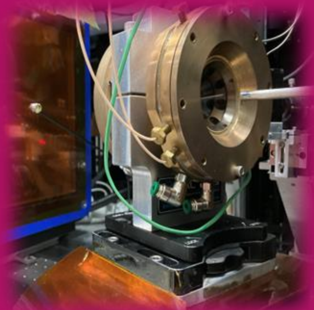
High Pressure measurements with **X-rays**



Stella Chariton

The University of Chicago

Center for Advanced Radiation Sources

GSECARS (Sector 13, APS)

NXS – 08/14/23

Talk Overview

- The pressure scale
- Why apply high pressure? – Experiments at extreme conditions
- High pressure generation devices
  - *Focus on Diamond Anvil Cells*
- Why synchrotron radiation? – Overview of X-ray techniques at high pressures
- High pressure techniques for X-ray scattering
  - *Focus on X-ray Diffraction*

The pressure scale

$$Pressure = \frac{Force}{Area}$$

The Pascal unit

- 1 atm = 101325 Pa
- 1 Pa = a dollar bill resting on a flat surface
- 2 kPa = pressure of popping pop-corn
- 1 MPa = pressure of average human bite
- 360 GPa = pressure in the center of the Earth
- 1 TPa = 100 Eiffel towers stacked on top of a penny

Fun Facts check: [Orders of Magnitude – Wikipedia]

Why apply high pressure?

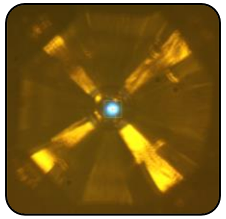
Pressure cookers
Steam pressure allows higher temperatures to break down tough tissue

Physical, chemical & optical **properties** of materials change with **pressure !**

Liquefied Petroleum Gas tanks
Pressure and cooling turn gas into liquid for easy storage

Why apply high pressure?

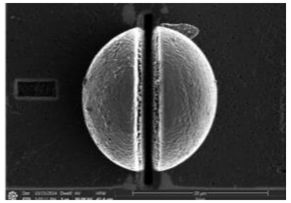
Superconductors



LaH_{10} (~249 K, 150 GPa)

Sun et al. 2021, Nature Com

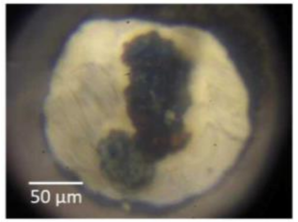
Super-hard Materials



Nanodiamond balls

Dubrovinsky et al. 2022, Nature

High Energy Materials

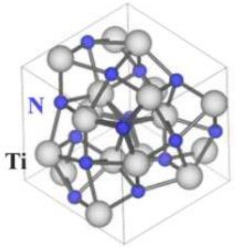


Salts of Polynitrogen anions

Laniel et al. 2019, Nature Com

Physical, chemical & optical **properties** of materials change with **pressure !**

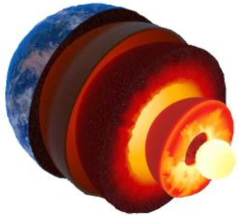
Semiconductors



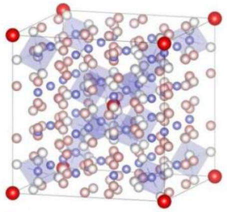
Cubic Ti_3P_4

Bhadram et al. 2018, Phys. Rev. Mat.

Deep Planetary Interiors



Thermoelectric Materials



$In_xCo_4Sb_{12}$, Skutterudites

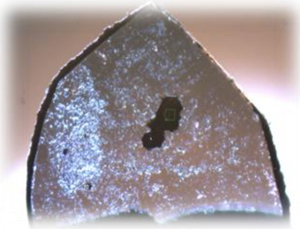
Leszczyński et al. 2017, J. Alloys Compd.

Experiments at Extreme Conditions

High Pressure


Courtesy of COMPRES


Courtesy of Lucy Moorcraft/SINE2020



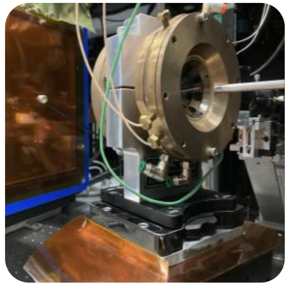
Large Volume Presses

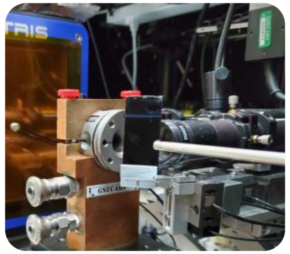
Diamond Anvil Cell

Paris-Edinburgh Cell

Made by Nature

High Temperature



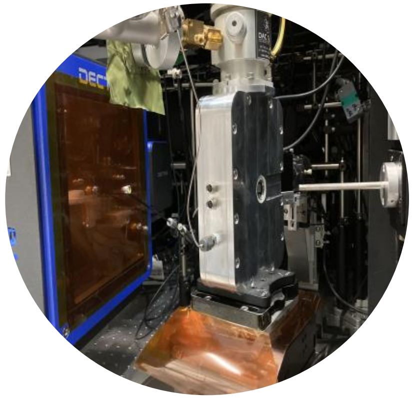


Laser Heating

Furnace Heating

> 7000 K

Low Temperature

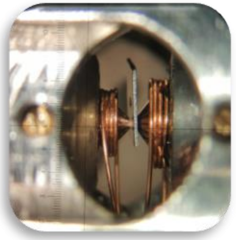


Cryostat enclosures

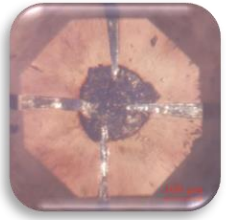
Cryogenic jets

as low as 0.03 K

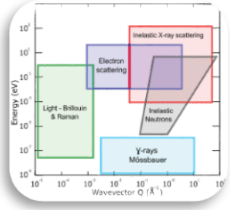
Magnetic Fields


Courtesy of Thomas Meier, BGI, HPSTAR

Electric Fields

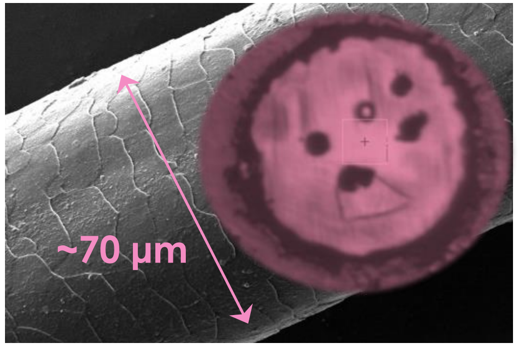

Courtesy of Sergey Medvedev, Max Planck Inst

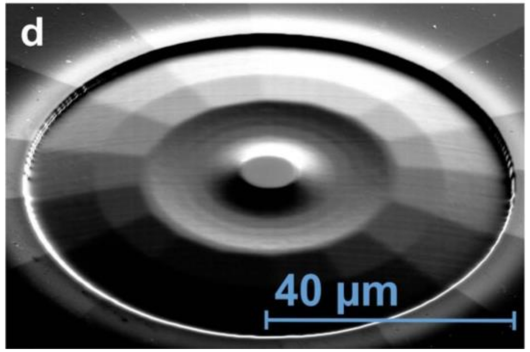
Radiation Flux


Shen & Mao, 2017, Rep. Prog. Phys.

Experiments at Extreme Conditions

Tiny & Unique





Dubrovinsky et al. 2022, Nature

Challenging sample
preparations & measurements

" The Synchrotron Life"

Argonne Guest House

Every single second of
beamtime matters

History of High Pressure Science

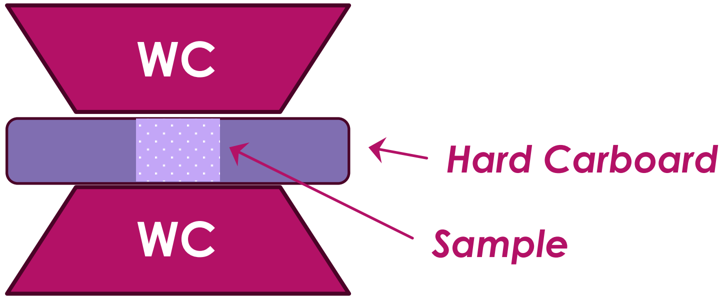
Percy Williams Bridgman (1882-1961)

Father of modern high-pressure research

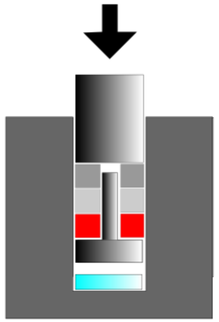
- Achieved ~40 GPa in the laboratory
- New pressure apparatus & Self-sealing gasket
- Nobel Prize in 1946 for his work in the field of high-pressure physics
- Earth's most abundant mineral, bridgmanite $(Mg,Fe)SiO_3$, is named after him

Source: Wikipedia, Britannica

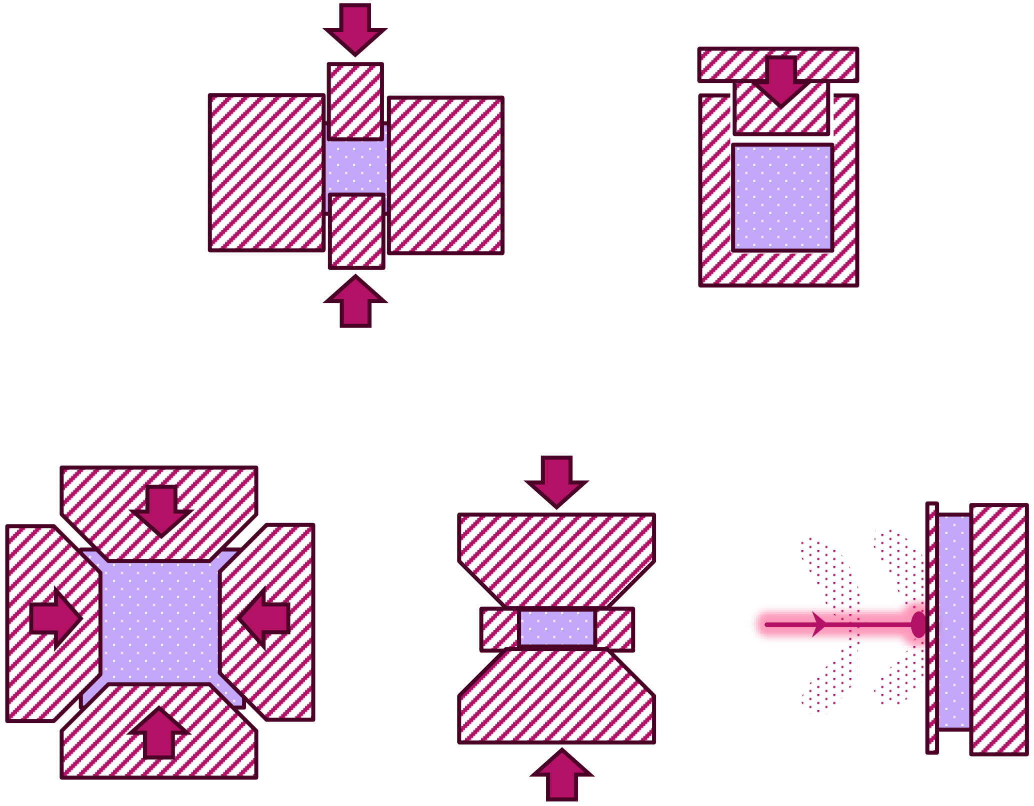
Bridgman anvils



Bridgman Seal



High pressure generation devices



Materials

- ✓ Tungsten Carbide
- ✓ Tempered high strength steel
- ✓ Diamond

Pressures

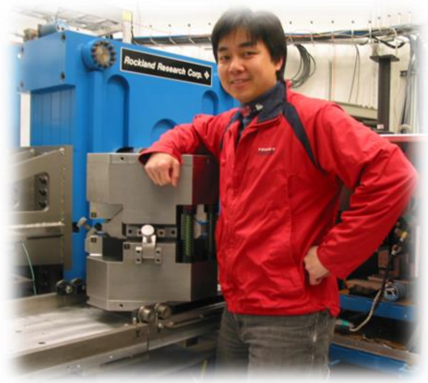
- ✓ 0 – 1000 GPa
- ✓ Hydrostatic or not
- ✓ Static or dynamic

Types

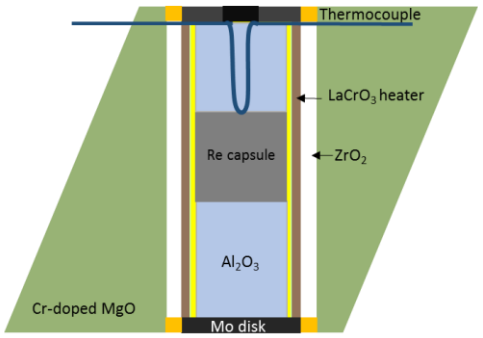
- ✓ Piston / Cylinder
- ✓ Anvils
- ✓ Laser Shock waves

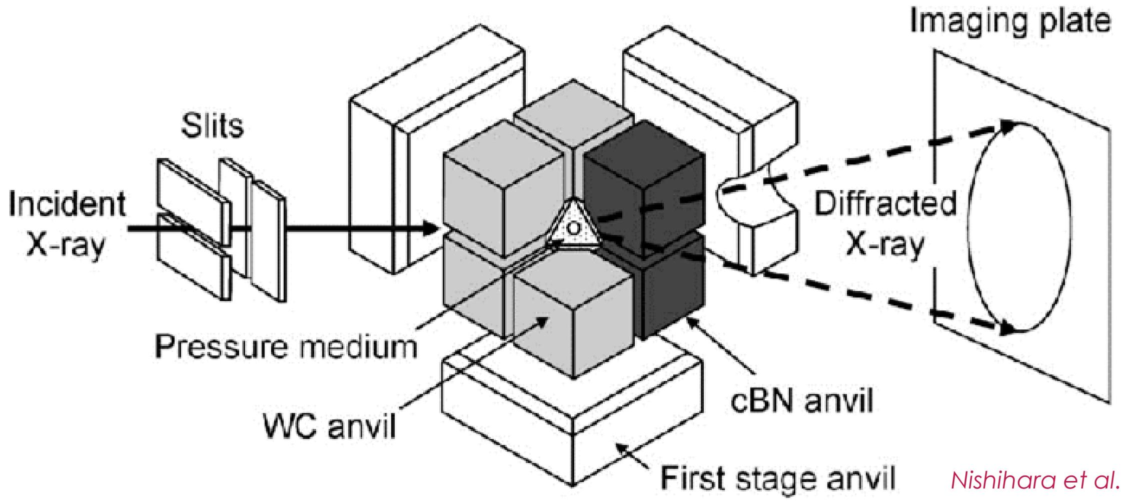
Large Volume Press

multi anvil apparatus

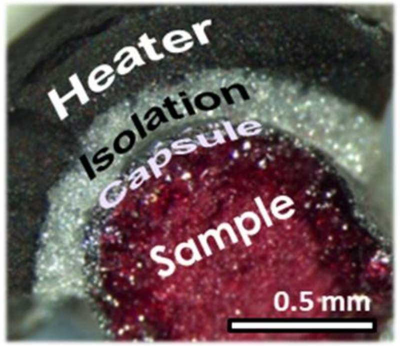


Tony Yu, Beamline scientist at 13IDD, APS



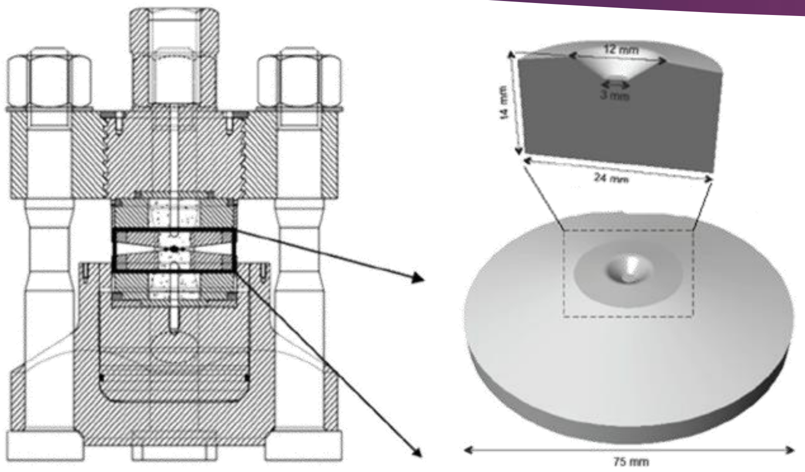


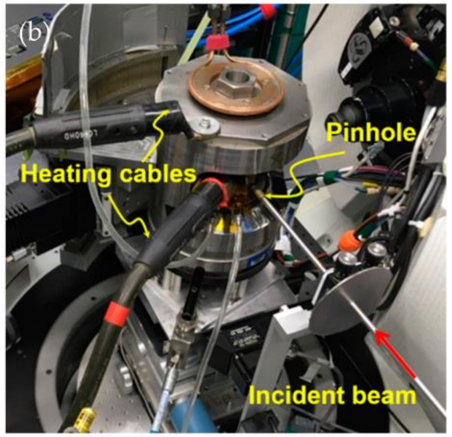
Nishihara et al. 2009, JSR



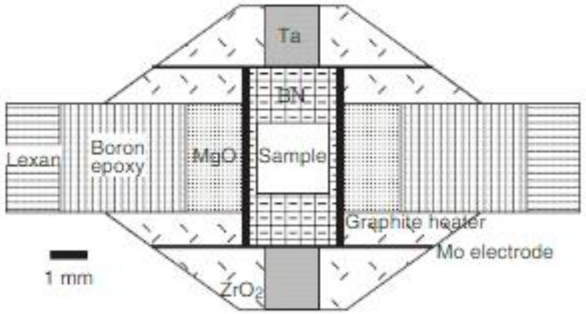
- ✓ Anvils made of WC, cBN, sintered diamond
- ✓ Anvil truncation size defines the pressure range
- ✓ $LaCrO_3$, graphite or capsule material used as heaters
- ✓ Typical conditions 0-30 GPa (max ~95 GPa), ~3000 K
- ✓ Working in deformation or hydrostatic mode
- ✓ X-ray transparent materials allow measurements at synchrotrons

Paris-Edinburgh Cell





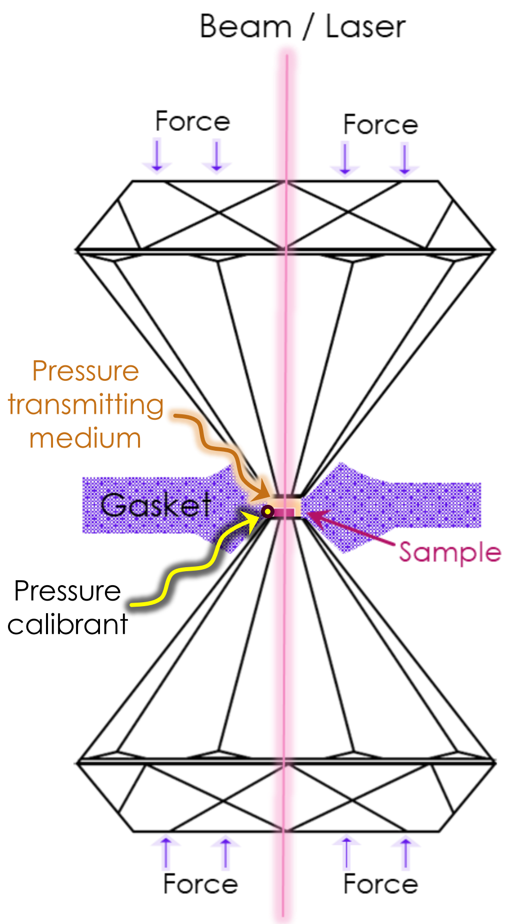
Yu et al. 2019, Minerals



Kono et al. 2013, PEPI

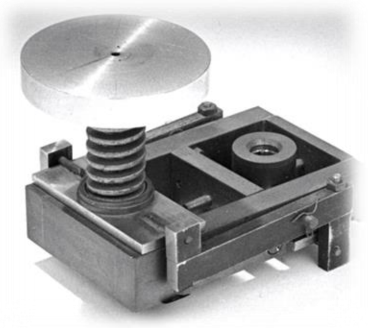
- ✓ Anvils made by sintered materials (WC, diamond, BN)
- ✓ Portable
- ✓ Typically can hold large volumes of sample 1-100 mm^3
- ✓ Modified versions for Neutron diffraction and study of liquid phases using X-rays

Diamond Anvil Cell



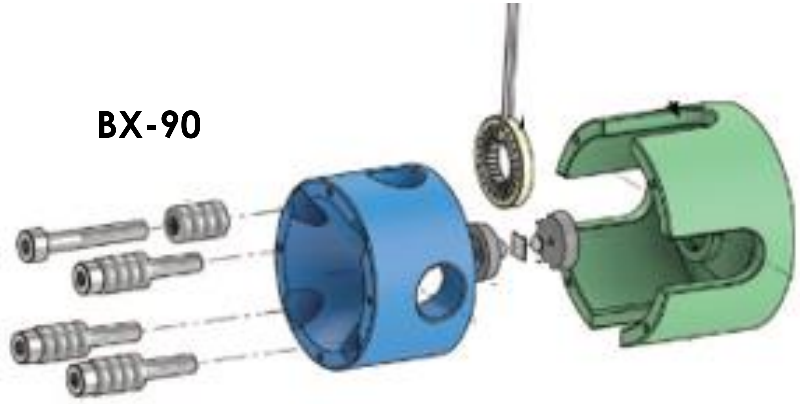
DAC is the most popular high-pressure device for X-ray experiments, because diamond has :

- ✓ Highest known hardness & optically transparent
- ✓ Fracture toughness, highest known thermal conductivity, low friction and adhesion, ultra high melting point, highest electron dispersion, high dielectric breakdown, radiation hardness, high magnetic field compatibility, biocompatibility



First diamond anvil cell created in 1957-1958 (NIST museum)

BX-90



Kantor et al. 2012, Rev Sci Instrum

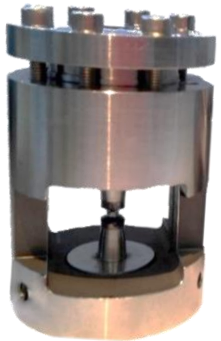
Diamond Anvil Cell
Variety

Remote program during pandemic
GSECARS-June-2020

DAC components that can vary :

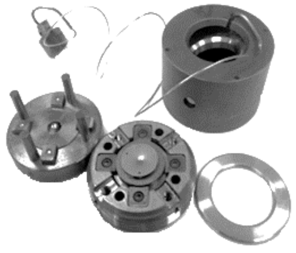
- ✓ Cell body
- ✓ Supporting seats
- ✓ Diamond anvils
- ✓ Gasket material
- ✓ Pressure transmitting medium
- ✓ Pressure calibrant
- ✓ Sample arrangement

Diamond Anvil Cell
Variety



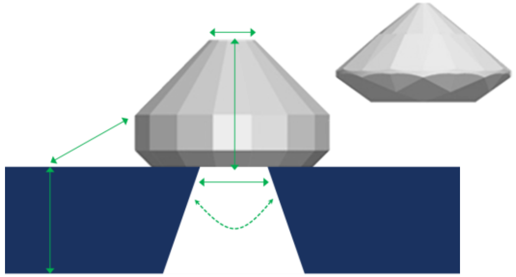
Panoramic DAC with Be gasket
Nuclear Resonant Inelastic X-ray Spectroscopy or Radial X-ray Diffraction

BX90 & Diacell120 with Boehler-Almax seats and diamonds
Single-crystal X-ray Diffraction
Brillouin Spectroscopy
or Non-crystalline X-ray Diffraction (PDF)

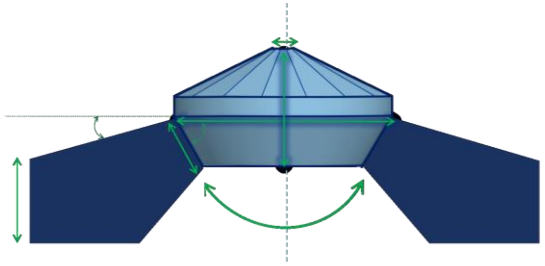


LeToullec pressure driven cell or others
A can with an inflating membrane allows remote pressure increase

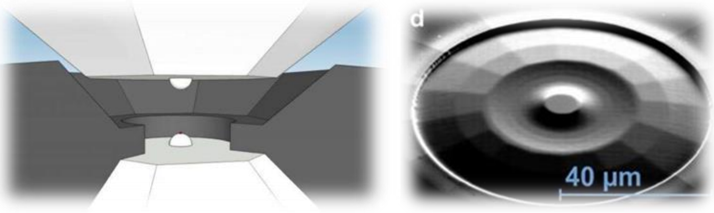
Standard symmetric cell
Powder X-ray Diffraction
Nuclear Forward X-ray Scattering (or SMS)
IR, Raman Spectroscopy



Standard seat WC or cBN standard or Brilliant cut diamond
X-ray and optical opening ≤ 60º

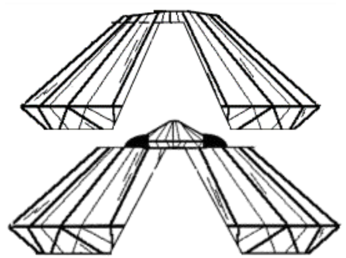


Boehler-Almax seat and anvil
X-ray and optical opening ≥70º



Double stage diamond anvils and Toroidal Anvils
Ultra high-pressure generation

Dubrovinsky et al. 2015 & 2022, Nature



Perforated Diamonds
Removed Material for X-ray Spectroscopy studies.

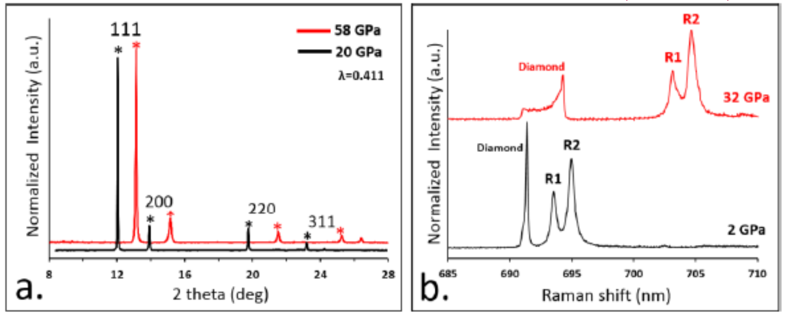
Dadashev et al. 2001, Rev Sci Instrum

Diamond Anvil Cell
Supporting Tools

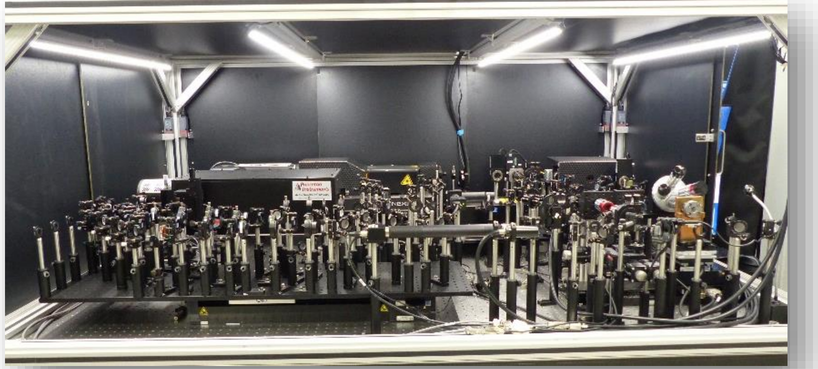
Rivers et al. 2008, High Pres Res

Gas loading system COMPRES/GSECARS, APS

Chariton, PhD thesis, 2019



Holtgrewe et al. 2019, High Pres Res



Advanced laser system at GSECARS
Raman, IR, UV, CARS, laser heating

Common Pressure Transmitting Media (PTM)

Gases: He, Ne, Ar, Xe, CO_2, N, H

Liquids: ethanol/methanol, silicon oil

Solids: NaCl, KCl, KBr, MgO, SiO_2

Common Pressure Calibrants

Au, Pt, Ruby, YAG, Diamond Raman edge, Equations of state of common samples

Diamond Anvil Cell
Supporting Tools

Micromanipulator at GSECARS

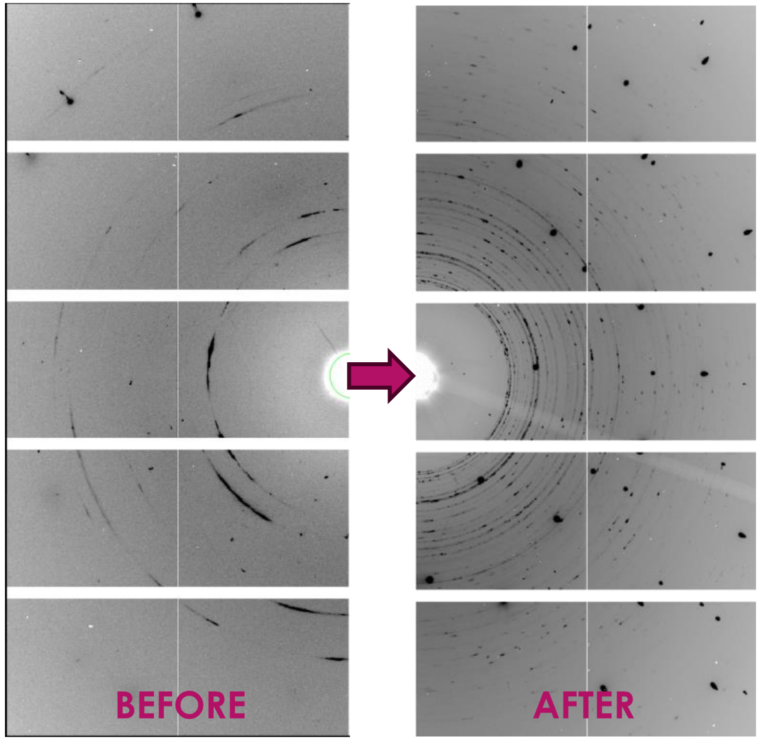
Gasket laser drilling system at GSECARS

Glovebox for DAC loadings at HPCAT

Microscopes at HPCAT

Examples of common DAC supporting infrastructure available to users

Diamond Anvil Cell
Temperature control



- ✓ Double-sided Laser Heating
- ✓ Resistive Heating
- ✓ Cryogenic treatment
- ✓ Cryogenic + laser heating

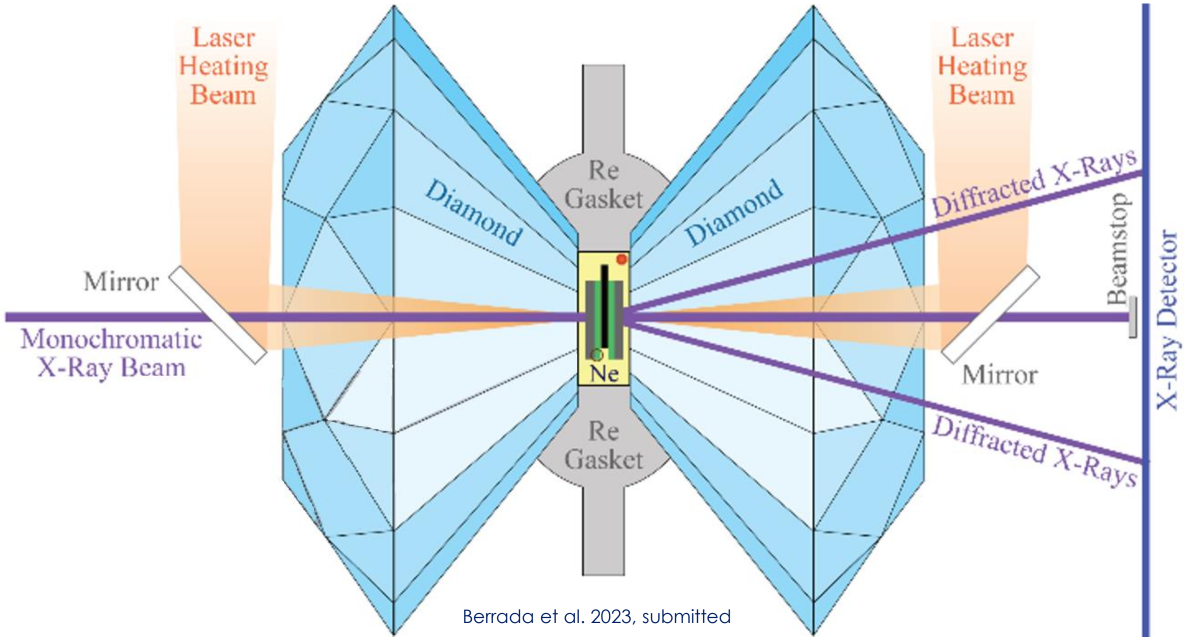
Application of pressure and temperature promotes:

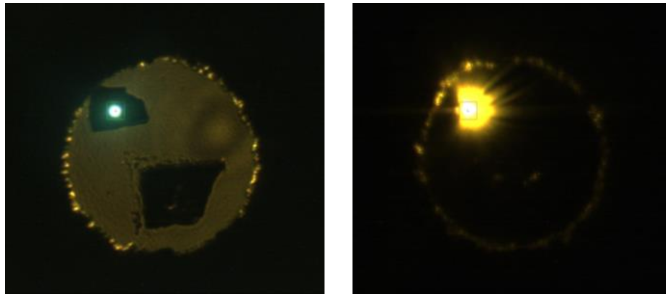
- New optical, physical properties
- Phase & structure transitions
- Crystal growth & recrystallization
- Reaction chemistry

Diamond Anvil Cell
Temperature control

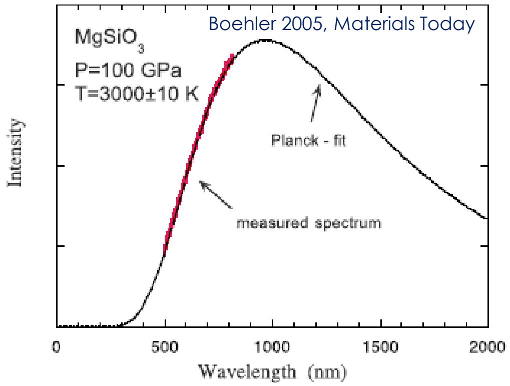
✓ Double-sided Laser (internal) Heating

YAG or CO_2 lasers , Continuous or Pulsed mode





X-ray and lasers are aligned.
A crystal couples with the 1064 nm laser and heats at 2400 K, 35 GPa.



Thermal emission is measured.

The spectrum is fitted using the Planck equation.

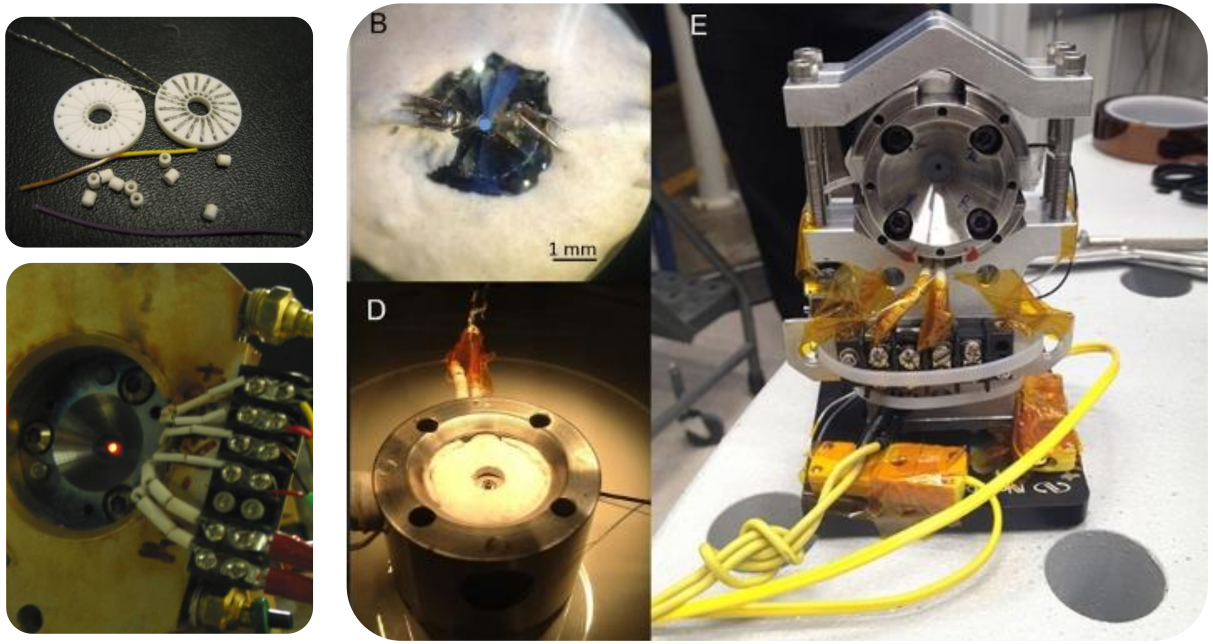
Temperature is estimated.

~500 to >7000 K

Diamond Anvil Cell
Temperature control

✓ Resistive (external) heating

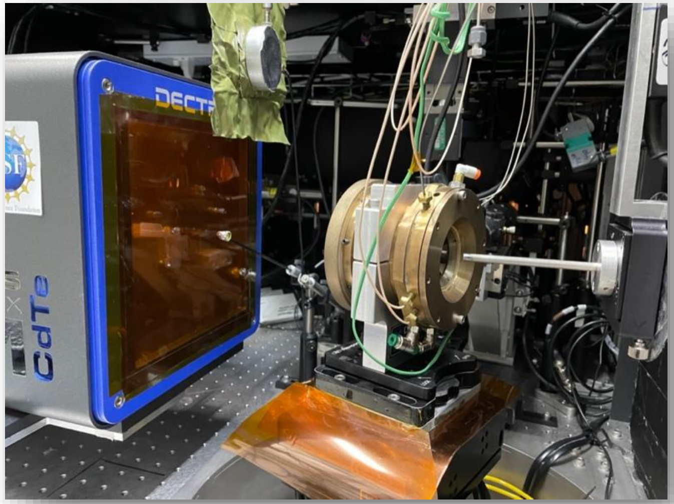
Ceramic furnaces, graphite inserts, others



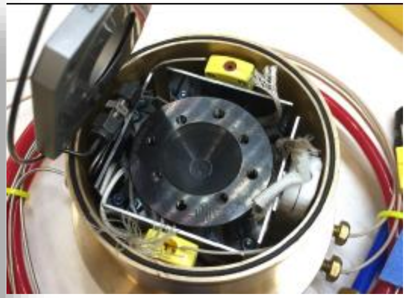
Lai et al. 2020, JOVE

External heating provides precise and well controlled heating.

However, it is limited to low temperatures (< 800 K) due to risk of diamond anvil graphitization and failure.



GSECARS & Bin Chen, University of Hawaii



EH-DANCE external heating enclosure
Allows stable heating up to ~1300 K

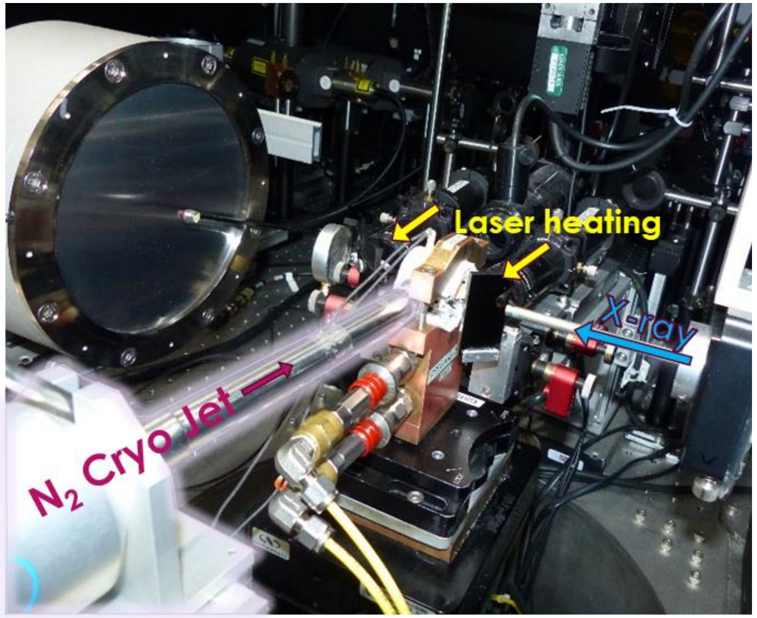
Diamond Anvil Cell
Temperature control

✓ Cryogenic Treatment

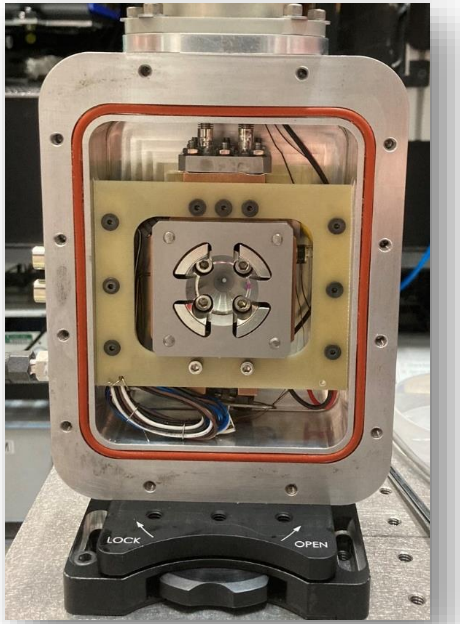
Nitrogen flow in air or in vacuum

Cryogenic temperatures as low as 0.03 K can be achieved

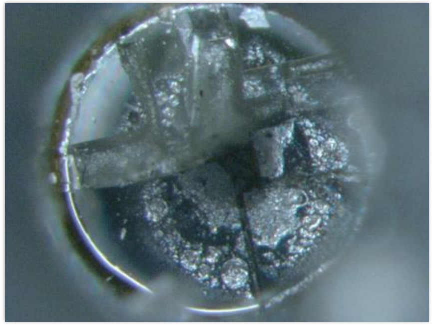
DAC cooling allows safer laser heating sessions of sensitive sample configurations or crystal growth of low temperature phases



Cryo Jet, 13-IDD, APS

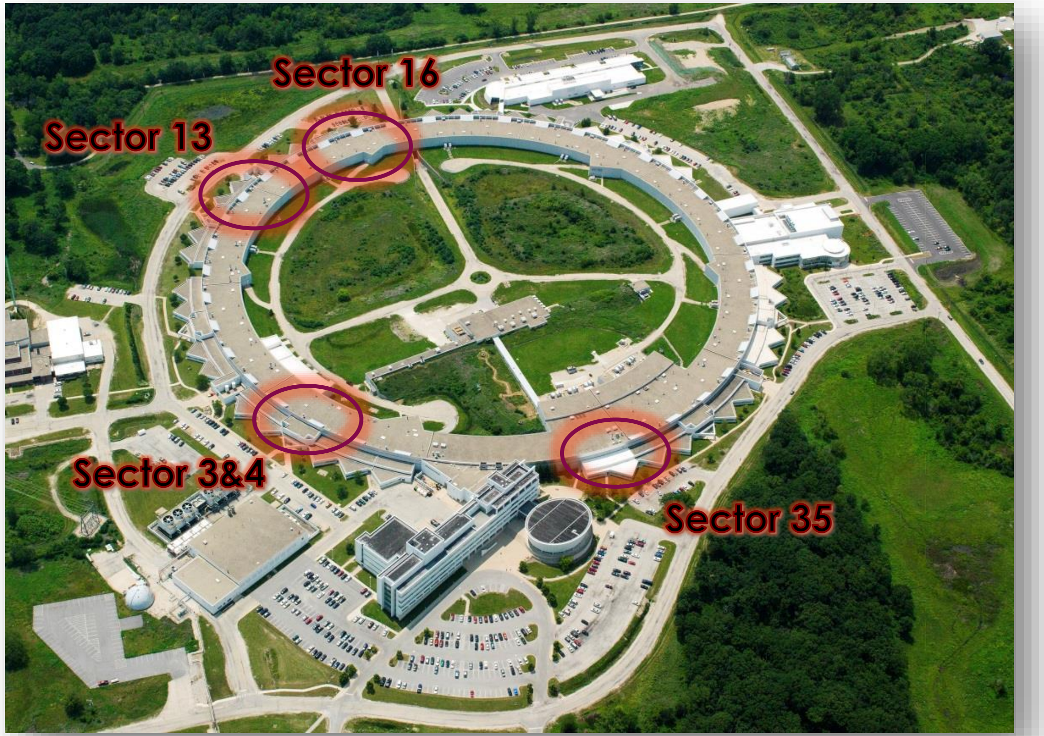


Cryostat enclosure, 13-IDD, APS



Alkali metals + H_2
=
most challenging for DAC

Why synchrotron radiation?



High Pressure Science at APS

High pressure = tiny sample volumes

typically, ~ 0.003mm^3, < 30 μm thick

Synchrotrons provide a highly stable X-ray beam ideal for high pressure studies

- ✓ High Intensity, brightness
- ✓ Coherent X-ray beam & low divergence
- ✓ Broad energy range, tunable energy
- ✓ Pulsed time structure
- ✓ Polarized radiation

X-ray synchrotron-based techniques
at high pressures

X-ray Diffraction

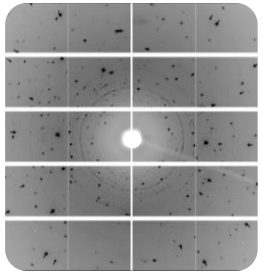
Powder (PXRD)

Single-crystal (SCXRD)

Polycrystalline

Amorphous

Radial



X-ray Spectroscopy

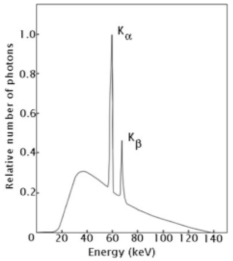
X-ray Absorption (XAS)

X-ray Emission (XES)

X-ray Absorption near edge (XANES)

X-ray Absorption fine structure (XAFS)

X-ray Fluorescence (XFS)



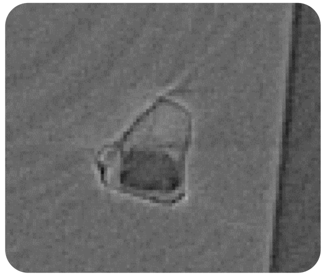
X-ray Imaging

Radiography

Tomography (CMT)

Phase contrast

Coherent diffraction



X-ray Inelastic Scattering

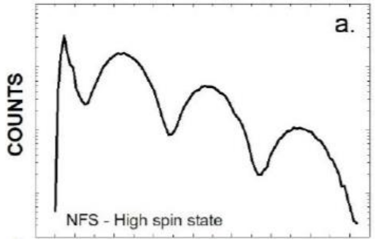
Non-resonant X-ray Inelastic scattering (NIXS)
(X-ray Raman scattering)

Resonant X-ray Inelastic scattering (RIXS)

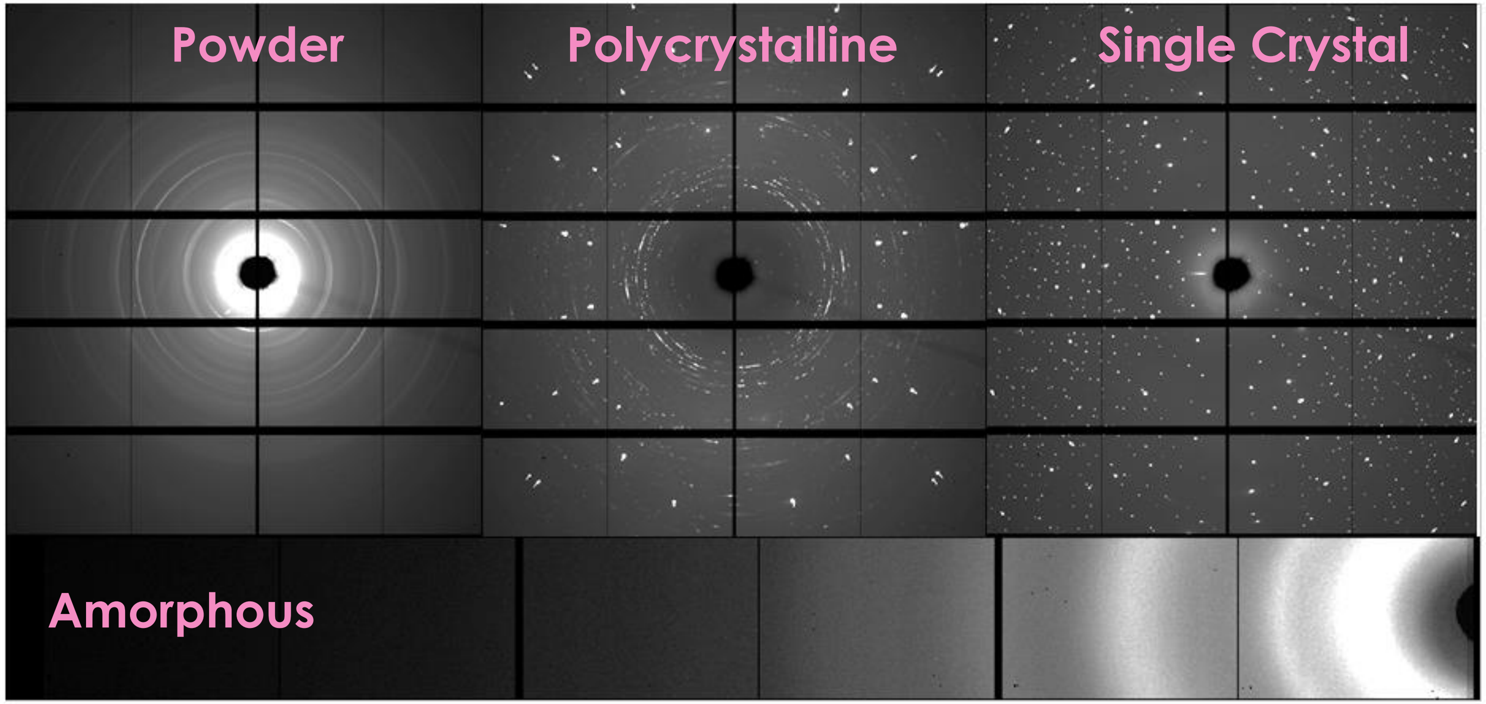
Nuclear Resonant Inelastic X-ray scattering (NRIXS)

Nuclear forward X-ray scattering (NFXS)

Compton Scattering (CS)

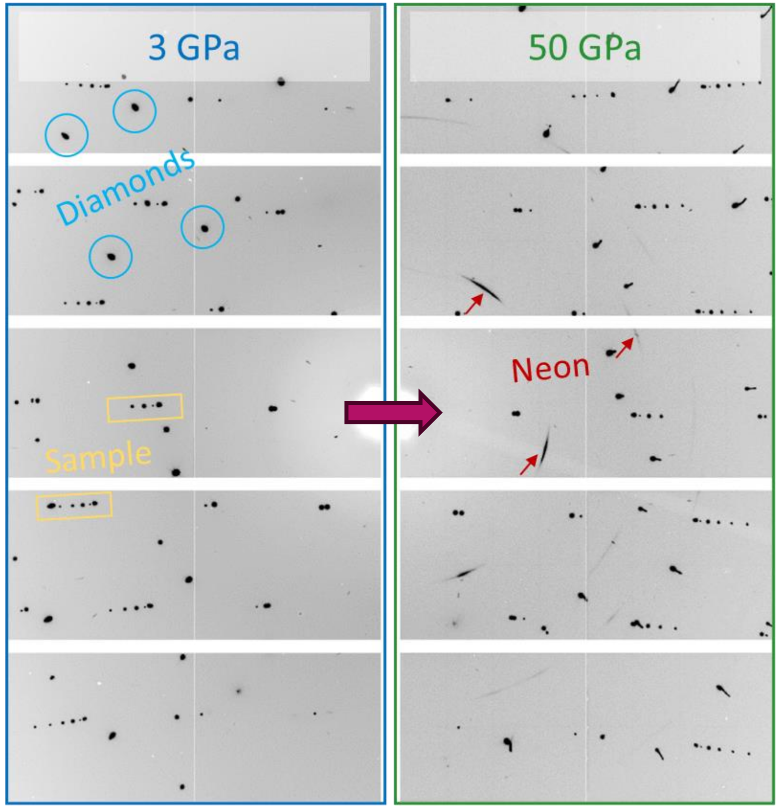


X-ray Diffraction

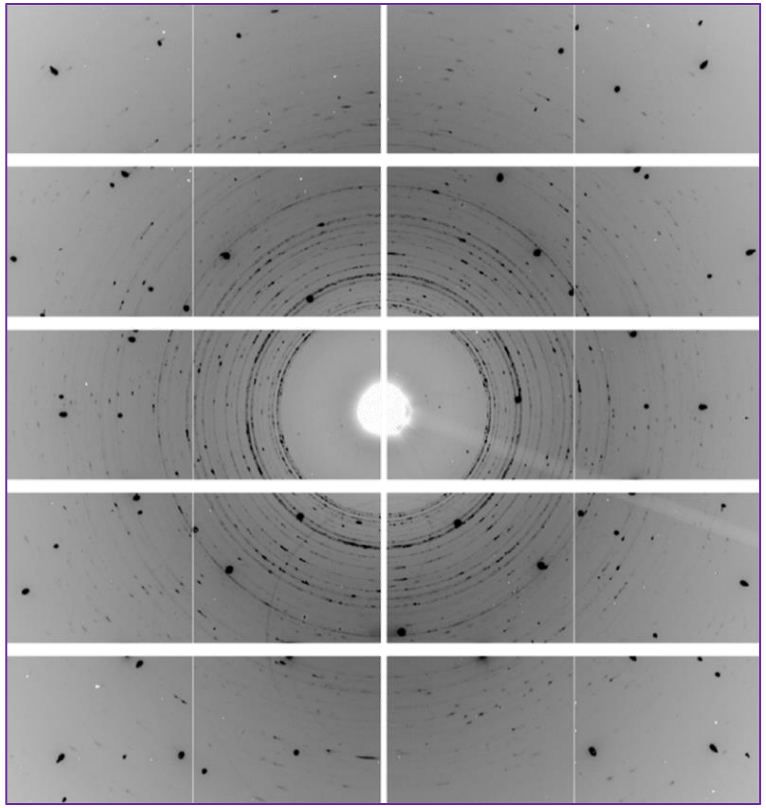


What is different at high pressure?

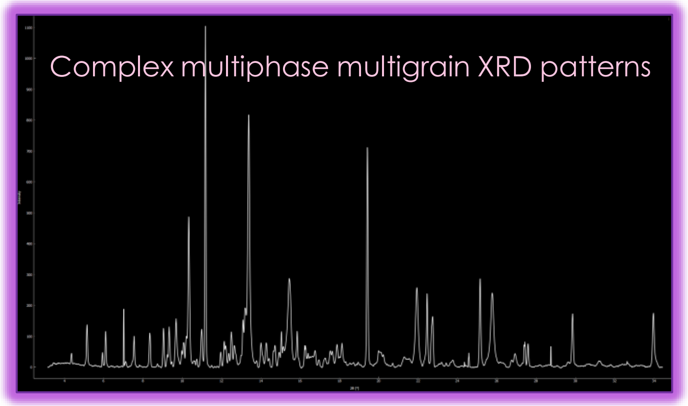
X-ray Diffraction



Single crystal Re_2C loaded with Ne pressure medium



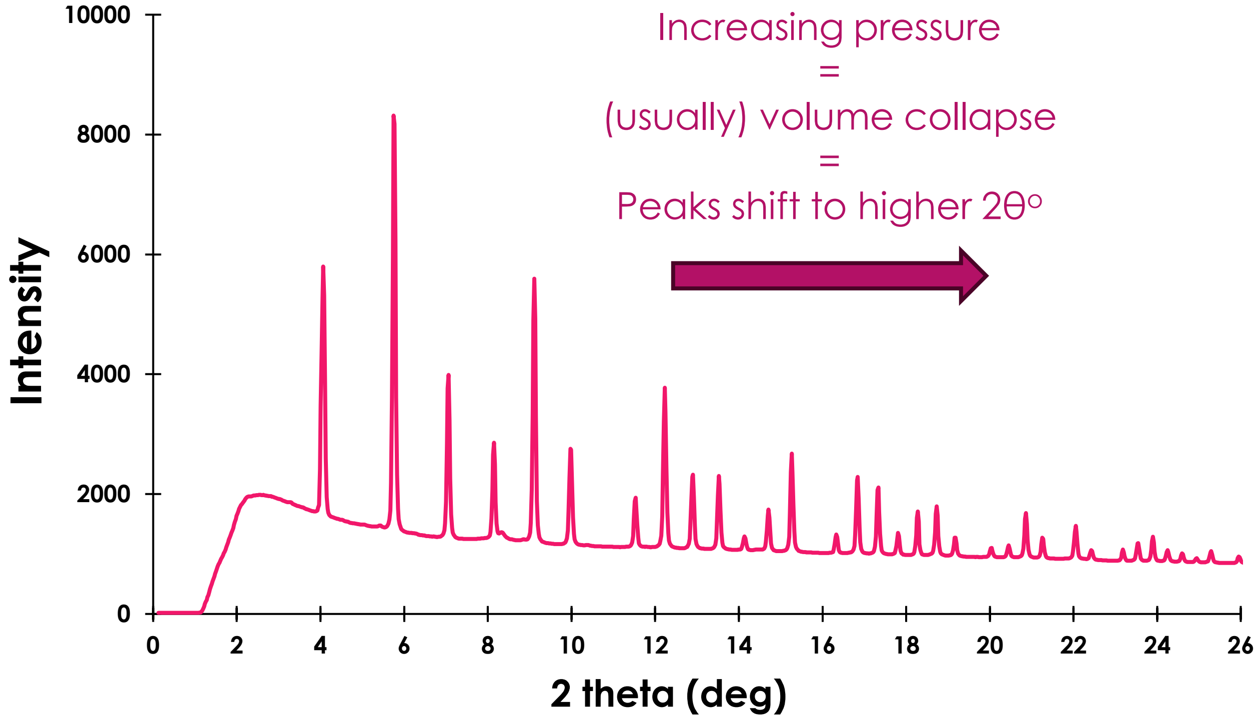
A laser heated sample has decomposed in various phases

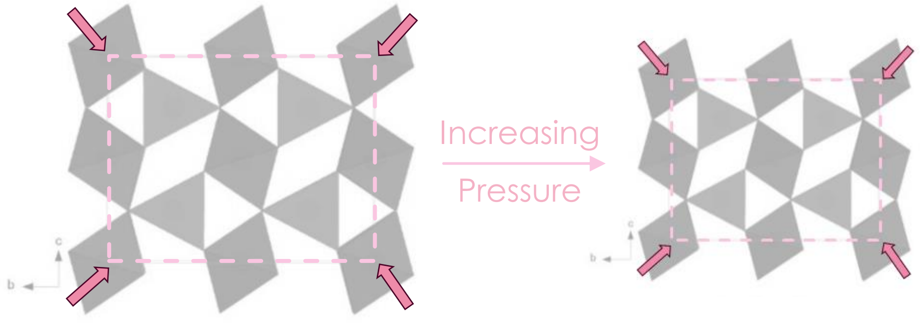


Reflections in a high-pressure environment

✓ Starting material
✓ Diamond anvils
✓ Pressure transmitting medium
✓ Decomposition products
✓ Gasket material
✓ Thermal insulators
✓ Pressure markers
✓ Satellite reflections …

X-ray Diffraction



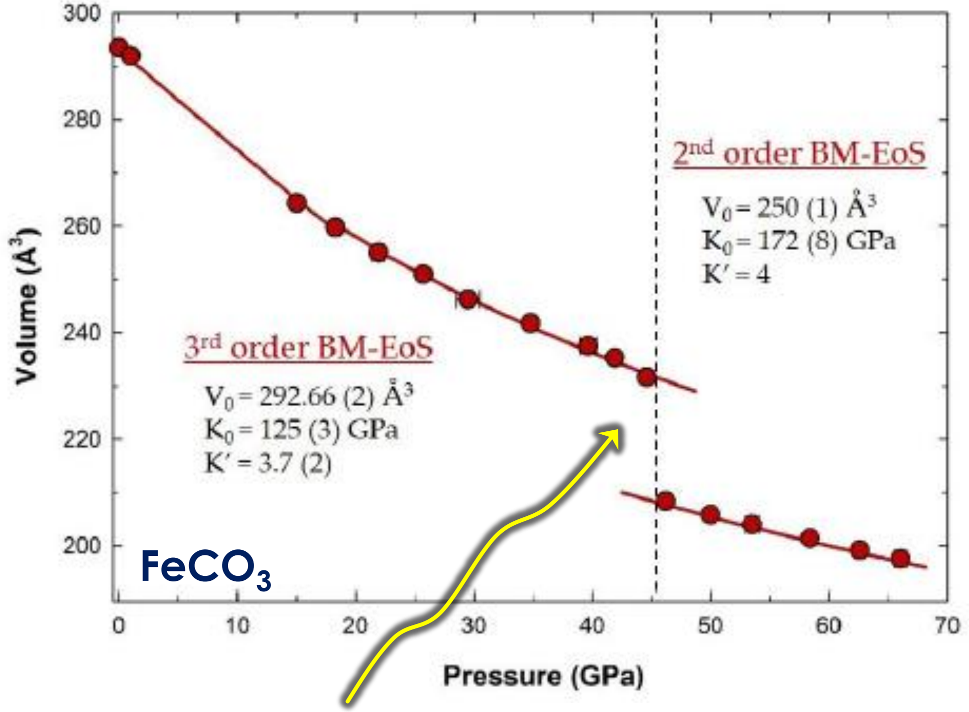


When will new reflections appear at extreme conditions?

- ✓ *Structure/symmetry has changed*
- ✓ *A phase has decomposed*
- ✓ *Crystals have change orientation*
- ✓ *An amorphous phase has crystallized*

X-ray Diffraction
Equations of State

Chariton et al. 2020, Am Min



Sudden volume collapse indicates drastic changes in the structure.

Check why in slides 37-41

Birch-Murnaghan equation of state

$$P(V) = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(K_0' - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$$

P – pressure

K_0 – bulk modulus at zero pressure

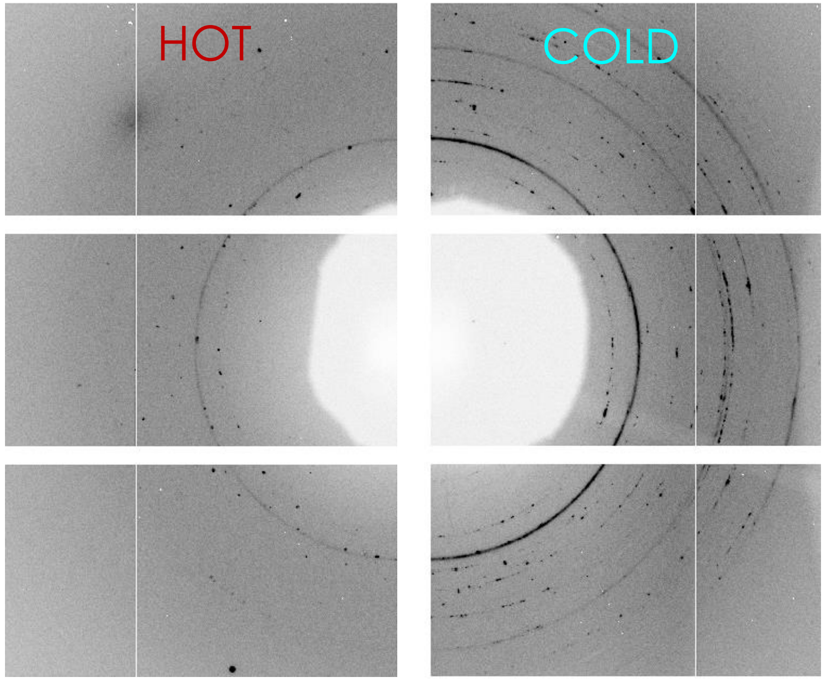
V_0 – volume at zero pressure

K_0' – derivative of bulk modulus with respect to pressure

The bulk modulus describes how compressible a material is.

High K_0 = harder to compress

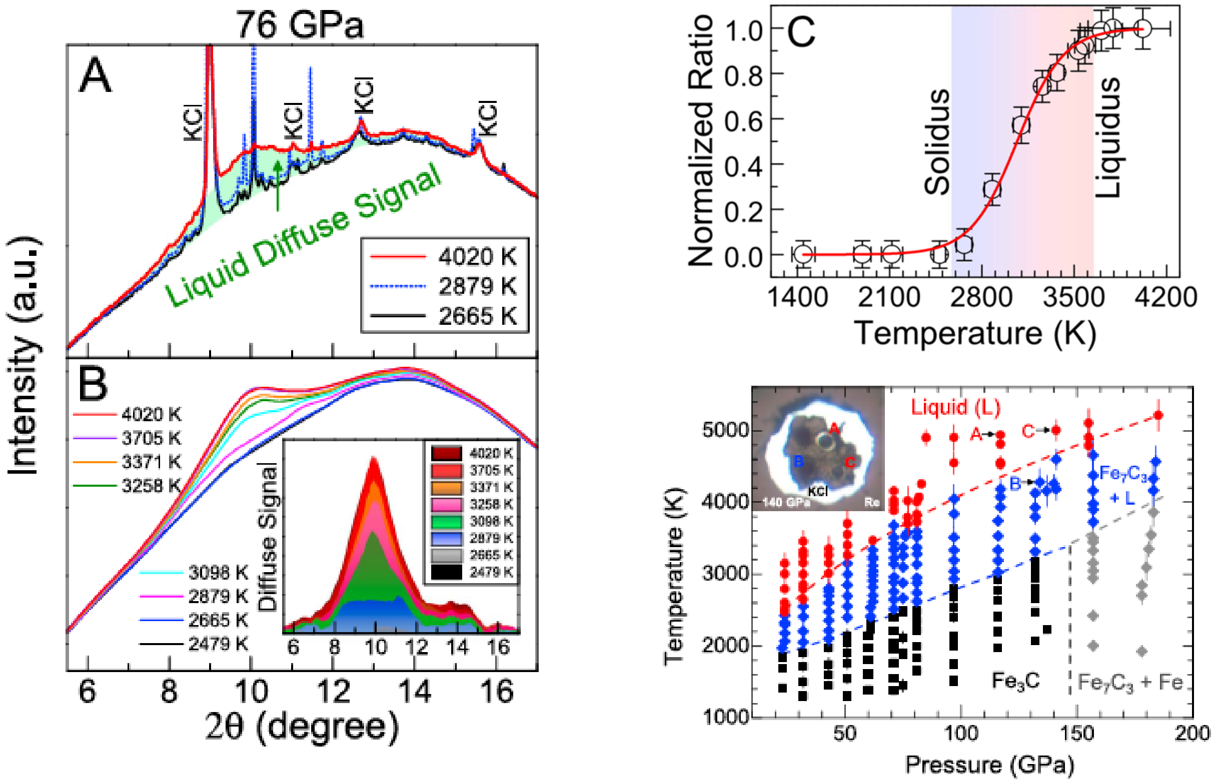
X-ray Diffraction
Melting curves



When a phase melts, peaks disappear, and diffuse scattering appears due to the liquid phase

Fe_3C and Fe_7C_3 up to 185 GPa and 5200 K

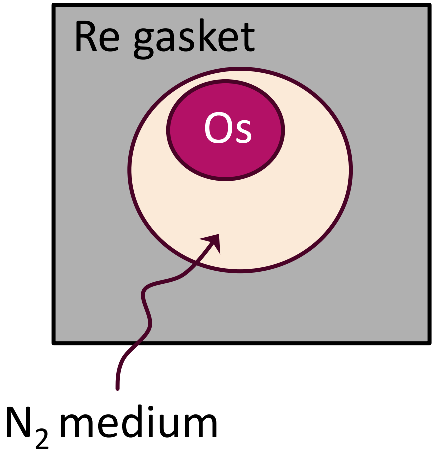
Liu et al. 2016, GRL

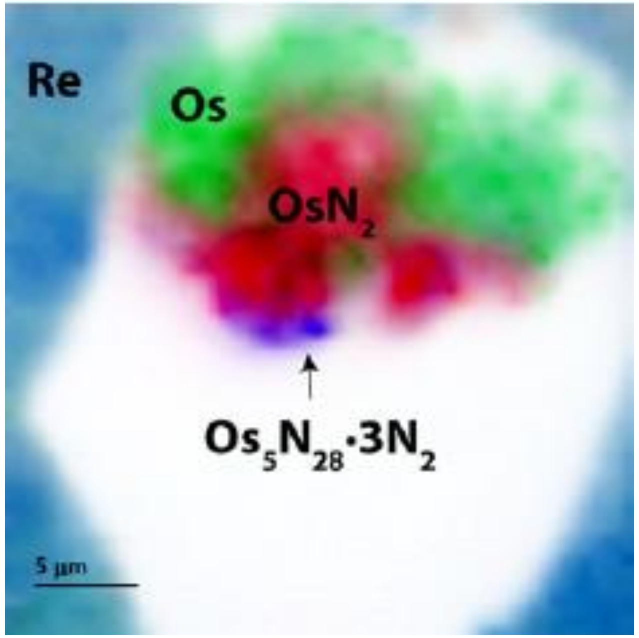


X-ray Diffraction

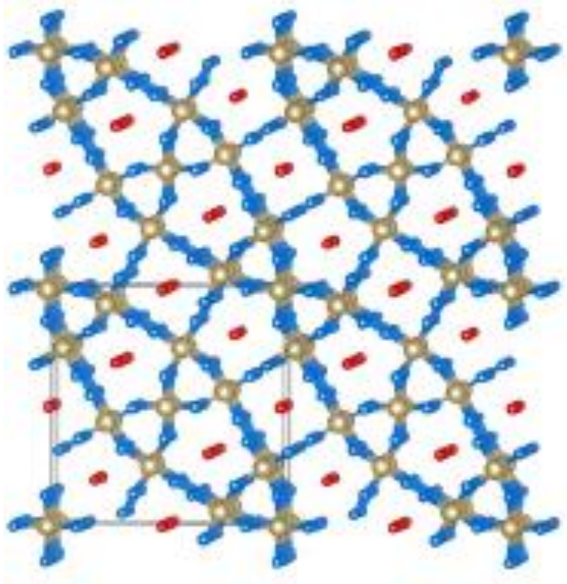
Chemical reactions

Laser heated at 105 GPa, 2800 K





Detailed XRD map allows localization of the various decomposition products within the sample chamber



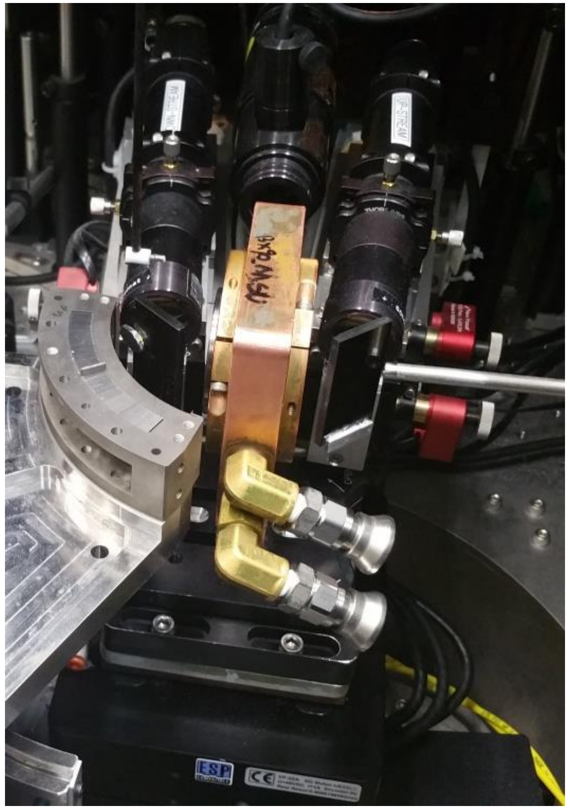
$Os_5N_{28}\cdot 3N_2$

Single-crystal XRD approaches on a multigrain/multiphase dataset allow structure solution of a novel phase

Bykov et al. 2020, Angew. Chem. Int. Ed,

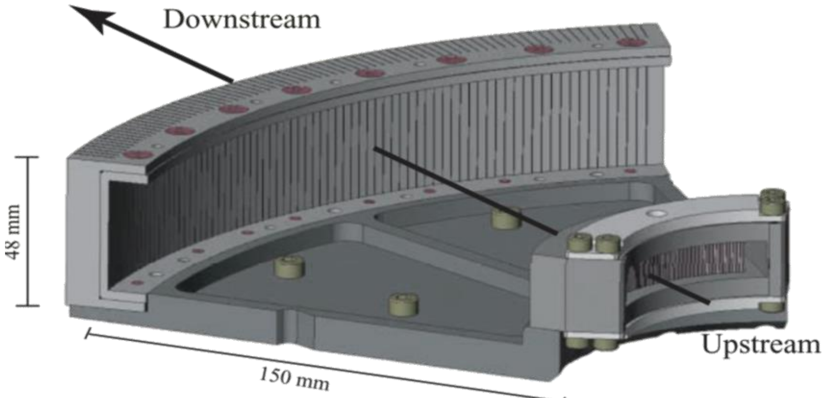
X-ray Diffraction

non-crystalline structure

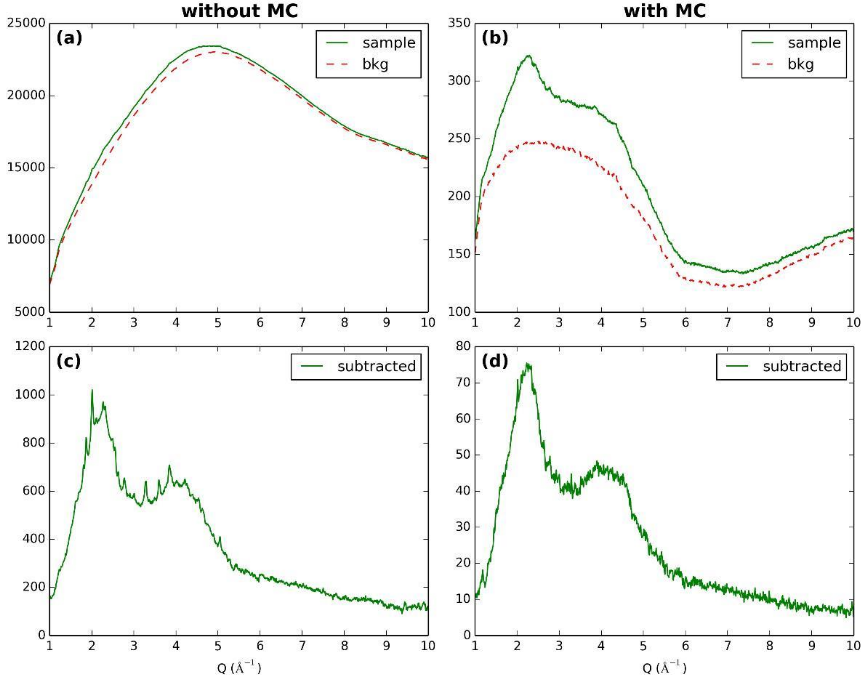


MCC system coupled with laser heating at 13-IDD

The Multi Channel Collimator designed to reduce background from the sample high pressure environment.



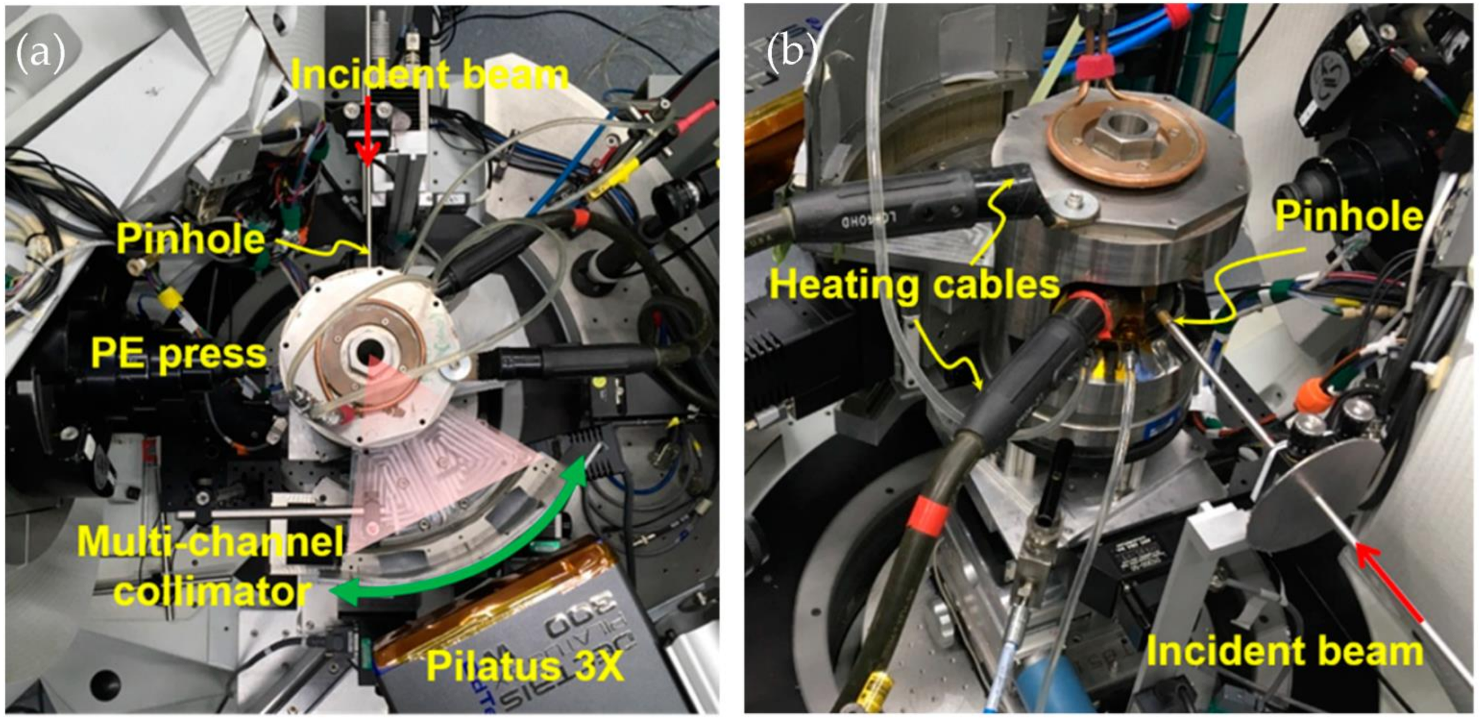
Morard et al. (2013) Rev. Sci. Instrum. **84**, 063901

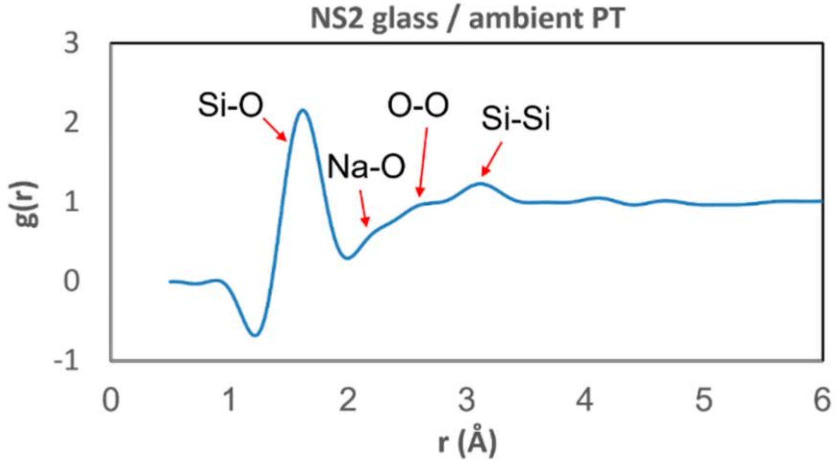


Information accessed: *Polymerization, structure factors, radial distribution functions, densities etc...*

X-ray Diffraction
non-crystalline structure

Multi Channel Collimator and Paris-Edinburgh cell to study liquids

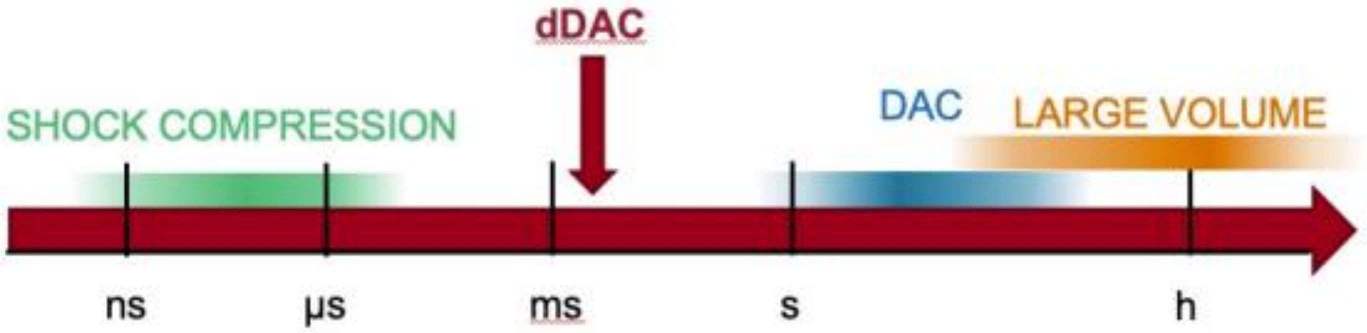




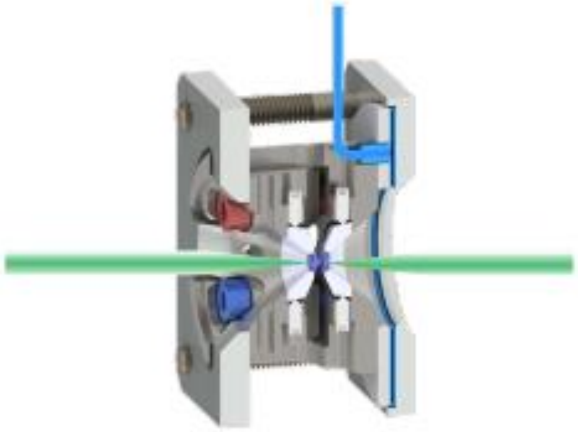
Pair distribution function g(r) of Na_2SiO_3 glass.

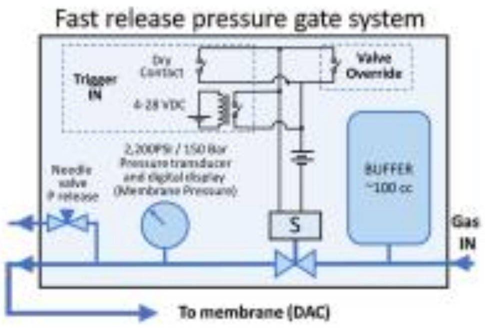
Peaks show atomic distances.

X-ray Diffraction
dynamic compression

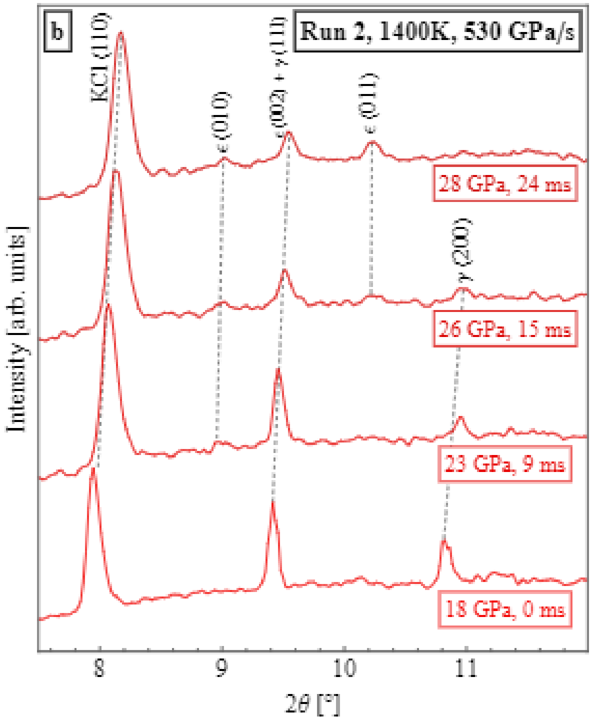


dDAC setup
Compatible with
13IDD double-sided
laser heating





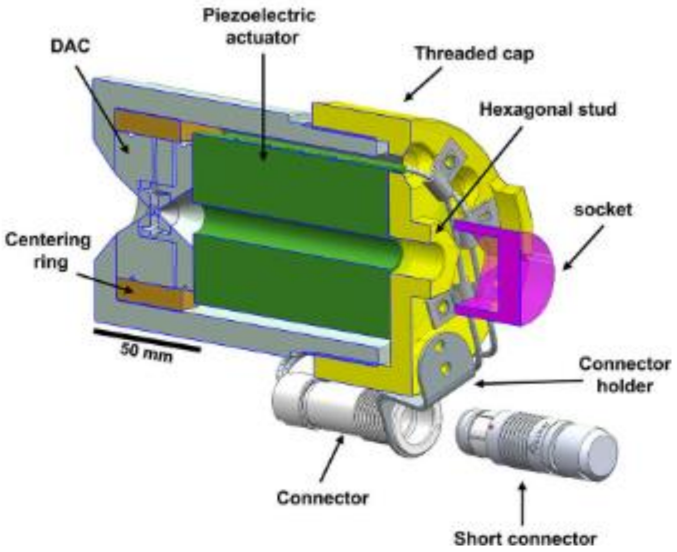
Courtesy of S. Pandolfi, SLAC

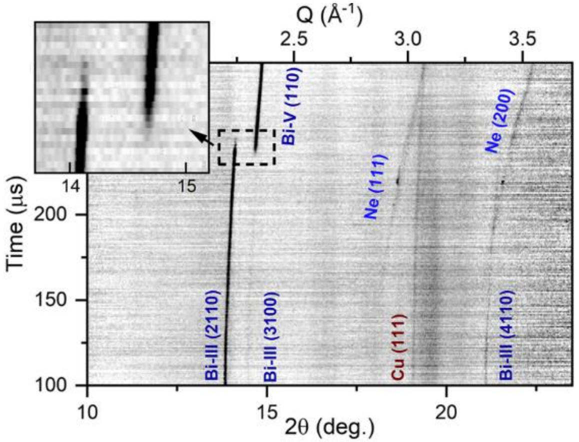


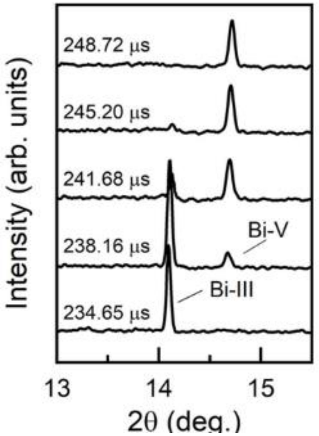
Ricks et al. 2023, submitted

X-ray Diffraction
MHz dynamic compression

Husband et al. 2023, JSR







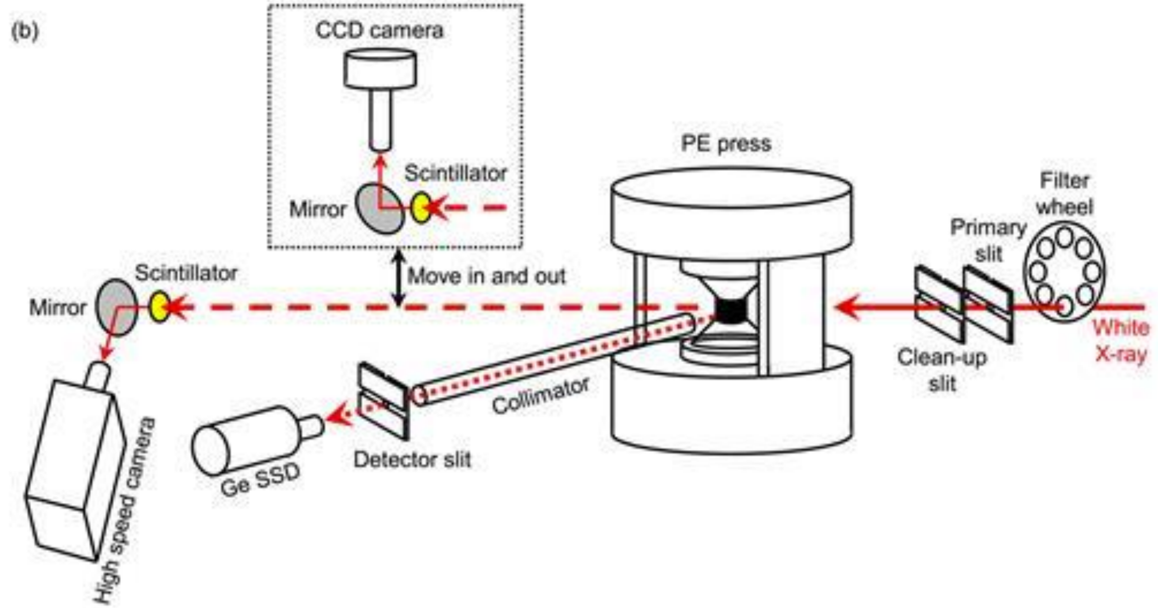
XFEL facilities provide faster X-ray diagnostics.

At EuXFEL, X-ray pulses are produced in repetition of 4.5 MHz.

In combination with dDACs we can study material behavior in the ≤ 550 μs time window.

X-ray Imaging
PE cell

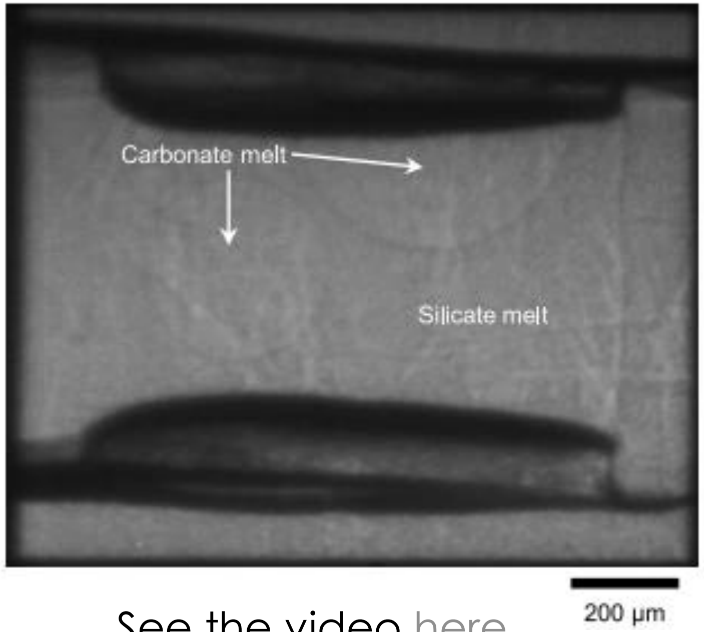
Schematic of setup at 16BM-B beamline, HPCAT, APS



Kono et al. 2015, Rec Sci Instrum

NaAlSi3O8 + CaCO3 at 2.5 GPa, 1400oC melting

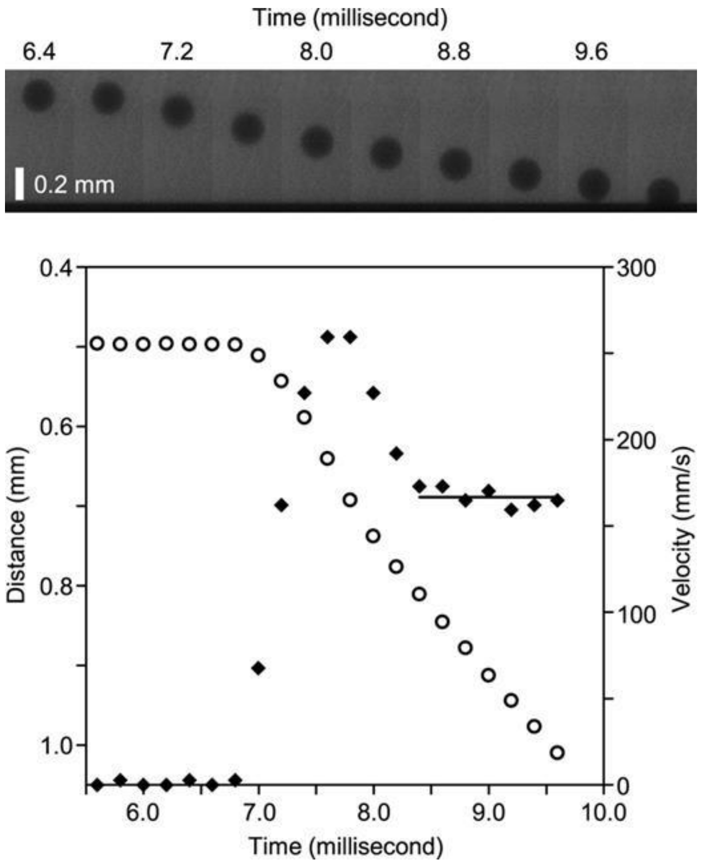
The 2 melts coexit with boundaries enhanced by phase contrast



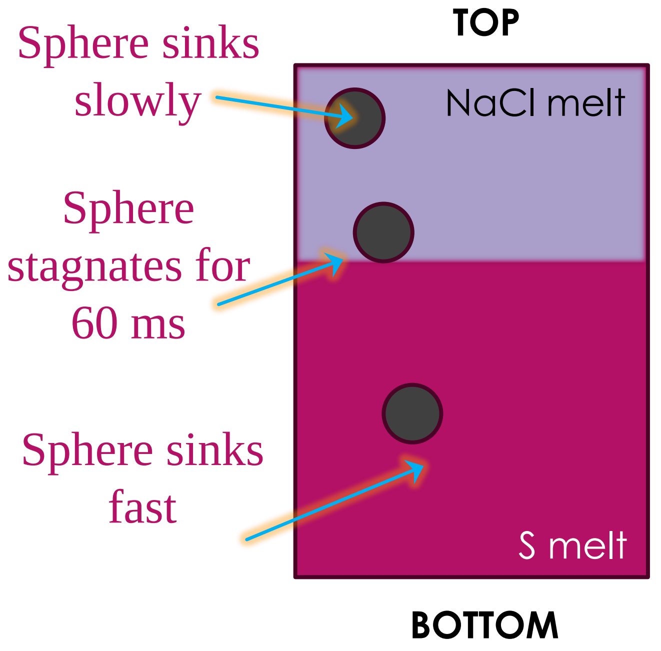
See the video here

X-ray Radiography

viscometry



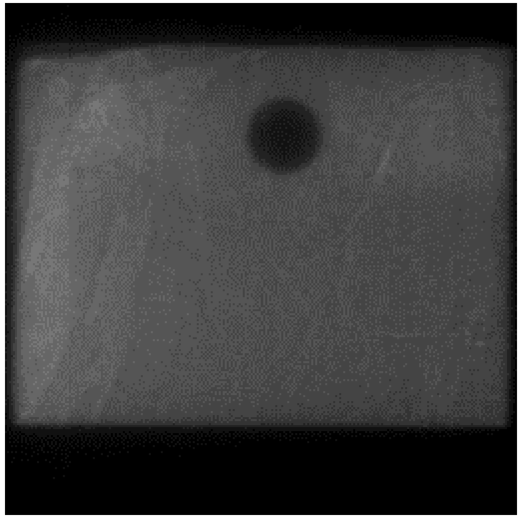
Kono et al. 2015, Rec Sci Instrum



Falling Sphere method

A WC sphere starts sinking in NaCl melt and then passes in liquid sulfur.

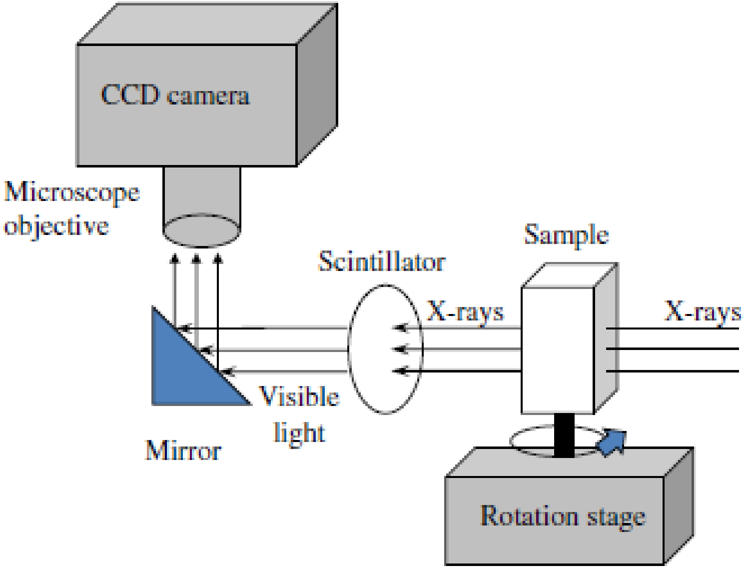
The two melts have different viscosity.

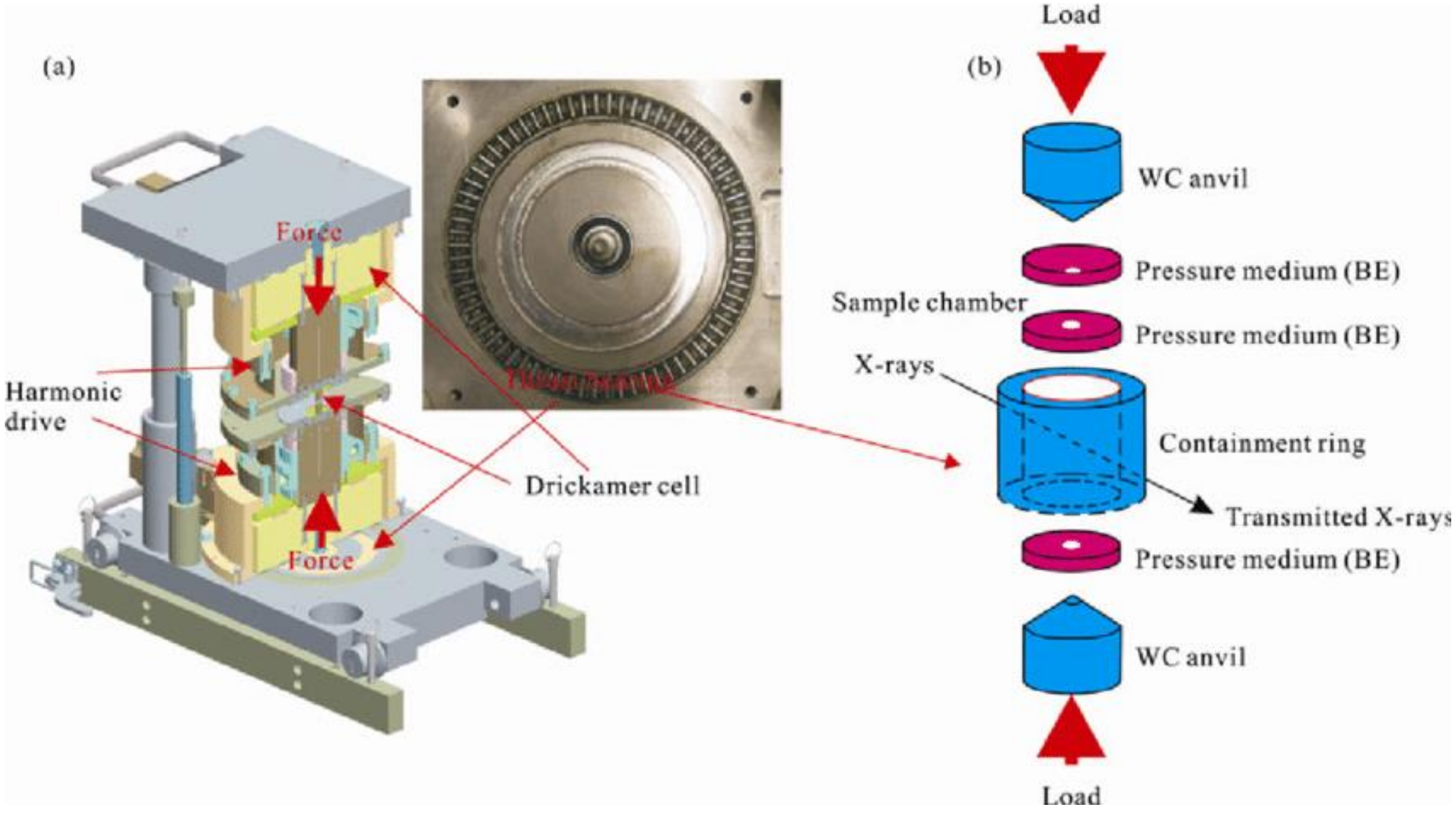


Plays 200 times slower

3D X-ray Tomography
high pressure

Principle of Microtomography set-up

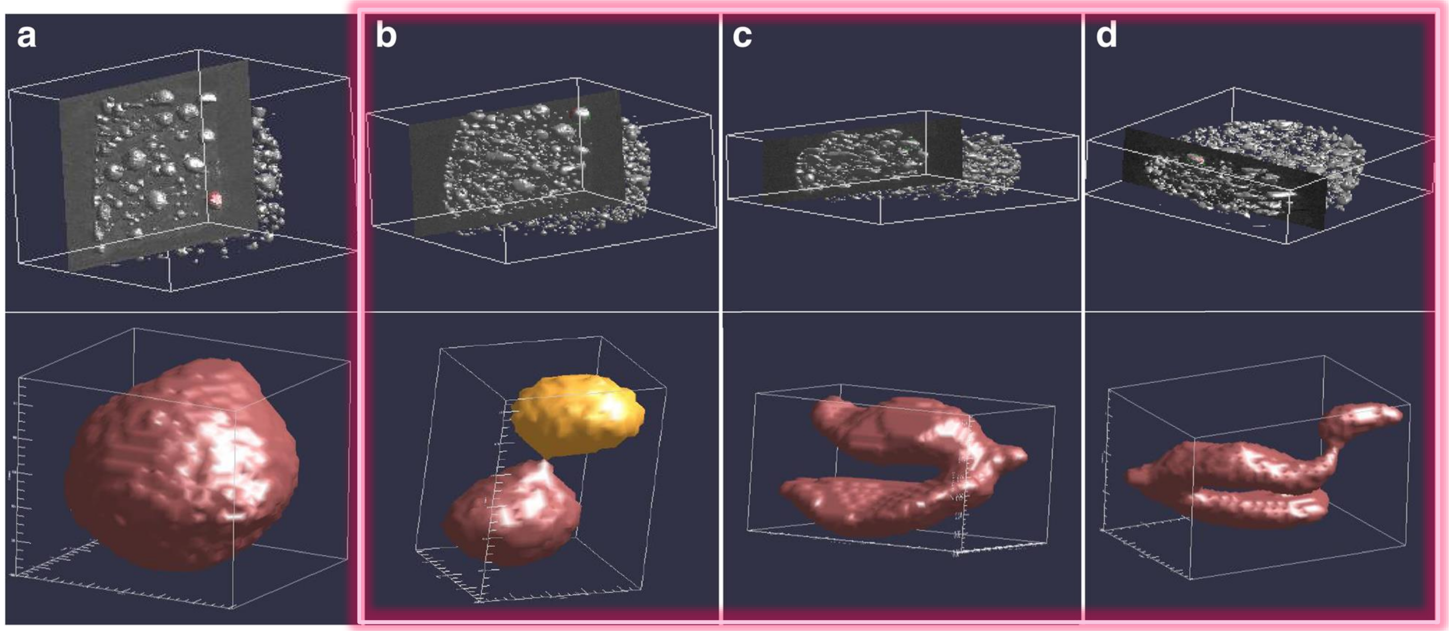




Yu et al. 2016, PEPS; Wang et al 2010, J Earth Sci

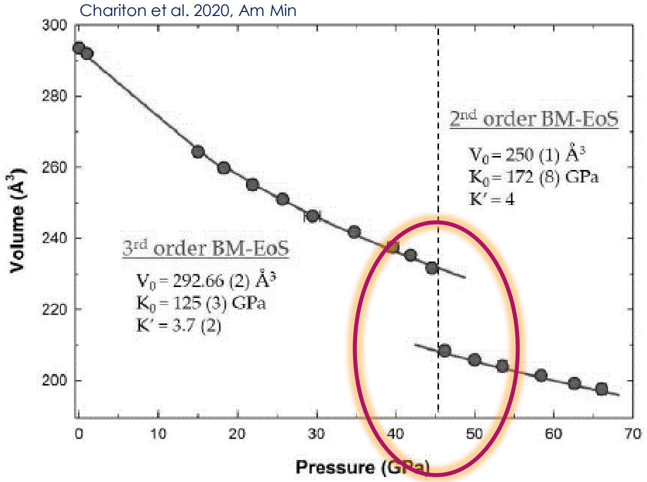
3D X-ray Tomography
study shear strain

Olivine $(Mg,Fe)_2SiO_4$ and Fe-Ni-S composite at high pressure and temperature.
While the anvils are twisted producing shear strain, 3D tomography images are collected and reconstructed.
Thanks to phase absorption contrast the olivine matrix is removed and alloy blobs are shown.



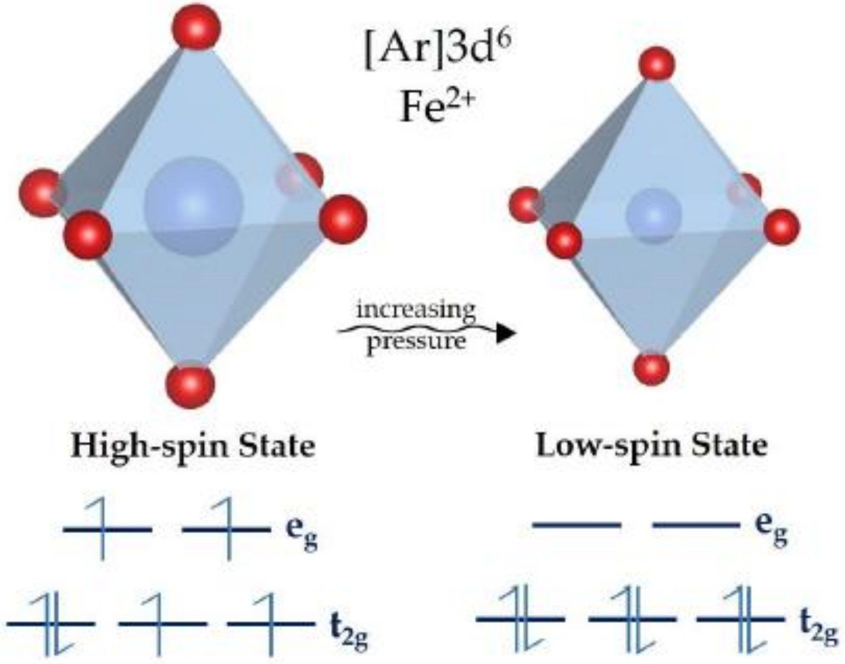
Yu et al. 2016, PEPS

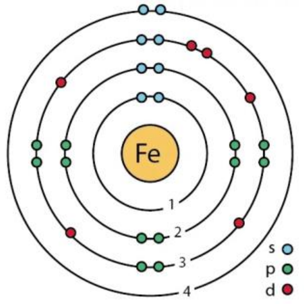
Multiple techniques combined
the story of siderite $FeCO_3$



X-ray diffraction shows a sudden volume collapse at ~45 GPa.

This is due to the Fe^{2+} pressure-induced spin transition.





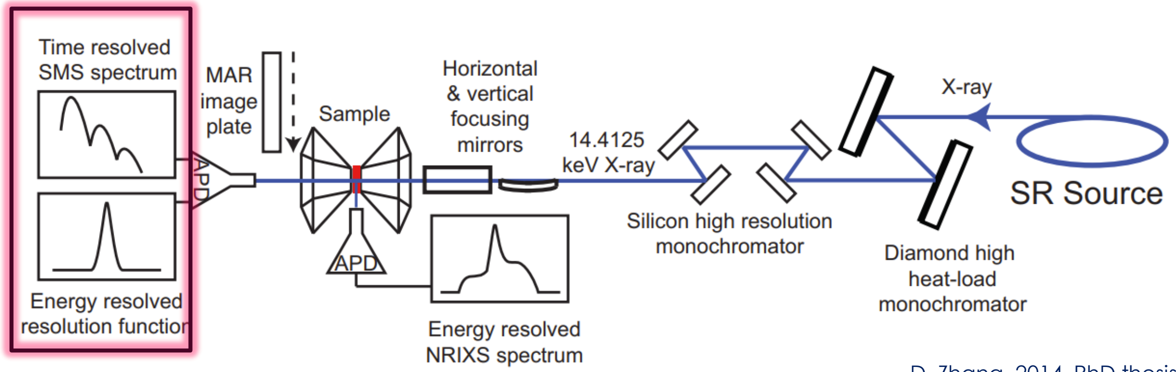
Let's see how other X-ray techniques note this transition…

Nuclear Forward X-ray Scattering (NFXS)

Synchrotron Mössbauer Source (SMS)

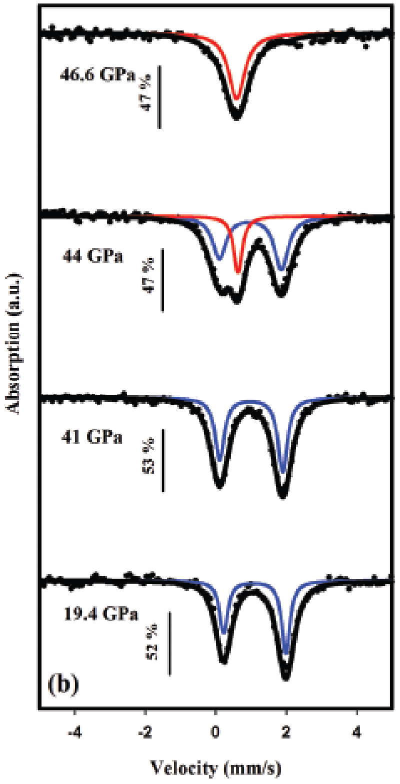
About the methods

- ✓ Phonon densities of state
- ✓ (Time-resolved) Mössbauer information
- ✓ Isotope specific (here ^{57}Fe)
- ✓ Energy at beamline tuned at 14.4 keV

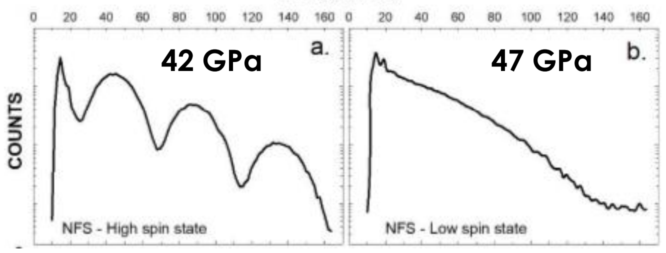


D. Zhang, 2014, PhD thesis

Cerantola et al., 2015, Am Min



Chariton et al., 2019, Am Min



NFXS

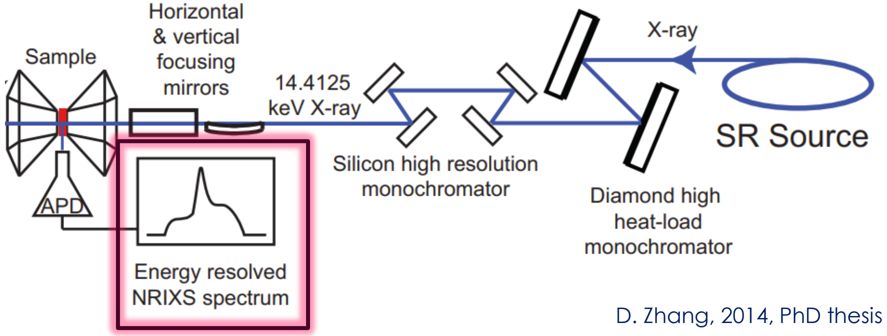
SMS

The spin crossover is clearly evident

Nuclear Resonant Inelastic X-ray Scattering (NRIXS)

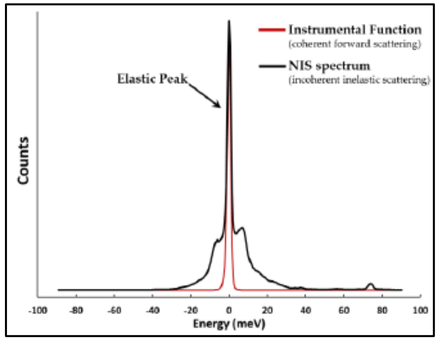
About the method

- ✓ Phonon densities of state
- ✓ Debye sound velocities
- ✓ Isotope specific (here ^{57}Fe)
- ✓ Energy bandwidth optimized in the meV range

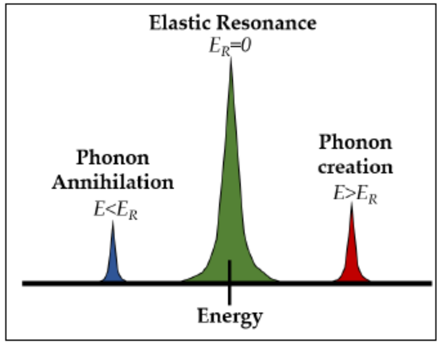


D. Zhang, 2014, PhD thesis

Chariton, 2019, PhD thesis

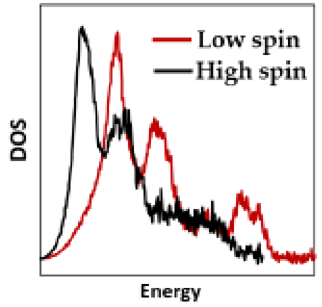


A typical NRIXS spectrum

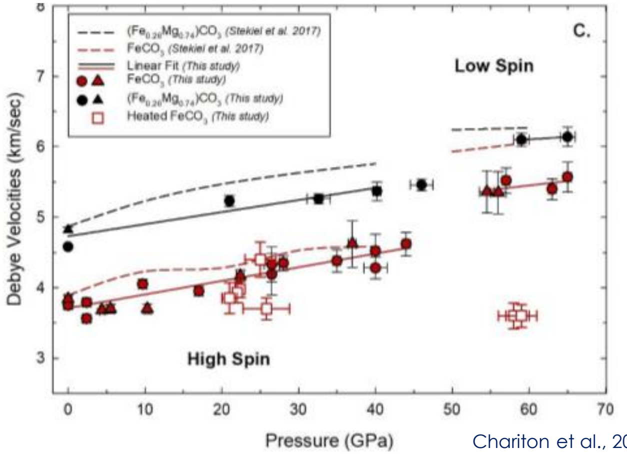


The principles in a NRIXS spectrum

Abrupt change in the density of phonon state



Sound velocities suddenly increase



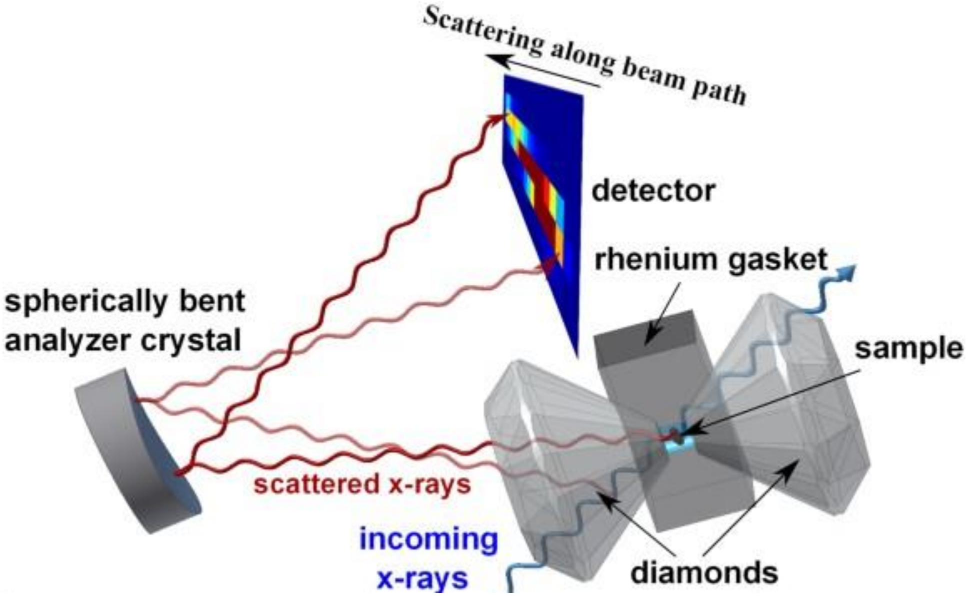
Chariton et al., 2019, Am Min

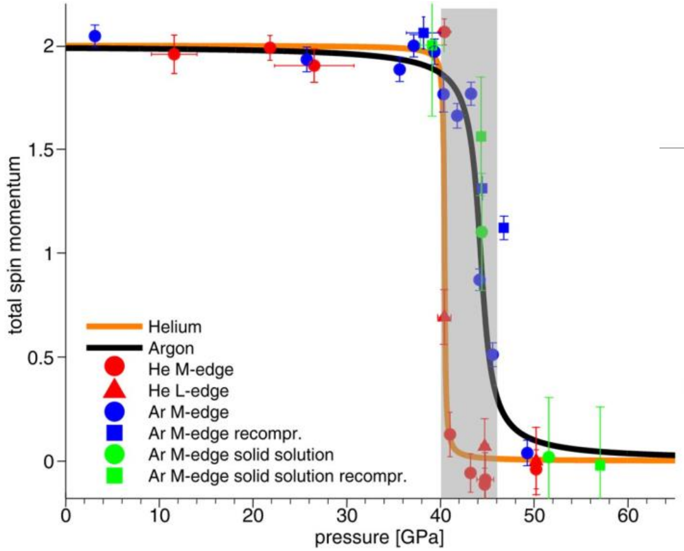
Non-resonant Inelastic X-ray scattering (NIXS) X-ray Raman scattering (XRS)

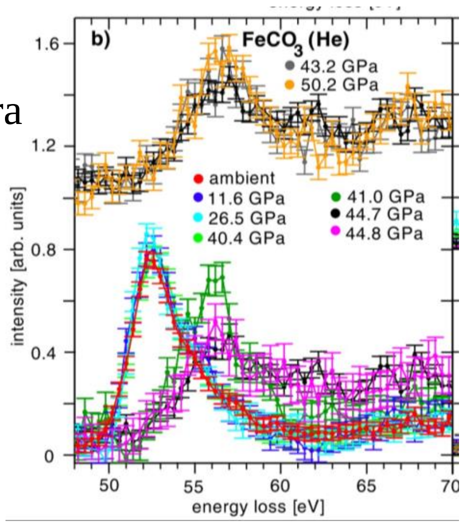
About the method

- Probe low energy absorption edges
- Sensitive to local atom coordination and oxidation state

Abrupt shift of XRS spectra





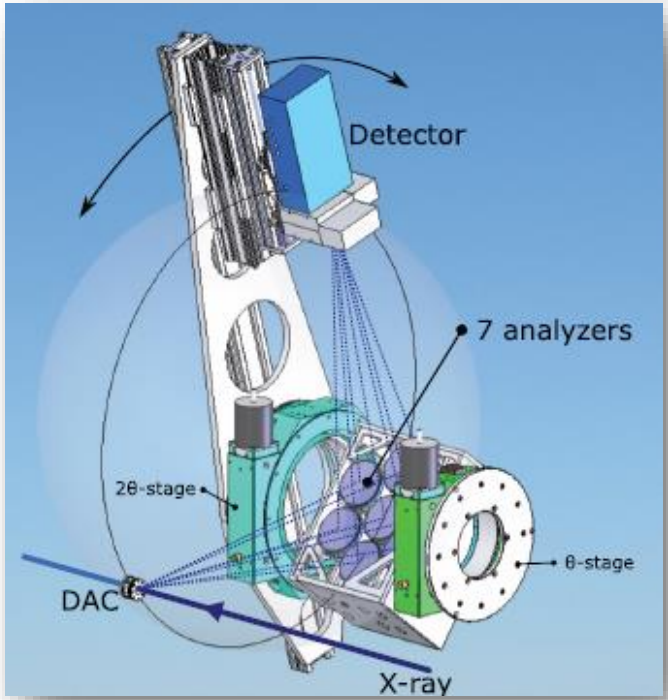


Sudden drop of spin total momentum

Different hydrostatic media suggest different onset of

Weis et al., 2017, Scientific Reports

X-ray Emission Spectroscopy (XES)



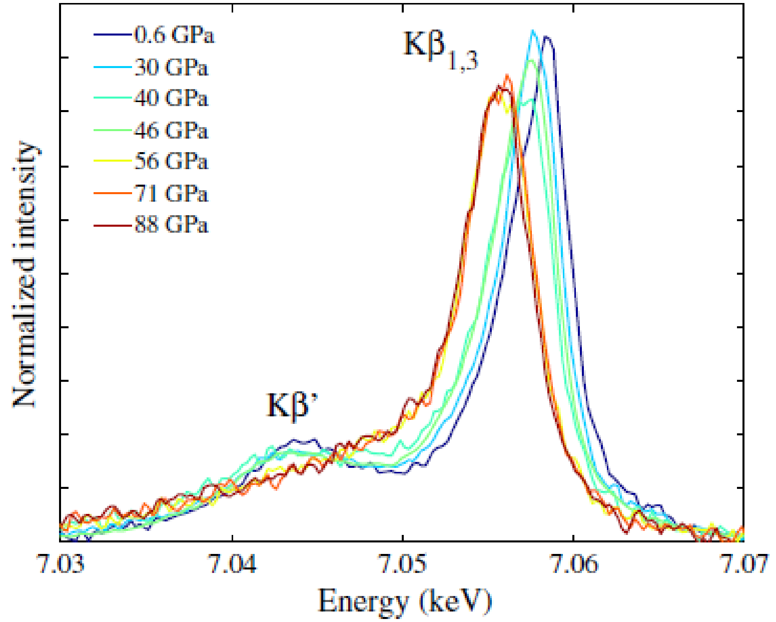
Rowland Circle spectrometer

Courtesy of Eric Rod

About the method

- ✓ Deep core electrons excited by X-rays
- ✓ Fluorescence radiation is collected
- ✓ Information on the filled electronic states
- ✓ The excitation X-ray source needs to have higher energy that that of the fluorescent photons.
- ✓ Diamond becomes increasingly absorbant of X-ray energies below 10keV, thus various geometries have been developed

Mattila et al. 2007, J Phys Condes Matter

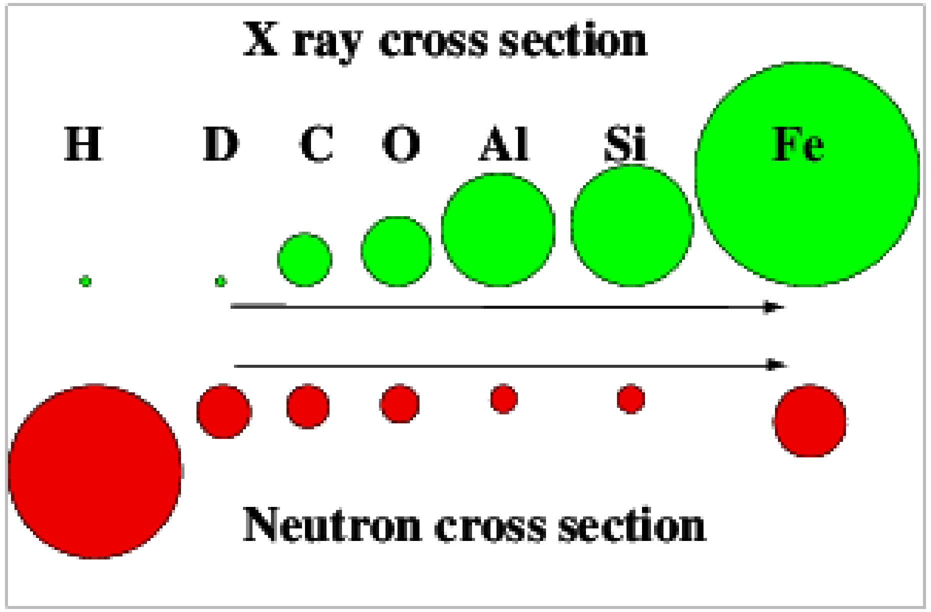


Collapse of the Kβ' satellite intensity above 50 GPa

Loss of Fe magnetic moment

Neutron Diffraction in the DAC

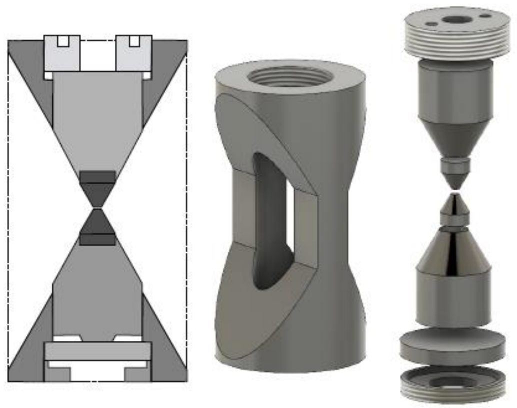
Doster, 2007, AIP conf proc



Ideal to investigate the structure of hydrous/hydride phases

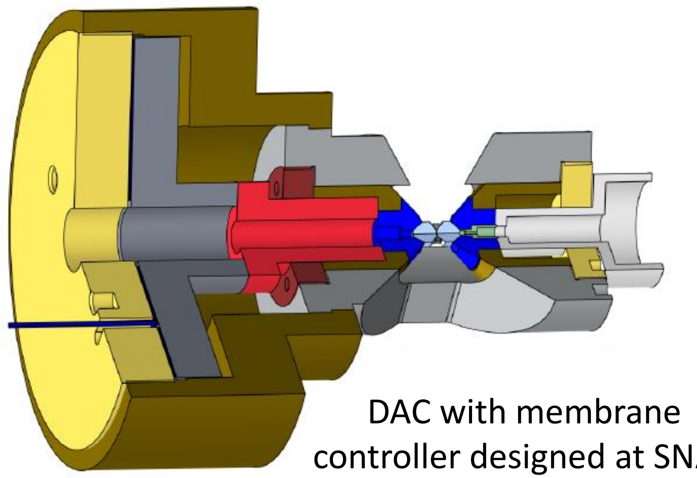
However, sufficient sample volumes are required to obtain reasonable scattering signal

Special assemblies & DACs exist for neutron measurements



Clamped DAC, Versimax anvils

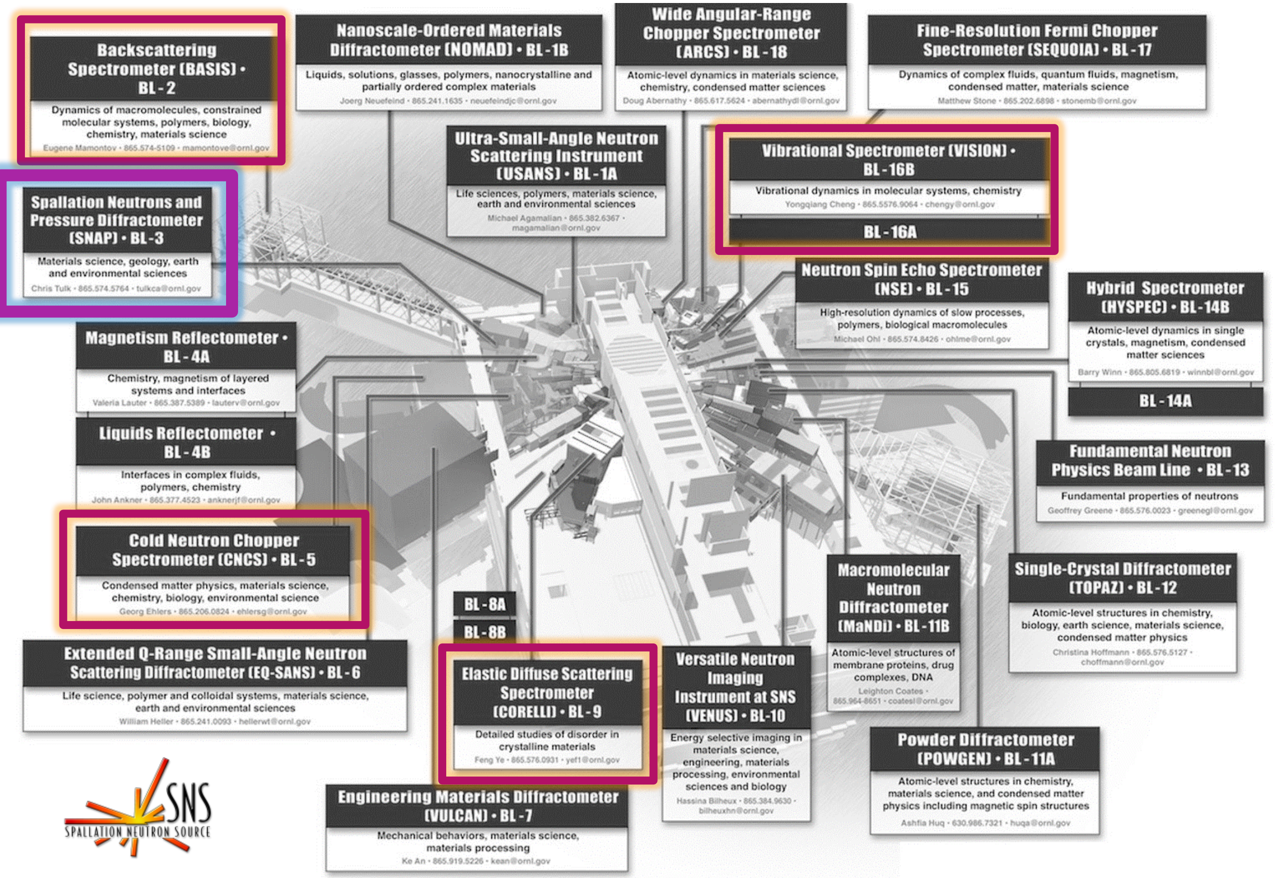
Haberl et al. 2017, High Pres Res

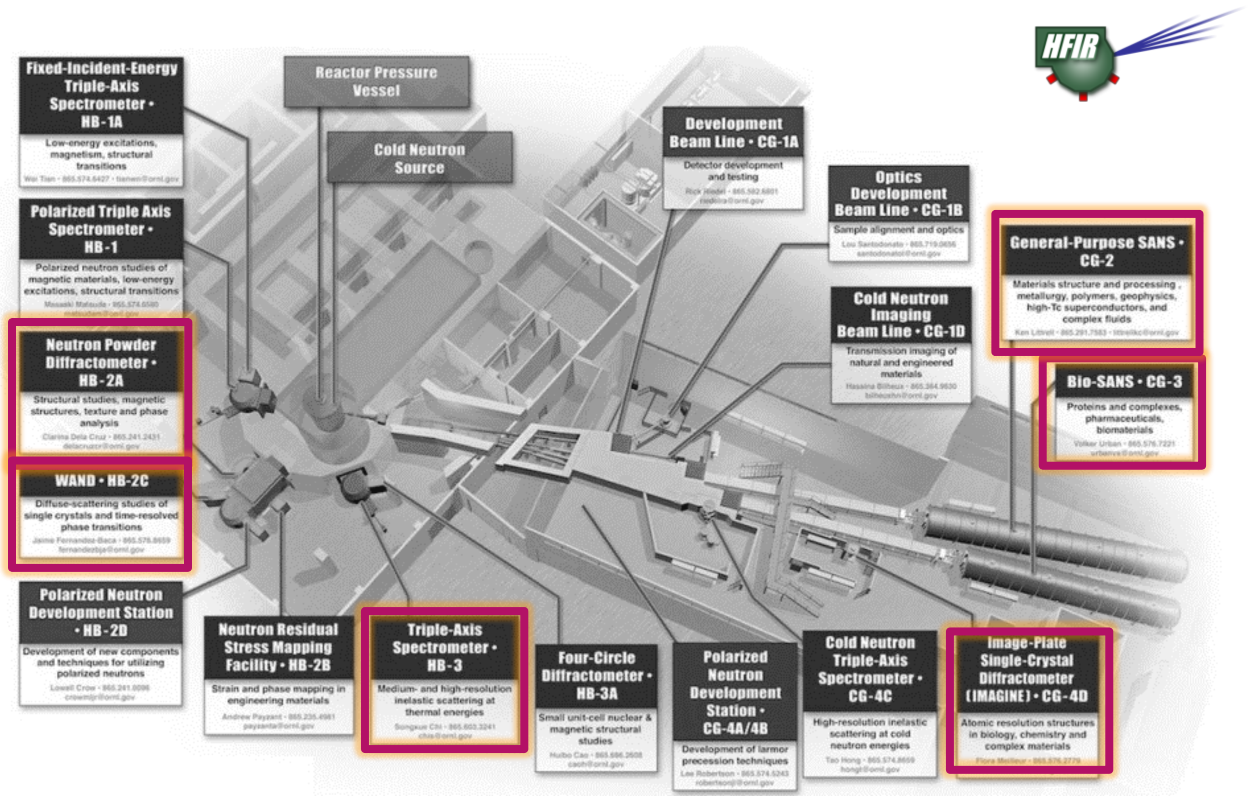


DAC with membrane controller designed at SNAP

Boehler et al. 2017, Rev Sci Instr

High pressure science in SNS and HFIR





Additional material

- Laser Shock Compression Experiments
- Paris-Edinburgh Cell
- Review – High Pressure devices at Synchrotron
- Review – DAC studies using X-rays
- Crystallography at extreme conditions
- Materials at TPa pressures in the DAC
- 3D X-ray microtomography under pressure
- Neutron diffraction at megabar pressures
- Nuclear resonant X-ray techniques in the DAC
- High pressure X-ray Emission Spectroscopy at APS

Thank you for your attention!

Any questions ?

stellachariton@uchicago.edu