X-ray Powder Diffraction from Solid Deuterium

Recent optical studies have demonstrated that solid hydrogen exhibits three crystalline phases mainly based on the difference in the orientation of molecules (Fig. 1) [1]. In the diagram, only the crystalline structure of phase I has been determined.

Structural studies of solid hydrogen by X-ray diffraction technique are severely restricted because of the low scattering efficiency of hydrogen and the small size of the sample at high pressure. Because the intensity from a single crystal reflection is higher than that for a polycrystalline sample, the X-ray diffraction experiment with solid hydrogen was first carried out by the use of single-crystal technique at 5.4 GPa, and the crystal structure of phase I was determined to be hcp [2]. Measurements at higher pressures were impeded by the drastic reduction in diffracted intensity due to a significant reduction in the volume of the sample chamber and/or the fragmentation of a crystal under pressure. Louberyre *et al.* have overcome the difficulty with the excellent technique of growing a single crystal in helium and the application of high brilliance third generation synchrotron X-ray sources. By these means, the pressure-volume relation of solid hydrogen and deuterium have been determined to 120 GPa at room temperature [3].

In spite of the low intensity from a polycrystalline sample, the powder diffraction technique is still important because it is simple and convenient, and moreover, single crystals frequently fragment at structural transition accompanying a discontinuous change in volume.

In this work, our interest is focussed on whether or not the powder technique can be used for structural studies of solid hydrogen at high pressures and to determine the crystalline structure of phase II. The transition boundary between phase I and phase II exhibits a strong isotope effect and this shifts to a higher temperature and a lower pressure for deuterium (dotted curve in Fig. 1) [1,4,5]. The powder X-ray diffraction experiments of solid deuterium were carried out in this way.

A diamond anvil cell (DAC), with a tungsten carbide hemispheric seating and a cone-shaped aperture to detect diffracted X-rays, was used for high pressure generation. The top surface of the anvil was 0.3 mm. An Re gasket was pre-indented to 50 μm and a hole of 110 μm diameter was made as a sample chamber. The high-pressure experiments were carried out at beamline **BL10XU**. The wavelength was tuned with an Si (111) double-crystal monochromator to 0.6196 Å. An X-ray refractive lens made of molded PMMA (polymethyl methacrylate, density 1.19 g/cc) was inserted in the X-ray path to enhance the density of the incident beam. The sample was exposed to an X-ray beam through a pinhole collimator of 26 μm diameter. The cell was oscillated within ±5 deg. The typical exposure time was 30 min. The powder patterns were obtained by an angle-dispersive method with an image plate detector.

Figure 2 shows two-dimensional diffraction images from solid deuterium at 62.3 GPa and 300 K. In the figure, two different areas around the Debye-Scherrer rings are selected because the

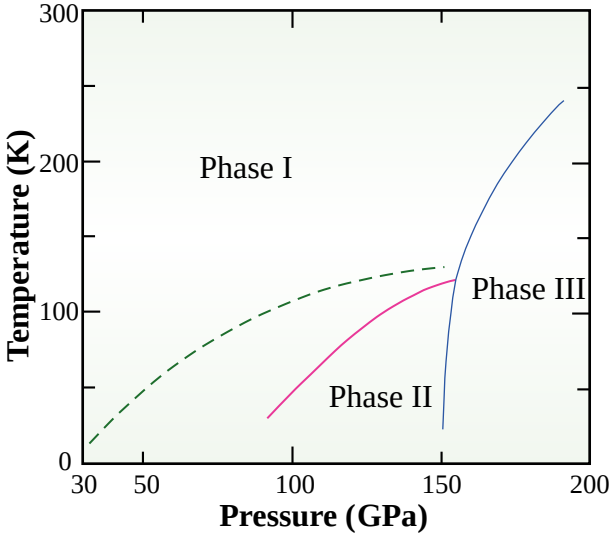

Fig. 1. Schematic phase diagram of solid hydrogen. The dashed line represents the boundary between phase I and phase II for solid deuterium.

diffraction around the ring was not uniform. Three diffraction rings from solid deuterium can be observed. These are assigned to the 100, 002 and 101 diffraction rings from an hcp lattice. There were strong arcs from the rhenium gasket. Figure 3 depicts the one-dimensional diffraction pattern integrated around the whole ring. The signal-to-noise ratio of the 101 diffraction line of solid deuterium was about 11. The lattice constants at 62.3 GPa and 300 K were a = 2.015 and c = 3.237 Å. The derived cell volume and the c / a ratio were consistent with single-crystal data [3].

The pressure cell was cooled to 83 K. During the course of cooling, pressure increased greatly to 94 GPa due to the thermal shrinkage of the body of the pressure cell. The pressure was estimated from the pressure-volume relation of the rhenium gasket because the ruby signal was lost in measurement. The pressure was slightly overestimated because of the large compressibility of deuterium, the diffraction profile, however, should be obtained from phase II. Three diffraction arcs from the sample can be observed (Fig. 4), which are also assigned to the 100, 002 and 101 diffraction lines of the hcp lattice. The lattice constants are a = 1.964 and c = 3.145 Å (c/a = 1.601). The center of each molecule is still on the hcp lattice point in phase II.

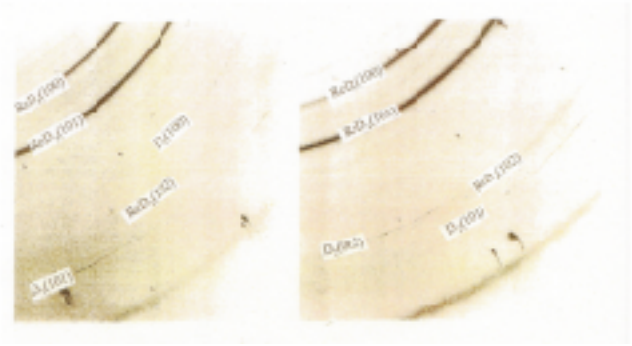

Fig. 2. Two-dimensional diffraction images from solid deuterium at 62.3 GPa and 300 K. Two different areas around the Debye-Scherrer rings are selected because the diffraction intensity was not uniform around the ring.

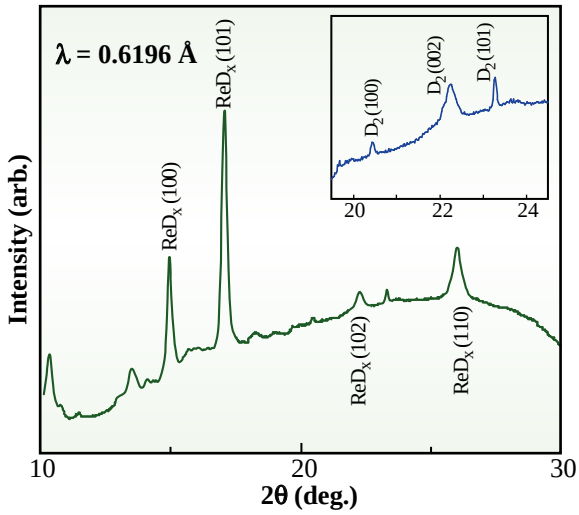

Fig. 3. Integrated one-dimensional diffraction pattern obtained at 62.3 GPa and 300 K. The inset shows an expanded scale of intensity between 2θ = 19 and 25 deg.

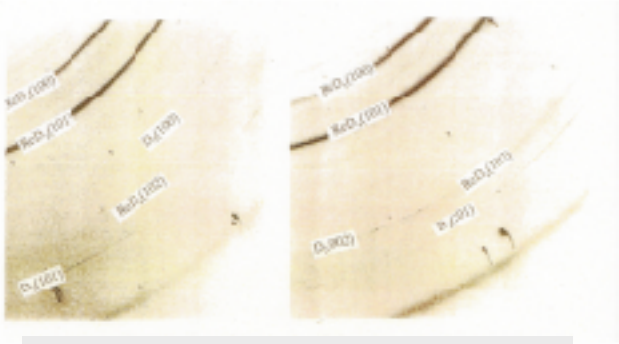

Fig. 4. Two-dimensional diffraction images from solid deuterium at 94 GPa and 83 K.

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