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Structural changes of filled ice Ic hydrogen hydrate under low temperatures and high pressures from 5 to 50 GPa

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Low-temperature and high-pressure experiments were performed on the filled ice Ic structure of hydrogen hydrate at previously unexplored conditions of 5–50 GPa and 30–300 K using diamond anvil cells and a helium-refrigeration cryostat. *In situ* x-ray diffractometry revealed that the cubic filled ice Ic structure transformed to tetragonal at low temperatures and high pressures; the axis ratio of the tetragonal phase changed depending on the pressure and temperature. These results were consistent with theoretical predictions performed via first principle calculations. The tetragonal phase was determined to be stable above 20 GPa at 300 K, above 15 GPa at 200 K, and above 10 GPa at 100 K. Further changes in the lattice parameters were observed from about 45–50 GPa throughout the temperature region examined, which suggests the transformation to another high-pressure phase above 50 GPa. In our previous x-ray study that was performed up to 80 GPa at room temperature, a similar transformation was observed above 50 GPa. In this study, the observed change in the lattice parameters corresponds to the beginning of that transformation. The reasons for the transformation to the tetragonal structure are briefly discussed: the tetragonal structure might be induced due to changes in the vibrational or rotational modes of the hydrogen molecules under low temperature and high pressure. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4746017>]

I. INTRODUCTION

Hydrogen and water are the most abundant materials in the universe according to the cosmic abundance of the elements. Hydrogen hydrates have been reported to be potentially ubiquitous in space objects such as proto-stars, extra-solar planets, and their satellites.^{1,2} One type of hydrogen hydrates, i.e., the clathrate structure, has recently received significant interest as an environmentally clean hydrogen storage material.^{3,4} Gas hydrates, including hydrogen hydrates, are known to form several structures that incorporate various guest species under high pressure.^{5–10} A systematic outline of the effects of pressure and guest size on the structural changes at room temperature has been proposed.^{11,12} Clathrate hydrate structures comprise host cages formed by hydrogen-bonded water molecules with encapsulated guest species.⁵ At higher pressures, some clathrate structures transform to filled ice-type structures.^{13,14} Detailed crystal data for the individual structures have been summarized from the experimental data reported.¹⁵

Three hydrogen hydrate phases are known to be stable under high pressure: a clathrate structure II (sII)² and two filled ice structures called compound 1 (C1) and compound 2 (C2).^{16,17} Structure II (sII) consists of 16 dodecahedral

cages (5¹²) and 8 hexakaidecahedral cages (5¹²6⁴). Previously, it was believed that the sII hydrogen hydrate did not form because the guest was too small, although its existence was inferred due to equilibrium data.¹⁸ Recently, the sII structure of hydrogen hydrate was successfully synthesized at low temperature and features four hydrogen molecules forming a cluster that occupies the hexakaidecahedral cages to stabilize the structure.^{2,19} The filled ice structures consist of a host ice framework that forms a H₂O sublattice and hydrogen molecules that are contained in the voids of the host ice framework. The H₂O sublattice of C1 is similar to that of ice II; thus, C1 closely resembles helium hydrate.²⁰ The sublattice of C2 has a diamond-like structure similar to ice Ic, in which hydrogen molecules occupy small voids in the H₂O sublattice (Fig. 1). C2 can be recognized as an ice VII structure with one H₂O sublattice completely replaced by rotationally disordered H₂ molecules;¹⁶ thus, the molecular ratio of hydrogen to water is 1:1. At room temperature, C1 forms above 0.9 GPa and transforms to C2 at ~2.5 GPa.

High-pressure studies of C2 of hydrogen hydrates (referred to as HH-C2 in this paper) performed at room temperature revealed interesting properties. For example, HH-C2 survived above 80 GPa with structural changes occurring at about 40 GPa and 60 GPa.^{21,22} The first structural change was explained to be relating to symmetrization of the hydrogen bond; this explanation was inferred from the lattice parameters measured via x-ray diffractometry (XRD)

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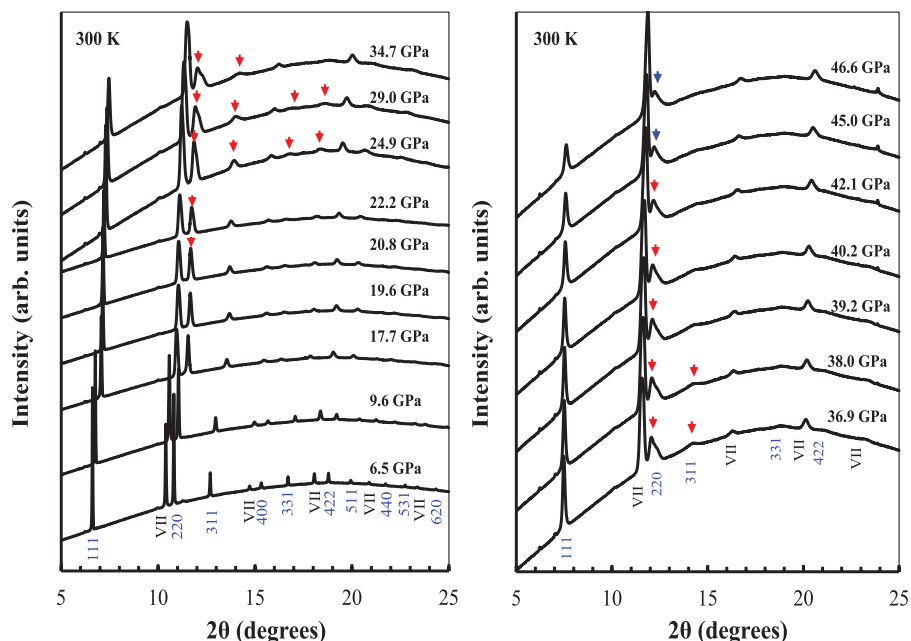


FIG. 3. Changes in XRD patterns with pressures from 6.5 to 46.6 GPa at 300 K. The 220, 311, 400, and 331 diffraction lines split above 20 GPa and 25 GPa, respectively. Above 45 GPa, the split reduced. Red arrows show the splitting diffraction lines of the tetragonal phase and blue arrows show those of the HP-phase.

III. RESULTS

Figure 3 shows representative XRD patterns with a pressure change from 6.5 GPa to 46.6 GPa at 300 K (path 1 in Fig. 2). Below 20 GPa, all diffraction lines were indexed as the HH-C2 cubic structure. Above 20 GPa, the 220 diffraction line that describes the cubic structure began to split to a higher angle; these splitting diffraction lines were indexed as 220 and 202 for the tetragonal structure. Above 24.9 GPa, splitting of the 311, 400, and 331 diffraction lines was also detected: these lines were indexed as 311 and 113, 400 and 004, and 331 and 313 for the tetragonal structure. However, the 111 diffraction line did not split at these conditions. The magnitude of splitting of the diffraction lines increased with increasing pressure until it reached its largest value at about 34.7 and 36.9 GPa; the degree of splitting of the 220, 311, 400, and 331 lines then reduced until it was barely visible at 45.0 and 46.6 GPa. At this point, another change became evident: the 111 diffraction line became asymmetric. With decreasing pressure, the peak splitting evident below 45 GPa continued until about 20 GPa; below 20 GPa, the peaks converged and the XRD patterns were the same as those of the cubic phase. The splitting and convergence of the peaks occurred reversibly with increasing and decreasing pressure, respectively. In our previous study performed at room temperature up to 80 GPa, similar splits of the 220 diffraction line above 40 GPa and the 111 line above 60 GPa were observed although the symmetry corresponding to the patterns could not be determined as fewer diffraction lines were observed in that study.²¹ The present experiments were performed at pressures up to 50 GPa at room temperature and the results are consistent with those of the previous study within the pressure range examined. Representative peak separations for the split diffraction lines are shown in Fig. 4; the splitting of the cubic single peaks into doublets is clearly shown.

Figure 5 (left) shows the changes in the XRD patterns with increasing pressure from 24.5 to 55.5 GPa at 100 K (path 4 in Fig. 2). Splitting of the 220, 311, and 400 diffraction lines was observed at 24.5 GPa, reached a maximum at 42.0 GPa, and then decreased until it was barely visible at 48.9 GPa and 55.5 GPa, at which point the 111 diffraction line became asymmetric. The changes above ~ 48.9 GPa suggest a phase transition to another high-pressure phase, as observed at 300 K. With decreasing temperature from 270 to 74 K (path 8 in Fig. 2), the 220 and 311 diffraction lines began to split below 170 K, and the split increased until 74 K. With increasing temperature from 84 to 300 K (path 9 in Fig. 2) (Fig. 5, right), the split peaks were evident until about 250 K, above this temperature they converged. At ~ 41 GPa with decreasing temperature from 300 to 90 K (path 5, Fig. 2), splitting of the diffraction lines was observed for all the XRD patterns; in contrast, at ~ 7 GPa, the diffraction lines did not split in the

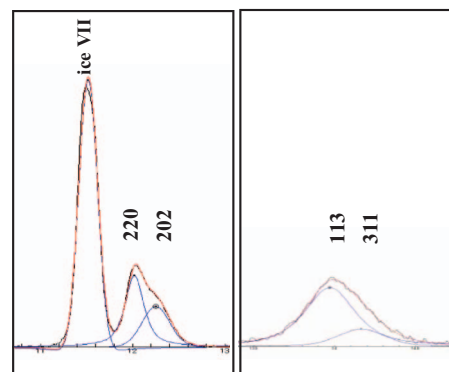


FIG. 4. Peak fitting of the split 220 and 311 peaks at 34.7 GPa and 300 K (left) and at 24.9 GPa and 300 K (right). The split peaks are indexed as a tetragonal structure.

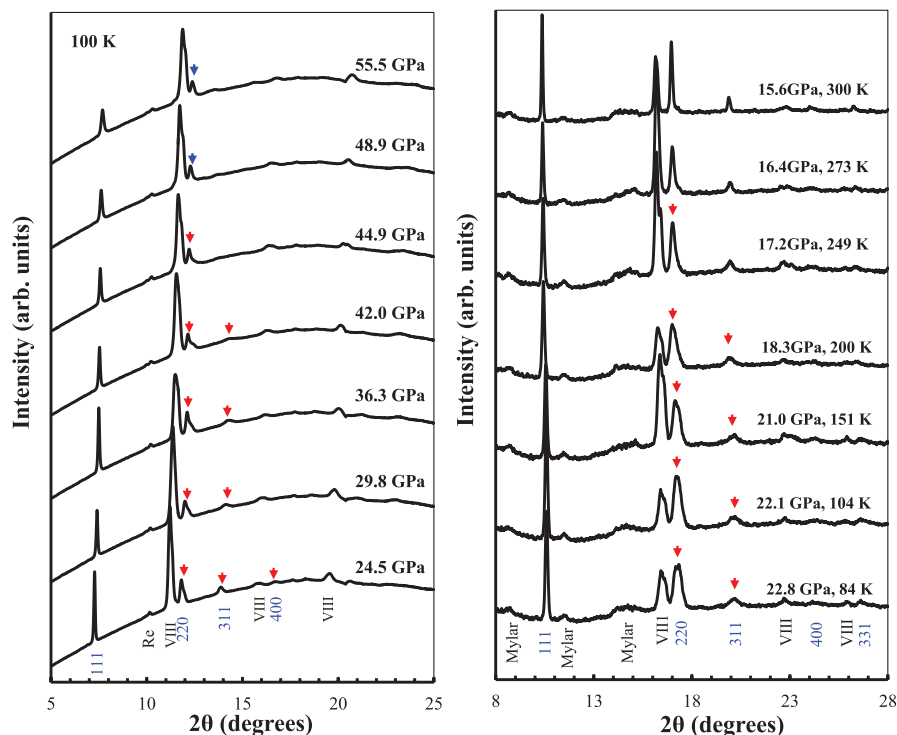


FIG. 5. (Left) Changes in XRD patterns with pressure from 24.5 to 55.5 GPa at 100 K. (Right) Changes in XRD patterns with increasing temperature from 84 to 300 K. Red arrows show the splitting diffraction lines of the tetragonal phase and blue arrows show those of the HP-phase.

temperature range of 300–30 K (path 10, Fig. 2). At 84 K, splitting was observed above 10 GPa, which illustrates that this is the pressure at which transformation to the tetragonal phase occurred. All observed phase changes are summarized in Fig. 6.

Variations of the lattice parameters with changing pressure at 300 and 100 K are shown in the top and bottom of Fig. 7, respectively. At 300 K and below 20 GPa, the structure of HH-C2 was assigned as cubic; above 20 GPa, the structure was determined to be tetragonal (Fig. 7, top). The effects of pressure on the slopes of the *a* and *c* axes differed, which suggests a change in axis ratio with pressure; the *c* axis was more incompressible than the *a* axis. The variations of the lattice parameters and the change in the axis ratio observed at 300 K were in close agreement with theoretical calculations below 45 GPa at 300 K.²⁸ At the structural transition from cubic to tetragonal at about 20 GPa, the change in volume was almost continuous, which indicates a second order transition. At 100 K, the transition to the tetragonal structure started at a lower pressure, and the *c* axis remained more incompressible than the *a* axis. Although theoretical calculations of the lattice parameters were performed only at 300 and 0 K, and not at 100 K,²⁸ the experimental values for the lattice parameters at 100 K were essentially consistent with those calculated by the theoretical study. The lattice parameters also converged again at about 55 GPa (Fig. 7, bottom); this result will be described below.

IV. DISCUSSION

All experimental results reveal that the cubic structure of HH-C2 transforms to a tetragonal structure and that this

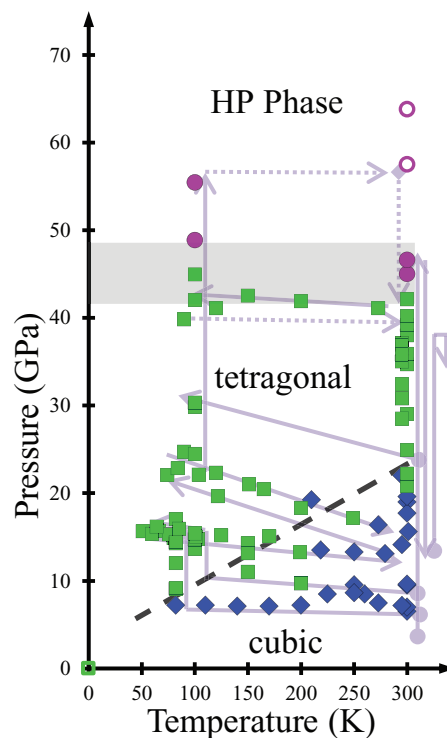


FIG. 6. Summary of phase changes. Reaction diagram incorporating all experimental data from the 11 paths of five samples. The solid blue rhombuses, green squares, and pink circles indicate the cubic, tetragonal, and high-pressure phases, respectively. The open pink circles indicate the high-pressure phase reported previously.²¹ The open green square at 0 K indicates the calculated tetragonal phase.²⁸

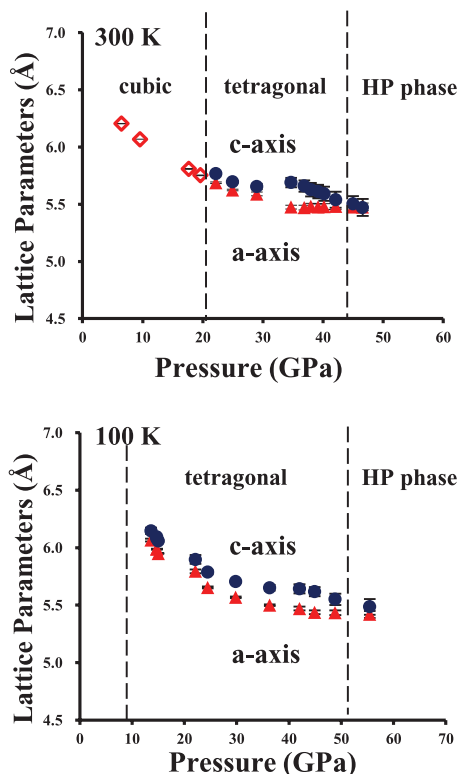


FIG. 7. Variation of lattice parameters with pressure change at 300 K (top) and 100 K (bottom).

transformation occurs over a wide low-temperature and high-pressure region (Fig. 6). From the distribution of the cubic and tetragonal structures, the boundary between the two structures can be inferred to exist along the points at ~ 20 GPa and 300 K, 15 GPa and 200 K, and 10 GPa and 100 K (represented by the dashed line in Fig. 6). The observed lattice parameters and axis ratios are in good agreement with those of the theoretical study below ~ 45 GPa; the phase above 50 GPa is discussed next. The experimental results confirmed the existence of a HH-C2 tetragonal structure and also the effect of pressure and temperature on the axis ratio. Thus, the present study experimentally confirms the predictions of the theoretical study.²⁸ Recently, a low-temperature phase that was either tetragonal or trigonal was found in a narrow pressure range from 0.3 to 0.8 GPa between sII and HH-C1.²⁴ However, the XRD patterns in the present study were completely different from those reported. These differences cannot be explained by the pressure shift. The tetragonal XRD patterns in the present study are modified from that of cubic HH-C2; therefore, they resemble that of cubic HH-C2. In contrast, the positions of the diffraction lines were completely different in the XRD patterns in that study,²⁴ which suggests another structure. Therefore, the present tetragonal phase is completely different from that reported in the previous study.²⁴

As for the phase above ~ 50 GPa, there is a difference in the results between the present experiments and the theoretical calculations.²⁸ The lengths of the *a* and *c* axes of the tetragonal structure converge again at ~ 45 and 50 GPa at 300 and 100 K, respectively, within the present experimental conditions (Fig. 7). In contrast, the theoretical calculations predicted the difference in the *a* and *c* axes to begin to ap-

pear at ~ 20 GPa, then gradually increase with pressure, and then above 55 GPa the axes are largely separated, although the lattice parameters were calculated as the same tetragonal structure.²⁸ The experimentally observed conversion of the lattice parameters suggests the beginning of a phase transition to another high-pressure phase rather than just a change in the axis ratio within the tetragonal structure, as claimed by the theoretical study.²⁸ In our previous study up to 80 GPa at room temperature, changes in the XRD patterns were observed despite the lower XRD quality: The 220 line similarly split to a higher angle at ~ 40 GPa, converged at ~ 50 GPa, and then split again above 55 GPa but to a lower angle; the 111 line also split above 60 GPa.²¹ That study clearly showed the presence of another high-pressure phase above 50 GPa at room temperature. Thus, the change observed at about 45–50 GPa in the present study likely corresponds to the beginning of the phase transition to the high-pressure phase, as previously observed. Since the present experimental conditions were limited to below 50 GPa, the phase boundary between the tetragonal phase and the high-pressure phase was not clearly elucidated. Details of the high-pressure phase have not yet been clarified.

A possible reason for the formation of the tetragonal structure is discussed below. In our previous study, the change detected at 40 GPa was thought to be caused by a structural change induced by the symmetrization of the hydrogen bond. This supposition was based only on the oxygen–oxygen distances that were estimated from a cubic lattice parameter and not from experimentally determined atomic positions.²¹ However, in the present experiments a similar transformation to the tetragonal structure at 20 GPa and 300 K, 15 GPa and 200 K, and 10 GPa and 100 K was observed. If this change is induced by symmetrization of the hydrogen bond, the present results imply that this occurs at very low pressures in the low temperature region. However, at such low pressures, the oxygen–oxygen distance is much longer than that expected for symmetrization of the hydrogen bond.³¹ Therefore, there must be a more reasonable explanation for the change to the tetragonal structure. The vibrational modes of the hydrogen molecules in the cubic HH-C2 structure are thought to be rotationally disordered at ambient conditions;¹⁶ however, changes in the rotational or vibrational modes of the hydrogen molecules are likely to occur at low temperature and high pressure. It is possible that such changes may induce deformation of the cubic lattice.

The reasons for the transformation of HH-C2 to a tetragonal structure have not yet been fully elucidated. To further explore this issue, Raman spectroscopy should be performed to determine the vibrational and rotational modes of the hydrogen molecules, and further neutron study and theoretical calculations are also required.

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