Materials Diffraction Suites (MaDiS) for NSLS and NSLS-II

A White Paper

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Prepared by

John B. Parise

and

Members of a proposed Beamline Advisory Team (BAT) to establish a Powder Instrument Next Generation (PING-BAT)

and

Individuals as noted in the text

PING-BAT

Simon Billinge (spokesperson)	Columbia University
Peter Chupas	Argonne National Laboratory
Lars Ehm	Stony Brook University/BNL
Jon Hanson	Brookhaven National Laboratory
James Kaduk	Ineos Technologies
John Parise	Stony Brook University
Peter Stephens	Stony Brook University

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Executive Summary

The recommendations of two recent workshops (July, 2007 and Jan 2008) are that a Powder Instrument Next Generation (PING), a unique resource for the materials community, be built as part of the NSLS-II project. This white paper outlines the opportunities for *Materials Diffraction* at this instrument, and PING's unique place in the DOE and worldwide inventory of powder diffraction instruments. The workshop held January 17-18 brought together a diverse group of materials scientists in five breakout sessions: 1) Materials Diffraction 2) Metrology 3) Engineering 4) High Pressure Science and 5) Surfaces and Interfaces. Despite overlaps in scientific approaches, it became clear that no one document can hope to represent the needs of all five groups adequately. The white papers from other break-out sessions are submitted separately. However it is clear that the build-out of a Materials Diffraction Suite (*MaDiS*) at NSLS *and* at NSLS-II would satisfy many of the needs of the diffraction community articulated in the separate white papers. PING provides both leading edge technology in the instrumented hutch (PING #1 in Fig. 1) and provision of un-instrumented hutches for the transitioning of instruments, existing and being developed at NSLS, to MaDiS at NSLS-II.

The importance of knowing where the atoms are: A quantitative knowledge of the atomic scale structure of materials (preferably under the condition of synthesis and operation) is a prerequisite for understanding exiting materials, tailoring their properties and designing new ones. The current frontiers in structural science are related to the complexity, heterogeneity, size and imperfections of the structures of interest in a diverse array of special conditions and environments. The determination of atomic arrangements and mechanical properties for real materials requires a suite of beamlines covering specific energy ranges and with the ability to span the variety of experimental set-ups required by the diverse materials community. This can best be accomplished in partnership between NSLS and NSLS-II facilities and the community, through the BAT.

For the bulk materials scattering community PING represents a unique instrument, best envisioned as a starting point for a broader effort to establish MaDiS. PING is optimized to use high energy (E > 50 keV) x-rays for real- and reciprocal-space diffraction studies of real materials including powders, single crystals, nano-materials and heterogeneous samples. The ability to create small beams with high flux and well controlled sample positioning will allow heterogeneous samples such as real working devices to be studied in great detail. The hard x-rays are well suited to PDF studies of nanostructure, and to studies of materials in special environments, where high penetration and tight collimation to discriminate against parasitic scattering are required. The high flux and efficient detection will allow small sample volumes to be probed, time resolved measurements and high throughput studies. A modular design will allow complementary data to be readily collected on the diffraction line and the PDF side-station, and the other MaDiS components (Fig. 1). Coupled with state of the art data analysis and

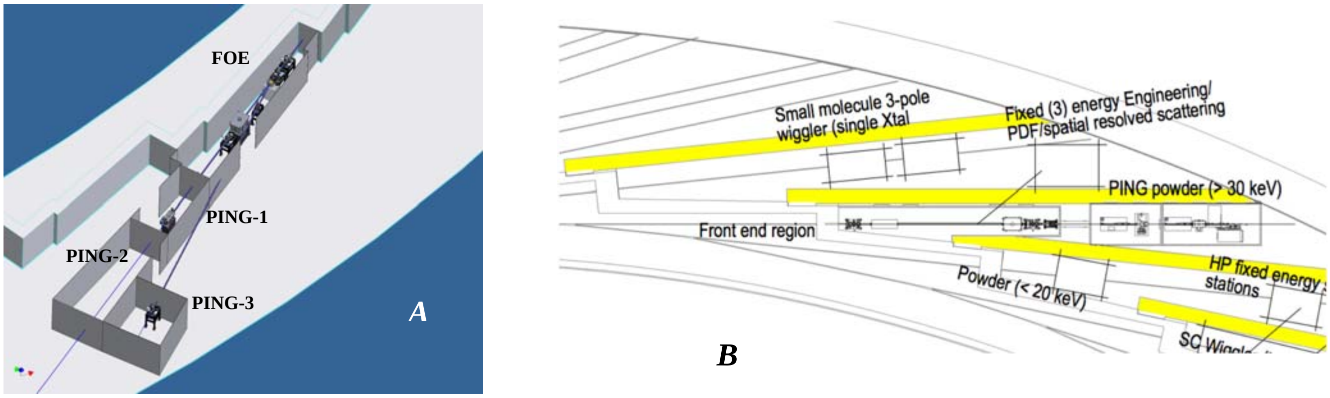


Fig. 1 Conceptual views of (***A***) the PING beamline and a partial view of (***B***) the Materials Diffraction Suite (MaDiS) extending over at least 2 - sectors. The PING project beamline (***A***) consists of a fully built out hutch for high energy high resolution scattering (PING-1) and two un-instrumented hutches, PING-2 operating in serial with -1 and useful for experiments with long set-up times such as catalysis and high P experiments. PING-3 operates in parallel and will be useful for total scattering studies. PING-2, -3 will also provide a stopgap for programs currently using X7, X-16 and X-17 at NSLS prior to the build-out of other beamlines at NSLS-II thereby ensuring a minimum of beamtime to keep research programs "ticking along". MaDiS will include 3-pole wiggler based (E < 20 keV) powder and single crystal diffraction, and superconducting wiggler-based sectors - just visible at the bottom of scheme (***B***) allowing increased access to diffraction at extreme conditions and to beams suitable for burgeoning PDF studies . Further details are given in section 3.

modeling software integrated into the beamline infrastructure, and complementary spectroscopy and anomalous diffraction capabilities elsewhere at NSLS-II, will position NSLS-II as a unique place to carry out Total Crystallography studies. Provision of two un-instrumented stations, along with a fully optimized high-resolution station, will allow scientists to transition capability from NSLS. This will allow ramp-up of research programs during start-up of NSLS-II (Fig. 1).

Key recommendations for NSLS-II

1) *PING will represent a radical departure from existing powder instruments and there is a clear need for such a unique instrument in the US and worldwide inventory*. PING will be optimized for 1) high energy (50 - 100 keV) scattering 2) high angular resolution 3) high time resolution and 4) studies at non-ambient conditions and 5) high spatial resolution. Currently operational beamlines emphasize some of these options (e.g. 1 and 3 at 11-ID at APS; 1 and 2 at ESRF). *The increased emphasis on extreme conditions, complexity and heterogeneity is where the science is heading*.

2) *The PING-BAT advises that the PING instrument be designed in such a way to take advantage of "BNL proprietary"* developments in detectors and optics, along with several user initiatives in environmental cells, to build the first fully optimized powder diffraction beamline for high energy scattering at extreme conditions. Some of these developments include Laue analyzer crystals, focusing Laue monochromators, Si-strip and energy discriminating area detectors. On the user side a plethora of user-friendly ultra high temperature, high pressure and apparatus designed for the study of materials *in operando*, are designed and built. It is critical that the 5-year horizon to the construction of PING and MaDiS be accompanied by efforts to prototype environmental chambers, and to push ahead with ever more suitable high time, angular and spatial resolution optics and detectors.

3) *The use of radial collimation to exclude parasitic scattering from environmental cells is critical* and should be integrated with sample cells.

4) *PING will introduce and implement the concept of "designer" extreme environments at synchrotron sources.* The PING-BAT advises the staffing profile of the beamline include an engineer whose duties focus on design/integration of extreme environments. The community recognizes that enabling transformative measurements at extreme conditions will require that sample cells for extreme environments be considered as an extension of the beamline design. *A holistic approach is required to integrate optics, cells and detectors*.

5) *The on-going need for anomalous diffraction studies* for PDF and diffraction for chemically complex problems (that need complementary data sources) should be accommodated at a spectroscopy beamline. Edge studies are best done at a beamline where the upstream optics are optimized for this kind of measurement. PING-BAT spokesperson Simon Billinge has obtained a conditional commitment from Bruce Ravel in principle to establish a diffraction capability on the EXAFS line.

6) *Software development* will be critical for all aspects of PING, including rapid data collection and analysis. These developments should be coordinated across MaDiS, and all beamlines doing bulk scattering.

7) *The community needs an integrated, broad-based diffraction capability, and a cross-disciplinary approach*: *PING should be seen as a beginning not an end.* PING emphasizes high-energy (> 50 keV) powder scattering. It is clear that 3-pole wiggler (< 30 keV) based powder and single crystal instruments are needed. A Materials Diffraction Suite (*MaDiS*) will provide beamlines optimized for particular set of experiments across the disciplines. For example, determination of atomic arrangements and mechanical properties under extreme conditions is now of importance to such diverse groups as Materials Chemists (hydrogen storage) Earth and Planetary Scientists (planetary interiors) Environmental Scientists (carbon sequestration) Condensed Matter Physicists (GMR and superconductors) and Materials Engineers (materials under intense radiation), to emphasize but a few emerging areas. No one beamline or sector can be optimized to cover this territory. However *cross-disciplinary BATs can ensure the best use of the resource by the broadest user community.*

8) *A MaDiS BAT for NSLS (see below) should establish now what labs are needed for implementation of in operando diffraction.* For example The Materials Chemistry, Catalysis, Environmental Sciences users require a

"wet" chemistry lab with dry, inert atmosphere glove boxes to ensure samples are viable between transport from home laboratory and the beamline. The engineering community requires ready access for large pieces of equipment and samples. Work at extremes of pressure will require specialized gas loading equipment and requisite safety reviews, while work on highly activated samples from contaminated sites or highly irradiated reactor parts will require appropriate labs. *A holistic approach is required and where synergies or incompatibilities exist these should be recognized early on.*

9) *No one beamline or sub-discipline should be responsible for the breadth of materials diffraction research. Provision of a truly multi-disciplinary approach, the natural synergies at Brookhaven National Laboratory, such as complementary expertise in nanofabrication and characterization, high performance computing, and so on, need to be utilized to the fullest extent possible to maximize the scientific impact of NSLS-II in Materials Science.* A nexus for these activities, and potentially a means to popularize scattering, engage the NE scientific communities and to launch multi-institution multi-facility initiatives, might be a focus at the Joint Photon Sciences Institute (JPSI).

Key recommendations for NSLS

1) *The build-out of X-17A and establishing NSLS-MaDiS will dramatically impact potential PING users and influence NSLS-II MaDiS design*. X-17 is the only high-energy beamline at NSLS capable of prototyping many of the optic and detector options proposed for PING. Apropos to point (6) above it is vital that a cross-disciplinary culture and a facility diffraction capability continue to grow at NSLS. The only viable high-energy diffraction resource at NSLS is X-17 and it is vital this resource is supported and expanded in preparation for NSLS-II.

a) A MaDiS needs to be established at NSLS, incorporating X-17A, which when operational will mimic many of the features of the PING-beamline in terms of scope and operation.

b) *At a minimum, X-17A,* X-16 (high-resolution powder) and a single crystal crystallography beamline built around a commercial, user-friendly, instrument should be the core of NSLS-MaDiS. The NSLS SAC should consider widening NSLS-MaDiS as resources permit.

c) The advisory team for NSLS-MaDiS will be an excellent prototype for the sort of cross-community collaboration required to get NSLS-II-MaDiS off the ground.

d) NSLS management and the NSLS-SAC should carefully consider the growing need for *in operando,* extreme conditions and high energy (E > 50 keV) total scattering studies (see Appendix 2) in the larger materials diffraction community, and how best to deploy resources, and foster initiatives likely to have the greatest scientific impact.

2) *To harness the expertise in the community of materials diffractionists,* the PING-BAT recommends that NSLS beginning exploring the possibility of standardizing environmental cell mounts for use on several beamlines (see point 4 to NSLS-II). As a straw man proposal: kinematic mounts, such as those used routinely in optics experiments, could be distributed to uses as possible means of interfacing their equipment and making it portable between beamlines. Several break-though environmental chambers are described in this document and several more will be developed. In order to integrate a large variety of capabilities for extreme conditions from day 1, the community will need to be engaged at NSLS.

3) *It is vital the developments described by Siddons on detectors continue apace* and that the Si-strip detector be deployed for users. Developments for NSLS-II will immediately benefit users of the NSLS as more efficient detectors are distributed to diffraction beamlines.

4) *It is vital a commercial single crystal instrument is made available for chemical crystallography.* This instrument should be user friendly and allow at last users in the NE to have rapid access, with appropriate lab-support facilities for low temperature work on air and temperature sensitive compounds.

5) *A MaDiS BAT for NSLS should establish now what labs are needed for implementation of in operando diffraction (see recommendation 7 for NSLS-II).* A holistic approach is required and where synergies or incompatibilities between disciplines exist these should be recognized early on.

1. Introduction to Scientific Theme

Two workshops, held July, 2007 and January, 2008, concentrated on the present and future needs of the Materials diffraction community. Large attendances (> 90 attendees) at both meetings are testament to the enduring and expanding need for high-resolution (time, spatial, and angular) powder diffraction, single crystal diffraction and diffraction from materials at extreme conditions

The advent of dedicated synchrotron sources in the '80s and their proliferation in the past decade spurred enormous progress in the characterization of materials. The frenzy of activity in the area of synthesis and engineering of functional materials for devices illustrates the symbiotic relationship between synchrotron facilities and materials development. While these experiences suggest solutions to society's needs for discovery and engineering of new materials are well in hand, there is a critical need to accelerate solutions to energy and environmental problems. Incremental improvements in materials properties, and understanding of the fundamentals of condensed matter reactivity, will not provide solutions that address the full magnitude of the problems on necessary time-scales. Transformational discoveries, with timely characterization, are sought. It is likely that the materials that provide solutions to pressing problems in materials science will be chemically and structurally complex across a range of length scales from Å-nm-µm-mm-m. It is also increasingly likely that the new functional materials will have to be processed or operate at extreme conditions of time, temperature, pressure, radiation, corrosion, magnetic and electrical fields.

The proposed suite of instruments at NSLS-II and upgraded instruments at NSLS will provide crucial capabilities to enable such transformative studies, changing the way we do materials science by taking us from traditional *"in vitro"* approaches to giving capabilities for *"in situ"* and *"in operando"* materials studies:

Materials Science v1.0 "In vitro": experiments on materials in glass capillaries

Materials Science v2.0 "In situ": experiments on materials in special environments

Materials Science v3.0 "In operando": studying materials in operating devices

In operando studies inherently imply two key aspects to materials experiments for which NSLS-II is excellently suited: spatial resolution and time resolution. Accurately defining gauge volumes in heterogeneous samples is a challenging problem since it requires focusing and positioning hard x-rays, which penetrate the volume of a sample, with high precision. This is currently an active area of development in the synchrotron community.

Spatial resolution is required because devices and the environment are inherently heterogeneous. Time resolution is required because the material state is evolving with time as the device runs, for example, a battery discharging.

An additional aspect inherent in MS*v3.0* is integrating device engineers and product R&D into the basic discovery, tending to blur the traditional distinction between Research and Development. This presents both a challenge and an opportunity to the community and to NSLS-II. As materials chemists and materials scientists become more familiar with self-assembly and nano-fabrication the processes and the hetero-structures produced inherently become more complicated. Remaining with the same set of characterization tools necessarily means the information available from any given experiment is limited. The community needs to address this situation.

In operando studies promise a new way of following complex processes and it will require building more power sources and instrumentation, and taking a more holistic approach to data collection and analysis than is currently practiced. It is vital that source, optics, and environmental cells be tightly integrated from the beginning. The BAT concept is new but the NSLS provides excellent opportunities to test concepts such as interchangeable mounts so that the same cells can be interchanged seamlessly between instruments (IR + high energy X-rays for example). Complex modeling will be developed to address the need to address from different information sources, such as complementary scattering experiments, non-scattering data. Complex modeling is in its infancy, but should be developed in tight integration with experimental capabilities at NSLS-II to gain the greatest benefit from this unique source.

In situ scattering and its popularization throughout the materials community will provide significant increases in capability and productivity. A critical development to take us from MS*v1.0* to MS*v3.0* is to make an interface to the research community that allows access to scientific information from scattering experiments to non scattering-experts. Requirements will be different beam access modes, cyber-infrastructure and scientific user support that satisfy the needs of scientists and engineers doing novel science, but not necessarily being expert scatterers. The currently enormously successful mode of working in collaboration with an expert at the facility needs to be augmented and democratized. Specialized expertise and infrastructure is needed in data analysis and visualization software, using modern modular programming paradigms that allow for rapid feature extensions driven by scientific need.

No one beamline or sub-discipline should be responsible for the breadth of materials diffraction research. Provision of a truly multi-disciplinary approach, the natural synergies at Brookhaven National Laboratory, such as complementary expertise in nanofabrication and characterization, high performance computing, and so on, need to be utilized to the fullest extent possible to maximize the scientific impact of NSLS-II in Materials Science. A nexus for these activities, and potentially a means to popularize scattering, engage the NE scientific communities and to launch multi-institution multi-facility initiatives, might be a focus at the Joint Photon Sciences Institute (JPSI).

2. The Growth, Expansion, and Transition of NSLS Scientific Programs

To continue to service new users of scattering it is imperative that the capacity for high-energy, in situ, time-resolved scattering be increased at NSLS. The build-out of X-17-A1 and a commitment to engage the community in design and installation of environmental cells will allow the community to explore new scientific opportunities and prepare a knowledgeable user base to take advantage of the Powder Instrument Next Generation (PING) and a proposed suite of powder and single crystal instruments at NSLS-II (see below). It is crucial that PSD and area detectors with moderate energy resolution (~300 eV) and sub-ms time resolution, based on silicon technology, be available as soon as possible at NSLS. To take full advantage of the high energy available at PING the possibility of equivalent or better resolutions in a germanium-based detector are required. Continued support of the existing bulk powder lines (X7A and –B and X16) is vital to allow new science to blossom and to test scenarios for NSLS-II over the next seven years.

The prospect of a commercial single crystal instrument on an end station at NSLS, with appropriate staffing would greatly enhance the prospects for chemical and materials crystallography (see below)

It is imperative the design of environmental cells begins immediately and that they be compatible with existing beamlines. Implementation of "standard" fixture to the beamline, a common kinematic mount, would greatly enhance the throughput at powder beamlines.

Tight integration of software, beamline optics, detector and sample environment from the start would greatly enhance the capabilities of the environmental user community and its productivity. Search algorithms for micro-diffraction to readily identify phases. A strong software development effort in areas of data acquisition, analysis, simulation, and visualization is needed. Interpretation of data with poor signal-to-noise discrimination will require integrated simulation along with representations of dynamical processes as 2D or 3D movies. The aim is ease of and real time evaluation of data to improve the confidence level in data quality and higher productivity.

Potential new users

A list of committed users and contributors is given in Appendix 4.

There is considerable potentially new demand for a technique that is as well known as materials diffraction. Home laboratory-based X-ray diffraction (XRD) on bulk samples and single crystals plays a crucial role in research missions of many academic, industrial and government research programs. It is also amongst the first techniques taught to undergraduate and graduate students and so provides a ready entry point to synchrotron radiation. Increasingly the community is moving towards national laboratory-based radiation sources as these provide unique opportunities because of orders of magnitude increases in spatial, temporal and angular resolution. The following are growth areas: a) Combined hard X-ray microdiffraction and fluorescence for simultaneous identification of phase, composition and contaminant sorption on the µm scale; b) The use of pair distribution function (PDF) techniques in combination with XAFS to determine the local, intermediate and long-range structures and to correlate these structures with functionality d) Time resolved and in situ measurements of reaction pathway and kinetics - increasing in combined measurements to determine chemistry or local structure; e) Combined SAXS/WAXS/PDF to simultaneously explore nanomaterials on the Å-nm-µm length particle during particle nucleation-ripening-growth and transformation; f) measurements under extreme conditions (pressure, temperature, acidity). In the next decade the user friendliness of facilities and their ability to deliver results (data analysis and modeling) will be critical to attract and maintain a potentially vast user base for these techniques

3. Proposed Suite of Beamlines (Broadbent contribution)

Materials Diffraction Suite (MaDiS) and Powder Instrument Next Generation (PING)

3.1 Technical Requirements and Specifications for PING

Following the January 2007 User workshop, the following criteria were listed for the beamline design:

- High energy operation is required; desired range is 40-100 keV (ideal) with optimization at ~80 keV
- The first end station will allow high-energy powder diffraction studies to be conducted. A range of basic sample environments will be provided, and the emphasis will be on maximizing the throughput of the station; a robot will be included to assist with this.
- Second endstation is for ´long setup time´ experiments and will not be fitted out within the Project scope. The equipment for this station will be transferred from NSLS and/or purchased with funds and grants from other sources. The equipment anticipated is listed later in this section.
- There is a strong desire to pursue a parallel operating fixed energy side station for PDF experiments at ~80keV.
- The source for the beamline will be a full length 7 m long damping wiggler to get the highest possible flux at the highest energy.
- PING will not be optimized for anomalous scattering investigations. There is an on-going need for anomalous diffraction studies for PDF and diffraction, as chemically complex problems need complementary data sources. Edge studies are best done at a spectroscopy beamline where the upstream optics are optimized for this kind of measurement. PING-BAT spokesperson Simon Billinge has obtained a conditional commitment from Bruce Ravel in principle to establish a diffraction end station on the EXAFS line.
- The energy of the beamline should be tunable, however it is expected that 2-3 sets of crystals should be provided to allow relatively fast switching of a small number of fixed energies and/or permit different thicknesses and/or different crystal cuts. The primary emphasis will be on working conveniently at 50keV or 80keV with +/-5keV variation possible at each of these energies.
- A later upgrade in the second hutch would allow a primary focus and slits at the first hutch position and then refocusing mirrors in the second hutch to produce a 20μm focus in the second hutch; this would be unique at these energies.
- The beamline design should not be compromised by trying to cover too much, should be relatively simple to operate, and reliable.

Instrumentation Requirements.

The previous sections and appendices 1 - 3, describe scientific objectives best met with a high flux, high energy beamline that is set up to do not only a range of "standard" powder diffraction experiments as well as a dedicate PDF station, but also allows complex experiments with long set up times to be accommodated. The proposed beamline meets these requirements by harnessing the huge flux from a damping wiggler, and carefully manages the heatload, such that the beam can supply three hutches, two of them simultaneously. Very considerable efforts will be made to ensure that a wide range of sample environments are made available to the User community, in part by making full use of expertise already available locally.

Source Properties

NSLS-II is designed to deliver photons with high average spectral brightness and high flux over a wide energy range. The damping wigglers will provide brightness exceeding 10^{17} ph/mm^2/mrad^2/s/0.1%BW at energies up to 100keV, with spectral flux will exceeding 10^{13} ph/s/0.1%BW up to 80keV. This high flux comes at the cost of extreme power loadings (65kW); for this beamline, concentrating on the high energies provides a good route to power management by:

- Allowing very significant filtering (reducing the flux below 40keV), as well as,
- Aperturing in the vertical (giving disproportionately more high energy photons per unit power, and removes the need for a collimating mirror), and,
- Using Laue monochromators.

These factors will all reduce the power load seen by the optics to a manageable level. The beamline will be optimized for use between 40keV and 100keV.

Beamline Instrumentation and Layout for PING

The beamline will include a standard optics enclosure, two in-line experiment stations for standard and long set-up experiments, as well as a side station devoted to PDF studies.

The conceptual layout for the NSLS-II powder diffraction beamline is shown in Figs. 1 and 2. The beamline consists of the following optical components: note that this excludes the usual high heat load front end components.

ID-inboard (main) beamline.	Start	Center	Fixed Pos	End	Length
Shielded Wall			**26,724**	26,724	
spool piece	26,724	26,874		27,024	0,3
White Beam Slits	27,024	27,574		28,124	1,1
Pre-Filter (all water-cooled)	28,124	28,424		28,724	0,6
Bellows	28,724	28,824		28,924	0,2
Attenuators (all water-cooled)	28,924	29,224		29,524	0,6
Bremsstrahlung collimator	29,524	29,774		30,024	0,5
Bellows	30,024	30,124		30,224	0,2
Single side bounce Laue Mono	30,224	30,574		30,924	0,7
Bellows	30,924	31,024		31,124	0,2
spool piece	31,124	32,074		33,024	1,9
spool piece	33,024	33,924		34,824	1,8
Double Laue Monochromator	34,824	35,424		36,024	1,2
Bellows	36,024	36,174		36,324	0,3
Bremsstrahlung stop	36,324	36,524		36,724	0,4
Monochromatic slits / beam monitoring	36,724	37,024		37,324	0,6
Bellows	37,324	37,474		37,624	0,3
spool piece	37,624	38,774		39,924	2,3
Photon shutter	39,924	40,124		40,324	0,4
Hutch wall - FOE length 13,6 m	40,324	40,574		40,824	0,5
flight tube	40,824	41,824		42,824	2
Bellows	42,824	42,974		43,124	0,3
Horizontal Focussing Optics (Mirror & ML)	43,124	43,524		43,924	0,8
Exit window	43,924	43,974		44,024	0,1
open space	44,024	45,024		46,024	2
Hutch wall - 1st Exp.Hutch 5,45 m	46,024	46,124		46,224	0,2
open space	46,224	50,324		54,424	8,2
Hutch wall - Exp.Hutch 8,4 m	54,424	54,524		54,624	0,2 2nd

ID-outboard (branch) beamline	Start	Center	Fixed Pos	End	Length
Shielded Wall			**26,724**	26,724	
spool piece	26,724	26,874		27,024	0,3
White Beam Slits	27,024	27,574		28,124	1,1
Pre-Filter (all water-cooled)	28,124	28,424		28,724	0,6
Bellows	28,724	28,824		28,924	0,2
Attenuators (all water-cooled)	28,924	29,224		29,524	0,6
Bremsstrahlung collimator	29,524	29,774		30,024	0,5
Bellows	30,024	30,124		30,224	0,2
Single side bounce Laue Mono	30,224	30,574		30,924	0,7
Bellows	30,924	31,024		31,124	0,2
spool piece	31,124	42,074		53,024	21,9
Endstation ID-out					

The filtering of the beam is performed with high heat load, commercially available white beam filter units as supplied to a number of facilities worldwide. The Laue monochromator will be an adaptation of a Laue mono developed at BNL [2-4]. All other beamline components are available as standard commercial items from a number of vendors.

The focus size on the main beamline will be adjustable from ~3mm(v), (ie fully collimated) x 5mm(h) down to ~200 microns in both the vertical and horizontal. The useful flux in the focused condition will be $>3\times10^{12}$ photons/sec/0.1%BW at 50 keV and $>10^{12}$ photons/sec/0.1%BW at 80 keV.

Fig. 2. Floor layout of the NSLS-II Project Beamline for Powder Diffraction (PING) showing location of a proposed bending magnet (BM) based crystallography area, e.g. commercail single crystal apparatus (see Appendix 2). These would be part of a larger MADiS (Fig. 1).

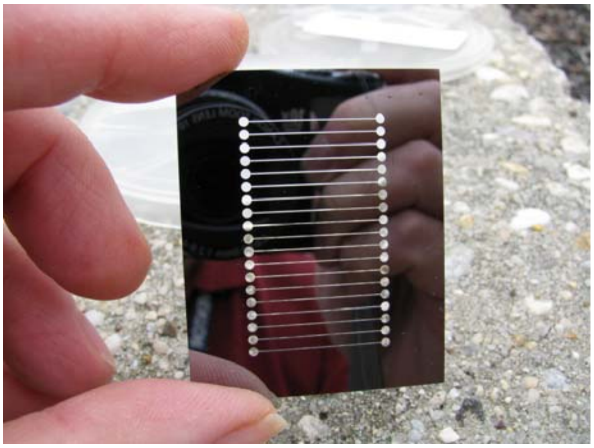


Fig. 3 High-energy analyzer developed by Siddons at BNL

We wish to retain the possibility of pink beam (i.e. strongly filtered white beam) operation for some of the Materials Engineering applications, this can be done reasonably easily with such a beamline design although care will have to be take with the experiment stations due to the high energies present.

PING #1 (Fig. 1, 2)

The first experiment station will be ~3m wide x 4m long with the focus position roughly in the middle of the hutch. This would be very similar to modern, highly productive, stations at the ESRF, SLS, APS, ASP but cater to a wide range of Users interested in higher energies (>50keV).

The diffractometer would be fitted with a high-energy analyzer developed at BNL (Fig. 3). This device developed by Siddons *et al.* works on a Roland circle geometry diffracting the scattered x-rays through the crystal (based on a Silicon wafer) in a Laue geometry, to a detector. This detector will be a custom multi-element germanium detector, made in-house by the NSLS Detector Development Group. In addition to the high-resolution setup, a longer term objective will be to implement a Germanium based micro-strip detector, again, optimized for higher energies. This will directly detect the scattered x-rays, and does not require crystals; the coverage angle is large with many individual 125 micron wide “strips” providing good angular resolution (typically 250 microradians when used on a 0.5m radius). The detector is made from many (~11) individual modules tiled to provide the necessary angular coverage (~100 degrees). This detector will be used for time-resolved studies and will be unique; currently a few synchrotrons (including NSLS) use similar, in-house built, detectors on a silicon substrate at lower energies.

PING #2 (Fig. 1, 2).

The second station will be built as large as the existing floor allows, with a focus position ~2m into the hutch. The access and facilities will be designed to allow very flexible setups with reasonably easy changeover of experiments. The science is described elsewhere, but the list below is provided to give examples of the sorts of experiment envisaged in the hutch.

Technique and equipment	Size of equipment (typical)	Weight (approx)
HP Earth and Materials Sciences: 2000T press to give routine 50 GPa at sample.	4m x 4m plus plumbing (hydraulics) plus accessories.	2000 kg
HP Earth and Materials Sciences: Double sided laser heating (2500K) for routine experiments up to 200 GPa.	3m x 2m plus plumbing and accessories.	100kg including laser and stand.

Catalysis cells with goniometer and detector on 1m arm.	2m x 2m plus gas handling and analysis equipment.	500kg
Carbon sequestration and catalysis. High pressure CO_2 cell. (See App. 1)	1m x 2m plus accessories.	1000 kg including cell, rotation stages, area detector etc.
Engineering applications (white beam, fixed angle EDX, high capacity 0.5µm resolution x/y/z translating table, for scattering in the vertical and horizontal).	3m x 3m	2000 kg
Single crystal set-up concentrating on higher energy experiments and heavier loads (complements standard set up beamline proposed on adjacent BM line).	~2m x 2m	1000 kg

Side station (PING #3)

The PDF side station shall be ~4m x 4m. The concept for this station is based on APS beamline 11-ID-B which features a single horizontal bounce design. A thin bent Silicon crystal in the Laue geometry will kick the beam sideways and simultaneously provide horizontal focusing, it should be noted that this is at the expense of bandwidth, although this will not be an issue as 10^{-3} bandwidth is sufficient for PDF studies.

- Energy needed is ~80 keV (as high as possible but giving sensible beam separation).
- The CRL could be common to both branches, but the there is a preference to put independent CRLs on each branch, after the individual monos.
- The horizontal focus is <300 microns.
- The energy will be switchable through the implementation of a double crystal setup (one on top of the other, which just translate vertically through the beam to switch over).

3.2 MaDiS - "conventional" beamlines

The powder diffraction program at NSLS-II will be covered at the high energies by the project PING beamline operating at 50-100 keV and described below. The more conventional powder diffraction studies will be covered with a three pole wiggler beamline optimized for ~5-30 keV. The beamline will use the common well-proven format of a vertically collimating mirror, a double crystal monochromator with sagittal bender (for horizontal focusing), and then a vertical focusing mirror. A preliminary specification (Fig. 1) is as follows;

Source Three pole wiggler (standard)

Energy range 5-30 keV

Energy resolution <2x10E-4

Crystals Si[111] and Si[311]

Mirrors Si, Rh, Pt coated, 2-3 mrad incidence angle, VCM - collimates beam, VFM - focuses beam in vertical

Harmonic contamination <<1%

Focus size, adjustable from 1 mm(v) x 5 mm(h) down to ~200 microns in vertical and horizontal

The end station would be set up to enable the majority of powder diffraction experiments to be done relatively easily. Extensive use would be made of standard mounts for sample chambers, and there would be two detectors available, rotating about a common axis of the diffractometer. Firstly, a high-resolution array of detectors based on crystal analyzers and scintillation counters (similar to that being built at Diamond, especially in terms of energy range), but also in use at the APS, SLS, ESRF and elsewhere. Secondly a modular silicon microstrip detector will be built in-house at BNL (a design for these modules already exists within BNL), this would be similar to detectors available at SLS and Australian Synchrotron. The advantage of the second detector is speed, and whilst this comes at a cost of angular resolution, it should be noted that this type of detector has become the prime choice for about 80% of experiments at the SLS, and would permit many time resolved experiments not possible with the crystal analyzer. The standard sample environments would include cryostream and hot air type devices, as well as cryostats and furnaces. We would anticipate that a robot would be included to allow long uninterrupted runs of standard samples. The key point about this type of set up is not the new or unique equipment, if will be the ease of changing sample environments, and the user-friendliness of the software, both designed to help the User obtain high scientific productivity.

4. Beamline Specifications and R&D Needs

The NSLS recognized the increasing demand for experimental capabilities using high-energy synchrotron radiation and will address this need by building a beamline dedicated to research using high-energy X-rays. The beamline will be located on port A at the superconducting wiggler X17 (Fig. 4). The scientific focus of the beamline X17A will include X-ray total scattering coupled with Pair Distribution Analysis (PDF), investigation of buried interfaces and single crystal diffuse scattering. A detailed scientific case is laid out in Appendices 2 and 3. At the current stage, the following beamline layout is proposed.

4.1 High Energy Beamline X17A Specifications: Energy: fixed, 65 keV (Fig. 4)

Optics: The beamline will operate at a fixed energy of 65 keV (λ ~ 0.1907 Å). The energy will be selected by a side scattering sagittally focusing bend Laue monochromator (Fig. 4). This single crystal monochromator will allow focusing in two dimensions to a minimum spot size of ~ 100 × 100 μm^2. The expected energy resolution of Δ*E/E* of 10^{-3} is sufficient for investigation of structural changes in materials. X17A will be the first beamline that will use this new monochromator design and therefore serve as testing ground for application of this kind of monochromator at NSLS-II.

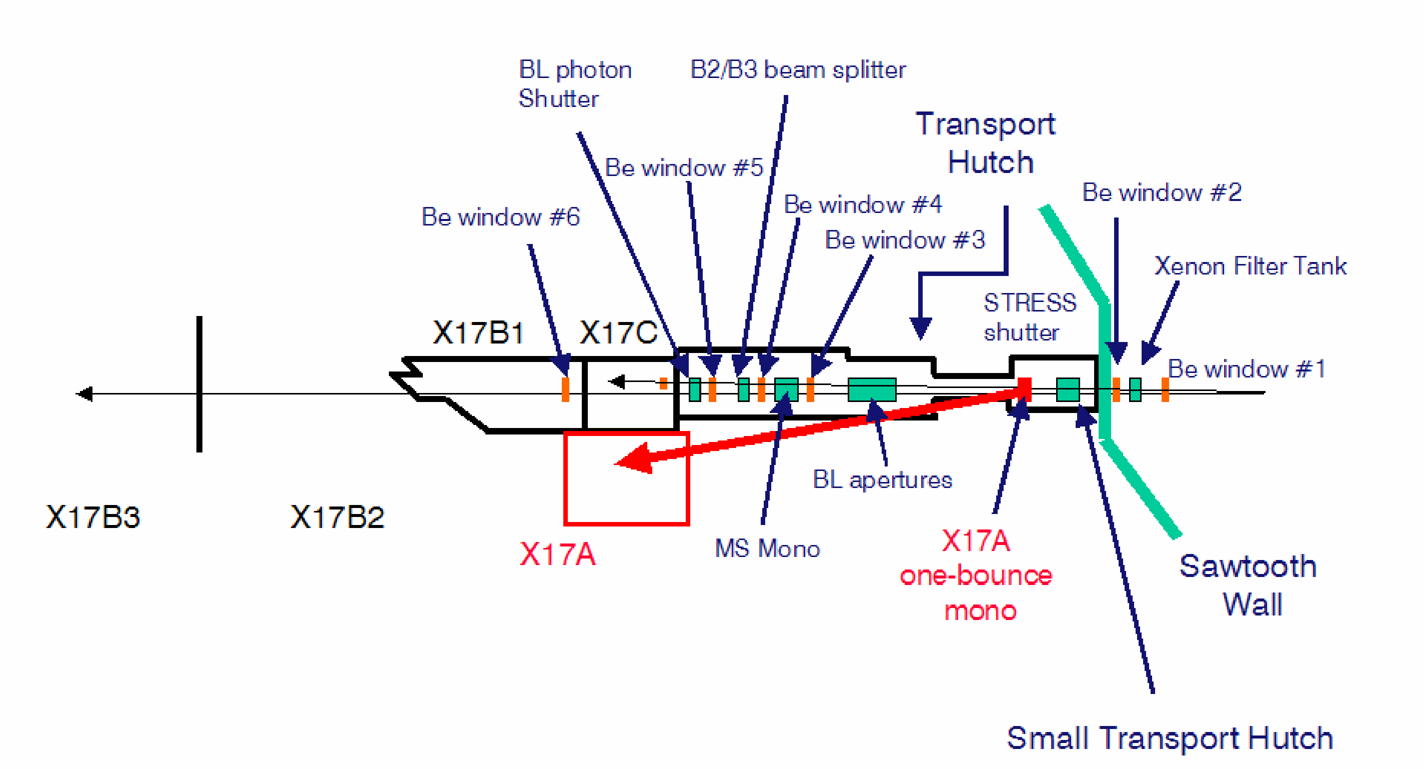


Fig. 4 Schematic view of the beam path of X17A.

Equipment: A four-circle diffractometer in standard or κ-geometry will serve as base for the different experiments. Additional translation in *x, y, z* direction will allow positioning the sample and sample environments in the beam. The main detector option at X17A will be an online image-plate detector. Additionally, a point detector usable with and without analyzer crystal will be available. For total scattering experiments at ambient conditions a robotic sample changer needs to be installed, facilitating rapid sample change and high-throughput data collection.

Sample Environment: The investigation of materials *in situ*, at variable environmental conditions is a central theme in modern material science. It is planed to outfit the beamline with cutting edge pressure cells, furnaces and low temperature equipment, for experiments at non-ambient conditions. In contrast to the usual add on approach for sample environments, a tightly integration of the environmental cells during the design phase with the experimental capabilities is planed. This approach will serve as a test case for integration of beamlines and sample environments at NSLS-II.

Modes of operation: We anticipate that the user base is comprised of mainly two types of users.

1. The material scientist and materials chemist interested in total X-ray scattering and PDF analysis for characterization of newly synthesized materials at ambient conditions.
2. Scientist from various disciplines performing high-energy scattering experiments *in situ* at non-ambient conditions.

The first category of users is usually interested in a rapid access to the beamline to characterize only a few samples structurally, before additional properties are measured at other facilities or their home laboratory. The most efficient way to serve this part of the user community is by providing a rapid access proposal system combined with a mail-in service. In this model, the beamtime is very efficiently used, since there is no learning curve for the users, as the data will be collected and fully automatically preprocessed and checked by experienced staff on the beamline who have much greater feel for what will and not work. The use of a sample change robot on the beamline in conjunction with highly automated data processing software will allow a most efficient use of the limited beamtime. Once this operation mode is established and a large enough user base is build, it is not unreasonable to expect 20 to 40 papers a year.

The second category of users is interested in investigation of structural changes in materials *in situ* at non-ambient conditions. For theses experiments the user need to be present at the beamline and needs to be trained. The user base for such experiments can be increased dramatically, by supplying the sample environment at the beamline. This would allow users to perform experiments at extreme conditions, which have no infrastructure for experiments at non-ambient conditions at their home institution, but have materials at hand with interesting scientific problems to solve.

4.2 Plans for Single crystal diffraction - (with significant input from Simon Teat, ALS)

The state of play at NSLS for "routine single crystal diffraction" is not satisfactory. Significant opportunities are being lost by not having a commercial instrument with commercial software familiar to the majority of chemical crystallographers. A well appointed beamline, at NSLS and suitable for transfer to the NSLS-II would look like this

Single crystal Beamline Specifications: Energy range: 5 – 30 keV

Optics: This energy range would allow access to the first row transition elements starting at the K-edge of V and extending to Mo and from the L-edges of Cs to the end of periodic table. However access to energies in the region of 40 - 80keV would be desirable for charge density studies and reciprocal space mapping of single crystal diffuse scattering (see Appendix 3) and for sample environments with restricted opening angles (diamond anvil cells for example). A spot size: ~100 x 100 μm (FWHM) is desirable. Again smaller spot sizes may be useful for very high pressure DAC work, consistent with the ability to track or map sample movement out of the beam because of sphere of confusion issues. The sample will be rotated about at least two axes, omega and phi, therefore a sphere of confusion with a maximum diameter of 10 μm will be required for a 100 μm spot. Assuming the spot is Gaussian in shape, then a spot of 100 x 100 μm will only have a uniform intensity region of 10 x 10 μm. For small molecule work then the useable area is 20 x 20 μm. For good charge density data collection, the crystal must be bathed in a very uniform beam therefore access to a large spot size would be necessary, however, this type of experiment does not always demand high flux. The focusing could then be relaxed or removed.

An energy resolution of 10^{-3} (structure determination) or 10^{-4} (resonant scattering) is required. For structural data collection, the maximum energy resolution is not required, where as the additional flux would be useful. A double crystal multi-layer monochromator would be suitable. For resonant scattering experiments higher resolution is required, which could be achieved by a double crystal silicon 111 monochromator.

Equipment: An off-the-shelf fully commercial CCD area detector system with goniometer can be used with minor modifications. One such modification would involve mounting it so the omega and two theta axes are parallel to the horizontal plane, to circumvent the drop off of intensity due to the polarization term. The advantage of a commercial system is that it comes with all the software needed to collect data once aligned. The users, with a similar instrument in their lab, will be able to start work with the minimum of training. The software provided with most commercial systems cannot only handle conventional data but also twinned and incommensurate. For diffuse scattering and some incommensurate studies, a detector with high dynamic range would be required. The intensity differences between the strong Bragg peaks and the weak incommensurate satellites or diffuse features are so great that on a CCD, the Bragg peaks would be saturated if the collection was optimized for the weak data. The weak peaks would be lost in the background if the data collection was optimized for the Bragg peaks. At present the best detector for these types of experiments are image plates. The science case is presented in Appendix 3

4.3 The need for a single crystal (and powder) service, now at NSLS, and at NSLS-II

Small molecule diffraction stations can be highly productive in terms of papers generated. Once a couple of years into full user operation, it is not unreasonable to expect 30 to 50 papers a year, if the user base is large enough, as there are a limit to the number of papers that can be written by a individual user. One efficient way to increase this user base, within the limited amount of beamtime available, is by offering mail-in service.

There are three main advantages for the station and the users. There is no learning curve for the users, as the data will be collected and processed by experienced staff on the beamline who have much greater feel for what will and not work. Beamtime can be used more efficiently. The uncertainty involved in single crystal experiments revolves around the suitability of the crystal, i.e., will it diffract well enough and strongly enough to give a useable data set? In general there is no way to test a sample to see whether it will diffract well enough before being brought to the beamline: some will, some will not. This produces two scenarios: the chemist with only a few samples, and the user with beamtime and a higher-than-expected failure rate. For the chemist with too few samples, there is a risk of a completely wasted trip and the costs that would be incurred; therefore these samples should be submitted to the service. Whereas the user with beamtime and the higher failure rate of samples may run out of samples before the end of their allotted beamtime, as not all will work. In this case, the service samples could be run in the remaining beamtime. There would be faster access to beamtime though the service than having to go through the normal application process which can take up to 9 months, from application to date of experiment; in that time the crystals may have degraded. The service would provide a fast turnaround as long as frequent and adequate service beamtime is available.

There are two main service access modes: data collection and initial processing; and data collection to fully refined structure. Those envisaged using the first mode would be those who are capable of solving and refining their data. These academics have programs that only produce a small number of crystals on an irregular basis, which makes traveling to the synchrotron combined with the subsequent learning curve an impractical proposition. Staff crystallographers who have no funds with which to travel would also use this mode of access.

The second mode would be for the materials chemists, who normally access crystallographer via collaboration rather than have one in house. In this case the collaboration would be with the service staff at the beamline.

5. Recommended Transition/Construction Sequence

The NSLS-MaDiS would initially consist of X-17A, X16 and a dedicated single crystal diffraction facility. The high-resolution powder and single crystal instruments should be maintained on bending magnet lines at NSLS to provide continuity for work at NSLS-II. In preparation for PING and to service the user base (see Appendix 3) X-

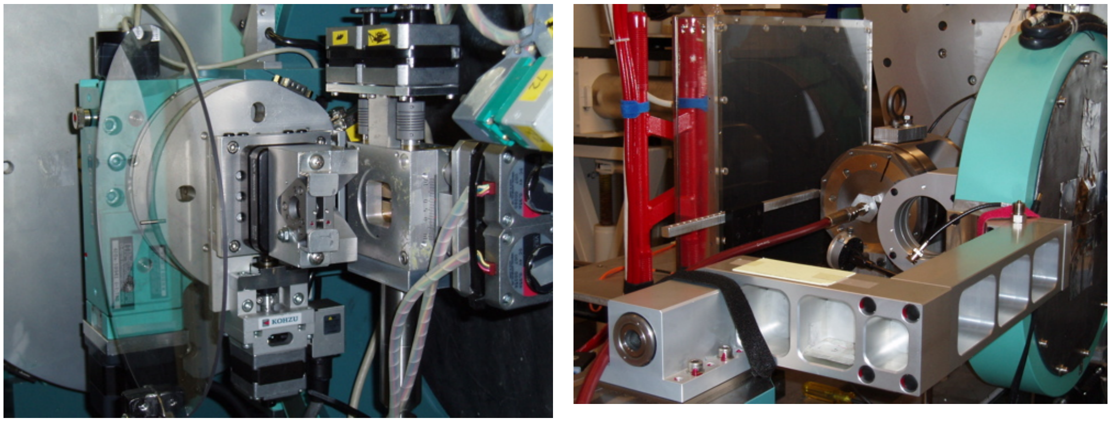


Fig. 5 (left) Diamond anvil cell (DAC) mounted in a kinetic mount on the 1-ID-C beamline with the beam entering to the right. (right) One of the PE VX cells proposed for purchase, mounted on the 11-ID-B beamline with the beam entering from the right. The GE detector is the grey plate in back.

17A needs to be built out and *a comprehensive cross-disciplinary BAT established to advise on its mission and design.* PING is designed to give the users of all powder-related research at X-17, X-7B and X16 the opportunity to keep their research "ticking along" until a full suite of specialized instrumentation is available at NSLS-II. The "empty" hutches will allow transition of work at extreme conditions to be carried out while providing world-class access to high-resolution powder diffraction at extreme conditions in the first hutch.

6. Facility Infrastructure at NSLS-II

6.1 Ancillary Equipment:

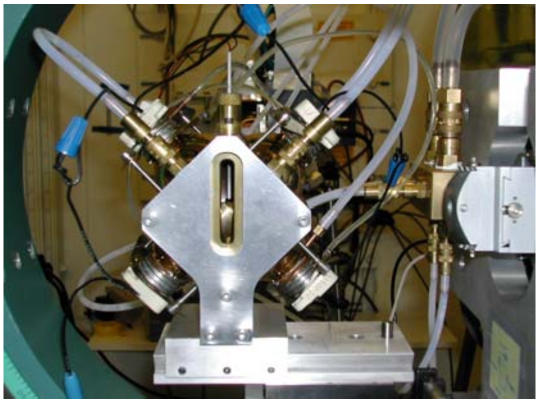


Fig. 6 Quadrapole furnace, 1800°C (Kriven, UI)

A variety of ancillary equipment is required for experiments under non-ambient conditions, for example the high P devices shown in Fig. 5. All of this equipment should be available from day one at NSLS-II and as soon as practical at the NSLS powder lines, especially X-17A, B and C, since these are the best approximation of the PING beamline, and other diffraction beamlines at NSLS-II dedication to ms3.0 (see introduction). To facilitate this the community should be actively engaged at NSLS and concepts such as a standardized kinematic mount, designed to fit on several beamlines, should be shipped to investigators. These investigators are already used to designing kit for synchrotron or home laboratory use. By harnessing the community's considerable expertise in non-ambient studies, especially for HP and HT cells, these can be integrated from day one. For example Waltrud Kriven produces furnaces capable of temperatures up to ~1800°C and uses these at both NSLS and APS (Fig. 6). Other users have different designs. This community should be engaged to help construct other devices and JPSI could be a clearinghouse, providing expertise and small starter funds to encourage the innovation of he community to be translated into devices that are designed specifically for the NSLS-II environment, after having been tested at NSLS. These devices should include flow cells that allow control of gas or liquid flow across the sample while simultaneously heating/cooling (80 K to 1200 K) of example a nitrogen open flow cryostream with a temperature range from 80 to 400 K. Solid media pressure cells, such as the VX-1 Paris-Edinburgh cell, capable of pressures up to 10 GPa shown below mounted at 11-ID-B at the APS (Fig. 5). Diamond anvil cell (DAC) of various designed (a simple Merrill-Bassett DAC is shown mounted at APS Figs. 5, 7).

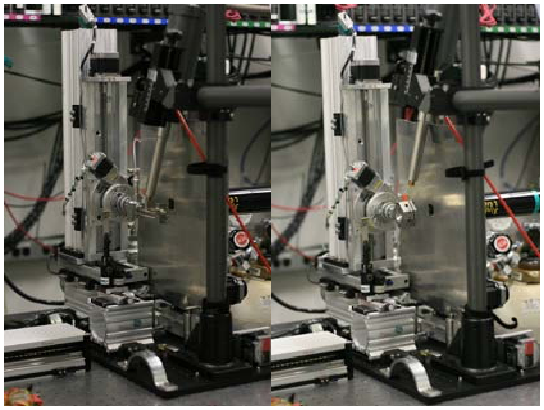


Fig. 7 Assembled (a) flow through apparatus and (b) diamond anvil cell (DAC) experiments. The equipment package, mounted on a portable breadboard, includes beam-defining pinholes, alignment stages, shielding, sample alignment and rotation stages, and the beamstop. This prototype could serve as a template for what will be possible at NSLS-II and an upgraded powder instrument suite at NSLS. Going forward it will be important to have community buy-into planning a limited number of standard beamline interfaces for work at extreme conditions.

6.2 Possible standard interfaces to a suite of powder instruments

Prototyping applications demonstrate the viability of an approach to standardize mounts. For applications where the equipment can be miniaturized, it is convenient to transport from beamline to beamline on a standard platform. Recent work by Chapman and Chupas (Fig. 7) allows standard DACs, compatible with external heating and cooling, using a standard Cryostream®, to be mounted and easily aligned on a variety of beamlines.

6.3 Overview of the CO_2 sequestration and catalysis cell (see also Appendix 2)

This is a first generation stage primarily designed for polymer studies under sub- and super-critical CO_2. Design criteria for this are -40 to 200ºC and up to 125 Bar with inert gases (Fig. 8).
A second-generation stage specifically designed for CO_2 sequestration and catalysis work is in early concept stage. Conditions are as per down-hole and so they are Challenging. Design targets for this are 300 bar, 300ºC (or 500ºC if easily achievable for catalysis studies), flooded operation (keep sample wet at high temperatures), high chloride concentrations (brine), down to pH3, flammable gases (methane), sour-gas-capable (H_2S). Operation on both lab (reflection AgKα) and synchrotron (transmission) sources is required from the same cell.

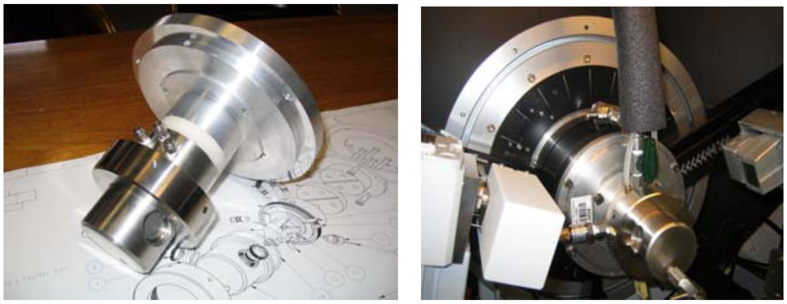


Fig. 8 The high pressure CO_2-apparatus mounted on a standard laboratory diffractometer (right, courtesy of Pamela Whitfield, NRC, Canada [1].

6.4 Equipment from the High Pressure Hutch at NSLS.

The image in Fig. 9 shows a HP studies setup at NSLS. It is anticipated that this equipment could be setup on wheeled bases to allow easy roll-in capability for the PING beamline experiment station.

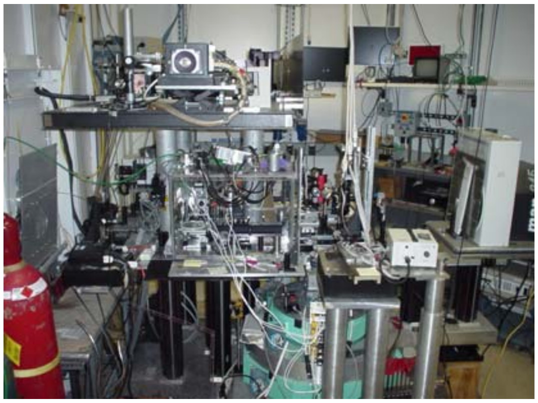


Fig. 9 The set-up for P studies at X-17B3 at NSLS; a prototype for operations at PING#2 (see Figs. 1, 2)

6.5 Sample Preparation Facilities:

A MaDiS BAT for NSLS should establish now what labs are needed for implementation of *in operando* diffraction. Many of the considerations for this work will carry over to NSLS-II. For example The Materials Chemistry, Catalysis, Environmental Sciences users require a “wet” chemistry lab with dry, inert atmosphere glove boxes to ensure samples are viable between transport from home laboratory and the beamline. The engineering community requires ready access for large pieces of equipment and samples. Work at extremes of pressure will require specialized gas loading equipment and requisite safety reviews, while work on highly activated samples from contaminated sites or highly irradiated reactor parts will require appropriate labs. *A holistic approach is required and where synergies or incompatibilities exist these should be recognized early on.* Other equipment includes oven for ex-situ sample dehydration access to User machine shops, which are available in the event that samples fixtures need to be fabricated or customized. The ability to collect diffraction data on radioactive materials needs to be coordinated closely with the appropriate group at BNL.

6.6 Computer Support for Data Collection, Analysis and Reduction

At both NSLS and at NSLS-II data rates will increase with the design/construction/acquisition of strip and area detectors capable of much faster data readout rates. Significant improvement in the computational infrastructure will also be needed. These fast readout rates, coupled with the large sizes of a single 2-diminsional data file (> 8 MB at 33 Hz or faster), make stringent demands on the ability to both store and process data efficiently and effectively. Significant data reduction needs to occur concurrently with the data collection at the beamline. The 2 dimensional data files need to be corrected for dark current background and radially integrated to yield a simple data file of Q (or 2θ) vs. scattered intensity. The availability of an onsite data storage system and processing environment will enable beamline users to process their data while at Brookhaven, and to leave their experiments with reduced data, increasing both efficiency and user satisfaction.

Current data rates are approximately 200 to 400 GB of data per week of raw unprocessed data, which corresponds to ~4 TB per 3 months scheduling cycle (i.e. 12 TB per year). Once the raw data files are corrected, ~200 GB generally reduce to ~10 GB. It is expected that data rates will grow to as much as 1 TB per week (~45 TB a year) following the beamline upgrades scheduled for FY2007. In the current situation users are responsible for backing up their own data using principally portable hard drives to take data home with them. With the acquisition of a dedicated detector we propose on making available a data storage system that will benefit users by allowing them to leave only with the reduced data, which is corrected for detector dark current etc. This reduced data is then in a form that can be later used in data analysis, while the raw data will be backed up by the beamline. The computer system envisioned for the beamline consists of two *Workstations*, one used for detector control and the other for online data processing. Both these *Workstations* will access a *Primary Storage Server*, which will allow both fast access to the data and will retain data for up to 3 weeks, while the *Backup Storage Server* will be used to retain data for the longer term (1 year).

In terms of user satisfaction and productivity, it will be critical to reduce *and* interpret these vast quantities of data and a concerted effort along the lines of the DANSCE initiative will be required. An excellent example of burgeoning areas of research is desperate need of software development is the construction of models to fit the elastic diffuse scattering from single crystals (See Appendix 3 for an example [5]).

Appendices: State of the Art and Future Materials Diffraction

Appendix A1: High Resolution Powder Diffraction: state of the art and future prospects

Many of the contemporary topics in solid-state chemistry and condensed matter science involve complex materials with large unit cells [6]. Single crystal techniques, where the Bragg scattering is well separated, are the mainstay for structure determination. Many important materials do not occur as sufficiently large crystals, or they form powders upon structural transitions that occur *in operando*. For these materials powder diffraction provides the most information for unambiguous structure determination. Further, many technologically important materials crystallize as highly crystalline powders but with structures that involve very subtle changes in aristotype (basic) structure [7]. The perovskites are the most important members of this class of materials. Chemical ordering, structural or magnetic frustration can lead to subtle splitting of Bragg peaks, build-up of diffuse scattering and the presence of weak super lattice reflections. Single crystal technique (see Appendix 2) provides an excellent means of reciprocal space mapping, even for exceedingly small samples if electron techniques are used [8, 9]. For *in operando* studies there is no more viable, and user-friendly technique than powder scattering.

High-resolution techniques began at the NSLS with the construction of X-7A and the work of David Cox [6]. Since that time increasingly complex materials, usually studied at ambient conditions have been tackled. These include important zeolite catalysts and separators [10-13], structurally frustrated materials with subtle lattice distortions [14] and a plethora of superconductors and GMR materials. More recently the technique is applied to pharmaceutical and other organics.

The breadth of the user base for versatile HRPD powder diffraction requires than provision be made for the expanding uses of the technique, which is trending towards studies at extreme condition. This will require studies to high Q, higher energy beams to penetrate cells, excellent collimation to discriminate against parasitic scattering from sample environments, and higher angular resolution to study increasingly complex materials. At the same time the highest possible flux/brightness are required to study smaller heterogeneous materials and to carry out parametric studies [15]. It is possible that a combination of multiple single crystal samples will be required to study anisotropic diffuse scattering. For the majority of users however a versatile high energy, focused beam with a choice of low noise detectors to provide either/both high time/angular resolution, along with a choice of sample environments, will open up new important areas of research.

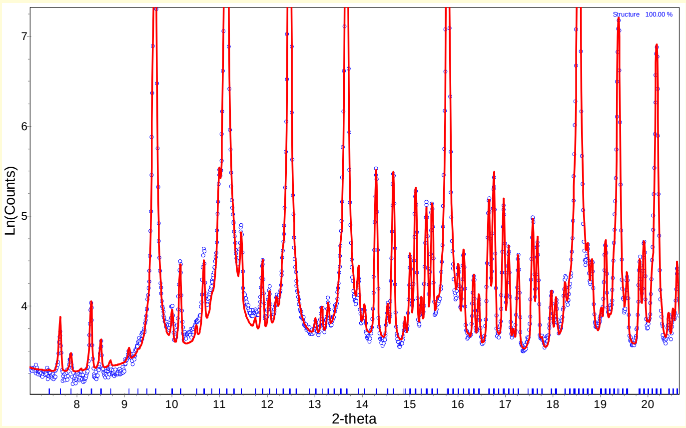


Fig. A1.1 Synchrotron X-ray diffraction data collected on ZrP_2O_7 at beam line X7A of the NSLS; 2° to 67.062° 2θ, λ = 0.8013 Å selected with a Ge(111) channel cut crystal monochromator and a step size of 0.01 on a flat plate sample.

Increasingly, complex materials [16-21] will require a variety of approaches and input from several techniques. Computational techniques will become increasingly important and modeling in particular. Examples of the use and potential of HRPD, as stand alone technique or combined with other studies to solve problems are given below.

A1.1 ZrP_2O_7: An example of structural frustration [22, 23]

Upon cooling to ambient conditions the structure of ZrP_2O_7 undergoes a transition to a structure with 3 x 3 x 3 supercell containing 50 atoms in the asymmetric unit and 11 unique sites for phosphorous; this remarkable number of P-sites is confirmed by solid state NMR [22, 23]. Here has been considerable debate in the literature about the true room-temperature structure of ZrP_2O_7 and related materials. The combination of information from solid-state ^{31}P NMR and high resolution powder diffraction data was used to determine the structure of this 136 unique-atom material. The structure was solved using a combination of simulated annealing and Rietveld refinement performed simultaneously on X-ray and neutron diffraction data. Despite the close to cubic metric symmetry of the material, its true orthorhombic structure (space group Pbca) can be refined to a high degree of precision since the high angular resolution data (Fig. A1.1) provide well-separated peaks and excellent precision for weak peaks necessary to define the subtle deviation from the cubic substructure.

A1.2 Organic materials at elevated pressure

HRPD has found important applications to organic materials. Many organics are polymorphic, meaning that they can appear in different crystal structures. This can have a profound effect on their biological availability (with great economic and health impact), as dramatized by the case of retonavir [24]. HRPD using a synchrotron source played a key role in explicating a polymorphic transformation of Zopiclone with implications for quality control of commercial dosage forms [25]. New polymorphic forms, which can be useful even if metastable at ambient conditions, can be produced by crystallization at high pressure [26]. The importance of understanding structural transformations in organic materials, at ambient and elevated pressure, is not restricted to pharmaceuticals. Explosives can degrade in time by polymorphic transformations, and transformations under pressure may be important to their detonation characteristics. While some experiments have been published, for example on polymorphic transformation of the well-known explosives HMX [27] and RDX [28] there is a serious dearth of understanding of the structural behavior of energetic materials. Several of the studies cited here were carried out on single crystals, which, as noted above, is the method of choice when they are available. Structures have been solved and refined from powders of organic materials in diamond anvil cells [29], but there are very few examples. Because of the complexity of the structure of these materials, with many atoms in the irreducible unit cell, high-resolution powder diffraction is an important resource for further understanding. Advanced optics at NSLS-II combining a very small beam with high resolution will be a significant advance in the capability to carry out such experiments.

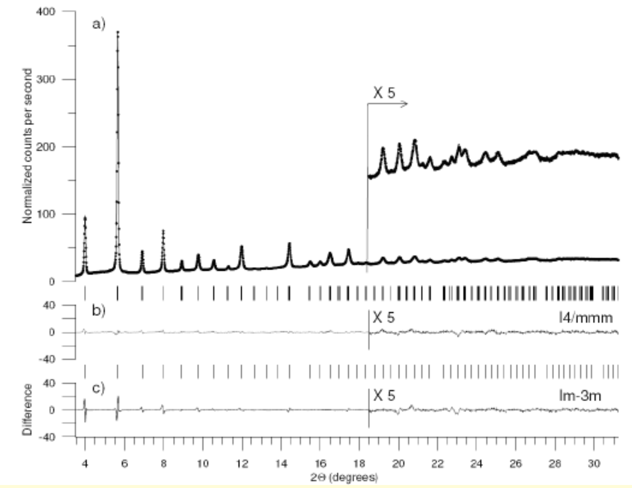


Fig. A1.2 Powder diffraction pattern of $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ at 12.2 kbar, showing a subtle improvement in quality of fit, visible in the difference pattern, in tetragonal (b) *vs.* cubic (c) space group.

Molecule based magnets constitute another group of materials with a strong response to applied pressure. For example, one material, $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ which is based on two interpenetrating Prussian blue lattices, has a peculiar magnetic hysteresis at ambient pressure, which reverts to a more normal response under the application of modest pressure (10 kbar). Powder x-ray diffraction measurements in a diamond anvil cell suggest a transformation from a cubic to a tetragonal lattice, but the data are marginal [30]. (Fig. A1.2) A gas pressure cell would be the ideal environment to study such behavior in a wide variety of materials, and the proposed diffractometer combining high resolution with high energy would allow the beam to penetrate the cell, exert accurate control of the gauge volume, and give the resolution required to observe small distortions.

A1.3 "Routine" structure solution from high resolution powder diffraction

The need for powder diffraction to contribute structural information in support of materials research can only grow. Many applications do not require particular environments or parametric studies, just good data that can be used as the basis to solve and refine crystal structures. For example, in 2007 and the first three months of 2008, ten new crystal structures were published from data collected at ambient pressure and temperature with the unfocused beam at X16C. The productivity of this "bread and butter" capability is limited more by the human factors of a skilled base of users than by any aspect of beamline hardware. However, it depends on having a stable instrument available for data collection without having to schedule and reconfigure a beamline from other tasks. We anticipate the demand for a beamline essentially dedicated to that task through the remaining life of NSLS, as well as at NSLS-II. Experience is that an unfocused beam at about 0.7Å wavelength is suitable, and so we call for a diffraction station similar to X16C based on a three-pole wiggler at NSLS-II. This could be implemented with many of the components of the current X16C beamline.

Appendix A2: In situ techniques: state of the art and future prospects

Pair distribution function methods represent a powerful and rapidly growing set of technique capable of probing the local-, intermediate- and extended-range order in technologically important materials for which the structure underlying relevant physical properties often deviates from perfect crystalline order including dynamically disordered, inhomogeneous, nano-scale and amorphous systems. The MaDi suite of instruments, anchored on the PING beamline on the DW source at NSLS-II, and anchored on X17 at NSLS, provide excellent opportunities for research in an area that is expanding in importance. New detectors and optics will allow extremely weak/dilute features to be probed with unprecedented accuracy, facilitate time-resolved studies to monitor chemical reactions, enable bonds of similar length to be resolved, and accordingly impact the research programs of the PI's, their collaborators, the NSLS general users and the rapidly growing PDF community.

Background to PDF techniques

In order to study aspects of short-range order it is important that the total elastic scattering, the Bragg scattering as well as the diffuse elastic scattering, be included in the analysis. For determination of structural information in disordered or amorphous materials, full-profile fitting of the pair distribution function (PDF) derived by Fourier transformation of the total scattering has proven a powerful complementary or alternative technique to Rietveld analysis, and is routinely performed using data collected at ambient conditions. Extensions to extreme conditions will require continuous efforts by the community over the coming years in the areas of hardware and software development.

The PDF, G(r), gives the probability of finding an atom at a given distance r from another atom and can be considered as a bond length distribution [31]. It is obtained from the powder diffraction (X-ray or neutron) via a Fourier transform of the normalized scattering intensity, S*(Q)*:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ$$

where $\rangle(r)$ is the microscopic pair density, $\rangle_0$ is the average number density, and Q is the magnitude of the scattering vector (Q = (4□sin ⎝)/⎣). Experimentally it is not possible to measure data up to infinite Q, and the cutoff at finite values of Q_{max} decreases the real space resolution of the PDF. This causes some aberrations in the form of “termination ripples” which propagate through $G(r)$ as high frequency noise. For both X-ray and neutron scattering experiments, high energies are required in order to access high values of Q_{max} to obtain the most accurate Fourier transform of the reduced structure function $F(Q)$.

Conventional high real-space resolution measurements typically make use of energy resolving point detectors, such as high-purity germanium, that are scanned over wide angular ranges. The DW PING source will greatly advance studies requiring the highest possible peak-background discrimination and rejection of scattering from environmental cells. For example, for large volume high pressure devices such as the Paris-Edinburgh cell the use of a point counter with tight collimation provides excellent signal-to-noise discrimination, and data collection times will improve by at least an order of magnitude compared to comparable high energy sources, decreasing an 8 hr experiment to ~1 hr.

For the highest time resolution, studies of small samples ($V < 10^{-2}$ mm^3) in diamond anvil cells (DACs) area detectors are preferred [32-34]. Combining high energy X-rays (> 60 keV) with area detectors to measure the scattered intensity to moderately high values of momentum transfer ($Q_{max} < 30$ Å^{-1}), in combination with modified environmental cell designs [34, 35] enables previously impractical parametric and in-situ studies of complex functional materials. Consequently, such studies based on this approach have become more routine/widespread and this approach has rapidly become the method of choice for PDF measurements for a growing number of users.

A2.1 Studies in situ and in operando

Detectors with fast readout, coupled to the NSLS-II DW source will allow allows sub-millisecond time resolved studies to study chemical reactions such as oxidation/reduction reactions, the formation of nano-particles through nucleation/precipitation mechanisms, operating catalysts, determination of phase diagrams and studies of materials at extreme conditions. The viability of extracting high quality PDF data at the fastest readout has recently been demonstrated to study the reduction of PtO_2 under hydrogen to form metallic Pt particles at sub-second time resolution (Fig. A2.1). Chupas *et al.* [33] applied *in-situ* PDF methods to study how metallic Pt particles form during reduction of Pt(IV) salts on high surface area TiO_2. Using differential PDF methods, the atom-atom correlations involving only Pt were selectively recovered by subtracting out those arising from the support oxide, thus we were able to directly probe the formation of Pt particles. Development of low noise short readout time detectors coupled with DW source will dramatically improve abilities to carry out a range of measurements important to several sub-disciplines of condensed matter science. *The following is a highly selective summary of contributions from potential users MaDiS at NSLS and NSLS-II.*

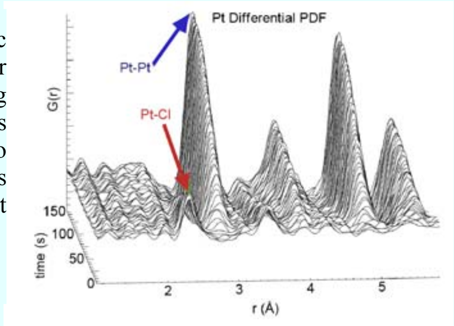


Fig. A2.1: In-situ/time-resolved PDF (0.5 sec resolution) of the reduction of Pt(IV) under H_2. Disappearance of Pt-Cl correlations during reduction and appearance of Pt-Pt contacts is evident. The Pt-Pt correlations continue to grow in intensity after the Pt-Cl contacts disappear due to formation of larger Pt particles.

Measurements requiring high sensitivity.

New detectors, with energy discrimination and fast readout, coupled with the increased brightness at high energies will greatly enhance sensitivity. A dramatic example of what is possible now using current generation detectors and sources allows weakly scattering or highly dilute features such as those encountered in solutions, hydrogen storage systems and protein cores to be probed. The differential PDF, obtained experimentally through direct subtraction of a reference PDF measured for the vacant apo-host or substrate from that of the guest-loaded host, directly probes molecular scale interactions associated with guest binding/supported metal particles by selective recovery of only the atom-atom correlations (interatomic distances) arising from guest-framework or guest-guest interactions [36-38].

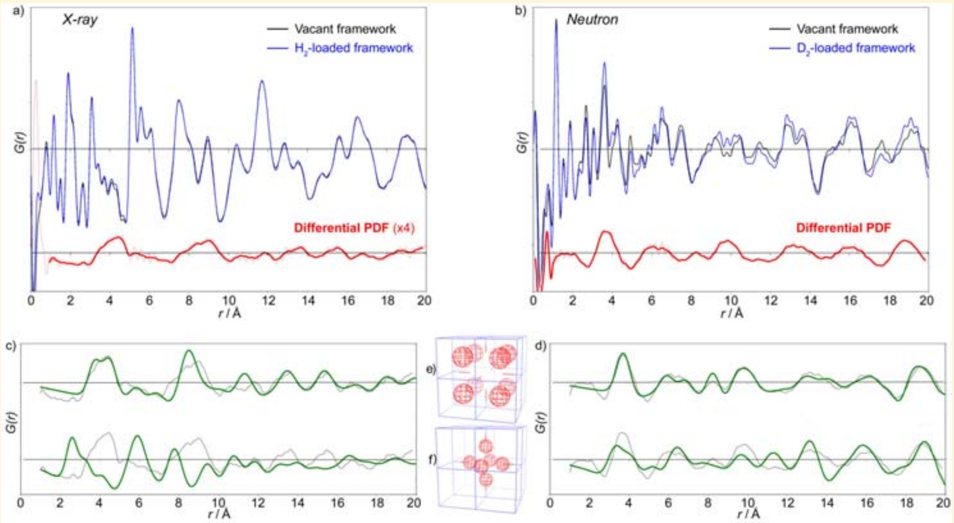


Fig. A2.2 PDFs, *G(r)*, for vacant and loaded framework and the corresponding differential PDFs from the X-ray (a) and neutron scattering data (b). The differentials, raw (dotted) and *r*-averaged over normalisation ripples (continuous), are shown. Calculated X-ray (c) and neutron (d) differential PDFs for models consistent with Van der Waals interactions (e, upper curves) and with binding at the accessible Mn^{II} sites (f, lower curves). experimental differentials in (gray).

Encapsulated materials (Chupas, Chapman, Parise).

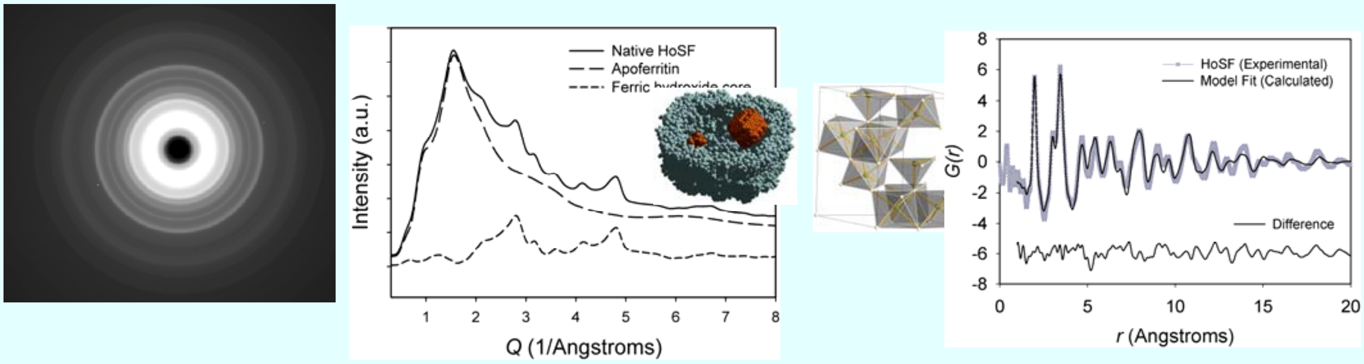
Hydrogen storage [38]

Pivotal to the rational development of host materials with increased H_2 storage capacities, approaching projected DOE targets for practical applications, is the understanding of the nature of the H_2framework interaction and the factors that influence H_2 binding strength and storage capacity. However, few structural studies have directly probed the adsorption sites in these systems when loaded with H_2. As such, the principal mechanism for H_2 sorption remains controversial/speculative, with the current views developed from attempts to correlate observed sorption behavior with the structural features and chemical functionality of the apo-host (e.g., surface area and volume; surface polarizability and potential coordination sites).

The structure of local H_2-framework interactions within the H_2/D_2loaded Prussian Blue analogue, $Mn^{II}_3[Co^{III}(CN)_6]_2$, by using both high-energy X-ray and neutron scattering data (see Fig. A2.2) contradicts accepted models and provides no evidence for binding interactions with the accessible Mn^{II} sites [38].

Protein cores and structures in capsids*:*

Biological macromolecules, such as protein cages and viruses are templates for the synthesis of nanoscale particles of inorganic materials [39-41]. Further, iron storage proteins known as ferritins are essential for the regulation of iron in most living organisms. This roughly spherical protein has evolved with the remarkable ability to absorb soluble Fe^{2+} species into its hollow interior and reversibly store the iron as an insoluble, nano-sized ferric oxyhydroxide particle (Fig A2.3). While it is long recognized that the Fe^{3+} core resembles the mineral ferrihydrite, a quantitative structure model was lacking. Analysis of high-energy total x-ray scattering data collected from native horse-spleen ferritin, and utilizing the differential PDF approach, shows a recently-determined structure model for ferrihydrite [42], rather than the accepted arrangement, describes the nanocrystalline iron core [43] (Fig. A2.3).



(**a**) (**b**) (**c**) (**d**) (**e**)

Fig. A2.3 The raw scattering data collected from native horse spleen ferritin (HSfn). The signal of interest (dashed line in **b**) from the iron-oxide hydroxide core (**c**) is obtained by difference between signals from HSfn (solid line) and apo-fn (long dash). This differential signal, transformed to give G(r) is fitted (**e**) with the model in (**d**).

A2.2 Future studies using PDF across the disciplines

Gains in time resolution would extend the differential PDF approach to a broader range of materials with potential energy-storage applications, including other coordination framework materials, porous carbons and clathrates. Furthermore, we anticipate that the present results will redirect efforts in the targeted development of framework materials for H_2 storage towards pore geometries that best complement the H_2 molecule to maximize interactions with the pore surface. Upgrades of X-17 at NSLS and particularly the PING suite with the brighter DW source and newly developed detector will dramatically impact this area of research over the next decade. The significant contribution to the background from scattering from environmental cells will need to be addressed for studies of glasses, melts and light elements, since in these cases Compton scattering can overwhelm the signal of interest. The increase in flux on sample must be complemented with energy discriminating area detectors. The proposed BNL strip detector designed by Siddons and to be installed at NSLS and on PING at NSLS-II will greatly enhance signal-to noise discrimination. Other solutions will arise from the community as well and this should be encouraged. For example the high pressure community has a great many techniques now being developed to enhance weak signals from cells including the design of large volume "gem" cells using large synthetic anvils, including diamond [41, 42]. These new devices allow a large sample volume to be taken to pressures above 35 GPa and have been used at the 11-ID beamline without focusing. In those cases where the sample is sufficiently large to allow tight collimation, the problem of Compton and parasitic scattering from high P cell components is greatly reduced.

A2.3 Selected examples of studies at extreme conditions

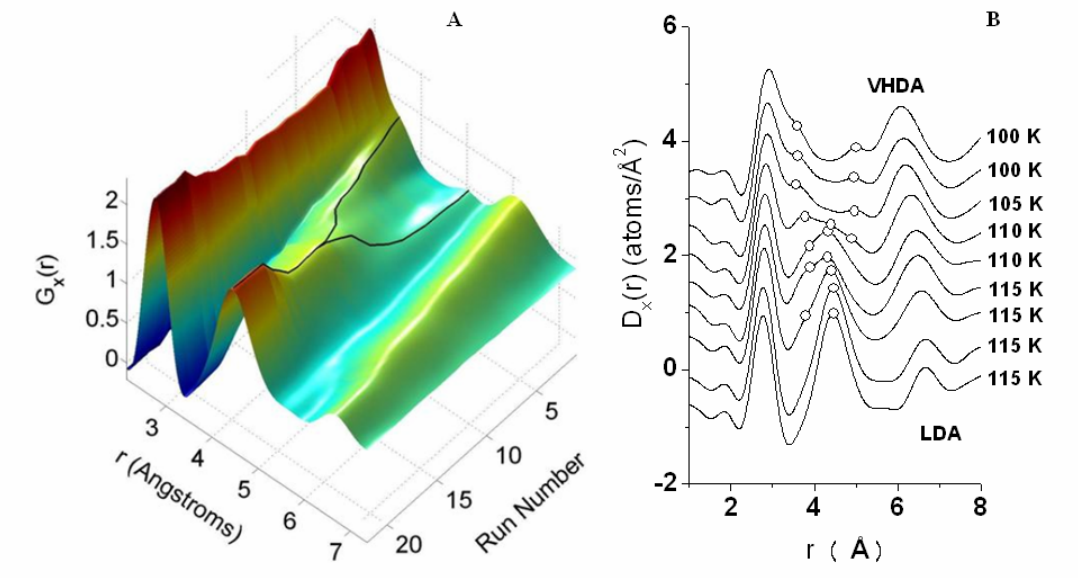
Speciation in solution [44]

A predictive understanding of the mobility, fate, and transport of heavy-metal contaminants under geologically relevant conditions requires metrical knowledge about the dissolved species. The chemistry of the uranyl ion (UO_2^{2+}) in near neutral or basic groundwater is complicated by hydrolysis, complexation and oligomerization reactions that result in dissolved aggregates, colloids, and amorphous precipitates. This chemistry is exemplified in groundwater with higher concentrations of dissolved silicate. Known to form precipitates at higher pHs and concentrations, a molecular level understanding of speciation has remained elusive because the short-range order (as probed by XAFS) appears very similar despite chemical changes in the solutions and their precipitates. Most of the work to date on these very important solutions and amorphous materials are carried out at APS. The upgrade of X-17A and especially the construction of PING at NSLS-II will greatly enhance our ability to look at other important solution speciation systems, including the toxic heavy metals (Cd, Pb) and potentially trace elements important in soil geochemistry in the critical zone (Mo for example).

Ices and clathrates (Tulk and Benmore)

Recently, a new form of amorphous ice, known as the Very High-Density Amorphous (VHDA) form, has been identified and characterized [45-48]. High energy X-ray have some advantages over the neutron experiment because of the far greater weighting of the X-ray oxygen-oxygen partial structure factors, which are roughly 6 times that for neutrons (at Q=0 Å-1).

It is now clear from the measured structure factor data and the resulting radial distribution functions that major changes in the packing of the oxygen atoms are responsible for the increased density (A2.4). Specifically, the interstitial oxygen that characterizes the structure of the more common High Density Amorphous (HDA) form is moved significantly closer to the first coordination shell, while, on average, the hydrogen bond lengthens to accommodate this increase in coordination number. The caveat to these reports is that the experiments have all been conducted on pressure-quenched samples at low temperature upon annealing. The missing key element in all these efforts are X-ray structural investigations to investigate more fully the role of the oxygen-oxygen structure *in situ* at high pressure and at simultaneous low temperature (under conditions where the second critical point is expected to exist). The small sample size plus addition of the complicated sample environment (cryostat and



(a) **(b)**

Fig. A2.4. **(a)** The short range ordering region of the *Gx r* functions. Increasing run number represents decreasing sample density. (right) *Dx r* showing the locations of some of the data points (open circles) along the line overlaid on the plots in **(a)**.

pressure cell) coupled with the need for large q-space coverage itself require a high energy (> 65 keV) focused X-ray beam and a detector capable of capture as wide an angle as possible, with energy discrimination, makes these experiments cutting edge and, possibly, feasible at NSL with the strip detector. This is an ideal experiment for the proposed focused high-energy PING beam, with new pressure cells and large angle detector being proposed.

Novel high pressure clathrates (Tulk, Klug, Guthrie, Parise)

The discovery of novel clathrate hydrates at HP has led to significant new interest in these materials [49] The prospect for significant H_2-, CH_4- and other gas-storage adds further interest [49-52]. Clathrate hydrates are composed of light elements, organics, and water molecules that form regular cages in which atoms or small molecules are enclosed. There are both practical and fundamental reasons to study the properties and structures of these materials. These include the search for new hydrogen storage materials [53], along with fundamental understanding of the molecule-molecule interaction under extreme conditions. As a demonstration experiment we obtained excellent HEX scattering data on several phases formed by applying pressure to Xe-clathrate (Fig. A2.5). These data were obtained in DACs with drilled diamonds and allowed derivation high quality PDFs from the total scattering data and high quality Fourier maps. Low temperature-high pressure total scattering studies of structural transformations in clathrates are well matched to the capabilities of the PING beamline. The DAC fitted with perforated diamonds [35, 54, 55] are ideally suited for moderate pressure (< 5 GPa) and low temperature studies.

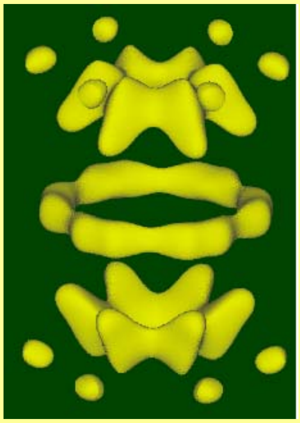


Fig. A2.5: High energy x-ray diffraction studies of guest disorder in Str II and Str H noble gas clathrate hydrates. Upon applying pressure in the 10-20 kbar range, Kr-clathrates transform to a structure with poorly understood disorder of Kr. HE X-ray scattering emphasizes scattering length contrast Radial distribution functions (RDF) show correlations between atoms over the local and intermediate radial distance from 0 to 20 Å. Guest atoms in the large cage of Structure II are not located at the cage center, as has been previously refined in all models, changes the way we think about the guest-water (host) potential. Work by Tulk, Chakoumakous – ORNL; Ehm, Parise – Stony Brook; Klug – NRCC.

Environmentally important earth materials (Parise, Whitfield, Grey, Reeder)

Beyond the range of structural coherence it is important to follow processes such as incipient precipitation, nano-particle nucleation, ripening and shape change as a function of possessing under different environmental conditions. While wide-angle X-ray scattering (WAXS) say above Q=2 $Å^{-1}$, provides information about interatomic distances, modeling the small angle X-ray scattering (SAXS) provides information on particle size and morphology. Both SAXS/WAXS measurements should ideally be performed simultaneously on the same sample contained in a sample environment, in real time. While beamlines capable of such measurements are available none are optimized for the samples and sample environments likely to be of interest to the environmental scientist. Just as importantly, the researchers versed in these techniques are not environmental scientists and training opportunities for junior researchers in these areas are limited.

Measurements under extreme conditions: The long-term viability of a number of engineered solutions to environmental problems depends critically on *in situ* measurements to test the consequences of contaminant sequestration on earth materials. For example the viability of CO2 sequestration depends on the stability of the various rock formations in contact with supercritical CO_2 (sc-CO_2) and various fluid mixtures – many of the possible fluids in sequestration sites are above their critical points. Significant experimental challenges accompany *in situ* experiments in supercritical media. For example a mixture of water and sc-CO_2/H_2S forms a Lewis acid, which is capable of rapidly corroding steel. Sc-CO_2 in many aspects behaves like a ketone due to its slight dipole so it is a good solvent for many organics, including polymers.

CO_2 sequestration: in-situ HP powder diffraction (Whitfield, Kaduk)

Injection of Carbon (CO_2) as a means of oil recovery [56] is a mature technology and is also seriously considered as a means of effective carbon sequestration. Despite a number of modeling studies [57] there are relatively few experimental studies [58] to examine the chemical processes that may occur down-hole when supercritical CO_2 is injected. One study [58]showed dramatic changes in the solution chemistry raising questions about the long-term stability of injected CO_2 due to changes in the chemical environment. This environment may vary considerably with different minerals, brine concentration, pH, T, P. Whitfield [1] pursues an *in operando* approach to examining the effects of these variable on the super-critical CO_2-rock interaction (Figs. A2.6a and b).

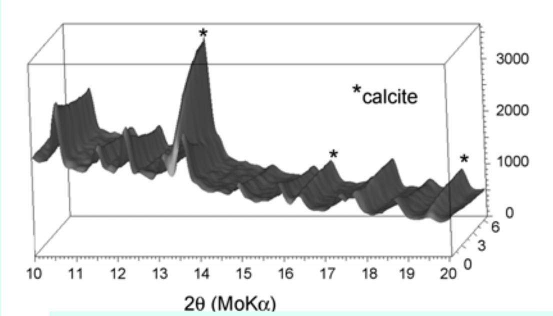


Fig. A2.6a. Phase evolution of damp wollastonite during carbonation at 60ºC under 500psi CO_2

Initial studies in the laboratory [1] using a modified cell (Fig. A2.6b), which might serve as a prototype for NSLS and NSLS-II, show high-pressure carbonation of wet wollastonite carbonation under relatively mild conditions (45-73ºC),

$$CaSiO_3 + CO_2 \xrightarrow{H_2O} CaCO_3 + SiO_{2\,(amorphous)}$$

followed by quantitative analysis of the data using the Rietveld method are consistent with results of thermal analysis results and more time consuming techniques [59]. At 60ºC the carbonation reaction is pressure independent. Collecting data from a reaction at different temperatures provides activation energy. The slower reactions at low temperature can be performed at the home laboratory, albeit unconventional since they require penetrating radiation (MoK〈) new generation PSD detectors. The existing stage has serious limitations in terms of accurately replicating the conditions present for the rock-liquid interactions down-hole and other mineral sequestration approaches.

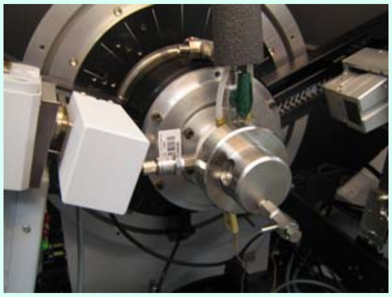


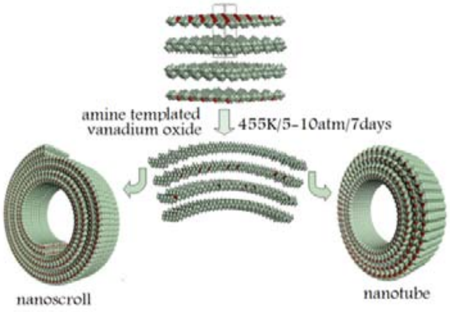
Fig. A2.6b. High pressure CO_2 stage mounted on lab diffractometer. Gas and recirculating fluid lines enter at the top, the transducer on the left and the thermocouple from below.

What could feasibly be done? A custom 2nd generation stage, designed specifically to replicate conditions that may be found down-hole with supercritical CO_2 injection and optimized to operate on a high brightness high energy source is needed. The 2nd generation stage would operate at higher PT (300°C and 300 bar), with flammable gases, H_2S, concentrated brine under acidic conditions. *The upgrades to X-17A and PING NSLS-II will allow in operando simulation of down-hole conditions for realistic sequestration scenarios.*

In Situ Studies of Lithium Rechargeable Batteries (Grey, Chupas, Upreti, Whittingham)

The current generation of lithium-ion batteries (LIBs), while meeting many of the criteria required for lap-tops and other portable electronics, are too slow to charge and discharge, and are associated with safety issues. Changes in the structure of electrode materials for LIBs, during battery cycling and as a function of temperature, can be followed using the *in operando* techniques that will be built into PING from day 1. The PDF methods are particularly suited to studies of disordered layered materials encountered in LIBs (Fig. 2.7) intermetallic anode materials such as InSb and Cu_6Sn_5, which are often nanoparticulate in size, and cathode materials such as $LiFePO_4$, where distortions of the metal coordination geometry will be probed during cycling.

Fig. A2.7 (Whittingham) hydrothermal synthesis produces nano-scrolls of layered V- oxides, that may be potentially useful as LIB anode. Following the formation, structural changes upon Li-insertion in operando will benefit from developments of a high energy powder scattering program focused on *in operado* studies.



A2.4 Framework Materials and their responses

Negative Thermal Expansion. (Chapman, Wilkinson, Chupas).

Materials that shrink when heated, behavior known as negative thermal expansion (NTE) and incorporated in composites, can be tuned to exhibit a preferred intermediate (*e.g.* zero) thermal expansion behavior. NTE behavior occurs across a broad of materials, including members of the oxide-based and more recently in cyanide-bridged molecular framework materials including the $M(CN)_2$ $LnM(CN)_6$ and Prussian Blue [60] structural families . The complete understanding of the fundamental mechanisms underlying this unusual behavior and how it can be influenced/controlled and tailored by factors such as compositional and topological structure, is pivotal to the development applications involving NTE materials and in the tailoring of the thermal expansion behavior towards specific applications. The dynamic nature of these NTE materials means that the local structural distortions associated with the thermally induced vibrations etc can only be resolved using local probes such as PDF methods.

Cyanide Bridged Molecular Frameworks (Chapman)

High throughput studies at a DW beamline with fast, low noise detector will facilitate systematic studies of cyanide-based molecular framework materials to investigate the factors that can influence NTE behavior including composition, topology, guest inclusion and polyhedral rigidity/flexibility. For example, within the Prussian Blue family of NTE materials formed by cyanide-linked octahedral metal cations, phases exist with vacancies at up to 1/6th of the $M(CN)_{6-n}$ sites with the remaining 'under coordinated' metal ions expected to form more flexible coordination polyhedra [60]. Using PDF methods to accurately extract the bond lengths defining the coordination polyhedra and hence to identify polyhedral distortions in both vacancy-free and vacancy-containing phases, we hope to explore the validity of the rigid unit mode model and its importance in NTE behavior.

High Pressure PDF Studies (Parise, Wilkinson, Hriljac, Chupas, Chapman, Martin).

When either pressure or stress are applied to matter, atoms are brought closer together, ultimately altering a material's structural, electronic and mechanical properties in radical and often unexpected ways: pressure causes proteins to unfold, s-metals to become d-metals, materials to reach their yield strength, and phase transitions, including amorphization, to occur. Non-ambient studies provide fertile ground for the formation of new materials, the measurement of mechanical properties in crystalline and nano-crystalline materials. This is evidenced by myriad new transitions in the most basic materials, such as H_2, H_2O, nano-materials and glasses. *Entirely new classes of substances and phenomena are appearing under compression, and understanding their functionality requires precise in situ studies of their atomic structure in their crystalline and glassy state.*

Pressure induced amorphization (PIA) and polyamorphism ZrX_2O_8 (X - Mo, W) (Wilkinson)

Interest in the behavior of NTE materials at high pressure arises from the rich phase behavior that is observed, including crystalline to crystalline phase transitions and pressure induced amorphization and the fundamental importance of high pressure vibrational spectroscopy when trying to understand the origin of NTE. Initial work examining PIA in $ZrMo_2O_8$ and ZrW_2O_8 [61] demonstrated that the structural changes that occur on going from the cubic crystalline materials to the initially formed glasses are different for these two compounds. Total scattering (PDF) will provide information on metal-metal correlations that does not show up in XAS data. *In-situ* high pressure total scattering studies [35, 62, 63] of the amorphization are challenging experiments that will be facilitated by upgrades of scattering capabilities at NSLS and especially NSLS-II. *These challenging experiments are necessary however to completely avoid the issue of structural relaxation that is always present when samples are recovered from high pressure and studied ex operando.*

A2.5 Glass-glass and liquid-liquid transitions (Benmore, Tulk, Weber, Parise)

Glasses and liquids at high pressure and very high temperatures.

Knowledge of the structural changes induced by variation of temperature and pressure is essential for understanding changes in physical properties of glasses, liquids and melts. While structural studies are necessary to establish structure-property relationships for glasses and liquids of technological and geological importance [64], until recently [55, 65] few *in situ* studies have been carried out under pressure. With the availability of high-energy (HE) synchrotron X-ray beamlines, and the ability to focus HE X-ray [54, 66] *in situ* studies, rather than work on samples recovered after compression, becomes an exciting and viable prospect. A quantitative understanding of the structural basis for phenomena such as polyamorphism could have high technological impact, if persistent metastable solid phases, densified glasses for example, could be recovered from high pressures, or if chemical routes could be found to reproduce the phenomena discovered. The former strategy is familiar in crystalline substances where various polymorphs of the same element or compound (e.g. graphite and diamond) have very dissimilar, and valuable, properties. Superconductive [67-69] and GMR materials [70] provide examples of how [70] pressure studies inspire chemical modification to stabilize novel materials at low pressures. *To understand polyamorphism, systematic in situ and quantitative HP studies of the structure of suitably chosen compositions is required to help establish the presence and the nature of this phenomenon.*

The existence of polymorphism is well known in the crystalline state; the soft mode transitions in the perovskites [71] are accompanied by large changes in, for example, sound velocities easily observed in ultrasonic measurements or in the inelastic neutron scattering spectrum. While the transitions in glasses may not be abrupt [65] they share some remarkably common features with polymorphic transitions in crystalline solids. Some of these similarities have only recently been demonstrated using combined PDF-elasticity measurements (Figs. A2.8, A2.9). For example, there is evidence that changes in glasses under pressure involve coordination change [55, 65] and changes in the S-wave velocity reminiscent of soft mode behavior. While evidence of this "polyamorphic" [72, 73] behavior under pressure is mounting, an understanding of thermodynamically distinct phases in the liquid/glassy state requires analysis of scattering data collected *in situ* and to high *Q*.

Glass-glass and liquid-liquid transitions (Parise, Chupas, Chapman, Benmore, Tulk)

Examples of new phenomena observed at HP in glasses include softening of shear wave velocities (Fig. A2.8) Indicative of structural transitions in the glassy state [55]. Compositions in the Ge-Se system, and $GeSe_2$ in particular, are archetypal network glass, which comprises of both edge and corner sharing tetrahedra arranged in a distribution of ring sizes. A signature of the intermediate range order in glassy $GeSe_2$ is indicated by the presence of a first sharp diffraction peak (FSDP) in the measured structure factor, although chemical ordering (associated with the principal peak at Q~2 Å-1) has also been associated with extended range ordering in real space (Fig. 10). Isotopic substitution neutron diffraction experiments on recovered samples pressurized to 10 GPa and in-situ monochromatic high energy X-ray diffraction measurements using a DAC (Fig. A2.8) up to pressures of 9.3GPa show that the conversion from edge to corner sharing tetrahedra at high pressure is associated with a slight elongation of Ge-Se bond length and a substantial distortion of tetrahedra. The first sharp diffraction peak decreases in intensity and has almost disappeared at the highest pressure without any significant coordination number change (Fig. 10). The gradual density increase by 18% at 9.3 GPa, is associated with a similarly gradual increase in intermediate range ordering, which is attributed to increased chemical range order in the glass.

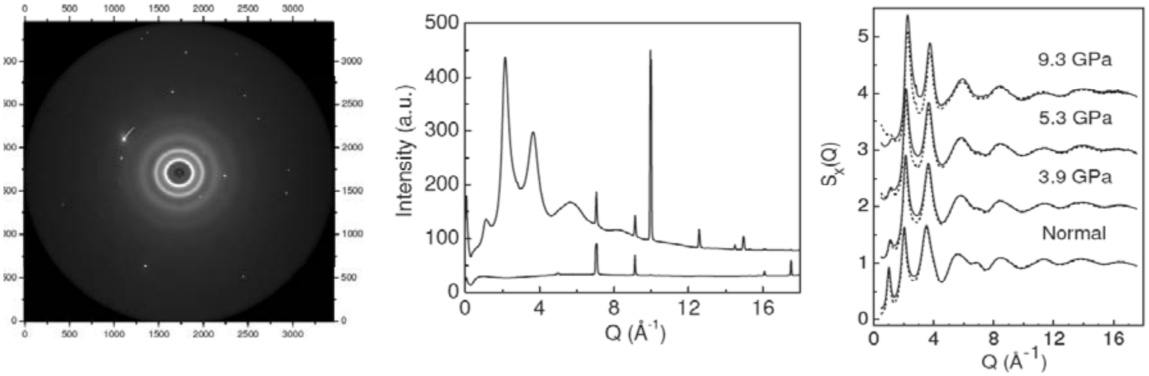


Fig. A2.8 (left) Raw X-ray (E = 80 keV) data obtained from the Mar345 image-plate for glassy $GeSe_2$ in a diamond anvil cell (DAC) at 5.3 GPa. Spots are Bragg peaks from the single crystal diamonds and diffuse rings are the diffraction pattern for the $GeSe_2$ glass. (Middle) The integrated intensity measured using high-energy x-rays for glassy $GeSe_2$ in a DAC at 5.3 GPa (upper curve) and for the empty DAC at ambient pressure (lower curve). The additional sharp peaks arise from single crystal ruby (used for pressure calibration) Bragg scattering. (Right) Total structure factors obtained from scattering data.

These preliminary data suggested the existence of a polyamorphic [72, 74] transition in this system. Gradual structural transitions in glasses and liquids as a result of increasing pressure are inherently difficult to identify however, due to their disordered nature. Acoustic experiments, on the other hand, measure compressional and shear velocities, which in particular are sensitive to network rigidity. Apart from characterizing the framework structure using X-ray and neutron scattering at HP, we also observe a minimum in the shear velocity (Fig. 11) and associated anomalous behavior in Poisson's ratio at 4 GPa, indicative of a second order-type transition in $GeSe_2$ glass. This is the first time both the scattering and a physical property so associated with 2nd order phase transitions have been observed in a framework system [75]. We previously characterized the anomalous Poisson ratio in cristobalite [76]. The S-wave minimum and associated changes in elastic properties at HP are attributed to a competition between two densification mechanisms. At pressures up to 3 GPa, a conversion from edge-to-corner sharing tetrahedra results in a more flexible, floppy network (6). This is contrasted by a gradual increase in coordination number with pressure, which leads to an overall stiffening of the glass.

The data shown in Figs. A2.8 and A2.9 document the relationship between structural changes in $GeSe_2$ glass, derived from the scattering data right, and changes in the physical properties, the shear wave propagation shown left. We attribute the ultrasonic anomaly to changes in the structure of the glass, which are revealed upon careful analysis of the PDF; $GeSe_x$ coordination number increases from x = 4.0(2) at 0 GPa to x= 4.5(2) at 9.3 GPa. The mechanism of close packing of the network maybe by conversion of edge sharing to corner-sharing tetrahedra at low pressure (0-3 GPa) and by distortion of tetrahedra at higher pressure (3-9 GPa). These first-time observations suggest a very rich behavior for glasses at HP. *These measurements represent the current state-of-the-art. In order to conduct studies of glasses containing lighter components, water and silicates in particular, requires a detector system with greater sensitivity and better signal-to-noise discrimination, and larger sample volume at high pressures. The initiatives to develop the infrastructure to allow larger sample volume and a cleaner signal are the focus of the PING project and the upgrade to facilities at NSLS.*

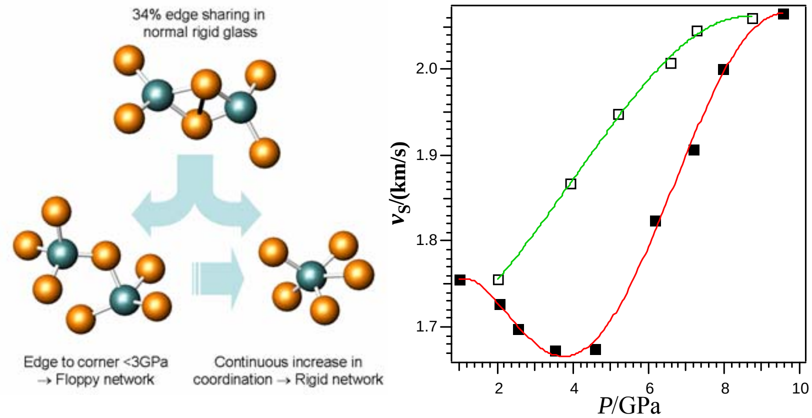


Fig. A2.9 (Left) Densification mechanisms in $GeSe_2$ glass at HP. (Right) Variations with pressure in shear velocity (V_S). Lines are polynomial fits as a guide to the eye (compare to Fig. 10).

Network forming oxide melts and glasses at VHT (Wilding, Benmore, Tulk).

The study of liquids and amorphous materials under extremes of pressure and temperature is developing into a very rich field. Neutron and high-energy X-ray diffraction are critical to the understanding changes in structure, associated with both gradual and abrupt changes in mechanical and optical properties of these materials. Measurements on pure liquid silica on 11-ID-C have revealed the persistence of a strong covalently bonded network up to at least the fourth nearest neighbor in the liquid state [77]. Changes in the silica (or alumina) liquid network upon the addition of a modifier can produce unusual structural transitions with temperature and/or pressure if the concentration of the network former is sufficiently depleted. We have begun to study a series of these liquid and glassy structures for several geologically and technologically important binaries in the system CaO/MgO/FeO : Al_2O_3/SiO_2 (Figs. A2.10, A2.11). The investigation of structural changes versus composition between two purely network forming melts i.e. $SiO_2 : Al_2O_3$ is also underway.

Levitation experiments (Fig. A2.10, right) provide evidence of a similar fragile-strong transition occurring upon supercooling liquids at intermediate compositions between $MgSiO_3$ and Mg_2SiO_4 [78, 79]. The containerless processing of high temperature levitated liquids also provides a unique technique for vitrifying materials, which cannot otherwise be, glass-quenched e.g. Mg_2SiO_4. An aerodynamic glass fabrication facility set up at the APS for

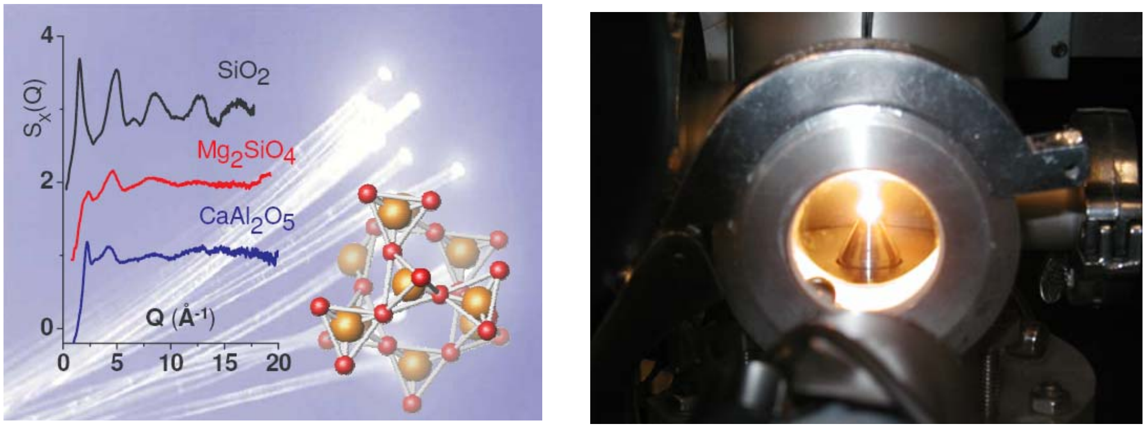


Fig. A2.10 High energy X-ray diffraction data for aerodynamically levitated liquids: pure SiO_2, MgO-SiO_2 and CaO-Al_2O_3 at temperatures around 2000K. Containerless quenching of these liquids together with fast large area detectors allows a measurement of the supercooled liquid structure as it jams during the transition into the glassy state.

making these exotic samples for combined X-ray/neutron and high pressure studies will greatly accelerate the pace of these experiments.

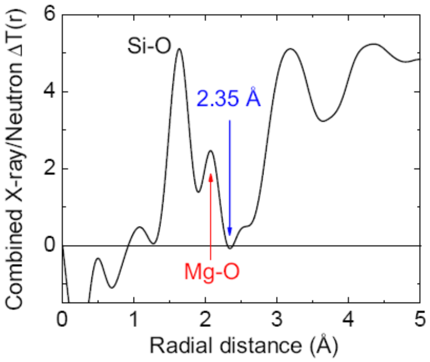


Fig. A2.11 Diffraction measurements on MgO-SiO$_2$ glasses show a discontinuous change in structure with composition, from a strong SiO$_2$ dominant network in MgSiO$_3$, to a fragile MgO$_n$ (n=4,5,6) polyhedral network in Mg$_2$SiO$_4$, and are associated with a 15% increase in Mg-O coordination number over a narrow interval. A combination of x-ray and neutron diffraction data have been used to obtain detailed information of the Mg-O environment by eliminating the overlapping O-O peak at ~2.35Å from the pair distribution function in MgSiO$_3$ (opposite).

Another classic example is CaO:Al$_2$O$_3$ glasses (Fig A2.10), which have potential applications as infrared optics, laser hosts and high strength optical fibers. Neutron/X-ray experiments on these glasses have found a low Ca-O coordination number of ~4 at some compositions [80], and this has been attributed by molecular dynamics simulations to an asymmetric distribution of Ca-O correlations which extend out to ~3.0Å. Aerodynamic levitation experiments have shown that these Ca-O correlations broaden considerably in the liquid state. This behavior may be related to changes in the Al$_2$O$_3$ framework, and possibly the formation of OAl$_3$ triclusters in the melt.

A2.6 *In situ Search for New Materials Under Extreme Temperature Conditions (Kriven)*

High throughput synthesis (HTS; [81, 82]) especially when combined with high energy synchrotron X-ray powder diffraction , is a versatile means for discovery of novel materials with useful properties, and for the elucidation of phase diagrams [83]. Extensions of HTS to extreme conditions will require a concerted effort in the development of ancillary equipment compatible with the optics and detectors currently being developed for next generation sources. *Rapid survey using high energy X-ray powder scattering, will take NSLS and NSLS-II into the realm of MS 3.0.*

In situ Chemical Reactions and Structural Evolution as Studied Rietveld and PDF Synchrotron

The kinetics of chemical reactions e.g. oxidation at elevated temperatures can be followed by high temperature powder diffractometry. Rate constants can be measured there from. Similarly, crystallization kinetics can be determined *in situ*, from Rietveld and PDF measurements (Fig. A2.11).

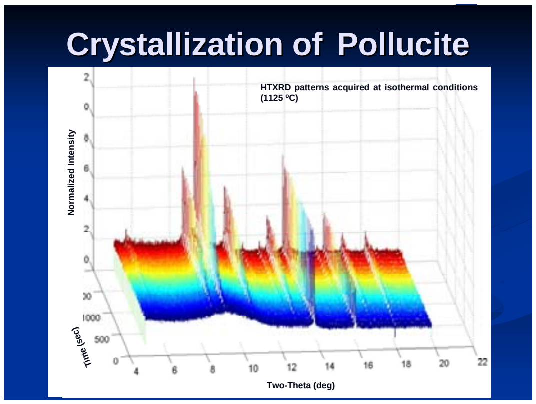


Fig. A2.11. In situ high temperature powder diffractometry observing the crystallization of pollucite (Al$_2$O$_3$•Cs$_2$O•4SiO$_2$) from the amorphous hydrated geopolymer precursor, taken with a curved image plate detector within 22 min.

Accelerated Design of Advanced Structural Ceramics (Kriven, Croft)

Once new materials have been identified and the volume and unit cell shape changes as well as transformation temperatures have been identified, structural ceramic composites can be designed and fabricated for *in situ* studies of stress-induced transformation toughening. Specifically, knowing the thermal expansion coefficients of candidate matrices and toughening phases, chemically compatible composites having matched thermal expansion coefficients will be engineered as laminates or fibrous monoliths, or even as fiber-reinforced composites. Bulk samples of such composites will then be pre-notched and evaluated by *in situ* straining stage experiments as observed by highly penetrating synchrotron rays. The mechanisms of stress-induced transformation and the resultant redistribution of stress states, clamping forces of a propagating crack tip and overall toughening of the ceramic component will be demonstrated. A specific example to illustrate such a composite would be transformation weakening of enstatite ($MgO•SiO_2$) as a potentially debonding interphase in forsterite ($2MgO•SiO_2$), as illustrated in Fig. A2.12.

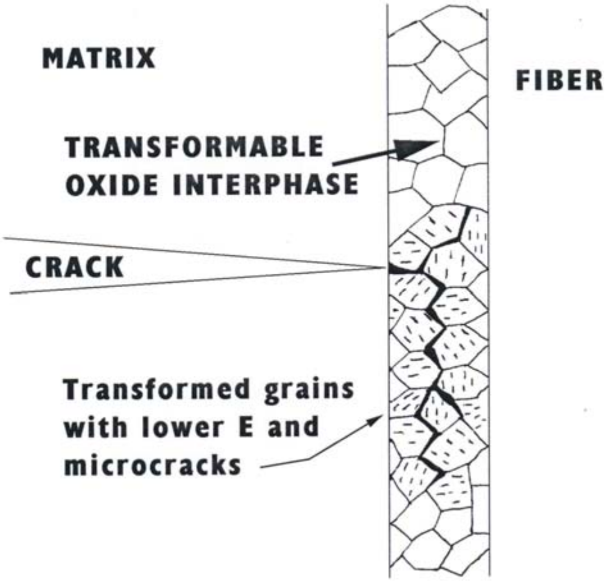


Fig. A2.12. Schematic diagram illustrating “transformation weakening of ceramic interphases” leading to overall toughening of a ceramic matrix composite. In thermally induced transformations, all interphases are pre-transformed before the approach of a crack, with some consequent loss of overall strength of the material. In the ideal, shear stress induced case, a propagating crack induces a transformation in its immediate environment, with strength only minimally reduced throughout the bulk. Maximum toughening is achieved, since the propagating crack needs to do work to overcome the nucleation barrier and cause transformation, and onset of the other synergistic toughening mechanisms (e.g., microcrack formation) occurs.

Accelerated In situ Elucidation of Phase Diagrams

The measurement of phase diagrams can be significantly expedited by *in situ* studies at high temperatures and with special resolution of diffusion couples. When two end phases are joined and heat-treated, they mutually interdiffuse, forming compounds according to their phase diagram at thermodynamic equilibrium for a given temperature. It is envisaged that using a collimated beam to step across the diffusion couple it would be possible to crystallographically identify the phases formed and co-existing in equilibrium with each other. Once the individually phases have been identified, they can be heated separately and their individual behavior in terms of thermal expansion coefficients and possible phase transformations can be measured.

How to do it

Use the quadrupole lamp furnace (QLF) capable of temperatures to 2000°C in air with temperature accuracy of ± 5°C to 1830 °C and ± 10 °C above it. In conjunction we would advocate the use of a fast (30 sec readout) curved image plate detector [84] (CIPD) or silicon-based (millisecond) curved strip detector. This set up is shown with operator in Fig. A2.13.

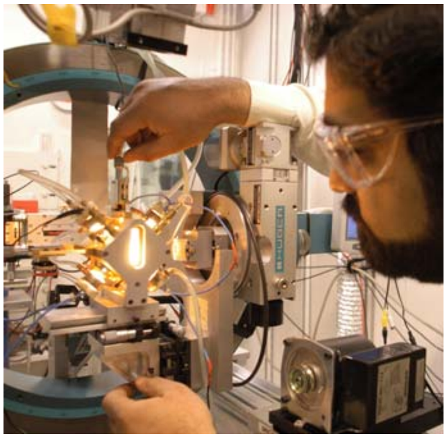


Fig. A2.13 Quadrupole lamp furnace (QLF), exit port view.

Appendix A3: Single Crystal Techniques: state of the art and future prospects *(Contributions from James Martin and Simon Teat)*

A3.1 Introduction

For materials chemistry to meet the challenges of today and the future, it is necessary to correlate the physical properties of materials with their structures. Without these structure-property relationships, rational design is not possible and any advances are by pure luck. Combining synchrotron radiation with 2-D area detectors allows high quality Bragg diffraction data to be rapidly collected from small and weakly diffracting crystals that otherwise show little or no diffraction using a laboratory source, and allows rapid survey of reciprocal space for studies of weak diffuse scattering. This combination also allows "problem crystals", such as twins or stacked plates, to be cut to a size where these problems might be mitigated, and still provide high quality data. Unlike a laboratory source, the synchrotron wavelength can be tuned to better suit the sample, i.e., long wavelength for weakly diffracting light atom structures or short wavelength for highly absorbing samples. This ability permits anomalous dispersion based studies, making it possible to discriminate isoelectronic species. The wavelength can also to tuned to minimize absorption, maximize resolution and maximize the data coming out of the restricted geometry of some environmental cells.

A3.2 Structural Chemistry

Small molecule x-ray diffraction is the most powerful tool for determining the arrangement of atoms and molecules in a single crystal. Today chemists are producing larger and more complex materials; not surprisingly they have a tendency to be small and weakly diffracting, however, there are many smaller and simpler molecules, which refuse to produce lab size crystals. Often x-ray diffraction is the only way for the chemists to work out what they have made; in particular, some technologically important materials such as microporous materials, small molecule magnets etc, are extremely difficult to characterize with most other analytical methods. Without the structure it is impossible to work out the origin of the physical properties and improve on these properties by rational design. Even if crystals of a suitable size for a lab instrument are grown, there is no guarantee that there will be enough diffraction to generate a solution. Twinned and disordered crystals experience serious degradation of diffraction intensity as a function of 2θ; many of these samples will fail to solve on a lab source due to a lack of higher resolution data. Regular access to the synchrotron can accelerate structural chemistry programs especially when the crystals grow slowly over a number of months until they are large enough to investigate on a conventional lab system. Regular access allows these crystals to be studied when they are smaller and either data can be collected or the sample rejected and re-crystallized sooner. Often for these types of compounds, they produce better small crystals than large, since as the crystal grows it loses the order it initially had and becomes increasingly disordered. By the time it is large enough to be studied conventionally, the additional volume is actually a handicap.

A3.3 Anomalous Dispersion/ Resonant Diffraction

Absolute structural determination

Wavelengths longer than copper allow better absolute structure determination on light atom structures as the anomalous terms f” for C, N and O are much higher. This is important in the pharmaceutical industry, as the wrong handedness can be dangerous.

Oxidation state determination

f’ and f” rapidly change around the absorption edge of an element; how this changes is determined by the oxidation state of the element itself. This allows the position of the same element with different oxidation states to be ascertained. This information helps to understand the physical properties of materials, such as super-paramagnetic magnets and framework catalysts, leading to the design of better materials by tailoring the properties as required.

A3.4 Microporous materials and magnetic metal clusters

In microporous materials or poly-metal clusters, it is important to know where specific metal atoms are situated in order to understand the material’s function. When these metals are isoelectronic or near neighbors this can be difficult, as there is little or no contrast. By tuning around the edges of the elements where f’ is changing rapidly, it is possible to modify the scattering factor of each atom in turn to increase the contrast and allow the position and occupancies to be determined.

A3.5 Structures under change

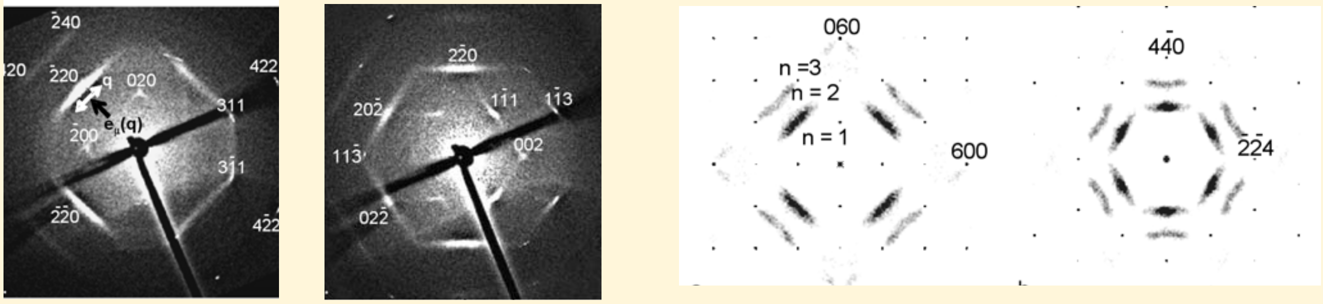
Most materials are collected in such a way that only a limited snapshot of the structure at one temperature and under ambient pressure is determined, so the structural dependence on environmental influences is not known. Pressure and temperature are two such influences that can induce structural changes, such as coordination and bonding; these can be used to modify the properties such as color, magnetism etc. Technologically important compounds such as microporous materials operate at high temperatures, pressures and gas atmospheres, which are very different to the normal low temperature data collection from which the structures are normally determined. Processes such as dehydration, rehydration or gas/vapor absorption can be studied by combining the high intensity of the synchrotron and a small crystal. The smallest practical crystal size is required to give a higher surface area to volume ratio to allow better diffusion into and out of the sample, as these materials are likely to be used as powders it better matches the real process conditions. The ability to collect data rapidly allows numerous temperature steps to be collected in a short period, allowing properties such as negative thermal expansion to be investigated and understood. For some of these types of experiments, environmental cells are required to attain the more extreme conditions. These cells have limited opening angles and increased absorption therefore short wavelengths can be used to alleviate these problems.

A3.6 Charge density studies

Charge density studies allow the derivation of the physical properties of materials by understanding the chemical interaction within the crystal. By the collection of high-resolution data, properties such as electrostatic moment, electrostatic potentials, electric field and quadrupole couplings can be determined. Systematic errors such as extinction and absorption can be reduced at the synchrotron by choosing a smaller crystal and by collecting the data at higher energies. By studying these properties in systems such as microporous materials it allows an understanding of the potential interactions available between the material and the feedstock upon which it acts catalytically, resulting in better design of catalysts.

A3.7 Disordered Materials (Martin, Chupas)

With the return from point to modern area detectors, it is once again apparent that Bragg peaks are not the only diffraction features present in reciprocal space. Diffuse features and incommensurate peaks are now visible and can explain the deficiencies in the structural model that is based purely on the Bragg intensities and problems in processing what otherwise looks like good data. These types of feature are indicators of disordered material where atoms or molecules are displaced from their mean position as determined by a conventional single crystal model and the normal certainty at finding an atom or molecule at a position now becomes a probability instead. Such compounds can have interesting dielectric properties, for example, and only by understanding how the structure and properties are related can better materials be designed.



(**a**) (**b**) (**c**) (**d**)

Fig A3.1(a) A 5° rotation angle images near <001> orientation around the [020]* and (b) [1,-1,0] orientation around the [2,-2,0]* reciprocal lattice directions. (c) and (d) Calculated diffraction patterns in projection along (a) [100] and (b) [111] respectively after Monte Carlo relaxation. Taken from the work of Martin, NC State.

Diffuse Scattering [5]: Time resolved powder diffraction for mechanistic studies, such as those described above in Appendix 2, have produced stunning results. For many materials of interest the complex geometries and 3-D nature of the elastic diffuse scattering is smeared out for samples in the powder form. "Single" crystals, even if twinned, split or aggregated to give textured "pseudo single crystal patterns" provide information to allow the nature of the deviation from the average crystal structure that are important for material properties. An example is recent work from Martin's group at NC State. The diffuse scattering of plastic crystalline CBr_4 is extremely anisotropic (Fig. A3.1) suggesting the need the need to mount efforts to develop software for analysis of 2 and 3-D PDF.

2-D single crystal synchrotron X-ray diffraction of the high temperature plastic phase of CBr_4 reveals relatively sharp, G ± 1/2 {110}* sheets of diffuse intensity (where G represents the set of average structure Fm-3m allowed Bragg reflections). This intense and highly structured diffuse scattering arises from the large amplitude excitation of transverse polarized displacive modes of distortion and shows that a set of six possible orientations of the individual CBr_4 molecules in the plastic phase are strongly coupled with displacive relaxational degrees of freedom. Using Monte Carlo simulations to model the diffuse intensity, the displacive relaxations are shown to be along the molecular nearest neighbor 1/2 <110> real space directions associated with the relative orientations of individual and nearest neighbor CBr_4 tetrahedra.

Appendix 4: Potential Users of MaDiS at NSLS and NSLS-II/User comments

Directors of Institutes containing several senior investigators

First name	MI	last name	Institution	email	tel
Russell	J	Hemley	Director, Geophysical Laboratory, Carnegie Institution ofWashington, 5251 Broad Branch Rd. NW Washington, DC.	Hemley@gl.ciw.edu http://cdac.ciw.edu	202-478-8951 (off) 301-523-7596 (cell) 202-478-8901 (fax)
Malcolm		Nicol	Director, UNLV High Pressure Science and Engineering Center, Department of Physics and Astronomy, University of Nevada Las Vegas, Las Vegas, NV 89154-4002	nicol@physics.unlv.edu	702-895-1725
Camden	R	Hubbard	Leader, Diffraction and thermal physics group, Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6064	hubbardcr@ornl.gov http://html.ornl.gov/dtpgrp/staff/hubbard.html	865-574-4472 865-574-3940 (fax)
Stanley	M	Wittingham	Director, Institute for Materials Research, SUNY Binghamton, NY 13902-6000	stanwhit@binghamton	(607) 777-4623
Donald	J	Weidner	Director, Mineral Physics Institute, Stony Brook	Donald.Weidner@sunysb.edu	(631) 632-8211
Peter	Y	Zavalij	Director, Crystallographic Center, Chemistry, University of Maryland	pzavalij@umd.edu http://www.chem.umd.edu/facility/xray/	(301)405-1861

Individuals responding with specific ideas. A full list of workshop attendees is available at

http://www.nsls.bnl.gov/newsroom/events/workshops/2008/lsdp/mse/registrants.asp

Selected comments from potential users of the Solid State Chemistry Community

Ken Poeppelmeier (Northwestern University)
a purposeful, "user interface" is needed from providing stipend resources, travel funds, to an effective software, web-friendly interface (much as we do with the journals)....this MUST be built in from the get-go...not left as a promise that gets underfunded or not funded at all down the road. There simply are no funds in the grants of the PI to do this !!!

Ray Schaak (Penn State University)
One of my main interests in this area would be analyzing structures of nanoscale solids, most likely PDF-type analysis. We've not done it yet, but that is a very definite emerging need. We and others sometimes observe the formation of phases, as nanocrystals made at low-ish temperatures, that are "new" or typically only observed under higher temperature or pressure conditions. Probing these structures… will be critical.

Ram Seshadri (UCSB)
Temperature control, particularly below 10 K is what all diffractometers miss that we need.

Cora Lind (University of Toledo)
A setup with a highly focused beam (for the small opening of the DAC), ability to choose a short wavelength (to get data with a 22 degree cone opening), and most importantly a good detector (we have to run a gazillion data corrections every time before we can do anything useful) are highly desirable.

Hanno zur Loye (University of South Carolina)
It would be nicest if we could simply send a capillary containing our powder and have someone run it and send us the data back. Variable temperature capabilities, to look for phase transitions would be great (though I realize this cannot be done via mail in). Having some decent computers there for data collection, data conversion and analysis would be helpful. Maybe we can graduate from VMS.

Svilen Bobev (University of Delaware)
Advanced capabilities at NSLS to do high resolution powder and single-crystal diffraction. Special environments for low/high T and under magnetic field will be fantastic.

Mike Lufaso (University of North Florida)
One aspect that I would find particularly useful is the implementation of a 'mail-order program' for routine powder diffraction measurements.

First name	MI	last name	institution	email	tel
Angus		Wilkinson	Chemistry, Georgia Institute of Technology, Atlanta, GA 30032-0400	angus.wilkinson@chemistry.gatech.edu	404 894 4036
Ravindran	R	Thoguluva	Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW Washington, DC.	rthoguluva@ciw.edu	202-478-8995
Hanno		zur Loye	University of South Carolina, Chemistry, 631 Sumter Street, Columbia, SC 29208	ZURLOYE@mail.chem.sc.edu http://www.chem.sc.edu	(803) 777-6916 work (803) 777-8508 fax
Muhetaer		Aihaiti	Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW Washington, DC.	maihaiti@ciw.edu	202-478-8932
Jiuhua		Chen	CSMEC, , Florida International,VH-140, University ParkMiami, FL 33199	jchen@notes.cc.sunysb.edu	
Chris	C	Tulk	Neutron Scattering Sciences, Oak Ridge National Lab, Oak Ridge, TN 37830 USA	tulkca@ornl.gov	
Quentin		Williams	Geosciences, UC Santa Cruz	quentw@pmc.ucsc.edu	
Allen	W	Burton	100 Chevron Way, Richmond, CA 94802	buaw@chevron.com	510-242-1810
Bao-sheng		Li	Geosciences, Stony Brook NY 11794-2100	bli@notes.cc.sunysb.edu	
Ashfia		Huq	Neutron Scattering Sciences, Oak Ridge National Lab, Oak Ridge, TN 37830 USA	huqa@ornl.gov	(865)574-7923
Douglas		Buttrey	University Delaware	dbuttery@udel.edu	
Peter	C	Burns	Geo Notre Dame	Prof.peter.c.burns@gmail.com	
Edwin		Kugler	Chemical Engineering, West Virginia University, Morgantown, WV 26506-6102	edwin.kugler@mail.wvu.edu	(304) 293-2111 ext 2414
Galen		Stucky	Chemistry, UC Santa Barbara, CA, 93106	stucky@chem.ucsb.edu	
Meigan		Aronson	Department of Physics and AstronomyStony Brook University , Stony Brook NY	maronson@bnl.gov	631-344-4915
Thomas		Duffy	Geosciences, Princeton NJ 08648	duffy@princeton.edu	
Pamela		Whitfield	NRC Canada, 1200 Montreal Road, Ottawa Ontario K1A 0R6, CANADA.	pamela.whitfield@nrc.gc.ca	(613) 998 8462
Scott		Misture	Materials Science NYS College of Ceramics at Alfred University,Alfred, NY 14802	misture@alfred.edu	607-871-2438 Fax 607-871-2354
Patrick		Woodward	Chemistry, Ohio State, Columbus OH 43210-1185	woodward@chemistry.ohio-state.edu	614-688-8274
James		Martin	Chemistry, NCstate,	Jim_Martin@ncsu.edu	919-515-3402
Clare	P	Grey	Chemistry, Stony Brook	Clare.Grey@stonybrook.edu	631-632-8241
Peter	P	Khalifah	Chemistry, Stony Brook/BNL	Peter.Khalifah@stonybrook.edu	631-632-8359
Karena		Chapman	APS, Argonne Naaional Laboratory	chapman@aps.anl.gov	

In addition the following have professed interest in PING but were unable to attend the original workshop; the interest of this group is mostly in work at high pressures using large volume and DAC HP apparatus

Alexander Goncharov	Carnegie Institution of Washington	James A Tyburczy	Arizona State University
David Walker	Columbia University	Jung-Fu Lin	The University of Texas at Austin
Michael Kruger	University of Missouri	Pamela C. Burnley	University of Nevada, Las Vegas

Andrew Campbell	University of Maryland
Surendra Saxena	Florida International University
Shun-ichiro Karato	Yale University
Kanani Lee	Yale University
Justin Hustoft	Yale University
Takaaki Kawazoe	Yale University
Mainak Mookherjee	Yale University
Tomohiro Ohuchi	Yale University
Kazuhiko Ostuka	Yale University
Zhicheng Jing	Yale University
Sang-Heon Dan Shim	Massachusetts Institute of Technology
John Tse	University of Saskatchewan
Alexandra Navrotsky	University of California at Davis
Isaac Silvera	Harvard University
Yanbin Wang	University of Chicago
Michael Vaughan	Stony Brook University
William Durham	Massachusetts Institute of Technology
Li Li	Stony Brook University
Yanzhang Ma	Texas Tech University
Hyunchae Cynn	Lawrence Livermore National Laboratory

Murli H. Manghnani	University of Hawaii
Larissa Dobrzhinetskaya	University California at Riverside
Oliver Tschauner	University of Nevada, Las Vegas
Markus Hücker	Brookhaven National Laboratory
Viktor Struzhkin	Carnegie Institution of Washington
Mark Rivers	University of Chicago
Yanbin Wang	University of Chicago
Lili Gao	University of Illinois, Urbana-Champaign
William J Evans	Lawrence Livermore National Laboratory
Li Chung Ming	University of Hawaii

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