Retention of filled ice structure of methane hydrate up to 42 GPa

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High-pressure experiments on methane hydrate were performed in the pressure range of 0.2–42 GPa using diamond-anvil cell. *In situ* x-ray-diffraction study revealed that methane hydrate of a high-pressure form, filled ice structure, survived up to 42 GPa. Pressure versus volume data were obtained in the pressure region. The filled ice structure represented large anisotropic compressibility and the volume change attained 40% at 42 GPa. The anisotropic compressibility was explained by the characteristic channel framework of the filled ice structure.

I. INTRODUCTION

Methane hydrate, referred to as "fiery ice," is considered a fruitful natural resource on the Earth and is also thought to be the dominant constituent of the outer planets and their moons. Gas hydrates consist of hydrogen-bonded water molecules forming cages and of included guest molecules or atoms in these cages. Under ambient pressure, two typical structures, structure I (sI) and structure II (sII), and a hexagonal structure (sH) containing a large guest molecule have been described.[1–3] It is already known that the hydrate structure is selected by the size of the guest molecules under ambient pressure. However, high-pressure studies, in contrast to the selection rule, have demonstrated that small guest species such as N_2, Ar, and even H_2 selected sII. The 16-hedra cages in such sII structures are occupied by two N_2 molecules,[4] by two Ar atoms,[5] and by a cluster of four H_2 molecules,[6] respectively. In addition, several different structures, i.e., a hexagonal structure, a tetragonal structure, and an orthorhombic filled ice structure were found for methane, argon, and other hydrates under high pressure.[7–13] In the case of methane hydrate, well-known structure I was transformed to a hexagonal caged structure at approximately 1.0 GPa, and the caged structure collapsed at above 2 GPa, thus transforming into a filled ice structure.[7,10,14] The filled ice structure was related to the ice I_h structure, and methane molecules filled the channels of an ice I_h-like structure.[15] Other recent studies have shown that argon hydrate and nitrogen hydrate finally transformed into the identical filled ice structure at approximately 1.0 and 1.6 GPa, respectively, although these hydrates represented different low-pressure structures and medium-pressure structures from those of methane hydrate.[8,9,16] These findings suggest that the filled ice structure is a common, stable structure at pressures above 1–2 GPa in the case of gas hydrates; the guest sizes of these gas hydrates range between that of argon and methane. Of particular interest in this regard would be to determine whether or not a "post filled ice structure" exists under additional

higher pressure and how the hydrogen bonds change under such high pressure; this would be of interest from the point of view of basic material science in water-methane system, as well as from the perspective of planetary science. To date, the understanding of methane hydrate remains limited at pressures below 10 GPa. The present study describes the high-pressure behavior of methane hydrate at pressures above 10 GPa by using a diamond-anvil cell (DAC) and x-ray diffractometry (XRD); the filled ice structure of methane hydrate survived at pressures of up to 42 GPa with large anisotropic compressibility.

II. EXPERIMENTS

A lever-and-spring-type DAC was used in these high-pressure experiments. The ruby fluorescence method was used for the pressure measurements. The XRD experiment was performed using synchrotron radiation on BL-18C and BL-13A at the Photon Factory, High Energy Accelerator Research Organization (KEK). A monochromatized beam with a wavelength of 0.061 98 nm was used. The initial material was methane hydrate powder, which was prepared using a conventional ice-gas interface method under the following conditions: 15 MPa and $-3\,°C$. This powder consisted of almost pure methane hydrate with full occupancy, according to gas chromatography and a combustion analysis. The sample powder was placed into a gasket hole in a vessel cooled by liquid nitrogen in order to prevent the decomposition of the sample. The sample was sealed by loading the anvils to approximately 0.2 GPa at a low temperature, and then the DAC was warmed to room temperature. The XRD study and optical observations were conducted at room temperature in a pressure range from 0.2 to 42 GPa.

III. RESULTS

The representative XRD patterns observed with increasing pressure are shown in Fig. 1. In the pressure region be-
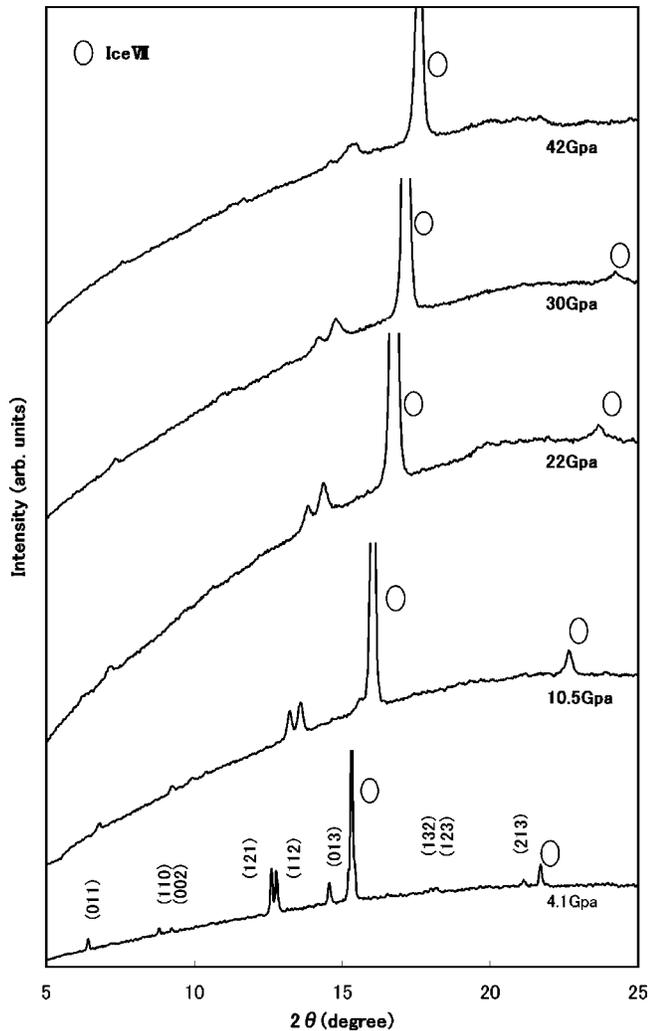
FIG. 1. Representative XRD patterns with increasing pressure.

FIG. 2. Variation in volume ratios (V/V_0) with pressure.

FIG. 3. (a) Changes in unit-cell parameters, a, b, and c axes with pressure. Solid square, solid triangle, and solid circle indicate b, c, and a axis, respectively. (b) Filled ice structure, illustrated based on the structural analysis (Ref. 15). The large tunnels perpendicular to the c axis and four-membered rings along the a axis are observed.

low 2 GPa, the initial structure I of methane hydrate (MH-sI which was called MH-I[10]) became hexagonal structure [MH-sH (MH-II[10])] at approximately 1.0 GPa and was further transformed into an orthorhombic filled ice structure [MH-iceI$_h$ (MH-III[10])], as has previously been noted.[7,10,14] Up to a pressure of 20 GPa, the XRD patterns of the filled ice structure were clear. The diffraction peaks became broader, but the typical diffraction peaks (e.g., 011, 110, 002, 121, and 112) of the filled ice structure were observed until 42 GPa. Solid methane was not detected in the pressure region examined. Under an optical microscope, no additional phase changes were observed at pressures above 2 GPa. At 42 GPa, the sample was heated at 150 °C for 12 h by placing the entire DAC in an oven in order to reduce inhomogeneous strain due to uniaxial compression, and also in order to examine the stability of the filled ice structure at 42 GPa. After the heating, the diffraction pattern became somewhat clear, and solid methane did not appear. This result suggests that the filled ice structure is stable at 42 GPa. With decreasing pressure, the filled ice structure reverted to the MH-sH (MH-II) at approximately 2.0 GPa and to MH-sI (MH-I) at 1.0 GPa. These low-pressure structures were reproduced even after the compression of 42 GPa, and the same
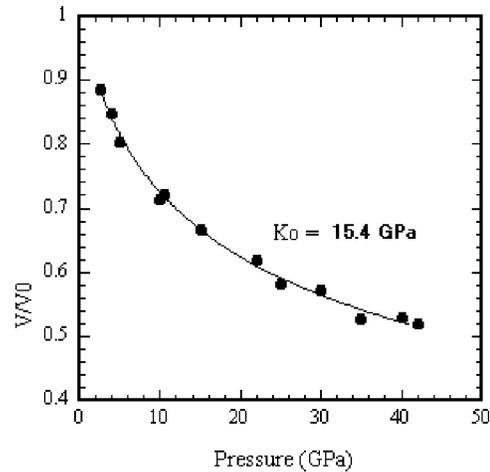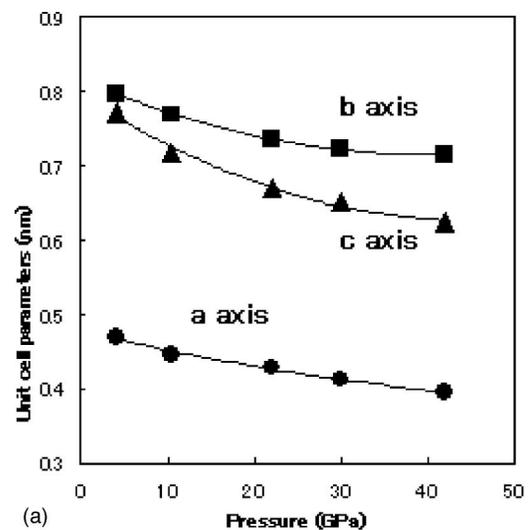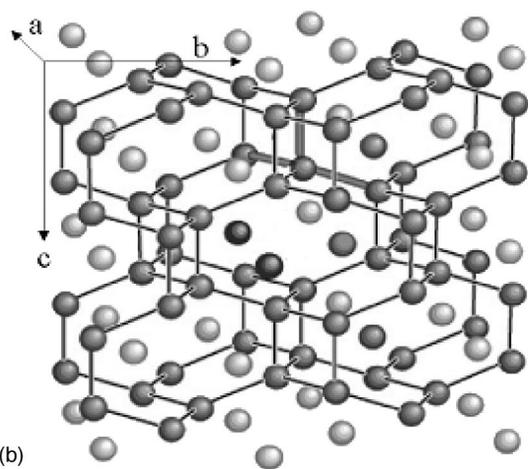
TABLE I. Unit-cell parameters at high pressures obtained by the present experiment and the theoretical calculation (Ref. 18).

Pressure (GPa)	a obs (nm)	b obs (nm)	c obs (nm)	Volume (nm^3)
4.1	0.4687	0.7974	0.7704	0.2879
10.5	0.4446	0.7685	0.7165	0.2448
22.0	0.4276	0.7350	0.6691	0.2103
30.0	0.4125	0.7226	0.6517	0.1942
42.0	0.3953	0.7148	0.6239	0.1762
Pressure (GPa)	a cal (nm)	b cal (nm)	c cal (nm)	Volume (nm^3)
3.0	0.4665	0.7932	0.7815	0.2892
10.0	0.4407	0.7594	0.7123	0.2384
20.0	0.4221	0.7316	0.6703	0.2070
30.0	0.4101	0.7127	0.6458	0.1888
40.0	0.4011	0.6983	0.6280	0.1759

result was observed with good reproducibility for seven experimental runs.

IV. DISCUSSION

To confirm the reliability of the pressures measured, the relationship between the pressure and the volume of ice VII coexisting with the filled ice was compared with an established relationship of ice VII that had been reported previously.[17] The present data were closely superimposed on that relationship, indicating that the pressures measured were sufficiently reliable. Figure 2 shows variation in volume ratios (V/V_0) with pressure for the filled ice structure. It is of note that the volume change reached 40% at 42 GPa. Fitting by Birch-Murnaghan's equation of state as $K' = 4$, and the bulk modulus K_0, was calculated to be 15.4(5) GPa. In the previous paper by the present authors, the bulk modulus was calculated to be 25 GPa,[7] although the method of calculation was same. Considering the bulk modulus of ice VII, 23.7GPa,[17] the present value is appropriate. And, the present value is consistent with that reported, 15.2 GPa.[15]

The changes in the unit-cell parameters with pressure are shown in Fig. 3. A considerable difference in compressibility was observed among the axes; the c axis was dominantly shortened, compared to the a and b axes; the a axis was less shortened than the b axis. This anisotropic compressibility was not caused by nonhydrostatic compression as described later, but rather by an intrinsic property. The filled ice structure is similar to that of ice I_h when viewed along the c axis.[15] Both structures are composed of the layers with six-membered rings of water molecules, the rings of which form hexagonal channels running along the c axis. But the manner of interlayer linkage differs between the filled ice structure and ice I_h. In the case of ice I_h, the water molecules in a six-membered ring are linked to the upper and lower layers alternatively, whereas in the case of the filled ice structure, three adjacent water molecules in a ring are linked to the

upper layer, and the other three adjacent atoms are linked to the lower layers. Such a linkage manner consequently forms large spaces (tunnels) perpendicular to the c axis,[15] which may lead to the larger compressibility of the c axis, as was observed. On the other hand, this type of linkage in a filled ice structure results in belts with four-membered rings along the a axis, which differs from the belts with six-membered rings in ice I_h. The water molecules in the four-membered rings are closely linked. The smaller compressibility of the a axis may be due to the belts with the four-membered rings. Very recently, a theoretical calculation using the first-principle molecular-dynamics method reported that the filled ice structure of methane hydrate was maintained at pressures of up to 80 GPa.[18] That study also showed anisotropic compressibility among the axes. The unit-cell parameters obtained by the present experiment and by the theoretical calculation are given in Table I. Both data show good agreement. Although the present experiments were conducted under conditions of nonhydrostatic compression, the results were consistent with the theoretical calculations under conditions of ideal hydrostatic compression.

Under such extremely compressed state, it is speculated that symmetrization of hydrogen bonds might occur in the filled ice structure as predicted by the theoretical study.[18] Another example involving symmetric hydrogen bonds was reported in a clathrate hydrates, H_2O-H_2.[19] That clathrate has water molecules in an arrangement similar to pure ice I_c and VII, in which the symmetric hydrogen bonds are produced in the pressure range of 30 to 40 GPa.[19] It is of interest that symmetrization of hydrogen bonds occurs at significantly lower pressure than that for pure H_2O.[20,21] As regards methane molecules, the intermolecular distances of methane molecules were speculated to become very short, because these distances determined at 3 GPa, i.e., 0.3852 and 0.4053 nm,[15] were already shorter than the typical van der Waals diameter of methane molecules. Thus considerable interac-

tion might have taken place between the methane molecules and also between the methane and the water frameworks, which might be related to the retention of the structure at such high pressures.

The present finding that the filled ice structure of methane hydrate survives at pressures of up to 42 GPa leads to a new understanding on ice-related material science. The retention of methane hydrate at such high pressures could influence the modeling of internal structures and evolution of outer planetary bodies such as Uranus and Neptune. A spectroscopic verification of the symmetric hydrogen bonds will be a future work.

[1] E.D. Sloan, *Clathrate Hydrates of Natural Gases*, 2nd ed. (Marcel Dekker, New York, 1998), p. 11.

[2] G.A. Jeffrey, *Inclusion Compounds*, edited by J.L. Atwood, J.E. D. Davies, and D.D. MacNichol (Academic, London, 1984), p. 150.

[3] J.A. Ripmeester, J.S. Tse, C.I. Ratcliffe, and B.M. Powell, Nature (London) **325**, 135 (1987).

[4] W.F. Kuhs, B. Chazallon, P.G. Radaelli, and F.J. Pauer, J. Inclusion Phenom. Mol. Recognit. Chem. **19**, 65 (1997).

[5] H. Itoh, J.S. Tse, and K. Kawamura, J. Chem. Phys. **115**, 9414 (2001).

[6] W.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).

[7] H. Hirai, Y. Uchihara, H. Fujihisa, M. Sakashita, E. Katoh, K. Aoki, K. Nagashima, Y. Yamamoto, and T. Yagi, J. Chem. Phys. **115**, 7066 (2001).

[8] H. Hirai, Y. Uchihara, T. Kawamura, Y. Yamamoto, and T. Yagi, Proc. Jpn. Acad., Ser. B: Phys. Biol. Sci. **78**, 39 (2002).

[9] H. Hirai, Y. Uchihara, Y. Nishimura, T. Kawamura, Y. Yamamoto, and T. Yagi, J. Phys. Chem. B **106**, 11 089 (2002).

[10] J.S. Loveday, R.J. Nelmes, M. Guthrie, S.A. Belmonte, D.R. Allan, D.D. King, J.S. Tse, and Y.P. Handa, Nature (London) **410**, 661 (2001).

[11] I-Ming Chou, A. Sharma, R.C. Burruss, J. Shu, H.K. Mao, R.J. Hemley, A.F. Goncharov, L.A. Stern, and S.H. Kirby, Proc. Natl. Acad. Sci. U.S.A. **97**, 13 484 (2000).

[12] A.Y. Manakov, V.I. Voronin, A.V. Kurnosov, A.E. Teplykh, E.G. Larionov, and Y.A. Dyadin, Dokl. Phys. Chem. **378**, 148 (2001).

[13] A.V. Kurnosov, A.Y. Manakov, V.Y. Komarov, V.L. Voronin, A.E. Teplykh, and Y.A. Dyadin, Dokl. Phys. Chem. **381**, 303 (2001).

[14] H. Shimizu, T. Kumazaki, T. Kume, and S. Sasaki, J. Phys. Chem. B **106**, 30 (2002).

[15] J.S. Loveday, R.J. Nelmes, M. Guthrie, D.D. Klug, and J.S. Tse, Phys. Rev. Lett. **87**, 215501 (2001).

[16] J.S. Loveday, R.J. Nelmes, D.D. Klug, J.S. Tse, and S. Desgreniers (unpublished).

[17] R.J. Hemley, A.P. Jephcoat, H.K. Mao, C.S. Zha, L.W. Finger, and D.E. Cox, Nature (London) **330**, 737 (1984).

[18] T. Iitaka and T. Ebisuzaki, Phys. Rev. B (to be published).

[19] W.L. Vos, L.W. Finger, R.J. Hemley, and H.K. Mao, Chem. Phys. Lett. **257**, 524 (1996).

[20] K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, Phys. Rev. B **54**, 15 673 (1996).

[21] A.F. Goncharov, V.V. Struzhkin, M.S. Somayazulu, R.J. Hemley, and H.K. Mao, Science **273**, 218 (1996).