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Structural changes of filled ice Ic structure for hydrogen hydrate under high pressure

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High-pressure experiments of hydrogen hydrate, filled ice Ic structure, were performed using a diamond-anvil cell in the pressure range of 0.1–80.3 GPa at room temperature. *In situ* x-ray diffractometry (XRD) revealed that structural changes took place at approximately 35–40 and 55–60 GPa, and that the high-pressure phase of hydrogen hydrate survived up to at least 80.3 GPa. Raman spectroscopy showed that the changes in vibrational mode for the hydrogen molecules in hydrogen hydrate occurred at around 40 and 60 GPa, and these results were consistent with those of the XRD. At about 40 GPa, the intermolecular distance of host water molecules constituting the framework attained the critical distance of symmetrization of the hydrogen bond for water molecules, which suggested that symmetrization of the hydrogen bond occurred at around 40 GPa. The symmetrization might introduce some structural change in the filled ice Ic structure. In addition, the existence of the high-pressure phase above 55–60 GPa implies that a denser structure than that of filled ice Ic may exist in hydrogen hydrate. © 2008 American Institute of Physics.

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I. INTRODUCTION

Hydrogen hydrate is expected to be a workable storage medium for hydrogen molecules because it can store and release the hydrogen molecules easily with water as the only oxidation product. Hydrogen hydrate is an inclusion compound consisting of water-hydrogen system. Recently, a clathrate hydrate of hydrogen hydrate, structure II (sII), was shown to be formed at 220 MPa and 249 K.^{1–4} In sII, four hydrogen molecules and one hydrogen molecule are contained in the large cages and small cages, respectively.⁴ At room temperature, filled ice structures for hydrogen hydrates, filled ice II and filled ice Ic (Fig. 1), are formed above 0.8 GPa.^{5–7} The filled ice structures consist of ice structures that form frameworks and of guest molecules contained in voids in the frameworks. The filled ice II and the filled ice Ic are formed by including the hydrogen molecules into ice II and ice Ic, respectively. The molecular ratios of hydrogen molecules to water molecules for the filled ice II and the filled ice Ic are 1:6 and 1:1, respectively. The filled ice Ic structure (FIICs) resembles the ice VII structure. Ice VII consists of two interpenetrating ice Ic. The FIICs can be recognized as an ice VII structure in which one ice Ic is completely replaced by hydrogen molecules.⁵

The authors of previous studies reported that the filled ice II structure was synthesized at around 0.8 GPa and that the filled ice II structure was transformed to the FIICs at 2.3

GPa.^{5–7} The FIICs was maintained to 60 GPa at room temperature, and at 30–40 GPa, symmetrization of the hydrogen bond in host water molecules constituting the framework was predicted to occur.⁶ Vos *et al.*⁶ examined the O–H stretching modes of host water molecules in the FIICs by Raman spectroscopy. They estimated the pressure for the symmetrization based on the extrapolation of the frequencies, but symmetrization was not detected. Also, phase changes in the FIICs above 30 GPa have not yet been clarified. Therefore, clarifying the phase changes in the FIICs as well as the symmetrization of the hydrogen bond in hydrogen hydrate would be of interests. In this study, high-pressure experiments with hydrogen hydrate were carried out, and *in situ* x-ray diffractometry (XRD) combined with Raman spectroscopy revealed the phase changes in the FIICs above 30 GPa. We also examined the symmetrization of the hydrogen bond for host water molecules.

II. EXPERIMENT

A lever-and-spring type diamond anvil cell (DAC) was used in the high-pressure experiments. For pressure measurements, a ruby fluorescence method was used. A sample was loaded by filling the cell with distilled and de-ionized water and an air bubble. Then, the cell was placed in a gas loading vessel, in which the air bubble was replaced by supercritical hydrogen fluid (99.99999%) at 80–150 MPa. After the gas loading, the sample was compressed and hydrogen hydrate was formed by the reaction between water and fluid hydrogen. Four samples with different compositions of hydrogen

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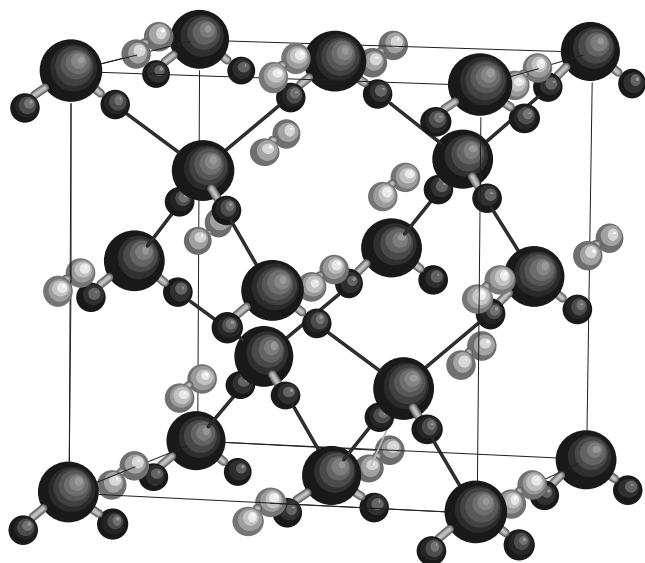


FIG. 1. A structural model of the FIcS illustrated from the structural analysis (Ref. 5). The black spheres indicate the atoms of water molecules, and the small and big ones indicate hydrogen atoms and oxygen atoms, respectively. The gray spheres indicate the hydrogen atoms of hydrogen molecules. Under high pressure, hydrogen atoms of water molecules move to the midpoint between oxygen atoms (symmetrization). After the symmetrization, water molecules dissociate to form an ionic crystal of hydrogen atoms and oxygen atoms.

and water, $H_2:H_2O=40:60$, $50:50$, $60:40$, and $70:30$, were prepared. The composition was estimated from the volumes of water and fluid hydrogen and the known molar volumes of the pure components.^{5,8} Optical microscopic observations, XRD, and Raman spectroscopy were conducted in a pressure range of 0.1–80.3 GPa at room temperature. XRD experiments were performed using synchrotron radiation on BL18C at the Photon Factory of the High Energy Accelerator Research Organization. A heating treatment for annealing of the sample was performed using a heat gun at 70.2–80.3 GPa and 490–500 K.⁹

III. RESULTS

Under an optical microscope, water and fluid hydrogen were observed to react and to form the filled ice II structure at 0.8 GPa, and at 2.3 GPa the transition to the FIcS was observed. Then, changes of the vibron, in the vibration mode, in the FIcS up to 76.1 GPa were examined by Raman spectroscopy. Figures 2(a) and 2(b) show the Raman spectra of the vibron and the variations of the Raman shift with pressure, respectively. At low pressure, only one mode of vibron for the FIcS was observed. At 42.2 GPa, a new mode of the vibron appeared at lower frequencies. This mode almost disappeared at 61.6 GPa. At 64.9 GPa, another new mode was observed at higher frequencies. The original mode of the vibron became weaker, and the new mode became stronger with pressure. In addition to the splitting, the slopes of the Raman shifts versus pressures also changed at approximately 40 and 60 GPa [Fig. 2(b)].

Figure 3 shows the representative XRD patterns observed with increasing pressure at room temperature, and variations of the d -values for the diffraction lines with pres-

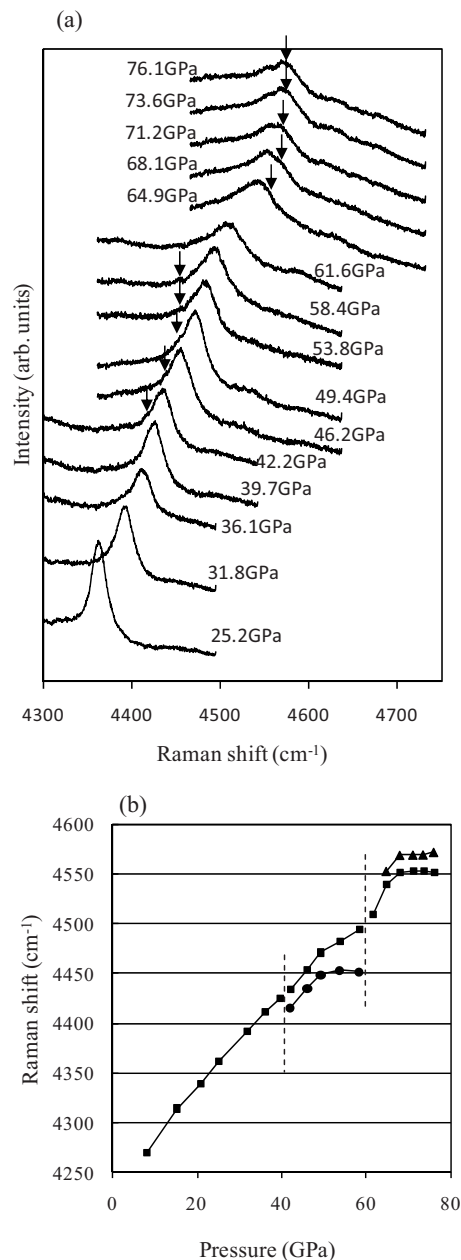


FIG. 2. (a) Representative Raman spectra of the vibron for hydrogen molecules in the FIcS. The arrows indicate the new splitting mode of the vibron. The Raman spectra were obtained with decreasing pressure. (b) Variations of the Raman shift of the vibron for the FIcS with decreasing pressure. The black squares, circles, and triangles indicate the original mode of the FIcS, the splitting mode that appeared at lower frequencies than the original one, and the splitting mode that appeared at higher frequencies, respectively. The changes in the slope of the Raman shift vs pressure were observed at approximately 40 and 60 GPa, in addition to the splitting.

sure are shown in Fig. 4(a). The XRD patterns were obtained from the sample with a composition of $H_2:H_2O=60:40$. At 3.2 GPa, the typical diffraction lines of the FIcS (111, 220, 311, 400, 331, and 422), as well as unreacted ice VII (110), were observed. The reaction of ice VII and hydrogen proceeded with time, and ice VII completely reacted at 30.8 GPa. The diffraction line of ice VII, 110, was not observed at 30.8 GPa. The diffraction lines of the FIcS became broader and weaker with increasing pressure, and only three lines of the FIcS (111, 220, and 311) were observed at 38.9 GPa.

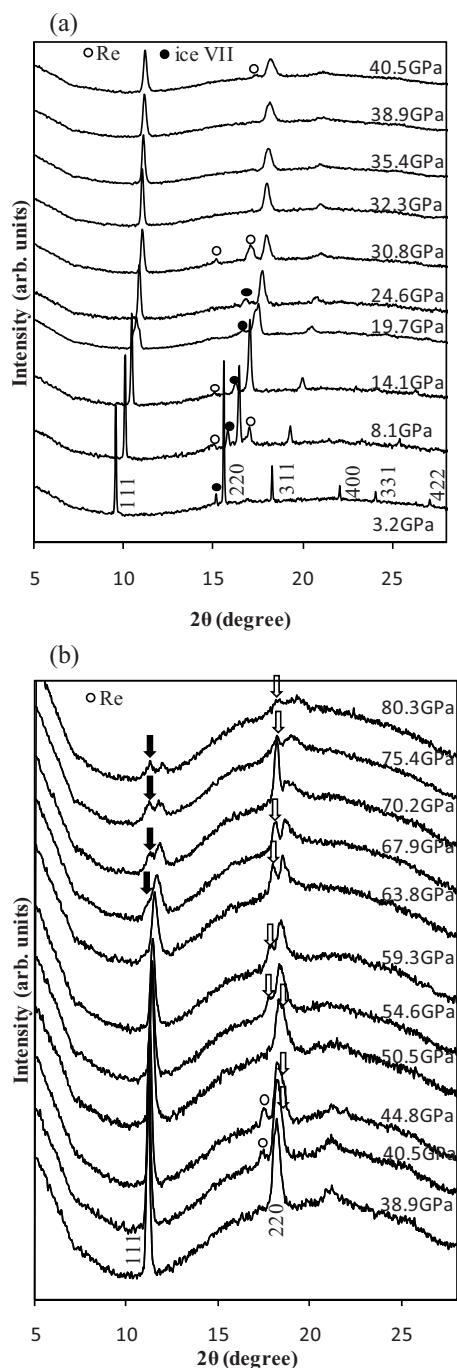


FIG. 3. Representative XRD patterns of hydrogen hydrate with increasing pressure observed from 3.2 to 40.5 GPa (a), and at enlarged patterns from 38.9 to 80.3 GPa (b). The x-ray wavelength is 0.6179 Å. The open and black circles indicate diffraction lines from the rhenium gasket and ice VII, respectively. The arrows indicate the new diffraction lines of hydrogen hydrate. Annealing treatments were carried out at 70.2, 75.4, and 80.3 GPa. After the annealing treatments, the diffraction lines became clear. At 70.2 GPa, the intensity of the new line of 220 was larger because the diffraction spots were also obtained.

Above 40.5 GPa, the XRD patterns were clearly changed. The enlarged patterns above 38.9 GPa are shown in Fig. 3(b). A splitting of the diffraction line of 220 was observed at 40.5 GPa; that is, a new line appeared at the higher angle. These diffraction lines were confirmed not to be those from a rhenium gasket.¹⁰ In the previous study,⁶ the splitting of the 220 diffraction line was also reported beyond 30–35 GPa,

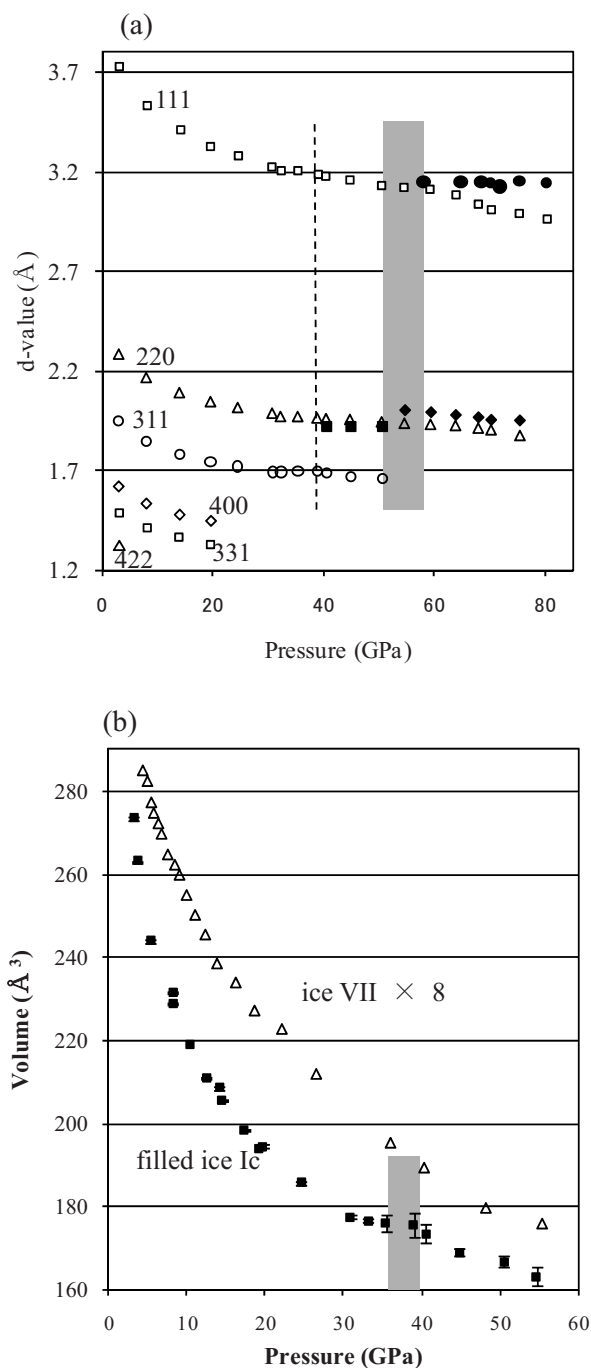


FIG. 4. (a) Variations of the d -values with pressure. The d -values for three samples were plotted together. The black marks indicate the d -values of the new diffraction lines. The gray area around 55–60 indicates the transition region. (b) The volumes of the FIIcS and the eightfold value of ice VII. The black squares and open triangles indicate the volumes of the FIIcS and the eightfold value of ice VII (Ref. 11), respectively. The lines in the black squares indicate the deviations in indexing. A change in the slope of the volume vs pressure was observed at around 40 GPa. The gray area at around 35–40 GPa indicates the transition region.

although the pressure was a little different. At 54.6 GPa, this diffraction line disappeared and another new line was observed at the lower angle of 220. In addition, at 67.9 GPa, a splitting of the diffraction line of 111 was also observed. Annealing treatment was carried out at 70.2 GPa because the XRD pattern was broad, and the splitting line of 111 was observed as a shoulder of the original one. After annealing,

the diffraction lines became clear. Above 70.2 GPa, four diffraction lines were observed up to at least 80.3 GPa.

In another sample with the composition of $\text{H}_2:\text{H}_2\text{O}=60:40$, the reproducibility of the splitting for the diffraction line of 111 was confirmed. In that experiment, the sample was kept at 62.8 GPa for two weeks, at which time the pressure was decreased to 58.1 GPa, and the new diffraction line, 111, also appeared. Therefore, the transition was thought to start between 58.1 and 62.8 GPa and to proceed with time. Figure 4(b) shows the variations of volume with a pressure change calculated as the FIcS. Above 55 GPa, the volumes could not be calculated because the main diffraction lines split above 54.6 GPa. The volume decreased continuously until 40 GPa, at which point a change in the slope versus the pressure was observed. In addition, the deviations in indexing volume became larger above 35 GPa. These results thus show that the FIcS phase transformed to a new high-pressure phase at around 35–40 GPa and that it further transformed to another high-pressure phase at around 55–60 GPa. As described above, in the Raman spectra clear changes were observed at around 40 and 60 GPa with decreasing pressure. Therefore, the Raman results were consistent with those of the XRD studies. For the structural changes in hydrogen hydrate at around 35–40 and 55–60 GPa, the similar results were obtained in the XRD and Raman studies for the other samples with the composition of $\text{H}_2:\text{H}_2\text{O}=40:60$, 50:50, and 70:30.

The phase changes observed at around 35–40 and 55–60 GPa showed that the FIcS transformed to other new structures of hydrogen hydrate, or that the FIcS for hydrogen hydrate decomposed into ice VII and solid hydrogen. In order to examine whether the FIcS decomposed or the FIcS transformed into the new structures, the XRD patterns of the samples were compared with those of ice VII, because the solid hydrogen could not be detected by a conventional XRD study. The XRD patterns of the samples were clearly different from those of ice VII. These results thus showed that the XRD patterns observed above 40 and 60 GPa were intrinsic for new high-pressure structures of hydrogen hydrate.

IV. DISCUSSION

In the present XRD studies, new diffraction lines were observed at around 40 and 55–60 GPa. In the Raman spectra, splitting of the vibron of hydrogen molecules was also observed at around 40 and 60 GPa. The splitting of the Raman spectra could be induced by the change in the number for the guest hydrogen molecules such as the saturation of the voids in the host framework. The saturation implies that some hydrogen molecules in the FIcS move to other voids in the framework, and thus that the FIcS for hydrogen hydrate partly decomposes. The decomposition of the hydrogen hydrate produces the appearance of solid hydrogen and ice VII. In the present experiments, however, additional ice VII was not observed at around 40 and 60 GPa. Therefore, the changes in vibration mode of hydrogen molecules may be induced by the structural change in hydrogen hydrate.

To examine the structural change in the FIcS at around 40 GPa, we checked the indexing of hydrogen hydrate on the

assumption that the FIcS was kept above 40 GPa. Below 33.1 GPa, the deviations between the calculated and observed d -values were less than 0.46%, indicating that the indexing as the FIcS was appropriate. Above 35.4 GPa, the deviations between the calculated and observed d -values grew to 1.42% and the deviations in volume became larger (1%–1.5%) [Fig. 4(b)]. Therefore, indexing of the diffraction lines as the FIcS above 35.4 GPa is not appropriate, which suggests that the structural change in FIcS to a new high-pressure structure may occur at around 35 GPa, although the appearance of the new diffraction line was observed at around 40 GPa. The deviations were not so large, and thus the new high-pressure structure above 35–40 GPa may be a modified structure of the FIcS.

The volumes of the FIcS were compared with that of ice VII,¹¹ because the FIcS is related to the structure of ice VII. The FIcS has a lattice parameter of almost twice that of ice VII.⁵ The volumes of the FIcS and the eightfold values of ice VII (Ref. 11) are shown in Fig. 4(b). A decrease in the volumes of the FIcS with increasing pressure was greater than the eightfold value of ice VII below 40 GPa; i.e., the compressibility of the FIcS was larger than that of ice VII. The FIcS is supported by one framework of ice Ic under external pressure, while ice VII is supported by two frameworks. This might produce a larger compressibility of the FIcS than of ice VII. However, this trend stopped at 40 GPa, and the compressibility of the FIcS became less than that of ice VII above 40 GPa. This result indicates that the framework of the FIcS for hydrogen hydrate becomes stiffer above 40 GPa. The change in the compressibility of the FIcS was also shown by a bulk modulus. Fitting by Birch–Murnaghan's equation of state below 32.3 GPa was fixed at $K'_0=4$, and V_0 and the bulk modulus K_0 were calculated to be 303 Å³ and 18.8(3) GPa, respectively. When K'_0 was not fixed at 4, the parameters were calculated as $V_0=303$ Å³, $K_0=15.7(10)$ GPa, and $K'_0=4.8(3)$, and the present values were consistent with those reported in a previous study, $V_0=304$ Å³, $K_0=15.6$ GPa, and $K'_0=4.3$.⁶ We then attempted to fit using the data from 35.4 to 54.6 GPa on the assumption that the FIcS was kept above 35 GPa. The parameters were calculated as $V_0=242$ Å³ and $K_0=62.2(8)$ GPa when K'_0 was fixed at 4. These analyses also clearly showed that the structural change occurred above 35.4 GPa and that the bulk modulus of the new structure was larger than the FIcS, although the reliability of the parameters obtained from 35.4 to 54.6 GPa was lower because few sets of data were used for the fitting above 35.4 GPa.

In a previous study, the authors predicted that symmetrization of the hydrogen bond in host water molecules would occur.⁶ Symmetrization of hydrogen bond implies that hydrogen atoms of water molecules move to the midpoint between oxygen atoms (Fig. 1). After the symmetrization, water molecules dissociate to form an ionic crystal of hydrogen atoms and oxygen atoms. Therefore, the symmetrization of hydrogen bond could induce the structural change as well as the vibrational change. Thus, the symmetrization of the hydrogen bond in hydrogen hydrate was discussed with regard to the O···O distance of the water molecules. In the case of ice VII, symmetrization of the hydrogen bond occurred when

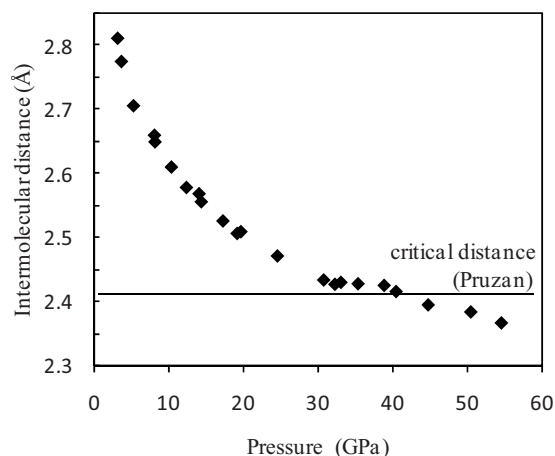


FIG. 5. The intermolecular O \cdots O distance of water molecules in hydrogen hydrate. The horizontal line at 2.42 Å is the critical distance of symmetrization (Ref. 12).

the O \cdots O distance of water molecules attained 2.42 Å, which was the critical distance.¹² The O \cdots O distance reached 2.42 Å at approximately 60 GPa in the case of ice VII,¹¹ and the symmetrization of the hydrogen bond was experimentally confirmed to occur at around 60 GPa, using IR and Raman spectroscopy.^{13–15} In the symmetrization of the hydrogen bond, the change in the compressibility of ice VII structure occurred and the bulk modulus increased.^{11,16} We examined the O \cdots O distance of the host water molecules in the present hydrogen hydrate (Fig. 5). The O \cdots O distances were calculated by the lattice parameter a as $d_{\text{O}\cdots\text{O}} = (\sqrt{3}/4)a$, on the assumption that the fcc structure of the FIcS was kept above 40 GPa. At 40 GPa, the O \cdots O distance became less than 2.42 Å, which was the critical distance. Therefore, the symmetrization for host water molecules might occur at around 40 GPa. The changes in the compressibility presently observed at around 40 GPa [Fig. 4(b)] and the changes in the bulk modulus are consistent with the features of ice VII.

Symmetrization of the hydrogen bond does not always induce structural changes. Actually, the ice VII structure does not change after the symmetrization of the hydrogen bond, although in the case methane hydrate, the present authors showed in an earlier study that the symmetrization for host water molecules might induce a structural change.⁹ A high-pressure structure of methane hydrate, filled ice Ih structure, has large spaces (tunnels), which leads to a large structural anisotropy,^{9,17,18} which might produce a structural change in the symmetrization of the hydrogen bond. In the case of hydrogen hydrate, the FIcS does not have the structural anisotropy. However, the symmetrization of the hydrogen bond might induce changes in intermolecular interactions between host water molecules and guest hydrogen molecules in the FIcS as well as an orientational ordering. These interactions were considered to produce the changes in the structures and in the vibration states in the guest molecules.

In addition to the structural change at 35–40 GPa, new diffraction lines were clearly observed at around 55–60 GPa, and in the Raman spectra, splitting of the vibron was observed at around 60 GPa. These results clearly show that hydrogen hydrate transforms to another new high-pressure structure at 55–60 GPa and that the new phase is maintained up to at least 80.3 GPa. This implies that a denser structure than that of the FIcS exists under high pressure in hydrogen hydrate.

In the present studies, the symmetrization of the hydrogen bond in the FIcS was detected by analyzing the O \cdots O distance. Our results also suggested that a denser structure than that of the FIcS above 55–60 GPa exists. These results may help in the understanding of the structural changes and the symmetrization of host water molecules in hydrogen hydrate and other gas hydrates. The analysis of the structures of the two high-pressure structures for hydrogen hydrate will be a future subject of study.

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- ¹W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, and Y. Zhao, *Science* **297**, 2247 (2002).
- ²S. Patchkovskii and J. S. Tse, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 14645 (2003).
- ³W. L. Mao and H. K. Mao, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 708 (2004).
- ⁴K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H. K. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, *Phys. Rev. Lett.* **93**, 125503 (2004).
- ⁵W. L. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, *Phys. Rev. Lett.* **71**, 3150 (1993).
- ⁶W. L. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, *Chem. Phys. Lett.* **257**, 524 (1996).
- ⁷H. Hirai, S. Ohno, T. Kawamura, Y. Yamamoto, and T. Yagi, *J. Phys. Chem. C* **111**, 312 (2007).
- ⁸R. L. Mills, D. H. Liebenberg, J. C. Bronson, and L. C. Schmidt, *J. Chem. Phys.* **66**, 3076 (1977).
- ⁹S. Machida, H. Hirai, T. Kawamura, Y. Yamamoto, and T. Yagi, *Phys. Earth Planet. Inter.* **155**, 170 (2006).
- ¹⁰H. Hirai, K. Konagai, T. Kawamura, Y. Yamamoto, and T. Yagi, *Chem. Phys. Lett.* **454**, 212 (2008).
- ¹¹R. J. Hemley, A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, *Nature (London)* **330**, 737 (1987).
- ¹²Ph. Pruzan, *J. Mol. Struct.* **322**, 279 (1994).
- ¹³A. F. Goncharov, V. V. Struzhkin, M. S. Somayazulu, R. J. Hemley, and H. K. Mao, *Science* **273**, 218 (1996).
- ¹⁴K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, *Phys. Rev. B* **54**, 15673 (1996).
- ¹⁵A. F. Goncharov, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, *Phys. Rev. Lett.* **83**, 1998 (1999).
- ¹⁶E. Sugimura, T. Iitaka, K. Hirose, K. Kawamura, N. Sata, and Y. Ohishi, *Phys. Rev. B* **77**, 214103 (2008).
- ¹⁷J. S. Loveday, R. J. Nemes, M. Guthrie, D. D. Klug, and J. S. Tse, *Phys. Rev. Lett.* **87**, 215501 (2001).
- ¹⁸H. Hirai, T. Tanaka, T. Kawamura, Y. Yamamoto, and T. Yagi, *Phys. Rev. B* **68**, 172102 (2003).