High pressure X-ray studies at NSLS

The National Synchrotron Light Source offers the COMPRES community a considerable opportunity for x-ray studies using the superconducting wiggler at X17. This beamline has a steep history of high pressure innovations including diamond anvil studies and large volume studies. The superconducting wiggler continues to provide an x-ray source that is competitive with third generation sources for x-ray diffraction studies. In addition, the current plans to build the next x-ray synchrotron at Brookhaven (NSLSII) provides a significant future at the NSLS that requires the presence of COMPRES research to assure access to the NSLSII.

With this vision of the NSLS, we held a workshop on February 25 – 26 to assess the community needs and hopes for the next five years. Forty five attendees discussed the strengths and weaknesses, the science goals and technical limitations. We enumerated the needs for support staff and the needs for new equipment to enable initiatives. We set priorities and estimated budgets. Here we present the results of the workshop and provide a budget plan for the next five years. We include a list of participants and the agenda for the workshop as appendices. Here we address some of the conclusions of the workshop followed by the detailed proposal for the next five years.

Phase transitions

Experimental and theoretical investigations of phase transitions in Earth and planetary materials under pressure and temperature conditions of their interiors are of fundamental importance to our understanding of the nature and dynamics of planetary bodies in the solar system. A number of recent findings have led to major paradigm shifts in Earth’s interior models. The discovery of the perovskite to post-perovskite transition in the predominant phase of the Earth’s mantle may be considered “the discovery of the decade” in mineral physics, with multidisciplinary impact on the study of the core-mantle boundary (Murakami et al. 2004; Lay et al. 2005, Hernlund et al. 2005). The recent controversies regarding the post-spinel transition has challenged the established view of the transition zone and stimulated extensive research on pressure calibration at high temperatures, which is the basis for comparing field observations with laboratory measurements (Irifune et al. 1998; Shim et al.; Fei et al. 2004). With the unsettled claims of the beta-phase by experimentalists and the bcc phase by theoreticians, the issue of the structure of iron under core conditions also remains uncertain (e.g. Saxena et al. 1996; Alfè et al. 2002 ; Andrault et al. 2000; Ma et al. 2004).

In the next five years, new data on phase transitions in the following areas have been identified as of primary interest to the study of the Earth and planetary interiors. For crustal and upper mantle materials, new experimental data on the phase transitions in ultra-high-pressure metamorphic rocks are needed to assist the study of deep focus earthquakes. A thorough investigation of the post-spinel transition will help interpret detailed seismic observations on the transition zone, including the magnitude, sharpness, lateral heterogeneity, and topography of the 410 and 660-km discontinuities. Further studies of the post-perovskite transition including the determination of the Clapeyron slope are necessary for unraveling the mysteries concerning the D” zone and ultra-low-velocity-zone at the core-mantle boundary. A new class of phase transition in planetary
materials such as CAIs, chondrules, and basaltic glasses from the Moon promise to shed light on the origin and evolution of the early Earth.

Phase transition is sensitive to stress conditions. A poorly understood factor is the effect of non-hydrostatic stress on the conditions of phase equilibrium. From the technical point of view, holding pressure constant while monitoring phase transformation is an overlooked issue that deserve more attention. In most experiments with static compression, pressure is not directly measured. It may be more meaningful to determine phase transitions at a given strain state instead of pressure.

It has been recognized that the presence of the second phase may affect the transition conditions of the phase of interest (Stixrude 1997). Phase boundary may also be sensitive to the amount of minor or trace elements in the sample. Although many current research have focused on single phase systems, natural geological systems contain multiple components, among which chemical reaction may take place upon changes in pressure, temperature and composition. Studying chemical reactions in multi-component systems under high pressures and high temperatures that are prevalent in the Earth’s deep interior is a frontier in the phase transition study.

As pressure increases, the experimental sample size becomes smaller. To ensure that the experimental data collected at micron or sub-micron scale are applicable to the Earth, we must understand the effect of grain size, surface effect and the presence of nanometer-sized inclusions on phase transitions.

Before equilibrium is reached, phase transition proceeds as a function of time. Investigating the kinetics of phase transition is important for assessing the fate of the subducted slabs and understanding the dynamics of the core-mantle boundary.

A variety of experimental techniques are available to detect a phase transition, including x-ray diffraction, various spectroscopic methods, imaging (also known as x-ray radiography), and resistivity measurements. Special techniques such as magic angle diffraction may be useful in eliminating the effect of non-hydrostatic stress on phase transition.

In addition to structural phase transition, there is a resurgence of interest in electronic spin crossover in the lower mantle minerals (Badro et al. 2003, Li et al. 2004; Badro et al. 2004; Jackson et al. 2005; Li et al. 2005). This is an example of non-quenchable transition that must be studied using in-situ experimental techniques. Another novel type of phase transition is liquid-liquid transition, which may be important for understanding high-pressure melt including silicate magma in the crust and mantle and metallic magma in the core.

Specific topics were defined that help define the technological challenges:

**Topic: An accurate petrogenetic grid.** An accurate petrogenetic grid to 30 GPa with good coverage would allow an accurate mapping of the P-T plane, giving access to pressure and temperature knowledge in high-pressure devices that do not allow in-situ P-T measurements. The grid could be used for detailed P,T measurements in offline high-pressure devices, and samples of a particular composition could be used as internal standards in measurements of phase equilibria in any system. The location of some invariant points as anchor points or standard reference points for the P-T plane would also be very useful (similar to the use of the triple point of H2O as a standard reference point for temperature, for example). The creation of such a grid will require:
A. In-situ x-ray diffraction measurements of univariant boundaries.
B. A set of independent primary standards valid at the relevant P-T conditions. Some workers have mentioned the possibility of a set of “internally compared” standards based on one primary standard. However, this introduces unnecessary propagation of random or systematic errors from the primary data set. A better method will be to measure many standards (using elasticity and volume measurements, for example) and treat each one as a primary standard, with inter-comparisons as a cross-check. Elasticity and volume measurements of these standards (such as NaCl, MgO, CsCl, Au, Pt, W, etc.) will need to be performed at all the P, T conditions and an equation of state agreed upon for each in order to create this series of standards.
C. The determination of the pressure effect of thermocouple emf needs to be pursued. The Johnson Noise equipment created by Ivan Getting, and relocated to a beam line or other appropriate facility, will be a good mode of action for this (Sector 13 at GSECARS may already be doing this).
D. High-pressure, large-volume assemblies with lower thermal gradients will be needed to increase the accuracy of these measurements. Cell assembly development will thus need to continue.
E. High d-spacing accuracy and resolution will be needed for the phase equilibrium measurements at the beam line. This should be negotiated with the experts at the beam line.
F. Long duration runs may be necessary to reach a state of equilibrium in many cases. This will benefit from the existence of side stations and multiple experimental apparati.

**Topic: Lower mantle phase equilibria.** The complexity of phase behavior in the lower mantle is just being uncovered. The phase transition in CaSiO₃ perovskite, expected in the mid-lower mantle, and the post-perovskite phase transition in (Mg,Si)O₃, are very recent discoveries and it is assured that detailed studies of the phase equilibria and properties will be necessary to apply these findings to the mantle in appropriate detail. Transition pressures will need to be more accurately determined, including the effects of secondary elements on the pressures of the transitions. The partitioning of secondary and minor elements will be important in understanding the chemical evolution of the Earth. The property changes caused by the phase transitions are now an issue. Stress effects, kinetics will need to be known. These studies will benefit from improvements in x-ray resolution, temperature measurement in the diamond-anvil cell, creation of isothermal temperatures in the laser-heated diamond-anvil cell, and the performance of associated experiments such as spectroscopy and elasticity measurements (for example to more precisely locate and characterize the symmetry transition in CaSiO₃, since the x-ray effects very close to the transition may be too subtle to see).

**Topic: Melting.** In a field dominated by x-ray diffraction measurements, the determination of the onset of melting is a difficult problem. However, the onset of melting, and the phase equilibria of melting including solidus and liquidus locations, element partitioning, as well as the mechanics and geometry of melting, are all important in Earth’s evolution and structure. The high temperatures and chemical reactivity of
melts also lead to problems in containment and pressure measurement that need to be continually solved as they arise. High-resolution imaging of samples in the LVP, combined with marking of the melts with heavy incompatible elements, could help in locating onset and geometry of melts (though the effect of the dopants on the melting needs to be considered). A combined energy- and angle-dispersive facility for the laser-heated DAC could be used to switch between accurate d-spacing measurements (angle-dispersive) and the easier identification of melting (energy-dispersive) (suggested by Tom Duffy). Associated optical and spectroscopic measurements would also be very useful.

Equation of state of melts are important in defining the thermodynamics of melting and motivate new studies. For example, the notion of phase transitions within melts is important to define. Certainly coordination changes occur for elements such as silicon or magnesium with increasing pressure. Whether these changes are sudden or gradual affects our understanding of melts. X-ray absorption studies can define density. X-ray diffraction can yield the pair distribution function. The first of these studies is currently in progress at X-17B2 using an imbedded reference sphere in a melt. The PDF studies require a wide range in Q and very low background. We propose below to purchase a solar slit system, such as the one in use at the ESFR. This system can yield the required low background for these measurements.

**Topic:** Effect of stress on phase transitions. The pressure/temperature conditions and kinetics of phase transitions are affected by stress, and in the low-stress limit this is applicable to phase transitions in subducting slabs and other deforming environments in the mantle. The understanding of this will require the accurate control and measurement of stress and strain. *In-situ* stress/strain measurements are active parts of the D-DIA, R-Drickamer and R-DAC programs at present, and the application to phase transitions is in the formative stages. Problems such as the effect of stress on the forsterite to wadsleyite phase transition in subducting slabs would be of keen interest in mineral physics, for phenomena such as deep earthquakes. Technical developments include high resolution stress detection, high dynamic range for the initial detection of phase transitions in a strained solid, magic angle diffraction for isolating the “stress-free” state, high-resolution radiography and tomography for imaging of phases and cracks (using metal markers, for example), and ultrasonic measurements of events in the sample coupled with imaging. Such studies of stress will be of interest in materials science as well as mineral physics. One distinction to make is the presence of stress as a “problem” in phase transitions when the equilibrium behavior at isostatic pressure is desired, as opposed to the use of stress as an imposed variable whose effects on phase transitions are of primary interest (Harry Green).

**Topic:** Effect of grain size/surfaces on phase transitions. This is an active part of the study of nanomaterials. Grain size and surface energy have significant effects on phase transitions, allowing metastable phases to be accessed and changing phase diagrams. Materials scientists are interested in the phase behavior of compounds with well-characterized grain sizes in the nanoscale range. This can also apply to nanophases or nano-inclusions (nuclei) in natural minerals, in which metastable behavior has been observed (TiO2 inclusions in natural minerals was mentioned by Harry Green).

**Topic:** Second-order phase transitions. In order to better see the small lattice splittings near second-order phase transitions, good control of hydrostaticity and high-resolution x-
ray measurements are needed. The detection of second-order or nearly second-order transitions is also aided greatly by the use of complimentary methods, such as Raman, IR and other lattice dynamic measurements.

**Topic: Non-conventional phase transitions.** Spin transitions (high-spin to low spin) in transition metals and polyamorphous phase transitions (glass to glass or liquid to liquid transitions) are unusual types of phase transitions requiring special measurements. High-q radial distribution function measurements (both x-ray and neutron) are useful for polyamorphous transitions, while nuclear forward scattering (NFS) and other specialized techniques are needed to study HS-LS transitions. For Earth compositions such as (Mg,Fe) SiO3 with smaller amounts of the transition metal, higher-resolution x-ray diffraction would be useful for discriminating the small lattice parameter differences between HS and LS states.

**Topic: Thermodynamic measurements.** The accessible properties of phase transitions that can reveal the thermodynamics of systems are the P-T slopes of univariant phase transitions, molar volumes of crystalline solids available by x-ray measurements, melt volumes by falling sphere, radiography, or tomography measurements. These can be combined with other data, such as heats of solution, vibrational measurements, and calculations, to obtain the full thermodynamic characterization of complex systems.

**Topic: Binary (and higher multicomponent) phase equilibria.** As the detailed studies of mantle systems continue, it is becoming more and more important to be able to interpret the phase equilibria of systems with more components from in-situ measurements. For example, in the study of the effects of Fe, Ca, Al, and other elements on the post-perovskite phase transition in MgSiO3, it is necessary to interpret the phase behavior of a multi-component system using x-ray diffraction at ultrahigh pressures. This and other multi-component systems require good discrimination of d-spacings, accurate simultaneous measurement of P and T, and low thermal gradients to map out binary and higher phase diagrams. This is in its infancy and will rely on technical developments in both large-volume and diamond cell research.

**Topic: High-pressure boiling and critical points.** This will require the identification of liquids and gases in situ, which can be done with imaging and with liquid structural measurements. Very high temperature furnaces will also be required.

**Topic: Kinetic studies.** For slow kinetics, turrets of diamond cells and multi-anvil side stations would be very useful for taking occasional measurements without occupying the beam unnecessarily. For very fast kinetics, techniques of more rapid data collection would be highly desirable.

**Topic: Incommensurate structures.** The study of incommensurate structures, such as are found in the post-close-packed structures of alkali metals, for example, requires the detection of small superlattice reflections, which in turn will rely on high dynamic range and x-ray sensitivity. The needs are similar to those for second-order phase transitions.

**Topic: UHP metamorphism.** The creation of more detailed phase diagrams for crustal rocks will be needed to unravel the new metamorphic grades that have been found in ultrahigh-pressure terranes.

**Melt and glass structure**

High resolution x-ray diffraction for crystallographic studies and high energy x-ray scattering for pair distribution function (PDF) studies of non-crystalline materials
(melts and glasses) at high pressure temperature has drawn great attention among the participants at the workshop. While properties of crystalline minerals have been extensively studied from the crystallographic point of view, melts and glasses increasingly become of geophysical interest because melts and partial melting play an important role in mantle dynamics.

Structure determination of glasses and melts at high-pressure (P) and temperature (T) require high quality data. These data must be free from parasitic scattering from cell components, such as: anvils, gaskets, and furnace materials. Several methods are used to eliminate or reduce background scattering and are applied either in the data processing stages or during data collection. These include: background measurement and subsequent subtraction from high PT data or the use of slit systems to completely eliminate parasitic scattering from reaching the detector. In practice, it is generally not enough to simply collect backgrounds or blanks at ambient conditions and apply these to high PT data because backgrounds change with P and T, and may not be easily determined at high PT. On the other hand, Soller slit systems, such as the one illustrated in Figure 1, can be used to completely eliminate parasitic scattering from reaching the detector and are functional at any PT conditions. Soller slits, when properly installed and aligned, can provide high quality data.

Soller slits are currently being used with multi-anvil [1] and Paris-Edinburgh [2] pressure systems. An example of liquid diffraction data collected using a Paris-Edinburgh press, with and without Soller slits, is displayed in Figure 2. This figure illustrates a very important point about liquid (melt) and glass scattering. Namely, melts and glasses are very weak scatters and their signals can be “washed out” by parasitic scattering. However, it is immediately clear that Soller slits are remarkable at removing parasitic scattering and allow the collection of high quality diffraction data necessary for structure determination of glasses and melts at high PT conditions.

**Elasticity**

The most robust fingerprint of chemical and thermal state of the Earth’s interior are the elastic properties of the materials. Recovered by seismology, the radial variations in seismic velocity points to phase transitions, melting, and general pressure increase. Painted as blue and red, lateral variations in seismic velocity lead to dynamic modeling as the colors transform to temperature or composition, and further to buoyancy. These transitions require the input of a comprehensive understanding of the elastic properties of earth materials as a function of all of the relevant variables. These last few years has seen tremendous growth in our data base as well as our experimental tools for defining this information. Here we outline some of this excitement with a focus on the next phase of development.

*Recent Highlights – Equations of State*  

P-V-T Equations of state of mantle and core
minerals are essential to interpreting the observed seismic structure of the Earth in terms of its mineralogy. Recently numerous important advances in measuring equations of state (EOS) have been made using synchrotron x-ray diffraction at high pressure. Measurements of room temperature EOS of minerals remain important. Recent examples include the compression curves for the newly discovered post-perovskite phase of (Mg,Fe)SiO₃, which may be an important constituent of the lowermost mantle D" region (Mao et al., Princeton group).

High-P,T EOS of minerals (e.g., MgSiO₃ perovskite (ESRF); CaSiO₃ (Shim et al.; hcp-Fe (Dubrovinsky et al.)) have been measured using laser heating in diamond anvil cells. These advances illustrate the tremendous potential of this technique. The precision and accuracy of this powerful tool will benefit further from continued development.

Evaluations of high-temperature pressure standards are of critical concern to further development in high pressure science. A recent comprehensive study by Fei et al. (2004) examined the high-P,T equations of state of numerous candidate pressure calibration standards (e.g., MgO, Au, Pt, W, Mo, Pd), and documented inconsistencies between previously determined EOSs of these materials. This study was carried out using a multi-anvil press with synchrotron x-ray diffraction to determine cell volumes, and reached pressures up to 20 GPa and temperatures of 2000 °C. The inconsistencies highlighted in this study allowed a critical assessment of the earlier equations of state, and made recommendations regarding the most reliable pressure calibrations at high T. A related study focussed on the widely used ruby fluorescence scale in relation to the compression of a number of metals at room temperature (Dewaele et al.).

Recent Highlights – Elasticity A variety of techniques are now being used to determine acoustic velocities of materials at high pressure. These include Brillouin spectroscopy, NRIXS, inelastic x-ray scattering, and ultrasonic interferometry.

Brillouin spectroscopy in the diamond anvil cell continues to provide novel and important results. A recent example is the measurement of acoustic velocities in polycrystalline, Al-bearing silicate perovskite to 45 GPa (Jackson et al., 2005). These data point to Al content as a plausible explanation for lateral shear wave velocity variations in the lower mantle. Additionally, a Brillouin spectroscopy system has recently been installed at the GSECARS sector of APS. The combination of Brillouin spectroscopy and simultaneous x-ray diffraction can provide an absolute pressure scale, which will be welcomed by the high pressure community.

Inelastic x-ray scattering methods have recently been developed for high-pressure applications, and used to study the elastic properties hcp-Fe, the principal component of the Earth’s inner core (e.g., Fiquet et al., 2001; Lin et al., 2004). This tool may well be an important component of the NSLSII program.

Simultaneous ultrasonics + XRD investigations in the multi-anvil press permit the equation of state and acoustic properties of minerals to be evaluated under high-P,T conditions. An example is the recent study of MgSiO₃ perovskite to 9 GPa and 873 K by Li and Zhang (2005). In principle this technique can be extended to 20 GPa and high temperatures. Gigahertz ultrasonic techniques are also being carried out at very high pressures in the diamond anvil cell.

Finally, it should be noted that with synchrotron XRD techniques, characterizing stress and strain is now done routinely in a variety of high-P,T experiments. This is an important advance over past experimental methods, in which the stress/strain state of samples were commonly uncertain or unknown.

Scientific challenges – Equations of state Equations of state of deep Earth materials are essential in the interpretation of seismological properties and geodynamics of the planet’s interior. The emergence of synchrotron radiation sources has allowed tremendous advances
in the development of technologies that can soon be used to precisely measure these pressure-volume-temperature relationships under extreme conditions of P and T. In addition, synchrotron XRD of an internal calibrant is commonly used to determine pressure in studies of phase equilibria, crystallography, acoustic properties, and other measurements at high-P,T conditions. Now that these methods are being employed, it is imperative that their accuracy and precision be validated.

In the last few years a number of studies have revealed significant inconsistencies between several high-P,T pressure standards that are widely used. The efforts to correct this situation have focussed on the pressure range below ~20 GPa, normally accessible using the multi-anvil press. It is apparent that a similar, and probably worse, situation exists among pressure standards that are now being used in laser heated diamond anvil cell studies. A key challenge to the high pressure community is to develop standards that can be used as internal pressure calibrants for x-ray diffraction experiments in the laser heated diamond anvil cell. This should also include the cross calibration of multiple standards, because no single standard is appropriate for use in all experiments. A comparison of these calibrations across different beamlines will be helpful to strengthen the standardization of the adopted equations of state, and also to identify any difficulties in making inter-facility comparisons of data.

A related concern is the lack of pressure calibrants for use in high temperature experiments that take place at users’ home institutions, where x-ray diffraction is not an available method. The development of a tool, similar to the ruby fluorescence scale, that can be used to determine pressure at high temperatures without XRD would be of tremendous benefit to the high pressure community.

The determination of P-V-T equations of state of liquids, by synchrotron x-ray radiography, is recognized as a promising direction for future studies. The properties and dynamics of melts are critical to understanding many geophysical processes.

Scientific Challenges – Elasticity
The interpretation of seismological profiles of the Earth’s interior has long been the principal motivation for measuring the acoustic velocities and the elastic tensors of minerals, both at ambient and high P or T conditions. As the resolution of seismological studies continues to improve, the need for more and better elasticity data, under simultaneous high pressures and high temperatures, increases.

Two specific challenges that can be highlighted include: the interpretation of seismic anisotropy throughout the planet, from uppermost mantle to inner core conditions; and understanding lateral variations of compressional and shear wave velocities ($\partial V_p$ and $\partial V_s$) in terms of composition and/or temperature variations. These goals require the mineral physics community to provide complete characterization of elastic anisotropy, as well as aggregate acoustic velocities, in minerals, and also the variation of these properties with pressure, temperature, and composition.

As mentioned above, there are several technologies that hold promise in this regard. These include Brillouin spectroscopy, inelastic x-ray scattering, and ultrasonic interferometry, all of which have been demonstrated to be useful at high pressures and/or high temperatures. Each of these techniques has its own unique advantages, and all are expected to provide important contributions toward these goals.

In order to further develop the ultrasonic studies at X17B2, a 2000-ton press with exchangeable modules is immediately needed to expand pressure ranges of a variety of experiments, including equation of state, phase transformation, and ultrasonics. Sintered diamond cubes are needed for expanding the pressure to the top of the lower mantle pressures to narrow gap/expand the overlap in pressure range between diamond anvil and large volume apparatus to ensure consistency from different techniques. These new acquisitions will benefit the experiments for equation of state, ultrasonics, lattice strain studies.
Rheology

The quantitative relationship between stress, strain, and time in minerals forms the basis for our view of the evolving Earth. Plate tectonics, earthquakes, volcanic eruptions all respond to these intrinsic properties of Earth materials. Laboratory studies have recently made a significant breakthrough in capability for defining these properties at mantle pressures and temperatures using x-rays generated by synchrotrons at national laboratories. This progress has set the stage for new and exciting research efforts.

Significance of deviatoric stress measurements at high pressure. Thermal convection in Earth’s deep interior cools the planet and in the process generates earthquakes and volcanoes, moves tectonic plates, and disturbs the uniform chemical layering of a differentiated Earth. Laboratory measurements of the relationship between deviatoric stress and deviatoric strain rate of rocks and minerals at high pressure are driven by the need to understand this circulation at depth. Characterizing the state of deviatoric stress during experiments under high confining pressure is also critical in a number of other mineral physics studies that have important bearing on the frontiers of solid Earth science (e.g., accurate characterization of seismic velocities of high-pressure phases). Current research on global geodynamics strongly suggests that the dynamics and evolution of this planet are controlled largely by materials properties under deep Earth conditions, including rheological properties, phase relationships, elastic properties and chemical properties such as the diffusivity and solubility of certain elements [e.g., Bercovici and Karato, 2003; Kellogg, et al., 1999; Schubert, et al., 2001; Tackley, 2000; van Keken, et al., 2002]. For instance, the lateral and radial variation of viscosity have an important influence on the convection pattern and generation of deep earthquakes [e.g., Bunge, et al., 1996; Christensen, 1984; Green and Houston, 1995; Green and Marone, 2002; Karato, et al., 2001; van Keken and Ballantine, 1998], whereas the solubility and diffusivity of elements in various phases control the chemical evolution associated with mantle convection [e.g., Hart, 1988; Hofmann, 1997; Van Orman, et al., 2002]. Also, the way in which materials are distributed or the flow pattern in Earth can, in principle, be inferred from seismological observations, but the interpretation of seismological data relies entirely on our understanding of elastic and anelastic properties of minerals under deep Earth conditions [e.g., Jackson, 2000; Karato and Karki, 2001; Karki, et al., 2001; Liebermann, 2000].

Recent progress. During the last few years, there has been important progress in measuring the state of stress of samples during high-pressure experiments. Firstly, there have been significant advances in high-pressure, high-temperature deformation apparatuses, in particular, the successful development of two instruments: the Deformation DIA (D-DIA) [Wang, et al., 2003], and the Rotational Drickamer apparatus (RDA) [Xu, et al., 2004; Yamazaki and Karato, 2001], by which quantitative rheological experiments have become feasible well beyond a pressure of ~4 GPa. Insights provided by these new instruments will be key to better understanding of the evolution and dynamics of terrestrial planets. An
important new dimension currently in its early stages is development of ways to use the
diamond anvil cell (DAC) to extend such deformation studies to much higher pressures.

Secondly, there is an increased appreciation of the importance of stress in the
experimental studies of equations of state (EOS) and elasticity [Wang, et al., 1998; Weidner,
et al., 1992] Some discrepancy in reported EOS is likely due to the influence of deviatoric
stress that causes systematic differences in the positions of x-ray diffraction peaks. For an
anisotropic material such as brucite, values of bulk modulus reported from synchrotron
studies in the 1990s varied by a factor of two owing to the uncorrected effect of deviatoric
stress at high pressure [Xia, et al., 1998]. Improved stress measurements are also critical to
multianvil studies of elasticity. For example, acoustic measurements of EOS in a multianvil
apparatus are hindered by the lack of knowledge of sample dimensions at high pressure. It is
now possible to use the D-DIA to hold sample length constant during acoustic measurement
[Li, et al., 2005a]. At this point direct imaging is used as feedback. As we are able to resolve
differential stress levels below the elastic limit and achieve higher resolution of sample
dimensions, we will be able to bring even finer control to acoustic measurements and, by
intentionally imposing a differential stress, begin to define third order elastic moduli.

Thirdly, it is often critical to measure many phenomena such as phase equilibria or
diffusion coefficients in a purely hydrostatic environment. Yet, cell assemblies are often
elastically anisotropic, so that when compressed “hydrostatically” in a multianvil apparatus, a
non-zero state of deviatoric stress is unavoidable. If, however, deviatoric stress can be
determined, then steps can be taken (e.g., operation of D-DIA anvils) to reduce the stress
state to hydrostatic.

We have recently developed a method for measuring stress in a sample under high-
pressure and temperature conditions in a multianvil apparatus using x-ray diffraction from a
synchrotron source [Li et al, 2004]. The spacings of the lattice planes are measured both
parallel and perpendicular to the principal stress axes. The stress is then derived from this
measured elastic strain using the elastic moduli [Singh, et al., 1998]. We have used both
white x-ray and monochromatic techniques. For the white beam studies, we have used a
multi-element solid-state detector that was designed for EXAFS studies. With it we use four
elements that are positioned at 90° from each other. A conical slit system was designed and
built to fit the detector. Because of the small diameter of detector, we could not build a slit
system that optimized the optics such as the acceptance angle and spatial resolution.
Nevertheless, we obtain precision of 100 MPa. The number of detectors in our current system
precludes defining the orientation of the principal stress axes projected on the plane of the
detectors (so they must be known a priori), and the dimensions of the slits limits the x-ray
resolution. The monochromatic system yields about the same precision, with a greater ability
to define the axis of the stress field because a 2-D detector is used. However, the
monochromatic system cannot readily collimate the diffracted x-ray beam, so the background
due to diffraction from the pressure medium and parts of the sample assembly can easily hide
diffraction from the sample, which limits our choices of building materials.

At the workshop the following issues were expressed:
• In order to characterize the flow properties of many important earth phases, we
need higher pressure. Although the DAC can provide much wider pressure range
than LVP, there are still concerns about whether the DAC is an appropriate tool
for the characterization of flow laws.
• Although some concern was expressed about trying to characterize the behavior
of too many phases, we need to cognizant that crustal phases are returned to the
mantle and subducted to great depth.
For rheology studies: Quantify effect of H_2O on rheology
Progress has been made but there is more work to be done especially at high pressure.

We do not fully understand where water resides – in crystals? Along grain boundaries? Does water stay in the same place upon quench? Do we need to look for in-situ techniques that will allow us to probe the structural sites for water at high pressure and temperature? Or are quenched samples representative?

Making good measurements at low stress levels will be important for properly characterizing activation volumes

making sure that we measure the flow mechanisms appropriate to the mantle

We need to better understand the effect of other volatiles and impurities on rheology.

We need to better understand the character of grain boundaries at high pressure and temperature as they are likely to become more like defects (or grain boundaries in metals). If atoms on the grain boundary behave as if they are in the liquid state then we can anticipate a larger pressure effect on their behavior than we might otherwise anticipate.

Grain boundary characteristics will be important for grain boundary sliding.

The small probe size of NSLS II opens up the possibility of nano-imaging or tomography techniques that will allow us to observe defects in-situ during deformation.

Techniques that allow us to create high strains will be important for studying the development and effects of lattice preferred orientation and the development and effect of rock textures (e.g. two phase mixtures, foliated or textured rocks etc.)

Challenges:

- **Strain measurement** of 10^-6 would allow us to do anelasticity measurements with small source size. At NSLS II this would be possible.

- Need to build optics to enlarge the image before we convert it to light (x-ray microscope)

- This higher resolution would also improve deformation measurements in the DAC (their sample size is small which limits their ability to measure strain.)

- Possibly single crystal Q experiments combined with polycrystalline Q experiments would allow us to examine “micro-creep” vs “macro-creep” and therefore shed light on the interpretation of post glacial rebound data.

- Perhaps we can establish equations that relate micro-creep and macro-creep.

- Rotational diamond cell? (future potential tool that could be useful)

- Strength increases with pressure therefore, we need to go to much higher temperature to get low stress to compensate. Therefore, we need to develop cells that can go to higher temperatures than we currently achieve.

- Software data processing issues: need to get high precision stress/strain results in real time.

Current status at X17B2. We now have an MRI proposal pending at the NSF requesting funds to upgrade the conical slit system with a new detector that is optimized for stress resolution. We expect that we can achieve 10 MPa precision with the new system if funded. We have also recently purchased (with a grant from the Air Force) a MAR345 imaging plate detector which will be used with monochromatic x-rays. We will be able to refine stress
measurements with this system. We are nearing the final design of a D-T-cup which is a deformation system similar to the DDIA, but using the T-cup tooling. We expect that this system will allow us to carry out deformation experiments at high temperature and pressures exceeding 20 GPa. We currently have funds for the purchase of this system.

References