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Raman scattering and x-ray diffraction experiments for phase III of solid hydrogen

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Abstract. Raman scattering experiments were carried out at pressure up to 296 GPa at low temperature. The behaviors of spectral data were consistent with previous results. The frequency of the vibron, however, did not show linear pressure dependence, contrary to the previous report. Darkening of the hydrogen sample was observed above 270 GPa. The band gap closure of solid hydrogen is expected to be 400 – 450 GPa. Diffraction data of phase III were obtained with monitoring the transition into phase III by in situ measurement of Raman vibron frequencies of hydrogen.

1. Introduction
Pressure-induced metallization of solid hydrogen, which has been first predicted by Wigner and Huntington [1], is one of the most fascinating problems in high pressure physics. High-Tc superconductivity of the metallic phase predicted by Friedli and Ashcroft [2] has also stimulated the research of solid hydrogen. Optical studies due to the development of diamond anvil cell techniques have established that solid hydrogen exhibits three crystalline phases [3]. Phase I, low pressure phase, is an orientationally disordered phase and crystallizes into an hcp structure [4]. With increasing pressure at room temperature, Phase I directly transforms into Phase III, which is an orientationally ordered phase. At cryogenic temperature, solid hydrogen successively transforms from Phase I into Phase III via intermediate Phase II with increasing pressure. Structural studies of Phase III by diffraction techniques have not been reported so far. Johnson and Ashcroft have predicted that solid hydrogen becomes a molecular metal before breakdown to a monatomic solid under pressure [5]. Phase III is thus considered to be turned into metallic state at extremely high pressure.

Goncharov et al. have reported Raman scattering and visible to near-infrared absorption spectra at pressures up to 285 GPa and estimated the metallization pressure of solid hydrogen to be 325 – 495 GPa [6]. On the other hand, Loubeyre et al. have succeeded to measure the absorption edge of molecular solid hydrogen above 300 GPa and evaluated the metallization pressure to be 450 GPa by the extrapolation to 0 eV [7]. They have also reported that hydrogen becomes opaque to visible light at

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320 GPa. Recent CARS measurement of solid deuterium by Baer et al. has also estimated the metallization pressure as 460 GPa [8].

Recently, we have reached static pressures in the range of 400 GPa using a DAC with anvils of double bevel geometry and developed a diamond anvil Raman gauge up to this pressure on the basis of the primarily pressure scale; the equation of state of Pt [9, 10]. Thus, we performed Raman scattering and x-ray diffraction measurements for Phase III of solid hydrogen based on our new pressure gauge.

2. Experimental
Merrill-Bassett diamond anvil cells (MBC) were used for high-pressure generation. Diamond anvils with top surface of 120 μm and with that of 25 μm were used for diffraction experiments and Raman ones, respectively. Raman scattering experiments were carried out at pressure up to 296 GPa at low temperature of 90 K and 100 K. An He-Ne laser (632.8 nm = 1.96 eV, 35 mW) or an Ar ion laser (514.5 nm = 2.41 eV, 50 mW) was used as an excitation source for Raman measurements. X-ray experiments at 100 K were carried out using monochromatic SR source on the BL10XU station at SPring-8 with monitoring the transition into phase III by in situ measurement of Raman vibron frequencies of hydrogen. The diamond anvil Raman gauge calibrated at room temperature [10] was used to estimate pressures at low temperatures with neglecting the temperature effect.

3. Results
At the x-ray diffraction experiments, we measured vibron frequencies of hydrogen in situ to monitor the transition into Phase III and succeeded to obtain two diffraction lines of Phase III, which can be assigned to an hcp lattice. No discontinuity of their d-values was observed when crossing the II-III phase boundary with the increase in pressure. The c-axis decreases with increasing pressure, while the a-axis is almost kept constant. The constant decrease in the c-axis may be responsible for the great increase in IR absorption intensity at the II-III transition [11]. The details of the X-ray results will be described elsewhere.

![Figure 1](image-url)

**Figure 1.** Raman spectra of the main vibron (a) and lattice modes (librons) (b) of solid hydrogen at 296 GPa and 90 K.

Raman scattering experiments were carried out at pressures up to 296 GPa at low temperature. A Raman spectrum obtained at 296 GPa and 90 K is shown in figure 1. The main vibron band is shown in (a) and libron mode range in (b). The spectral feature of phase III is consistent with previous results [6, 7]; that is, large broadening of a main vibron band and ten libron modes below 900 cm⁻¹. Figure 2 shows the pressure dependence of the line width of the vibron band. The line width increases discon-
continuously at the II-III transition and rapidly increases with increasing pressure. The half width at half maximum of the band reaches to 200 cm$^{-1}$ at 296 GPa, which is also consistent with the previous result [7]. The increase in a line width is caused by the increase in an intermolecular interaction. At the II-III transition, the reorientation of molecule or the shortening of intermolecular distance might discontinuously take place.

![Figure 2](image1.png)

**Figure 2.** Pressure dependence of the line width of the main vibron. Crosses indicated previous results [6, 7]. The line is guide for eyes.

![Figure 3](image2.png)

**Figure 3.** Pressure dependence of vibron frequency. A dotted line and a cross are from previous reports of [7] and [6], respectively. The difference scale is responsible for the discrepancy.
Pressure dependence of vibron frequencies is depicted in figure 3. The vibron frequency decreased to 3355 cm\(^{-1}\) at the highest pressure of 296 GPa, which value is nearly equal to the value at 316 GPa obtained by Loubeyre et al. The frequency of the vibron, however, did not show linear pressure dependence, contrary to their result [7].

Darkening of the hydrogen sample was observed above 270 GPa. At 296 GPa, no transmitted light through hydrogen sample was observed under irradiation of an Ar ion laser (2.41 eV), while the sample scarcely transmitted the light of an He-Ne laser (1.91 eV). Thus, the exciton level of solid hydrogen is estimated around 2 eV at 296 GPa. Since the pressure determined by Loubeyre et al. [7] is overestimated by about 20 GPa compared with our pressure scale [10], the value of 2 eV at 296 GPa is coincident with the results of reference 7. This means that the metatllization pressure of 450 GPa evaluated by Loubeyre et al. should be lowered by more than 20 GPa. Further, a structural phase transition should be occurred before the band gap closing to zero, because the zero gap state is unstable due to the degeneracy of bonding and anti-bonding states. The metallization of solid molecular oxygen is a good example. The metatllization pressure of oxygen was evaluated to be 110 GPa by the extrapolation of the band gap energy to 0 eV [12]. The transition into metallic state, however, was observed at 96 GPa [13]. Thus the metatllization of solid molecular hydrogen might be occurred at pressure around 400 GPa. Metallic hydrogen will be obtained experimentally before long as static pressures obtained by the use of a diamond anvil cell are now reached to 410 GPa.

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