70 YEARS OF CREATING TOMORROW

Los Alamos NATIONAL LABORATORY

# Total Scattering Developments for Nanoscale Research

Katharine Page
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UNCLASSIFIED

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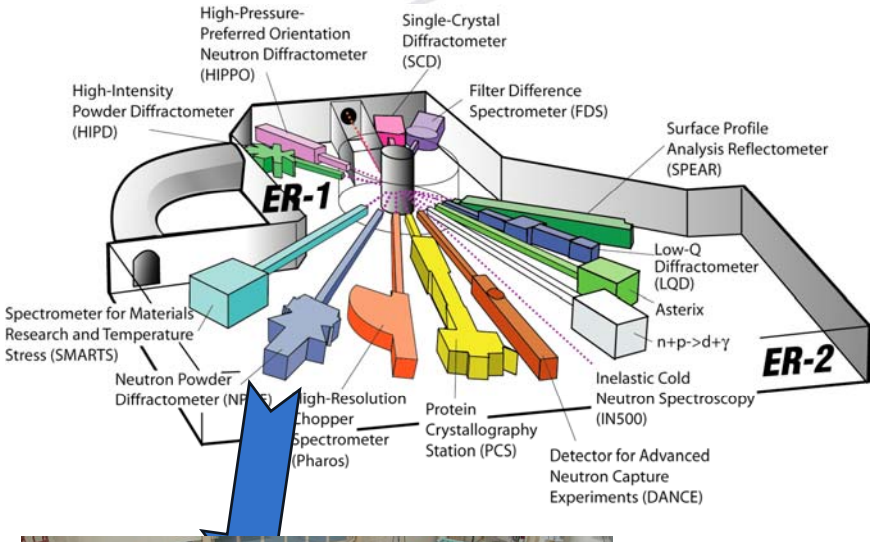
NNSA National Nuclear Security Administration

# Total Scattering at the Lujan Center

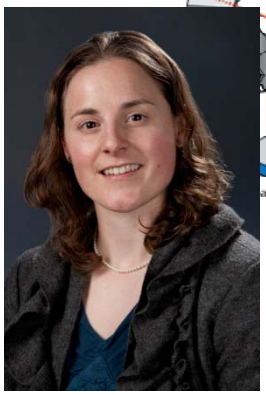


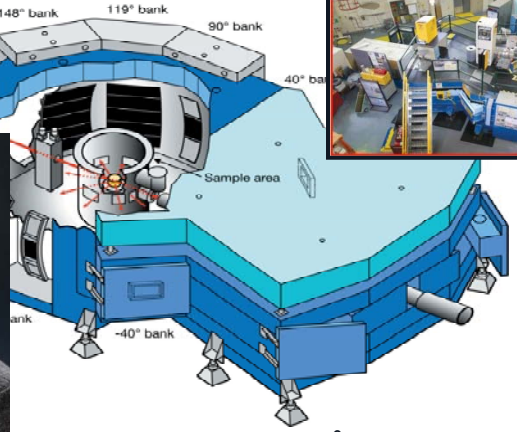

**Building a high resolution total scattering powder diffractometer – upgrade of NPD at MLNSC**

T. Proffen[1,*], T. Egami[2], S.J.L. Billinge[3], A.K. Cheetham[4], D. Louca[5], J.B. Parise[6]

# Total Scattering at the Lujan Center

## Neutron Powder Diffractometer (NPDF)






L1: 32m, Qmax=50 Å-1, Δd/d=0.15 %

Typical PDF measurement 1 - 4 hrs

Sample amounts down to 200 mg

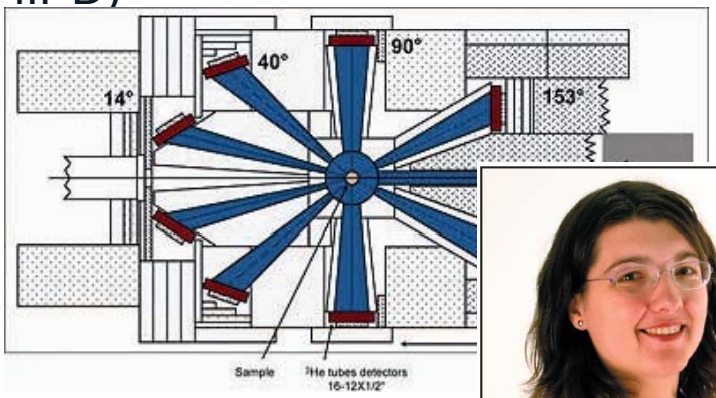
Ancillary: 15 K-1100 K

Web based instrument interface

Automatic creation of PDF

kpage@lanl.gov

## High-Intensity Powder Diffractometer (HIPD)






L1: 9m, Qmax=50 Å-1, Δd/d=0.3 %

Typical PDF measurement 3-4 hrs

Sample amounts down to 200 mg

Ancillary: 4 K-800 K, pressure cell 10 kbar

Web based instrument interface

Automatic creation of PDF

allobet@lanl.gov

**May 1 proposal deadline → http://lansce.lanl.gov !!**

# Lujan's Total Scattering Team

**Katharine Page**
NPDF Instrument Scientist - kpage@lanl.gov
**Research interests**: Nanostructure in ferroelectrics, phase change materials, total scattering methods, nanoparticle structure modeling.

**Anna Llobet**
HIPD Instrument Scientist - allobet@lanl.gov
**Research interests**: Total scattering analysis, magnetism, multiferroic materials.

**Joan Siewenie**
NPDF Instrument Assistant - siewenie@lanl.gov
**Research interests**: Amorphous materials, RMC modeling, instrumentation.

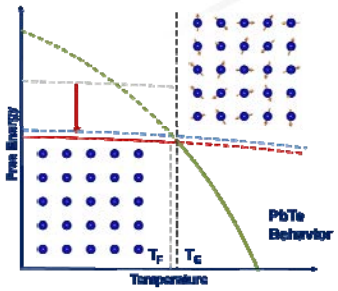
**Claire White**
Director's Postdoctoral Fellow - whitece@lanl.gov
**Research interests**: Molecular dynamics (MD) and Density Functional Theory (DFT) modeling, geopolymers, PDF techniques.

**Graham King**
HIPD Postdoc - gking@lanl.gov
**Research interests**: PDF analysis, RMC modeling, magnetism, complex oxides.

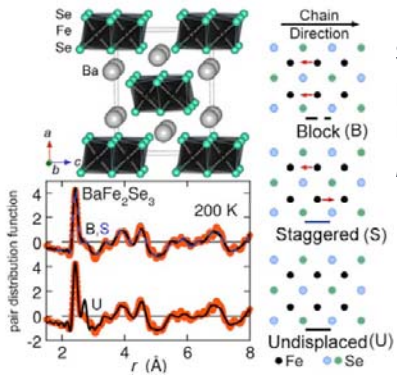
**Graduate Students & Summer Students:**
2012-2013: Joe Peterson, NMSU
2013: Michael Brusowski, USNA

**http://totalscattering.lanl.gov**

# Last 10 Years

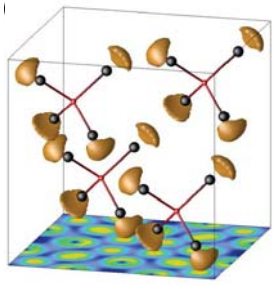



E. Bozin, *et al.*, Entropically Stabilized Local Dipole Formation in Lead Chalcogenides, *Science* **330**, 1660 (2010).




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

*Total Scattering established and seeing rapid growth for disordered crystalline materials*



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).

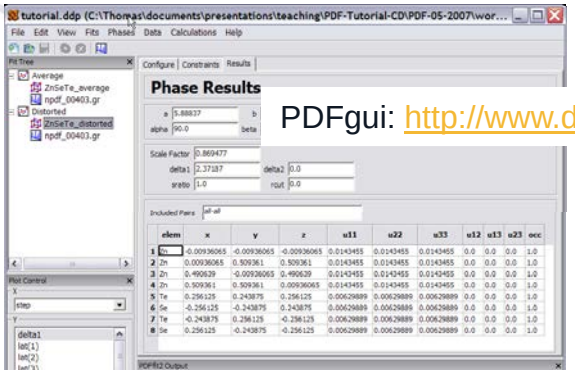
# Atomic PDF Modeling

## 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




PDFgui: http://www.diffpy.org/

## Large Model: Reverse Monte Carlo

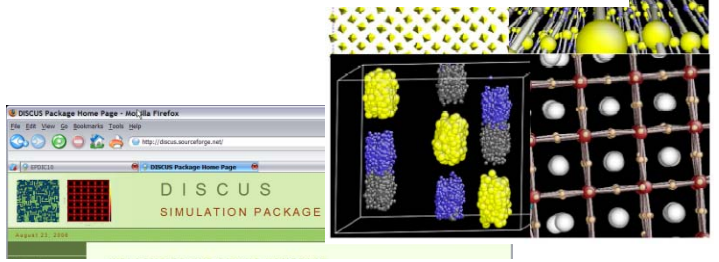
20000 + atoms

Fit X-ray and neutron *F(Q), G(r)* , Bragg profile

Constraints utilized

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

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



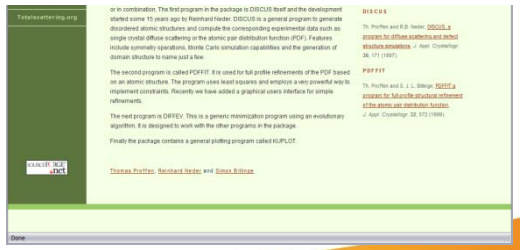

DIFFEV and DISCUS: http://discus.sourceforge.net

## Multi-level /Complex Model: General Minimization

Refine higher level parameters (not each atom)

Example nanoparticle: *diameter, atom spacing, stacking fault probability*

Choose minimization



## Emerging: *ab initio* and force-field based approaches

Density Functional Theory

Molecular Dynamics

# Methods Developments Driven by Materials Problems

- Corrections for Hydrogen Background Scattering
  - → Nanoparticles with surface ligands
  - → Pyrolized catalysts
- Amorphous and Crystalline Phase Quantification
  - → Phase change chalcogenide
  - → Intact sandstones
- Finite Nanostructure Modeling & Future Developments

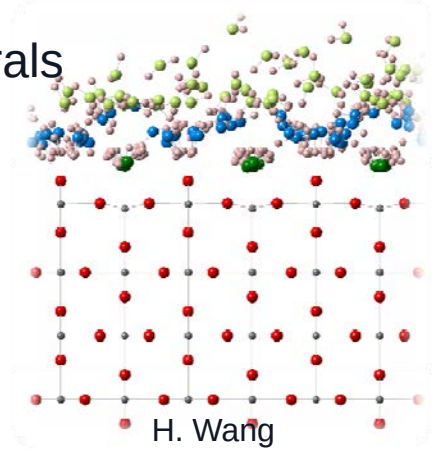
# Corrections for Hydrogen Background Scattering in the neutron PDF

K. Page, C. E. White, E. G. Estell, R. B. Neder, A. Llobet, and T. Proffen, J. Appl. Cryst. 44 (2011) 532-539.

And some nanomaterial examples…

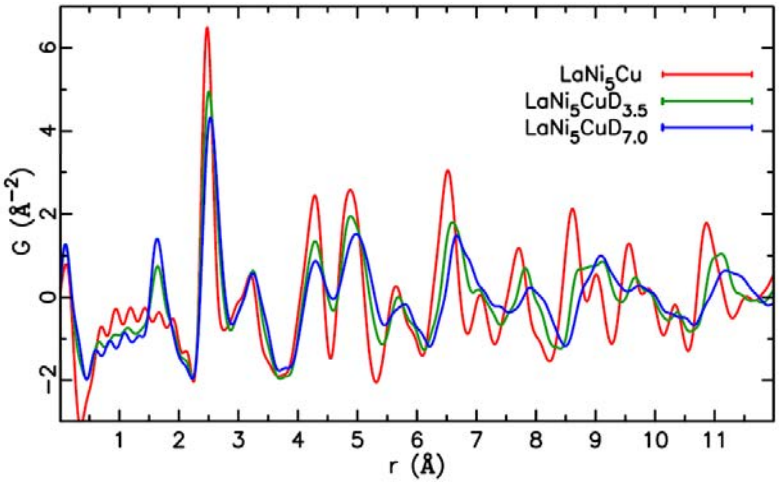
# Materials Problems Featuring H

Hydrated Clays & Minerals



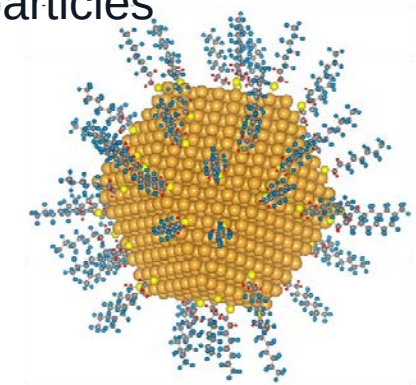
H. Wang

Metal Hydrides



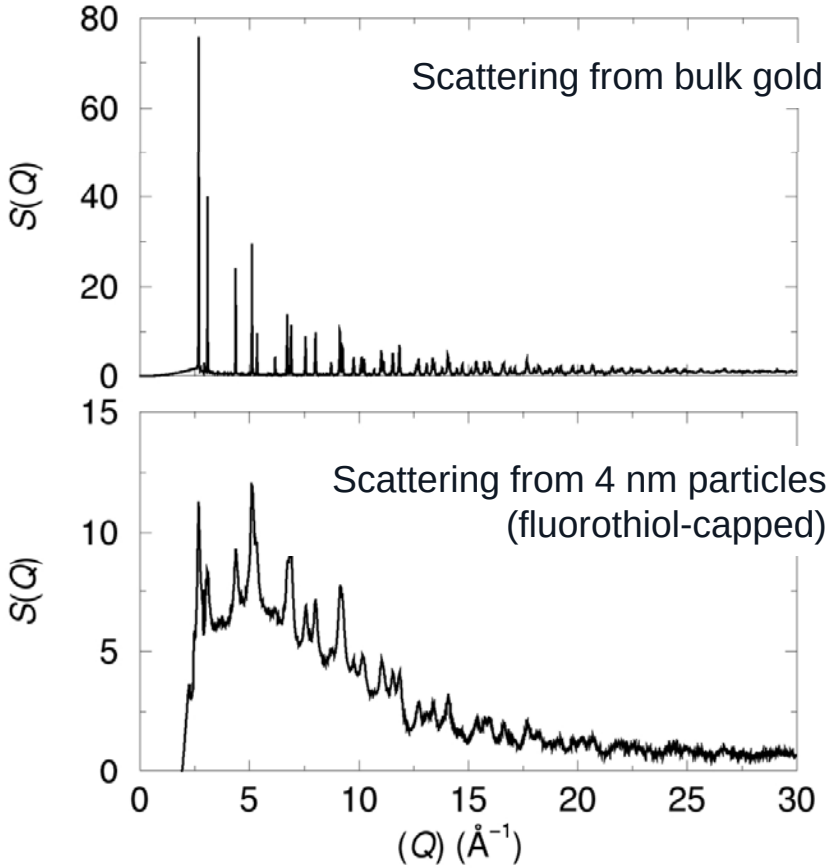

H. J. Kim

Stabilized Nanoparticles



- *and* MOFs, organic molecules, polymers, etc.
- Deuterating can be expensive, time-consuming, or impossible.

# The Problem with H



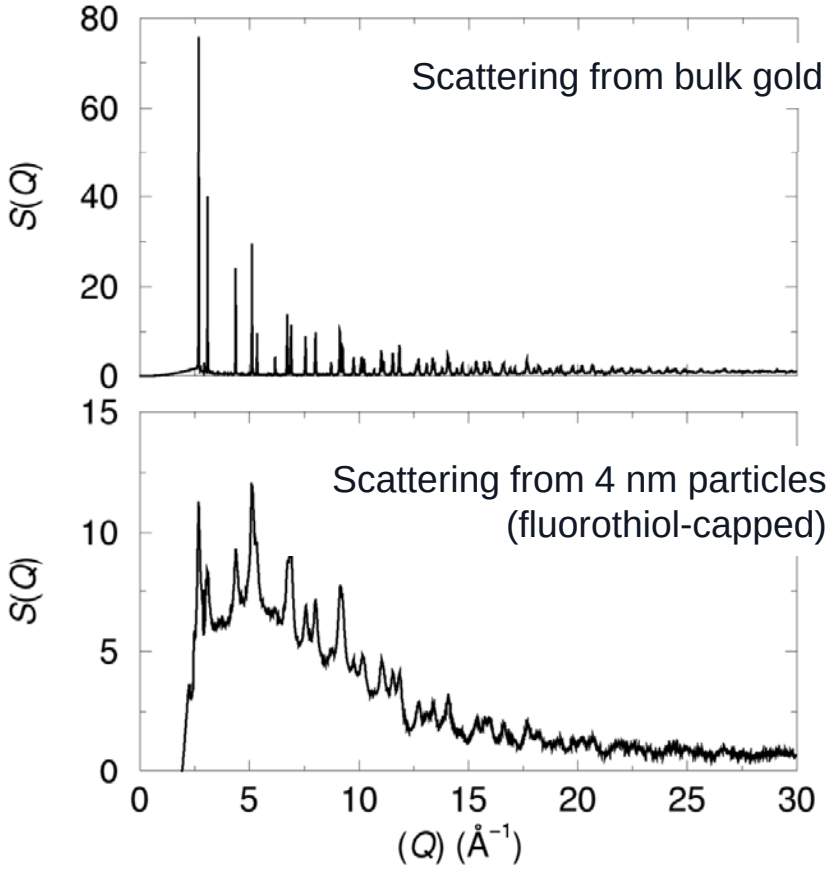

What is the 'mound'?

Inelastic incoherent scattering contributions (incoherent cross section of nuclear scattering from different nuclei in a sample). Large when energy exchange between neutron and atom is significant.

Results in significant low-r intensity and baseline errors in the PDF (unfortunately where contributions from H coherent scattering are expected).

Page, Proffen, M. Terrones, H. Terrones, Lee, Yang, Stemmer, Seshadri, Cheetham, *Chem. Phys. Lett.* **393** (2004) 385-388.

# The Problem with H




- We are far from understanding the nature of this scattering even for very simple systems. It must be empirically subtracted when present.

A. K. Soper, *Mol. Phys.* 107 (2009) 1667-1684.

- Isotopic substitution is sometimes an option.

- And some procedures (work) for liquids:
  - -Subtracting reference data
  - -Extrapolating to 0 in real space
  - -Placzek correction

# 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)*

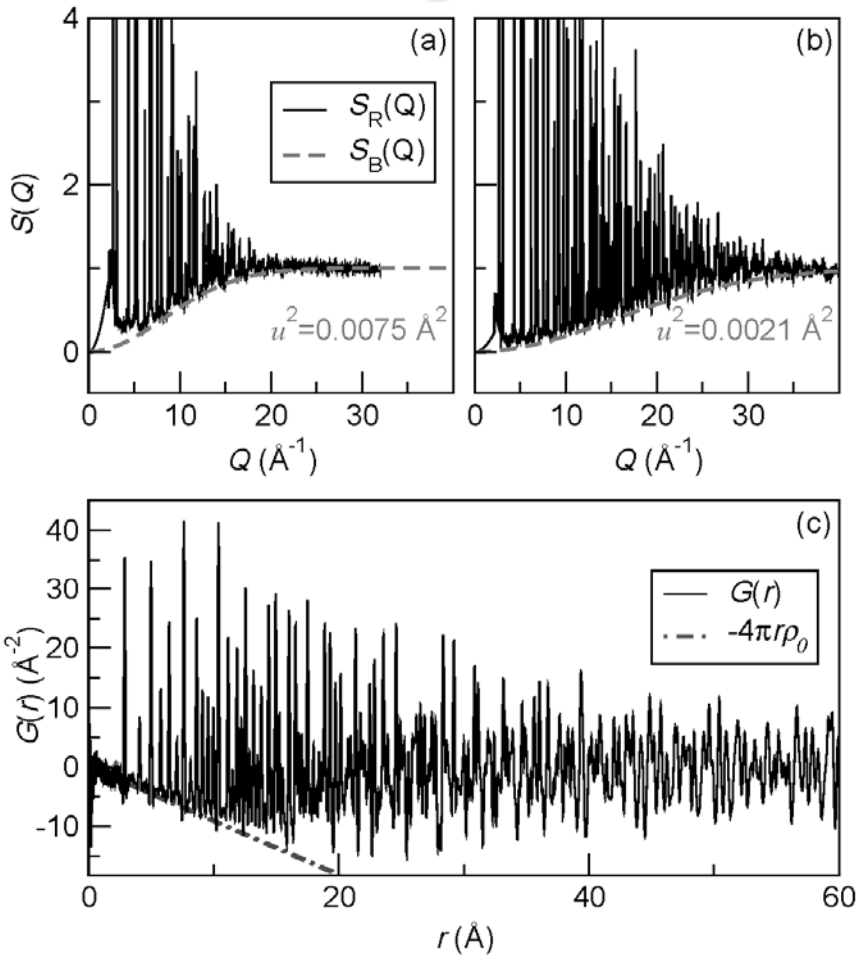
$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{\left|\sum c_i b_i\right|^2} + 1 \qquad Q = \frac{4\pi \sin\theta}{\lambda}$$

*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.

# Typical Behavior




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

Sine Fourier transform

The Pair Distribution Function (PDFFIT Notation): $G(r)$

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

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

*average density*

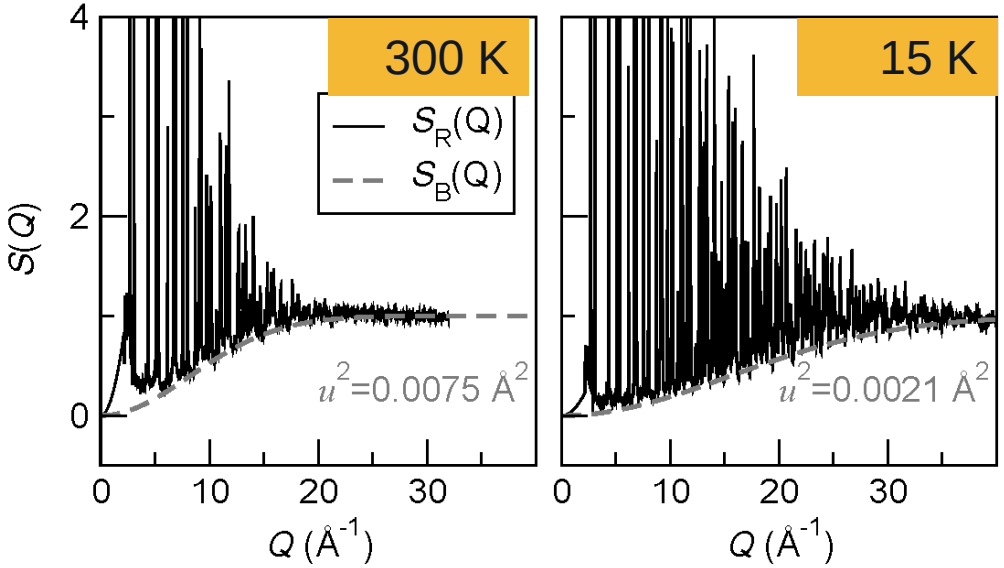
*pair density*

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

*distance between i and j atoms*

# Typical Behavior

## $S_B(Q)$: Characteristic Background Function




Experimentally measured function is affected by thermal motion and disorder, damping the function at high-*Q*.

The Debye-Waller approximation incorporates lattice vibration effects into crystallographic analysis with a Gaussian Function, incorporating the atomic displacement parameter *u.*

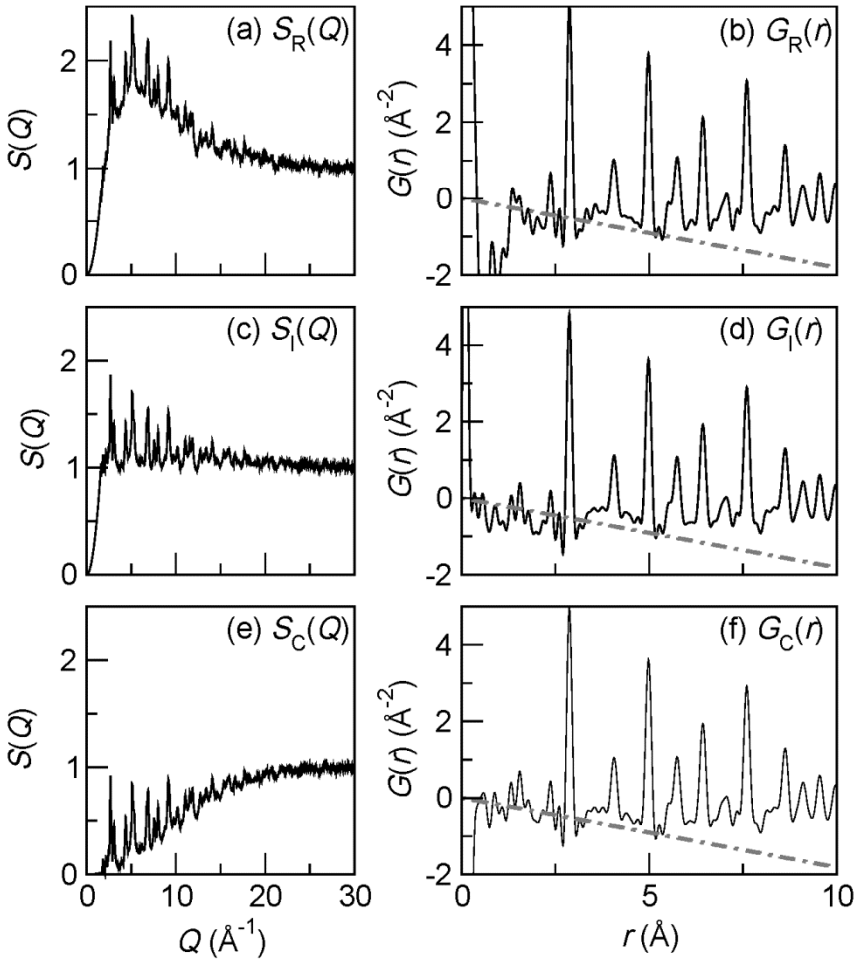
*Laue diffuse scattering term*
*(self part of nuclear coherent scattering)*

$$S_{\mathrm{B}}(Q) = \exp\left(-\langle\langle u_i^2\rangle\rangle Q^2\right)L + 1 - \exp\left(-\langle\langle u_i^2\rangle\rangle Q^2\right)$$

*Debye-Waller factor*

Since we know the expected behavior, can we empirically correct for incoherent inelastic scattering from H?

# Empirical Background Correction




**$S_R(Q)$: Measured**

Conventional data reduction steps applied

**$S_I(Q)$: Intermediate**

Background is subtracted from each bank of data (an iterative fitting procedure is applied)

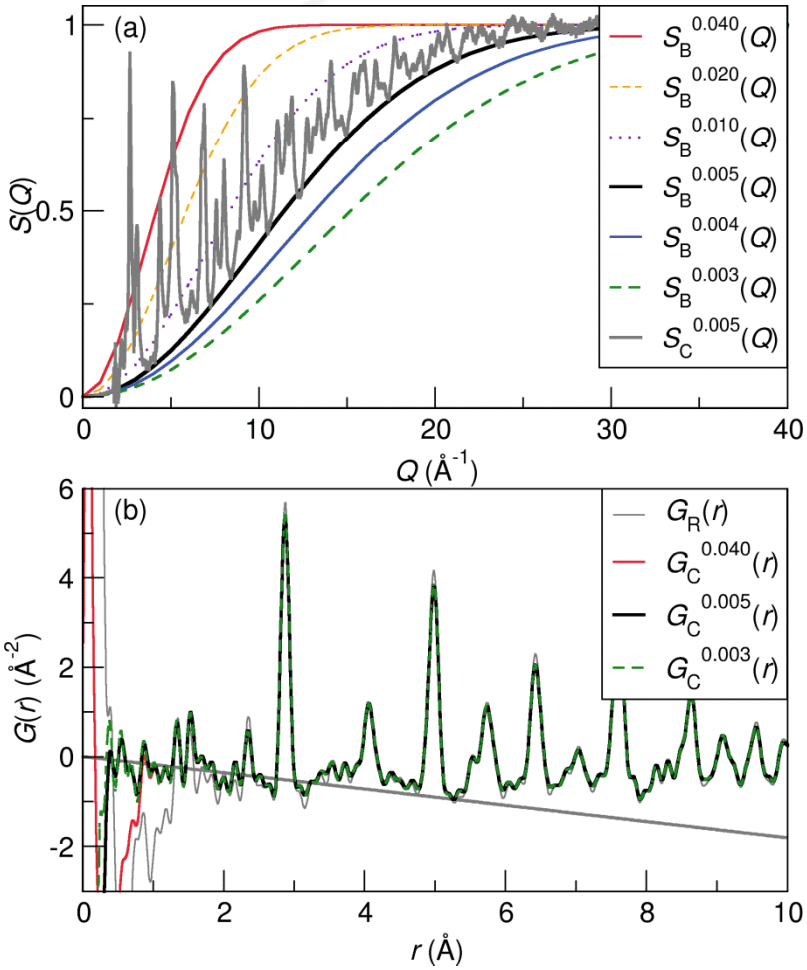
**$S_C(Q)$: Corrected**

Added characteristic background term to intermediate data

*Implemented in PDFgetN using DIFFUSE package add-on.*

P. F. Peterson, et. al., J. Appl. Cryst. 33 (2000) 1192.
Th. Proffen & R. B. Neder, J. Apply. Cryst. 30 (1997) 171-175.

# Corrected *S*(*Q*) and *G*(*r*)



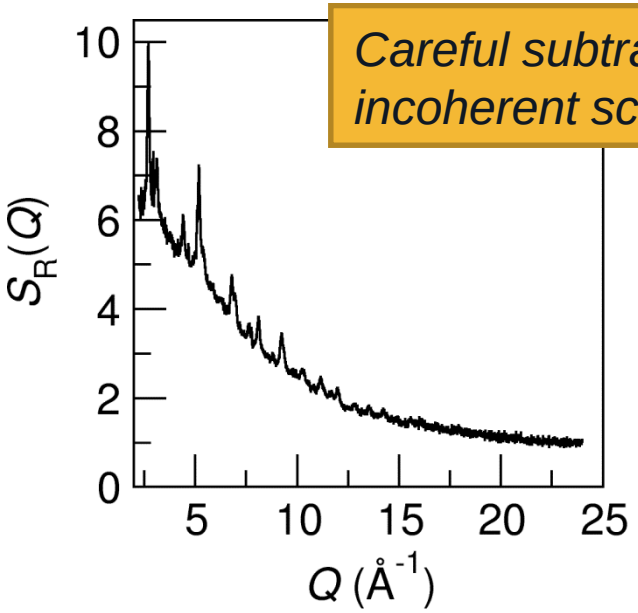

Requires a user value for the Debye-Waller factor.

From:
-Reference material
-Refinement of *G*(*r*) data derived from intermediate structure function
-Rietveld refinement (if available)
-Your favorite theorist

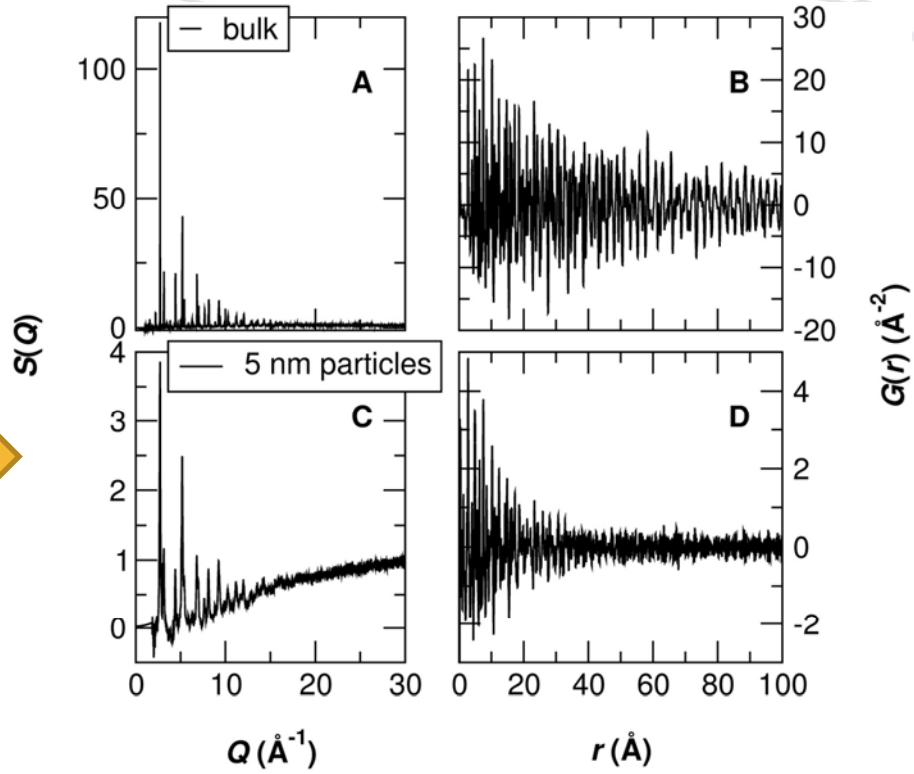
Appears to work… **So what?**

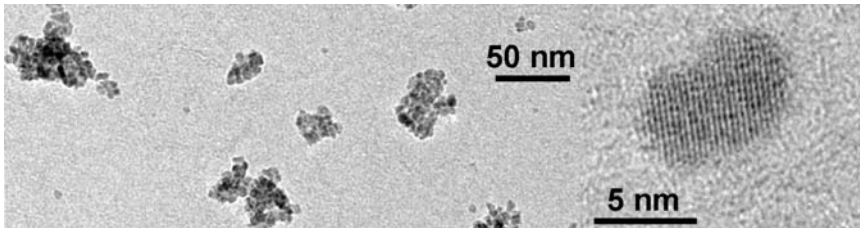
# Example: Nanoparticles

Approx. 1 g samples of 5 nm $BaTiO_3$ (Markus Niederberger) studied by neutrons (NPDF, Los Alamos National Lab):




*Careful subtraction of incoherent scattering*

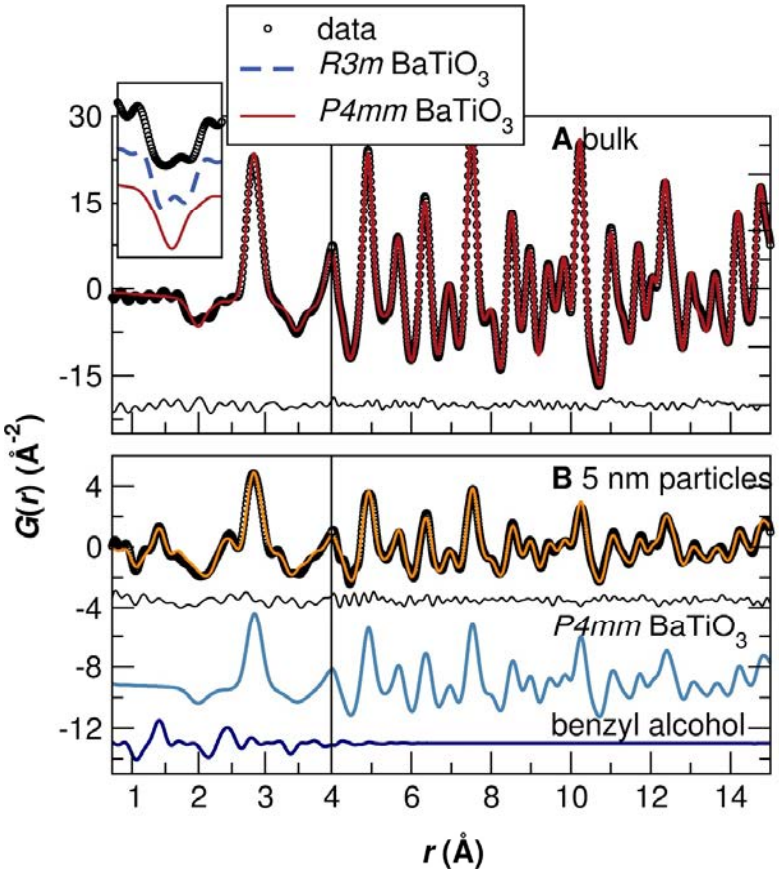


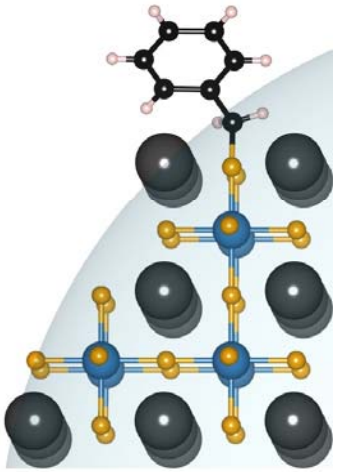




Page, Proffen, Niederberger, Seshadri, *Chem. Mater*. (2010).

# Example: Nanoparticles

The PDF: Bulk $BaTiO_3$ is tetragonal with a split (*R3m*) first Ti-O peak.
The 5 nm particles appear cubic but are *strongly* distorted.



Capping groups observed by scattering for the first time (for any polydisperse nanoparticle system).

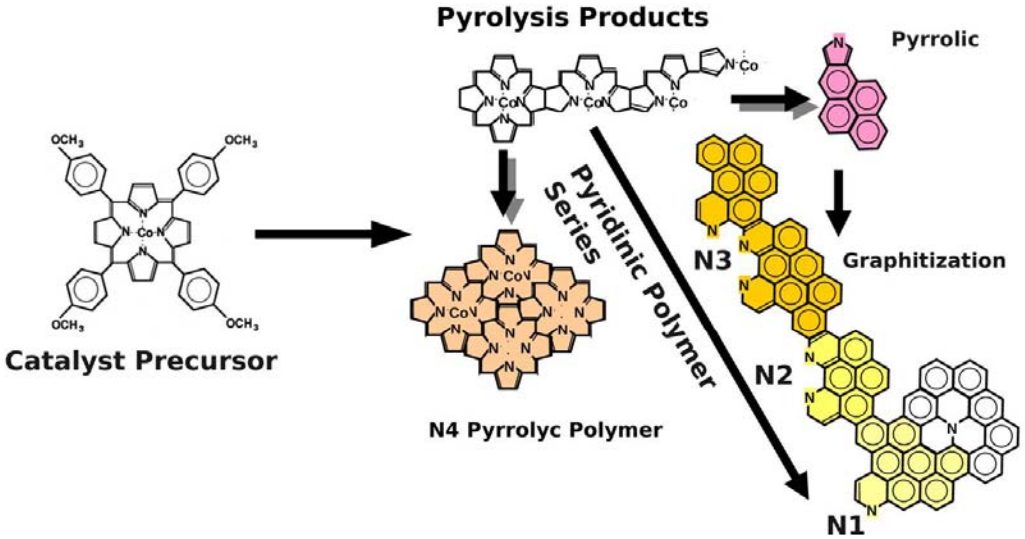
Phase ratios consistent with size, TGA *etc.*

Page, Proffen, Niederberger, Seshadri, *Chem. Mater*. (2010).

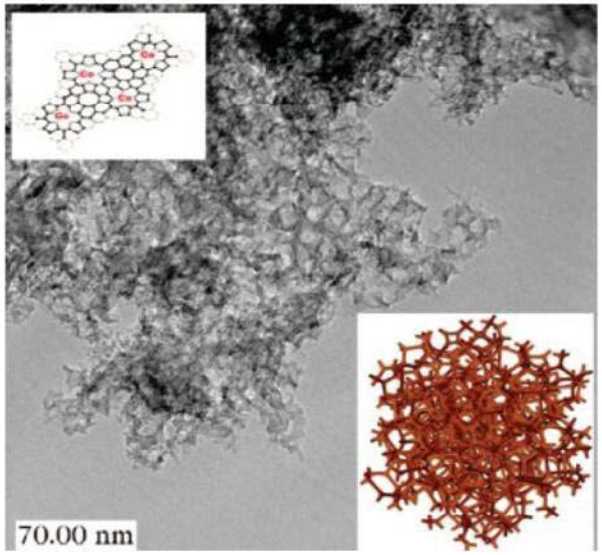
# Example: 'Amorphous' Catalyst

CoTMPP (Co-tetramethylphenylporphyrin)

When CoTMPP is pyrolized (several hour heat treatment in an inert atmosphere), its catalytic activity for oxidation reduction increases. This effect is not understood.



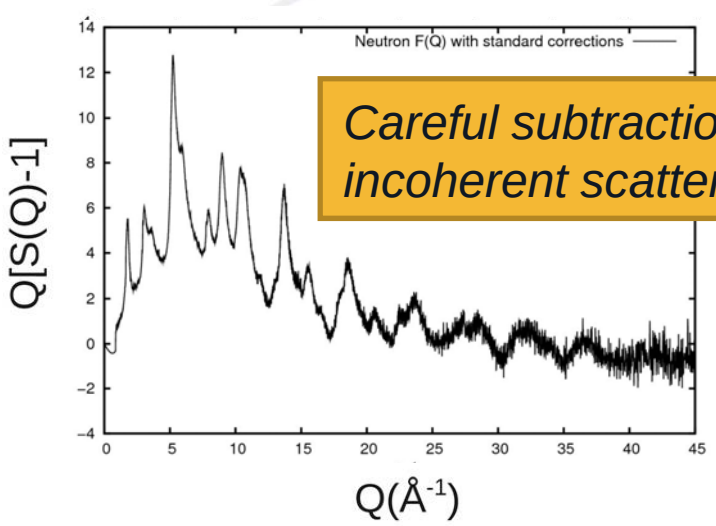

Hypothetical pyrolysis products, T. Olson, UNM (2008).



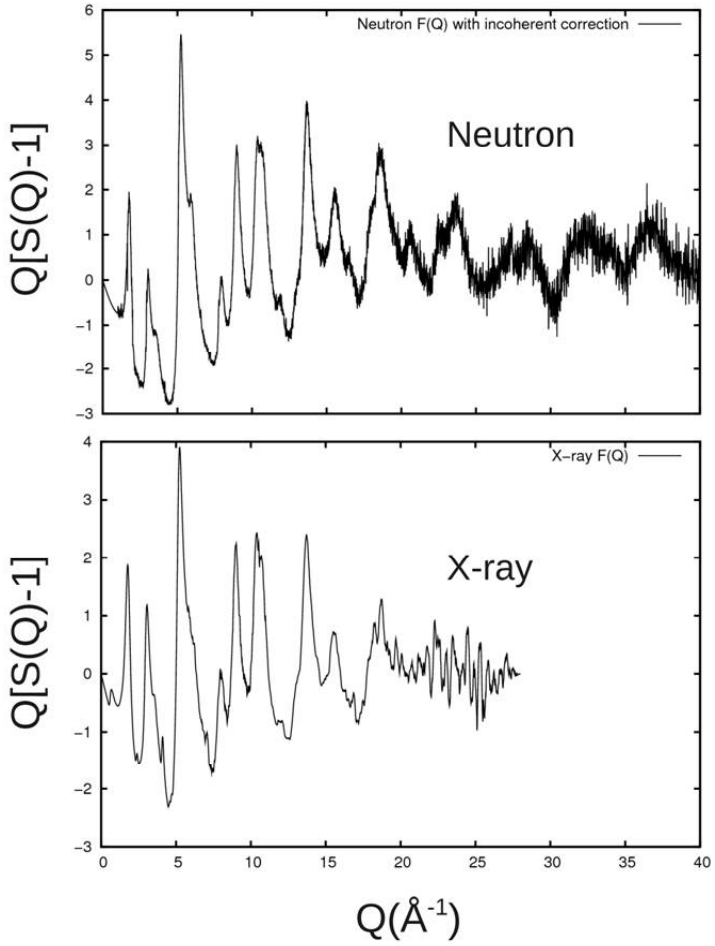

Described as 'amorhphous' and 'balled-up' carbon structure in the literature.

J. Zielgelbauer, et al., J. Phys. Chem. B, 112 (2008) 8839-8849.

# Example: 'Amorphous' Catalyst




*Careful subtraction of incoherent scattering*

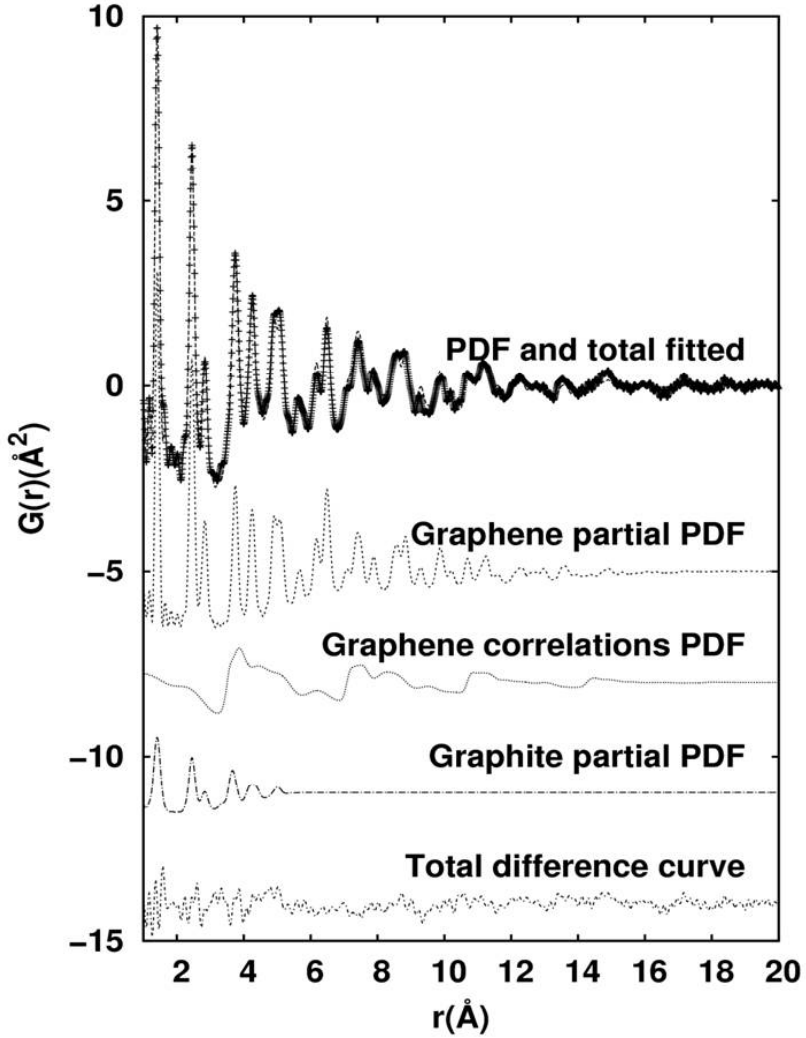



Composition from XPS:

| | |
|---|---|
| C | 0.814 |
| O | 0.120 |
| N | 0.060 |
| Co | 0.006 |

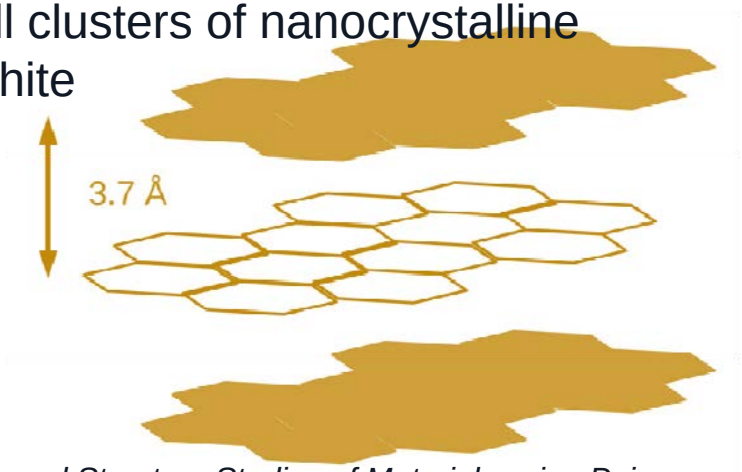
Neutron *S*(*Q*) reveals H content

# Example: 'Amorphous' Catalyst




Three length scales associated with this structure (fit with small-box model):

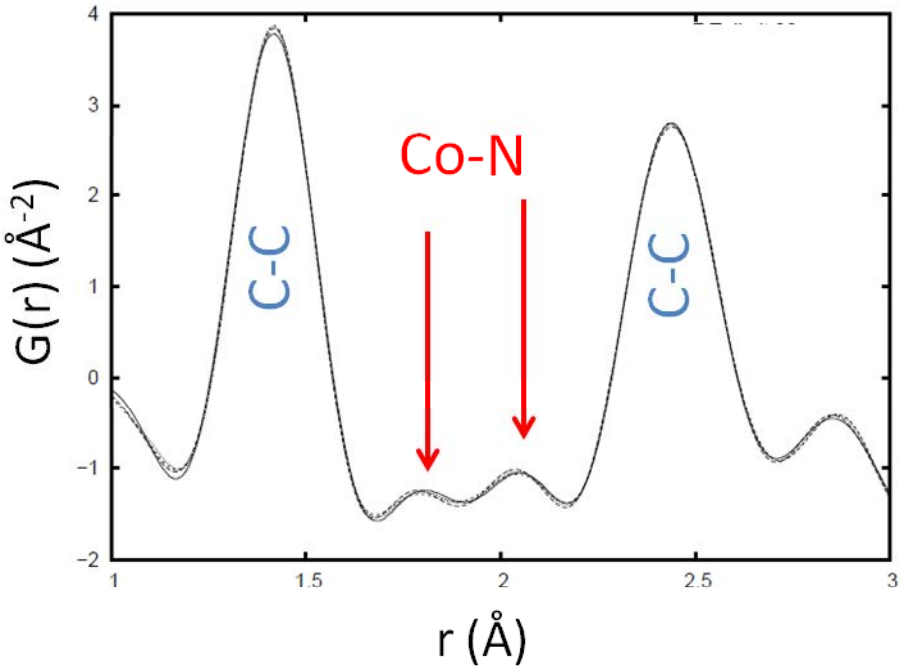
1. graphene-like disks ~18 Å in diameter
2. coordination of graphene layers one to another (at a distance relaxed from graphite-like layer stacking at 3.7 Å)
3. small clusters of nanocrystalline graphite

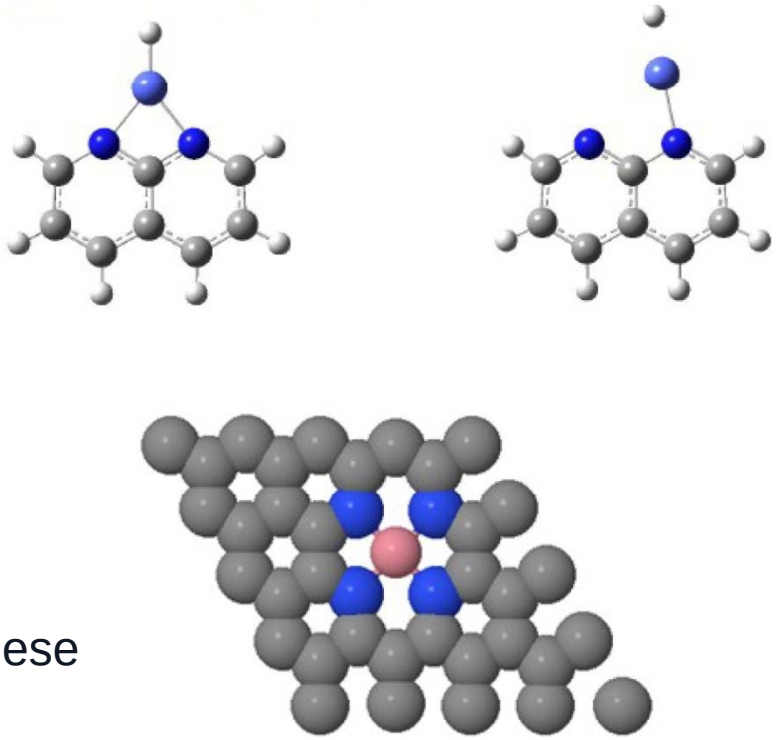



J. Peterson, *Local Structure Studies of Materials using Pair Distribution Function Analysis*, PhD Thesis, NMSU (2013)

R. E. Franklin, Acta Crystallographica, 3 (1950) 107.

# Example: 'Amorphous' Catalyst



X-ray PDFs reveal trace Me-X bonding in these materials.

DFT, EXAFS, and INS support both edge (long) and embedded (short) Co-N bonding is present.

DFT calculations provided by B. Keifer, NMSU.

# H Background Correction

- Empirical correction of H background in Total Scattering $S(Q)$ is allowing local atomic structure studies of functional materials previously assumed inaccessible.
- The correction has been applied successfully to nanoparticles, pyrolized porphyrin materials, MOFs, hydrated clays, and geopolymers.
- *Caveat: A more robust statistical determination of the background scattering is desirable, and will allow error propagation in data reduction software (currently incorrect).*
- Experimental removal of H background scattering with elastic PDF (as opposed to energy integrated) is planned.

# Determining Crystalline and Amorphous Phase Fractions with PDF

J. Peterson, J. TenCate, Th. Proffen, T. Darling, H. Nakotte, and K. Page, J. Appl. Cryst., 46 (2013) 332-336.

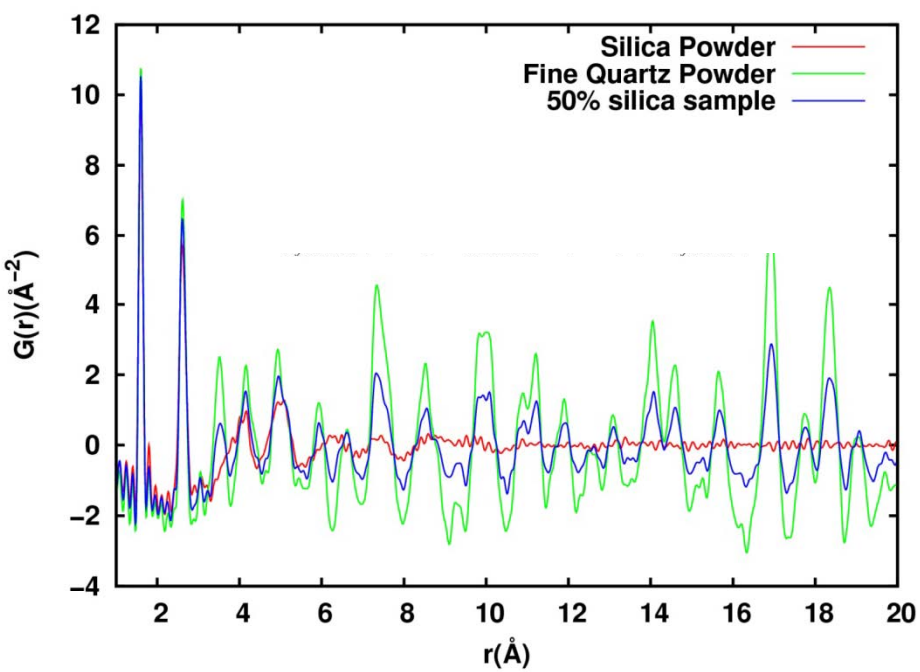
And examples from functional materials and rocks…

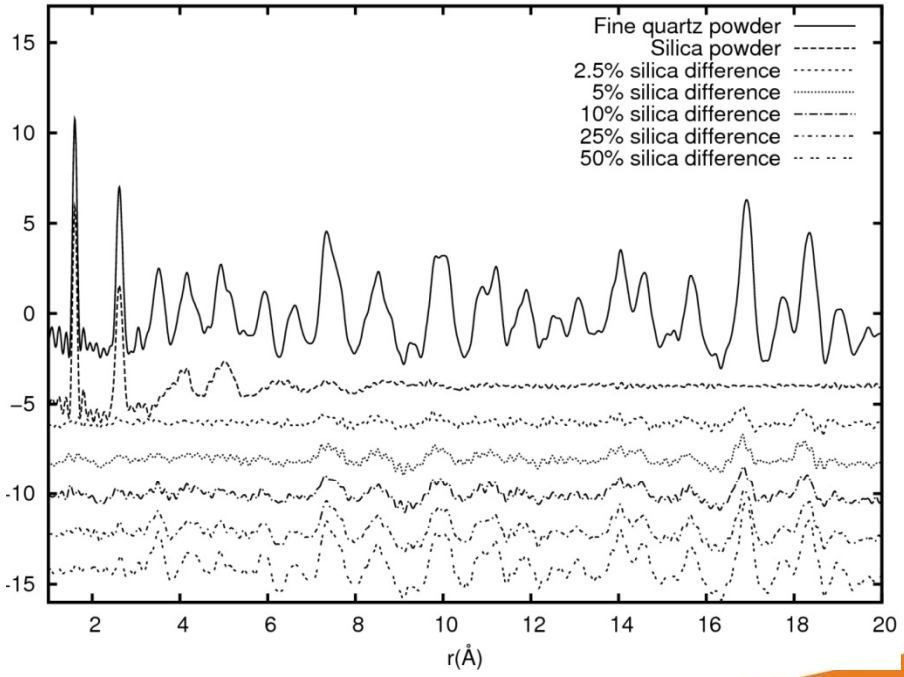
# Materials Problems Featuring Crystalline & Amorphous Phases

- Phase fraction determination based on Rietveld methods are accurate within a few percentage points (Cline *et al*., 2001; Stalick & Toby, 2001), but the nature of the amorphous phase is not revealed.
- Examples using PDF analysis in the last decade:
  - Tungsten particles in bulk metallic glass (Proffen *et al* 2005)
  - Graphitic poisoning in transition metal carbide catalysts (Page *et al*., 2008)
  - High temperature phase formation in geopolymers (White *et al*., 2010)
  - Ligand-capped nanoparticles (Page *et al*., 2010, 2011)
  - Surface or binding structure interactions (Billinge *et al*., 2005; Harrington *et al*., 2010; Chupas *et al*., 2011; Newton *et al*., 2012)
  - Guest-host structure interactions (Chapman *et al*., 2009; Kim *et al*., 2009; Damdournet *et al*., 2011; Zhao *et al*., 2011)
- Sensitivity was not proven.

# Determining Amorphous Content

- Collected high quality NPDF data for 10 g mixtures of quartz and silica powders (2.5, 5, 10, 25, and 50 wt. %)
- 2.5% amorphous content appears visually detectable with PDF.



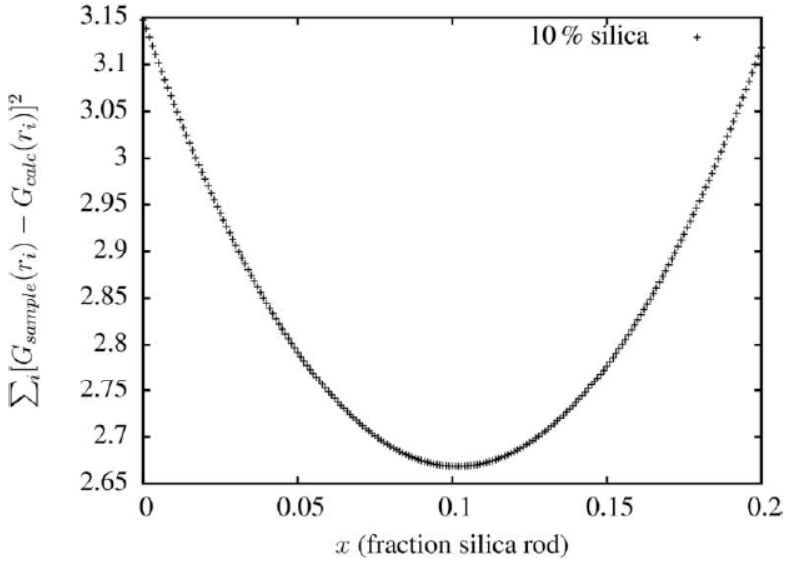
# Determining Amorphous Content

- Amorphous content is easily calculated with reference data sets and a simple minimization scheme.

$$G_{\text{calc}}(r) = x\, G_{\text{amorphous}}(r) + (1 - x)\, G_{\text{crystalline}}(r)$$

$$\sum_{i}^{N} [G_{\text{sample}}(r_i) - G_{\text{calc}}(r_i)]^2$$

- Accurate across complete range of real space data.

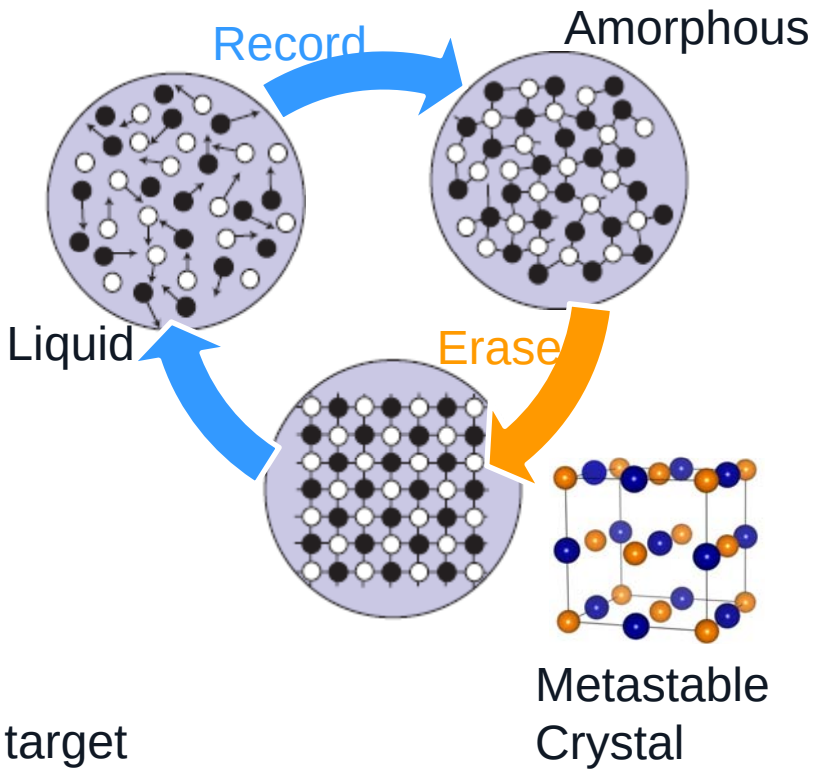



| Actual (%) | Calculated (%) |
|---|---|
| 2.5 | 0.2 |
| 5 | 2.9 |
| 10 | 10.5 |
| 25 | 26.3 |
| 50 | 50.7 |

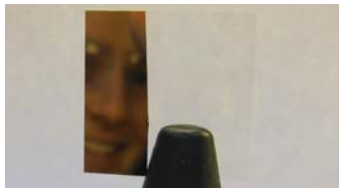
# Example: $GeSb_2Te_4$ thin films

**Challenges**

- Metastable phase is often only accessed in thin film (or nanoparticle) form
- Many studies are completed on pulverized thin films
- Few tools to capture and model amorphous and crystalline structure




**$GeSb_2Te_4$ Samples**

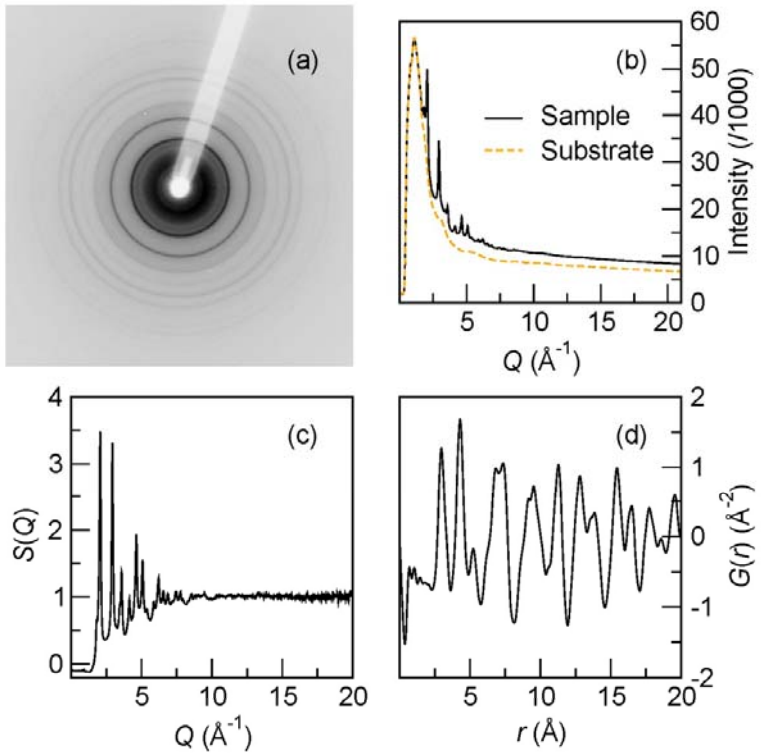


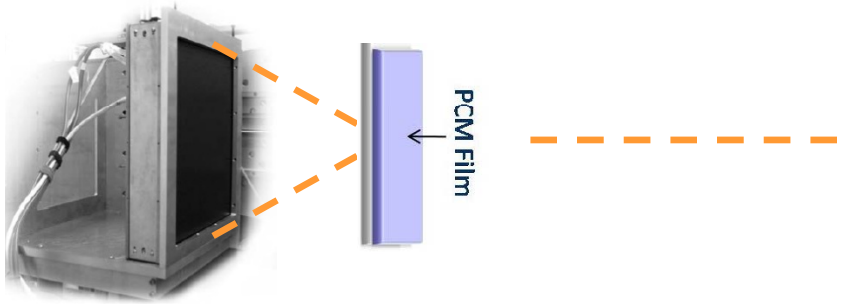
- Prepared by sputtering from a stoichiometric target
- Crystallized with thermal annealing

# Example: $GeSb_2Te_4$ thin films

Image Plate Detector at 11-ID-B, APS, Argonne

P.J. Chupas, K.C. Chapman, P.L. Lee, *J. Appl. Cryst.* **40**, 463-470 (2007).

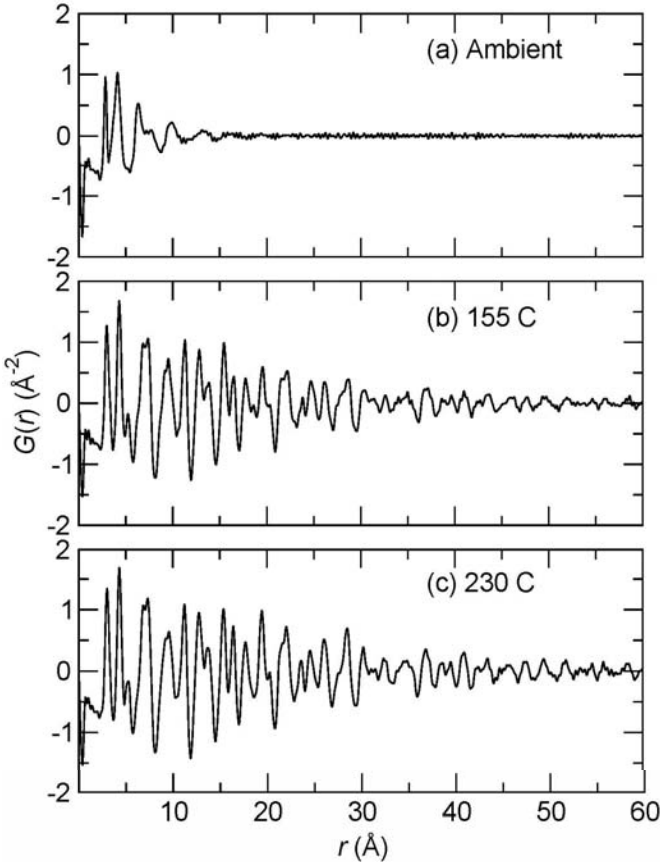


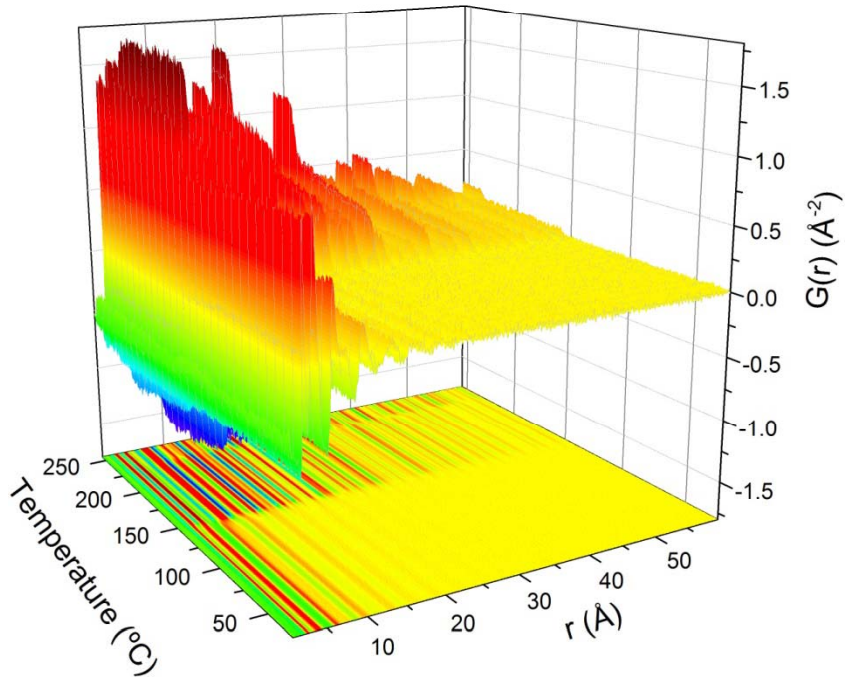

Data collected for 1 µm films deposited on kapton , thermally annealed in situ under flowing He to 155 C and measured at ~60 keV in transmission.

K. Page & J. K. Baldwin, in preparation.

# Example: $GeSb_2Te_4$ thin films

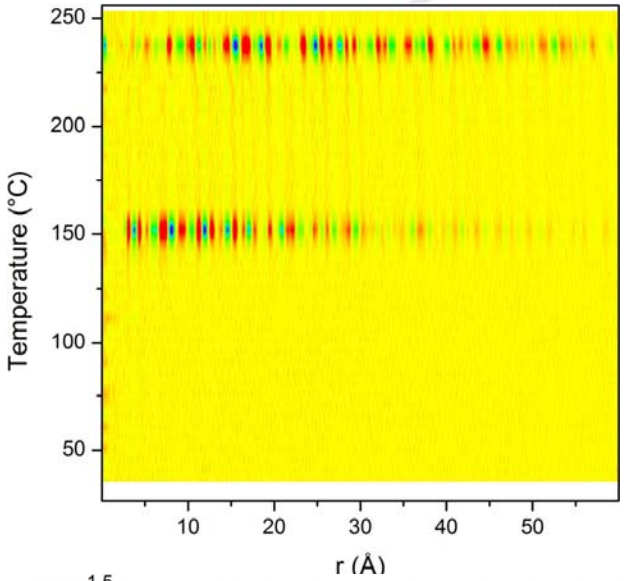


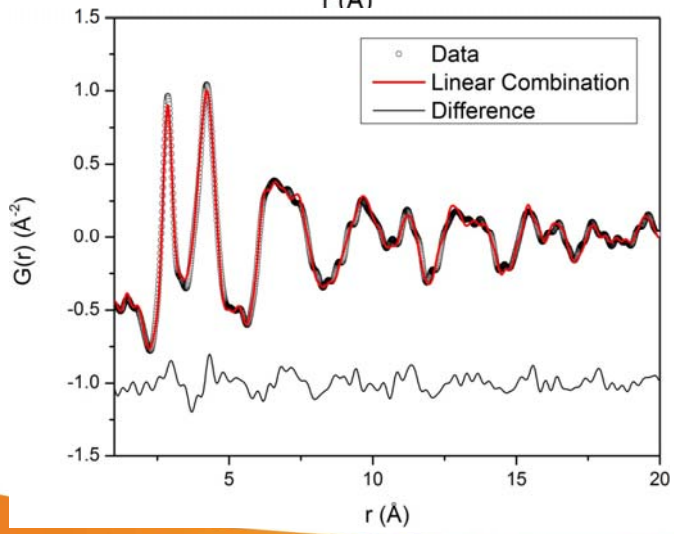

We have temperature dependent data (over 600 steps) for several ramping rates.

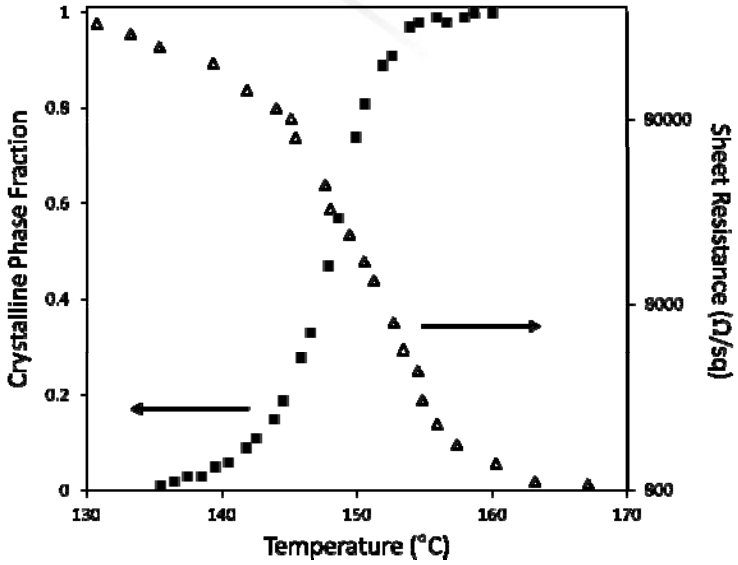



Models: correlation length scale, bond lengths and distribution of nearest neighbors, chemical short range order (ordering of Ge, Sb, and vacancies)

# Example: $GeSb_2Te_4$ thin films



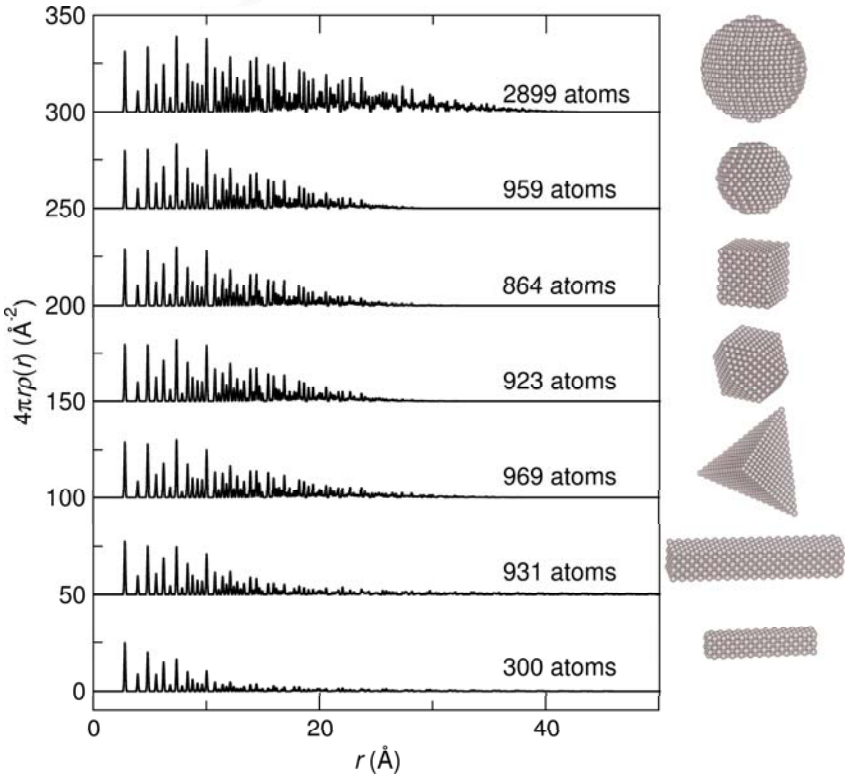

- Phase content links to reflectivity, charge transport, *etc.* across amorphous to crystalline phase transition
- Intermediate structure simply a superposition of end members

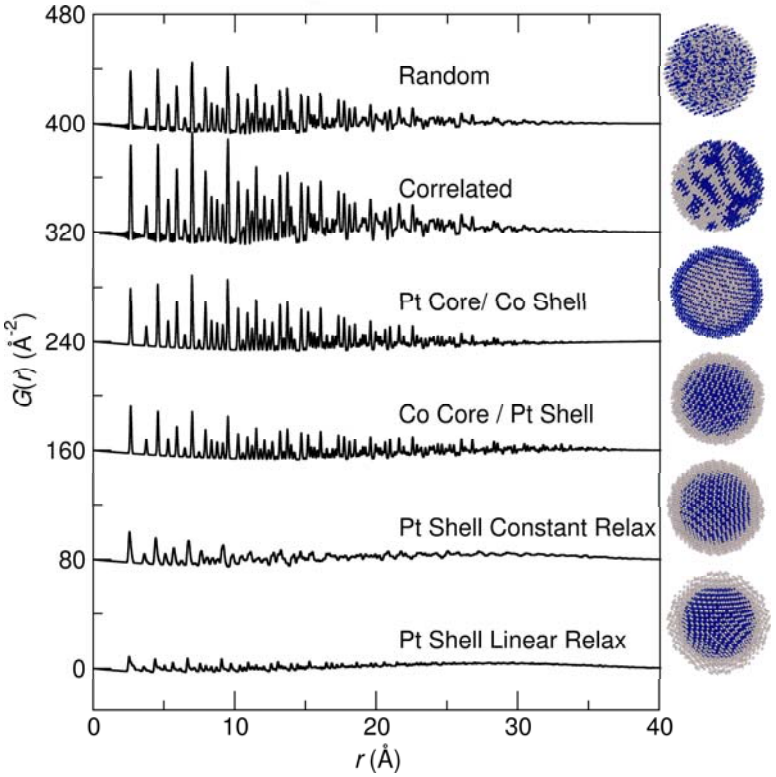
# Finite Nanostructure Modeling

K. Page, T. C. Hood, Th. Proffen, and R. B. Neder, J. Appl. Cryst. 44 (2011) 327-336.

The next 10 years…

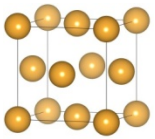
# Promising Prospects for Nano



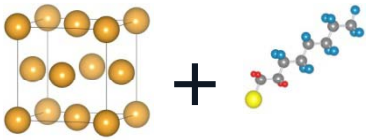




Atomic PDF has indirect sensitivity to size, shape, and architecture of finite materials because it is a distribution of all atom-atom pairs in the scattering volume… this is **a modeling challenge**.

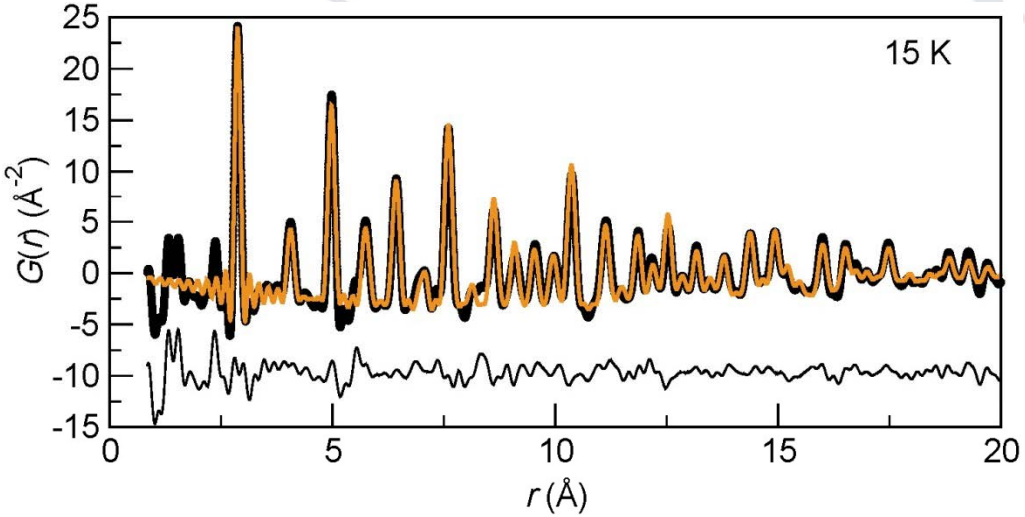
# Modeling is Moving Forward

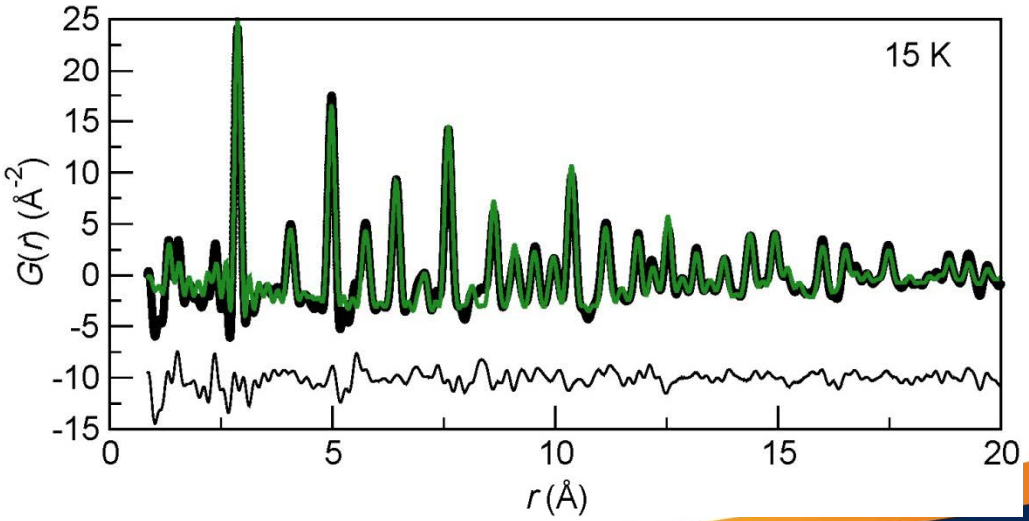


*The conventional PDF nanoparticle approach… no ligand modeling.*



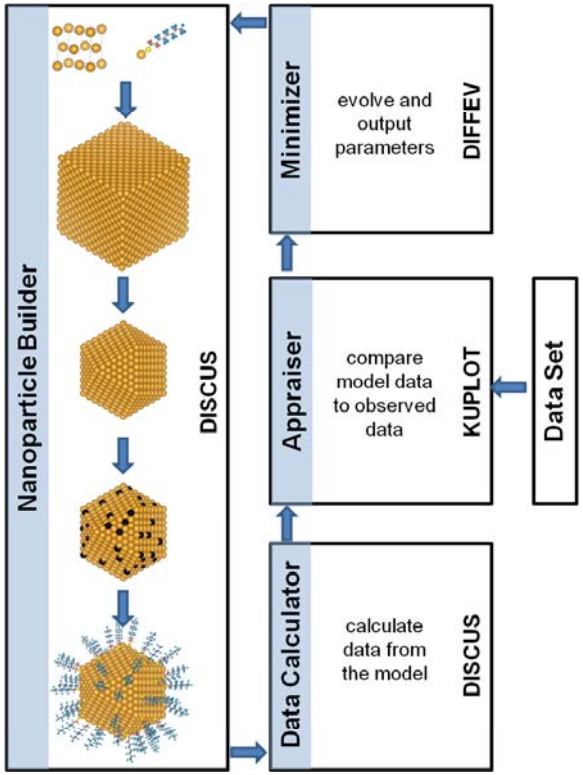
*The limit of what can be done with conventional approaches.*



# Modeling is Moving Forward

Our approach: the particle is modeled as a whole. An *fcc* Au particle is constructed with a shape. Ligands are located randomly at the particle surface with a defined surface density and defined Au-S distance, orientated out from the particle center.

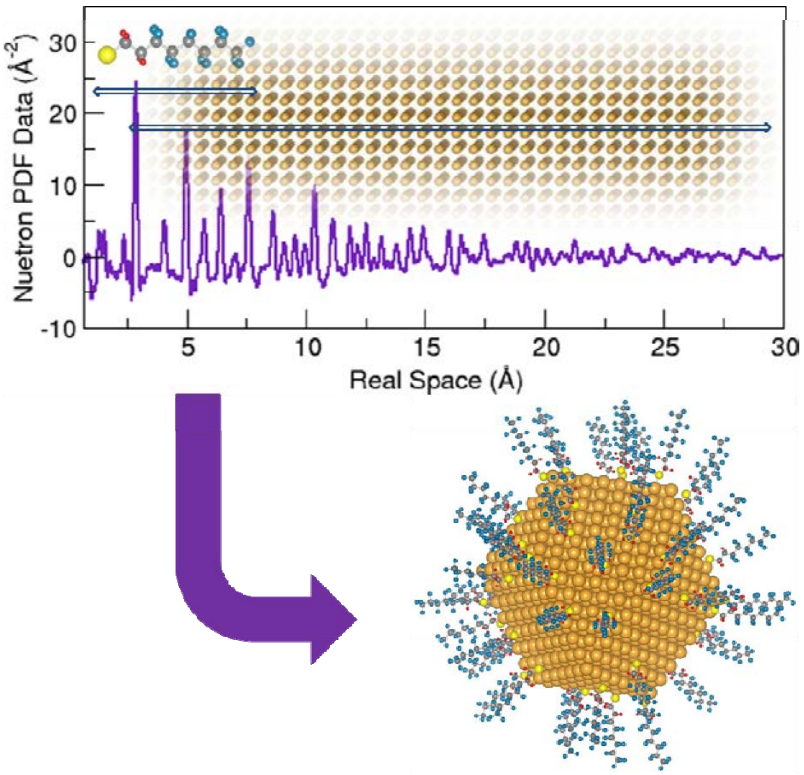



Refined with DIFFEV
Au *fcc*: $a$, $u_{iso}$(Au)
Ligand: surface density, angle with respect to particle face, Au-S distances

The refinement is run (takes several days) on a supercomputer cluster.

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

# Modeling is Moving Forward



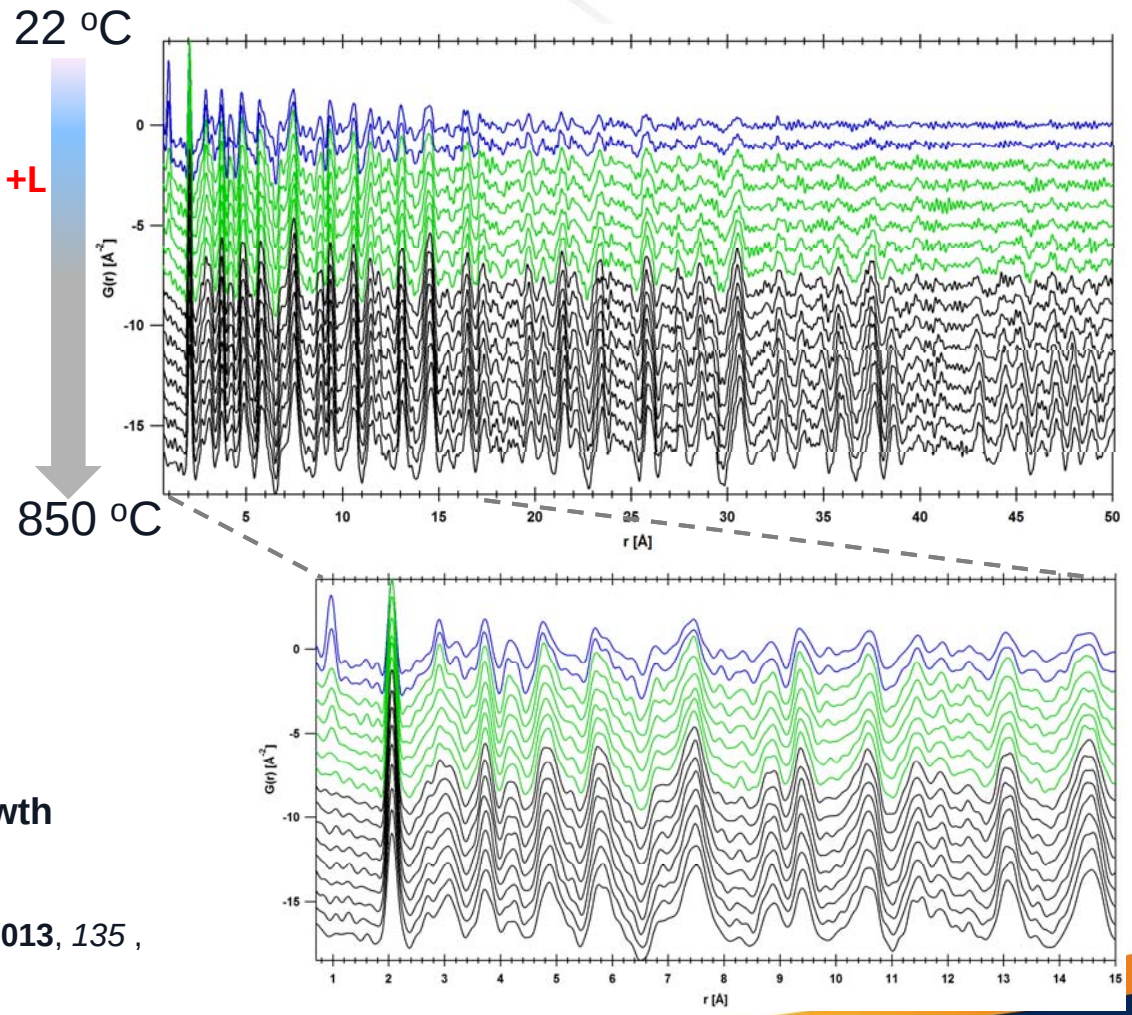

We are just now catching up to data collected nearly 10 years ago (2004).

**Next 10 Years**

- Quantifying experimental capabilities
- Exploring additional data inputs
- Experimenting with weighting of data sets and parameters
- Modules or user interfaces

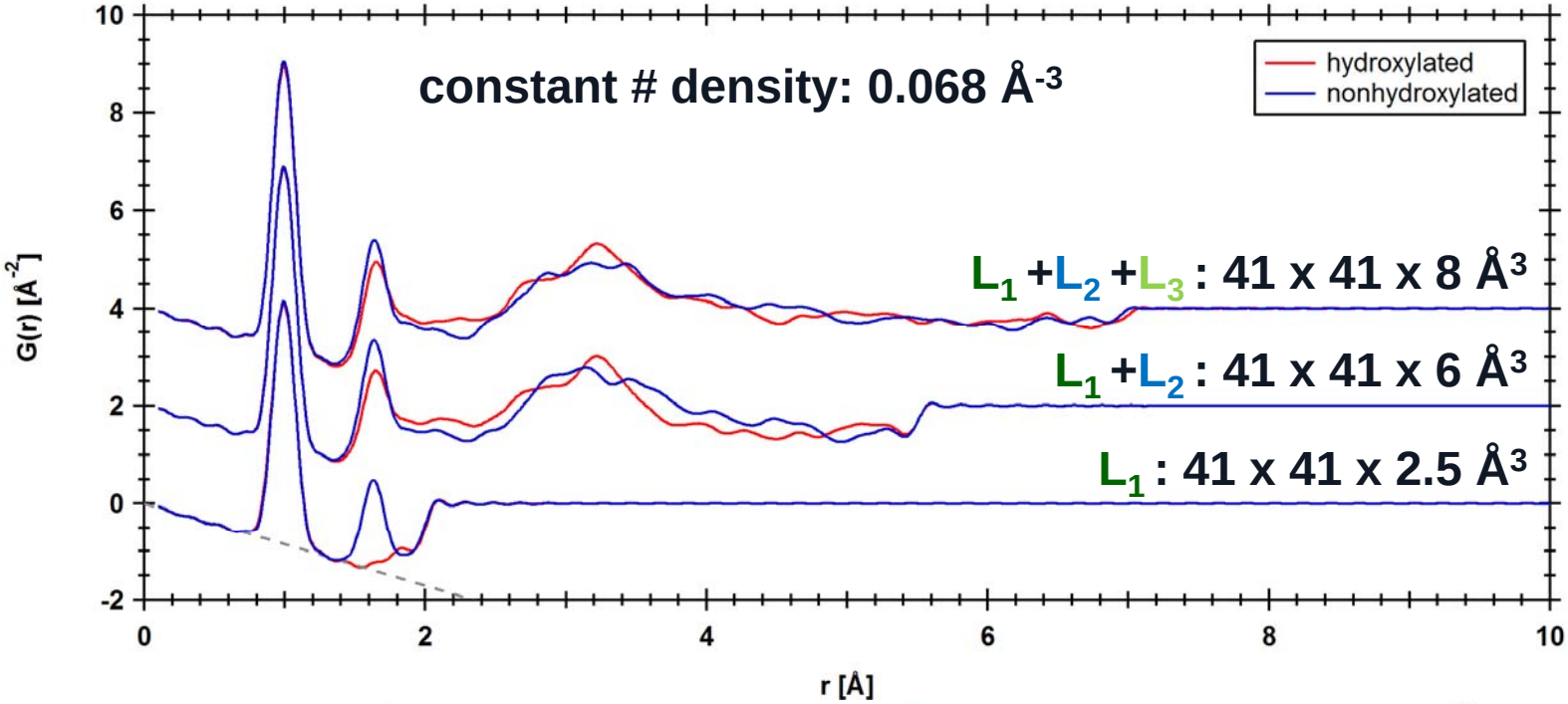
# Instrument Capabilities are Growing: In situ Dehydration, NOMAD, SNS

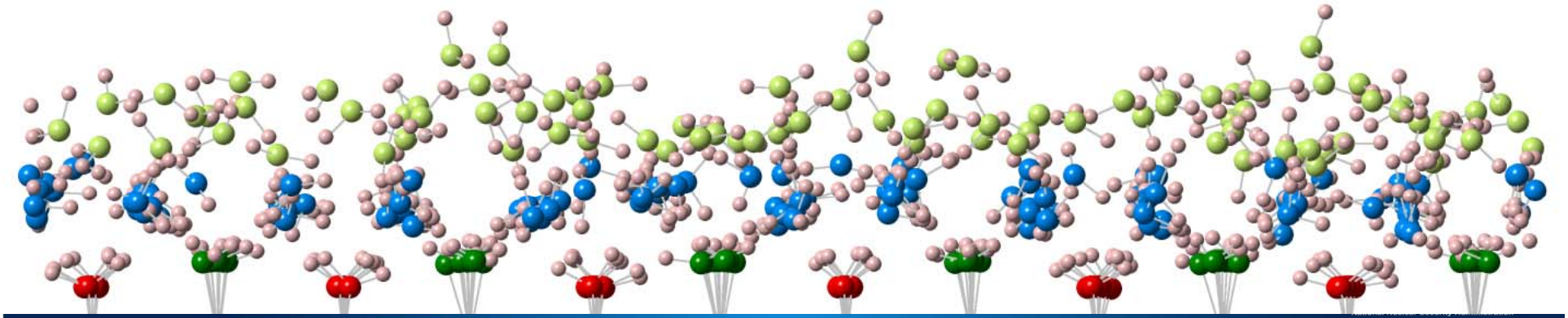
- **Starting with full coverage ($L_1$ +L +$L_3$ )**
- **Blue lines:**
  **22 and 50 ºC - $L_1$ +$L_2$ +$L_3$**
- **Green lines:**
  **50 to 350 ºC ( with 50 ºC increments) - $L_1$ +$L_2$**
- **Black lines:**
  **400 to 850 ºC ( with 50 ºC increments) – $SnO_2$ grain growth**




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

# MD Simulation of PDF



# Conclusions

- Corrections for Hydrogen Incoherent Inelastic Scattering
  →Try neutron PDF on your hydrogenous systems
- Amorphous and Crystalline Phase Quantification
  →Try PDF for your multi-phase system
- Signatures of Nanostructures in PDF
  →Data and modeling are improving
  →Continue maturing data reduction and modeling software
  →Benchmark local structure methods with materials studies

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Joe Peterson
Heinz Nakotte
Boris Keifer

**GST Thin Films (LANL)**
Kevin Baldwin

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