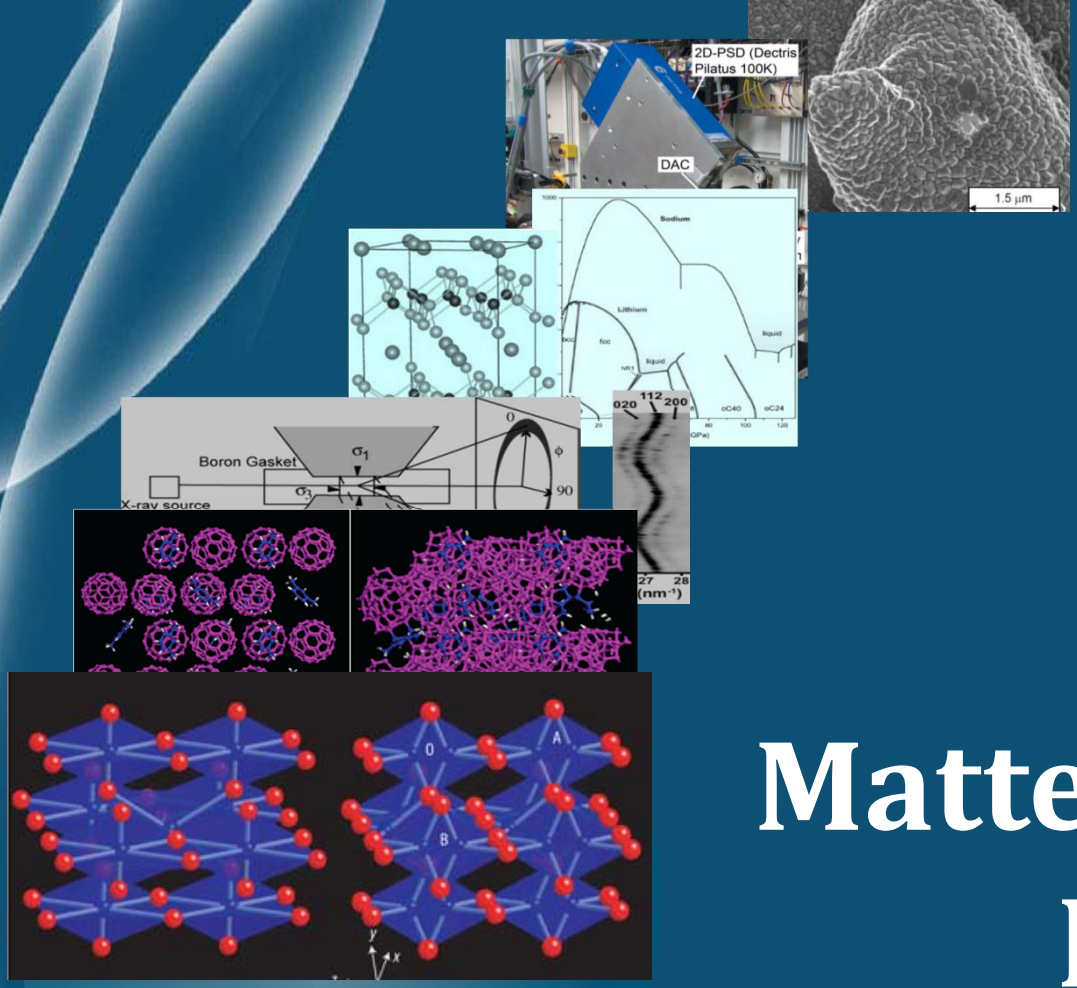

Advances in

Matter Under Extreme Conditions

HPCAT Workshop Report

October 10-12, 2012

Office of Science

National Nuclear Security Administration

Carnegie Institution for Science

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Organizing Committee:

Thomas Duffy (Princeton University)
David Funk (Los Alamos National Laboratory)
Chi-chang Kao (SLAC National Accelerator Laboratory)
Christian Mailhiot (Lawrence Livermore National Laboratory)
Guoyin Shen (Carnegie Institution Washington)
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Reaching 0.5 TPa and Beyond
Thomas Duffy (Princeton University)
Stanimir Bonev (Lawrence Livermore National Laboratory)

Time-dependent Off-Hugoniot Processes
William Evans (Lawrence Livermore National Laboratory)
Shengnian Luo (Los Alamos National Laboratory)

New Materials Discovery
Jonathan Crowhurst (Lawrence Livermore National Laboratory)
John Tse (University of Saskatchewan)

Novel States of Matter
Dana Dattelbaum (Los Alamos National Laboratory)
Andrew Cornelius (University of Nevada at Las Vegas)

Deformation and Transport Properties
Rudy Wenk (University of California Berkeley)
Yusheng Zhao (University of Nevada Las Vegas)

Liquid and Amorphous Materials
Chris Benmore (Argonne National Laboratory)
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New Technologies and Instrumentation
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EXECUTIVE SUMMARY

The study of matter at extreme conditions represents a forefront area of research activity across the sciences, including physics, chemistry, materials science and even biology. Advancing the frontier of extreme conditions science requires powerful micro-sampling probes to access minute samples through the vessel walls and to separate weak sample signals from the background signals arising from the much more massive surrounding vessel materials. The development of synchrotron radiation sources has provided the essential breakthrough.

During the last decade, the High Pressure Collaborative Access Team (HPCAT), a consortium to advance compression science and technology using synchrotron radiation at the Advanced Photon Source (APS) of Argonne National Laboratory, has pioneered key developments in high pressure technology for extreme conditions science using third-generation synchrotron radiation. A plethora of x-ray diffraction and x-ray spectroscopy techniques has been developed and integrated with high pressure, high/low temperature capabilities at HPCAT. High pressure x-ray diffraction, using energy or angular dispersive modes, provides comprehensive crystallographic, bonding, elastic, and deformation information from single-crystal, polycrystalline, nanocrystalline, and noncrystalline substances. High pressure x-ray spectroscopy, using emission, inelastic, or nuclear resonant scattering techniques, yields phonon dynamics, charge dynamics, electronic and spin states of materials under high pressure and high/low temperatures. These new tools, integrated with hydrostatic or uniaxial compression, static or dynamic loading, laser heating, cryogenic cooling, and large volume presses, have enabled investigations of high pressure structural, vibrational, electronic, and magnetic properties that were unimaginable only a decade ago.

The discovery and observation of new phenomena have become the norm in daily operations at HPCAT. Research carried out at HPCAT has provided fundamental knowledge of the behavior of materials in a broad range of environments, such as pressure, temperature, radiation, and deviatoric stress, including both static and dynamic phenomena. Investigations of structure, equations of state, and electronic and magnetic properties provide critical data for code validation and tests of fundamental theory. Measured structure-property correlations help to establish predictive models for developments of new materials and new applications. Data on materials properties at conditions occurring within the Earth and planetary interiors provides essential keys for understanding the mineralogy, dynamics and composition of the Earth and other planets.

A decade of forefront scientific investigations at HPCAT has provided the basis to launch and chart the next generation of high-pressure synchrotron research. At the same time, the HPCAT facility is aging and has reached a critical stage for a major upgrade to stay at the cutting edge. The workshop attendees enthusiastically concluded that a major upgrade of HPCAT is necessary in advancing compression science using synchrotron radiation and developing novel high energy x-ray diagnostic probes optimal for studying materials at extreme conditions. Taking full advantage of the APS Upgrade Program (APS-U) for unmatched brilliance and matching optics and novel integrated techniques, HPCAT can significantly improve both spatial and temporal resolution and provide the superior

tools for the community to lead the next level of development of compression science. In addition to traditional “static” or “dynamic” experiments, there will emerge developments that will provide novel x-ray capabilities covering a time domain that fills the gap between “static” and “dynamic” compression.

As a result of the many successes of HPCAT, extreme conditions science is now one of the major thrust areas of the APS, the nation’s most brilliant hard x-ray synchrotron radiation source, and its facility operated beamlines. Many specialized beamlines with unique capabilities have been built for various experiments and hold great potential to be further integrated for extreme conditions science. The High Pressure Synergetic Consortium (HPSynC) was established to facilitate the next level of scientific advancement in this field by working with high pressure scientists and beamline staff at these specialized beamlines. The goal of HPSynC is to collaborate with these sectors at the APS through the coordinated development of high pressure devices and expertise to make extreme conditions science a site-wide emphasis. The creation of Dynamic Compression Sector at APS (DCS@APS) will augment this thrust by bringing the expertise, instrumentation, and user community in dynamic compression to the APS.

Together with the APS-U in parallel with the arrival of DCS@APS, this is clearly an opportune time for high compression science to take full advantage of this confluence of expertise in extreme conditions research, along with the unmatched brilliance and significantly improved spatial and temporal resolution that the facility-wide upgrade will provide. The interaction and coordination provided by a dedicated NNSA center for extreme conditions research at the APS will not only facilitate key breakthroughs for high compression science, but will at the administrative level take advantage of cost sharing for projects at multiple beamlines, beamtime allocation for complementary experiments and feasibility tests, and the sharing of unique equipment (e.g., fast detectors). This Center, interacting with the facilities and personnel at HPCAT and DCS, along with other complementary APS beamlines, will form the structure of a research environment for extreme conditions science that is unique in the world. This coordinated effort will also serve as a model for planned activity at future light sources, such as NSLS-II at BNL and MaRIE at LANL.

This report documents the proceedings of the workshop, "Advances in Matter under Extreme Conditions," held at the APS in October 2012. A retrospective of the successes of HPCAT over the past 10 years, as well as opportunities for addressing key grand challenges in future of extreme conditions science were discussed by over 120 people from the US and abroad. Emerging from the workshop and its discussions is a clear signal of the outstanding opportunities for the future of extreme conditions science at the APS in the years to come.

I. HPCAT TODAY

1. BACKGROUND AND OVERVIEW

Figure 1: *HPCAT: an integrated high pressure facility located at Sector 16 of the Advanced Photon Source.*

During the past decade, HPCAT has taken advantage of the nation's most brilliant high energy synchrotron source and developed a multitude of integrated synchrotron radiation techniques optimized for high pressure research. These x-ray probes, integrated with hydrostatic or uniaxial compression, static or dynamic loading, resistive or laser heating, and cryogenic cooling, have enabled users' investigations of structural, vibrational, electronic, and magnetic properties at high pressure and high/low temperature that were not possible a decade ago. Numerous discoveries and observations of new phenomena have been observed at the facility over the years. Research work at HPCAT provides fundamental knowledge of the behavior of materials in a broad range of environments, such as pressure, temperature, radiation, and deviatoric stress, including both static and dynamic phenomena. Investigations of structure, equations of state, and electronic and magnetic properties provide critical data for code validation and tests of fundamental theory. The measured "structure-property" correlations help to establish predictive models for developments of new materials and new applications. Data on materials properties at conditions occurring within the Earth and planetary interiors provides essential keys for understanding the mineralogy, dynamics and composition inside the Earth and other planets.

HPCAT started in 1999 with a DOE-BES grant to the Carnegie Institution of Washington (CIW) and a one-time CIW-endowment seed fund. Soon afterward, DOE-NNSA funded Lawrence Livermore National Laboratory (LLNL) and University of Nevada at Las Vegas (UNLV) to join as HPCAT Members, and several years later, University of Hawaii (UH, a 5% Member supported by a DOD grant, discontinued after 3 years) and the DOE-NNSA funded Carnegie/DOE Alliance Center (CDAC) also joined as HPCAT Members. Together this consortium developed the integrated HPCAT facility including the insertion-device (16ID) beamline which has two branches operational independently, and the bending magnet (16BM) beamline which is split into two branches and operates independently by dividing the radiation fan.

The main features of the HPCAT facility are: (1) Science driven – the techniques are chosen for their maximum impact in the multidisciplinary and interdisciplinary high-pressure sciences. (2) Optimized for high pressure devices - the x-ray energy, energy resolution, x-ray beam size, background discrimination, detector configuration, etc. are optimized with consideration of high pressure vessels and samples at high pressure conditions. (3) Integrated capabilities - the multiple techniques at HPCAT are integrated for complementary information to enhance the common scientific goal. (4) Comprehensive support equipment - a number of supporting instruments have been developed for controls and measurements of pressures and temperatures, complementary optical and magnetic measurements, and sample handling and preparation.

HPCAT has been exceedingly successful and productive in advancing high-pressure science and technology using synchrotron radiation. More than 230 individual users performed experiments at HPCAT in each of the past three years. Many are partner users and returning users, making the "person-visits" more than 500 each year. Among them, more than 60% are students and post-doctoral associates. Every year, there are about 10 Ph.D. theses and 3-4 Master degree theses completed based partly on experiments at HPCAT. In addition to numerous reports to the federal programs, HPCAT experiments have resulted in >1.5 peer reviewed papers per week, among which >23% appear in high profile journals with impact factors ≥ *Physical Review Letters*.

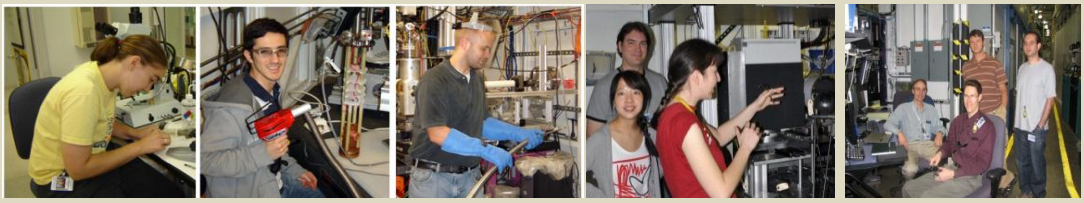
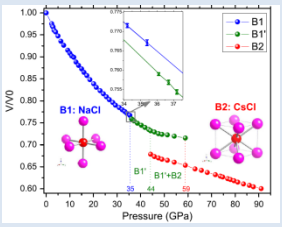
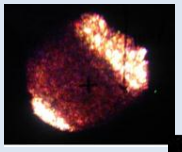


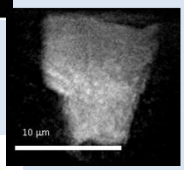
Figure 2: *More than 230 individual users each year performed experiments at HPCAT. Among them, more than 60% are students and post-doctoral associates.*

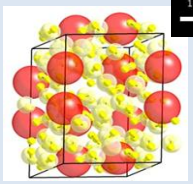
ESTABLISHED HPCAT CAPABILITIES

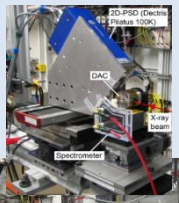
- ***Probing structures at various scales of space and time***: By using x-ray diffraction and x-ray imaging techniques, structures of materials at various scales—from amorphous, nano- and polycrystalline, single crystal, to microstructure of composite materials—can be determined *in situ* at high pressures and high/low temperatures. Fast imaging and diffraction measurements can be performed at the sub-millisecond to 100 ns level for high pressure samples to be recorded with time-resolved information in materials transport property, metastability, and transition kinetics.
- ***Measuring electronic, phonon, and magnetic properties:*** By using x-ray spectroscopy and inelastic x-ray scattering techniques pioneered at HPCAT, measurements of phonon dynamics, charge dynamics, and electronic and spin states of metals, alloys, oxides, nitrides, hydrides, new superconductors, and new superhard or other super-durable materials at *in situ* high pressures and high/low temperatures can be performed at HPCAT.
- ***Multi-megabar pressures and temperatures from 4 K to over 6000 K***: With a typical probing size of 3-5 μm, materials behavior at multi-Mbar pressures (>350 GPa) can be investigated at the HPCAT facility. Use of cryostats equipped at beamlines allows for exploring properties of materials at temperatures down to 4K. With online or portable laser heating systems, we can reach temperatures over 1 eV (>11,000 K) on compressed samples; however, reliable temperature determination is still within the range below 6000 K.

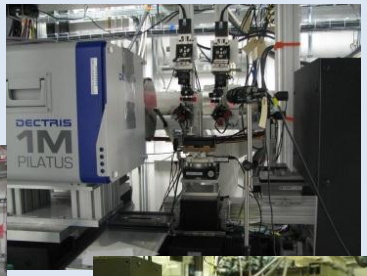


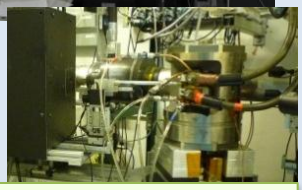


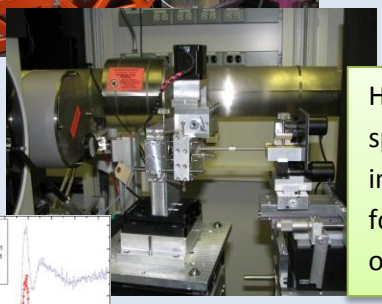




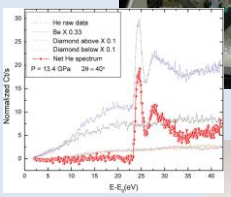


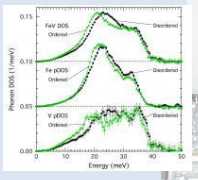






High-pressure diffraction, spectroscopy, and imaging techniques in four independent operational beamlines





Support equipment

2. AN INTEGRATED FACILITY

Dedicated for high pressure research, an array of x-ray techniques in diffraction, spectroscopy, and imaging have been developed or pioneered at HPCAT for addressing fundamental questions in physics, chemistry, materials sciences, geosciences, and biosciences. There are four simultaneously operational beamlines at HPCAT (16-ID-B, 16-ID-C/D/E, 16-BM-B, 16-BM-D), with specialized x-ray optics and high pressure synchrotron radiation instruments in nine stations. Further details are given in Appendix A.

2.1 High Pressure X-ray Diffraction (XRD)

XRD has long been the essential and versatile probe for *in situ* determinations of phases, structures, charge distributions, and materials elastic properties and plastic deformations, etc. It is by far the most widely used technique by users. The HPCAT beamline 16-ID-B is fully dedicated for XRD; large portions of 16-BM-D (>90%) and the 16-BM-B (>50%) operations are used for XRD programs. At 16-ID-D, complementary XRD is established as an integrated component.

- Angle dispersive XRD (ADXD): Using a monochromatic x-ray beam and an area detector, HPCAT has advanced and refined ADXD with a small focused x-ray beam (3-5 μm) of sufficient flux suitable for performing XRD experiments. HPCAT offers a wide energy range (12-70 keV) for various experimental needs, excellent collimation systems for small, clean, focused beam, and detector selections of CCD, imaging plate, or Pilatus. Typical resolution in d-spacing is $\Delta d/d$ ~1-3x10^{-3}.
- Energy dispersive XRD (EDXD): Using a polychromatic x-ray beam and an energy dispersive detector, EDXD is mainly used for studying liquid and amorphous materials, where one takes the EDXD advantages of high depth resolution, low background, and large coverage in reciprocal space. The EDXD technique at 16-BM-B is integrated with a Paris-Edinburgh cell which is capable of generating pressures up to 12 GPa and temperatures over 2500 K.
- Anomalous XRD: When x-ray energy is tuned near an absorption edge of a specific element, XRD provides detailed information on the selected element.
- Radial XRD: While typical XRD experiments are carried out at HPCAT with the incident x-ray beam passing through the loading axis of diamond anvil cell, in the radial XRD geometry the incident x-ray beam impinges upon the sample at a $90^{o}\pm30^{o}$ angle relative to the loading axis through an x-ray transparent gasket. Radial XRD provides a wealth of information on lattice preferred orientation, lattice strain, and materials deformation and strength.
- Single-crystal XRD: The small x-ray beamsize and high-precision sample control systems at HPCAT allow for conducting single-crystal XRD on micro-size crystals at Mbar pressures. Single-crystal XRD provides robust information on phase identification and crystal symmetry (space groups). It has advantages in dealing with samples of low symmetry structures and/or multiple phases. The diffraction intensity, when properly measured, can be used to derive detailed structural information on atomic positions, order-disorder, thermal parameters, and charge distributions.

- Amorphous XRD: Both ADXD and EDXD are routinely used at HPCAT for studying amorphous and liquid materials at extreme conditions. With ADXD, several methods have been developed for accurate background subtraction, together with high energy x-rays and diamond anvil cells with large openings for large coverage in reciprocal space. EDXD is integrated with a Paris Edinburgh cell as described above. Amorphous XRD provides information for understanding the local and intermediate range ordering of amorphous and liquid materials.
- Laue XRD: provides information on texture of crystalline materials, and strain, dislocation arrangements, domain structure, and slip systems of single crystals. The use of a polychromatic beam provides large reciprocal coverage and eliminates the need for rotating samples. This technique has great potential in studying materials deformation and defects evolution in a time-resolved manner.
- High-resolution XRD: In many high *P-T* transitions, such as electronic and topological transitions, magnetic collapse, and piezoelectric transitions, the structural changes are subtle and difficult to detect with normal ADXD. HPCAT has improved d-spacing resolution of high-resolution XRD, which is essential for studying the behavior of the subtle transitions.

Established Techniques at HPCAT

- **X-ray Spectroscopy**
  - X-ray absorption (XANES, XAFS, PFY)
  - X-ray emission (XES, RXES)
- **Inelastic X-ray Scattering**
  - Inelastic x-ray scattering (x-ray Raman, 1eV)
  - X-ray nuclear resonant inelastic scattering (NRIXS, 2meV)
  - X-ray nuclear forward scattering (Mössbauer)
- **X-ray Diffraction**
  - μ-XRD integrated with laser heating, cryostats
  - μ-XRD integrated with XAS
  - Single crystal XRD
  - Laue XRD
  - X-ray PDF (for amorphous and liquid materials)
- **X-ray Support Equipment**
  - Double sided laser heating
  - Various cryostats
  - Paris-Edinburgh cell
  - A numbers of on-line and off-line systems
  - Software

Key Features of the HPCAT Facility

- Four simultaneously operational beamlines
- Probing x-ray beam size suitable for high pressure equipment
- Tunable x-ray energies for various x-ray measurements
- High energy resolution (1eV-1meV) for x-ray scattering and spectroscopy
- Precise collimation systems for optimal S/N ratios
- User friendly operation

2.2 High Pressure X-ray Spectroscopy (XRS) and Inelastic X-ray Scattering (IXS)

HPCAT has pioneered developments in XRS and IXS techniques which provide unique probes for studying electronic structures and phonon dynamics. HPCAT beamline 16-ID-D is fully dedicated for XRS and IXS, where multiple XRS and IXS techniques have been developed. These techniques are compatible with each other, with minimum switch-over

time between different measurements. Several techniques, including XRD, can be integrated for simultaneous measurements on high pressure samples. The beamline 16-BM-D is also partially used for XRS. HPCAT has put significant effort toward optimizing the efficiency, accuracy, and sensitivity of each technique using various geometries and state-of-the-art detectors and x-ray optics.

- X-ray absorption near edge spectroscopy (XANES): With monochromatic x-ray beams scanning tens of eV across absorption edges, XANES provides information on electronic states in the conduction band, revealing properties including valence state, orbital-occupancy, hybridization, charge transfer, and electronic ordering.
- X-ray absorption fine structure (XAFS): The fine absorption features hundreds of eV above the absorption edges reveal element-specific information on local atomic arrangement that is particularly valuable for amorphous materials and in low concentration materials.
- X-ray (resonant) emission spectroscopy [(R)XES]: In XES experiments, the core electrons are excited by incident x-rays and the decay emission x-rays are collected by an XES spectrometer with sub-eV energy resolution. XES characterizes core electrons and occupied density of states with weak influence of nearest neighbor species. The established XES at HPCAT has been widely used as a unique probe for the diagnosis of pressure-induced spin transitions in transition elements. RXES, or partial fluorescence yield (PFY) spectroscopy, has also been successfully utilized at HPCAT. RXES may be viewed as a combination of XES and XAS. Instead of collecting transmitted x-rays as in XAS, emission spectra are measured at each step as the incident beam energy is changed or scanned across an absorption edge. This resonant method significantly enhances footprints of electron states, and has a remarkable sharpening effect in projected spectra (RXES or PFY).
- X-ray fluorescence spectroscopy (XFS): This method permits determination of solubility of minerals in fluids at a few ppm level, and can be used for multi-element analytical probes and for studies of dissolution kinetics. In XFS experiments the fluorescence signals (e.g., K_{α}, K_{β}, or both) are collected by a solid-state energy dispersive detector. A confocal geometry is used for minimizing unwanted background signals.
- Inelastic x-ray scattering (IXS): With ~1eV energy resolution, IXS (often called x-ray Raman spectroscopy) is emerging as a powerful x-ray spectroscopic probe. Through IXS, fundamental electronic structure and dynamics of electron gas, strongly correlated systems such as superconducting materials, excitons, plasmons, and their dispersions can be obtained, which provides critical data for code validation and tests of fundamental theories. Either momentum resolved or momentum integrated IXS can be measured for various needs. Soft x-ray absorption spectra may be acquired with high energy x-rays which provide penetrating power through walls of a high-pressure device. For example, K edges of light elements (Be, B, C, N, O…) under conditions can be measured by IXS.
- Nuclear resonant inelastic x-ray scattering (NRIXS): Using incident x-rays of meV resolution tuned near the exceedingly narrow nuclear resonant line (at neV level), the NRIXS is measured using time discrimination electronics because of the narrow nuclear absorption. At HPCAT, we have established NRIXS for ^{57}Fe Mössbauer isotope. NRIXS

provides information on phonon density of states, from which one can derive important dynamic, thermodynamic, and elastic information.

- Nuclear forward scattering (NFS): Using the time structure of synchrotron radiation, NFS records Mössbauer effects in the time domain. The nuclear hyperfine signals are very sensitive to internal magnetic fields, electric field gradients, and isomer shifts, and are widely used to study magnetic collapse, site occupancy, and valence and spin state. Compared to other nuclear resonant techniques, NFS measures the transmission signals which are relatively strong and may be collected in a fast manner.

Figure 3: *HPCAT staff (October 2012): From left to right, Guoyin Shen, Stanislav Sinogeikin, Eric Rod, Ho-kwang Mao, Dmitry Popov, Agnes Mao, Jesse Smith, Veronica O'Connor, Yoshio Kono, Paul Chow, Yue Meng, Arunkumar Bommannavar, Zhisheng Zhao, Daijo Ikuta, Hongping Yan, Yuming Xiao, Changyong Park, Curtis Kenny-Benson.*

2.3 High Pressure X-ray Imaging (XRI)

HPCAT has developed a variety of XRI techniques for different imaging purposes, such as radiography and tomography, using the full-field imaging method or the position scanning method. XRI is an important component in all experimental stations. Recently, high-pressure topography has been developed using polychromatic x-rays at beamline 16-BM-B.

- X-ray radiography: provides density contrast or phase contrast imaging through which the sample configuration inside the pressure device may be visible. The radiographic imaging, both by position scanning method or the full-field method, is essential in almost all synchrotron experiments, and provides information on sample allocation/configuration, sample and anvil deformation, etc. Integrated with a Paris-Edinburgh cell, x-ray radiography has wide applications in determinations of density, viscosity and ultrasonic velocity of liquid materials at high pressures.
- X-ray tomography: By rotating a sample under load, radiographic images can be collected at small angular intervals at high pressure, allowing for reconstructing 3D tomography images of an object. This technique has been used for measuring volume of amorphous materials for EOS determination and 3D microstructure of composite materials under shear deformation.
- X-ray topography: Using polychromatic beam, the x-ray topography technique has been established at 16-BM-B. Multiple x-ray topography images can be recorded corresponding to reflections from different crystallographic planes. The low divergence of synchrotron radiation provides high resolution composite images of topography images, suitable for studying internal strain and defects in single crystal materials, such as CVD diamonds at various growth conditions.

2.4 Support Equipment

High *P-T* technology has undergone rapid development in areas of maximizing pressure, precise pressure control and measurement, control of hydrostatic media, strain rate, or stress fields, as well as integrating high/low temperature techniques and other extreme conditions (magnetic fields, electric fields, etc.). Non-synchrotron high-pressure techniques are an important part of the HPCAT program, providing a comprehensive set of techniques. The support facility has played an important role in the success of these experiments. It also makes it possible to carry out collaborative work between HPCAT staff and scientists who do not have high-pressure facilities at their home institutions or users from other beamlines at APS.

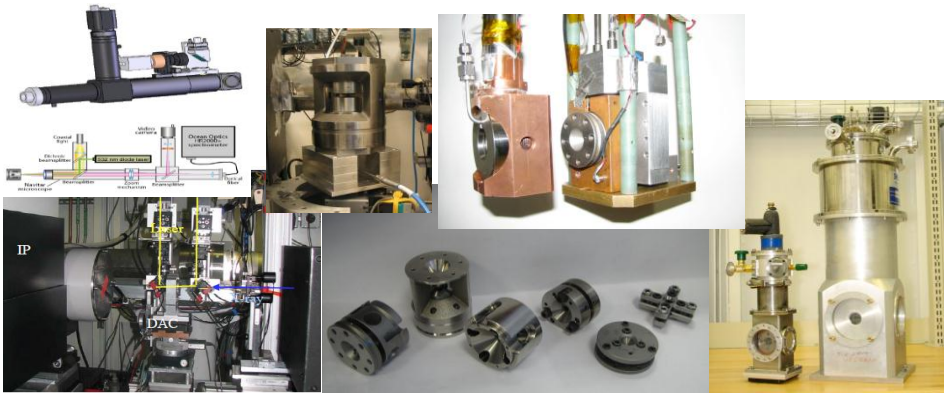


Figure 4: *HPCAT has established a comprehensive set of supporting equipment for controlling and measuring pressure and temperature, and for sample preparation and non-synchrotron characterization.*

- Pressure controls and measurements: A number of devices (membrane, gear box) have been established for remote and automatic pressure controls in high *P-T* synchrotron experiments. Meanwhile, HPCAT has established a number of portable online optical systems for ruby fluorescence pressure measurements and *in-situ* Raman sample characterization. These online optical systems, capable of measuring pressure in cryostats, resistively heated cells, and at room temperature, are available at all four experimental stations at HPCAT. Combined with remote pressure control systems, they significantly increase the capability and efficiency in high *P-T* synchrotron experiments.
- Temperature controls and measurements: Besides pressure, temperature is also a routine parameter widely manipulated by users at HPCAT, greatly facilitated by the established support equipment. HPCAT has established laser heating systems for heating samples from 1000 K to several thousands of degrees (>6000 K). Resistive heating techniques are used for relatively modest temperatures at up to 1200 K for diamond anvil cell and 2500 K for Paris-Edinburgh cell, respectively. Specially designed cryostats, suitable for various x-ray measurements, are used for temperatures down to 4 K.
- Complementary characterization techniques: The results from x-ray measurements are often compared with those from complementary techniques at HPCAT, including a micro-Raman spectroscopy, electrical resistivity, and magnetic measurements which can often be performed at *in situ* high pressure conditions. HPCAT has close collaborations with other laboratories at the Argonne National Laboratory for examining samples after pressure release.

- Sample preparation facility: For efficient use of beam time, samples should be always prepared before the assigned beam time. However, samples and/or pressure devices may be subject to unpredicted changes or even failures as experimental conditions vary. It is essential to have facilities for sample preparation on site. At HPCAT, we have established support facilities for sample preparation and characterization. The support equipment also makes it possible to carry out collaborative work between HPCAT staff and scientists who do not have high *P-T* facilities at their home institutions or users from other beamlines at APS.
- Software: High *P-T* experiments are often dynamic; users need to make decisions based on the collected data so far. It is essential to have software for timely data evaluation on site. HPCAT has developed a number of software routines for determinations of pressure, temperature, unit cell parameter, etc.

2.5 High Pressure Synergetic Consortium (HPSynC)

Many specialized beamlines with unique capabilities have been built for various experiments and hold great potential to be further integrated for extreme conditions science. To fully utilize the synchrotron power, a dedicated team called High Pressure Synergetic Consortium (HPSynC) was established to work with high-pressure scientists and beamline scientists to facilitate the next level of science and technical integration. Co-managed by the Geophysical Laboratory and the APS, HPSynC has improved both high-pressure devices and beamline parameters interactively to optimize the extraordinary capabilities for novel high-pressure experiments.

The HPSynC scientists collaborate with beamline scientists at specialized beamlines, including 16 sectors at APS (Sectors 1, 2, 3, 4, 6, 7, 9, 11, 12, 13, 15, 16, 20, 30, 32, and 34). They propose high-impact research projects, adapt apparatus to fit the specific beamline requirements, and bring in various portable equipment systems to develop novel high pressure synchrotron techniques. They work on time-resolved, dynamic studies using the fs laser to catch the structural dynamic change under extreme *P-T* condition. They have taken the advanced capabilities of new synchrotron sources, like high flux, low emittance, high energy, high energy resolution, polarization, coherence, and short-pause radiation to perform advanced high pressure research on diffraction, spectroscopy, imaging and time-resolved studies.

Microbeam high-pressure XRD has been advanced to an order of magnitude higher spatial resolution (200-500nm), which provides a platform for ultra-high pressure research, grain-grain interaction, single crystal study in powder samples, and inter- and intra-granular response under pressure. High-pressure melts and clusters have been investigated by high-energy XRD, anomalous XRD, and small-angle XRD, where the nanoparticle size, bonding distance and intermediate-range ordering can be probed. The Bragg coherent diffraction imaging technique has been combined with diamond anvil cell high pressure study, and individual nano particles have been investigated *in situ* to explore the nanoparticle morphology and internal strain distribution with 3d spatial resolution at 30 nm, while the plastic flow induced rheology can be viewed as pressure increases. X-ray 3D tomography with 30 nm resolution has opened new research areas in measuring

compressibility of amorphous materials, the nanoporous distributions, etc. By tuning the incident beam energy, the charge transfer, valence transition, chemical composition and even spatial distribution of pressure induced spin transition can be mapped via the newly developed XANES-tomography approach. The tailored improvements of the diamond anvils, gaskets, DACs, and portable laser-heating and cooling systems have greatly enhanced myriad of XRS techniques.

3. SELECTED SCIENCE HIGHLIGHTS

3.1 Complexity in "Simple" Alkali Metals

Science Achievement

Lithium and sodium are often considered as model simple metals. However, high pressure experiments at HPCAT have shown that these alkali metals behave in manners that are anything but simple. They display unusual "melt-down" phenomena induced by quantum effects. When they eventually solidify at lower temperatures, the simple metals adopt a range of highly complex structures not previously observed in any element.

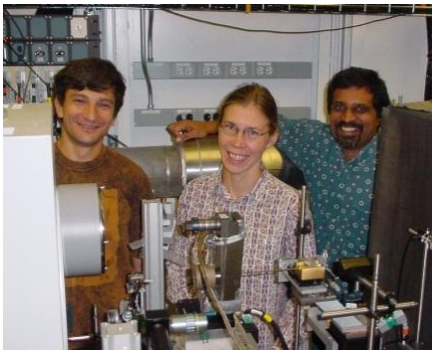


Figure 5: *Gregoryanz, Degtyareya, and Somayazulu work together to reveal complexity in "simple" elements.*

Significance and Impact

The complexity of these simple metals is a surprise. It means that the quantum effects are clearly at play at high compressions. The zero-point energy could increase significantly under compression, and eventually plays a significant role in shaping the phase diagrams. These studies demonstrate the significant enhancement of quantum effects at high pressure and pave a pathway to "construct" a system possessing a metallic liquid ground state.

Research Details

Using powder and single crystal high pressure diffraction techniques, phase diagrams of Li and Na have been mapped to 130 GPa. Melting is clearly signified by the appearance of diffuse scattering from the liquids. Na remains a liquid at room temperature at 110 GPa, while Li has a melting point at 190 K at 45 GPa, by far the lowest melting point among the elemental metals.

Using both resistive heating and cryostat techniques, single crystal diffraction experiments reveal a number of complex crystal structures with large unit cells for both Li and Na, which have never been predicted theoretically.

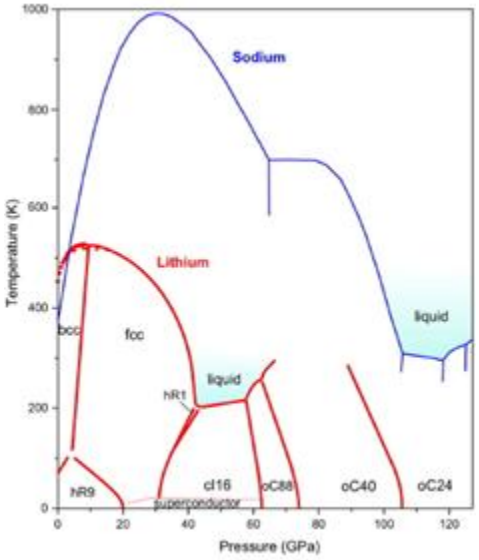


Figure 6: *Complexity in phase diagrams of Li (red) and Na (blue). Huge "melt-down" is shown for both Li and Na. The "simple" metals adopt a number of complex structures at high pressures. (After O. Degtyareya)*

C. L. Guillaume, E. Gregoryanz, O. Degtyareva, et al., *Nat. Phys*. **10**, 1038 (2011).
E. Gregoryanz, O. Degtyareva, M. Somayazulu, et al., *Phys. Rev. Lett*. **94**, 185502 (2005).

3.2 Ordering State in Materials

Science Achievement

The atomic structure of materials may be classified by ordering state, such as the short-range order of liquids and amorphous materials or the long-range periodicity in crystalline materials. Recent experiments at HPCAT have demonstrated a new category of materials with a crystalline structure formed by amorphous C_{60} clusters [1]. In contrast, high pressure experiments on metallic glasses revealed a glassy state with a long-range level of order, referred to as the perfect glass state [2].

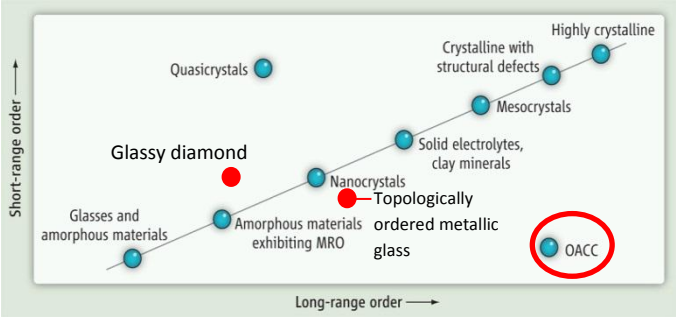


Figure 7: *An order-disorder diagram (modified from Science 337, 812-813, 2012) which shows that short-range order in most materials is correlated to long-range topological order. Recent discoveries at HPCAT extend our current knowledge of ordering state (indicated in red).*

Significance and Impact

In general, short-range order in materials is correlated with the long-range-order as shown in Figure 7. The discoveries at HPCAT extend our current knowledge of the ordering state of materials by expanding into regions where amorphous clusters can form a periodic lattice or where a glass is a single crystal at heart. These studies open the door for exploring materials with various degrees of ordering state with the potential for a huge variety of physical and chemical properties.

Research Details

- When solvated C_{60} buckyballs were subjected to high compression, individual balls were crushed into disordered clusters of carbon atoms, but the amorphous clusters were arranged in an ordered crystal lattice.
- By compressing a $Ce_{0.75}Al_{0.25}$ glass at 25 GPa, the glass turned into a face-centered cubic single crystal. Upon pressure release, the new structural order was preserved.

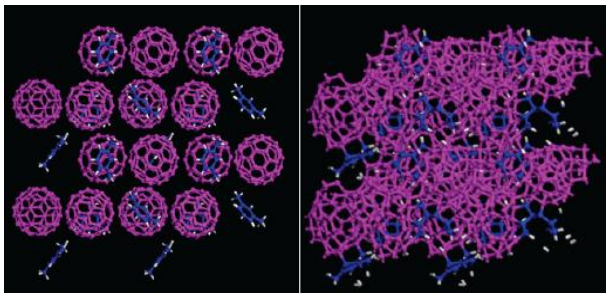


Figure 8: *(Left) C_{60} starting material showing buckyballs arranged in periodic order. (Right) under pressure buckyballs were crushed, but leaving the disordered clusters still arranged in a periodic long-range order. [1]*

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[1] L. Wang, B. B. Liu, W. G. Yang, et al., *Science* **337**, 825-828 (2012).
[2] Q. Zeng, H. W. Sheng, Y. Ding, et al., *Science* **332**, 1404-1402 (2011).

3.3 Superconductivity at High Pressure

Science Achievement

Iron selenides display superconductivity below 30K, but superconducting transition temperatures (T_c) decline with the application of pressure up to 9 GPa. Upon further compression, however, a surprising reemerging superconductivity has been observed with T_c above 48K, which sets a new record of T_c for iron-based selenide superconductors.

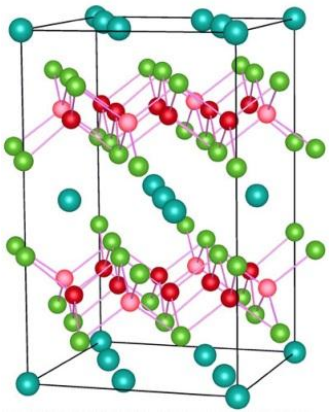

Figure 9: *Initial crystal structure of iron selenides persisted throughout the disappearing and reappearing superconductivity. [1]*

Significance and Impact

Iron selenides together with iron arsenides and cuprates are classified as three families of high temperature superconductors. Despite many different physical properties, the three families share the common structural unit with charge reservoir layers for electron or hole doping and conducting layers responsible for superconductivity. The reemergence of superconductivity at higher pressure with higher transition temperatures indicates the essential role of charge carriers in the superconducting mechanism. The finding points to possibility of searching for new superconductors with higher transition temperatures at ambient pressure.

Research Details

- Using six different iron selenide samples in single crystal form, measurements of crystal structure, electric resistance, and magnetic susceptibility were performed at high pressures up to 15 GPa. Experimental data confirmed the disappeared superconductivity at around 9 GPa. At higher pressures, the measurements on all six samples yield the same reemergence of superconductivity.
- The initial crystal structure persists throughout the pressure range studied. The disappearance of superconductivity in the low-pressure cycle and the re-emergence of superconductivity with higher T_c in the high-pressure cycle reflect detailed structural variances within the basic unit cell itself.

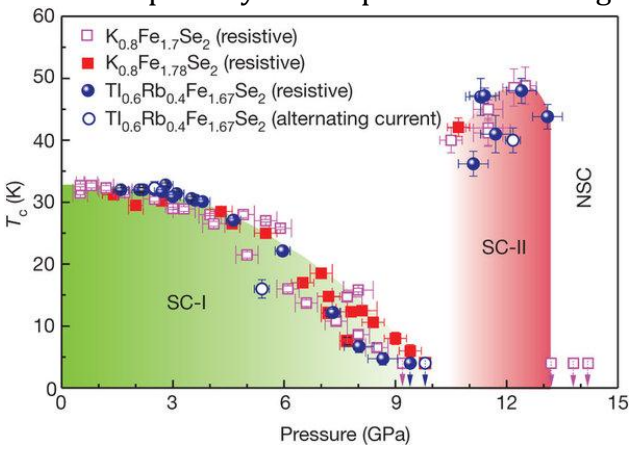

Figure 10: *Disappearing and reappearing superconductivity at high pressures. The maximum T_c is 48.7K at 12.5 GPa. [1]*

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[1] L. L. Sun, X. J. Chen, J. Guo, et al., *Nature* **483**, 67-69 (2012).

3.4 High Pressure X-ray Induced Chemistry

Science Achievement

Pressure can change chemical bonding and reactivity. HPCAT experiments show that the photochemical effects can be greatly enhanced by pressure. At ambient conditions, the mixture of H_2 and O_2 reacts explosively and forms H_2O, but at 10 GPa, samples of H_2O ice VII irradiated by x-rays were converted into a molecular compound of coexisting O_2 and H_2 [1]. Similarly, irradiating a fluid mixture of N_2 and O_2 at 2 GPa with x-rays broke the strong covalent bonds and formed a stable ionic compound (NO^+NO_3) with an interesting layered structure [2].

Figure 11: *High pressure spectroscopy setup at HPCAT.*

Significance and Impact

The kinetic stability of the new materials at high pressure implies that there are energy minimum states separated from simple molecular systems (H_2O or N_2-O_2 mixture) by large energy barriers. The barriers may be too high to cross by thermal energy alone. The high energy x-rays provide access to a large range of local energy minimum states, opening many intriguing scenarios in studies of simple molecular interactions and applications to energy storage.

Research Details

- When subjected to high pressure and extensive x-radiation, H_2O molecules cleaved, forming O–O and H–H bonds. The oxygen and hydrogen framework in ice VII was converted into a molecular alloy of O_2 and H_2. X-ray diffraction, x-ray Raman scattering, and optical Raman spectroscopy demonstrated that this crystalline solid differs from previously known phases. It remained stable with respect to variations in pressure, temperature, and further x-ray and laser exposure.
- Applying hard x-ray photon radiation to a mixture of liquid N_2 and O_2 in a diamond-anvil cell, an ionic phase of $NO_2^+NO_3^-$ was observed at 0.5 GPa. The decomposition of this phase to a new ionic NO^+NO_3 phase was discovered at 2 GPa. Samples were characterized by optical Raman spectroscopy and x-ray diffraction.

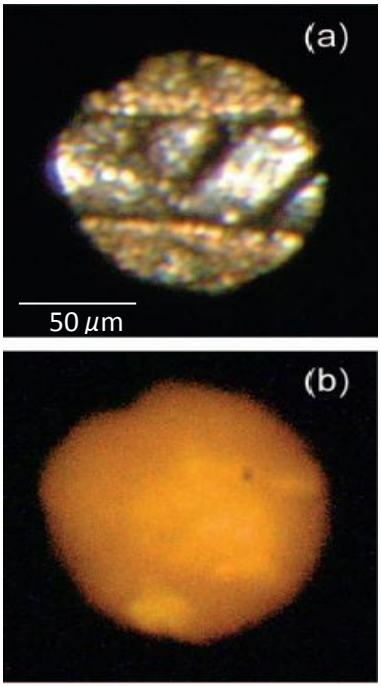

Figure 12: *X-ray induced chemistry at high pressure. (a) The mark by irradiation. (b) The new ionic NO^+NO_3 formed. [2]*

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[1] W. L. Mao, H. K. Mao, Y. Meng, et al, *Science* **314**, 636-638 (2006).
[2] Y. Meng, R. B. Von Dreele, B. H. Toby, et al., *Phys. Rev. B* **74**, 214107 (2006).

3.5 Noble Gas Chemistry at High Pressures

Science Achievement

The normally un-reactive, closed shell xenon was predicted by Linus Pauling to react and form chemical bonds with highly electronegative fluorine and oxygen. While ambient pressure chemistry essentially reflects this, we have shown that under pressure, xenon forms novel chlorides and iodides. In addition, it forms a whole suite of stoichiometric, van der Waal (vdW) compounds with H_2 molecules. In addition, the vdW compound $Xe(H_2)_7$ is stable to pressures as high as 2.5 Mbar.

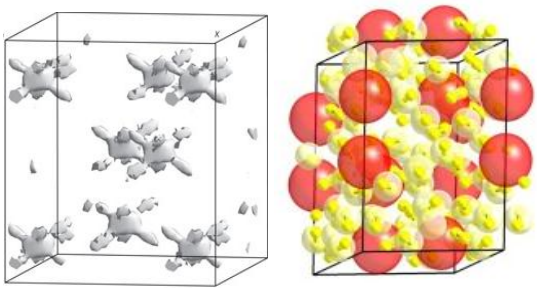

Figure 13: *(Left) Electron density distribution shows the spread of electrons between the Xe atoms. (Right) The xenon atoms are surrounded by freely rotating hydrogen molecules. [1]*

Significance and Impact

The fact that pressure induces reactivity in xenon may not come as a surprise considering that by itself xenon is known become metallic at high pressures. What is surprising however is that a number of unexpected compounds dissimilar to those synthesized at ambient pressures are synthesized at high pressures (and high temperatures) and some of them are retrieved at ambient pressures on pressure release. For example, we have identified $Xe(H_2)_{15}$ which can be synthesized at 4.2 GPa and room temperature and retrieved at 1 atm and at 90 K. Similarly, we have synthesized a strikingly red $XeCl_2$ solid at pressures above 1 GPa but can retain it at pressures as low as 200 atmospheres and at room temperature. These discoveries open the possibility of synthesizing a whole new class of compounds that have unexpected electronic properties due to xenon.

Research Details

- Using powder and single crystal diffraction techniques in combination with Raman and infrared spectroscopy, we have obtained the structures, stoichiometry and the bonding nature of these compounds.
- While high pressures were achieved with diamond anvil cells, simultaneous high temperatures were needed for many of the syntheses and this was achieved by resistive and laser heating of the samples using specialized gaskets to minimize interaction with gasket materials at the high *P-T* conditions.

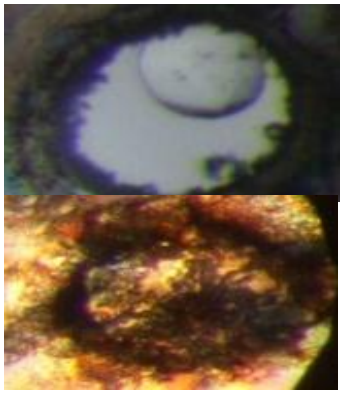

Figure 14: *(Top)Single crystal of $Xe(H_2)_{15}$ in a diamond cell. (Bottom)The metallic XeI_2 sample synthesized at 14 GPa and 1880 K. (Courtesy: M. Somayazulu)*

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[1] M. Somayazulu, P. Dera, A. Goncharov, et. al, *Nature Chem*. **2**, 50-53 (2010).

3.6 Strength and Deformation at High Pressure

Science Achievement

Using radial diffraction geometry, diffraction patterns document elastic deformation by shifts in d-spacings (sinusoidal variations) and plastic deformation resulting in crystal rotations and corresponding intensity changes. Deformation experiments in a polycrystalline $(Mg_{0.9},Fe_{0.1})SiO_3$ post-perovskite yield information on stress and lattice preferred orientation for the plastically deformed sample in the diamond anvil cell. The lattice-preferred orientations suggest that slip on planes near (100) and (110) dominate plastic deformation under the Earth's core-mantle boundary conditions, providing essential deformation parameters in modeling the anisotropy of this dominant mineral at the core-mantle boundary.

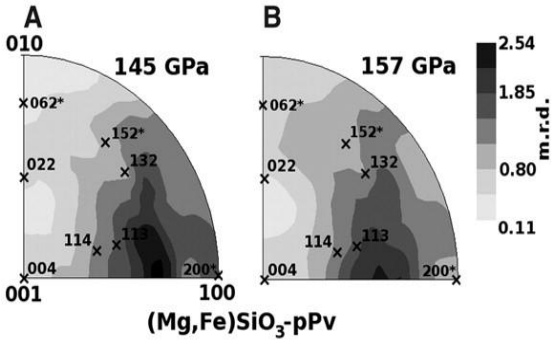

Figure 15: *Inverse pole figure showing the preferred orientation pattern in (Mg,Fe)SiO_3-pPv in compression measured (A) at 145 GPa just after converting the material to the pPv phase, (B) at 157 GPa. [1]*

Significance and Impact

The work demonstrated that the detail deformation mechanism can be studied for samples at multi-Mbar nonhydrostatic conditions. The established methodology is applicable to study the stress-strain-time relationships in solids which are vital to addressing rheological properties and deformation textures at extreme conditions. The results have significant implications in modeling the structure and dynamics of the interiors of the Earth and other planets.

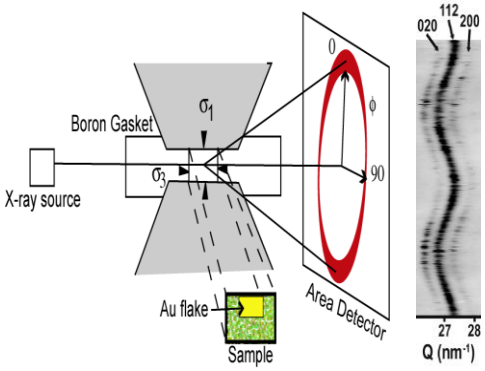

Figure 3: *Geometry of a radial diffraction experiment with a diamond anvil cell which provides uniaxial stress (left). The corresponding changes are visible in "unrolled" Debye rings (right). (Courtesy: H. R. Wenk)*

Research Details

- High pressures and high temperatures were generated in a laser-heated diamond anvil cell with large openings to allow radial x-ray diffraction. The sample was loaded in a 40-μm diameter hole in a beryllium gasket compressed with beveled diamond anvils.
- The relative intensity variations of the diffraction peaks are used to calculate the orientation distribution function which contains information about the crystallite orientations and can be used for deformation mechanisms analysis.

S. Merkel, A. K. McNamara, A. Kubo, et al., *Science* **316**, 1729 (2007).
S. Merkel, A. Kubo, L. Miyagi, et al., *Science* **311**, 644 (2006).

3.7 4*f* Electron Delocalization and Volume Collapse

Science Achievement

Electronic delocalization transitions are of great interest because they signify large scale electronic correlations in materials. High pressure x-ray emission experiments at HPCAT have shown that the development of multiple electronic configurations with differing 4*f* occupation numbers can be directly and quantitatively measured, thus providing the key quantum observable related to the delocalization of the strongly correlated 4*f* electrons, such as in cerium [1] and praseodymium [2].

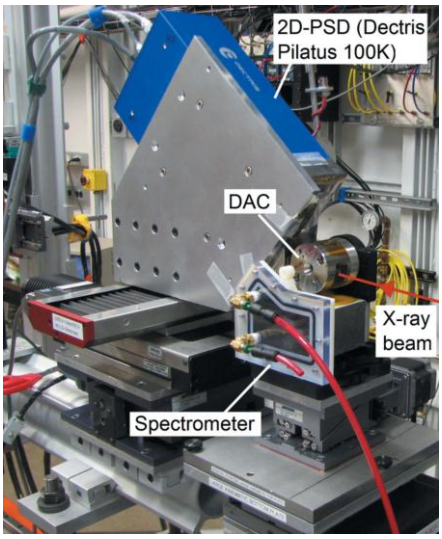

Figure 17: *X-ray emission spectroscopy setup at HPCAT.*

Significance and Impact

These experiments demonstrate a general methodology for analogous work on a wide range of strongly correlated *f*-electron systems. The intimate connections between the 4*f* electronic structure and the volume-collapses are described by experimental observables and provide direct comparisons of the electron delocalization with the dynamic mean field theory (DMFT) predictions. The results serve an important anchor in future discussions of 4 *f* delocalization.

Research Details

- Ce and Pr samples were loaded in diamond anvil cells with great care to maintain pure samples. X-ray emission spectroscopy (XES) or resonant XES (RXES) was used to measure electronic structures.
- The Ce-$L_{\gamma 1}$ XES spectra provide a measure of bare atomic 4*f* moment <J> for Ce as a function of pressure. For Pr, the L_{α} RXES is sensitive to the changes in electron occupancy, providing the relative quantum weightings of the different *f* orbitals.

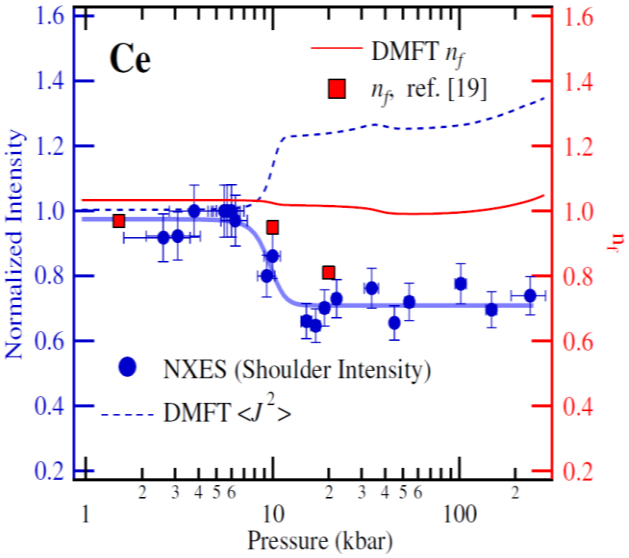

Figure 18: *Comparison of experimental data with DMFT predictions. The predicted <J²> changes in the opposite direction than does the experimental data. Right axis: Number of 4f electrons nf. [1]*

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[1] M. J. Lipp, A. P. Sorini, J. A. Bradley, et al., *Phys. Rev. Lett.* **109**, 195705 (2012).

[2] J. A. Bradley, K. T. Moore, M. J. Lipp, et al., *Phys. Rev. B* **85**, 100102(R) (2012).

3.8 Spin Transitions in the Earth's Mantle

Science Achievement

Iron is the most abundant transition metal in the Earth's deep interior, and its presence can affect a wide range of earth materials properties in the region. A series of high-pressure experiments at HPCAT have shown that iron ions in lower-mantle minerals can undergo an electronic high-spin to low-spin transition at high pressures and temperatures. A spin crossover of Fe^{2+} in ferropericlase has been observed to occur at conditions corresponding to the middle part of the lower mantle. The consequences of the transitions have been studied in terms of their implications to deep-Earth geophysics, geochemistry, and geodynamics.

Significance and Impact

The advent of the synchrotron x-ray spectroscopies permitted first observations of the spin-pairing transitions and their effects at high pressures. The low-spin phase displays unusual physical and chemical properties as a result of the spin-pairing transition. The effects of the transition can thus affect our understanding of the Earth's interior. These results are recently integrated with the long-range spin-spin interaction potentials to help reconcile seismic observations and particle and mineral physics data with significant deep-Earth implications.

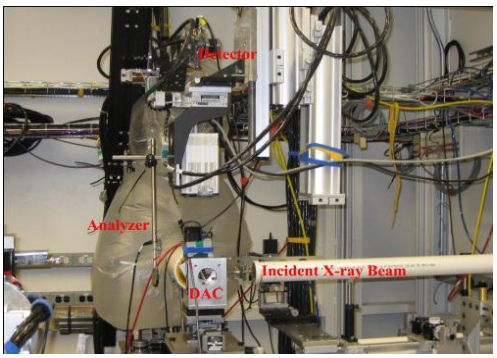

Figure 19: *X-ray emission spectroscopy in a DAC to detect spin states of iron at HPCAT.*

Research Details

- Using x-ray emission and Mössbauer techniques at HPCAT, the spin and valence states of iron in lower-mantle minerals have been studied up to 136 GPa and high temperatures. The spin-pairing transition was observed through changes in Fe K_β emission spectra and hyperfine parameters. The total spin momentum of Fe^{2+} in the octahedral site of the crystals vanishes at approximately 40 GPa.
- Using x-ray diffraction in a heated diamond anvil cell, thermal pressure-volume relationship (equation of state) of the minerals reveals a volume collapse with enhanced density and incompressibility for the low-spin state.

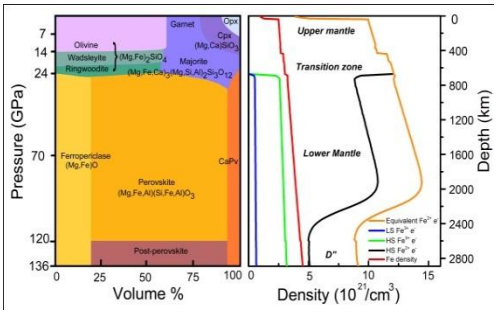

Figure 20: *Mineralogy (left) and electron density across the spin transition (right) in Earth's mantle. The transition of Fe^{2+} occurs in lower mantle ferropericlase. [1]*

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[1] L. R. Hunter, J. E. Gordon, S. Peck, et al., *Science* **339**, 928-932 (2013).
[2] J. F. Lin, V. V. Struzhkin, S. D. Jacobsen, et al., *Nature* **436**, 377-380 (2005).

3.9 Expanding the Phase Diagram of CO_2

Science Achievement

Under standard conditions, carbon dioxide (CO_2) is a simple molecular gas and an important atmospheric constituent, whereas silicon dioxide (SiO_2) is a covalent solid, and one of the fundamental minerals of the planet. The remarkable dissimilarity between these two group IV oxides is diminished at higher pressures and temperatures as CO_2 transforms to a series of solid phases. The CO_2 phase diagram is expanded in pressure-temperature space, showing similarities between CO_2 and SiO_2 polymorphs. In the high-pressure stishovite-like phase, carbon atoms manifest an average six-fold coordination within the framework of sp^3 hybridization.

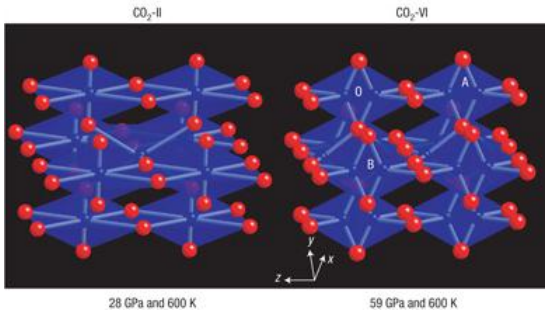

Figure 21: *Structural models for CO_2-II and CO_2-VI based on in situ X-ray diffraction measurements. [1]*

Significance and Impact

Considering the rich abundance of carbon, oxygen and silicon in the Earth's mantle, the new high-density form of six-fold CO_2 may offer new concepts in geo- and mineral chemistry. CO_2 could exist in the Earth's mantle as four- and six-fold covalent solids and within solid solutions with SiO_2 and/or other minerals. The structural similarities between CO_2 and SiO_2 polymorphs would presumably enhance their mutual solubility and chemical reactivity at the pressure–temperature conditions of the Earth's mantle. The structural instability of six-fold CO_2 at low pressures and its enhanced ionic character on decompression would help account for the carbonate minerals originating from the Earth's interior as well as for the high-temperature origin of carbonates in martian meteorites.

Research Details

- Samples were loaded into an externally heated membrane driven diamond anvil cell (mDAC). The use of resistively heated mDACs provided precise control over both pressure and temperature. Furthermore, the mDAC can apply a constant load to the sample during external heating to 1,200 K at a given pressure, thus allowing isobaric heating experiments.
- X-ray diffraction data were obtained *in situ* at controlled pressure-temperature conditions by using focused (~5 μm) x-rays and an image plate detector.

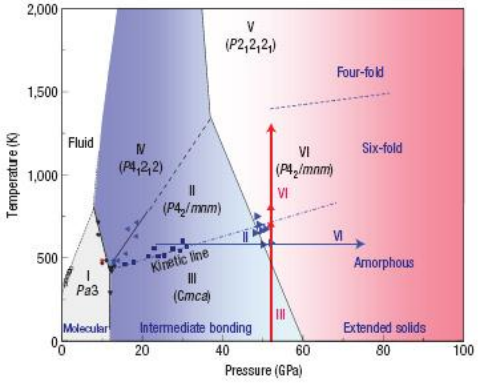

Figure 22: *Phase diagram of carbon dioxide illustrating the molecular to non-molecular phase transitions to four- and six-fold coordinated carbon atoms. [1]*

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[1] V. Iota, C. S. Yoo, J. H. Klepeis, et al., Nat. Phys. 6, 34-38 (2007).

3.10 Synthesis of Transition Metal Nitrides

Science Achievement

Transition metal nitrides are of great technological and fundamental importance because of their strength and durability and because of their useful optical, electronic, and magnetic properties. Although numerous metals react with nitrogen, nitrides of the noble metals can only be synthesized at high pressure-temperature conditions. Following the first report of the synthesis and recovery of noble metal Pt nitride [1], several durable noble metal nitrides were discovered containing Ir [2] and Os [3]. These new compounds have bulk moduli comparable with those of traditional superhard materials.

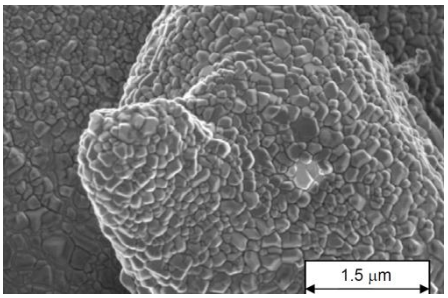

Figure 23: *SEM image of recovered PtN_2. [2]*

Significance and Impact

These discoveries demonstrate the potential of high pressure synthesis because high pressure significantly alters materials chemistry. The new chemistry of nitrogen under extreme conditions offers great promise for both a new understanding of the phase diagram of nitrogen at extreme conditions as well as the design of materials with interesting and useful properties, strengthening the hope of finding potentially hard high-pressure phases outside the B-C-O-N system, i.e., with large volumes per atom but high coordination.

Research Details

- Metal samples in powder form were loaded in diamond anvil cells. Nitrogen was then loaded into the DAC either cryogenically or by a gas-loading system. Laser heating was applied to the sample at high pressures.
- The x-ray diffraction and Raman spectroscopy instruments at HPCAT provided diagnostic probes.

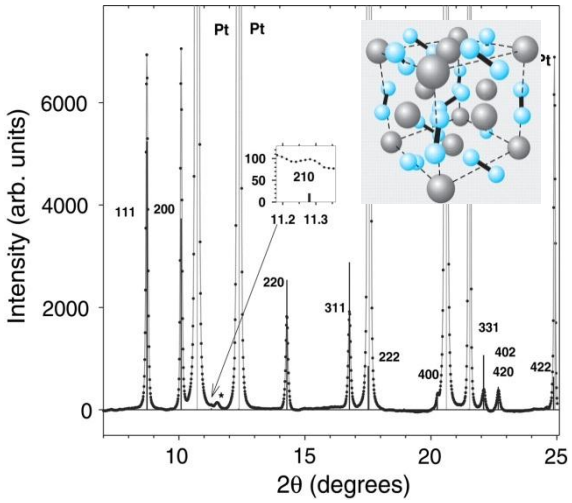

Figure 24: *Powder x-ray diffraction pattern of PtN_2 obtained from the recovered sample. Insert: Diagram of the proposed pyrite structure of PtN_2. [2]*

[1] E. Gregoryanz, C. Sanloup, M. Somayazulu, et al., Nature Mater. 3, 294-297 (2004).
[2] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, et al., Science 311, 1275-1278 (2006).
[3] A. F. Young, C. Sanloup, E. Gregoryanz, et al., Phys. Rev. Lett. 96, 155501 (2006).

II. NEW CHALLENGES AND OPPORTUNITIES

A decade of forefront scientific investigations at HPCAT has provided the basis to launch and chart the next generation of high-pressure synchrotron research. The ongoing facility-wide APS upgrade will provide synchrotron radiation with unmatched brilliance in the next few years. More advanced detectors and x-ray optics will significantly improve both spatial and temporal resolution in high pressure synchrotron research. A number of novel x-ray techniques have recently, or will soon, become available for integration with high pressure devices. In addition, there are numerous developments in high pressure technology in recent years, for example static pressure beyond 0.5 TPa, dynamic loading with controlled strain rates, pressure cells with controlled stress conditions, extremely high or low temperature capabilities, and micro-engineered sample configurations. In the three-day workshop, extensive discussions took place to (1) articulate foremost scientific challenges in the field of extreme conditions science; (2) identify the science and technology breakthroughs needed to address these challenges; and (3) define research directions in the area of high-pressure synchrotron science to advance the exploration of matter under extreme conditions.

The workshop attendees enthusiastically concluded that a major upgrade of HPCAT is necessary for advancing compression science using synchrotron radiation and developing novel high energy x-ray diagnostic probes suitable for studying materials at extreme conditions. A number of research directions were identified together with scientific and technical challenges in the next decade through discussions in the following breakout panels:

Panel 1 – Reaching 0.5 TPa and beyond
Panel 2 – Time-dependent off-Hugoniot processes
Panel 3 – New materials discovery
Panel 4 – Novel states of matter
Panel 5 – Deformation and transport properties
Panel 6 – Liquids and amorphous materials
Panel 7 – New technologies and instrumentation

Priority thrusts were in turn identified by each panel. These are described after each panel summary.

Among the important conclusions from the panel reports is the need to establish an infrastructure that brings together expertise, instrumentation, and the user community in both static and dynamic compression science using synchrotron radiation. The synergies of HPCAT with HPSynC, DCS and other APS beamlines will set the stage for a unique center for extreme conditions science, and will enhance the coordination of various programs at APS (e.g., HPCAT, DCS, and APS-operated beamlines) and beyond (NNSA sponsored laboratories, other synchrotron facilities). The center will also provide training and support to students and young scientists in using state-of-the-art synchrotron techniques for obtaining fundamental knowledge of the behavior of materials in a broad range of environments.

PANEL 1: REACHING 0.5 TPa AND BEYOND

Chairs:

Thomas Duffy, Princeton University
Stanimir Bonev, Lawrence Livermore National Laboratory

Panel Contributors:

Reinhard Boehler, Carnegie Institution of Washington
Alexandra Navrotsky, University of California, Davis
Eugene Gregoryanz, University of Edinburgh
Brent Fultz, California Institute of Technology
Richard Scalettar, University of California - Davis
Carl Greeff, Los Alamos National Laboratory

Introduction

Over the past fifty years high-pressure experiments have had a major impact in fundamental studies in physics, chemistry, materials science, geology, and planetary science. Static compression studies have produced remarkable findings and have been a rich source for the discovery of new phenomena up to pressures of several megabars and temperatures ranging from near zero to several thousand Kelvin. Much information has been obtained on crystal structures, equations of state and other thermodynamic properties. Many new high-pressure phases have been discovered and their chemical and physical properties explored. Novel magnetic, electronic, and superconducting states have been probed. The concurrent advances in theoretical techniques using density functional theory over this same time period have contributed greatly to understanding the observed phenomena. The combination of theory and experiment provide a stringent test of our understanding of condensed matter at high compression.

Synchrotron radiation facilities have played a major role in the growth and development of high-pressure science. The high brilliance of third-generation synchrotron sources and the wide transparency of diamond anvil cells together with improvements in x-ray optics and detectors have led to dramatic advances in material property measurements at high pressures. HPCAT has been a leader in these developments for the past decade. It has pushed the limits of established techniques such as x-ray diffraction while fostering the development and application of many new x-ray spectroscopy and x-ray imaging techniques that have greatly advanced capabilities for studying thermodynamic, elastic, and electronic properties.

Structure, bonding, and thermodynamic properties are among the most fundamental properties of interest in high-pressure investigations. They are and will undoubtedly remain the subject of many high-pressure experiments in the coming years. The high pressure synchrotron facilities provide a unique capability for exploring these fundamental properties of matter over the widest range of pressures and temperatures. This panel identified the following priorities for research and outlined new opportunities at high pressure synchrotron facilities in the following five areas: (1) The ultrahigh pressure frontier; (2) Bridging the strain rate gap between static and dynamic experiments; (3)

Thermodynamics and kinetics and high *P-T*; (4) Complex, heterogeneous materials across a range of *P-T* conditions; and (5) Elasticity, strength, and rheology at Mbar conditions.

P1.1 Ultrahigh Pressure Frontier

Application of pressure to 1 Mbar or beyond produces fundamental changes in the nature of a material. In most cases, there will be one or more phase transitions occurring over this range. As compression energies at these pressures are comparable to bonding energies, significant changes in atomic bonds are expected. Ionic or covalent solids may transform into metals or superconductors. Molecular solids may transform into extended solids. There may be profound changes in chemical processes and thermodynamic properties in a system. At the same time, there are large changes in elastic moduli, strength, and deformation behavior which may fundamentally alter mechanical and rheological properties.

The maximum pressure that can be achieved with diamond anvil cells is limited by the strength of diamond and the achievable culet size. The vast majority of diamond cell experiments are performed at pressures below 300 GPa, and it becomes increasingly difficult to create and probe conditions above this level. Some pioneering experiments have explored the higher pressure regions [1]. Recently, using hemispherical micro-balls (10-50 μm) as a second-stage anvil, it was possible to achieve pressures up to 640 GPa (Figure 25) [2].

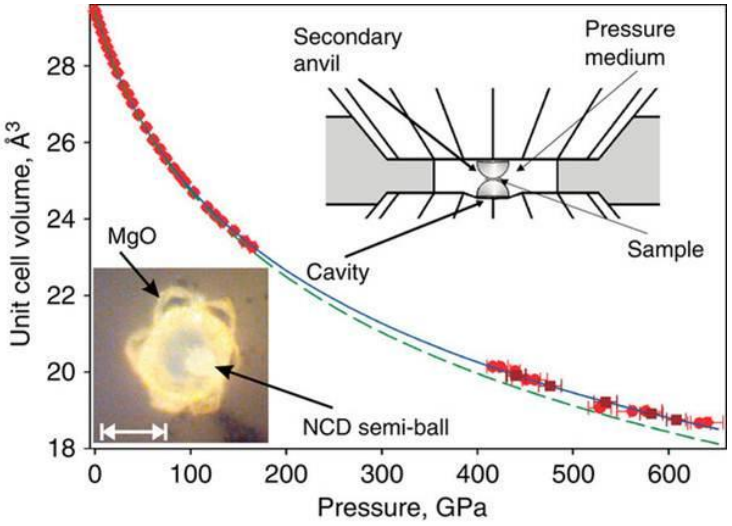

Figure 25: *X-ray diffraction data to 640 GPa on rhenium [2]. The inset shows the double-stage geometry with second-stage micro-ball nano-diamonds in a DAC.*

Research Directions

Expanding the achievable pressure range, the types of experiments that can be performed, and their accuracy at ultrahigh pressures will reveal many novel and interesting phenomena. Atomic coordination and structures of materials are governed, to first order, by the geometric relation of "hard-sphere" radii. This simple concept is one of the oldest guidelines in searching for possible high pressure polymorphs based on low

pressure analogs of the next row elements on the Periodic Table. For instance, germinates were used as analogs for predicting high pressure silicate minerals of the Earth's mantle. The classic NaCl-CsCl (B1-B2) transition was predicted on the basis of ionic radii, and later verified in all alkali halides. However, because compression affects electron orbitals of different symmetry in different ways, there are numerous examples of intriguing and poorly understood phenomena, many of which were not predicted or simply unexpected. For instance, many elements (e.g., S, P, Fe, Li) becomes superconductors at high pressure, while some metals (e.g., Li, Na) becomes insulators at ultra-high pressure. The revealed novel incommensurate structures demonstrate that the crystal structures at high pressure may become much more complicated than previously thought. At significant compression, valence electrons may localize in the interstitial regions and the relative bandwidth decrease monotonically, leading to band narrowing, electronic densities with interstitially centered maxima.

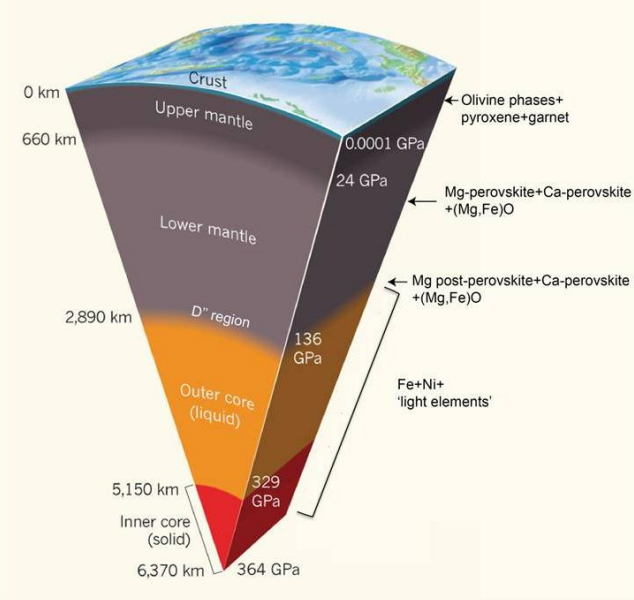

Figure 26: *Cross-section through Earth's interior. (Courtesy: T. Duffy)*

The pressure range of the Earth's inner core extends up to 364 GPa (Figure 26). There is uncertainty about the crystal structure and properties of iron at Earth core conditions as theoretical calculations have suggested that hexagonal close packed, body centered cubic, face centered cubic, or a stacking disordered phase of iron may be stable under core conditions. Recently, the first static diamond anvil cell experiments have achieved inner core conditions, reaching up to 377 GPa and 5700 K [3]. Many more studies at these conditions are needed to fully characterize the behavior of core materials. Thermodynamic and transport properties are needed to understand the origin of the geodynamo that produces Earth's magnetic field. Direct measurements of elastic and rheological properties are also needed to explain inner core elastic anisotropy, hemispherical dichotomy, radial variability, and possible super-rotation [4].

Aside from the Earth, there is a vast unexplored *P-T* range relevant to giant planets. The central pressures of ice giant planets (Uranus and Neptune) reach as high as 800 GPa, whereas the center of Jupiter is as high as 7 TPa. In addition to the planets of our own solar system, there is significant interest in the interior structures of many extra-solar planets that have now been detected in our galaxy. Existing models of the interior of extra-solar planets are based on long, uncertain extrapolations of experimental data and theoretical calculations, and better experimental equation of state (EOS) data and other properties at multi-megabar pressures are needed to test and improve these models [5].

Scientific and Technical Challenges

Developing new anvil and cell designs to achieve multi-megabar pressures with larger sample volumes is one of the most exciting frontiers for high-pressure science. A variety of new developments including multi-stage or specially shaped anvils, multi-carat single-crystal CVD diamond, nano poly-crystalline diamond, and designer anvils all provide potential avenues for expanding the feasible pressure range.

The development of techniques to achieve simultaneous high temperatures while at multi-megabar pressures also represents a major challenge. As mentioned above, for example, to reach conditions of the center of the Earth, one needs to achieve 3.6 Mbar and greater than 6000 K. Methods are thus needed to heat solids to well-controlled, uniform conditions without catastrophic weakening of the diamonds and support structure. New developments are needed to overcome complications including diamond deformation, limited sample thickness, and lack of thermal insulators that make achievement of uniform temperature states and application of spectroradiometric measurement techniques difficult under these conditions.

It is also necessary to develop accurate and precise probes of the range of material properties of interest. High-sensitivity measurement techniques are necessary because of the minute amount of sample that can be subjected to such extreme conditions. X-ray diffraction will no doubt remain one of the principle techniques for high-pressure studies. Development of nanometer-sized x-ray probes will enable the probing the smaller volumes which will enhance the capabilities to achieve ultrahigh pressures. High-spatial resolution probes are also needed for detailed sample mapping. New developments in single-crystal x-ray diffraction to pressures above 1 Mbar are especially promising as this technique provides a more detailed picture of high-pressure structures than can be achieved using powders. The capability of nanoprobe techniques to select a single crystal for study from a multi-grain aggregate is especially promising.

At present, measurements above about 150 GPa are challenging. Initial efforts should focus on development of compression techniques and improved probes from 1.5–4.0 Mbar while also exploring technologies for even higher pressures. Accurate characterization of pressure, stress, and temperature are essential and will require development of new heating techniques, pressure standards and pressure-transmitting media that are effective and well characterized at such conditions.

Potential Impacts

At ultrahigh pressures, there are large ranges of *P*-*T* space that cannot be accessed with current static or shock wave techniques. These regions are terra incognito and are ripe for new scientific discoveries. Theoretical studies are proposing many new phases and novel behavior under multi-megabar conditions [6, 7], but there is limited or no experimental data on many systems. Experimental measurements under such conditions are very likely to reveal new, unanticipated behavior and properties in materials.

For example, solid molecular hydrogen and its potential metallization have been a challenge for condensed matter theory and experiment for decades [8]. Atomic metallic hydrogen at high pressure has many potentially novel properties including new quantum states as a low-temperature metallic superfluid or a room-temperature superconducting superfluid. The development of new ultrahigh pressure techniques is a key to unraveling the complex behavior of this fundamental solid but current investigations are limited to approximately 250-300 GPa where hydrogen remains a molecular insulator. Recent experiments have been controversial [9], and studies have reached conflicting conclusions regarding metallization at ultrahigh pressures (Figure 27). Recent theoretical predictions of dissociation of hydrogen into a monoatomic body-centered tetragonal phase near 500 GPa [10] are a strong motivation to push experimental techniques to higher pressures for studies of this fundamental material.

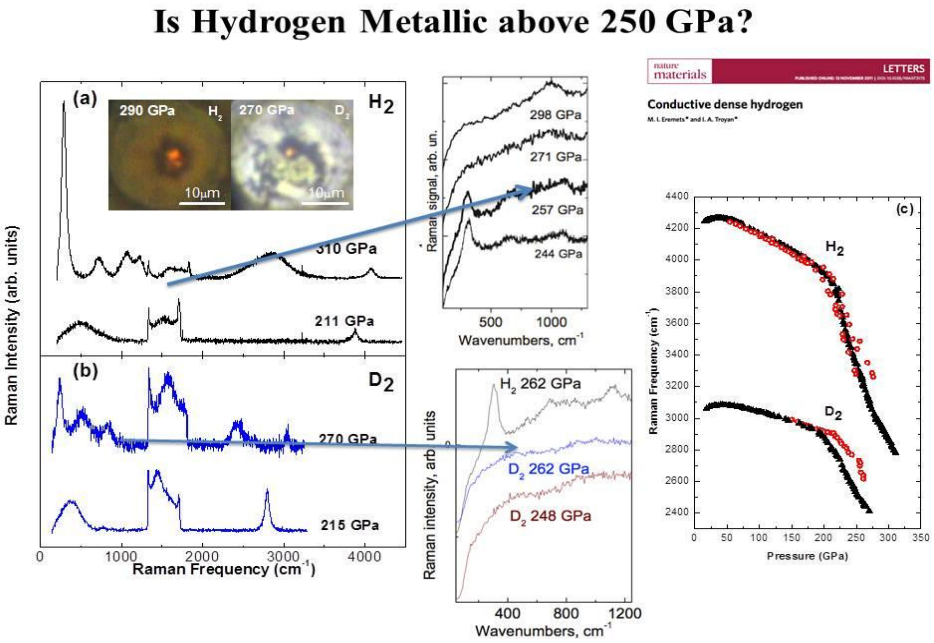

Figure 27: *Raman spectra of hydrogen and deuterium at high pressures. (Courtesy: E. Gregoryanz)*

At pressures above 200 GPa, equations of state, thermodynamic properties, and phase transitions are wide open for exploration. In addition to H_2, a large range of fundamental materials including elements, alloys, simple molecular compounds, oxides, carbides, nitrides, and silicates need to be explored at these pressures. Recent studies of elements have revealed a rich complexity in structures and physical properties at very high pressures. The conventional thinking that pressure produces simple structures is now known to be incorrect. Furthermore, theoretical studies [11] are now predicting highly unusual stoichiometries in simple chemical systems at very high pressures which will require new, challenging experimental methodologies to explore.

Ultrahigh pressure experimental technique development also has the potential to have profound impacts in Earth and planetary sciences. The interior structures of Jupiter, Neptune, and other giant planets are still poorly understood. The interior structure of the wide range of possible extra-solar planets also requires new experimental data for

understanding. Knowledge of these interior structures is essential for testing models for the formation and evolution of planets and planetary systems.

P1.2 Bridging the Strain Rate Gap

Dynamic and static compressions are complementary means of probing material behavior at extreme conditions. Shock compression techniques can achieve substantially higher pressures than static techniques, but shock waves are associated with large amounts of entropy production and corresponding heating. This temperature rise limits the ability to dynamically compress materials to high density, and usually produces melting at very high pressures, so that it is the liquid phase that is being probed. Ramp compression is a newly developing dynamic compression technique that achieves quasi-isentropic compression, resulting in lower temperatures and higher states of compression. Both shock and ramp loading involve many orders of magnitude higher strain rates than static compression

The time scale that lies between traditional static and dynamic experimental techniques is largely unexplored, and interesting new phenomena are likely to be found in this region. Phase transitions, reaction rates, kinetics, and metastability are all functions of loading rate as are mechanical properties such as strength and deformation mechanisms. Integrated models and theories that can describe the thermodynamic and constitutive properties over the wide range of timescales between static and shock conditions are needed.

Scientific and Technical Challenges

The high brightness and timing structure of the Advanced Photon Source are well suited for characterizing dynamic and time-resolved behavior. Among the major challenges are developments of high pressure devices operating with precisely controlled loading or heating rates and the ability to cycle pressure or temperature rapidly. Recent emerging advances in these areas include the dynamic diamond anvil cell and pulsed laser heating techniques. Time-resolved laser heating techniques can reach higher temperatures than continuous heating techniques and are especially useful for avoiding effects of diffusion and undesirable chemical reactions. There is also a need to develop a new generation of detectors with the time (and spatial) resolution and the sensitivity required for these experiments. A variety of new time-resolved probes (spectroscopy and diffraction) will be needed to interrogate materials across different timescales. Extension of such techniques to multi-megabar pressures in combination with development of dynamic ramp compression techniques to such pressures will allow the rate dependence of materials to be studied to much higher pressures than currently possible.

Potential Impacts

Development of controlled drives and diagnostics will result in a unique ability to create and probe dynamic processes. It will provide new tools to understand the constitutive response and deformation behavior of materials under extreme conditions. Major phenomena to be explored under dynamic conditions include phase transitions, reaction rates, disordering, and kinetics. Equilibrium phase diagrams are not sufficient to

describe material behavior in dynamic processes. Following chemical reactions using time resolved synchrotron techniques will provide a new way to probe reaction kinetics and mechanisms.

The development of the Dynamic Compression Sector (DCS) at APS provides the first ever opportunity to combine dynamic high pressure capabilities with the intense brightness of third-generation light sources. This is an outstanding opportunity for HPCAT in collaboration with DCS to address many fundamental questions concerning the relationship between static and dynamic material behavior that have been unanswerable until now. We expect that the synergy between HPCAT with expertise in synchrotron techniques and DCS with expertise in dynamic compression will lead to new breakthroughs in this area.

Impact phenomena and shock processes are of major importance in materials science, geophysics and planetary science. One of the main limitations of traditional dynamic experiments is the lack of structural diagnostics (i.e. x-ray diffraction). For example, SiO_2 has been the subject of extensive experimental studies using dynamic techniques for decades now due to its fundamental importance in materials science and in understanding impact phenomena in geology and planetary science. Dynamic experiments have documented a complex transition for low-density silica phases to a dense stishovite-like high-pressure phase with a complicated transition pathway and exhibiting metastability and kinetic effects. The capability to study dynamically compressed silica with x-ray diffraction promises to lead to major breakthroughs in understanding this complex and enigmatic material and will open the door to wider applications.

P1.3 High Pressure Thermodynamics and Kinetics

Phase transitions, equations of state, and other thermodynamic properties are and will likely continue to be a major focus of research. These studies explore the fundamental question of how the thermodynamics of solids change under pressure and temperature. In addition, studying reaction kinetics is essential to understand the processes controlling transformations (nucleation and growth process) at high *P-T* conditions.

The equation of state (EOS) is one of the most fundamental properties of condensed matter. It is essential for modeling planetary interiors as well as simulation of dynamic processes such as planetary impacts. The EOS also provides a critical point of comparison between experiment and theoretical calculations using density functional theory for a given material. Macroscopic thermodynamic processes are closely connected to atomic level dynamics. The study of lattice dynamics at high pressures and temperatures is essential for understanding phase diagrams, phase transformations, and other properties such as thermal expansion. Areas of focus include phonon dispersion, high-frequency collective dynamics, phonon-phonon interactions, phonon-electron coupling, and dynamic instabilities.

High pressure has strong effects on electrons and electronic excitations. As thermodynamic and bonding properties are explored at ever higher pressures (P1.1), a key question centers on the role of semi-core and core electron interactions for determining

the structural and thermodynamic properties of solids and liquids. Under such extreme conditions, is there core-electron chemistry in the same sense as valence-electron chemistry?

Scientific and Technical Challenges

The last decade is marked by the maturation of an array of high-pressure synchrotron techniques that have extended beyond examination of the static structure and have focused on dynamic behavior. Nuclear resonant inelastic scattering and nuclear forward scattering are used to study the phonon density of states and Mössbauer effect. Deep core-level electron bonding states are studied by the x-ray Raman effect. Charge and spin states are probed using x-ray emission spectroscopy. Inelastic x-ray scattering can be used to study phonon dispersion in crystals and for determination of high-frequency collective dynamics in glasses and liquids

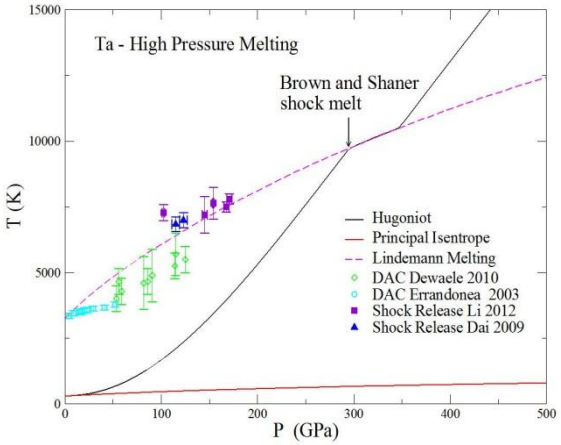

Figure 28: *Synthesis of static, dynamic, and theoretical calculations for the melting behavior of tantalum. Melting curves remain one of the most controversial thermodynamic properties at high pressure with many disagreements among static and dynamic experiments and theoretical calculations. (Courtesy: R. Boehler)*

These experiments typically require access to lower energies (5-15 keV) and very long x-ray exposure times, limiting the types of experiments that can be performed. Future developments in cell designs with enhanced samples volumes and less absorbing anvils or containment materials are needed. Dynamic behavior at simultaneously high *P-T* has been hardly explored due to the challenges of stable heating over the long x-ray exposure times. There is also a need to extend these measurements to higher pressures, such as achieving studies of the lattice dynamics of iron and iron alloys under core conditions. Advances in spectroscopic techniques should be coupled with other complementary experimental techniques outside of HPCAT.

Improvements in cell stability, heating techniques, and temperature measurement will also benefit studies of melting behavior, thermal expansion, and thermal equations of state. Well-characterized absolute standards for pressure determination are needed as well. More broadly, we recognize a need for the establishment of on-line, accessible databases for thermodynamic properties at high pressures and temperatures. There is also a strong need for closer interaction between experimentalists and theorists. For example, anharmonic theory by perturbation methods needs to be extended, or better results need to be extracted from molecular dynamics methods. Further development of density functional theory and techniques such as quantum Monte Carlo is needed. HPCAT should seek opportunities to more explicitly engage theorists in combined experimental theoretical investigations.

Potential Impacts

Advances in inelastic scattering techniques have broad applications to understanding phonon dispersion and high-frequency collective dynamics. Fundamental properties of interest in materials science and geophysics can be constrained including elastic constants, sound velocities, interatomic forces, and phase transition mechanisms. These methods also provide insight into dynamical instabilities, phonon-phonon interactions, phonon-electron interactions, and relaxation behavior. Technical advances will lead to the ability to better utilize phonon methods to measure the sources of entropy in compressed solids.

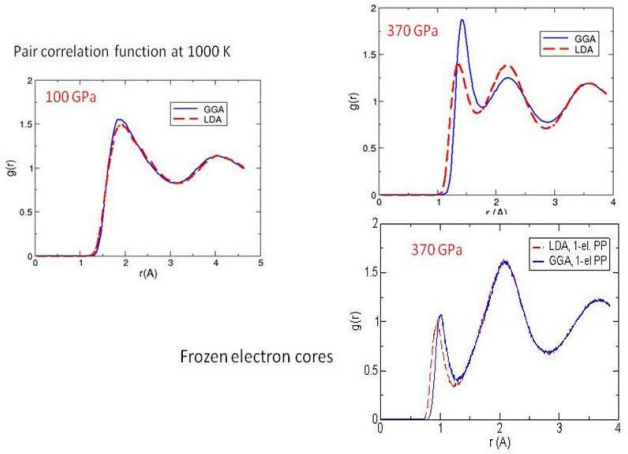

Figure 29: *Example of the significance of exchange interactions among the core electrons in Li. Molecular dynamics simulations are performed on liquid Li at 100 and 370 GPa. At 370 GPa there is an overlap between the core electrons. In both cases, the simulations are performed with two different exchange-correlations approximations (LDA and GGA). In the low P case they give identical results, but diverge significantly at high pressure. However, when the core electrons are frozen, the differences diminish again. This illustrates that the exchange interactions among core electrons are indeed non-trivial, and the choice of exchange approximation matter. [Courtesy: C. Greeff]*

One specific area of importance is the understanding of melting at extreme pressures. New diagnostic techniques are needed to resolve long-standing controversies regarding the melting curves of transition elements and other materials (Figure 28). Extending melting curves to higher pressures, and achieving an integrated understanding of melting via static and shock experiments and theoretical calculations is needed.

To address whether density functional theory-based methods (within local and generalized gradient exchange approximations) are accurate at extreme densities where interactions between, and modifications of, core electrons begin to play a significant role, there is a need for experimental data that would allow sufficiently precise comparison with theoretical calculations in order to validate the required level of theory for simulation of materials at extreme pressures (Figure 29).

P1.4 Complex Heterogeneous Materials

Just as important as the drive to achieve ever higher pressures and temperatures is the capability to study materials of increasing complexity and heterogeneity. New probes and techniques are enabling study of finer-level structure, which opens new opportunities to understand material behavior at a more fundamental level and to tailor the properties of interest in synthesized compounds. Areas of focus include nanocrystalline materials, disordered or amorphous solids, and liquids. Materials consisting of nanometer-sized crystals have unusual physical properties compared to their bulk counterparts. Complex

materials include multi-phase aggregates such as natural peridotites and basalts that are representative of the complex assemblages in deep planetary interiors. Another important category is that of strongly correlated materials that involve interactions of spin, charge, and orbital degrees of freedom. The complicated pressure-temperature phase diagrams and volume collapse in rare earth metals provide an example of such behavior (Figure 30). These materials are difficult to model theoretically, and the study of strongly correlated materials under high pressures has led to the discovery of many unique and novel properties [12].

Heterogeneous systems have also come under increasing recent experimental and theoretical scrutiny in materials science [13, 14]. One theme is how the deliberate introduction of disorder can weaken strong correlation effects (e.g. magnetism and

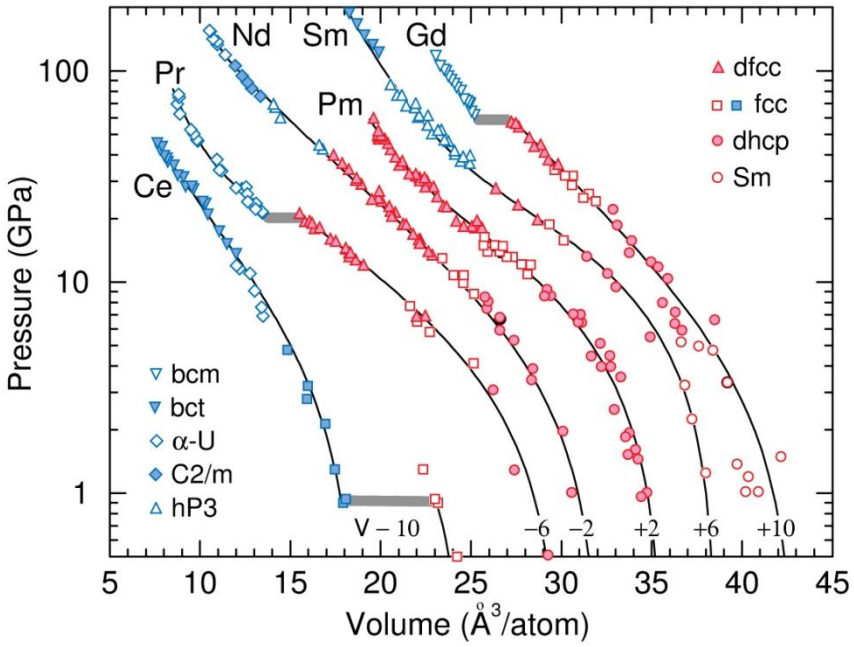

Figure 30: *Volume collapse transitions in the rare earths [16]. Kondo singlet formation occurs in transition from expanded (high volume) phase to compressed (low volume) phase under pressure. In general, the structures exhibited at high pressure are of lower symmetry, reflecting the increased participation of 4f electrons in bonding, and providing an illustration of the increased structural complexity under compression discussed in panel 1.*

superconductivity) and lead to greater insight into their underlying mechanisms. A second thrust has been on layered heterostructures, especially those which have strong electron-electron interactions, which can exhibit novel, and technologically useful, properties. High pressure will provide an especially useful diagnostic on these systems since it directly tunes the lattice geometry, a key element in the heterogeneity.

In fact, a recent focus of computational efforts for strongly interacting solids has been on the equation of state of such heterogeneous materials. The key observation is that certain regions of such systems can act as 'entropy reservoirs', effectively lowering the temperature of other regions and allowing the emergence of strongly correlated states of matter there. These computations have also been examining the effects of the ratio of the

interaction strength to the kinetic energy, which is the more canonical knob with which to tune strong correlation physics, and which is directly altered by the application of pressure.

Scientific and Technical Challenges

Studies of complex and heterogeneous materials require the development of techniques to determine chemistry and structure at the nanoscale. Nano-scale imaging techniques such as 3D x-ray diffraction microscopy, coherent x-ray diffraction imaging, and nano-tomography are examples of new techniques for diamond anvil cell applications. Techniques with high-spatial resolution are required for detailed reconstruction of single grains at the nanoscale and to obtain constraints on the variations in phase and composition along pressure and temperature gradients in samples. Also needed are methodologies for detailed mapping of stress and strain distributions in the high-pressure sample chamber. Due to the complexity of such materials, multiple diagnostics must be combined for complete sample characterization. This will require integration of *in situ* synchrotron measurements with post-run high-resolution analysis techniques such as nano-secondary ion mass spectrometry (SIMS) or focused ion beam techniques.

An additional need is for tailored anvils that provide multiple intelligent probes and/or can measure new physical properties. One example is the capability to perform Nuclear Magnetic Resonance (NMR) measurements in the DAC. NMR is an ideal diagnostic tool to investigate the microscopic properties of materials under extreme conditions. The nuclear spins in materials couple to the local spin and charge and therefore the evolution of the local structure and electronic environment can be probed as a function of temperature and pressure via an *in situ* NMR coil. Through the quadrupolar coupling between nuclei and the local electronic charge environment, NMR provides local information about the structure, supplementing k-space probes such as x-ray and neutron scattering. A central goal is the fabrication of an NMR sensing coil directly on the diamond culet. Many of the same issues which are central to ultra-high pressure, such as achieving high sensitivity, are fundamental to an NMR effort.

Potential Impacts

Techniques for the study of complex, heterogeneous materials have the potential to lead to major breakthroughs by using newly developing structural and chemical probes to characterize the micro- and nanoscale sample environment in ways that were not possible previously. A key component of this effort is to recognize the importance of integrating experimental studies with theoretical approaches. In this way, we can understand, for example, how unusual properties emerge in highly correlated atomic and electronic systems. Potential advances can also be made in the study of inhomogeneities and their possible role in transport and thermodynamics/phase transitions. One example in this area is the effect of inhomogeneities on antiferromagnetic order and superconductivity in high T_c superconductors.

Measuring x-ray total scattering as a function of temperature and pressure enables the determination of structure on both the local and intermediate length scales [15]. This is a

powerful technique for studying changes in the atomic structure of materials with varying degrees of disorder from crystalline to nano-crystalline to amorphous. Such work is leading to new understanding of the effects of crystalline size on thermodynamic properties, elasticity and mechanical properties, and solid-state phase transitions.

Static pressure can further be used to create and characterize materials with controlled levels of disorder or grain size, leading to novel properties. Examples include high-density amorphous materials and ultra-strong nano-phase materials. Breakthroughs will lead to understanding of how disorder can be introduced into materials at various length-scales to control specific properties and for particular applications. More generally, advanced probing and characterization techniques will enhance our ability to synthesize new materials with important scientific and technical applications. These include super hard materials, high-temperature superconductors, multi-ferroic materials, and energy storage materials.

P1.5 Elasticity, Strength, and Rheology

Mechanical and constitutive properties such as elasticity, strength, and rheology are important but poorly characterized properties of materials at elevated pressures and temperatures. Constraining these properties at extreme conditions is challenging as mechanical response is sensitive not only to pressure, temperature, and loading rate but is also a function of phase(s), microstructure, defects, and impurities. There is also a need to characterize the complete stress state in materials subjected to high *P*-*T* conditions. Despite such complications, characterization of these properties will lead to a range of applications that include enhancing material performance, development of superhard materials, development of wide-ranging constitutive models, and understanding of the dynamics of planetary interiors.

The single-crystal elastic properties, for example, are of fundamental importance for understanding stress-strain relations, elastic wave propagation, phase transition mechanisms, and other properties of solids. However, high-precision experimental methods for determination of anisotropic elasticity remain very limited above 20 GPa, and measurements at simultaneous high pressures and temperatures are even scarcer. These technical limitations greatly limit our understanding of high-pressure mechanical behavior.

Scientific and Technical Challenges

The scientific needs are for development of quantitative methods to constrain deformation mechanism and yield strength. These properties vary in complex ways and depend on pressure, temperature, stress, strain rate, grain size, hydration state, etc. Advances are needed to transform the diamond anvil cell into a quantitatively reliable deformation apparatus with spatially resolved and accurate measurements. Also needed is the capability to vary strain rates as well as pressures and temperatures. Further advances in other types of deformation devices (multi-anvil, Drickamer device) will provide access to different regimes of environmental and material conditions.

For complex, multi-phase aggregates, techniques will also be needed for determination of full variation in stress state and strain across the micro- or nano-structure of a material at high resolution. Development of techniques for 3D tomographic mapping of strain in grains of aggregate materials is also needed. There is also demand for high-precision techniques—for determination of single-crystal and aggregate elastic properties, especially shear moduli—that can reliably reach megabar pressures and thousands of Kelvin.

All these techniques will need to be applied to a wide range of materials of interest in materials science and geoscience. There is a need to develop databases of important thermoelastic and rheological properties that are easily and widely accessible to the community. As with other research directions, we see a strong need for integrated approaches combining theory and experiment. HPCAT should foster such interactions through workshops, meetings, and by placing theorists on staff at the APS.

Potential Impacts

Potential impacts in this area include the development of materials that are superhard or have other extreme or novel properties such as high compressive strength, bulk modulus, shear resistance, thermal conductivity, melting temperature, etc. Further developments in techniques for characterization of strength and rheology will lead to better understanding of the atomic structure and bonding characteristics of these unique materials, and hence will provide new insights into their synthesis, recovery, and potential technical applications.

Studies of the rheological and elastic properties of geological materials will lead to advances in understanding physical properties and deformation behavior of the deep Earth, which is necessary to interpret seismic observations. Most current rheological and elasticity studies are limited to pressures of the upper mantle (less than 24 GPa), and vast ranges of the Earth's lower mantle and core are still unexplored. The elastic and rheological properties of the major phases in the deep Earth, perovskite, post-perovskite, and iron alloys, remain mostly unknown.

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PANEL 2: TIME-DEPENDENT OFF-HUGONIOT PROCESS

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Introduction

Phase transformation pathways are strongly influenced by the time-dependence of the drive (compression, thermal transfer, strain, irradiation, etc). For example, shock-induced transitions often result in small grains or even nanoparticles, whereas static compression typically leads to large grains or even single crystals. Rapid cooling rates can transform metals from crystalline phases to metastable phases including technologically valuable bulk metallic glasses. Strain rates outside of the range of conventional gas gun and explosive drives (off-hugoniot) access dramatically different regimes of quasi-static and non-equilibrium conditions. Development of integrated x-ray systems and methodologies for probing the time-dependent evolution of structural dynamics are a frontier challenge with significant scientific and technological impact.

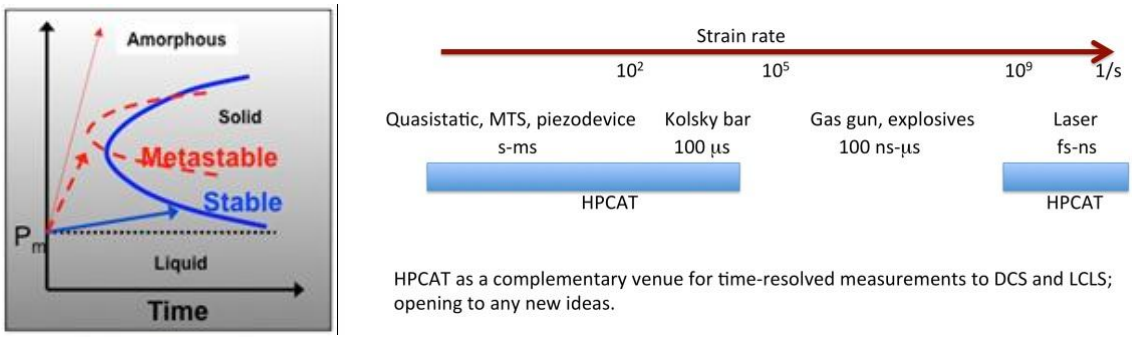

Figure 31: *HPCAT as a complementary venue for time-resolved measurement to DCS and LCLS (Courtesy: Left - W. Evans, Right – D. Hooks).*

Time-resolved x-ray studies of transformation dynamics can provide unparalleled insights into the atomic-scale mechanisms. Establishing this class of research will enable the discovery of novel metastable structures arising from non-equilibrium phase boundaries, quantitative determination of transformation kinetics, and an understanding of materials metastability - one of the most important scientific challenges in modern materials research. The scientific understanding of the dynamics of chemical and structural

transitions will be dramatically advanced through the development of time-resolved x-ray diagnostics integrated with a variety of impulsive drives (pressure, temperature, photo-chemistry, strain). These advances will broadly address dynamic processes including reaction chemistry, material performance, technological material synthesis, geoscience and basic science.

Current Status

Time-dependent x-ray studies of dynamic processes have been limited by instrumental limitations. Some of the key limitations to x-ray based time-resolved approaches have been timescales of phase transitions (sub-nanosecond), sufficient x-ray intensity, and detector performance. Advances in the brightness of x-ray sources and high-speed detector technology are overcoming these limitations. Third generation x-ray sources, such as the APS, delivering fluxes of $\sim 10^{13}$ photons per second are achieving the requirements for time-resolved studies at the millisecond scale. Leading edge gate-able detectors with high efficiency (e.g., Pilatus) complement the synchrotron performance allowing precise timing and rapid data collection. Current efforts are focused on integrating these technologies with various drives, including pressure (dynamic DAC), temperature (ramped laser heating) and photo-chemistry (laser-induced).

The science of time-dependent transformations is dominated by phenomenological and statistical-mechanical models, such as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation. These approaches have been largely dictated by the limited data available for model development and validation. Significant scientific advances can be realized with the increased availability of detailed data on phase transformation nucleation and growth processes.

Challenges and Opportunities

An ideal experimental capability would be a system capable of collecting a continuous record of x-ray scattering data from a single transformation event. Studies of this type would provide unprecedented insight into the transformation pathways, nucleation, growth and metastable phases. Variations in the drive characteristics (rate, intensity) would identify controlling factors and potentially identify methods for achieving specific transformation products. There is a broad range of scientific issues that such a capability would address. Notable areas include:

- Non-equilibrium transformations and “equilibrium” phase boundary, e.g., superheating/supercooling, over-/under-pressurization.
- Studies of the dynamics of a wide variety of materials, hard/soft materials including proteins, and processes.
- Nano-, microscale microstructure interactions and evolution
- Atomic rearrangement: lattice structure and interface (scattering/imaging), including nanomaterials.
- Dynamics of changes in valence (EXAFS); spin (e.g., domain walls); photon, electron, spin, phonon interactions; chemistry (spectroscopy).

- Correlation of structural dynamics with complementary physical properties: mechanical, electrical, magnetic, transport, etc.
- Dynamics/kinetics for thermo-mechano-chemical pathways: phonons, phase changes, chemical reactions, plasticity (loading, detection).

While compelling, these scientific challenges pose formidable technical challenges. The approaches must deliver data on time and spatial scales relevant to the structural dynamics. The x-ray data collection for 10-1000 nanoseconds exposures (time interval between bunches) for durations of up to several milliseconds results in 105 separate data files. Not only does this place demands on the detector hardware, but also processing of large data sets. The proposed variety of drives (pressure, temperature, photo-chemistry) would require an x-ray source that can be easily manipulated to provide a variable spot size. Achieving adequate x-ray photon flux and appropriate energy ranges would require a tunable source with the possibility of shifting from monochromatic to pink beam modes for increased flux. These and additional technical challenges must be addressed for a credible experimental program:

- Effective diagnostics
    - spatially/temporally resolved scattering/diffraction
    - imaging
    - spectroscopy
    - XANES tomography (composition and microstructure)
    - coherent diffraction imaging
    - X-ray sources
- Spatially coherent + monochromatic; high flux; focused and unfocused beams.
    - Tunable, high flux (pink beams), monochromatic light (radiation damage)
    - Shorter pulses – preserving flux are preferred (1 ps vs. 100 ps).
    - Time structure: 100 ps (time resolution limit); repetition rate (4 APS modes)
- Pulsed drive/loading techniques
    - Pressure/temperature, photons (lasers), electromagnetic fields
    - IR, UV lasers; fs laser
- Detectors
    - High speed: gating (single pulse), and framing (exposure time 100s ns to ms)
    - Large area for diffraction
    - Direct and indirect x-ray detection; indirect, fast and efficient scintillators; point spread function
- Synchronization of drive/loading, x-ray pulses and detectors
- Software
    - Timing, loading, and detector controls
    - Big data processing: storage, transfer, and processing, including physics and data mining

Concluding Remarks

X-ray studies of time-dependent transformations are a challenge to current synchrotron capabilities, but hold the promise of unprecedented insights into the dynamics of phase

changes. Despite the challenges, many experiments can proceed with existing resources, albeit at either lower data collection rates, or with decreased time resolution. These initial experiments will undoubtedly spur and capitalize on technological advances and enhance the state of the art, driving kinetic models from a phenomenological basis toward a more fundamental atomistic approach.

P2.1 Nanoscale Interactions

Studies of interactions and structural evolution at the nanoscale are important to advancing the understanding of nucleation, growth and control of microstructure. X-ray studies are particularly compelling because it directly measures particle sizes and crystal structures. The dependence of these properties on environmental conditions impacts both fundamental scientific understanding of kinetics and technological materials development.

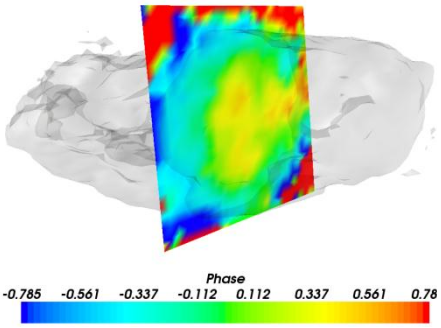

Figure 32: *Coherent Diffraction Imaging (CDI) of individual voids (Courtesy: W. Yang).*

Research Directions

Use low angle scattering/imaging (small/wide angle x-ray scattering & coherent diffraction imaging) to characterize the evolution of nanoscale material distributions in time and space upon rapid heating or compression. Specific research goals include:

- Nanoscale mixing kinetics/chemistry
- Quench/passivate nanoparticles for recovery at room pressure
- Characterize defect migration under dynamic conditions

Scientific and Technical Challenges

The scientific challenges largely relate to poorly understood parameters that control nanoscale interactions. This research thrust seeks to measure such properties, but initial work will be highly exploratory.

- How can nucleation at the nanoscale be controlled by pressure?
- How do surface chemistry and grain boundary interactions depend on pressure?

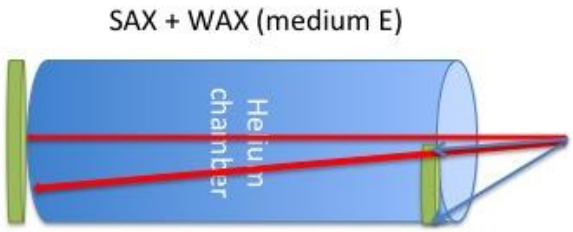

Figure 33: *Small Angle X-ray Scattering (SAX) & Wide Angle X-ray Scattering (WAX) to cover sufficient Q-space and collect statistically averaged data.*

The length scale (nm) poses one of the greatest technical challenges to this effort. Environmental conditions need to be well characterized and preferably controlled at nanometer scales. In addition diagnostic

probes will likely sample large numbers of particles yielding statistical averages.

- Difficult to observe nanoscale material dynamics under a wide variety of initial conditions
- Requires precise control and characterization of the thermodynamic state

Potential Impacts

Success of this research direction will impact the fundamental understanding of kinetics and dynamics of nanoscale materials and features.

P2.2 Influence of Strain/Compression Rate on Structural Dynamics and Constitutive Properties

There is a striking gap between the strain rates achieved in conventional dynamic experiments (high strain rate > 10^5/s) and static experiments (low stain rate <10^{-3}/s). Data in this intermediate regime addresses this gap and characterizes the rate dependence of various deformation mechanisms (diffusional flow, phonon drag, phase transition kinetics, metastability, adiabatic heating, etc.). Comprehensive experimental studies of material response to low, intermediate and high strain rate are needed to develop and benchmark accurate models of strength and constitutive properties.

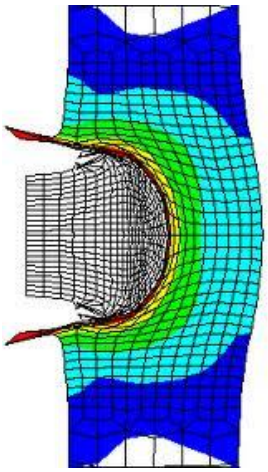

Figure 34: *Finite element model of projectile impacting a target with associated deformation.*

Research Directions

Various strain techniques integrated with x-ray scattering techniques will determine the dependence of constitutive properties and phase transitions. Specific research goals include:

- Strength of materials and the dependence on strain rate
- Measurement of stress-strain relationships under well-characterized loading conditions
- Phase transition kinetics and metastability

Scientific and Technical Challenges

The challenges associated with this research direction include characterization of the loading conditions, fast physical property diagnostics and association of measurements with bulk properties. In order to make accurate comparisons with result from complementary platforms and predictive models, it is necessary to determine the stress condition of the sample, be it in a DAC, shearing press, or dynamic drive. Similarly, the microscopic measurement using synchrotron x-rays must be scaled up to the macroscopic behavior of a material. Effective averaging techniques or rapid measurements are needed to eliminate statistical variations of individual measurements.

- Are the microscopic x-ray measurements representative of the bulk sample?
- How can the stress conditions of the sample be accurately determined?

The technical challenges relate to the performance limitations of the pressure platform, and diagnostic techniques with the spatial and temporal resolution consistent with the time-dependence of the pressure drive.

- What are the highest compression rates that can be reliably achieved?
- Determining/stabilizing the pressure variation and stress change following a pressure ramp/jump
- Coupling pressure-drive to laser heating techniques for achieving simultaneous pressure-temperature increases

Potential Impacts

Detailed experimental measurements of constitutive properties and associated stress environments under a range of strain rates will provide crucial data for developing and validating predictive models and finite element codes. Data of this type is unprecedented and will be instrumental in guiding and validating computational modeling efforts.

P2.3 Time-dependent Phase Dynamics and Non-equilibrium Transitions

The evolution of microstructure is an exceedingly rich area of study, relevant to fundamental natural processes and development of advanced materials. Conditions driving such changes include a broad range of chemical & physical stimuli such as pressure, temperature, strain, chemical environment, photo-chemical/mechanical, etc. Time-resolved studies of the evolution of materials in these environments can provide unparalleled insights into the controlling mechanisms and kinetics of transformations.

Research Directions

The evolution of physical, chemical and microstructure is an exceedingly rich area of study, relevant to fundamental natural processes and development of advanced materials. Conditions driving such changes include a broad range of chemical & physical stimuli such as pressure, temperature, strain, chemical environment, photo-chemical/mechanical, etc. Time-resolved studies of the evolution of materials in these environments can provide unparalleled insights into the controlling mechanisms and kinetics of transformations (Figure 35).

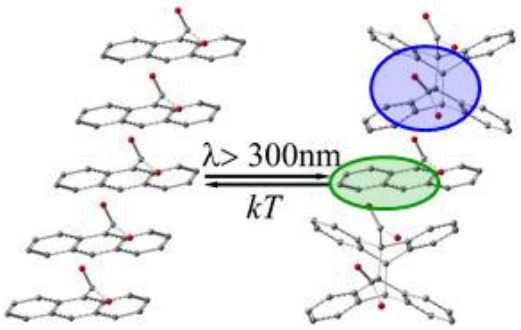

Figure 35: *Investigation of chemical/structural changes using time-resolved approaches to measure structural transformation mechanisms (from Ref. [4]).*

Coupled with phase transition dynamics is the possibility of accessing non-equilibrium states (Figure 36). Provided sufficiently rapid

drives, systems can be driven into non-equilibrium states that may be metastable and persist indefinitely. This will provide information regarding nucleation, growth and stability of energetically competitive phases. As an example, this research direction would support the understanding and development of bulk metallic glasses – disordered materials with inherent radiation damage resistance that could be used as structural components in advanced nuclear reactor designs.

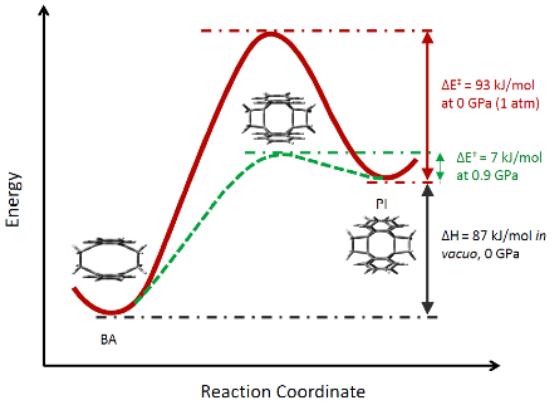

Figure 36: *Studies of mechano/photo/pressure/thermal-catalysis of transformation mechanisms (from Ref. [3]).*

Research Directions

Research goals include:

- Time-resolved measurement of structural evolution induced by pressure, strain, particle/crystalline domain size, etc.
- Kinetics of
  - Polymorphic crystalline phase changes
  - Photo-mechanical changes
  - Mechano-chemistry
  - Protein folding
- Characterization of the formation of materials in non-equilibrium situations
  - Coherent chemistry
  - Very rapid unloading and/or temperature quench
  - Anisotropic chemistry
  - Non-thermal kinetic energy distribution

Scientific and Technical Challenges

This research direction has broad applicability across a range of fields. Time-resolved measurements of transformations not only provide information on the mechanisms, but also give insights for tuning and control of these transformations. Understanding materials at this basic level will be a key enabler of achieving materials with tailored properties. While the benefits are compelling, the scientific challenges are also significant. For example, characterizing the nature of a disordered material (a bulk metallic glass) using diffraction is not a simple matter. Scientific advances will be necessary to address the following issues:

- Identifying suitable physical properties to diagnose the material behavior (atomic rearrangement, charge transfer, spin transitions, order/disorder, recrystallization, chemical reaction/dissociation)
- Evaluating structural changes in macromolecules, crystal structure and crystalline disorder
- Understanding the dynamics of phase transitions:

  - Microscopic (nucleation)
  - Macroscopic (growth)
  - Influence of compression rate
  - Microstructure evolution
- Is it possible to find higher yield/cheaper synthesis methods using non-equilibrium phenomena?
- Is it possible to recover previously unknown metastable materials? Understanding the time-dependent dynamics is the key to explore the potential synthesis methods.

The technical challenges of this research direction are mainly related to the performance demands of the time-resolved detection. In order to collect time-resolved structural data, the detection system must have the required temporal and spatial resolution. In addition, managing the data stream and prompt analysis tools will be needed.

- Time and spatial constraints
  - μ-sec and sub-μsec time resolution
  - 1-10 micron sized sampling areas
  - control and monitor μsec and sub-μsec dynamic pressure drives
- Integrating a variety of pressure-drives and experimental diagnostic techniques for measuring property changes at high compression rates
- High probing fluxes balanced against radiation damage
- Stability and reproducibility of pump-probe experiments
- Fast acquisition versus signal-to-noise
- High-speed, high-efficiency, high-resolution detectors
- process/analyze large data sets
- drives (dDAC, laser, explosive, strain,…) with micro-positioning
- X-ray beam with variable focus (sub-micron to mm's)

Potential Impacts

Success within this research direction will provide unprecedented observation of dynamics at a microscopic level. Experimental observations of transformations will provide the opportunity for close comparison of molecular dynamic simulations and experiment during processes rather than simply initial and final states. This enhanced level of knowledge will enhance our understanding of transition dynamics and enable advances in the development of materials with tailored properties.

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PANEL 3: NEW MATERIALS DISCOVERY

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Introduction

Pressure is a versatile and controllable external parameter to alter the electronic structure of materials. Recent experimental investigations have shown that through careful control of pressure it is possible to tune the magnetic and conductivity properties, and to promote solid state chemical reactions by overcoming the activation barriers through hybridization leading to bond breaking and forming. Compression also provides a means to study continuous change in short, intermediate and long range structural ordering linking the progression from nano clusters to bulk solids. Since 2002, HPCAT has provided the high pressure community reliable and well maintained investigative tools. To face the challenges of the next decade and to continue to be a world leader in high pressure instrumentation, HPCAT must evolve to keep pace with the cutting edge advancements in synchrotron radiation technologies and techniques. Fundamental understandings of pressure driven phenomena, such as those mentioned above, will require new and refined instrumentation.

Current Status

High pressure science used to be the research domain of physicists and geophysicists. The advent and availability of practical and versatile synchrotron based techniques, such as those provided by the HPCAT, has led to recent widespread use of high pressure in materials research. A recent experiment has revealed a long range topological ordering in Ce-Al metallic glasses [1] which raised a fundamental question concerning the underlying structure of metallic glass and, in a broader context, the exact nature of intermediate and long range ordering in amorphous materials. Another example is that a new superhard form of carbon consisting of both ordered and disordered components was made by compressing crystalline carbon C_{60} clusters embedded in a solvent [2]. This finding may lead to the development of a new strategy to synthesize novel materials with desirable or unique properties. Obviously pressure is a powerful external variable to alter the short, intermediate and long range ordering in solids. Apart from fundamental scientific reasons it is essential to understand the interplay of structure and ordering in order to fully exploit the new discoveries for practical applications. A possible avenue is to monitor *in-situ* the structural evolution with applied pressure. HPCAT already has the capability of measuring

long range (*e.g.* x-ray diffraction) and short range (x-ray absorption) structural correlation. New high pressure techniques bridging the intermediate range to meso-scale are highly desirable. The complete suite of structure characterization techniques will provide a holistic understanding of structural transformation of a solid induced by pressure and may lead to a new perspective on the principles of structural stability and the relationship between ordered and disordered solids.

At HPCAT, the nominal x-ray beam size for diffraction is 4 μm x 5 μm. It is now possible to perform experiments on (sub)-micron-sized single crystals and this has paved the way for structural determination under extreme pressure (> 100 GPa). A very small beam size also offers the opportunity to study the effect of strain on the sample. The strain is the result of non-hydrostaticity and is often discarded as a nuisance. Instead, the effect of a pressure gradient can be exploited by taking advantage of the extremely small beam size to perform raster scanning on the specimen. The diffraction patterns provide valuable structural information on different micro-crystallite grains, a prerequisite for the understanding of grain-grain interactions and structural transformation mechanisms. The described approach has important practical implications since in nature the pressure condition is rarely quasi-hydrostatic. The challenge is to realize the improvement in high speed data collection detector technology and the simultaneous development of software for fast online data reduction.

The characterization of the electronic structure of materials under pressure is a subject of great importance particularly in the design of new high pressure materials for technological applications. For this purpose, the development of new capabilities for simultaneous measurement of several properties will be highly beneficial. For example the identification of the structure at the superconducting state at low temperature is essential to clarify the suggestion concerning the co-existence of a charge density wave-distorted incommensurate structure and superconductivity. There is increasing theoretical evidence suggesting that under extreme compression the valence electrons are pushed into the interstitial regions leading to electron localization and the formation of electrides. Furthermore, the interaction between electrons from the penultimate core levels will become important. Electron spectroscopies, such as x-ray absorption, resonant (RIXS) and non-resonant x-ray scattering (x-ray Raman, XRS) have been demonstrated to be indispensable techniques. Currently, high pressure x-ray Raman is routinely employed for the study of materials consisting of first row elements. There are two possible approaches that can expand the information content of XRS. The polarization property of synchrotron radiation can be utilized on single crystal samples for the mapping of the electronic energy dispersion (band structure) of the empty states. In addition, since the symmetry of the final state of an electronic excitation is dependent on the momentum transfer, measurement of IXS spectra at different values of momentum transfer will provide detailed information on the orbital contribution to the unoccupied electronic density of states. XRS however, requires a large photon flux in order to be practical. The major technical hurdles are to significantly increase the photon flux on the sample and to simultaneously enhance the detector(s) sensitivity.

Challenges and Opportunities

Recent discoveries at HPCAT have shown that the traditional boundary between disordered and ordered structures can no longer be clearly defined at high pressure. Observations of pressure-induced transformations to crystalline-like structures in metallic glasses and mesoporous aerogels highlight the relevance of pressure in the investigation of the connection between long and short range order in solids. Spatially resolved diffraction under non-hydrostatic conditions can be exploited to provide information on the elasticity of small grains and grain-grain interactions. There are few ways to probe electronic structure at high pressure. Non-resonant and resonant inelastic scattering have emerged as power spectroscopic techniques in the characterization of electronic structures and electron correlation effects but require significant improvements in photon flux and focusing optics. If this can be realized, the electronic factors underlying novel structural transitions in elemental solids and superconductivity can be studied.

P3.1 Bridging the Gap: Nano to Macro, Disorder to Order

It is fair to say that the biggest impact of synchrotron radiation on high pressure science is the possibility of *in-situ* structural determination, either by powder or single crystal diffraction. X-ray crystallography will likely remain in future the key instrument in high pressure research. The surprise discovery of a myriad of complex structures in simple elemental solids at high pressure starting in the late 1990s has refuted the textbook notion that simple structures such as face-centered cubic or hexagonal close packing are favored under high pressure [3]. This revolutionized our perspective on the nature of chemical bonding and the new phenomenon of electron localization. Eventually this led to the bold prediction of the possible occurrence of an insulating state in lithium [4, 5]. More recently, it was demonstrated that a lanthanide metallic glass, by definition a disordered solid, can be ordered by compression [1]. Although glasses are common materials and well-studied, the structures of glasses are not fully understood. The observation opens a new dimension in glass science. Did this astonishing observation suggest an inherent "hidden" order? Is the phenomenon just a manifestation of a change in the electronic structure? The conversion of fullerene to diamonoid often requires high pressure and high temperature. It was shown lately that compression of solvated xylene in fullerenes at room temperature and relatively low pressure led to the formation of a superhard amorphous crystal formed by severely deformed fullerenes, but that surprisingly retained the translational symmetry [2].

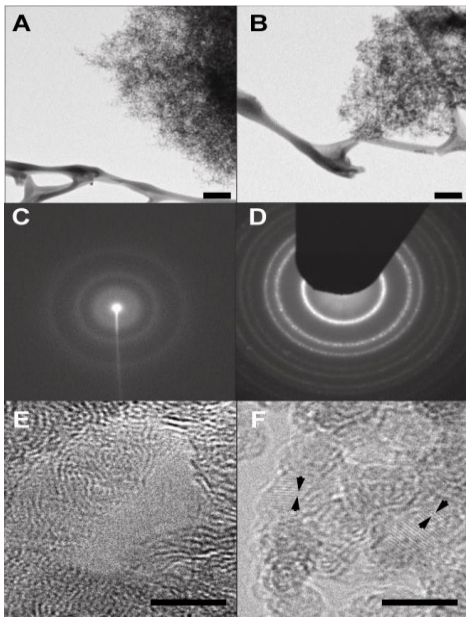

Figure 37: *Amorphous carbon aerogel (A, C, E) and recovered nanocrystalline diamond aerogel (B, D, F) after exposure of precursor to high pressure and temperature in a neon medium (from Ref. [7]). Scale bars in A and B: 200 nm, and in E and F: 5 nm.*

Similarly, compression experiments have shown that, using an appropriate approach, porous amorphous carbon materials can be made to convert under high pressure and temperature to nanocrystalline diamond-like structures that retain porosity, despite the high pressure and the radical reorganization of the atomic structure [6, 7] (Figure 37). These pioneering studies, among many others, have demonstrated the potential of *in-situ* high pressure synthesis. However, in order to assess the practicality of scaling up small scale (*e.g.*, diamond cell) synthesis to industrially relevant quantities the community will require a thorough understanding of the relevant mechanisms and the controlling variables, implying in turn careful and systematic experimental investigation.

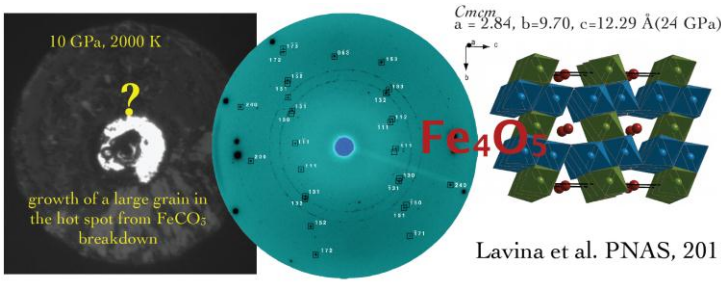

Figure 38 *Synthesis and determination of the novel compound Fe_4O_5 using the laser heated diamond anvil cell and in-situ x-ray diffraction. Discovery was dependent on higher data resolution than previously possible and the ability to quickly adjust the data collection strategy during a given experiment.*

The determination of new high pressure structures and their compressibility is essential to the discovery of new materials and the interpretation of their properties. Recent advances in high pressure x-ray micro-diffraction tools have led to impressive discoveries (Figure 38) and a much more accurate description of structures and how they deform upon compression. Recent high resolution single crystal x-ray diffraction studies on pressure-induced spin transition in Fe-bearing minerals have advanced the understanding on how the structural effects of an electronic phase transition can provide detailed evidence of an elastic component of the pressure-induced spin transition. These studies also reveal the complexity of micro-crystallite grains generated by non-homogenous temperature, pressure and chemical gradients. This, however, offers a unique opportunity to study grain-grain interaction and the strain effect on spin transitions.

Research Directions

- Order to Disorder – Nano to Macro
- Using pressure as a probe to study progressive transformations in solids at different length scales
- Structural polymorphism in non-periodic solids
- To reveal the fundamental factors governing the structural transformations in metallic glasses, in particular the amorphous to crystalline transition
- Real space quantitative electron density map
- A direct probe of the change in chemical bonding, hybridization and the electronic factor in driving structural phase transitions
- Determination of melting curves and polymorphic transitions in transition metals
- Reconcile differences between different experiments and with theory; produce and identify new polymorphs.

Scientific and Technical Challenges

New methodology and instrumentation for structural characterization of disordered solids from the nano to mesoscale are needed. Diffraction using hard x-ray (>100 keV or 0.1 Å) increases the Q-range and can provide much better resolved distribution functions at intermediate correlation distances [4-6]. The technical difficulties to be overcome are the development of software for data reduction, background removal and the elimination of spurious scattering, e.g. from the diamond anvil cell. For the latter, anvils made from nano-polycrystalline diamonds may be useful. In contrast diffraction at very small angle (i.e. low Q) can be used to investigate mesoscale structures such as chemical aggregates, and engineered mesostructures from the measurement of the density fluctuations due to structural differences on the order of ca. 10-100 Å. The challenge is to construct a high pressure high resolution small angle scattering x-ray diffraction instrument. A plausible solution is to adopt the Bonse-Hart geometry [9]. 2-D raster x-ray scattering in a very small area (ca. 20×20 μm^2) under high pressure and high temperature conditions can provide a detailed mapping of a sample texture and structure; this approach would allow studying the effects of inhomogeneous pressure and temperature on micro-crystallites strain, chemical gradients, and structure. This will require a highly focused beam (ca. 1 μm) with high spatial resolution of the sample stage and an ultrafast detector. The development of efficient software to handle voluminous data sets and data reduction is essential.

HPCAT has already demonstrated the ability to study metals under extreme conditions; measurements will need to be extended to the range of up to 10,000 K at simultaneous > 100 GPa pressures. At the same time, undesirable reactions with the other materials in the DAC must be avoided. Rapid and highly sensitive x-ray diffraction measurements will be required together with exceptional temperature and pressure control and measurement.

Potential Impacts

The proposed research direction will contribute significantly to the scientific knowledge of the structures of ordered and disordered solids, structural stability, atom correlations and polymorphism in amorphous materials. The information is relevant to a broad community of materials scientists and condensed matter physicists. From a practical perspective, new atomically-ordered materials synthesized by pressure tuning of disordered solids are expected to have numerous applications. For example a mesoporous diamond structure derived from an amorphous precursor may find application in the development of tunable and optically efficient antireflective coatings, optical quantum bits, and cellular biomarkers. Phase equilibria between minerals determine to a large extent the behavior of the interior of the Earth as well as other planets. The determination of the phase diagrams of relevant minerals is therefore of utmost importance. The information is needed in the interpretation of seismic data and geodynamic modeling of rheological and transport properties. Likewise, spin transitions in iron bearing minerals have a direct effect on the fundamental physical properties of the Earth's mantle including radiative thermal conductivity, electrical conductivity, thermal expansion, heat capacity, density, incompressibility, sound velocities and elastic moduli. Mean field models predict that the spin crossover should occur with gradual density changes and a large hysteresis. The

prediction apparently is at odds with the suggestion that stratification in the lower mantle is due to a spin transition. The proposed high pressure-high temperature single crystal diffraction will help to resolve this discrepancy. In addition, grain interactions may affect the anisotropy of the elastic properties modifying the local texture and residual stresses of microstructure. Extending the precise determination of melting curves of various materials including metals will provide data with which to rigorously test current state-of-the-art first principles approaches; such data will also be expected to improve geophysical and geochemical models of planetary interiors.

P3.2 New Physics in Extreme Conditions

Recent observations of the existence of complex incommensurate structures, superconductivity, metal → insulator transitions, spin transitions etc. are all directly related to the underlying electronic structure. Owing to the confined environment of the diamond anvil cell, only all photon (i.e. photon-in photon-out) spectroscopic methods (e.g. x-ray emission XES, x-ray absorption XAS) are applicable for characterization of electronic structures under high pressure. Inelastic x-ray scattering (IXS), an energy loss technique, is a powerful spectroscopic tool compatible with high pressure environments [11]. It is bulk sensitive, elemental and orbital specific. IXS is a versatile technique and has been used widely for measurement of phonon band structures [12], iron vibrational density of states [13] and electronic excitations [11]. On the latter, IXS also has the distinct advantage of not being limited by dipole selection rules. For electronic excitations, the current instrumentation somewhat restricts the high pressure applications to first row elements due to their relatively large cross sections [14]. There are several outstanding scientific problems, especially in highly correlated systems, such as valence fluctuations in rare earths, spin crossover and Mott-Hubbard insulator-metal transitions in transition metal compounds, and electron localization at high pressure in which high pressure IXS experiments can play a pivotal role. The technical challenges are to extend the applicability of the IXS technique to shallow core levels of elements beyond the first row with higher sensitivity and increased energy resolution.

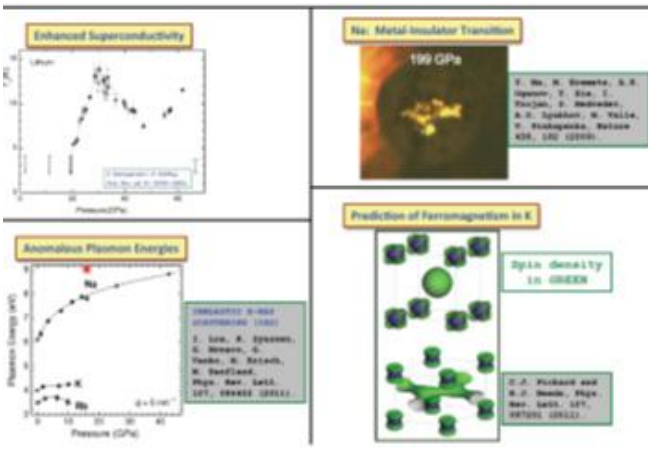

Figure 39: *Several examples of anomalous behavior observed in alkali metals under high pressure (after Schilling et al.). In situ and direct determination of corresponding electronic structure (using, for example, nuclear resonant inelastic x-ray scattering [23]) would be helpful for better understanding this behavior.*

The origins for the magnetic collapse, insulator-metal transition, valence fluctuations and Kondo-like behavior in highly correlated *d*- (transition metal) and *f*- (rare earth) materials are challenging topics in contemporary physics. At present, there are no conclusive answers to explain these physical phenomena. For example, there is not sufficient evidence to indicate that the disorder → order structural transformation in the

rare earth Ce metallic glasses mentioned earlier is the result of volume collapse due to the Ce $4f \rightarrow 6d$ transition. In the closely related EuO, it was found by nuclear resonant inelastic scattering that the pressure evolution of the Eu valence electronic configuration is much more complicated than the simplistic $Eu^{3+} \rightarrow Eu^{2+}$ description. In fact the Eu electronic state changed from well-defined fractional $4f$ and $5d$ occupation at low pressure to a mixed valence state and then reentrant to the Eu^{2+} valence state at higher pressure [15]. This observation highlights the important connection of electronic structure to the magnetic and transport properties of a material. Recently, the long-sought after prototypical Mott insulator $\rightarrow$ metal transition in NiO was confirmed from conductivity measurements. Apart from the historic significance, the experiment suggested a novel high to low spin transition prior to metallization [16]. Resonant and non-resonant IXS [17] are techniques of choice to provide unambiguous information to validate this hypothesis.

More than a decade ago it was pointed out that subjecting the alkali metals Li and Na to extreme pressures forced their ion cores into contact, thereby leading to an increasing localization of their conduction electrons into interstitial lattice sites [18]. Highly anomalous properties in all solid state properties were predicted, including strong deviations from free-electron behavior, a narrowing of bandwidths relative to bandgaps, metal-insulator transitions, and strong electron-lattice coupling culminating in superconductivity at relatively high temperatures (Figure 39). More recently theoretical calculations have predicted that the increased conduction band localization leads to s-band ferromagnetism in potassium metal at pressures near 20 GPa [19]. Bandwidth widening of heavier alkali metals can be probed with XES. Conduction band structure can be determined using angular and momentum resolved IXS spectroscopy on single crystals.

Research Directions

- Spin dynamics under high pressure
  - Investigate relationship between spin and transport properties
  - Electron correlation effect in transition metal and rare earth compounds
  - Mott-Hubbard transition in transition metal compounds
- Electronic structure of simple elements
  - Characterization of valence and conduction band structures
  - Study of electron localization effect
  - Search for paramagnetic electronic state in metallic elements

Scientific and Technical Challenges

In non-conventional superconductors, superconductivity often emerges in a strongly correlated electron system near the antiferromagnetic quantum critical point. Recent reports show that the antiferromagnetic spin fluctuations of recently discovered $CaFe_2As_2$ superconductor in the normal state is suppressed under hydrostatic pressure but does not completely vanish. Thus, Mott-Hubbard insulating, magnetic and superconducting (SC) states are intimately related through the spin dynamics. To investigate the potential link, pressure is the best control parameter to tune interactions systematically. Resonant and non-resonant IXS will provide complementary information on the evolution of the spin

state through the transitions. These experiments, however, must be performed under high magnetic field, variable temperature and high pressure conditions, preferably simultaneously. These requirements may pose some technical challenges. The specimen in the diamond anvil cell must be loaded in a cryostat and/or with laser heating. Apart from the usual increase of phonon flux, the development of a new detection system to increase the signal sensitivity and simultaneous measurement of different momentum transfers over a wide angular range is essential. Since spin coupling between the valence levels and shallow core level is expected to be much stronger than that of the probed element, information obtained from IXS will also be much richer. Thus, it is beneficial to explore IXS using the M-edges of transition metals. A critical component to the success of the proposed research is theoretical and software development. The observed IXS spectra can be fitted to theoretical models to extract meaningful and useful parameters. An example is the determination of the crystal field parameter from spin-multiplet calculations employing a model atomic Hamiltonian [21]. This will lead to a proper understanding of the physical nature of the pressure dependence of the Hubbard on-site repulsion parameter, U.

IXS is now routinely used to probe the electron density of states of the unoccupied states in compounds containing first row elements [14]. The technique in principle can be extended to the study of single crystals under high pressure. Conceivably the experimental setup may be similar to that required for the measurement of phonon band structure. A single crystal in the diamond anvil cell is oriented with respect to the incident photon beam. A technical challenge is to maintain the direction of the momentum transfer of the scattered phonon while the crystal momentum direction is altered. If this could be achieved IXS can be used to map the electronic band structure of the empty states.

Potential Impacts

Probing electronic excitations is important to resolve the existing ambiguities in the mechanism of the Mott-Hubbard insulator metal transition and valence fluctuation in transition and rare earth compounds. The research will provide critical information on current debate on the coexistence of magnetic order, spin fluctuations and superconductivity in high T_c cuprates and recently discovered iron pnictides. First principles electronic structure calculations of highly correlated *d*- and *f* electron systems are a considerable challenge. The experimental results will become the test ground for theoretical development. The knowledge of the electronic structure and orbital characteristic of empty states is essential to rationalize the very rich and exotic phase diagram of alkali metals near the solid-liquid boundary [22].

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PANEL 4: NOVEL STATES OF MATTER

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Introduction

"Extreme conditions" chemistry is arguably the next chemistry frontier for attaining breakthrough discoveries in new bonding motifs and the synthesis of novel materials with unprecedented properties. In this context, "extreme conditions" refers to the thermo-mechanical conditions of *P*-*T*, and even dynamic compression (high *P*-*T*, strain rate) conditions, as well as these conditions combined with other "extremes" such as high electric or magnetic fields [1]. There is enormous potential for substantially different materials to be created under extreme conditions in nearly every field, from high energy density materials to superconductors and superhard materials, to energy or hydrogen storage materials. In addition, studies of chemical structures under these conditions provide a foundational understanding of how chemical bonds and electrons behave in extreme environments.

Pressure has one of the largest ranges of any variable, and invokes multiple important effects on atomic and molecular structures [2]. The application of low pressure drives densification (condensation, solidification) via atomic ordering. Further compression of crystalline lattices overcomes interatomic repulsive forces, and eventually promotes more significant structural reorganizations and chemical bonding changes through an interplay of atomic (molecular) and electronic interactions. Extended solids may form on the way to amorphous or ionic structures. As the compression energy begins to approach the chemical bond energy, delocalization of electrons can be observed, and filled valence shell atoms become chemically reactive. The many recent discoveries of novel bonding and properties of materials in extreme conditions indicate that our conventional descriptions of atomic and electron behaviors are wholly inadequate under these conditions. For example, the periodic table at extreme high *P*-*T* conditions bears little resemblance to the one at ambient conditions.

Current Status

HPCAT has been at the forefront of new materials discovery since its initial commissioning in 2002 as a dedicated high-pressure facility at the Advanced Photon

Source. Key capabilities of the HPCAT facility that have enabled these breakthroughs include the brilliance of the APS synchrotron source, the availability of small (few-10 μm) x-ray beams, remote sample positioning, resistive and in-hutch pulsed laser heating, and *in-situ* x-ray spectroscopies, all coupled to high pressure diamond anvil cell and related devices [3]. The past decade has revealed a tremendous richness in the phase diagrams of the "simplest" of molecules, such as H_2[31], N_2, CO_2 and H_2O (see sidebars), formic acid [4], and atomic B [5], Na [6], and Li [6]. There have been surprising behaviors observed at "extreme" conditions, such as negative melting curves, and the presence of liquid phases (melt) at ambient temperature at high pressures in the alkali metals [6], with complex phases observed near the melt minima. Superhard materials (those with a Vickers hardness HV> 40 and bulk modulus greater than diamond) have been discovered in covalently bonded structures based on boron [5], carbon and nitrogen [7] within diamond anvil cells, and under complementary shock compression conditions. The hydrogen intramolecular covalent bond has been shown to be weakened at high pressure [6, 32], with symmetrization of hydrogen bonding occurring in a number of simple molecules.

In addition to inducing complex structural transformations, compression drives unexpected chemical reactivity. The formation of extended solids (polymers) is a common observation under high-pressure conditions. Polymeric cg-N is a sought-after high energy density target [8], and p-CO has been prepared at high pressures, recovered to ambient conditions, and shown to be highly energetic in its conversion back to CO(g) [9]. An example of the unprecedented reactivity and bonding that has been observed to occur under extreme conditions is the reactivity of xenon (and dihydrogen) at high pressures forming novel xenon-hydrogen compounds [10]. Mixtures of Xe-H_2 at modest pressures (4.9, 5.4 GPa) were found to sequentially form high-hydrogen content xenon complexes $Xe(H_2)_7$ and $Xe(H_2)_8$ with intact H_2 groups (Figure 40). The structures contain an exceptionally large molar equivalent of bound hydrogen, important for potential hydrogen storage applications. High-hydrogen compounds were also prepared from mixtures of SiH_4 and H_2 [11].

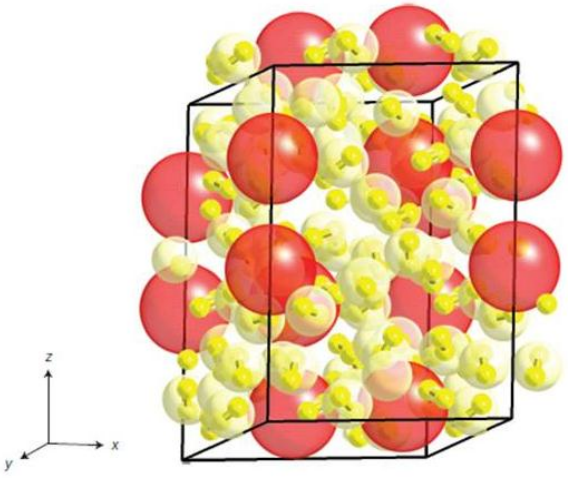


Figure 40: *Structural representation of $Xe(H_2)_7$ formed at 4.9 GPa from Xe-H_2 mixtures. Xe atom pairs are stabilized by the freely rotating H_2 molecules. (after Ref. [10]).*

The combination of 3rd generation synchrotrons and modern diamond anvil cell techniques have made many of these recent discoveries possible, by allowing exquisite interrogation of small samples created in extreme conditions.

Challenges and Opportunities

The principal overarching challenge in this topical area is the need to define the new "rules" of chemistry in extreme environments so that we may exploit them, in a predictive way, to prepare novel materials. To do so, there must be improved integration of theory with experiment, working hand-in-hand to understand the effects of extreme environments on local-to-extended structures and electron behaviors, predict new synthetic targets and their properties, and aid in the interpretation of experimental discoveries with refinement of structure theories as needed.

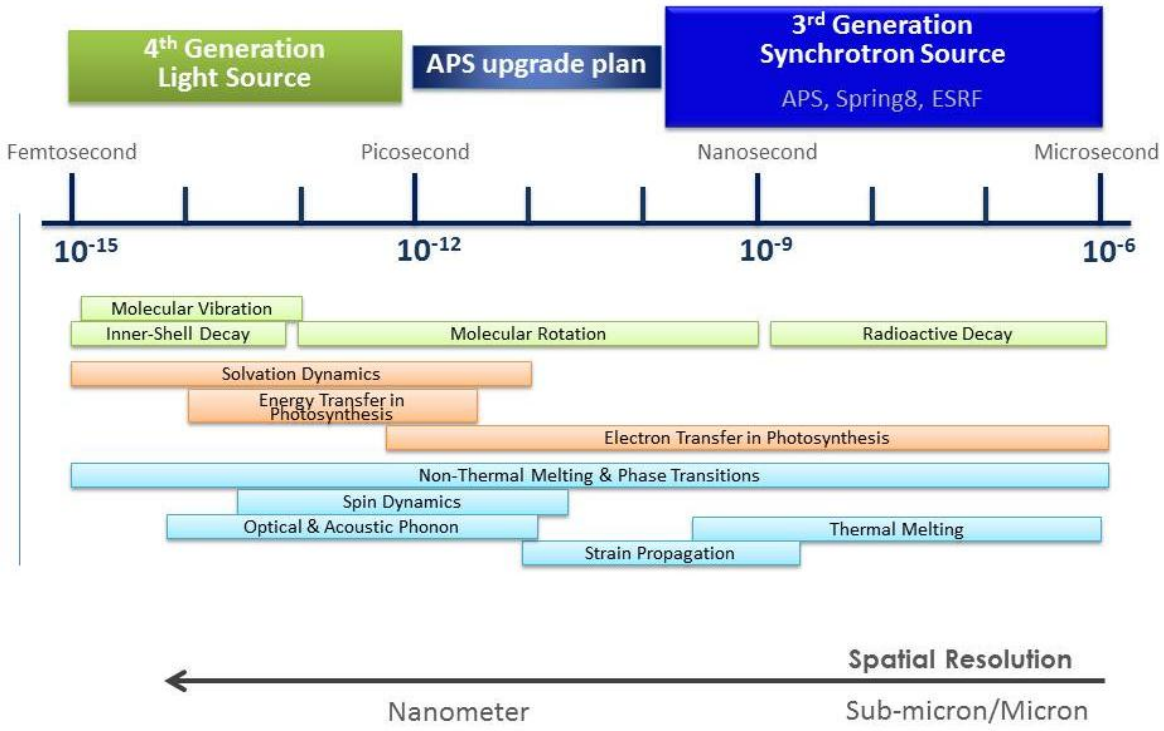


Figure 41: *Advances in synchrotron sources are expected to bridge the gap between 3rd and 4th generation light sources, and allow for measurements of electronic and chemical reaction phenomena on the nanometer to micron length scales (bridging the so-called "micron gap"). This figure illustrates some of the temporal and spatial processes that will be accessible at extreme conditions with the APS upgrade at HPCAT. (Courtesy: D. Dattelbaum).*

Secondarily, many of the most novel behaviors (superconductivity, extended solids) are predicted or observed to occur either perilously close to, or beyond, the limits of today's high-pressure experimental capabilities. A second overarching theme must be the continued investment in technique developments for reaching new thermodynamic phase space. Examples include reaching higher pressures at variable temperatures in diamond anvil cells, and developing an ability to prepare larger volume samples at higher pressures. Furthermore, new environments could be combined such as high heating and strain rate (pressurization) conditions, high pressures with high magnetic and electric fields, and introduction of chemical environments within the diamond cell. The details of material

structures and properties must then be probed using combinations of *in situ* probes (structural, optical, transport properties) under these conditions.

Advances in light source technology, the upgraded APS synchrotron source or a 4th-generation light source, is marked by high peak brilliance, short pulse size and high coherence of the light source. These advancements are expected to result in enhanced resolution in both temporal and spatial domains, ultimately to femtosecond and nanometer scale, and enable investigation of electronic and atomic processes in real time scale with nanometer spatial resolution (Figure 41). Three thrust areas emerged from this panel: from prediction to discovery: new paradigms in extreme condition chemistry; *in situ*, in real time: defining the details of chemical transformations in extreme conditions; and photon-induced chemistry.

P4.1 New Paradigms in Extreme Condition Chemistry

Over the past decade, new materials and novel phenomena have been discovered and predicted at high pressures and temperatures. Many of these phenomena are fundamental chemistry problems, reflecting how chemical bonds break and form, how atoms and molecules organize over short- and long-ranges, and how kinetics and thermodynamics govern materials stability.

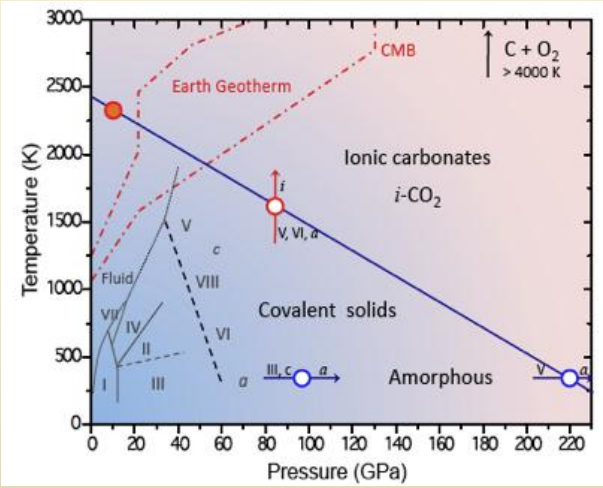
Research Directions

At Mbar pressures, the compression energy rivals the chemical bond energies and the transformation of molecular solids into more compact structures with itinerant electrons (such as metallic and non-metallic extended phases) occurs [12]. Non-molecular extended solids, particularly those composed of low-Z molecules, constitute a new class of high-energy-density solids. These new solids store a large sum of chemical bond energy in their three-dimensional network structure (~ several eV/bond). The large cohesive energy of singly bonded or sp^3 hybridized electrons gives rise to an extremely stiff lattice and novel electronic and optical properties. Importantly, non-molecular solids with three-dimensional network structures, held together by strong covalent bonds, have high kinetic barriers against reversal, offering opportunities to recover these novel materials at ambient conditions.

Broadly speaking, molecular-to-non-molecular transitions occur due to electron delocalization manifested as a rapid increase in electron kinetic energy at high density. The detailed mechanisms, however, are more complex and the transitions often exhibit path dependent phase boundaries and phases, large strains in lattice, and structural distortions—all of which are controlled by mechanisms well beyond thermodynamic constraints to chemical kinetics [13]. As a result, the equilibrium phase boundary is difficult to precisely locate (experimentally or theoretically) and is often obscured by the presence of metastable phases (ordered or disordered), as observed in carbon dioxide (sidebar 1) [14] and water (sidebar 2) [15].

Carbon Dioxide: Tuning at Bond Energies

Carbon dioxide exhibits a richness of high-pressure polymorphs with a great diversity in intermolecular interaction, chemical bonding, and crystal structures [1]. It ranges from a typical molecular phase I observed below 10 GPa to fully extended, polymeric phases of V, VI and *a*-carbonia above 40 GPa, with crystal structures similar to those of SiO_2. These extended solids are fundamentally new materials exhibiting interesting optical nonlinearity, low compressibility, and high energy density. The large disparity in chemical bonding between the extended network and molecular structures, on the other hand, results in a broad metastability domain for these phases, to room temperature and almost ambient pressure. Yet, all known extended phases of CO_2-V, VI, *a*-carbonia, and coesite-CO_2 become non-metallic amorphous solids with enhanced ionic characters in the CO bonds at higher pressures above 100-200 GPa and room temperature. At high temperatures these extended solids further transform into carbon dioxide carbonate (*i*-CO_2) - a fully extended *2D* ionic layer structure of the post aragonite of $CaCO_3$ (*$P2_12_12$)*. Hence, the present results clearly suggest revisiting the assumption of high stability of CO_4 tetrahedra to 1000 GPa [2]. The presence of such ionic carbonate solid at the pressure-temperature near the core-mantle boundary provides a geochemical mechanism for transporting carbon dioxide from near the Earth's surface to anhydrous silicates in the mantle and iron core and, thus, offers a critical constraint on the deep carbon cycle. These are important findings underscoring the periodic analogy between CO_2 and SiO_2; yet, the absence of *in-situ* real-time structural information at high pressures and temperatures often obscures the details and results in controversies [3-5].



Phase/chemical equilibrium diagram of CO_2.

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Scientific and Technical Challenges

Understanding phase metastability is critically important in materials research, as nearly all man-made materials have been developed based on knowledge of metastability. This includes nanoparticles, energetic materials, polymers, plastics, and many other hydrocarbons. Because the metastability arises from local energy minimum configurations existing along many kinetically controlled pathways on a complex potential energy landscape, it is important to understand the associated transition kinetics at atomistic/molecular levels over a large range of pressure, temperature and strain rate. Yet, despite the acknowledged importance and decades of research on chemical kinetics, the kinetic properties are still studied almost exclusively in terms of temperature and composition – not in a pressure domain (static and dynamic alike). This is in part due to technical challenges in precisely controlling pressure and compression rate and obtaining time-resolved structural information under dynamic conditions. As a result, it undermines the acknowledged significance of pressure and compression rates and results in incomplete thermodynamic (i.e., G (T, μ) at constant P) and kinetic (e.g., TTT at constant P) descriptions of solids under extreme conditions [16].

There are also significant challenges in validating theory against experimental observables. $O(N^3)$ and exponential scaling, and computational limitations on periodicity and numbers of atoms are challenges to be overcome to perform simulations on large numbers of atoms over durations that scale with experiment. Furthermore, for chemical reactions, the computations of energy landscapes (potential surfaces and transition states) in extreme conditions can be cumbersome, and there are computational limits on the dynamics (at the ps timescale). Lastly, many of our computational tools for treating structural evolution in extremes or even dynamic chemical events (such as ReaxFF [17], or LATTE [18]) often do not tackle the potential role of electronic excited states in reaction pathways.

Potential Impacts

The impacts of this research direction are the potential for synthesizing new materials with properties not attainable by conventional means. New synthetic targets are diverse and offer the potential for impacting fields from energy materials to engineering or structural materials, to defense materials.

P4.2 Chemical Transformations in Extreme Conditions

Chemistry is the study of structure and bonding changes going beyond static properties and stable structures. Therefore, a major future direction must be the development and application of time-resolved, *in situ* measurements for following chemical reaction mechanisms and their kinetics in extreme conditions.

Research Directions

The preparation and isolation of new materials under extreme conditions must exploit competitions between kinetic and thermodynamic pathways. To do so, we must improve our understanding of the potential energy landscape along reaction paths, and delve into reaction mechanisms and their kinetics in real time. The bunch sequences of the APS allow for a variety of *in situ* time-resolved diffraction experiments ranging from nanosecond time resolution, few-"frame" techniques, to essentially continuous, millisecond-to-second x-ray pulse-averaged measurements. Recent experiments have shown the enormous potential of applying x-ray probes in understanding the details of dynamic or chemical events. For example, time-resolved diffraction was recently used to decipher the chemical transformations associated with combustion processes in Ni/Al mixtures by streaking diffraction rings across an image plate detector at HPCAT [23]. Dynamic phase contrast imaging has recently shed light on shock front homogeneity, and dynamic compaction of porous materials such as polymeric foams and glass beads with single frame "snapshots" the event [19]. Time-resolved Laue diffraction has also been used to follow solid-solid phase transformations under shock loading [20], important to the development of phase-aware, multi-phase equations of state and strength models for metals. Continued advances in detector physics and the APS upgrade will enable multiple "snapshots" or frames at even faster temporal resolution for the investigation of structure and bonding evolution under rapid compression (shock, dynamic DAC, load frames), laser- or x-ray photo-excitation, or other events (electric or magnetic fields, thermal heating or ignition, etc.).

Solid-state transformations are often diffusion limited, as in the most (if not all) transitions occurring in static high pressures. The diffusion process in solids occurs in an intermediate time (μs to ms) scale between conventional static (<1 GPa/s) and shock wave (>10^7 GPa/s) experiments, which can be obtained, precisely and in controlled ways, using dynamic-DACs and related techniques [21, 22]. Dynamic-DACs are nearly a perfect match to the x-ray pulse structure of third-generation synchrotrons for obtaining time-resolved structural information of solids under dynamic conditions. Therefore, it is a priority in high-pressure research to integrate dynamic-DAC and time-resolved x-ray diffraction [23] (or time-resolved spectroscopy [24]) and investigate the dynamic structural (chemical) responses of solids under rapidly modulating pressures across various chemical and phase transformations.

A major focus for the future of HPCAT must be the further development of time-resolved diffraction techniques capitalizing on the synchrotron bunch sequences and fast CCD and CMOS detectors (such as the Pilatus 1M and Perkin-Elmer). Here, dynamic-DACs, pressure- and temperature-jump techniques, and shocks from static high *P-T* conditions offer pathways to new states, and require pump-probe experimentation to probe transient states along the compression/heating pathway. For example, strain rates as high as 1 s^{-1} to 10^2 s^{-1} have been reported using the piezoelectric-driven dDAC [21], and pressure-jump approach [22], respectively, filling in an important regime of the "strain-rate gap" between static and dynamic compression experiments. These types of experiments can shed light on many questions. Can all of the structural phase transformations kinetically occur as one compresses across the *P-T* phase diagram? Are phase transformations driven to completion or are there retained low pressure or metastable phases formed? What are the kinetics of

melting and re-freezing in extreme environments? X-rays for structural determination cannot be the only probe in experiments focused on chemistry. Both optical and x-ray spectroscopies (as possible), and *in-situ* measurements of electrical resistivity provide essential probes of electronic and bonding changes as reactions proceed under these conditions.

Scientific and Technical Challenges

Challenges to studying the mechanisms and kinetics of chemical reactions (and the phase transformation leading up to them) under extreme conditions include the single event nature of the experiments (having the right sample condition at the right time, and low experimental through-put), current limitations in detector physics (temporal resolution limited by detector read-out times and number of frames), and the challenges associated with focusing multiple probes (x-ray, optical, laser heating beams etc.) on micron-sized samples within diamond anvil cells at high *P-T* conditions. Some of these challenges, such as detector physics (and related source brilliance), and sample positioning, will diminish continually as new developments are made in a broader sense. Others will require focused efforts at dedicated beamlines like HPCAT and the related DCS at APS.

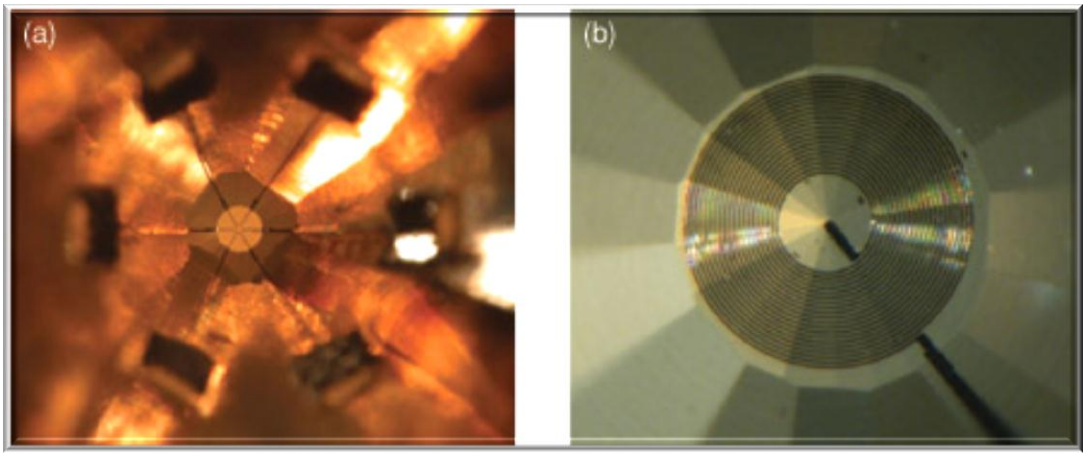


Figure 42: *"Designer" diamond anvils made for (a) electrical transport and (b) magnetic susceptibility (after Ref. [25]).*

Going forward, it will be increasingly important to adequately diagnose the states of matter at faster timescales, *in situ* using multiple probes to perform simultaneous measurements in high-pressure cells. These measurements include x-ray diffraction, x-ray scattering, thermodynamic, and optical to name a few. The advantages, in addition to optimization of measurement time, of using multiple probes are many fold. Much research focuses on determining *P-V-T* phase diagrams where simultaneous measurements avoid the pitfall of 'matching' *P-V-T* condition for data from multiple measurements. Also, a common problem in comparing data sets is the variation of local stress conditions on physical properties; simultaneous measurements assure that the different physical properties are measured at the same *P-V-T* and stress state. Another advantage lies in the ability to measure the properties of high-pressure states that are recoverable at ambient conditions.

An example of multiple *in situ* probes is the combination of simultaneous electrical resistance (transport) and x-ray diffraction measurements (structure). Performing electrical transport measurements on the small samples used in a DAC has long been a technological challenge. The work of a Lawrence Livermore/University of Alabama, Birmingham collaboration has been at the forefront of measurements using 'designer' anvils that have electrical contacts made using lithography followed by diamond chemical vapor deposition to perform transport [25] as well as magnetization measurements [27]. A picture of the designer anvils is shown in Figure 42.

An example illustrating the importance of applying both techniques is a recent study of a FeSe-type superconductor. The Fe-based superconducing systems in general show a strong correlation between structure and superconducting properties. It was found that the structure of the low temperature superconducting state in FeSe was not the same as the room temperature structure [28]. Subsequent simultaneous measurements [29] clearly show the proper correlation between structure and transport properties.

Another area of future development is the simultaneous application of x-ray diffraction and x-ray scattering. Many beamlines around the world are currently capable of performing XRD and other x-ray scattering measurements. Sector 16-BMD at HPCAT allows one to perform both XRD and XANES measurements. Two recent examples relating to Fe inside the Earth illustrate this well. Andrault et al. were able to better explain solid-liquid partitioning (Figure 43) in the deep mantle that can better explain the core-mantle boundary which in turn provides a better idea of how the mantle evolved and how the plumes feed hot spot volcanoes such as the ones in Hawaii [30]. Inelastic x-ray scattering was used along with XRD to test Birch's Law (linear relationship between sound velocity and density) at high *P-T* conditions relative to the Earth's core [31]. This is important as extrapolations are typically used to estimate data under these conditions.

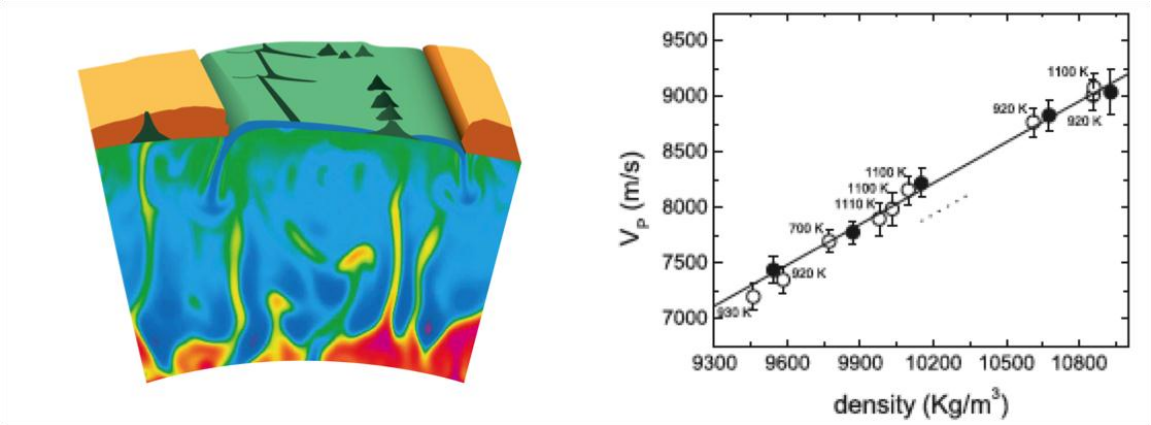
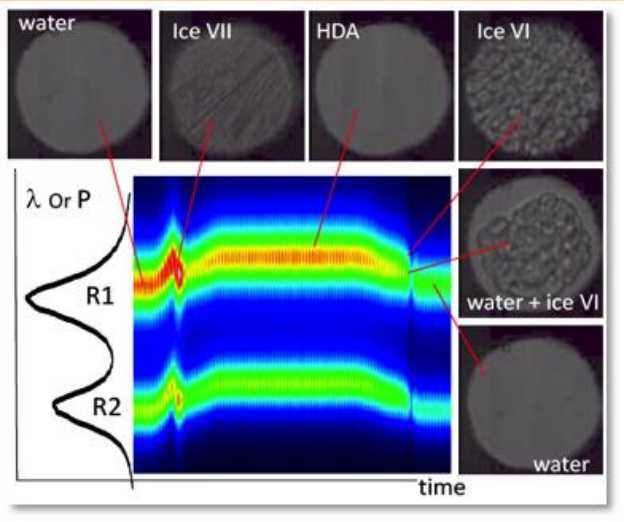


Figure 43: *(Left) Illustration of mantle plumes from the core-mantle boundary region reaching the Earth's crust [30]. (Right) Aggregate sound velocity versus density for Fe at ambient and enhanced temperatures taken from [30]. The linearity shows behavior consistent with Birch's Law.*

Ices: Amorphization and Metastable Phases

Abundant in nature, water is a major constituent of planets and living organisms alike. The phase diagram of water is both unusual and complex, exhibiting a large number of polymorphs with great diversity in crystalline structure, chemical bonding, and collective interactions. The hydrogen bond angles and topology of relatively weak hydrogen bonds (with respect to covalent OH-bonds) are subject to large distortions, which in turn lead to proton and structural disorders and a myriad of phases – both stable and metastable (including amorphous) [1]. Hence, the phase diagram of H_2O is governed by mechanisms, beyond thermodynamic constraints, to chemical kinetics – exclusively written in structural evolutions associated with crystal nucleation and growth, proton ordering, amorphization, and interfacial structural miscibility.



High density amorphous (HDA) ice forms from metastable ice VII at 300 K and 1.6-2.1 GPa under rapidly modulating pressures.

Recently, the evidence was found for HDA ice formed well above the crystallization temperature at 1 GPa – well inside so-called the "no-man's land" (Figure). It forms from metastable ice VII in the stability field of ice VI under rapid compression, resulting *presumably* from structural similarities between HDA and ice VII. Interestingly, the HDA formation follows an interfacial growth mechanism unlike the melting process. Yet, it forms along the extrapolated melt line of ice VII and resembles the ice Ih-to-HDA transition. These results were primarily based on the broad Raman spectra of governing phases, which often encountered challenges in resolving individual phases and associated transition dynamics. Therefore, the structural information is critical to better understand the exact structure of metastable ice VII and HDA, as well as the origin of pressure-induced amorphization.

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Optical pump and probe techniques, coupled to structural methods, will also be increasingly important for kinetic studies. In particular, time-resolved vibrational spectroscopic probes coupled to dynamic pressure- or temperature-jump experiments, with complementary x-ray diffraction, are essential tools for studying the evolution of chemical bonds as reactions proceed in extremes. Simultaneous Raman and transport measurements have recently led to claims of showing behavior consistent with one of the "holy grails" of high pressure science – namely the metalization of hydrogen [32]. In the future, there will be increased demand for synchrotron beamlines to offer multiple measurement techniques to be used concurrently with XRD at high pressures. HPCAT should take an active role to be at the forefront of such development.

P4.3 Photon-Induced Chemistry

The absorption of photons by reactant molecules may cause reactions to occur by bringing the molecule to the necessary activation energy, and by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction pathway. Using the wide spectral range of photons of the high brilliance light sources, and adjacent optical or free electron laser sources, to induce and direct chemical reactions and to create new chemistry, is a promising research direction in high-pressure research. This approach, together with the advanced capabilities promised by an upgraded synchrotron source or a 4th-generation light source, provides a promising way to initiate and potentially control a chemical process and allows us to design, initiate, and direct the chemical and physical behavior of materials.

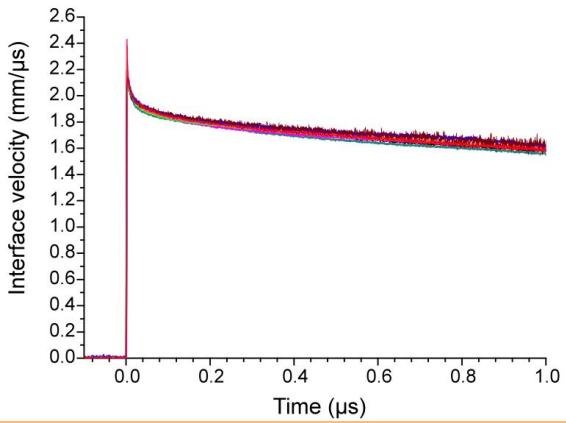
Research Directions

The high peak brilliance, short pulse duration and high coherence of 3.5 to 4th generation light sources offer enhancements in both the temporal and spatial domains, ultimately to offer interrogation of matter at the femtosecond and nanometer scales. In the research area of photon-induced chemistry under high pressure, the opportunities brought about by the upgraded APS synchrotron source or a 4th-generation light source can be summarized as:

(1) Selective use of photon energy (ultraviolent, soft x-ray and hard x-ray) for targeted bond breaking in initiating chemical reactions.
(2) Combining the control of photon peak brilliance with pulse size can be used to control the level of "damage" to the sample. Short pulse can reduce or eliminate photon "damage."
(3) Study the temporal evolution of chemical bond of reactants breaking and reforming on their natural time scales as they form a sequence of intermediate states, and possibly observe the processes involving electrons, spins, atoms in chemical reactions.
(4) Spectroscopy and structural studies at nano-scale regions.
(5) Ultra-high pressure research on submicron samples.

Detonation Chemistry

The detonation of high explosives is driven by chemical reactions proceeding under the extreme conditions created by shock compression. Despite our maturity in understanding the wave dynamics associated with detonation propagation, our ability to predict the sensitivity or chemical reaction zone of an explosive is nearly non-existant due to a lack of understanding of the first and subsequent reaction steps behind the shock front. In one of the simplest explosives, nitromethane (CH_3NO_2), the first reaction step is believed to be an intermolecular proton transfer reaction forming an aci-ion intermediate [1]. Subsequent exothermic decomposition proceeds over the ~ 100-150 ns of the chemical reaction zone (see Figure below) to form small molecule products [2].



Detonation wave profile for nitromethane. The reaction zone is ~ 100-150 ns long [2].

The reaction chemistry of larger explosive molecules, such as RDX, is predicted to be substantially more complicated [3]. Static and dynamic compression experiments coupled with the x-ray source of the APS can shed light into the processes leading up to and during detonation in explosives. The leading edge of a detonation ties the unreacted, quiescent explosive to a high *P-T* condition on the unreacted equation of state surface (Hugoniot) of the explosive. Static experiments give information on the explosive's crystalline structure, compressibility and presence of phase transitions along the pathway to this condition. Mixtures of simple molecules (H_2O, N_2, C, HCOOH) under warm, dense conditions serve as models for detonation product mixtures, necessary for establishing product mixing rules and equations of state. Dynamic experiments of shocked and detonating explosives can give insights into the real-time structural and chemical evolutions through the reaction zone. The application of novel x-ray probes, such as x-ray absorption spectroscopy or inelastic x-ray scattering, can give information regarding the carbon (and other atom) bond hybrization (s) at various temporal and spatial scales behind the shock front, where optical probes are inaccessible. We expect that the intersection of synchrotron techniques with static to dynamic compression experiments will aid in the answering of long-standing questions about the mechanisms of the shock initiation of explosives, role of phase transformations in the initiation sensitivity of crystalline explosives, and the interplays of explosive microstructures with localization of energy (in pressure and temperature "hot spots") and the onset of chemical reactions.

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Photon induced new chemistry has been demonstrated by the chemical reactions of O_2 and N_2 molecules under high pressure to form ionic phases of nitrogen oxide reported previously [33]. Nitrogen and oxygen do not react with each other at ambient temperature due to the large covalent bond energy of the molecules. Irradiating a liquid mixture of O_2 and N_2 contained in a diamond anvil cell under pressure with a 10.2 keV synchrotron x-ray radiation caused dissociation of O_2 and N_2 molecules and induced chemical reaction to form

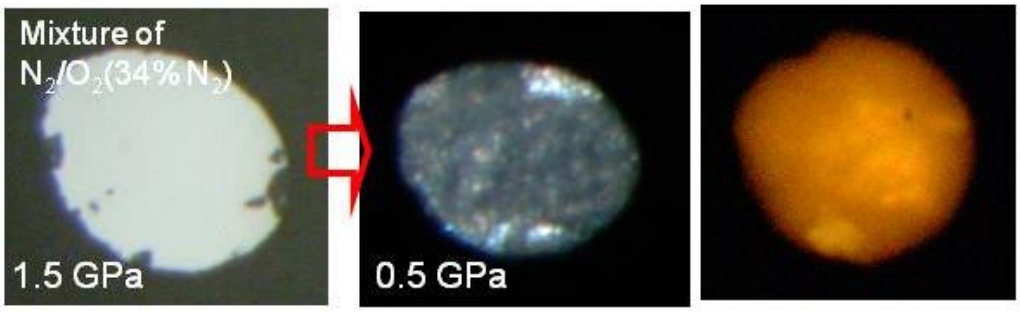

Figure 44: *a) $NO_2^+NO_3^-$, an ionic phase of N_2O_5 after x-ray radiation of the N_2/O_2 mixture [33]. b) A known phase previously found only at low temperatures $NO^+NO_3^-$ at 1.7 GPa after x-ray radiation of $NO_2^+NO_3^-$ at 2 GPa for 12 hours. (c) a new phase [33].*

$NO_2^+NO_3^-$, an ionic phase of N_2O_5 (Figure 44b). The mechanism for the hard x-ray photon-induced dissociation of O_2 and N_2 is the same as that by soft x-ray photons, in which the photon produces an inner-shell core hole, and the fragmentation of the molecules is caused by a valance (bonding) electron filling the core hole. Compared to soft x-ray photons, the absorption cross-section of hard x-ray photons is much smaller. Ultraviolet photons can also be used to break the triple bond of nitrogen and the double bond of oxygen, but through the mechanism of ionizing the valence electrons of the molecule. In the same work, it was also shown that x-ray radiation can facilitate further transformation of $NO_2^+NO_3^-$ to NO^+ NO_3^- by dissociating NO_2^+ to a more stable configuration of NO^+ at higher pressures (Figure 44c).

Scientific and Technical Challenges

The principal scientific challenge in this area is to develop an ability to control chemical reactions using photons, and follow those reactions using in-situ x-ray and optical methods. While traditional optical pump-probe experiments have been successful for studying visible light-driven photochemistry for decades, controlled chemical reactions driven by x-ray-to-visible photons at extreme pressures is a new territory.

Hard x-rays in the 2-100 keV range at the APS have also been shown to induce decomposition in a variety of simple compounds, such as NH_3BH_3, $KClO_3$ and $NaClO_3$, in both glass capillaries at ambient conditions and at high pressures within diamond anvil cells. Examples of the chemical reactions are given below:

$$2KClO_3 + h\nu \rightarrow 3O_2 + 2KCl$$
$$n(NH_3BH_3) + h\nu \rightarrow (H_2NBH_2)_n + nH_2 \rightarrow (HNBH)_n + 2nH_2$$
$$O_2 + 2H_2 + h\upsilon \rightarrow 2H_2O$$

$$3N_2H_4 + h\upsilon \rightarrow 4NH_3 + N_2$$

The hard x-ray induced decomposition of small molecules into gas phase mixtures may be a pathway to useful hard x-ray induced chemistry wherein highly controllable reactions never before achieved in sealed environments (e.g. high pressure and/or high temperature ovens) catalytically via irradiation.

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PANEL 5: DEFORMATION AND TRANSPORT PROPERTIES

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Dmitry Popov, Carnegie Institution of Washington
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Introduction

Most high pressure studies in the past decades focused on the behavior of materials under hydrostatic (or assumed to be hydrostatic) conditions. This is appropriate to quantify crystal structures at *P-T* conditions and establish ideal phase diagrams. Real materials are far more complex. Single crystals are stacked with dislocations and other defects, many introduced during deformation. In polycrystalline materials deformation produces changes in grain shape and grain orientation which have a profound influence on mechanical properties. Most materials become anisotropic. This applies to metals, ceramics, polymers as well as Earth materials down to the inner core. When crystals contain defects, this changes their thermodynamic properties and stability [1]. The goal of this section is to address these issues by proposing new research directions that have become feasible with technical advances.

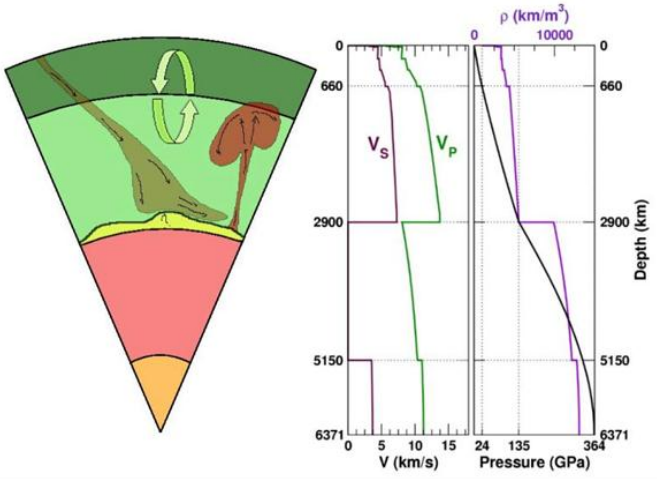

Figure 45: *Schematic Earth structure with mantle (green and yellow), liquid outer core (red) and solid inner core (brown). Seismic velocity changes and density with discontinuities (right side).*

An understanding of the stress-strain-time relationships in solids is vital to addressing rheological properties, strength and stiffness of materials at extreme *P-T* conditions. It is widely agreed that knowledge of rheological properties of Earth materials is critical for our understanding of the dynamics and evolution of Earth (and other planets). Rheological and constitutive properties of engineering materials often differ from equilibrium elastic properties and equations of state. For example, high pressure promotes plasticity in solids, including nanocomposites [2]. Also rocks in the deep Earth and planetary systems are subject to large-scale convection and deformation, producing seismic anisotropy (e.g. [3, 4], Figure 45). Application of shear deformation

under pressure may cause significant reduction of phase transformation pressure and induce new phases that cannot be achieved without shear.

Anisotropy of materials is expressed both in physical properties and microstructures, including crystal and shape preferred orientation. Deformation is also apparent as residual stresses, expressed by local lattice strains in crystal structures. Investigation of the stress-strain-microstructure behavior of composites at ultrahigh pressure and temperature is still at an exploratory stage and further development of experimental techniques, data analysis and data interpretation are of critical importance. The enhanced HPCAT, coordinating with other beamlines at the APS as well as other synchrotron sources, can play an important role.

Current Status

As mentioned briefly in the introduction, changes that occur under nonhydrostatic stress conditions are critical for understanding material behavior and this has been a central topic in materials science [5]. Most of this work was performed at ambient pressure but elevated temperature. In earth sciences there has been a tradition to perform deformation experiments also at high pressure (e.g. reviews in [6]). While in metallurgy a wide variety of deformation geometries were explored, in geosciences most experiments were done in axial compression until recently when torsion apparatus were developed [7], though with a very limited pressure range (<2 GPa). This has changed with the development of the D-DIA multianvil apparatus [8] where 15 GPa can be reached.

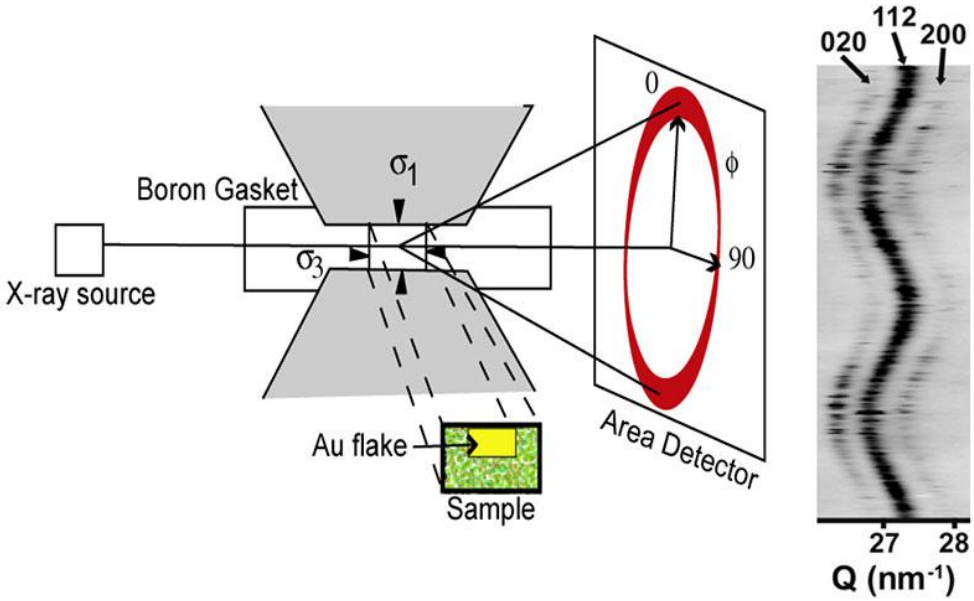

Figure 46: *Geometry of a radial diffraction experiment in the DAC. Diamond pistons not only apply pressure but also induce stress (left). The corresponding changes are visible in "unrolled" Debye rings (right). They are sinusoidal due to elastic distortion of the crystal lattice under stress and show intensity changes due to rotations produced by dislocation glide. (after H. R. Wenk)*

For higher pressures diamond anvil cells can be used. If the sample is contained between diamond anvils without a weak medium, anvils also act as pistons and transmit stress. In radial diffraction geometry (Figure 46, left), first introduced by Kinsland and Bassett [9], diffraction patterns document elastic deformation by shifts in d-spacings (sinusoidal variations) and plastic deformation resulting in crystal rotations and corresponding intensity changes (Figure 46, right). This proved to be a very efficient method to study elastic anisotropy [10] and preferred orientation [11]. Amazingly even stiff ceramics such as olivine and periclase deform ductily at 10 GPa and room temperature. During deformation in the DAC preferred orientation develops during dislocation glide which can be used to infer slip systems. Radial DAC experiments have identified deformation mechanisms at 200 GPa in ε-iron which composes the Earth's inner core [12](Figure 47, top), as well as for the high pressure phase $MgSiO_3$ postperovskite up to 185 GPa, which dominates convection in the core-mantle boundary [13](Figure 47, bottom).

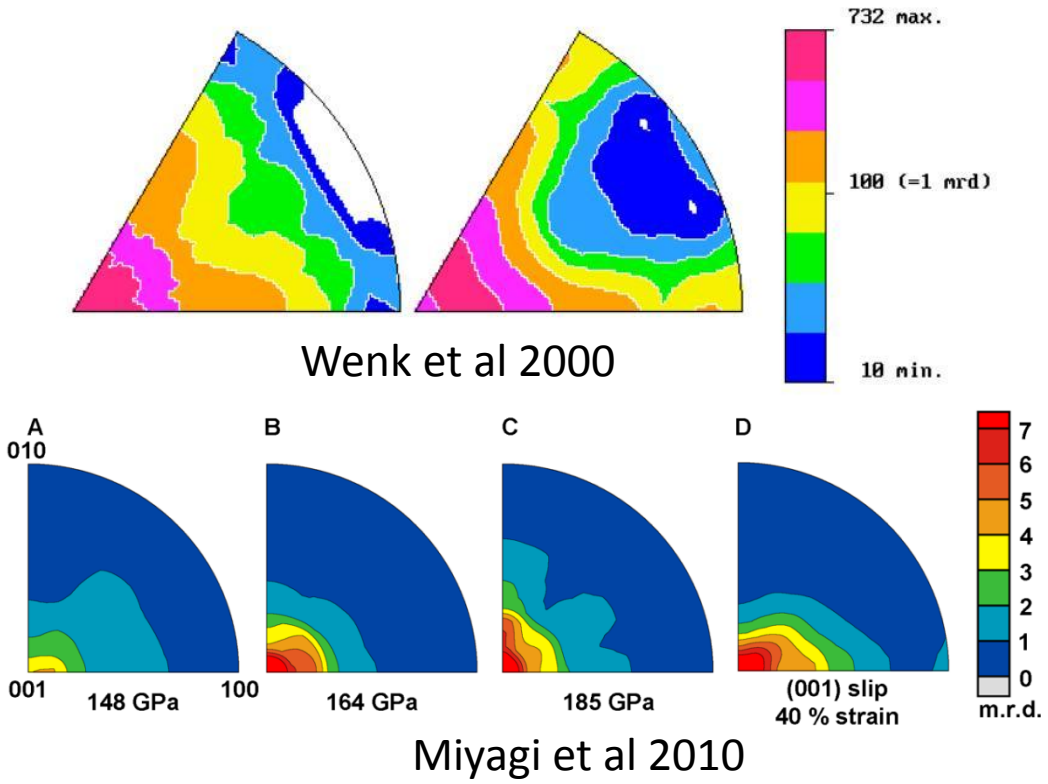

Figure 47: *(Top left) Inverse pole figure of iron at 200 GPa documenting the preferred orientation developing during compression at high pressure. (Top right) corresponding orientation pattern generated by polycrystal plasticity modeling with dominant basal slip. (Bottom) Evolution of preferred orientation in $MgSiO_3$ postperovskite observed in the DAC with increasing pressure and stress (A-C). D corresponding polycrystal plasticity simulation with dominant (001) slip which appears to be the main active slip system in the lowermost mantle of the Earth [13].*

Deformation in an electrochemical reaction of battery anode/cathode also provides an example that can be well simulated in the high pressure experiment. The Li^+ ion transport in a battery can be compromised by mechanical deformation of electrodes due to large

strains caused by lithium intercalation/extercalation during charge-discharge cycle. The volume changes in electrodes of up to 300% without fracturing are equivalent to internal pressures more than 10 GPa. Understanding the dislocation density at high pressure is the key for information on sustaining the excessive internal elastic/plastic energy, which directly contributes to the extreme strength of the material (Figure 48).

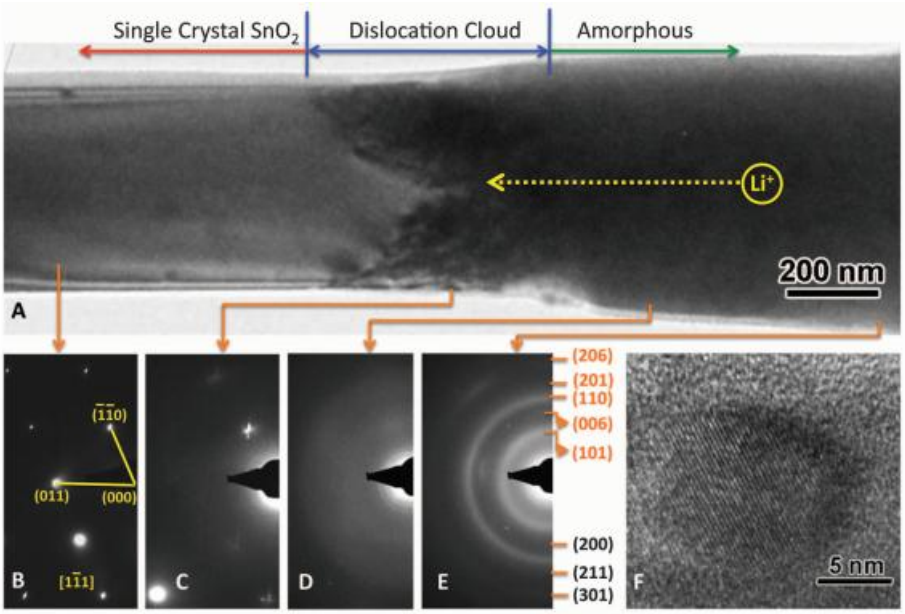

Figure 48: *Structural and phase characterization of SnO_2 nanowire anode by TEM micrograph and EDPs from the different sections of the nanowire: (A) of the nanowire showing a reaction front (C & D "dislocation cloud") separating the reacted (E "amorphous halo") and nonreacted (B "pristine single-crystal SnO_2") sections; (F) A HRTEM image from a charged nanowire showing Sn nanoparticles dispersed in an amorphous matrix [14].*

Overarching Challenges and Opportunities

The next technical advances in the field of mechanical properties and deformation will need to address a wider and more reliable pressure-temperature range. Reliable temperature control with resistive and laser heating emerges as an important issue. Also, in addition to studying fine-grained powders, single crystals need to be explored to investigate the local orientation and stress state. This can be done with the Laue technique but requires coordination. Also, larger grain size in deformation processes is a significant factor influencing the flow process and new instrumentation needs to be designed.

As with high *P-T* experiments to establish phase diagrams, also for deformation studies, temperature is a critical factor that influences deformation mechanisms, phase transformations under stress, nucleation and growth, and recrystallization. Much progress has been made with heating in DACs but especially for radial DACs this is still far from a routine. With laser heating there are large temperature gradients and intermediate temperatures are difficult to reach though recent work with mobile systems is very promising [15]. Resistive heating, on the other hand, has been limited to low temperatures and has been subject to contamination (e.g. [16, 17]). Recently exploratory experiments

were done at ALS 12.2.2, combining resistive and laser heating, temperatures of close to 2000K were reached, with resistive heating over extended periods, but also this needs to be improved [18] (Figure 49). A flexible and reliable heating system for general users would be an invaluable addition at HPCAT and could serve as a model for other facilities. In recent HPCAT experiments tremendous possibilities of the mobile laser system were discovered but this sophisticated system needs modifications to make it available for more routine applications.

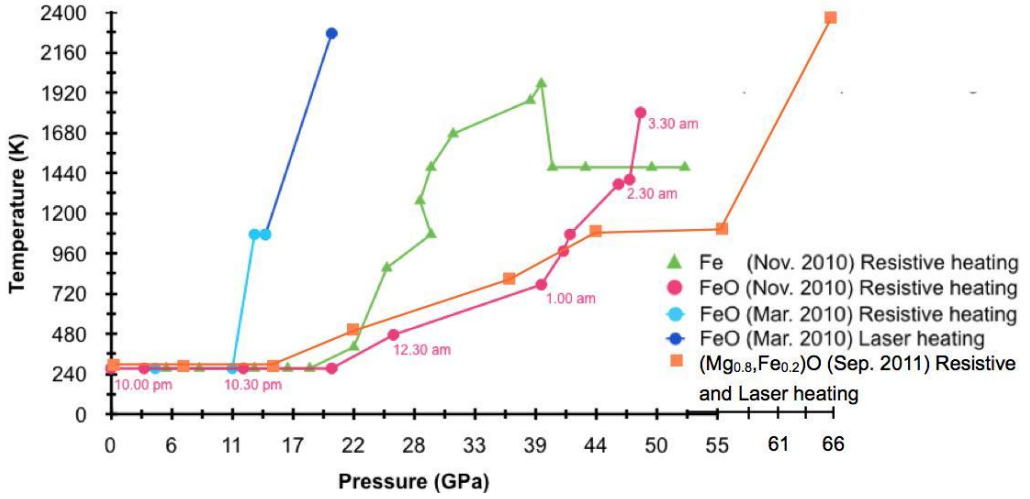

Figure 49: *High temperature experiments with resistive and laser heating on a radial DAC conducted at ALS [18].*

Experiments alone do not produce results. Data need to be analyzed with sophisticated software and here experiments need to be designed to make the data analysis more quantitative and straightforward. Much software is available such as XMAS [19] for interpreting residual strain and orientation, GSAS [20] and FULLPROF [21] for regular diffraction images, MAUD [22] for diffraction images of anisotropic materials, but this software needs to be constantly upgraded to take facility development into account.

Improvements in hardware at extreme conditions produce large amounts of very complex data. Many of these data are never or only incompletely analyzed. It requires modern user-friendly software and training of users. Clearly, this is outside of the main mission of HPCAT, but the HPCAT consortium could play a significant role in promoting coordination in software development at different facilities such as XMAS for orientation and strain identification from Laue patterns (e.g. [23]), heXRD for monochromatic single crystal strain and orientation analysis (currently in development by Joel Bernier, LLNL), and the sophisticated Rietveld code MAUD (Materials Analysis using Diffraction) for polycrystal image analysis [22]. Equally important, but more removed from the facility is the scientific interpretation of the derived material properties in terms of material behavior. With polycrystal plasticity theories deformation mechanisms can be assessed based on crystal orientation patterns. It is critical to educate users, e.g. by organizing focused interdisciplinary workshops to bring scientists of different expertise (e.g. physics, materials science, chemistry, earth sciences) together and exchange ideas.

Concluding Remarks

Exploring the role of ultrahigh pressure experiments to investigate the deformation behavior at extreme conditions is not at all a mature field. Facility improvements at a synchrotron scattering beamline could play a critical role as described in more detail below in the priority section. Relatively minor additions can establish a powerful Laue beamline at HPCAT to complement oversubscribed facilities such as APS-34 or ALS 12.3.2 which are mainly used for ambient condition experiments. An important improvement, also shared by other panels, is the establishment of reliable and quantitative heating capabilities for DAC experiments. In addition to radial-DAC for compression, rotational-DAC for shear experiments needs to be advanced to enable *in situ* crystal rotation studies. Further along, the large volume press needs to be advanced to provide experiments with larger sample size.

P5.1 Time-resolved Laue X-ray Diffraction

Using a white x-ray beam, Laue diffraction provides information on crystal lattice defects and deformations *in situ* under external stress in time resolved mode. Using a microfocus beam, this has been very powerful in mapping local heterogeneities in a wide variety of materials (e.g., [24, 25]) and is currently used at APS (sector 34), ALS (12.3.2) (Figure 47 left) and ESRF. Application of white beam for this kind of research provides better time resolution with respect to a monochromatic beam because sufficient reciprocal space can be accessed without the need to rotate the sample, which drastically reduces collection time and overcomes the problem of "sphere of confusion". Implementation and development of a HPCAT Laue setup is important because the Laue beamline in sector 34 at APS is highly oversubscribed and not available for routine high pressure and other experiments conducted under external stress. In contrast to ALS, the higher x-ray energy at APS has advantages because a higher Q-range can be recorded, which is particularly important for DAC applications with a limited 2Θ range. It is recommended that HPCAT work with existing white x-ray beamlines on topics including hardware, instruments, and data analysis [19].

Research Directions

As most deformations are controlled by both dynamical and kinetic factors, measurements in time resolved mode are essential for understanding the deformation process. The white Laue beamline will provide a powerful tool for measurements on texture, strain, dislocation arrangements, and operational slip systems [26, 27]. Among a large list of possible applications, we identify two research directions as examples.

Obviously studies of phase transformations such as structural phase transitions, processes in melting or dissolving crystals, and crystal growth are important for understanding behavior of materials at high pressure. For a thorough understanding of the transformations, however, it is necessary to have information about defects and deformations of crystals. Application of a white beam to samples in DACs is technically feasible in both axial and radial geometries, thus opening a research direction of studying

crystal defects and deformation. Exploratory results on phase transformations on iron in a DAC were very promising (Joel Bernier, LLNL). Figure 50 (right) shows a map over an iron crystal in a DAC, with red areas indicating where iron has transformed to the high pressure ε-phase. In such experiments not only phases can be identified but also residual strains (e.g. dislocation densities) can be mapped to determine their influence on phase transitions, together with orientation relations with high precision (<0.1°). Establishment of a dedicated white Laue beamline at HPCAT would be important not only for phase transformation studies, but for addressing strains and deformations during the transformations.

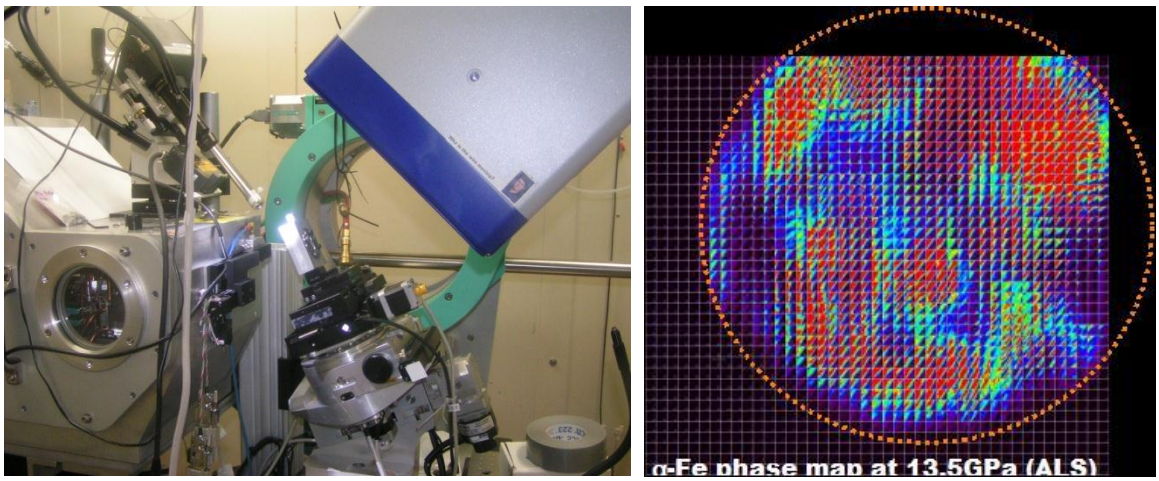

Figure 50: *Experimental configuration at ALS microfocus beamline 12.3.2 with DAC on sample stage (left). Mapping the Fe bcc-hcp phase transition in 1 micron steps (right). The blue regions in this single crystal have transformed to hcp. (Courtesy: J. Bernier)*

Another important research direction is the study of plastic and elastic deformation which also requires spatially and time resolved data on strain and defects. This work also will be done in DACs in the conditions of strong nonhydrostatic or uniaxial stress. With the white Laue beamline, different stress generation devices (e.g. [28]) will be considered in order to get more precise values of external stress and strain, integrated with the x-ray microscopy approach [27]. Deformation mechanisms of polycrystalline materials directly define many of their properties [29]. Understandings of deformations will be enriched by (1) measuring of rotation of selected grains with respect to the stress direction in similar way as it was done before using a monochromatic beam [30], (2) grain boundary studies [31], (3) modeling selected single-crystals using stress generation devices like a micro-indenter [32].

Scientific and Technical Challenges

The major scientific challenge is the development and improvement of physical models to describe the phase transformations and plastic deformation. Examples of the existing models include polycrystalline materials deformation [25, 33] and strengthening mechanism due to interphases blocking propagation of dislocations [34].

The major technical challenges are introduced by beam focusing, stress generation, and data reduction software. The current 5μm focused beam is not small enough because

typical spatial variations of strain and parameters of dislocations take place in the micron and submicron scale [26]. This is why most x-ray microscopy dedicated facilities operate with 0.5-1μm beam. In order to get such a beam available at the HPCAT, the beamline requires a reconfiguration to be able to implement more powerful focusing optics. The use of 1 μm beam would provide data from much more specific elements of dislocation structures, as well as enable studies of dynamics of grain boundaries with improved precision, even in DACs. With different stress generation devices like mechanical testing machines it should be possible to implement differential apertures. Application of devices alternative to DACs also introduces some challenges because they have to be accommodated to the sample environment, one has to follow the requirement of optimal sample thickness and keeping the point of interest in the beam during deformation [28].

As was mentioned above and also pointed out by other panels, improvements in hardware at extreme conditions produces large amounts of very complex data. Clearly, this is outside of the main mission of HPCAT, but specific scientific tasks of HPCAT Laue setup most likely will require development of some software which is not currently available. A comprehensive package for indexation of Laue diffraction patterns [19] will be the basis for any new software needed.

Potential Impacts

The experimental methods for measuring strain-stress relationship, dislocation arrangement, orientation of crystalline blocks, and grain boundary at high pressures in a time resolved manner are still lacking. White Laue diffraction will fill the gap and provide an essential complementary component in high pressure synchrotron technology.

P5.2 Complex Strain Geometries

Most high pressure deformation experiments are conducted in axial compression including DAC in radial diffraction (described above) and D-DIA (e.g. [8]). With the D-DIA samples can also be deformed in axial extension. There is a need to explore the behavior at lower strain geometries, and particularly in earth sciences deformation in plane strain (simple shear and pure shear) are significant since they correspond more closely to deformation in the Earth. This is why for low pressure a torsion apparatus was developed [7] and has been widely applied. More recently the Drickamer apparatus was modified to allow torsion experiments at higher pressure [35]. In current experiments samples were analyzed after deformation *ex situ*. But especially at highest pressures the behavior of materials needs to be characterized *in situ*. This is where HPCAT could play a significant role by modifying existing equipment and applying it to high pressure shear deformation. For highest pressures the rotational diamond anvil cell (rDAC) could be modified to determine simple shear deformation behavior at ultrahigh pressures [36]. Further along the large-volume press (LVP) can enable deformation of larger samples, including larger grain size.

Research Directions

A rotational Drickamer apparatus (RDA, Figure 51, left) is designed to work at pressures up to 30 GPa temperatures up to 3,000K, and specimen sizes of mm^3, in complex stress environments, as well as in simple shear for radiographic tomography studies. A rotational rDAC (Figure 51, right) can superimpose extensive shear in addition to compression and thus add another dimension for materials study.

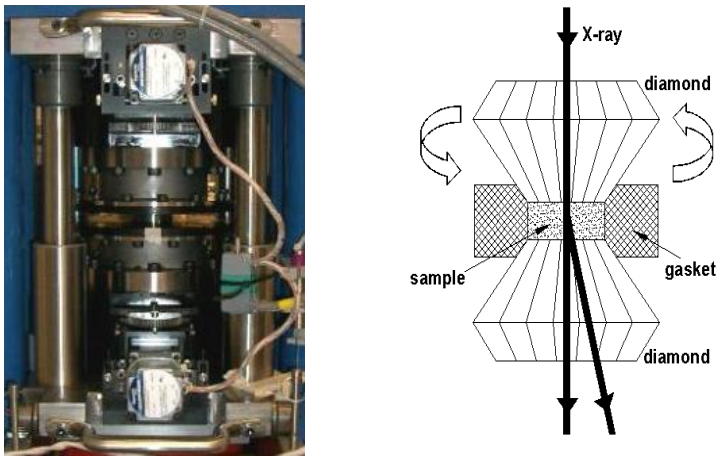

Figure 51. *(Left) A rotational Drickamer cell for shear experiments. (Right) Schematics of a Rotational DAC .*

The large volume press (LVP) is an important tool for high pressure research. It creates well-controlled pressure-temperature environments that enable scientists to perform tailored stress-strain studies to understand constitutive/rheological materials properties. Some of the most advanced and mature high-pressure techniques are based on LVPs, such as plastic deformation study, acoustic velocity measurement, and thermal and electric conductivity measurements. State-of-the-art facilities are the D-DIA at GSECARS-APS (e.g. [8]) and in Japan (e.g. [37]). There are currently initiatives to build new high pressure apparatus for use at APS. They include the next generation Tri-Axial Press (TAP_6x300, Figure 52, a six-cylinder cubic compression system) that extends the stress field applications into a true-triaxial loading geometry, i.e. $\sigma 1 \neq \sigma 2 \neq \sigma 3$ in order to fully manipulate the material strains for comprehensive deformation-constitutive-rheological studies. A TAP prototype is being developed at UNLV for synchrotron or neutron synthesis experimental usages, with a loading capacity of 300-tons for each of the six hydraulic piston-cylinders.

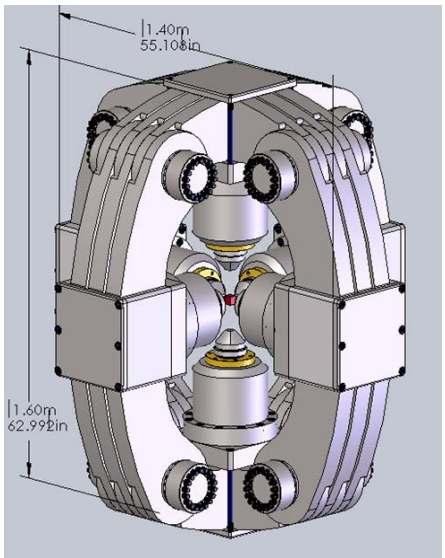

Figure 52: *TAP_6x300, a compact true-triaxial press in cubic compression with six piston-cylinder hydraulic loadings of 6x300 ton. (Courtesy: Y. Zhao)*

The LVP is designed with high-strength alloy steel plates, advanced welding techniques, and is compact to build a super bolt bundling frame. The high capacity loading frame is compact enough for mounting on a robust goniometer and/or translational stages such that synchrotron and neutron beam alignments can be made for many kinds of diffraction/scattering/radiography positions. Experiments include material synthesis (superhard, thermoelectric, battery materials, etc.), deformation mechanisms, sound velocity, thermal and electric conductivity, calorimetry and phase transition measurements.

Scientific and Technical Challenges

Shear deformation can be significant and here the rDAC as well as the rotational Drickamer apparatus have great potential. It has been observed that plastic shear reduces the phase transformation pressure by a factor of 2 to 10, promotes the formation of novel phases, makes some reversible phase transformation irreversible and leads to strain-controlled kinetics [38]. However, rDAC experiments have not yet been used to study *in situ* preferred orientation changes. Also Drickamer experiments, mainly conducted at SUNY with white x-rays, do not currently address changes in orientation distributions. It would be an excellent opportunity for HPCAT to take a leading role. Clearly there are challenges: deformation by torsion produces very heterogeneous strain and both for rDAC and RDA the sample must be scanned from the center axis to the edge to document changes.

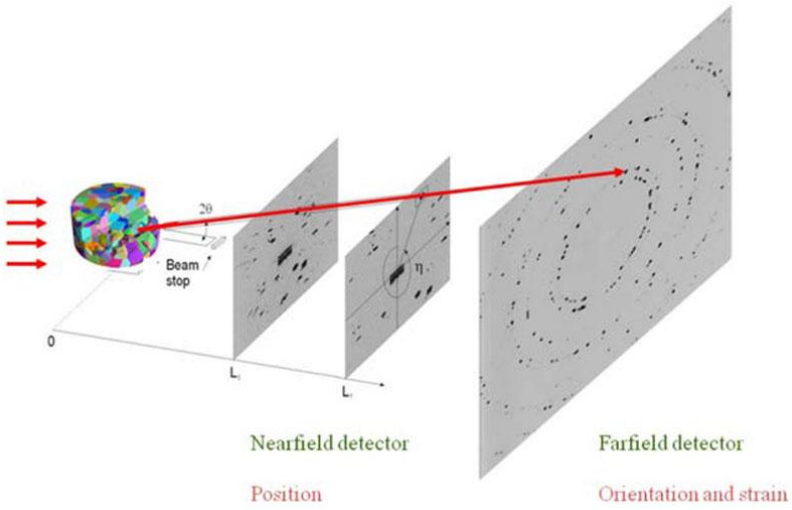

Figure 53: *Experimental setup for strain tomography. (Courtesy: J. Bernier)*

Another approach for coarser samples is to use a rotation method [39]. The sample is illuminated by a full field monochromatic beam and 2D transmission diffraction images are taken using the rotation method (Figure 53). With a large area far-field detector and reconstruction software, the full orientation, elastic strain tensor, and unit cell refinement can be determined for every grain within the illuminated volume. The detailed local grain boundary information can also be achieved with the use of a high resolution detector. In this way, correlations between kinetics and local microstructural heterogeneities can be probed. The ability to collect grain-by-grain kinetics on a statistically significant number of grains rather than just measuring a powder-averaged value, will allow more realistic models to be developed that incorporate the true kinetic distributions of behavior due to the inhomogeneous nature of all polycrystalline materials.

Potential Impacts

By adding rDAC, rotational Drickamer and LVP to the HPCAT inventory, completely new capabilities will be added to study mechanical properties of materials at high pressure. Characterization *in situ* by high energy diffraction would make this a unique facility world-wide. While much of the equipment can be based on existing apparatus, considerable development is required and a dedicated team will be indispensable. It has been mentioned earlier that data analysis is often difficult. This will be all the more true for materials with

heterogeneous deformation and anisotropic properties. Also here equipment development and software advances have to go hand-in-hand.

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PANEL 6: LIQUIDS AND AMORPHOUS MATERIALS

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Malcolm Guthrie, Carnegie Institution of Washington
Magnus Lipp, Lawrence Livermore National Laboratory
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Introduction

For a proper understanding of property-structure-dynamic relations in a material, a detailed understanding is needed at the atomic level. X-ray diffraction from single crystal diffraction experiments in three dimensions allow absolute structure determination, whereas crystalline powder materials exhibit sharp Bragg peaks which may be accurately indexed with a lattice and displacement parameters corresponding to a well-defined space group. The liquid or amorphous state however has an inherently disordered structure on intermediate- and long-range length-scales, making absolute structural determination much more difficult. Consequently, multiple probes are often required to provide an insight into the connection between a material's structure, dynamics and property behavior. For the past 80 years x-ray diffraction has held a vital role as a primary technique for the structure determination of liquids and amorphous materials through the extraction of the pair distribution function. The advantage of this function is that it can be directly compared to theory and simulation results. The same applies to the dynamical x-ray structure factor from which information can be extracted on collective excitations in liquids and glasses. Equally important, x-ray imaging enables the measurement of many important material properties including density and viscosity in liquids. In this report we address the current status of the capabilities of HPCAT as they pertain to liquid and amorphous materials and in light of scientific trends explore future possibilities and avenues of research. Our recommendations for priority research directions span all aspects of high-pressure research, from x-ray instrumentation developments, to cell design, to combining data from multiple techniques.

Current Status

At the present time HPCAT is equipped with a wide array of x-ray scattering and imaging techniques for investigating the liquid and glassy state. This includes methods for measuring not only the structure but also important melt properties such as volume, sound velocity, and viscosity. Current capabilities include

- 16BM-B:
    - Paris-Edinburgh press (VX-3) with heavy resistive heating capability

  - Energy dispersive x-ray diffraction
  - White-beam radiography volumetry
  - Ultrasonic velocity measurements
  - Falling sphere viscometry
- 16ID-B:
  - DAC laser heating capability
- Portable Paris-Edinburgh press (VX-5)
  - Independent control unit compatible for virtually all APS beamlines
  - The same capabilities (listed above) of the VX-3 press

Overarching Challenges and Opportunities

In the past decade it has become increasingly apparent that the liquid state is not simply a blank, randomly disordered void as is so often implied by a glance at the phase diagram. Rather a considerable number of transitions, both gradual and abrupt, occur in the liquid and fluid states, which has researchers now penciling in transitions and bands along with the well-documented crystalline transitions. Such transitions have been found to be structurally associated with changes in electronic structure, coordination number changes, variations in topology and polymerization to name a few.

As may be expected, structural rearrangements with pressure and temperature are normally associated with corresponding kinks in thermodynamic and physical properties such as density, viscosity, and conductivity. Consequently the processing of liquids and amorphous materials at high pressure provide unique opportunities to make new families of materials with different properties and characteristics than those possessed at ambient conditions. Transitions at extreme conditions, particularly at high pressures, include

- liquid to liquid and amorphous to amorphous transitions
- metastable states
- pressure induced amorphization
- new glasses quenched from pressure minima

The idea of polyamorphism, i.e. multiple structures of liquids with the same composition separated by a first order phase transition, remains a fundamentally important and unresolved phenomenon. Although theoretically possible, unambiguous evidence has yet to be presented in the liquid state for any system, despite several indications that this may occur from experiments on glassy and amorphous materials. In addition,

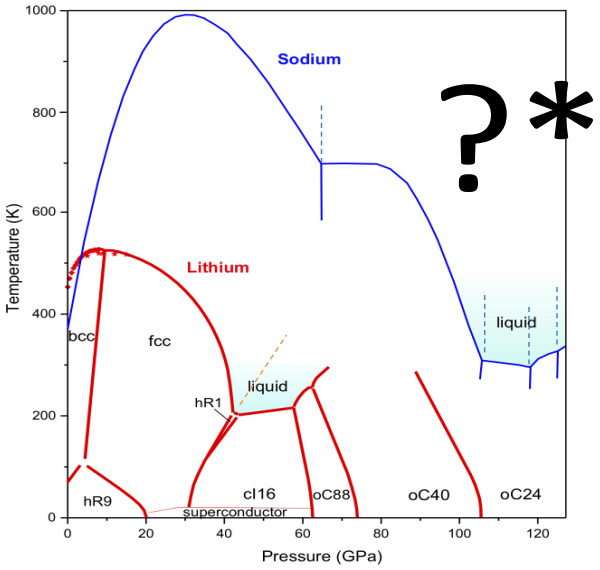

Figure 54: *The phase diagram of lithium and sodium [1]. Arbitrary dashed lines are extrapolated into the liquid state to emphasize the fact that so little is known about the structure and structural transitions that occur in the liquid state generally.*

identifying second order and other gradual transitions in disordered materials may well prove equally important for technological advancements in the field.

Concluding Remarks

The future of the application of x-ray diffraction and imaging to liquid and amorphous materials lies in advances in instrumentation, dedicated sample environment equipment and software development. Advances in focusing optics and more intense photon beams will lead to smaller beam sizes which may address the question of structural heterogeneity between the ergodic and non-ergodic regimes during glass formation through faster time resolved measurements. The combination of x-ray and neutron or anomalous scattering data has not yet been fully exploited by the high pressure community to explore structural changes with pressure at the partial structure factor level in liquid and amorphous materials. Coherent high energy photons from x-ray free electron lasers (X-FEL) hold the promise of extracting 3-dimensional images of disordered material structures using the technique of "ankylography", although at the time of writing the limits of the technique are still controversial.

P6.1 Transitions in Liquids and Amorphous Materials

Pressure induced amorphization, whereby the long range order in a crystalline material disorders considerably at high densities, is a poorly understood phenomenon, but the structural transformation can change a material's properties significantly [2, 3]. The study of liquids generally lends itself to investigations at high temperatures, but transitions are often density driven and could therefore occur over a wide range of pressures. Prime candidates for liquid-liquid transitions under pressure are those materials (elements) for which two different slopes of the melt-line dT/dP between are observed. Especially interesting are the cases when the slope at low pressure is found to be negative and the one at higher pressure positive, as for example in cerium and bismuth or silicon. Figure 55 shows the phase diagram of cerium and the melt-line minimum at 3.3 GPa. Below the critical temperature of ~480 K cerium exhibits

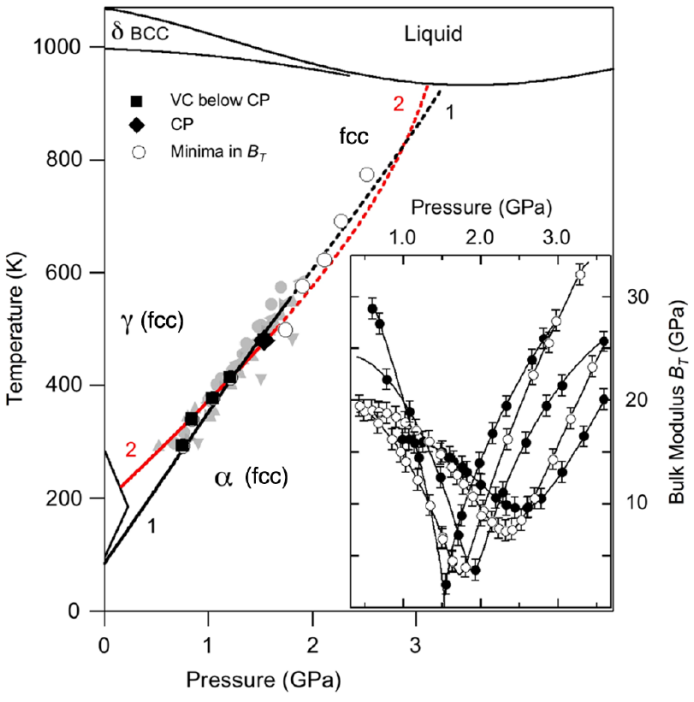

Figure 55: *Phase diagram of cerium [4]. Black and grey solid symbols represent the observed boundary between γ- and α-phase below the critical temperature; the hollow circles the location of the dip in the minimum of the bulk modulus delineating the γ-type material from the α-type. This dip becomes shallower, wider and moves to higher pressure with increasing temperature (see inset).*

the famous volume collapse between isostructural fcc phases. The inset demonstrates how the minimum in the bulk modulus as a continuation of the volume collapse above the critical temperature becomes shallower and wider with higher temperature and moves to higher pressure. The question is whether a remnant of the γ- and α-type phase – or in extension for all materials with differing melt-line slopes - remains in the liquid.

Since the Clausius-Clapeyron equation connects volume and entropy change across the transition with the melt-line slope via $dT/dP = \Delta V/\Delta S$ and $\Delta S \geq 0$, this implies a negative volume change on the low pressure side, meaning the liquid has a higher density than the solid. This stands in contrast to the "normal" behavior on the higher pressure side where the liquid has a lower density than the coexisting solid. Such a behavior points to a liquid-liquid phase transitions based on density arguments alone and should be measured by tracking the density of the liquid under pressure alone. In other words, an isothermal equation-of-state measurement provides essential evidence of transitions in liquids. Structure measurements on the other hand, while they cannot provide direct proof of the order of the transition, are indispensable in providing a physical explanation of the atomic or molecular rearrangements that accompany the density change.

Research Directions

This independent measurement of the volume (and thus the density) can be achieved in principle by viewing the sample via x-ray radiography. At present the two pressure devices generating the extreme condition sample environments are the large volume press and the diamond anvil cell, the first one allowing larger volumes and steady electric heating, the later megabar pressures albeit at tiny volumes. HPCAT provides access to a very versatile large volume press system, a so-called Paris-Edinburgh cell (PEC) capable of pressures in excess of 10 GPa and temperatures in excess of 2000 K. Appropriately filtered incoming x-ray photons deliver a shadow-image on a scintillator crystal that gets imaged onto a camera. An example of an EOS obtained this way is shown in Figure 56 below.

In this case the sample was manufactured with a square base and the image allowed the determination of the volume by showing width and height. Similar efforts have been undertaken for high-Z amorphous materials in a DAC whose EOS is otherwise inaccessible by x-ray diffraction [5]. It appears that the distinction of γ-type and α-type cerium extends to the liquid phase as well, a somewhat unexpected result when plotting the maximum of the second pressure derivative of the bulk modulus as a measure of the strength of the effect at higher temperatures (Figure 56).

Scientific and Technical Challenges

Currently the PEC technique described above cannot deliver results as good as angle dispersive x-ray scattering (see scatter of data-points in Figure 56). But a determination of the isothermal EOS in the liquid state with this technique would be highly desirable. Improved accuracy could be achieved by a better optical system, better control when manufacturing the samples, the ability to rotate the sample while under pressure (all hardware issues), and improved software allowing a more consistent contrast

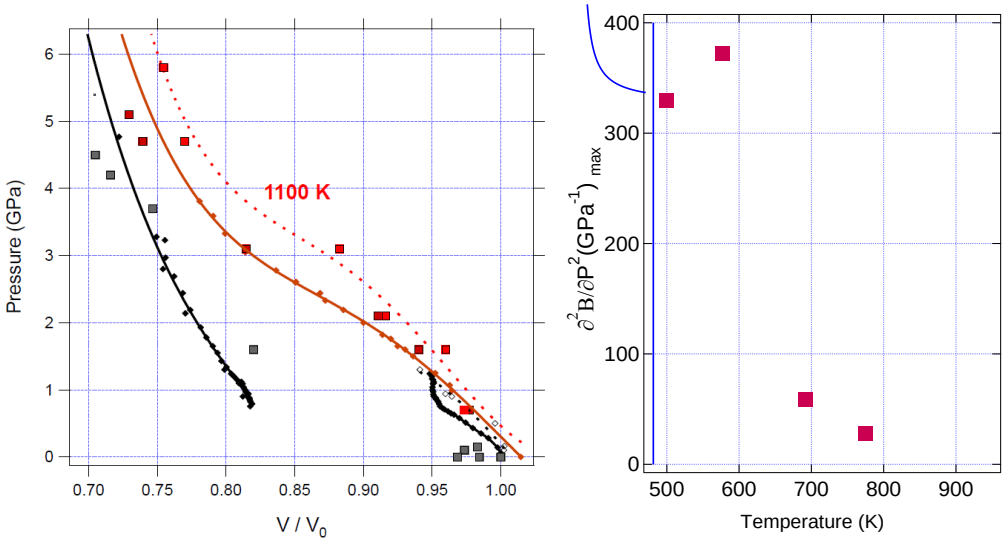

Figure 56: *(Left) EOS of cerium. Solid lines show the room temperature (RT) EOS (black) and the 775 K EOS (dark red) as determined by angle dispersive X-ray diffraction. The square symbols show the data-points acquired by radiography (grey: RT, dark red: 775 K, and bright red: 1100 K). The dashed line is a guide to the eye for the 1100 K isotherm. (Right) Maximum of the second derivative of the bulk modulus with pressure (see also inset to Figure 55) indicates a weakening of the γ- and α-type distinction with increasing temperature leaving no γ- and α-type remnant in the liquid since the temperature of the melt-minimum in cerium is at about 930 K. (Courtesy: M. Lipp)*

determination as well as 3D-reconstruction (tomography). Technical challenges in this panel therefore include the development of sintered diamond PEC, the custom design of WC and DACs, and the advancement in the area of new heater materials.

Potential Impacts

The main impacts of transitions in liquids and amorphous materials are twofold. Firstly, the ability of a liquid to change its properties (density, viscosity, specific heat, etc.) on either side of a *P-T* transition line opens the door to a completely new fundamental phenomenon. Given the ubiquitous nature of liquids in everyday life, the potential for technological applications is widespread. Secondly, the ability to induce amorphous materials by pressure, especially those that can be recovered to ambient conditions, provides a way of tuning materials properties that are most likely unobtainable using any other method.

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P6.2 Structure of Non-crystalline Materials

Since the observation of 'halos' in the first x-ray diffraction experiments from liquids [1] and viscous oils [4] it has been known that even non-crystalline systems possess a distinct local structure. However, these amorphous systems lack long-range periodicity and liquids, in particular, are distinguished from solids by the ability of their constituent atoms or molecules to move freely in response to their potential environment. Correspondingly, a wide range of local atomic (or molecular) arrangements may be explored within a macroscopic volume of liquid. Despite this structural ambiguity, in 1997 Poole et al. [5] speculated that discontinuous change in local species, permitting the coexistence of "multiple liquid phases distinguished by density" along a 1st-order transition line may be possible. Indeed, preceding this speculation, a wealth of indirect evidence for such transitions had already been established in I [6], Se [7], S [8], SiO_2 [9-11], GeO_2 [12, 13] and H_2O [14]. And, it was not long before the direct observation of the stable coexistence of two distinct phases of liquid P at 1000 K and 1 GPa was reported S15].

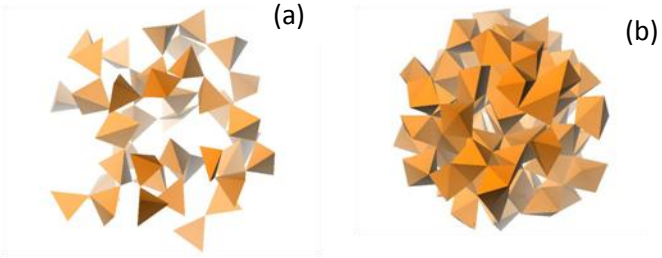

Figure 57: *RMC structural fits [2] to x-ray diffraction data [3] measured from GeO_2 before (a) and after (b) the tetrahedral to octahedral phase transition around 15 GPa illustrating the dramatic changes both in local and intermediate-range structure. The octahedral form of the glass does not exist at ambient pressure but it was possible to characterize its structure by in situ high-energy x-ray diffraction.*

Research Directions

It seems now that this behavior may be rather general: there have since been observations of "liquid polymorphism" [5] in several elements (Fe [16], Si [17], Cs [18]), liquid II-VI compounds such as CdTe [19] and theoretical predictions of transitions in liquid C [20] and H_2 [21]. Strikingly, the observed phase behavior of these liquids is clearly distinct from that found in the solid state and it is, therefore, fundamentally important to determine the underlying mechanisms.

In addition to structural transitions, the high-pressure investigation of melt lines has uncovered complex behavior including strong maxima in several systems (including Cs [22], Na [23], Li [24], C [25]). In the case of liquid Li, this has led to the observation of pressure induced reduction of the melting temperature such that at 45 GPa it is liquid down to 190K! This counter-intuitive behavior may be related to the phenomenon of pressure-induced amorphization, which has previously been observed in H_2O [14], SiO_2 [$S_2$6], GeO_2 [27] and linked to metastable 1st-order phase transitions bound within the crystalline or glassy state [5]. In its first decade of operations HPCAT has made great strides in providing qualitative data to address these many important and interesting phenomena. In the next phase the goal must be to pursue quantitative data from these systems.

Scientific and Technical Challenges

In order to achieve the full potential of non-crystalline diffraction techniques at HPCAT, two prerequisites must be met: firstly, it is essential to extend these measurements to as high momentum transfer (Q) as possible in order to achieve sufficient real space resolution. Secondly, it is critical to pursue information on the individual partial-correlation functions of the material of interest.

The first requirement (of a large Q-range) is justified by considering the nature of a diffraction measurement on a non-crystalline system. The intensity of radiation scattered from the material of interest is directly related to its structure factor S(Q). The experimentally-measured S(Q) is extremely sensitive to changes of structure, however, it can be complicated to interpret it directly. The pair distribution function g(r) provides a far more intuitive characterization of local structure as it gives the probability of finding one atom at a given distance from another. The function g(r) is obtained by Fourier transformation of S(Q) and the basic properties of this operation inform us that the resolution of this real-space structure is inversely proportional to the highest momentum transfer we measure. A high real-space resolution is essential in determining accurately the bond lengths and angles comprising the local structure, information that is vital for reliable comparison with theory. It is also essential for performing a full pair-distribution function analysis employing computational techniques such as reverse Monte Carlo analyses [2] and empirical-potential structural refinement [28]. Underscoring this imperative, Figure 58 illustrates clearly that the information content of S(Q) extends out to at least 35 Å^{-1}.

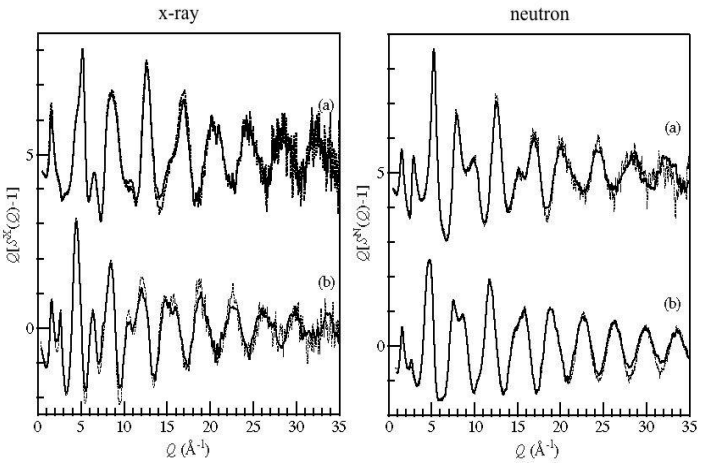

Figure 58: *Structure-factor S(Q) data from glassy SiO_2 (a) and GeO_2 (b) measured with x-rays (left) and neutrons (right). Note the quality of the neutron data at high Q relative to the x-ray data. (Courtesy: C. Benmore)*

A key requirement for accessing high Q (in particular for important low-Z materials) is to maximize sample volumes, while minimizing background signals (typically dominated by Compton scattering from diamond anvils). Recently developed large-volume neutron DACs have permitted the taking of 1.5mm culet anvils to almost 60 GPa. Adapting neutron cells for HPCAT (and optimizing beamline optics to take advantage of large samples) is one clear route to improve signal levels. The successful use of the Paris-Edinburgh (PE) press on BM-B is one example of this, however, the basic PE press is now 20 years old and more recent developments should be exploited.

Secondly, offering the option of higher monochromatic energies (~50-60 keV) with appropriate optics is a way to maximize Q-range for fixed-aperture pressure cells. Losses in terms of decreased flux, scattering cross-section, detector efficiency and increased

Compton scattering must be offset by increased sample volume and optimized backgrounds. *Maximum Q is defined by loss of sample signal relative to background, not by maximum Q-vector at which photon's can be counted.*

The key to obtaining quantitative information from amorphous/liquid systems for which scattering information is angularly averaged (both in reciprocal and real space) is to separately extract distinct contributions from each partial. If there are M atom types in a material, the number of partial pair-correlations is given by M(M+1)/2 and this quadratic increase in complexity means that interpreting the diffraction data rapidly becomes intractable. By "experimentally tuning" the scattering strength of an atom, it is possible to select specific correlations. There are several ways to do this.

- By tuning incident x-ray energy, anomalous scattering can be used to amplify or de-amplify scattering from specific atomic species. However, the energies required may cause problems e.g. if they are so low that sample and cell attenuation is a significant factor.
- By using alternative diffraction techniques, principally neutron scattering, where scattering strength follows isotopic species in a complex manner, and can often be very different from the monotonic Z-dependence of x-ray cross-sections.

The need for comparative x-ray and neutron studies and high Q-range data is established orthodoxy within the liquid and glass communities, but has not generally been achieved in studies under extreme conditions. HPCAT, managed by Carnegie, has a unique opportunity to do this as the institution also has a rapidly evolving neutron program. Communication and collaboration between x-ray and neutron facilities could be a highly synergetic endeavor. An obvious example would be to initiate collaborations between BM-B and the SNAP high pressure beamline at the SNS, both facilities are currently using the same pressure cells, so collaboration would be natural and would benefit both facilities. Recent advances have extended the pressure range for amorphous neutron diffraction up to ~17 GPa, which is comparable with present capabilities on BM-B. Future plans to develop large-volume laser heating of diamond cells at SNAP would potentially be an important technique for HPCAT.

Potential Impacts

In summary, it is clear that the greatest impacts can be achieved by capitalizing on the broad capabilities. In particular, new designs of pressures cells should be pursued with larger volumes, minimal "window" scattering and maximized angular apertures. We have noted that recent developments in neutron cell technology could be modified to be advantageous for HPCAT. In addition, the opportunities for complementary scientific collaboration with key neutron facilities (such as the SNAP and NOMAD instruments at SNS, or HIPPO at LANSCE) should be fully exploited. An existing access model from Sector 11-IDB provides a precedent, whereby a successful proposal on the NOMAD neutron instrument (ORNL) guarantees matching time at the APS. While we recognize the increased difficulties for high pressure/temperature experiments, such intra-lab collaboration should still be pursued, especially given Carnegie's footprint, both at APS and SNS.

In terms of HPCAT instrumentation, work should be done to assess the 'sweet spot' for amorphous diffraction in terms of energy, and to further optimize optics, etc. to match this. This work should be done in parallel with new cell developments, recognizing that the real Q_{max} is defined by signal levels and not intrinsic instrumental capabilities. With these developments, HPCAT is well positioned to extend its position as a world leader in the study of not only liquids and amorphous systems but, increasingly, technologically important nano-scale materials.

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P6.3 Liquid Dynamics

The dynamic structure factor S(Q,ω) provides detailed information about the behavior of a condensed system, so it poses a stringent test to any model of liquids or amorphous

solids. Measurements over pressures and temperatures that bracket regions such as glass transitions and triple points will tell us about previously unexplored physics.

Research Directions

The dynamic structure factor S(Q,ω) carries a tremendous amount of information about the arrangement and motion of particles in a condensed system. In fact, it carries so much information that, as Ercan Alp commented during the conference, it is extremely challenging for any theory to correctly reproduce it over a large range of Q and ω. HPCAT is well equipped to measure this quantity via inelastic x-ray scattering [1], and measuring it over a range of pressures and temperatures can map out in a detailed way how the properties of a system change with its thermodynamic state.

One region of interest is the glass transition. Connections have been drawn between the fragility of a supercooled liquid and S(Q,ω) of the corresponding glass [2]. In this case, S(Q,ω) is easier to interpret theoretically because a vibrational approximation accurately describes motion in the glass. No one has examined this behavior at the range of pressures that HPCAT can access, so measuring S(Q,ω) as a function of pressure for glasses would help test how broadly the proposed connections hold.

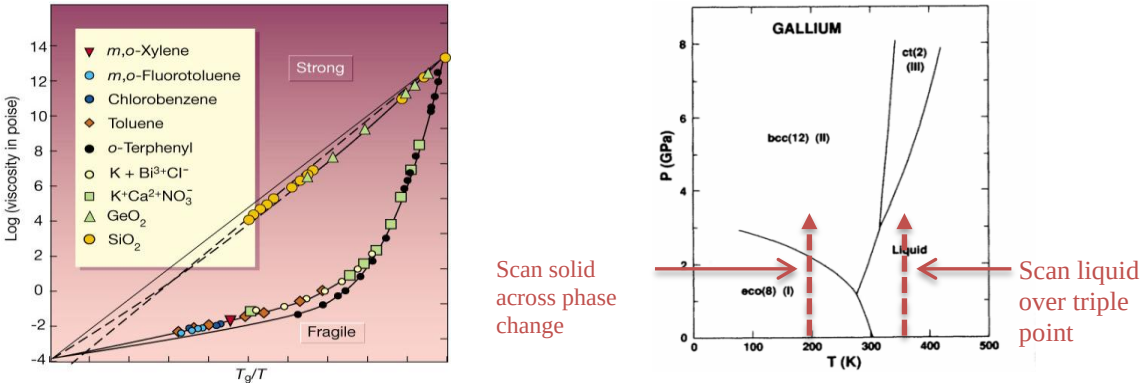

Figure 59: *(Left) Viscosity vs. temperature for strong and fragile liquids. This shows the clear separation into two classes, which may be mirrored by the behavior of S(Q,ω)in the glass. (From [3].). (Right) A proposed experiment to examine changes in both solid and liquid phases in the vicinity of a triple point. (Adapted from [5].)*

The dynamic structure factor is more difficult to interpret in liquids, because the motion of liquid atoms is not purely vibrational. However, it has been argued that by one particular decomposition of liquid motion into vibrations and diffusive steps, the vibrational part alone can account for the dispersion relation of the Brillouin peak of S(Q,ω) [4]. An area of particular interest is a solid-solid-liquid triple point, where the properties of the solid change abruptly but the liquid less so. Differences between electronic structure of the solid and liquid phases govern the slope of the melt curve and the volume and entropy changes across it; the phase diagram of gallium in Figure 59 shows dramatic shifts in the melt curve slope at a low-temperature, low-pressure triple point. How the structure of the liquid, as reflected in S(Q,ω), changes as one increases pressure over the triple point is entirely unexplored and unknown; so mapping this region in both solid and liquid regions would be valuable.

Scientific and Technical Challenges

Measurements with very high resolution in energy are necessary to see details of the dynamic structure factor, and such techniques have only recently been developed. Also, the extraction of other dynamical quantities such as vibrational spectra from $S(Q,\omega)$ is highly theory-dependent, and in fact different theoretical paradigms (e.g. potential energy landscape vs. generalized hydrodynamics) do not even extract comparable quantities. Nonetheless, matching $S(Q,\omega)$ remains a more stringent test for liquid than amorphous solid modeling, because the harmonic approximation works well in amorphous solids.

Potential Impacts

Studies of soft condensed matter have become more important over the last decade, as more theoretical and experimental techniques have been developed to tackle the complexities that liquid and amorphous phases exhibit but solids lack. Since almost all experimental work to this point has been confined to ambient pressure, any information about pressure dependence of detailed liquid structure, with the most detailed being $S(Q,\omega)$, will provide new information in unexplored territory.

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P6.4 Structure-Property Correlations

Property-structure-dynamics relations are vital for understanding the behavior of liquid and amorphous materials and for constructing predictive models. The density, viscosity, sound velocity, thermal and electrical conductivity are ultimately the manifestation of the structure and dynamics. These macroscopic properties are likely subject to changes due to polyamorphic phase transitions beyond the conventional critical point [1]. Density, for example, is a critical parameter for characterizing any disordered system and constructing structural models [2, 3].

Research Directions

In order to study the direct link between structure and properties, integration of multiple techniques in a high pressure device is essential. There are numerous opportunities in this area. For example, the polyamorphism of liquid can be directly addressed by simultaneously determining the density and short range order structure. The in-situ density measurement is arguably the most critical component of integration in high-

pressure and high-temperature liquid studies. Simultaneous determination of density is also helpful to construct the structure-elasticity correlations. Viscosity anomaly with pressure (e.g., a negative correspondence to an increase of pressure or a kink in trend) is another example of benefits which can be obtained by an integrated setup. Electric and thermal conductivity is ultimately due to the transport phenomena and manifestation of the structure and dynamics. Therefore, it is critical to establish a facility that can combine techniques to measure density, ultrasound velocity, viscosity, electric and thermal conductivity together with simultaneous measurement of structure.

The current status of HPCAT can mostly be described by its structure measurement capability. Recently, a few new capabilities (ultrasound velocity and viscosity) have been integrated with the structure measurement, especially in the technique utilizing the Paris-Edinburgh type large volume press. The integration opens great potentials as illustrated below.

A comparative study of liquid structure of polymerized silicate (jadeite) melts to the known viscosity behaviors as a function of pressure has been recently reported (Figure 60) [4]. The polymerized silicate melts show negative pressure dependence versus the log of the viscosity up to 6 GPa. The pattern is surprisingly reproduced by the structural connectivity correlations, as seen by metal-metal distance and metal-oxygen-metal angle, indicating that there is an explicit relationship between structure and viscosity. The result is intriguing because no clear explanation has been suggested for this behavior: what kind of structural parameter must be defined to express the degree of polymerization and how the parameter can be used to predict the viscosity behavior, especially for the decrease with increasing pressure, are totally unknown.

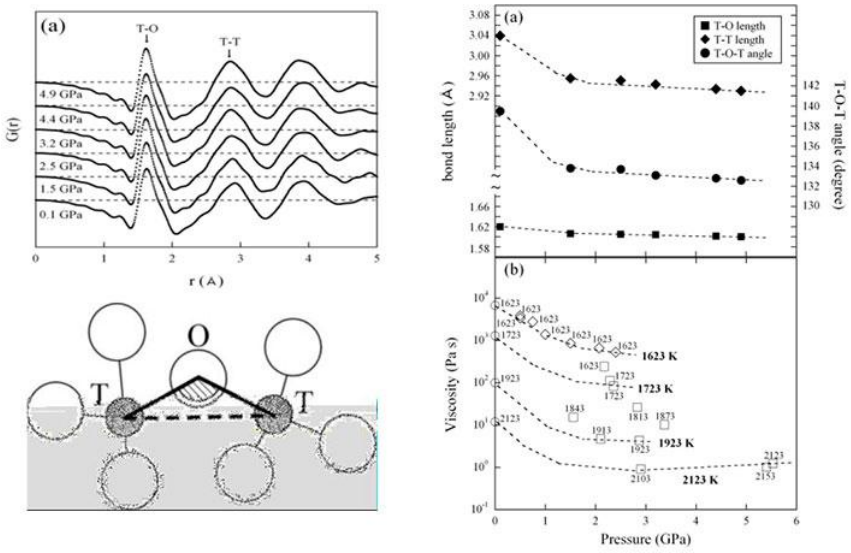

Figure 60: *Comparison of structural behavior (upper-left and upper-right panels) to viscosity variation (lower right) as function of pressure for a polymerized silicate (jadeite) melts (from [4]). The geometric configuration of polymerized silicate unit is given in lower left corner.*

The observation of viscosity and structure correlation lead to a need for an integrated instrumental setup to perform more reliable and systematic investigation for various different liquid materials. A falling sphere viscometry setup for measuring viscosity of various liquids, especially for low viscosity liquids like water, ionic liquids, pure metals, etc., at high pressure has been recently established at HPCAT, 16-BM-B beamline [5] using a PEC that has been previously integrated with multi-angle energy dispersive x-ray

diffraction technique for structure measurement [6]. A viscosity anomaly of liquid KCl around 2 GPa just above the melting temperature and its strong correlation to the intermediate range order (IRO) structure has been observed showing distinct kinks in both viscosity and r2/r1 ratio and continuing plateau up to 6 GPa (Figure 61). Here, r1 and r2 are the first and second pair distribution function peaks, respectively, obtained from the pair distribution function, g(r), measured just after the viscosity measurement. In this case, the effect of ion size is likely playing a role to determine the behavior.

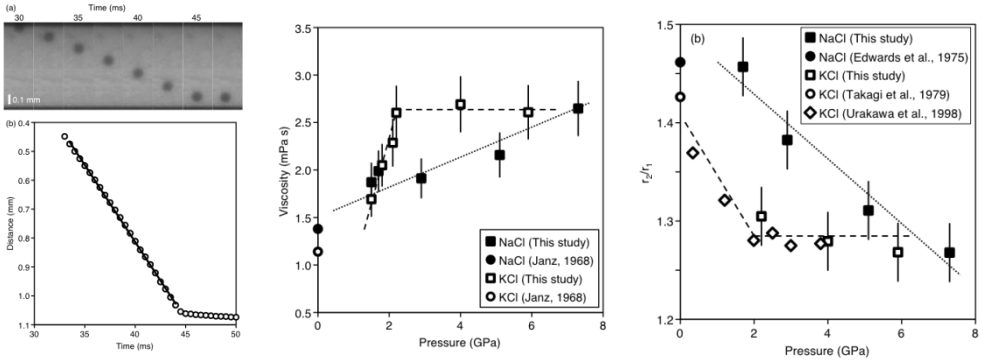

Figure 61: *Snapshots of falling spheres having reached to the terminal velocity (left), viscosity measured for KCl and NaCl as function of pressure with previously published data (center), and the corresponding r2/r1 ratios of pair distribution function determined from static structure factor S(Q) simultaneously measured at the same liquid conditions (right). (after [6])*

In addition to the integration of viscometry and structure measurement, ultrasonic elastic wave velocity measurement also has been integrated to enable simultaneous investigation of the structure and elasticity behavior of liquids and amorphous solids at high pressure and high temperature conditions (Figure 62) [7]. The first demonstration was made for SiO_2 glass compressed up to 7 GPa and 500 °C, in which the compressional wave velocity (V_p) is almost linearly correlated with the shrinkage in the IRO of silicate framework, as seen by shift in the first sharp diffraction peak (FSDP) of static structure factor, S(Q), while the behavior of shear wave velocity (V_s) is rather complicated and not fully characterized within the range of pressure investigated. The results indicate the collapse of void spaces to form denser solid silica glass during the early compression stage.

Scientific and Technical Challenges

Pressure dependent correlations between property, structure, and dynamics in liquids and amorphous solids are intuitively evident, however not well described by either theory or experiment. Experimentally, the difficulties arise from ambiguity in determining the disordered structure and the lack of mutually constraining information. For example, in many cases, determination of short range order in a liquid structure at high pressure is poorly constrained due to the lack of critical information, such as density, which needs to be precisely measured in-situ and independently. While the individual studies for structure and property are often cross-referenced, the integrated setups which are capable of simultaneous measurements of both structure and properties (i.e., density, viscosity, sound velocity, and conductivity) have not been well established.

The currently established integrated setup at HPCAT lacks the most important component of the property measurement, i.e., the density. The 2D radiography with white x-rays at 16-BM-B beamline is used for full volume measurement, but only in limited cases that the shape of sample is securely maintained with a known form (e.g., a perfect cylinder) during the compression, which is not always possible depending on the system to be investigated. Not only these technical limitations, but also the lack of theoretical and computational descriptions of measured structure factor, remains to be overcome. Recent development of *ab initio* molecular dynamics calculations may have different capabilities to predict stable phases of liquids and amorphous solids at given pressure and temperature, but are yet to be properly constrained or validated with precisely measured structure and property data. Typically, a technical development is sharply focused on a single subject to achieve the state-of-art application. In liquid and amorphous solid studies, however, integration of multiple techniques without compromising each capability is required.

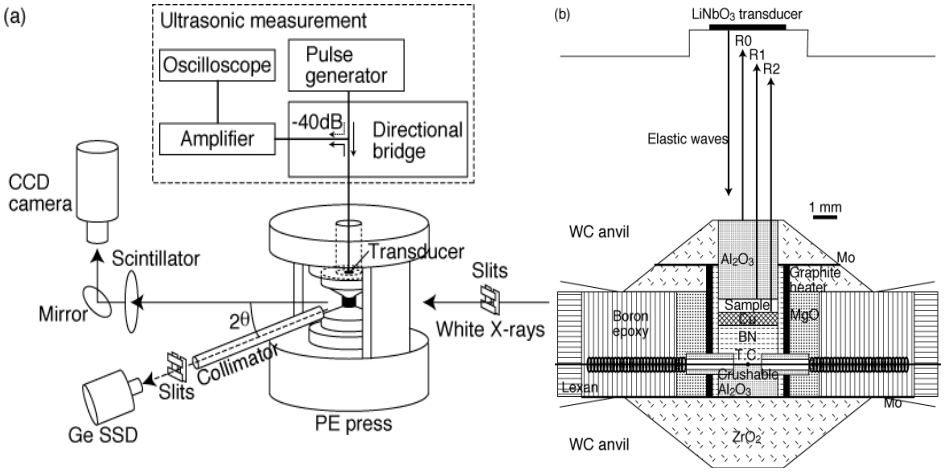

Figure 62: *Schematics of (a) integrated setup for ultrasonic elastic wave velocity and multi-angle energy dispersive diffraction measurement using a PEC at HPCAT, 16BM-B beamline and (b) sample assembly specifically designed for the experiment. Note that white x-ray radiography setup is also integrated to determine the sound travel distance.*

Potential Impacts

The direct link between microscopic structure and macroscopic properties of liquids and amorphous solids can enormously promote our understanding of various different phenomena observed from nanomaterials to planets. For example, nano-crystal nucleation from as-quenched amorphous metallic glasses and subsequent control of particle growth by dynamic compositional change can be better understood through *in situ* measurement of structure and phase segregation in multiphase composite materials including amorphous diffusion barrier. In earth and planetary sciences, there has been an argument that the degree of polymerization of silicate melts strongly depends on the chemical compositions and it would have a direct effect on the viscosity of magmatic fluids as seen by a strong correlation between types of igneous activities and the chemical compositions. The polyamorphism in liquids still remains to be verified, for which the integrated

approach confirming both structure and physical property data, changing discontinuously across the critical boundary, can unequivocally address this phenomenon. Electrical resistivity and thermal conductivity of metallic liquids under high-pressure conditions remains yet to be surveyed, especially in conjunction to the liquid-liquid phase transitions.

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PANEL 7: NEW TECHNOLOGIES AND INSTRUMENTATION

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Introduction

HPCAT is a dedicated high pressure research facility which pioneered third-generation synchrotron radiation technology for extreme conditions science [1]. Since the beginning of its operation a decade ago, HPCAT has developed and integrated an arsenal of novel x-ray diffraction and spectroscopic high pressure and high/low temperature synchrotron radiation techniques, as well as complementary optical and electromagnetic probes, at a single sector to advance cutting-edge, multidisciplinary, high-pressure science and technology. These tools, integrated with hydrostatic or uniaxial compression, laser heating, and cryogenic cooling, have enabled users' investigations of structural, vibrational, electronic, and magnetic properties at extreme conditions that were not possible a decade ago.

Current Status

The integrated HPCAT facility has established four independent, simultaneously operating beamlines with specialized x-ray optics and synchrotron radiation instrumentation – two bending magnet beamlines and two insertion device (undulator) beamlines.

The bending magnet (BM) beamline is spatially divided into two x-ray fans, providing x-rays to two independent experimental stations (16-BM-B and 16-BM-D) for x-ray diffraction and x-ray imaging experiments. 16-BM-B is dedicated to energy dispersive and white Laue x-ray diffraction. The majority of 16-BM-B experiments are performed with a Paris-Edinburgh large volume press (to >7GPa and >2500K), including amorphous and liquid structural studies, electrical resistance and thermal conductivity measurements, x-ray radiography combined with high-speed camera for falling sphere viscosity and density measurements of liquids, and ultrasonic elastic sound wave velocity measurements of amorphous solids, liquids and melts. The methods of measuring strain, deformation, and studying phase transitions with white beam Laue techniques in the diamond anvil cell are also under development. 16-BM-D is a monochromatic beamline for powder and single

crystal angle-dispersive micro-diffraction at high pressure and high (resistive heating) / low (cryostats) temperature. The additional capabilities include on-demand high-resolution powder x-ray diffraction, and x-ray absorption near edge structure (XANES) spectroscopy integrated with x-ray micro-diffraction.

The insertion device (ID) beamline of HPCAT has two undulators in canted mode (operating independently) which feed two independent ID beamlines for x-ray diffraction (16-ID-B) and x-ray spectroscopy (16-ID-D) experiments. Liquid nitrogen cooled silicon side branching and vertical offset monochromators provide a large range of energies (13-43 keV for 16-ID-B and 4.5-37 keV for 16-ID-D). 16-ID-B is a micro-focused (4-7 μm beam) angle-dispersive monochromatic x-ray diffraction beamline which provides unique experimental capabilities for structural studies of materials under extreme conditions. It mainly focuses on high-pressure powder and single crystal micro-diffraction in a DAC at high temperatures (double-sided laser heating to several thousand K, and resistive heating to several hundred K) and low temperatures (various cryostats down to 4 K). The modern instrumentation allows high-quality diffraction at megabar pressures from light elements (such as H_2, Li), fast experiments with pulsed and modulated laser heating, fast dynamic experiments with the Pilatus-1M detector, as well as high pressure total scattering structure measurements on amorphous and liquid materials. 16-ID-D is dedicated to x-ray spectroscopy for materials under high pressure in a DAC. The available x-ray inelastic scattering techniques include nuclear forward scattering (Mössbauer) for spin and valence state studies, nuclear resonant inelastic x-ray scattering (NRIXS) with 2meV energy resolution for determining phonon density of states, sound velocities and Grüneisen parameters, x-ray Raman spectroscopy with 1eV energy resolution for the study of chemical bonding, x-ray fluorescence for element and concentration determination, energy-loss spectroscopy (1 eV) for the study of collective and single-particle excitations and dynamics, and x-ray emission spectroscopy (including resonant emission, partial fluorescence yield) for the study of spin states and inner shell transitions. Measurements can be done at low temperature (down to 4K) or at high-temperature with resistive or portable laser heating with in situ pressure determination. Diffraction can be integrated into a number of these setups.

Over the last several years HPCAT has developed and implemented a number of support equipment and apparatus to expand the available pressure-temperature range of experimental conditions, increase efficiency and productivity of the beamlines, improve the quality of experimental data, and integrate additional methods of sample characterization with synchrotron investigations.

A considerable effort has been put into developing instrumentation for remote and automatic pressure control with DACs. These developments include a number of mechanical devices (gearboxes) for controlling pressure in DACs at a variety of pressure and temperature conditions which can be used for automated data collection along predefined *P-T* paths. HPCAT also designed and implemented a double-diaphragm (membrane) pressure control system which can be integrated with many types of DAC and allows accurate sample pressure control at various temperature conditions – from cryogenic to laser heating.

Another development area in HPCAT supporting facilities is sample environment control. This includes development and implementation of a variety of compact cryostats for different synchrotron techniques (powder and single crystal diffraction, inelastic scattering, etc.). HPCAT cryostats can accommodate a variety of standard and custom DACs, can be easily integrated with remote pressure control devices, and allow a variety of high-pressure measurements to be performed at temperatures down to 2-4 K. Another sample environment development at HPCAT includes whole cell heaters for various DACs, devices (pneumatic and piezo) for fast unidirectional and cyclic pressure change in DACs, as well as the development of new types of DACs for various diffraction and inelastic techniques.

One of the strengths of HPCAT is the abundance of stationary and portable optical supporting devices. A number of portable online optical systems are dedicated for ruby fluorescence pressure measurements and in situ Raman sample characterization during synchrotron experiments. Combined with remote pressure control systems, they significantly increase beamline productivity during high-pressure experiments. HPCAT staff have also designed and implemented a number of offline optical systems for pressure and Raman measurements, offline laser heating, IR laser micro-drilling/micromachining system for sample/gasket preparation, and so on. While some of these devices are still under development, most are fully operational and have been successfully used by HPCAT users for years.

Overarching Challenges and Opportunities

Currently the APS is undertaking a major upgrade (APS-U) to increase source brilliance and flux. In parallel to the APS-U, HPCAT is undergoing a major upgrade as well for the next generation of high pressure experiments. The challenge of the HPCAT upgrade is to take full advantage of the APS-U for unmatched brilliance and develop matching optics and novel integrated techniques which will significantly improve both spatial and temporal resolution and provide the superior tools for the community to lead the next level of high pressure experiments.

The HPCAT upgrade will result in orders-of-magnitude improvements of crucial parameters: including the x-ray source brilliance, source flexibility, beam stability, on-sample x-ray flux, micro-nano focusing size, sampling spatial resolution, temporal resolution, diffraction d-spacing and energy resolutions. Such improvements require a systematic upgrade of key components, including the undulator source, the x-ray optics train, the focusing systems, and detectors, using the newest technologies that have only become available very recently. The upgraded HPCAT will provide the U.S. research community with a superior facility for pursuing next-generation high pressure science, including submicron diffraction, submicron imaging, Mbar single crystal diffraction, Mbar spectroscopy, high-resolution x-ray diffraction, time-resolved synchrotron instrumentation, and optimized medium energy resolution inelastic x-ray scattering. These techniques will each open an entirely new branch of high pressure science which does not exist or is in its infancy.

Concluding Remarks

HPCAT development is predominantly science driven. The goal of HPCAT is not only to remain the current frontier, but look forward and develop new techniques and new capabilities for the next generation of high pressure synchrotron research. The main questions facing HPCAT are:

- What are the primary research directions in multidisciplinary high pressure science?
- What are the key issues to bring the state-of-the-art synchrotron techniques for high pressure research?

The panel has identified the following directions:

- Maximizing on-sample flux to increase temporal resolution
- Improving/optimizing x-ray beams to increase spatial resolution
- Developing and implementing signal conditioning devices and utilizing advanced detector technologies
- Further developing support facilities and extending sample environment (pressure and temperature range, as well as strain rate).

The important aspects of future development include (1) integration of signal detection techniques and using multiple analyzers during a single x-ray exposure (i.e. combined IXS and XRD for phase identification, structure/lattice parameter determination, and single crystal orientation inside the DAC), (2) efficient (pre)processing of huge amounts of data produced by fast detectors (e.g. Pilatus) and synchronization and processing of synchronous data (e.g. diffraction and temperature measurements during pulsed and laser heating), (3) engineered/designer samples/diamonds/gaskets, (4) preparation and fabrication of sample geometries for laser heating and other geometry-sensitive experiments. These aspects often go unnoticed in a facility, yet they are extremely important for successful high pressure experiments and advancement of high-pressure technology.

P7.1 Maximizing Flux on the Sample

One of the ever present challenges of static high pressure research is extremely small sample size (typically in the nanoliter range), and the volume of the sample material further decreases with increasing pressure. This small sample is typically surrounded by relatively massive surrounding materials absorbing both the incident beam and useful signal from the sample. Thus in order to obtain high-quality reliable information about the properties of materials from such minute samples within a reasonable amount of time the x-ray flux on the sample should be maximized, especially for time-sensitive experiments and experiments where the scattering cross-section is very small (e.g., diffraction from liquids and light elements, and photon-hungry inelastic measurements).

Research Directions

There is a whole suite of various experiments which will become possible provided the flux can be increased by an order of magnitude. Some examples include fast dynamic diffraction experiments with either fast ramp compression (kinetics studies, extreme strain rate experiments), or fast repetitive/stroboscopic experiments (e.g. studies with d-DAC [5, 6] or pulsed laser heating [2, 7]). An appreciable increase in x-ray flux together with advanced fast detectors (e.g. Pilatus [4, 8] for x-ray signal detection) will allow a significant increase in expanding pressure-temperature conditions [9, 10] as well as an increased temporal and spatial resolution of the experiments.

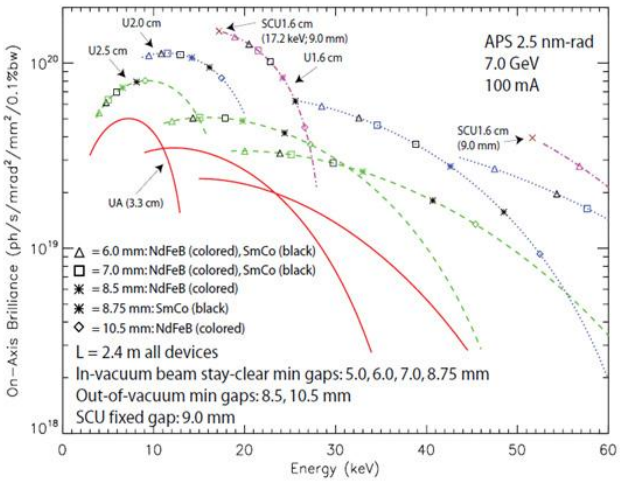


Figure 63: *Brightness from hybrid permanent magnet undulators and a superconducting undulator with 16 mm period (beam parameters from APS).*

Undulators are typically optimized for relatively low energy (<20 keV). Taking into account that the current available detectors like Pilatus are often optimized for relatively low energy, this combination is beneficial for fast and flux-hungry studies. However, for many high-pressure diffraction experiments the geometric constraints require higher energies to effectively penetrate window material and cover a reasonable reciprocal range. Despite the fact that nowadays in some diamond cells [11] a diffraction angle as large as 90 degrees in transmission geometry (and larger in side geometry) can be achieved, relatively low energies such as 20 keV are far from optimal for high-pressure diffraction experiments on single crystals, structure determination, low symmetry materials and so on. An order of magnitude increase in flux would allow reliable structural studies of amorphous and liquid materials (PDF / total scattering), as well as structural studies of light element compounds.

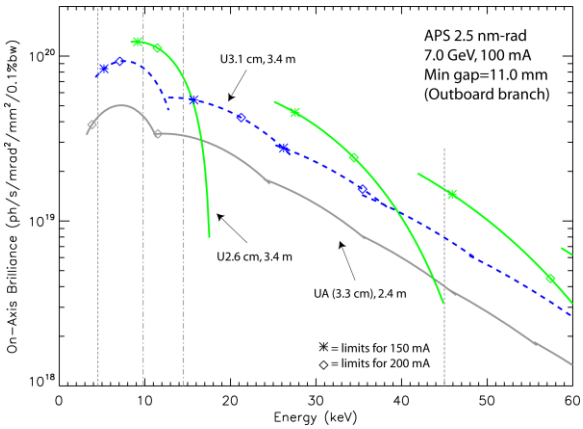


Figure 64: *On-axis brilliance of existing 16-ID-B APS-UA 2.4m 3.3 cm undulator and proposed revolver 3.4m long U2.6 cm (optimized for brilliance at 30-40 keV) and U3.1cm with energy coverage from 10 to 50 keV.*

Scientific and Technical Challenges

There is no single, most important component of the beamline completely responsible for the x-ray flux on the sample. Thus careful consideration should be given to every particular element of the beamline, including undulators, monochromators, and beam condensing and focusing optics. During the APS-U the beam flux and brilliance will be significantly increased, which will increase available flux by at least 1.5 times. To further

increase flux on the sample HPCAT should consider using a longer straight section and replacing the existing 2.4 meter undulators with longer (3.4 meter) revolver-type undulators. The availability of two interchangeable magnetic structures in a revolver undulator allows for better optimization of the x-ray flux for various energy regions. This will not only further double the available flux throughout the usable energy range, but also will allow up to 2 time higher brilliance at high energy (e.g. 30-40 keV, Figure 64). Another option to consider for significant flux increase at high energy is to use superconducting undulators which now are under development at APS [12, 13]. This option should be carefully considered when superconducting undulators become available. For bending magnet beamlines superbend superconducting bending magnets [14-16] should be considered if technically feasible. Replacing regular bending magnets can increase the available flux and brilliance by an order of magnitude [14].

One of the options for flux increase that should be investigated and considered is the use of front end compound refractive focusing before the monochromators [17]. A water-cooled compound refractive lens as a white beam collimator has been successfully implemented at APS (Sector 3) [18]. The collimation of the beam plays a double role due to decreased divergence of the beam – first it increases the efficiency of the monochromator, and second, it decreases beam size at the end station, allowing the focusing mirrors to intercept a larger fraction of the beam or even the whole beam.

Perhaps the most effective way to increase flux is to increase bandwidth of the monochromator by using different materials for monochromating either undulator of bending magnet beam. One potential option is employing multilayer monochromators. The major advantage of multilayer monochromators over crystal-based devices is larger spectral bandwidth and higher photon flux [19]. Thus at 2-BM beamline at APS the use of a multilayer double-monochromator results in 20-40 times flux increase compared to Si111 crystal at 3-11 keV [20]. The efficiency of multilayer monochromators at high energy, as well as the feasibility of using it with undulator beams, need to be further explored.

Another way of increasing the beam flux at the sample is the use of more efficient focusing optics with larger throughput and cross-section, capable of intercepting a larger fraction of the beam. This includes large regular Kirpatrick-Baez (KB) benders, compound refractive focusing lenses, and fixed-bent multilayer mirrors working at a given specific energy.

Potential Impacts

An order of magnitude increase in on-sample flux and brilliance (combined with improved focus and advanced detectors) will have a revolutionary effect on high-pressure technology, allowing the next generation of high pressure experiments. It will further enhance the developments in ultra-high-pressure techniques and high-pressure time resolved studies, such as using pulsed laser heating and fast strain control devices (d-DAC). It will also effectively increase productivity of high-pressure experiments and expand deliverable beamtime for increased user activities.

P7.2 Optimizing X-ray Beams

Because of the nature of high-pressure research the majority of the studied samples in diamond anvil cells are extremely small – on the order of hundreds of cubic micrometers or smaller, and the sample size progressively decreases with increasing pressure, often reaching a size of only a few microns at multimegabar pressures. Therefore focusing of the x-ray beam is a must for high-pressure research. Optimizing x-ray focusing optics for tighter focus and maximum possible on-sample flux is critical; it should be a major priority in HPCAT technical development. With the improvement in photon brilliance in the APS-U by having longer straight sections, revolver undulator configuration, and higher operation current, it is timely and urgent to enable high pressure synchrotron research with a beamsize reduction by one order of magnitude.

At all HPCAT beamlines the x-ray beam is focused into tight spot with KB mirrors. Currently there are two types of KB mirrors – short (typically 100-200 mm long) mirrors capable of focusing the x-ray beam to a 4-5 μm spot, and long 1 meter mirrors in optical hutches focusing the beam to 10-50 μm. While this is adequate for moderate-pressure diffraction and spectroscopy studies, it is critical to improve x-ray focusing optics to reach sub-micron beamsize for enabling quantifications of microstructure and grain-to-grain interactions under pressure, precise determinations of equations of state and pressure calibration, combinatorial studies of a large array of samples, density determinations for amorphous/liquid materials, and isolation of a μm-size single crystal from a polycrystalline aggregate.

Research Directions

Optimized beam is essential for any advanced facility and, by integration with high pressure devices, it becomes an important factor in advancing the high-pressure synchrotron-radiation science and technology, for example, (1) to enable high-pressure x-ray diffraction and spectroscopic studies with μm to sub-μm incident x-ray probes, (2) to enable high-pressure x-ray imaging and tomography studies with <30 nm spatial resolution, and (3) to obtain sufficient statistics and/or finer time resolution in high pressure dynamic experiments.

The needs of x-ray beam focusing often depend on the specifics of a particular experiment. For the majority of high-pressure multi-megabar DAC experiments a 1-3 μm beamsize would be an excellent beam size. Nevertheless specific experiments may require either larger or smaller focus size. For example, many diffraction experiments would benefit from larger focus size in the order of 10-50 μm for better powder statistics although larger focus is easier to obtain by moving mirrors toward the sample and focusing between the sample and the detector, or even on the detector plane for highest resolution. While conceptually straightforward, this capability of fast changing focus size at a variety of working energies should be enabled in the future mirror system design.

At the same time it is extremely important for HPCAT to establish submicron probe capability dedicated and optimized for high-pressure synchrotron research. Such submicron probes will significantly expand the scope of high-pressure research, and will

result in high impact scientific discoveries leading to new high compression physics and chemistry. Some examples of valuable information obtained with using submicron beam include: information on anvil nano-strains and nano-x-ray imaging techniques, which will prepare HPCAT for next generation high-pressure equipment beyond 1TPa; measuring single crystal diffraction from micron/submicron-sized grains in polycrystalline samples with poor powder statistics; obtaining quality diffraction information from samples under large pressure/stress gradient at multimegabar pressures, especially from compound double-stage DACs with single micron-sized samples, and so on.

Scientific and Technical Challenges

Several APS beamlines (Sectors 2, 26, 34) have established a variety of x-ray optics and advanced nanobeam capabilities down to tens of nm. The high pressure vessels and multiple techniques, however, are often incompatible with the primary setups at these specialized nano beamlines. Because focus size is roughly inversely proportional to demagnification ratio, the working distance at these nano-focusing beamlines are typically only several millimeters, which is unacceptable for the majority of high-pressure work. It is important to develop a dedicated high-pressure beamline with a modest beam size of 100-500 nm but with proper working distance for integrating high pressure devices. Such a dedicated beamline can be located in 16-ID-E, 75 meters from the source, providing a high demagnification factor suitable for submicron focus with a long working distance of 75 mm. The completion of such a project will make HPCAT the first beamline in the world equipped with submicron probes dedicated and optimized for high pressure research, and will enable a variety of submicron x-ray techniques including diffraction and spectroscopy (absorption, emission, synchrotron Mössbauer). The unique, relatively long working distance of up to 75 mm should allow for accommodating cryostats for low temperature and laser heating systems for very high temperatures.

While development of sub-micron focusing is extremely important in opening up new horizons in high-pressure science, it is not practical for the majority of high-pressure synchrotron work, especially x-ray powder diffraction because of (1) relatively large beam divergence which causes peak broadening and decreases the resolution, and (2) inadequate powder statistics due to limited scattering volume. Thus 1-3 μm beam focus remains an optimal size for most high-pressure experiments.

Currently the focusing mirrors at HPCAT are based on Kirpatrick-Baez (KB) benders. They are installed at every station and are being used for the whole usable energy range. KB focusing is based on complete external reflection, with critical angle inversely proportional to x-ray energy. For example at 30 keV a 200-mm mirror at ~2 mrad will effectively intercept only about 300 μm of the beam, which, in two dimensions, constitutes about 20% of the whole beam flux. Using larger mirrors (i.e. 320 mm) significantly improves mirror throughput, intercepting the whole beam at lower energies, but still significantly cuts the beam at higher energies. In addition using large mirrors increases working distance, decreases demagnification, and results in larger focused spot unless they are used as pre-focusing devices. Thus at higher energy it may be advantageous to use Compound Refractive Lenses (CRL) [21, 22] (commonly used, for example, at ESRF) which can effectively intercept the full high-energy beam. Using CRL for focusing higher energy

has the additional advantage of relatively easy focus change. Even though the CRL are not achromatic and their focal distance is energy dependent, the advantage is that CRL will not change the direction of the beam (unlike KB or multilayers). Changing the number of individual lenses along the beam path, e.g. by using a commercially available transfocator [21], will change the focus size, making the CRL focusing system very flexible, allowing fast beam focus changes from microns to all the way to unfocused beam without changing beam position on the sample.

Another option for focusing the whole beam is using multilayer mirrors [23, 24] which show high reflectivity at significantly larger critical angles. Unlike regular KB mirrors they are not achromatic and are optimized for a narrow energy band at relatively low energies (<15 keV). The huge advantage of multilayer mirrors is their large acceptance angle, which is significantly higher than that of regular KB mirror. This high acceptance angle allows intercepting full beam with a short mirror.

In summary, because HPCAT stations are versatile and deal with different experiments at different energies, and require different focus and divergence characteristics for different experiments, it is practical at each experimental station/table to have a series of focusing devices optimized for specific energy values.

Two technical aspects which should be paid special attention while considering focusing issues are sharpness of the beam and beam focus/sample stability to within beam focus size. The quality of the beam focus is determined not only by the full-width at half maximum (FWHM) but also by the beam tail, which can be detrimental to tight focusing. This is particularly critical for high pressure experiments because the small high pressure sample is always embedded by massive surrounding materials (anvils, gaskets, windows). Because tighter focus usually results in larger divergence of the beam, especially when attempting to focus full beam to micron or submicron level (i.e. with fixed-bent, short-length, graded multilayer mirrors), HPCAT needs to make an effort in designing a new generation of cleanup slits/pinholes for cutting beam tails, optimized for long working distance (>25 mm), small focus (0.1-3 μm), large divergence setups. It is obvious that focused beam (x-ray delivery and optics) and sample position stability is another important aspect which should be considered and paid special attention in sub-micron probe development.

P7.3 Signal Devices and Advanced Detectors

While x-ray flux and beam focus are important in high-pressure experiments, the signal to noise ratio (S/N) is the ultimate result in experimental measurements. Increasing the signal to noise ratio can effectively decrease the collection time and improve quality of the data by orders of magnitude, or simply allow new types of high-pressure measurements which would otherwise not be feasible. While important to all high-pressure x-ray techniques, signal to noise ratio improvement is particularly important in high-pressure spectroscopy where signal level is typically low.

Research Directions

Any high-pressure setup is typically quite complicated and elaborate; it consists of anvils (which can be diamonds or other material), steel or other gasket, pressure standard, pressure medium and so on where the sample constitutes only a tiny volume compared to the rest of the material. Therefore in many high-pressure experiments parasitic signal from the various elements of the high-pressure setup can overwhelm the signal from the sample. Thus one of the primary tasks in high-pressure experiments, especially inelastic scattering and diffraction measurements on amorphous materials [25]/light elements, is to significantly improve the S/N ratio and eliminate/minimize parasitic scattering from gasket, diamonds, and other components of the high-pressure setup. This requires high collimation for discriminating unwanted signals from the surrounding materials, and high throughput x-ray optics for collecting weak signals from small samples imbedded in the surrounding high pressure cell. This will dramatically improve the quality of the data, as well as will significantly decrease data collection time.

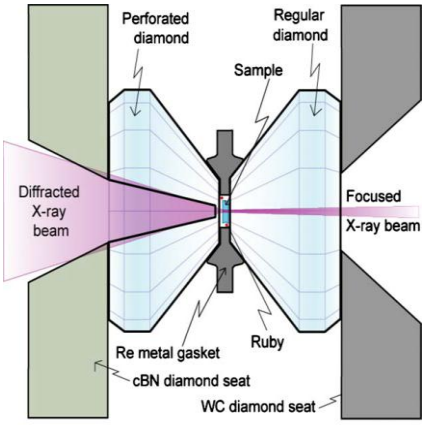


Figure 65: *A schematic drawing of the DAC with one partially perforated diamond. (Courtesy: S. Sinogeikin)*

Scientific and Technical Challenges

Even though there are numerous ways of minimizing the parasitic scattering from the sample surroundings for improving S/N ratio and decreasing the collection time, technically these methods are either extremely challenging, or are only in the development stage. Below we list a few novel ways of signal conditioning for diffraction and inelastic scattering experiments.

The diamond itself in diamond anvil cells often plays a major role in contributing experimental background, either by providing strong scattering signal (e.g. diffraction and Campton) or attenuating the useful signal from the sample. One way to mitigate these problems is to reduce the anvil volume and use perforated diamonds. Perforation techniques have been widely used in both diffraction experiments [25, 26] and inelastic scattering/spectroscopy experiments [27, 28]. Although the strength of anvil is affected by perforation, causing limited accessible pressure range, the use of such machined diamonds can dramatically decrease the signal absorption by the diamond and reduce parasitic scattering.

One of the common ways to reduce the scattering from anvil and gasket materials both in a diamond cell and large volume press (LVP) is to slit out the parasitic signal and collect signal only from the area where the x-ray beam intersects the sample. While simple fixed or tweezer-type slits can do a decent job in cleaning the signal, they also significantly cut the intensity of the collected signal. Thus more sophisticated and higher throughput beam conditioning devices should be used. One of the most effective and relatively simple and straightforward devices for signal conditioning in both DAC and LVP work is Soller slits,

which are commonly used at multiple beamlines [29, 30]. It will be beneficial to develop customized slits for specific types of experiments, e.g. fixed (tapered Soller slits) or adjustable (both angle and opening) circular ring slits for angular collimation with known angular relations. More specific cases like engineered beryllium gasket with built-in slits or local integrated Soller slits should also be considered.

One of the modern collimating/conditioning devices which should be seriously considered is polycapillary optics for IXS spectroscopy [31, 32]. Due to its relatively small field of view the use of polycapillary collecting optics will not only minimize parasitic scattering from the sample but will also allow, when combined with a proper position-sensitive detector (i.e. Pilatus 100K), simultaneous signal collection from the sample at multiple scattering angles, thus increasing the efficiency of data collection and decreasing collection time by orders of magnitude. Using multilayer focusing optics for signal collimation and conditioning is another viable option which should be explored.

An area of interest for dramatically increasing signal-to-noise ratio and reducing collection times is exploiting the electron bunch mode for time-resolved and synchrotron Mössbauer experiments. One of the recent examples involves using a high-speed periodic shutter synchronized with APS beam pulses near the focal spot of a micro-focused x-ray beam at 3-ID of the APS [33]. This fast shuttering technique operates without a high-resolution monochromator and produces much higher signal rates, while offering orders of magnitude more suppression of unwanted electronic charge scattering, which results in delivery of a very pure beam of Mössbauer photons with previously unavailable spectral brightness. Such a shuttering technique will allow both Mössbauer spectroscopy in the time domain, with the many advantageous characteristics of synchrotron radiation, and new opportunities for measurements using x-rays with ultra-high energy resolution. This development reduces data collection time by a factor of 100, down to a few seconds of data collection, which in combination with remote pressure control devices, will increase productivity of the beamline significantly.

Another direction which should be intensively pursued is active development and use of position-sensitive detectors and advanced analyzers which will allow one-shot or fast collection of inelastic and spectroscopy data. This direction has been started at HPCAT's spectroscopy beamline by developing a 17-element analyzer array for x-ray Raman and inelastic x-ray scattering. Another example of such development includes a miniature x-ray emission spectrometer (miniXES) for high-pressure studies in a diamond anvil cell, which was recently tested at HPACT [34]. Along with efficient spectrometers, HPCAT should invest time into developing the individual components of spectroscopic systems. For example, improving the quality of analyzers by using ultrafast laser- machined (as opposed to mechanical machining) diced analyzer crystals can significantly improve the quality of the data and reduce data collection time.

Further breakthroughs in the development of advanced, more efficient detectors capable of handling modern demands of collecting time, S/N ratio, etc., are critical for advancement of high-pressure technology. Detectors with adequate timing capability, high efficiency, and temporal/special/energy resolution with proper energy range and combined 3D position sensitive detectors with good energy resolution can revolutionize high pressure research. While the development of advanced detectors is beyond the scope

of HPCAT, it is necessary to track the development of new advanced detectors, and if possible collaborate in the development by providing required specifications. The advanced detectors not yet commercially available, but under development and of potential interest to HPCAT include: Area avalanching photo diode (APD) detectors with ns time resolution; 3D detectors – position sensitive / area detectors with good energy resolution; fast analog integrating pixel array detector (PAD) with internal memory capable of recording several hundred images at 6.5 MHz rate matching the APS beam bunch rate (APS project); high-energy fast CCD with 200 frames/s (LBNL-ANL project), and so on.

P7.4 New Sample Environments

Sample considerations are paramount in any experimental endeavor. Understanding and controlling the synthesis, composition, purity, modification, and manipulation of a sample and its surrounding environment allow for the precise and accurate characterization of materials properties. High pressure samples can be particularly challenging to work with. In order to reach extreme pressure conditions samples must be extremely small, sometimes just a few microns or less in any dimension. Furthermore, sample access is limited by the size, design, and materials of pressure generating devices and ancillary equipment. And clearly, high pressure phases and phenomena can frequently only be studied in situ inasmuch as they are typically not observed or cannot be recovered at ambient conditions. Mastery of the high pressure sample environment is a prerequisite to achieving the ambitious scientific goals set out for HPCAT over the next decade.

Much has been said in this report about the various developments that will be made possible by the upcoming APS Upgrade. The increased storage ring current together with state-of-the-art insertion devices will potentially offer the highest brilliance available at a third-generation light source. Complementary developments in front end optics and focusing devices will ensure the high flux of high energy photons can be delivered to the sample. These developments demand commensurate developments in sample preparation, control of the sample environment during experiments, and the ability to carry out detailed analysis of the sample following the primary experiment. In the context of sample environment, the goal for HPCAT during the next decade is two-fold. The first, more modest goal is to ensure that the high pressure experimentalist is never sample limited. The second, more ambitious goal is to optimize the sample environment tools, capabilities, and possibilities to the point that they help drive innovation by inspiring new avenues of research. Below we discuss a number of proposed developments to ensure these two sample environment goals are realized.

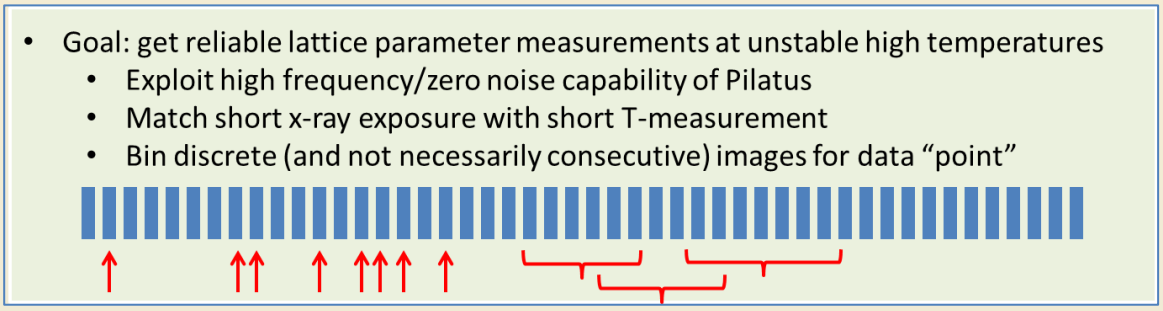
Research Directions

Future developments in sample environment can be divided into three primary areas:

- Sample preparation and loading
- Generation and measurement of in situ pressure-temperature conditions
- Post-experimental analysis

Reliable high temperature data from unstable heating

High power double-sided laser heating apparatus can effectively heat diamond anvil cell samples to thousands of degrees [1]. The key to obtaining stable high temperatures for an extended period of time is good thermal insulation between the high temperature sample and the thermally conductive diamond anvils, and perhaps engineered and micro-machined sample and sample environment [2]. At ultrahigh pressures, however, the efficiency of the thermal insulation is compromised by an extremely thin sample chamber, often just a few microns thick, which makes it extremely difficult to obtain steady state heating. The problem is further compounded by the possible need for longer x-ray exposures due to reduced scattering volume. During the course of an x-ray exposure lasting a few seconds, several discrete temperature measurements may reveal an unacceptable amount of fluctuation in the sample temperature. Advanced sample preparation methods are crucial in mitigating this difficulty by yielding thicker samples (and hence, thermal insulation layers). A complementary approach includes a stroboscopic data collection and processing technique made possible by fast pixel array (e.g. Pilatus) detector technology [3]. The Pilatus detector offers high-frequency data collection (with a readout time of less than 3 ms) combined with zero readout noise. This allows for the collection of several arbitrarily short, discrete x-ray images that can later be appropriately binned to yield a single high pressure, high temperature data point.



In the representation above, each blue bar represents an x-ray exposure. In the context of high temperature data, the exposure time is determined by (and matched with) the minimum exposure time required to obtain a reliable temperature measurement. The temperature data can later be analyzed and x-ray images binned according to the corresponding temperature measurements. The data may need to be binned discretely as indicated by the arrows, but may be binned in groups (as indicated by the by the brackets) for more stable conditions. If the data varies slowly with time, individual images may even contribute to more than one data point, as suggested by overlapping brackets. This sort of stroboscopic data collection, which is not possible with imaging plate and CCD detectors, could naturally be extended to other types of experiments with time-dependent data.

[1] Y. Meng, G. Shen, and H. K. Mao, *J. Phys.: Condens. Matt.* **18**, S1097 (2006).
[2] J. S. Pigott, D. M. Reaman, and W. R. Panero, *Rev. Sci. Instrum.* **82** (2011).
[3] C. Broennimann, E. F. Eikenberry, B. Heinrich, et al., *J. Synch. Rad.* **13**, 120 (2006).

Successful sample preparation and loading is crucial to the overall success of an experiment. As mentioned above, high pressure sample dimensions are typically a few tens of microns, and with the ever-present drive to reach higher pressures, it will be necessary to routinely load samples with dimensions of just a few microns. The onsite capability of machining accurate and precise chambers (gasket holes in DACs and sample assemblies in the Paris-Edinburgh Cell) is essential at HPCAT. Also, accommodations must be made to effectively handle materials sensitive to water/oxygen, as well as hazardous samples, for example, radioactive materials, explosives, and highly reactive samples. Finally, precise loading of liquids and gases should be available.

Control of *in situ* pressure-temperature conditions is the primary focus of development in terms of sample environment. Static multi-Mbar pressure generation is becoming a mature technique. Advancements in maximum attainable static pressure will depend on the ability to prepare samples on the smallest scale. Another important avenue in terms of pressure generation is pressure ramping—the rapid increase or decrease of pressure—to study the effect of different strain rates, the possibilities of metastable phases, and the dynamics of phase transitions.

HPCAT has had much success with research at non-ambient temperatures. Cryostats can go down to about 4K and laser heating experiments routinely reach several thousand Kelvin. In routine high pressure research there is currently a temperature gap, ~600-1000K, between resistive and laser heating that must be bridged. It will be beneficial to the broad user community to have dedicated equipment bridging this gap and extending the minimum and maximum temperature ranges across the entire experimental pressure range.

Analysis of the sample material following an experiment can be a crucial part of understanding and interpreting experimental results. A variety of processes including phase transitions (including melting and recrystallization), reaction, and decomposition can take place. Careful study with analytical tools, including conventional electron microscopy and related techniques such as energy dispersive elemental analysis, can give important insight to in situ modifications. It is important to establish these capabilities and make them available to users, possibly through partnership with neighboring laboratories or through shared facilities available at the proposed high pressure center at APS.

Scientific and Technical Challenges

Sample preparation and loading – There are a number of challenges associated with sample preparation and loading. For example, precise and accurate gasket drilling, sample assembly (including gasket materials, electrical leads, pressure transmitting media, miniature resistive heaters), sample orientation for some single crystals, and small sample size. One very important development in the near future should be a high energy pulsed laser for convenient, accurate, and precise micromachining. The first and most routine application would be micromachining single crystals. But such a device could also prove invaluable in micromachining electric leads and miniature resistive heating elements. It could also find great use for gasket drilling.

Anyone who has tried to load a DAC knows that it takes time, patience, and a steady hand. As we continue to push the limits of extreme conditions science, there will come a point when loading by hand may be impractical. Either the sample size is too small, or the loading geometry is too intricate. For example, there are already a number of publications demonstrating controlled sample geometry using deposition and FIB techniques. Also, the development of a robust and user friendly micromanipulator system could make the most extreme loading challenges more feasible.

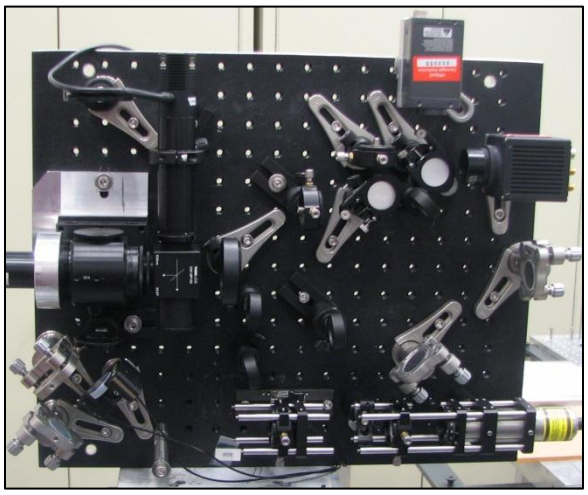


Figure 66: *Prototype portable laser heating system commissioned at HPCAT.*

HPCAT serves a broad, international user community from various research backgrounds. Because of this, it is imperative that it be able to handle a broad selection of sample materials. With the recent installation of a large, inert atmosphere glove box, HPCAT has taken an important step in offering users a better opportunity to study moisture and oxygen sensitive samples. Future developments should focus on the ability to handle other sensitive materials including radiological or explosive materials, and other hazardous substances. The high pressure community at the APS should work together to establish a centralized location for handling such materials. The facility would be furnished with various apparatus including glove boxes, fume hoods, supporting infrastructure, and disposal facilities.

Generation and measurement of in situ pressure-temperature conditions – An important thrust at HPCAT is the stable generation of ultrahigh pressures at high and low temperatures. The general goals are common in the high pressure field: push the current pressure-temperature boundaries, and equally important, improve the quality of pressure-temperature measurements.

In the context of pushing the current pressure boundaries, historically the goal has always been to go higher in pressure. Of course, this remains an important aspect. But as we have seen throughout the workshop, another important aspect is pressure control in the time domain. With more flux available than ever before and recent advances in detector technology, it is now possible to start looking at the time-dependent sample response to pressure changes. Currently at HPCAT the capability exists to rapidly increase pressure using conventional gas membranes. Exploratory work has yielded data from samples where the pressure is increased at a rate of a few Mbar per second. Future development should include so-called d-DACs which can modify the pressure "stroboscopically" and can be synchronized with fast detectors to examine, for example, phase transition dynamics and rate-related hysteresis.

The isothermal compression curves obtained by compressing crystalline materials at ambient temperature have yielded a wealth of fascinating phenomena and structural diversity. The move away from ambient temperature extends these curves into surfaces

and, not surprisingly, this added thermodynamic dimension brings with it an added layer of structural beauty and complexity.

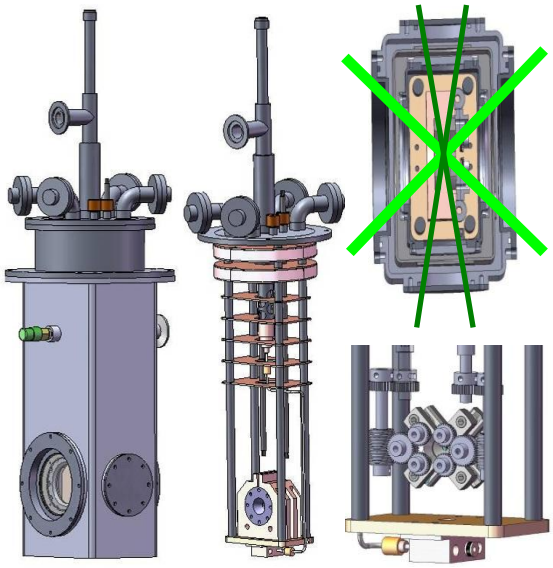


Figure 67: *Schematic view of proposed HPCAT He-flow diffraction/inelastic cryostat.*

Over the course of existence HPCAT has developed and implemented a number of cryostats for different synchrotron techniques (powder and single crystal diffraction, inelastic scattering, etc.) HPCAT cryostats can accommodate a variety of standard and novel DACs, can be easily integrated with remote pressure control devices, and allow a variety of high-pressure measurements to be performed to temperatures down to 2-4 K. Nevertheless there are capability gaps which require further attention and investment in the development of new cryogenic facilities. For example, at this moment there are two cryostats commonly used for diffraction: a large He flow cryostat and a compact cold-finger/combination cryostat. The large cryostat is used for powder diffraction measurements down to 4K and below. The obvious drawbacks of the cryostat include: small x-ray opening, large weight and horizontal transfer line (which make dynamic alignment and single crystal measurements impossible), and the large size makes it impossible to bring the cleanup pinhole close to the sample, resulting in either flux loss or inefficient cleaning of the beam. The size problem was mitigated by designing a compact combination cryostat. While this small cryostat can be used for both single-crystal (large x-ray opening, stable and reliable rotation) and powder diffraction, as well as inelastic measurements, its lowest temperature is limited to 10-12 K. Thus there is an obvious necessity in developing a new generation of optimized synchrotron (diffraction and inelastic) cryostats for extremely low temperatures which will be capable of performing single crystal and powder megabar experiments at 4K and below. The proposed prototype of such a cryostat is shown on Figure 67.

HPCAT also has a distinguished history of carrying out high pressure high temperature measurements using double-sided laser heating and, to a lesser extent, whole-cell resistive heating. A major effort should be made to cover the entire relevant pressure-temperature surface. One important step is to increase routine resistive heating capabilities to 1000K and above. Advances in both heater design and temperature measurement should help in achieving this goal. In terms of heater design, there are currently a handful of designs for small heaters (graphite or wound wire) that can be placed around the anvils and reach temperatures well over 1000K. To make their use more routine, it is imperative to develop non-contact (spectroscopic) temperature measurement at modest (below 1000K) temperatures. This would help ensure that temperature is measured at the sample location (as opposed to thermocouples, which can be unreliable depending on their location with respect to sample and/or heater) and it could help eliminate the need for thermocouples to be located close to the sample chamber.

Spectroscopic temperature measurement at modest temperatures would also help bring down the minimum useable laser heating temperature. The minimum temperature available for most laser heating systems is determined by the ability to measure the temperature reliably. Specifically, at lower temperatures the emitted radiation used to measure temperature gets to be too weak for a reliable measurement using conventional CCD detectors. By increasing the current maximum temperature of resistive heating and decreasing the minimum temperature for laser heating, the temperature gap can be effectively closed.

Finally, given the wide selection of measurement techniques available at HPCAT, and the ability to integrate techniques across beamlines, considerable effort should be put forth to offer additional high-temperature and low-temperature capabilities for as many types of high P measurements as possible. Figure 66 shows a portable laser heating system that has been effectively used in a number of nontraditional scattering geometries and applications. Future iterations should include additional capabilities and flexibility, for example the possibility to carry out single crystal diffraction at high temperature.

Time-resolved techniques – Fast detectors such as the Pilatus 1M, capable of shutterless sub-millisecond exposures and 130 Hz data collection rate, bring completely new capabilities of fast time-resolved experiments to HPCAT, and these capabilities will certainly be expanded with the expected future increase in flux. The scientific understanding of the dynamics of chemical and structural transitions can be dramatically advanced through the development of time-resolved x-ray diagnostics integrated with a variety of impulsive drives (pressure, temperature, photons, field) or pump-probe measurements. These advances will broadly address dynamic processes including reaction chemistry, phase changes, material behavior, thermodynamics and kinetics at high pressure-temperature conditions, technological material synthesis, and basic science.

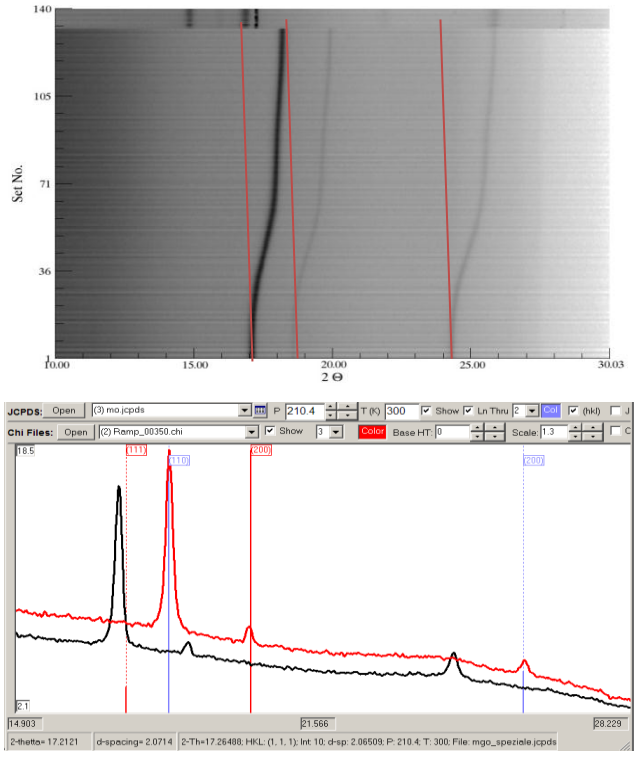


Figure 68: *Fast ramp-compression of Mo+MgO to 2.1 Mbar. The maximum compression rate is 2 MBar/sec. (Courtesy: S. Sinogeikin)*

The new Dynamic Compression Sector at the APS will concentrate on various shock type experiments (some of which were successfully tested at HPCAT [35]), while development of DAC-related fast dynamic techniques at HPCAT can help bridge the "strain rate gap," and link static to dynamic processes with new techniques and diagnostics. HPCAT has experience with time-resolved diffraction experiments. Some cyclic compression diffraction experiments with d-DAC have been

performed at HPCAT [5]. Recently HPCAT has developed a fast release gas membrane system which allows fast pressure ramp exceeding a rate of 2 Mbar/sec (Figure 68). With increasing x-ray flux and further development of fast detectors HPCAT should continue development of novel time resolved techniques over a range of time scales, working on fast compression/decompression ramp/jumps in pressure-temperature space and fast stroboscopic/repetitive measurements by developing appropriate membrane-driven and piezo-driven DACs.

This new experimental capability of dynamic loading paths to reach new phase space will allow a multitude of fast processes to be studied. The examples of new features/properties which can be studied include: formation of materials in non-equilibrium situations, rate dependence of phase transformations under intermediate strain rate compression, dynamic mechanical properties and deformation behavior, pathways through phase diagrams (non-equilibrium transformations and "equilibrium" phase boundary, e.g., superheating/supercooling, over-/under-pressurization), kinetics of melting/freezing, incomplete transformations/phase hysteresis/retained phases, very rapid pressure quench to retrieve and study otherwise unquenchable phases, and so on.

Post-experimental analysis – The techniques typically employed for detailed and quantitative post-experimental analysis require, for example, access to electron microscopy for visual examination and EDS measurements, and possibly focused ion beam milling for sample sectioning and lifting. It will be very beneficial to users to make these types of analyses available. It may not be feasible in terms of cost or personnel to maintain these types of instruments at one APS sector, however, it would certainly be a suitable part of a centralized high pressure center located at the APS site.

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III. CONCLUDING REMARKS

The identified research directions clearly raise the need for a major upgrade of HPCAT, taking full advantage of the APS-Upgrade for unmatched brilliance and matching optics and novel integrated techniques, thus significantly improving both spatial and temporal resolution and providing the superior tools for the community to lead the next level of development of compression science. In addition to traditional static or dynamic experiments, the HPCAT upgrade will provide novel x-ray capabilities covering a time domain that fills the gap between static and dynamic compressions.

Several research directions also require a scope beyond HPCAT, by establishing a center that brings together expertise, instrumentation, and user community in compression science at APS. By coordinating with HPSynC, DCS and other APS beamlines, (1) the Center will provide a focused team in effectively using and developing novel synchrotron techniques optimal to advancing compression science yet not included in the programs of HPCAT and DCS. These activities will make full use of the APS-Upgrade, and will also allow both HPCAT and DCS to stay focused on a few cutting-edge frontiers. (2) The Center will allow for staff to be hired in line with the needs of both HPCAT and DCS, thereby better serving the all-around needs of extreme conditions community in general (e.g., DCS users can get training at both HPCAT and DCS and vice versa on synchrotron techniques). This coordination is particularly important now, as 'static compression' scientists typically have much broader exposure to synchrotron techniques. (3) The Center will enhance the coordination of various programs at APS, for example by proper cost-sharing for projects at multiple beamlines, beam-time allocation for complementary experiments and feasibility tests of DCS, and sharing large or expensive equipment (e.g., fast detectors). With the established HPCAT support equipment that already serves users beyond HPCAT, the Center will provide enhanced support for users across the facility. (4) The Center will also serve as a model for science activity at future light sources (e.g., NSLS-II at BNL, MaRIE at LANL). (5) The Center will provide a training ground for students and young scientists in using the state-of-art synchrotron techniques.

APPENDICES

Appendix A: ESTABLISHED HIGH PRESSURE SYNCHROTRON TECHNIQUES AT HPCAT

A.1 Sector and Beamline Layout

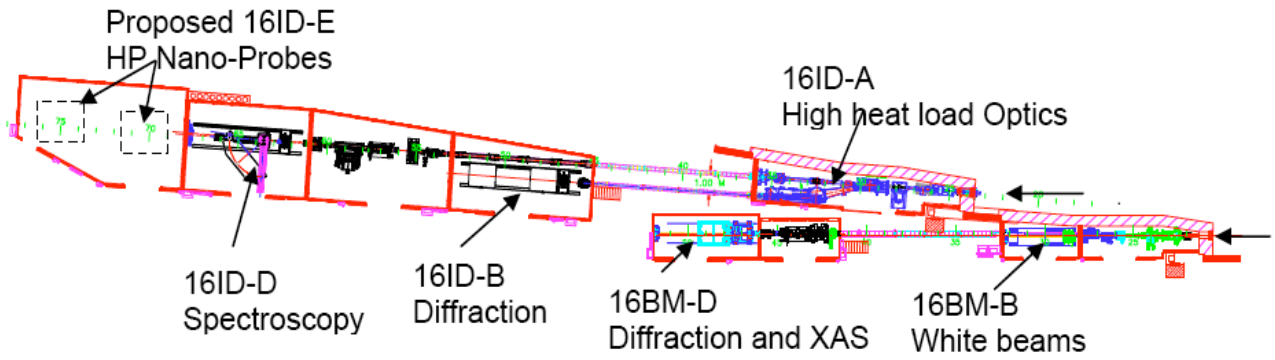

Figure 69: *HPCAT sector layout. The locations of four simultaneously operational stations are marked.*

The HPCAT sector is located at Sector 16 of APS, and consists of an insertion device undulator beamline (16-ID), a bending magnet beamline (16-BM), four support laboratories and an office area. The HPCAT design and construction effort began in 1998. A detailed technical design of the sector layout and an optical scheme were completed in 2000. The construction of optical enclosures and experimental stations began in April 2001. First x-rays were observed from 16-ID in March 2002 and from 16-BM in June 2003. The first HPCAT experiment was conducted at the end of 2002.

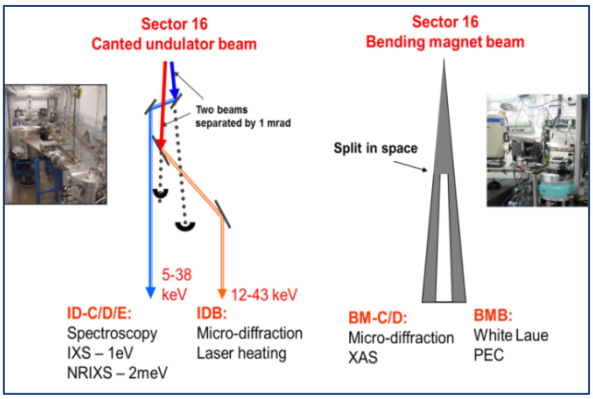

Figure 70: *HPCAT has established four simultaneously operational beamlines at sector 16 at the Advanced Photon Source.*

The HPCAT facility has established nine experimental stations (hutches) on the two beamlines of Sector 16, with five on the 16-ID line (sequentially downstream) 16-ID-A,-B,-C,-D, and -E, and four on the 16-BM line 16-BM-A,-B,-C, and -D (Figure 69). To increase the efficiency in utilization of precious beam time, the 16-ID and 16BM beamlines are each split into two branches for the maximum of four simultaneously operating experiments at hutches 16-ID-B, 16-ID-C or -D or -E, 16-BM-B and 16-BM-C or –D (Figure 70). The canted undulators allow for establishing two independent ID beamlines: the 16-ID-C-D-E branch for a range of x-ray spectroscopy techniques and the 16-ID-B branch for XRD. The white radiation fan of 16-BM is divided into two halves: one into 16-BM-B for EDXD and one into 16BM-C-D for micro XRD and XAS.

A.2 Micro-X-ray Diffraction

16-ID-B, an undulator-based monochromatic x-ray diffraction station, is a unique facility for micro-focused (~5 um) angle dispersive powder, amorphous, and single crystal x-ray diffraction under extreme *P-T* conditions. 16-ID-B is designed for performing high-pressure experiments at a variety of temperature conditions – from double-sided *in-situ* laser heating (several thousand K) to external resistive heating (several hundred K), down to cryogenic temperatures (4K) – and provides unique experimental capabilities for studies of crystal and amorphous structure, equations of state, high-pressure melting and phase transitions of various materials under extreme conditions to megabar pressures.

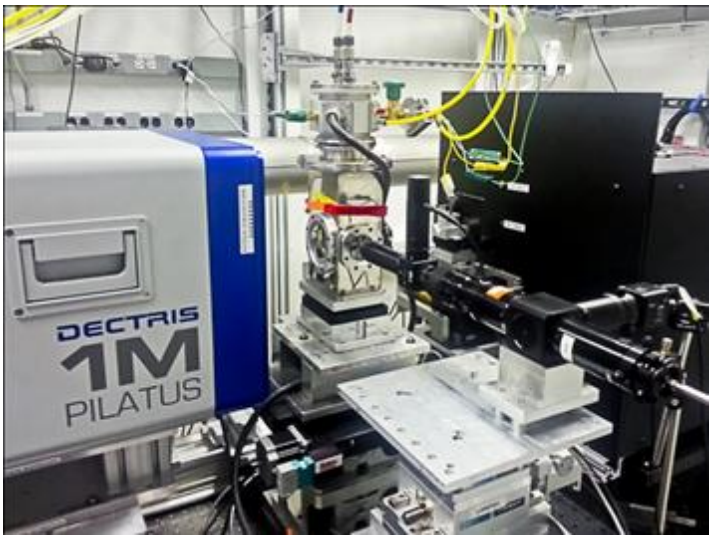

Figure 71: *Micro-diffraction setup in 16-IDB. Shown are high-temperature measurements with DAC in controlled gas enclosure, with IR temperature measurement, and Pilatus 1M detector.*

Recently 16-ID-B station was upgraded with a dedicated undulator in canted mode with optics optimized for source brilliance and source preservation. Also the water cooled Si220 Branching monochromator was replaced with a new 3-crystal (Si111, Si220, Si311) liquid nitrogen (LN) cooled monochromator with piezo-stabilization capability. The new monochromator expanded the energy range from ~25-35 keV to 12-43 keV. The low energy side provides very high flux (exceeding $1x10^{12}$ photons/s at 20 keV) beam for photon-hungry experiments (fast dynamic, low-Z), and the high energy side is optimized for regular diffraction, PDF total scattering, single crystal structure determination, and other various studies.

16-ID-B is equipped with two experimental tables. One, the laser heating table, is dedicated to double-sided *in-situ* laser heating with two 100W YLF fiber lasers, and the other, the general purpose table, is dedicated to cryogenic work, heavy (e.g. graphite and whole-cell) resistive heating, and special experimental and non-standard setups. General diffraction with standard setup, side diffraction and light resistive heating can be performed on either of the tables. The 16-ID-B station is equipped with two stationary/standard detectors – MAR 345 image plate and MAR CCD. Recently we have acquired a new shutterless pixel-array detector Pilatus 1M-F, capable of data collection at 130 frames per second rate. Combined with very high flux, the new detector allows diffraction data collection with sub-millisecond exposure, narrowing the gap between static and shock experiments.

A.3 *In situ* High *P-T* X-ray Diffraction

Laser heated DAC integrated with micro-focused x-ray diffraction is a unique experimental technique for studying structural properties of materials under simultaneously ultra-high pressure-temperature conditions (*P* to multimegabar and *T* to several thousand degrees). Figure 72 shows part of the experimental setup for the integrated system. Key features include:

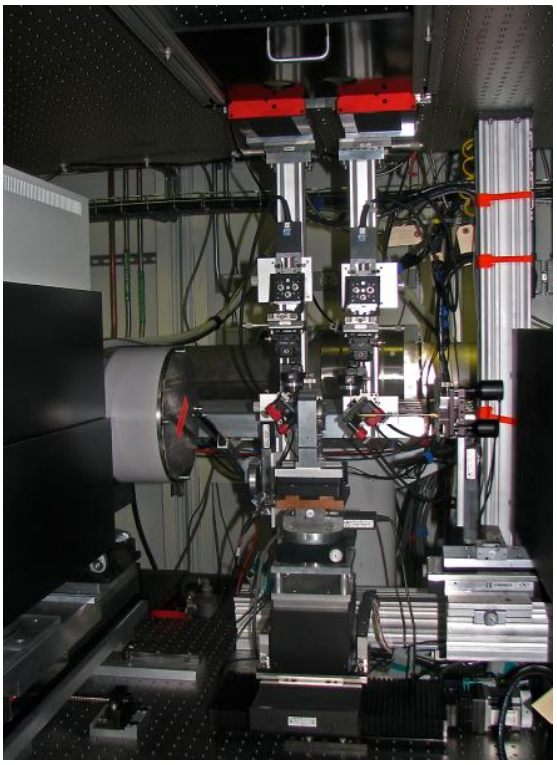

Figure 72: *Experimental setup of the on-line laser heating system at 16-ID-B for in situ micro-focused x-ray diffraction.*

- Double-sided heating w/2-100W YLF fiber lasers
- *In-situ* XRD with micro-focused x-ray beam
- Separate temperature measurement from both sides with imaging spectrometer
- *In-situ* variation of heating spot size (flat top 5 to > 60 μm, FWHM from 10 to >120 μm)
- Mirror pinhole setup allowing direct monitoring of the alignment of heating area, temperature measurement position, and XRD locations
- Pulsed heating and modulated heating capability
- Remote pressure control capability
- Water-cooled cell stage and holder for maximum stability
- User-friendly control interface; automatic data logging

Recently established new capabilities are driven by several issues in experimental studies such as timed resolved studies, *P-V-T* EOS, and high-pressure melting. Synchronized pulsed heating with fast data collection with a Pilatus detector allows time-resolved study providing important information on structural dynamics, phase transition dynamics, and chemical reactions under high pressure. The short heating pulse together with the fast data collection also allow the diffusive scattering of melt to be captured before it disperses into surrounding matrix; it also minimizes potential chemical reaction caused by extensive CW laser heating. One of our newly developed capabilities allows *in-situ* variation of laser heating spot size, which minimizes the effect of temperature gradient in phase transition and chemical reaction studies. Together with the mirror-pinhole setup it is now possible to reliably heat and conduct measurements on samples as small as 5 microns. These new developments provide new opportunities in several areas of research including *P-V-T* EOS and high-pressure melting.

A.4 Electronic Excitations

When x-rays impinge on a sample, many processes can occur. In inelastic x-ray spectroscopy, photons exchange energy and momentum with electrons in the sample and scatter from the sample. The double differential cross-section, which is proportional to the number of photons with a given energy, within an energy range, scattered into a solid angle, is measured. The spectrometer is designed to detect scattered photons of energies of interest with an energy resolution and momentum transfer corresponding to the physical process of interest. X-ray Raman yields information about the bonding of electrons and the electronic structure (energy levels and occupation of orbitals). The geometry of scattering can be selected to probe different bonding directions, for example in layered materials. If the photon energy-loss is on the order of a fraction of eV to tens of eV, one can study valance excitations and plasmons (collective excitations of the electron gas) with scattering close to the forward direction. This falls under the category of the spectroscopy of electronic excitations.

Presently, HPCAT has a spectrometer for the study of electronic excitations at low momentum transfer and x-ray Raman at larger scattering angles with about 1 eV energy resolution. We employ backscattering bent or diced Si(555) analyzers which scatter photons into a detector close to the sample. Multiple analyzers can increase the collection solid angle for low count-rate measurements. The incoming energy is scanned by the monochromator, with analyzer/detector geometry fixed to measure the Si(555) backscattering energy. HPCAT is developing the use of polycapillary optics to discriminate background due to gasket scattering (Figure 73). The polycapillary can have a limited field of view to collected scattered photons primarily from the sample. The capillary optics refocuses the photons which are then energy analyzed.

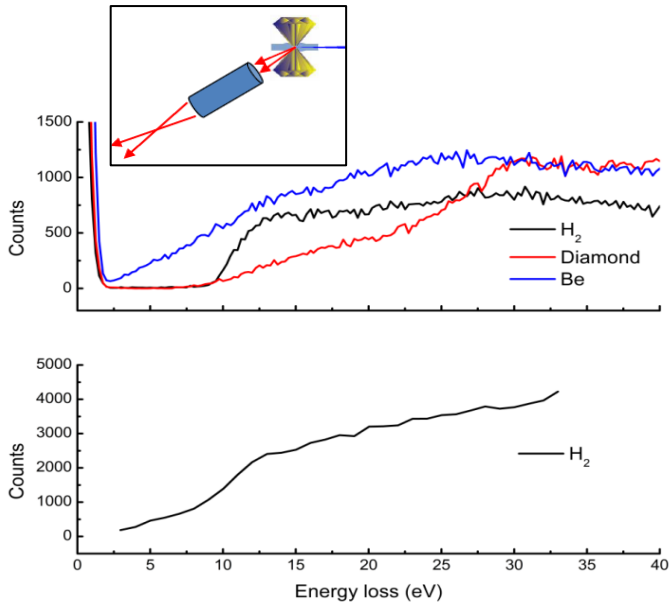

Figure 73: *In the bottom panel, the inelastic spectrum for H_2 at 10GPa using conventional slit collimation after the sample shows a large background from the diamond anvil cell. The upper panel (black line) shows the measured spectrum taken with a polycapillary optic (insert), which reduced the parasitic scattering effectively.*

A.5 X-ray Fluorescence Spectroscopy

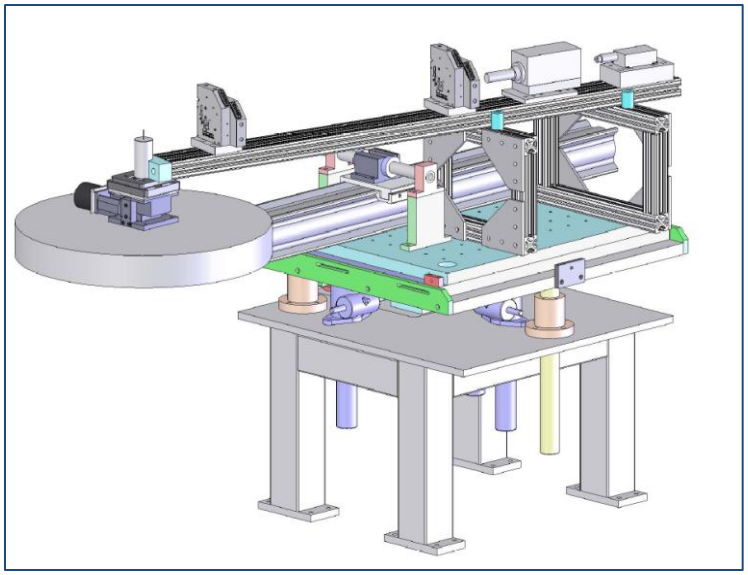

Figure 74: *Experimental setup for x-ray fluorescence spectroscopy at 16-ID-D HPCAT.*

The interaction of x-ray photons with atoms gives rise to the elastic and inelastic scattering of photons as well as photo-absorption. Ejection of a deep inner-shell electron by photo-absorption produces a vacancy in the electronic structure which relaxes ($\sim 10^{-15}$ s) by a radiative (x-ray fluorescence) or radiationless (Auger electron emission) mechanism. The set of energies of radiation emitted from atoms of a particular element arises because of its electronic energy levels and serves as a fingerprint for identifying the element. Thus, analysis of the emission spectrum can be used to identify the composition of an unknown sample. The intensity of a particular line is proportional to the concentration of that element, which is the basis of determining the elemental composition of a sample.

At HPCAT, a focused beam impinges on the sample in a diamond anvil cell. The number of photons with a given peak height are collected by a multi-channel analyzer. Via energy calibration, each channel is assigned an energy value. In this way, we can measure the number of photons of a given energy fluorescing from the sample. The spectrometer shown in Figure 74 employs a Vortex silicon drift detector in backscattering geometry due to the present requirements of the cell. The HPCAT setup is able to detect elemental composition at the tens of ppm level for a sample in a diamond anvil cell.

The UNLV group has extensively used the fluorescence technique for measuring dilute concentrations of elements in aqueous solutions. In their study, they used a hydrothermal diamond-anvil cell for *in situ* synchrotron x-ray fluorescence to quantify the concentration of Y, an important trace element often used as a proxy for the heavy rare earth elements in geologic systems, in a xenotime-saturated 2 M HCl-aqueous fluid at 1.19 to 2.6 GPa and 300–500°C. They find that the concentration of Y decreases with increasing fluid density.

Future developments at 16-ID-D will include 1x5 μm^2 focused beam for better special resolution and use of polycapillary optics for discriminating the unwanted background signals.

A.6 Resonant X-ray Emission Spectroscopy

Since its first application under high pressure in late 1990s, XES provides a unique probe for the diagnosis of pressure-induced spin transitions in materials by measuring satellite peaks of $K_{\beta 1,3}$ line for 3*d* transition metal elements and $L_{\gamma 1}$ line for 4*f* elements. Using the same experimental setup, RXES or PFY, experiments can be performed at various energies across the absorption edge. RXES may be viewed as a combination of XES and XAS. Instead of collecting transmitted x-rays as in XAS, emission spectra are measured at each step as the incident beam energy is changed across an absorption edge. This resonant method significantly enhances footprints of electron states, and has a remarkable sharpening effect in projected spectra (RXES or PFY), providing important information on electronic structure, such as intra-atomic multiplet coupling and inter-atomic hybridization.

At HPCAT, we have a 1-meter Rowland circle x-ray emission spectrometer which contains a 4-inch Si analyzer and an AmpTek solid state detector. A range of emission lines (4.5-21keV) can be studied by selecting proper Si analyzers. Since 2008, we have developed a new cryostat which can reach down to ~10K for R/XES studies on magnetic properties and spin transitions of many functional materials under high pressures and low temperatures.

To improve the efficiency of XES experiments, we have made a new design to implement more analyzers to increase the solid angle in data collection. We have also used both a miniXES and x-ray polycapillary optics for improving signal/noise ratio in data collection. The miniXES spectrometer (Figure 75, inset-A) contains a few small flat crystals which are placed close to the sample and arranged in Johansson geometry, together with a spatial filtering aperture and a low-noise x-ray position sensitive detector (Pilatus100K is used currently). Due to its close proximity to the sample, XES can be collected in a large solid angle. We also use a polycapillary with a focus length ~8.5mm and focus spot ~50μm for large solid angle data collection (Figure 75, insert-B).

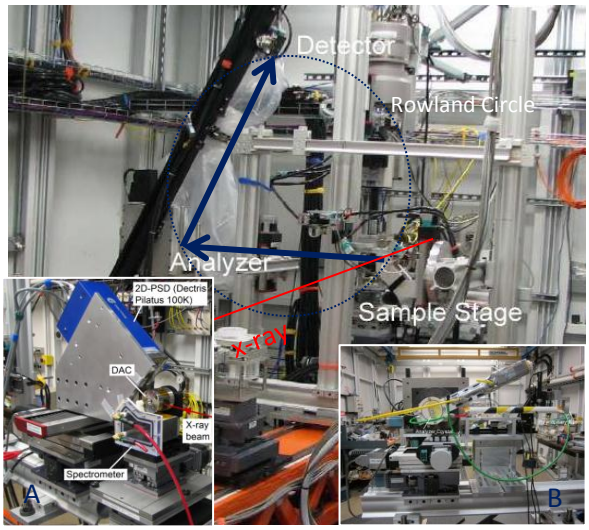

Figure 75: *The one-meter Rowland circle XES spectrometer setup at 16-ID-D. Inset-A: miniXES setup. Inset-B: The XES setup using a polycapillary.*

A.7 Nuclear Resonant Inelastic X-ray Scattering

Nuclear resonant x-ray spectroscopy has become feasible for high pressure research since the late 90's and is now widely used for studying lattice dynamics of materials. Nuclear resonant x-ray spectroscopy can be divided into two methods: NRIXS and NFS. NRIXS uses the possibility of simultaneous excitation of nuclear resonance and lattice vibrations, whereas NFS includes scattering processes that occur without recoil, i.e., without participation of lattice vibrations.

From NRIXS, partial density of states can be acquired and important dynamic, thermodynamic, and elastic information such as vibrational kinetic energy, vibrational entropy, and Debye temperature can be derived. This technique also allows determination of anisotropy of sound velocities, and mode Grüneisen parameters.

At HPCAT, the bandwidth of the undulator beam is reduced to ~1eV by a liquid nitrogen cooled Si(111) double crystal monochromator. After going through a high resolution monochromator (HRM), the bandwidth of x-ray beam is further reduced to ~2meV. The HRM consists of two channel cut silicon crystals [Si(440) and Si(975)]. The highly monochromatic x-ray beam is tuned to ^{57}Fe nuclear resonance at 14.414keV and is then focused at the sample position by KB mirrors. By using time discrimination electronics and a fast APD, the delayed signals caused by the narrow nuclear absorption provide NRIXS data carrying phonon dynamics information. We can now routinely measure NRIXS under high pressures using a panoramic DAC and two or three APD detectors in close proximity (Figure 76).

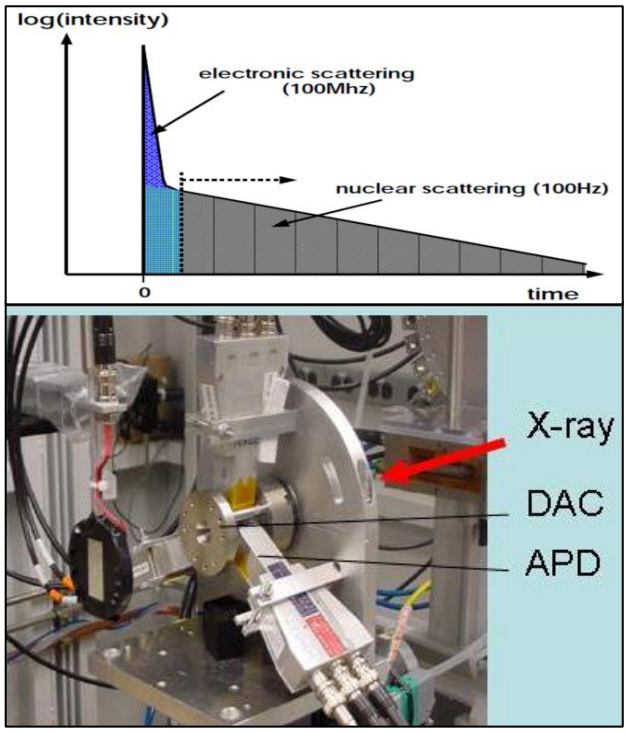

Figure 76: *Top: The delayed signals are a measure of nuclear scattering. Bottom: Photograph of HP NRIXS setup at HPCAT. 3 APD detectors are put close around a panoramic diamond anvil cell.*

NRIXS is highly isotope selective and is truly unique among techniques for the study of lattice vibrations. Materials surrounding the sample that do not contain resonant nuclei produce no unwanted background, and this feature permits high-pressure experiments in the megabar regime.

A.8 Nuclear Forward Scattering

Nuclear forward scattering (NFS), also known as synchrotron Mössbauer spectroscopy, permits determination of hyperfine interactions, and can provide information on spin state, valence state and magnetic ordering of samples. Compared to conventional Mössbauer spectroscopy using a radioactive source, NFS has advantages of the unique properties of synchrotron radiation: intensity, collimation, time structure, and polarization.

In NFS, the HRM is tuned to the nuclear transition energy and kept as stable as possible. X rays that are transmitted through the sample excite the resonant nuclei coherently. The re-emitted radiation is observed with the avalanching photo-diode detector in the forward direction. The timing circuit measures the elapsed time between excitation and re-emission and removes prompt events. The delayed events are the measure of NFS, resulting in the time spectrum of the nuclei in the sample. The HRM essentially plays the role of a bandpass filter around the nuclear transition energy. At HPCAT, a 2-meV HRM is used for ^{57}Fe nuclear resonance at 14.414keV (Figure 77).

In addition to the pressure dependent studies at room temperature, we have two cryostats coupled with membrane control and an online ruby system to do NFS experiments at low temperatures and high pressures.

Compared to other nuclear resonant techniques, NFS measures the transmission signals which are relatively strong and may be collected in a fast manner. For example, fast NFS experiments may be performed to determine high-pressure melting temperatures of iron by measuring the Lamb-Mössbauer factor which describes the probability of recoilless absorption. Similar to NRIXS, NFS is also isotope selective, which is particularly beneficial for high pressure experiments in discriminating unwanted background.

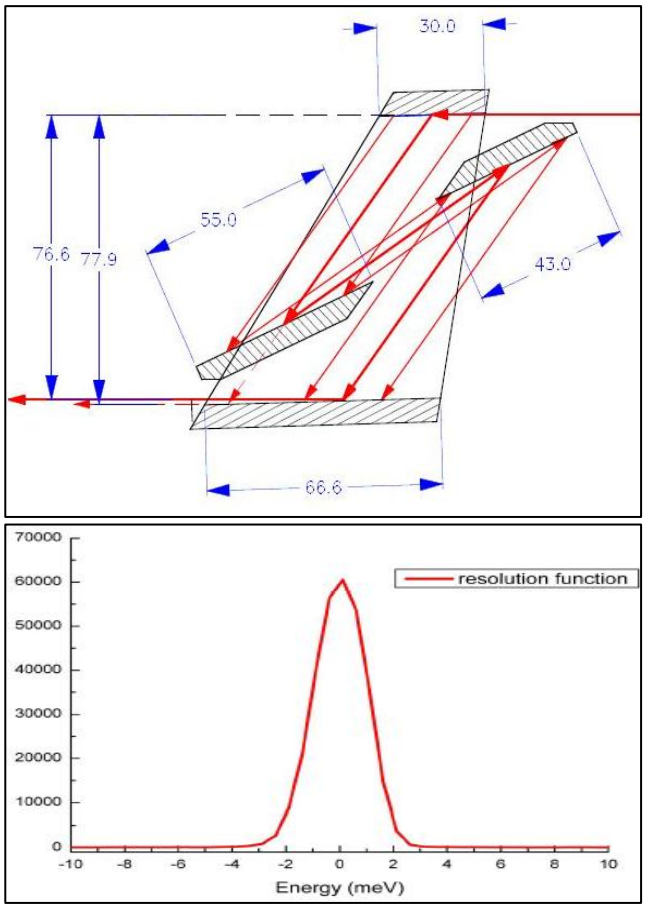

Figure 77: *Top: Schematic drawing of the 2meV HRM for ^{57}Fe at HPCAT. Bottom: A resolution function of the HRM.*

A.9 X-ray Diffraction at the Bending Magnet Beamline

The HPCAT 16-BM-D beamline is dedicated to general micro-x-ray diffraction (μ-XRD), high-resolution powder x-ray diffraction (HR-XRD), single crystal XRD and XAS.

The general μ-XRD configuration is the most widely used for studies of equations of state, phase transition, materials strength, etc. at various sample conditions including cryogenic cooling and resistive heating. The setup can be integrated with on-line Ruby fluorescence system and diaphragm membrane or gear box to control the pressures remotely. The typical beam size focused with KB-type mirrors is 5 μm (h) × 12 μm (v) at the full-width half-maximum. The photon flux is ~5 x 10^8 photons/sec at E = 30 keV, a typical energy used to minimize the x-ray attenuation through the sample cell. The energy is selected with a Si(111) double crystal monochromator in pseudo channel-cut mode. The range of energy covers 7-40 keV in normal operation and up to 60 keV when specially requested. Without being integrated with cryogenic cooling or a resistive heating setup, applications of the same diffractometer setup can be easily extended to single crystal XRD and XAS measurements. HR-XRD utilizes a Pilatus detector, which can improve the angular resolution of the diffracted beam when properly corrected for the x-ray efficiency.

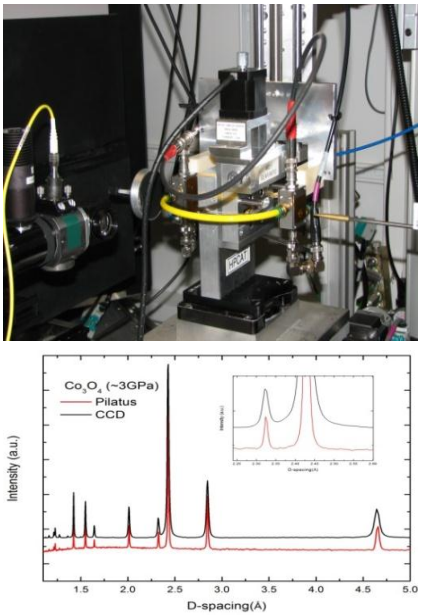

Figure 78: *Top: Switchable μ-XRD and XAS setup at 16BM-D. Bottom: Comparison of the diffraction peak width between Pilatus and CCD detectors.*

A switchable setup between the general μ-XRD and XAS has been recently developed. The detector configuration can be quickly converted from a large area detector (e.g., MAR345 IP detector) for diffraction to the ion chambers for energy scanning for x-ray transmission measurements without losing beam alignment or altering the sample condition (Figure 78). The fixed-exit, pseudo channel-cut Si(111) monochromator and the achromatic beam focusing optics with KB mirrors maintain the beam positions and sizes stable to within the ~40 μm pinhole aligned before the sample. The monitor and detector ion-chamber mount is pneumatically translated in and out to ensure the reproducible transmission geometry. The switchable setup without disturbing the beam alignment is useful to perform combined XRD-XAS experiment at an identical sample condition.

The resolution of HR-XRD at 16BM-D beamline has been improved by 3-5 times up to $\Delta q/q \sim 10^{-3}$ by using a Pilatus detector on a rotating two-circle diffractometer arm. Multiple diffraction images are collected at discrete 2θ angles and stitched together with proper geometric corrections to be integrated into a consistent diffraction pattern.

A.10 X-ray Laue Diffraction

This setup is for *in-situ* characterization of crystal lattice defects under external stress and for single-crystal x-ray diffraction studies in time resolved mode. It can provide information on texture of materials, strain, dislocation arrangements, domain structure, and operational slip systems of single-crystals. It is based on the high sensitivity of Laue diffraction to lattice rotations and deformations.

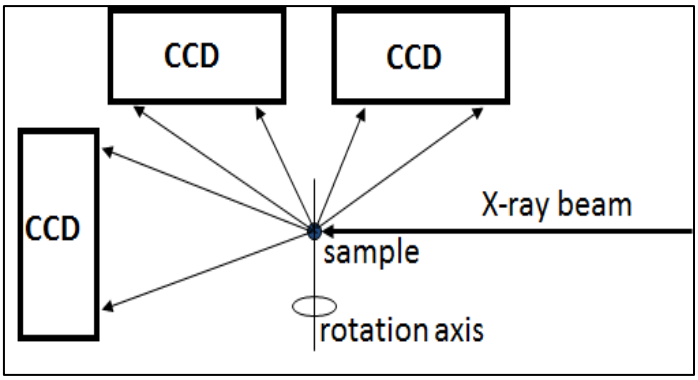

Figure 79: *Schematics of the Laue setup at HPCAT*

Experimental setup for Laue diffraction measurements (Figure 80) is available at HPCAT 16-BM-B beamline. X-ray white beam is focused down to 5-10μm by KB-mirrors. Typical energy range is 5-70kEv. A Si(111) channel cut monochromator provides monochromatic beam of ~ 40keV energy exchangeable with the white beam. It is used to measure d-values of selected reflections and for geometry calibration. Measurements are done in both forward and 90° geometries. Diffraction patterns are normally collected with Mar CCD area detector and test measurements with a Perkin Elmer detector, having better sensitivity at high energies, have been performed. Routine measurements can be done at low temperatures using cryostat (only in forward geometry) and at high temperatures with a resistive heating system.

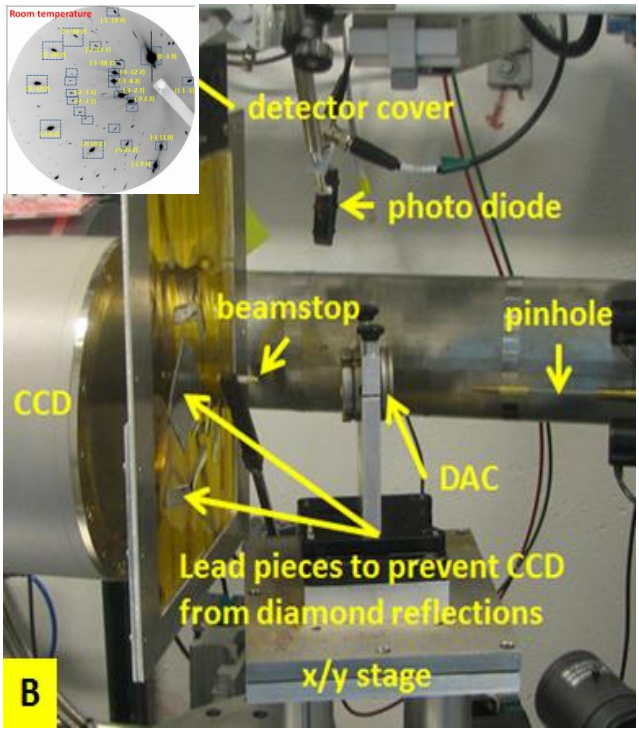

Figure 80: *HPCAT Laue setup at 16-BM-B. Insert: A typical Laue pattern.*

There is no need for rotating single crystal samples in white Laue diffraction measurements, a clear advantage in high pressure applications. Together with the fast data collection, the micro-white Laue technique has great potential in studying time resolved deformation and dislocation of materials in a controlled stress field and/or strain rate. Some case studies are currently underway.

A.11 Studies of Liquids with a Paris-Edinburgh Cell

An integrated setup for liquid structure, elastic wave velocity, and viscosity measurements with a Paris-Edinburgh (PE) cell at HPCAT, 16-BM-B station, provides a new way to investigate the link between microscopic structure and macroscopic physical properties of liquids and amorphous solids at high pressure and high temperature conditions (Figure 81).

Figure 81: *The Paris-Edinburgh cell at HPCAT 16-BM-B station.*

Static structure factor S(Q) of liquids, compressed in a PE cell, can be measured with the multi-angle EDXD technique at 16-BM-B white x-ray beamline. The PE cell is capable of compressing the sample up to 7 GPa and heating the sample up to 2000 °C using a graphite heater. The sample volume is typically >1 mm^3. Use of the large sample volume helps in obtaining signals from the weak scattering liquid, and is accompanied by a diffracted beam collimator with 50 μm or 100 μm slit size to effectively eliminate signals from surrounding materials. In addition, we recently developed ultrasonic elastic wave velocity and falling sphere viscosity measurement techniques in the PE cell. The elastic wave velocity is measured by ultrasonic pulse echo overlap method in conjunction with white x-ray radiography measurement for determining the wave travel distance. The falling sphere viscosity measurements are made with high-speed white x-ray radiography (>1000 frame/second). The liquid structure measurement can be combined with either elastic wave velocity or viscosity measurement.

Correlation between structure and physical properties of liquids and amorphous solids at high-pressure and high-temperature conditions can be investigated with the established instruments, providing a unique opportunity bridging the microscopic structure and the macroscopic properties of liquids and amorphous solids. The high-speed white x-ray radiography setup is capable of overcoming previous limitations in high-pressure viscosity measurement, which enables us to investigate a wide range of materials including very low viscosity liquids and fluids such as liquid metals, salts, and water (around 1 mPa) (Figure 82).

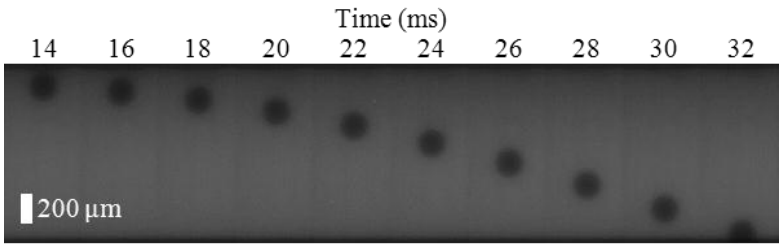

Figure 82: *X-ray radiographic images of a falling sphere (Pt, 200 μm in diameter) in liquid water at 1 GPa and room temperature.*

A.12 Support Equipment and Facilities

At HPCAT an array of novel x-ray diffraction and spectroscopic techniques has been integrated with high pressure and extreme temperature instrumentation. Over the last several years a number of support equipment have been developed and implemented to expand the available *P-T* range of the experimental conditions, increase efficiency and productivity of the beamlines, improve the quality of experimental data, and integrate additional methods of sample characterization with synchrotron investigations.

Figure 83: *HPCAT large diffraction cryostat and small cold finger large-opening diffraction/inelastic cryostat.*

A considerable effort was put into developing instrumentation which allows remote and automatic pressure control in DACs during synchrotron experiments. We have developed a number of mechanical devices (gearboxes) and double-diaphragm (membrane) pressure control system which can be integrated with virtually any type of DAC and allow accurate sample pressure control at a variety of *P-T* conditions – from cryogenic to laser heating experiments. Such devices can be used for automated data collection along predefined *P-T* paths. Pressure control devices for fast dynamic experiments, both ramping and stroboscopic, become available recently.

In order to fully utilize our remote pressure control capability we have designed a number of portable online optical systems for ruby fluorescence pressure measurements and *in situ* Raman sample characterization during synchrotron experiments. Now online optical systems are available for every experimental station at HPCAT. Combined with remote pressure control systems, they significantly increase productivity of beamlines during high-pressure experiments.

To further expand our cryogenic facilities we have designed and implemented a variety of compact cryostats for different synchrotron techniques (powder and single crystal diffraction, inelastic scattering, etc.) The cryostats can accommodate virtually any type of standard and novel DACs with remote pressure control, and allow various high-pressure measurements to be performed to temperatures down to 4 K.

We have also designed and implemented a number of offline optical system for pressure and Raman measurements, offline laser heating, IR laser micro-drilling/micromachining system for sample/gasket preparation, and so on.

Appendix B: WORKSHOP PROGRAM

Wednesday, October 10, 2012

17:00 *Registration - Argonne Guest House*

17:00 **Reception** *(concludes at 19:30) – Argonne Guest House*

Thursday, October 11, 2012

7:00 *Poster setup – in the Gallery, lower level APS Conference Center (Building 402)*

7:15 *Registration, Continental Breakfast – APS Conference Center (Building 402)*
Plenary Session 1 in Auditorium - Chair: Christian Mailhiot

8:15 **Welcome**, *G. Brian Stephenson*

8:30 **Charge of the Workshop**, *Christian Mailhiot*

8:45 **HPCAT: An Integrated Facility for High Pressure Research,** *Ho-kwang Mao*

9:35 **Compressing the Group-I Elements,** *Eugene Gregoryanz*

10:05 *Break*
Plenary Session 2 in Auditorium ----- Chair: Thomas Duffy

10:20 **Advances in Matter Under Extreme Conditions,** *Russell J. Hemley*

10:50 **Inelastic X-Ray Scattering Studies of Phonons, Thermodynamics, and Kinetics of Materials,** *Brent Fultz*

11:20 **Dynamic Compression Science at APS: *Scientific Challenges and Research Opportunities*,** *Yogendra Gupta*

11:50 **Photo** - *Front steps*

12:00 *Lunch - Gallery, lower level APS Conference Center*

13:30 **Break-out sessions**

Panel 1: Structure, bonding and thermodynamic properties reaching 0.5 TPa and beyond (room: A1100)
Chairs: *Thomas Duffy, Stanimir Bonev*
Panelists: *Reinhard Boehler, Brent Fultz, Carl Greeff, Eugene Gregoryanz, Richard Scalettar*

Panel 2: Time-dependent transformations and off-Hugoniot processes (room: C4200)
Chairs: *William Evans, Shengnian Luo*
Panelists: *Michael Armstrong, Jing-yin Chen, Eric Chronister, Daniel Hooks, Nenad Velisavljevic, Wenge Yang*

Panel 3: New materials discovery and applications (room: E1100)
Chairs: *Jonathan Crowhurst, John Tse*
Panelists: *Barbara Lavina, John Moriarty, James Schilling, Viktor Struzhkin*

Panel 4: Novel states of matter and new chemistry (room: E1200)
Chairs: *Dana Dattlebaum, Andrew Cornelius*
Panelists: *Valentin Iota, Yue Meng, Artem Oganov, Maddury Somayazulu, Philip Sterne*

Panel 5: Mechanical and transport properties of materials: strength, failure, rheology, transport properties (room: B5100)
Chairs: *Yusheng Zhao, Rudy Wenk*

Panelists: *Jon Almer, Joel Bernier, Changfeng Chen, Yan-zhang Ma, Dmitry Popov, Yanbin Wang*

Panel 6: Liquid and amorphous materials (room: A5000)
Chairs: *Chris Benmore, Howard Sheng*
Panelists: *Eric Chisolm, Malcolm Guthrie, Magnus Lipp, Changyong Park, Chris Tulk*

Panel 7: Advanced technologies and instrumentations (room: B2100)
Chairs: *Chi-chang Kao, Stanislav Sinogeikin*
Panelists: *Ercan Alp, Kevin D'Amico, Tim Graber, Vitali Prakapenka, Paul Chow, Jesse Smith*

16:00 **Poster cameo introduction** (1 min each, *in Auditorium*) *Chair: Stanislav Sinogeikin*

17:00 **Poster session -** *in the Gallery, lower level APS Conference Center (Building 402) – Chair: Stanislav Sinogeikin*

19:15 **Workshop dinner –** *Argonne Guest House*

Friday, October 12, 2012

7:00 *Continental Breakfast - APS Conference Center (Building 402)*

8:00 **Break-out sessions**

Panel 1: Structure, bonding and thermodynamic properties reaching 0.5 TPa and beyond (room: A1100)
Panel 2: Time-dependent transformations and off-Hugoniot processes (room: B4100)
Panel 3: New materials discovery and applications (room: E1100)
Panel 4: Novel states of matter and new chemistry (room: E1200)
Panel 5: Mechanical and transport properties of materials: strength, failure, rheology, transport properties (room: B5100)
Panel 6: Liquid and amorphous materials (room: B3100)
Panel 7: Advanced technologies and instrumentations (room: B2100)

10:00 *Break*
Plenary Session 3 in Auditorium ------ Chair: David Funk

10:15 **Novel Xenon Chemistry with a Diamond Anvil Cell,** *Maddury Somayazulu*

10:45 **Electron Correlation and Magnetism in f-Electron Metals under Pressure,** *Per Söderlind*

11:15 **Understanding f-electron itinerancy and magnetism using volume collapse,** *Joseph Bradley*

11:45 **Explosives Science**, *Daniel Hooks*

12:15 *Lunch - Gallery, lower level APS Conference Center*
Panel Report in Auditorium ---------- Chair: Guoyin Shen

13:30 **Report from break-out groups** (20 minutes each, in *Auditorium)*

15:50 **Path forward**

17:00 **Adjourn**

17:15 **HPCAT Tour –** *sign up at registration, meet outside Auditorium*

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