

High-Resolution Powder Diffraction Beamline

John Tse

Steacie Institute for Molecular Sciences,
National Research Council of Canada

Principal Contacts

Beamline Team Leader	John Tse SIMS, NRC John.Tse@nrc.ca
Beamline Development Scientist	De-Tong Jiang Canadian Light Source, University of Saskatchewan detong.jiang@lightsource.ca

Beamline Overview

Status	Recommended by the FAC as of December 31, 2001
Source	Insertion device
Monochromator	Double crystal
Spectral range	8–40 keV
Flux on sample	10^{13} photons/s/0.1% bandwidth
Brilliance	$\sim 10^{18}$ photons/mm ² /mrad ² /0.1% bandwidth
Resolution ($\Delta E/E$)	10^{-4}

The high-resolution powder diffraction beamline was recommended by the Facilities Advisory Committee in October of 2000, and was approved by the Board of CLSI in February, 2001. It is intended primarily for structural determination by powder diffraction of very small samples, such as materials under high pressure in a diamond anvil cell. The beamline will benefit a wide spectrum of research, both academic (materials science, chemistry, high-pressure science and geology) and industrial (materials science and pharmaceuticals).

CLSI has identified this beamline as a high priority project: construction will start when human and financial resources become available. The design team is now consulting with future CLS users, beamline scientists,

and users of high-pressure powder diffraction facilities at similar beamline installations (APS, ESRF, SPring-8, and Diamond). The team is working towards defining the insertion device source, the front-end design, and the layout of the experimental station.

Science

The CLS high-resolution powder diffraction beamline will be essential for high pressure science, a young and burgeoning area of research that owes its existence largely to the worldwide availability of high-brilliance synchrotron radiation.

High pressure is generated by the compression of a sample in a confined volume with a multi-anvil press or with a pair of opposing diamond anvils. With careful temperature control, conditions can be created in a small high-pressure cell that are similar to those in the Earth's core or those within the interiors of giant planets. This exploration of new physical and chemical phenomena will help to unravel the basic principles of the stability of matter under extreme conditions.

Beamline Team Research Activities

The following examples illustrate recent activities of Canadian researchers in the area of high pressure science. These projects are expected to continue at the CLS when the high-resolution powder diffraction beamline becomes operational. This world-class facility will trigger further important advances, not only in high pressure science but also in many other scientific disciplines.

Methane clathrate hydrate

J. Tse¹, D. D. Klug¹, J. S. Loveday² and R. J. Nelmes²

¹Steacie Institute for Molecular Sciences, NRC

²University of Edinburgh, UK

An important application of high pressure is the investigation of repulsive hydrophobic interactions between small molecules and water. Recently, the structures of several clathrate hydrates—crystals with open framework structures of water molecules and with “guest” atoms or molecules engaged in the cavities—

were studied by synchrotron X-ray and neutron powder diffraction under pressure [1]. It was found that instead of phase segregation, new crystalline structures were formed that were stable up to 10 GPa. This finding has made a significant contribution towards solving the riddle of methane on Saturn's satellite Titan.

An ice-related hydrate. The structure of one of the high-pressure hydrate phases (phase III) resolved from synchrotron X-ray and neutron powder diffraction data is particularly interesting [2]. It is a dihydrate in which a three-dimensional H-bonded network of water molecules forms channels surrounding the methane molecules (Figure 13·1). The network is closely related to that of ice Ih. The methane-water system appears to be the first in which a cage clathrate hydrate is transformed into an ice-related hydrate (or a “filled ice”). Thus, synchrotron X-ray diffraction studies of the high-pressure structures of hydrates provide experimental access to a completely unexplored regime of the guest-water interaction potential.

Solving Titan's methane riddle. The presence of methane in the atmosphere of Saturn's largest moon has been an enigma, because previous models predicted that this gas should have been destroyed long ago by photochemical processes. A study on the thermodynamic stability of methane hydrate, which was assumed to dissociate to methane and water at about 1 to 2 GPa, showed instead that the hydrate undergoes reversible phase changes and remains stable up to 10 GPa. This was an important development towards understanding gas hydrates and the evolution of conditions on Titan. The results implied that methane hydrate on Titan could have remained stable over time, eventually forming a near-surface layer that is continuously replenishing the methane in Titan's atmosphere.

The text of this report was adapted from an article in *Chemical & Engineering News*, April 9, 2001. The work was done at the SRS (Daresbury) and ISIS.

References

- [1] J. S. Loveday; R. J. Nelmes; M. Guthrie; S. A. Belmonte; D. R. Allan; D. D. Klug; J. S. Tse; Y. P. Handa. *Nature* **2001**, *410*, 661.
 [2] J. S. Loveday; R. J. Nelmes; D. D. Klug; J. S. Tse. *Phys. Rev. Lett.* **2001**, in press.

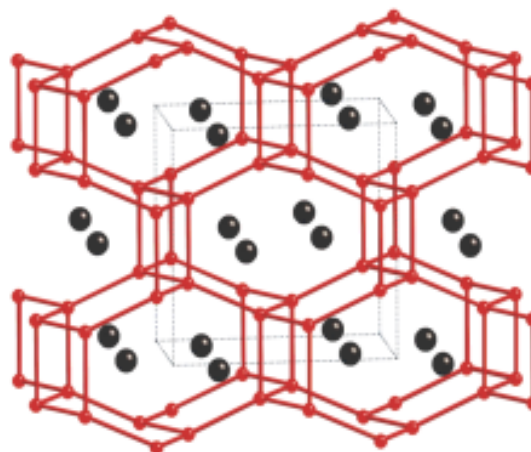


Figure 13·1 Structure of one of the high-pressure phases (phase III) of a clathrate hydrate as determined by synchrotron X-ray and neutron powder diffraction.

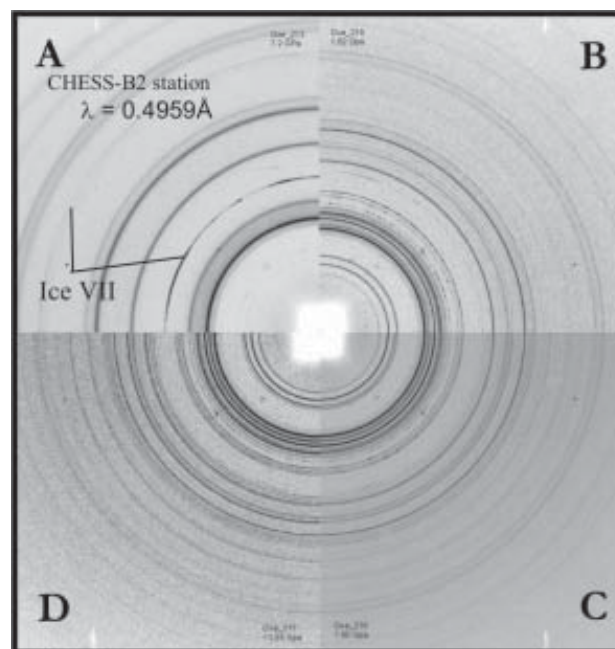


Figure 13·2 Sectors of full X-ray diffraction images of xenon hydrate under pressure in a diamond anvil cell. Sector A: at 7.2 GPa, a phase segregation is observed. Sectors B and C: at 1.60–1.62 GPa, an intermediate phase is recorded, which is derived from the structure I xenon clathrate hydrate (sector D) occurring at lower pressure.

Xenon clathrate hydrate

S. Desgreniers¹, I. Lepage¹, J. S. Tse²

and D. D. Klug²

¹University of Ottawa

²Steele Institute for Molecular Sciences, NRC

Xenon forms a H-bonded clathrate hydrate with the same crystalline structure as that of the CH₄/H₂O system. Our recent X-ray diffraction studies have shown the complete instability of the cage-forming structure (clathrate) at pressures in excess of 2.5 GPa, resulting in phase segregation to solid Xe and ice VII. The phase segregation, as inferred from the X-ray diffraction patterns, was preceded by a transition to an intermediate phase similar to the methane hydrate II phase [1]. X-ray diffraction images of the phase sequence recorded at room temperature as a function of pressure are illustrated in Figure 13-2. Structural refinement studies of the dense intermediate phase of Xe hydrate are now underway. The results could shed light on the unsolved structure of the methane hydrate II phase.

This work was performed at CHESS (Cornell U.).

Reference

[1] S. Desgreniers; R. Flacau; I. Lepage; J. Tse; D. Klug. High Pressure Studies of Clathrate Compounds. HPCr 2001 (International Workshop on Crystallography at High Pressures), Orsay, France, September 4–8, 2001.

Dense silicon clathrates

S. Desgreniers¹, W. Hou¹, D. Flacau¹, J. S. Tse²

and D. D. Klug²

¹University of Ottawa

²Steele Institute for Molecular Sciences, NRC

This was a study of the phase stability and the possible pressure-induced structural phase transitions in alkali-silicon clathrates (M-Si, with M = Na, K, and Rb). The M-Si clathrates share strong similarities with gas clathrate hydrates, since their structures are alike. Among other results, a possible unit cell instability was found in the K₈Si₄₆ compound: preliminary experimental results for the equation of state indicated a volume decrease anomaly (Figure 13-3). This anomaly could be driven by a phonon mode softening occurring at high density, as indicated by our recent calculations (Figure 13-4).

Single crystal elastic constants were extracted from the X-ray diffraction images of polycrystalline materials

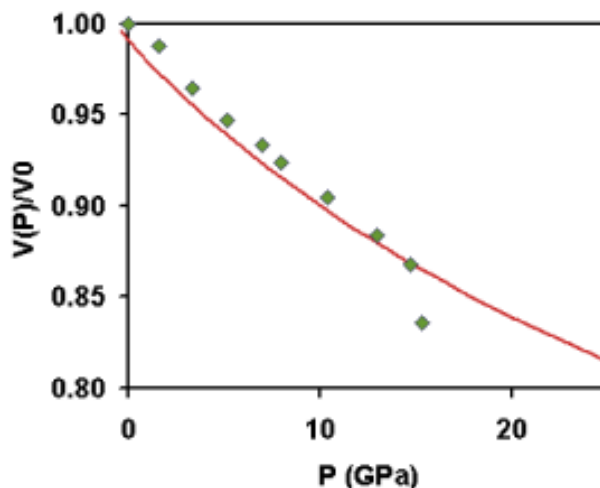


Figure 13-3 Experimental and calculated equation of state for the K₈Si₄₆ compound. A volume anomaly occurs at 16 GPa.

under pressure. Substantial progress has been made [1] in deriving the formalism needed to analyse the X-ray diffraction patterns of polycrystalline samples under non-hydrostatic pressure conditions in a diamond anvil cell. Deviatoric stresses give rise to deformations of what would otherwise be perfectly circular Debye rings. We have derived a system of equations that defines the variation of the Bragg angle as a function of the azimuthal angle (that is, along the Debye ring, for different rings) in terms of the maximum shear strength and the cubic elastic compliance tensor components

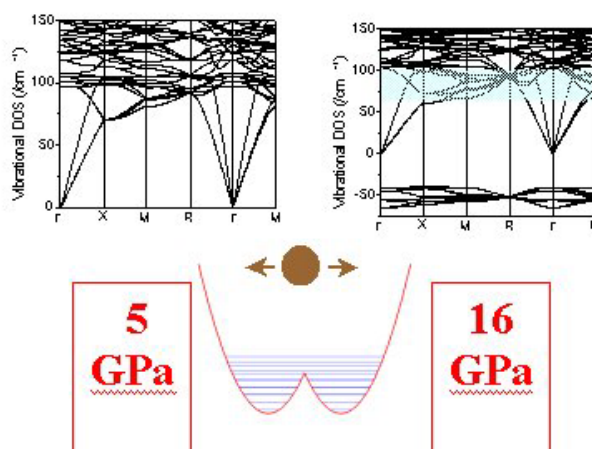


Figure 13-4 Calculations of the phonon density of states indicating a phonon softening in K₈Si₄₆ at 16 GPa.

of the material under study. A new diamond anvil cell was designed and constructed that allowed the recording of X-ray diffraction patterns from a non-hydrostatically compressed sample in a perpendicular geometry (normal to the load axis of the diamond anvil cell) through an X-ray transparent gasket. A preliminary test of the new pressure cell design was carried out at the CHESS B2 Station in May of 2001, and the first X-ray diffraction images were recorded.

These data were collected at CHESS (Cornell U.).

Reference

[1] W. Hou. M.Sc. Thesis, University of Ottawa, 2001.

X-ray diffraction of oxygen under pressure

F. Gorelli¹, L. Ulivi¹, M. Santoro¹, M. Hanfland²
and S. Desgreniers³

¹LENS, Florence, Italy

²ESRF, Grenoble, France

³University of Ottawa

Powder X-ray diffraction of pure oxygen and demixed oxygen-neon samples was carried out at the ESRF ID30 beamline at high pressure and low temperature [1]. We carefully scanned P with T fixed and T with P fixed, in the P - T range where the possible formation of O_2 dimer had been inferred by infrared spectroscopy. X-ray data analysis is still underway towards obtaining a complete mapping of the P - T phase diagram of solid oxygen.

This work was done at the ESRF (Grenoble, France).

Reference

[1] F. Gorelli; L. Ulivi; M. Santoro; M. Hanfland; S. Desgreniers. XXXIX European High Pressure Research Group Meeting, Santander, Spain, September 16–19, 2001.

Development of X-ray focusing glass capillaries

Y. Huang¹, D. Bilderback¹, J. Zha¹
and S. Desgreniers²

¹CHESS, Cornell University, Ithaca, NY

²University of Ottawa

We have been designing, fabricating, and testing glass capillaries for the purpose of focusing hard X-ray beams. The design [1] is aimed at producing a high X-ray flux into a $50 \mu\text{m}^2$ beam spot with an abrupt intensity profile

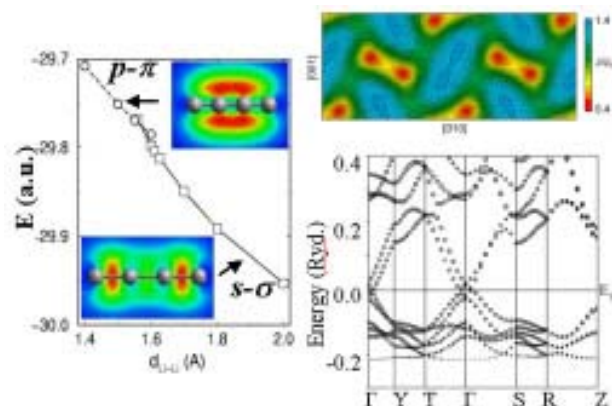


Figure 13-5 Unusual electron topology in high-pressure Li.

and a minimal (tolerable) beam divergence. Using focusing glass capillaries, we intend to make optimal use of the characteristics of the synchrotron radiation at the CHESS B2 Station. A small and intense hard X-ray beam will be required for studies of materials subjected to high pressure. The initial capillary tests have yielded very promising results: a 20-fold intensity increase at 25 keV with only twice the usual beam divergence as compared to the unfocused beam. More improvements of the glass capillary design are underway.

This work was performed at CHESS (Cornell U.).

Reference

[1] S. A. Hoffman; D. J. Thiel; D. H. Bilderback. *Opt. Eng.* **1994**, 33, 303.

Dense lithium

J. Tse and D. D. Klug

Steacie Institute for Molecular Sciences, NRC

It was found that when simple metals were compressed at high pressure, the normal notion of successive transformations into dense packing structures was not necessarily correct. For example, very diverse and even “open” structures were observed with the high-pressure phases of cesium. Recent theoretical studies by Neaton and Ashcroft (*Nature*, 2000) predicted a new symmetry-broken phase of lithium with very short $\text{Li}\cdots\text{Li}$ dimer-like contact and a very unusual charge density distribution (see Figure 13-5). We have developed a new bonding theory to explain the structures of simple alkali metals under high pressure. The essence of the theory is that

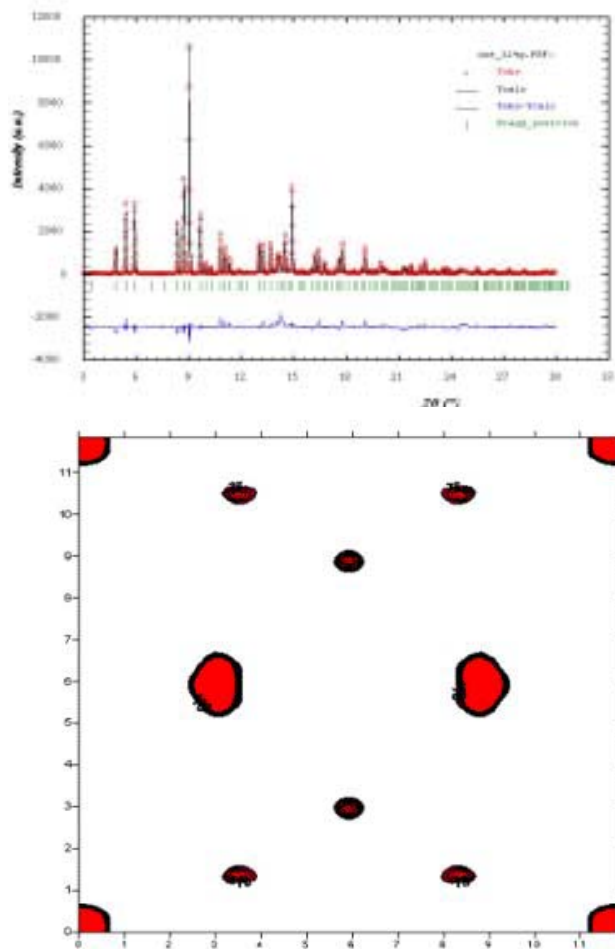


Figure 13-6 Upper figure: High-resolution X-ray diffraction data of xenon clathrate hydrate recorded at CHESS. Lower figure: xenon clathrate hydrate electron density map, obtained by the maximum entropy method.

Pauli repulsion dominates for densely packed atoms, and the valence electrons prefer to occupy interstitial space to alleviate these unpleasant interactions. In quantum mechanical terms, this is achieved by electronic transition to orbitals of higher angular momentum (higher kinetic energies), which are spatially more extended. An example is the high pressure phase of Li in which theoretical calculations show that $s \rightarrow p$ rehybridization occurs when the $\text{Li} \cdots \text{Li}$ contact is less than 1.5 Å. Consequently, instead of localizing the charge density directly along the $\text{Li} \cdots \text{Li}$ contact, the electron density is dispersed into the more open regions via p - π bonding.

This research was done at the Steacie Institute for Molecular Sciences, NRC (Ottawa).

Application of the maximum entropy method for high-density structure refinement

S. Desgreniers¹, J. S. Tse² and D. D. Klug²

¹University of Ottawa

²Steacie Institute for Molecular Sciences, NRC

The maximum entropy method (MEM) of X-ray powder diffraction analysis has proven useful in determining the electron density distribution of simple metals at very high pressure, where complete sets of structure factors are difficult to obtain experimentally.

We have applied MEM to powder X-ray diffraction patterns (recorded at CHESS) to construct the electron density maps of Xe clathrate hydrate. The MEM results are in excellent agreement with those of other methods. Electron density maps reconstructed from X-ray diffraction using MEM data were compared to computed density maps. High-resolution data recorded using synchrotron radiation were essential to the application of the MEM (Figure 13-6). MEM can be an important tool for solving the more complicated structures encountered in dense materials at high pressure, and we are pursuing its application to other materials.

Beamline Design and Beamline Team

Table 13-1 lists the design team involved in establishing endstation and beamline properties. Table 13-2 lists Canadian scientists currently active in high-resolution powder diffraction or who are potential future users. ✎

Table 13-1 XRD beamline design team

Canadian Light Source	De-Tong Jiang Emil Hallin Ingvar Blomqvist
Steacie Institute for Molecular Sciences (NRC)	John Tse Dennis D. Klug
University of Ottawa	Serge Desgreniers

Table 13-2 XRD beamline team and future users

Canadian Light Source and University of Saskatchewan	De-Tong Jiang Jeff Cutler
University of Ottawa	Serge Desgreniers
Steacie Institute for Molecular Sciences (NRC)	John Tse Dennis D. Klug