(Originally published in the CHESS Newsletter 2000)

Research Highlight

Studying Dense Materials by High Pressure X-ray Diffraction

Serge Desgreniers
Laboratoire de physique des solides denses
University of Ottawa,
Ottawa-Carleton Institute of Physics, Ottawa, Canada.
K1N 6N5

Prologue

I remember when I came, a number of years ago, to the control gate of the Cornell High Energy Synchrotron Source to register for the next scheduled set of experiments, I was told "my equipment had not been shipped yet". "What equipment?", did I reply? "The large high pressure apparatus which you will need for 4you experiment, Sir". I pressed on explaining to the CHESS operator that, albeit being right about our plans to study condensed matter under very high pressure conditions, all we needed for the next couple of days was what I carried in my briefcase and a large influx of hard X-rays! With further discussions, I convinced him how recent advances in techniques and methods in high pressure science, had made possible the study of high-density modifications in the atomic bonding and ordering in solids and materials in general. Interestingly, my host saw in my briefcase several diamond anvil cells, small devices containing samples at high pressure, ready to be put in the X-ray beam for study. In this article, I relate recent developments of high pressure X-ray diffraction and results derived from high pressure experiments carried out at CHESS.

ADXD is what we need!

Traditionally, high pressure studies at CHESS were linked to the use of the energy dispersive X-ray diffraction (EDXD) technique, at the B1 station also known as the "National High Pressure Facility at CHESS". EDXD is fast. A single X-ray diffraction spectrum, recorded in real time as a function of energy using a white synchrotron beam, covers real space interplanar distances spanning the approximate range of 5 to 0.4 Å.

The diamond anvil cell and the high pressure scale

Two opposed high-quality diamonds pressing against a sample constrained by a metallic foil, acting as a deforming gasket, constitute the core of the diamond anvil high pressure cell or DAC for short. Notwithstanding its relatively small size, a DAC can generate pressures exceeding that prevailing at the core of the Earth, i.e., above 360 GPa (100 GPa = 1 Mbar). The good transmissivity of the diamond for hard X-rays allows one to carry out powder or single crystal X-ray diffraction on a pressure-densified sample. Due to the small sample volume, a *sine qua non* condition to reach high pressures, the use of the high photon flux provided by synchrotron radiation at short wavelength is imperative. The DAC is a versatile tool. Other synchrotron-based experiments have been done on samples pressurized in a DAC: X-ray absorption and inelastic scattering. The DAC is also well suited for other physical characterization methods, e.g., luminescence, absorption, vibrational, and Mössbauer spectroscopy and electrical transport and magnetic measurements. Advances in DAC techniques and the availability of intense X-ray beams from second- and third-generation synchrotron sources have played a crucial role in the resurgence and the current vitality of high pressure science.

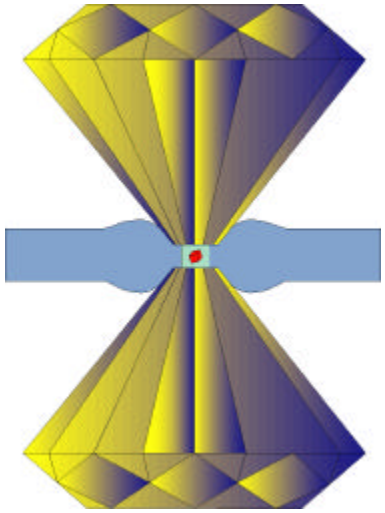

Figure 1. The diamond anvil high pressure cell

With EDXD, one has, however, to sacrifice resolution in *d*-spacing and accuracy of X-ray diffracted intensities. At best, EDXD provides $\Delta d/d \sim 2\text{x}10^{-2}$ and X-ray diffracted intensities requiring careful calibration, two impediments to solving pressure-induced, often times subtle, transformations in solids. The required d-spacing resolution and accuracy in X-ray diffraction intensities are more easily obtained by performing angle dispersive X-ray diffraction (ADXD) using monochromatic radiation of short wavelength. In brief, to pursue high pressure studies using X-ray diffraction, we had to develop the ADXD capability and expertise at CHESS. With the valuable help from the knowledgeable and dedicated CHESS staff, we have elaborated, tested, and refined the necessary equipment and analysis software and methods to make possible unprecedented high pressure studies of materials compressed in diamond anvil cells.

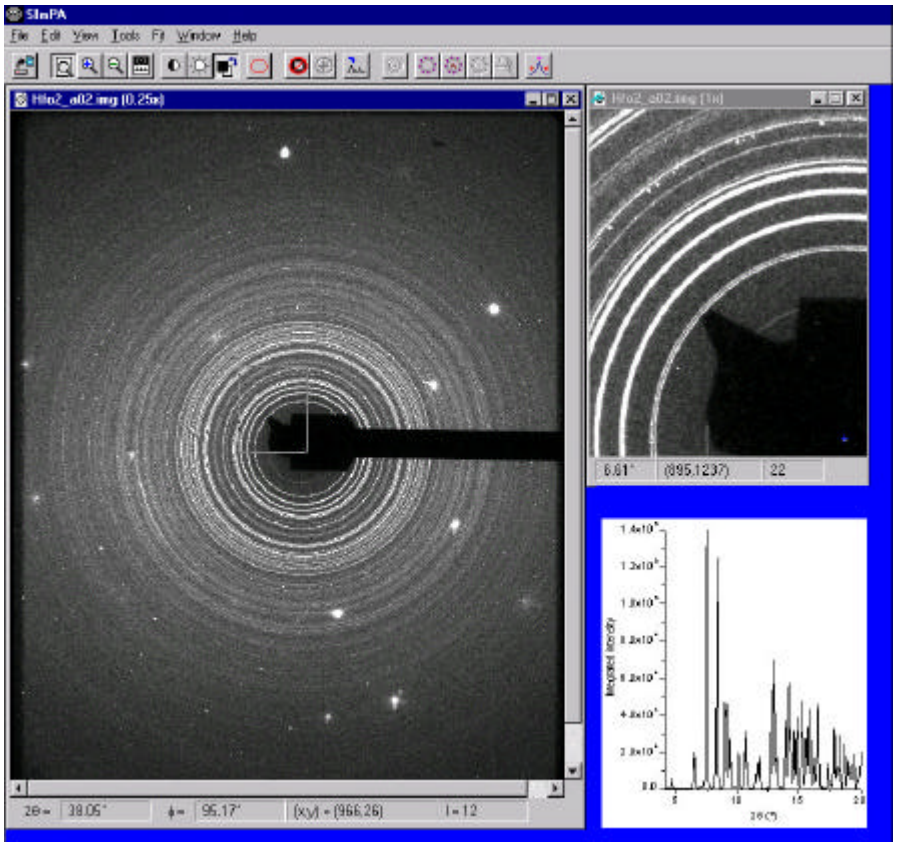

Figure 2. From the X-ray diffraction image to the diffracted intensity as a function of the Bragg angle using SimPA [1], The 2-θ plot shown here is obtained, following proper corrections and calibration, by an azimuthal summation along the Debye rings from the corresponding X-ray diffraction image recorded from polycrystalline HfO_2 at 1.2 GPa in a diamond anvil cell. The enlarged frame shows the attenuated undiffracted X-ray beam defining the center of the X-ray diffraction image and the first few Debye rings. Intense spots arise from Bragg reflections from the single crystal diamonds.

Putting it all together

High pressure in a diamond anvil cell (DAC; see Figure 1) comes at a high price: the diffracting volume is very small, typically around 100 nl. In order to record only the X-ray diffraction from the sample constrained in the DAC, it is necessary to use a microscopic X-ray aperture defining an X-ray beam impinging on the sample with a typical cross-section under 25 μm. The radiation from a double bounced Si (111) monochromator is normally utilized unfocussed, the natural divergence of synchrotron radiation and the bandwidth of the monochromator hence being the limiting factors of the X-diffraction linewidth. The complete Debye rings, resulting from the X-ray diffraction of the microscopic polycrystalline sample, are recorded on an area detector. Phosphor imaging plates are currently used. An X-ray exposure can last as long as several hours to ensure good counting statistics. To further improve the signal-to-noise ratio, all counts contained in each Debye rings are summed azimuthally, as a function of the Bragg angle measured from the center of the image indicated by the attenuated, undiffracted X-ray beam. The X-ray diffraction image processing, done by a software called SImPA [1], yields an X-ray diffraction pattern, i.e., a standard intensity *vs* 2-theta plot (see Figure 2). Experiments have been carried out so far on experimental stations where monochromatic hard X-rays are delivered, namely, D, F2, C1, and B2 lines .

Searching for ultrahard materials, the first steps

As a first example of a recent study for which ADXD at CHESS has played an important role, I will relate our first steps in searching for ultrahard materials. An initial study on Group IVB dioxides, done at CHESS using EDXD, unveiled the striking similarity between, for instance, the dense phases of ZrO_2 and HfO_2. At high pressure, both dioxides follow the same structural phase transitions over the same pressure range. The similarity between the two dioxides is normally attributed to the lanthanide contraction which give rise to the fact that Zr and Hf have equivalent sizes. In addition to similar phase diagrams, we could, for both dioxides, quench to room conditions an high-density phase occurring at pressures in excess of 30 GPa. The retrieved materials, according to the EDXD data, presented a high density and seemed to have a low compressibility. These observations could only be inferred by first determining the crystalline structure of the retrieved materials to calculate correctly both the density and the bulk modulus. Because of the low symmetry of the quench materials, ADXD was imperatively needed to solve the problem. ADXD images were recorded from the tiny amount of the pressure grown new phase and a complete structure refinement was carried out using the Rietveld method (Figure 3). Consequently, it was found that the quenched phase, for both dioxides, presented the orthorhombic symmetry (*Pnma*, Z = 4), with a reduced volume (with respect of the room conditions volume) of 0.87, and bulk moduli of 340 ± 10 and 440 ± 15 GPa, for HfO_2 and ZrO_2, respectively [2], as inferred from the measured equations of state (see Figure 4, for the case of HfO_2). For comparison, diamond has the largest bulk modulus of all known materials, namely, 455 GPa. If one assumes the relationship between bulk modulus and hardness, the new materials, synthesized by pressure, could be candidates for ultrahard materials. Other studies of dense oxides, as potentially ultrahard materials are underway. The ability to perform ADXD at CHESS is a key aspect to the success of our understanding of strong atomic bonding in dense oxides and how is it translates to hardness.

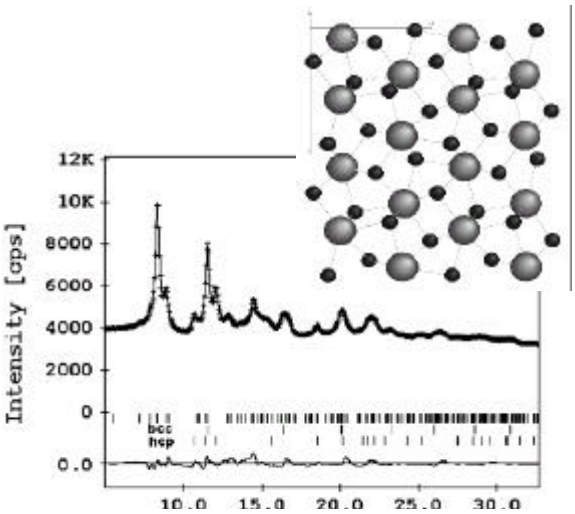

Figure 3. Rietveld refinement of a dense phase of ZrO_2. The ADXD data was acquired at the CHESS C1-line. The dense phase ZrO_2 recorded following a decompression from 65 GPa, has the *Pnma* space group with Z=4 [1] and is identical to the dense phase of HfO_2 synthesized under identical experimental conditions.

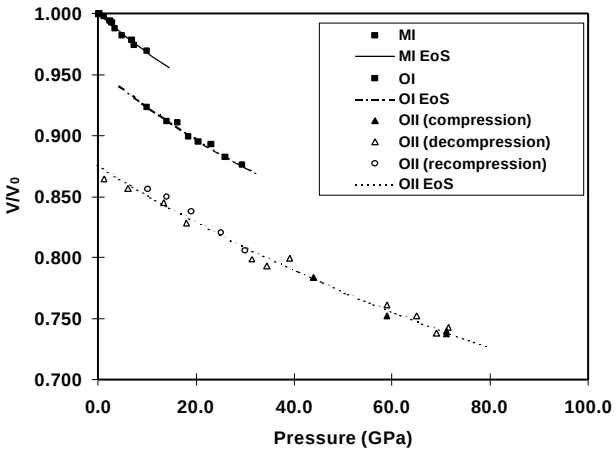

Figure 4. Relative volume change with pressure (equation of state) of dense phases of HfO_2. The high density phase, retrieved at room conditions from a pressure exceeding 70 GPa, presents a relatively high bulk modulus (B_0 = 340 ± 10 GPa) with a relative volume reduced to 0.87.

How to distort a cube

The application of pressure induces drastic instabilities in crystal lattices. The result: structural phase transitions. This is best exemplified by a recent study of dense zinc sulfide. At room conditions, ZnS is synthesized under two forms, a cubic phase also known as zincblende or sphalerite and an hexagonal phase known as wurtzite. In both forms, the coordination, the number of atomic neighbors, is identical and the atomic volumes are very close. In fact, under pressure, around 10 GPa, both forms transform readily to a very simple cubic lattice, the rocksalt structure. The pressure-induced transition is accompanied by a large volume change, of the order of 17%. As seen through the high pressure window of the diamond anvil cell under a microscope, one observes in fact a sudden contraction of single crystal of ZnS as the phase transition takes place. The same

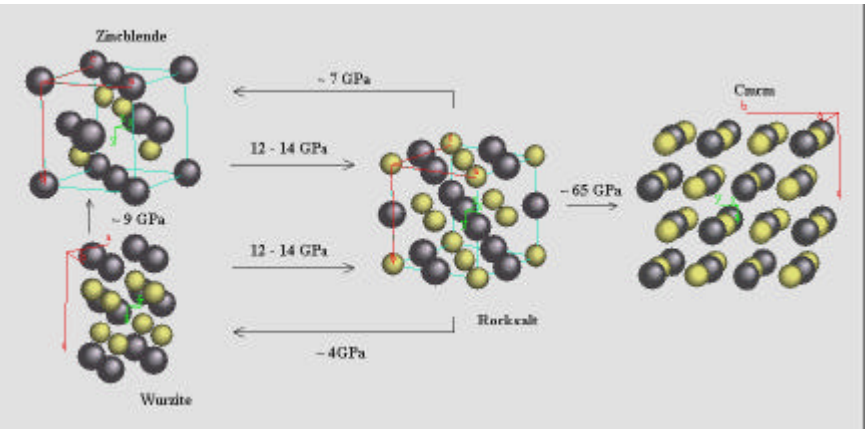

Figure 5. The sequence of crystalline structures adopted by ZnS as a function of increasing pressure.

and *c*-axis (Figure 5). The former effect is indicated by the appearance of reflections which would not otherwise be present for the cubic lattice whereas the latter yields a splitting of, for instance, the (002) and (022) cubic lines (Figure 6). Without the line resolution and the improved signal-to-noise ratio of the ADXD, the orthorhombic distortion in ZnS could not have been completely documented.

Epilogue

Angle dispersive X-ray diffraction is a key technique to study the structural modifications in dense materials. Using the equipment, software, and techniques developed in house and at CHESS, high quality structural data of samples in diamond anvil cells are now easily obtained at CHESS. The future of high pressure science at CHESS is bright. I will certainly continue to come to CHESS with my briefcase loaded with diamond anvil cells and come back with interesting and successful results. Undoubtedly, other scientists will do as well.

transition has been observed in other zinc and cadmium chalcogenides. It has also been shown recently among the chalcogenides [3], thanks to the advances in ADXD techniques using area detectors and synchrotron radiation, that pressure induces an orthorhombic distortion (*Cmcm)* of the cubic rocksalt structure. From ADXD data recorded at CHESS, we have observed and documented a similar transition in ZnS. When compressed in its rocksalt phase at pressures beyond 65 GPa, the orthorhombic *Cmcm* structure arises from a zigzag displacement of successive Zn and S atoms along the *b*-

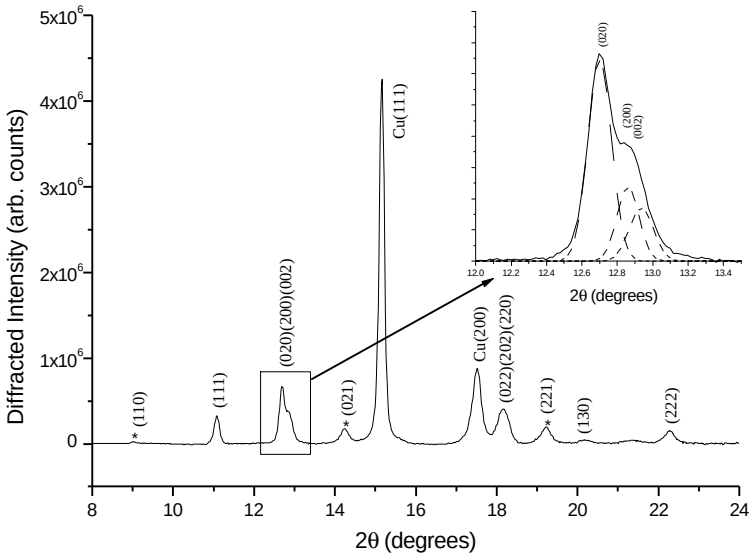

Figure 6 ADXD data indicating the orthorhombic distortion observed for pressures exceeding 65 GPa in ZnS. Lines labeled with by an asterisk arise from the displacement of atoms along the *c*- and *b*-axis and would be otherwise absent under the cubic symmetry. Note also the splitting of the (002) and (022) lines.

It is my great pleasure to acknowledge the invaluable help of Drs. K. Brister (formely at CHESS), C.-S. Zha, K. Finkelstein, and the entire CHESS staff. I am also grateful to former and present graduate students in my research group for helpful discussions, sample preparation, data acquisition, and analysis. The research presented has been mainly supported by The Natural Science and Engineering Research Council of Canada.

References

[1] Desgreniers, S. *SImPA User Guide and Tutorial* (1997); (www.physics.uottawa.ca/~lpsd/simpa/simpa.htm).
[2] Desgreniers, S. and Lagarec, K. *Phys. Rev.* B, **59**, 8467 (1999)
[3] Nelmes, R. J. and McMahon, M. I. In "*Semiconductors and Semimetals*", **54**, 145 (1998).
[4] Desgreniers, S., Lepage, I., and Beaulieu, L. *Phys. Rev.* B, **61**, 8726 (2000)