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X-ray powder diffraction from solid deuterium

H Kawamura[1], Y Akahama[1], S Umemoto[1], K Takemura[2], Y Ohishi[3] and O Shimomura[4]

[1] Faculty of Science, Himeji Institute of Technology, 3-2-1 Kouto, Kamigori, Hyogo 678-1297, Japan
[2] NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[3] JASRI, 1-1-1 Kouto Mikazuki, Hyogo 679-5198, Japan
[4] JAERI, 1-1-1 Kouto, Mikazuki, Hyogo 679-5198, Japan

E-mail: kawamura@sci.himeji-tech.ac.jp

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Abstract

X-ray powder diffraction from solid deuterium was first observed under high pressure at SPring-8. At pressures up to 62 GPa and room temperature, three diffraction lines (100, 002, 101) of the hcp lattice were observed. The derived cell volume and the c/a ratio were consistent with single-crystal data. At 83 K and 94 GPa, three diffraction lines were also obtained and assigned to the hcp lattice.

1. Introduction

Structural studies of solid hydrogen using the x-ray diffraction technique are very difficult 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, x-ray diffraction of solid hydrogen was first carried out by the use of the single-crystal technique at 5.4 GPa, which is just above the solidification pressure [1]. Measurements at higher pressures were impeded by the drastic reduction in the volume of the sample chamber and/or the fragmentation of a crystal under pressure. Louberyre *et al* [2] have overcome the difficulty by a sophisticated technique of growing a single crystal in helium and the application of high-brilliance third-generation synchrotron x-ray sources, and thereby the equations of state (EOSs) of hydrogen (deuterium) have been determined to 120 GPa at room temperature [2].

In spite of the lower intensity from a polycrystalline sample, powder diffraction techniques are important because the fragmentation of single crystals is frequently caused at the structural transition accompanying a discontinuous change in volume. Observations of x-ray powder diffraction from molecular hydrogen have been reported at pressures up to 50 GPa by Besedin *et al* [3]. They obtained the 101 reflection of the hcp lattice from a sample prepared by compression of hydrogen with nickel powder in a high-pressure chamber [3].

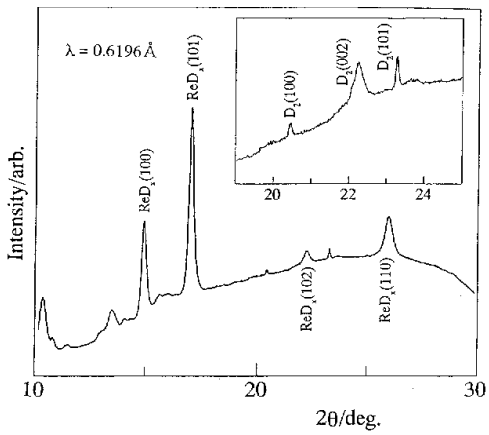

Figure 1. One-dimensional diffraction pattern obtained at 62.3 GPa and 300 K. The exposure time was 30 min. The inset shows an expanded scale of intensity between $2\theta = 19°$ and 25°.

Solid hydrogen exhibits three crystalline phases based on the differences in the orientation of the molecules [4]. The transition from phase I to II for deuterium is reported to shift to lower pressure [4–6]. In this paper, x-ray powder diffraction from solid deuterium at room temperature and low temperature is presented.

2. Experimental details

A diamond anvil cell (DAC) with a cone-shaped aperture to detect diffraction x-rays was used for high-pressure generation. The top surface of the anvils was 0.3 mm. The gasket material was rhenium with 0.25 mm thickness, pressed by the diamonds of the cell to 50 μm, and a sample hole of 110 μm was made. To fill deuterium into the sample hole in the gasket, the DAC was placed in a high-pressure vessel into which deuterium gas of 182 MPa was introduced. The x-ray diffraction experiments at room temperature and low temperature were carried out on the beam line BL10XU at SPring-8. An x-ray refractive lens made of moulded PMMA (polymethyl methacrylate, density 1.19 g cm^{-3}) 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 10°. Powder patterns were obtained by an angle dispersive method with an image plate detector. X-ray wavelength ($\lambda = 0.6196$ Å) and detector-to-sample distance (180 mm) were calibrated using a standard CeO_2 reference sample. Pressures at room temperature were determined by the ruby fluorescence method [7].

Diffraction experiments at low temperature were carried out by suspending a clamped cell in a liquid-nitrogen cryostat. Kapton film of 50 μm thickness was used for the x-ray windows of the cryostat. The temperature was measured by an Au–Fe/chromel thermocouple mounted on the upper diamond seating. The pressure at low temperature was estimated from the EOS of the rhenium gasket [8], because the ruby signal was lost in the measurements due to the usage of a Kapton window to diminish the background scattering. In this experimental run, the pressure was increased from 26.9 to 62.3 GPa at room temperature, and then the clamped cell was cooled down to 83 K.

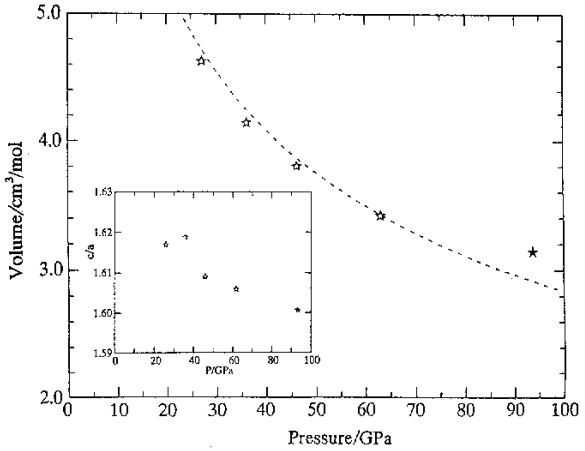

Figure 2. Pressure dependence of molar volume of solid deuterium. The 33 K EOS of the hydrogen isotopes determined from single-crystal data [2] is illustrated by the dashed curve, the inset shows the c/a ratio. Open symbols are at 300 K and closed symbols at 83 K.

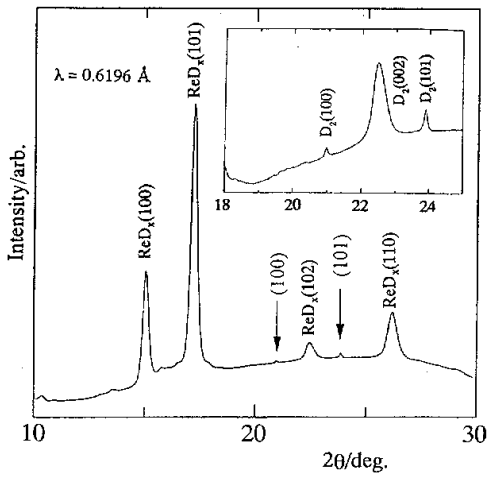

Figure 3. One-dimensional diffraction pattern obtained at 94 GPa and 83 K. The exposure time was 60 min. The inset shows an expanded scale of intensity between $2\theta = 18°$ and 25°.

3. Results and discussion

Figure 1 shows the one-dimensional diffraction pattern at 62.3 GPa and room temperature. The signal-to-noise ratio of the strongest lines from solid deuterium was about 11. The lattice constants are $a = 2.015$ and $c = 3.237$ Å. The derived cell volume and the c/a ratio at room temperature are consistent with single-crystal data [2]. Figure 2 shows the pressure dependences of the molar volume and the c/a ratio. In the figure, the 300 K EOS of the hydrogen isotopes determined from the single-crystal data is illustrated by the dashed curve [2].

Figure 3 shows the diffraction pattern at 83 K and 94 GPa. The pressure was determined from the Bragg reflections of the Re gasket at a point of 75 μm away from the centre of the anvil because the gasket immediately around the sample was expanded compared to pure rhenium due to the incorporated deuterium molecules. Three diffraction lines from solid deuterium

were observed, which are assigned to the 100, 002 and 101 lines of the hcp lattice. The lattice constants are $a = 1.964$ and $c = 3.145$ Å ($c/a = 1.601$). The molar volume and the c/a ratio are depicted in figure 2 by closed symbols. The molar volume at 83 K and 94 GPa is larger than the single-crystal data. This may be attributable to the pressure determination. The pressure to which the sample was subjected might be lower than that of the gasket because deuterium is more compressible than the gasket. The observed molar volume crosses the EOS curve at around 80 GPa. The sample, however, was compressed in a nonhydrostatic field because the pressure was strongly increased at low temperature in this experiment. In such a case, the volume obtained by our diffraction geometry apparently becomes larger, and hence the sample should be subjected to a pressure higher than 80 GPa. The diffraction pattern obtained at low temperature may thus be from phase II.

Acknowledgments

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