Raman scattering and X-ray diffraction studies on phase III of solid hydrogen

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Abstract. The structure of the phase III of solid hydrogen has been investigated from Raman scattering and X-ray powder diffraction experiments at low temperature based on the diamond anvil Raman gauge at pressures up to 300 GPa and 190 GPa, respectively. Observed splitting of low frequency Raman bands at around 230 GPa has suggested distinct lattice deformation of the hcp-like structure in phase III while X-ray diffraction data proposed that the molecular center was located in the vicinity of lattice points of hcp up to 190 GPa.

1. Introduction
Recently, the phase diagram of solid hydrogen around room temperature at multimegabar pressures has been updated by the observation of the phase IV [1-5]. The phase IV is considered to be a semiconductor with two kind of molecular sites. On the other hand, H₂ molecules in the phase III are considered to be an orientationally ordered state [6,7]. Spectroscopic studies reported the stability of phase III up to 340 GPa at low temperature below 100 K [4,8-10]. An X-ray diffraction study revealed that the molecular center in phase III was located in the vicinity of lattice points of hcp up to 183 GPa [11]. For this phase, theoretical studies predicted the transformation to metallic state without structural transitions around 400 GPa before breakdown to a monatomic solid [12,13]. Up to now, many structures are proposed for the ordered phase, such as Cmca [13,14] and C2/c [15,16]. The proposed structures basically differ in the orientation of molecules in a unit cell each other. However, the structure of phase III still remains unidentified experimentally.

Purpose of this study is to get the structural information of phase III of solid hydrogen. In this paper, we present the results of Raman scattering and X-ray powder diffraction experiments of solid hydrogen at pressures up to 300 GPa and 190 GPa, respectively and discuss the structure of phase III.

2. Experimental
Merrill-Bassett diamond anvil cells were used for high-pressure generation. Diamond anvils with typical top surface of 100 μm and 20 μm were used for diffraction experiments and Raman spectroscopy, respectively. Raman scattering experiments were carried out at pressure up to 300 GPa at low temperature of 90 K. An He-Ne laser (632.8 nm, 35 mW) or an Ar ion laser (514.5 nm, 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. Details of X-ray experiments have been described in elsewhere[11]. The diamond anvil Raman gauge calibrated by using the equation of state of Pt at room temperature [17-19] was used to estimate pressures at low temperatures.

3. Results and Discussion

3.1. Raman spectroscopy

In order to collect Raman spectra of phase III at pressure up to 300 GPa, three experimental runs were performed. Figure 1 shows the pressure change of the vibron frequency together with our previous data [10]. Present data are in good agreement with our previous results. Corresponding to the transition to phase III, the frequency drops by ~100 cm\(^{-1}\) at 165 GPa. With increasing pressure the vibron is softened with a coefficient of -5.07 cm\(^{-1}\)/GPa. However, the tendency becomes moderate above 230 GPa. The behavior, which was observed in our previous study, suggests certain change in the crystal lattice of phase III. However, the previous study at 100 K by Loubeyre *et al.* [9] has reported a linear pressure dependence up to 316 GPa. The difference in the behavior of the vibron frequency comes from the pressure determination method. Though they also used the pressure shift of the high frequency edge of the optical phonon band of the diamond anvil for pressure estimation, the pressure shift was calibrated to 200 GPa by using the pressure shift of the vibron and pressure more than 200 GPa was extrapolated from the calibration. Actually, in the present study, the vibron frequency decreases to 3355 cm\(^{-1}\) at pressure of 296 GPa but the value has been observed at 316 GPa by them. If the behaviour of the vibron above 230 GPa is true, certain change may be expected to the pressure dependence of low frequency Raman active modes.

![Figure 1.](image)

**Figure 1.** Pressure dependence of the vibron frequency together with our previous data [10]. Broken line corresponds to previous data by Loubeyre *et al.* [9] at 100 K. The vibron in phase III was softened with a coefficient of -5.07 cm\(^{-1}\)/GPa.
Pressure evolution of low frequency Raman spectrum of phase III is illustrated in figure 2. Low frequency modes, which mainly correspond to librons, are considerably broad and weak in intensity at pressure below 200 GPa. With increasing pressure, most of the bands split into two or three sharp bands at around 230 GPa. At 300 GPa eleven libron bands were identified below the frequency of 900 cm\(^{-1}\). The number of libron bands is consistent with previous studies [9,10] and may suggest a large unit cell. Since one Raman active vibron, one lattice phonon, one IR active vibron and two IR active librons have been observed up to now, the primitive cell of phase III would involved at least 4 molecules. Figure 3 shows the pressure change of frequency of observed bands. Though the frequency of each mode increases with increasing pressure, the tendency gradually becomes moderate, corresponding to the splitting around 230 GPa. The behavior is coincident with the anomaly of the vibron frequency. Clear splitting of Raman bands means asymmetrization of the hcp structure. Therefore, distinct change from the hcp-like structure occurs in phase III at around 230 GPa.

### 3.2. X-ray diffraction measurements

In order to collect X-ray powder diffraction patterns of phase III, we performed three different experimental runs in this study. The maximum pressure was extended to 190 GPa. In each run, only two diffraction peaks were observed in this phase. The observed \(d\)-values at each pressure are in good agreement with our previous report [11] shown in figure 4. The peaks correspond to the 100 and 101 diffraction lines of the hcp structure. The results meant that the molecular center is located in the vicinity of lattice points of hcp at least to 190 GPa. Therefore, assuming the hcp lattice, lattice constants \(a\) and \(c\) were estimated from the \(d\)-values. Obtained lattice constants are showed in the figure 5 as a function of pressure, together with our previous data [11]. After the II-III phase transition, the
lattice constant $c$ is more compressible compared with $a$. Present results reproduced our previous data. Considering the hydrogen molecule has an ellipsoidal shape and each molecular axis is ordered to tilt against the $c$ axis of the hcp structure, the lattice parameter, $c$ should contract. As a result, the $c/a$ ratio decreased to 1.55-1.56 at the transition and reached 1.54 at 190 GPa.

The decrease of the $c/a$ ratio in the phase III was theoretically predicted by Ashcroft [12] and Kitamura et al. [14]. According to the calculation by Kitamura et al., the $c/a$ ratio decreases from 1.583 in phase II (ordering of angular-moment states) at 130 GPa to 1.575 in phase III (classical orientational ordering of rotating hydrogen molecules) at 180 GPa because of an increase in the angle between the $c$-axis and the molecular axis. Though the present value at 190 GPa is larger than the theoretical one, the predicted behavior of the $c/a$ ratio is consistent with the present result. The decrease in the $c/a$ ratio with pressure in phase III would be related to the progress of orientational ordering, which was also inferred from the IR absorption study by Hanfland et al. [7]. The absorption intensity of IR vibron increased with increasing pressure up to 175 GPa. They pointed out that the absorption may continued to rise even further with increasing pressure above 175 GPa. Therefore, the structural behavior supports a classical feature of the orientational order of rotating hydrogen molecules for phase III [12,14,20].

![Figure 4.](image1.png)  
**Figure 4.** The $d$-values of observed two diffraction peaks from solid hydrogen at 100 K as a function of pressure together with our previous data [11].

![Figure 5.](image2.png)  
**Figure 5.** Pressure dependence of lattice constants $a$ and $c$, which were estimated from $d$-values assuming the hcp structure. Solid lines are guides to the eye.

Figure 6 shows molar volume of solid hydrogen as a function of pressure, together with our previous data [11]. The dependence shows an anomaly at the II-III phase transition. From the result, the volume reduction, $\Delta V$, of the transition was estimated to be 1% or less. The volume of the phase III is 2.33 cm$^3$/mol just after the transition and tends to show a larger decrease with increasing pressure. The tendency may result from an advance of the orientational ordering with pressure. The solid line shows the equation of state of phase I, $V_o= 23.0$ cm$^3$/mol, $K_o= 0.275(6)$ GPa, and $K'_o= 6.39(3)$, which was estimated from the pressure-volume data by a least-squares fit of Vinet fomula.
Figure 6. Molar volume of solid hydrogen as a function of pressure, together with our previous data [11]. The blue solid line shows the equation of state of phase I, $V_0 = 23.0 \text{ cm}^3/\text{mol}$, $K_0 = 0.275(6) \text{ GPa}$, and $K'_0 = 6.39(3)$.

In conclusion, from Raman scattering studies we obtained a structural information that a distinct lattice deformation of the hcp-like structure occurred at around 230 GPa in phase III. This strongly suggests necessity of X-ray diffraction experiments above the pressure for determining the structure of phase III.

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