2017 National School on Neutron and X-Ray Scattering

x-ray and neutron scattering &
High Pressure Science

Barbara Lavina
High Pressure Science and Engineering Center
University of Nevada, Las Vegas
barbara.lavina@unlv.edu
Outline

- high-pressure in the Universe
- significance of high-pressure research
- overview of pressure-generating devices
- high-pressure experiments and brilliance
- a very exotic world: some recent scientific highlights
- challenges of non-ambient experiments
- monochromatic high-pressure micro-diffraction and micro diffraction mapping of heterogenous samples: an example of problems and solutions in high pressure experiments
Pressure in the universe

- $10^{-17}$ Pa, intergalactic voids
- $\sim 10^{-7}$ Pa, APS storage ring
- $\sim 5$ GPa graphite turns to diamond
- $\sim 10$ GPa, at ambient T, He, H, Ne are solids
- $\sim 360$ GPa Earth’s center
- 500 GPa, hydrogen becomes a stiff metal
- $10^{13}$ Pa Jupiter interior
- $10^{16}$ Pa Sun’s core
- $10^{34}$ Pa inside neutron star


Metallic hydrogen
Dias & Silvera, Science, 2017
The composition, structure and evolution of the environment we live in depends on processes occurring deep inside the Earth. For instance,

• the atmosphere and the oceans (at least in part) were originated from the planet outgassing;
• ores formation in most cases occur at some depths;
• volcanoes and earthquakes can originate at great depths.

Large and small impacts are critical to planets formation and history. Extraterrestrial planets differ in whole composition and size but also in differentiation history. In order to understand their nature we must learn what phases might constitute their interiors.
National Security

• “As a core part of the NNSA’s advanced science and technology portfolio, the Office of ICF is working to produce thermonuclear burn conditions in the laboratory, to develop laboratory capabilities that will create and measure extreme conditions of temperature, pressure, and radiation of relevance to nuclear weapons, and to conduct weapons-related research in these environments.” (nnsa.energy.gov)

• NNSA supports large scale facilities where high-pressure research is being conducted and scientific opportunities are available.

NIF’s 192 laser beams routinely creating temperatures and pressures similar to those that exist only in the cores of stars and giant planets and inside nuclear weapons. https://lasers.llnl.gov/about

Z has so much energy that it can melt diamond, and in melting diamond to a puddle, Z scientists have been able to understand the material’s various states – from solid to liquid, with a mixed state in-between. http://www.sandia.gov/z-machine/
Material science

Pressure is a powerful tool to change properties and design materials. Areas of research include:

- superhard materials,
- superconductors & other materials with interesting electronic properties,
- high-energy-density materials and hydrogen storage,
- nuclear waste storage.

Biology and medicine

- pressure aided synthesis of pharmaceuticals
- food preservation
- life at high pressure
Understanding the behavior of matter at extreme conditions broadens and deepens our fundamental physics and chemistry knowledge. By applying pressure we can add extremely high energy to a system, dramatically affecting all physical and chemical properties. High pressure studies include:

• equilibrium phase diagrams and metastability,
• deformation (from atomic scale to bulk) in hydrostatic and non-hydrostatic conditions,
• electrical and magnetic properties,
• bonding and chemistry at extremes conditions.
High Pressure generation: common devices

Static
- the diamond anvil cell, with 50+ years of history is by far the most common device
- large volume presses
- Paris-Edinburg cells

Dynamic
- gas guns, powder guns
- laser shock

![Graph of pressure and temperature ranges](Recio et al. 2016)
The diamond anvil cell

The DAC is a small device that can generate pressures up to 1000 GPa. Temperatures range from few degrees K to several thousands degrees K. It is the most versatile instrument, with a range of designs that better suite experimental conditions and probing techniques. Several techniques are compatible exclusively with DACs.
The diamond anvil cell, recent breakthroughs

Record pressures were achieved by using a second stage nano diamond semi balls between two diamond anvils. Dubrovinskaya et al, Sci. Adv., 2016

Much increased sample volume in DACs were developed for neutron experiments.

Boehler et al. High Pressure Res., 2013
The multianvil press

These large devices can generate pressures of up to ~ 100 GPa. Temperatures range from ambient to ~2000 K. The sample is typically few mm large.

These presses are very suitable to high P-T studies, deformation of polycrystalline samples, synthesis of recoverable phases and studies of multiphase materials.
Paris-Edinburgh cell

The Paris-Edinburgh cell is the most common highP device at neutron sources as it provides relatively large samples in a relatively small device.

Max $P \sim 40$ GPa, max $T \sim 2000$ K


HPCAT, APS

https://neutrons.ornl.gov/snap/sample
Shock compression

Shock compression can achieve the highest P-T conditions

Samples are relatively large but very short-lived

Both guns and laser driven shock devices will be available at the APS, allowing for a broad range of pressure, temperature and strain rate to be achieved.
Samples under high pressure are:

• very small and/or,

• enclosed in bulky devices, access to samples is limited to semitransparent windows,

• in some case very short lived,

• often very complex (pressure gradients, multiphase, poorly crystallized)
In addition to the general advantage of brilliant source, probing high-pressure samples in situ requires

- **high flux** for the beam to penetrate the device and for scattered radiation to travel out, obtain a reasonable signal from small samples or to collect data in short time,

- **highly focused** beam in order to reduce parasitic scattering,

- **tunable energy** allowing to play with the absorption of device components and optimize resolution (diffraction).

**At high pressure you need all the brilliance you can get!!**
High Pressure at the APS

16 HPCAT 100%

13 GSECARS > 50%

4 40%

3 ~50%

35 DCS 100%
World's most intense pulsed, accelerator-based neutron source

**100% BL3-SNAP**

- **Backscattering Spectrometer (BASIS)** - BL-2
  - Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
  - Nevena Kostic - 865-241-1633 - nevena@ornl.gov

- **Nanoscale-Ordered Materials Diffractometer (NOMAD)** - BL-1B
  - Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
  - Jorgo Neumayer - 865-574-4387 - jorgo@ornl.gov

- **Wide Angular-Range Chopper Spectrometer (WARS)** - BL-1B
  - Atomic-level dynamics in materials science, chemistry, condensed matter sciences
  - Doug Anderson - 865-574-5064 - danderson@ornl.gov

- **Fine-Resolution Fermi Chopper Spectrometer (SERF)** - BL-17
  - Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
  - Matthew Stone - 865-241-5096 - matstone@ornl.gov

- **Ultra-Small-Angle Neutron Scattering Instrument (USANS)** - BL-1A
  - Life sciences, polymers, materials science, earth and environmental sciences
  - Michael Agrawal - 865-574-6367 - agrawalm@ornl.gov

- **Vibrational Spectrometer (VISION)** - BL-10D
  - Vibrational dynamics as molecular systems, chemistry
  - Victoria Chen - 865-576-4555 - victoria.chen@ornl.gov

- **Cold Neutron Chopper Spectrometer (CNCS)** - BL-5
  - Condensed matter physics, materials science, chemistry, biology, environmental science
  - Gregor Blundell - 865-574-0634 - gregor@ornl.gov

- **Extended Q-Range Small Angle Neutron Scattering Diffractometer (EQ-SANS)** - BL-6
  - Life science, polymer and colloidal systems, materials science, earth and environmental sciences
  - William Heeler - 865-574-0350 - heelerw@ornl.gov

- **Magnetism Reflectometer** - BL-4A
  - Chemistry, magnetism of layered systems and Interfaces
  - Valentina Lacerda - 865-241-5096 - valentina@ornl.gov

- **Liquids Reflectometer** - BL-4B
  - Interfaces in complex fluids, polymers, chemistry
  - Joone Andre - 865-277-6323 - andrejm@ornl.gov

- **Elastic Diffuse Scattering Spectrometer (CORELLI)** - BL-9
  - Detailed studies of disorder in crystalline materials
  - Pieter De 865-574-0351 - pieter@ornl.gov

- **Versatile Neutron Imaging Instrument at SNS (VENUS)** - BL-10
  - Energy selective imaging in materials science, engineering, materials processing, environmental sciences and biology
  - Raina Bilboue - 865-574-6360 - rnbilboue@ornl.gov

- **Hybrid Spectrometer (HYSPEC)** - BL-14B
  - Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
  - Barry Weid - 865-574-0819 - barryw@ornl.gov

- **Fundamental Neutron Physics Beam Line** - BL-13
  - Fundamental properties of neutrons
  - Geoffrey Greens - 865-574-6033 - georgeg@ornl.gov

- **Single-Crystal Diffractometer (TOPAZ)** - BL-12
  - Atomic-level structures in chemistry, biology, earth sciences, materials science, condensed matter physics
  - Christina Nefzger - 865-574-3527 - cnenfzger@ornl.gov

- **Powder Diffractometer (POWGEN)** - BL-11A
  - Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
  - Ashlee Hug - 865-886-7301 - huga@ornl.gov

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The Spallation Neutron Source is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.
The highest T superconductivity was measured at ~ 200 GPa in hydrogen sulphide
Drozdov et al., Nature, 2015

The finding was later further confirmed via nuclear resonant scattering
Trojan et al., Science, 2016
Prediction and synthesis of a stable compound of helium and sodium at high pressure. Dong et al., Nature Chemistry, 2017
Lithium isotope effect

The lightest metal still holds many surprises, even at modest P-T

Auckland et al. Science, 2017
Shocked silicon powder and crystals

Pink beam diffraction
DCS Sector 35

Time resolved shock compression of silicon allows observing the high-pressure phase at these conditions for the first time and study the reciprocal orientation of the crystals before and during the shock.
FeO$_2$ a compound first predicted from first principles calculations to be a plausible deep-Earth phase was obtained experimentally from the breakdown of FeOOH.
Synthesis of Na-H compounds

Two hydrogen-rich compounds, NaH$_3$ and NaH$_7$ were synthesized at high P-T. The characterization was performed via XRD and Raman analysis in combination with theoretical calculations.
Most synchrotron and neutron techniques can be applied to high pressure studies, but in most cases the data quality is decreased and the analysis is not straightforward.

Data are affected by limited access, absorption and scattering of the windows.

Samples might be non ideal in thickness and size, show severe strain range, coexistence of polymorphs and reacted and unreacted material.

• data analysis might require corrections and tailored manipulation,

• often the data interpretation is not unique, hence multiple techniques and theoretical calculations are necessary to solve a problem.

Synchrotron and neutron high-pressure techniques are very rapidly evolving allowing for new and better science to be performed.

This is indeed a very good time for high-pressure science as new experimental opportunities are becoming available!
XAFS, challenges of DAC measurements

DAC experiments are performed in different geometries:
• **radial**, sample thickness and uniformity are hardly ideal
• **axial**, glitches appear in the spectra due to diamond diffraction

Glitch removal algorithm
Hong et al., J.Phys.: Conf. Series, 2013

Nano crystalline anvils
Ishimatsu et al., J Synchr. Rad., 2012
Great efforts are made to obtain relatively high quality crystals, these include use of soft pressure-transmitting media and/or annealing.

Wide access conical anvils (Boehler & De Hansetters 2004) and/or semitransparent seats are critical for high-pressure crystallography.
Reciprocal space access

The DAC body determine large blind regions
- rotation range bounded by upstream cell opening
- diffracted beams are confined to a cone defined by the downstream opening

Merrill and Bassett, Rev Sci Inst, 1974

example of diffraction peaks distribution in the reciprocal space
Partial and overlapping peaks

Some peaks are discarded due to overlapping with parasitic scattering
Glitches caused by diamond diffraction

- the incident beam as well as the beam diffracted by the sample are attenuated by diamond diffraction events
- the intensity reduction is significant
- sample peaks are randomly affected by this problem
- it is possible but not practical to correct for diamond diffraction glitches
- the effect is minimized by collecting highly redundant datasets

Sketch down the vertical axis of a diamond anvil cell

Intensity of the beam transmitted through the DAC as a function of the rotation angle
Variable illuminated crystal volume

- **Crystal larger than the beam**
- **Similar size / centered**
- **Similar size / off center**
- **Small crystal**

- **\( \omega = 0^\circ \)**
- **\( \omega = 35^\circ \)**
  - **\( \text{SoC} \approx 0 \)**
  - **\( \text{SoC} \neq 0 \)**

Figure 1: The figure shows a schematic projection down to the vertical axis of a range of settings encountered in HP SXD experiments viewed down to the vertical axis. The crosshair with the two horizontal axes along the beam and perpendicular to the beam define the instrument center, the circle center defines the emergence of the \( \text{SoC} \) axis. The beam profile is represented with a color scale. The crystal is shown in blue.

Figure 2: The first three sketches show a misaligned crystal nor a large sphere of confusion instrument viewed perpendicularly to the beam direction at three values of \( \omega \) rotation. The beam is assumed to have a nearly gaussian shape where yellow/orange and red show areas of low/medium and high intensity. The sketch on the right represents the x-ray flux on the same crystal when multiple oscillations images are collected at three different horizontal positions. The x-ray flux on the misaligned crystal is highly variable in a single oscillation, the effect is smoothened by collecting multiple oscillations.
Variations of $I^*V_{cr}$: Empirical correction

- In case of crystals much larger than the beam, the volume of crystal in the beam shows a simple variation ($\cos \omega$)
- An empirical correction can be obtained for high symmetry structures
- After eventual corrections for DAC absorption, we can study the $\omega$-dependence of the relative difference between the intensity of a reflection with respect to the average of the set of equivalents: \( \frac{I_{hkl} - <I_{hkl}>}{<I_{hkl}>} \)
- We can express such changes as an $\omega$-dependent correction to be applied to the incident flux and the initial volume of crystal intercepting the beam
Comparison of refined parameters from raw and corrected data with the literature

<table>
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<th></th>
<th>Rint %</th>
<th>R1 %</th>
<th>Rall %</th>
<th>wR2 %</th>
<th>Goof</th>
<th>u</th>
<th>$U_O$ (Å²)</th>
<th>$U_T$ (Å²)</th>
<th>$U_M$ (Å²)</th>
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<td>Sasaki (1997)</td>
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<td>0.2555(2)</td>
<td>0.0084(4)</td>
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<tr>
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<td>5.3</td>
<td>5.3</td>
<td>0.253(1)</td>
<td>0.001(3)</td>
<td>0.003(2)</td>
<td>0.001(2)</td>
<td></td>
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</tr>
<tr>
<td>corrected</td>
<td>7.3</td>
<td>1.8</td>
<td>1.8</td>
<td>0.2552(4)</td>
<td>0.008(1)</td>
<td>0.0078(5)</td>
<td>0.0062(5)</td>
<td></td>
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</tr>
</tbody>
</table>

• The comparison suggests that the empirical correction can be very effective for high-symmetry crystals

• Although model-dependent, such correction may be derived, with caution, from $F_O$-$F_c$ values
Rastering oscillation images

- In some cases the instrument and sample alignment are hardly controllable. This is for instance the case of cryostat measurements requiring bulky equipment with external pipes that apply a torque on the sample stage, increasing the instrument sphere of confusion.

- A possible solution consists in the collection of multiple diffraction images at different positions at $\omega_0$.

The use of a microsphere allows excellent focusing and reproducible positioning.

Schematic view perpendicular to the beam of a rotating crystal and “three beams”.

~4 µm Re sphere.
Application: Single crystal diffraction of FeCO$_3$ to 90 GPa

Siderite at lower mantle conditions and the effects of the pressure-induced spin-pairing transition

Barbara Lavina,$^1$ Przemyslaw Dera,$^2$ Robert T. Downs,$^3$ Wenge Yang,$^4,5$ Stanislav Sinogeikin,$^4$ Yue Meng,$^4$ Guoyin Shen,$^4$ and David Schiffer$^1$

Structure of siderite FeCO$_3$ to 56 GPa and hysteresis of its spin-pairing transition
Accurate bond lengths measurements
High P-T Synthesis: New Iron Oxides

Heated spot
15-50 μm Ø
1500-2500 K

Temperature gradients cause severe heterogeneities

HPCAT-161DB
Laser heating system
Meng et al. RSI 2015
Challenges In Synthesis And Characterization

- minimal samples strain are important to characterize structures with relatively large unit cells, in a soft medium grain growth exacerbates thermal gradients
- large thermal gradients may cause chemical gradients in addition to grain size and phase heterogeneity
- non stoichiometry and defect structures are to be expected in Fe-O compounds
- such problems are much greater in systems with complex phase diagram

Most syntheses result in highly heterogeneous samples with respect to phase and grain size
As a result of thermal gradients, laser-heated samples might develop a range of grain sizes. Often, no ideal powder or single crystal patterns can be collected. It is apparent that data collection, reduction and analysis strategies needs to be tailored to the grain size.
$\text{Fe}_5\text{O}_6$ Large Grains Patterns From Selected Locations
Proper structural analysis of LH-DAC samples: Mapping, powder, SXD, multigrain analysis

In a video-publication, the procedures that led to the discovery of Fe$_4$O$_5$ are thoroughly described.

http://www.jove.com/video/50613
https://barbaralavina.wordpress.com/
Two New High-P Iron Oxides

**h-Fe₃O₄**

**Fe₄O₅**

**Fe₅O₆**

**Discovery of the recoverable high-pressure iron oxide Fe₄O₅**

**Unraveling the complexity of iron oxides at high pressure and temperature: Synthesis of Fe₅O₆**
Barbara Lavina* and Yue Meng*

PNAS | October 18, 2011 | vol. 108 | no. 42 | 17281–17285

Interesting phase mapping can be obtained reasonably fast.

The distribution of synthesized iron oxides (red: $\text{Fe}_4\text{O}_5$, blue: $\text{Fe}_5\text{O}_6$, green: wüstite) supports the inferred composition of $\text{Fe}_5\text{O}_6$, the new phase is chemically intermediate between wüstite and $\text{Fe}_4\text{O}_5$ and is in fact more abundant in between the two known oxides.

There are no evidences in the P-T range investigated of a “continuum” of $\text{Fe}_3\text{O}_4$+FeO compounds!
Summary

• The high-pressure world is extremely fascinating and exotic, far from being fully understood and explored, even for elements.

• High-pressure experiments are uniquely challenging, including achieving desired conditions, probing samples, processing and interpreting data.

• Large scale user facilities such as the APS and the SNS but many others in the USA and around the world provide unique and constantly improving research opportunities.

• Probing matter and processes as they occur in controlled environments is exciting and certainly will have an even greater role in the future.
Suggested readings

- An Introduction to High-Pressure Science and Technology
  J. Manuel Rojo, J. Manuel Menéndez, Alberto Oliver de la Roza

- Scottish Graduate Series
  High-Pressure Physics
  Edited by John Loveday

- Materials Under Extreme Conditions
  Molecular Crystals at High Pressure
  Roberto Bini, Vincenzo Schettino

- High-Pressure Crystallography
  From Fundamental Phenomena to Technological Applications
  Edited by Elena Bolzoni

- Springer