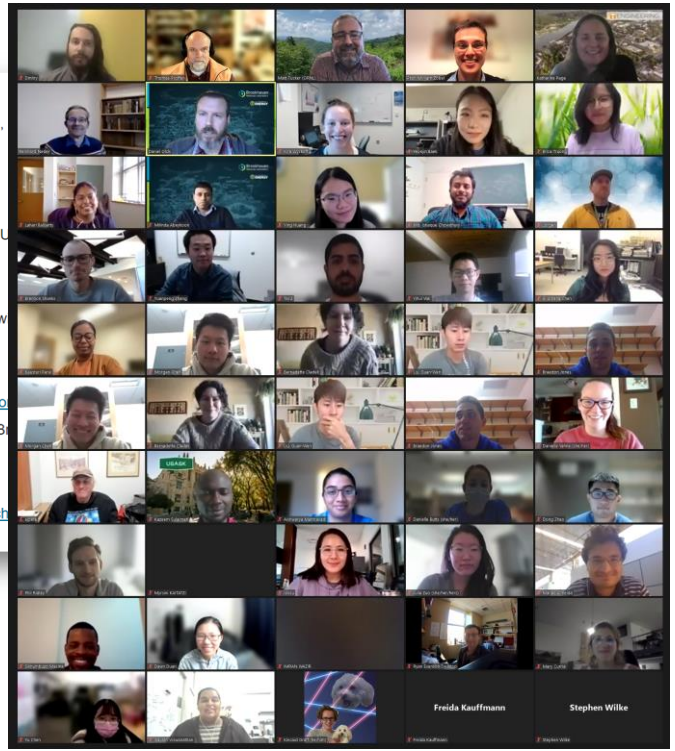
Disorder and diffuse scattering in materials chemistry: Andrew Goodw

November 5

Of Spins and Pseudospins- Magnetic PDF as a powerful probe of sho correlations: Ben Frandsen, Department of Physics and Astronomy, B

November 10

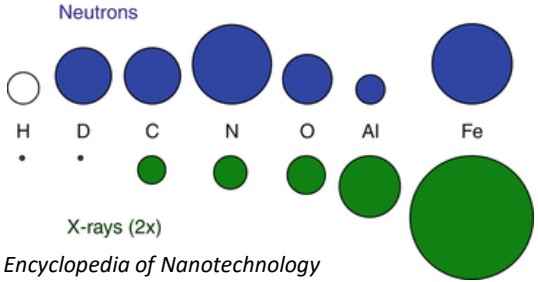
Pushing insight from laboratory PDF data and why we still need synch Institute of Crystallography, RWTH Aachen University, Germany



BIG ORANGE BIG IDEAS

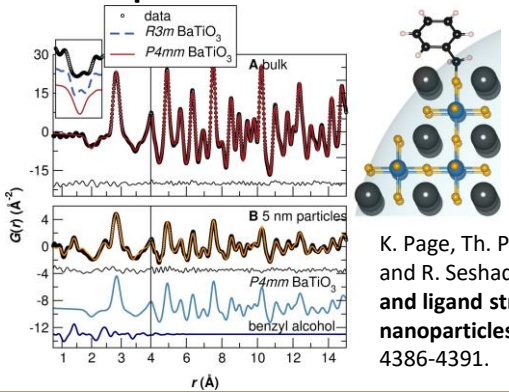
Neutron Total Scattering

Light Atom and Neighboring Atom Species



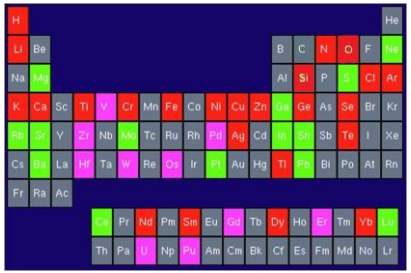
M. Laver, *Encyclopedia of Nanotechnology* (2012), 2437-2450.

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.

Isotope Substitution

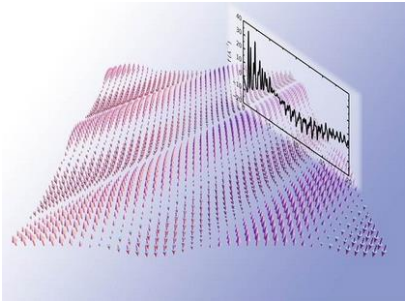


J. E. Enderby, D.M. North, P. A. Egelstaff, **Partial structure factors of liquid Cu-Sn,** *Phil. Mag.*14 (1966) 131.

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

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.

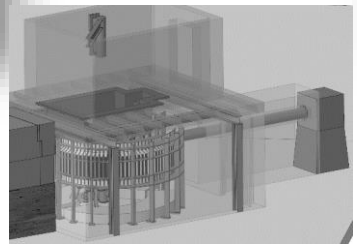


Nondestructive

Penetration of Sample Environments

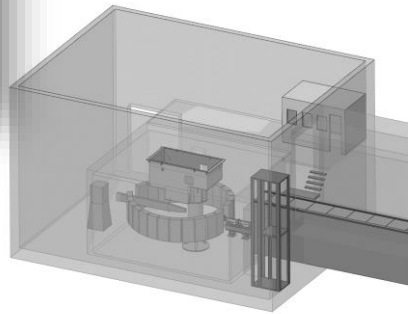
Existing/Future FTS Powder Suite

NOMAD: high intensity diffractometer



DISCOVER: medium resolution total scattering diffractometer

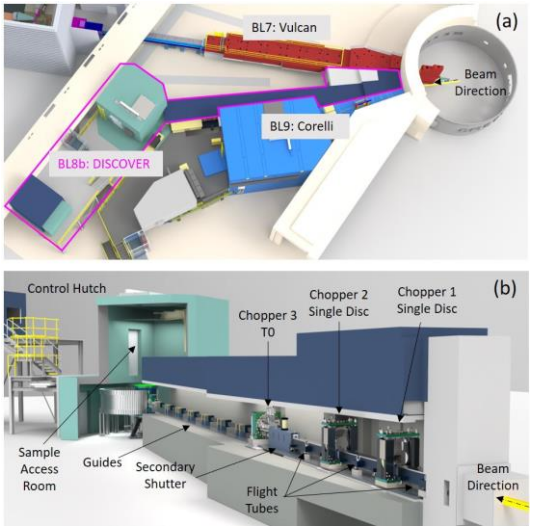
POWGEN: general purpose diffractometer

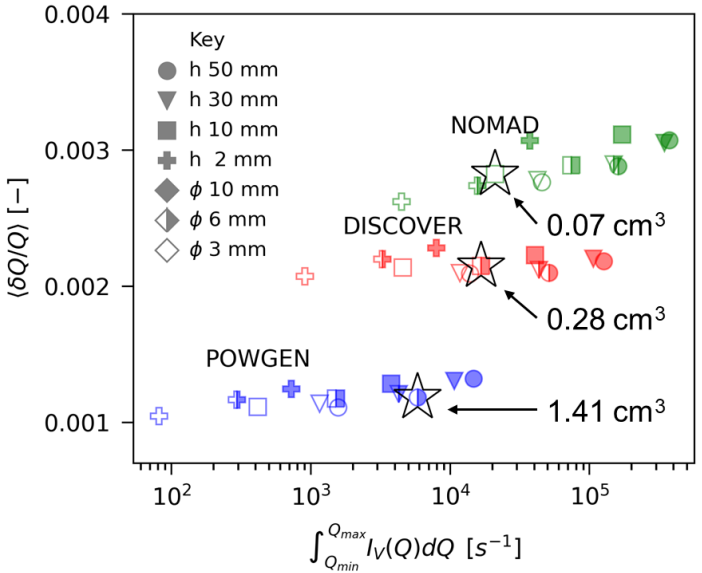


HiResPD: highest resolution diffractometer (for FTS)

DISCOVER Beamline

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





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

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

BIG ORANGE BIG IDEAS

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?

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ScatteringPage.utk.edu

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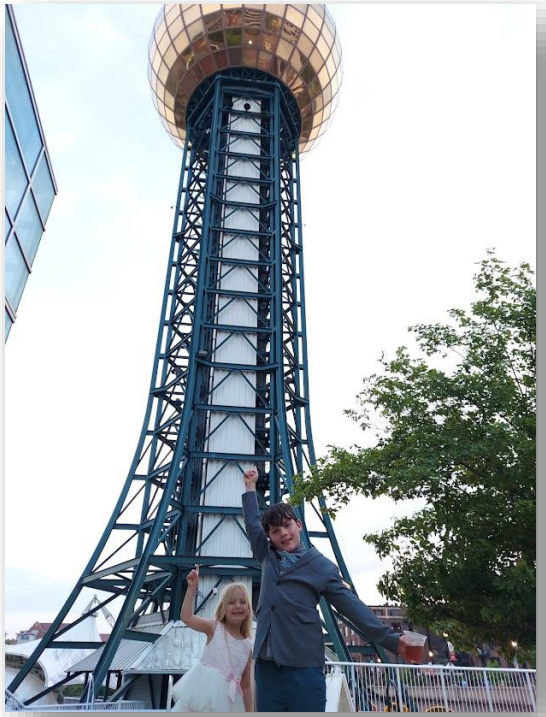

BIG ORANGE BIG IDEAS

Survey for this lecture:

Lecture – 8:30 – 9:30
PDF Analysis - Katharine Page
https://forms.office.com/g/B72AQcXhGv