High Pressure PDF at 11-ID-B

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The Pair Distribution Function, G(r)

G(r) is related to the ***probability*** of finding an atom at a distance ***r*** from a reference atom.

It is the Fourier transform of the total structure factor, ***S(Q)***.

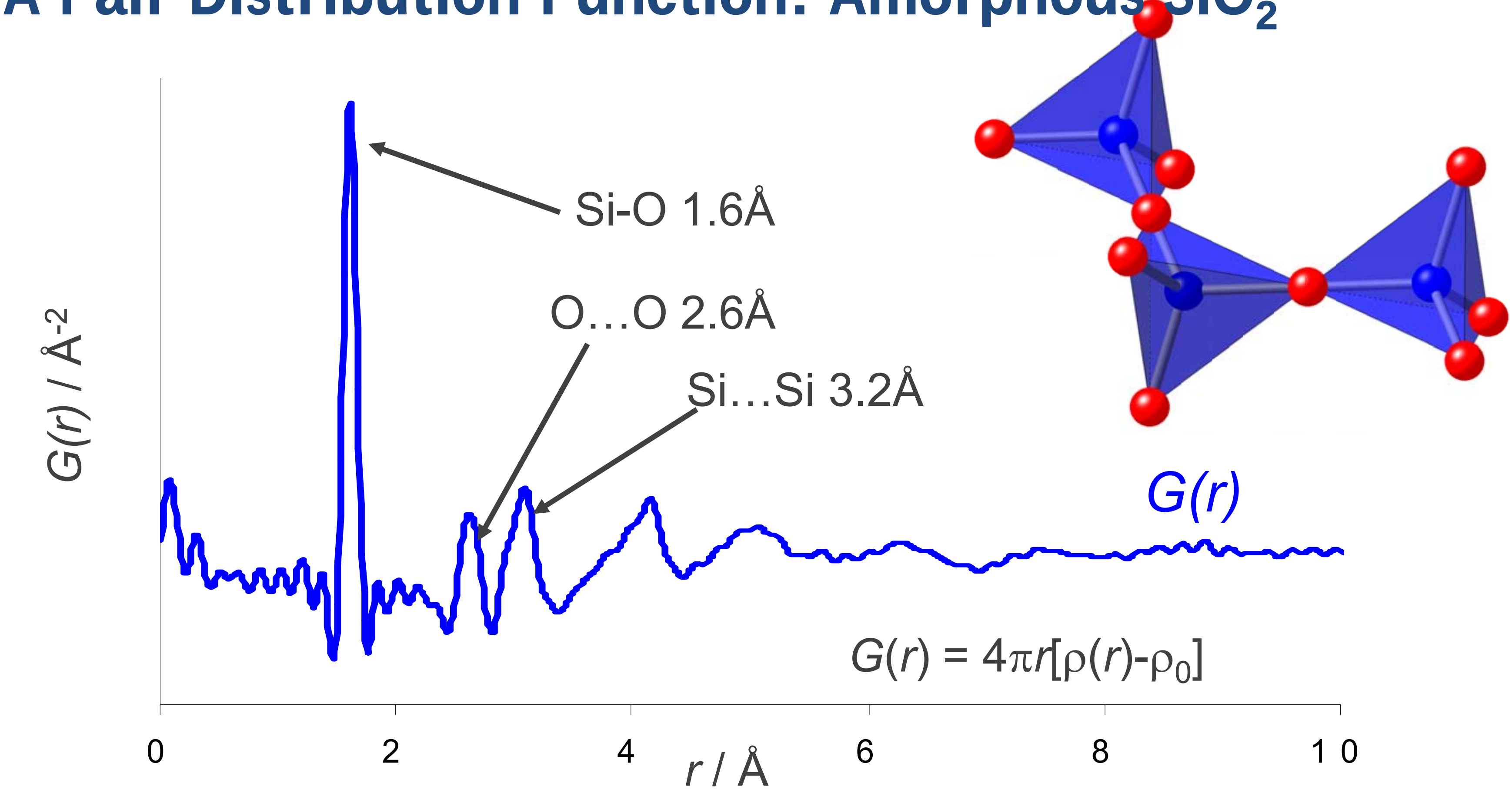
$$G(r) = 4\pi r\,\rho_0[\underbrace{g(r)}_{\text{probability}}-1] = (2/\pi)\int Q[\underbrace{S(Q)}_{\text{structure factor}} - 1]\sin(Qr)\,dQ$$

The structure factor, ***S(Q)***, is related to coherent part of the diffraction intensity

$$S(Q) = 1 + [\underbrace{I^{coh}(Q)}_{\substack{\text{diffraction intensity}\\ \text{(corrected)}}} - \sum c_i|f_i(Q)|^2]/|\sum c_i f_i(Q)|^2$$

Apply corrections for background, absorption, Compton & multiple scattering

A Pair Distribution Function: Amorphous SiO_2

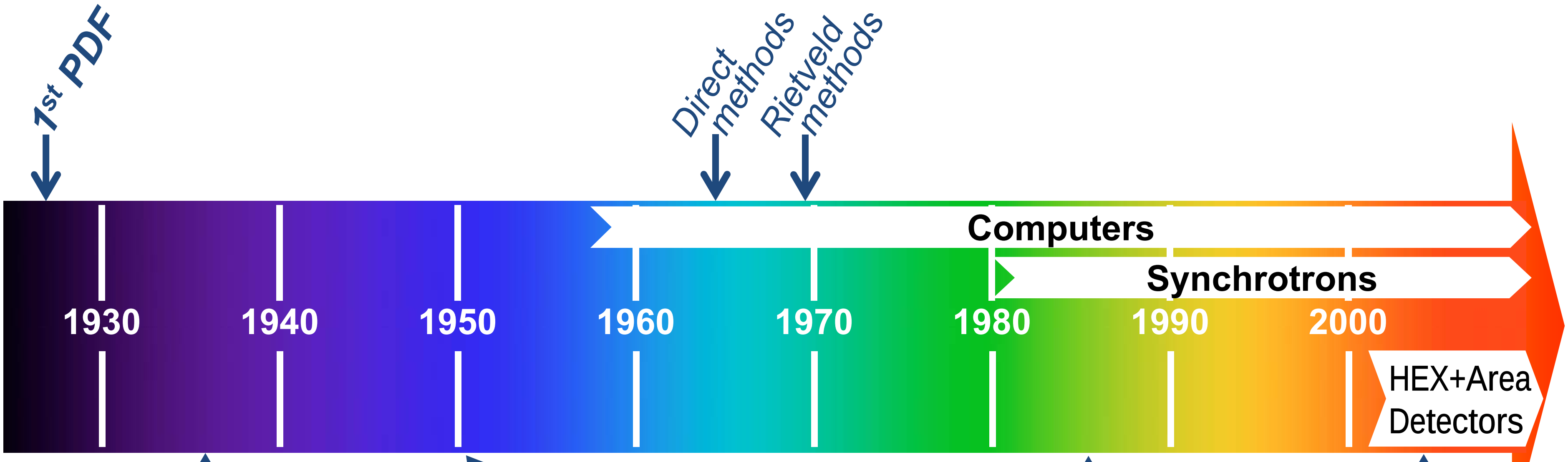


$G(r) = 4\pi r[\rho(r)-\rho_0]$

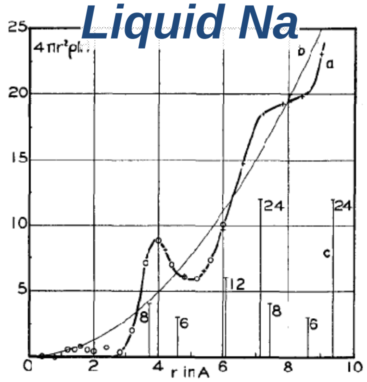
Peak position	Bond length / distance
Peak area	Coordination #, scattering intensity
Peak width	Disorder
Peak r_{max}	Particle size, coherence

Structural Modeling

A brief history of X-ray PDF measurements

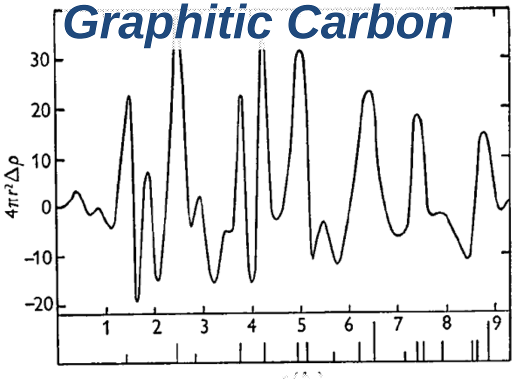


Liquid Na



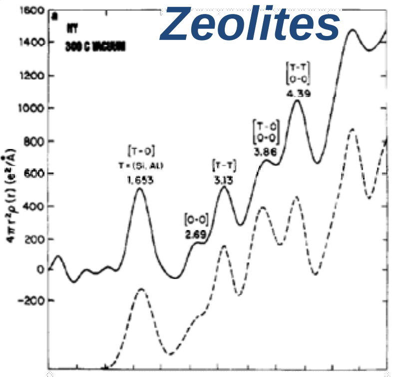
Tarasov & Warren *J.Chem.Phys.*(1936)

Graphitic Carbon



RE Franklin *Acta. Cryst.* (1950)

Zeolites



RD Shannon *J.Phys.Chem.*(1985)

Readily Accessible PDF Data

PJ Chupas *J.Appl.Cryst.*(2003)

Modern PDF measurements: High energy X-rays

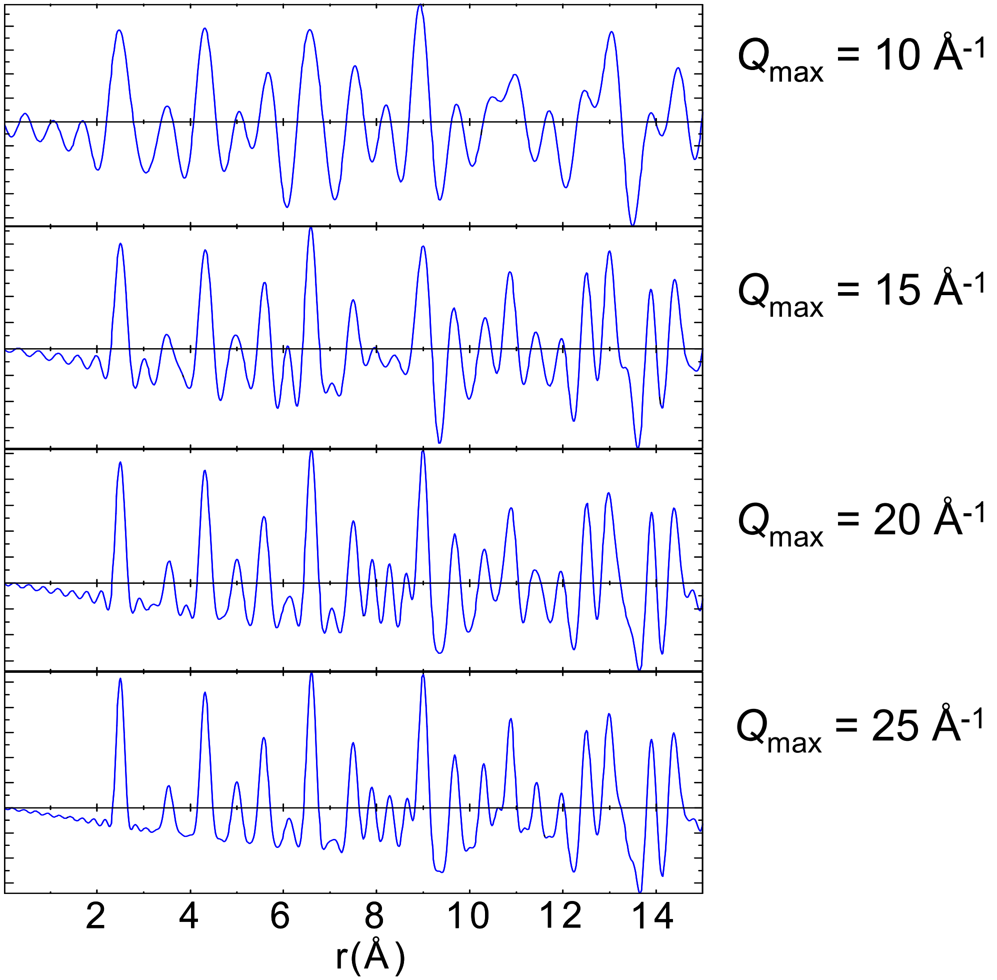
High energy X-rays → *High* Q_{max} → *High real space resolution*

$$Q_{max}=4\pi\sin\theta/\lambda$$

for Cu Kα, $\lambda=1.54$Å, $2\theta=180^{o}$

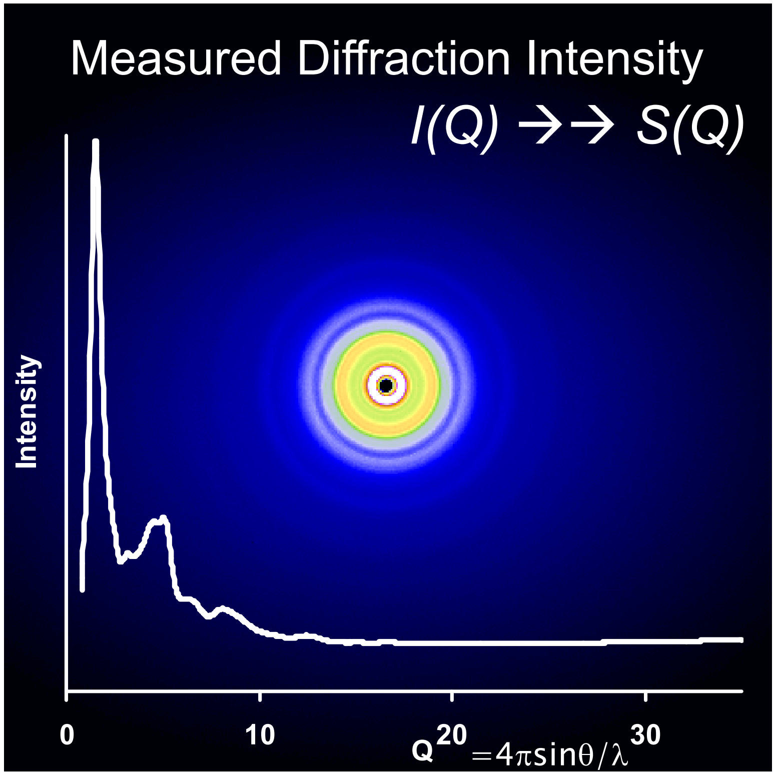
$$Q_{max} = 4\pi\sin90/1.54 = 8\ \text{Å}^{-1}$$

We typically use wavelengths between 0.20 and 0.08 Å

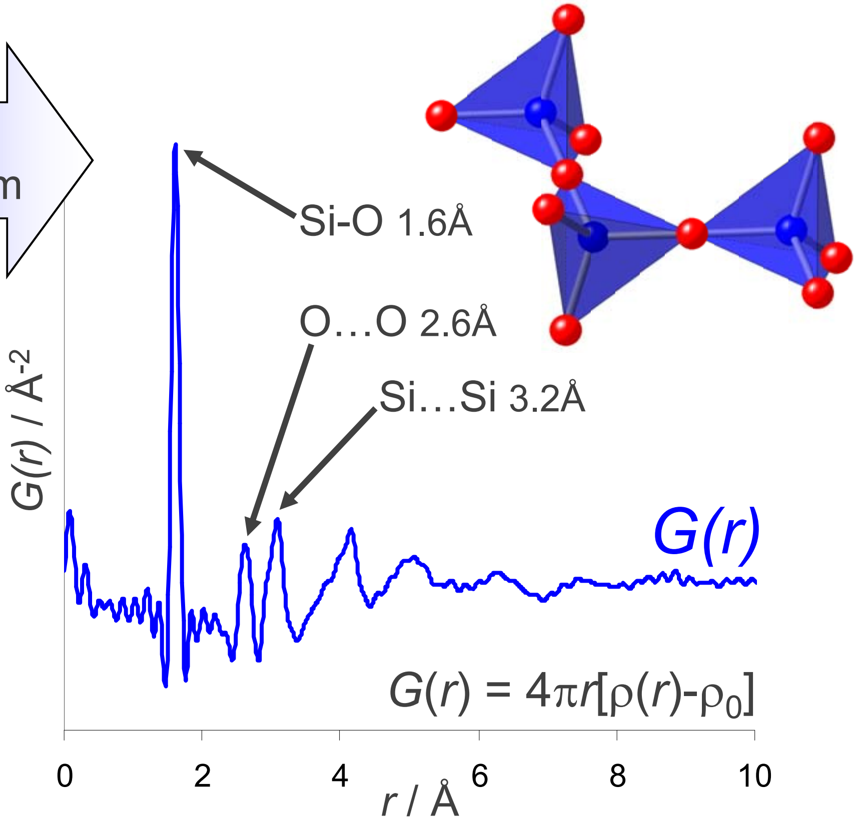


Modern PDF measurements: Area detectors

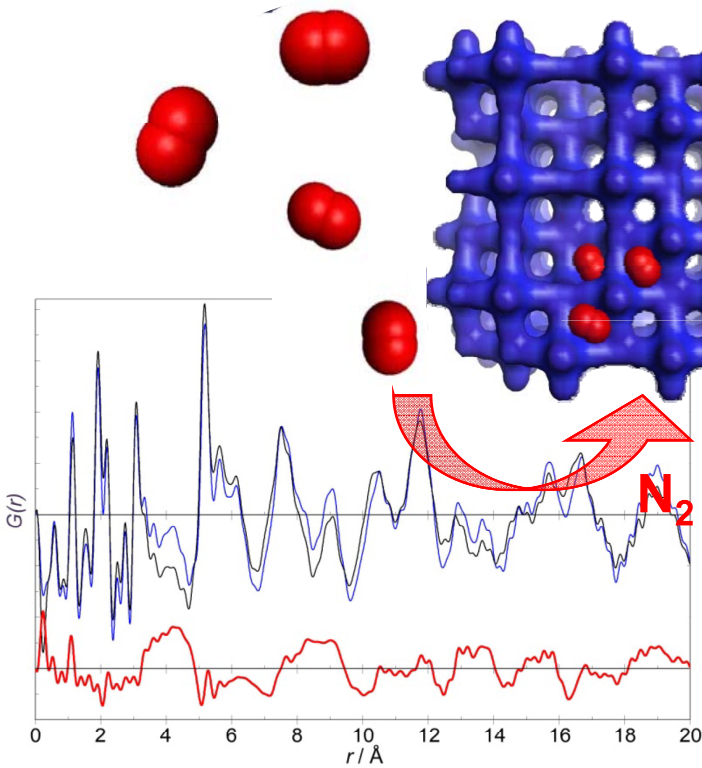
- The structure factor S(Q) measured as a function of diffraction angle using monochromatic X-rays
- Area detectors collect all data simultaneously to yield more rapid measurement

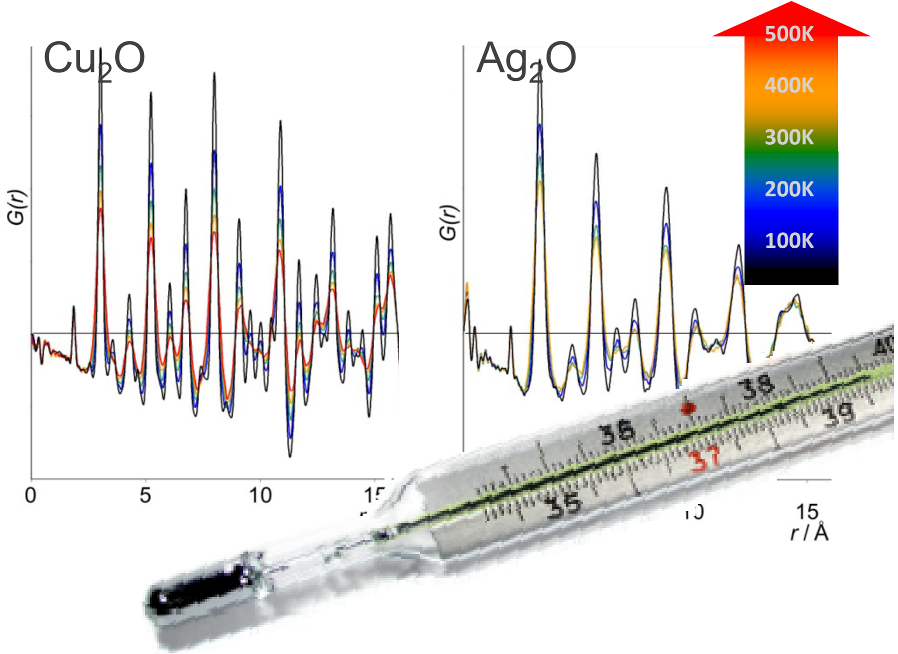


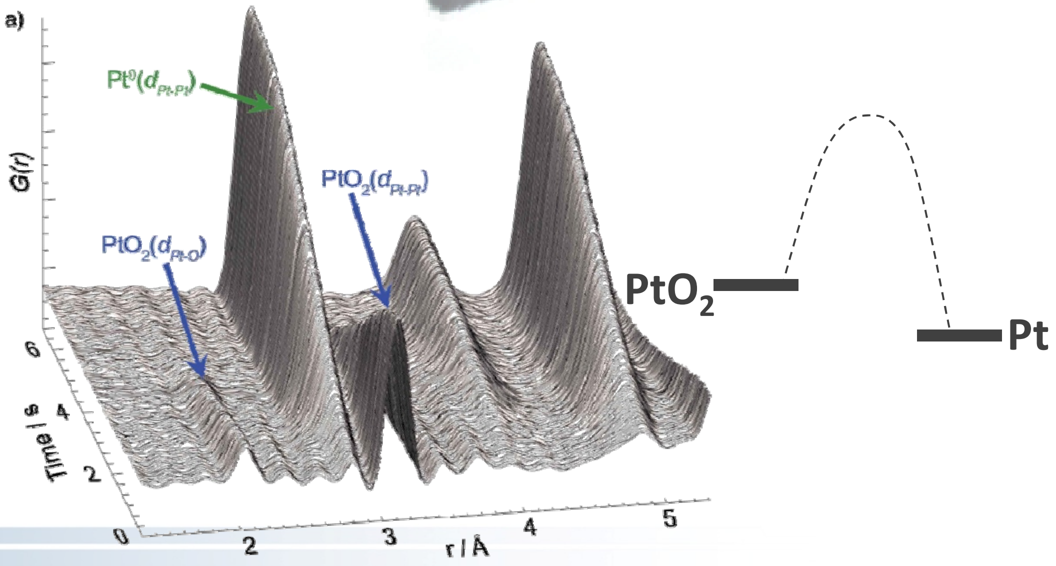
Fourier Transform



PDF as a function of temperature, reaction progress and guest-loading now relatively routine





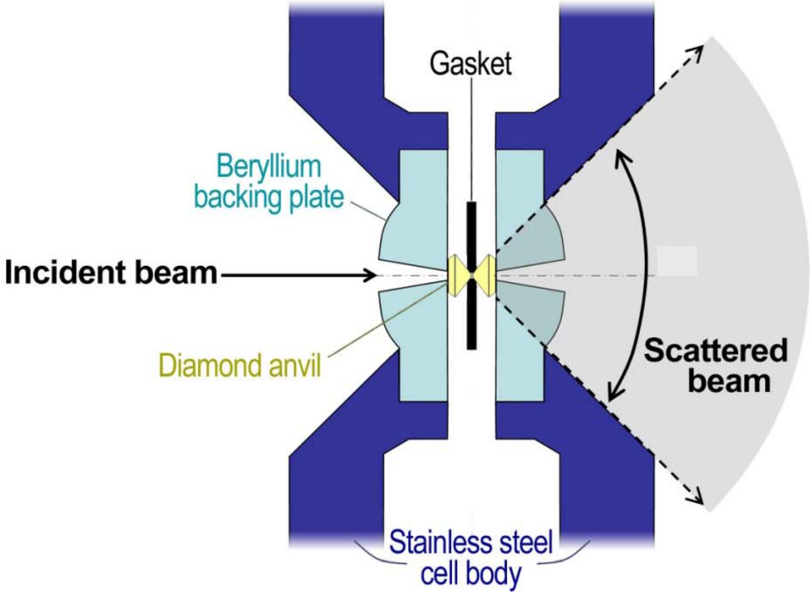


PDF is well suited to study HP phenomena

- Pressure-induced amorphization
- Phase-transitions

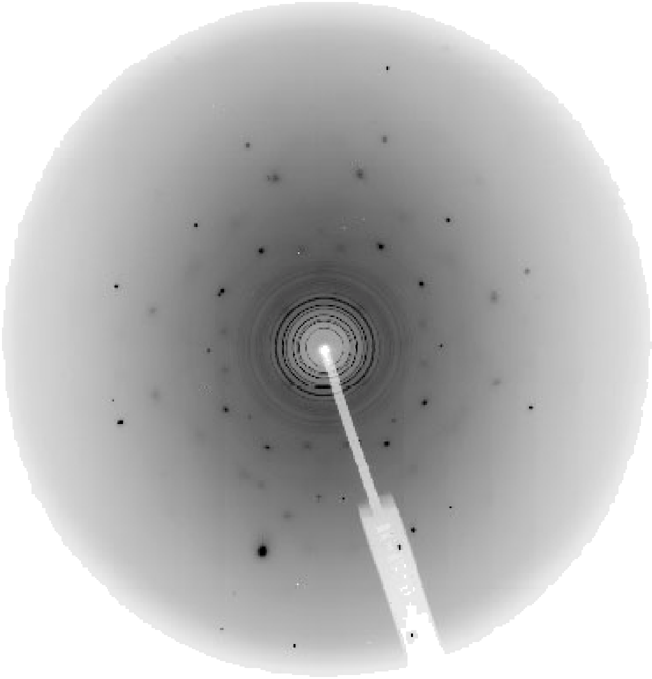
High pressure measurements

High pressure apparatus, such as diamond anvil cells, use small, highly encapsulated samples resulting in low sample-to-background scattering ratios. The limited aperture for the scattered beam limits the accessible *Q*-range.



PDF measurements

High quality, accurate PDFs require that X-ray scattering data with a good *signal-to-noise ratio* is collected, rigorously *normalized* and Fourier transformed to *high values of momentum transfer* ($Q > 20$ Å^{-1}).

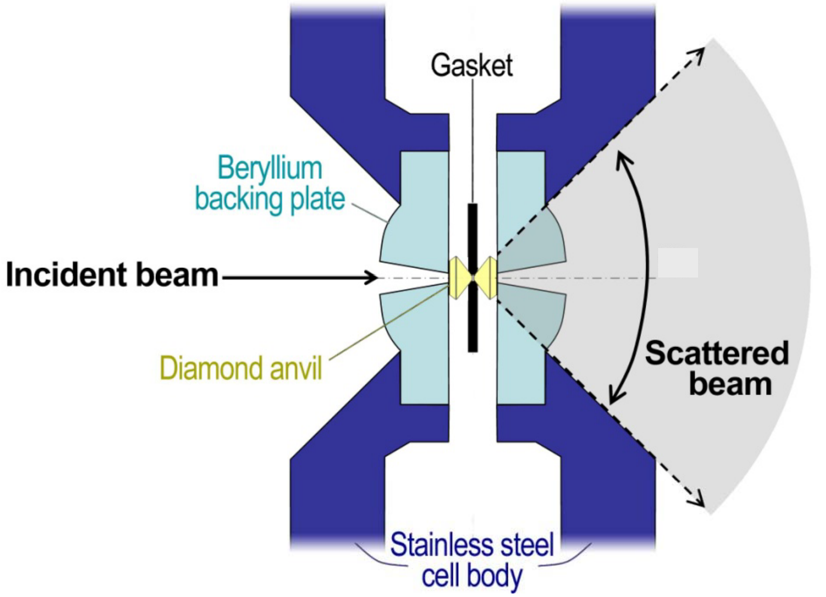


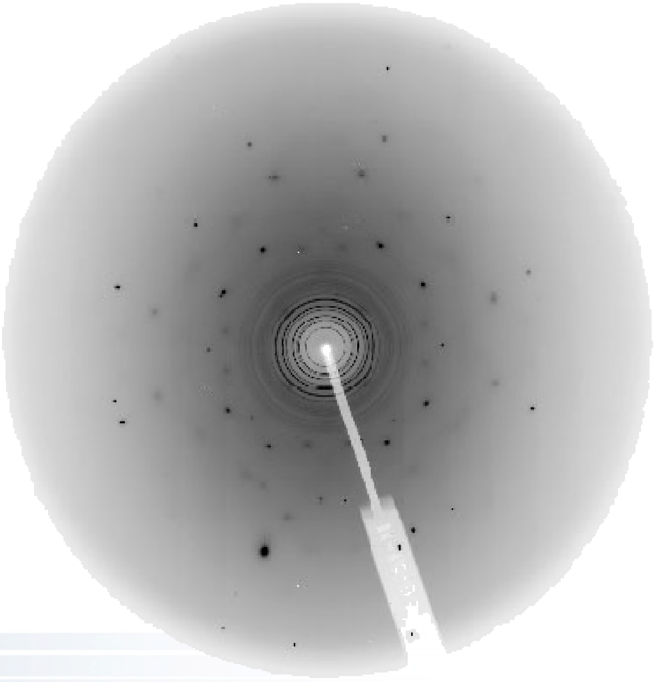
High pressure vs PDF: Divergent needs?

High Pressure	Pair Distribution Function	Handicap
Sample volume: Small ~0.1 mm	Sample volume: Large ~1mm	**1:10**
Small beam = low flux: 0.1 x 0.1 mm	Larger beams: 0.5x0.5 mm	**1:25**
Background: Large diamond anvils Poor sample-to-background ratio	Background: Thin-walled capillaries Good sample-to-background ratio	**1:30**
Background: Pressure-dependent	Background: Accurately determined	**?**
Data: limited by DAC apertures	Data: to high Q (> 20 Å^{-1}) HEX + large scattering angles	**?**

Many coupled parameters

- Instrument Parameters:
  - Photon energy
  - Beam size / shape / focusing
  - Detector type / positioning
- Pressure Cell Parameters
  - Target pressure range
  - DAC design
  - Diamonds
  - Backing plates
  - Pressure transmitting media
- Data Reduction
  - Masking diamond reflections





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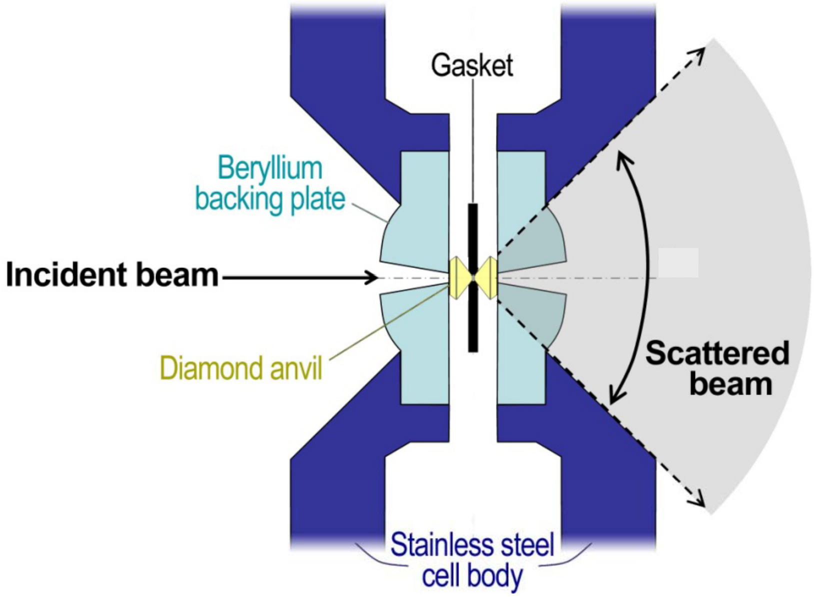
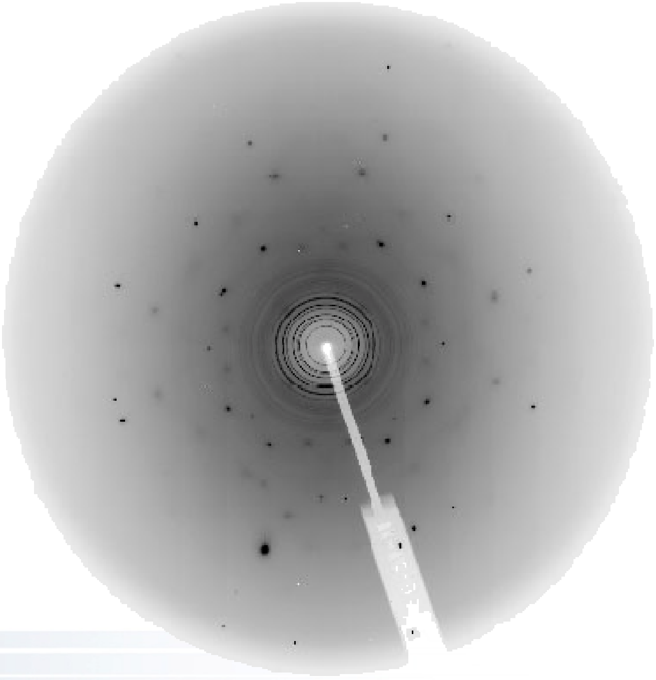
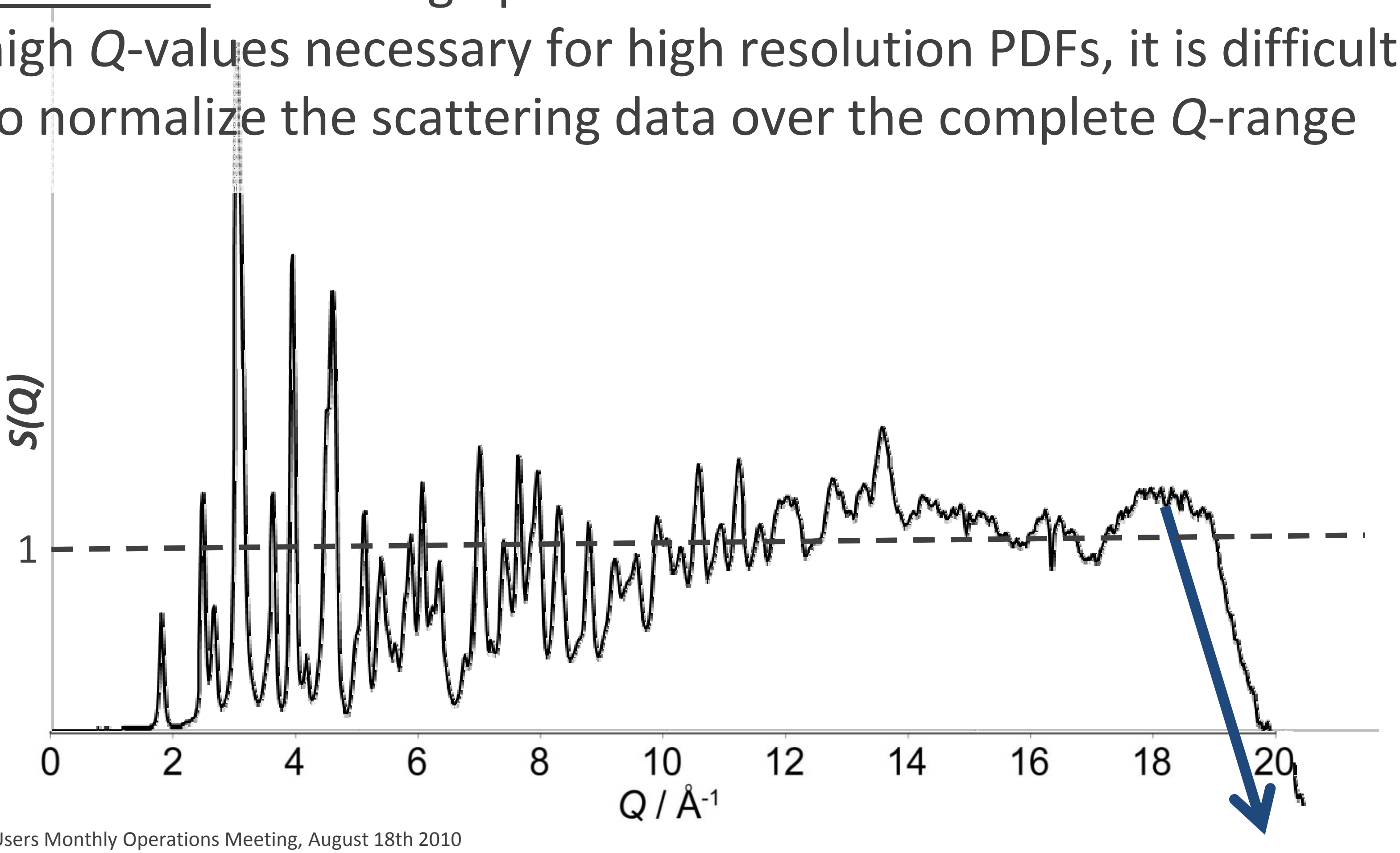




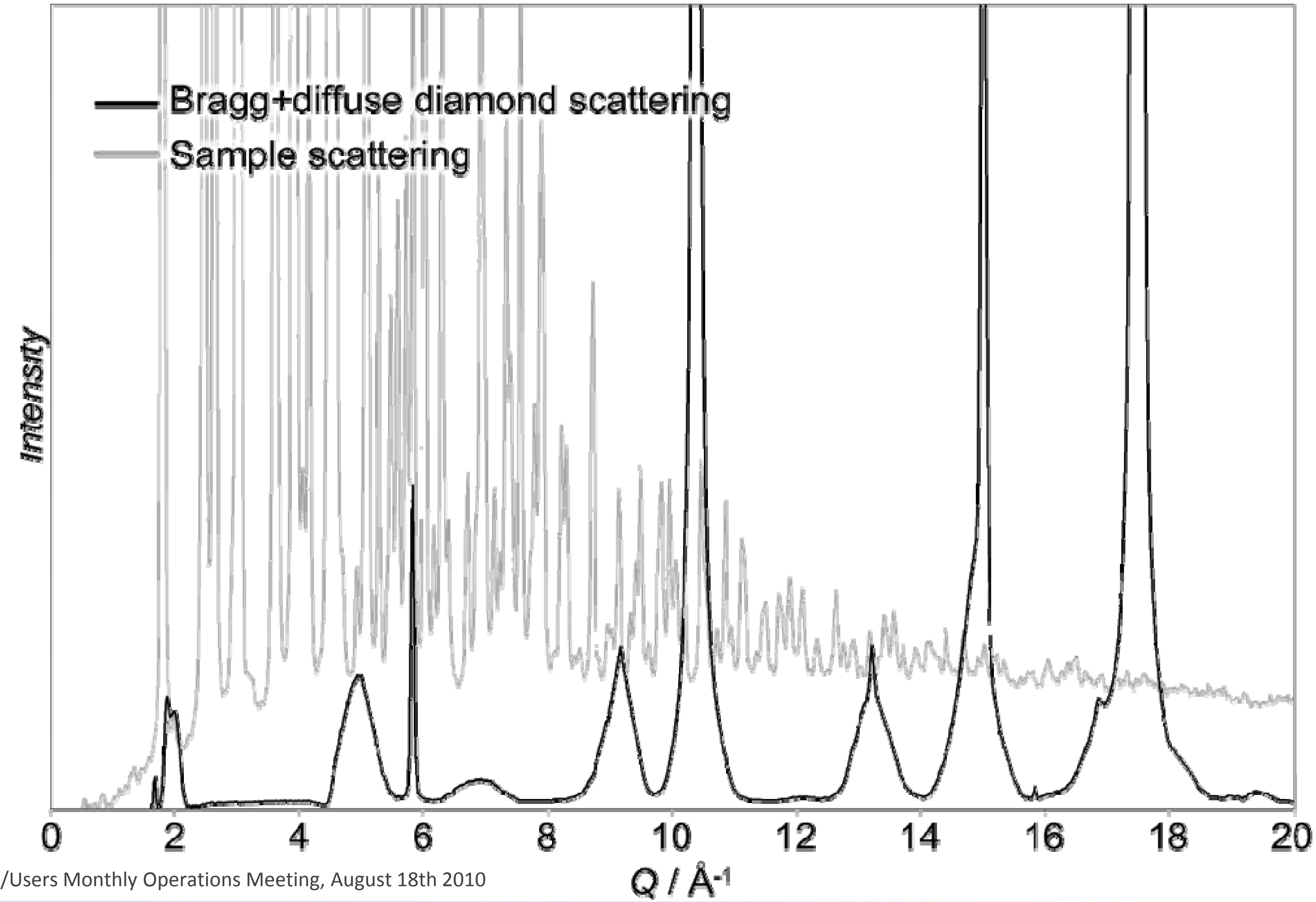
The limited Q-range problem: a background issue

Observation: While high pressure data can be collected to the high *Q*-values necessary for high resolution PDFs, it is difficult to normalize the scattering data over the complete *Q*-range

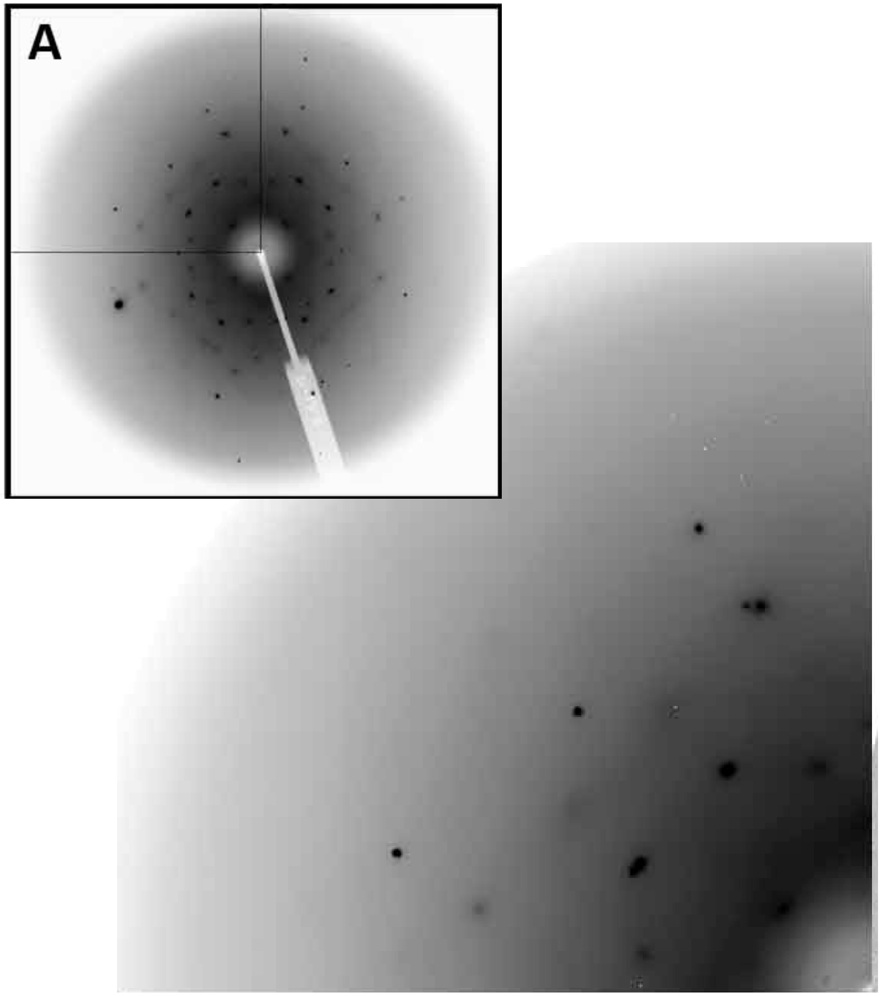


Diamond anvils: Single crystal Bragg and diffuse

The structured single crystal diffuse scattering from the diamond anvils is of similar intensity to the sample scattering.

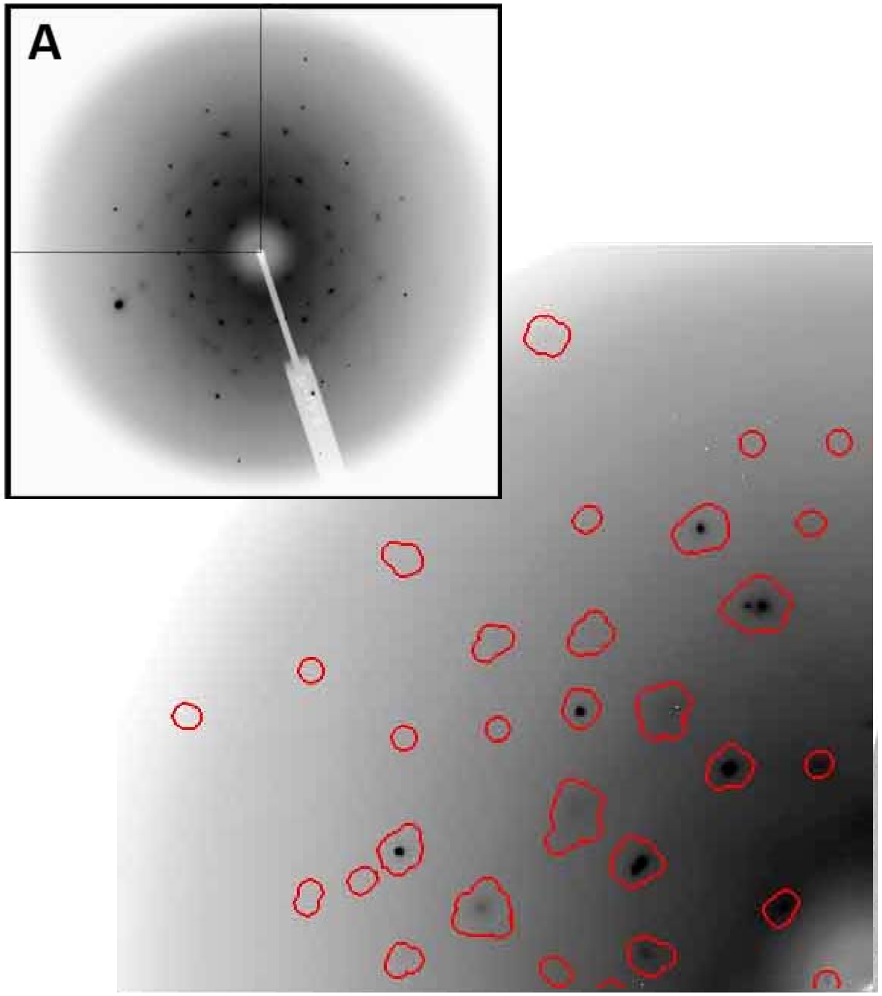


Diamond masking limits usable Q-range



- The single crystal diffuse features are pressure (strain) dependent and are “masked” in the images.
- In practice, constructing a **<u>complete</u>** mask is extremely challenging
- Due to the magnitude of the diamond contribution, **ANY** inadequacies in the masking limits the usable *Q*-range.

Diamond masking limits usable Q-range



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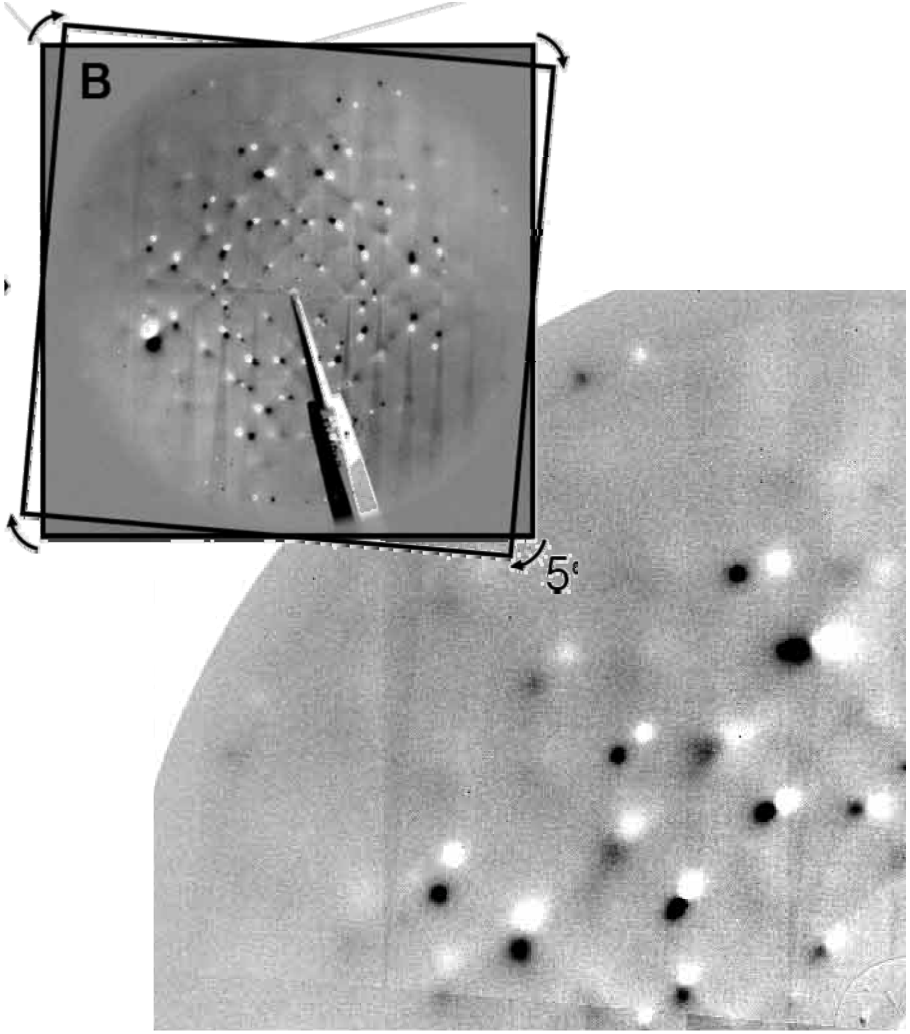
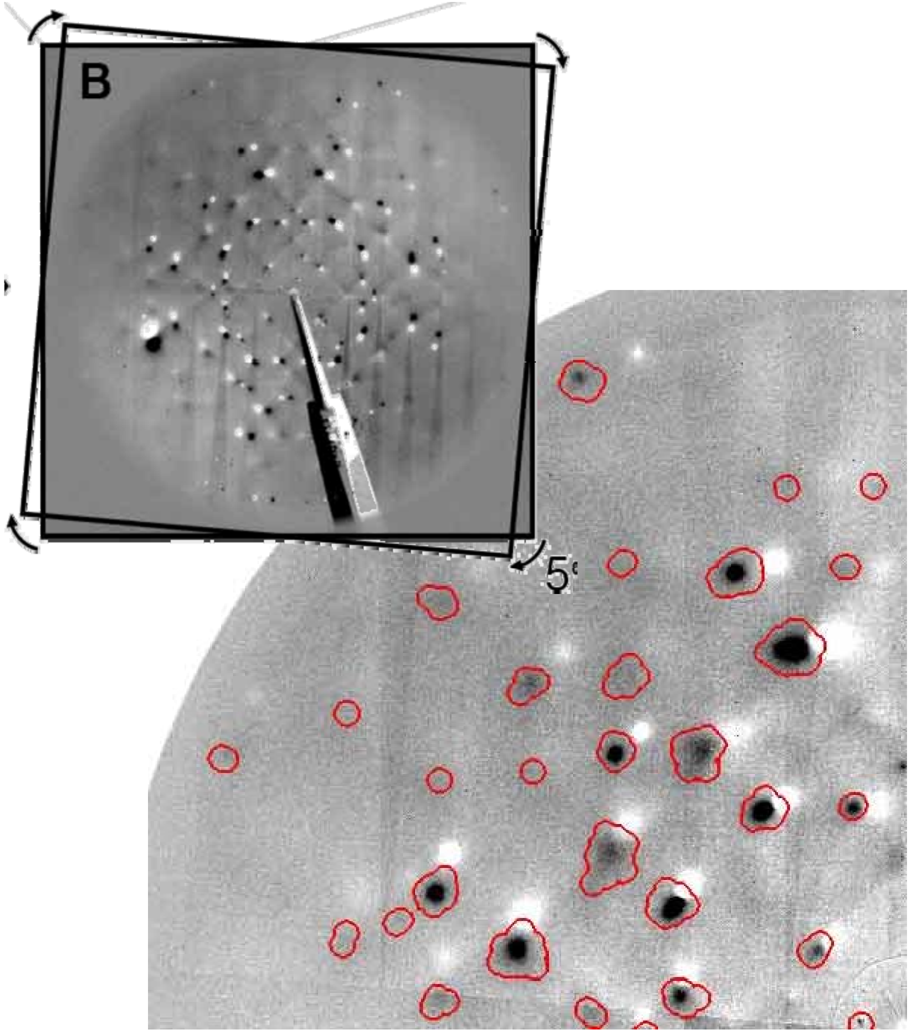
Diamond masking limits usable Q-range



- By subtracting the radially symmetric scattering, the structured diffuse can be more readily identified.
- This is achieved by rotating an image around the beam center and subtracting from the original image

Diamond masking limits usable Q-range



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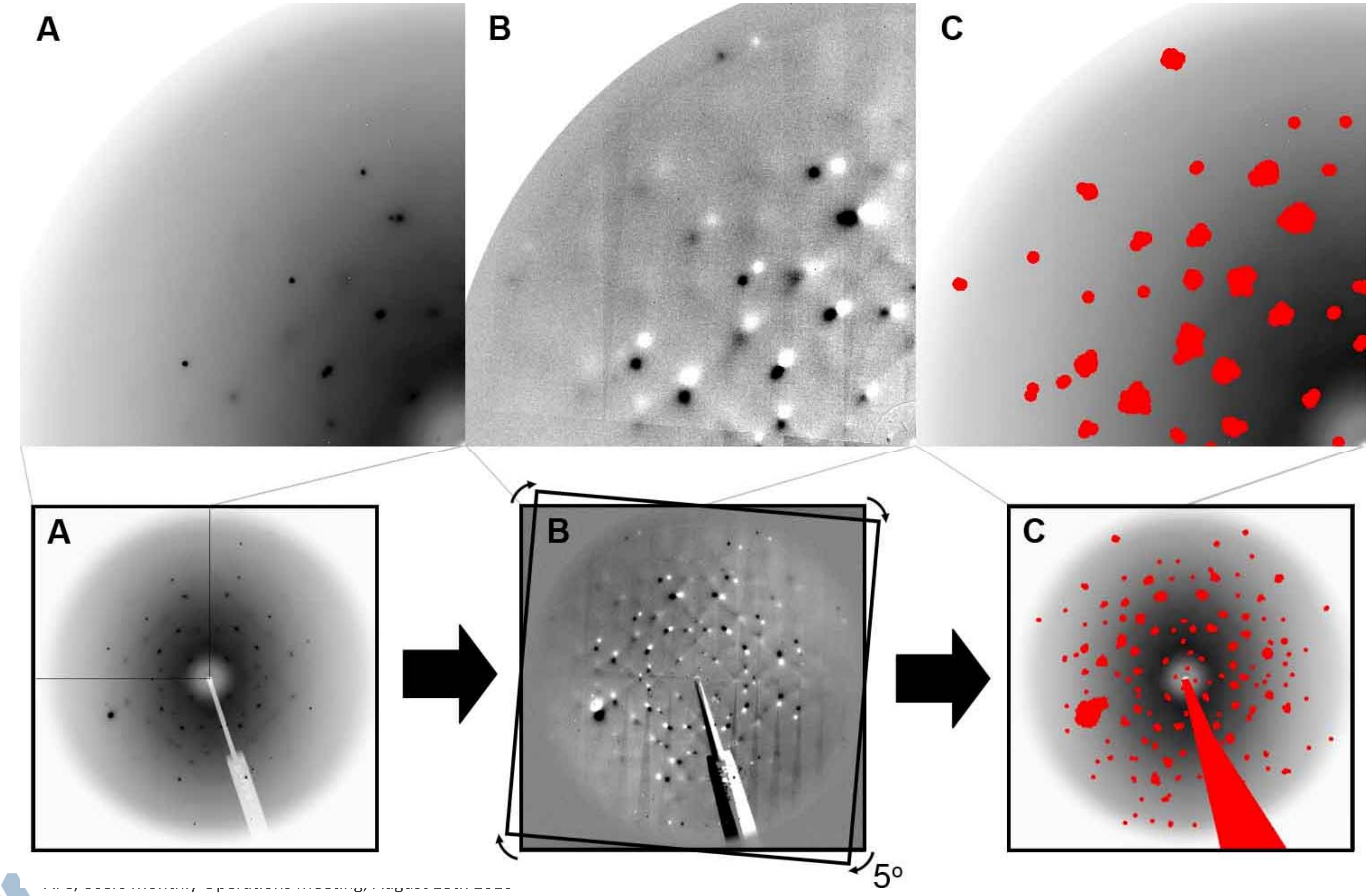
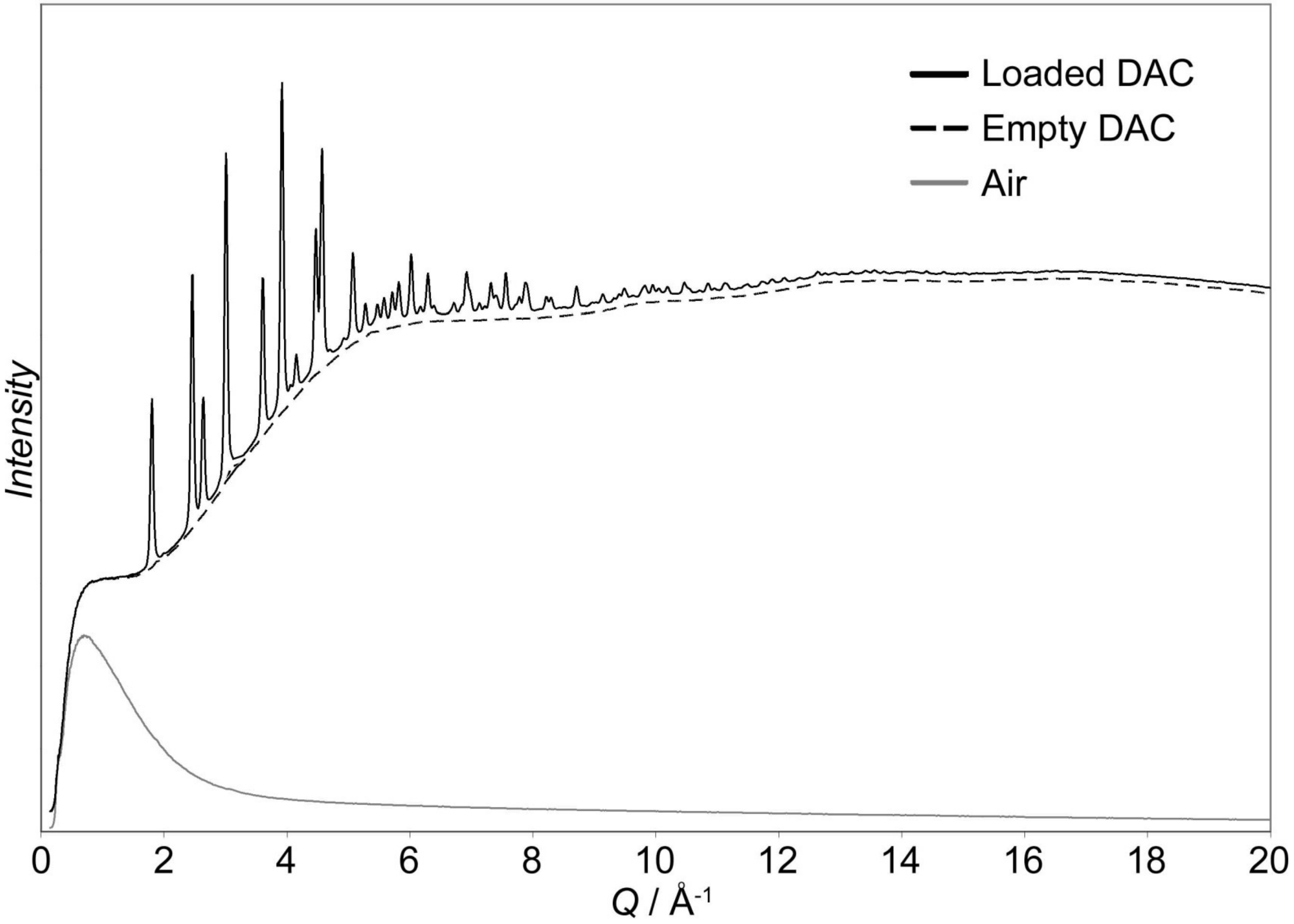
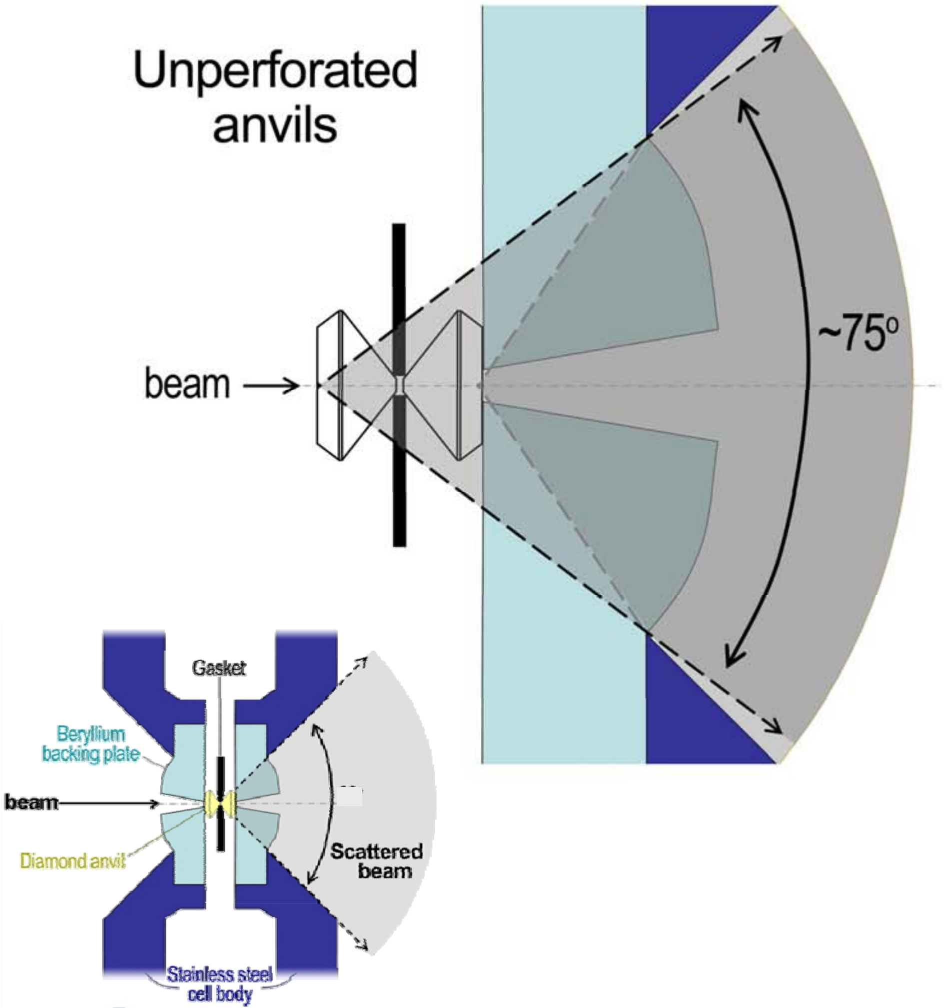
Effective masking strategy expands usable Q-range

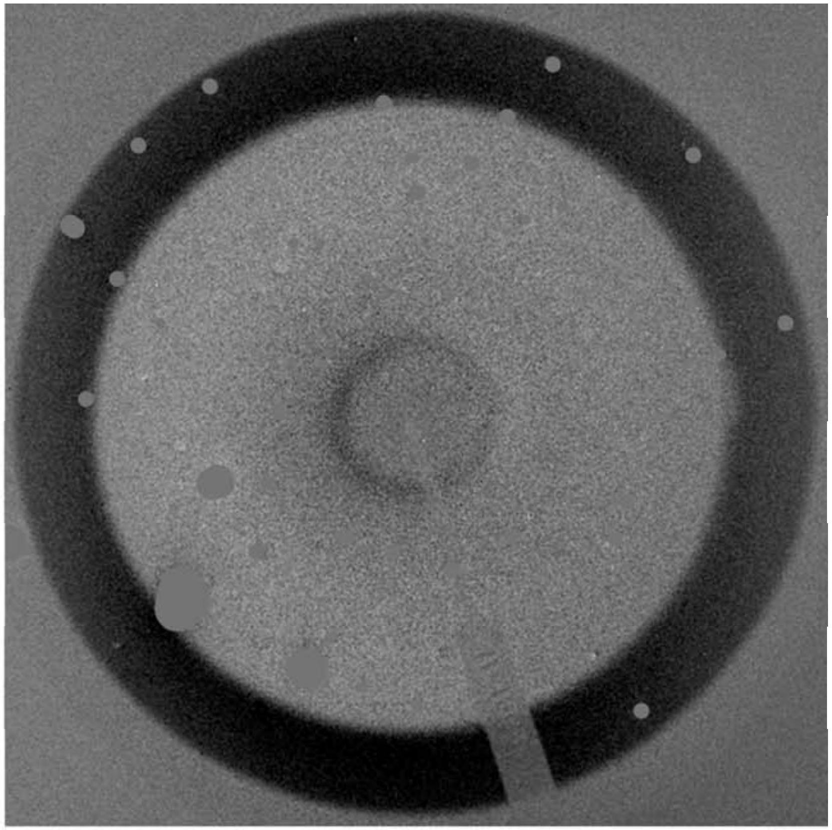


Diamond anvils: a large Compton contribution

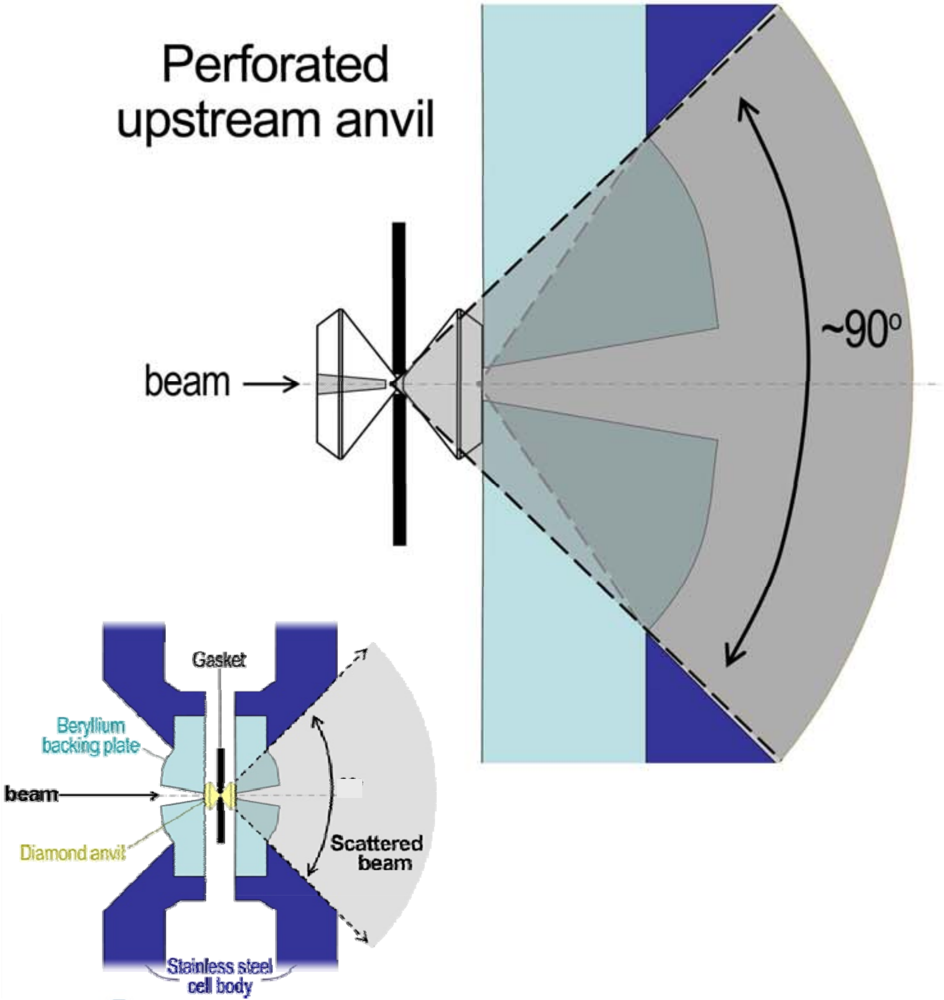


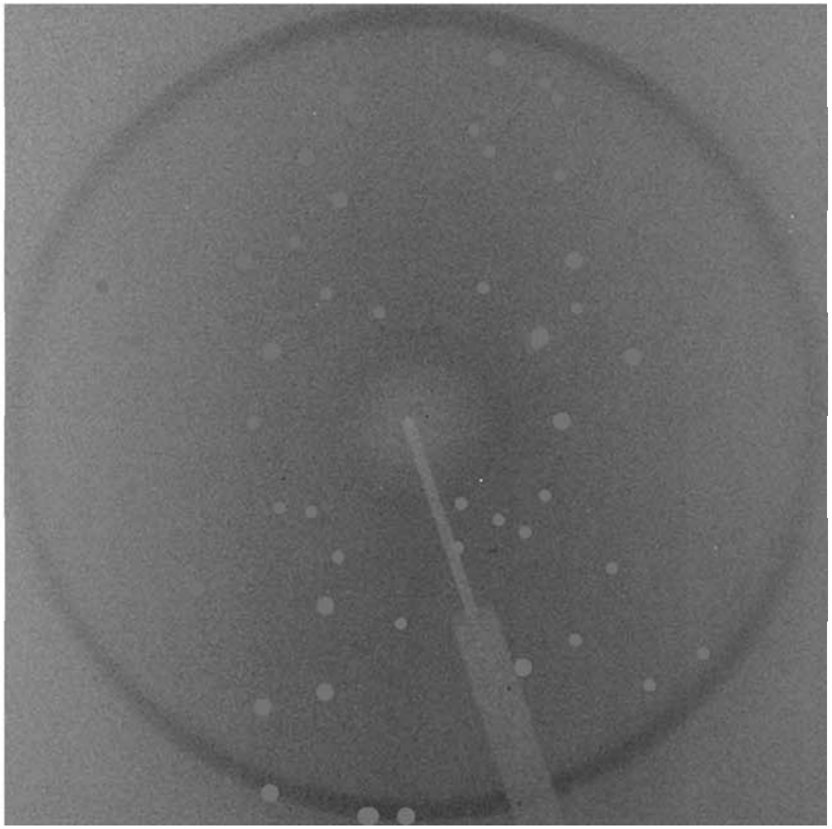
Diamond anvils: limit usable Q-range





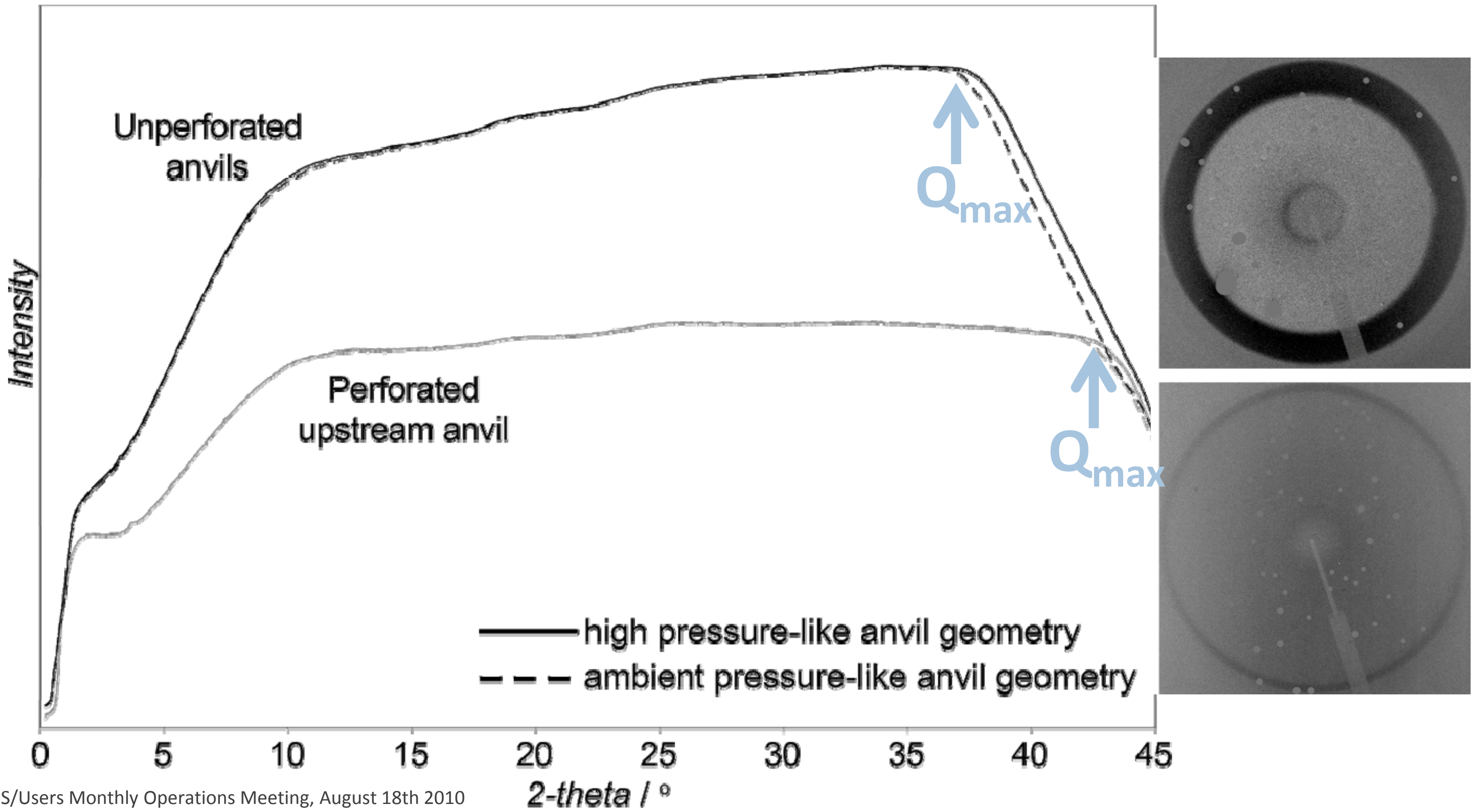
Diamond anvils: limit usable Q-range



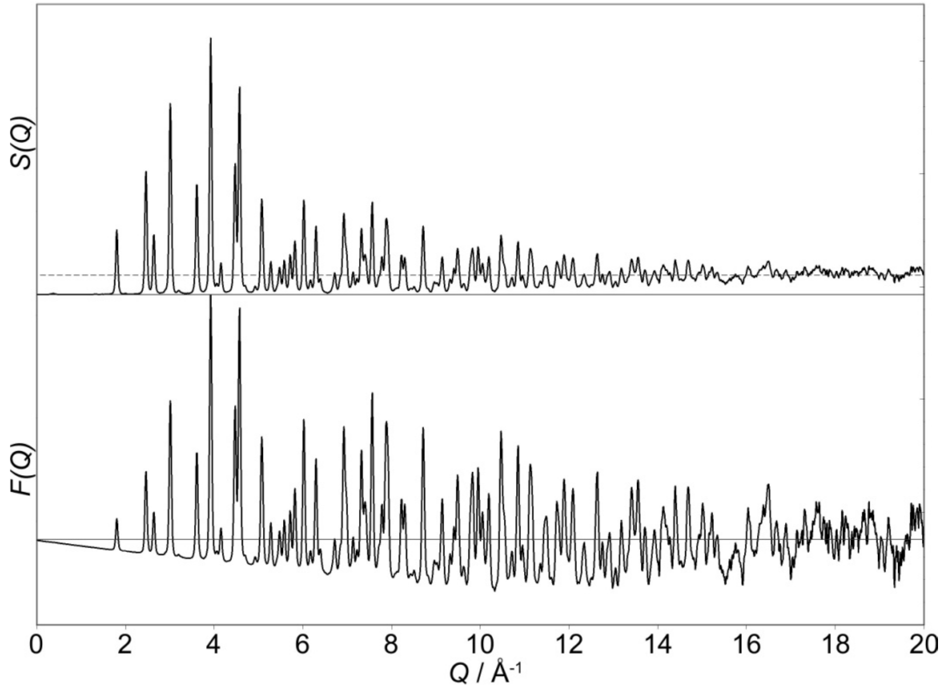


Diamond anvils: limit usable Q-range

Shadowing of scattering from the upstream anvil by the cell body shifts under pressure. By installing a partially perforated upstream anvil, and eliminating this pressure dependent shadowing, high pressure data can be accurately normalized over the full Q-range.



Some data….

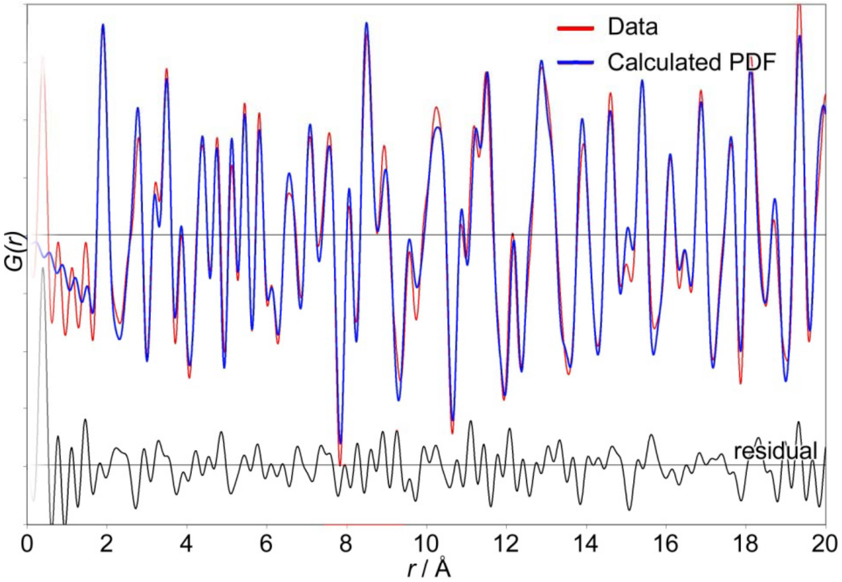


alpha-Al$_2$O$_3$ in DAC at ambient P

60keV

Q$_{max}$ = 20 A^{-1}

(2-theta ~43°)



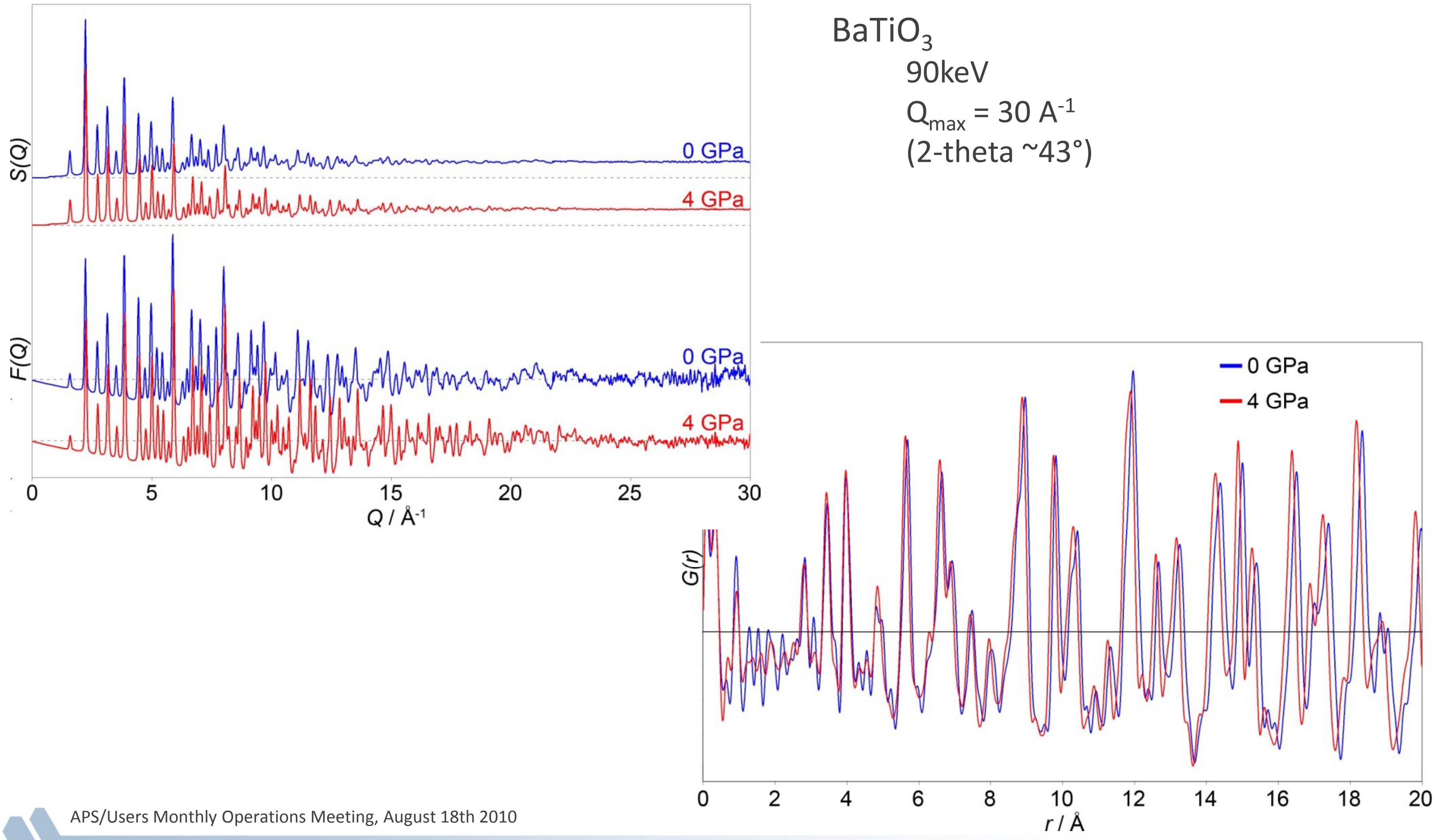
Some data…

BaTiO$_3$

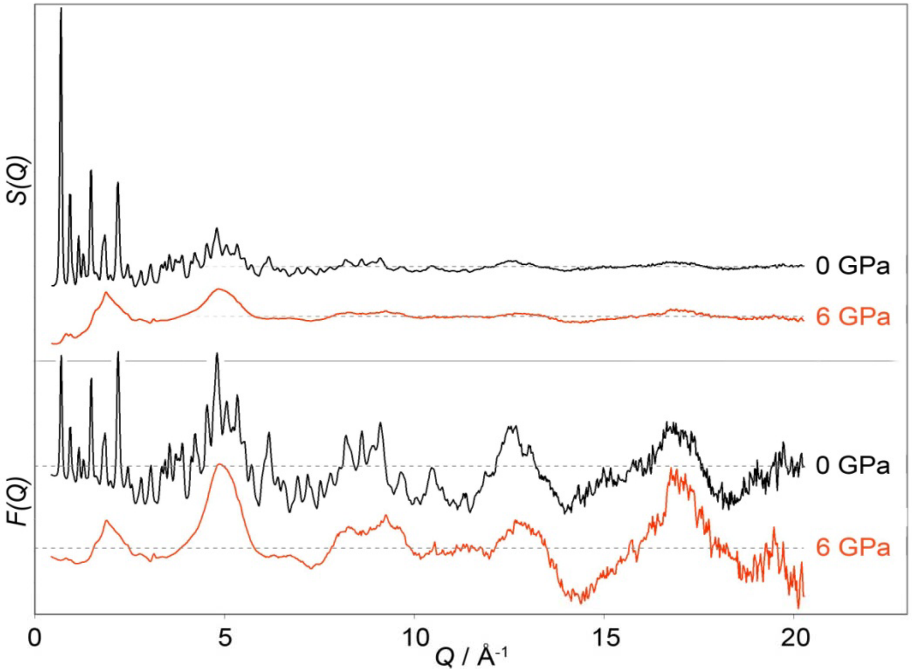
90keV

Q$_{max}$ = 30 A^{-1}

(2-theta ~43°)



Some data…

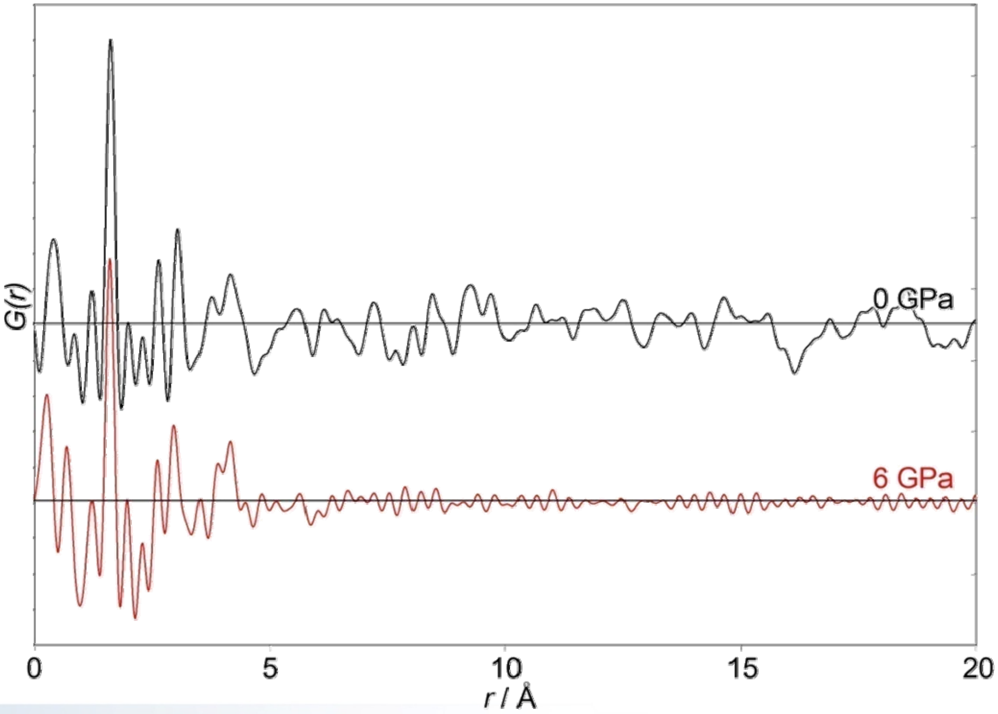


Zeolite (SiO_2)

60keV

Q_{max} = 20 A^{-1}

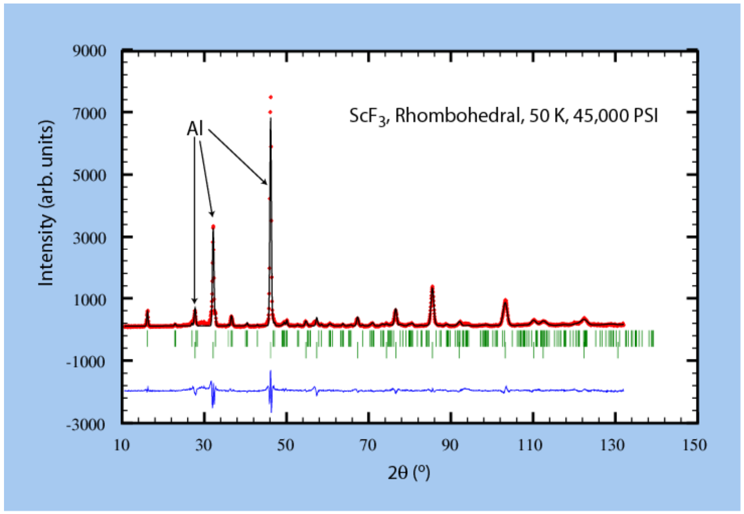
(2-theta ~43°)



Gas pressure cells for neutron scattering

- Large volume helium pressure cells can provide accurately known pressures, but scattering from the sample cell can be a major problem

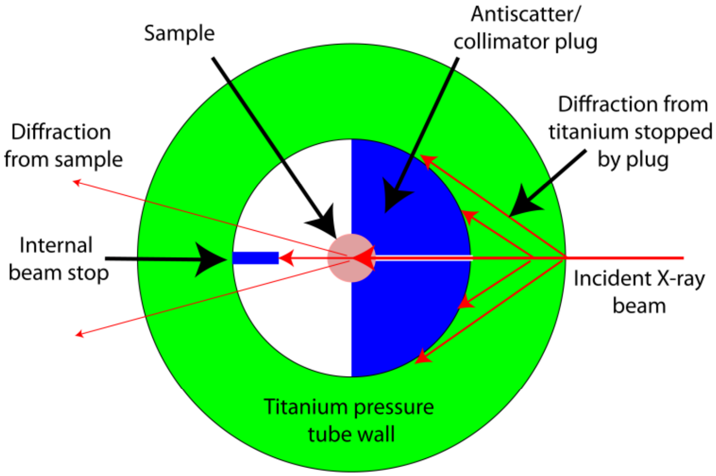
Bragg peaks from the aluminum pressure cell are ~10 x stronger than those from the sample!



Gas pressure cell from Harwood Engineering

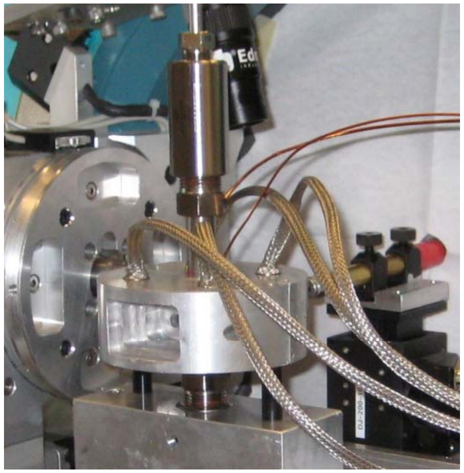
Eliminating the Bragg peaks

- Bragg peaks from the pressure cell body can be reduced by careful collimation
  - Radial collimator outside the pressure cell to attenuate scatter from the walls e.g. Soller slits
  - Attenuating slit+beam stop <u>inside</u> the pressure cell
    - Can give Rietveld quality diffraction data!

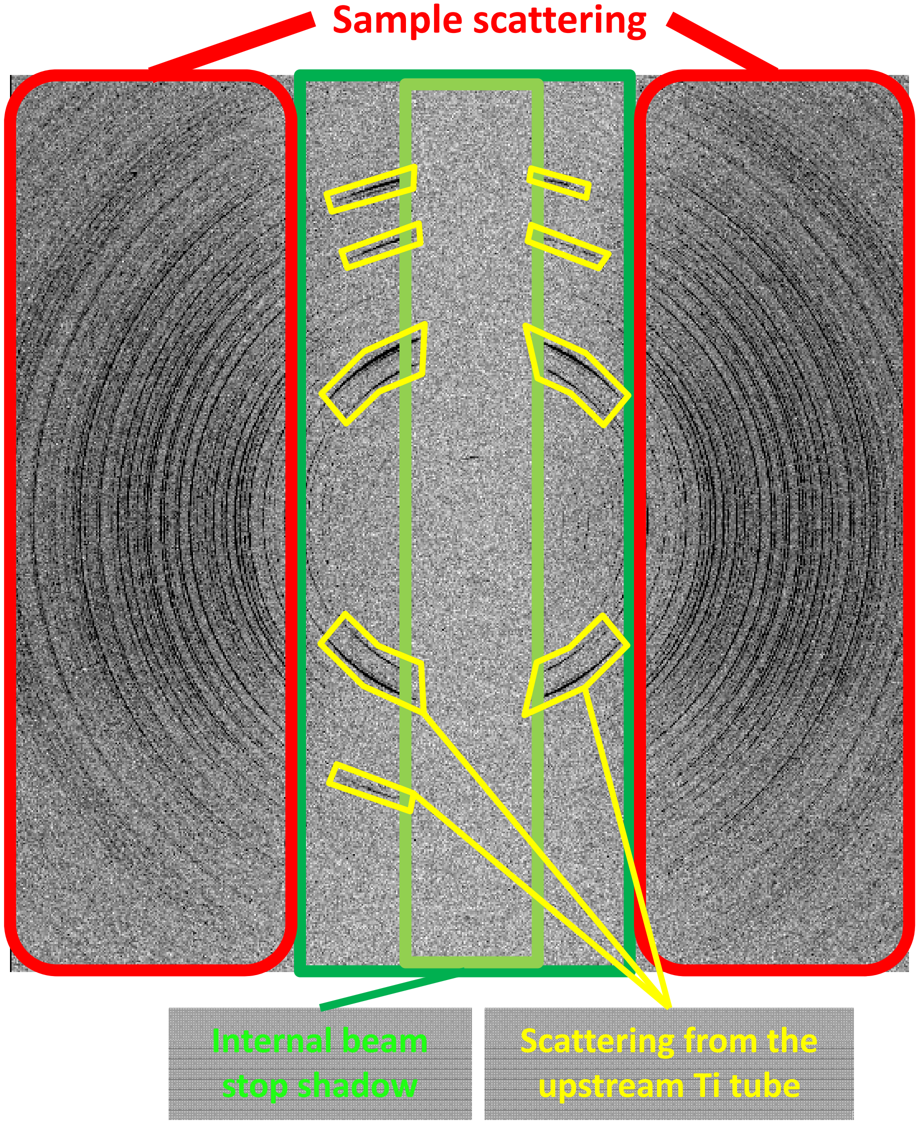


X-ray cells for modest P and T

- Grade 5 Titanium pressure tubes
  - 20,000 psi (5/16” i.d., 9/16” o.d.)
  - 40,000 psi (1/4” i.d., 9/16” o.d.)
- Tungsten internal slit and beam stop
- Aluminum heater block around pressure tube
- Silicone oil hydrostatic pressure medium
- Stability of the cell position under stress from the high pressure hose is important!
  - Very small movements will introduce systematic errors into measured lattice constants that are highly significant when trying to determine bulk moduli and CTEs!!!!



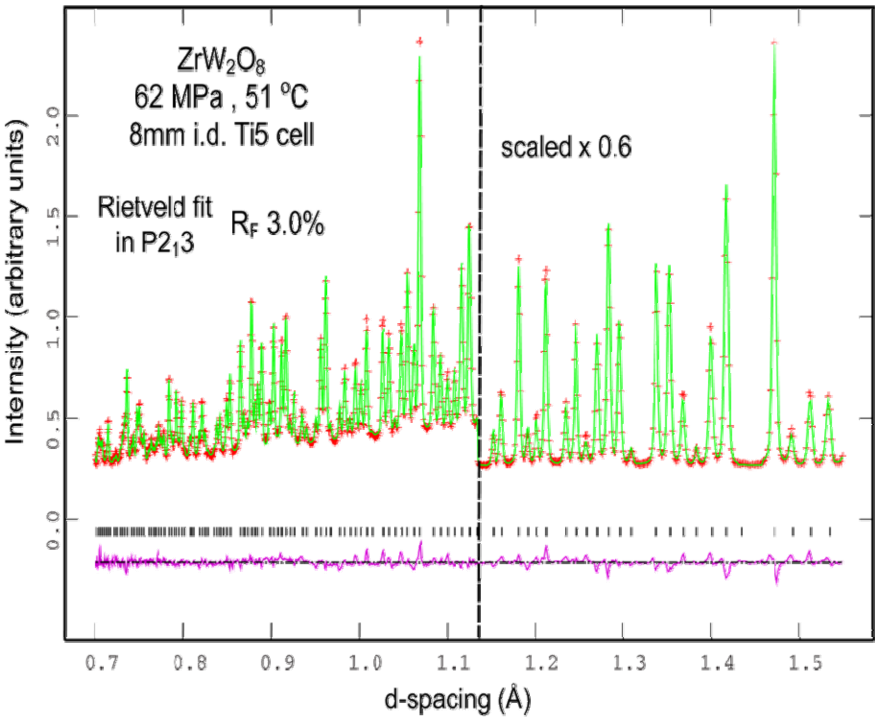
The internal collimator



Sample scattering

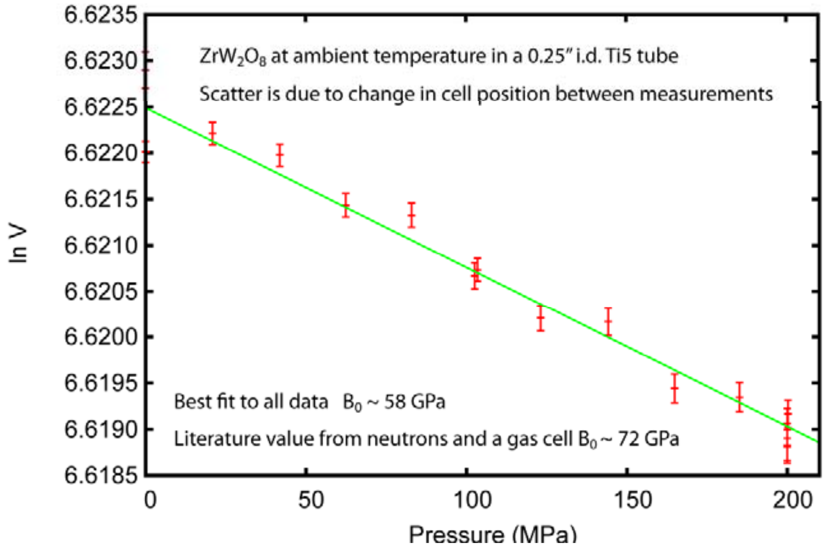
Internal beam stop shadow

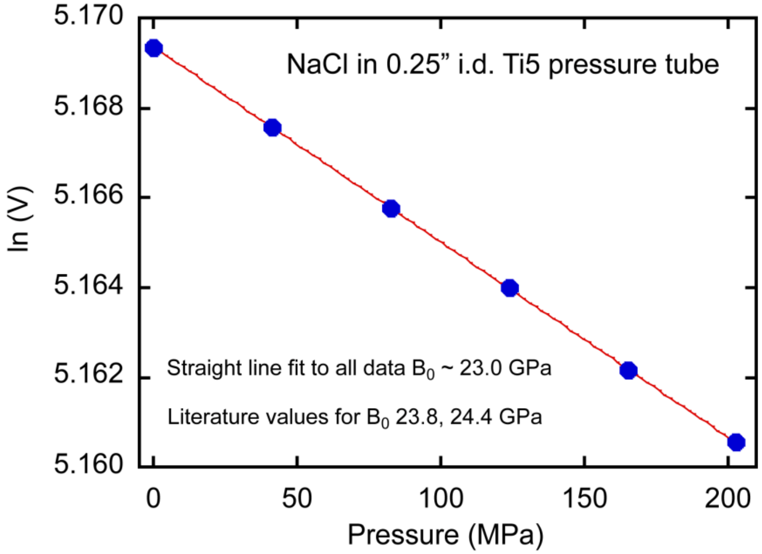
Scattering from the upstream Ti tube



Accurate measurement of lattice constants

- Cell design is suitable for accurate lattice constant determination by Rietveld or Le-Bail fitting, but the cell must not move due to stress from the plumbing!





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<u>High pressure PDF</u>

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- Benjamin Greve (Georgia Tech)
- Chad Ruschman (Georgia Tech)
- Joseph Hriljac (Birmingham)

Peter J. Chupas

Angus P. Wilkinson Gregory J. Halder

Chad J. Ruschman Benjamin K. Greve

Joseph A. Hriljac

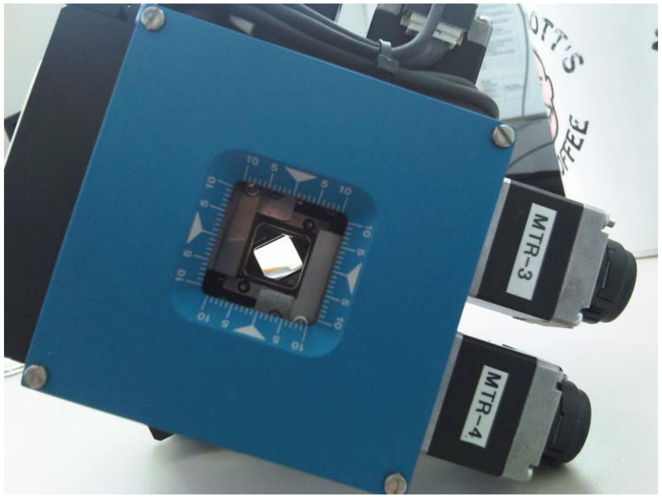
Charles Kurtz

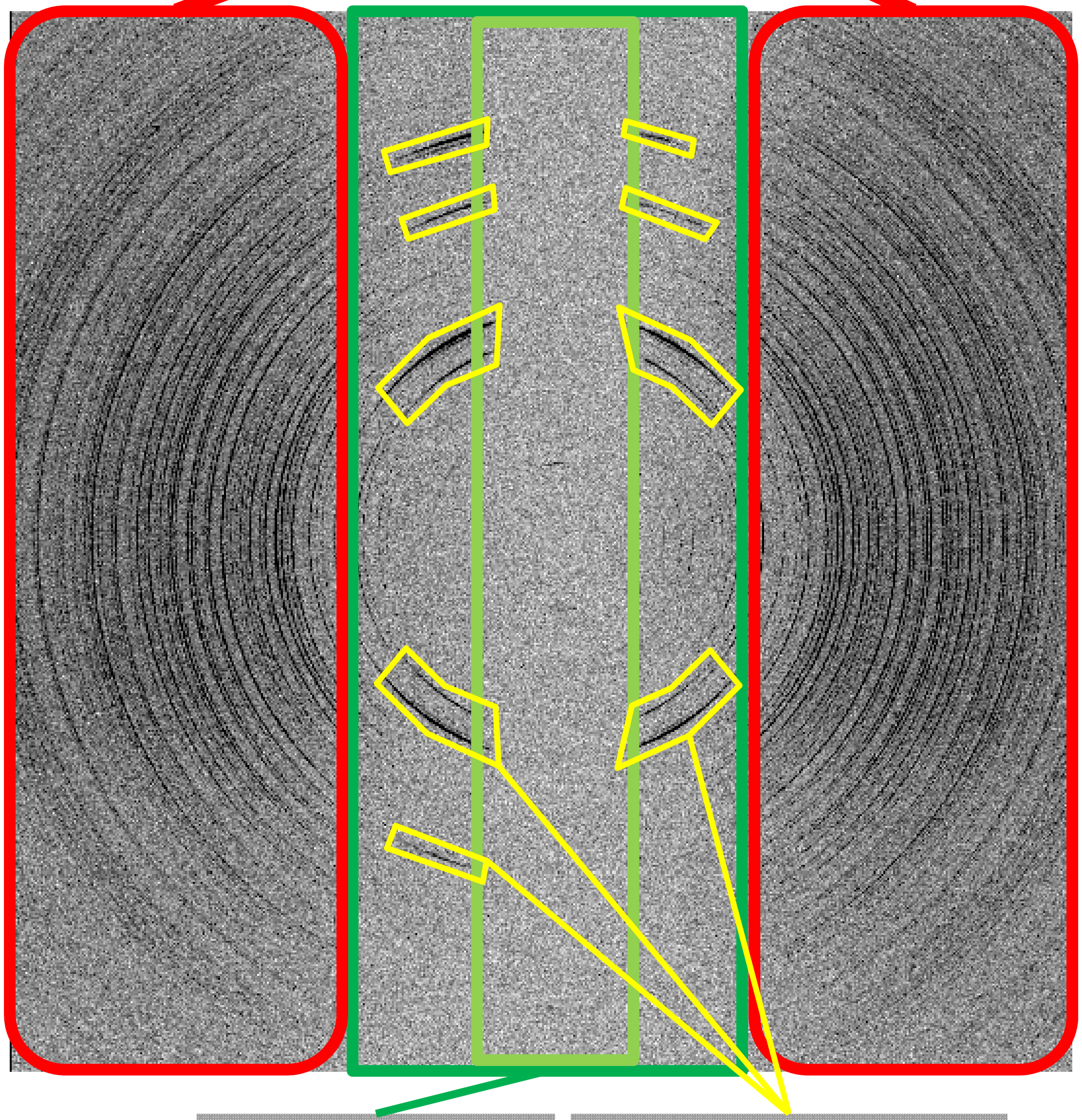
http://www.wordle.net/.

Future developments in PDF@HP at 11-ID-B

- Two-dimensional focusing with Al compound refractive lenses to be installed

- A new incident beam defining aperture will be installed. This will define a beam more closely matched to the circular gasket hole, to maximize the sample area illuminated while reducing the risk of unwanted scattering from the gasket.





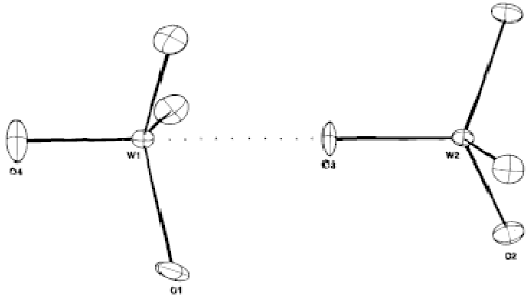
Sample scattering

Internal beam stop shadow

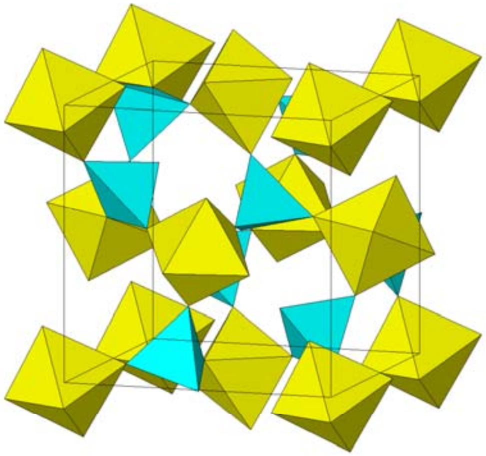
Scattering from the upstream Ti tube

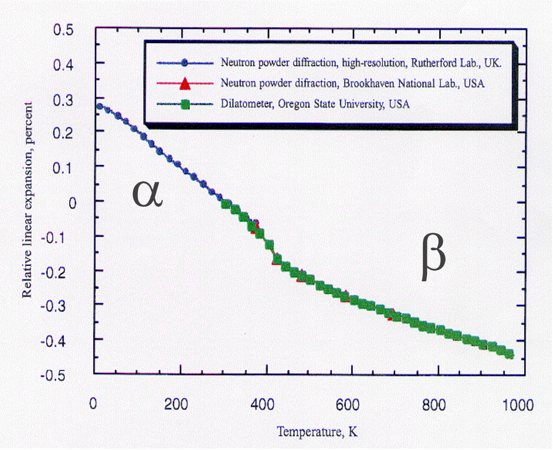
Order-disorder in the NTE material ZrW2O8

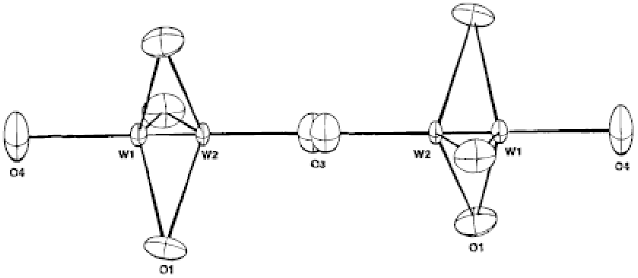
- ZrW_2O_8 displays an order disorder transition at ~400K
  - How does this transition depend on pressure?
  - What happens to the bulk modulus on disordering?



Ordered arrangement of XO_4tetrahedra in the alpha structure





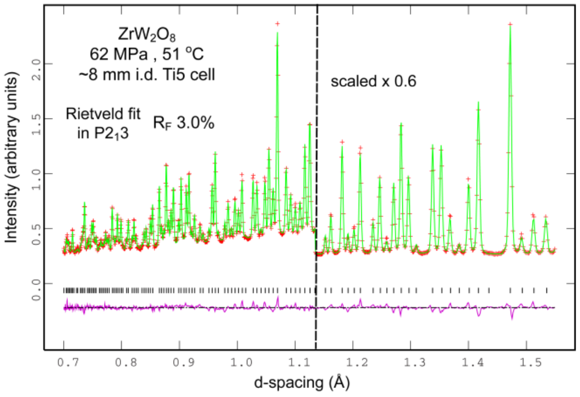


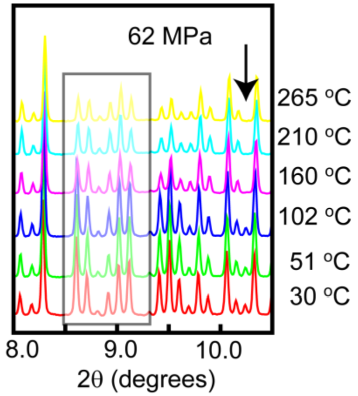
Disordered arrangement of XO_4tetrahedra in the beta structure

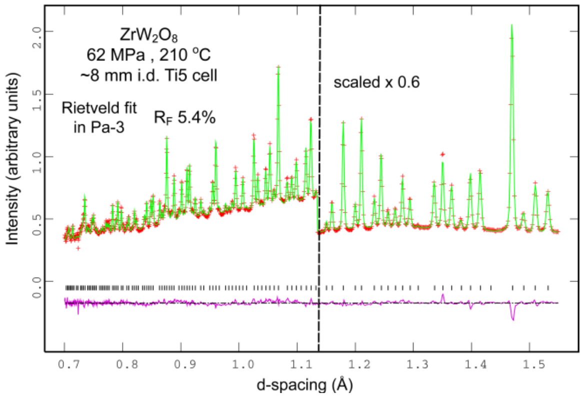
J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian and A. W. Sleight, "Negative Thermal Expansion in ZrW_2O_8 and HfW_2O_8," *Chem. Mater.* **8**, 2809-2823 (1996).

ZrW_2O_8 at modest pressures

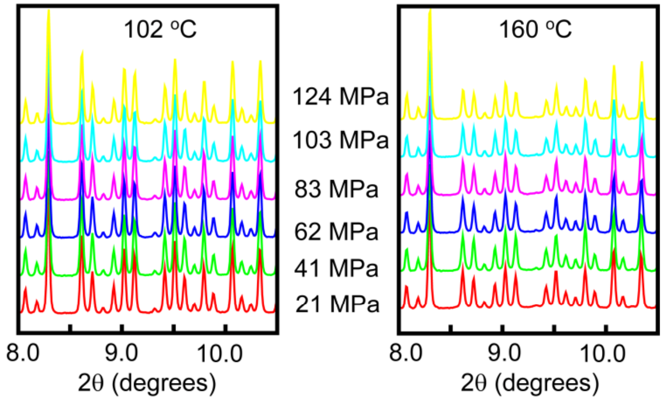
- Phase transition lies between 102 and 160 °C over the full pressure range initially examined (0 – 124 MPa)







Good quality Rietveld fits obtainable between 0.7 and 1.55 Å d-spacing with detector ~90 cm from sample and 58 keV X-rays

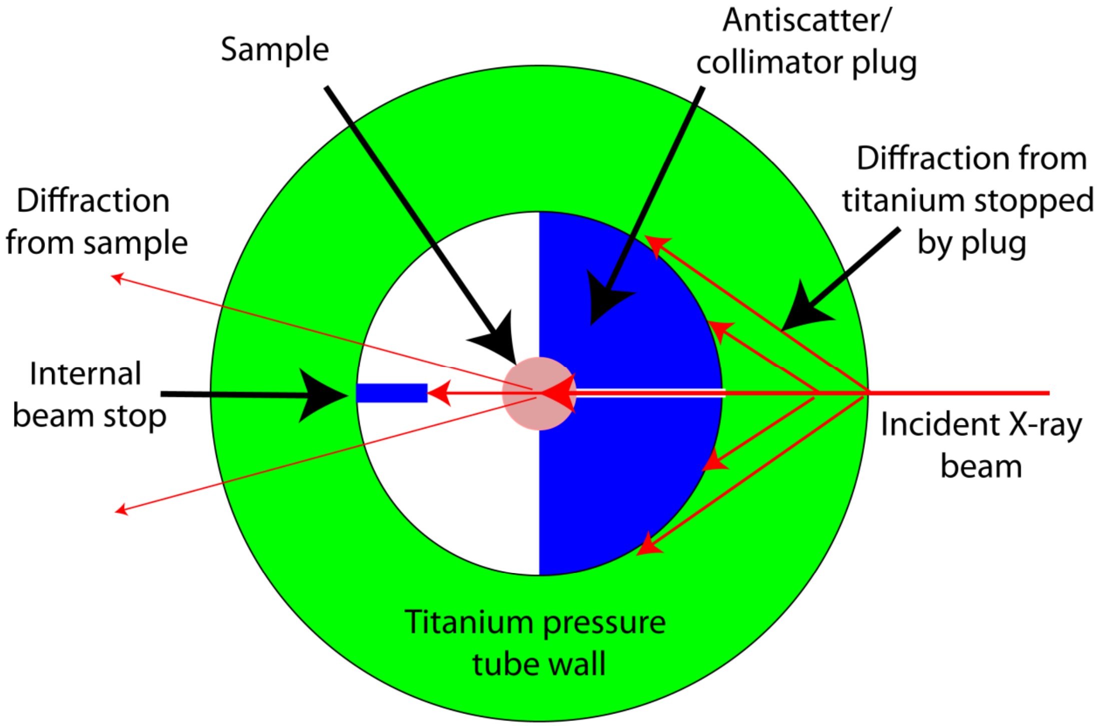


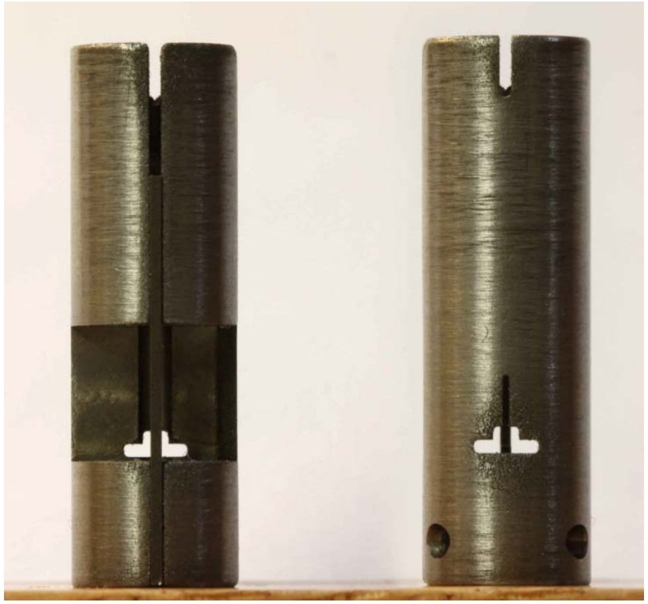
Data below 0.7 Å d-spacing is corrupted by attenuation from the beam stop

Fluid Pressure Cells

- Lower pressure accessed (<0.5 GPa) but with more control
- Strong heavy walled tubes to contain high pressure fluid
- Stainless steel or Ti
- Attenuates incident/scattered beam
- Tube scattering dominates measured intensity
- Need collimator / Söller slits etc. ($$$) to isolate contribution from the sample

An internal collimator





High precision VT-HP measurements