Atomic Pair Distribution Function (PDF) Analysis
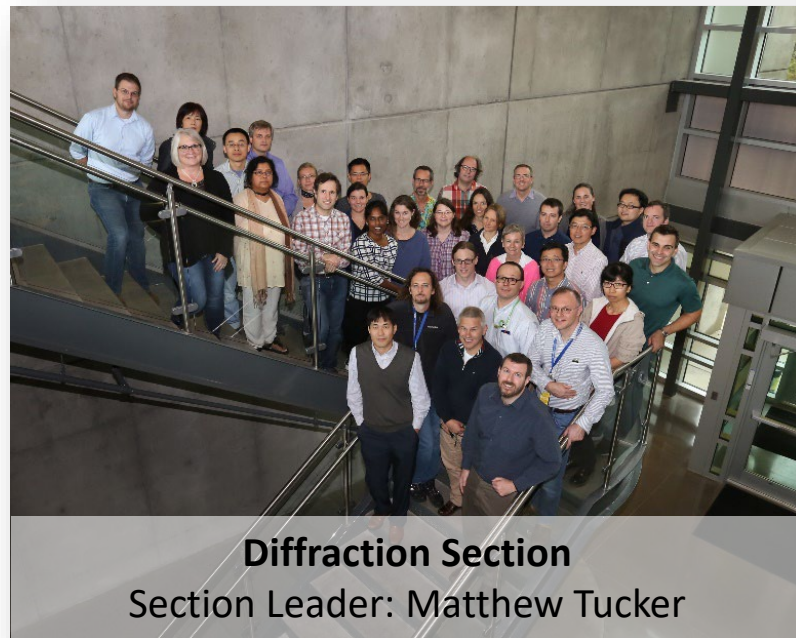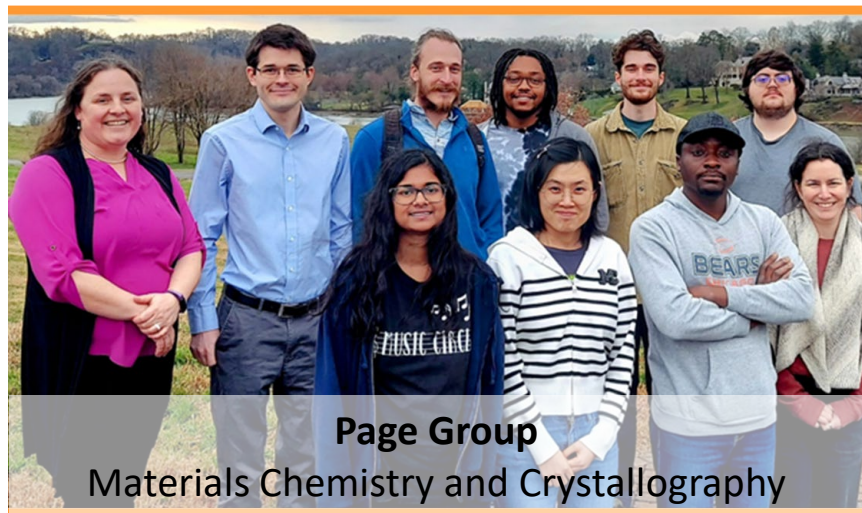
Katharine Page

Materials Science and Engineering Department
& Oak Ridge National Laboratory

THE UNIVERSITY OF TENNESSEE KNOXVILLE

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Page Group
Materials Chemistry and Crystallography

Diffraction Section
Section Leader: Matthew Tucker

ScatteringPage.utk.edu

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
- Extension 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)
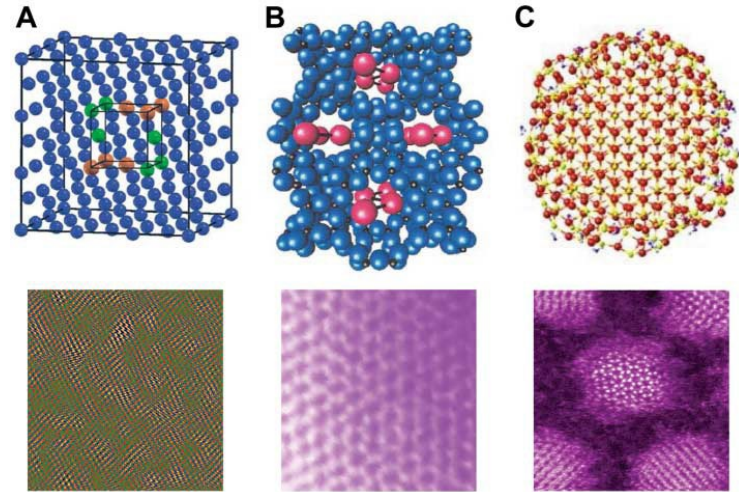
S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).
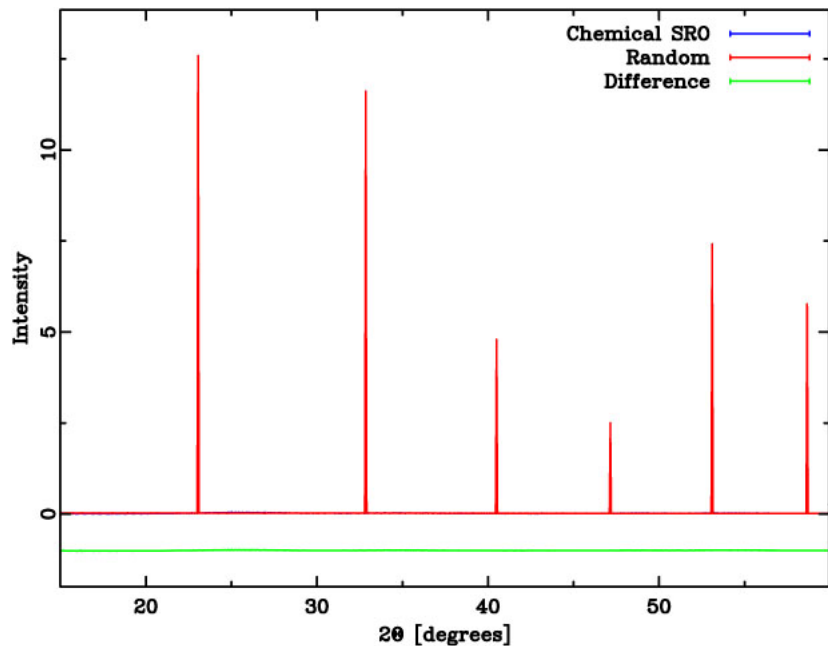
D. A. Keen and A. L. Goodwin, **The crystallography of correlated disorder**, *Nature* 521, 303–309 (2015).
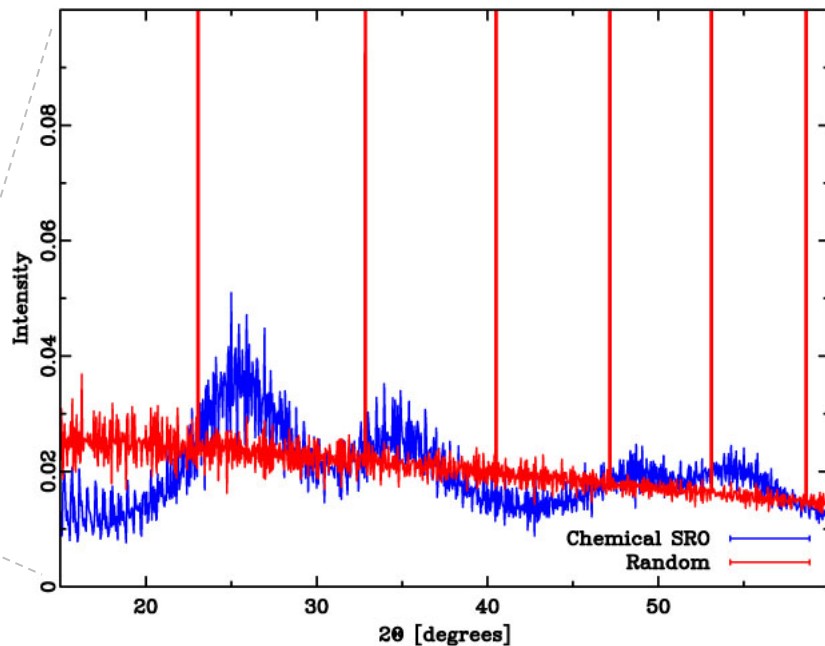
What is *total* scattering?
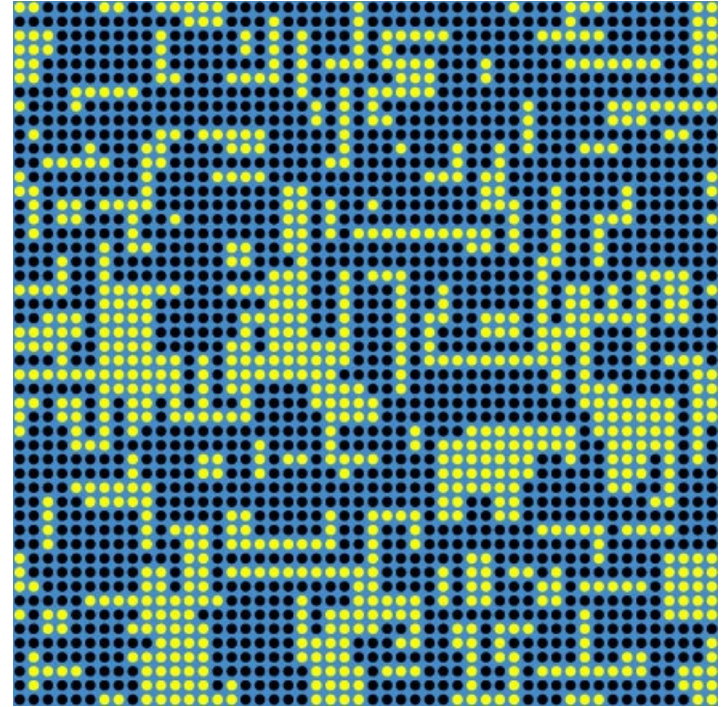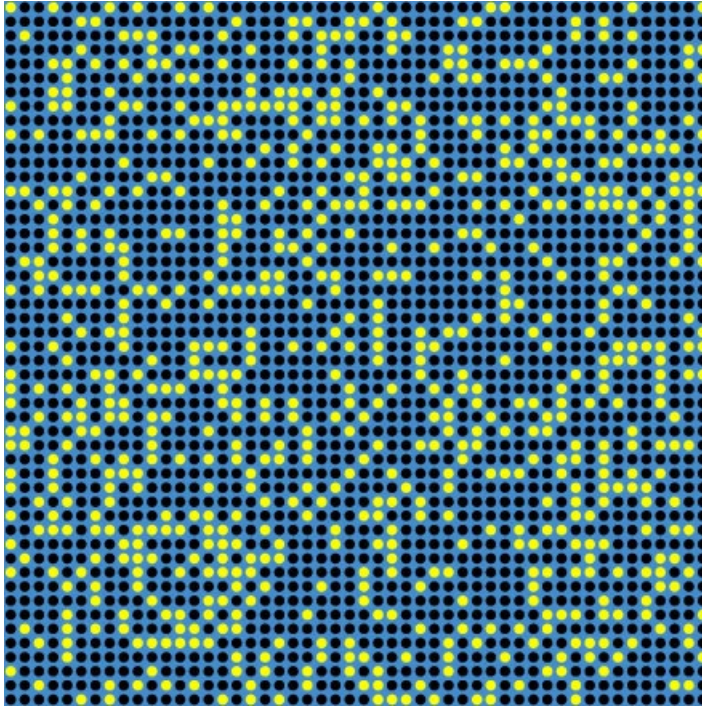
Cross section of 50x50x50 unit cell model crystal consisting of 70% blue atoms and 30% *vacancies*.
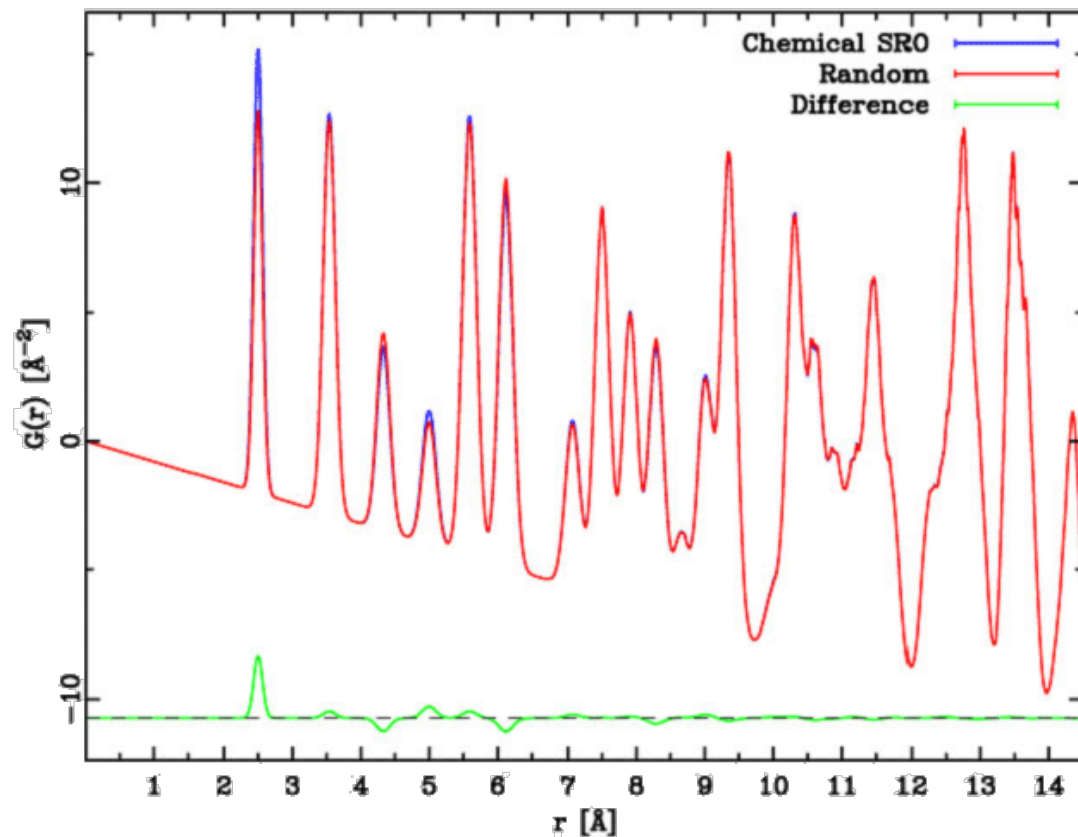
Bragg Scattering and CSRO

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
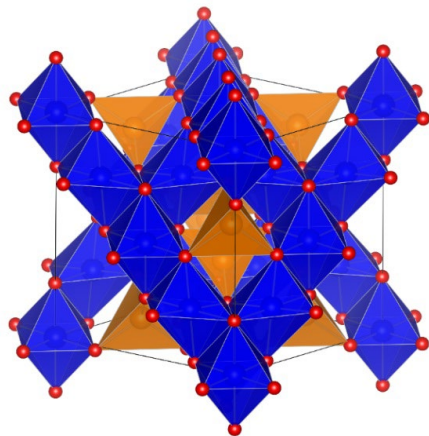
Interested in learning more?

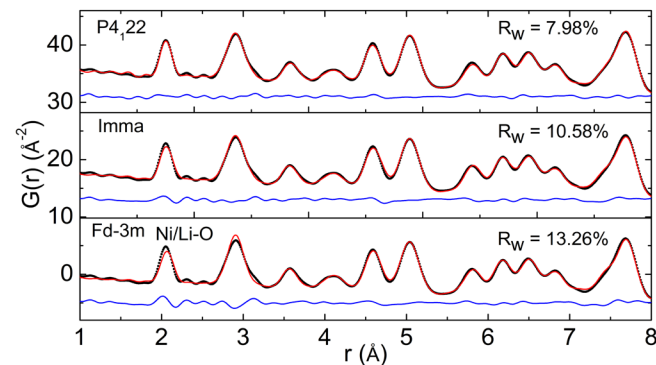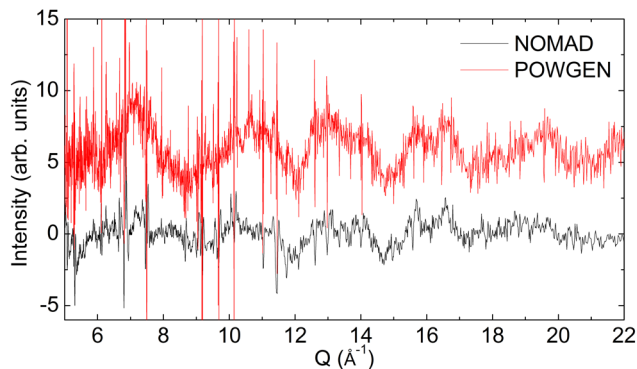Apply to attend the 5th Annual School on US Total Scattering Analysis
http://conference.sns.gov/e/VirtualTS-School/

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.
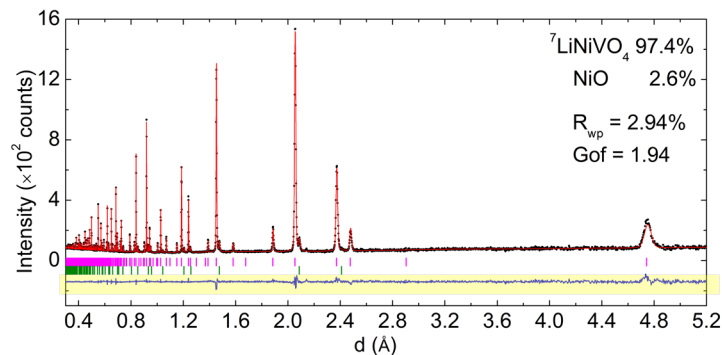
B-site cation ordering in inverse spinel oxides: LiNiVO$_4$

(V)[LiNi]O$_4$
S.G. Fd-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.
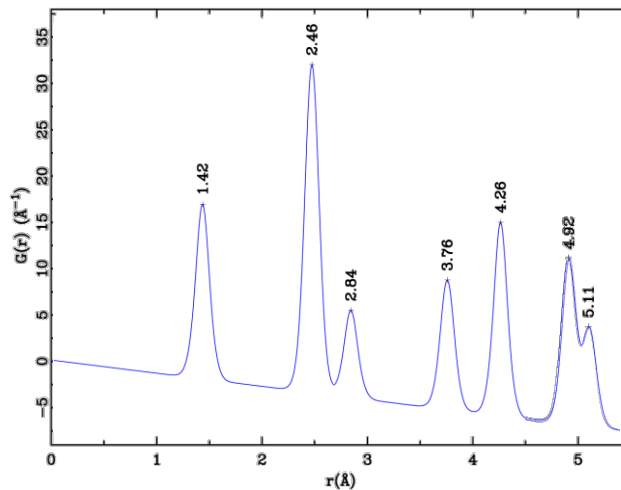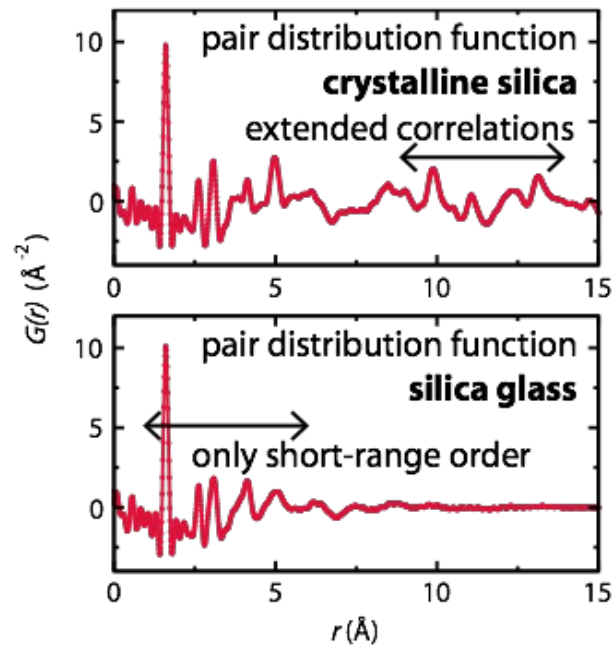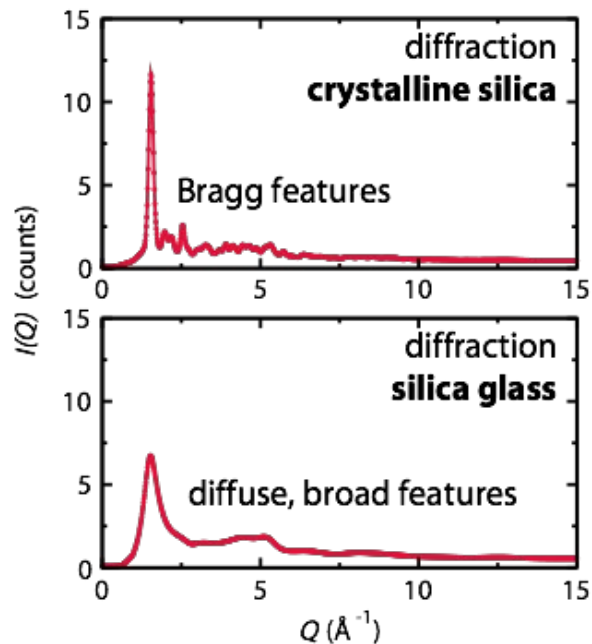
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What is a PDF?
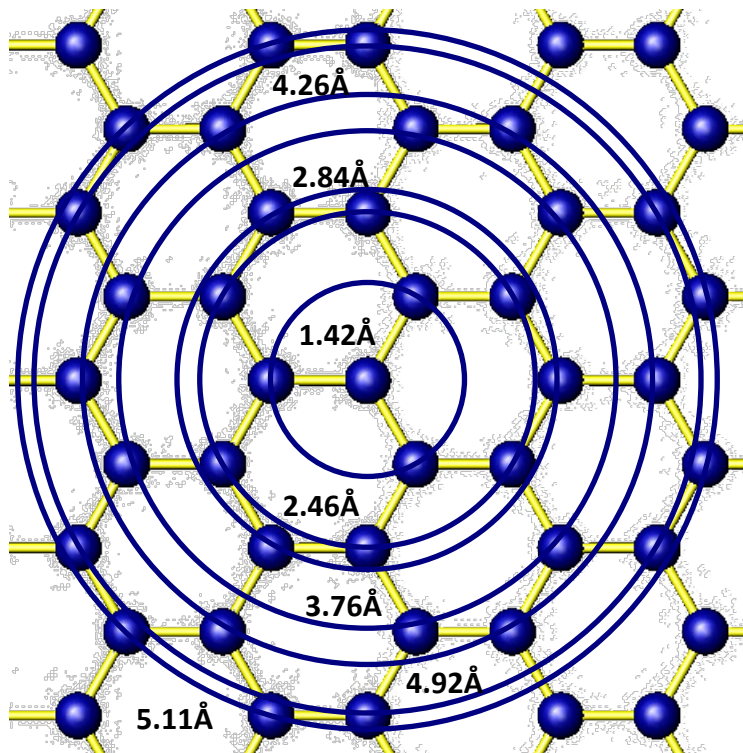
The **Pair Distribution Function (PDF)** gives the probability of finding an atom at a distance "r" from a given atom.
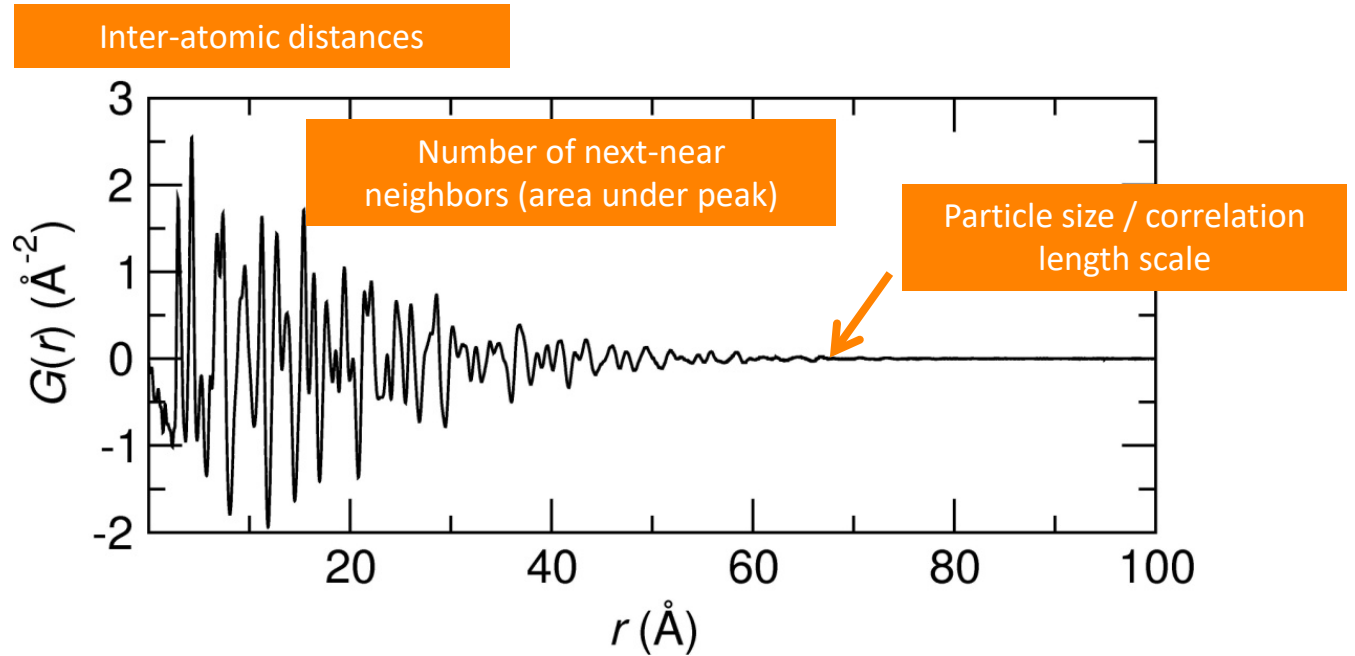
Pair Distribution Function

Sine-Fourier transform of **all** scattered neutron/X-ray intensity (crystalline and amorphous)
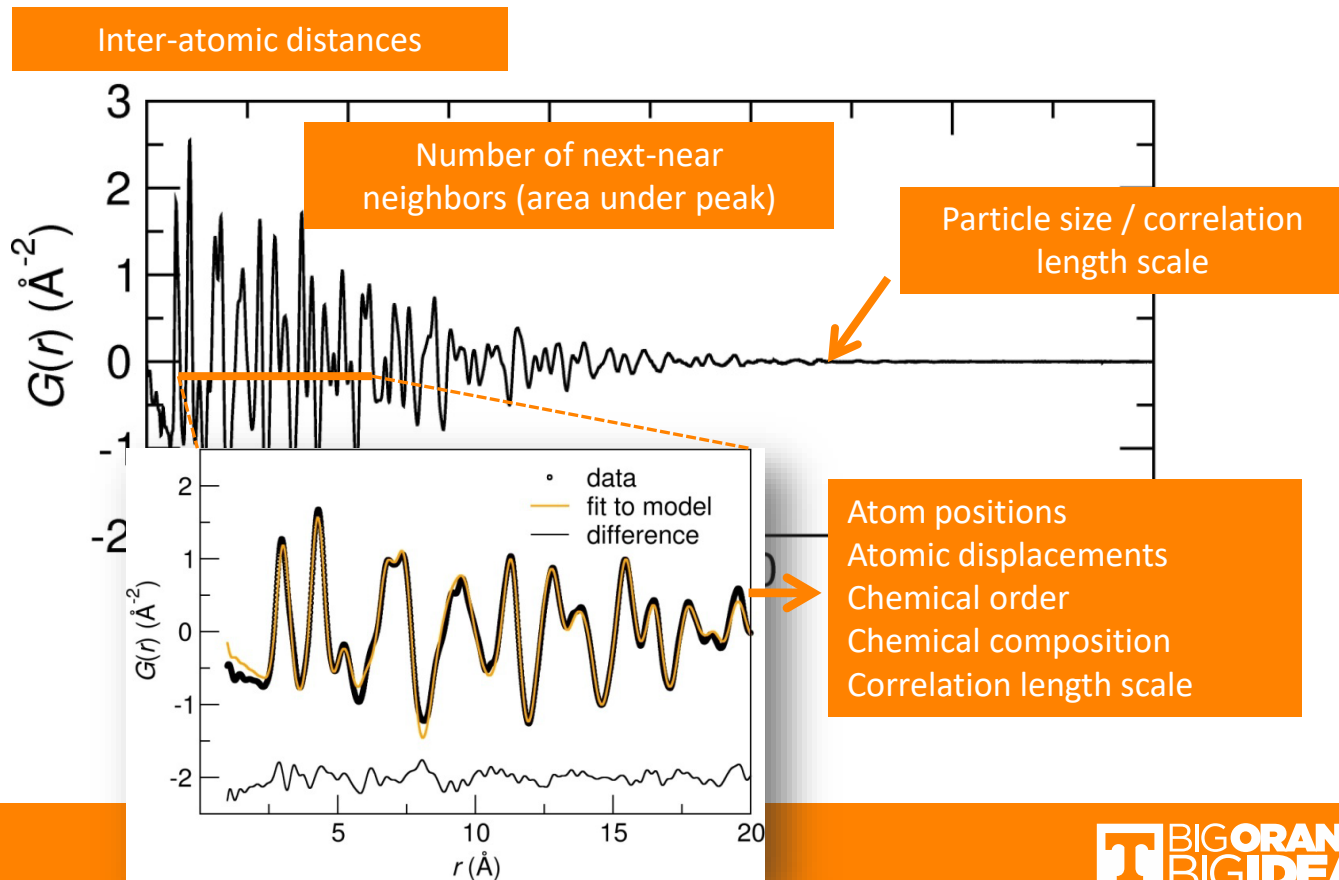
→*Experimental, ensemble, real-space, atom-atom histogram*

Pair Distribution Function

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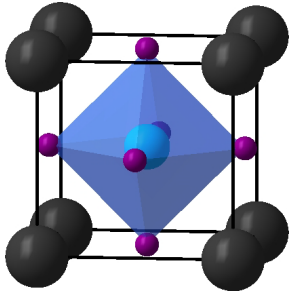
Inter-atomic distances

Number of next-near neighbors (area under peak)

Particle size / correlation length scale

Pair Distribution Function

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

Inter-atomic distances

Number of next-near neighbors (area under peak)

Particle size / correlation length scale

Atom positions
Atomic displacements
Chemical order
Chemical composition
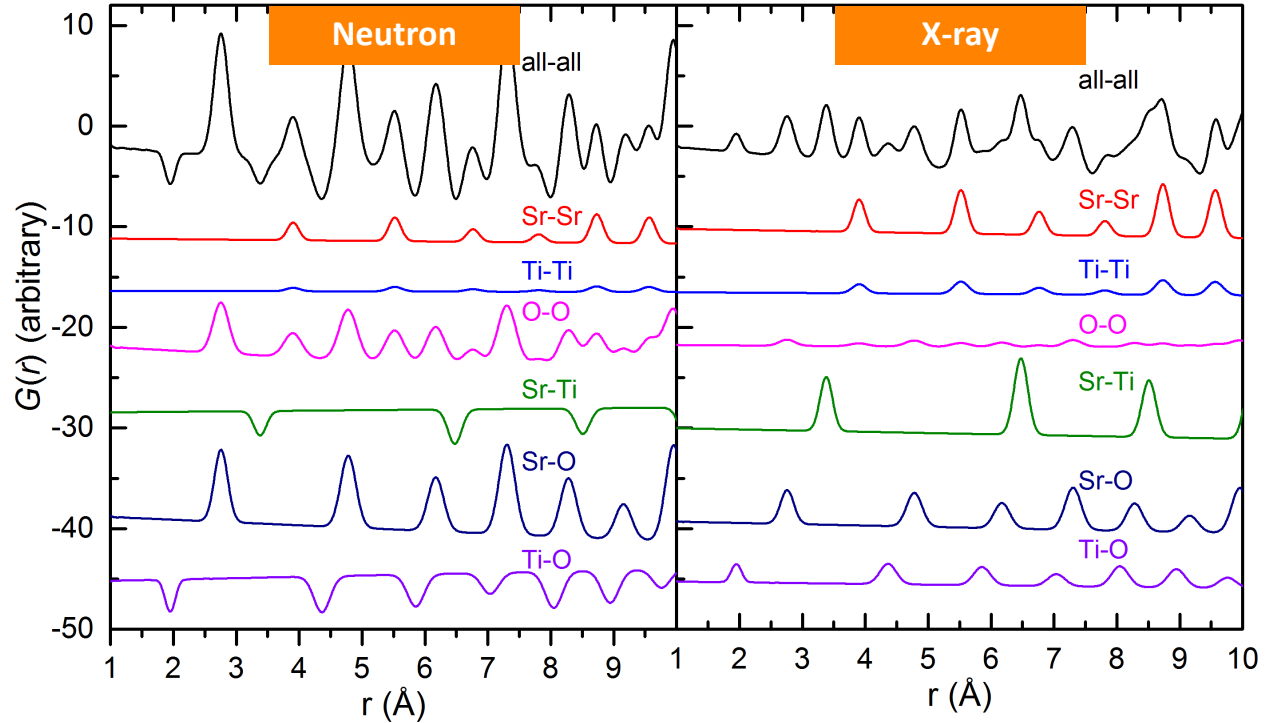Correlation length scale

Partial PDFs

SrTiO$_3$

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

Neutron and X-ray PDFs are often highly complementary

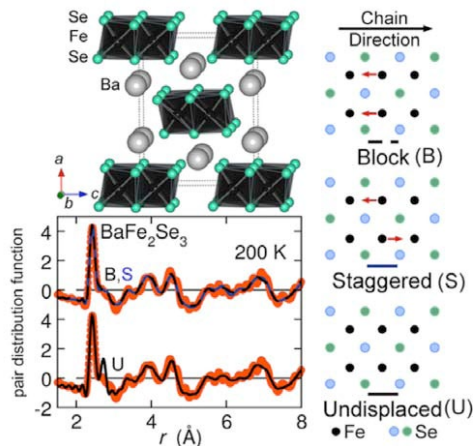# WHAT TYPES OF STUDIES CAN BE DONE WITH THE PDF TECHNIQUE?

Local Distortions
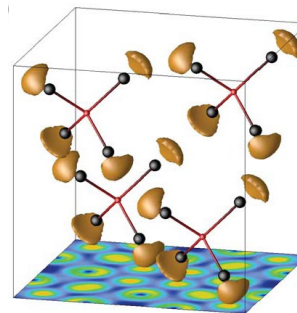Chemical Short-Range Ordering
Nanostructures
Amorphous Structures

Local distortions *via* PDF

- Local dipoles

- Local Jahn-Teller distortions

- Frustrated lattices

- Orbital ordering

- *etc.*

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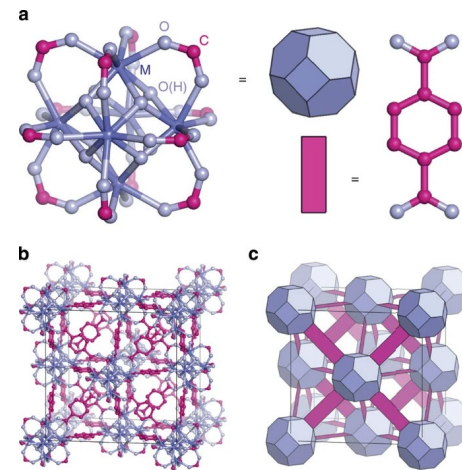

D. Louca, e*t al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).
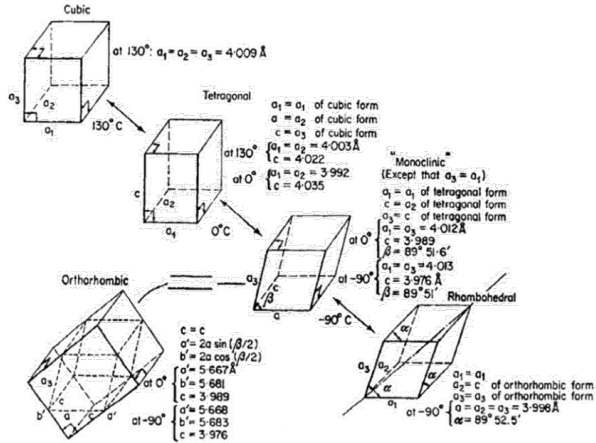

M. J. Cliffe, *et al.*, Correlated defect nanoregions in a metal–organic framework, *Nature Communications* **5**, (2014).
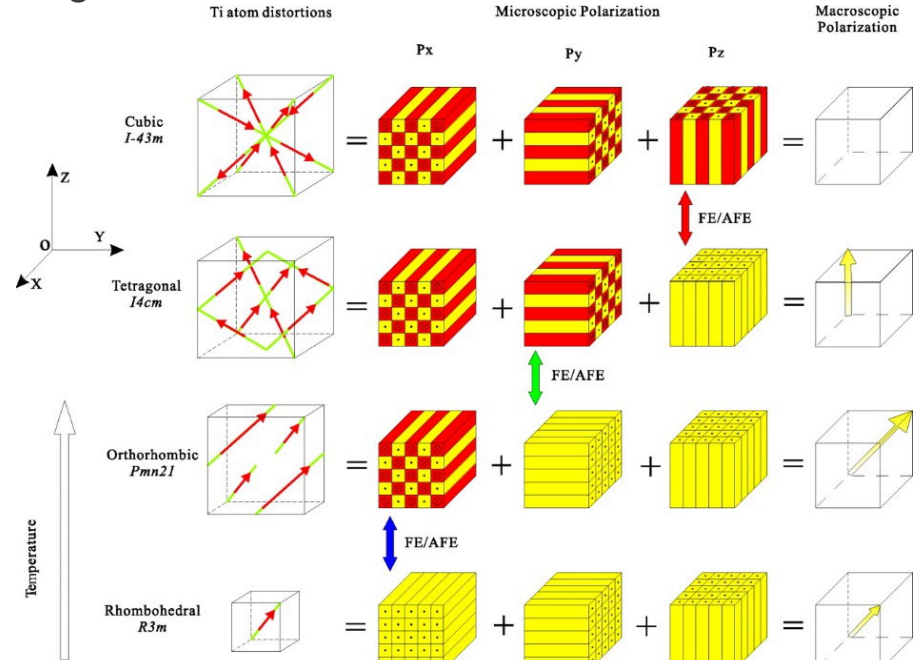
Example: Local structure in BaTiO$_3$

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).
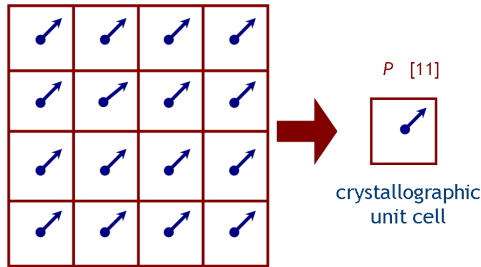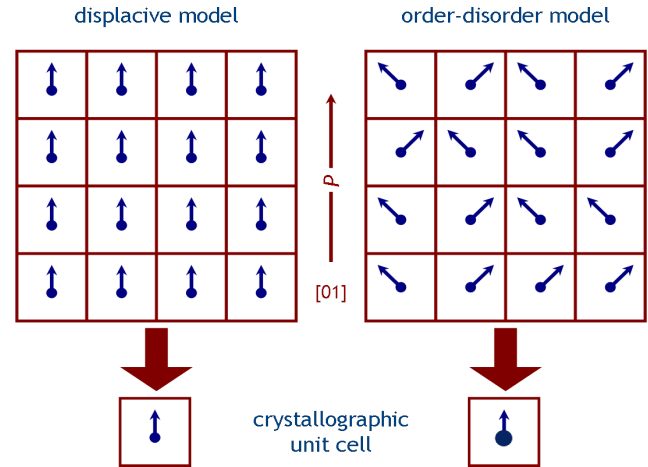
Example: Local structure in BaTiO$_3$

BaTiO$_3$: Ferroelectric oxide, a rhombohedral (*R3m*) ground state and a room temperature tetragonal (*P4mm*) structure
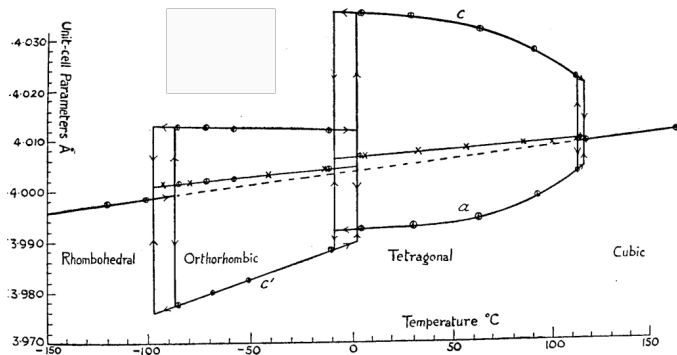
A 2D model where local and average motifs are the same

crystallographic unit cell

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

displacive model

order-disorder model

crystallographic unit cell

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).
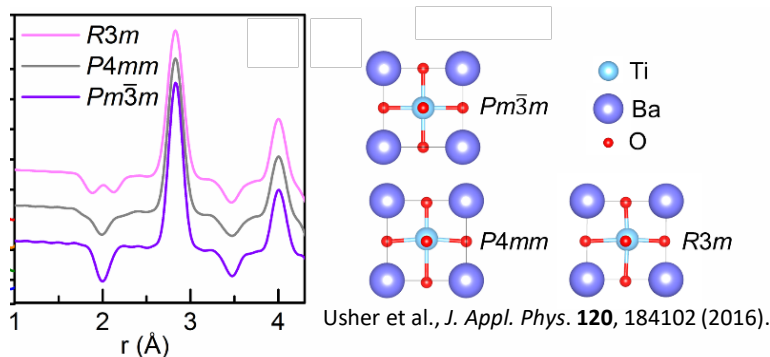
Experimental BaTiO$_3$ PDFs

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
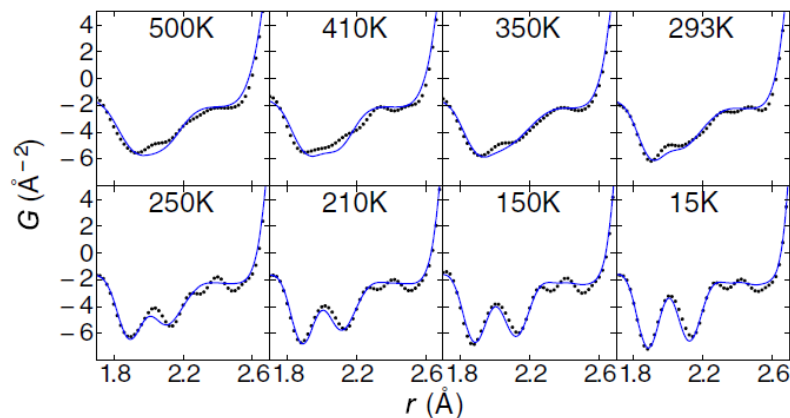
Chemical Short-Range order *via* PDF

- 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**, (200   2) 47–50.
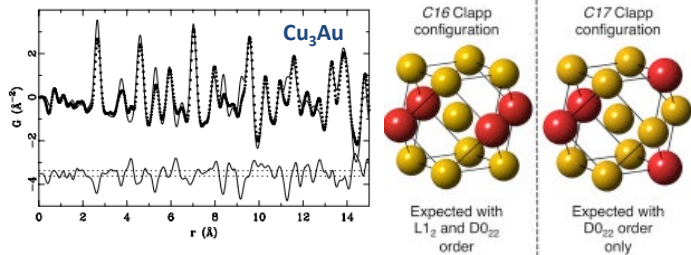
Cu₃Au

L.R. Owen, H.Y. Playford, H.J. Stone and M.G. Tucker, Analysis of short-range order in Cu₃Au using X-ray pair distribution functions. *Acta Materialia* (2017) 125, 15-26.
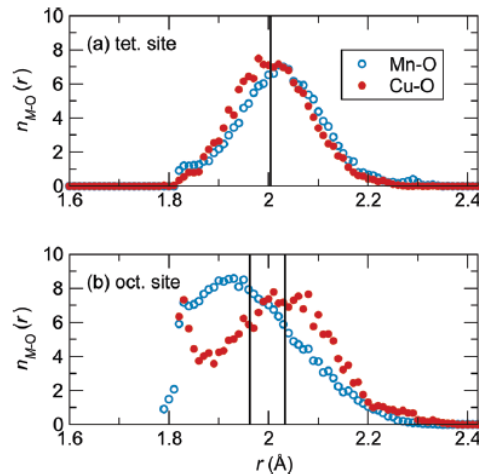
D. P. Shoemaker, J. Li, and R. Seshadri, Unraveling Atomic Positions in an Oxide Spinel with Two Jahn-Teller Ions: Local Structure Investigation of $CuMn_2O_4$, *J. Am. Chem. Soc.* **131,** 11450 (2009).

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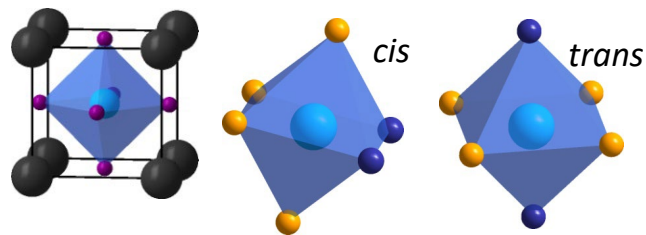
K. Page, *et al*., Local atomic ordering in $BaTaO_2N$ studied by neutron pair distribution function analysis and density functional theory, *Chem. Mater.* **19** (2007) 4037-4042.

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

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$_3$32* or *P4$_1$32*) via extended post-annealing at 700 °C to 600 °C

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

We studied the nature and length-scale of local cation ordering in this system and related it to electrochemical performance
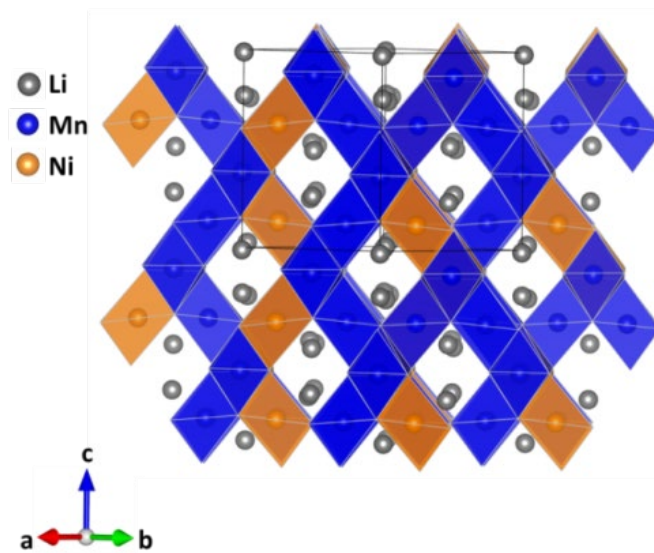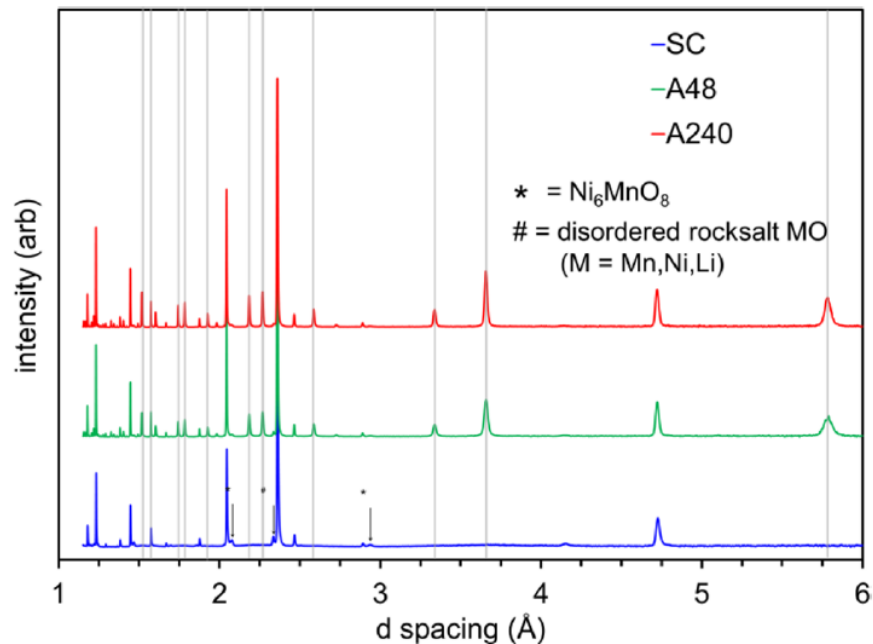
Example: High Voltage Spinel Cathode $^7LiNi_{0.5}Mn_{1.5}O_4$

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

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

Annealed (A48): 48 hours at 700°C

**Annealed (A240):** 240 hours at 700°C

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

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

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

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. $P4_332$)

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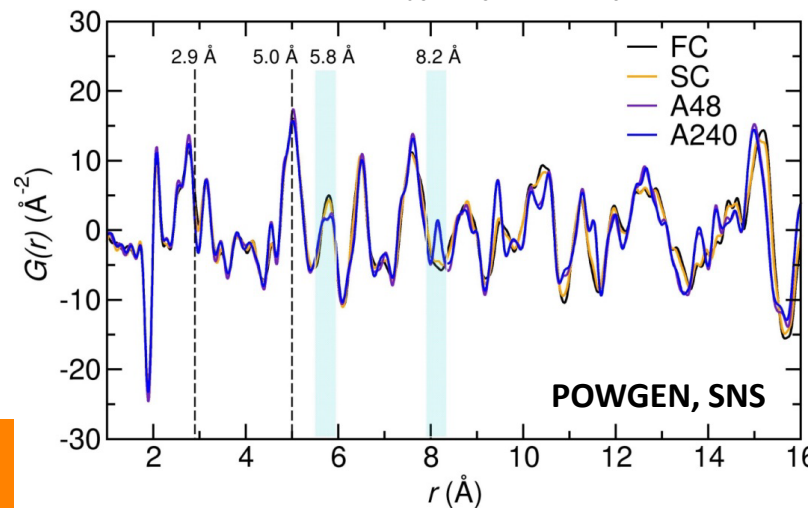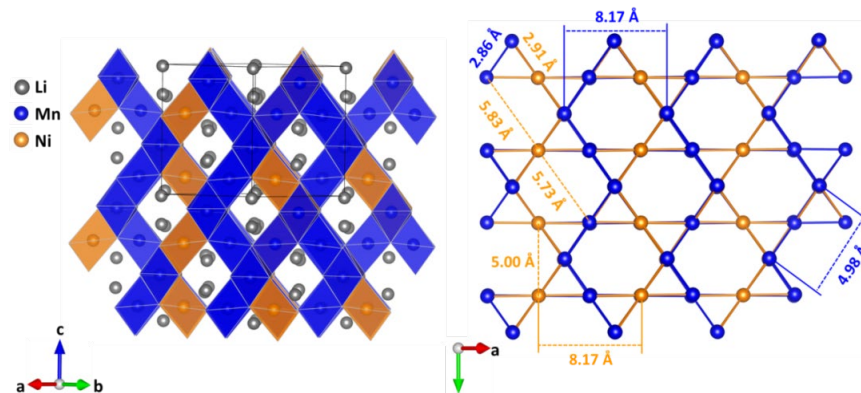
Liu J., Huq A., Moorhead-Rosenberg Z., Manthiram A., Page K., **Nanoscale Ni/Mn Ordering in the High Voltage Spinel Cathode $LiNi_{0.5}Mn_{1.5}O_4$**, *Chemistry of Materials,* 28**,** (2016) 6817–6821.

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

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?**
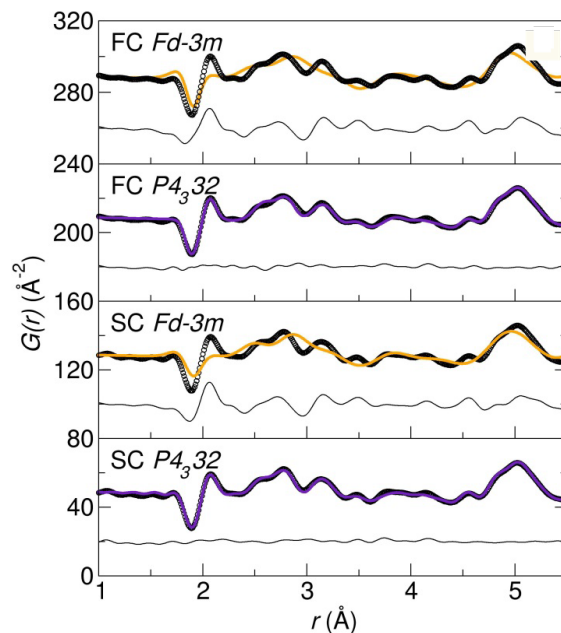
J. Liu, A. Huq, Z. Moorhead-Rosenberg, A. Manthiram, and K. Page, **Nanoscale Ni/Mn ordering in the high voltage spinel cathode LiNi$_{0.5}$Mn$_{1.5}$O$_4$**, *Chemistry of Materials*, 28, 19, 6817–6821, 2016.

Example: High Voltage Spinel Cathode $^7LiNi_{0.5}Mn_{1.5}O_4$
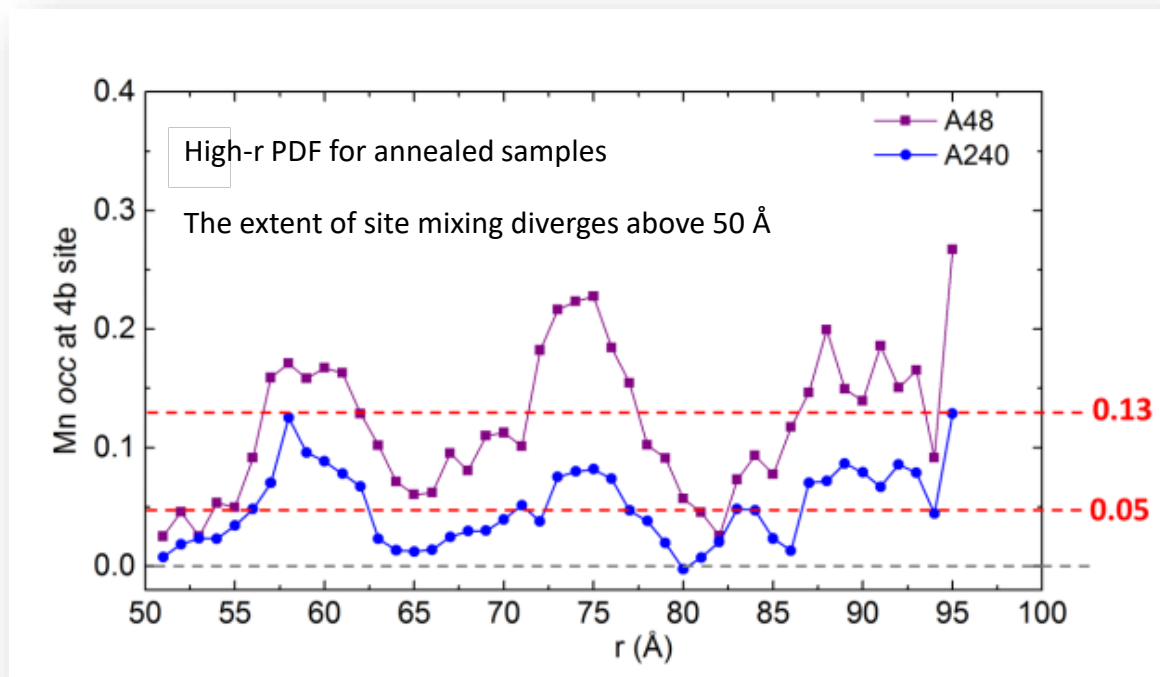
15 Å correlation length scale for SRO
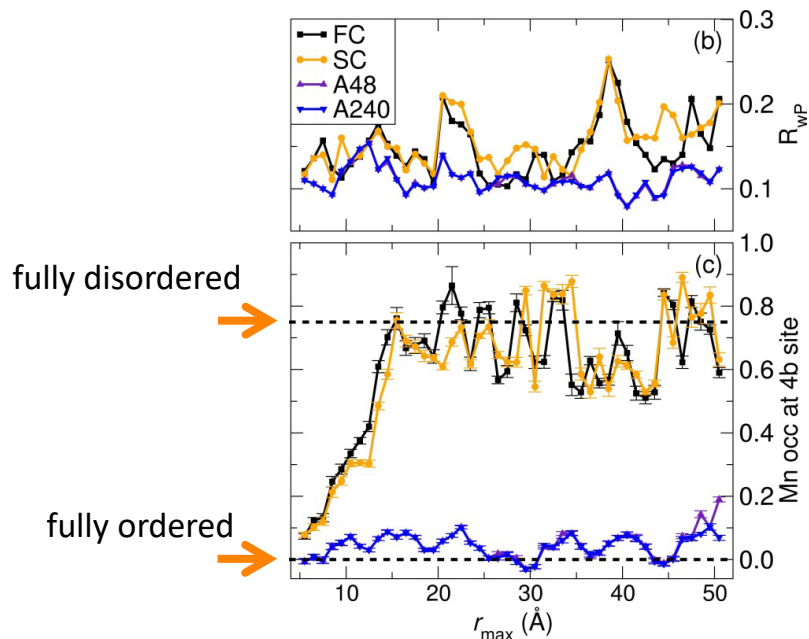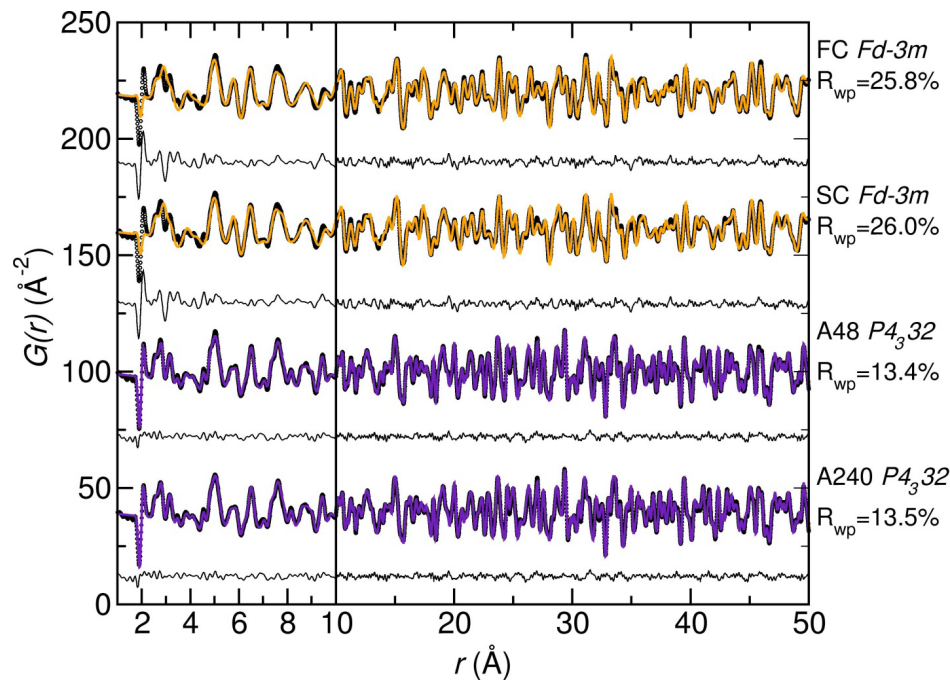
- 5% site mixing in the A48 and A240 patterns throughout the entire range
- FC and SC samples are nearly fully disordered at pair distances beyond 15.5 Å

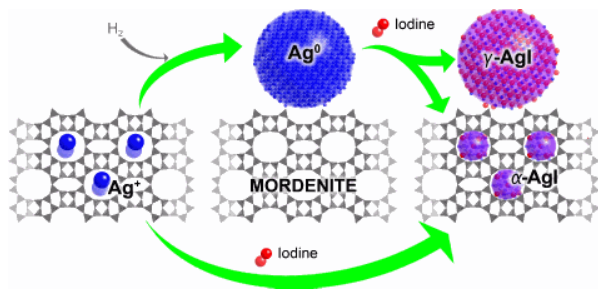# Example: High Voltage Spinel Cathode $^7LiNi_{0.5}Mn_{1.5}O_4$

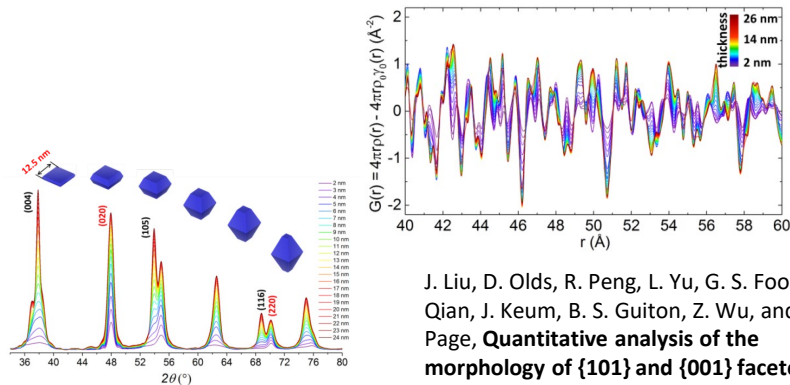Fit the PDFs within a 4.5 Å "box" in 1 Å steps (a "box-car" refinement)

High-r PDF for annealed samples

The extent of site mixing diverges above 50 Å

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

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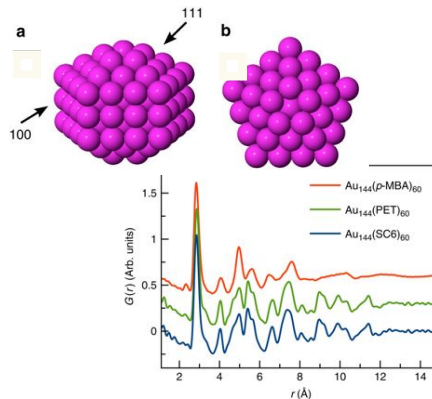
K. M. O. Jensen, P. Juhas, M. A. Tofanelli, C. L Heinecke, G. Vaughan, and C. J. Ackerson, **Polymorphism in magic-sized Au$_{144}$(SR)$_{60}$ clusters,** *Nature Communications* 7, 11859 (2016).

Example: SnO₂ Nanocrystals

~2 nm SnO₂ (cassiterite) nanocrystals capped with H₂O/OH or D₂O/OD groups
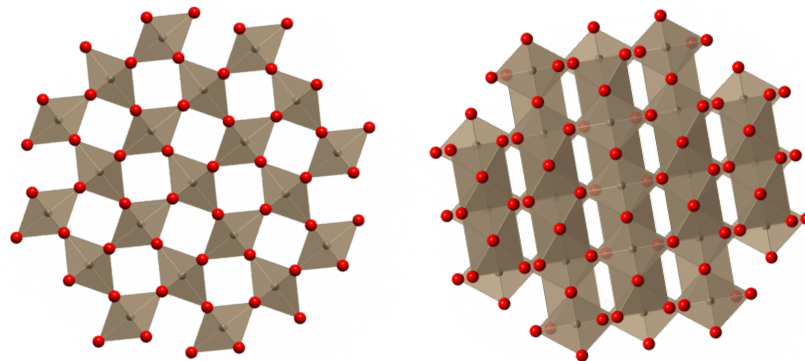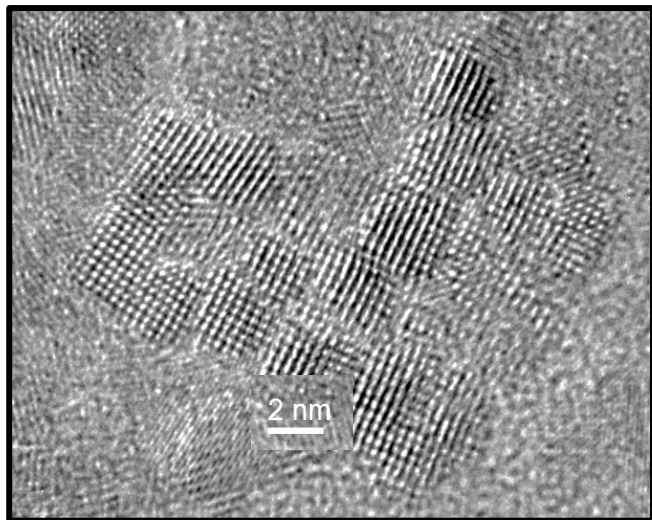
H.-W. Wang, D. J. Wesolowski, T. Proffen, L. Vlcek, W. Wang, L. F. Allard, A. I. Kolesnikov, M. Feygenson, L. M. Anovitz, and R. L. Paul, **Structure and stability of SnO₂ nanocrystals and surface-bound water species**, *J. Am. Chem. Soc.*, 135, 6885-6895, 2013.
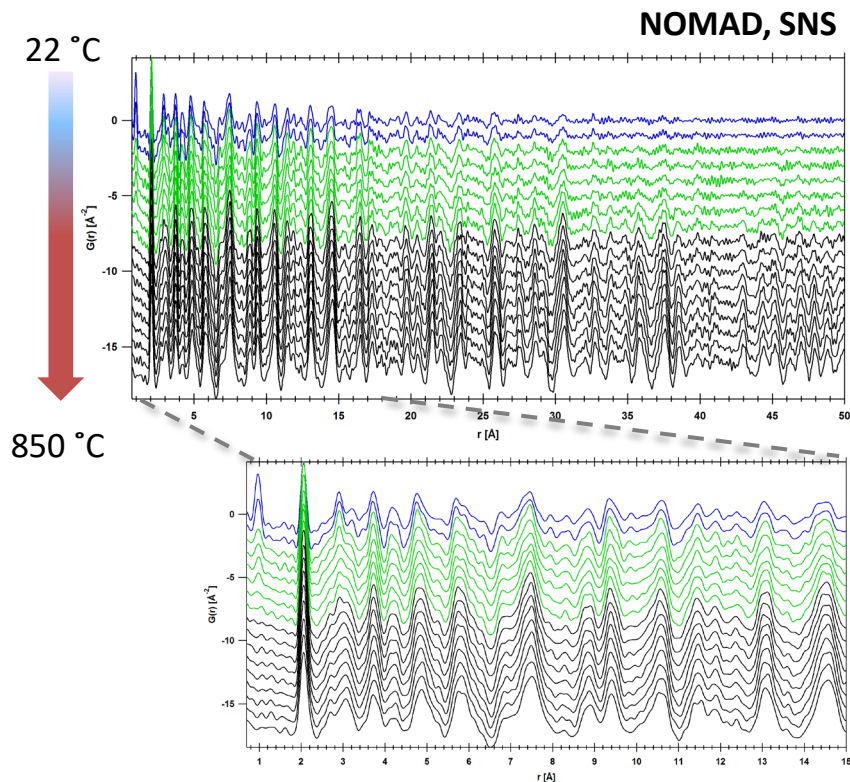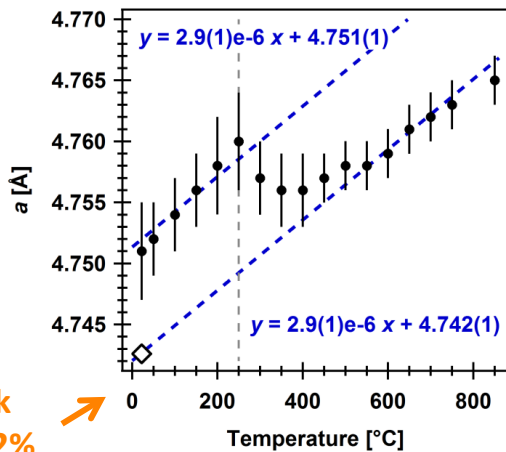
TGA suggests 2 steps dehydration.

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$_2$**
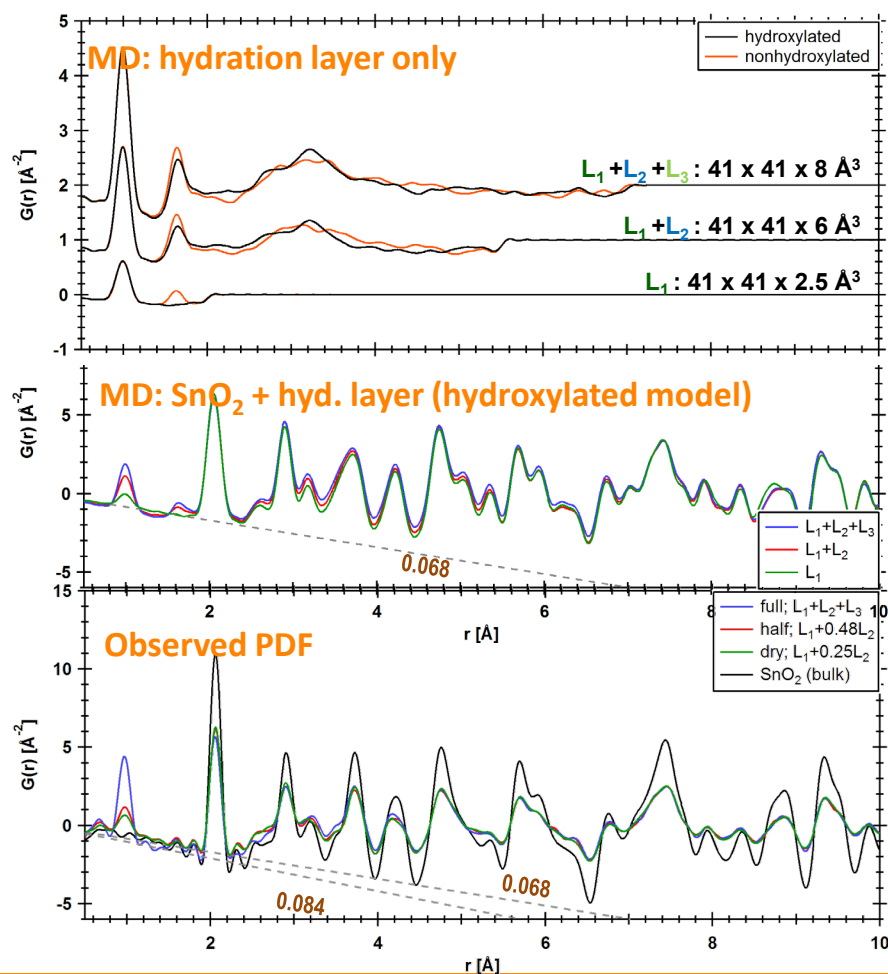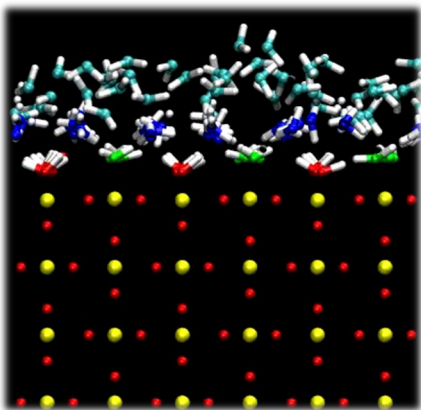
- **400 to 850 ˚C: SnO$_2$ grain growth**

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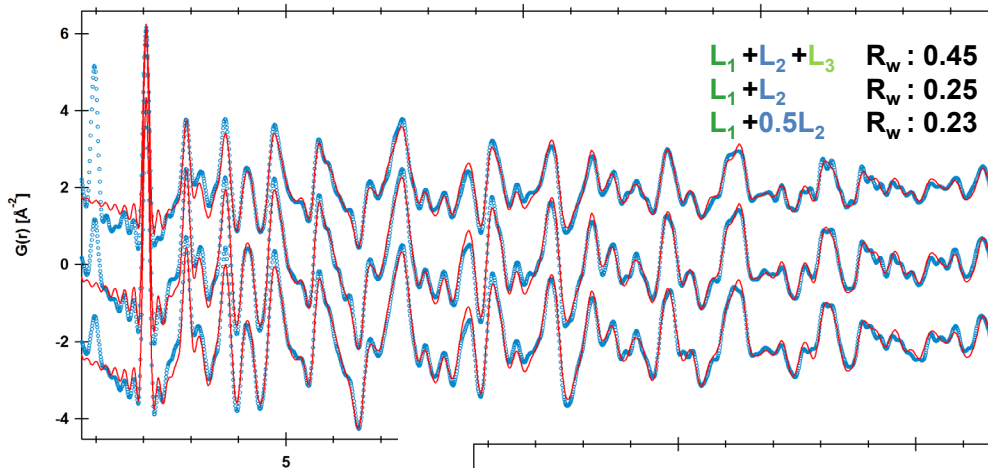
Box size: 41 x 41 x 23 Å^3 ; 2592 atoms; # density = 0.068 Å^{-3};
U_{iso} = 0.003 Å^2

MD: hydration layer only

L$_1$+L$_2$+L$_3$: 41 x 41 x 8 Å^3
L$_1$+L$_2$: 41 x 41 x 6 Å^3
L$_1$: 41 x 41 x 2.5 Å^3

MD: SnO$_2$ + hyd. layer (hydroxylated model)

Observed PDF

Example: SnO₂ Nanocrystals

Single phase model:
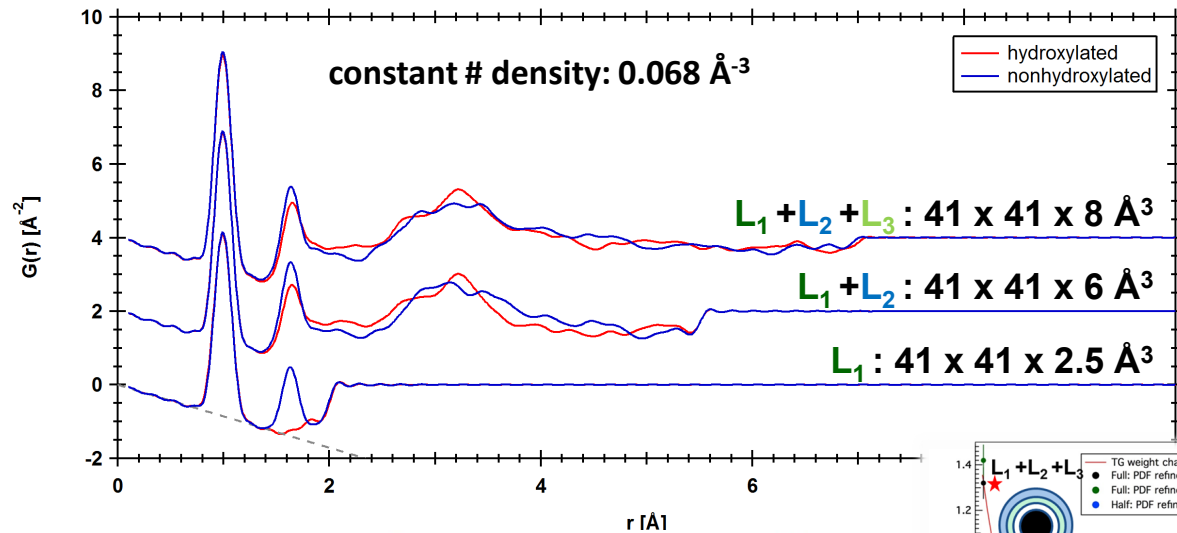
SnO₂ bulk structure,

refined particle

size = ~47 Å

Two phase model:

SnO₂ bulk + layered

MD water structure
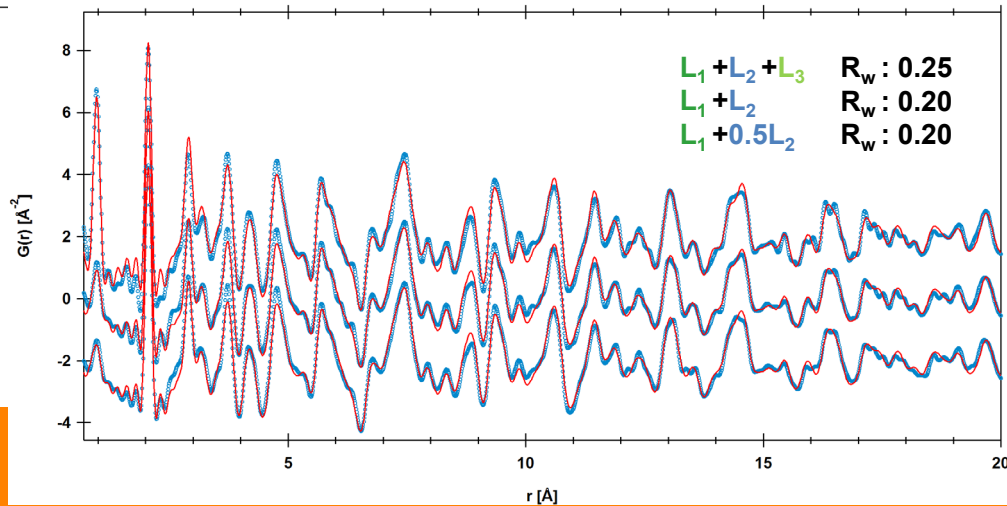
Example: SnO₂ Nanocrystals

constant # density: 0.068 Å⁻³

hydroxylated
nonhydroxylated

$L_1 + L_2 + L_3$: 41 x 41 x 8 Å³

$L_1 + L_2$: 41 x 41 x 6 Å³
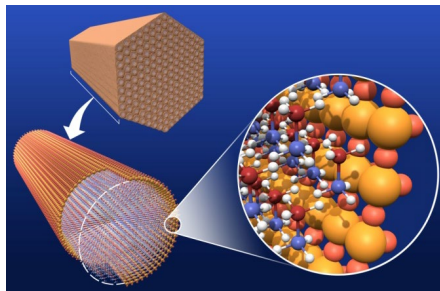
L_1 : 41 x 41 x 2.5 Å³

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 SnO₂ nanocrystals and surface-bound water species**, *J. Am. Chem. Soc.*, 135, 6885-6895, 2013.
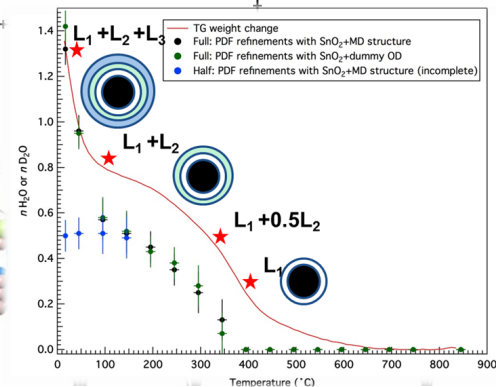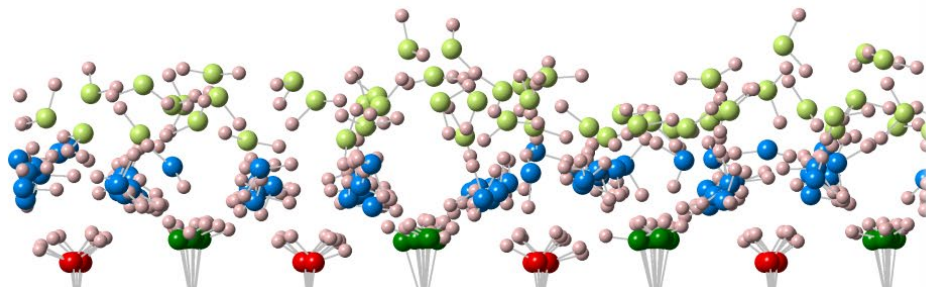
Amorphous structures *via* PDF

- Glasses

- Liquids

- Concretes

- Adsorbed/absorbed gasses

- *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 NH₃BH₃ 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).
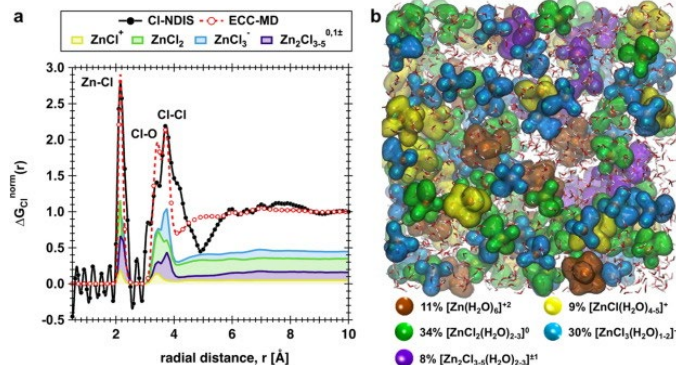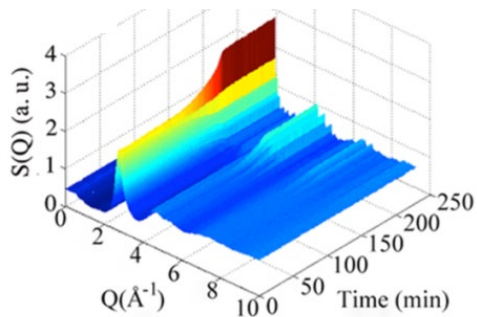
N. Rampal, H.-W. Wang; D. Biriukov, A. B. Brady, J. C Neuefeind, M. Predota, A. J. Stack, **Local molecular environment drives speciation and reactivity of ion complexes in concentrated salt solution**, *J. Molec. Liq.*, 340, 116898 (2021).

# Example: solvation structure of 18 m NaOD/H aqueous solution

Measured X-ray and neutron RDF patterns compared to RDFs predicted by MD simulation of high-dimensional neural network potentials accentuate complementary features:

Contributions of ion-ion (red lines), ion-water (black and green lines), and water-water (blue lines) interactions can be deconvoluted

M. Hellströma and J. Behler, **Structure of aqueous NaOH solutions: insights from neural-network-based molecular dynamics simulations**, *Phys. Chem. Chem Phys.* 17 (2017) 82-96.

D. Semrouni, H.-W. Wang, S. B. Clark, C. I. Pearce, K. Page, G. Schenter, D. J. Wesolowski, A. G. Stack, and A. E. Clark, **Resolving local configurational contributions to X-ray and neutron radial distribution functions within solutions of concentrated electrolytes – a case study of concentrated NaOH,** *Phys. Chem. Chem. C* 13 (2019) 6828-6838.
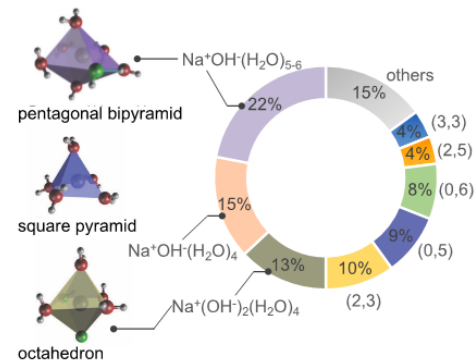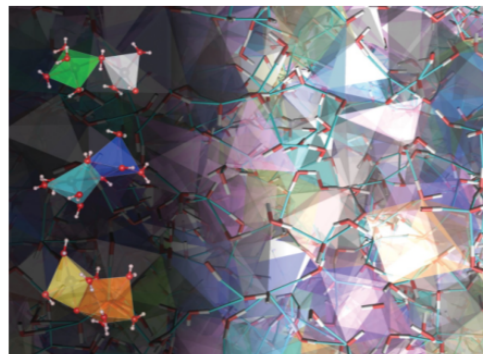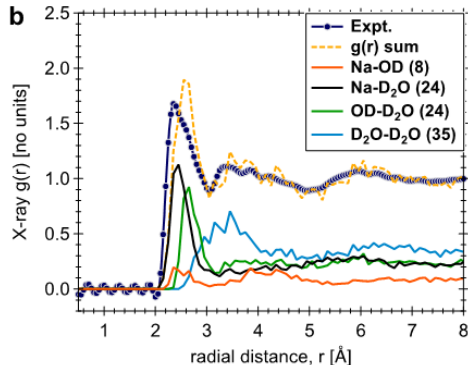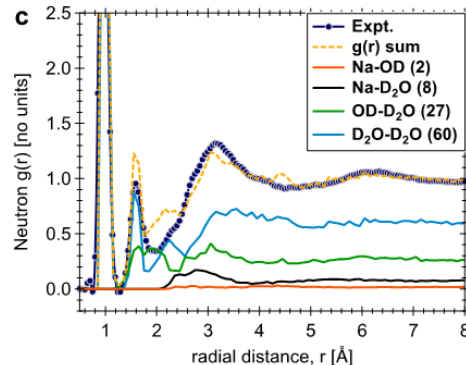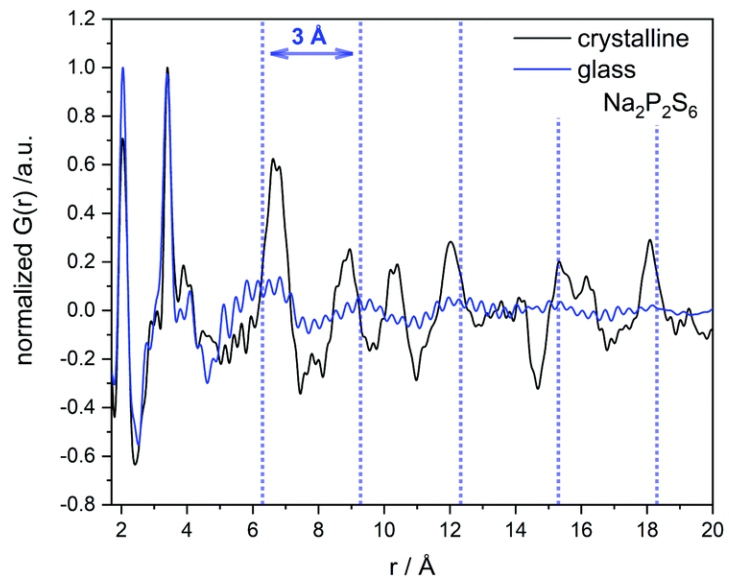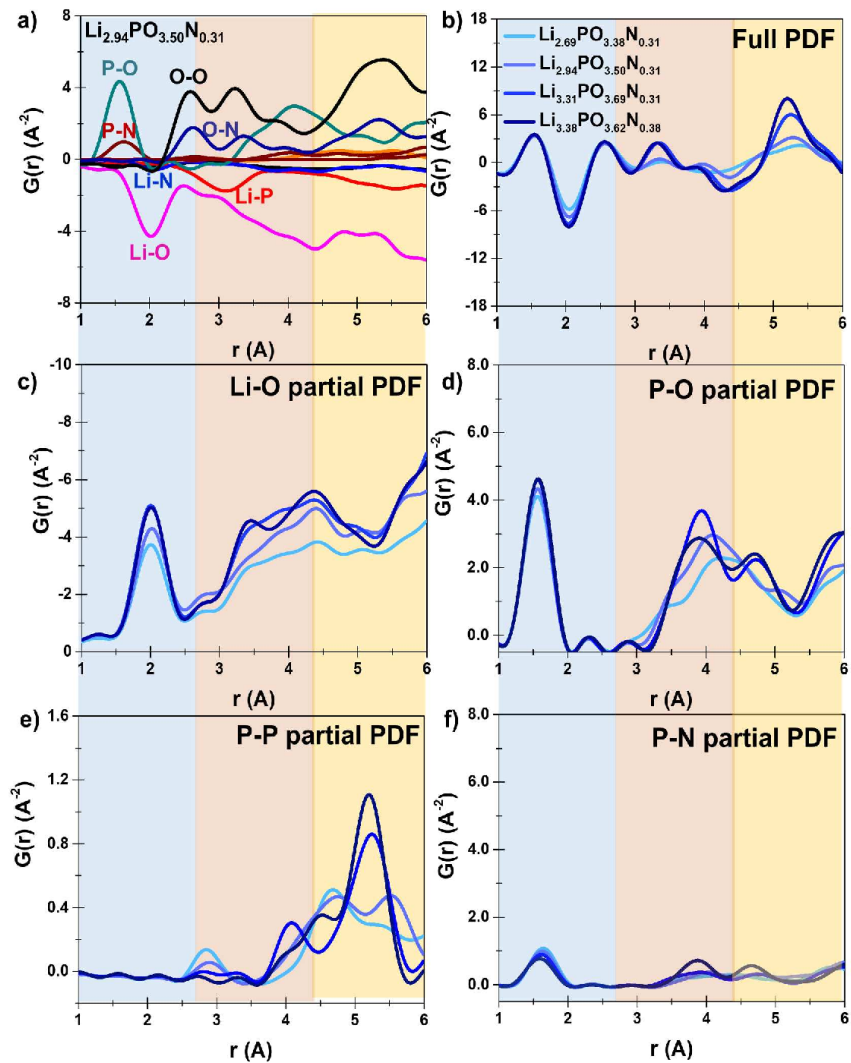
Example: amorphous ionic conductors

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$_2$P$_2$S$_6$ – elucidation of local structural changes by X-ray total scattering and NMR**, *Dalton Trans.*, 49 (2020) 1668-1673.

Questions?

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
- Extension 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)

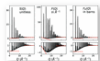$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{|\sum c_i b_i|^2} + 1 \qquad Q = \frac{4\pi \sin\theta}{\lambda}$$

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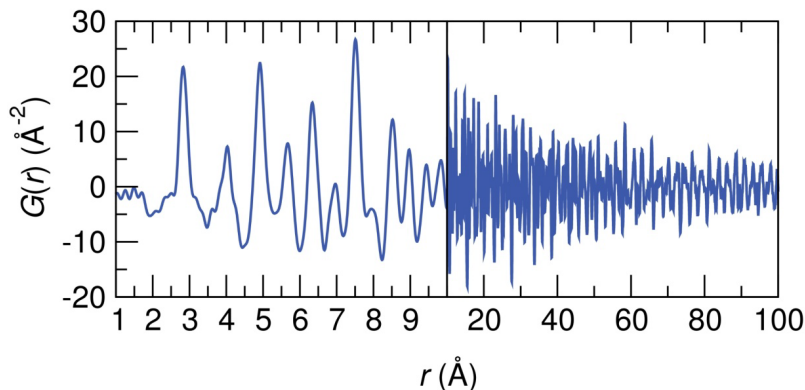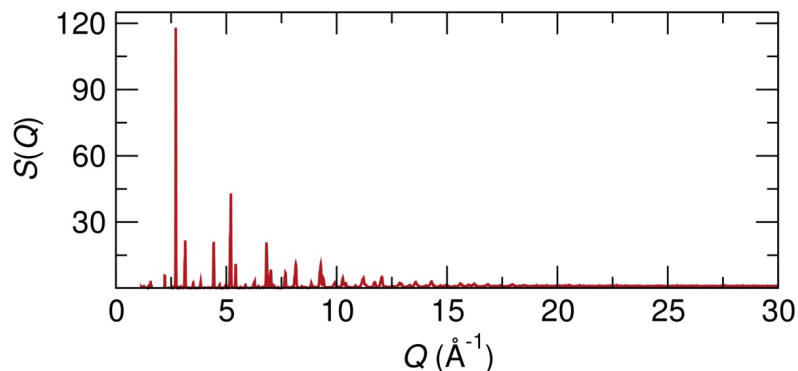
The total scattering structure factor: $S(Q)$

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

Sine Fourier transform

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

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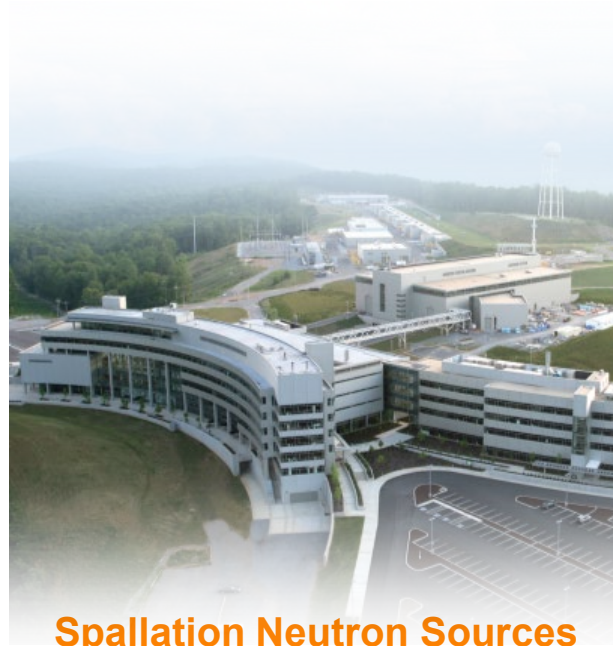
Obtaining High Quality PDFs

(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   **or**
(high energy X-rays)

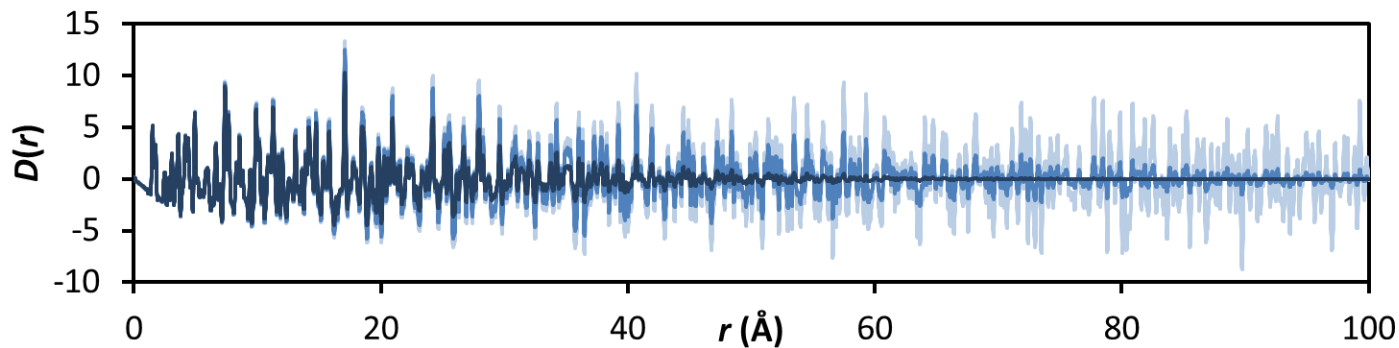**Spallation Neutron Sources**
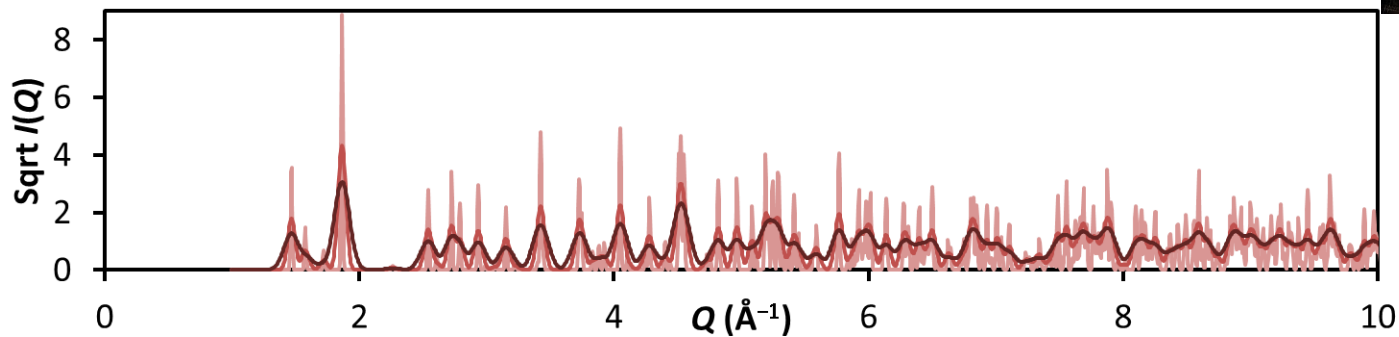**(reactor neutron energies are too low)**

Resolution Effect

Reciprocal space: Peak width, *dQ*

Real space: D
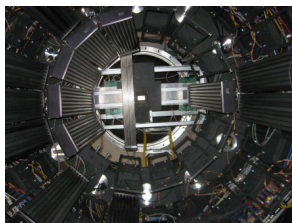
Q_{max} Effect
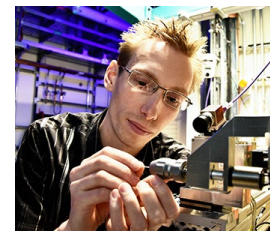
Δr resolution of a PDF is dominated by Q_{max}

- $Q = 2\pi/d = 4\pi\sin\theta/\lambda$

- $\Delta r \approx 2\pi/Q_{max}$
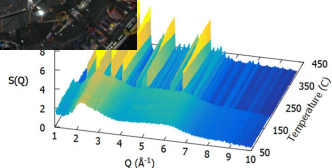
$AlPO_4$

Q_{max} 35 Å^{-1}
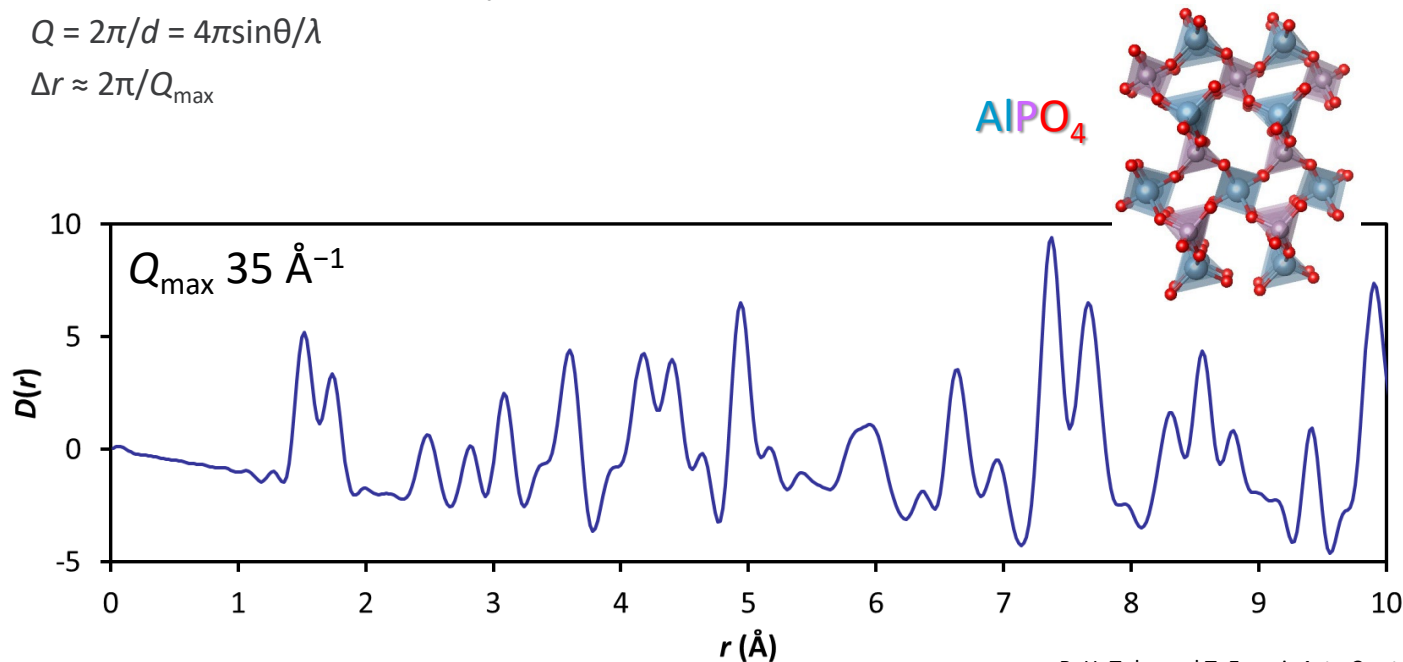
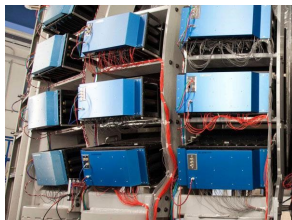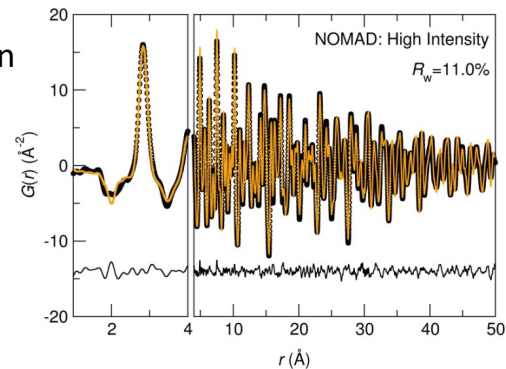B. H. Toby and T. Egami, *Acta Cryst. A*, **48** 336 (1992).

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 **~15 minutes to 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**
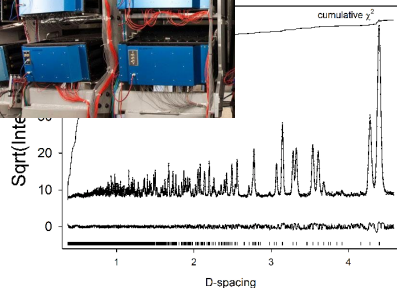
high resolution diffraction and PDF of crystalline materials
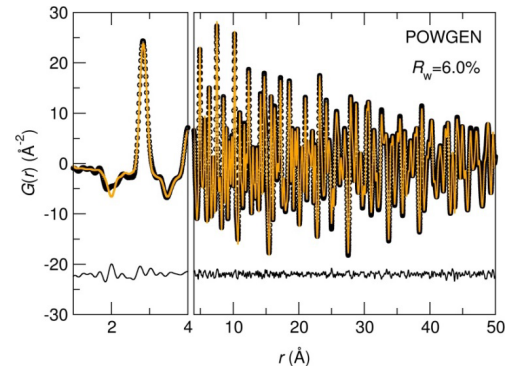
Mail-in programs available on both instruments

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).

Synchrotron Total Scattering: 2D Amorphous Si Detector
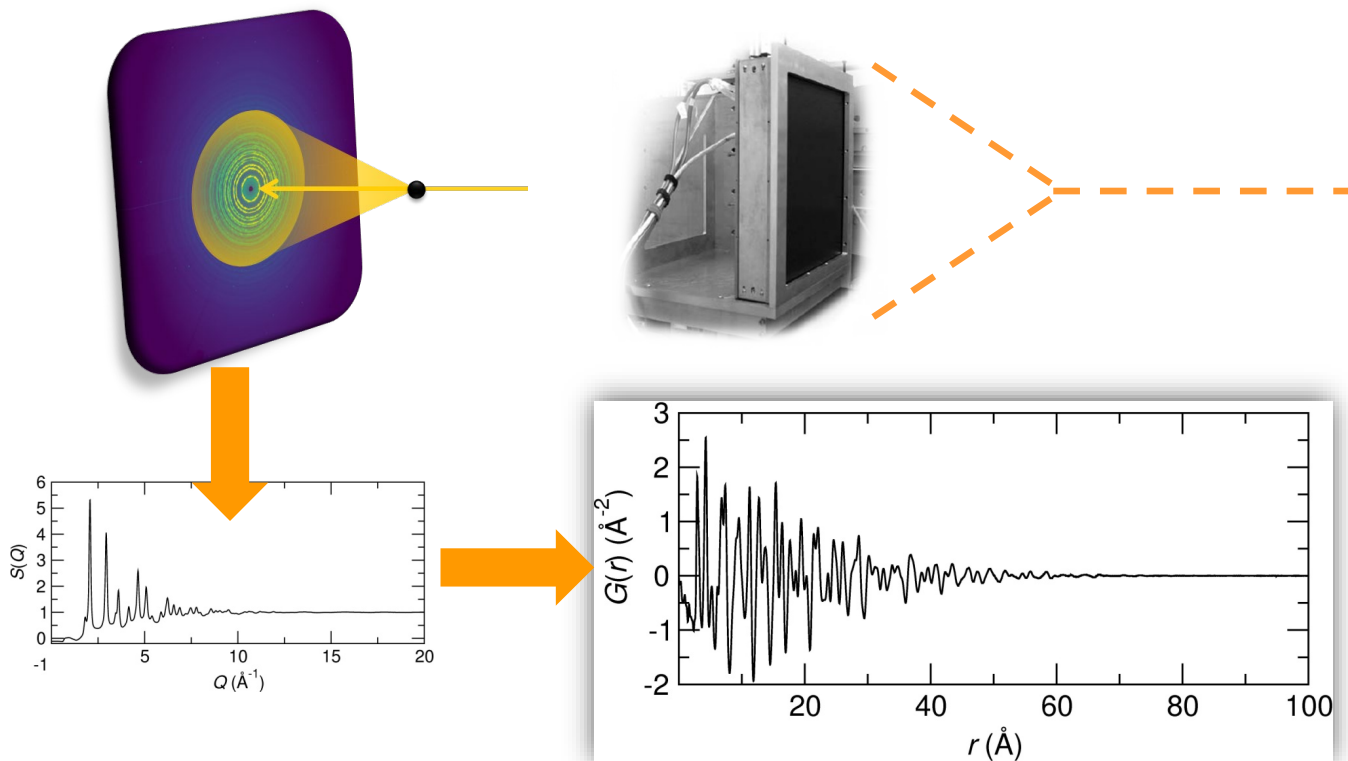
Examples of Dedicated User Programs in the US:

11-ID-B at APS

PDF at NSLS-II

10 mg sample can be measured in seconds to fractions of a second!

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

Combined methods

Pair Distribution Function

Based on the *radial distribution function* (RDF):
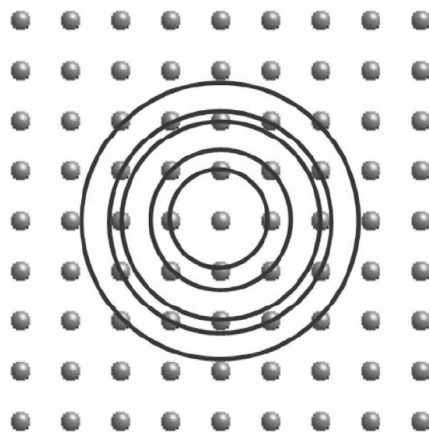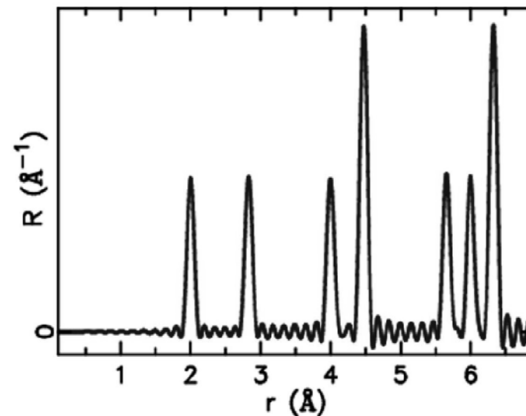
Atomic PDF (PDFFIT notation):

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

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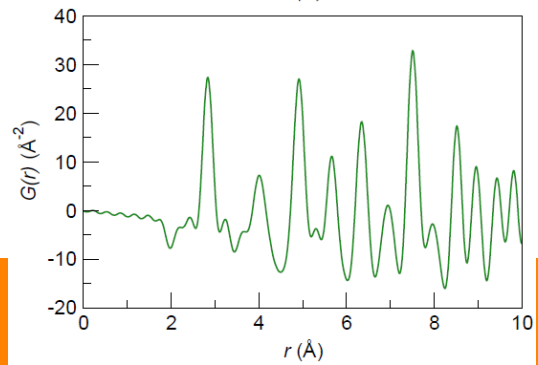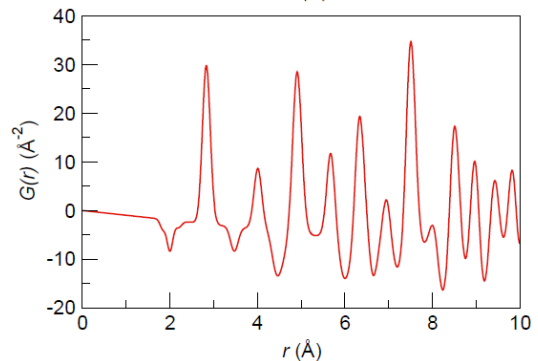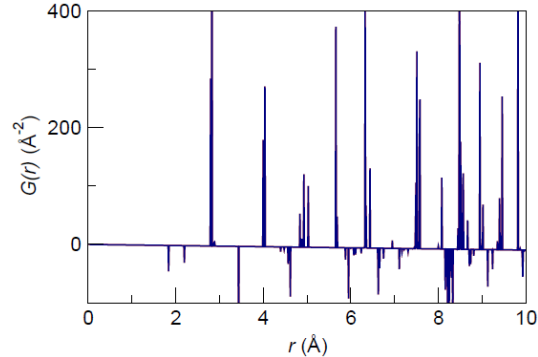
Large model: ensemble average of actual displacements (*RMCprofile*)

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
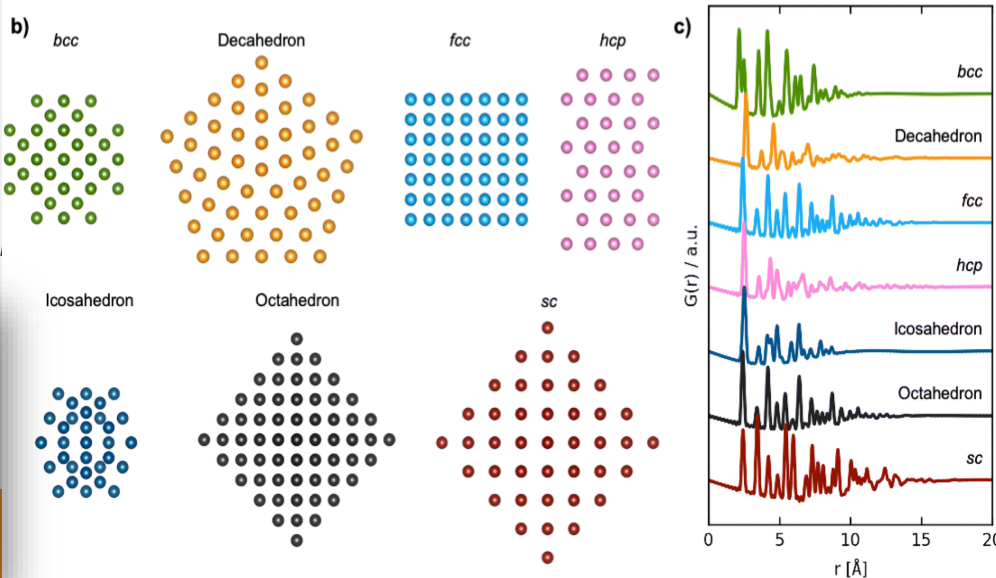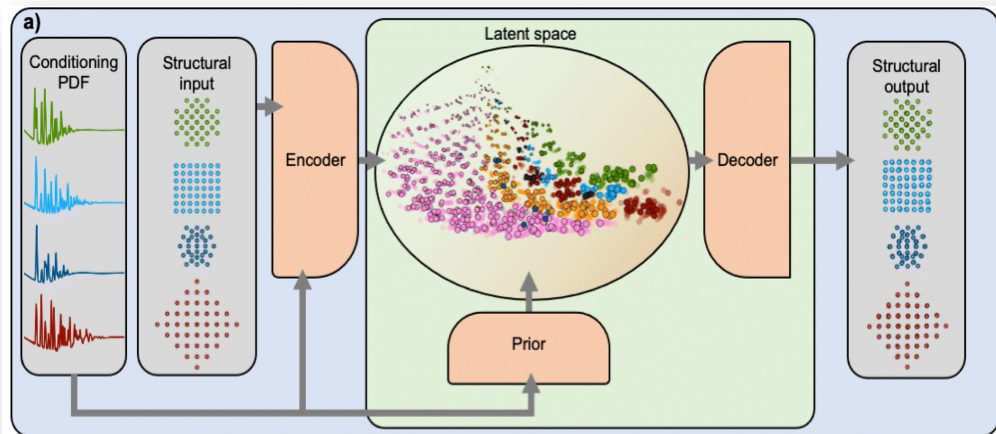Constraints utilized
Static 3-D model of the structure (a snap-shot)

Multi-level / Complex Modeling
Refine higher level parameters (not each atom)
Nanoparticle example: *diameter, layer spacing, stacking fault probab...*
Choose minimization scheme

ab initio, f...
Density Fu...
Molecular ...
Artificial In...

Small Box: Brief Software Comparison

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*

http://www.diffpy.org/
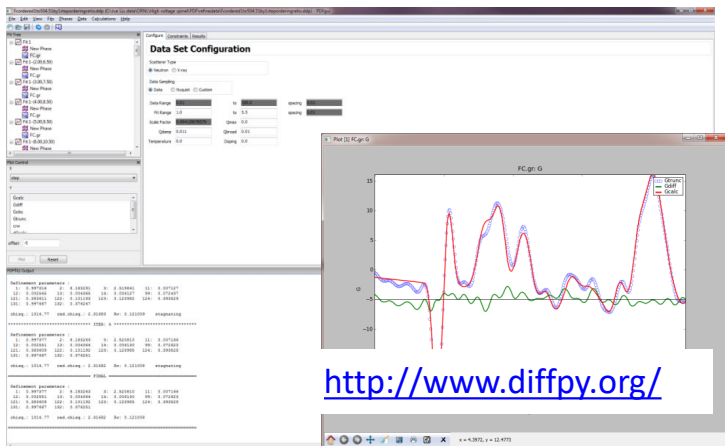
TOPAS PDF

+ Fast and flexible

+ Fit Bragg and PDF together

- Steeper learning curve

http://www.topas-academic.net

BIG ORANGE BIG IDEAS
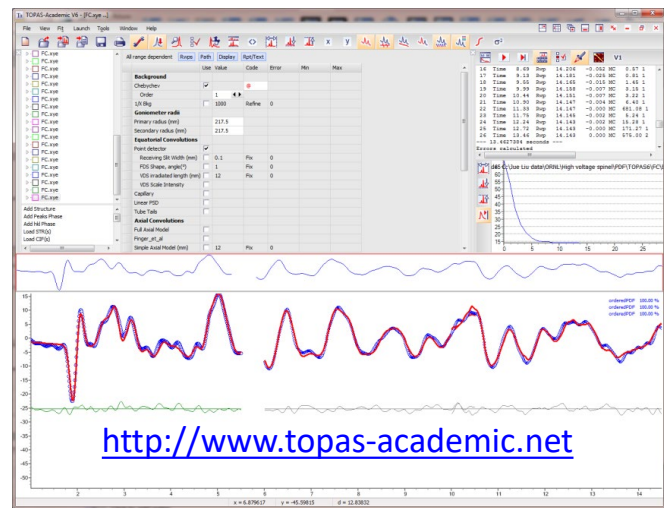
Large Box: Reverse Monte Carlo
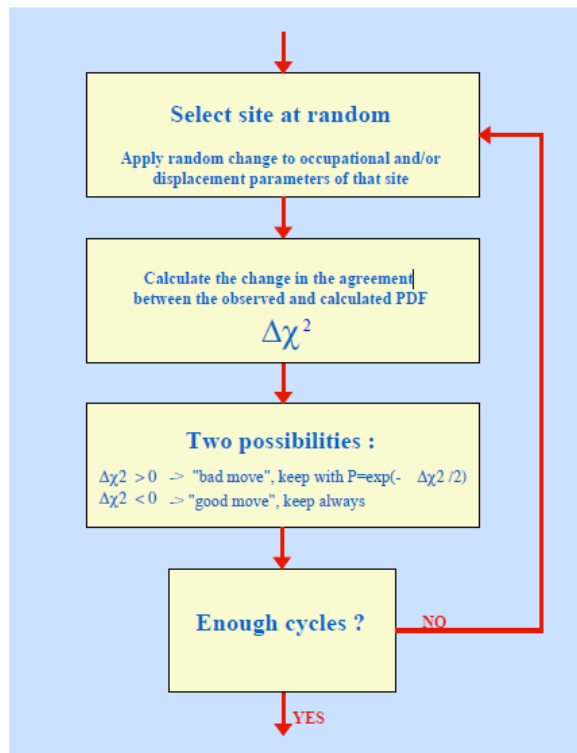
RMCprofile

- 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/

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

SQSs

DFT calculations to calculate the ground-state electronic structure using VASP/MS-Castep
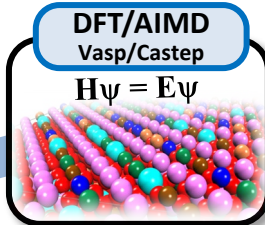
DFT/AIMD
Vasp/Castep
$$H\psi = E\psi$$

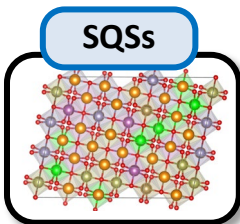Metropolis Monte Carlo simulations (MCS) utilized to estimate cation disorder and predict secondary phases

Bragg
GSASII/TOPAS

MCS

STEM/EDS

PDF

Neutron Synchrotron

XAFS

EXAFS analysis to constrain local chemical environment

Small-box
PDFgui/TOPAS

Big-box
RMCProfile

"Solved" structure

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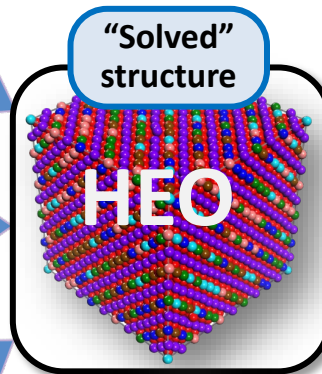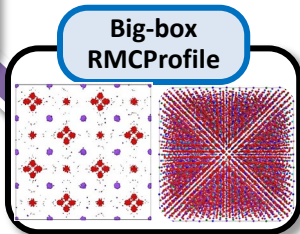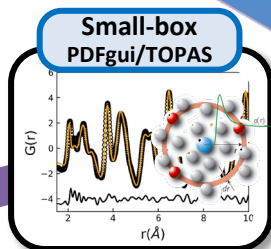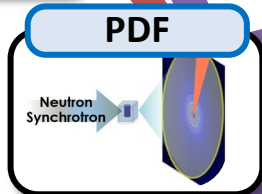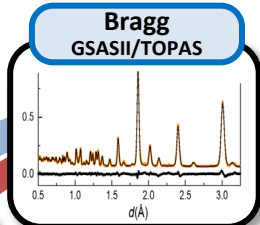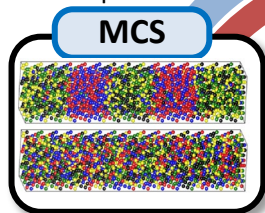
Pair distribution function PDF data analyzed by small-box modeling using PDFgui/TOPAS and by large-box Reverse Monte Carlo(RMC) modeling

Complex Modelling

BIG ORANGE BIG IDEAS
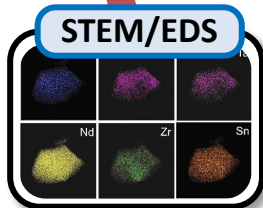
Small-box PDF fitting using DFT-relaxed SQS supercell

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

$Nd_2(Ta_{0.2}Sc_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$ $Nd_2(Ti_{0.2}Nb_{0.2}Sn_{0.2}Hf_{0.2}Zr_{0.2})_2O_7$
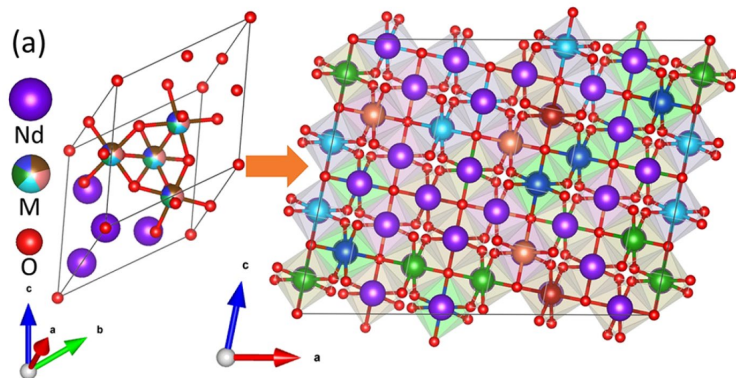
Primitive unit cell and Special Quasirandom Structures (SQS) supercell
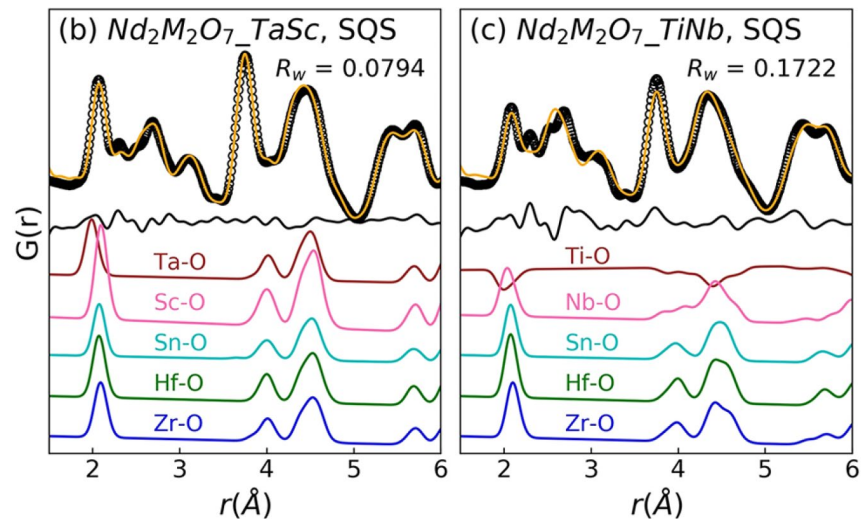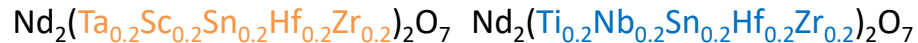
Total and decomposed partial PDFs from individual M−O pair−pair correlations

Bo Jiang et. al. *J. Am. Chem. Soc.* 2021, 143, 4193–4204.

"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.

5×5×5 supercell
11000 atoms

RMC

Fold to
RMC unitcell
'point cloud'

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

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

Fm-3*m*
structure

Fd-3m, Rietveld

(a)

(b)

Bo Jiang et. al. *J. Am. Chem. Soc.* 2021, 143, 4193–4204.
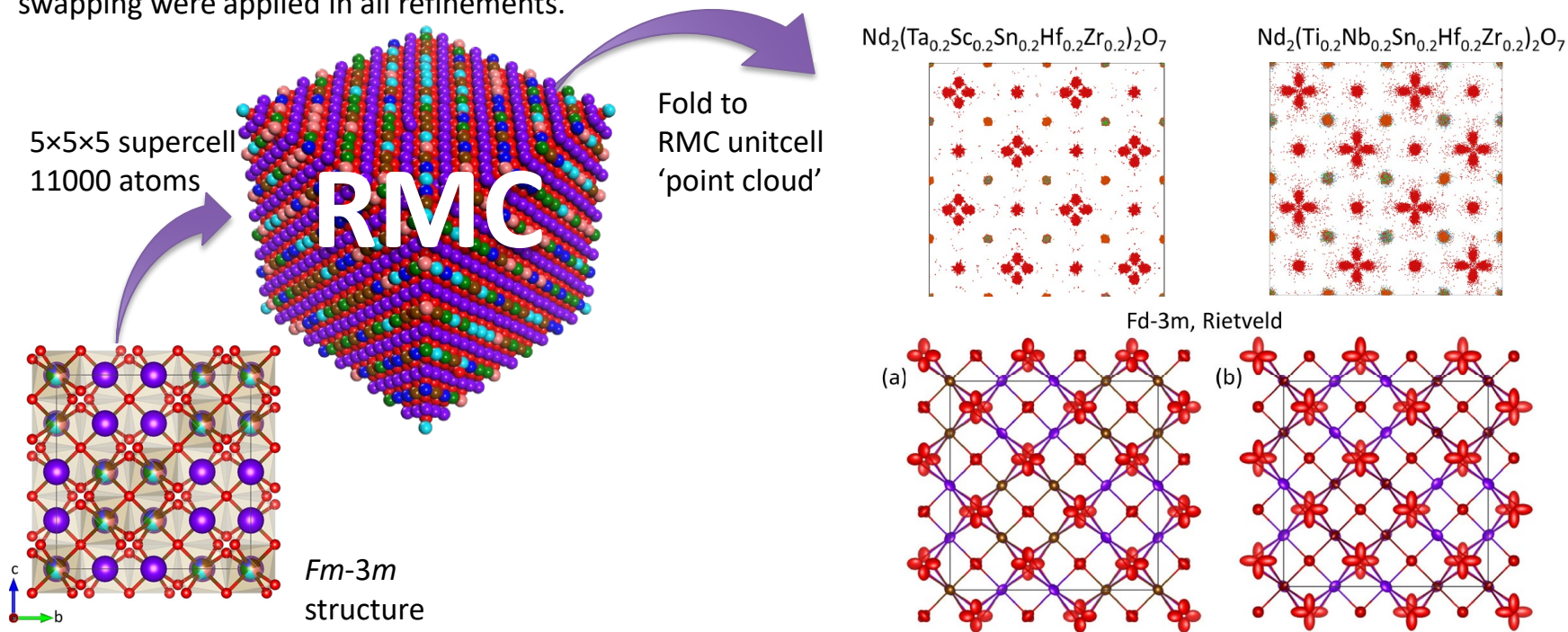
Nearest-neighbor M-O peaks

SQS
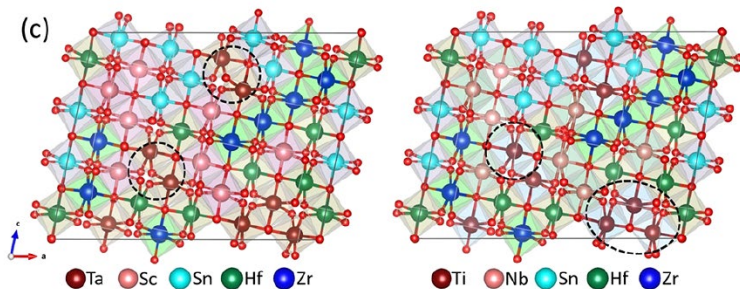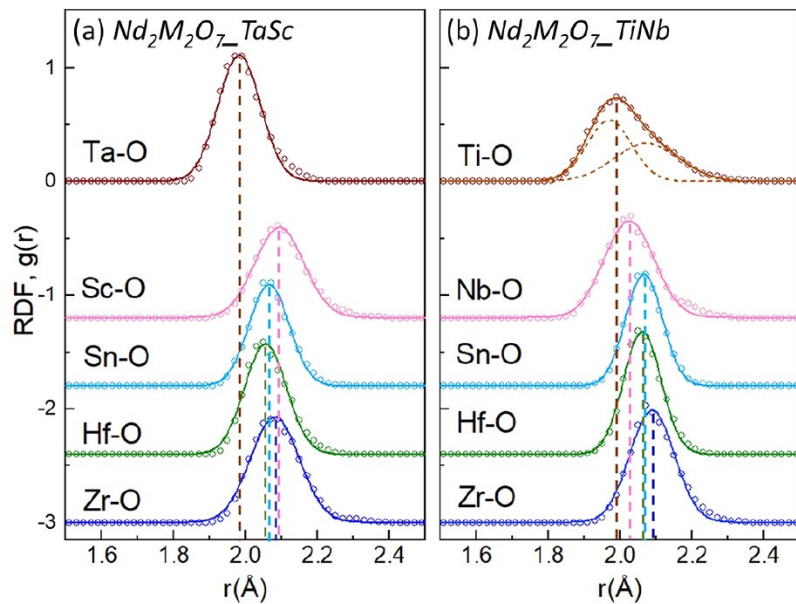
RMC
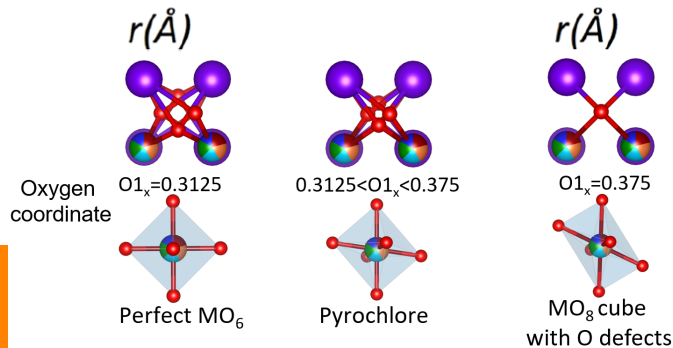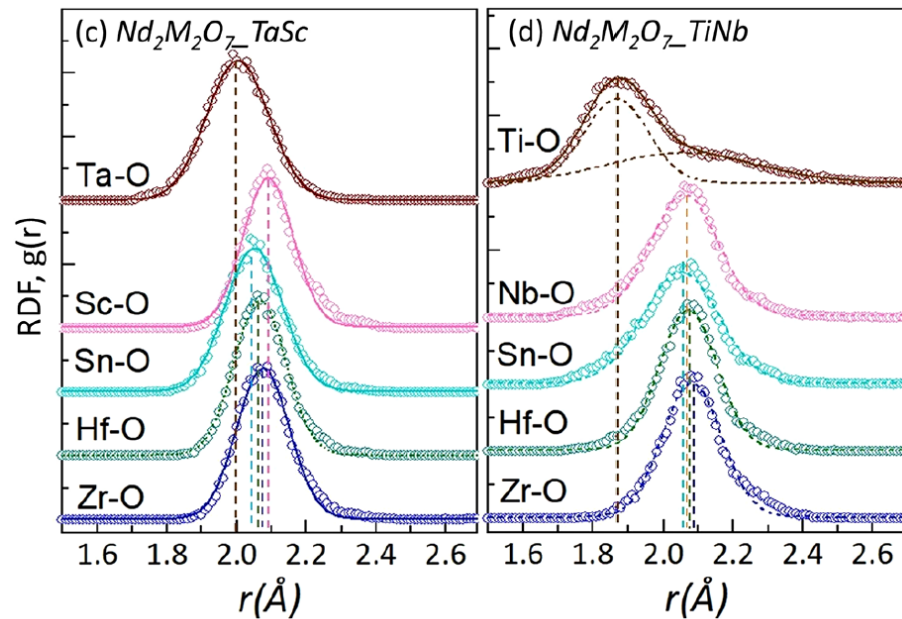
Neighbor correlations *n(r)* by RMC

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

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

(a) $Nd_2M_2O_7\_TaSc$

Ta-Ta
Ta-Sc
Ta-Sn
Ta-Hf
Ta-Zr

(b) $Nd_2M_2O_7\_TiNb$

Ti-Ti
Ti-Nb
Ti-Sn
Ti-Hf
Ti-Zr

A FEW EXTENSION AREAS

Magnetic PDF

Thin-Film PDF

Dynamic PDF

3D PDF

Sample Environments

Magnetic PDF: mPDF
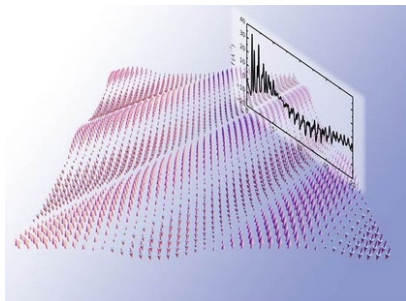
Direct access to long-range and short-range magnetic correlations in real space: **spin-stripe correlations in cuprate superconductors, spin fluctuations in frustrated magnetic systems, etc.**

Magnetic pair distribution function analysis of local magnetic correlations

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

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

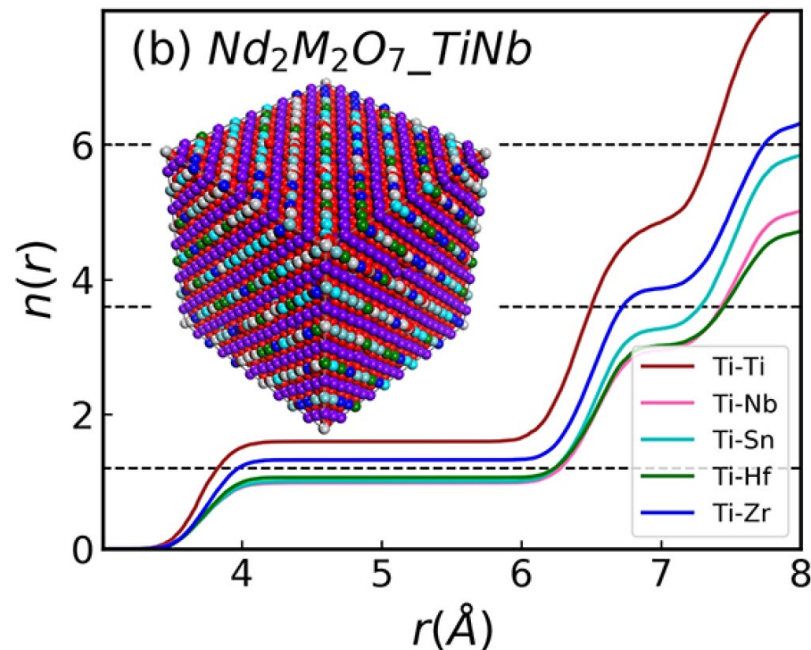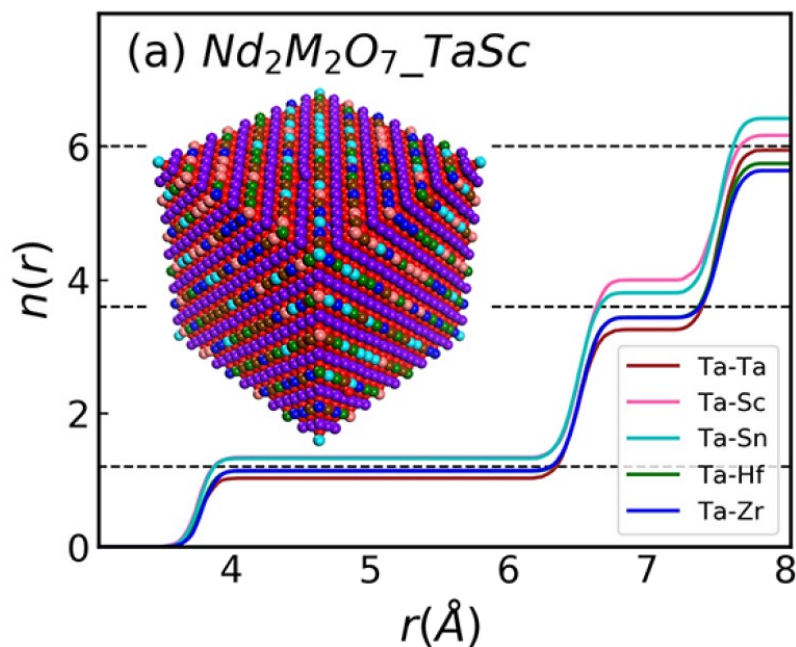Joseph A.M. Paddison[1,2], Harapan S. Ong[1], James O. Hamp[1], Paromita Mukherjee[1], Xiaojian Bai[2], Matthew G. Tucker[3,4], Nicholas P. Butch[5], Claudio Castelnovo[1], Martin Mourigal[2] & S.E. Dutton[1]

Thin Film PDF: tfPDF

1 μm $GeSb_2Te_4$ films deposited **on kapton**, thermally annealed in situ under flowing He
K. Page, J. K. Baldwin, Th. Proffen, unpublished.

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.

Dynamic PDF: DyPDF

PMN 450K

$Pb(Mg_{1/3}Nb_{2/3})O_3$
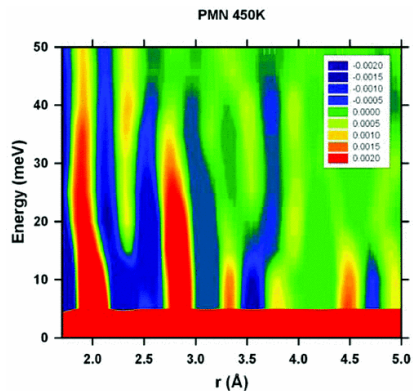
T. Egami and W. Dmowski, **Dynamic pair-density function method for neutron and X-ray inelastic scattering**, *Z. Kristallogr.* 227, 233–237 (2012).

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).
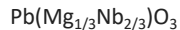
3D - PDF

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

$(Mn_{1-x}Fe_x)_2O_3$
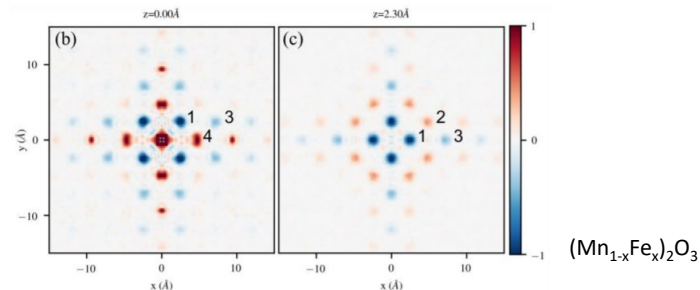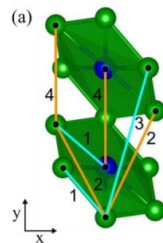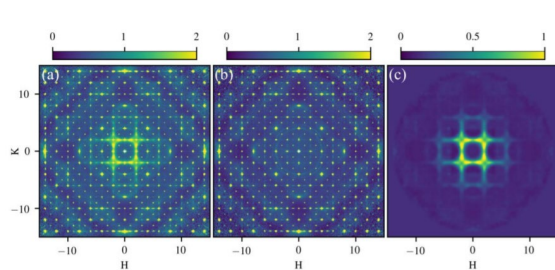
N. Roth, A. F. May, F. Ye, B. C. Chakoumakos, and B. B. Iversen, **Model-free reconstruction of magnetic correlations in frustrated magnets**, IUCrJ, 5, 410-416 (2018).

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, Diffpy: 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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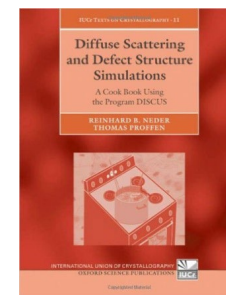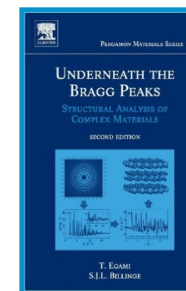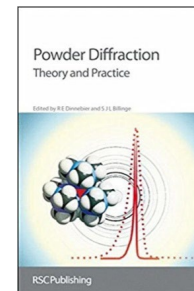
Try Diffraction/PDF Mail-in Programs for Users!

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 Total Scattering Analysis Online Video Library!

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 Goodwin

November 5

Of Spins and Pseudospins- Magnetic PDF as a powerful probe of short 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
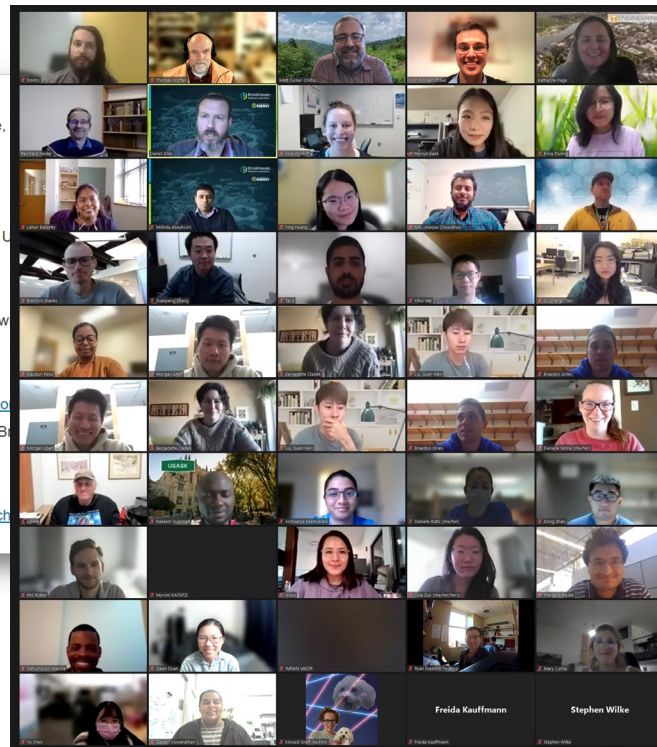
Stay tuned for announcements about our 7th annual school!

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

Survey for this lecture:

https://forms.office.com/g/VX885ZMVkz

NXS Lecture - Katharine Page:
"PDF Analysis"