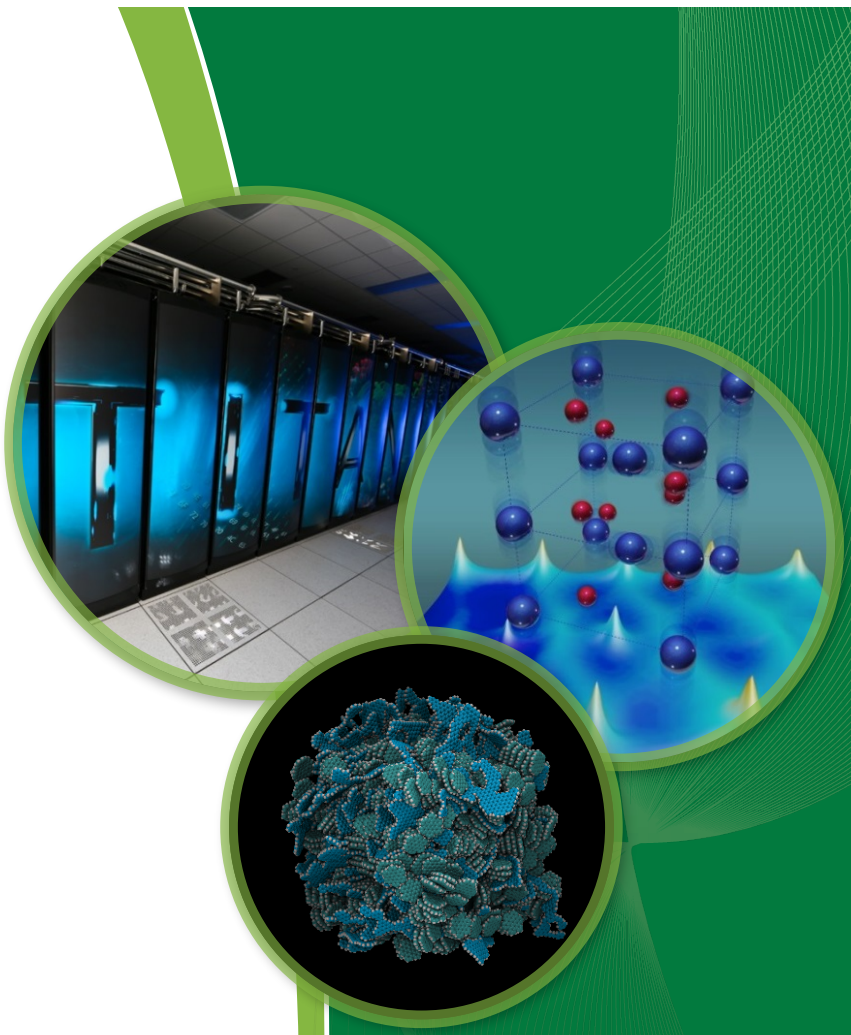
Introduction to total scattering and small box modeling



Simon A.J. Kimber

Diffraction group

Neutron Sciences Directorate

Oak Ridge National Laboratory

ORNL is managed by UT-Battelle
for the US Department of Energy

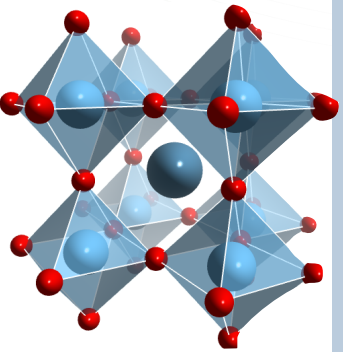
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

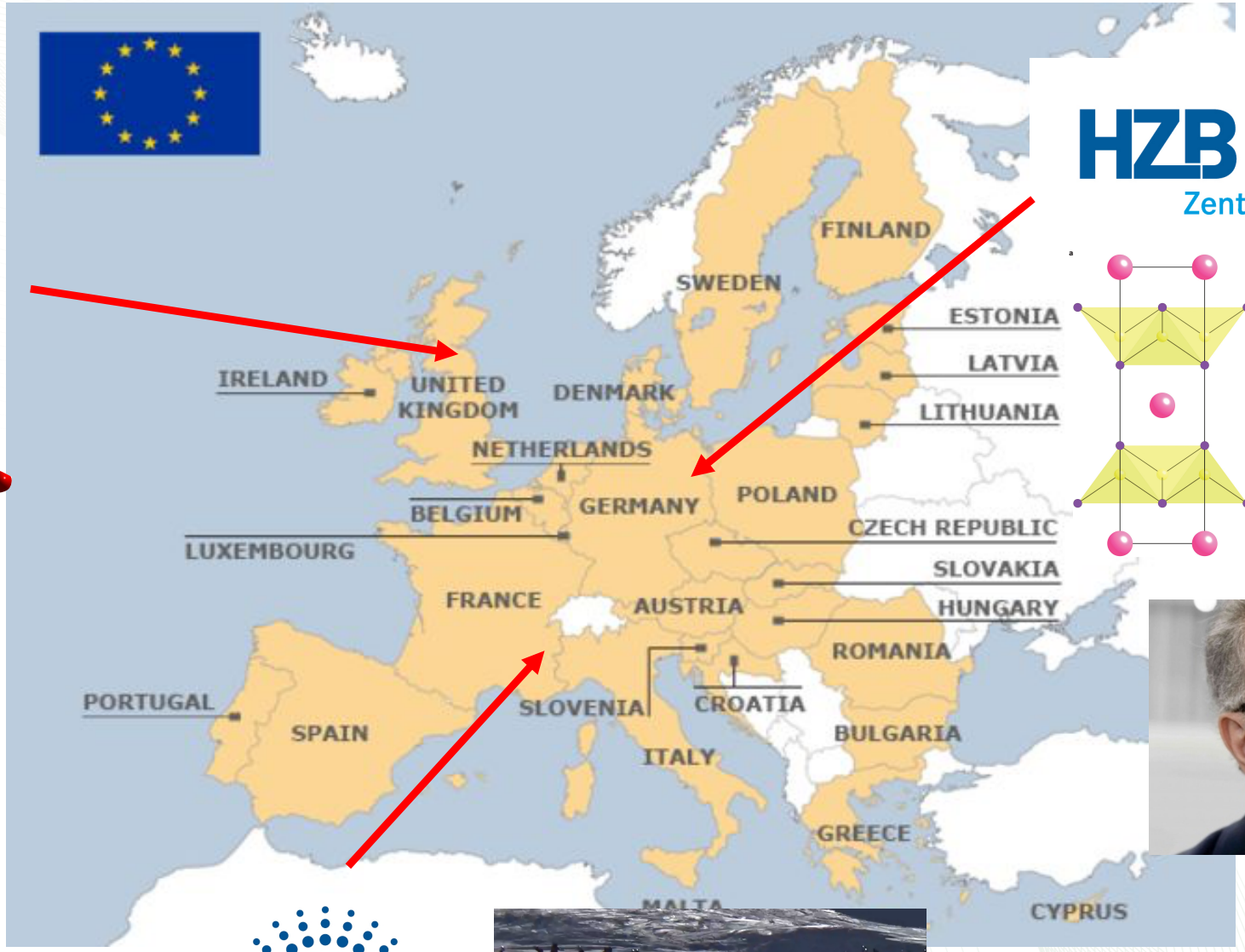
Outline

- About me, ORNL
- Why Fourier methods?
- Instrumentation for total scattering at ORNL
- What goes in the PDF?
- Small box modeling for total scattering
- Scientific examples, future techniques

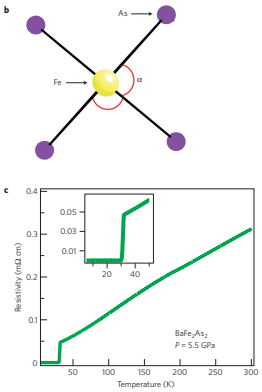
$$G(r) = 2/\pi \int_0^\infty Q[S(Q) - 1] sin(Qr) dQ$$

About me/ORNL





HZB Helmholtz Zentrum Berlin



(since Jan. 2017)

About me/ORNL

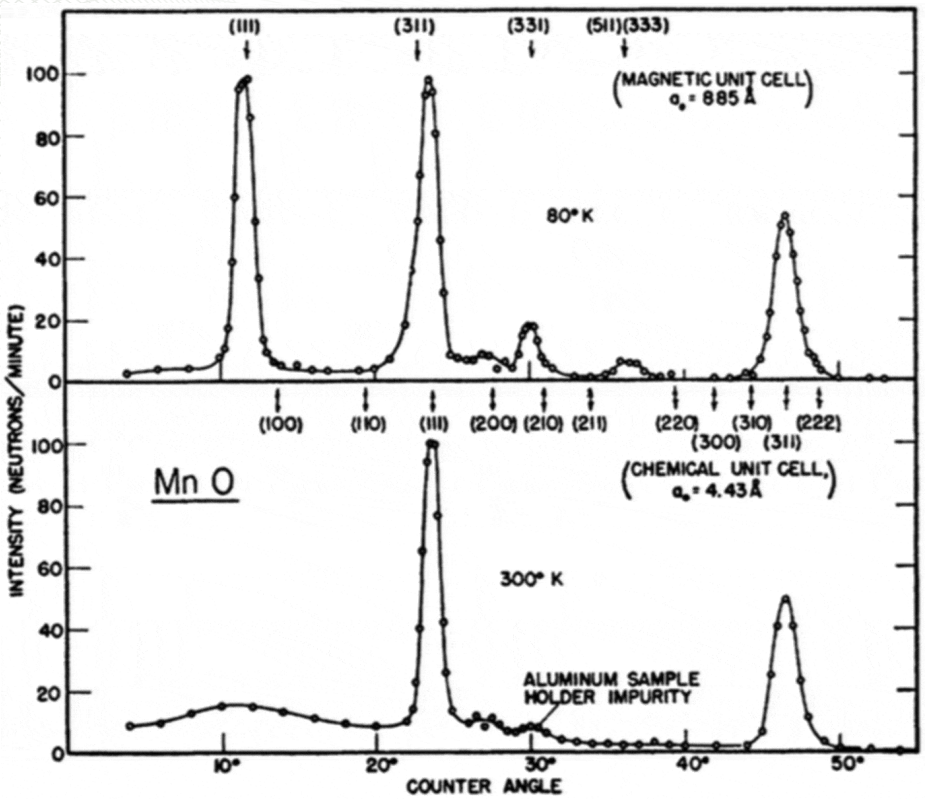
Tremendous privilege to work at (inter)national labs:

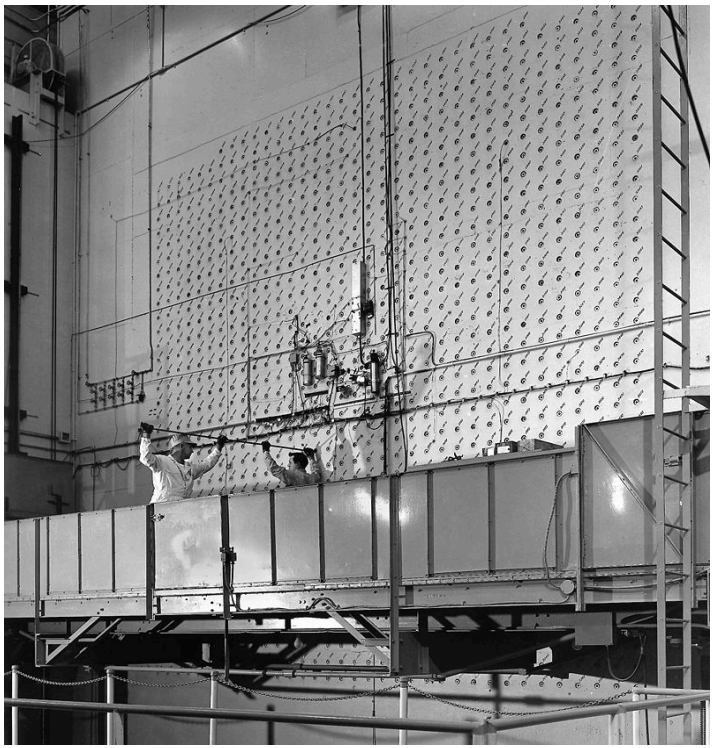
- Supporting user science, bring new methods to ‘market’

- Working toward strategic goals of laboratory, DoE and nation

<u>World leaders in neutron science</u>

About me/ORNL

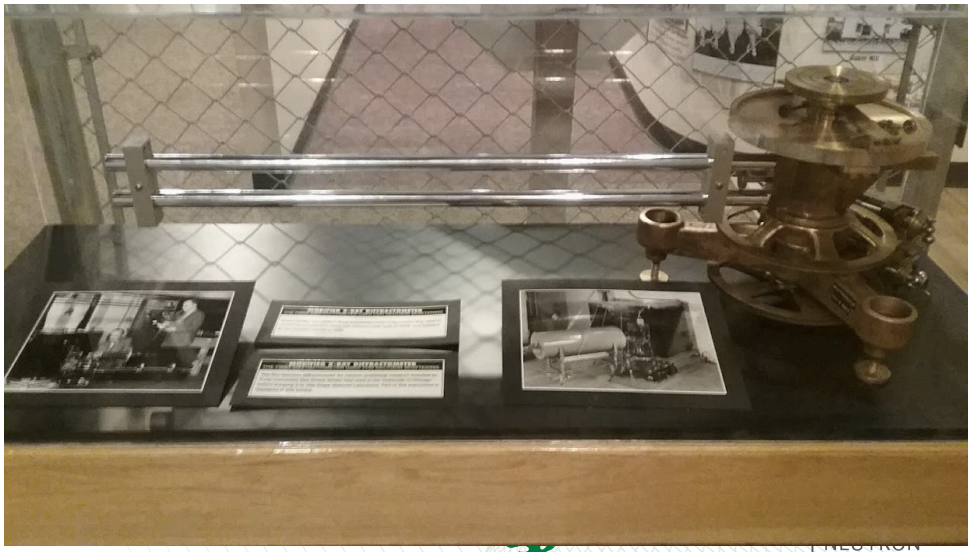




"Detection of AFM by neutron diffraction"

C.G. Shull, J. S. Smart, Phys. Rev., **76**, 1256-1257 (1949)

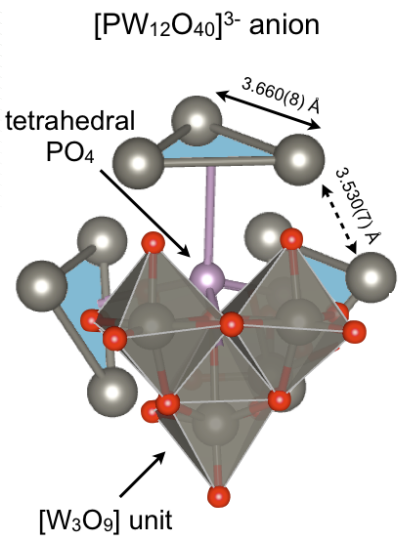
"*It has occurred to one of us (J.S.S.) that neutron diffraction experiments might provide a direct means of detecting antiferromagnetism*."

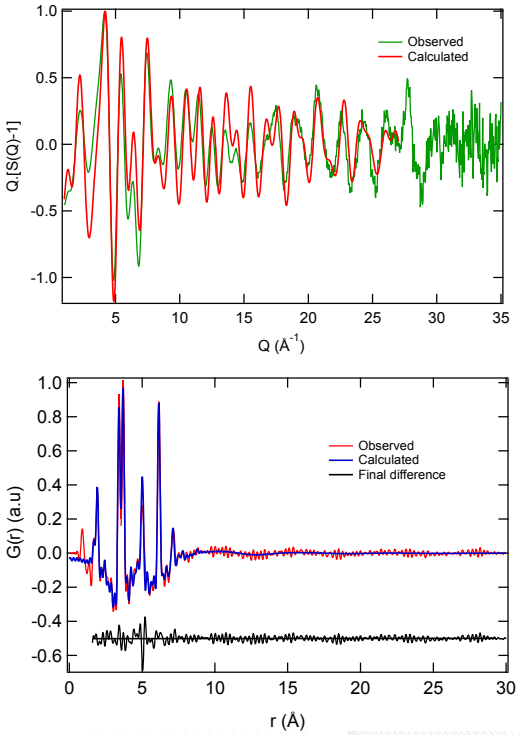


About me/ORNL

About me/ORNL

Why Fourier methods?





Information content of PDF = information content of raw data

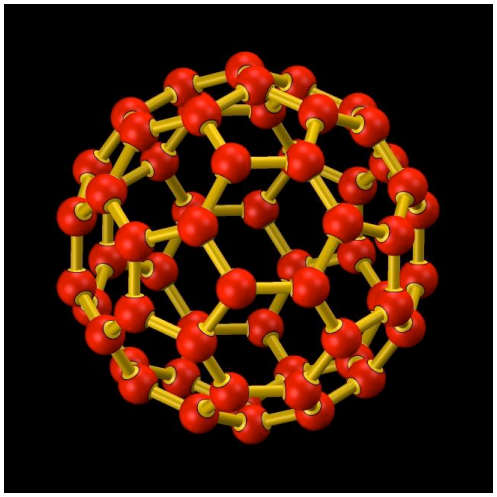
Broad signals better presented

Take advantage of Fourier filtering

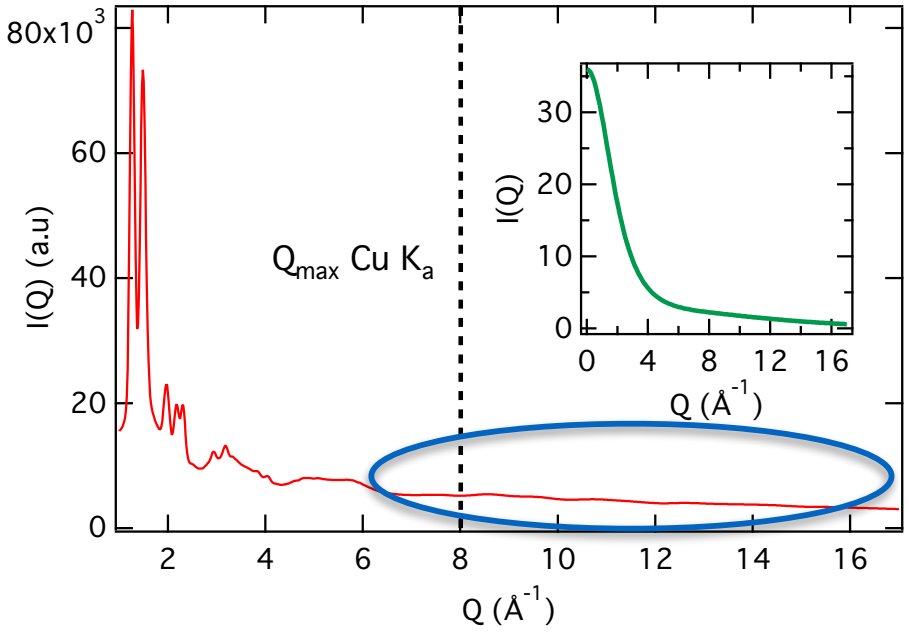
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

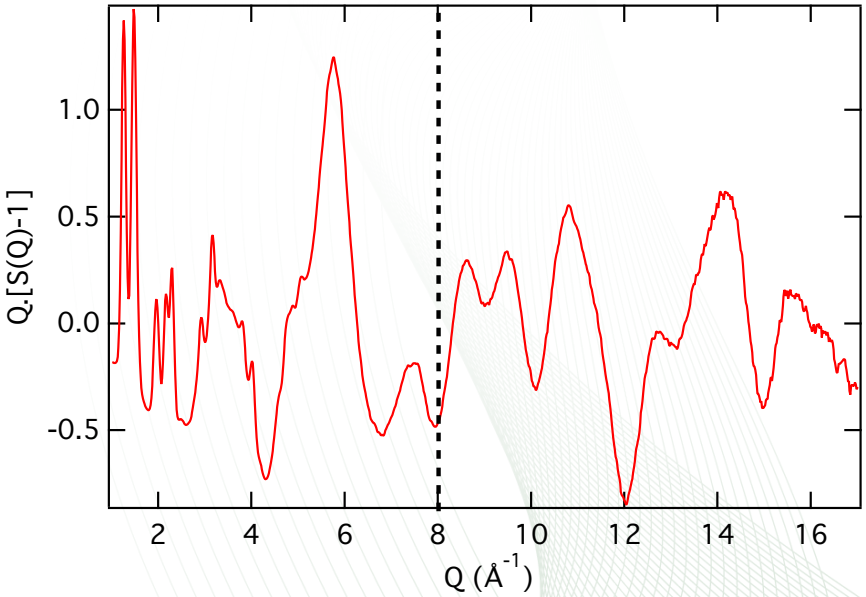
Why Fourier methods?

Best case is plastic crystal, with both long-range order (Bragg peaks) and short-range order (diffuse scattering)



$$Q = \frac{4\pi \sin(\theta)}{\lambda}$$





OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

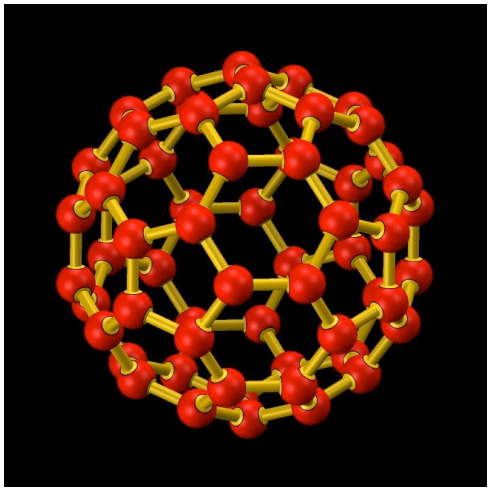
Why Fourier methods?

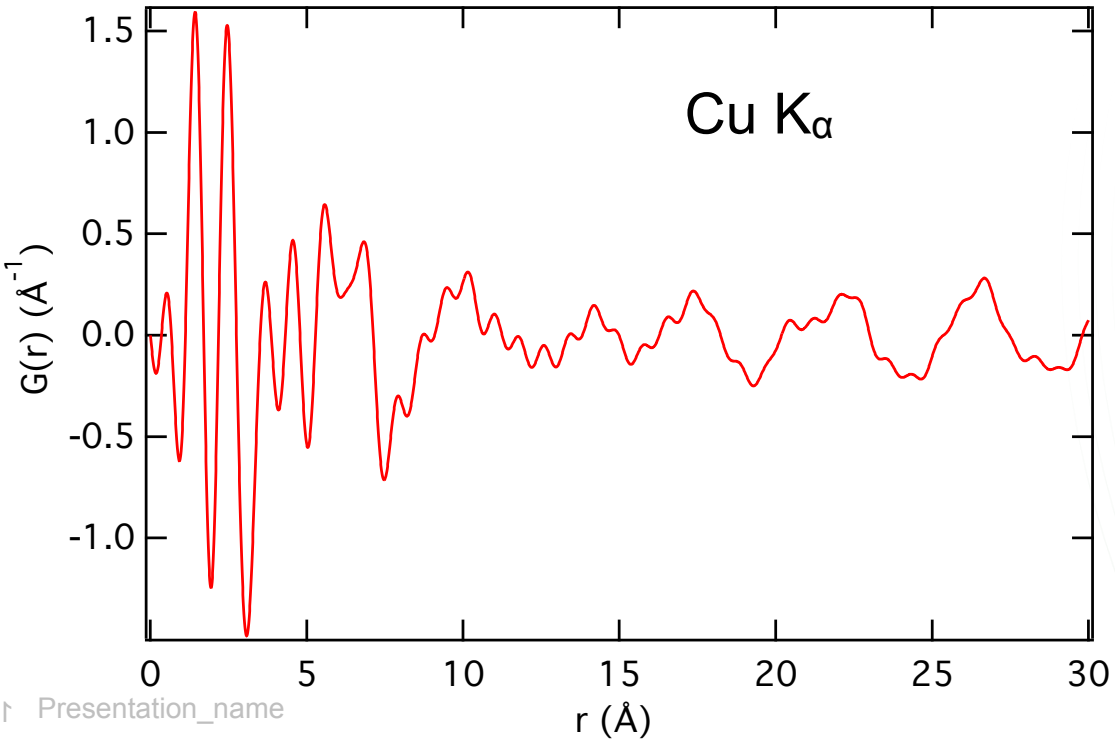
Fourier transform of Q.[S(Q)-1] taken using:

$$G(r) = 2/\pi \int_0^\infty Q[S(Q) - 1] sin(Qr) dQ$$

Result is a ‘pair distribution function’ or histogram of bond lengths

(model independent) information depends on ‘Q-max’, i.e. wavelength used





OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

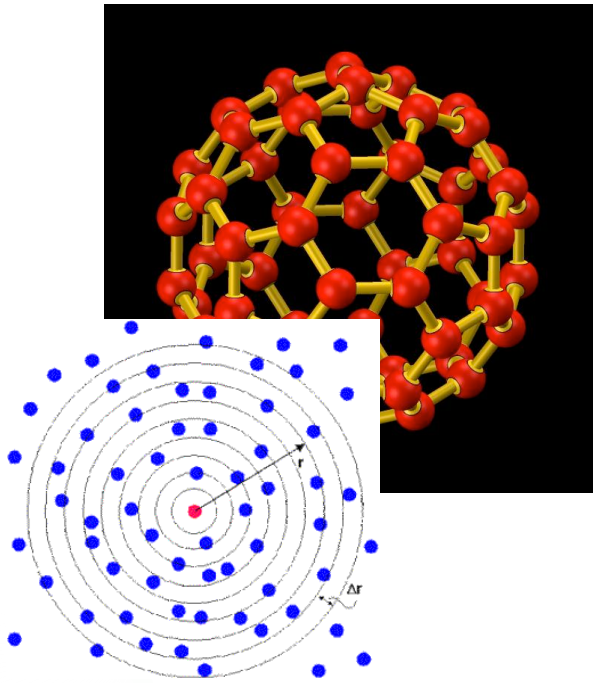
Why Fourier methods?

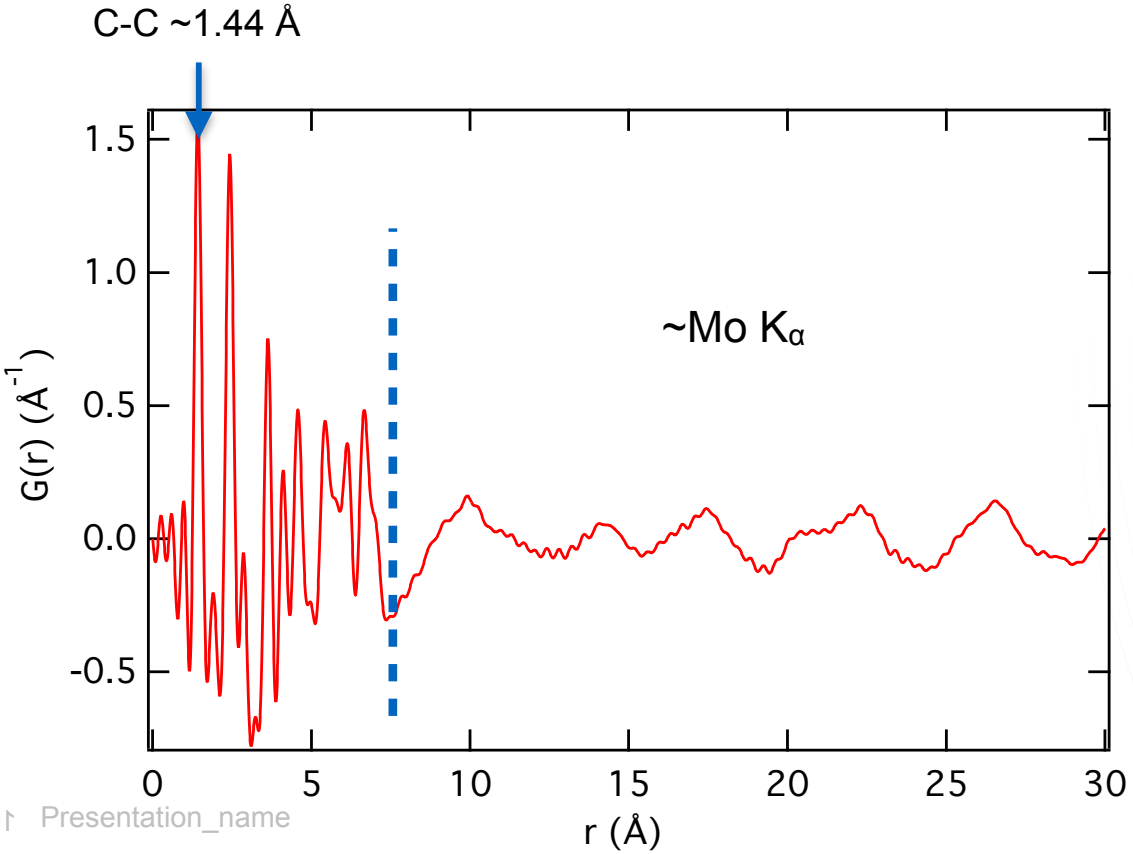
Fourier transform of Q.[S(Q)-1] taken using:

$$G(r) = 2/\pi \int_0^\infty Q[S(Q) - 1] sin(Qr) dQ$$

Result is a ‘pair distribution function’ or histogram of bond lengths

(model independent) information depends on ‘Q-max’, i.e. wavelength used





Pair distribution function connected to model:

$$G_c(r) = \frac{1}{r} \sum_i \sum_j \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

Peak positions related to oxidation states, intensities give atomic weights/coordination

Extent in *r* gives size of molecule

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

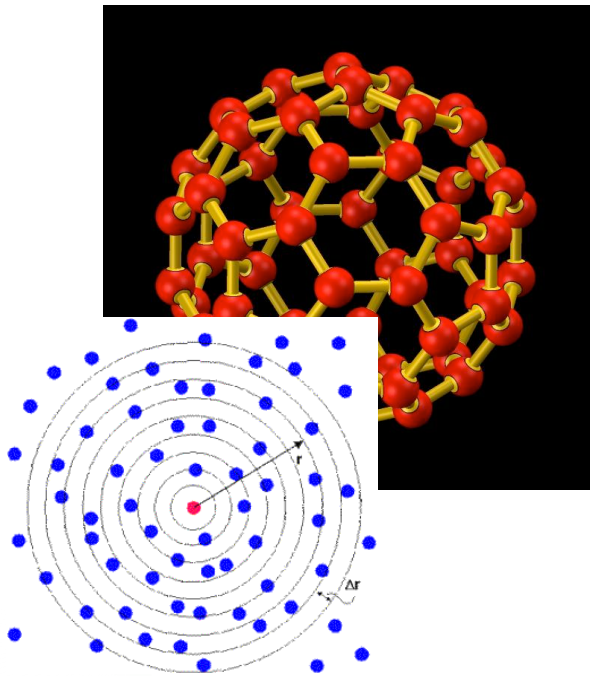
Why Fourier methods?

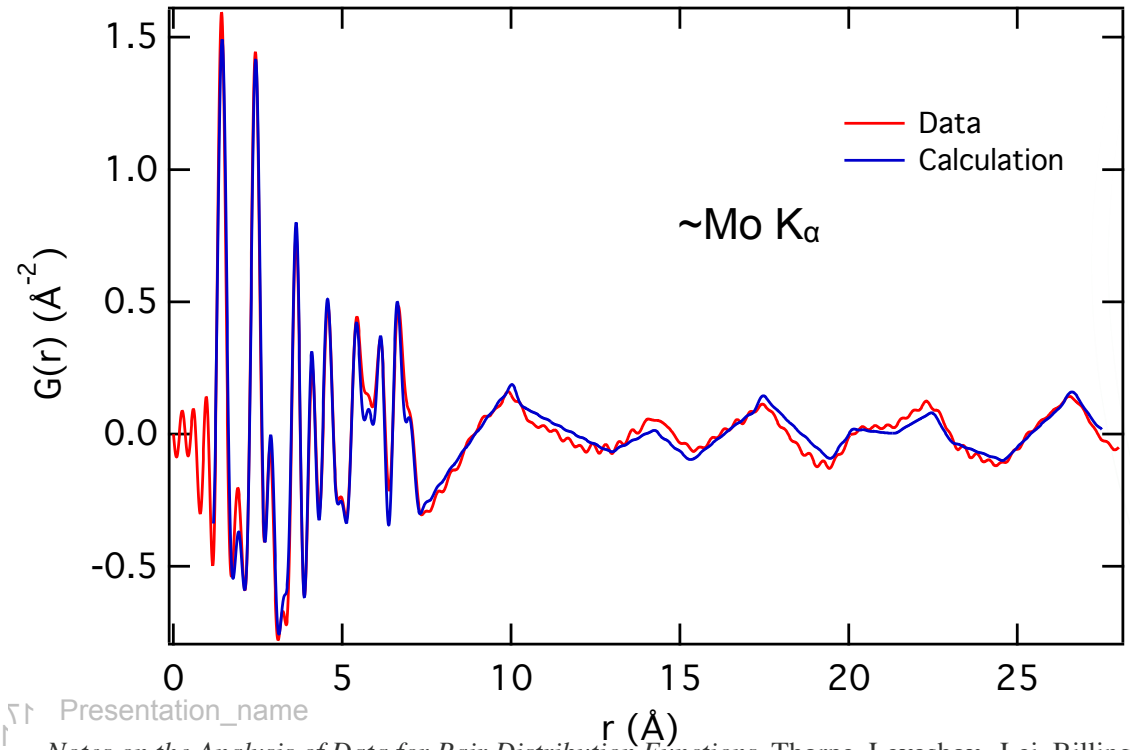
Fourier transform of Q.[S(Q)-1] taken using:

$$G(r) = 2/\pi \int_0^\infty Q[S(Q) - 1] sin(Qr) dQ$$

Result is a ‘pair distribution function’ or histogram of bond lengths

(model independent) information depends on ‘Q-max’, i.e. wavelength used





Pair distribution function connected to model:

$$G_c(r) = \frac{1}{r} \sum_i \sum_j \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

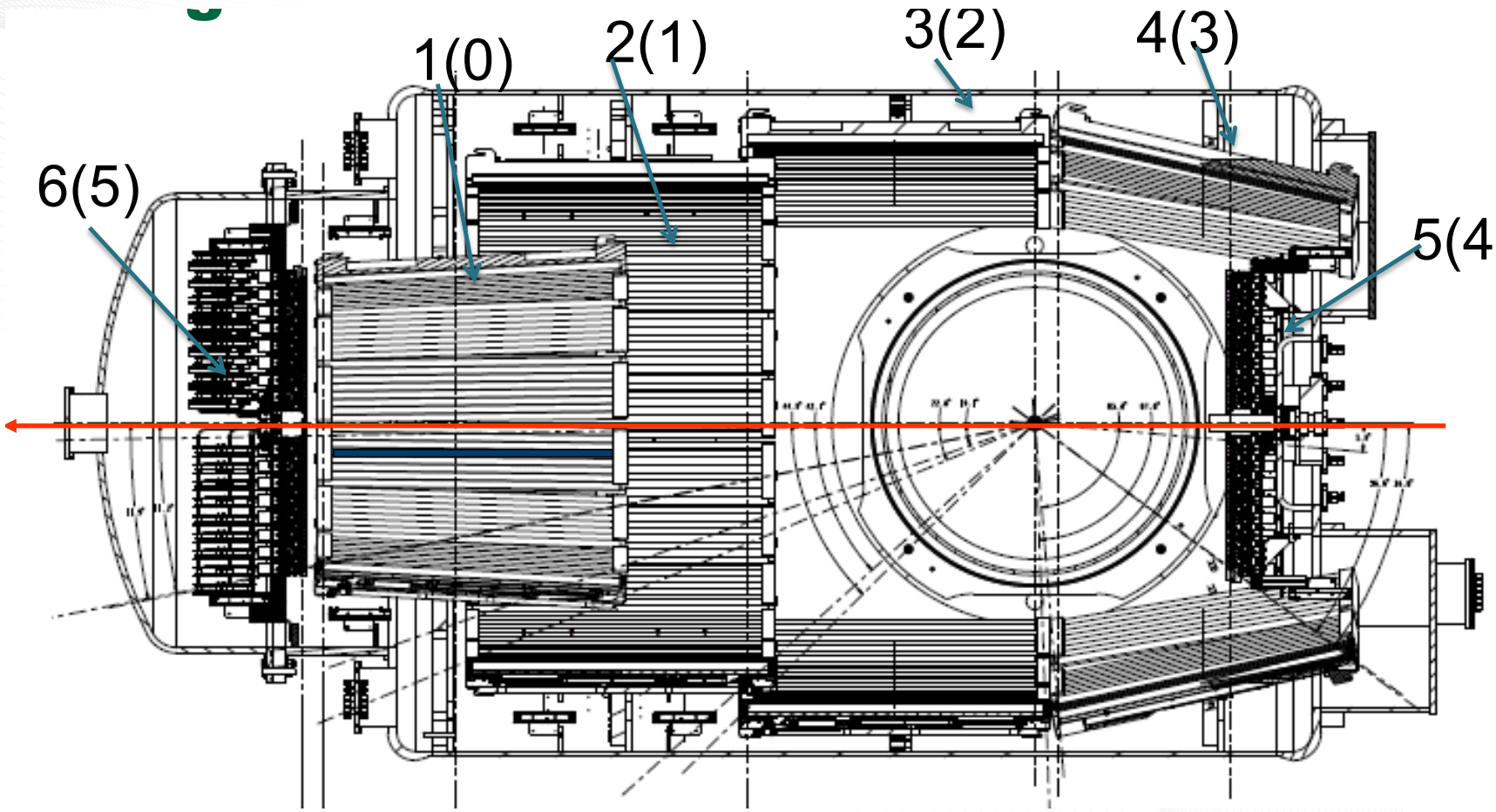
Peak positions related to oxidation states, intensities give atomic weights/coordination

Extent in *r* gives size of molecule

Notes on the Analysis of Data for Pair Distribution Functions, Thorpe, Levashov, Lei, Billinge, (2002)

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

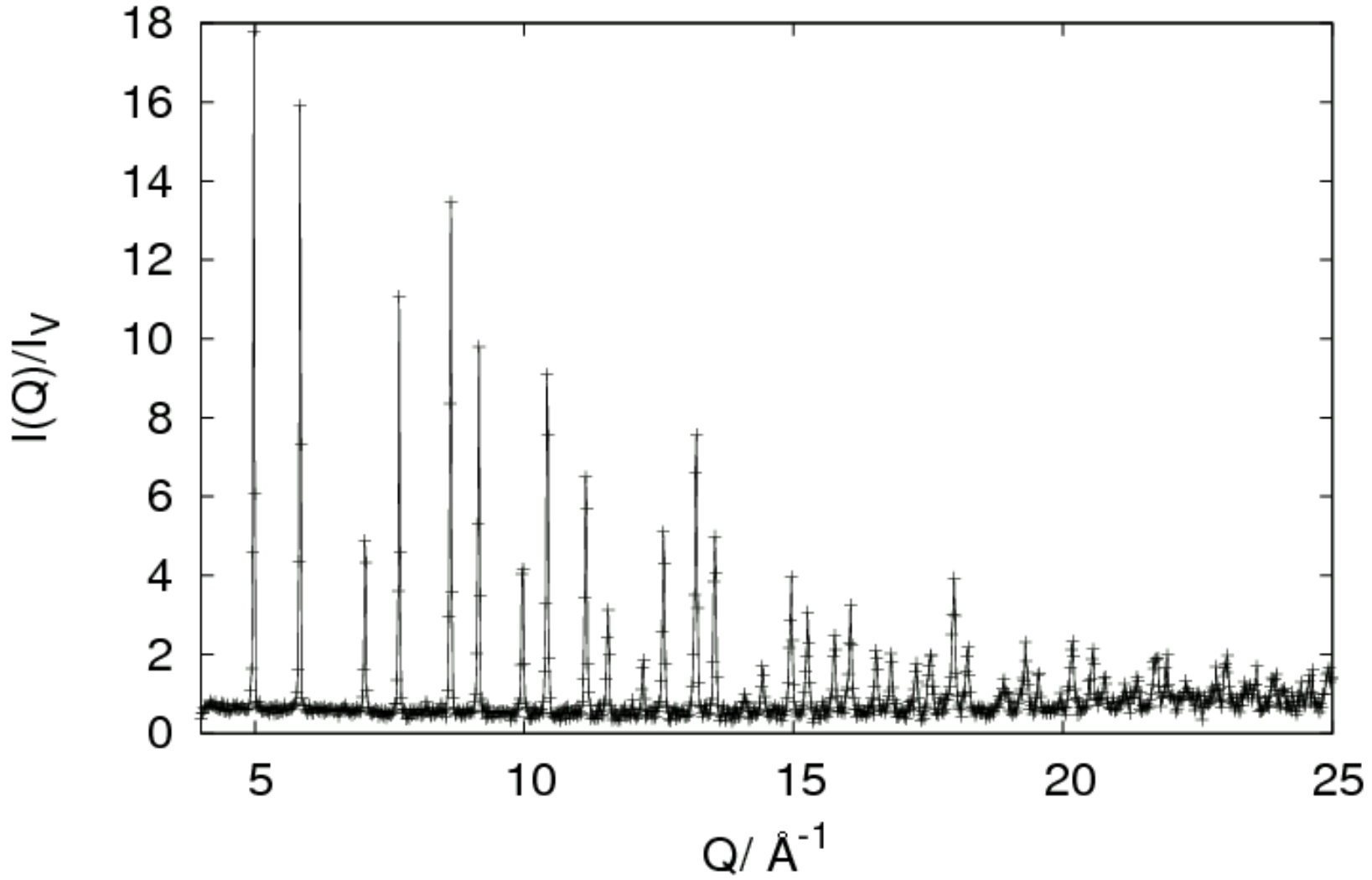
Total scattering at ORNL



19.5 m, decoupled poisoned supercritical hydrogen
4.0 sr detectors, $0.02 < Q < 100\ A^{-1}$

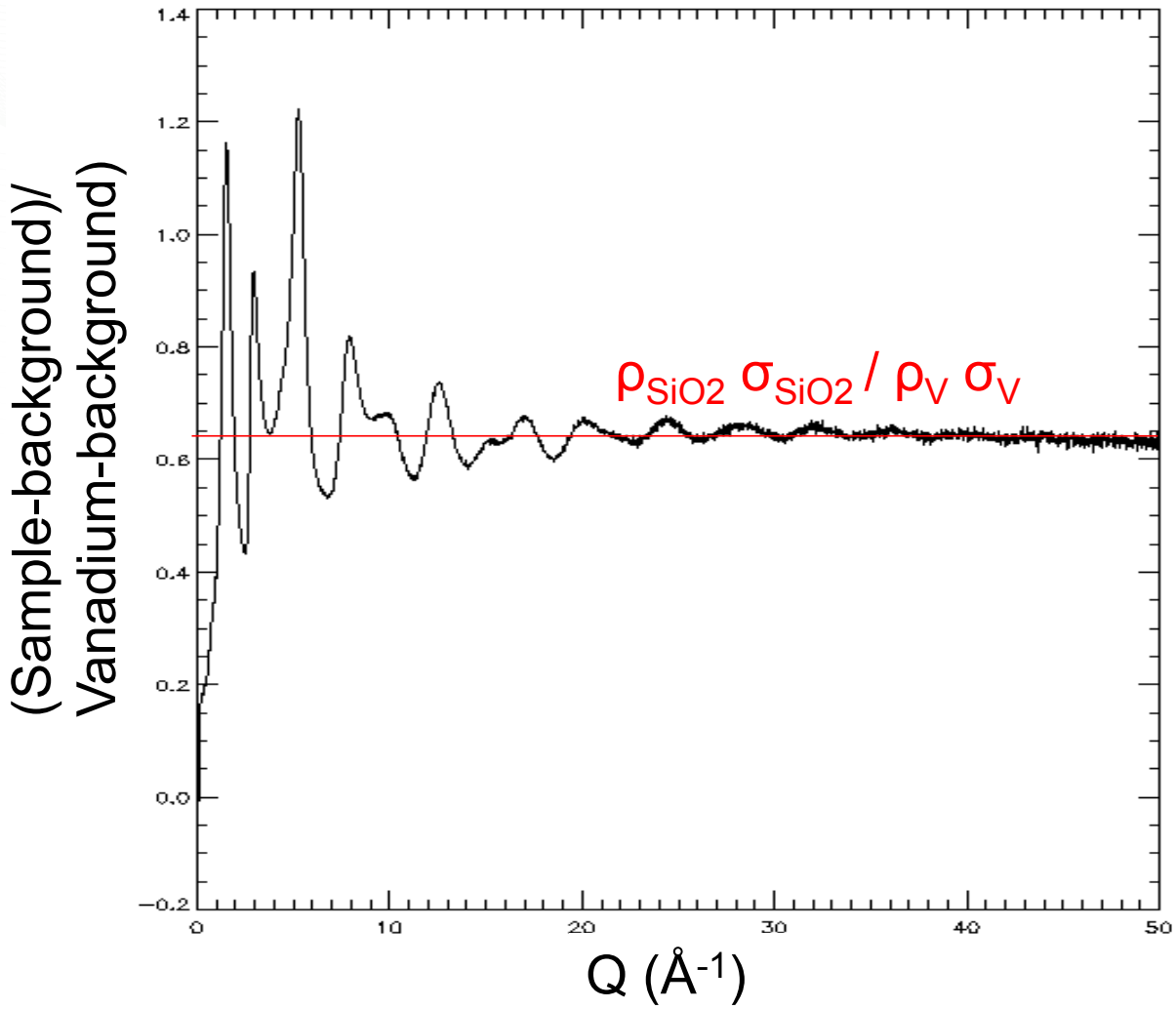
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Total scattering at ORNL



0.6 g of diamond in 1 s (backscattering banks only)

Total scattering at ORNL



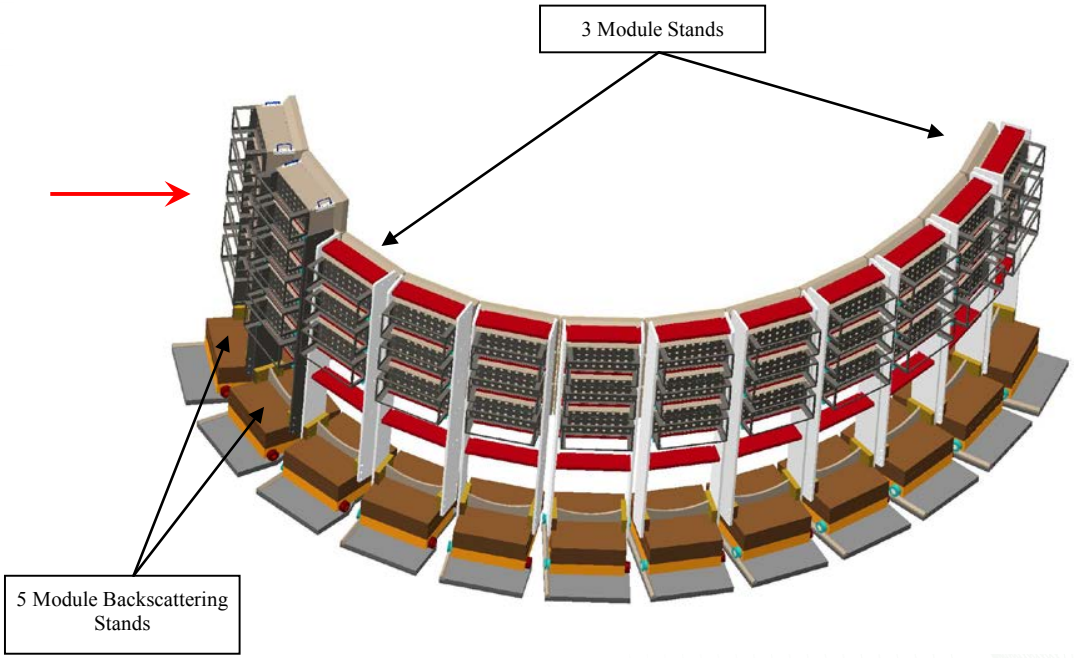
20 mins on glassy silica

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Total scattering at ORNL

POWGEN is narrow band width diffractometer

1 Å band width, 10-170 ° coverage

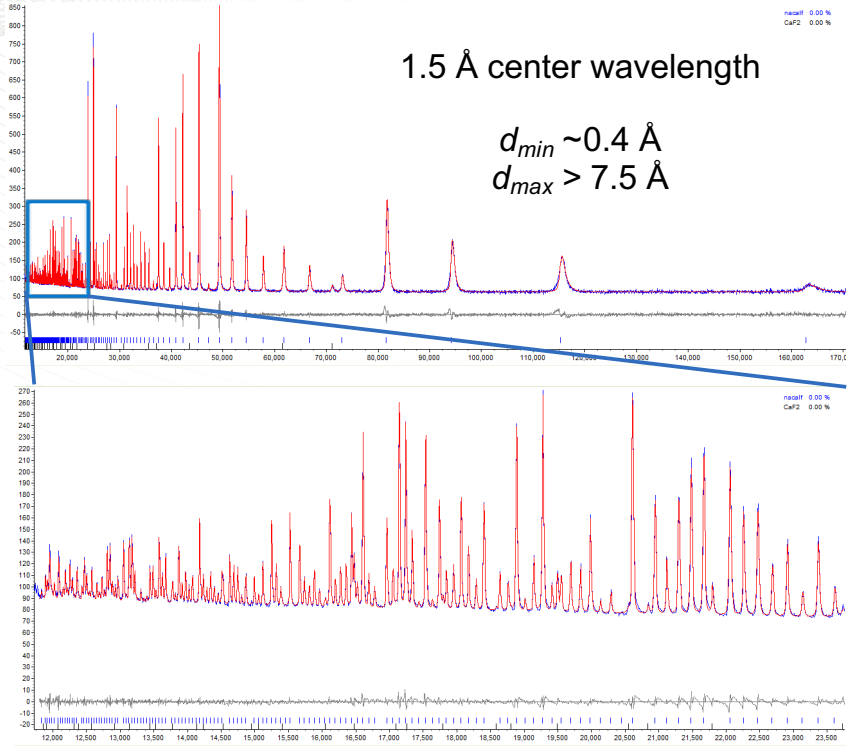


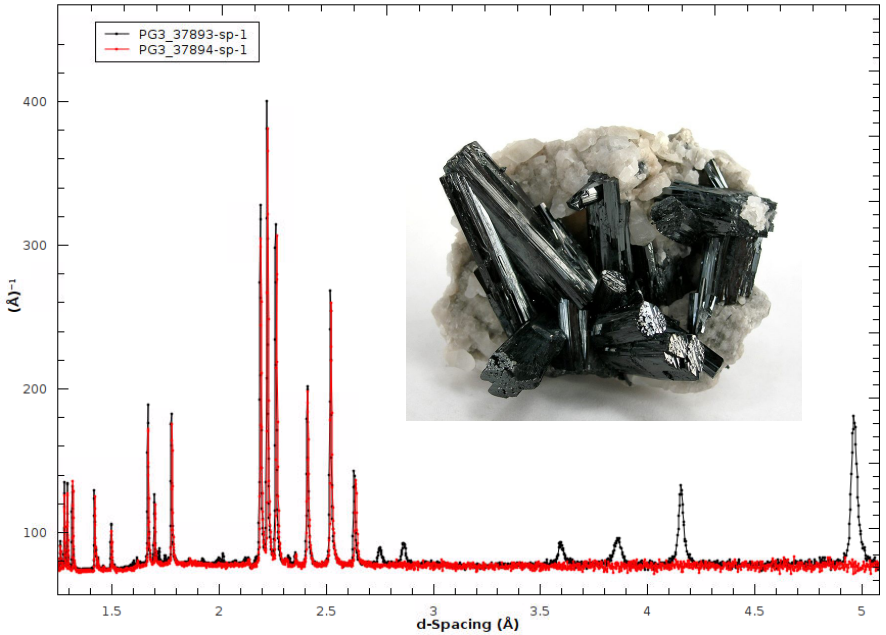
Layout of detectors now matches design philosophy

=> no banking

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Total scattering at ORNL





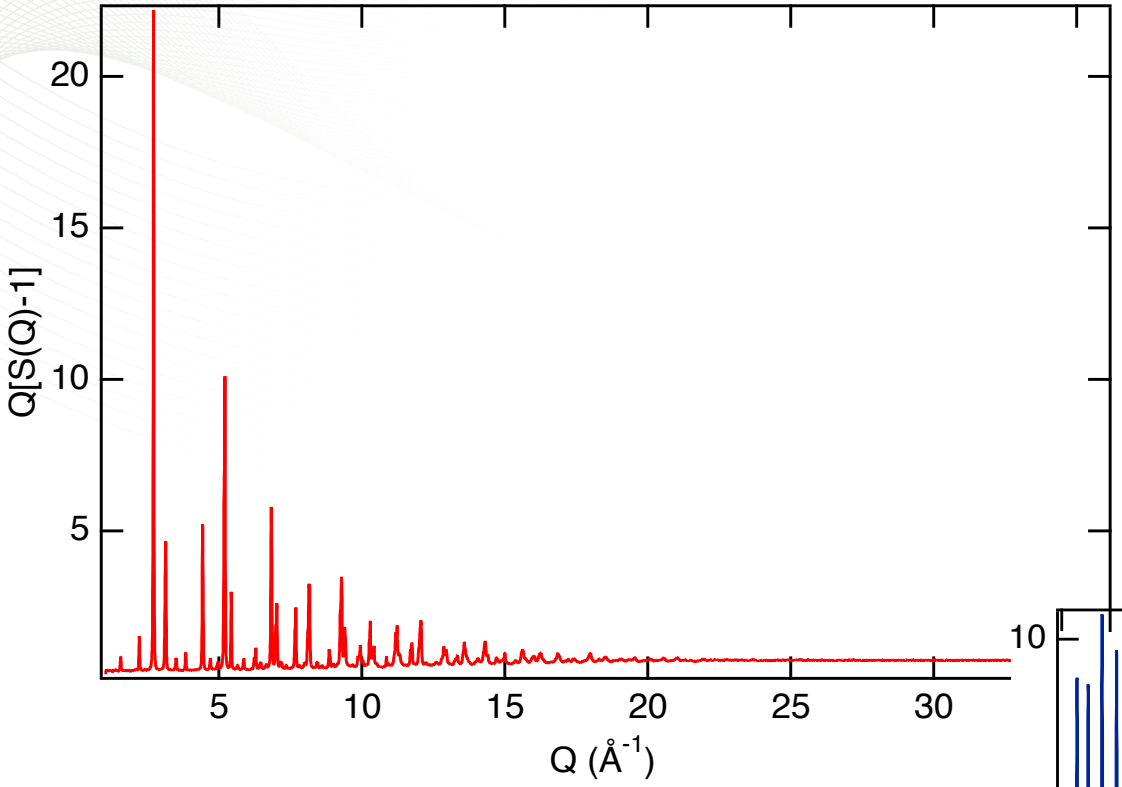
MnOOH

POWGEN is highest resolution NPD in North America

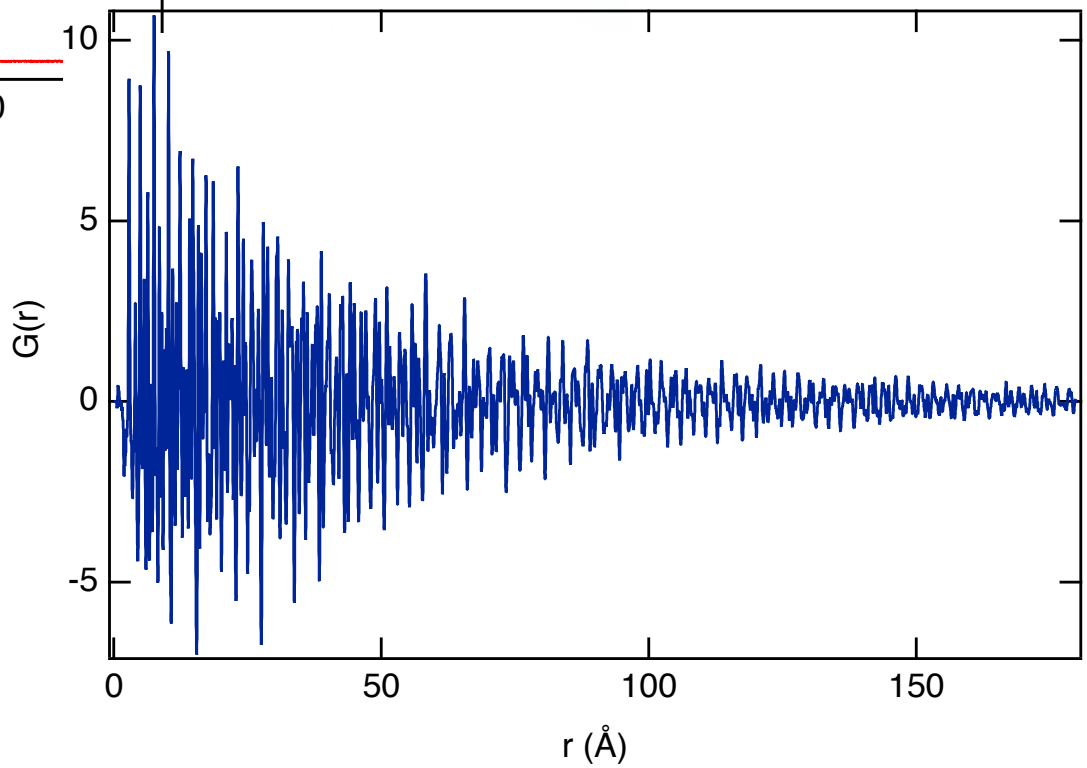
Highly flexible, typically use center wavelengths of 0.7, 1.5…. 4.7 Å etc

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Total scattering at ORNL



At 0.7 Å center wavelength, POWGEN covers sufficient Q-range for PDF in a single histogram



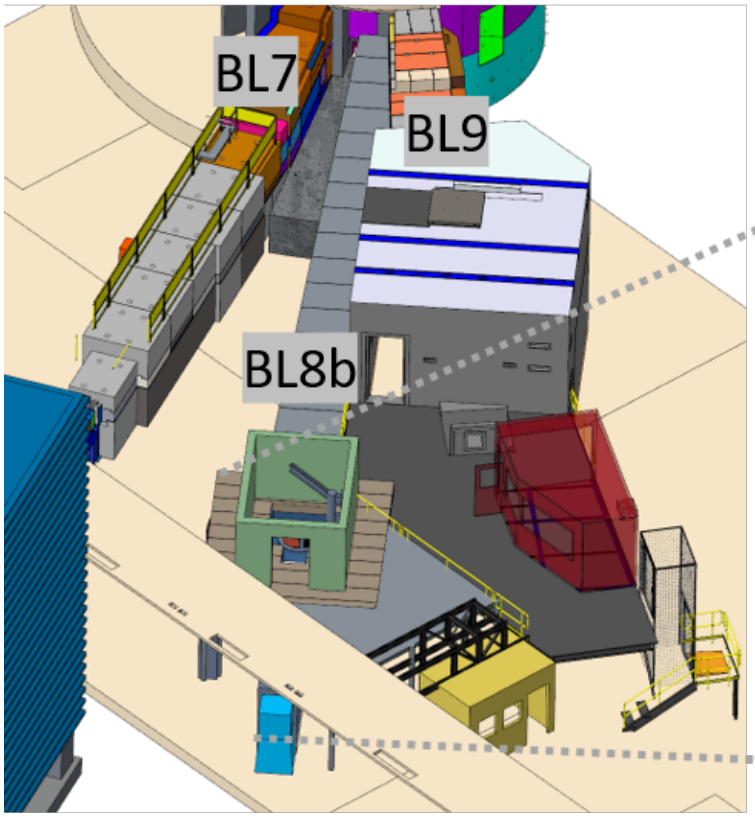
Data trivial to convert to r-space and easy to model

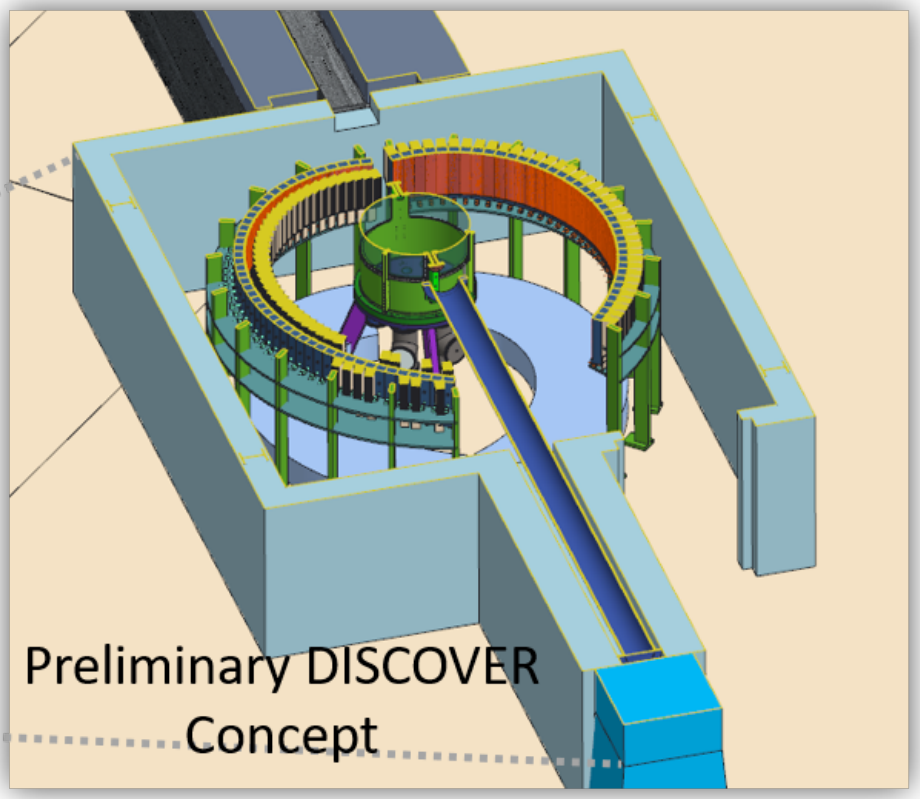
Total scattering at ORNL

Discover will be:

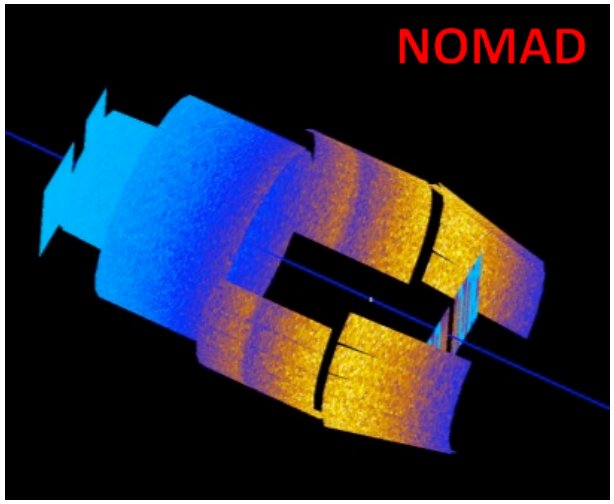
1- Viewing the poisoned 300 K water moderator

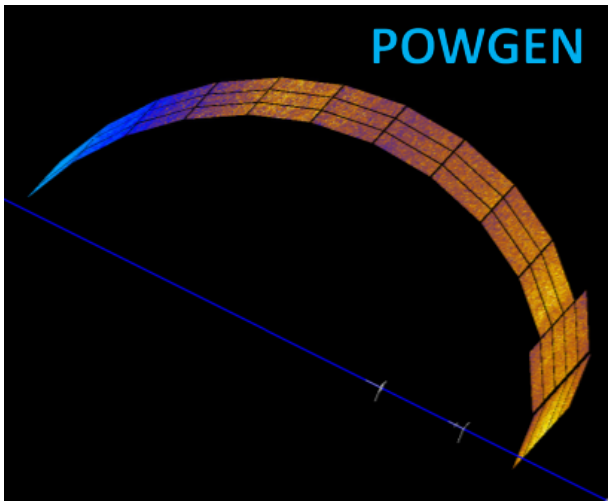
2- Around 32 m in length, and medium resolution

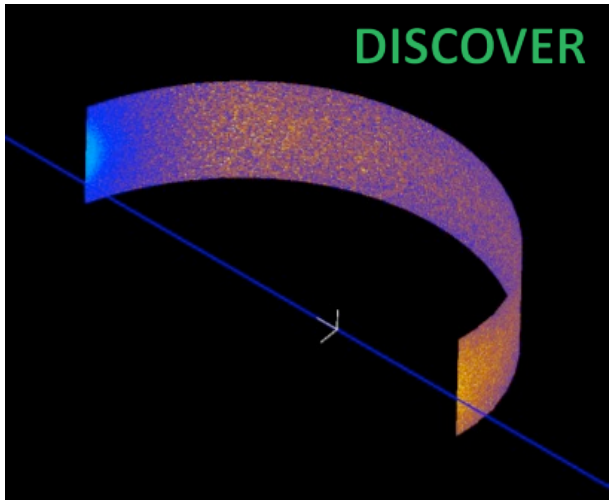


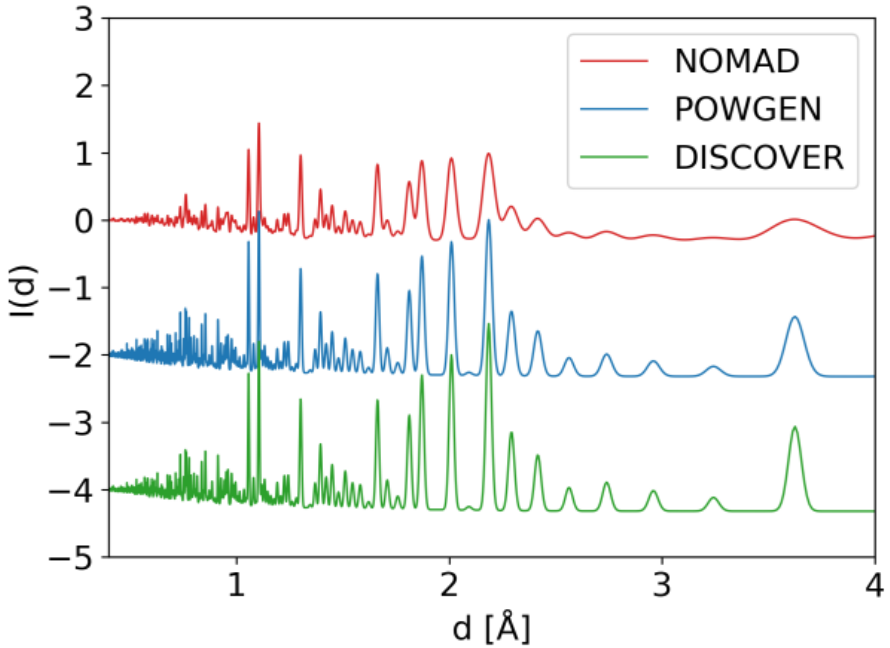


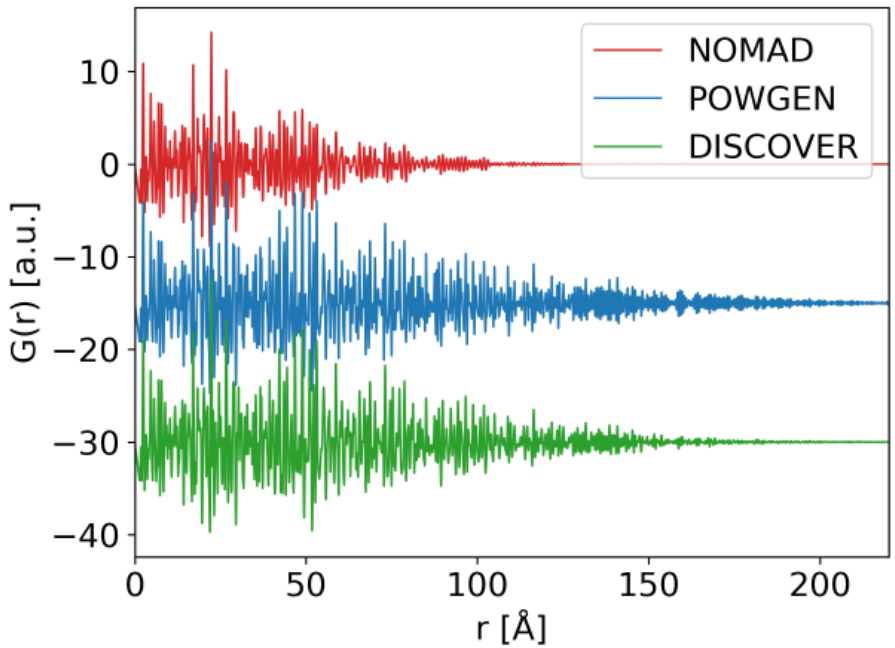
Total scattering at ORNL







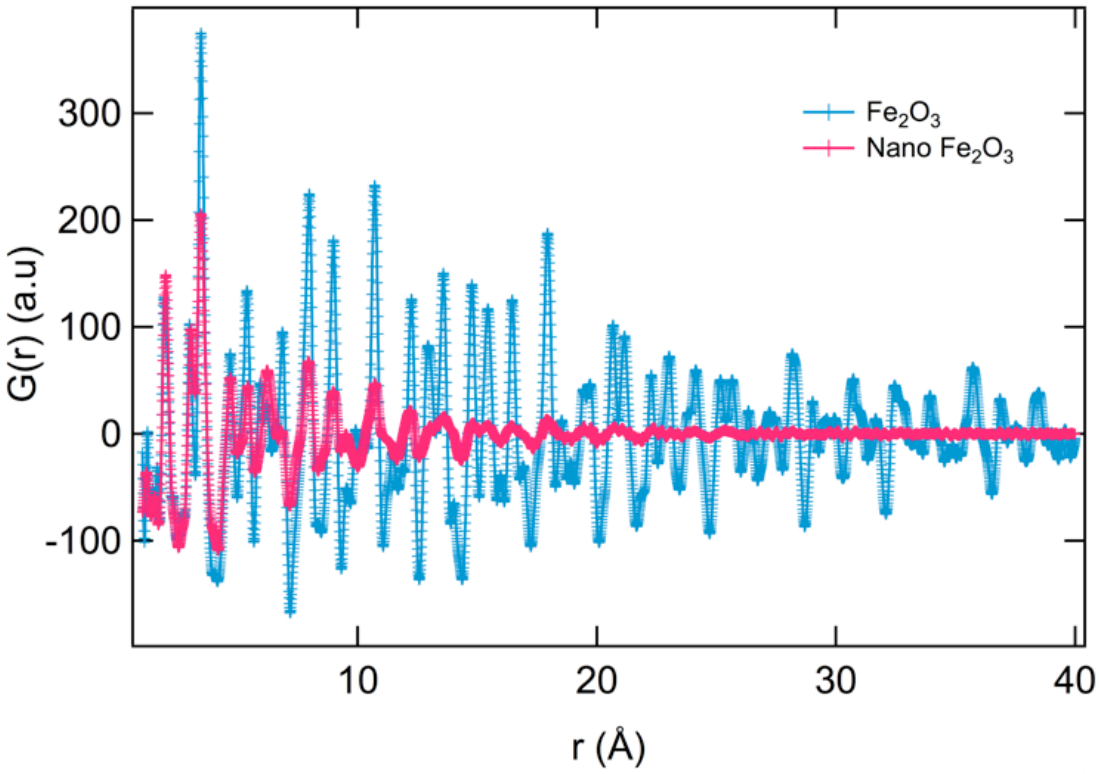




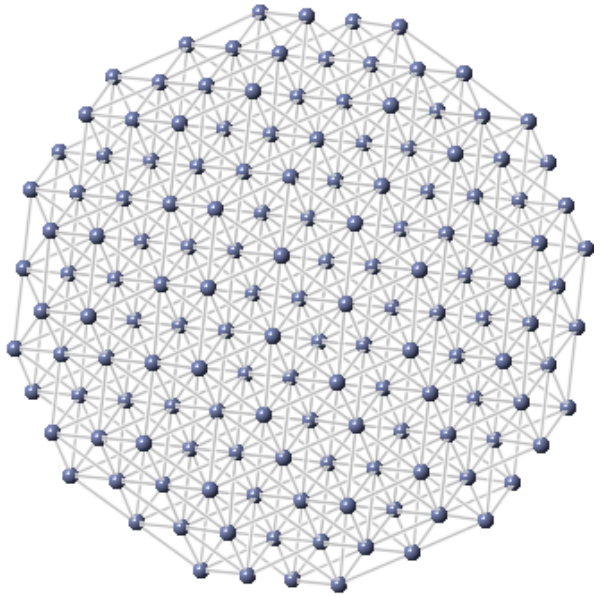
damping = exp-((rΔQ)²/2)

OAK RIDGE National Laboratory | NEUTRON SOURCE

What goes in the PDF?



$$1 - \frac{3}{2}\frac{r}{D} + \frac{1}{2}(\frac{r}{D})^3$$



Size/shape information

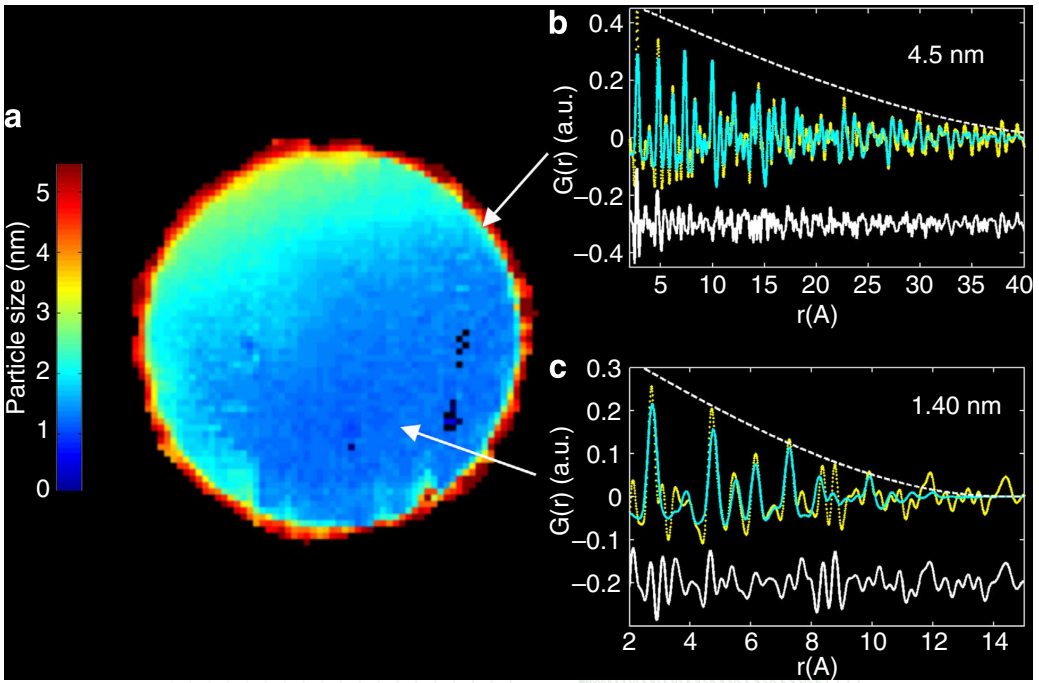
PDF is sensitive to the coherent domain size and particle shape

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

What goes in the PDF?

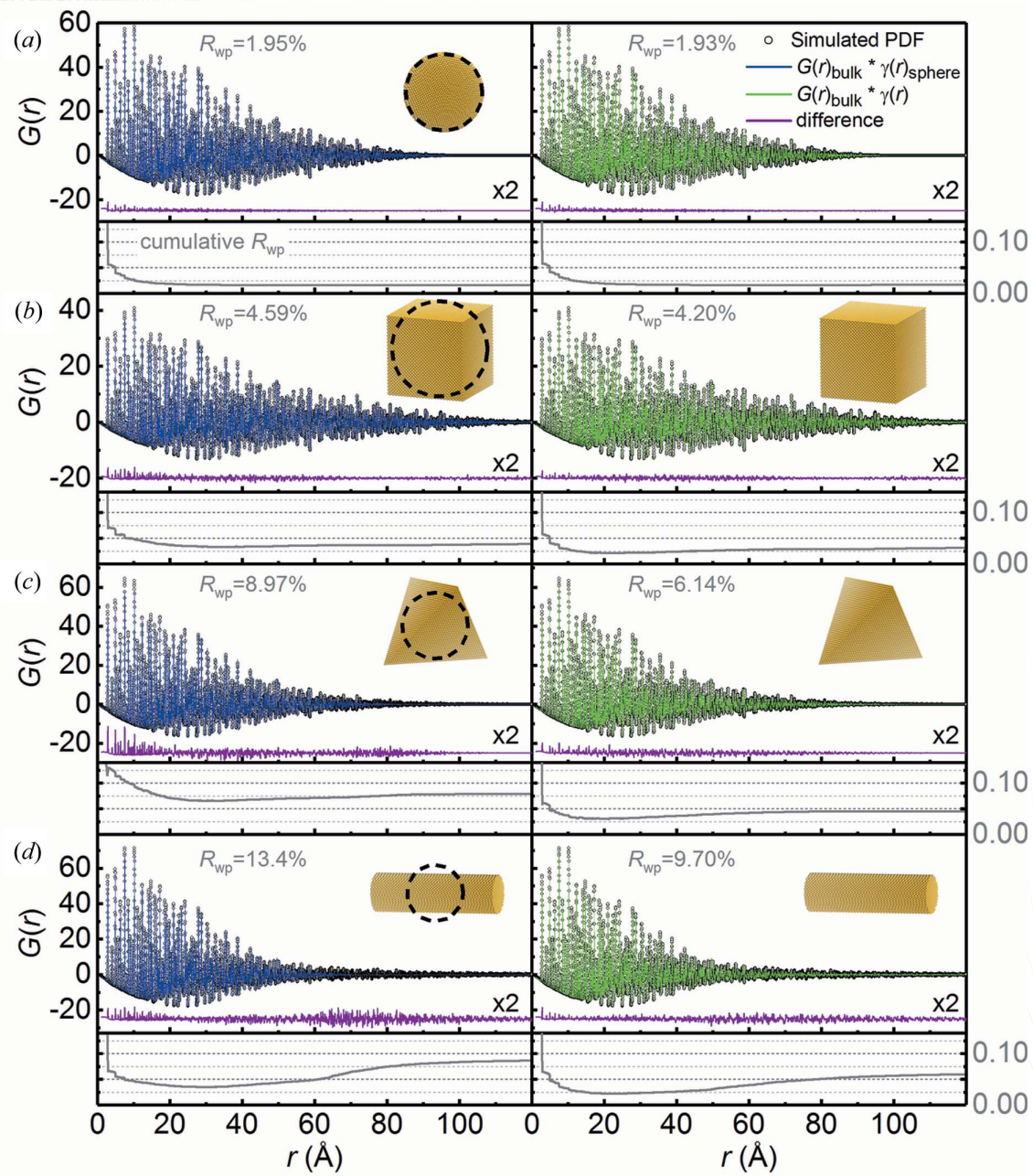
Fitting damping parameters allows mapping of nanoparticle sizes

=> supported catalysts



S.Jacques, M. Di Michel, SAJK *et al*, *Nat. Comm.*, **4**, 2536 (2013)

What goes in the PDF?



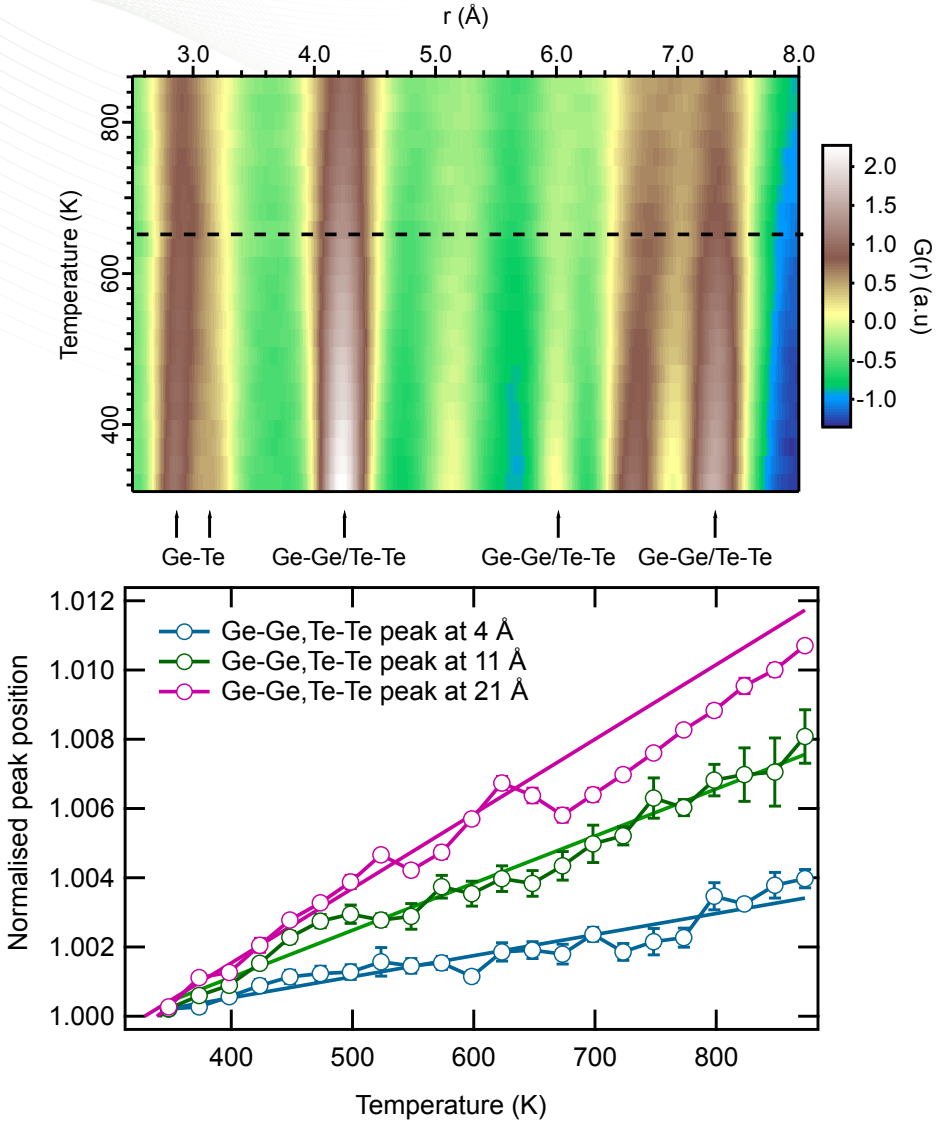
'High resolution' total scattering is sensitive to rather subtle shape changes

Constrains instrument design (need well behaved Q-resolution function)

Usher, Olds, Liu, Page, Acta A, **74**, 322 (2018)

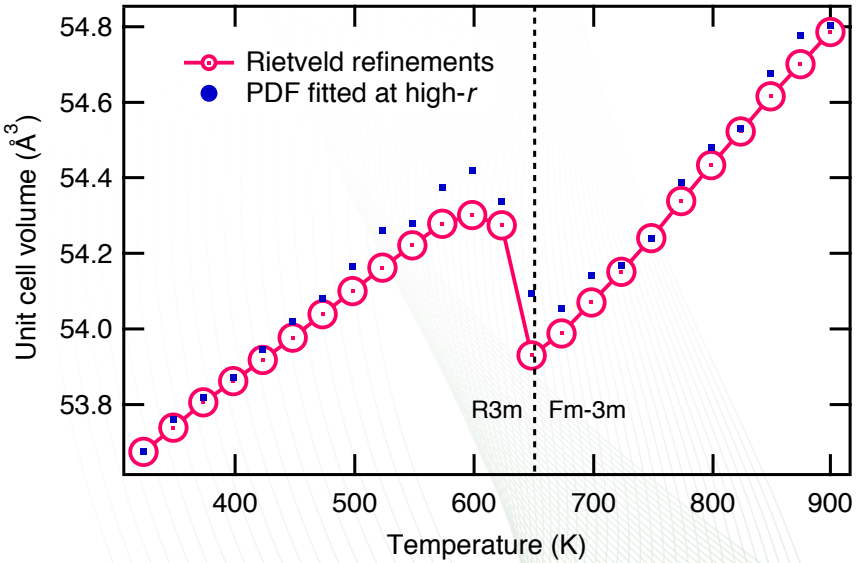
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

What goes in the PDF?



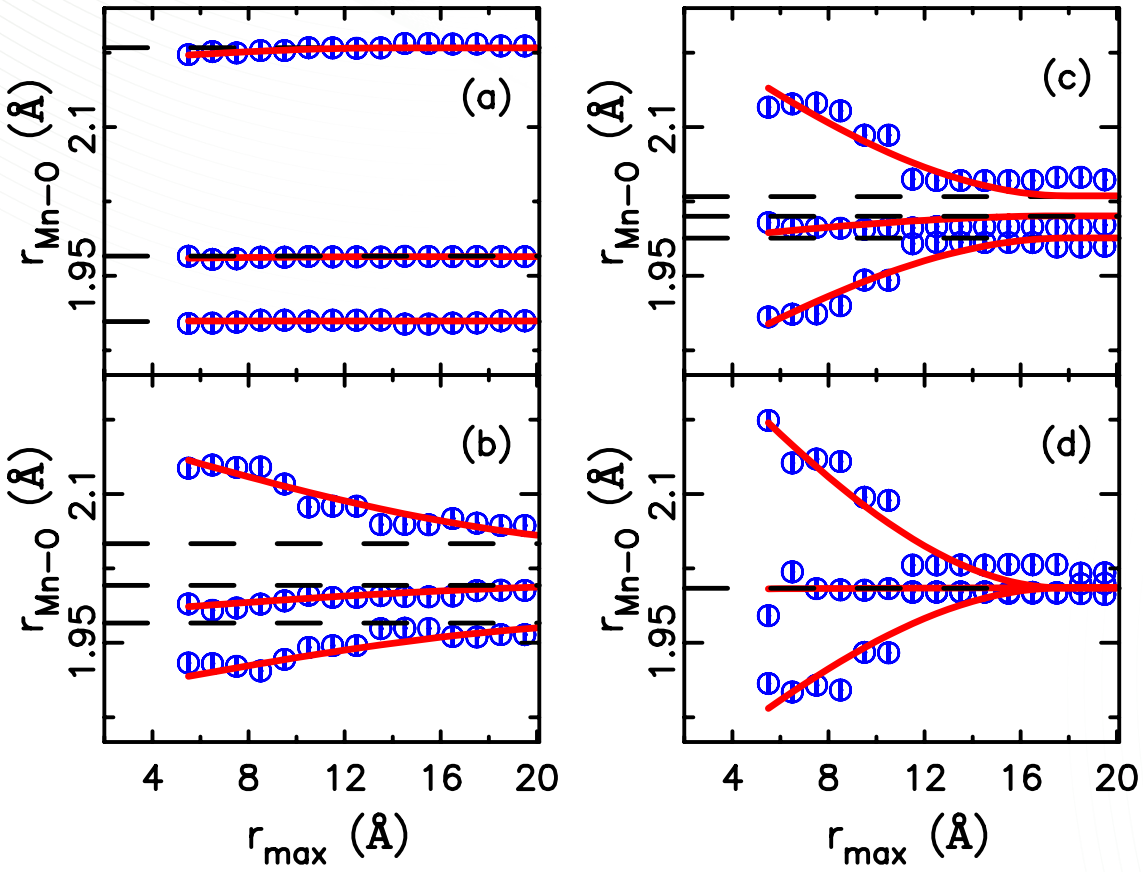
The PDF contains r-dependent information

e.g. interpolates between local structure and Rietveld result

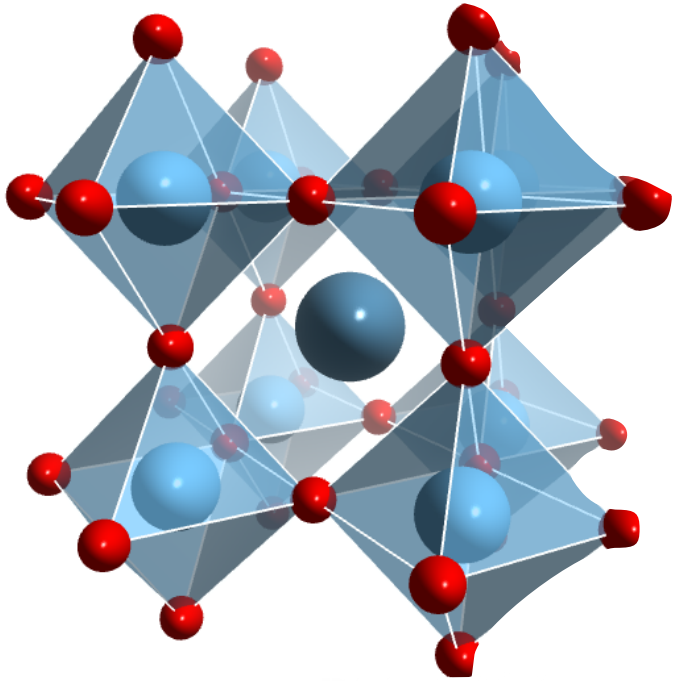


OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

What goes in the PDF?



Qiu *et al*, Phys. Rev. Lett., **94**, 177203 (2005)

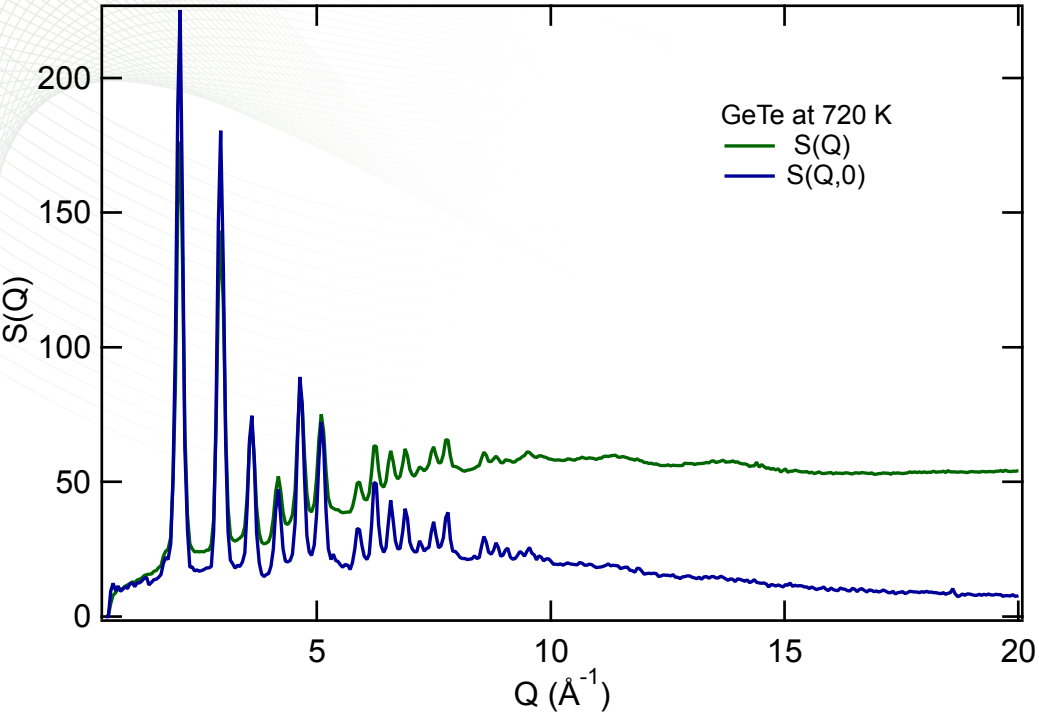


Long range Mn^{3+} orbital order disappears on heating through 750 K

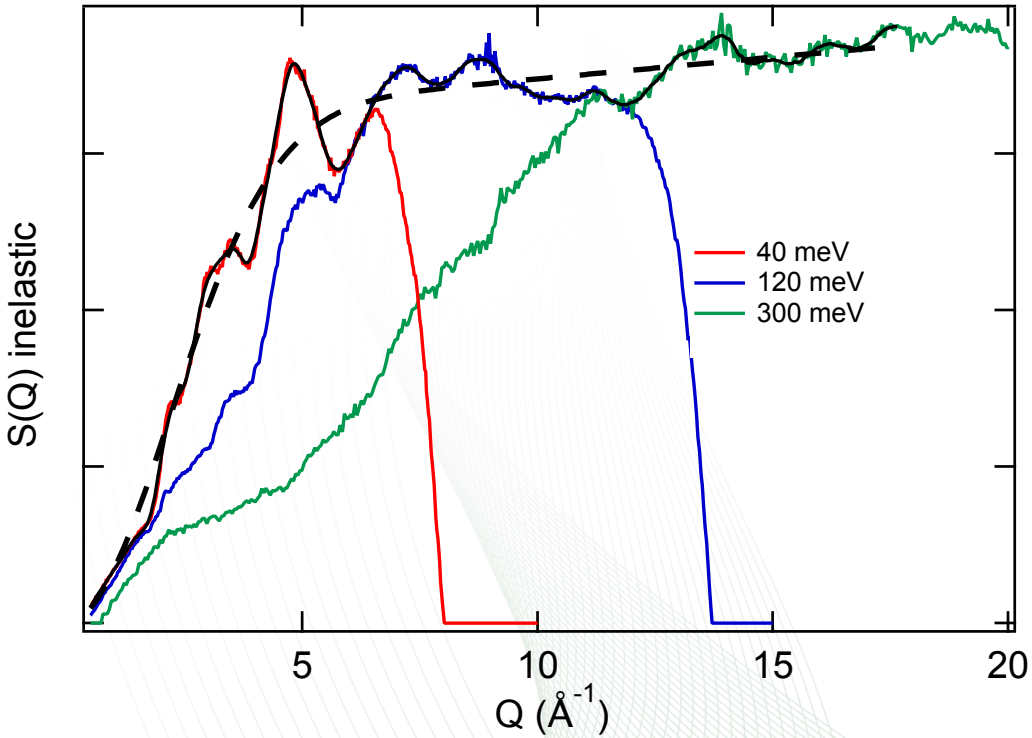
1.2 nm domains found by total scattering up to 1150 K

Box car fits used to extract correlation lengths

What goes in the PDF?



$$S(Q)_{elas} = S(Q).exp^{-Q^2\sigma^2}$$

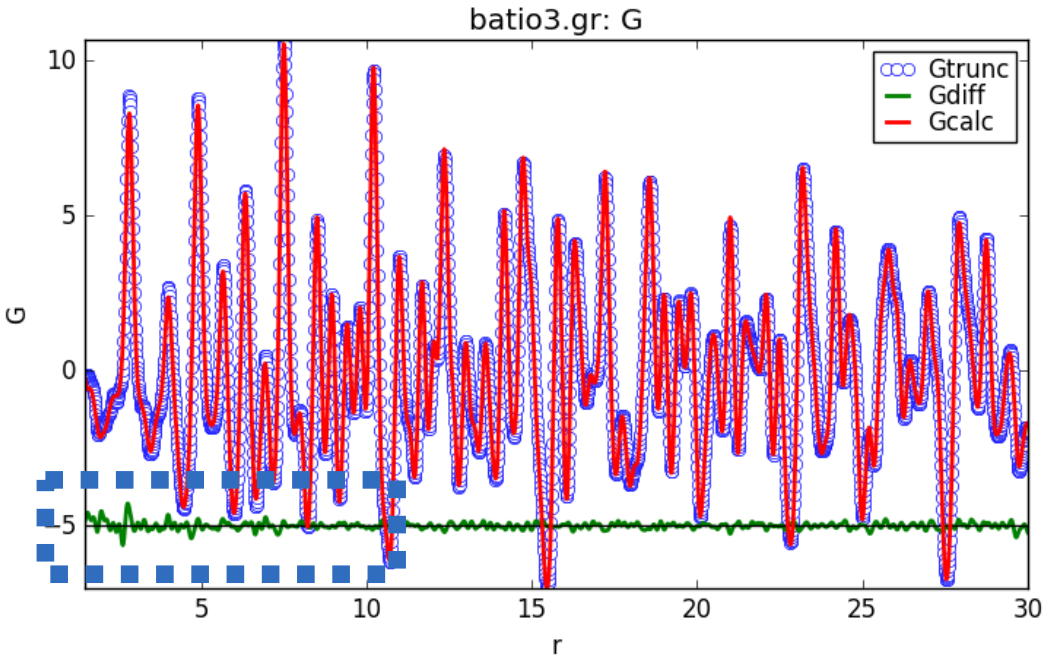


(unsurprisingly) phonon sum follows 1-DW

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Small box modeling

$$G_c(r) = \frac{1}{r} \sum_i \sum_j \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$



Small box modeling uses unit cell symmetry to reduce the number of parameters

Model is convolved with Gaussians for displacements parameters

Simple corrections for dynamic correlations, resolution functions, shape envelopes etc

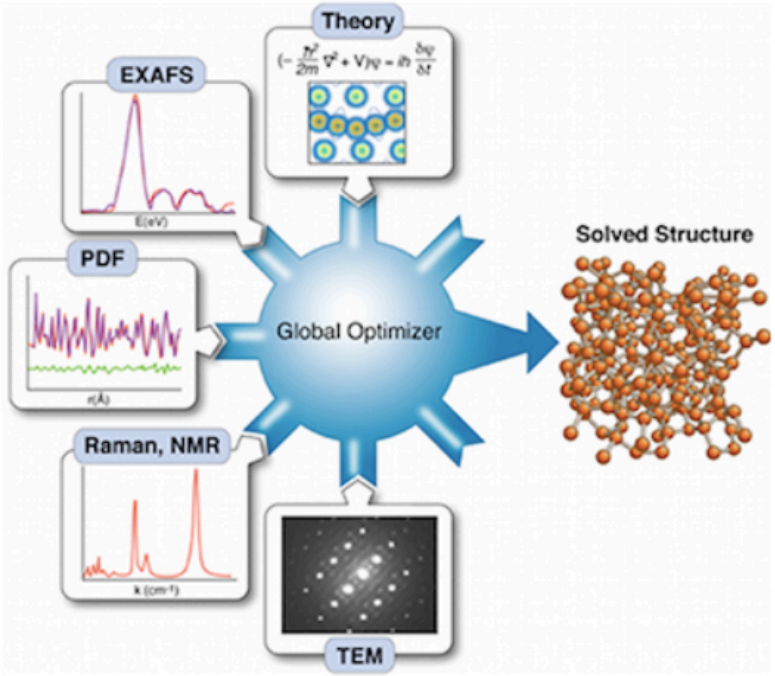
Extremely fast way of fitting PDF data and observing differences

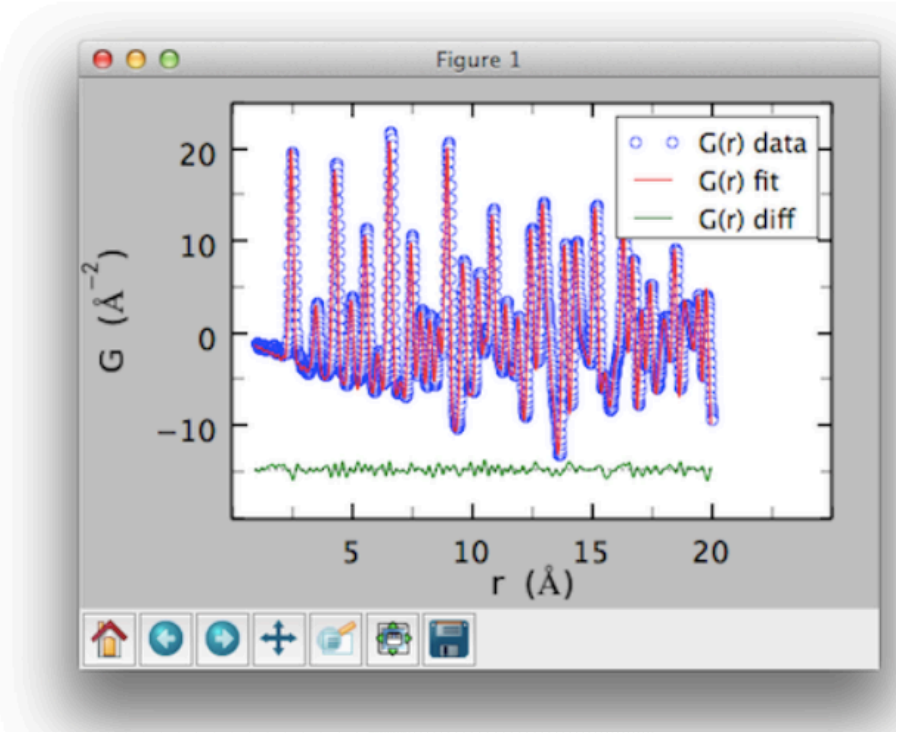
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Small box modeling

DiffPy - Atomic Structure Analysis in Python

A free and open source software project to provide python software for diffraction analysis and the study of the atomic structure of materials.





COLUMBIA UNIVERSITY

BROOKHAVEN NATIONAL LABORATORY

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE