PHYSICAL REVIEW B **82**, 060101(R) (2010)

Evidence from x-ray diffraction of orientational ordering in phase III of solid hydrogen at pressures up to 183 GPa

Yuichi Akahama,[1,*] Manabu Nishimura,[1,†] Haruki Kawamura,[1] Naohisa Hirao,[2] Yasuo Ohishi,[2] and Kenichi Takemura[3]
[1]*Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamighori, Hyogo 678-1297, Japan*
[2]*JASRI, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan*
[3]*NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

(Received 23 May 2010; revised manuscript received 15 July 2010; published 5 August 2010)

X-ray powder-diffraction experiments on solid hydrogen are performed at pressures up to 183 GPa and low temperature of 100 K. A transition into phase III is confirmed by *in situ* Raman-scattering measurements. Two diffraction peaks corresponding to the 100 and 101 lines of the hcp structure are observed above the II-III phase-transition pressure of 160 GPa, indicating that the hydrogen molecules in phases II and III are still in the vicinity of the hcp lattice point up to 183 GPa. Assuming a hexagonal structure for these phases, the lattice parameter, c decreases by 1.5% at the II-III phase transition. The behavior is consistent with a theoretically proposed feature of classical orientational ordering of rotating hydrogen molecules for phase III.

DOI: 10.1103/PhysRevB.82.060101 PACS number(s): 64.70.kt, 61.05.C−, 61.50.Ks, 62.50.−p

Optical studies have shown that solid hydrogen exhibits three crystalline phases, I, II, and III.[1] Phase I is a low pressure orientationally disordered phase that crystallizes into an hcp structure.[2] At cryogenic temperature, solid hydrogen successively transforms from phase I, via intermediate phase II, into phase III at around 160 GPa.[3] Phase III is considered to be an orientationally ordered phase due to the property of strong absorption of an IR-active vibron.[4,5] The transition from phase II to III is characterized by a large discontinuous drop in the Raman vibron frequency,[3] which shows a minor change at the transition from phase I to II.[1] From such optical behavior, the II-III phase transition has been considered to be the transition from the ordering of angular-moment states of hydrogen molecules to a classical orientational ordering of rotating hydrogen molecules and a larger change in the crystal structure has been expected. However, structural studies on phases II and III using diffraction techniques are severely restricted because of the low x-ray scattering efficiency of hydrogen and the small size of the sample at high pressure.

Up to now, two experimental studies to clarify the crystallographic structure of phase II have been reported.[6,7] In those experiments n-D_2 was used as the sample because of its low-transition pressure into phase II. We have performed x-ray powder-diffraction experiments for phase II and succeeded to obtain three diffraction lines. They are assigned to an hcp structure. We, thus, conclude that the center of each molecule is still on the hcp lattice point in phase II.[6] Goncharenko and Loubeyre[7] have performed neutron and x-ray diffraction experiments also for phase II of solid deuterium. They reported that an incommensurate peak appeared reproducibly at the I-II phase transition and proposed the structure of a unit cell with P-3 symmetry for phase II.

The ordered phase of molecular solid hydrogen is expected to become metallic at high pressure. Ashcroft and Johnson[8] have predicted that solid hydrogen becomes a molecular metal before breakdown to a monatomic solid under pressure. Up to now, many structures are proposed for the ordered phase, such as *Cmca* (Refs. 8 and 9) and $C2/c$.[10,11] The proposed structures basically differ in the orientation of molecules in a unit cell. However, the structure of phase III still remains unidentified. In this Rapid Communication, we present the results of x-ray powder-diffraction experiments of solid hydrogen at pressures up to 183 GPa and discuss the details of the II-III phase transition from the view point of the crystal structure.

Merrill-Bassett diamond-anvil cells (MBC) were used to generate high pressure. n-H_2 was loaded in the high-pressure cell using a gas-loading system operated at 180 MPa.[12] X-ray diffraction experiments at high pressure and low temperature were conducted by an angle dispersive method using a monochromatic synchrotron-radiation (SR) source (30 keV) and a cryogenic system on the BL10XU station at SPring-8.[13] After the MBC was cooled down to 100 K in the cryostat, the pressure was increased. A compound refractive lenses made from glassy carbon and SU8 polymer were used to focus light on the sample to overcome the low-scattering efficiency. Diffraction patterns were recorded on an image plate detector. High-pressure powder x-ray diffraction measurements above 100 GPa were performed for six runs of experiments. In the diffraction experiments, we performed *in situ* measurements of vibron frequencies of hydrogen to monitor the transition into phase III. The 002 diffraction line of the hcp lattice was usually missing because of strong preferred orientation and weak intensity. In one run, however, the 002 diffraction line was observed at 103 and 120 GPa. Then, the estimated errors of the lattice parameters, a and c from the 100, 002, and 101 diffraction lines were within $\pm 0.015\%$. In two runs using diamond anvils with a culet size of 120 μm diameter, the diffraction data for phase III were obtained at pressures up to 183 GPa.

Raman spectra were collected using a micro-optical spectroscopic system installed on the beamline. The excitation source was a 532 nm diode laser. A diamond Raman gauge calibrated at room temperature[14] was used to estimate pressures above 30 GPa at low temperature while neglecting the temperature effect. The temperature was measured with Si-diode resistance thermometers attached with a cell body. The obtained diffraction images were analyzed using the integration software FIT2D.[15]

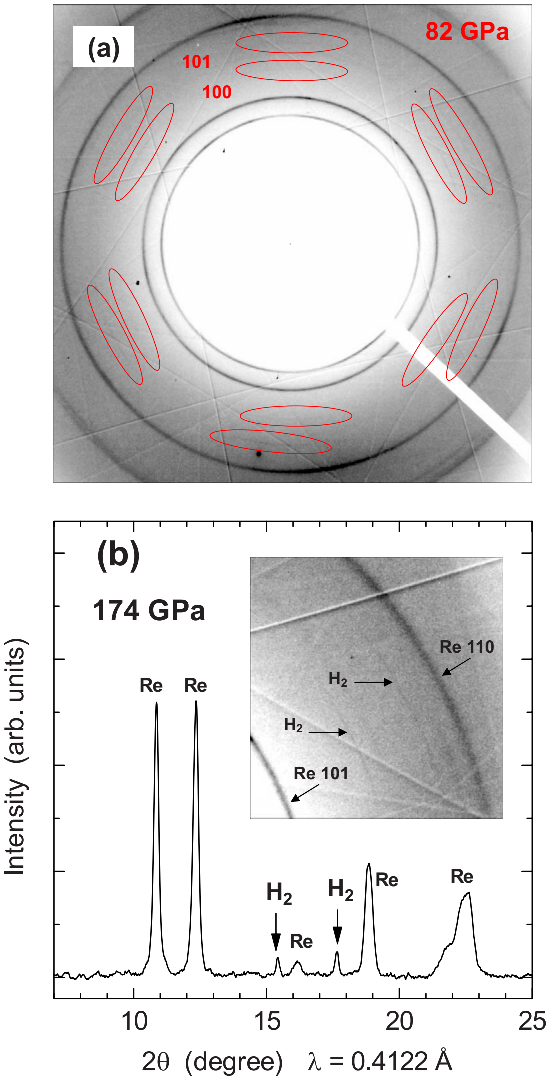

FIG. 1. (Color online) (a) Representative diffraction image of phase I of solid hydrogen recorded at 82 GPa and 100 K. The image shows a texture because of the preferred orientation of the powder sample and the Debye rings are defective. The texture maintained in phase III. This indicates a nonreconstructive mechanism for the transitions to phases II and III. (b) Typical x-ray powder-diffraction pattern of high-pressure phase III at 174 GPa. Two diffraction lines from the hydrogen sample are clearly observed. Lines labeled "*Re*" correspond to those from the rhenium metal gasket. Because the background due to Compton scattering x-ray from the diamond anvils was very strong and the intensity ratios of signal to background for the 100 and 101 lines were around 1/250 and 1/300, respectively, the background was numerically subtracted in the profile. Inset shows a part of the diffraction image at 174 GPa.

The diffraction images of solid hydrogen most commonly showed a texture because of the preferred orientation of the powder sample. The typical image shown in Fig. 1(a) corresponds to phase I of hcp at 82 GPa. The 100 and 101 reflections are clearly recorded and the 002 reflection is missing. The texture suggests that the hcp sample has a preferred orientation to the *c* axis. Namely, the *c* axis is directed along the direction of the incident x-ray beam, that is, the axial direction of the MBC. From the image it is found that the dispersion of the orientation axis is larger than ±8°. The Debye rings are defective and composed of six equivalent arcs of about 23°. This also suggests that the sample has a preferred orientation in the *c* plane of the hcp structure. With increasing pressure, two reflections corresponding to the hcp structure and their texture were maintained in phases II and III. The observation suggests a nonreconstructive mechanism for these phase transitions.[16] The sample condition also permits us to discuss the orthorhombic or monoclinic lattice distortion in phase III proposed by theoretical studies.

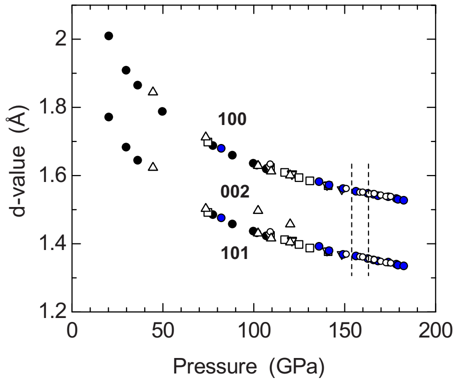

FIG. 2. (Color online) Pressure evolution of *d* values of diffraction lines from hydrogen detected in six experimental runs at 100 K. Different symbols represent the different runs. The lines corresponded to the 100 and 101 reflections of the hcp structure. Those of the 002 reflection observed at 103 and 120 GPa are also plotted.

A representative diffraction image and its one-dimensional profile in phase III obtained at 174 GPa and 100 K are shown in Fig. 1(b). The two diffraction lines from the hydrogen sample are sharp and the full width at half maximum is typically 0.13° though their intensities are weak compared with those from a Re metal gasket. The two lines correspond to the 100 and 101 reflections of the hcp structure of phase I. No diffraction peak other than the hcp structure was newly observed at pressures up to 183 GPa within the present experimental resolution. Furthermore, no splitting of diffraction peaks was detected. These results indicate that the orthorhombic or monoclinic lattice distortion is much smaller than those proposed theoretically,[11] and we can approximately consider the crystal structures of phases II and III as the hcp one.

At least the two reflection lines from solid hydrogen were detected in all six experimental runs. The collected *d* values are shown in Fig. 2; different symbols represent the different runs. The lines corresponded to the 100 and 101 lines of the hcp structure. The *d* values of these lines decrease continuously with increasing pressure, ignoring the slight scattering from run to run. In two experimental runs, diffraction patterns were successfully collected across the II-III phase boundary. In the figure, the broken lines represent the region in which Raman-active vibron lines of phases II and III coexist. The line width and relative intensity of the reflection peaks remained almost constant at the transition within the experimental accuracy. Thus, we can conclude that there is no major discontinuity of *d* values at the II-III transition. These experimental results suggest that the hydrogen molecules in phases II and III are still near the hcp lattice point

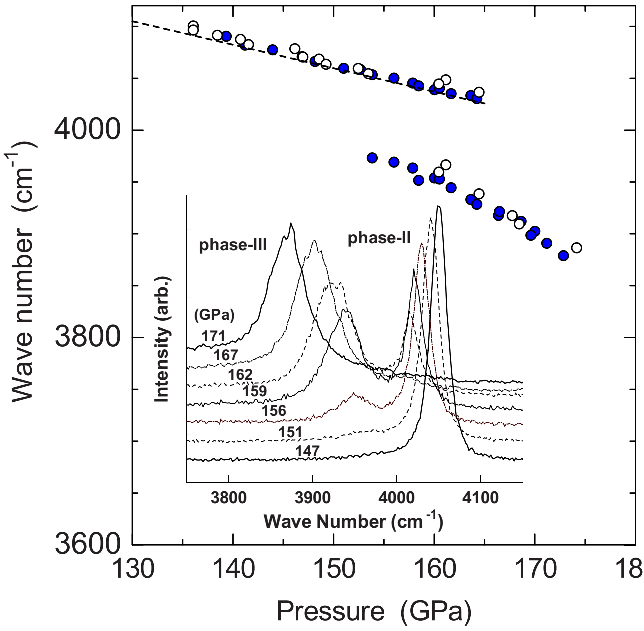

FIG. 3. (Color online) Pressure dependence of Raman-active vibron frequencies at pressures up to 175 GPa at 100 K. The Raman signal from phase III clearly appears at 156 GPa and the signal from phase II disappears at 166 GPa. Phases II and III coexisted at pressures between 155 and 166 GPa, and vibron frequency decreased by about 80 cm^{-1} at the II-III phase transition. The present results are consistent with those of a previous report shown by a broken line (Ref. 18).

and, thus, the crystal structures of phases II and III are expected to be hexagonal or slightly distorted hexagonal ones in the pressure range of the present experiments.

As mentioned earlier, the structure of phase III has theoretically been considered to be a superlattice of hcp phase I with six hydrogen molecules in the primitive cell[11] because a large number of molecular vibration modes (not less than 13) has been reported for phase III from Raman scattering and IR absorption experiments.[17,18] The structure is undoubtedly not hcp. But in this study no superlattice reflection was detected due to low signal-to-noise ratio. Therefore, we could not say more about the crystal symmetry. However, the structures of phases II and III can be approximated by a hexagonal structure in the presently studied pressure range. Accordingly, we can disclose the crystallographic aspect of the II-III transition since the transition was obviously monitored *in situ* by Raman-scattering measurements.

Figure 3 shows the results of Raman-scattering measurements to monitor the transition: Raman spectra and the pressure dependence of vibron frequencies at pressures up to 175 GPa at 100 K. The Raman signal from phase III clearly appears at 156 GPa and the signal from phase II disappears at 166 GPa. Thus, the vibron lines of phases II and III coexisted at pressures between 155 GPa and 166 GPa, and vibron frequency decreased by about 80 cm^{-1} at the II-III transition. The coexistence may come from pressure gradients in the samples. The present results are consistent with previous papers.[1,3,18]

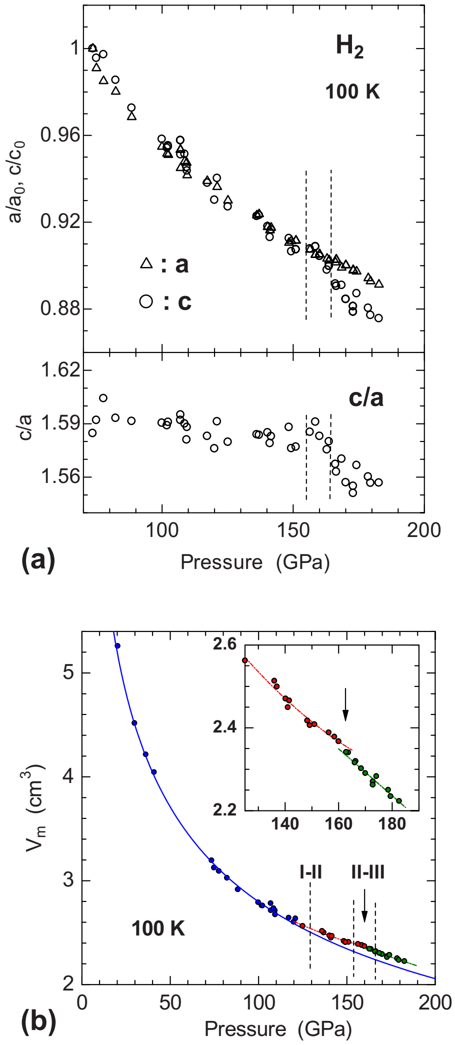

FIG. 4. (Color online) (a) Pressure dependences of lattice parameters a and c, and c/a ratio, which are determined by assuming an hcp structure for phases II and III. a and c were normalized with the values, 1.977 Å and 3.133 Å, respectively, at 73 GPa. Vertical broken lines represent the region in which phases II and III coexist. The lattice parameter c, decreases abruptly by 1.5% at the II-III phase transition. In contrast, the decreasing rate of a turns a little slower at the transition. The c/a ratio also decreases to 1.55–1.56 at the transition. (b) Pressure dependence of the molar volume. The solid line corresponds to the result of a least-squares fit of the equation of state by Vinet (Ref. 19) to the data for phase I, where the bulk modulus K_0=0.275(6) GPa and its pressure derivative K_0' =0.639(3) with the molar volume V_0=23.0 cm^3/mol at 0.1 MPa and low temperature. Dashed lines are guides for the eyes. The volume reduction, ΔV, in the II-III transition was estimated to be around 1% or less.

Assuming a hexagonal structure for phases II and III, the lattice parameters, a and c, and the c/a ratio were estimated from two diffraction peaks. The pressure dependence of a and c, which are normalized with the values 1.977 Å and 3.133 Å, respectively, at 73 GPa, are plotted as a function of pressure in Fig. 4(a). The lattice parameter, c decreases by 1.5% at the II-III phase transition. In contrast, the decreasing rate of a turns a little slower at the transition. The conflicting behavior of the lattice parameters may result in an insensible change in the pressure dependence of the d value of the 101 reflection. The decrease in c suggests a first-order transition and is responsible for the discontinuous decrease in frequency of the Raman-active vibron[1,3] and also for the great increase in intensity of infrared absorption.[4] As a result, the c/a ratio decreases to 1.55–1.56 at the transition. Considering the hydrogen molecule has an ellipsoidal shape and each molecular axis is ordered to be perpendicular to the c axis of the hcp structure, the lattice parameter, c should contract. The decrease in the c/a ratio in the phase III was first predicted by Ashcroft.[8] The theoretical calculation by Kitamura *et al.*[9] also indicated that 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. The predicted behavior of the c/a ratio is consistent with our results. Therefore, the structural behavior supports a classical feature of the orientational order of rotating hydrogen molecules for phase III.[5,8,9]

The transition boundary between phases I and II at 100 K is reported to be around 130 GPa.[1] The present result of the I-II phase transition was consistent with our previous result.[6] In the case of n-D_2, Goncharenko and Loubeyre have reported that the d values continuously decrease at the I-II phase transition with increasing pressure at constant temperature. The d value of the 002 peak, however, increases in the temperature cycle at constant pressure, and hence, the c/a ratio increases by about 0.1% at the transition.[7] The I-II phase transition is considered to be induced by a change in the quantum rotational state of molecules. Though the rotational states of n-H_2 and n-D_2 differ, similar behavior is observed. However, the present data do not show discontinuous change in the dependence of the c/a ratio within the present experimental resolution.

Figure 4(b) shows the pressure dependence of the molar volume calculated from the lattice constants. The dependence shows an anomaly at the II-III phase transition. From the result, the volume reduction, ΔV, 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.

In conclusion, in this study, we observed diffraction images from solid hydrogen at pressures up to 183 GPa by the powder x-ray diffraction technique using a third-generation SR source and presented the structural information about the II-III phase transition in terms of a crystallography; (i) the II-III transition was nonreconstructive one, (ii) the hydrogen molecules in phases II and III were still in the vicinity of the hcp lattice point at pressure up to 183 GPa, (iii) the lattice parameter, c decreased by 1.5% at the II-III transition, and (iv) the molar volume of the phase III was 2.33 cm^3/mol just after the transition. These results will provide important information for determining the crystal structure of dense hydrogen.

This work was performed under Proposal No. 2008B1216-ND2-np at SPring-8.

---

*Corresponding author; akahama@sci.u-hyogo.ac.jp

†Present address: KOBELCO Research Institute, 2222-1 Ikeda, Onoe-cho, Kakogawa, Hyogo 675-0023, Japan.

[1] H. K. Mao and R. J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).

[2] R. M. Hazen, H. K. Mao, L. W. Finger, and R. J. Hemley, Phys. Rev. B **36**, 3944 (1987).

[3] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **61**, 857 (1988); H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, *ibid.* **63**, 2080 (1989).

[4] M. Hanfland, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **70**, 3760 (1993).

[5] I. I. Mazin, R. J. Hemley, A. F. Goncharov, M. Hanfland, and H. K. Mao, Phys. Rev. Lett. **78**, 1066 (1997).

[6] H. Kawamra, Y. Akahama, S. Umemoto, K. Takemura, Y. Ohishi, and O. Shimomura, Solid State Commun. **119**, 9 (2001).

[7] I. Goncharenko and P. Loubeyre, Nature (London) **435**, 1206 (2005).

[8] N. W. Ashcroft, in *Molecular Systems under High Pressure*, edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p 201; K. A. Johnson and N. W. Ashcroft, Nature (London) **403**, 632 (2000).

[9] M. Kitamura, S. Tsuneyuki, T. Ogitsu, and T. Miyake, Nature (London) **404**, 259 (2000).

[10] C. J. Pickard and R. J. Needs, Nat. Phys. **3**, 473 (2007).

[11] J. S. Tse, D. D. Klug, Y. Yao, Y. L. Page, and J. R. Rodgers, Solid State Commun. **145**, 5 (2008).

[12] T. Kenichi, P. Ch. Sahu, K. Yoshiyasu, and T. Yasuo, Rev. Sci. Instrum. **72**, 3873 (2001).

[13] Y. Ohishi, N. Hirao, N. Sata, K. Hirose, and M. Takata, High Press. Res. **28**, 163 (2008).

[14] Y. Akahama and H. Kawamura, J. Appl. Phys. **100**, 043516 (2006).

[15] A. Hammersley, computer code FIT2D, version 10.27, reference manual, ESRF, Grenoble, France, 1998.

[16] P. Tolédano, H. Katzke, A. F. Goncharov, and R. J. Hemley, Phys. Rev. Lett. **103**, 105301 (2009).

[17] A. F. Goncharov, E. Gregoryanz, R. J. Hemley, and H. K. Mao, Proc. Natl. Acad. Sci. U.S.A. **98**, 14234 (2001).

[18] P. Loubeyre, F. Occelli, and R. Letoullec, Nature (London) **416**, 613 (2002).

[19] P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, J. Geophys. Res. **92**, 9319 (1987).