Meeting Report

COMPRES SPONSORED WORKSHOP

"Structure Determination by Single Crystal X-ray Diffraction (SXD) at Megabar Pressures"

In response to the proposal submitted last year to the Infrastructure Development Committee, COMPRES awarded us a budget of $20K to organize a workshop focused on the future of ultrahigh-pressure single-crystal XRD techniques, aimed at "building on the strengths of the existing high-pressure crystallographic community by bringing together the top experts from around the world to plan a coordinated way forward." This report summarizes the results of this successful two-day meeting, held on November 13-14, 2004, at the Argonne National Laboratory (Advanced Photon Source) in Chicago.

One of the main objectives of this workshop was to provide answers to the following questions:

1. Is it scientifically important/justifiable to develop megabar SXD techniques?
2. Is there enough interest and demand in the community for such development?
3. Is there a consensus among the experts on how such a task should be approached?
4. How can the effort be coordinated and managed most efficiently?

The meeting was very well attended, attracting over 60 participants, 14 of which came from outside US, representing 5 different countries. The high attendance of this relatively specialized workshop alone makes a strong case that there is indeed sufficient interest and demand in the community to develop high-pressure single-crystal techniques at the various synchrotron radiation sources. Our highly focused workshop was timed at a critical juncture in the early development of Mbar single-crystal techniques, and brought together nearly all the active experts and a wide range of supporters representing complementary specialties (such as microdiffraction). A complete list of workshop participants can be found at:

http://www.gl.ciw.edu/~pdera/sxd/index.html

The workshop participants can be grouped into four different categories:

1. High-pressure crystallography experts, who came to discuss cutting-edge technologies, early experiences with Mbar SXD, and their personal visions on which technologies and methods should be implemented.
2. High-pressure beamline scientists, who came to gauge the interest in the community of potential users, and to find out how best to equip their beamlines for SXD techniques in the future.

3. High-pressure researchers who are not using SXD technique now but recognize its importance and plan to use it in the future.
4. Synchrotron microdiffraction and detector technology experts, who were willing to help us implement their discoveries into our experimental setups, and hoped to gain something themselves by applying solutions developed in the high-pressure field to their own problems.

The workshop was divided into four sessions representing different branches of high-pressure crystallography experiments, and was supposed to guide the participants though the logical path leading from developmental motivation, through existing solutions (and problems), to technologies of the future:

(i) Structure solution from powder diffraction at ultrahigh pressure
(ii) Monochromatic single-crystal experiments at high pressure
(iii) White-beam single-crystal experiments at high pressure
(iv) Synchrotron microdiffraction

During the workshop, there were 29 oral presentations, featuring four one-hour long plenary talks given by distinguished experts (John Parise, Ross Angel, Keith Brister and Gene Ice) offering comprehensive introductions to the four major workshop themes. The rest of the talks within each session were 20-minute-long reports on the most exciting developments and recent experiments. The workshop themes and content attracted many last-minute attendees, who after reading the program (published on the web) decided that they could benefit from participation. We had five last-minute requests to attend the meeting during the three days prior to the meeting, and we had additional six participants who simply showed up. Most of the talks were innovative, some were provocative, and all were clearly custom-fit for this workshop. Perhaps the most memorable moment came when Gene Ice actually sang his conclusions in a roaring rendition of "Microdiffraction" (with guitar), which was so clever and catchy that most members of the audience joined in the chorus.

Of the most important topics covered by the speakers, one can distinguish:

1. Application of non-standard crystallographic techniques, such as Pair Distribution Function (PDF) analysis, to powder diffraction patterns of crystalline solids and the maximum entropy method (MEM), to modeling electron density distribution from high-pressure SXD data.
2. Utilization of combined information from powder and single-crystal XRD experiments to aid structure solution at high-pressure
3. Incommensurate structures and charge density waves
4. Solvothermal techniques, crystal growth at high-pressure, and sample annealing
5. Structure solution with the use of global optimization methods
6. Grain-size effects
7. Electronic and spin transitions
8. Time-resolved crystallography

9. Modern approaches to polychromatic diffraction at high pressure
10. Status of high-pressure beamlines in US and abroad
11. Perspectives of application of revolutionary x-ray optics and novel detector technologies in high-pressure XRD experiments

The collected abstracts are available for download from the meeting website. Since there were numerous requests for access to additional information and ideas presented at the meeting, we are in the process obtaining author permissions to post the PowerPoint presentations on the meeting website. Also, the Board of Editors of the Journal of Synchrotron Radiation has agreed to publish selected contributions to our workshop in a special 150-page issue of that journal, which will be edited by Przemek Dera, Charlie Prewitt and Steve Jacobsen.

It was clear from the talks that two (not mutually exclusive) concepts exist for the future development of ultrahigh-pressure synchrotron SXD, which will require prioritization.

1. Focus on monochromatic SXD
2. Focus on modern approaches involving combination of monochromatic and polychromatic SXD.

In the following section, both points of view will be summarized and a possible consensus proposed.

Monochromatic SXD: The technique is mature and well tested on laboratory diffractometers up to ~10-20 GPa, and has already been used at synchrotron sources for equation of state studies (cell parameters only) to >100 GPa on existing hardware, but remains largely untested for intensity data collection at US synchrotron sources. The recent proliferation of CCD detectors has provided higher resolution and increased sensitivity over earlier models, as well as decreased data collection time, but at the same time has introduced its own set of problems. Whereas CCDs are optimized for rapid intensity data collection, they are less well-suited for obtaining high-resolution peak profiles and high-precision cell parameters than are traditional point detectors. CCDs also introduce higher background because the diffracted beam (downstream) cannot be collimated. High-pressure experiments with a variety of diamond-anvil cells are possible with standard commercial hardware (three-circle or platform-type goniometer). Commercial software can be used for data processing, in combination with relatively simple custom high-pressure software tools. Although the intensity of X-rays available at synchrotron sources would allow the pressure range to be extended beyond 10 GPa (by decreasing the sample size), the necessity to rotate the sample during monochromatic data collection introduces a new set of mechanical challenges when the beam is nearly the same size, or smaller than the sample (as it will generally be at the synchrotron sources). While the necessary hardware (four-circle goniometers) is not yet available at the high-pressure beamlines, the monochromatic technique should be fairly easy and fast to implement, and will offer a rapid first step forward in terms of accessible pressure and quality of the SXD data. On the other hand, the intrinsic limitations of the method (rotation/absorption + background + angular access) may never allow it to work with sample sizes smaller than 10-20 micrometers (necessary for >100 GPa experiments). Undoubtedly, this technique is worth implementation at the beamlines, but preferably in a flexible setup that does not preclude other experimental approaches.

Polychromatic and combination SXD techniques: These techniques are now at the "proof of concept" stage at 3rd generation synchrotron sources (e.g. 16-BMB at HPCAT) and with one operational setup at the NSLS beamline X17. Single-crystal EDX is certainly not as mature and tested as monochromatic approach, but on the other hand offers some obvious advantages in the potential to study submicron-sized samples, depth-of-penetration resolution, and very short data collection times (sub-second with Laue). The polychromatic approach requires more sophisticated custom hardware and entirely custom instrument control and data processing software, but in return offers great flexibility if modifying and combining different techniques, including standard monochromatic SXD. While the monochromatic SXD technique has been developed and tested in laboratories, the requirement of availability of a high-intensity polychromatic x-ray beam makes the EDX/Laue approaches and their development constrained to synchrotron sources. The software development, which will permit fully automatic data collection is under way, but requires further financial support which is being sought through a recently submitted COMPRES I&D proposal. The development of this method for high-pressure work, and the software necessary to implement it, has attracted the attention and interest of experts from microdiffraction and detector technology communities, as well as from the protein Laue community. The EDX/Laue techniques will obviously benefit from a multi-disciplinary effort to develop them, and this workshop provided the first formal setting for members of the various interested parties to strategize and initiate a solid plan for future direction.

Regardless of the crystallographic approach chosen, one additional obstacle to performing ultra-high-pressure experiments at synchrotron sources is the general lack of DAC gas-loading apparatus. Experiments above 10 GPa require media such as He or Ne to be loaded into cells under pressure, but the necessary equipment has not been available, mostly due to facility safety concerns. Thus, investigators are required to load cells at their home laboratories and may have to abandon experiments if problems arise during their synchrotron beam time. It will be pivotal for the success of extending the pressure range of SXD experiments to make such gas-loading equipment available at synchrotrons.

From the discussions at the end of the meeting it was clear, that:

1. The high-pressure community, as well as high-pressure beamlines declared strong support and interest in the development of megabar SXD techniques.
2. COMPRES, as a representation of the HP community, should stimulate and support the efforts.
3. Considering the limited budget of COMPRES, the individual beamlines or the development team(s) should seek funding directly from funding agencies.

A major software development project will be critical to making the white beam techniques possible, requiring:

(i) a precisely defined goal and concept that can be implemented on several different beamlines.
(ii) the development team to be of reasonable size to assure proper coordination of the project. Individuals or groups at separate geographic locations will have to work intellectually very close together.
(iii) a common programming platform is necessary for coherent exchange and incorporation and of independently developed libraries or subroutines into one final product.

Based on the outcome of this workshop, we propose the following consensus as the future direction for Mbar SXD:

1. Form a high-pressure SXD expert working group composed of up to 10 scientists representing (i) high-pressure crystallography community, (ii) high-pressure beamlines scientists/management, (iii) synchrotron optics and detector technology experts.
2. Form a developer team of programmers, including microdiffraction partners.
3. Establish an Internet website and email discussion list that would serve the entire community as an information/software/consultation resource.

We wish to emphasize that although reaching megabar pressures with SXD techniques was the primary objective of our discussions, it soon became clear from the workshop presentations that the applications of the methodology developed for high-pressure research will have wider-reaching impact on other communities. The ability to sample submicron-sized grains with depth resolution, to solve crystal structures from XRD data collected within seconds (possibly during laser heating to several thousand K), and to spatially map the microstructure of deformation, has so far been in the area of dreams and wishes of geoscientists, materials scientists, and engineers. These applications may soon benefit from the development of ultrahigh-pressure SXD techniques, and surely we will also gain from the lessons and accomplishments already achieved by the microdiffraction community.

We would like to conclude by expressing our thanks to COMPRES for offering the financial support and initiating the idea of the workshop, as well as to all of the workshop speakers and participants, for their interest, time, and enthusiasm. We truly hope that the impulse this initiative created will bring major breakthroughs and exciting discoveries into high-pressure science within the next five years.

Przemyslaw Dera and Charles T. Prewitt