High Pressure Experiments with *in situ* X-ray and Neutron Measurements

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Talk overview

Why high pressure? - It is a great example for extreme conditions, and it is fun!

1. Background on high pressure
2. High pressure techniques for X-ray scattering
3. Opportunities for high pressure science with APS-U
4. High pressure neutron scattering: techniques, development and science examples

Extreme condition environments

Wikipedia:

"An 'extreme environment' contains conditions that are hard to survive for most known life forms."

- Alkaline/acidic: below pH 5 or above pH 9
- Extremely cold/hot: below -17°C or above 40°C
- Under pressure: e.g. habitats deeper than 2000 m
- Under radiation
- Hypersaline
- Without water or oxygen

Sandy desert

Mount Everest

Salt lake

Source: Wikipedia

Extreme condition environments

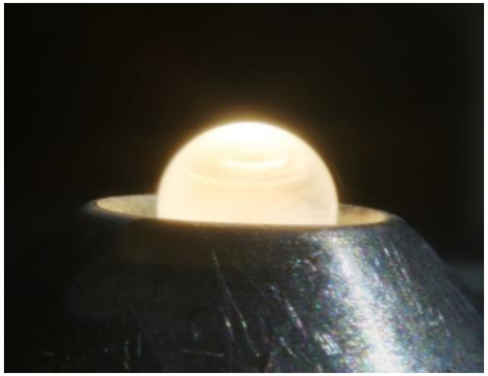
High radiation environments - In situ measurements on 'hot' samples

Courtesy of Ken Littrell,
GP-SANS, HFIR

High magnetic field environments

Low temperature environments – Cryostats and dilution fridges

High temperature environments – levitation for measurements of melts



Courtesy of Joerg Neuefeind,
NOMAD, SNS

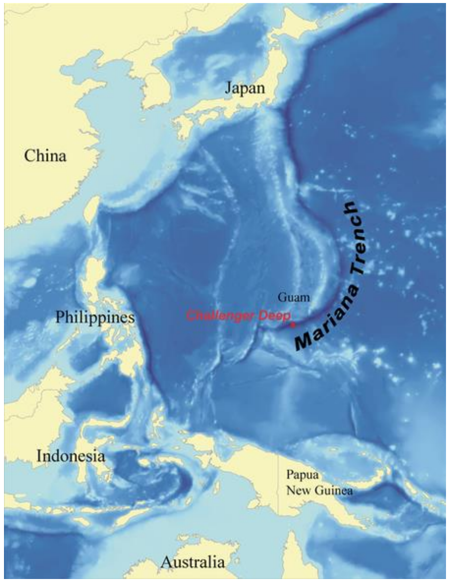
High pressure conditions

Ambient conditions:
1 atmosphere = 14.696 psi = 760 Torr = 1.013 bar = 101 kPa

High pressure conditions:
1 kbar = 0.1 GPa (= 987 atmospheres)

Wikipedia:
[Magnitude of pressure]()

Pressure of CO_2
400-600 kPa

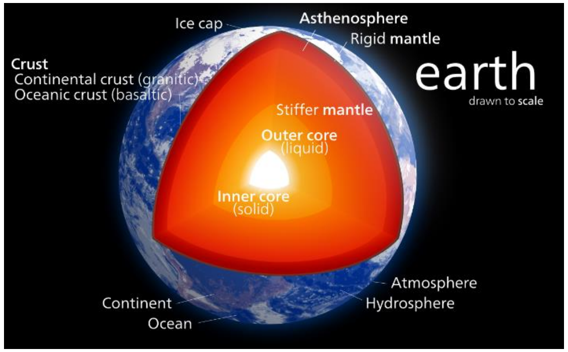


Deepest point of the ocean at depth of ~10900 m and ~0.1 GPa pressure

Photo Source: Wikipedia

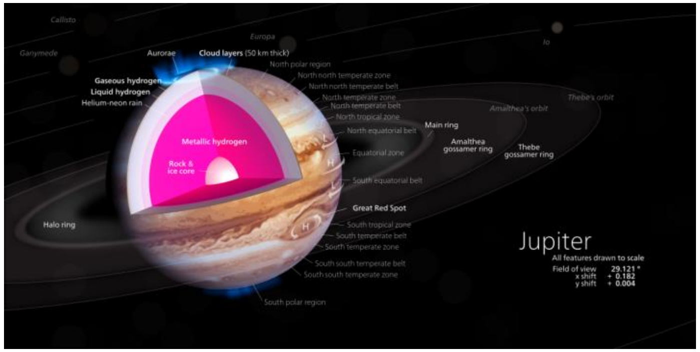
Planetary sciences

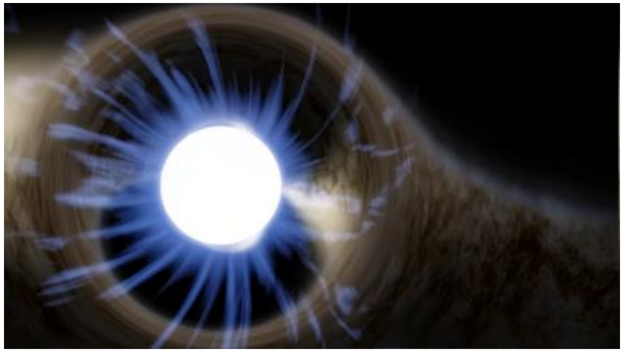
The understanding of the interior of planets and other solar bodies requires high pressure studies.



Pressure and temperature in the earth core ~360 GPa and 5000 K.

Pressure and temperature in Jupiter's core about 3000-4500 GPa and ~24000 K.





Neutron star, pressure from 3.2×10^{22} to 1.6×10^{25} GPa.

Photo Source: Wikipedia

High pressure, high temperature industry

High pressure is also important for industrial applications.

Haber-Bosch process for ammonia production occurs at 15-25 MPa and 400-500°C.

A historical (1921) high-pressure steel reactor at KIT, Germany

Polyethylene is often made by high pressure processing. The initial discovery applied 0.14 GPa for synthesis.

Diamond is made by high pressure, high temperature processing. The first diamonds were made under ~10 GPa and 2300 K.

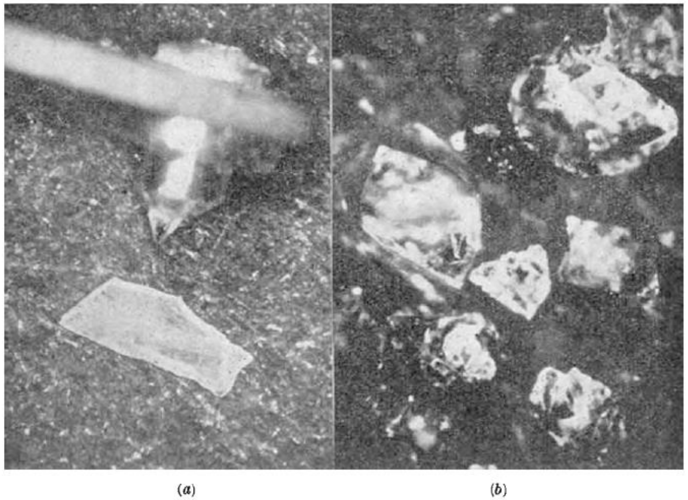


Fig. 3. Man-made diamonds. (a) 1-mm. diamond shown with phonograph needle. (b) 0·2–0·5-mm. octahedra

Bundy et al, Nature 176, 51, 1995.

Photo Source: Wikipedia

High pressure science

High pressure is becoming increasingly important in diverse aspects of science.

Food processing (high pressure pasteurization)

Room temperature superconductivity

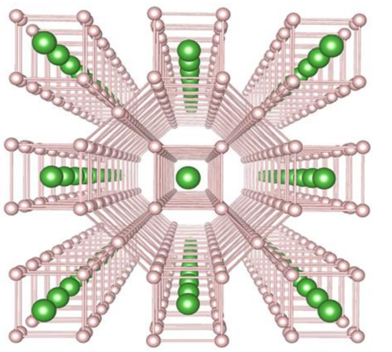
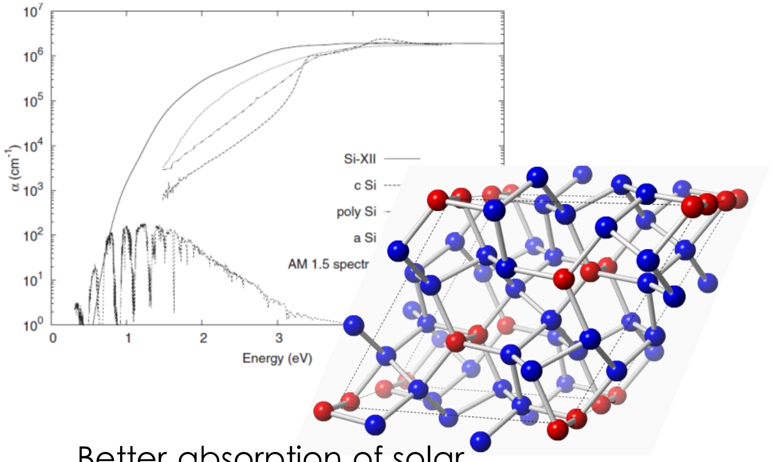


Image from Science News, LaH_{10} reported in PRL 122, 027001 (2019).

Novel semiconductors

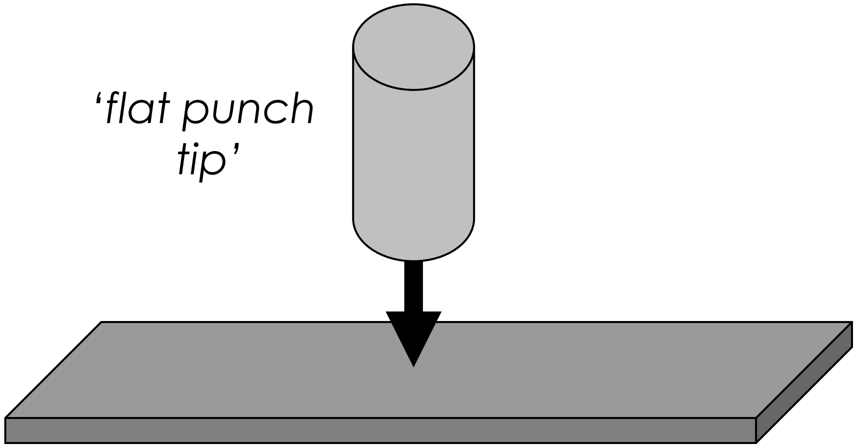


Better absorption of solar spectrum for r8-Si (Si-XII) in PRB 78, 161202(R) (2008).

What is pressure?

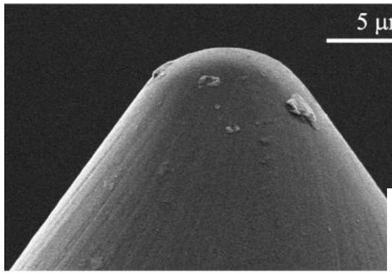
$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

For a radius of 2 μm,
an applied force of ~0.120 N
already achieves 10 GPa!

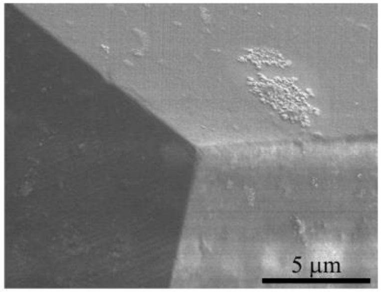


'flat punch tip'

Indentation:



spherical tip



Berkovich tip

History of high pressure science

Percy Williams Bridgman
father of high pressure studies

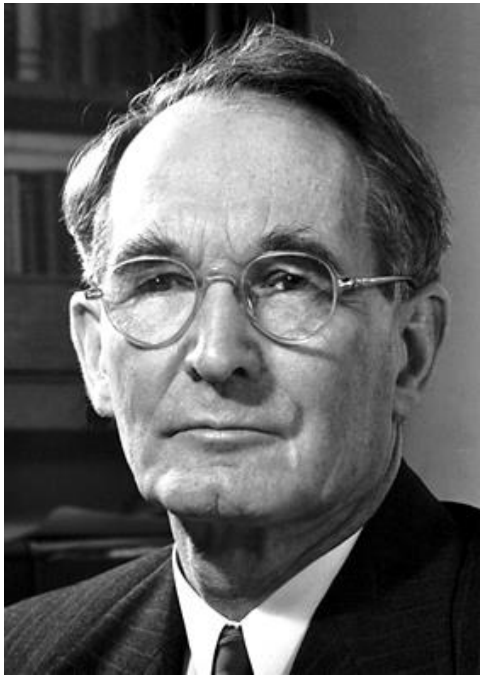
1919: appointed full professor in Harvard, aged ~37

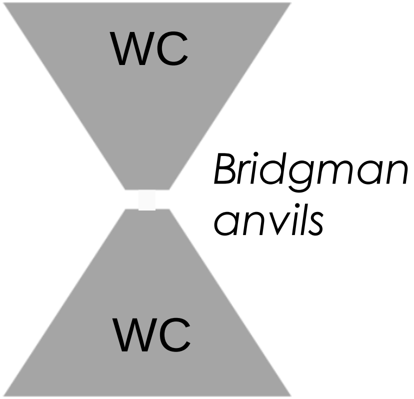
New pressure apparatus (1905), Bridgman anvils

Invented the Bridgman seal

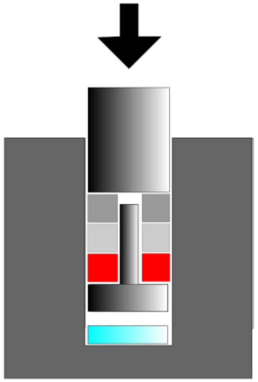
Studied over 100 materials under pressure

Received the Nobel Prize in 1946 for his studies of the properties of matter at high pressure and the invention of his high pressure apparatus.





Bridgman anvils

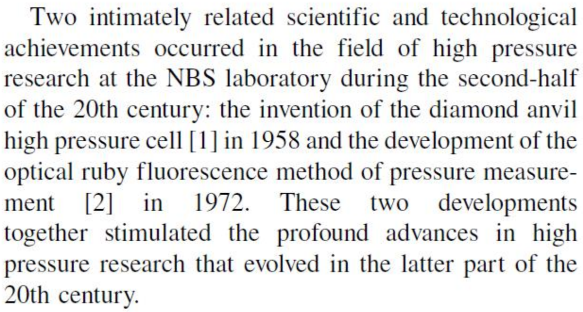


Bridgman seal

Photo Source: Wikipedia

History of high pressure science

Based on the shape of Bridgman anvils, the diamond anvil cell was developed at NIST.



Two intimately related scientific and technological achievements occurred in the field of high pressure research at the NBS laboratory during the second-half of the 20th century: the invention of the diamond anvil high pressure cell [1] in 1958 and the development of the optical ruby fluorescence method of pressure measurement [2] in 1972. These two developments together stimulated the profound advances in high pressure research that evolved in the latter part of the 20th century.

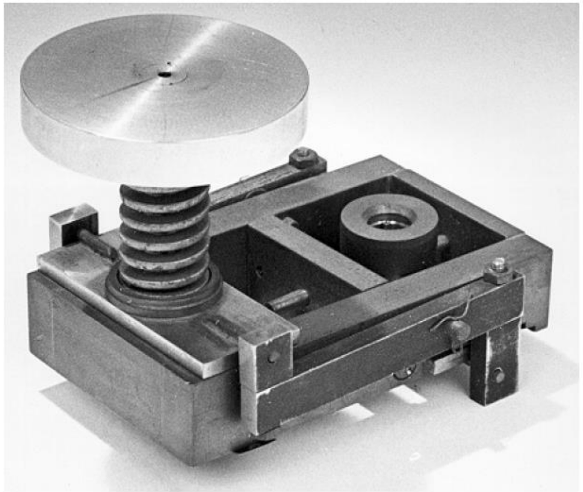


Fig. 1. The original DAC, on display in the NIST Museum.

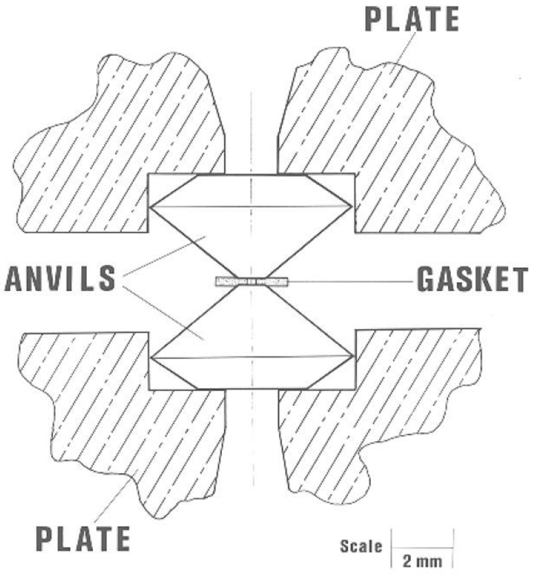


Fig. 4. A schematic diagram of the opposed diamond anvil assembly to illustrate the 180° optical transmission characteristics and the concept of Bridgman opposed anvils. A thin metal gasket containing a 250 µm diameter hole for encapsulating a sample (liquid or solid or both) is squeezed between the two anvils.

DAC development at NIST

2. High pressure X-ray scattering

Diamond cells for X-ray scattering

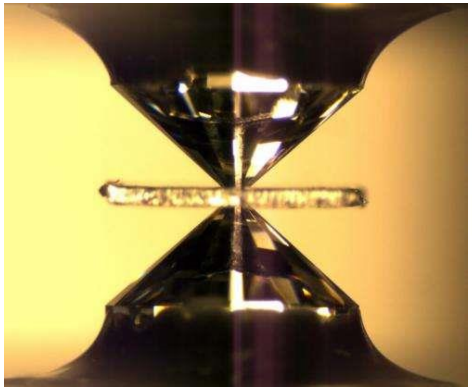
$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

For a radius of 200 μm, we now need to apply a force of ~1200 N (equivalent to ~130 kg) to achieve 10 GPa.

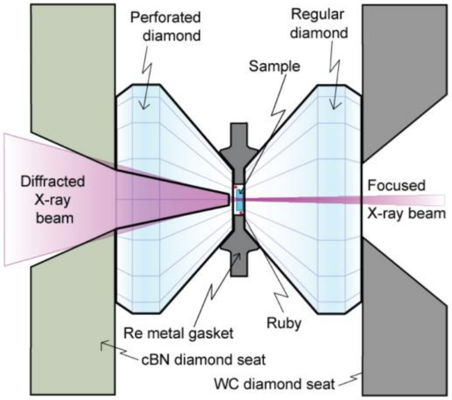
Such a radius enables sufficient sample size for X-ray experiments while loads/forces can be locked in with screws.

For X-rays the DAC is the main pressure device.

Diamond cells for X-ray scattering



from Phys.org

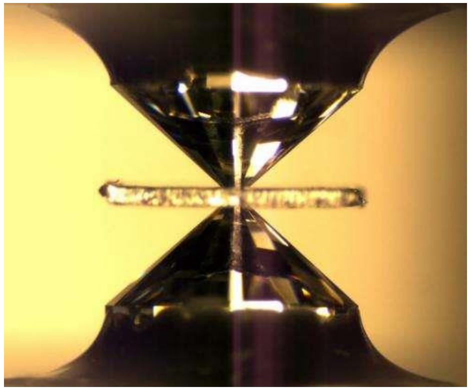


by Stas Sinogeikin (HCPAT)

The sample is loaded into the gasket together with a ruby (for pressure measurement) and a pressure transmitting medium (for hydrostatic conditions).

Pressure is then applied by bringing the anvils closer together and the gasket flowing inward.

Diamond cells for X-ray scattering



from Phys.org

- Large pressure range from very low pressures to ~300 GPa is accessible in a DAC.
- With double-stages, pressures up to 600 GPa have been reached.
- Large temperature range from ~1.4 K to ~5000 K can be additionally applied.
- Modifications allow easy adaption to more specific questions:
  - membranes for rate control on de/compression,
  - perforation for low signal samples,
  - designer anvils for transport measurements
  - additional dynamic compression etc.

Diamond cells for X-ray scattering

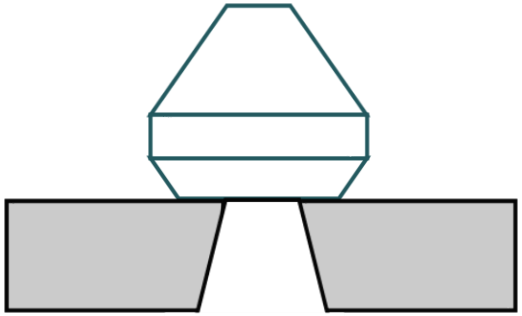
A large variety of different DACs have been created for different purposes.

Mao-type symmetric cells

Panoramic cells

Often used with Be gasket

Flat anvils



Seat made from WC or cBN (for transparency in beam)

Photo Source:
https://eel.stanford.edu/research/research-facilities

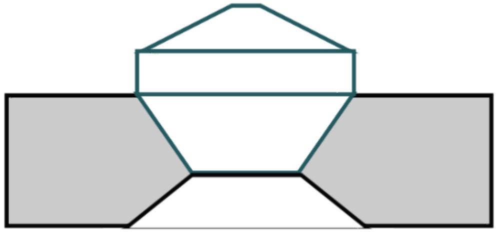
Diamond cells for X-ray scattering

A large variety of different DACs have been created for different purposes.

Deflection cell:

Boehler-Almax Plate DAC

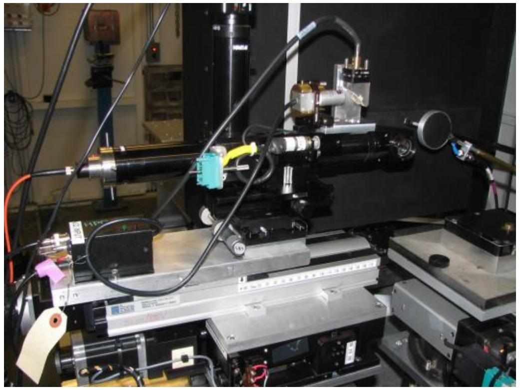
Conical anvils



Boehler-style cut

Diamond cells for X-ray scattering

DAC experiments require substantial support infrastructure.



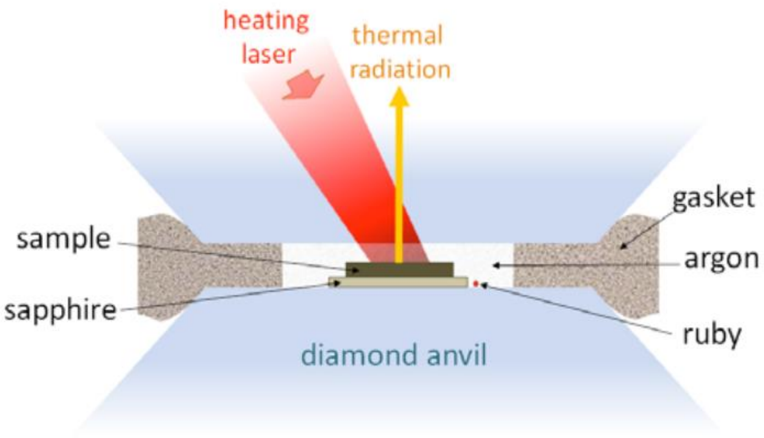
HPCAT online and offline ruby systems

GSECARS/COMPRES gas loader

HPCAT laser driller

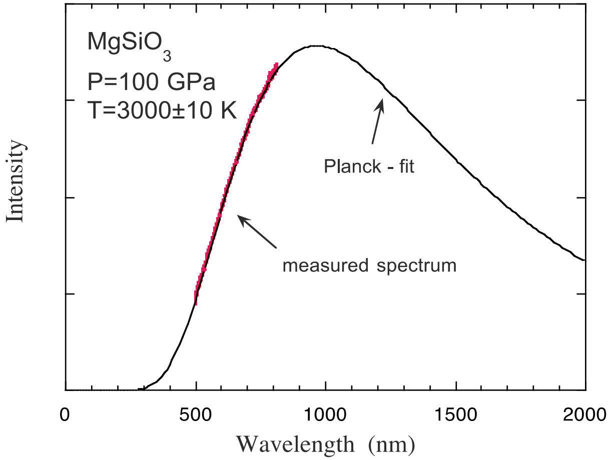
Laser-heating in the diamond cell

Samples can be heated to ~5000 K using a YAG or CO_2 laser. This can be done *in situ* during X-ray scattering.



Schematic of a laser-heated sample in a DAC [1]

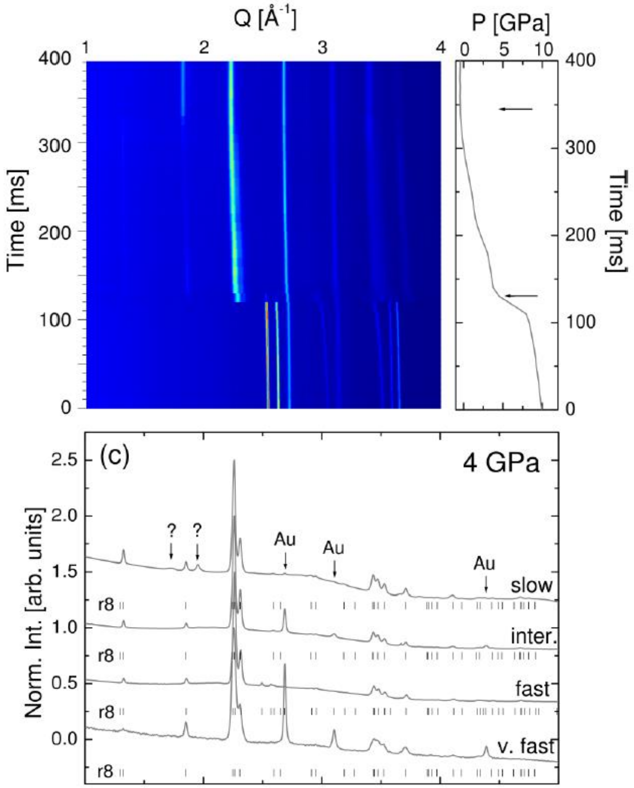
Temperature measurement using Planck equation [1]



DACs can also be combined with other extremes such as ultra-low temperatures or magnetic fields.

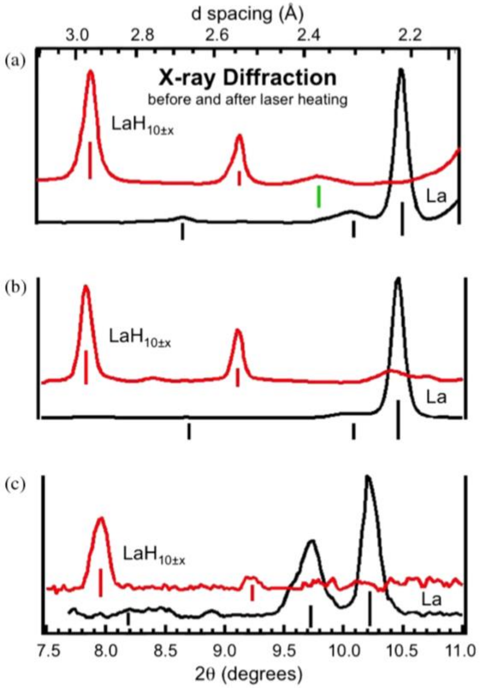
[1] R. Boehler, *Materials Today* **8**, 34 (2005).

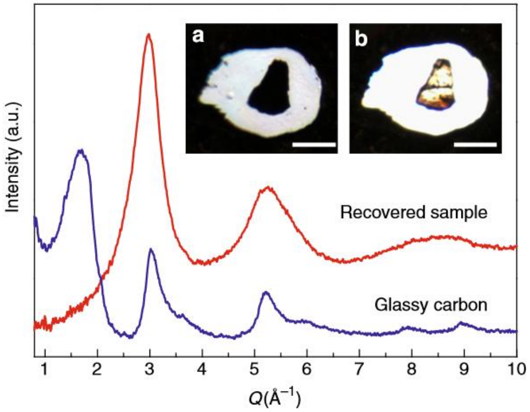
High pressure science with X-ray scattering



Rate dependence of metastable phase formation in germanium [1].

LaH_{10x} formed through laser heating in a DAC [2].





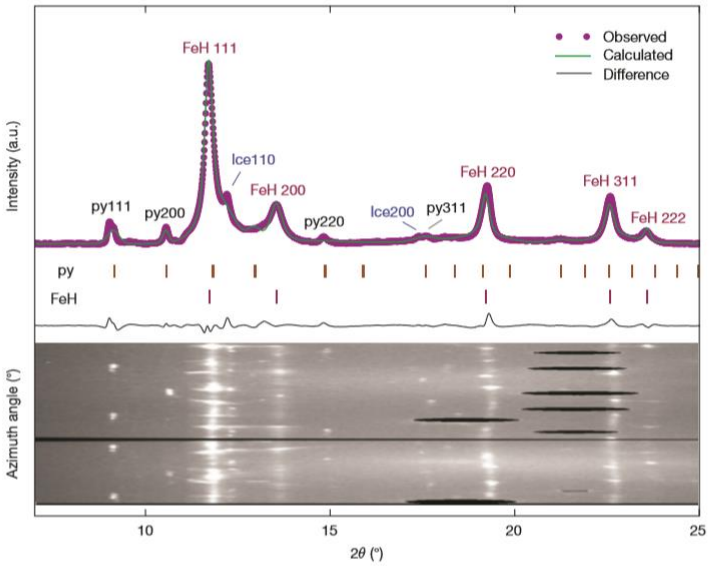
High pressure, high temperature synthesis of amorphous diamond [3].

[1] B. Haberl et al, PRB 89, 144111 (2014).

[2] Somayazulu et al, PRL 122, 27001 (2019)

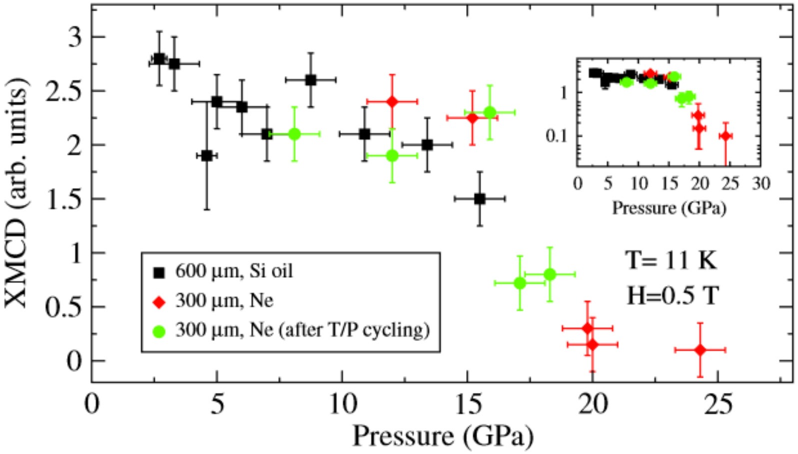
[3] Z. Zeng, Nat. Comm. 8, 322 (2017).

High pressure science with X-ray scattering



XRD pattern of Fe+H_2O reaction compound which suggests the possible presence of hydrogen-bearing iron peroxide in the lowermost mantle [1].

Pressure tuning of the spin-orbit coupled ground state of Sr_2IrO_4 measured for example through the pressure-dependence of the Ir L_3 edge [2].



[1] J. Liu et al, Nature 551, 494 (2017).
[2] D. Haskel et al, PRL 109, 27204 (2012).

Complications for X-ray scattering in a DAC

Most scattering techniques are also possible in a DAC although data quality is often inferior.

Powder diffraction: environment not hydrostatic enough for Rietveld.

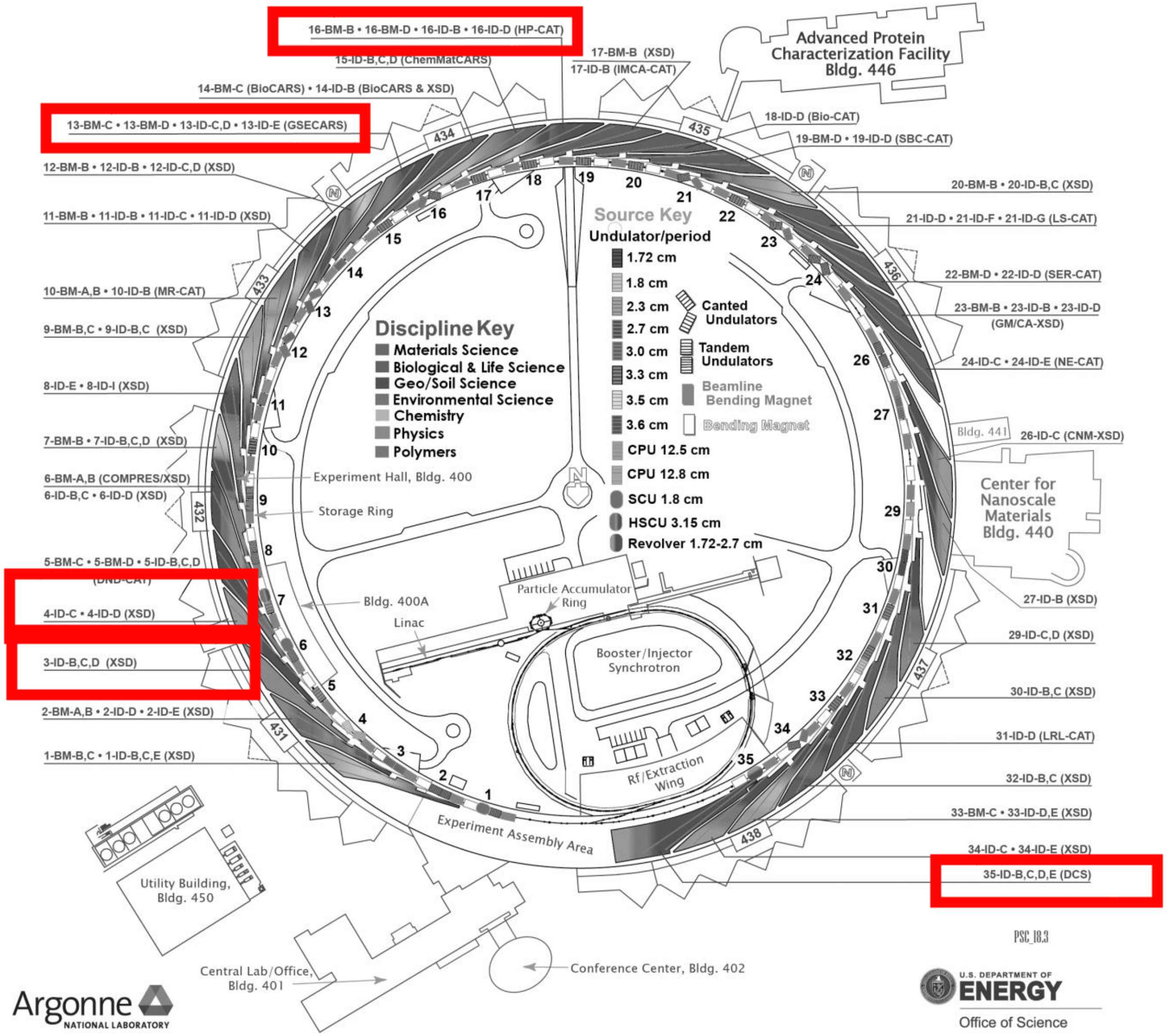
Laser heating: huge temperature gradients (1000 K!) that can even result in different crystal grain sizes.

EXAFS: Diamond glitches.

PDF: Limited diffraction aperture, background changes with pressure.

Single crystal diffraction: all of the above.

High Pressure Science at the APS



3. Opportunities for high pressure science with APS-U

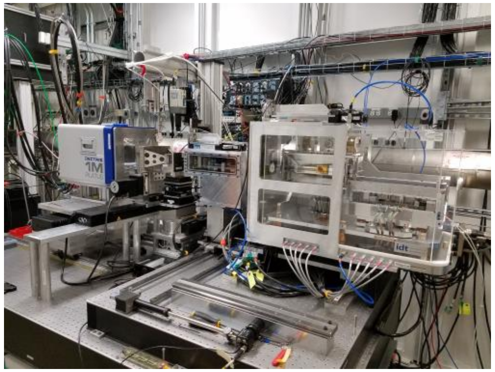
HPCAT, Sector 16

HPCAT offers 5 experimental stations and various offline laboratory support facilities

- **16-BM-B**: multi-array capabilities, including large volume Paris-Edinburg (PE) press for *in situ* viscosity measurements of melts/liquids, longitudinal and shear elastic moduli.
- **16-ID-B and 16-BM-D**: x-ray diffraction and *in situ* laser and resistive heating (ambient to >500 GPa, ~10K up to 4000+K) for multiphase P-T phase diagram development, understanding kinetics, and determining solid-melt boundary. X-ray absorption spectroscopy (XANES and XAFS) can be performed in tandem with diffraction in 16BM-D.
- **16-ID-D**: x-ray Raman spectroscopy, x-ray emission spectroscopy, inelastic x-ray scattering for understanding bonding and electronic structure.
- **16-ID-E**: an approved x-ray enclosure fielding special request and unique measurements.

Large volume press
At 16-BM-B

General purpose
table at 16-ID-B

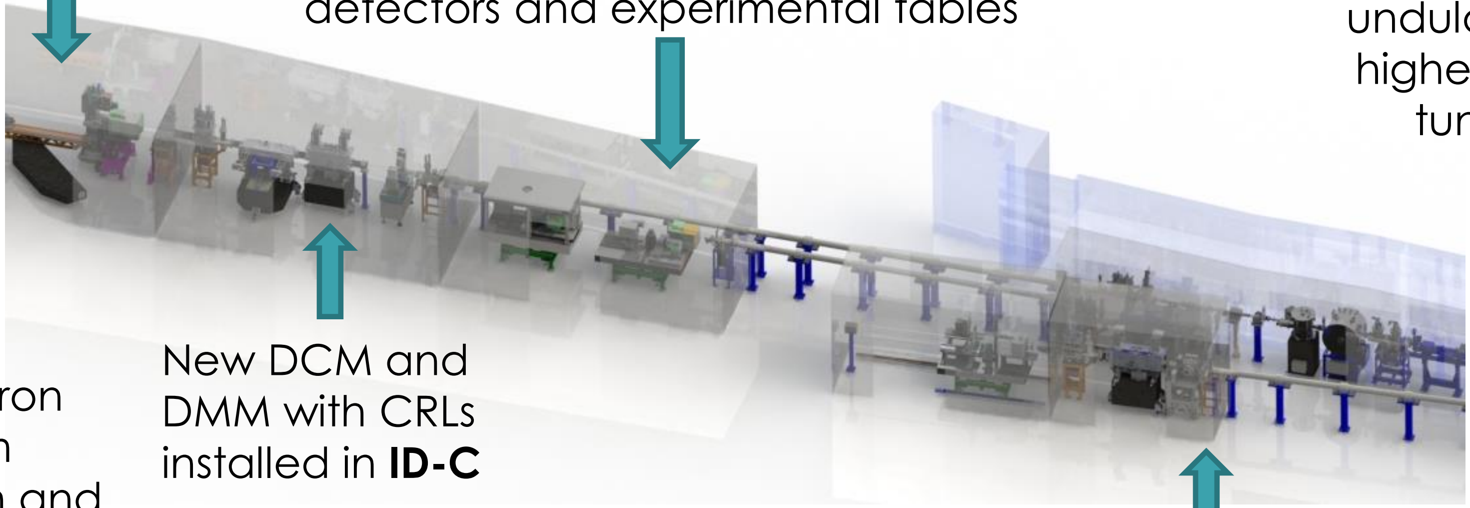


HPCAT, Sector 16, after APS-Upgrade

ID-D will facilitate SAXS, NRS, IXS

ID-B has new branching monochromator, focusing mirrors, detectors and experimental tables

Canted 21/25 Revolver undulators offer higher flux and tunability



sub-micron beam diffraction and tomography in **ID-E**

New DCM and DMM with CRLs installed in **ID-C**

BM line uses single source. PEC and XAS/XRD operate in tandem mode with new detectors, focusing optics and experimental tables

Contact:
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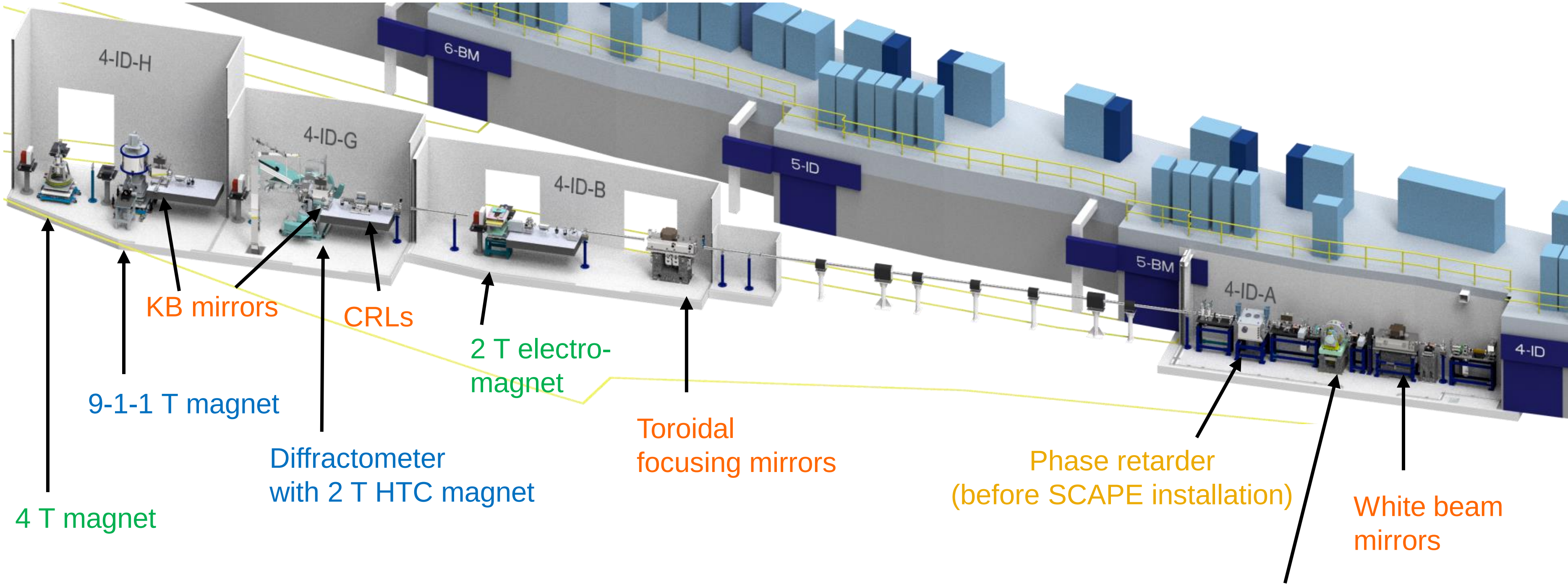
Argonne NATIONAL LABORATORY

APS-U beamline POLAR, to come online in 2024
Focus: Magnetism at extreme pressure conditions*



KB mirrors

CRLs

2 T electro-magnet

9-1-1 T magnet

Diffractometer
with 2 T HTC magnet

Toroidal
focusing mirrors

Phase retarder
(before SCAPE installation)

White beam
mirrors

4 T magnet

Monochromator

Contact:
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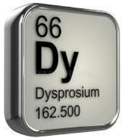
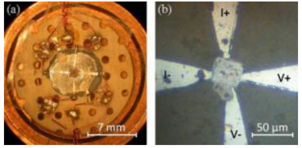
*See Appendix A

APS-U Polar beamline: brilliant focused beams for extreme pressure science*

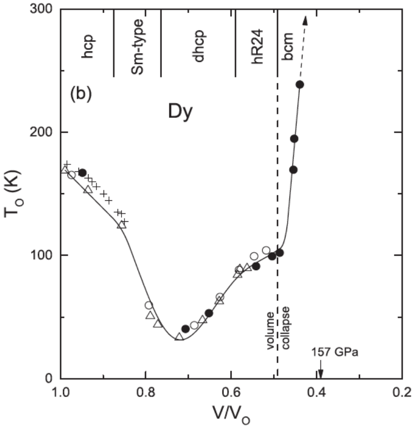
Brilliant sub-micron beams (400 nm) will enable *in situ* magnetic X-ray scattering and spectroscopy at multi-Mbar pressures (< 7 Mbar). Lanthanides/Actinides: Magnetism, Kondo/heavy fermion, mixed-valence superconductivity

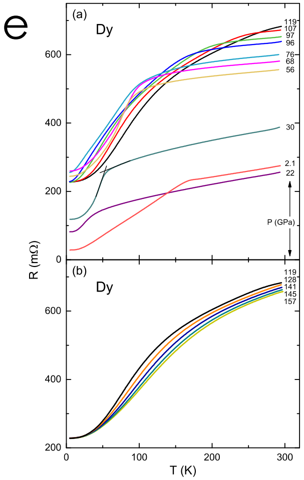
Anomalously high T_M above 1 Mbar





Electrical resistance



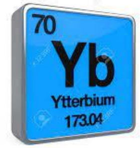


Needs to probe magnetic ordering directly

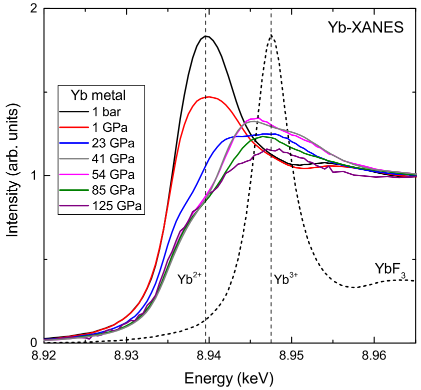
Lim et al. PRB 91, 045116 (2015)

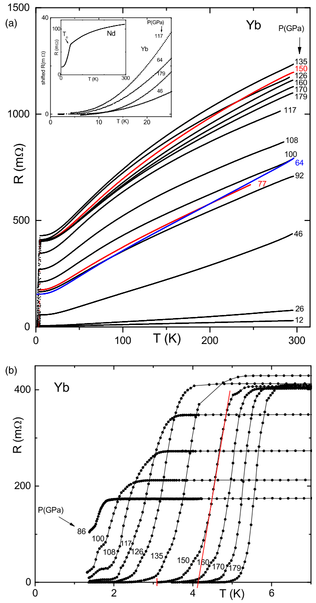
Jackson et al, PRB 71, 184416 (2005)

Pressure induced SC in Yb above 86 GPa



Electrical resistance





Mixed valence: Yb $4f^{14}$ non-magnetic; Yb $4f^{13}$ magnetic
Superconductivity mediated by spin fluctuations?

J. Song et al., PRL 121, 037004 (2018)

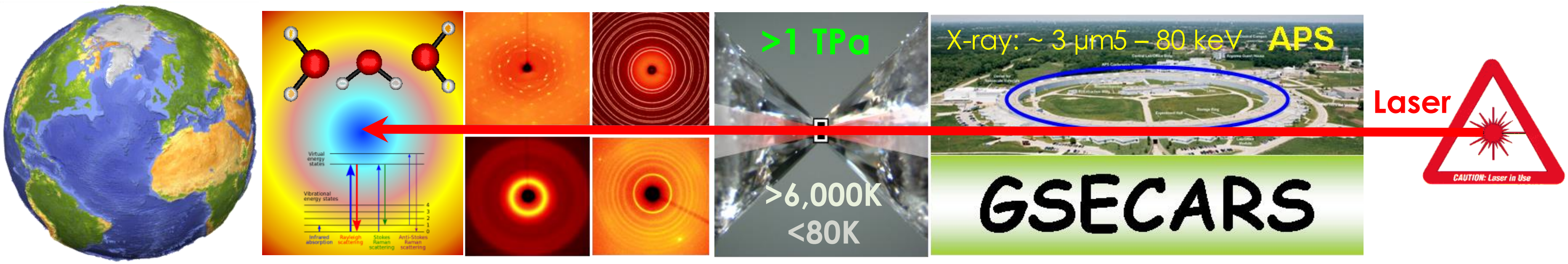
*See Appendix A

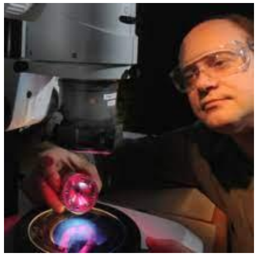
Diamond anvil cell program at GSECARS*

The DAC program at GSECARS provides state-of-the-art experimental techniques to study key geoscience topics in the entire pressure-temperature range of the Earth’s deep interior with full characterization of the sample *in situ* at high P-T conditions with combination of synchrotron x-ray probes and on-line optical techniques:

- **micro-x-ray diffraction (time resolved)**
- **inelastic x-ray scattering (x-ray Raman)**
- **x-ray emission spectroscopy**
- **x-ray fluorescence microprobe**
- **x-ray absorption and radiography**

on-line time resolved optical spectroscopy
(Raman, Brillouin, absorption, emission)
on-line laser heating (CW & pulse)





Contact:
Vitali Prakapenka
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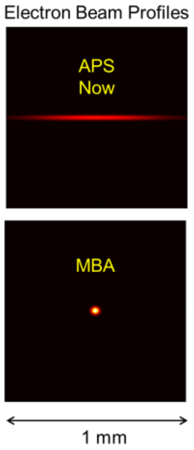
*See Appendix A

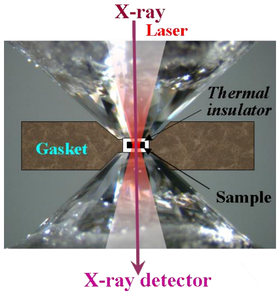
THE UNIVERSITY OF CHICAGO | GSECARS GeoSoilEnviroCARS
Argonne NATIONAL LABORATORY

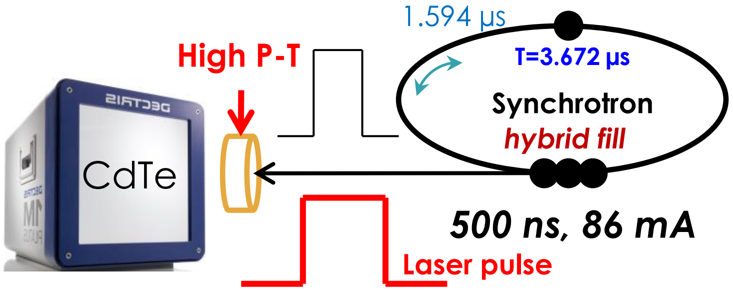
APS-U: MBA upgrade and DAC program

X-ray emission spectroscopy, time-domain experiments, dynamic compression and pulse laser heating are main techniques that will benefit from APS-U, not a new concept but **next level of experiments**.



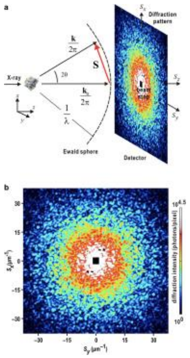
MBA: tightly focused (100-300nm), high brilliance, high energy x-ray beam – natural requirements for sophisticated DAC experiments





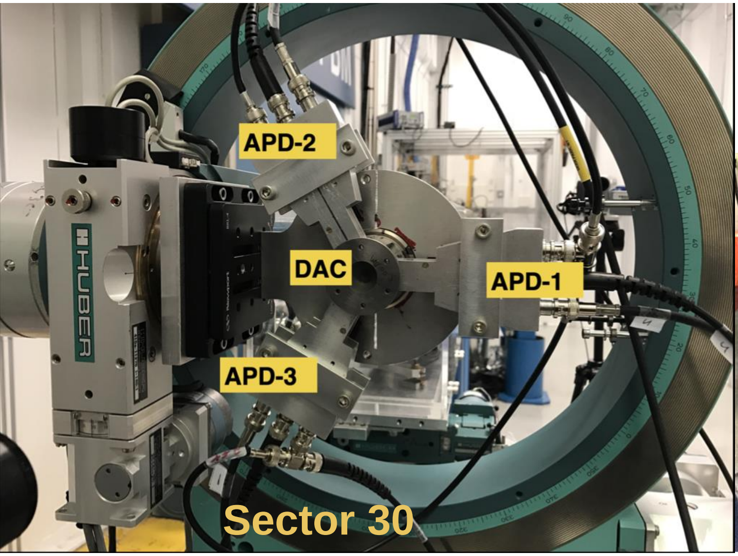
- Complexity of high-pressure phase diagram and melting covering the TPa range
- Element partitioning in the presence of molten phases
- Hydrogen reaction with minerals
- Water in the deep mantle
- Density and structure of silicate liquids and glass
- Structure solution of metastable phases (multi-grain single-crystal approach)
- Synthesis of novel materials
- ….

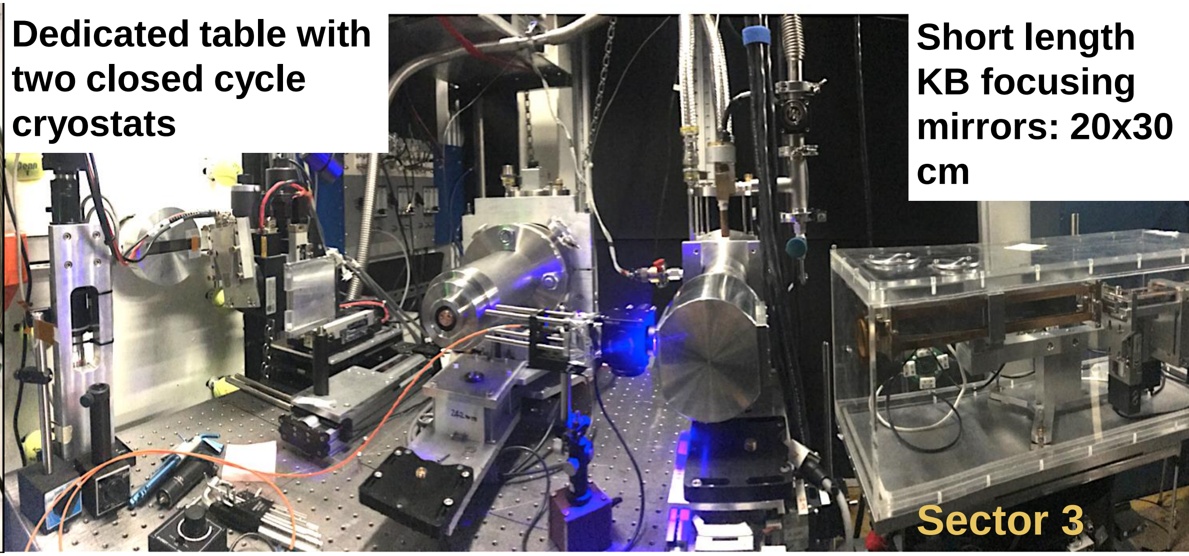
Coherent X-ray techniques: Scanning transmission x-ray microscopy, X-ray holography, Coherent x-ray diffraction imaging, Phase-contrast imaging, X-ray photon correlation spectroscopy, Ptychography, Magnetism



Extreme conditions programs at Sector 3 & 30

- The **Nuclear Resonance programs** at Sector 3 & 30 offer the following techniques:
  - Synchrotron Mössbauer spectroscopy (SMS)
  - Nuclear resonant inelastic x-ray scattering (NRIXS)
  - Mössbauer Microscope (MM)
- These techniques allow measuring *speed of sound, isotope fractionation, valence, phase fractions, texture, Mössbauer hyperfine parameters and magnetism*
- SMS and NRIXS measurement are routinely performed at extreme conditions:
  - low temperature, down to 4 K;
  - combined low temperature and high pressure (4 K, 150 GPa);
  - high pressure and high temperature (3500 K, 150 GPa).




Dedicated table with two closed cycle cryostats

Short length KB focusing mirrors: 20x30 cm

APS-U

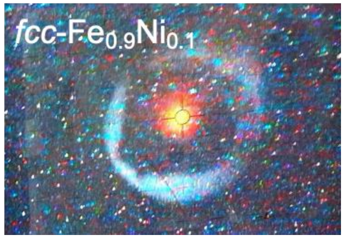
- ✦Reduced horizontal emittance will enable 1 μm focused beam
- ✦Increased current from 100 to 200 mA

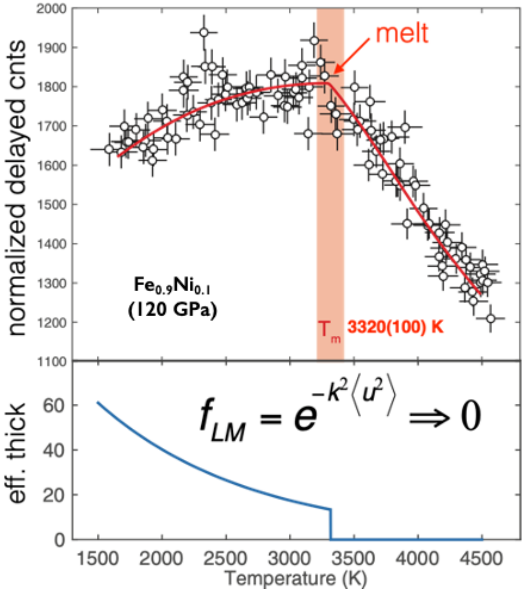
The APS-U brilliance enhancement will greatly benefit the extreme conditions programs at Sector 3 & 30 by:

- Enabling measurements at much higher pressures and temperatures to reach Earth core conditions.
- Resolve different phases synthesized in the diamond anvil cell, namely a high pressure Mössbauer Microprobe program can be envisioned;
- Allow more accurate measurements at high P, T in the laser-heated diamond anvil cell.

These improvements will boost studies of Earth and planets deep interiors as well as new extreme conditions for physics and chemistry studies.

Melting studies at the Earth core conditions using synchrotron Mössbauer spectroscopy

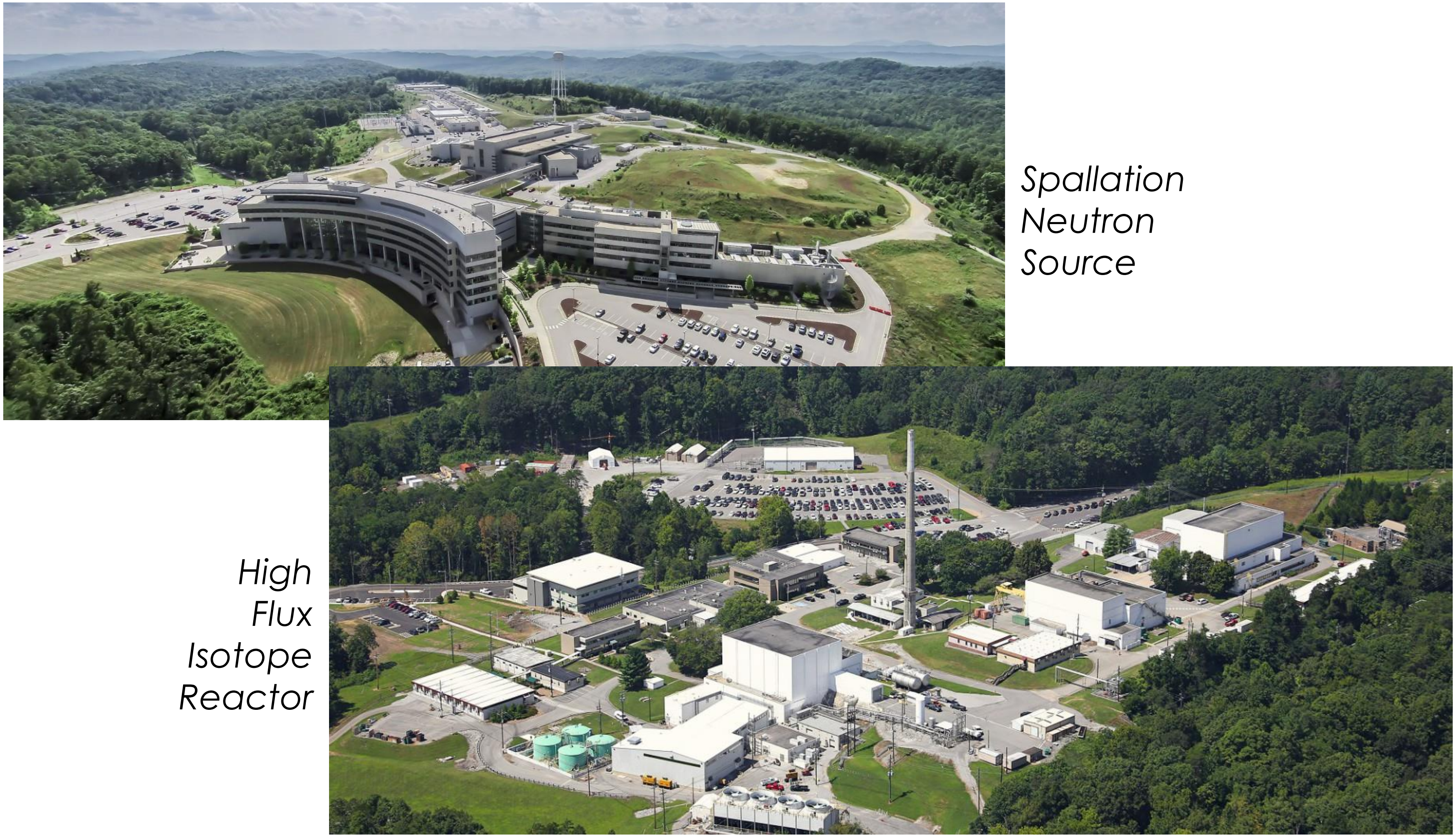




Contact:
Jiyong Zhao
jzhao@anl.gov

4. High pressure neutron scattering

Neutron scattering facilities at ORNL



Spallation Neutron Source

High Flux Isotope Reactor

Will focus on developments and science at ORNL although similar efforts are ongoing world-wide.

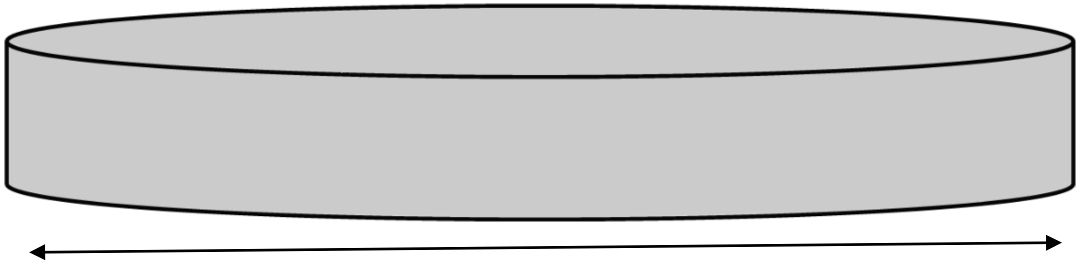
High pressure neutron scattering

The diamond anvil cell for synchrotron scattering or optical techniques is sufficiently versatile for most *in situ* studies.

BUT:

For a diamond with 200 µm culet diameter*, the volume of the sample chamber is 0.0003 mm^3.

The minimum-size on typical high flux instruments is ~1 mm^3 on well scattering samples.



OAK RIDGE National Laboratory

*Note that chamber diameter = below ½ culet diameter

High pressure neutron scattering

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

For a radius of 2 mm, we need to apply a force of ~120 kN to achieve 10 GPa. This is equivalent to 13 metric tons.

Photo source: Wikipedia

High Pressure Neutron Scattering

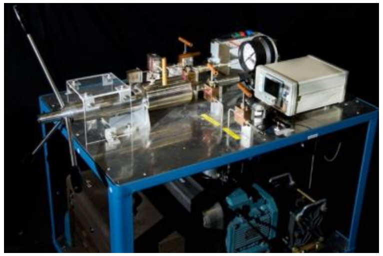
Fundamental challenge in high pressure neutron scattering:

Neutron scattering needs large samples, high pressure needs small samples.

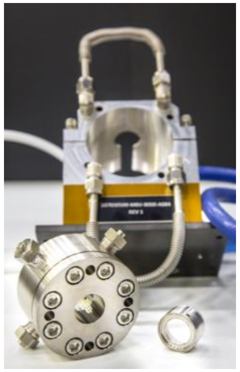
- To accommodate the necessary large sample volumes, a variety pressure cells exist for neutron scattering.
- These are often optimized for specific science questions and/or neutron scattering techniques.

High Pressure Neutron Scattering

Various dedicated high pressure cells* are used to enable a large variety of science from materials science, physics, geoscience and chemistry to soft matter science.



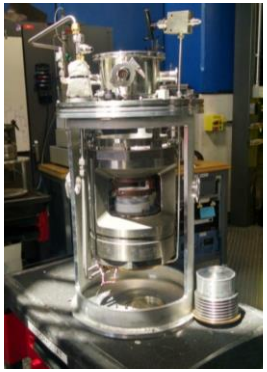
Gas cells for up to 0.7 GPa with gas intensifiers such as the SITEC

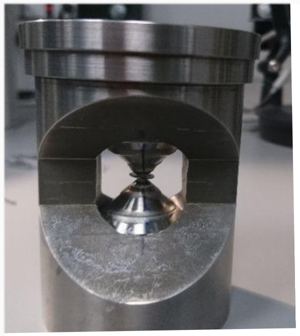


0.2 GPa extended McHugh cell for SANS

Clamp cells for up to 2 GPa at ultra-low temperature and high field

Paris-Edinburgh cells for up to 20 GPa



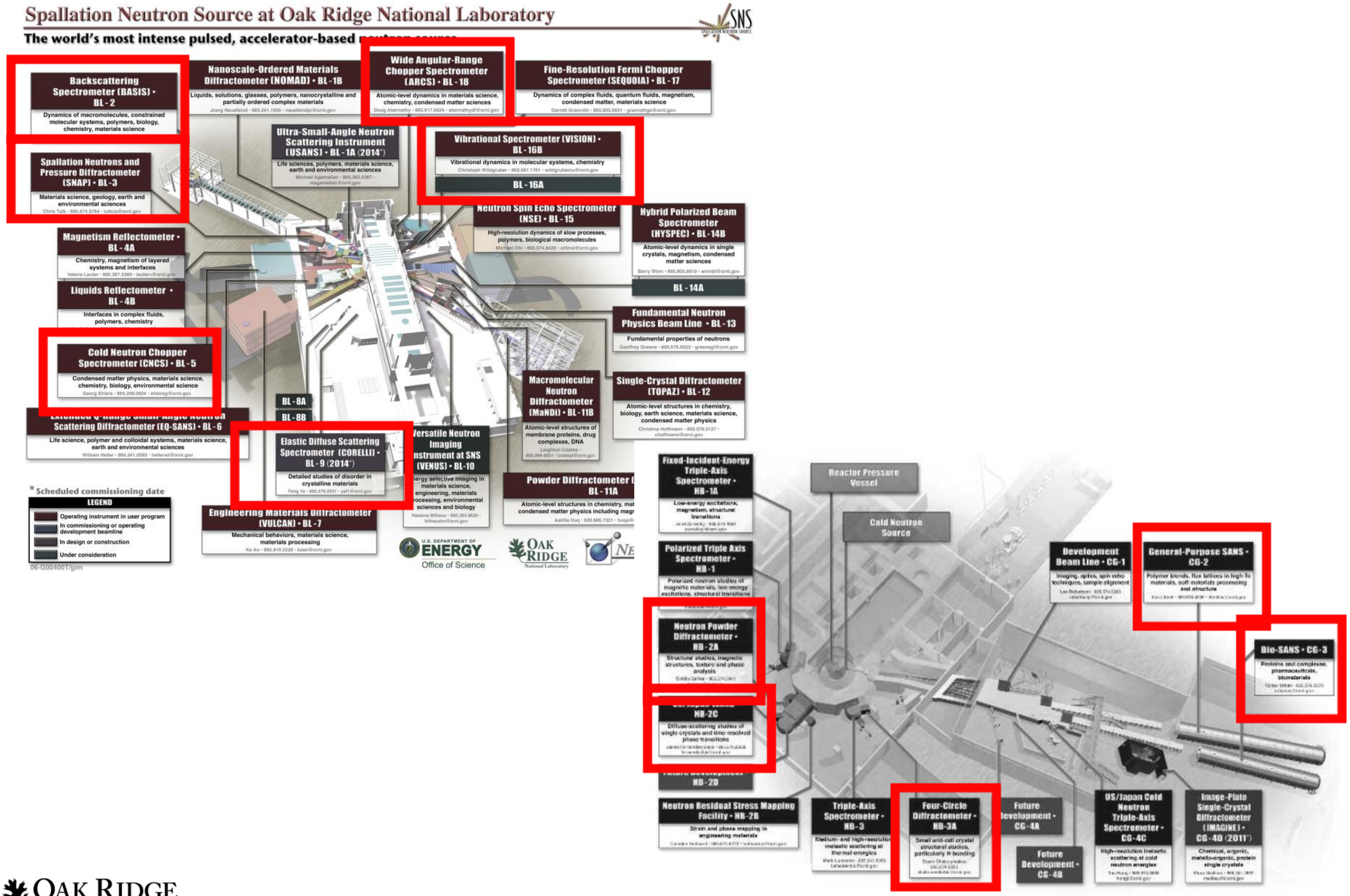


Diamond anvil cell for ultra-high pressures

Uwatoko palm-cubic cell for up 7 GPa

*See Appendix B

High Pressure Science at SNS and HFIR



Complications for HP neutron scattering

Most neutron scattering techniques are also possible within a neutron pressure cell.

Similar issues as for X-rays: hydrostaticity, diamond dips (glitches), limited apertures etc.

TOF white beam: background corrections can be highly complex and computationally intensive.

Additional key issue: the sample is (too) small and the background is (too) high.

Innovations in High Pressure Neutron Scattering

World-wide, many developmental efforts are under way to innovate pressure capabilities for *in situ* neutron scattering.

To provide new capabilities, there are several parameters that can be addressed:

- More neutron flux
- Reduced backgrounds*
- New/different pressure cells

Example: neutron diffraction in a DAC

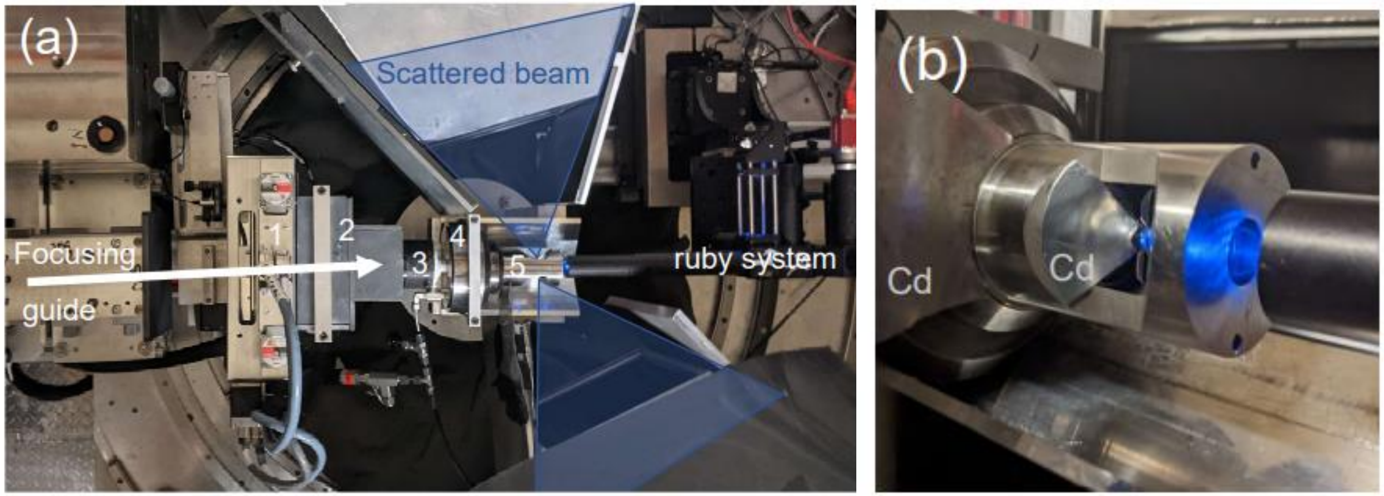
There is active research and development tackling all three components.

*See Appendix C

Megabar neutron diffraction

Many efforts are underway **world-wide** to develop neutron diffraction at megabar levels in the DAC.

Such development also occurs on SNAP, the SNS dedicated high pressure time-of-flight white beam diffractometer [1].



Neutron diamond anvil cell on SNAP [2]

[1] https://neutrons.ornl.gov/snap
[2] B. Haberl et al., JAP **130**, 215901 (2021).

Megabar neutron diffraction

Panoramic diamond cell inside a membrane press. The sample volume was ~0.05 mm^3 [1].

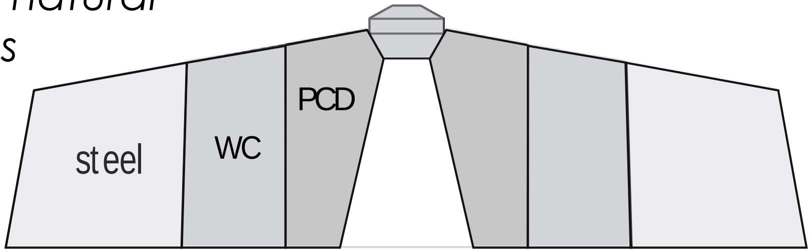
First generation diamond anvil cell developed on SNAP:

- Maximum pressures of 100 GPa were achieved.
- Single crystal diamond anvils allow removal of diamond peaks.
- Membrane press enabled online pressure increase.
- Gasket made from stainless steel.

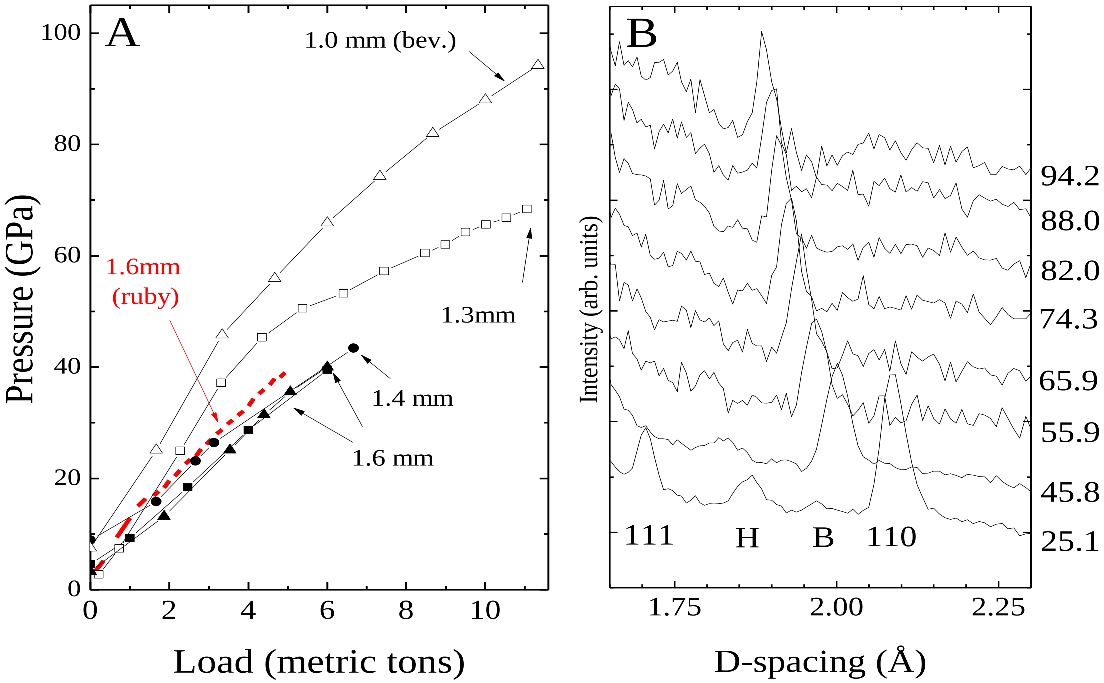
[1] R. Boehler, M. Guthrie *et al*. **High Pres. Res.** 33, 546 (2013).

Megabar neutron diffraction

Seat and natural diamonds used.



one anvil + seat:
$ 4500



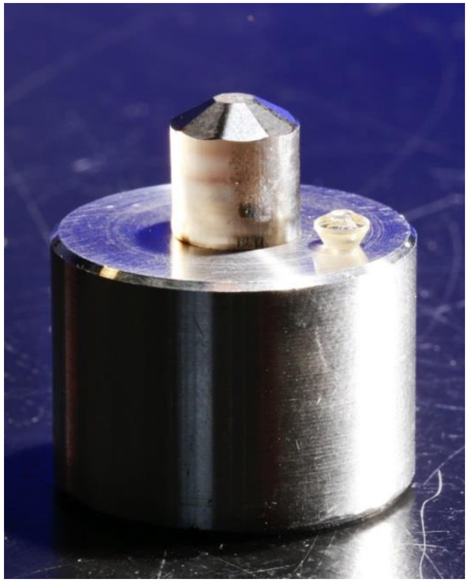
Neutron diffraction up to 94 GPa on ice. Sample volume at highest pressure was ~0.015 mm^3.

[1] R. Boehler, M. Guthrie *et al*. **High Pres. Res.** 33, 546 (2013).

Megabar neutron diffraction

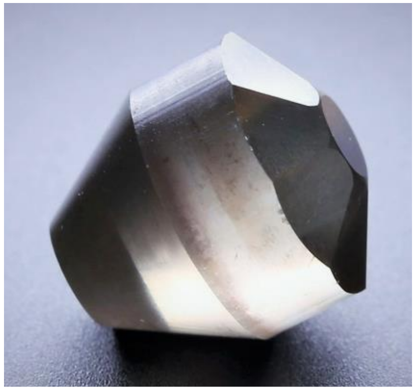
Then very large CVD anvils became available.

10 carat, 9 mm tall CVD anvil
with pyramidal design



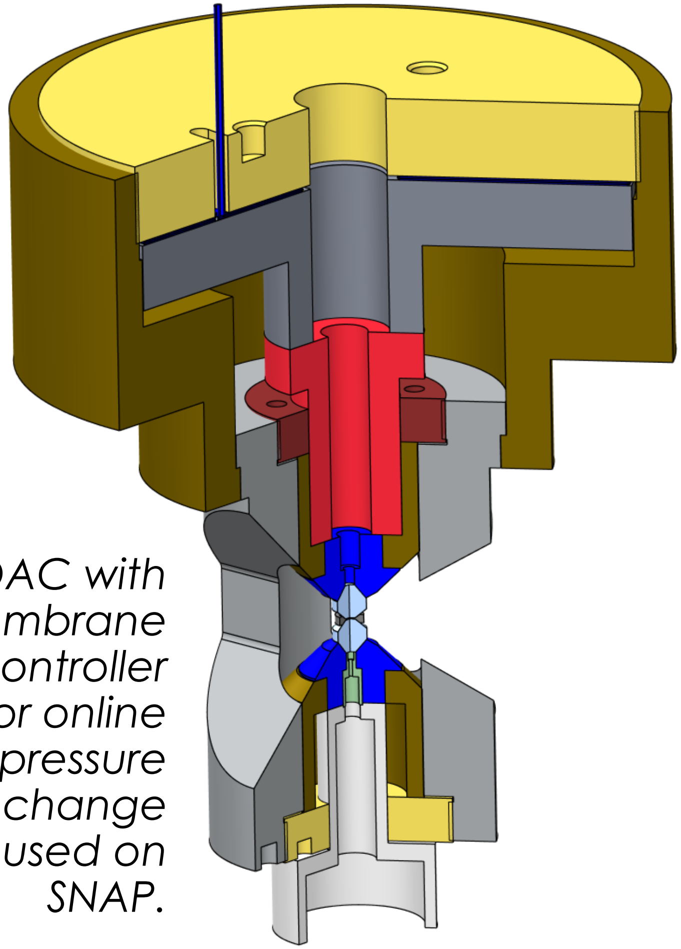
Cracked under 3 tons!

9 mm CVD anvil with
conical anvil design



Even 6 mm anvils have
been ok to 12 tons!

Megabar neutron diffraction



DAC with membrane controller for online pressure change used on SNAP.

Next generation DAC designed for SNAP [1].

- Opening aperture allows $Q = 1.3 – 22$ Å^{-1} on SNAP.
- Pressure can be increased online.
- Cell can be cooled to ~5 K.
- Maximum pressure of 45 GPa on ~0.15 mm^3.
- Incident beam is collimated with hBN right up to anvil.

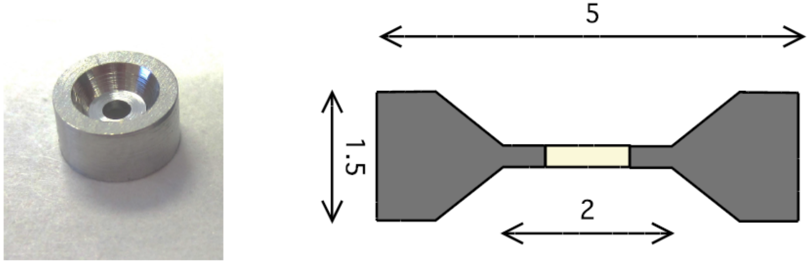
[1] R. Boehler, J.J. Molaison, B. Haberl, Rev. Sci. Instr. 88, 83905 (2017).

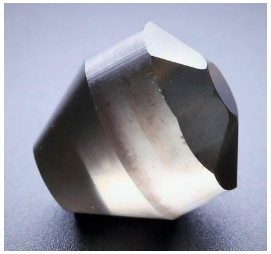
Megabar neutron diffraction

This particular design relied on two key components, large CVD anvils and machined gaskets for added support [1].

6 mm conical CVD anvils inside steel seats.

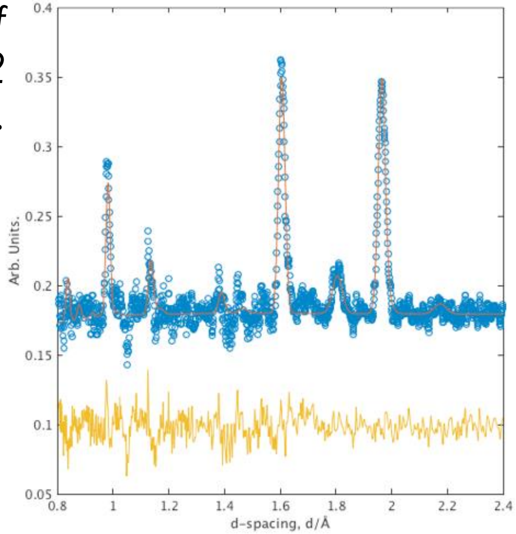
Machined stainless steel gasket





Conical anvil design.

0.06 mm^3 of ice-VII at ~62 GPa [2].



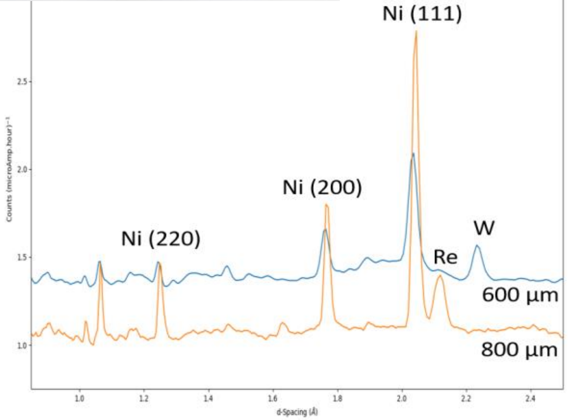
[1] R. Boehler, J.J. Molaison, B. Haberl, Rev. Sci. Instr. 88, 83905 (2017).
[2] M. Guthrie et al, PRB 99, 184112 (2019).

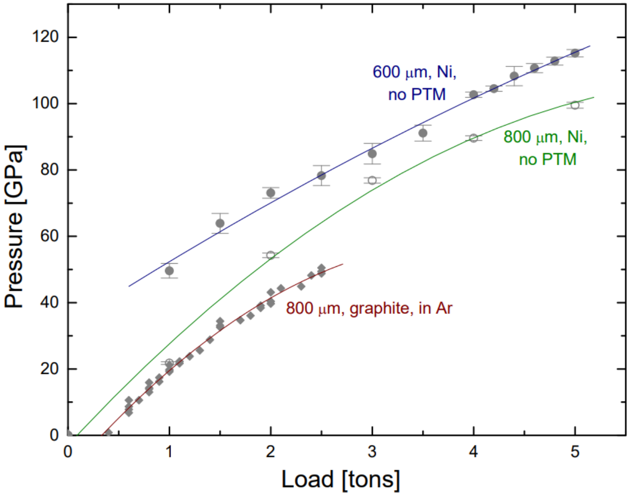
Megabar neutron diffraction

The latest generation SNAP DACs finally broke the ‘sound barrier’ of the megabar (=100 GPa).

New cell design [1]

Preparing a cell at SNAP

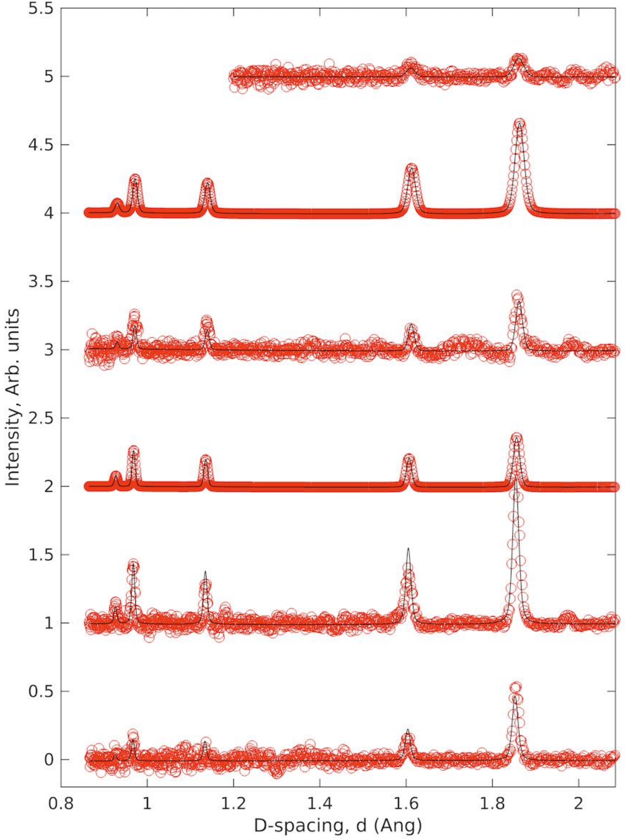


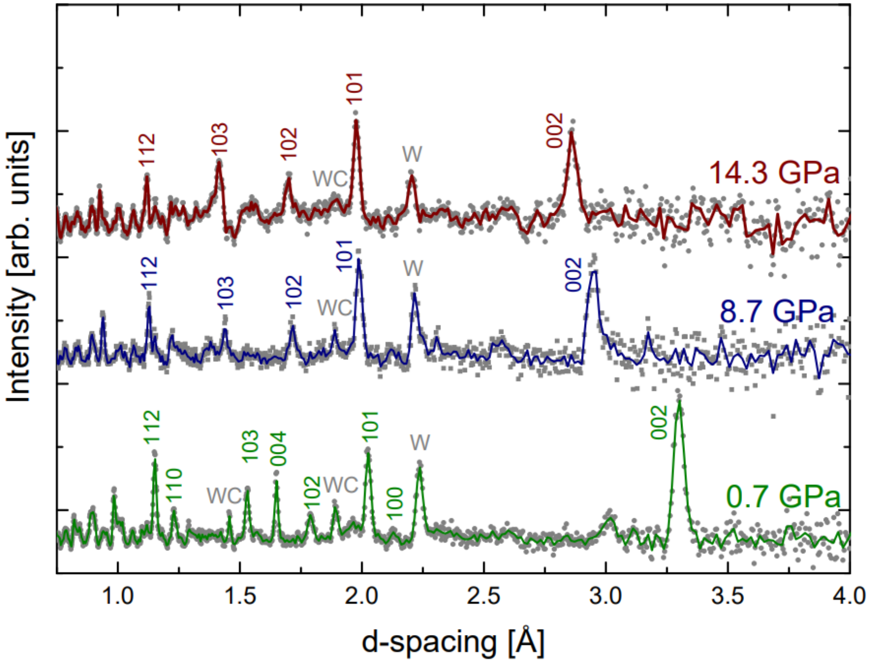


[1] R. Boehler, M. Guthrie, B. Haberl, manuscript in preparation.

Megabar neutron diffraction

Rietveld refinement of Ni at ~100 GPa. The data are refined while being kept separate in the individual columns of the detector [1]



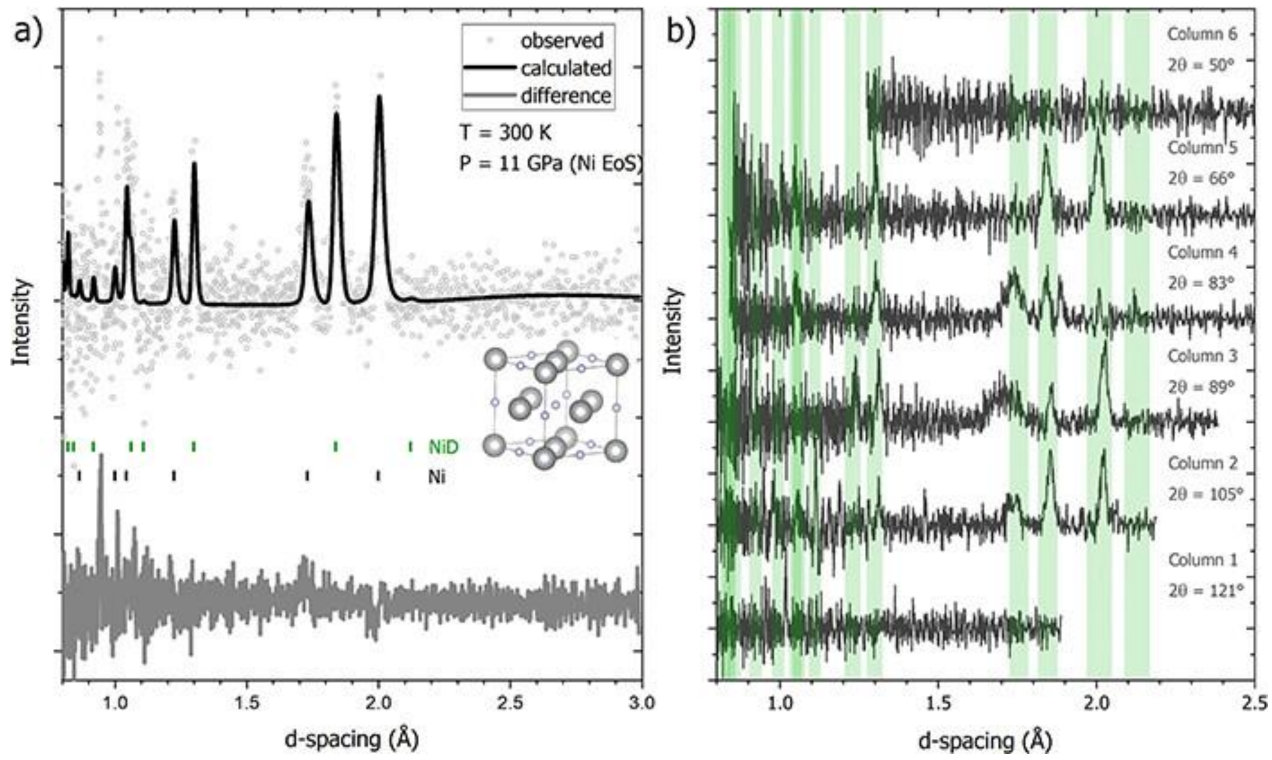


Graphite measured in a DAC gas loaded with Ar [1]

[1] R. Boehler, M. Guthrie, B. Haberl, manuscript in preparation.

Megabar neutron diffraction

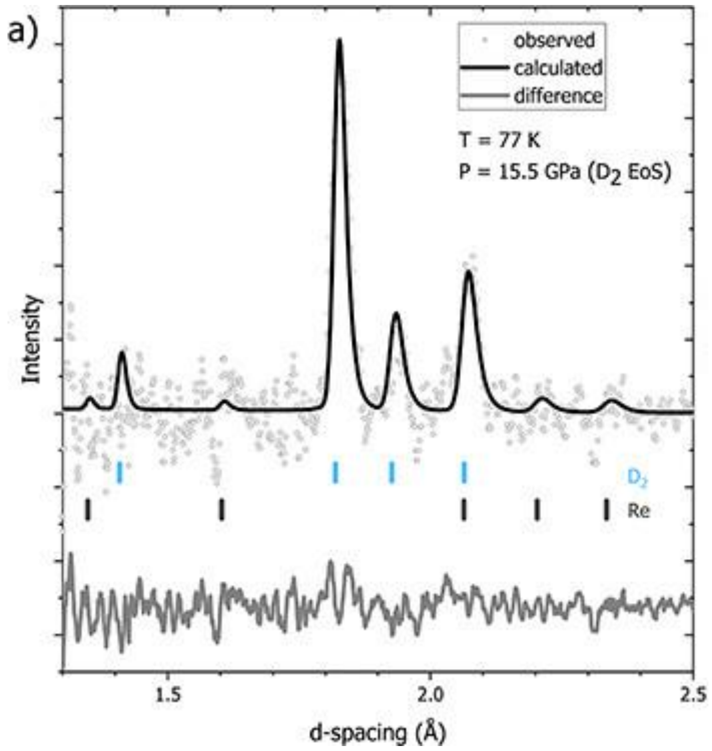
A key desire is science on hydrides. Here, nickel deuteride was synthesized inside a DAC. The angular resolution on SNAP was used to better assess (and eliminate) backgrounds.



[1] B. Haberl et al., JAP **130**, 215901 (2021).

Megabar neutron diffraction

D_2 loaded with amorphous Si flakes



Although the entire experiment was conducted below 120 K, the cell blew out at ~ 20 GPa.

We need to improve anvil technology for hydrogen compatibility.

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[1] B. Haberl et al., JAP **130**, 215901 (2021).

Conclusions

https://forms.office.com/g/eWZx7Wnibb

- High pressure experiments can be very hard.
- There are world-class high pressure facilities at the APS and SNS/HFIR. The earlier you communicate with us, the more we can help to design the best possible experiment.
- High pressure is fun!

Thank you!

Acknowledgment: Neutron DAC developments were in part funded through the ORNL LDRD scheme. Experiments used resources of the Spallation Neutron Source and the High Flux Isotope Reactor, a DoE Office of Science User Facility operated by the Oak Ridge National Laboratory and at the Advanced Photons Source, a DoE Office of Science User Facility operated by Argonne National Laboratory.

Reference Material

- “Techniques in High Pressure Neutron Scattering” by Stefan Klotz, CRC Press (2016).

- “High-Pressure Physics by John Loveday”, CRC Press (2012).

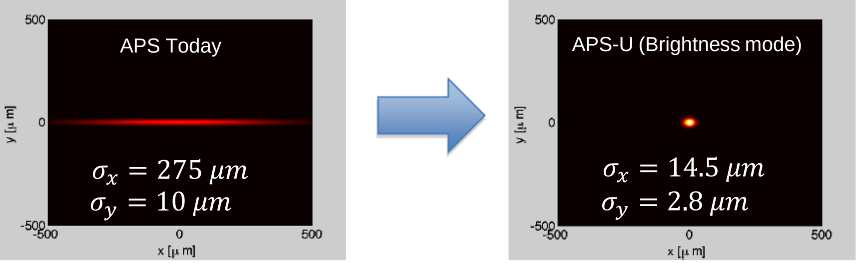
- “High-pressure studies with x-rays using diamond anvil cells” by Guoyin Shen & Dave Mao, Reports on Progress in Physics **80,** 016101 (2017).

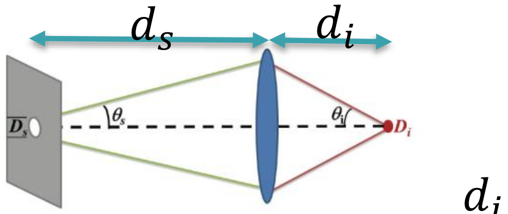
- “SPECIAL TOPIC: X-ray techniques at the HPCAT at the Advanced Photon Source”, Review of Scientific Instruments **86**, Issue 7 (2017).

A. Further details on APS-U & high pressure science

APS-U Polar beamline

APS-U
Electron source size
~ x 75 reduction
Focus: 10 um to ~100 nm

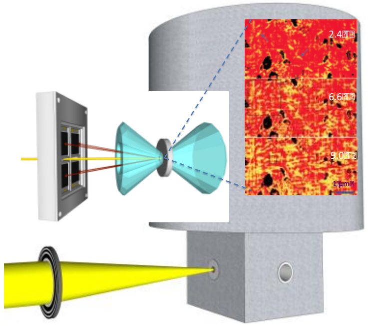




$$D_i \sim D_s \frac{d_i}{d_s}$$

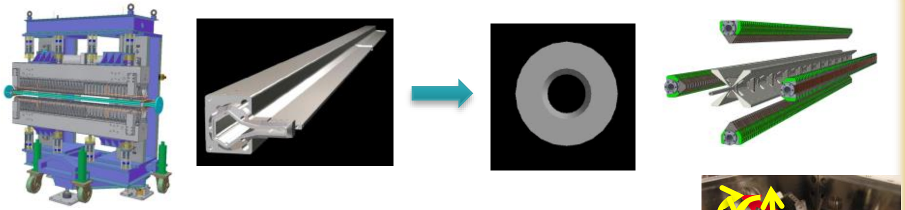
~ x100 flux gains in 100-300 nm beams

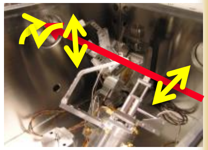
Electronic/magnetic response at high P
Mapping of phase/electronic inhomogeneity



Higher Pressures: x10 gains, to ~ 7 Mbar
Higher fields (new SC magnet): H=9/1/1 Tesla, 1.4 K
X-ray Circular/Linear dichroism

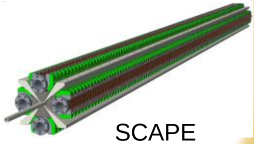
X-ray Circular/Linear Dichroism: X-ray polarization control
APS-U: Round undulator vacuum chambers





APS: Crystal optics (Diamond phase plates)
APS-U: Polarizing superconducting undulators
Linear H/V; Circular/Elliptical x-ray polarizat

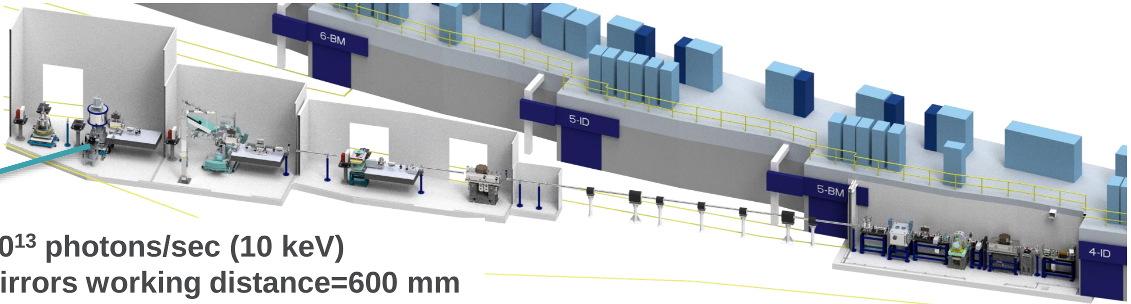
x10 flux gains vs phase plates E < 15 keV
Enables polarization control E >15 keV

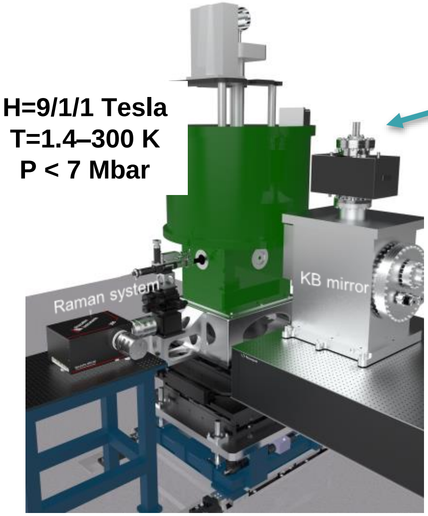


SCAPE
undulator

~ x1000 gains in polarized flux and polarized coherent flux in 100-300 nm beams
New frontiers in studies of electronic matter, especially at high pressures

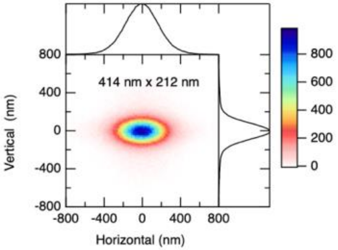
APS-U Polar beamline



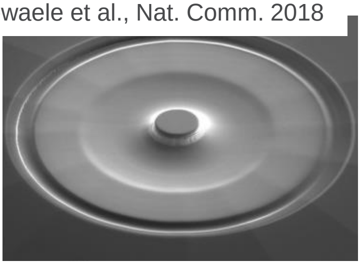


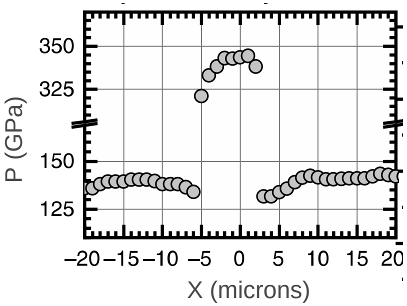
H=9/1/1 Tesla
T=1.4–300 K
P < 7 Mbar

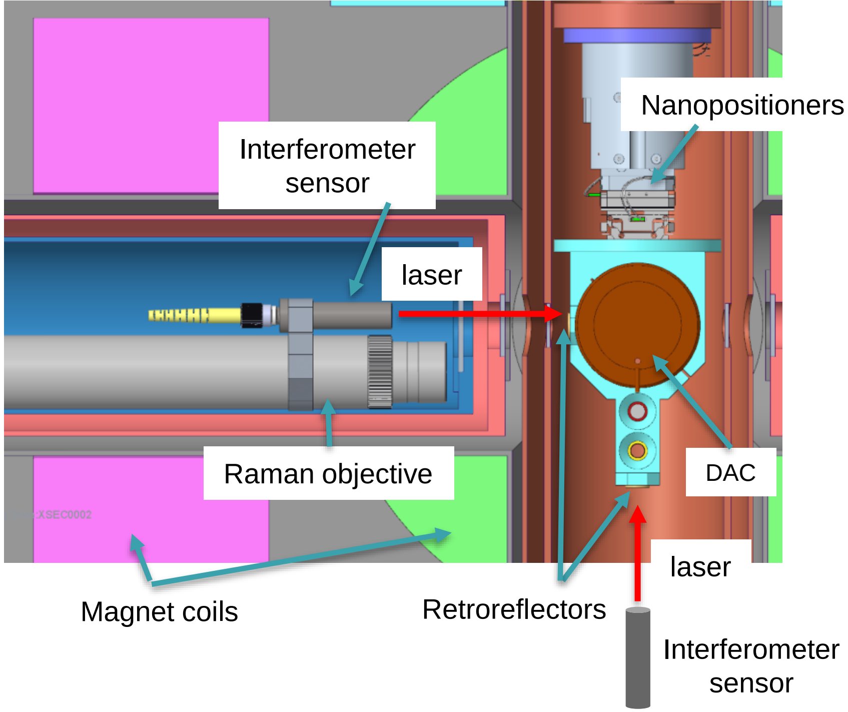
2.1×10^{13} photons/sec (10 keV)
KB Mirrors working distance=600 mm
Flux density gains ~ x100



Jenei et al., Nat. Comm. 2018
Dewaele et al., Nat. Comm. 2018





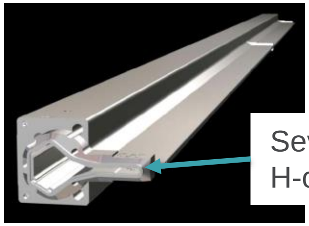


Extend pressure range of XAS/XMCD from ~ 1 Mbar to 6-7 Mbar
Also probe structural/electronic inhomogeneity ~ 300 nm resolution

X-ray polarization control at Polar beamline

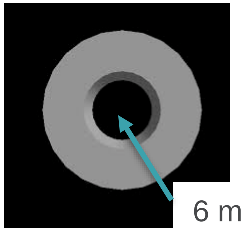
Undulator vacuum chamber

APS



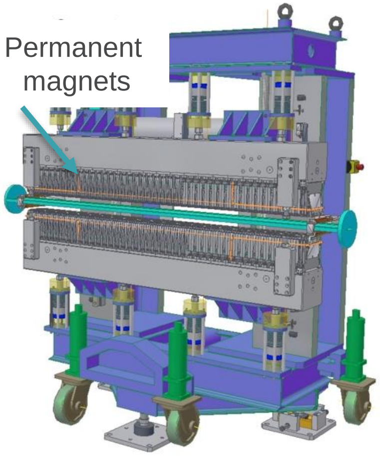
Several cm
H-opening

APS-U



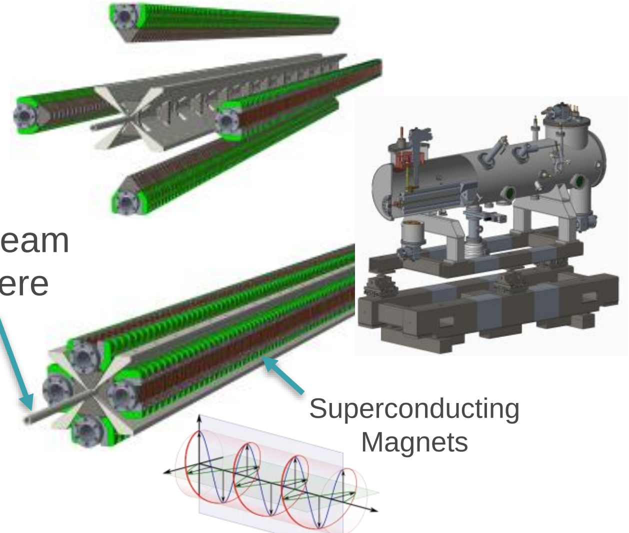
6 mm diameter

Permanent
magnets



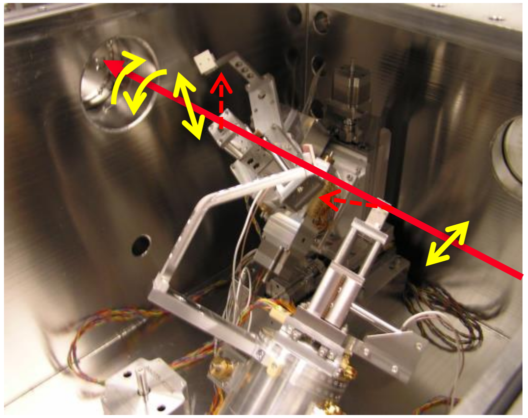
APS Undulator: vertical field
Linear horizontal polarization

e-beam
here



Superconducting
Magnets

APS-U undulator: L-H, L-V, RCP, LCP

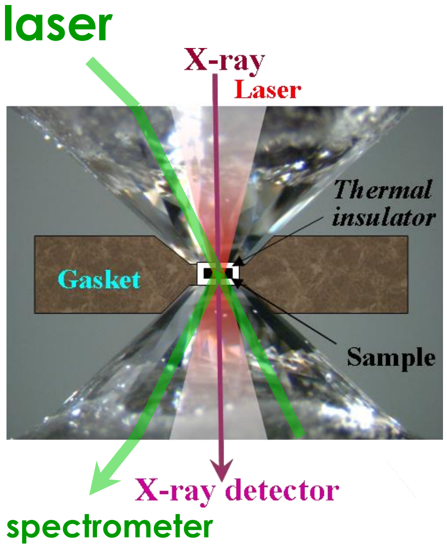


APS: diamond ¼ wave plates
LCP, RCP 2.8-14 keV, beam attenuation

APS-U: LCP, RCP, L-H. L-V 2.8-27 keV
Large flux gains below 14 keV (x5-30)
Access resonances 14-27 keV
5f element L-edge, 4d elements K-edge

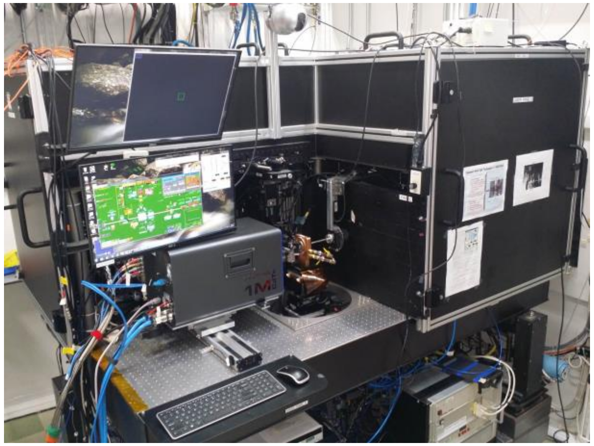
Diamond anvil cell program at GSECARS

Multiple optical axes (x-ray, lasers, spectroscopy/ imaging) should be aligned with sub-micron precision on sample in the DAC



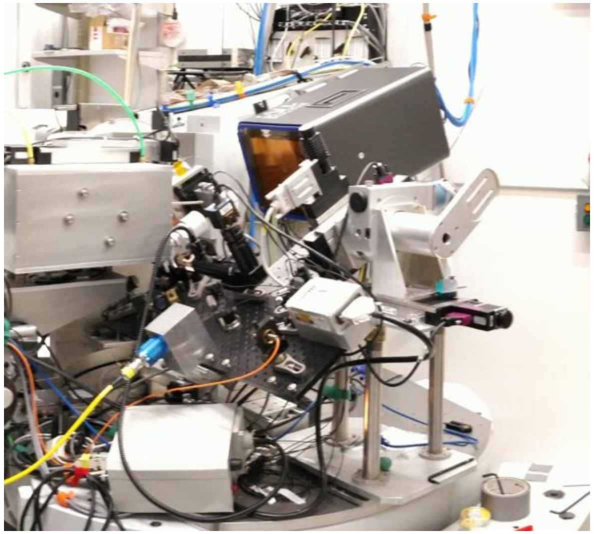
100 GPa equals 1 **million** bar (Mbar) or about 1 **million atmospheres**

13-IDD



X-ray energy 5-80 keV
beam size ~3 µm

XRD, sXRD, XES
on-line laser heating, Raman and VIS-IR spectroscopy

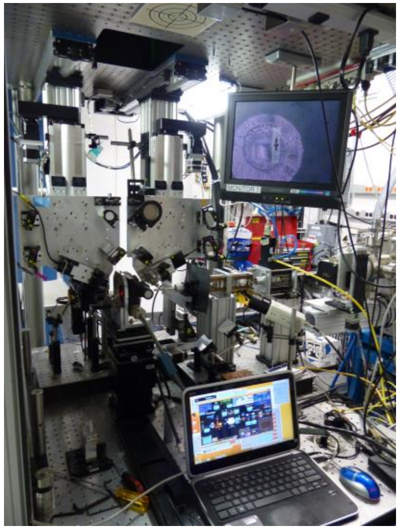


13-BMC

X-ray energy 15, 29 keV
beam size ~ 20 µm

sXRD
on-line laser heating, Raman and VIS spectroscopy

13-BMD



X-ray energy 5-80 keV
beam size ~6 x 12 µm

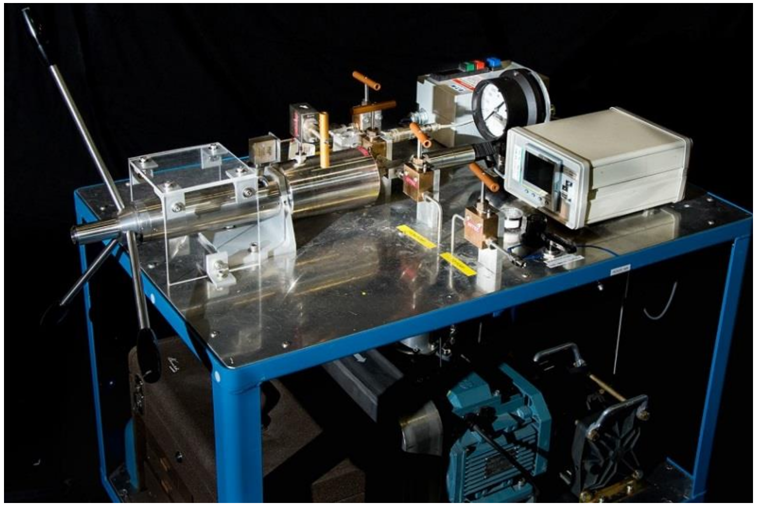
XRD, sXRD
on-line Brillouin, Raman
VIS-IR spectroscopy

B. Science examples using variety of neutron pressure cells

B. Neutron gas pressure cells

- Up to 0.7 GPa gas pressure,
- Inert gases as well as H_2/D_2 available,
- Cooling down to 5 K possible,
- Routinely used at many beamlines for diffraction and inelastic scattering,

Gas pressure cell with radial SNAP collimator [1]



SITEC Gas Intensifier rated to 7 kbar

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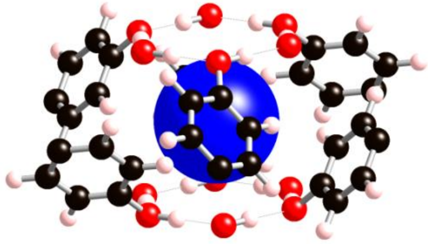
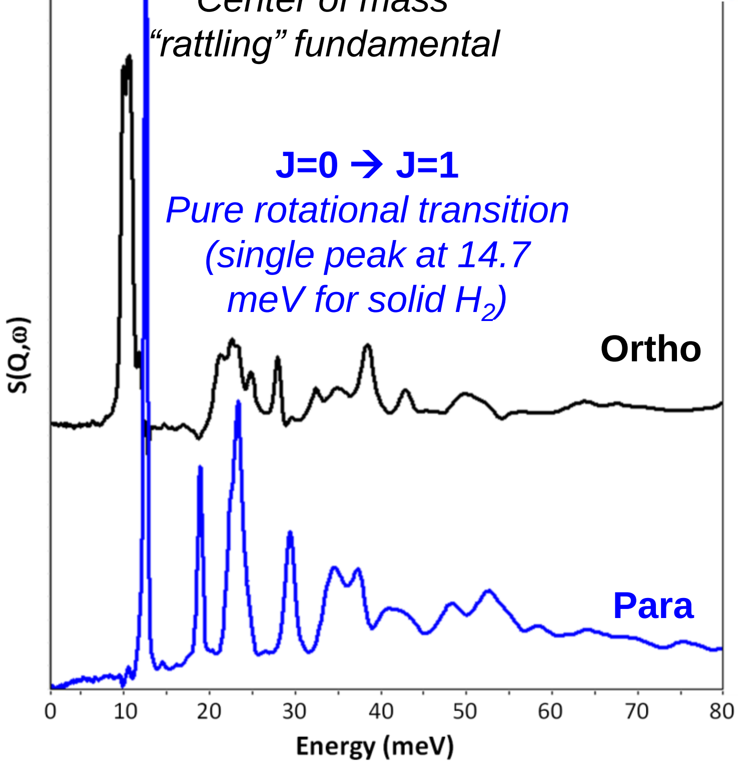
[1] A. dos Santos *et al.* accepted with Review of Scientific Instruments.

B. Neutron gas pressure cells

Gas pressure cell used on VISION

H_2 as 2D hindered rotor in organic clathrate cages measured on VISION.

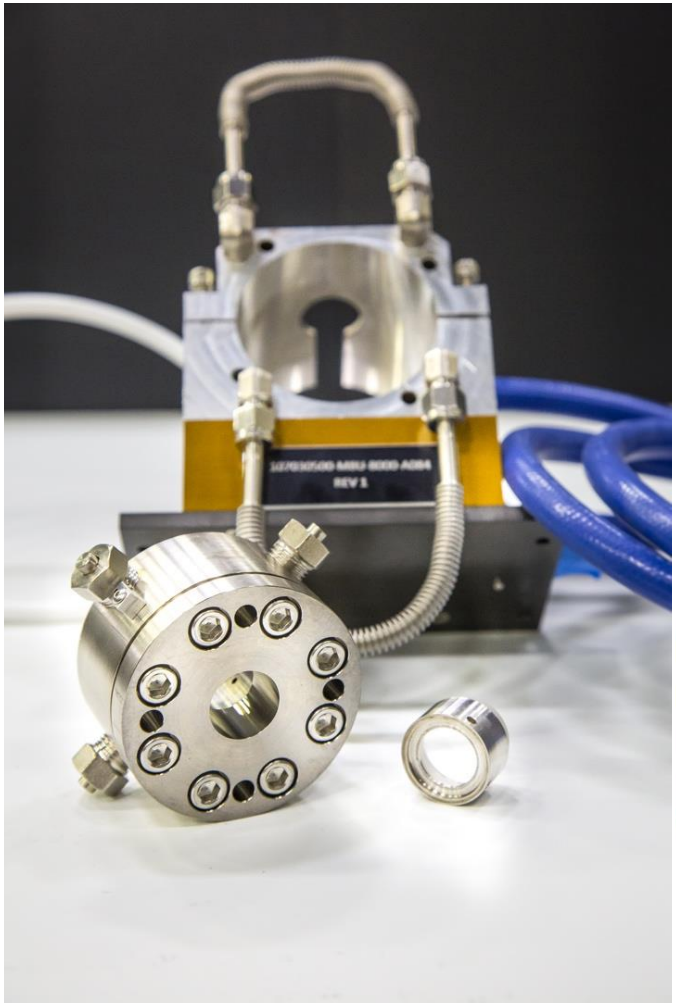




Diamond anvil cell gas loader can be used as portable H_2 intensifier

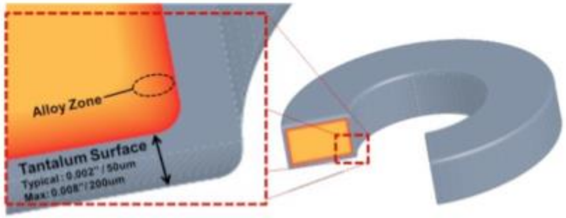
Source: Daemen (ORNL), see T.A. Strobel et al, PRL 120, 120402 (2018).

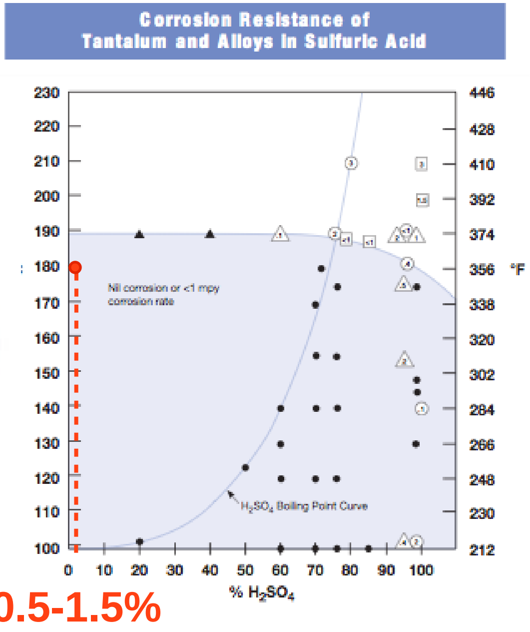
B. SANS pressure cells



Extended McHugh cells – SANS reaction cell for *in situ* pretreatment

- For acid pretreatments, stainless steel is not good but tantalum < 1 mpy corrosion rate
- Reaction cell - Stainless steel with surface alloyed tantalum



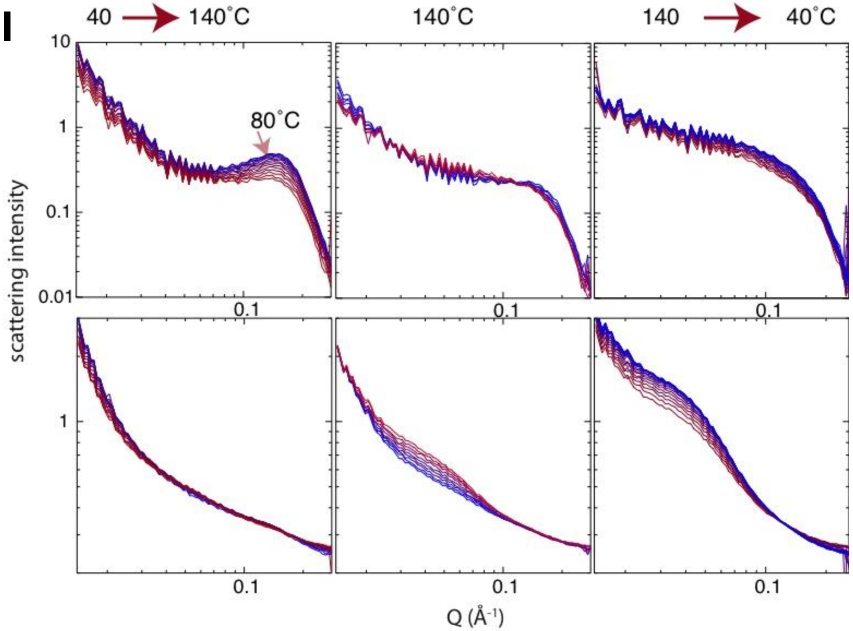

Corrosion Resistance of Tantalum and Alloys in Sulfuric Acid

Source: S.V. Pingali, Bio-SANS instrument team (ORNL)

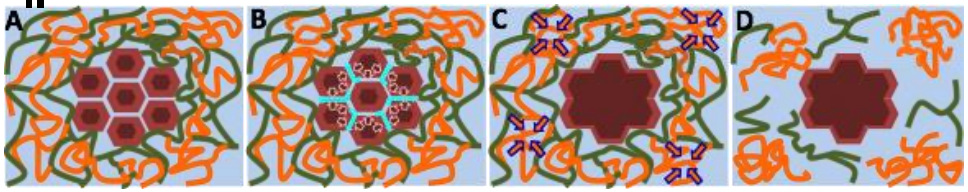
B. SANS pressure cells

Morphological changes in cellulose and lignin components of biomass occur at different stages during steam pretreatment

I



II



(I) *In-situ time-resolved neutron small-angle scattering data. Top row (horizontal sector) highlights cellulose morphological changes and bottom row (vertical sector) lignin.*

(I) *A schematic summarizing the fundamental processes responsible for the morphological changes of cellulose and lignin components during steam explosion pretreatment.*

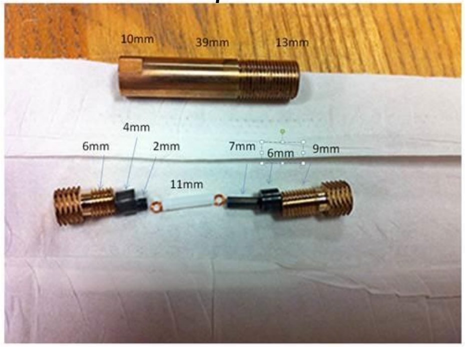
Pingali *et al. Cellulose* **21**, 873 (2014); Nishiyama *et al. Cellulose* **21**, 1015 (2014) ; Langan *et al. Green Chemistry* **16**, 63 (2014). Contact: Venky Pingali pingalis@ornl.gov.

B. Piston-cylinder clamp cells

Very useful for inelastic neutron scattering due to the large sample volumes possible, the relative ease of cooling and the possibility to insert cell into a magnet.

NiCrAl cell that can be cooled to 300 mK and allows maximum pressures of 2.2 – 3 GPa.

CuBe cell available through US-Japanese collaboration with a maximum pressure of 1.8 GPa.

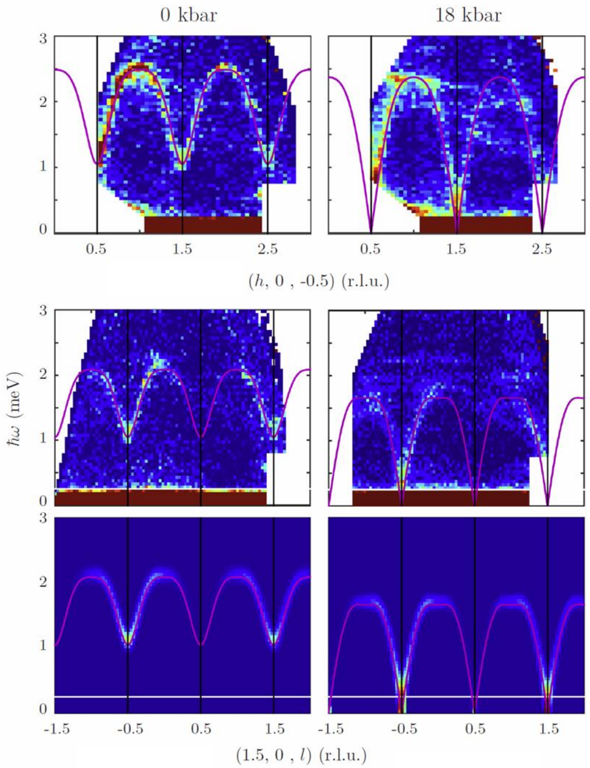


CuBe cell for maximum pressure of 2 GPa available with in situ optical pressure measurement. Sample size is 15 mm height and 4.5 mm diameter.

Source: Podlesnyak, Lumsden, Loguillo, Rucker, Tian, Matsuda (ORNL), Uwatoko (University of Tokyo)

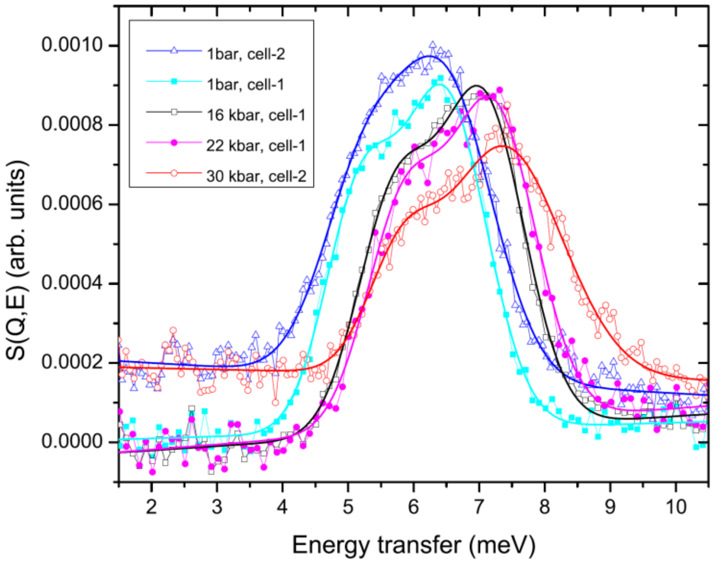
B. Piston-cylinder clamp cells

Inelastic neutron measurements on CNCS and SEQUOIA.



First publication using clamp cells on CNCS:
"Spin dynamics in pressure-induced magnetically ordered phases in ($C_4H_{12}N_2$)Cu_2Cl_6" [1].

"Pressure effect on hydrogen tunneling and vibrational spectrum in a-Mn"
Clamp cells and INS (CNCS and SEQUOIA) were used to measure the pressure effect of the tunneling mode and vibrational spectra of hydrogen in a-$MnH_{0.07}$ for pressures up to 3 GPa [2].

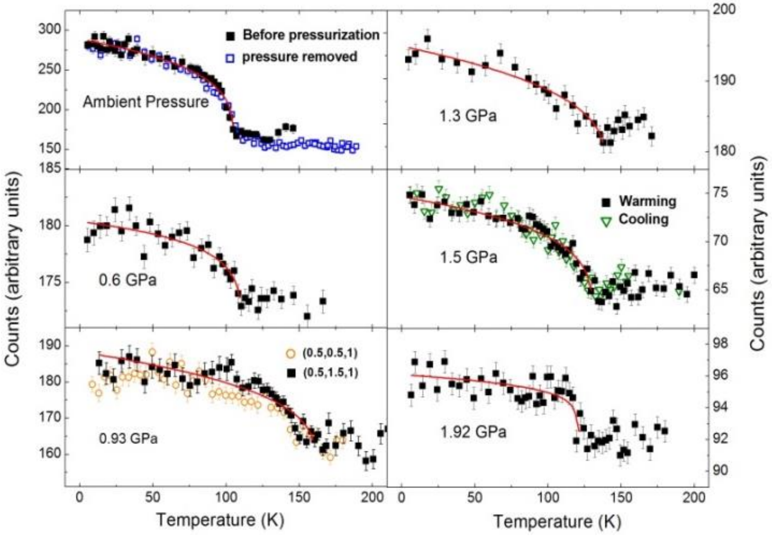


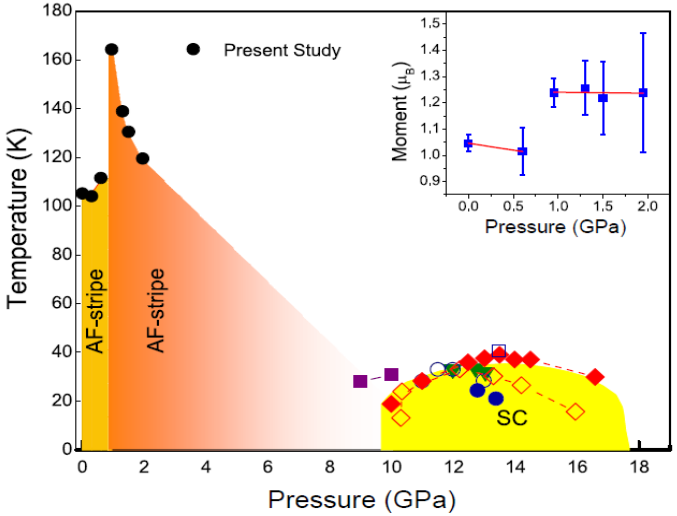
[1] G. Perren, *et al.* PRB 92, 54413 (2015), Editor's suggestion
[2] A.I. Kolesnikov *et al.*, PRB 94, 134301 (2016).

B. Piston-cylinder clamp cells

Single crystal diffraction at HB3A: Magnetic precursor of the pressure-induced superconductivity in Fe-ladder compound

Pressure-temperature phase diagram. The inset shows the size of the ordered moment as a function of pressure





Pressure-temperature phase diagram. The inset shows the size of the ordered moment as a function of pressure

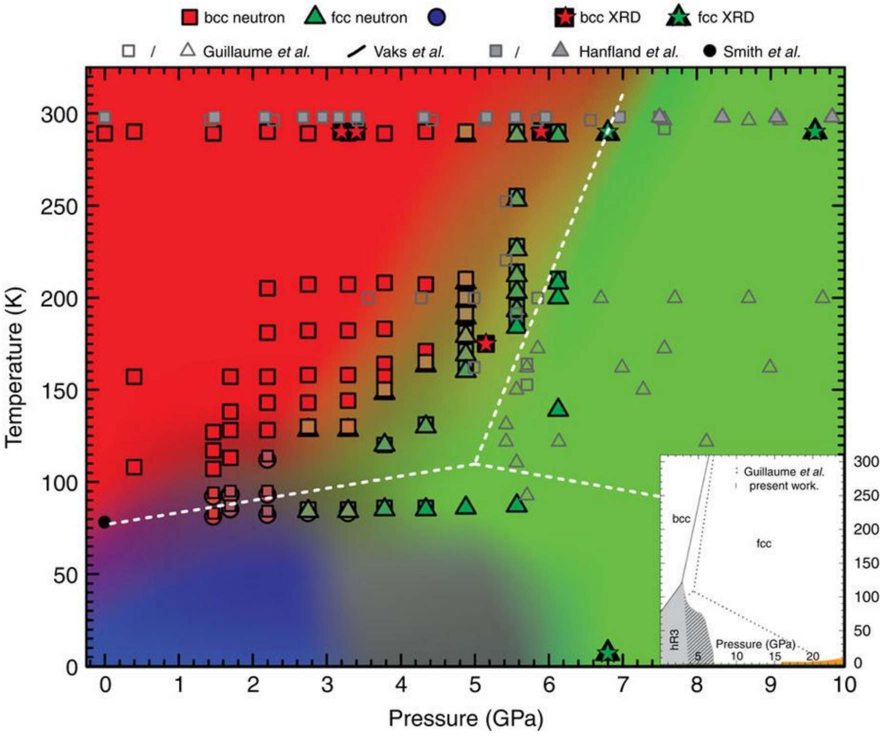
Source: Cao, HB-3A and HB-2C teams (ORNL), see S. Chi et al, PRL 117, 47003 (2016).

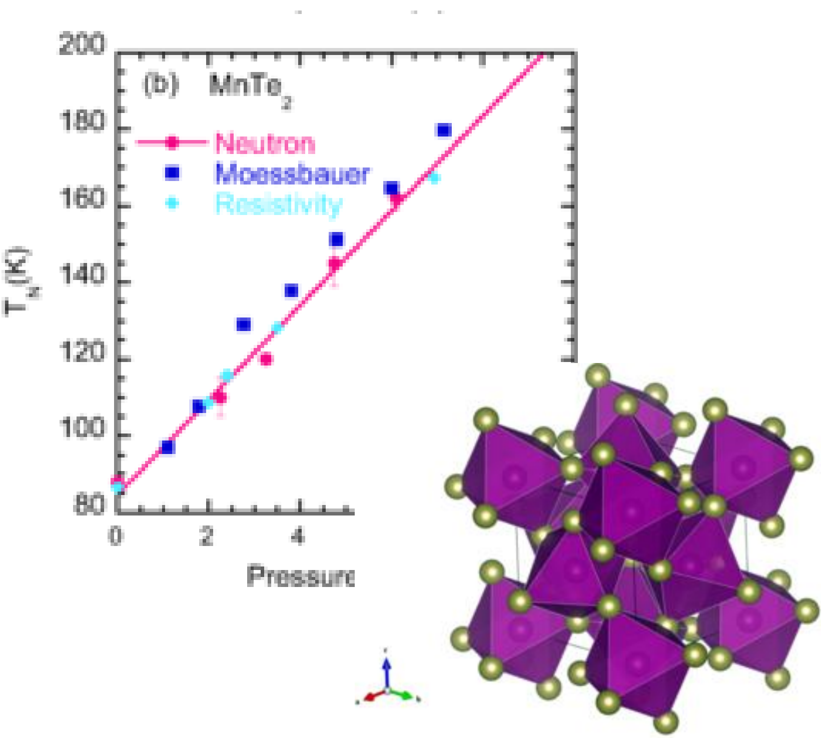
B. Diffraction on SNAP in the Paris-Edinburgh cell

- Key elements are a 200 ton press and toroidal anvils,
- 10 GPa with cubic boron nitride anvils,
- 20 GPa with polycrystalline diamond anvils,
- Cooling down to 85 K,
- gasket made from TiZr (no diffraction peaks).

B. Diffraction on SNAP in the PE cell

Understanding the phase diagram of lithium [1].





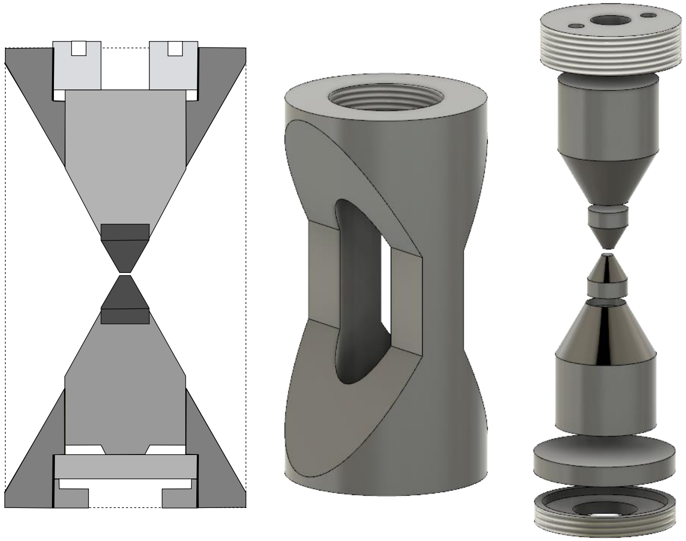
Pressure variation of the Néel temperature of $MnTe_2$ measured on SNAP in the PE cell [2].

[1] A. M. Schaeffer *et al*. Nature Communications 6, 8030 (2015).
[2] Tapan Chatterji, *et al*, Phys Rev. B 91, 104412 (2015).

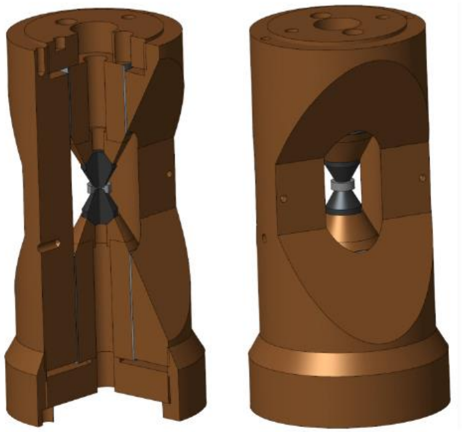
B. Clamped diamond cell with Versimax® anvils

- Opening aperture of 120º.
- Pressure is applied in press and clamped in via a simple spring mechanism.
- Cell can be cooled to ~5 K.
- Sample volume is up to 2 mm^3.

PCD anvil and gasket



Original Vascomax design [1]



Optimized CuBe design with conical anvils [2]

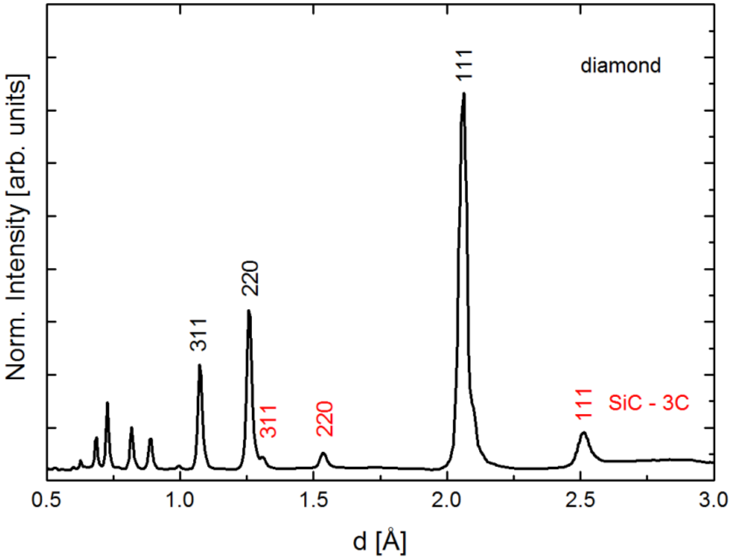
[1] B. Haberl et al, High Pressure Research 37, 495 (2017).
[2] B. Haberl et al, Re. Sci. Instr. **89**, 092902(2018).

B. Clamped diamond cell with Versimax® anvils

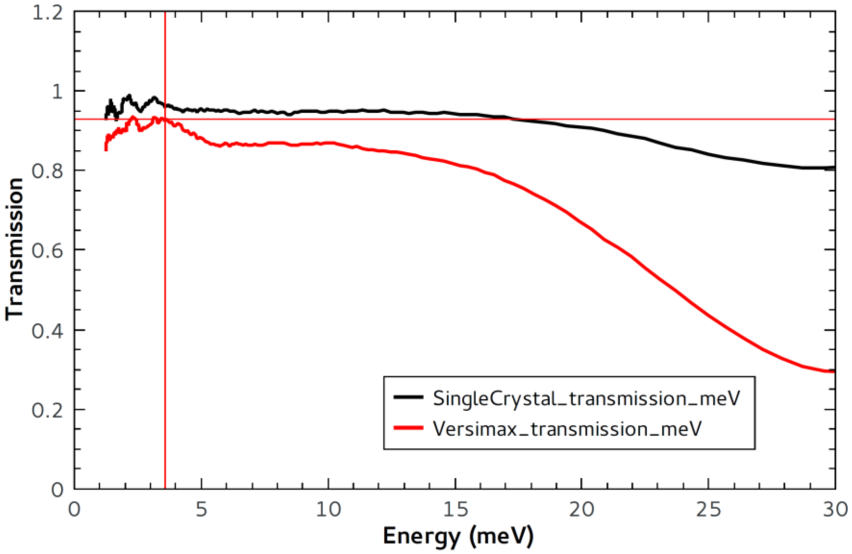
Properties of Versimax® (polycrystalline diamond sintered in SiC matrix from Sandvick):

- Diffraction pattern shows diamond-cubic SiC (3C) peaks.
- Held up to load of ~13 GPa without any support.
- Transmission on VISION is equivalent to single crystal diamond.

Powder diffraction data from SNAP.



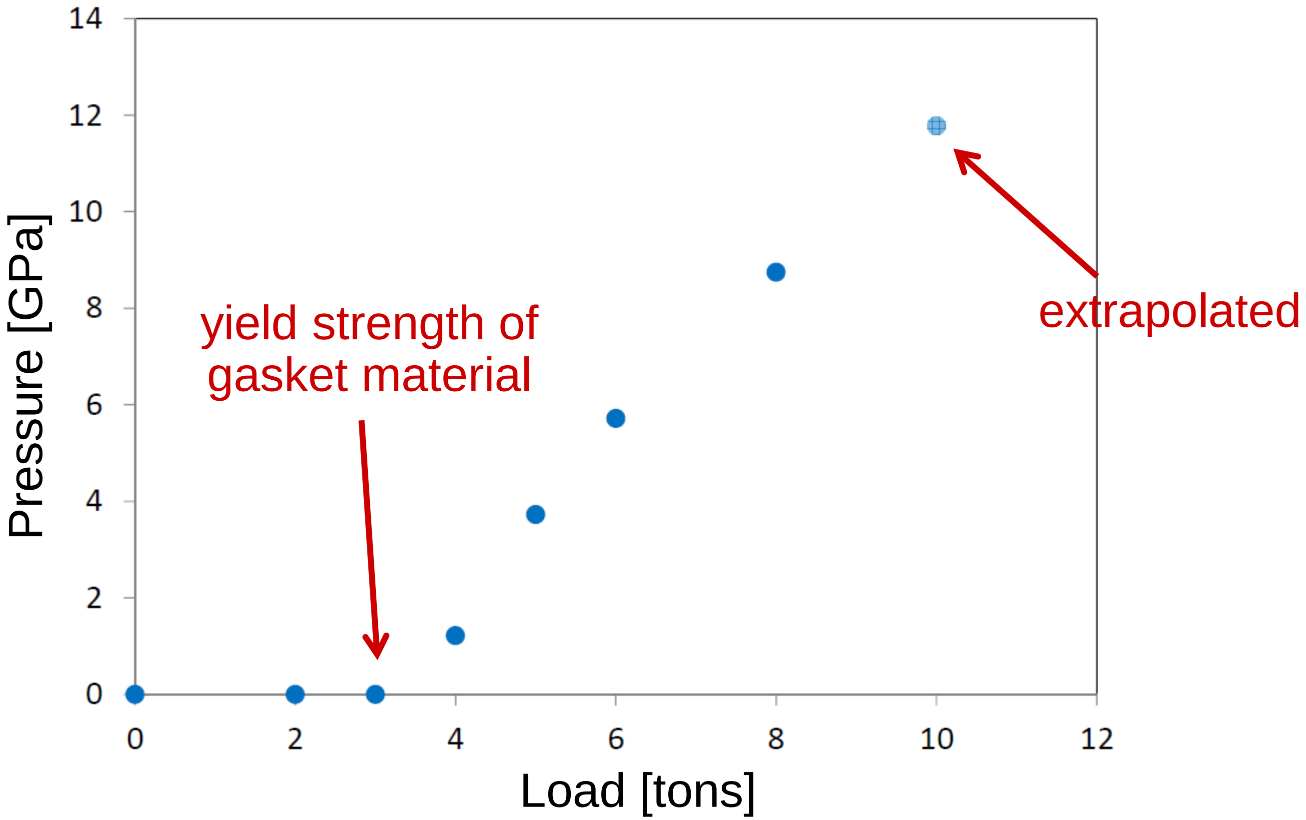
Transmission data from VISION.



[1] B. Haberl et al, High Pressure Research 37, 495 (2017).

B. Clamped diamond cell with Versimax® anvils

Versimax® is not transparent, so a pressure load curve for the 3 mm anvils was measured on SNAP using NaCl as pressure calibrant.

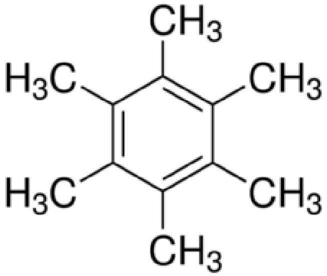


yield strength of gasket material

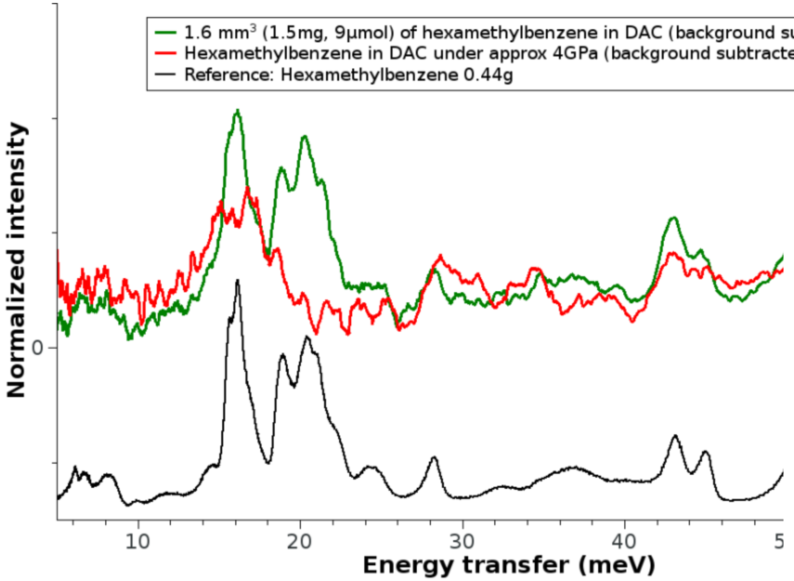
extrapolated

B. Clamped diamond cell with Versimax® anvils

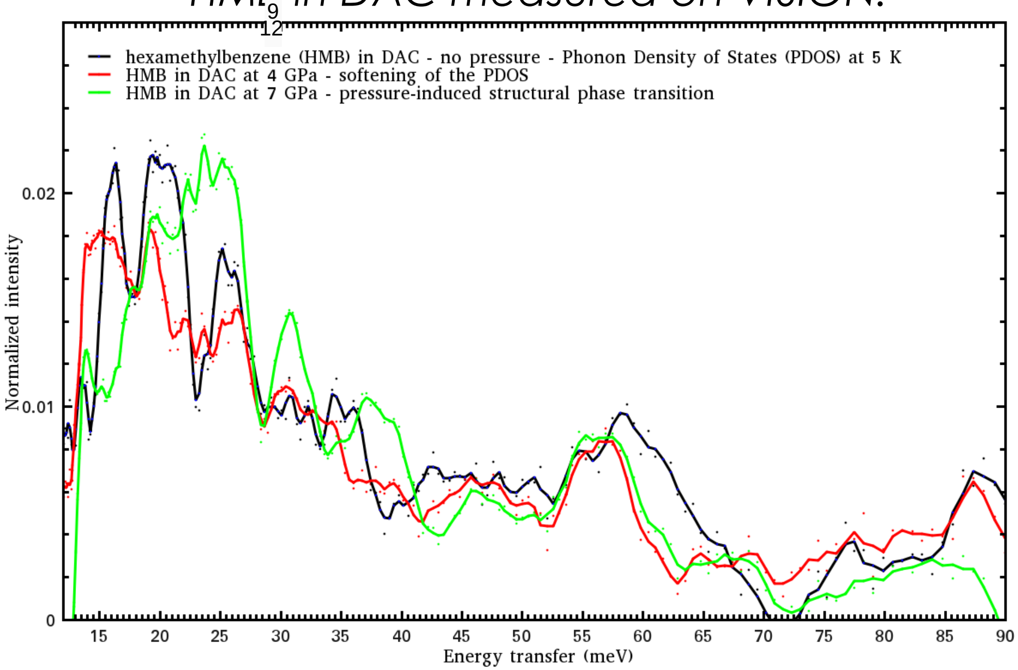
INS on hydrogen-rich samples is possible at SNS



Inelastic neutron spectrum from ~1.6 mm^3 of hexamethylbenze loaded into the DAC.



Preliminary INS data of pressurized HMB in DAC measured on VISION.



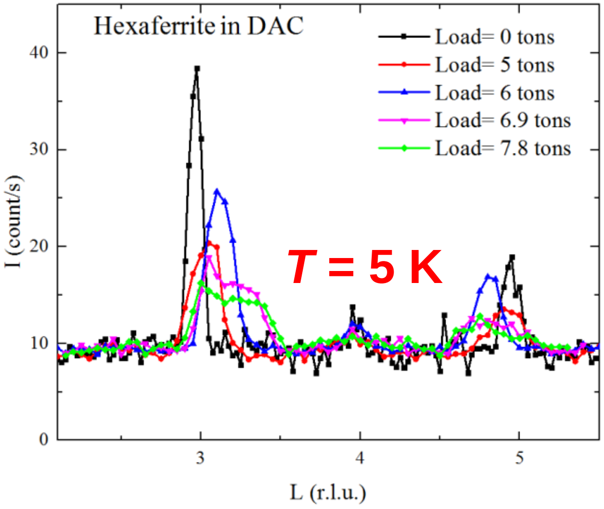
Source: Daemen, Haberl, Molaison, Boehle

B. Clamped diamond cell with Versimax® anvils

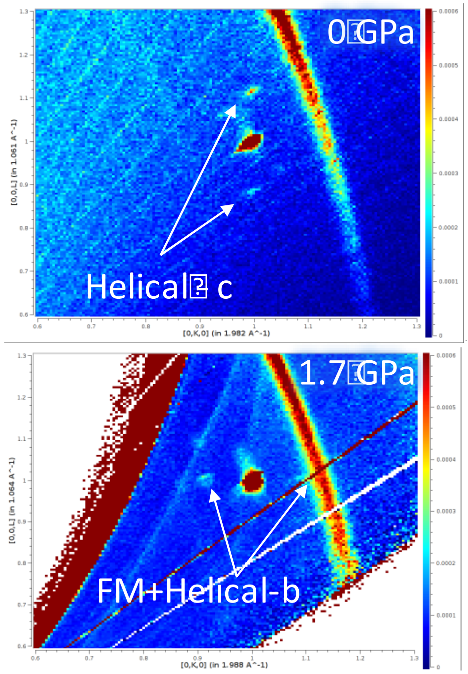
Single crystal diffraction is possible at SNS and HFIR.

HB-3A

Hexaferrite ~0.1 mm^3 crystal with Pb as pressure medium inside the DAC within CCR. Neutron wavelength λ=1.546 Å with half-lambda filter [2].

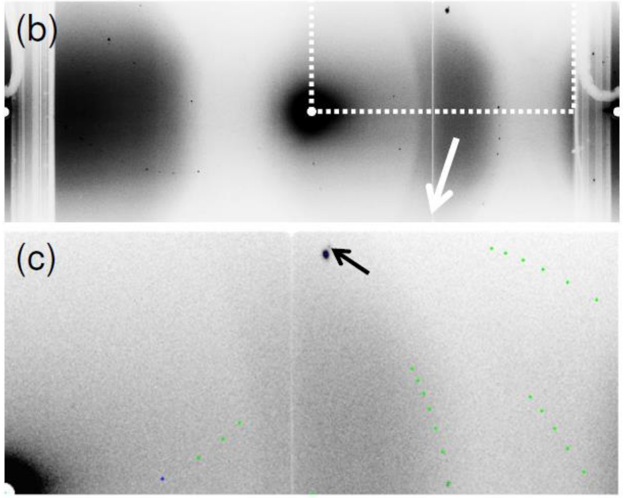


CORELLI



Single crystal diffraction from a ~240 μm thick single crystal of MnP loaded with KBr measured at 6 K [1].

IMAGINE



Hexaferrite ~0.1 mm^3 crystal with deuterated glycerin as pressure medium inside the DAC [2].

[1] B. Haberl et al, High Pressure Research 37, 495 (2017).
[2] B. Haberl et al, Re. Sci. Instr. **89**, 092902(2018).

C. Development in pressure cell specific collimation for neutron scattering

C. Incident and scattered beam collimation

Collimation (or shielding) is often critical to reduce background and remove parasitic cell scatter.

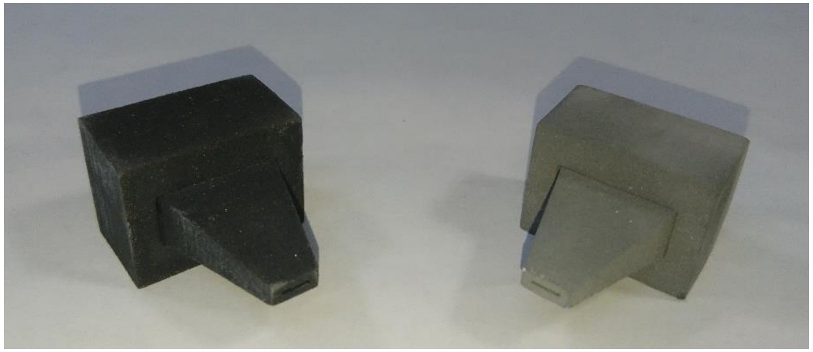
- Typically, cells were masked with neutron absorbing material, e.g. Cd, Gd, B.
- Very sophisticated masks are colloquially called incident beam collimation.
- Radial collimation instead is true collimation that collimates out unwanted scatter.

Wide-angle DAC covered in Cd.

C. Incident beam collimation

Custom collimation can be fabricated through 3D-printing:

- A form of 3D-printing (powder bed and inkjet printing) allows for 3D-printing of B_4C powder.
- The 3D-printed collimator is infiltrated with superglue which contains some hydrogen. This can now be replaced by infiltration with aluminum [1].



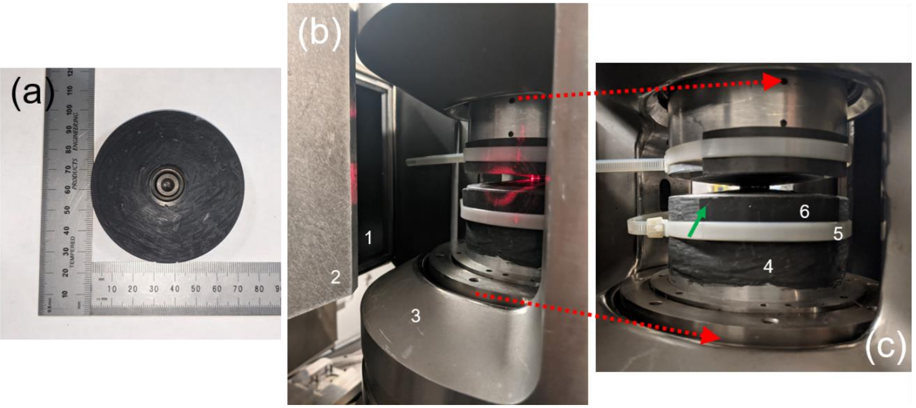
Superglue and aluminum infiltrated incident-beam B_4C collimators for Paris-Edinburg cell on SNAP [2].

OAK RIDGE National Laboratory

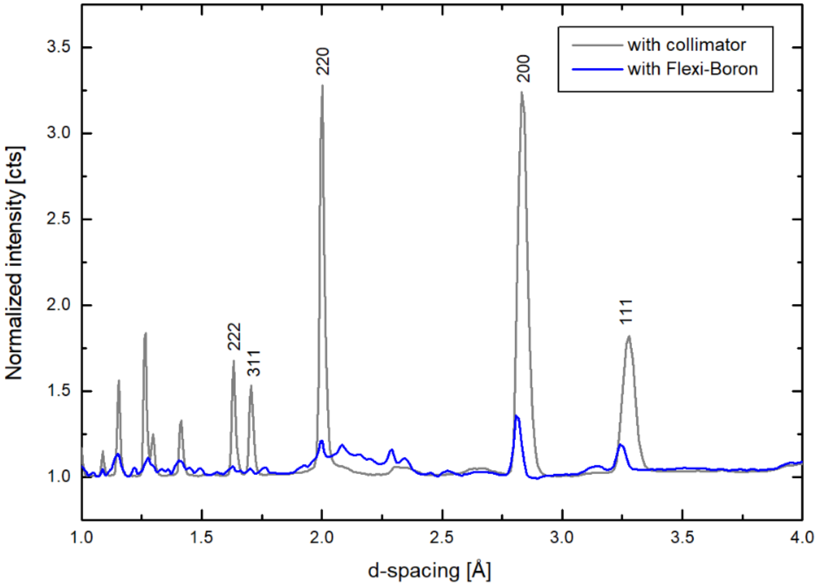
[1] C.L. Cramer et al, Materials and Design 180, 107956 (2019).
[2] B. Haberl et al, Review of Scientific Instruments **92**, 093903 (2021).

C. Incident beam collimation

'Old' set-up with Flexi-Boron



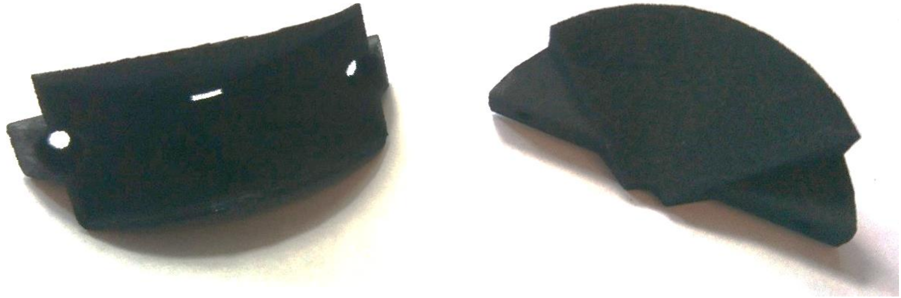
Collimator set-up



[1] B. Haberl et al, Review of Scientific Instruments **92**, 093903 (2021).

C. Incident beam collimation

3D-printing also allows for complex designs of hydrogen-free collimators from neutron absorbing materials.



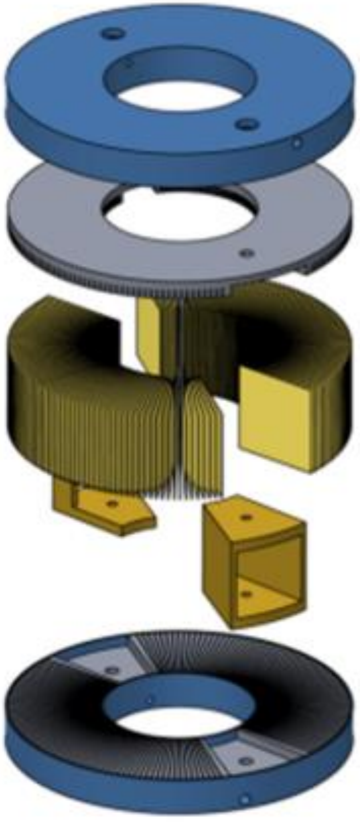
New collimator design printed from B_4C for single crystal diffraction in a wide-angle DAC typically used on SNS's CORELLI beamline [1]

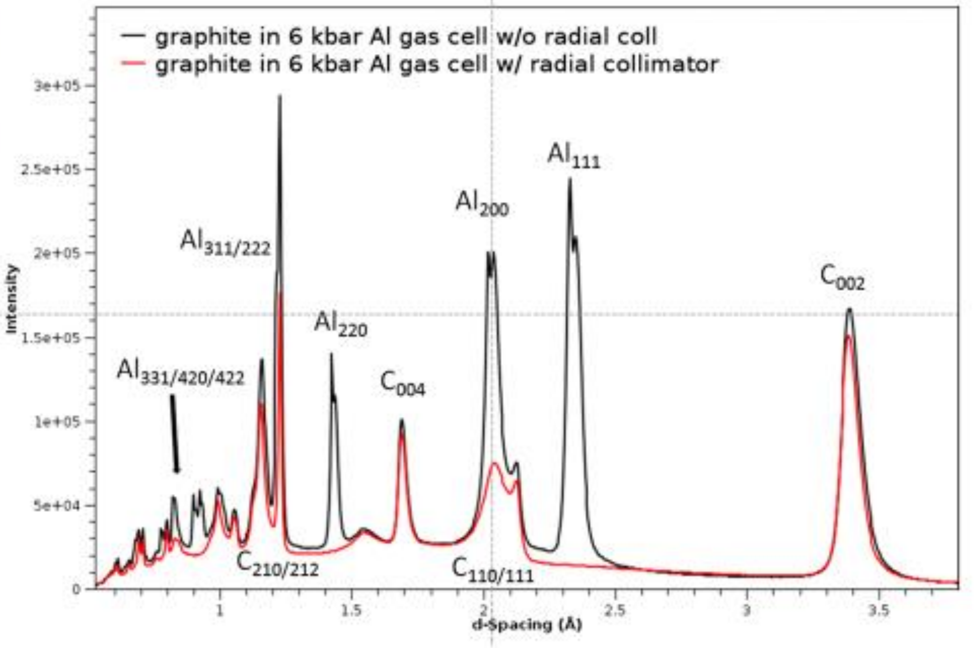
[1] B. Haberl et al, Review of Scientific Instruments **92**, 093903 (2021).

C. Scattered beam collimation

Radial collimation uses geometric considerations to only let scatter originated from the sample arrive on the detector.

Example of a radial collimator designed for a cylindrical gas pressure cell [1]

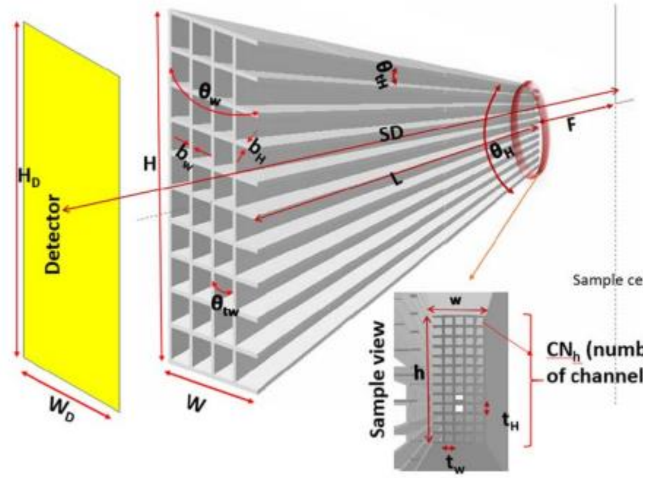




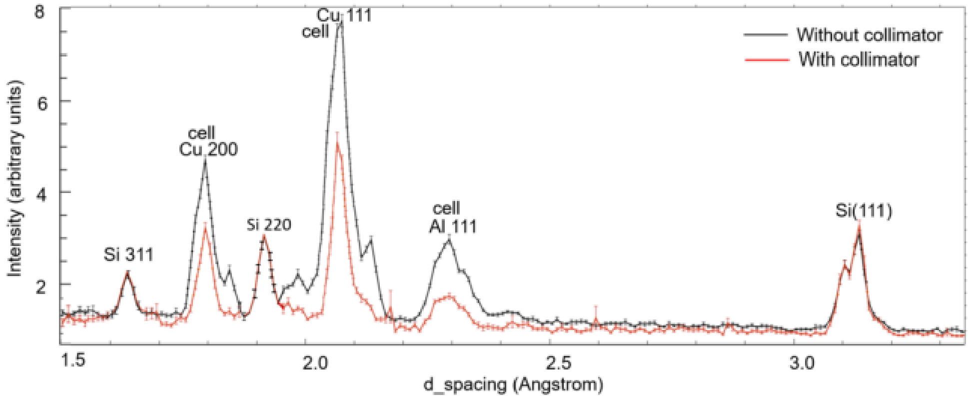
[1] A. dos Santos et al., Rev. Sci. Instrum. 89, 092907 (2018).

C. Incident and scattered beam collimation

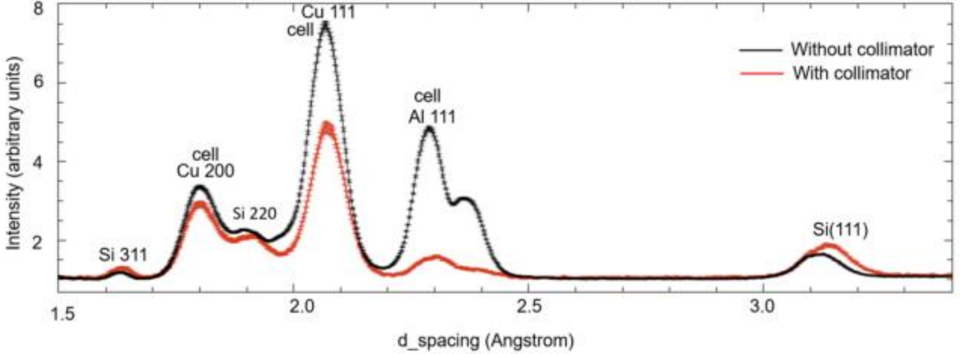
Monte Carlo Ray Tracing allows for further improved radial collimations through computer optimization[1]. Cell consists of a CuBe insert in an Al sleeve.



Simulation



Experiment



[1] F. Islam et al., Journal of Neutron Research 22 (2020) 155–168

C. Incident and scattered beam collimation

Collimation reduces cell scatter and increases ratio of sample-to-background signal:

- Incident beam collimation optimizes for illumination of the sample.
- Radial collimation selects for only sample scatter to arrive on the detector.

These developments are critical for high pressure neutron scattering since sample volumes and hence sample scatter are small.