High Pressure Measurements with X-rays and Neutrons

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Talk overview

- Why high pressure? - It is a great example for extreme conditions and it is fun!
- Background on high pressure
- High pressure techniques for X-ray scattering
- High pressure techniques for neutron scattering

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

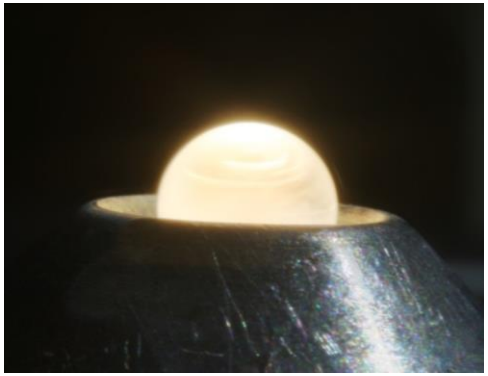
Courtesy of Ken Littrell, GP-SANS, HFIR

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

High magnetic field environments

Low temperature environments – Cryostats and dilution fridges

High temperature environments – levitation for measurements of melts



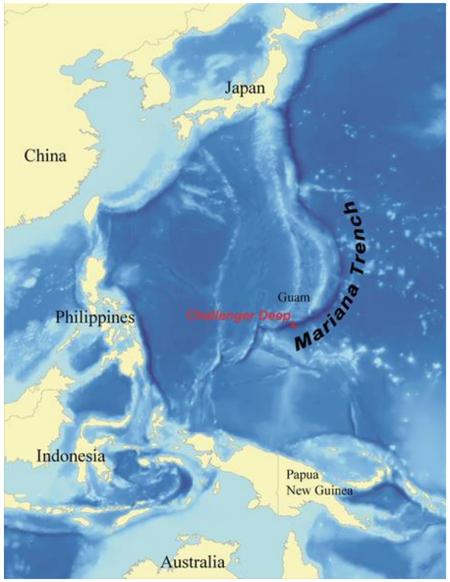
Courtesy of Joerg Neuefeind, NOMAD, SNS

High pressure conditions

Pressure of CO_2
400-600 kPa

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

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



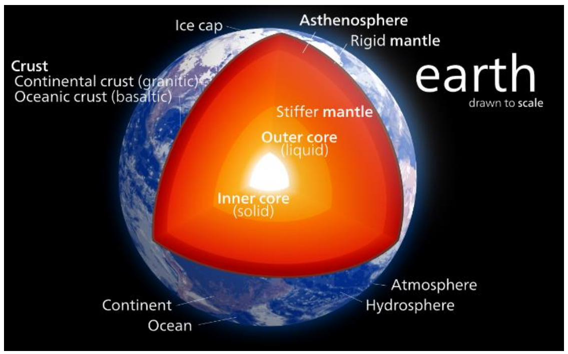
Deepest point of the ocean at depth of ~10900 m and ~0.1 GPa pressure

Wikipedia:
[Magnitude of pressure]

Photo Source: Wikipedia

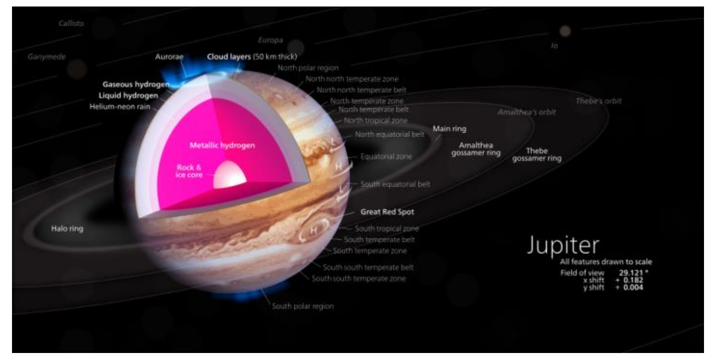
Planetary sciences

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.

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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.

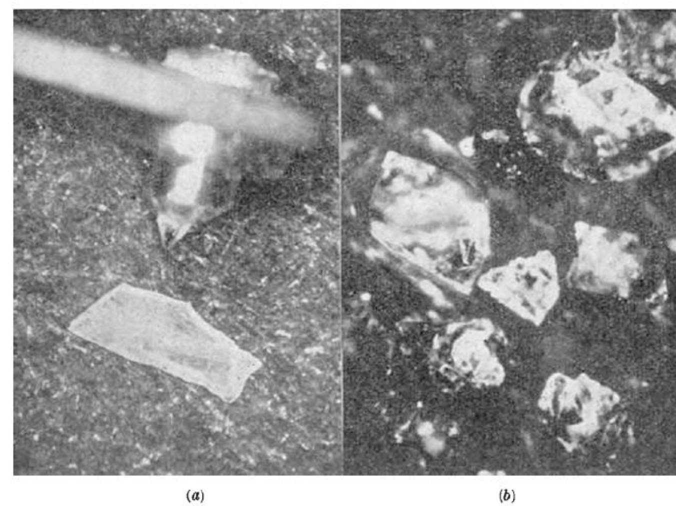


Fig. 3. Man-made diamonds. (a) 1-mm. diamond shown with phonograph needle. (b) 0·2–0·5-mm. octahedra

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

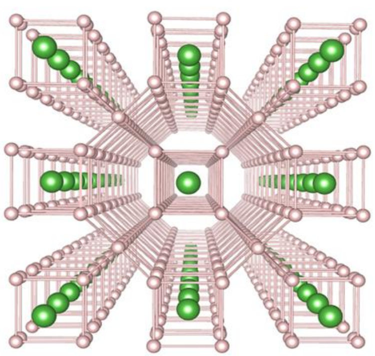
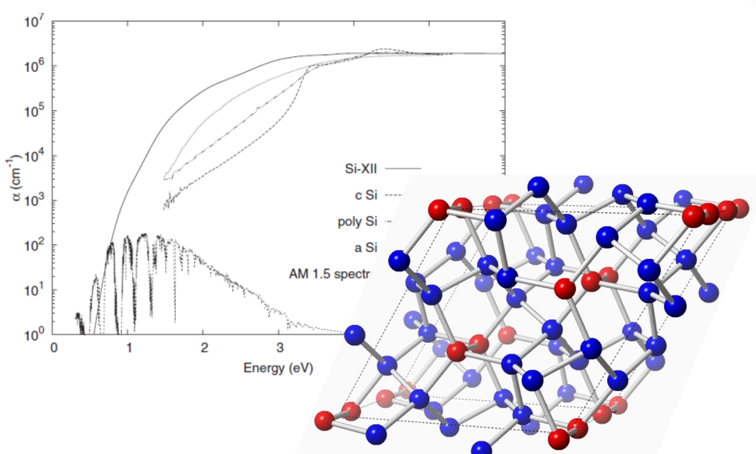


Image from Science News, LaH_{10} reported in PRL 122, 027001 (2019).

Novel semiconductors



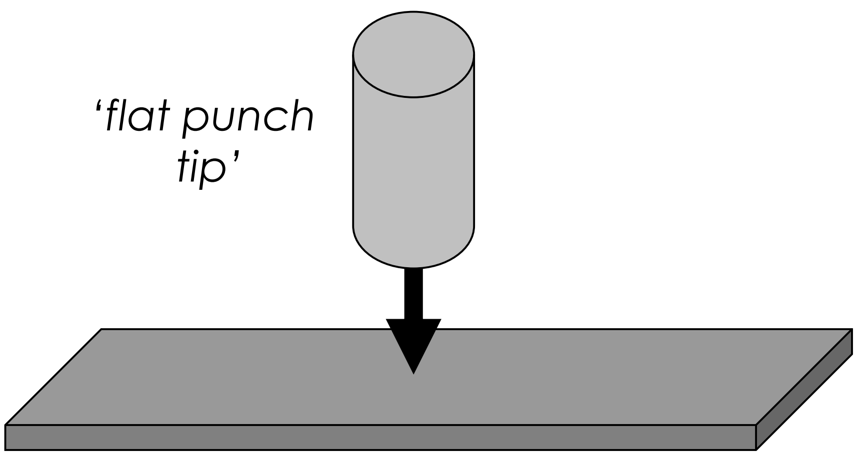
Better absorption of solar spectrum for r8-Si (Si-XII) in PRB 78, 161202(R) (2008).

What is pressure?

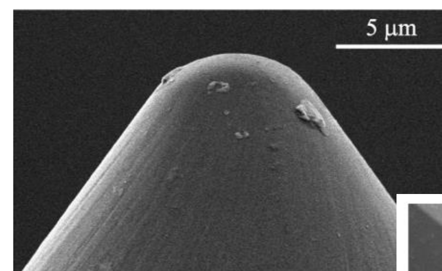
$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

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

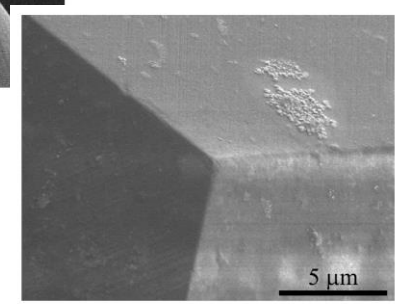
'flat punch tip'



Indentation:



spherical tip



Berkovich tip

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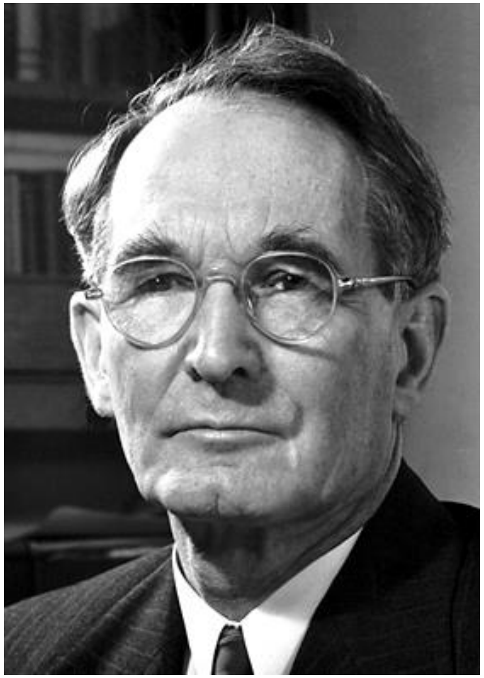
History of high pressure science



Percy Williams Bridgman

father of high pressure studies

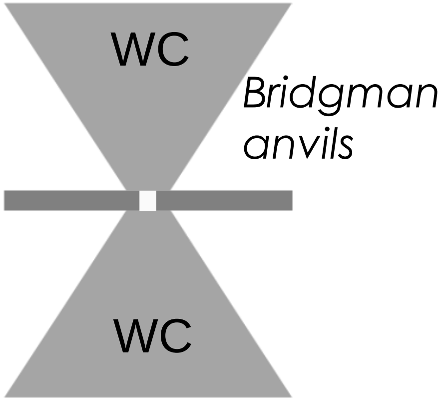
1919: appointed full professor in Harvard, aged ~37

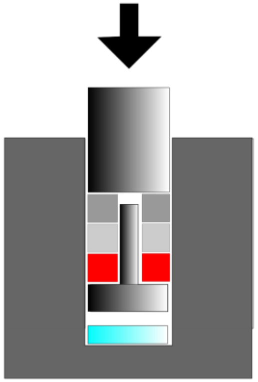
New pressure apparatus (1905), Bridgman anvils

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 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.

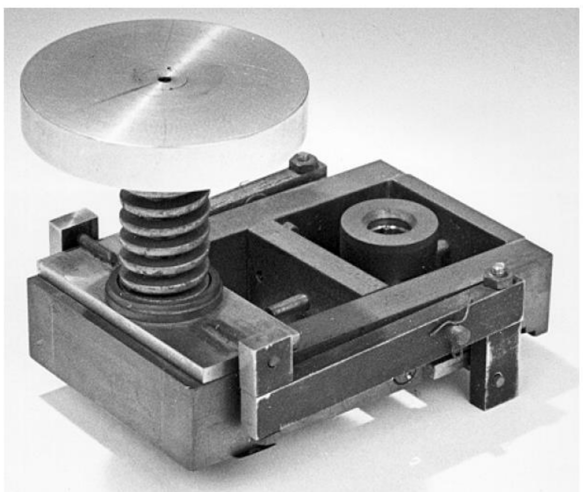


Fig. 1. The original DAC, on display in the NIST Museum.

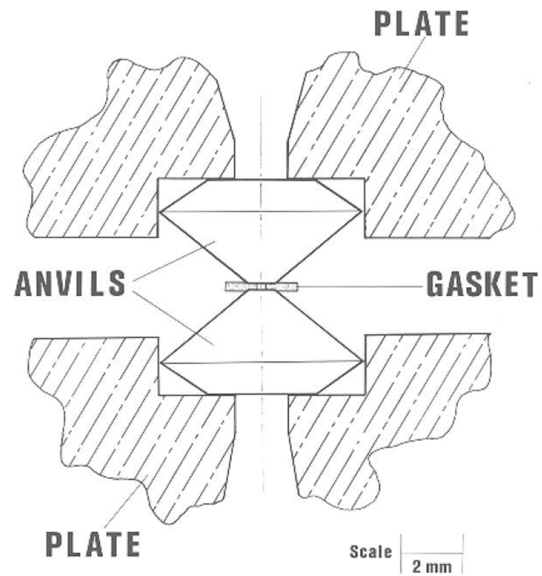


Fig. 4. A schematic diagram of the opposed diamond anvil assembly to illustrate the 180° optical transmission characteristics and the concept of Bridgman opposed anvils. A thin metal gasket containing a 250 μm diameter hole for encapsulating a sample (liquid or solid or both) is squeezed between the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

DAC development at NIST

Diamond cells for X-ray scattering

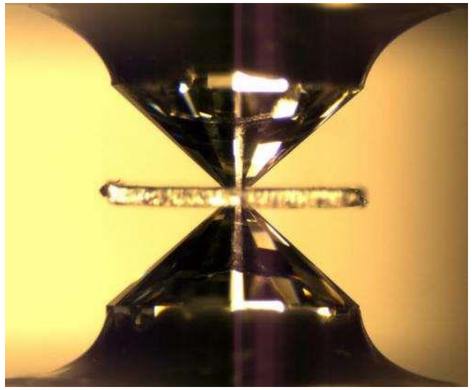
$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

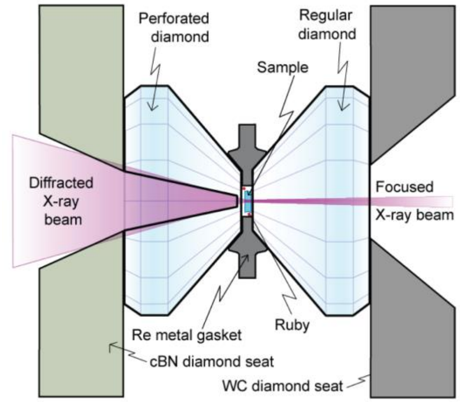
For a radius of 200 μm, we now need to apply a force of ~1200 N (equivalent to ~130 kg) to achieve 10 GPa.

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

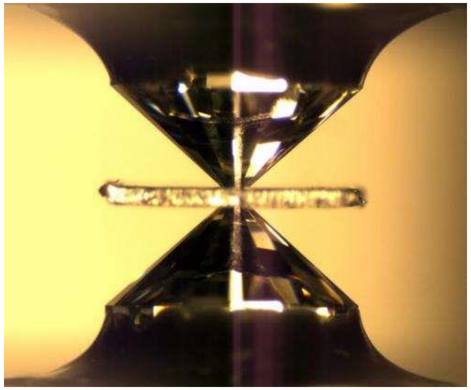


by Stas Sinogeikin (HCPAT)

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 ~0.1 mK 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

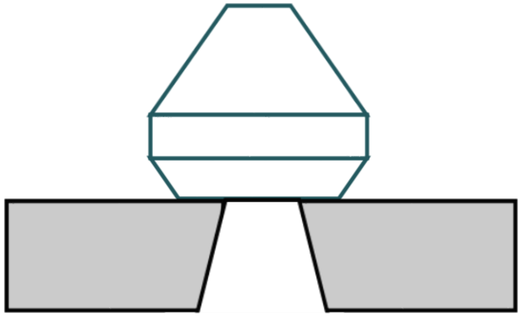
A large variety of different DACs have been created for different purposes.

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

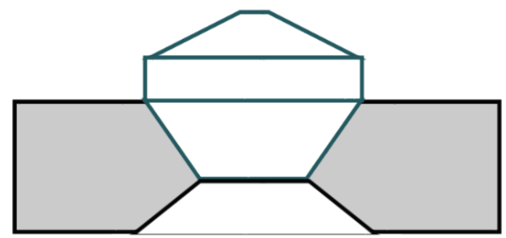
Diamond cells for X-ray scattering

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

Deflection cell:

Boehler-Almax Plate DAC

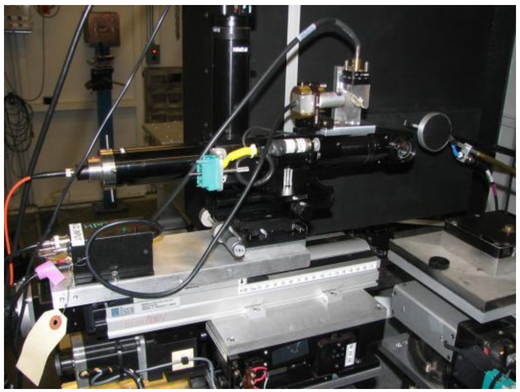
Conical anvils



Boehler-style cut

Diamond cells for X-ray scattering

DAC experiments require substantial support infrastructure.



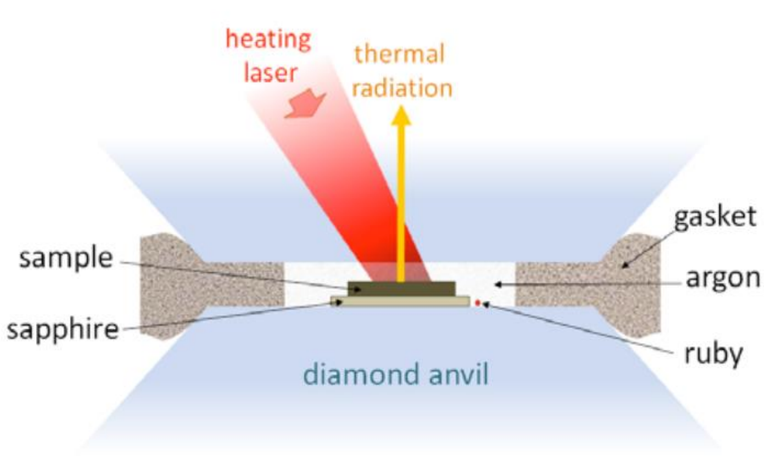
HPCAT online and offline ruby systems

GSECARS/COMPRES gas loader

HPCAT laser driller

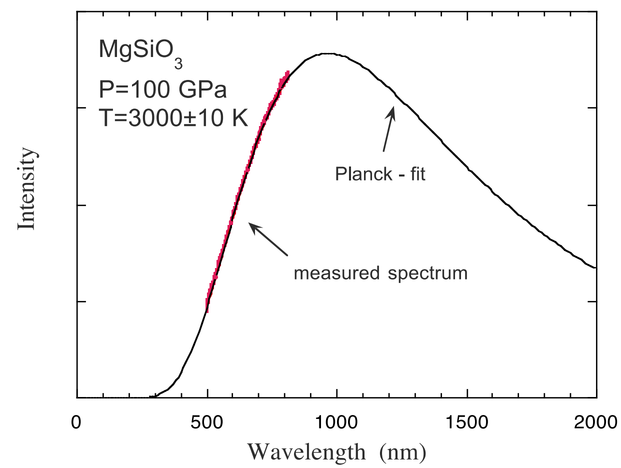
Laser-heating in the diamond cell

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]

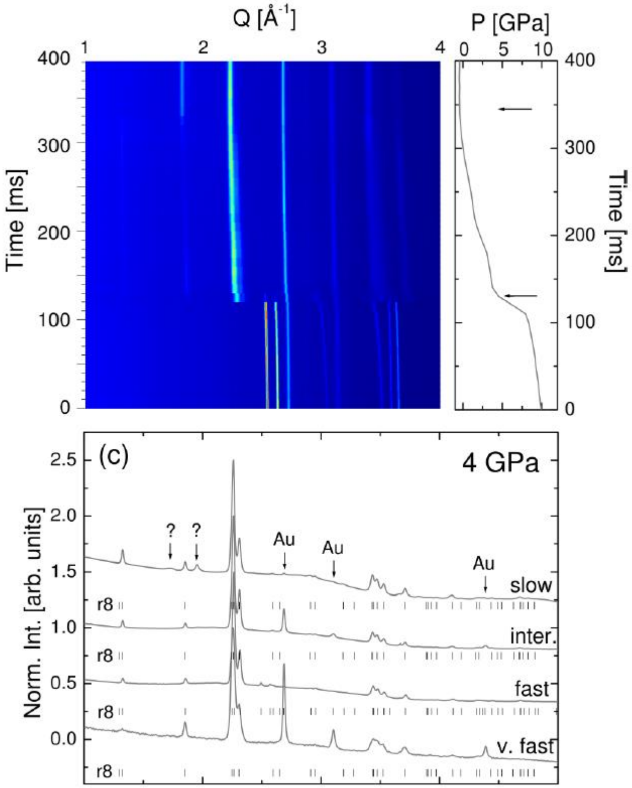
Temperature measurement using Planck equation [1]



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

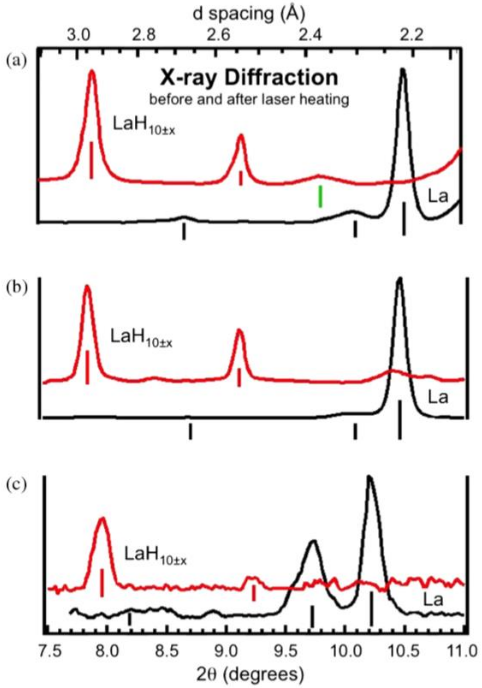
[1] R. Boehler, *Materials Today* **8**, 34 (2005).

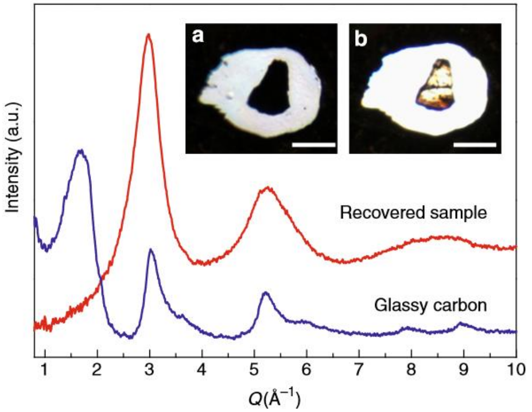
Examples for high pressure X-ray scattering



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

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

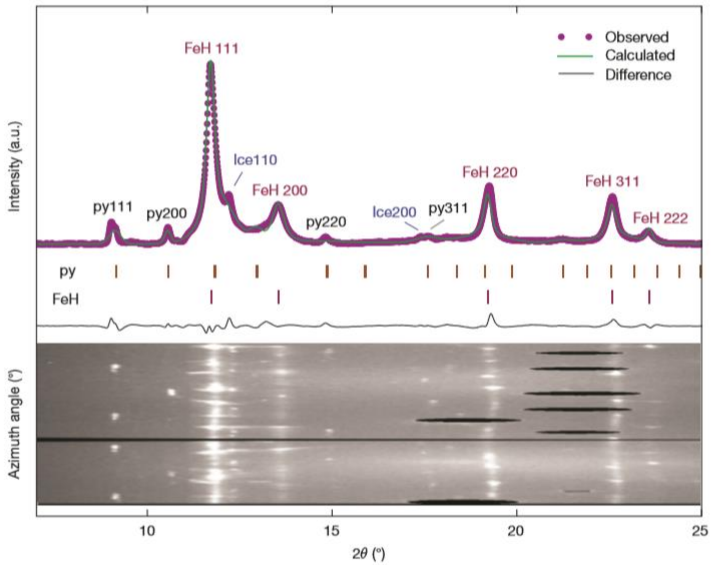




High pressure, high temperature synthesis of amorphous diamond [3].

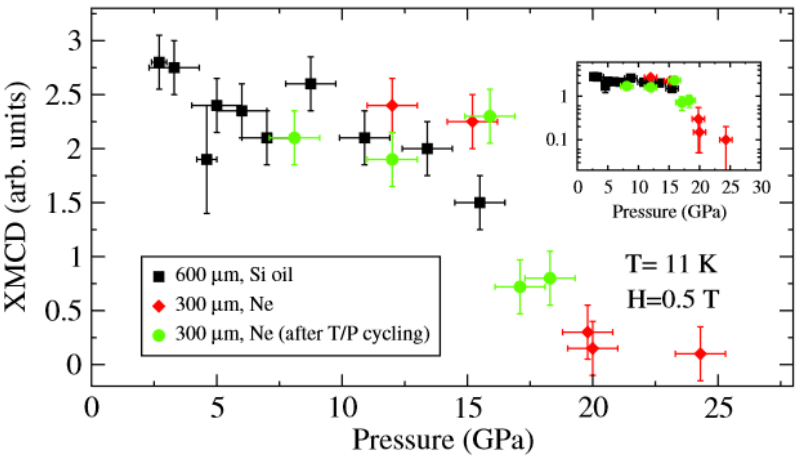
[1] B. Haberl et al, PRB 89, 144111 (2014).
[2] Somayazulu et al, PRL 122, 27001 (2019)
[3] Z. Zeng, Nat. Comm. 8, 322 (2017)..

Examples for high pressure X-ray scattering



XRD pattern of Fe+H2O 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 also possible in a DAC although data quality is often inferior.

Powder diffraction: environment not hydrostatic enough for Rietveld.

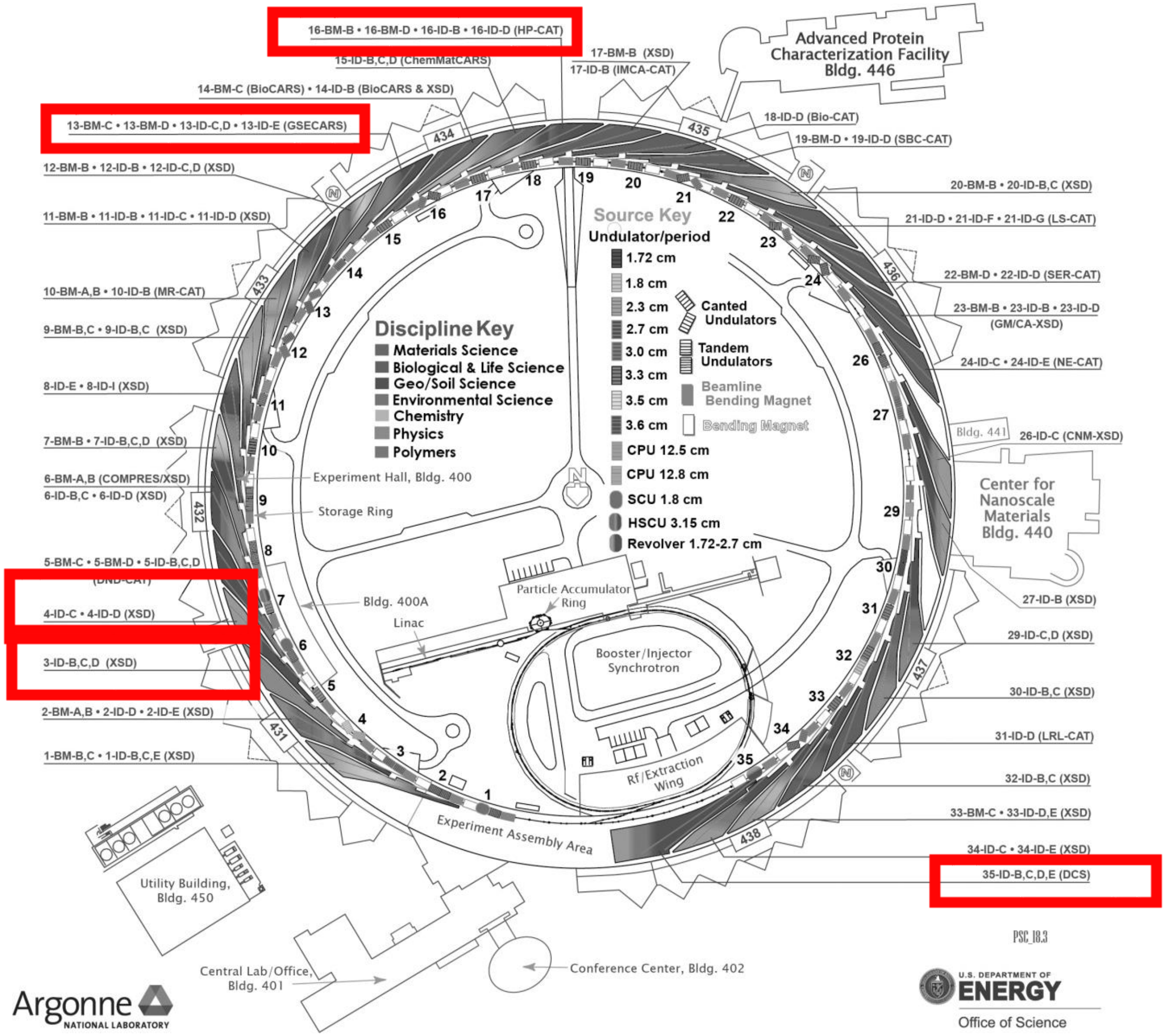
Laser heating: huge temperature gradients (1000 K!) that can even result in different crystal grain sizes.

EXAFS: Diamond glitches.

PDF: Limited diffraction aperture, background changes with pressure.

Single crystal diffraction: all of the above.

High Pressure Science at the APS



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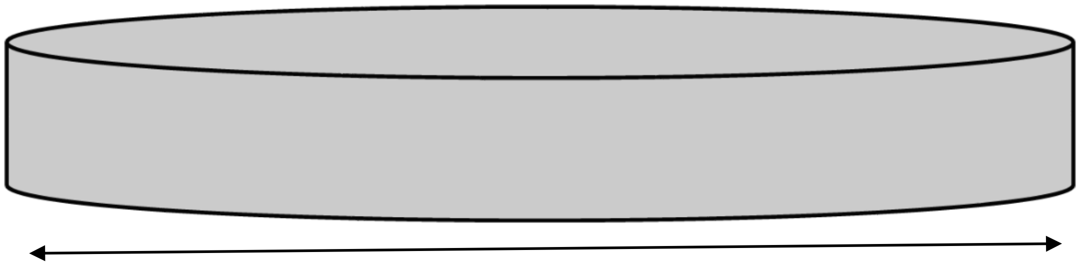
High pressure neutron scattering

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 0.003 mm^3.

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



*Note that chamber diameter = 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

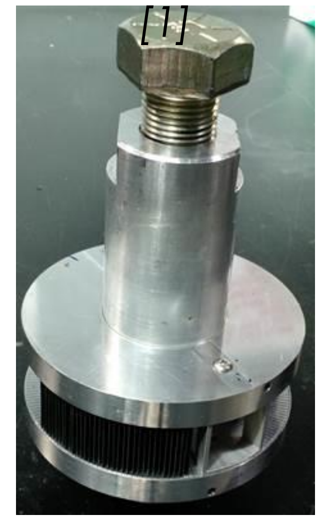
High pressure neutron scattering

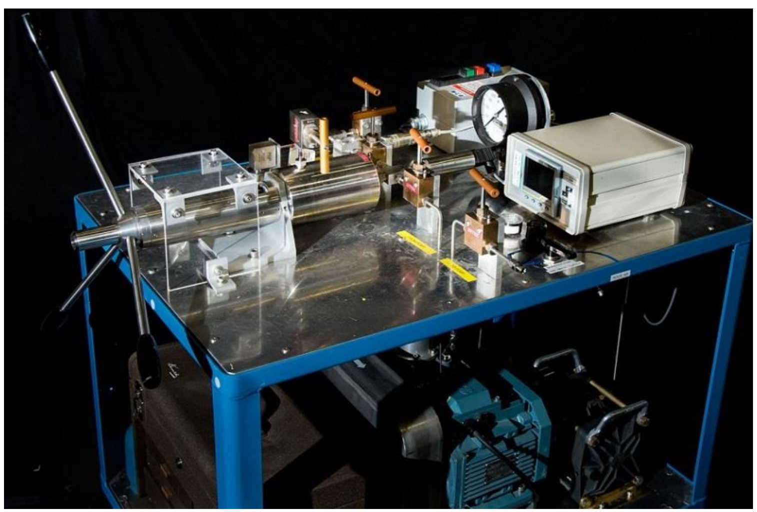
- To accommodate the necessary large sample volumes, a variety pressure cells exist for neutron scattering.
- These are often optimized for specific application.
- Many developmental efforts aim to increase pressure capabilities for *in situ* neutron scattering.

High pressure neutron scattering

- 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]





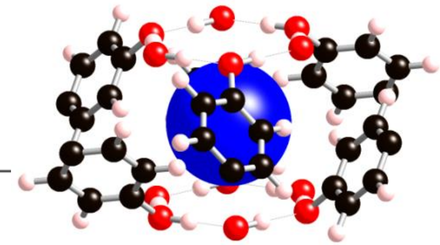
SITEC Gas Intensifier rated to 7 kbar

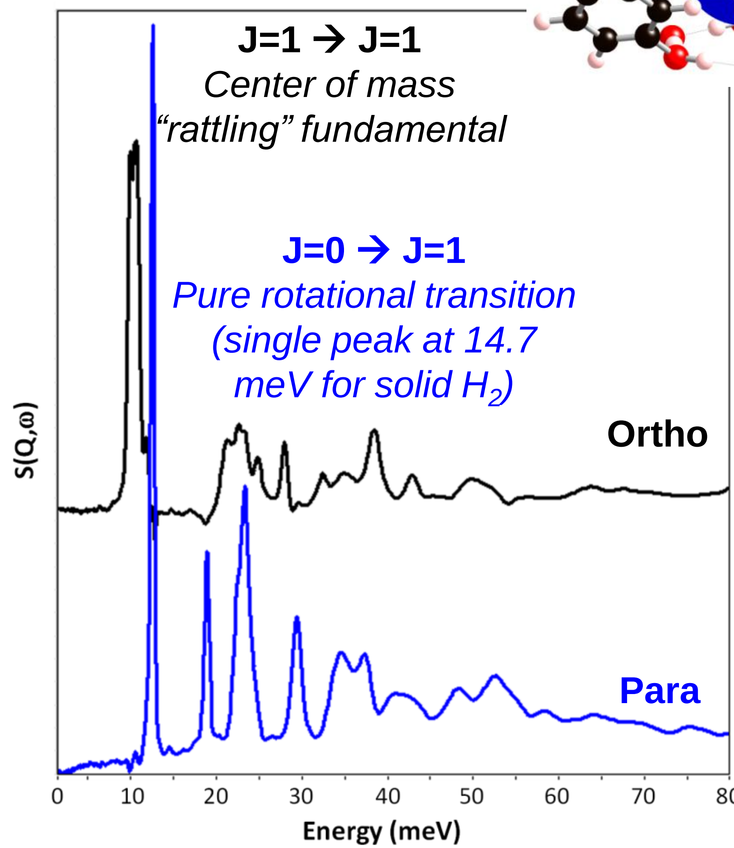
[1] A. dos Santos *et al.* accepted with Review of Scientific Instruments.

High pressure neutron scattering

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

Gas pressure cell used on VISION

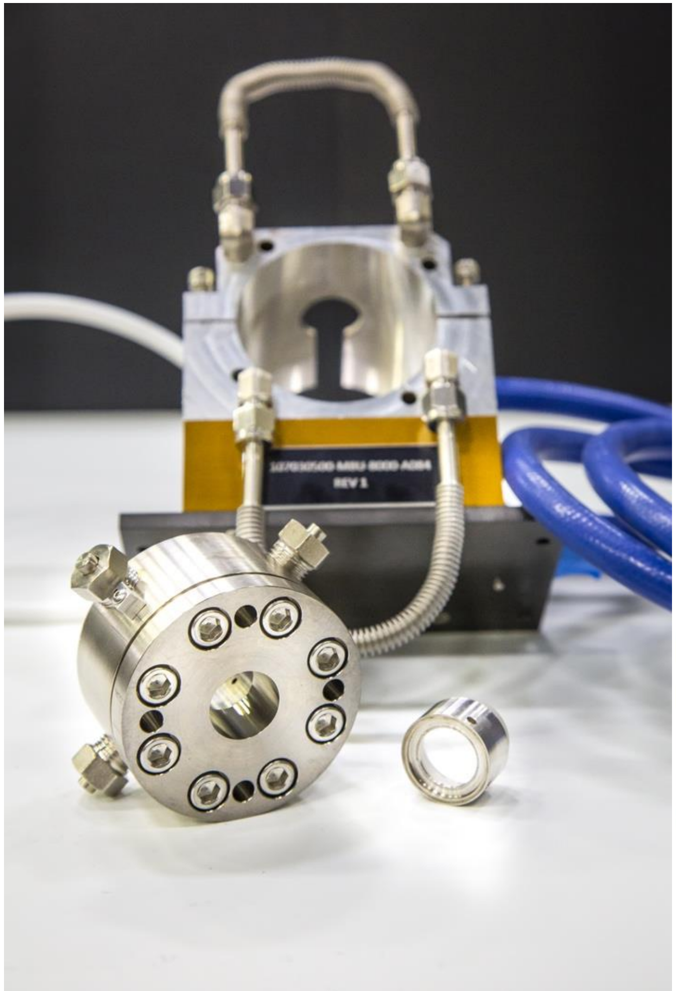




Diamond anvil cell gas loader can be used as portable H_2 intensifier

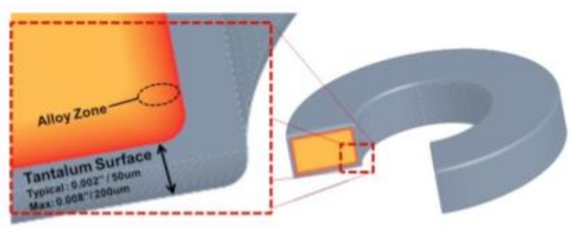
Source: Daemen (ORNL), see T.A. Strobel et al, PRL 120, 120402 (2018).

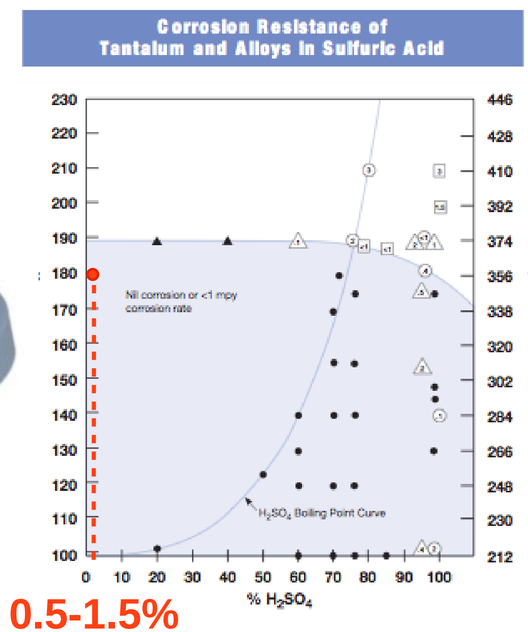
High pressure neutron scattering



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





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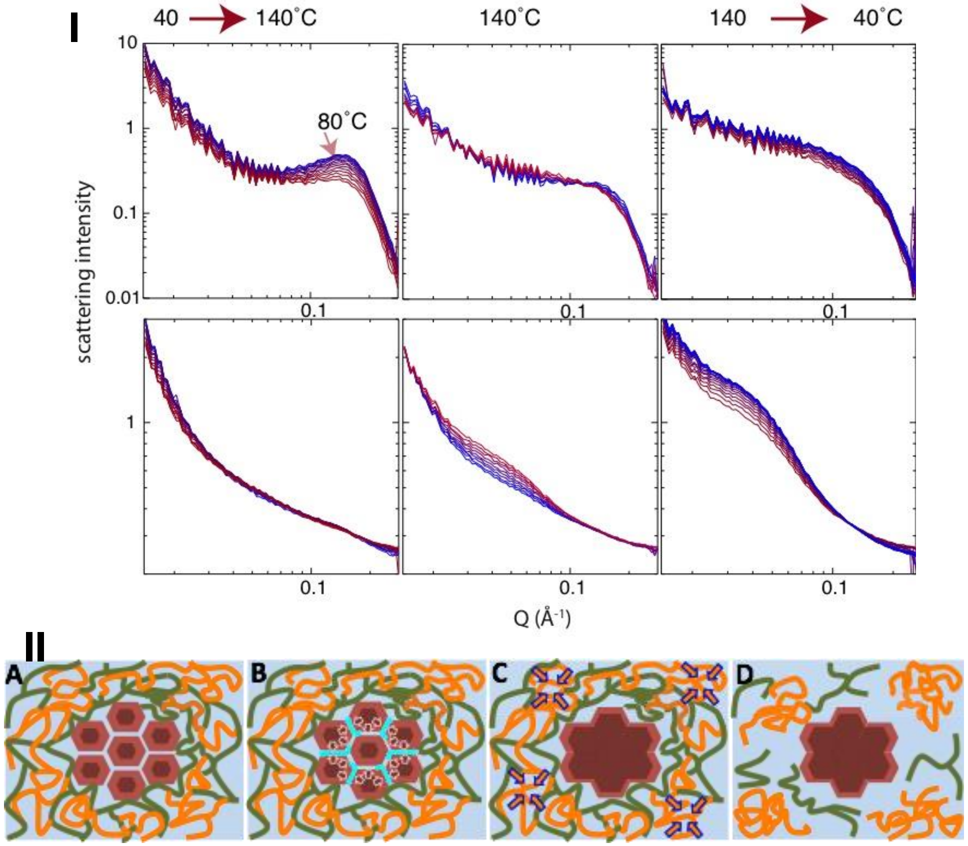
Source: S.V. Pingali, Bio-SANS instrument team (ORNL)

High pressure neutron scattering

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



(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.

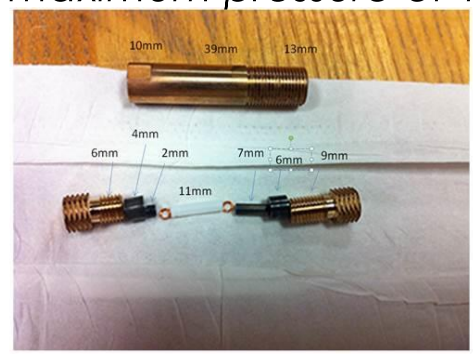
Pingali *et al. Cellulose* **21**, 873 (2014); Nishiyama *et al. Cellulose* **21**, 1015 (2014) ; Langan *et al. Green Chemistry* **16**, 63 (2014)
Contact: pingalis@ornl.gov.

High pressure neutron scattering

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.

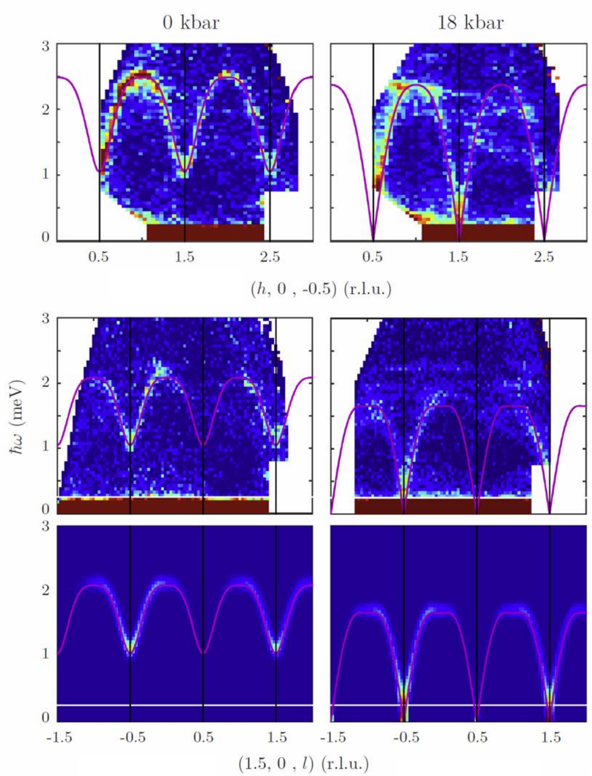


CuBe cell for maximum pressure of 2 GPa available with in situ optical pressure measurement. Sample size is 15 mm height and 4.5 mm diameter.

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

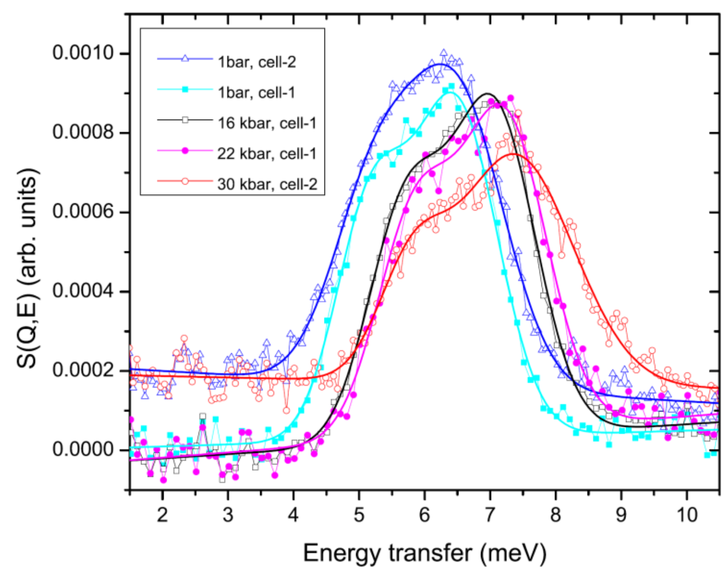
High pressure neutron scattering

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].

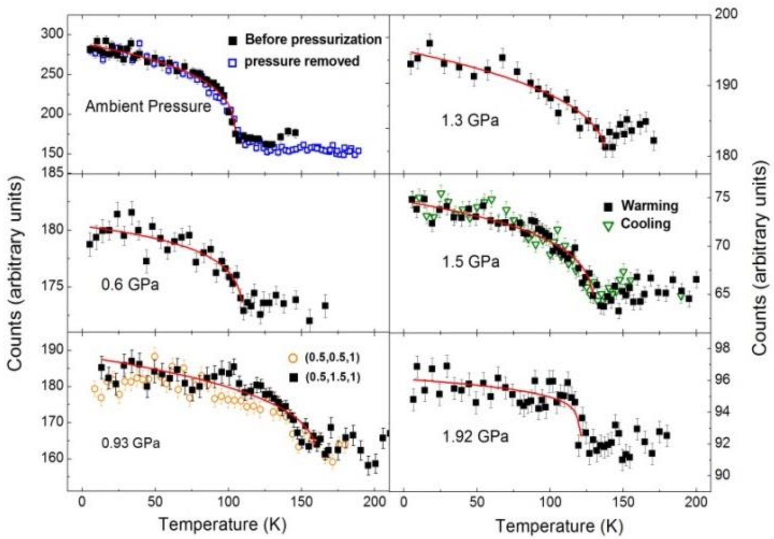


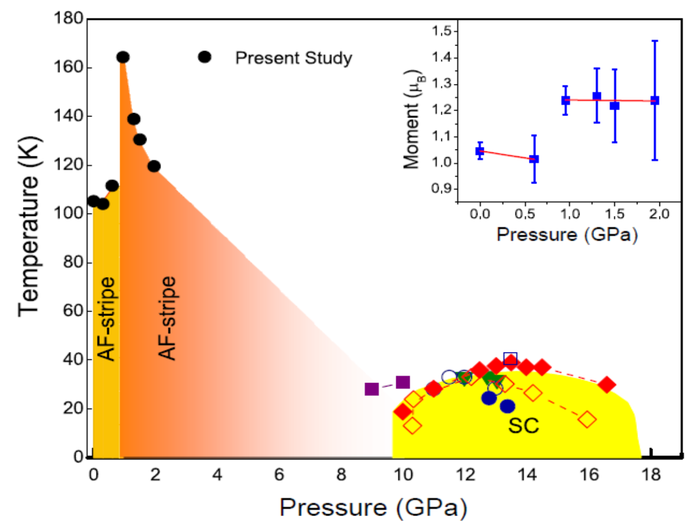
[1] G. Perren, *et al.* PRB 92, 54413 (2015), Editor's suggestion
[2] A.I. Kolesnikov *et al.*, PRB 94, 1343012 (2016).

High pressure neutron scattering

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

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

High pressure neutron scattering

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).

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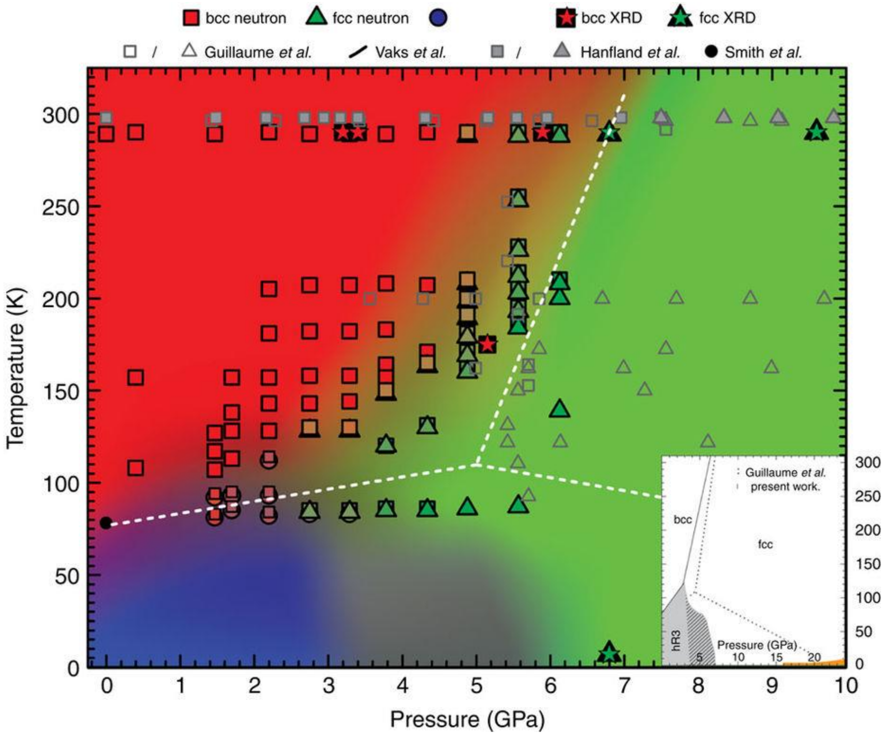
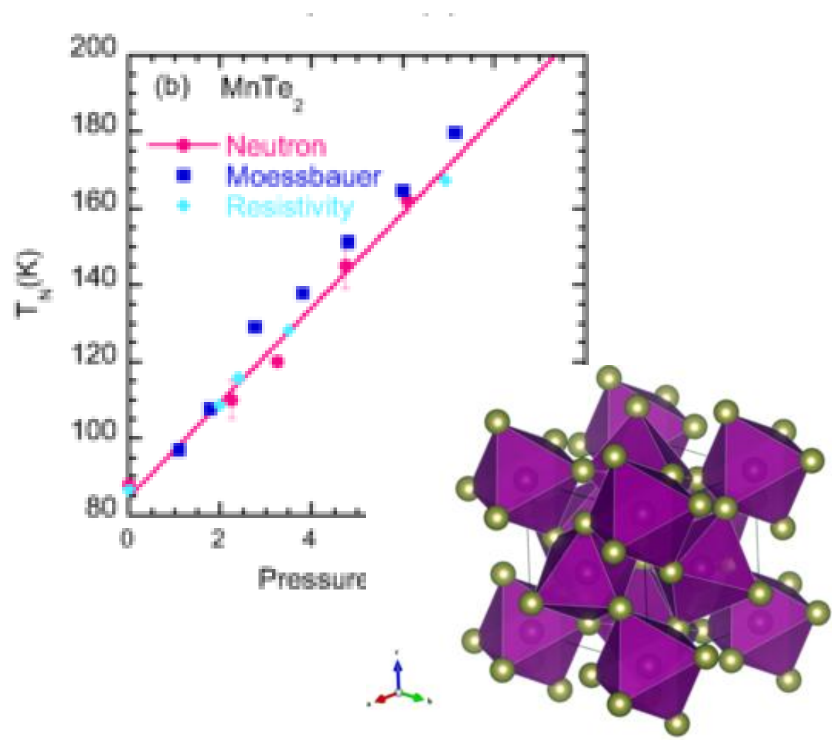
High pressure neutron scattering

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).

High pressure neutron scattering in the DAC

Panoramic diamond cell inside a membrane press. The sample volume is ~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.

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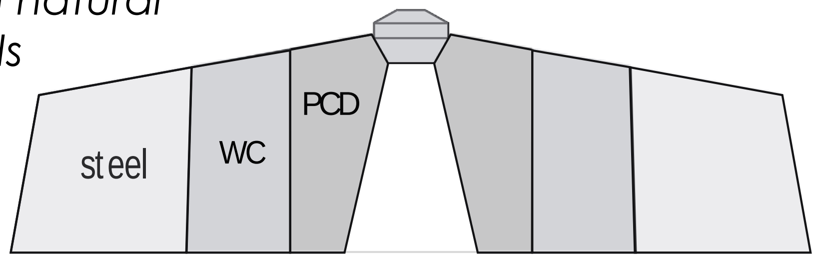
[1] R. Boehler, M. Guthrie *et al*. **High Pres. Res.** (2013).

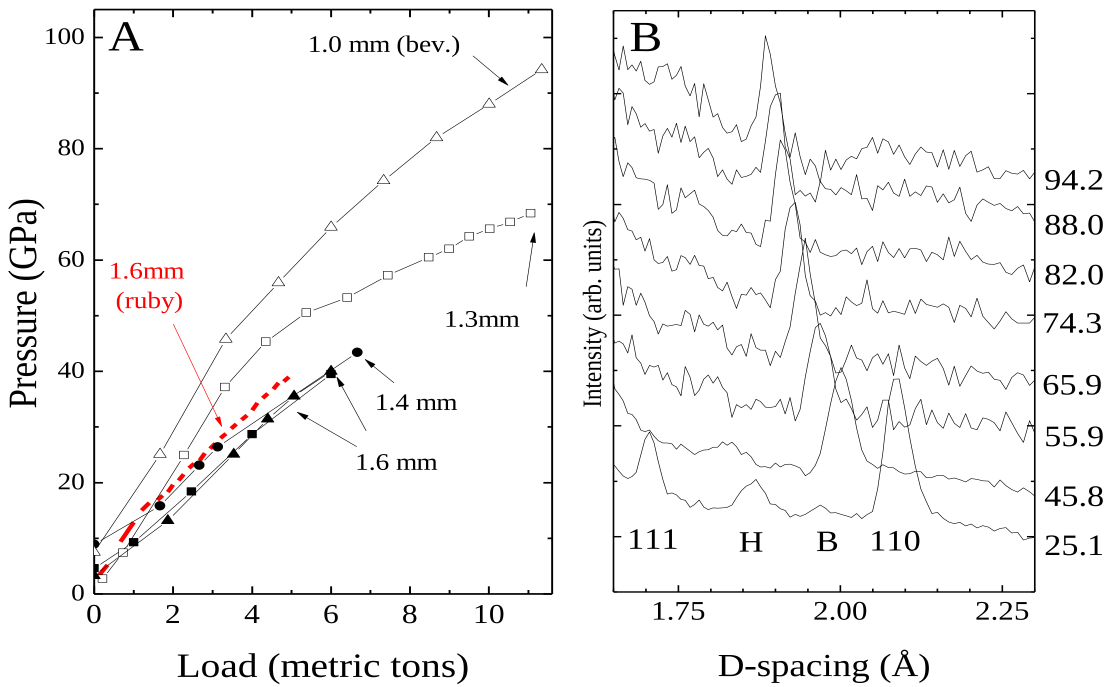
High pressure neutron scattering in the DAC

Seat and natural diamonds used.



one anvil + seat:

$ 4500



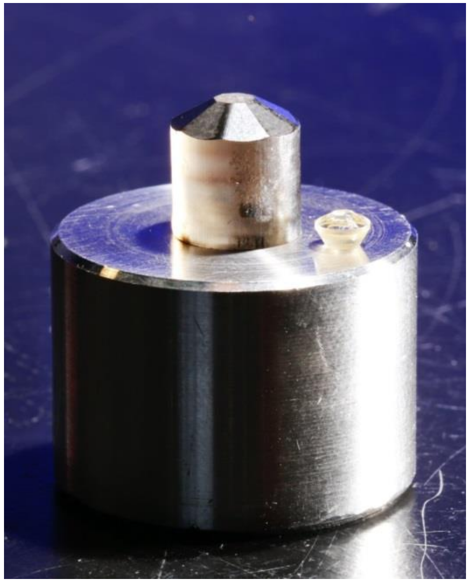
Neutron diffraction up to 94 GPa on ice. Sample volume at highest pressure was ~0.015 mm^3.

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

High pressure neutron scattering in the DAC

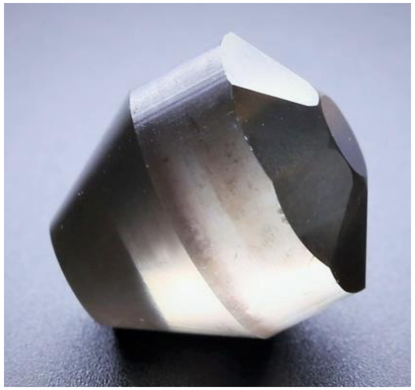
Then very large CVD anvils became available.

10 carat, 9 mm tall CVD anvil with pyramidal design



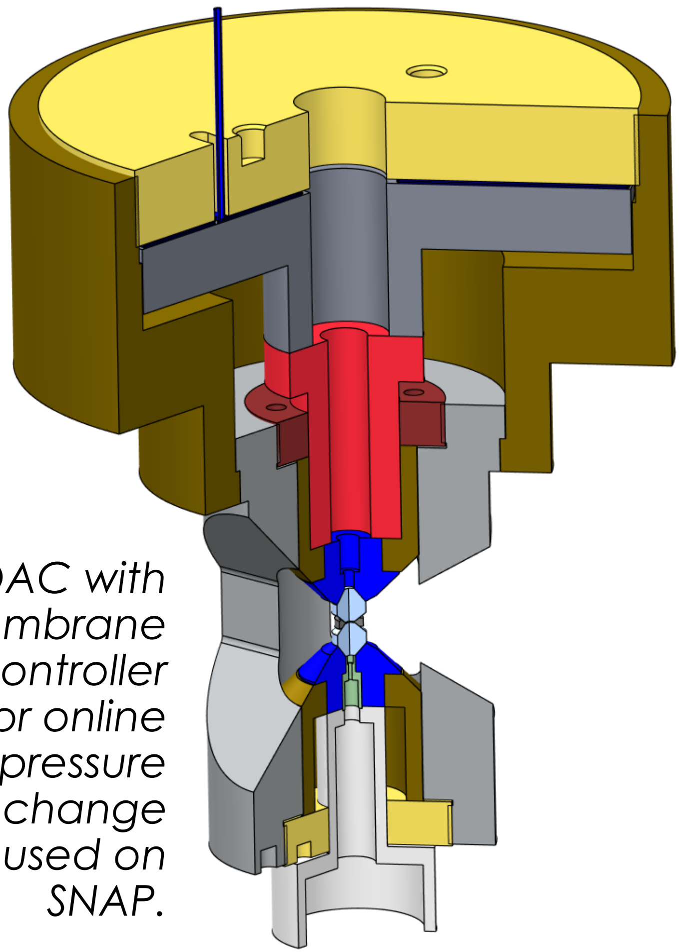
Cracked under 3 tons!

9 mm CVD anvil with conical anvil design



Even 6 mm anvils have been ok to 12 tons!

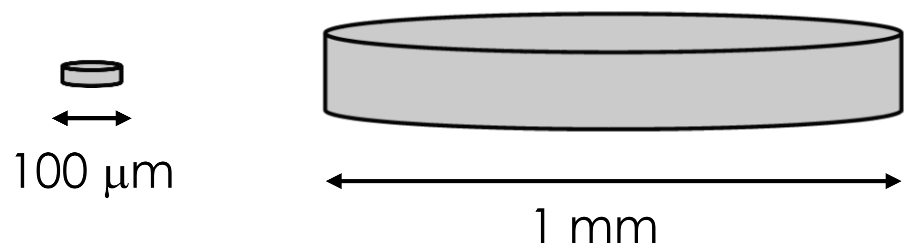
High pressure neutron scattering in the DAC



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

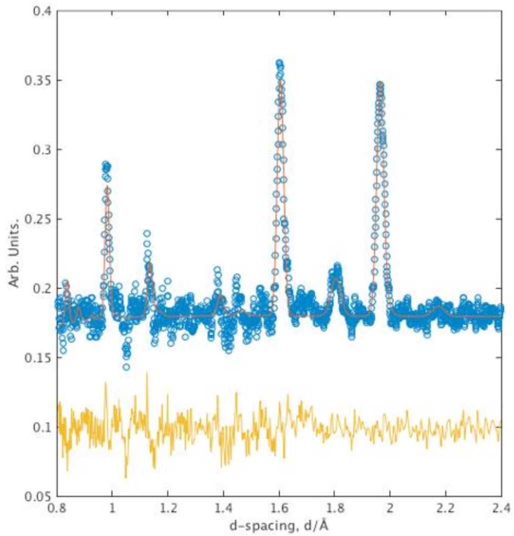
New diamond anvil cell designed for SNAP [1].

- 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.



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

High pressure neutron scattering in the DAC

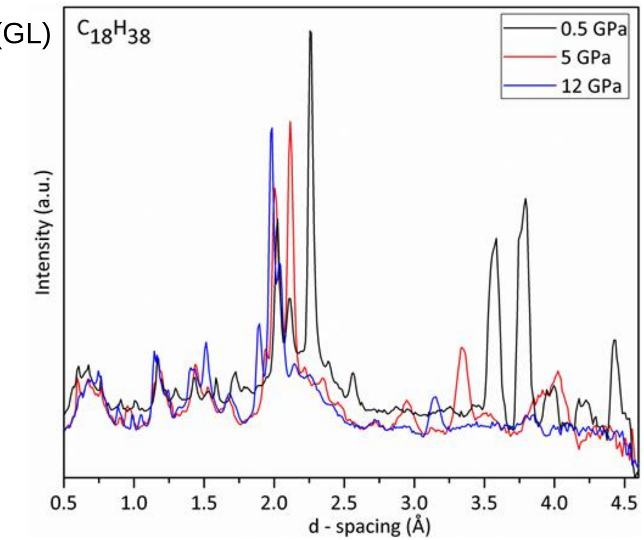


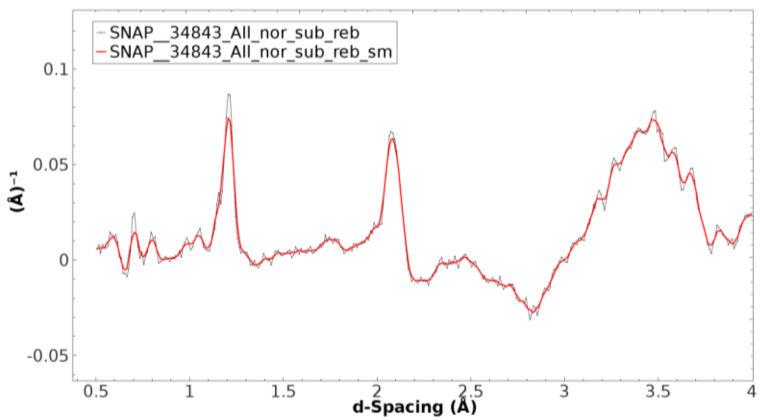
0.06 mm³ of ice VII at ~62 GPa [1].

Source: Guthrie (ESS)

0.06 mm³ of octadecane

Source: Basu (GL)





0.15 mm³ of glassy carbon at ambient pressure

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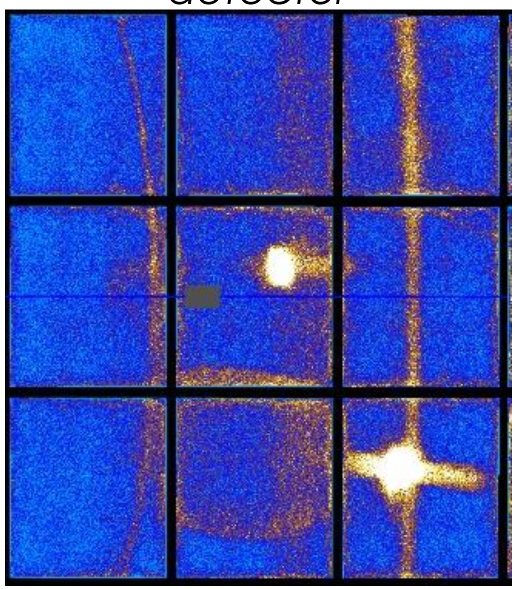
[1] M. Guthrie et al, PRB (2019).

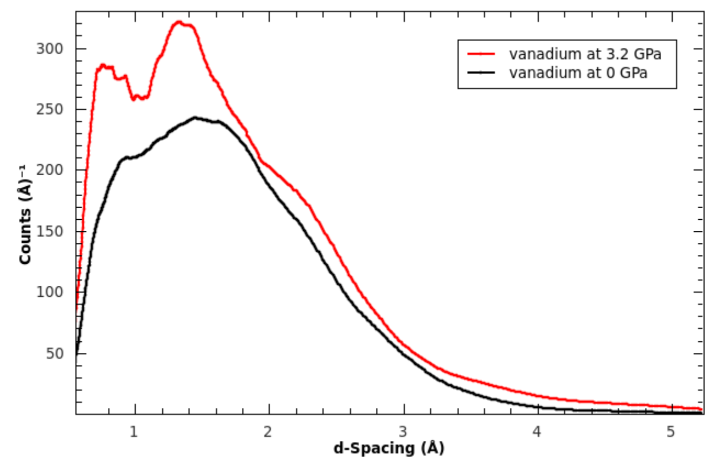
High pressure neutron scattering in the DAC

Background scatter from the cell significantly complicates data analysis. This background changes with pressure.

Diamond and gasket scatter on the SNAP detector



Change in vanadium signal observed with pressure change.



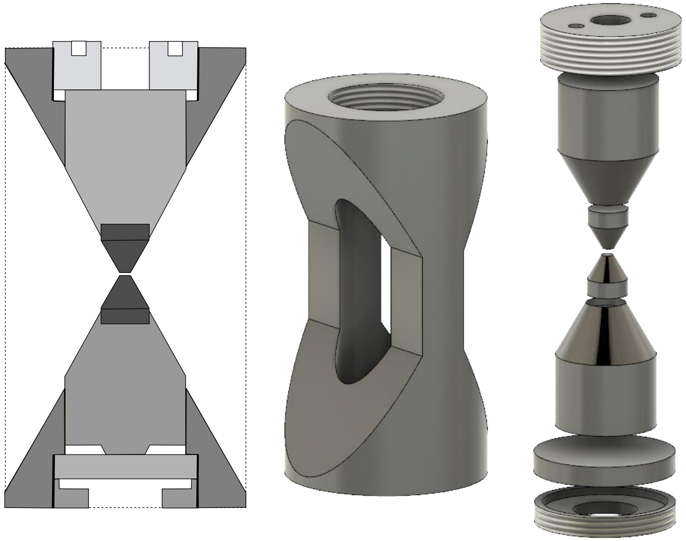
It is critical to consider what type of information is to be extracted from measurement in order to determine necessary corrections.

High pressure neutron scattering in the DAC

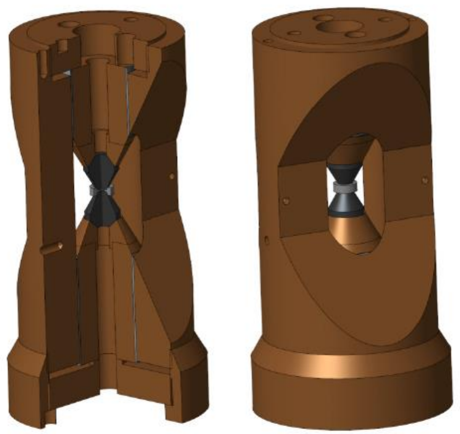
Clamped diamond anvil cell with Versimax® anvils:

- Opening aperture of 120°.
- 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]

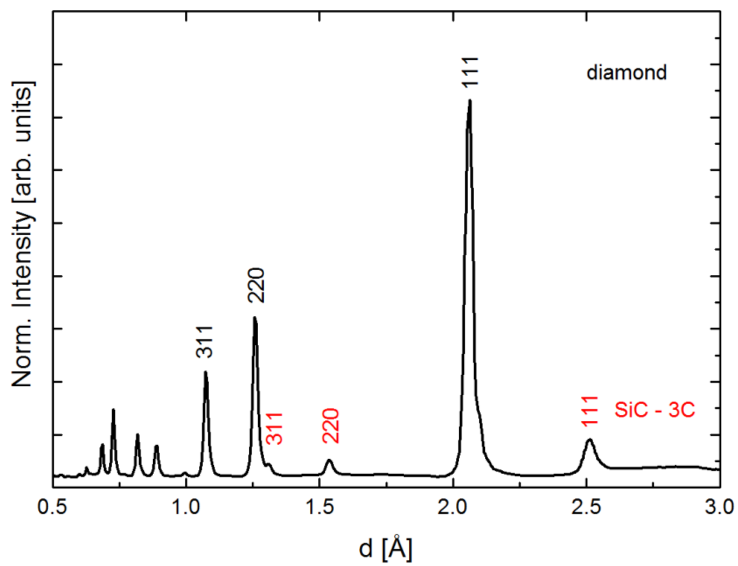
[1] B. Haberl et al, High Pressure Research 37, 495 (2017).
[2] B. Haberl et al, accepted Re. Sci. Instr. (2018).

High pressure neutron scattering in the DAC

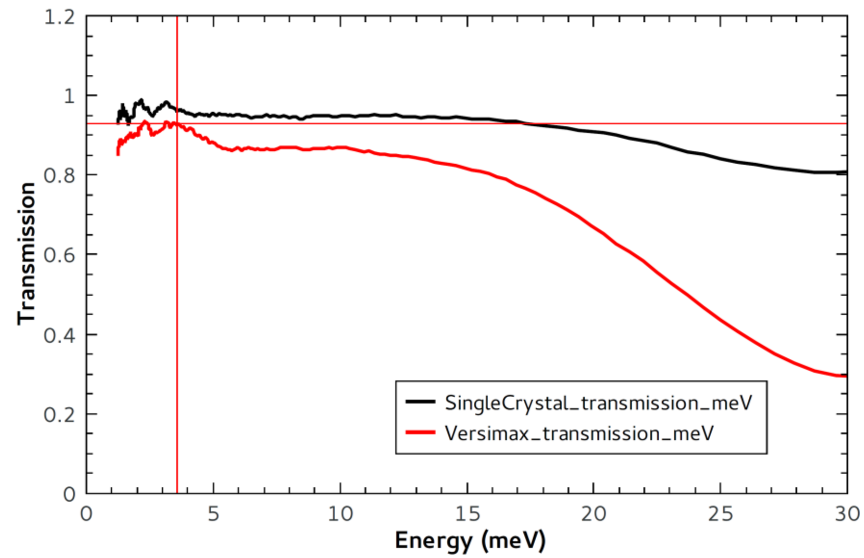
Properties of Versimax® (polycrystalline diamond sintered in SiC matrix from Sandvick):

- 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.



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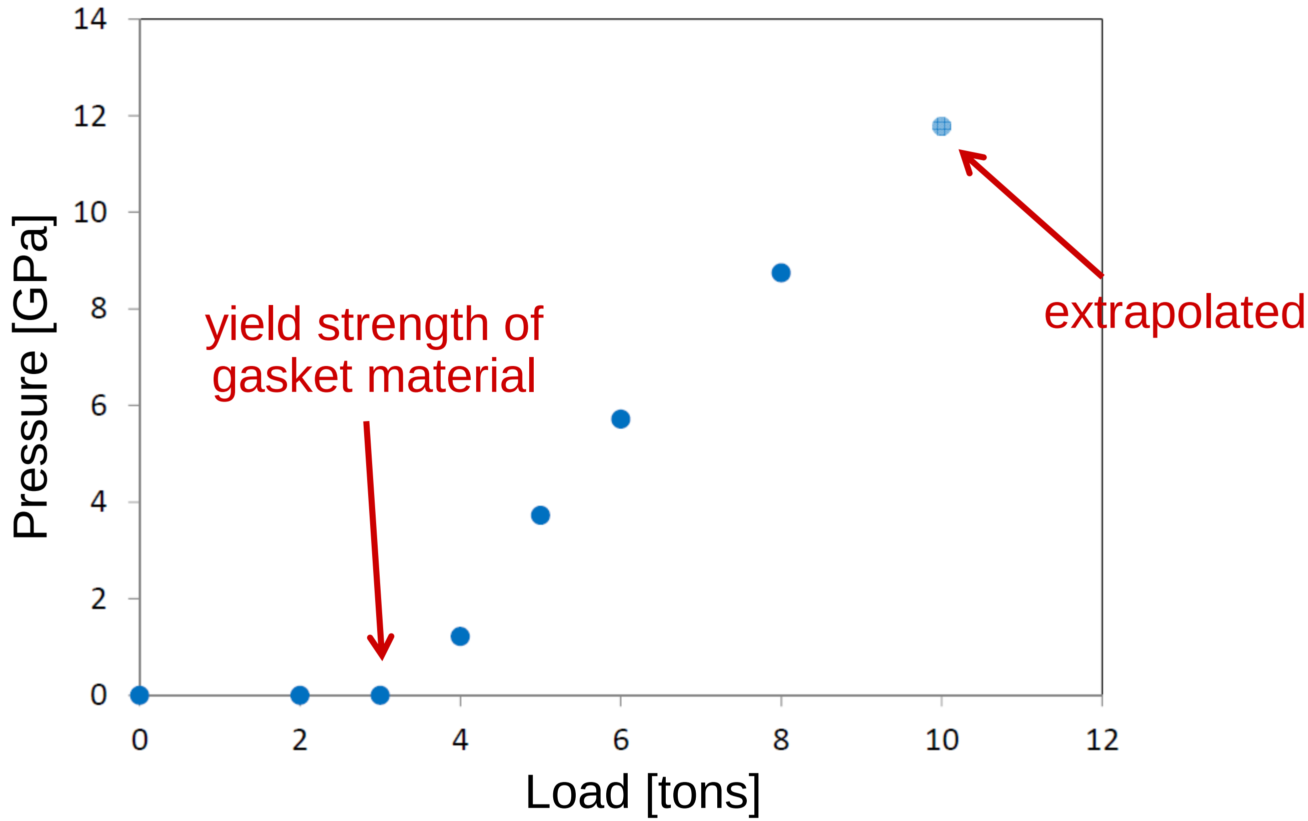
[1] B. Haberl et al, High Pressure Research 37, 495 (2017).

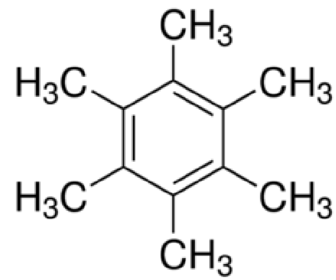
High pressure neutron scattering in the DAC

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

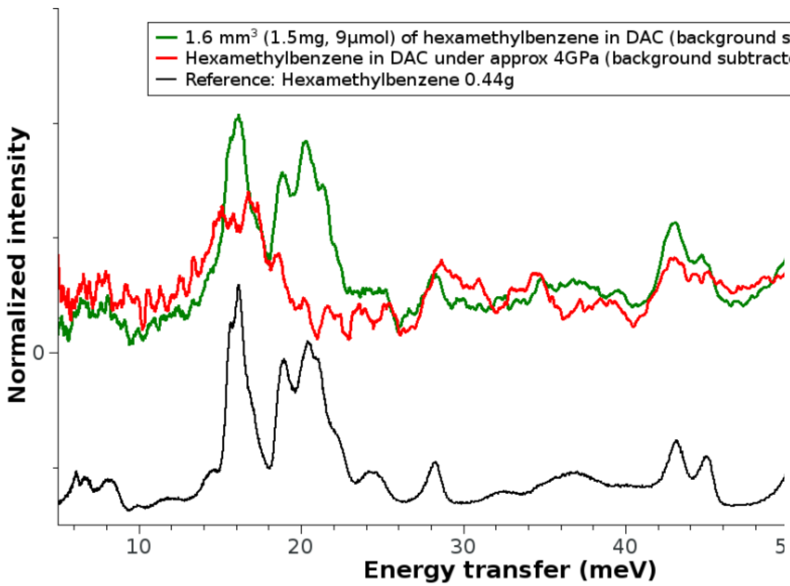


High pressure neutron scattering in the DAC

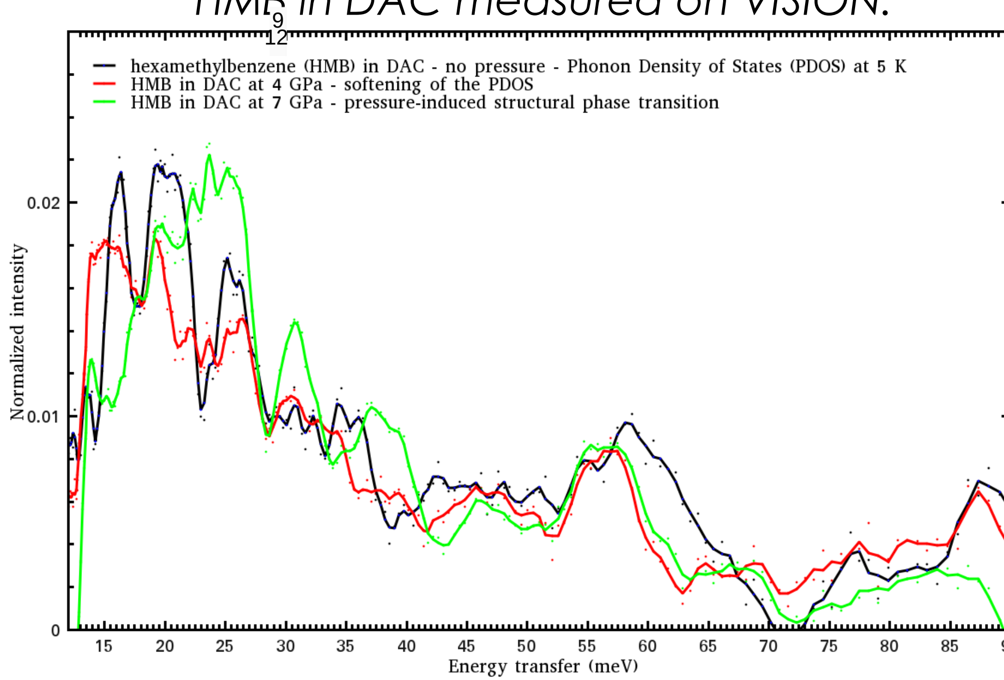
INS on hydrogen-rich samples is possible at SNS



Inelastic neutron spectrum from ~1.6 mm³ of hexamethylbenze loaded into the DAC.



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



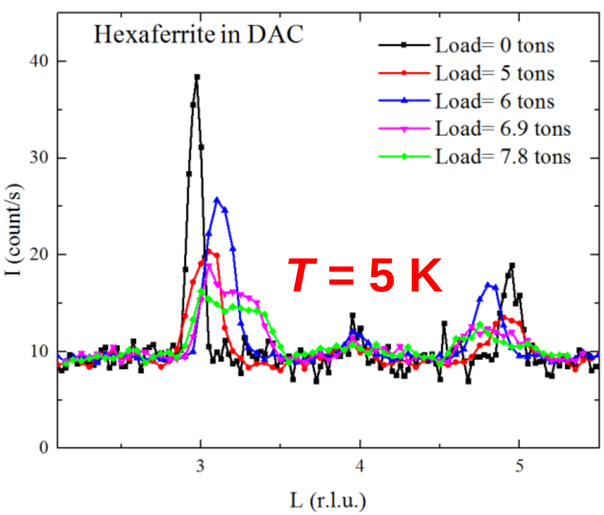
Source: Daemen, Haberl, Molaison, Boehler

High pressure neutron scattering in the DAC

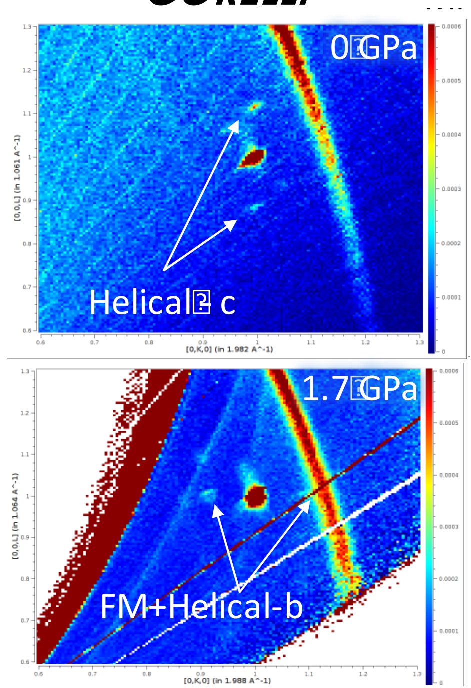
Single crystal diffraction is possible at SNS and HFIR.

HB-3A

Hexaferrite ~0.1 mm³ crystal with Pb as pressure medium inside the DAC within CCR. Neutron wavelength λ=1.546 Å with half-lambda filter [2].

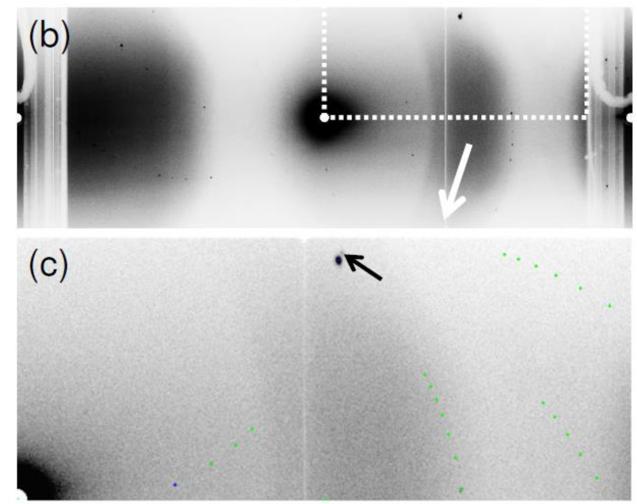


CORELLI



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

IMAGINE



Hexaferrite ~0.1 mm³ 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, accepted to Re. Sci. Instr. (2018).

Supporting equipment

- Offline and online ruby system
- Microdrillers and precision mechanical drillers
- Hydrogen-rated gas loader

Worlds largest single crystal of hydrogen grown in a liquid helium pressure medium

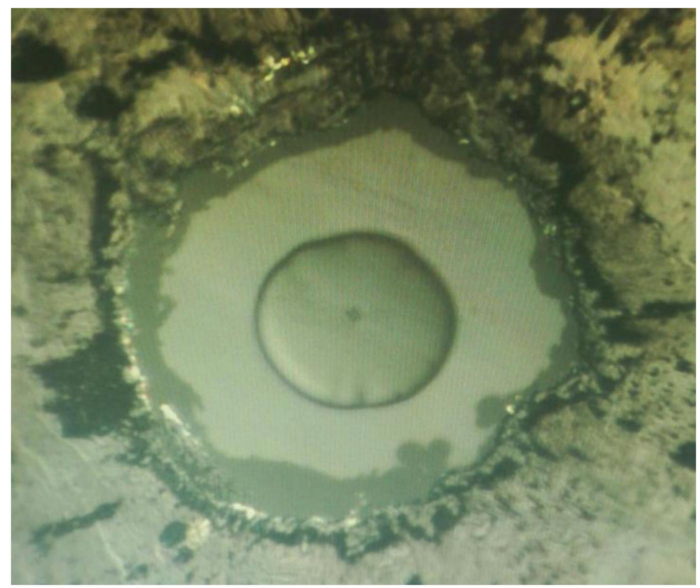
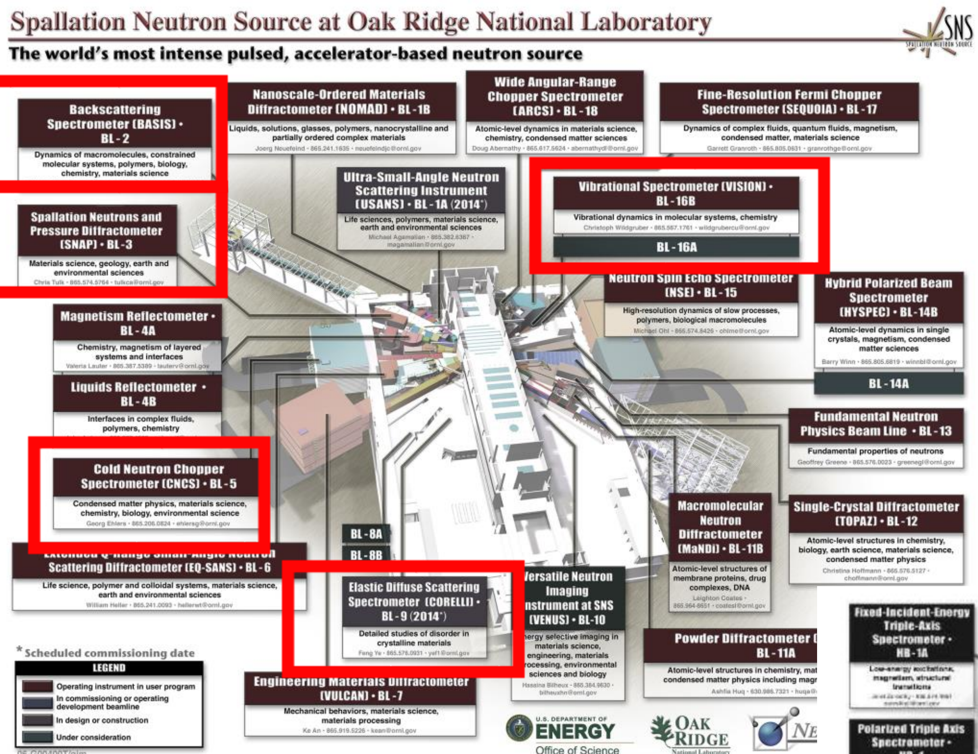
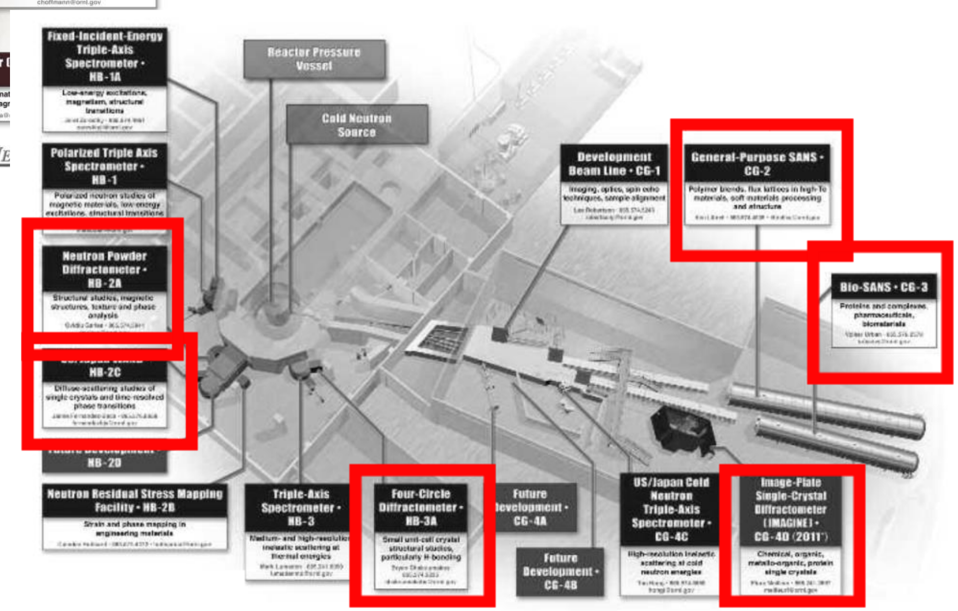


Image courtesy of B. Massani, U. Edinburgh

High Pressure Science at the SNS and HFIR





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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).

Conclusions

- 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.

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