Understanding the role of hydrogen in phase transformations through high pressure neutron diffraction

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

Neutron scattering facilities at ORNL

Spallation Neutron Source

High Flux Isotope Reactor

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

Outline

1) High pressure neutron diffraction
   1.1 Hydrogen in materials and minerals
   1.2 High pressure cells

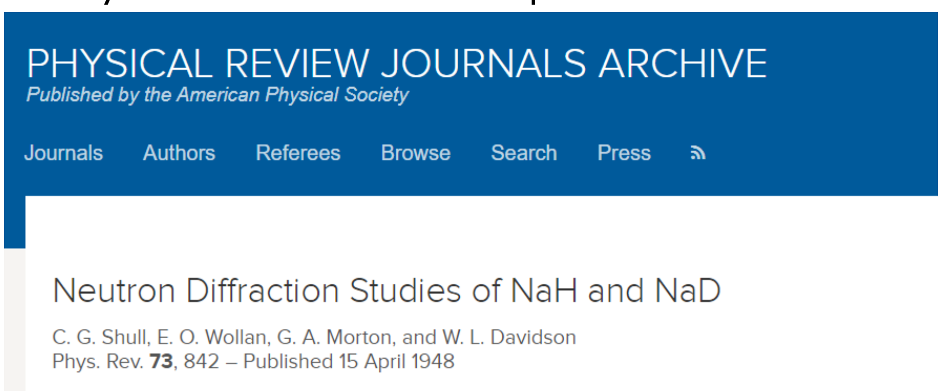
2) The diamond anvil cell project at SNAP
   2.1 Spallation Neutrons and Pressure Diffractometer
   2.2 Neutron diamond cells
   3.3 Recent science examples

3) Future directions at SNAP and beyond
   3.1 Single crystal diffraction
   3.2 Technical advances

1.1 Neutron diffraction and hydrogen

Neutron diffraction provides unique insight into atomic or magnetic structure of a material, specifically for light elements or isotopic differences.

Earliest neutron diffraction study on metal hydride at ORNL reported in 1948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Neutron Diffraction Studies of NaH and NaD
C. G. Shull, E. O. Wollan, G. A. Morton, and W. L. Davidson
Phys. Rev. **73**, 842 – Published 15 April 1948

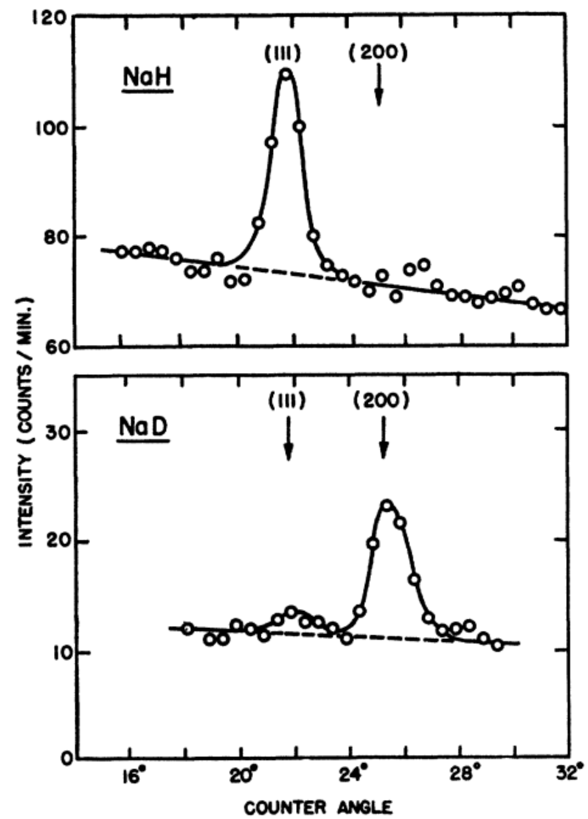

FIG. 1. Powder diffraction patterns over the (111) and (200) peaks of NaH and NaD. The diffuse scattering for NaH is seen to be much larger than that for NaD.

1.1 Materials physics: metal hydrides

Synthetic hydrides:

Numéro J. Phys. France
Volume 25, Numéro 5, mai 1964
Page(s) 454 - 459
DOI https://doi.org/10.1051/jphys:01964002505045400

J. Phys. France **25**, 454-459 (1964)
DOI: 10.1051/jphys:01964002505045400

The structure of HoD3

M. Mansmann et W.E. Wallace

ELSEVIER
Journal of Alloys and Compounds
Volumes 330–332, 17 January 2002, Pages 175-178

Structural study of metal–hydrogen interactions in cubic PrH_{2+x} and rare-earth analogues

G Renaudin, P Fischer, K Yvon

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Crystal structure of $YD_{1.96}$ and $YH_{1.98}$ by neutron diffraction

D. Khatamian, W. A. Kamitakahara, R. G. Barnes, and D. T. Peterson
Phys. Rev. B **21**, 2622 – Published 15 March 1980

EurJIC
European Journal of Inorganic Chem

Microreview Full Access

Solid-State Structures and Properties of Europium and Samarium Hydrides

Holger Kohlmann

First published: 25 May 2010 | https://doi.org/10.1002/ejic.201000107 | Citations: 25

Hydrides recovered from high pressure:

ELSEVIER
Journal of Alloys and Compounds
Volumes 330–332, 17 January 2002, Pages 110-116

Phase transformations, crystal and magnetic structures of high-pressure hydrides of *d*-metals

V.E Antonov

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Crystal structure and lattice dynamics of high-pressure scandium trihydride

V. E. Antonov, I. O. Bashkin, V. K. Fedotov, S. S. Khasanov, T. Hansen, A. S. Ivanov, A. I. Kolesnikov, and I. Natkaniec
Phys. Rev. B **73**, 054107 – Published 21 February 2006

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Neutron scattering study of tantalum dihydride

Mikhail A. Kuzovnikov, Vladimir E. Antonov, Alexandre S. Ivanov, Thomas Hansen, Stanislav Savvin, Valery I. Kulakov, Marek Tkacz, Alexander I. Kolesnikov, and Vladislav M. Gurev
Phys. Rev. B **102**, 024113 – Published 31 July 2020

In situ high pressure studies:

ELSEVIER
Physica B: Condensed Matter
Volume 174, Issues 1–4, October 1991, Pages 117-120

Neutron diffraction study of crystal structure and equation of state AlD_3 up to the pressure of 7.2 GPa

I.N. Goncharenko, V.P. Glazkov, A.V. Irodova, V.A. Somenkov

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Ac

Equation of state of lithium deuteride from neutron diffraction under high pressure

J. M. Besson, G. Weill, G. Hamel, R. J. Nelmes, J. S. Loveday, and S. Hull
Phys. Rev. B **45**, 2613 – Published 1 February 1992

AIP Publishing **Applied Physics Letters**

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Home > Applied Physics Letters > Volume 117, Issue 5 > 10.1063/5.0011646

Full • Submitted: 22 April 2020 • Accepted: 14 July 2020 • Published Online: 06 August 2020

Pressure-induced phase transition in barium hydride studied with neutron scattering

Appl. Phys. Lett. 117, 051902 (2020); https://doi.org/10.1063/5.0011646

E. Novak[1,2,3,a)], B. Haberl[2], L. Daemen[2], J. Molaison[2], T. Egami[1,4,5], and N. Jalarvo[2,3]

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Rapid Communication

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High-pressure structure and electronic properties of YbD_2 to 34 GPa

S. Klotz, M. Casula, K. Komatsu, S. Machida, and T. Hattori
Phys. Rev. B **100**, 020101(R) – Published 10 July 2019

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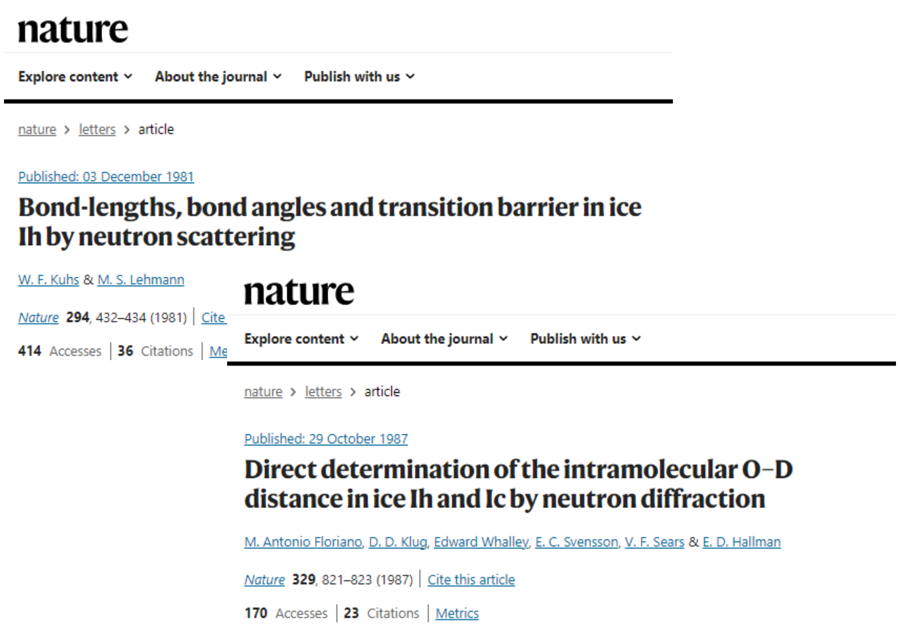
1.1 Planetary sciences: water ice

Neutron diffraction has been critical in understanding hydrogen bonds in various ices and is instrumental in identifying ice phases.



nature

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nature > letters > article

Published: 03 December 1981

Bond-lengths, bond angles and transition barrier in ice Ih by neutron scattering

W. F. Kuhs & M. S. Lehmann

Nature **294**, 432–434 (1981) | Cite

414 Accesses | **36** Citations | Me

nature

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nature > letters > article

Published: 29 October 1987

Direct determination of the intramolecular O–D distance in ice Ih and Ic by neutron diffraction

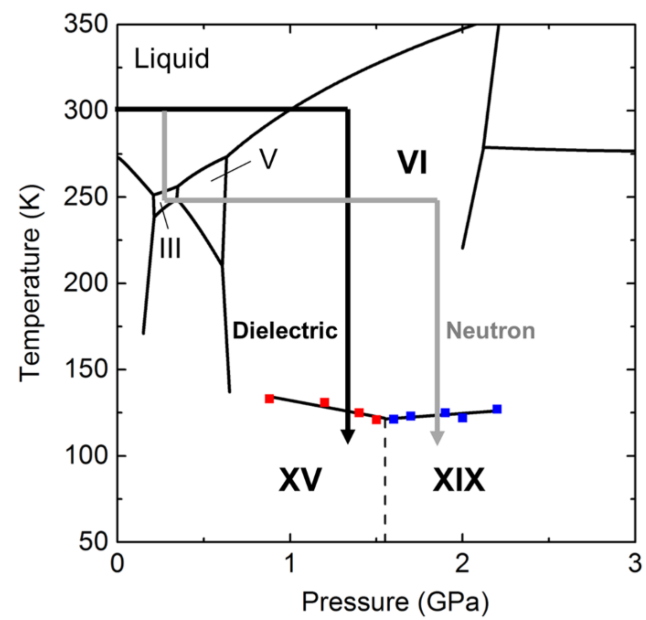
M. Antonio Floriano, D. D. Klug, Edward Whalley, E. C. Svensson, V. F. Sears & E. D. Hallman

Nature **329**, 821–823 (1987) | Cite this article

170 Accesses | **23** Citations | Metrics

Initial reports on the hydrogen bonds in ice at ambient pressure

Phase diagram of ice including the latest findings on the new phases, ice-XV and ice-XIX, taken from [1].



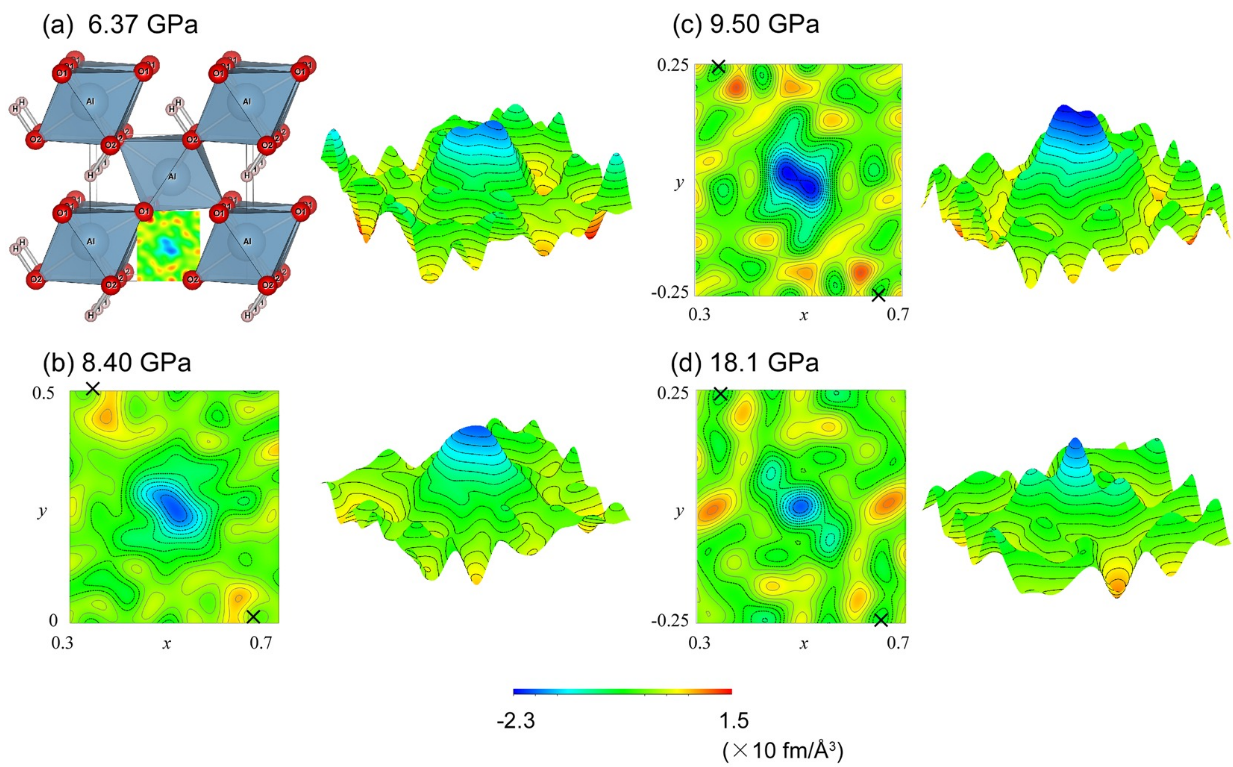
[1] R. Yamane *et al.*, Nature Communications **12**, 1129 (2021).

1.1 Mineral physics: hydrous minerals

Neutron diffraction can aid in the understanding of the pressure response of hydrogen bonds in hydrous minerals.

Diaspore: α-AlOOH [1].

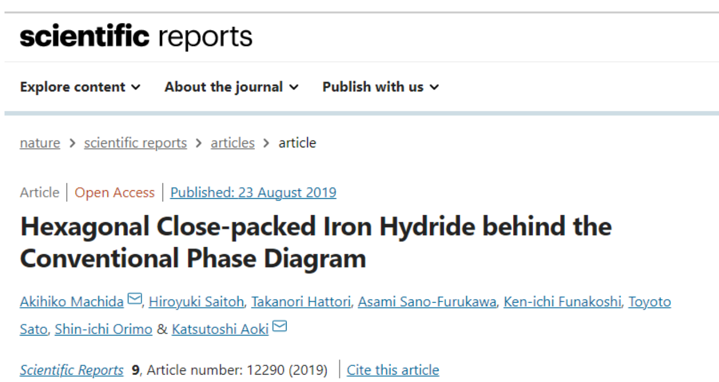
Difference Fourier maps of δ-AlOOH, a high pressure polymorph of diaspore, in sections containing H-bonds. The maps show changes in proton distribution under high pressure. Maps are based on experimental high pressure neutron diffraction data obtained at SNAP and PLANET. Taken from [2].



[1] Diaspore: Wikipedia
[2] A. Sano-Furukawa *et al.*, Scientific Reports **8**, 15520 (2018).

1.1 Mineral physics: metal hydrides

Various metal hydrides can also play a role in earth and planetary processes. For example, the formation iron hydride may explain the low density of Earth's iron core



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Article | Open Access | Published: 23 August 2019

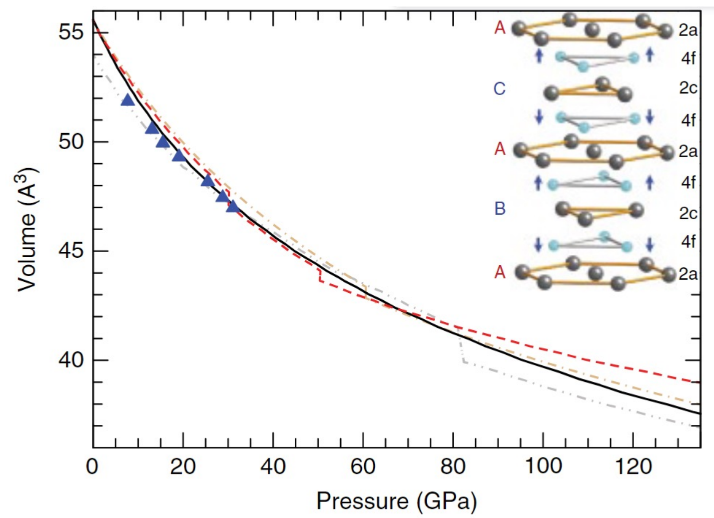
Hexagonal Close-packed Iron Hydride behind the Conventional Phase Diagram

Akihiko Machida, Hiroyuki Saitoh, Takanori Hattori, Asami Sano-Furukawa, Ken-ichi Funakoshi, Toyoto Sato, Shin-ichi Orimo & Katsutoshi Aoki

Scientific Reports **9**, Article number: 12290 (2019) | Cite this article

FeD_x observed by neutron diffraction in a cubic-type multi-anvil press to 7 GPa and 1070 K at PLANET, J-PARC.

Equation of state of FeD_x to 30 GPa measured by neutron diffraction in a DAC on SNAP (blue symbols) taken from [1]



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[1] C.A. Murphy, "*Hydrogen in the Earth's Core*" in "*Deep Earth: Physics and Chemistry of the Lower Mantle and Core*", *pp. 253-264* Wiley (2016).

1.1 High pressure neutron diffraction

While neutron diffraction has already been invaluable for understanding hydrogen bonding in materials and minerals, future works require robust high pressure capabilities.

The neutron diamond cell is a key device:

- It allows very high pressures,
- It is portable,
- It can be coupled with other extreme conditions,
- it is compatible with liquid and gas loading.

1.2 Background on diamond anvil cells

Based on work by Percy Bridgman, the first 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.

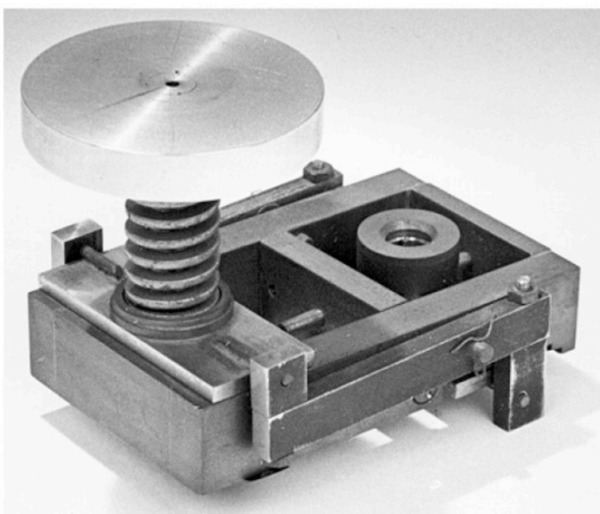


Fig. 1. The original DAC, on display in the NIST Museum.

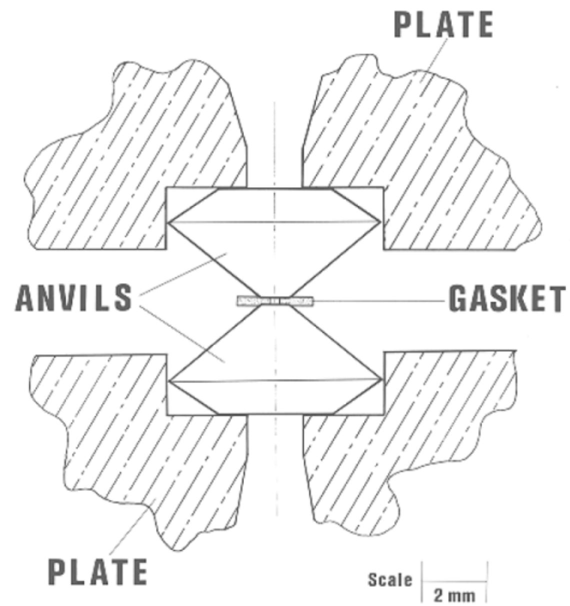
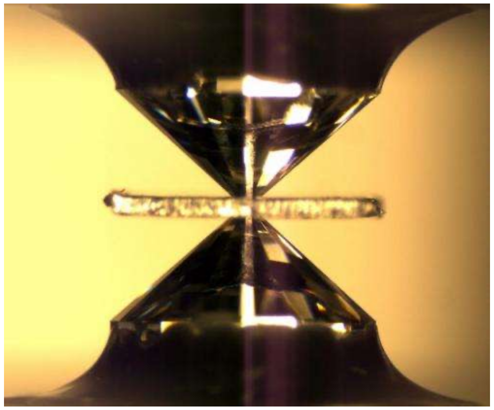
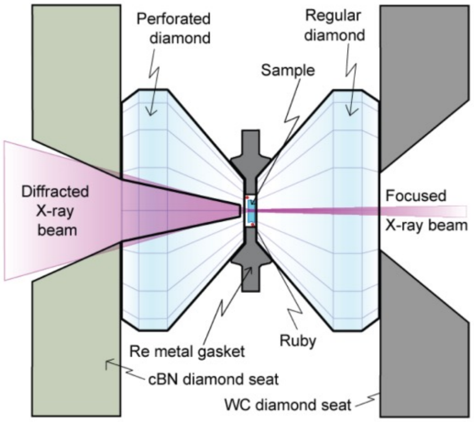


Fig. 4. A schematic diagram of the opposed diamond anvil assembly to illustrate the 180° optical transmission characteristics and the concept of Bridgman opposed anvils. A thin metal gasket containing a 250 μm diameter hole for encapsulating a sample (liquid or solid or both) is squeezed between the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

DAC development at NIST

1.2 Diamond cells for X-ray scattering



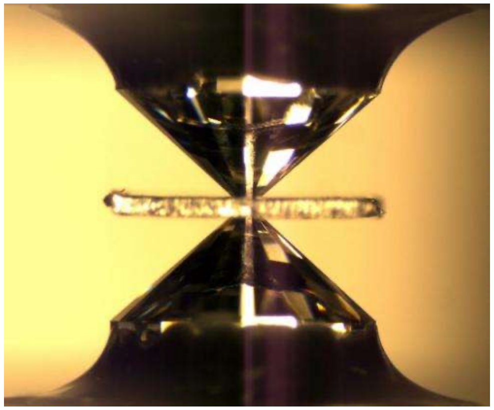


from Phys.org by Stas Sinogeikin (HCPAT, DACTools)

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.

1.2 Diamond cells for X-ray scattering



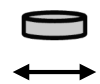
from Phys.org

- 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 ~5 K to ~5000 K can be additionally applied during *in situ* studies.
- 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.

1.2 Diamond cells for X-ray scattering

Standard DAC:

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



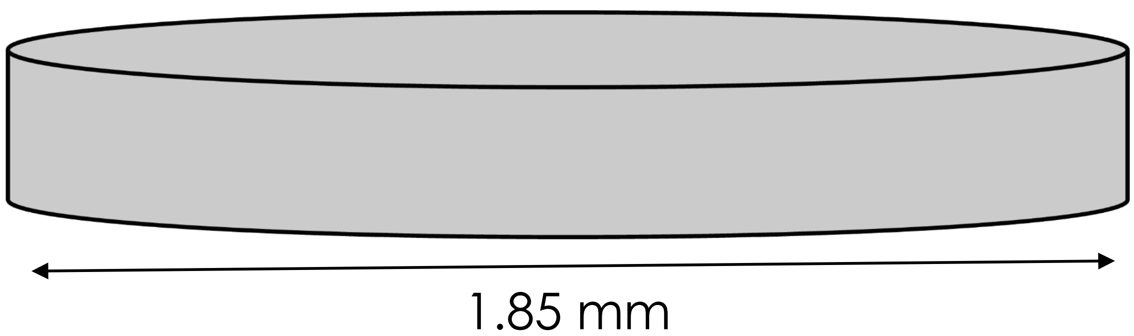
100 µm

- For a diamond with 200 µm culet diameter, the volume of the sample chamber is 0.0003 mm^3.
- Sample volumes are sufficient for most applications at synchrotrons or for Raman spectroscopy, transport measurements etc.

1.2 High pressure neutron scattering

BUT:

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



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

1.2 High pressure neutron scattering

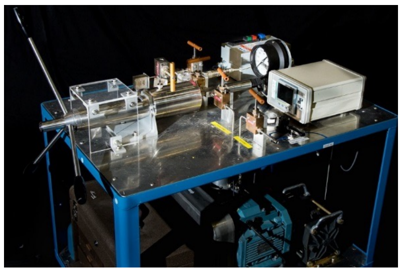
Fundamental challenge in high pressure neutron scattering:

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

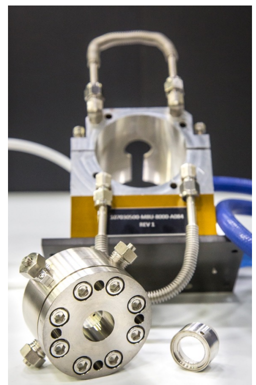
- To accommodate the necessary large sample volumes, a variety pressure cells exist for neutron scattering.
- These are often optimized for specific science questions and/or neutron scattering techniques.

1.2 Pressure cells for 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

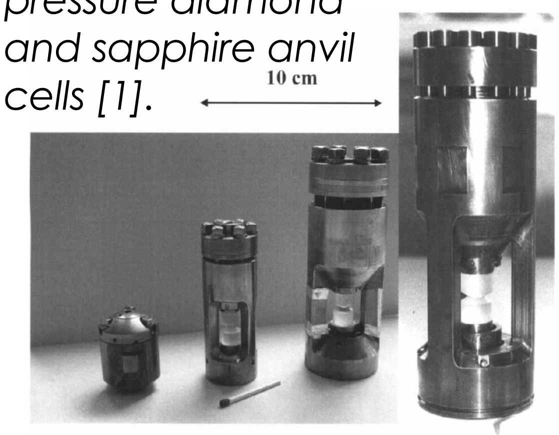
Paris-Edinburgh cells for up to 20 GPa

Uwatoko palm-cubic cell for up 7 GPa

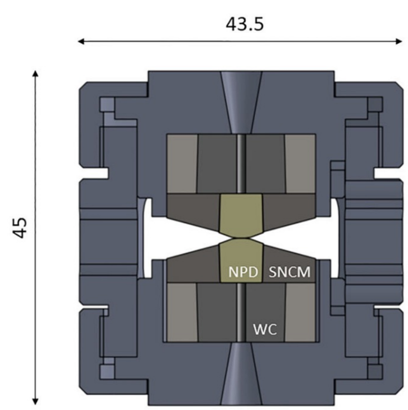
1.2 Neutron diamond anvil cells

The highest pressures, also for neutron scattering, are enabled by diamond anvil cells. Several projects world-wide aim to develop and optimize high pressure neutron DACs.

Kurchatov-LBB high pressure diamond and sapphire anvil cells [1].



DACs for single crystal neutron diffraction developed at Juelich [3]



DAC developed at J-PARC for use with nano-polycrystalline anvils [2].

[1] I.N. Goncharenko, High Pressure Research 24, 193 (2004).
[2] K. Komatsu et al., High Pressure Research 40, 184 (2020).
[3] "High-pressure with neutrons at the MLZ": weblink

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2. The diamond anvil cell project at SNAP

2. The diamond anvil cell project at SNAP

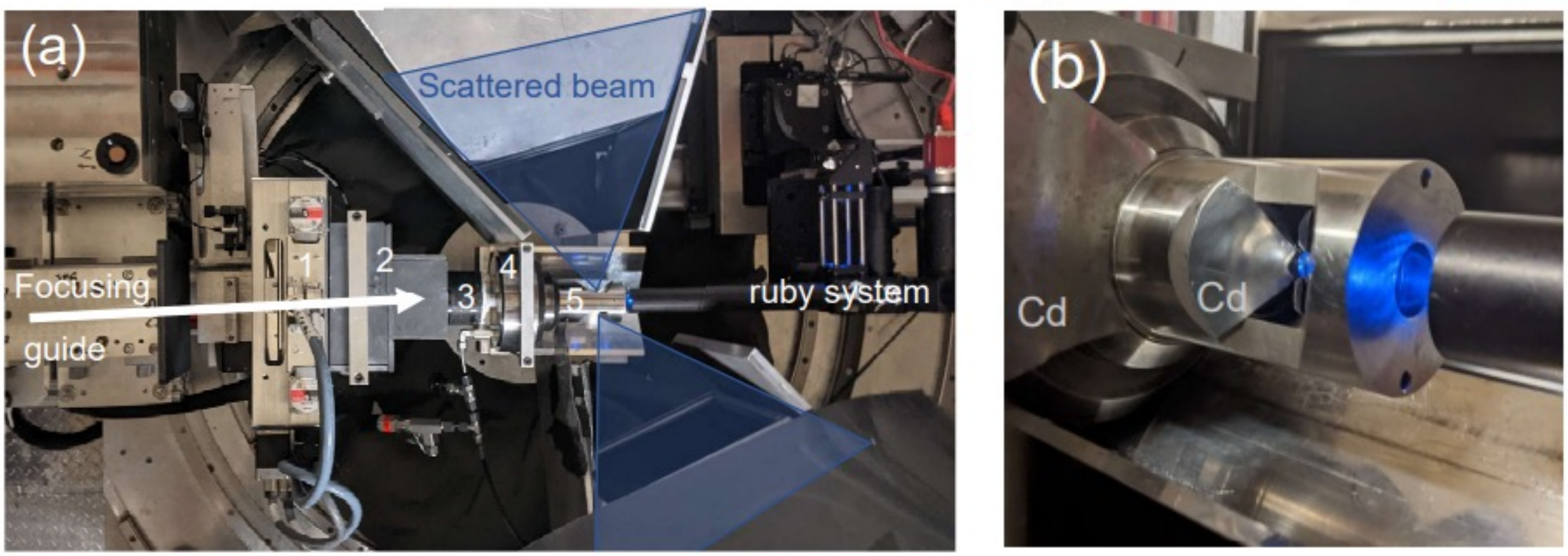
Neutron diffraction at megabar pressures requires:

- A neutron diffractometer optimized for high pressure applications.
- The necessary tools for analytical data analysis.
- A diamond anvil cell capable of achieving megabar pressures on sufficiently large sample volumes.

2.1 High pressure neutron diffractometer

The Spallation Neutrons and Pressure (SNAP) diffractometer is the dedicated high pressure time-of-flight white beam diffractometer at ORNL's SNS [1,2].

It is a high flux, moderate resolution instrument with a (for neutrons) very small beam (hotspot of ~2 mm).



Neutron diamond anvil cell on SNAP [3]

[1] https://neutrons.ornl.gov/snap
[2] S. Calder et al., RSI **89**, 092701 (2018).
[3] B. Haberl et al., JAP **130**, 215901 (2021).

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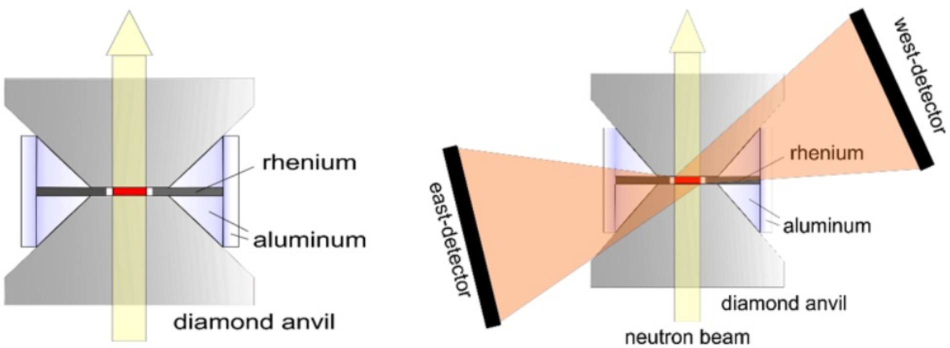
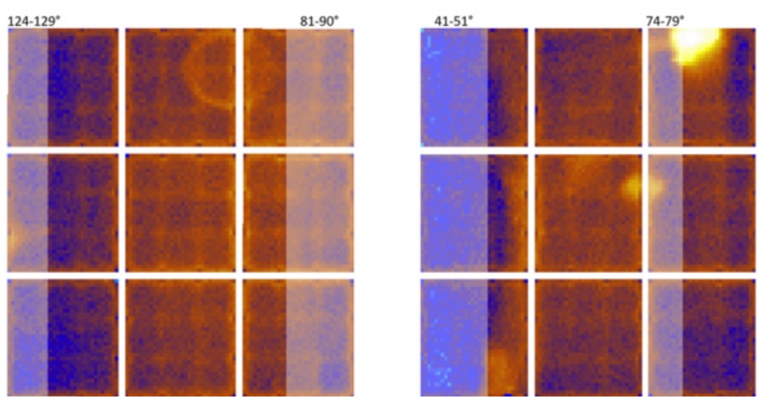
2.1 High pressure neutron diffractometer

TOF white-beam diffraction enables energy discrimination combined with an area detector. There, a full diffraction pattern can be extracted from neutrons scattered into even a small solid angle.





Set-up at SNAP [1]

Detector characteristics at SNAP [2]

Detector column	Average 2θ (deg.)	Minimum d-spacing (Å) for Rietveld	Maximum d-spacing (Å) for Rietveld	Resolution δd/d[a] (%)
1	121.79	0.65	2.13	0.69
2	104.33	0.65	2.32	0.85
3	88.30	0.67	2.63	1.09
4	83.49	0.67	2.85	1.13
5	65.77	0.68	3.60	1.49
6	50.00	0.94	4.90	1.90

[a]Note, for TOF diffraction δd/d is approximately constant in d-spacing.

[1] R. Boehler *et al.*, in "*Static and Dynamic High Pressure Mineral Physics*", Cambridge University Press (2022).
[2] B. Haberl *et al.*, JAP **130**, 215901 (2021).

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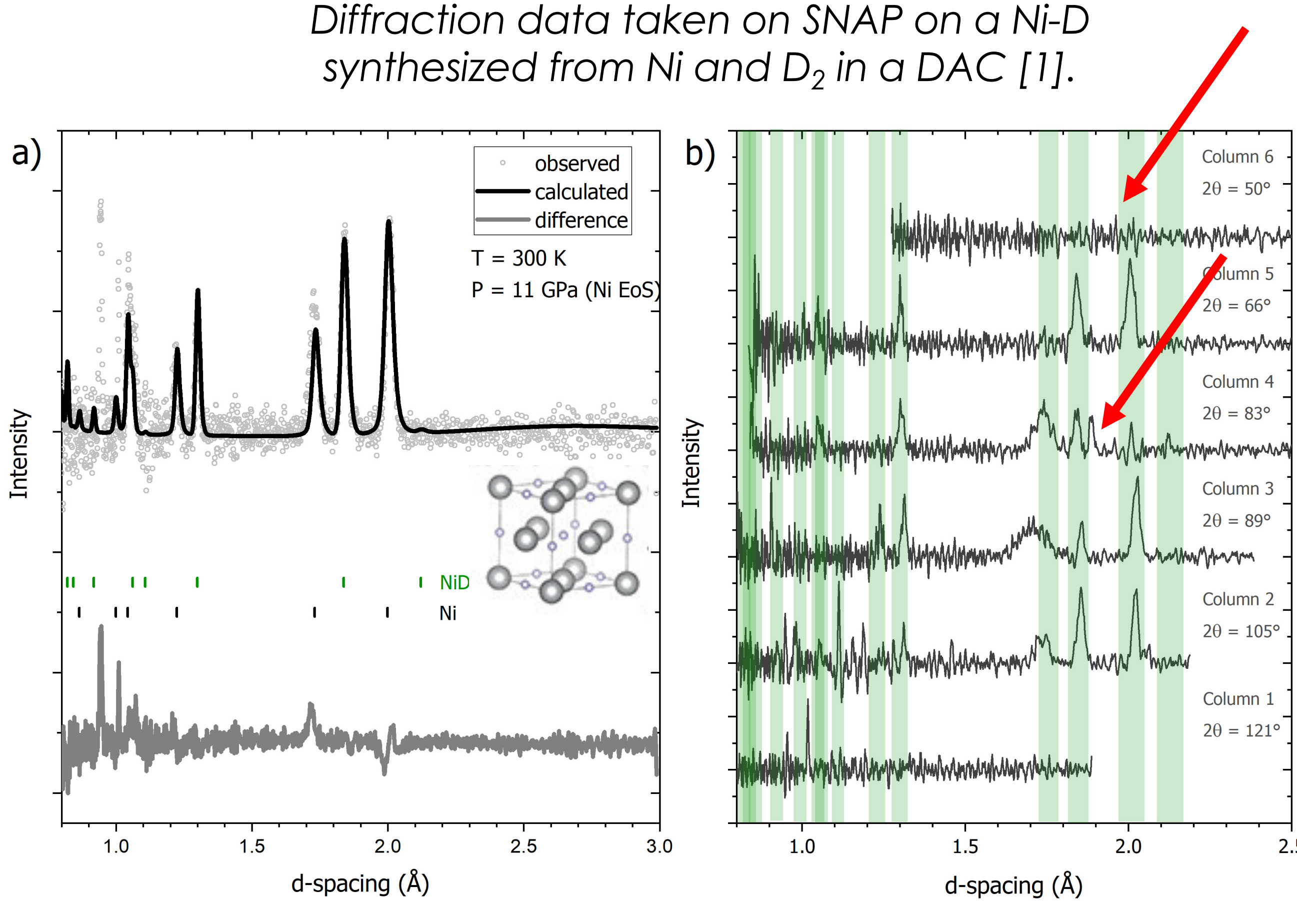
2.1 TOF white-beam neutron diffraction

The angular resolution on SNAP can be used to better assess (and eliminate) backgrounds as well as of powder quality on samples pressurized in a DAC.

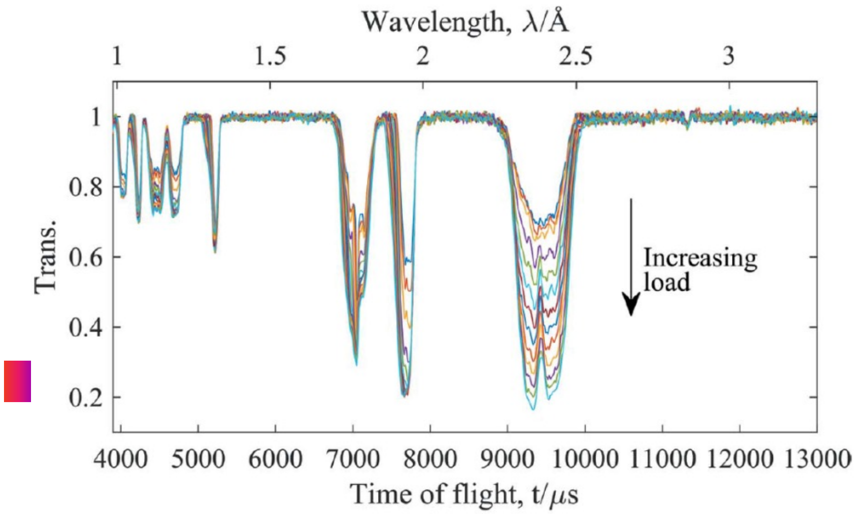
Diffraction data taken on SNAP on a Ni-D synthesized from Ni and D_2 in a DAC [1].

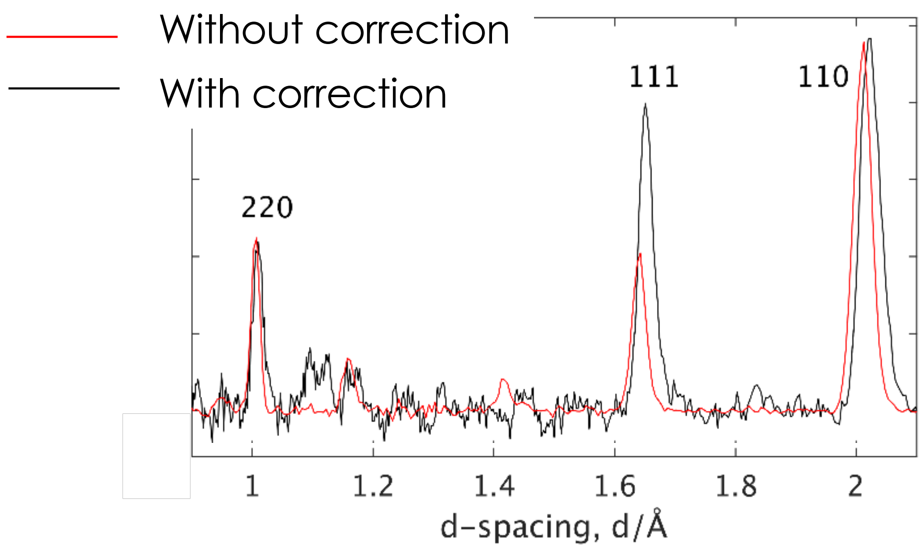


[1] B. Haberl *et al.*, JAP **130**, 215901 (2021).

2.1 Attenuation corrections

Significant attenuation due to Bragg scattering, which increases with pressure [1].





Effect on ice is considerable [2].

- 111 reflection strongly affected.
- Most sensitive to D position.

Corrections and angular analysis will be routinely implemented.

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[1] Guthrie M., *et al.,* J. App. Cryst. **50**, 76-86 (2017). [2] M. Guthrie *et al.*, PRB **99**, 184112 (2019).

2.2 Neutron diamond anvil cells

Panoramic diamond cell inside a membrane press. The sample volume was ~0.05 mm³ [1].

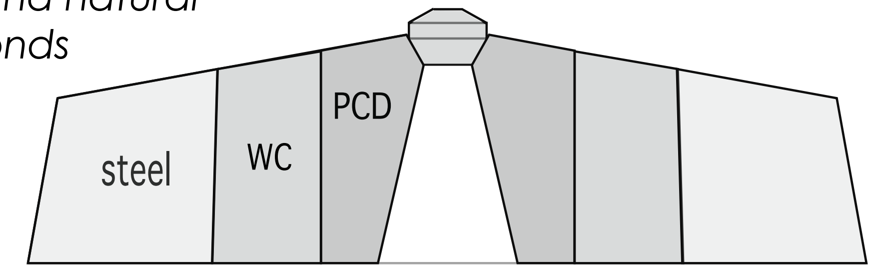
First generation diamond anvil cell developed on SNAP:

- Maximum pressures of almost 100 GPa were achieved.
- Single crystal diamond anvils allow removal of diamond peaks.
- Membrane press enabled online pressure increase.
- Gasket made from stainless steel.
- Limited Q-range due to need for elaborate binding rings.

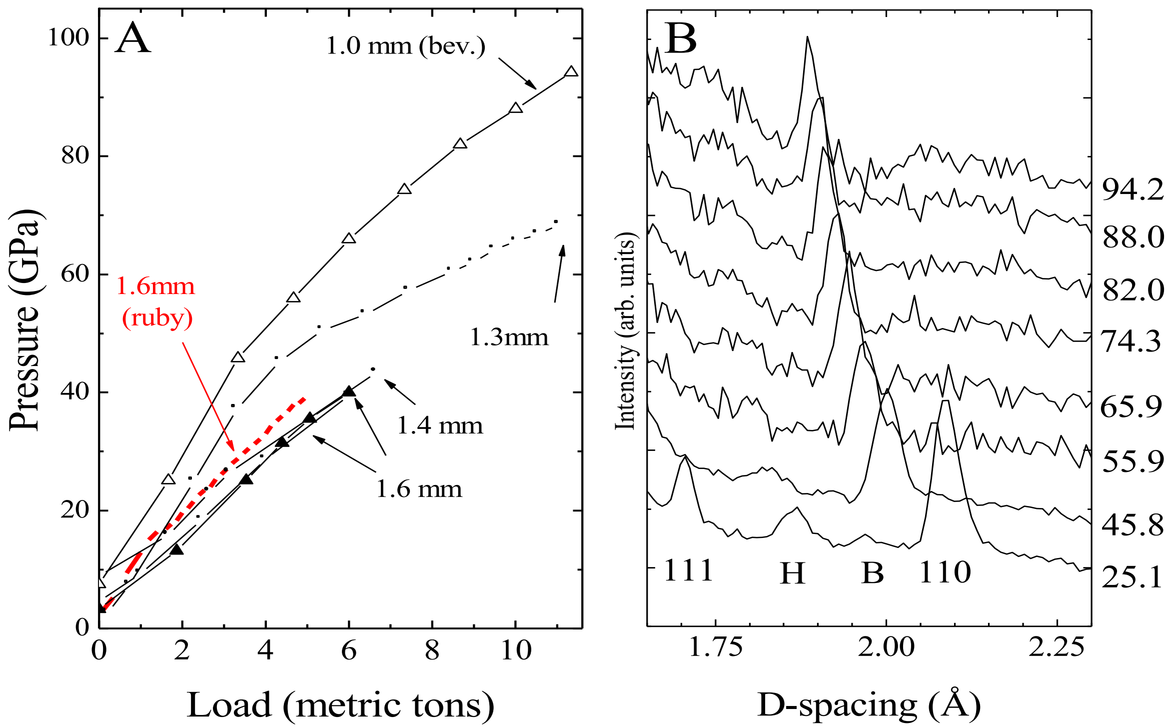
[1] R. Boehler, M. Guthrie *et al*. High Pres. Res. **33**, 546 (2013).

2.2 Neutron diamond anvil cells

Seat and natural diamonds used.



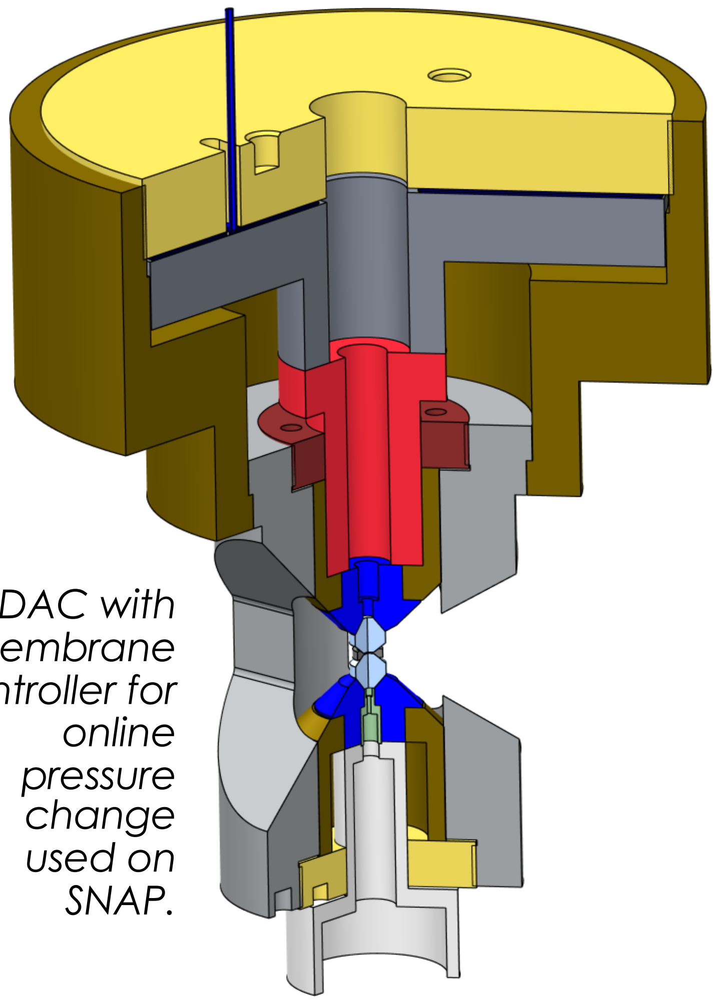
one anvil + seat:
$ 4500



Neutron diffraction up to 94 GPa on ice. Sample volume at highest pressure was ~0.015 mm³.

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

2.2 Neutron diamond anvil cells



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.

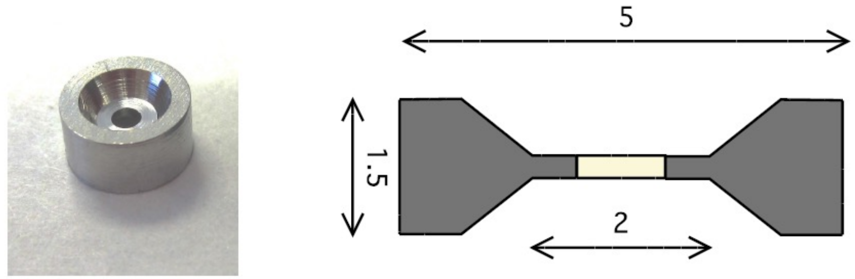
[1] R. Boehler, J.J. Molaison, B. Haberl, Rev. Sci. Instr. **88**, 83905 (2017).

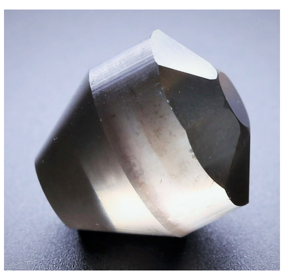
2.2 Neutron diamond anvil cells

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

6 mm conical CVD anvils inside steel seats.

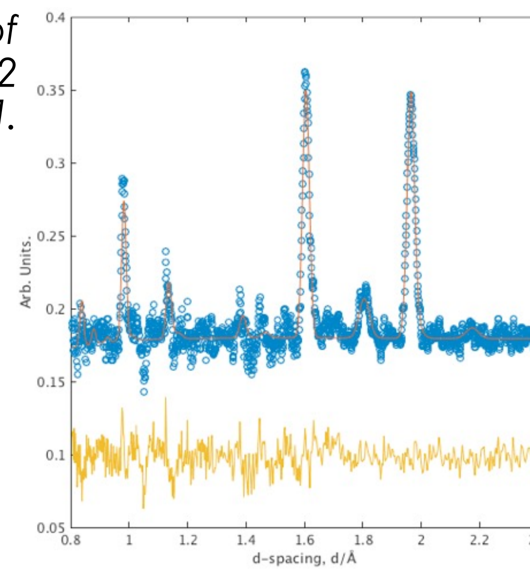
Machined stainless steel gasket





Conical anvil design.

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

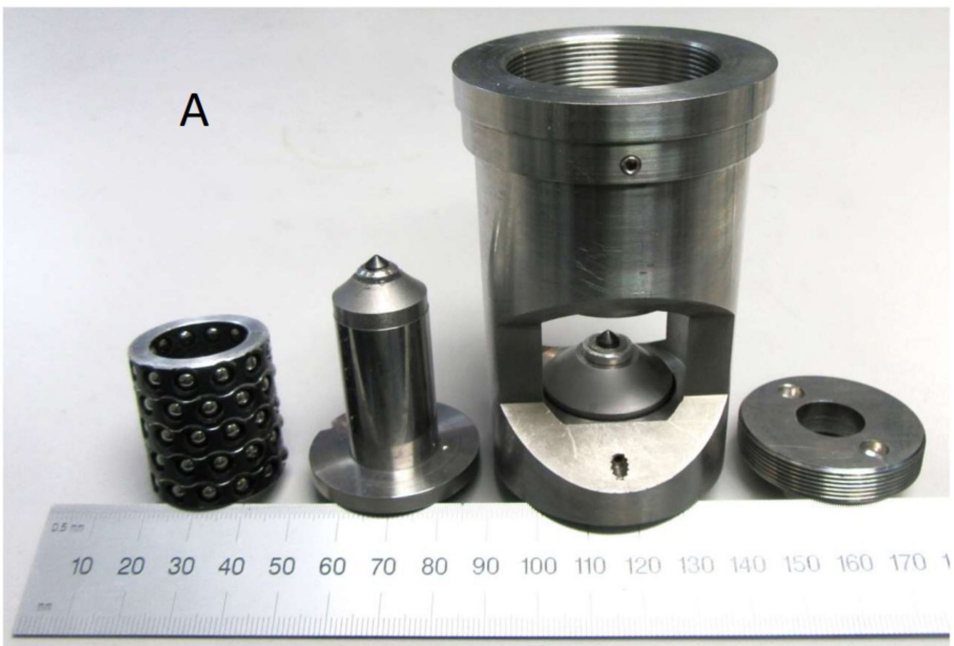


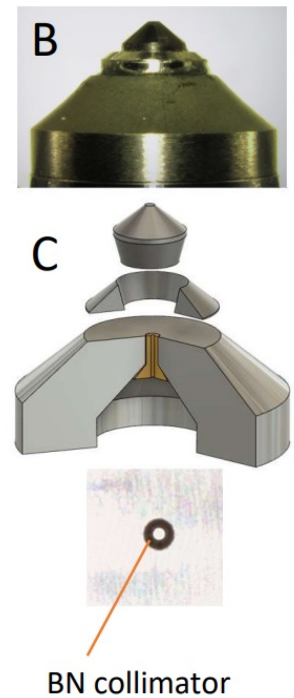
[1] R. Boehler, J.J. Molaison, B. Haberl, Rev. Sci. Instr. **88**, 83905 (2017).
[2] M. Guthrie *et al.*, PRB **99**, 184112 (2019).

2.2 Megabar neutron DACs

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

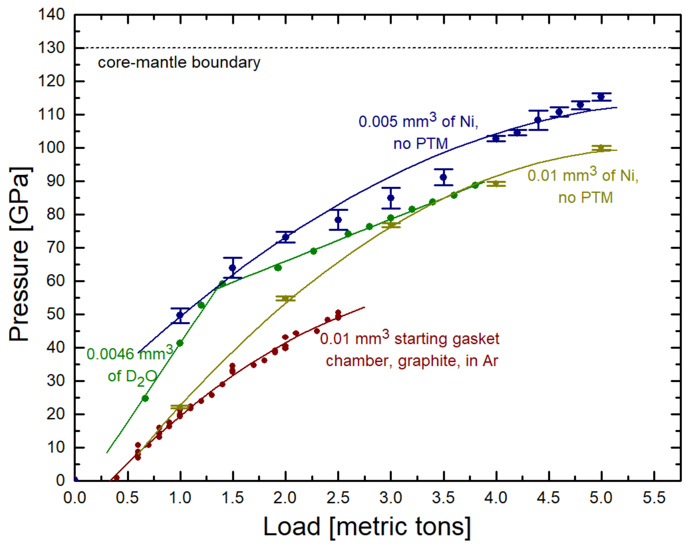
New cell design using roller bearings for ultra-high precision, flat radially supported anvils and in-seat collimation [1]





[1] B. Haberl, M. Guthrie, R. Boehler, Sci. Reports **13**, 4741 (2023).

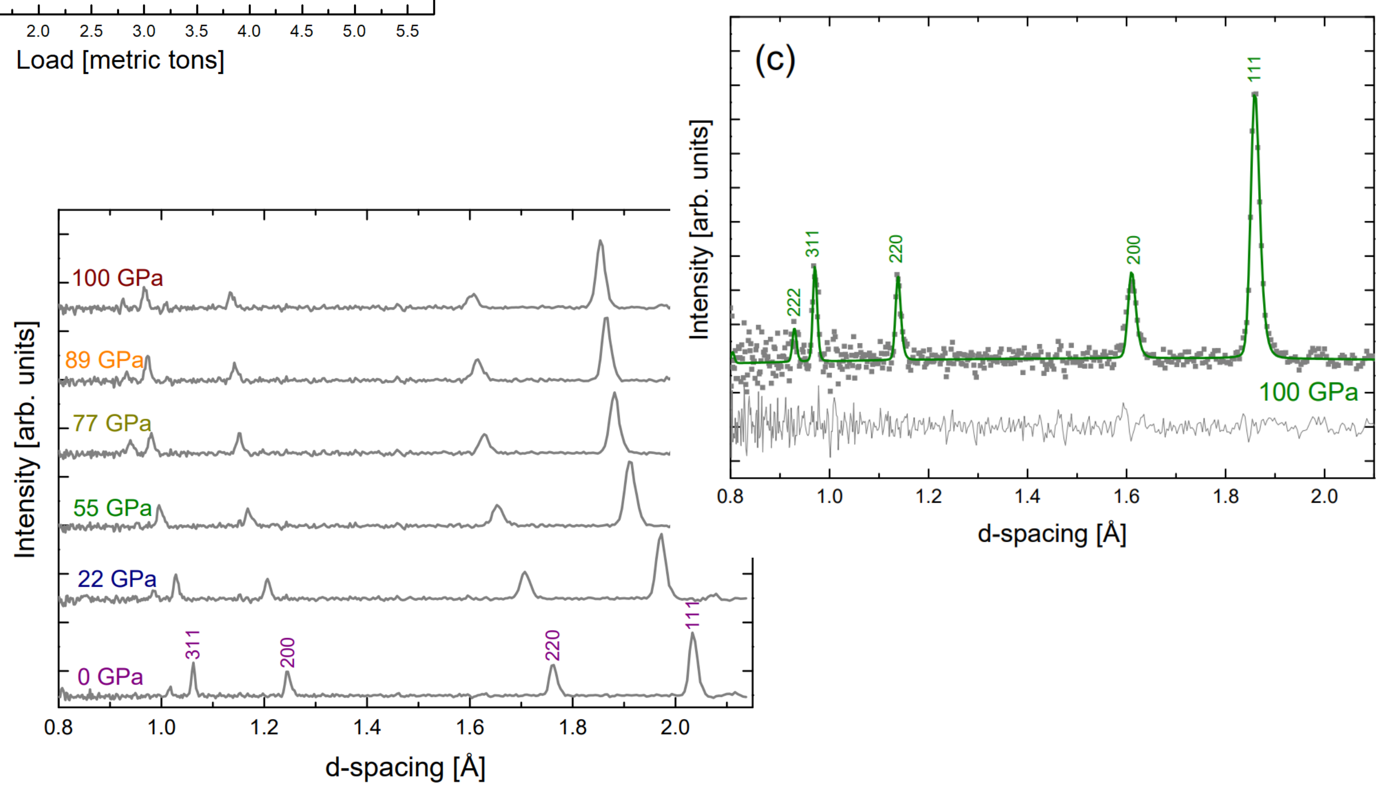
2.2 Megabar neutron DACs



A record pressure of 115 GPa was reached for Ni using 600 µm culets [1]

Preparing a cell at SNAP

100 GPa were reached for Ni using 800 µm culets while maintain data quality sufficient for full Rietveld [1]



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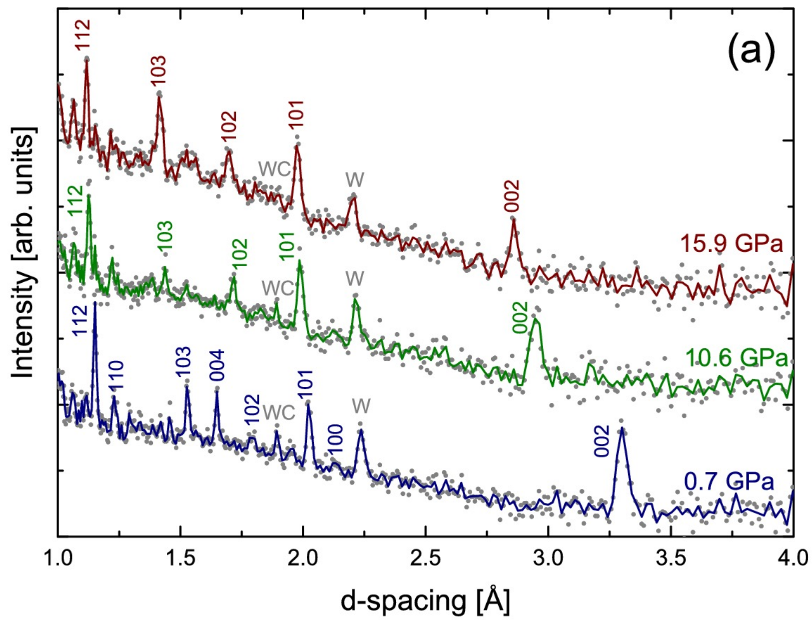
[1] B. Haberl, M. Guthrie, R. Boehler, Sci. Reports **13**, 4741 (2023).

2.3 Phase behavior of graphite

The phase behavior of graphite upon room temperature compression is complex and the nature of the high-pressure graphite polymorph is not yet fully known. High pressure neutron diffraction can yield new insights.



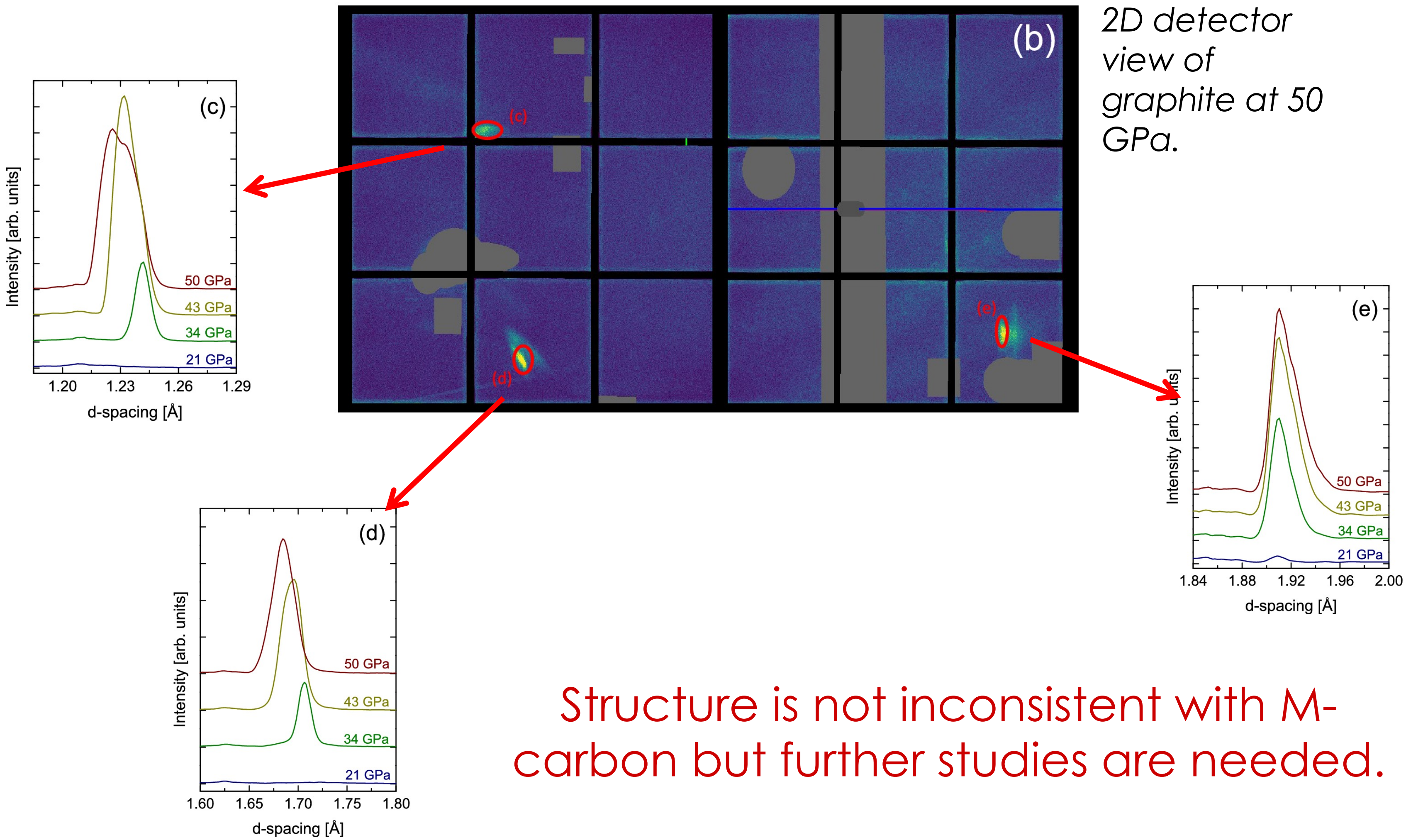
Room temperature compression of graphite loaded with Ar as pressure transmitting medium into a megabar DAC on SNAP [2]

On further pressure increase to ~21 GPa the hexagonal graphite structure dissolved over time.

[1] Graphite, Wikipedia
[2] B. Haberl, M. Guthrie, R. Boehler, Sci. Reports **13**, 4741 (2023).

2.3 Phase behavior of graphite

Pressure increase to 34 GPa and above yielded the nucleation of diffuse single crystal like features.



2D detector view of graphite at 50 GPa.

Structure is not inconsistent with M-carbon but further studies are needed.

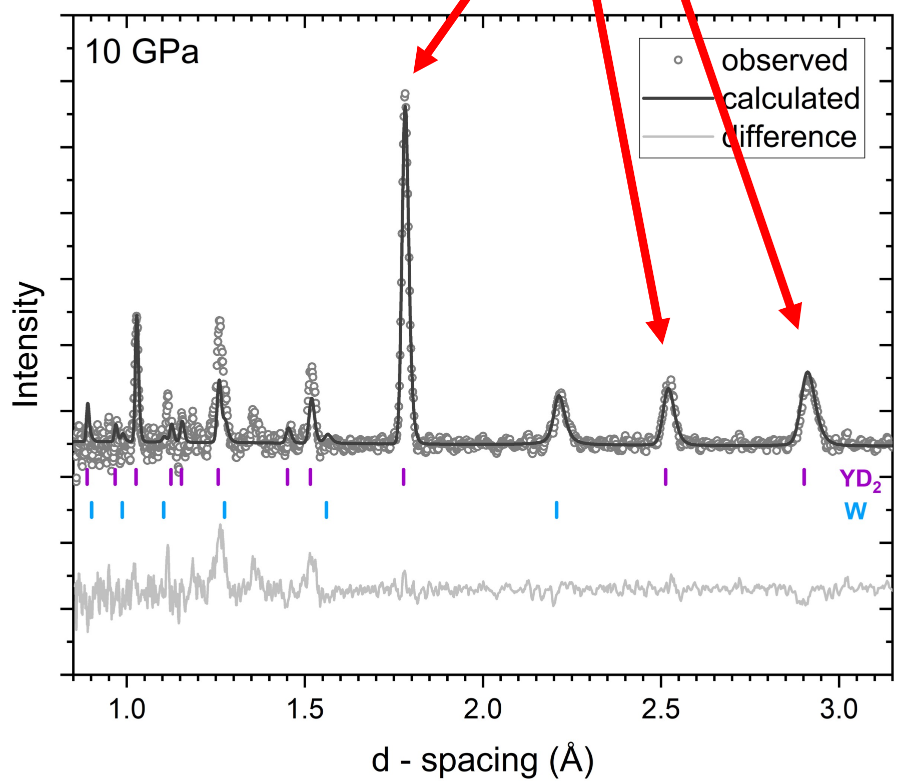
[1] B. Haberl, M. Guthrie, R. Boehler, Sci. Reports **13**, 4741 (2023).

2.3 Yttrium hydride – YD_2

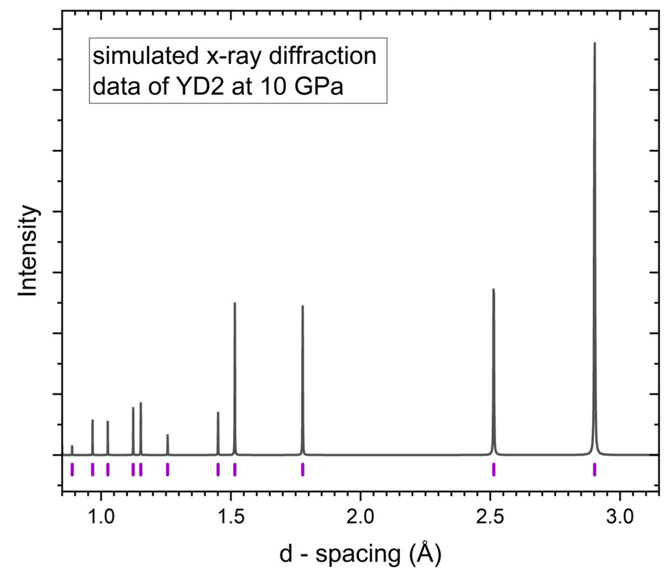
YD_2 was synthesized from a Y foil and D_2 at elevated temperature. It was compressed to 30 GPa under hydrostatic conditions and to 70 GPa under non-hydrostatic conditions.

Relative intensities yield D occupancy

YD_2 loaded with Ar as PTM

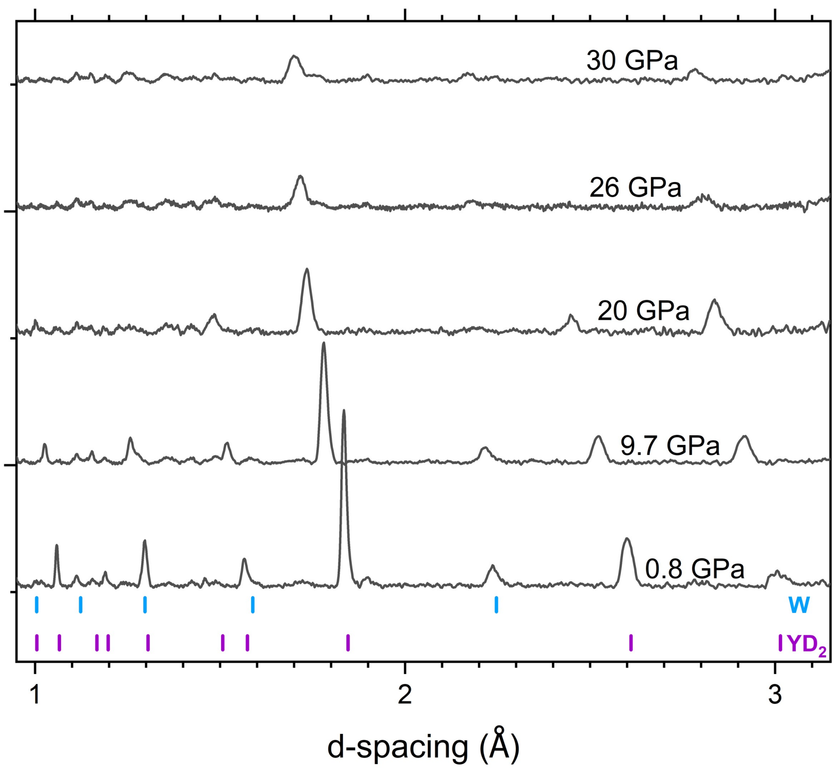


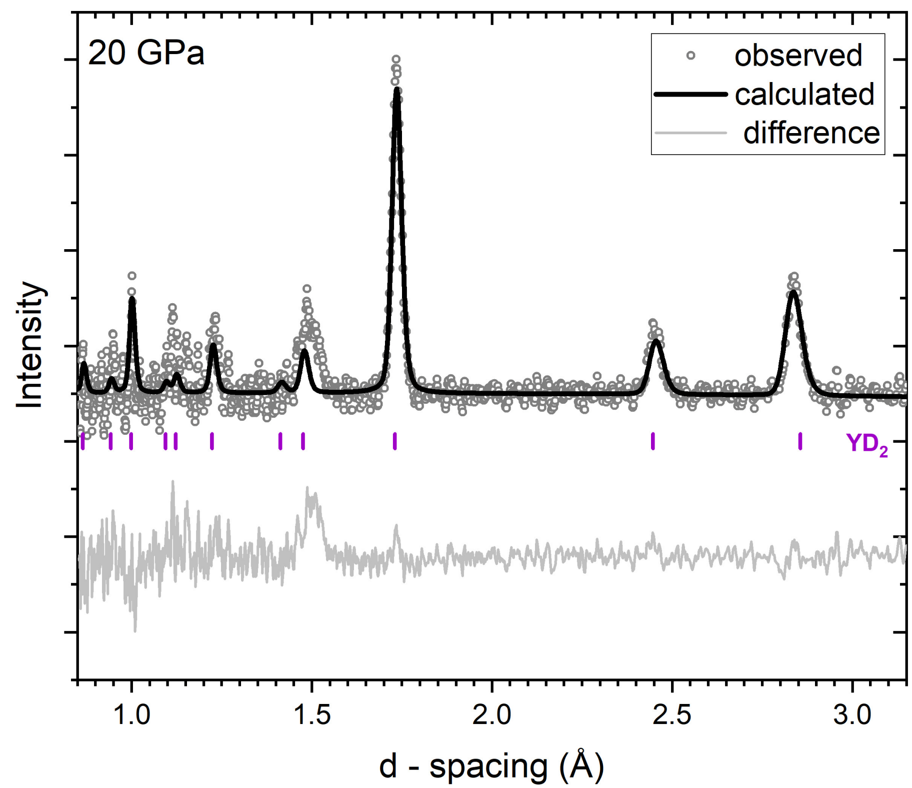
Simulated XRD pattern of YD_2 at 10 GPa – a cubic metal lattice without insight into relative intensities needed for occupancies.



2.3 Yttrium hydride – YD_2

Up to at least 20 GPa, all YD_2 data can be refined with the YD_2 structure (*Fm-3m*) and a D occupancy of ~1.8.



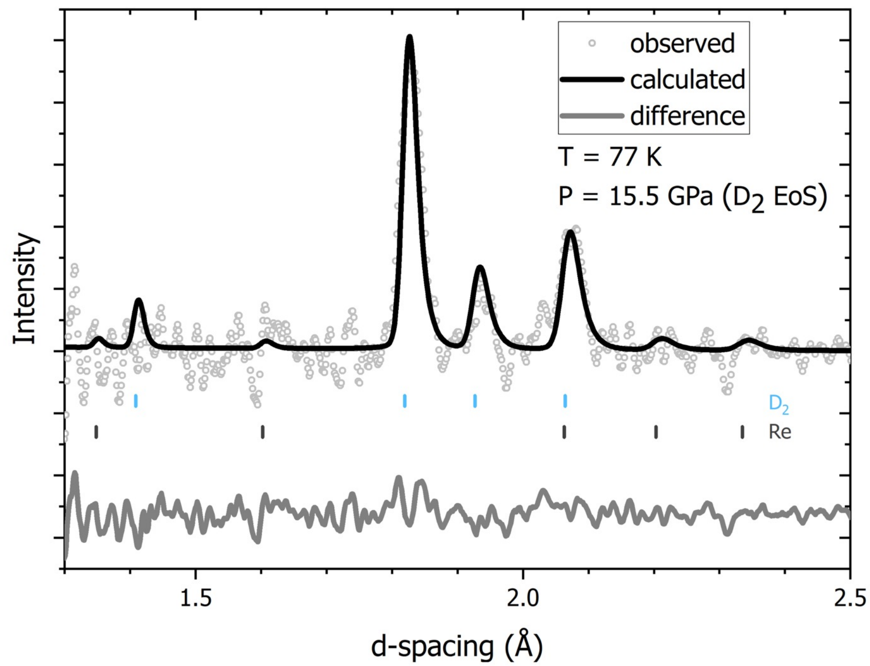


Neutron diffraction allows direct observation of deuterium related positions and stoichiometry.

2.3 Megabar neutron diffraction on hydrides

Beyond improvements to beamlines and development of megabar DACs, enabling work with hydrogen is critical.

D_2 loaded with amorphous Si flakes to create good-quality powder [1]



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

Large culets combined with hydrogen pose a particular issue and much effort is dedicated to diamond polishing and technology.

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

3. Future directions at SNAP and beyond

High pressure single crystal diffraction

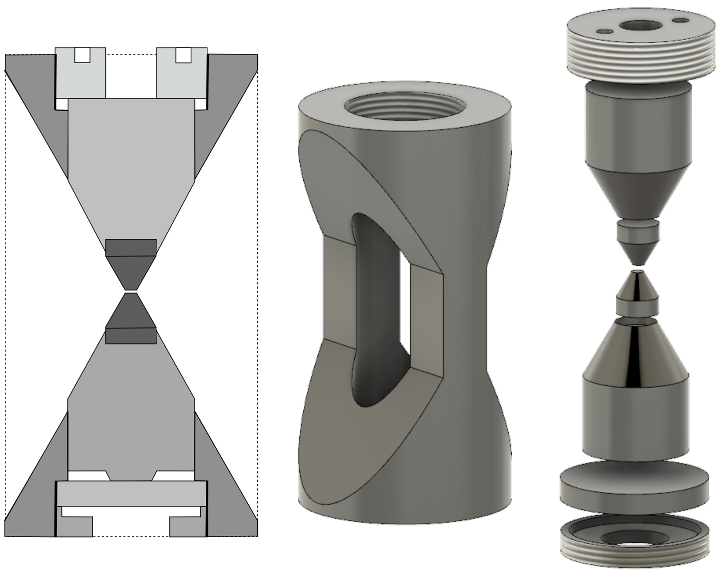
Technical advances at SNAP and diffractometers beyond.

3.1 High pressure single crystal diffraction

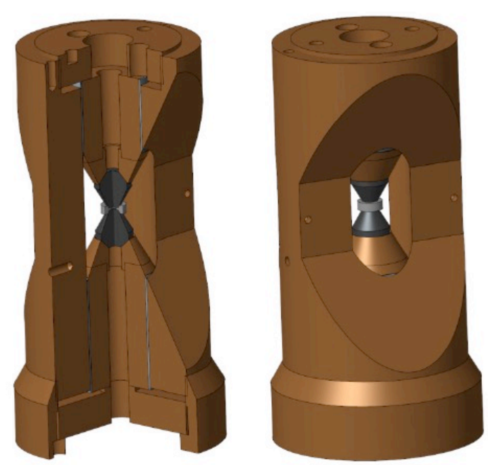
Clamped diamond anvil cell with Versimax® anvils:

- 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]

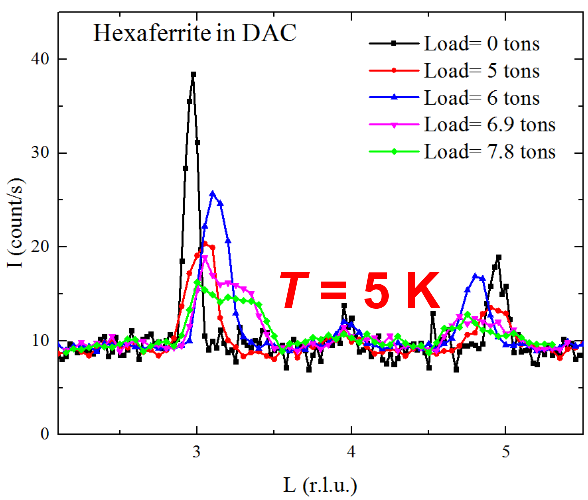
[1] B. Haberl *et al.*, High Pressure Research **37**, 495 (2017).
[2] B. Haberl *et al.*, Rev. Sci. Instr. **89**, 092902 (2018).

3.1 High pressure single crystal diffraction

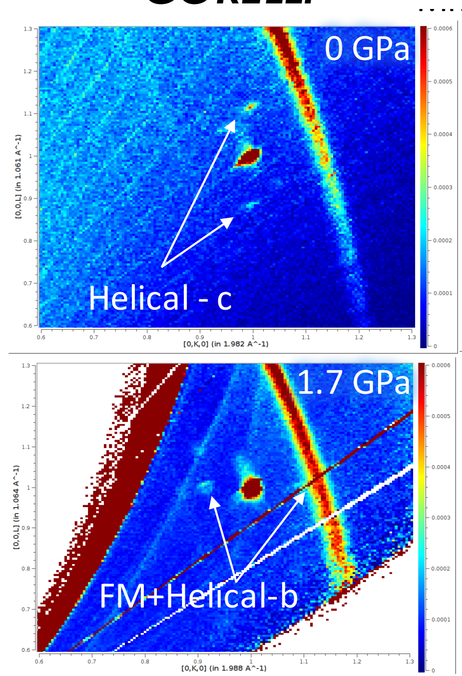
Single crystal diffraction to ~10 GPa is often used in studies focused on quantum materials. They typically focus on the observation of order parameters.

HB-3A

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

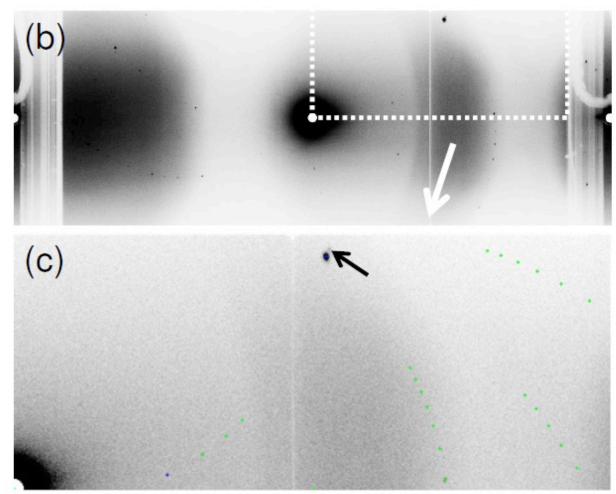


CORELLI



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

IMAGINE



~0.1 mm^3 crystal of hexaferrite 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.*, Rev. Sci. Instr. **89**, 092902 (2018).

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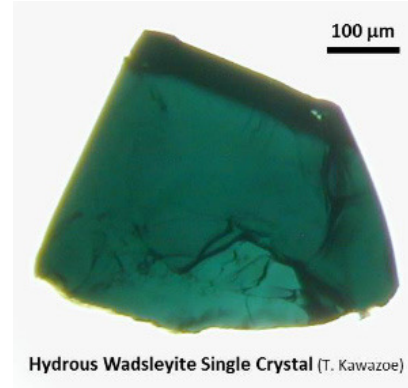
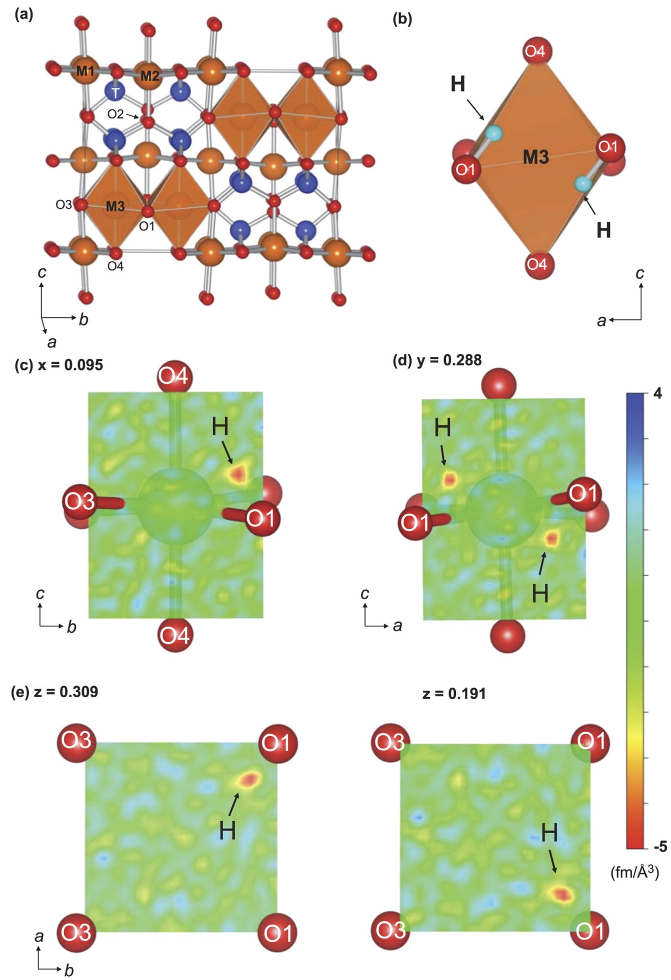
3.1 High pressure single crystal diffraction

Studies in geosciences are typically focused on quantitative analysis, for example of hydrogen sites and occupancy on hydrous minerals.



High-pressure polymorph of olivine: β-$(Mg,Fe)_2SiO_4$



Framework of wadsleyite crystal structure and difference Fourier maps observed by single crystal neutron diffraction at ambient pressure performed at ORNL's TOPAZ beamline. Taken from [2].

[1] Hydrous Wadsleyite: T. Kawazoe
[2] N. Purevjav *et al.*, Scientific Reports **6**, 34988 (2016).

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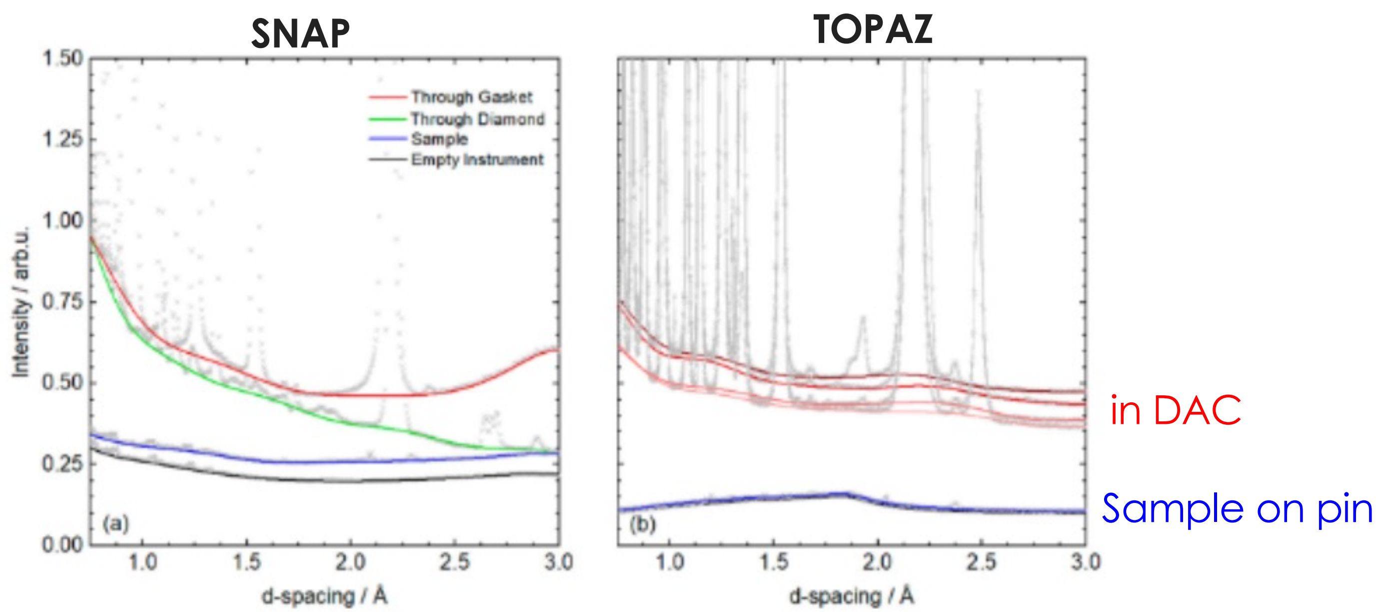
3.1 High pressure single crystal diffraction

SNAP and TOPAZ are equipped with the same type detectors, in principle quantitative single crystal diffraction can be deployed on SNAP. A proof-of-principle study [1] has explored this possibility.

Background comparison

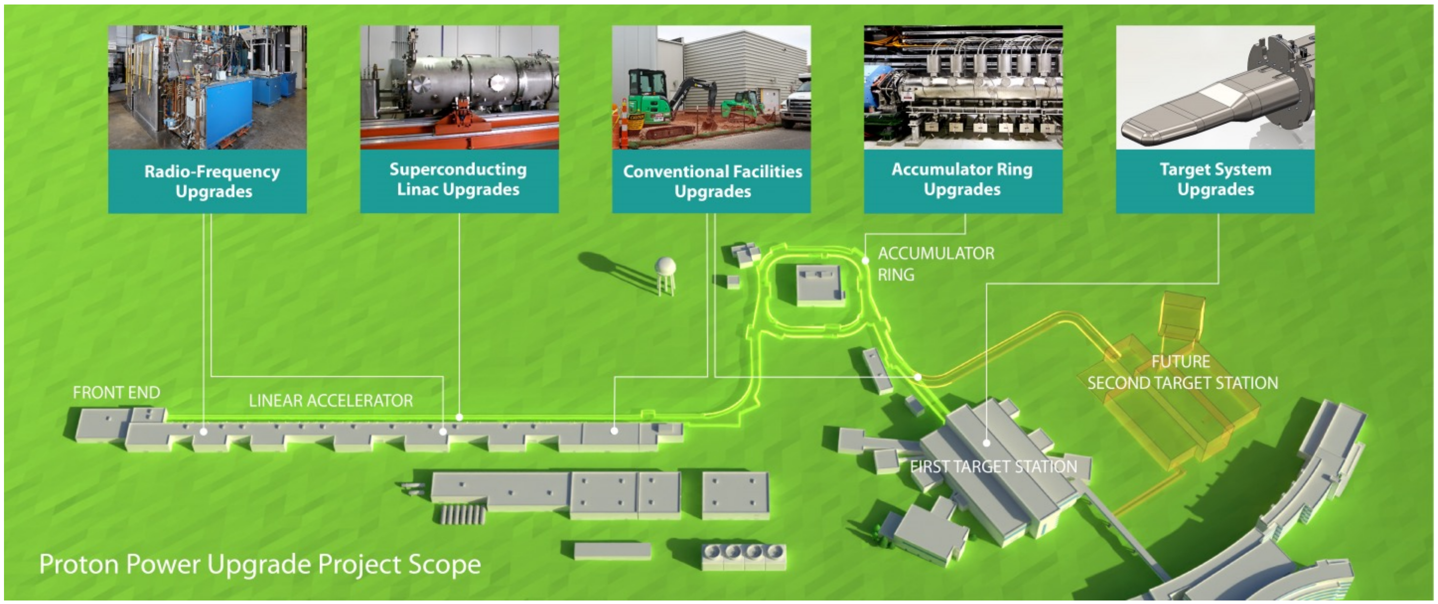


"…SNAP as it is setup presents some limitations but in principle similar data quality as on TOPAZ can be achieved and as such can yield accurate structural data." [1]

[1] B. Massani *et al.*, HPR **40**, 339 (2020).

3.2 SNS Proton Power Upgrade Project

The PPU will provide up to 40% more power the SNS and will be critical for the future Second Target Station (STS).

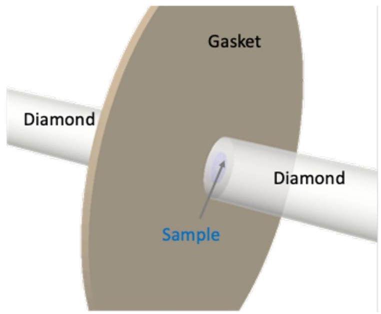


- More power will translate into the capabilities for smaller samples and hence higher pressures.
- More power will also translate into faster acquisition with a full spectrum becoming feasible within just one pulse.

Source: ORNL's PPU Project

3.2 New instrument concepts

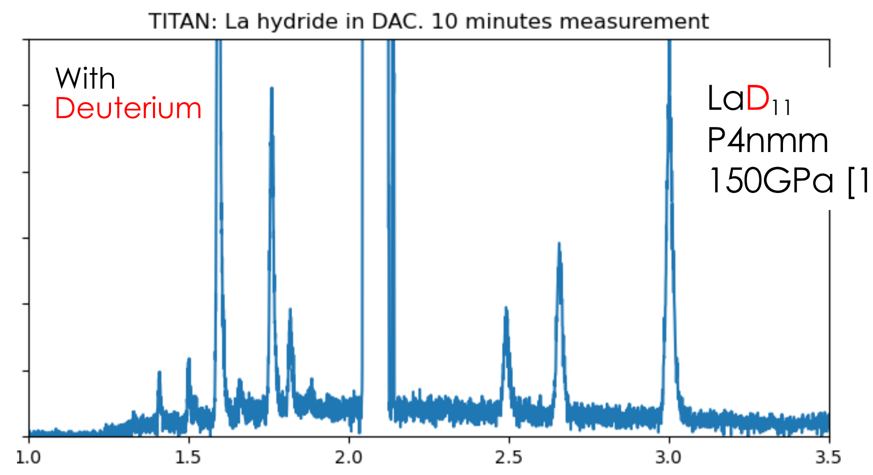
New instrument concepts and new sources provide even smaller focus spots for higher flux. An example is the TITAN concept proposed for ORNL's Second Target Station.



Simplified DAC model uses illuminated sample, part of gasket and part of diamond only

(sample vol. ~0.004 mm^3, 120 GPa)

La hydride in DAC: 10 min. measurement



[1] A.P. Drozdov et al, Nature 569, 528–531 (2019).

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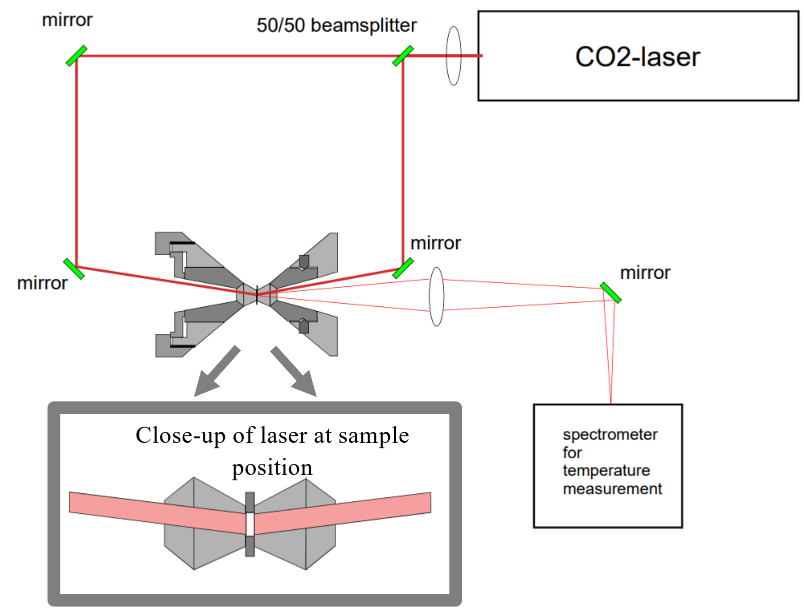
Source: Jiao Lin, Barry Winn, Garrett Granroth, et al. (ORNL)

3.2 Multi-extreme conditions

Addressing future science questions requires multi-extreme conditions, which necessitates the development of new extreme environments. Such new concepts include the laser-heated DAC [1].

Schematic set-up for laser-heating of a neutron DAC:
The laser beam of the CO_2 laser is split to facilitate double-sided heating on the sample position.

Close-up of the laser assembly at the sample position shows the use of a defocused beam that heats the entire sample volume contained between anvils and gasket.



[1] B. Haberl, *et al.* Review of Scientific Instruments **93**, 083907 (2022).

Conclusions

- Neutron diffraction can make an immensely useful contribution to research on hydrogen containing materials and minerals. Continuous development aim at higher pressures, better analytical tools, shorter collection times and the coupling of extremes
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2022 NXS Cohort

Acknowledgment: This work was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory managed by UT-Battelle, LLC, for the U.S. Department of Energy. This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

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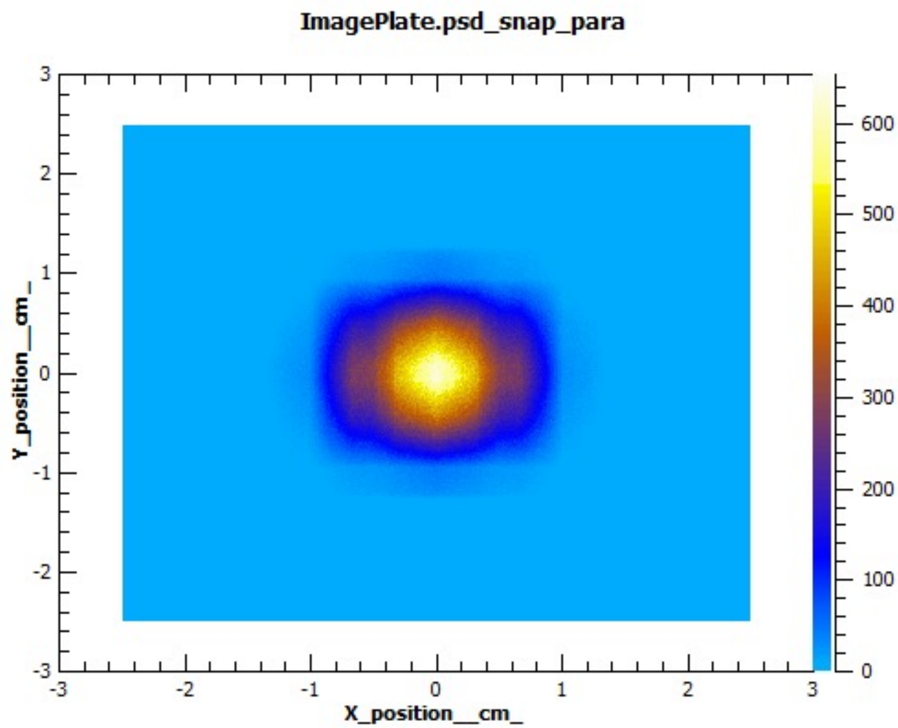
Appendix – Additional slides

A.1 High pressure neutron diffractometer

Unlike X-rays neutrons are not easily guided by optics. Yet improved guide technology now allows for smaller focal spots.



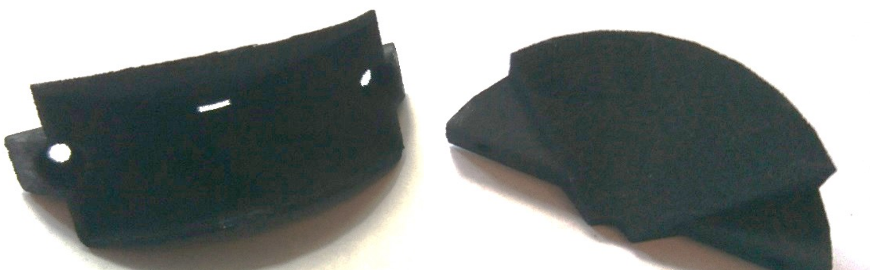
New logarithmic guide for SNAP: An overall beam spot of 20 x 20 mm allows for a ~2 x 2 mm hotspot

Source: Thomas Huegle

A.2 Incident and scattered beam collimation

Custom collimation is increasingly important for DAC and other pressure experiments, an application for which 3D-printing is explored:

- For example, powder bed and inkjet printing is used for 3D-printing collimators made from B_4C powder and later infiltrated with superglue or aluminum.
- This allows for complex designs of hydrogen-free collimators from neutron absorbing materials.



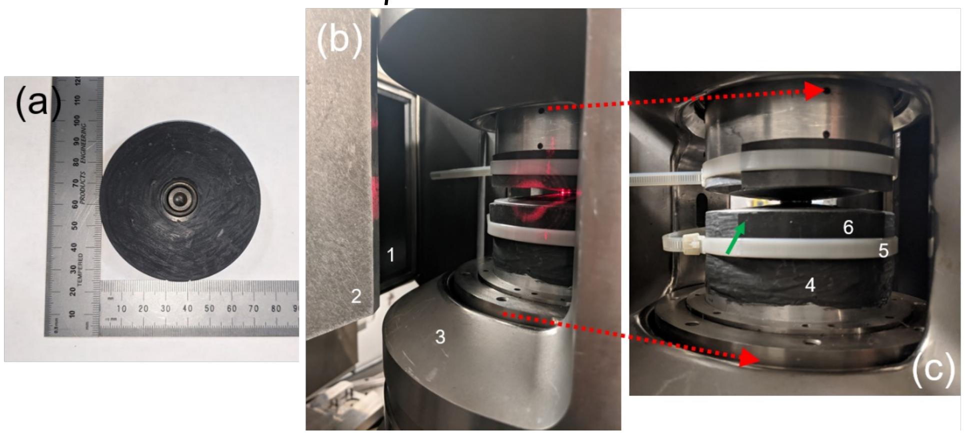
New collimator design printed from B_4C for single crystal diffraction in the wide-angle DAC.

Superglue and aluminum infiltrated B_4C collimators for PE cell on SNAP.

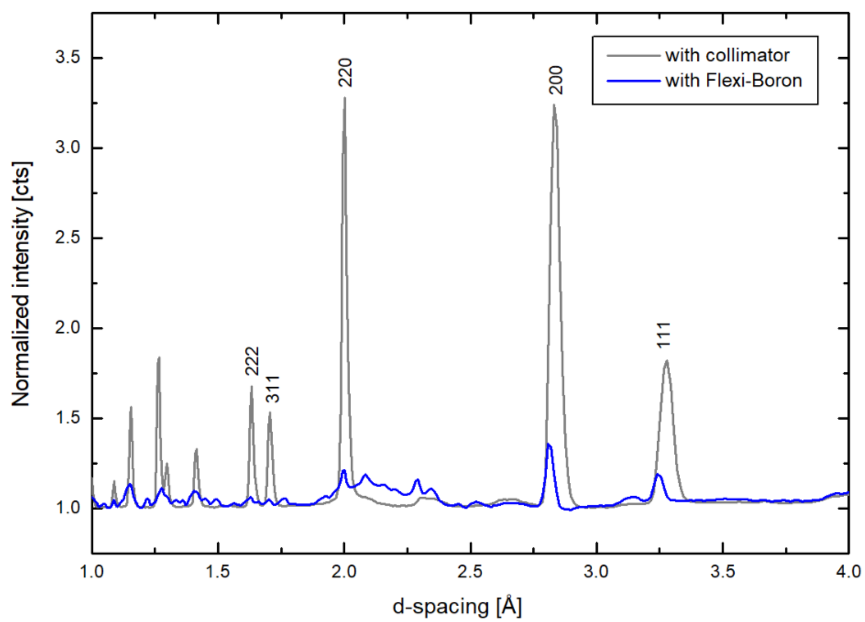
[1] B. Haberl *et al.*, Review of Scientific Instruments **92**, 093903 (2021).
[2] C.L. Cramer *et al.*, Materials and Design **180**, 107956 (2019).

A.2 Incident beam collimation

'Old' set-up with Flexi-Boron



Collimator set-up



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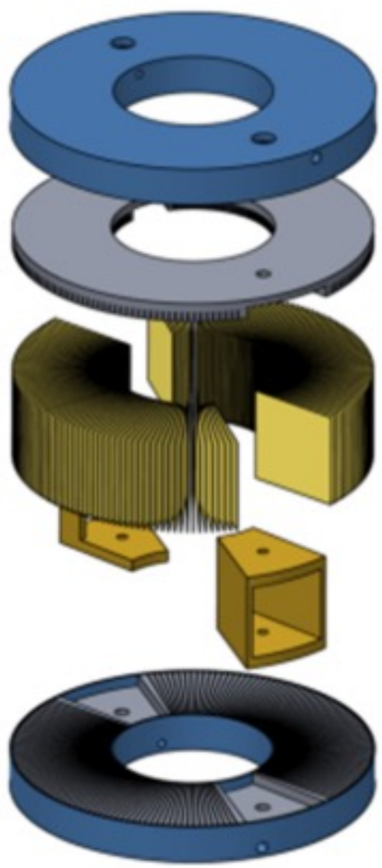
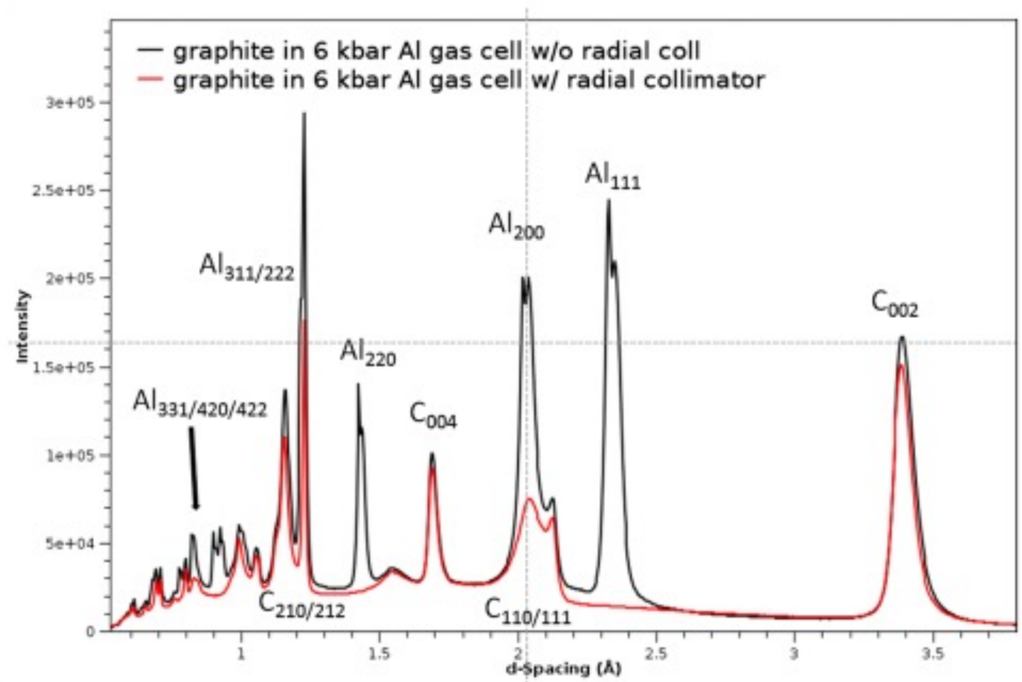
[1] B. Haberl et al, Review of Scientific Instruments **92**, 093903 (2021).

A.2 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]

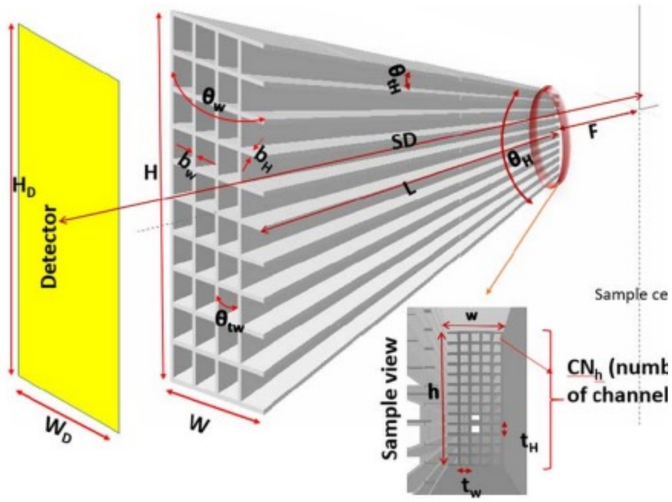




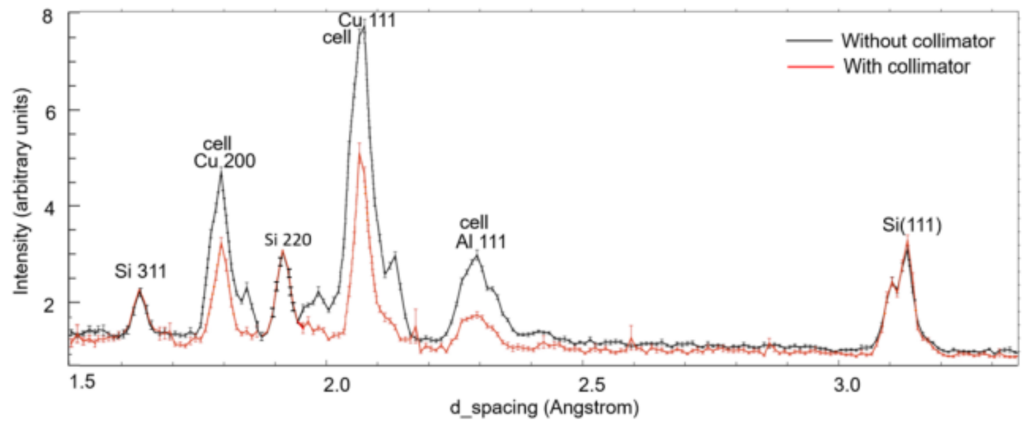
[1] A. dos Santos et al., Rev. Sci. Instrum. 89, 092907 (2018).

A.2 Incident and scattered beam collimation

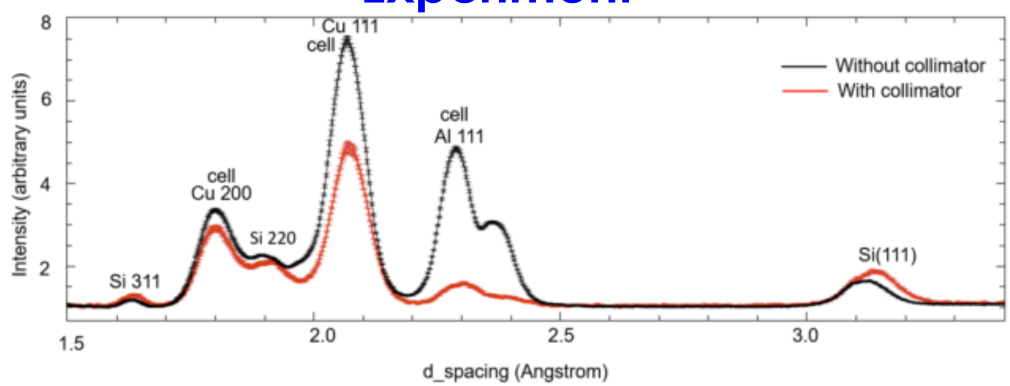
Monte Carlo Ray Tracing allows for further improved radial collimations through computer optimization[1]. Cell consists of a CuBe insert in an Al sleeve.



Simulation



Experiment



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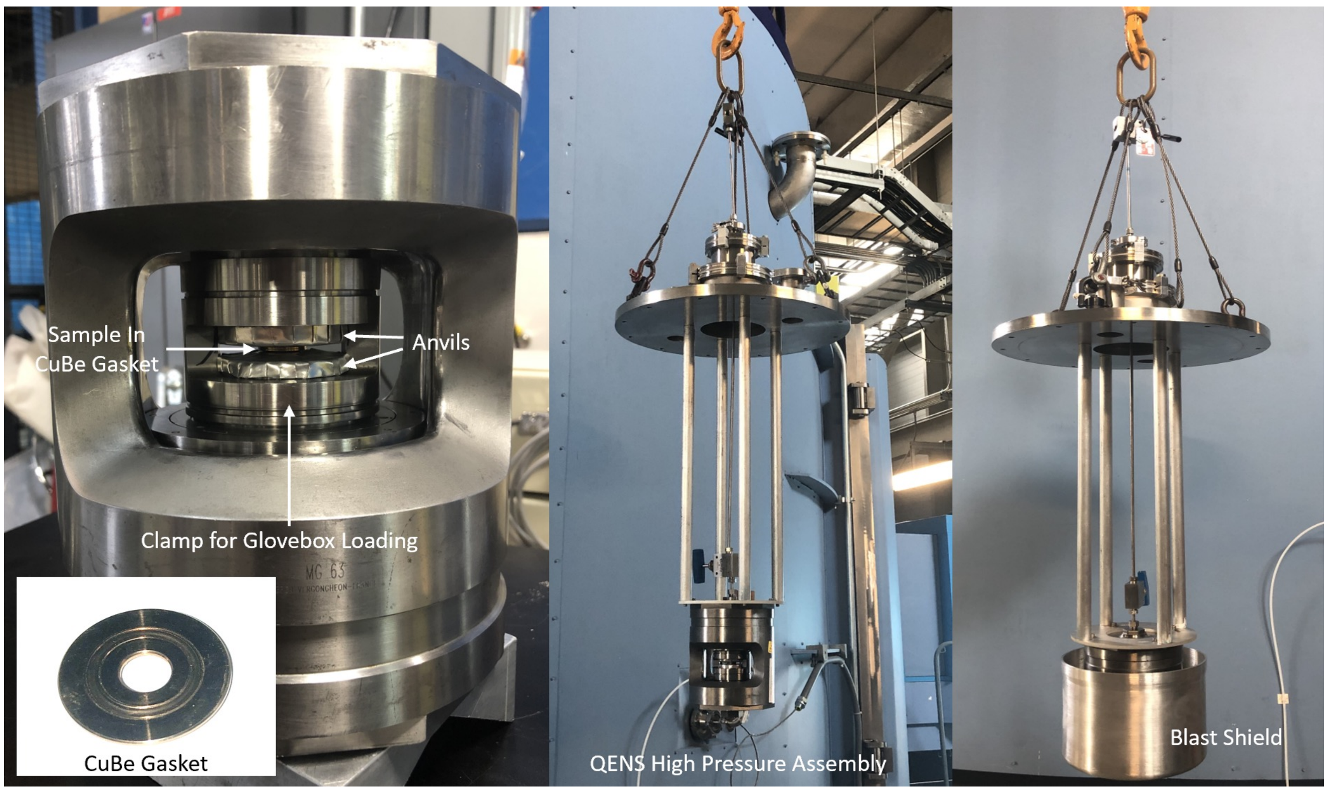
[1] F. Islam et al., Journal of Neutron Research 22 (2020) 155–168

A.3 Inelastic neutron scattering in the PE press

High pressure QENS was conducted on BASIS in the VX5 PE cell equipped with single toroidal anvils [1,2]. Gaskets were modelled after Bove & Klotz [3]. This set-up was also adapted for INS on the ARCS spectrometer using the VX3 PE cell.

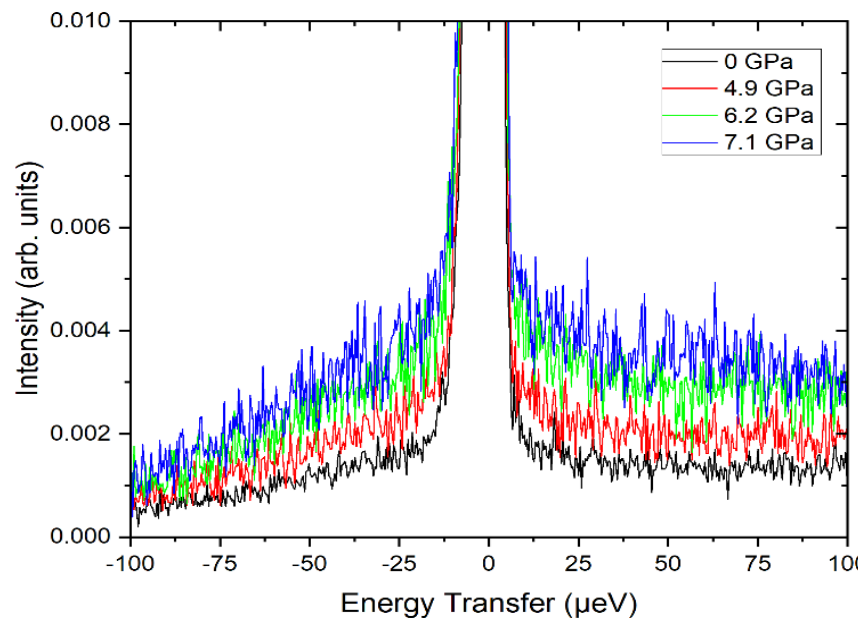


[1] E. Novak, B. Haberl, L.Daemen *et al.*, **APL 117**, 051902 (2020).
[2] E. Novak, Ph.D. Dissertation. University of Tennessee (2020)
[3] S. Klotz, T. Strassle, L. E. Bove, Appl. Phys. Lett. **103**, 193504 (2013).

A.3 Quasi-elastic neutron scattering

We conducted high pressure QENS on BaH_2 up to 7.1 GPa [1,2]. Pressure was determined based on a corresponding diffraction experiment on SNAP.

- Ambient pressure data yields the instrumental resolution where the hydrogen motion is essentially frozen.
- Under pressure we see quasi-elastic broadening which is directly related to faster dynamics.
- Timescales decreased from 24.4 ps (6.2 GPa) to 16.9 ps (7.1 GPa).



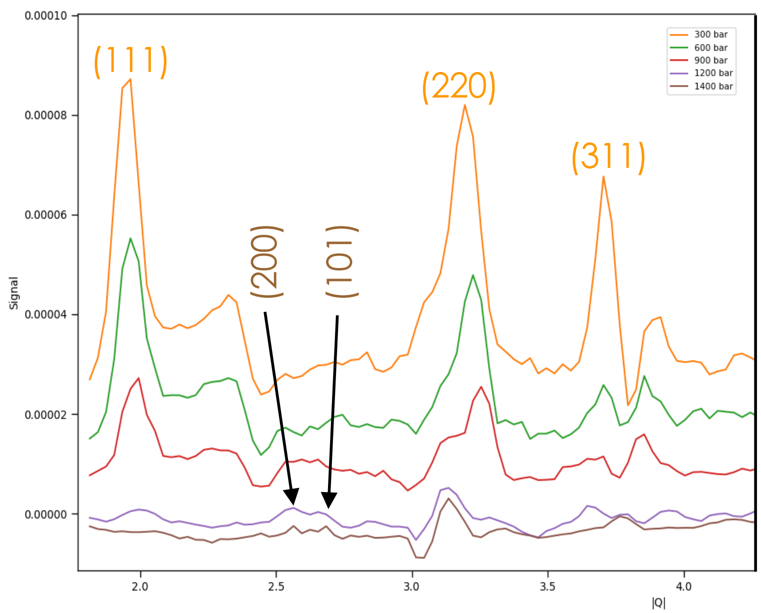
Larger sample volumes/longer exposures will be needed for more quantitative analysis.

[1] E. Novak, B. Haberl, L. Daemen *et al.*, **APL 117**, 051902 (2020).
[2] E. Novak, Ph.D. Dissertation. University of Tennessee (2020)

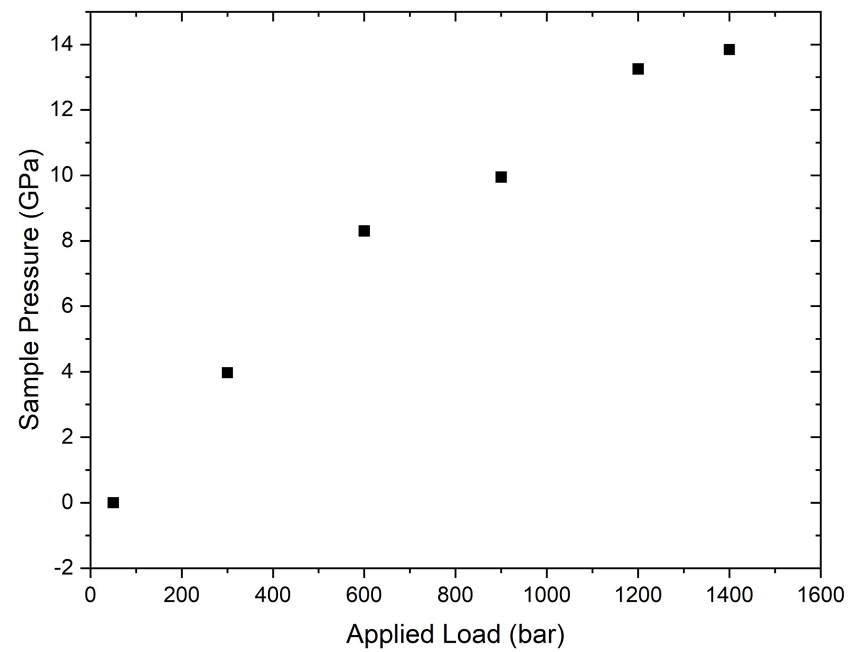
A.3 High pressure inelastic neutron scattering

We conducted high pressure INS on crystalline Ge up to ~14 GPa. Pressure was determined using the equation of state of Ge and *in situ* diffraction data from ARCS.

Diffraction data at increasing pressure



Pressure-load curve based on equation of state of Ge [1]



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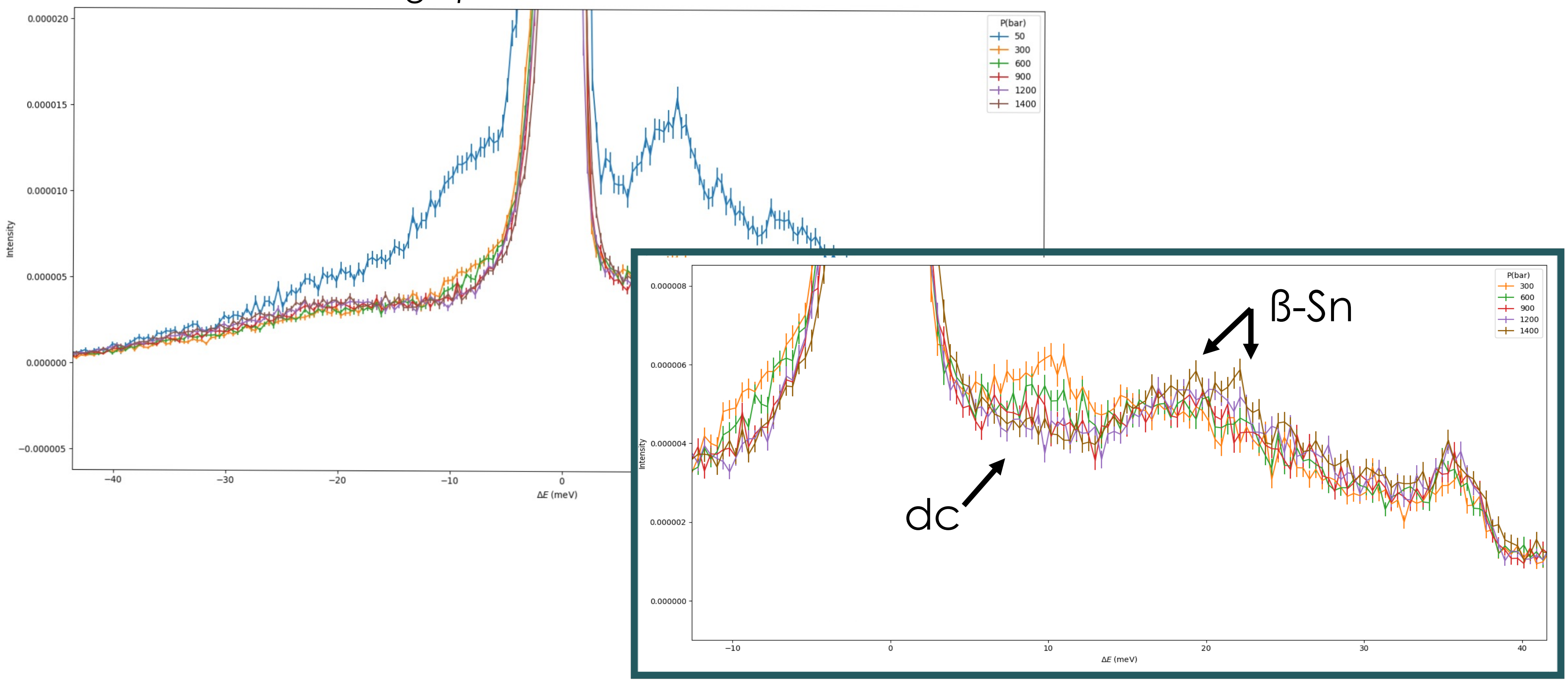
[1] C.S. Menoni *et al.*, **PRB 34**, 362 (1986).

A.3 High pressure inelastic neutron scattering

The INS data suggest a significant change in phonons at loads above 1200 bar. This corresponds to pressures of >10 GPa and hence metallization of Ge.

In situ high pressure INS at 50 meV



Detailed data analysis for conversion to phonon DOS and accompanying computation is in progress.