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High-pressure structures of methane hydrate observed up to 8 GPa at room temperature

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Three high-pressure structures of methane hydrate, a hexagonal structure (str.A) and two orthorhombic structures (str.B and str.C), were found by *in situ* x-ray diffractometry and Raman spectroscopy. The well-known structure I (str.I) decomposed into the str.A and fluid at 0.8 GPa. The str.A transformed into the str.B at 1.6 GPa, and the str.B further transformed into the str.C at 2.1 GPa which survived above 7.8 GPa. The fluid solidified as ice VI at 1.4 GPa, and the ice VI transformed to ice VII at 2.1 GPa. The structural changes occurring with increasing pressure were observed reversibly with decreasing pressure. The symmetric stretching vibration, ν_1 , of the methane molecule observed in the Raman spectra changed along with the structural changes. The bulk moduli, K_0 , for the str.I, str.A, and str.C were calculated to be 7.4, 9.8, and 25.0 GPa, respectively. The difference in the bulk moduli implies the difference in fundamental structure of the high-pressure structures. © 2001 American Institute of Physics. [DOI: 10.1063/1.1403690]

I. INTRODUCTION

Methane hydrate, containing guest methane molecules in cages of hydrogen bonded water molecules, lies globally under the oceans.¹ Methane hydrate is called “burning ice” and is a promising natural resource, while at the same time methane is a greenhouse gas that plays the most prominent role in global warming. In addition, outer planets and their satellite such as Uranus and Ganymede are thought to be composed partly of ice and methane hydrate. Many studies, therefore, have been carried out from wide viewpoints such as phase relations²⁻⁴ crystal structures,⁵⁻¹² physical properties,^{2,13} and nature of hydrogen bonding.¹⁴ Most of these studies, except for a few,¹⁴⁻¹⁶ were made at low temperature under ambient pressure. Therefore, high-pressure studies above 1 GPa have to be more intensively pursued to explore new materials in water-methane system, as well as, to survey their possible occurrence on the outer planets. Recently, the present authors reported an *in situ* x-ray diffraction study of methane hydrate at pressures of up to 5.5 GPa using a diamond anvil cell (DAC).¹⁷ This study showed that the structure I (str.I) of methane hydrate survived until 2.3 GPa by changing its cage occupancy. Another high-pressure study by x-ray diffractometry and Raman spectroscopy reported transformations to a hexagonal structure via the structure II.¹⁸ The other work by neutron and x-ray diffractometry described existence of a hexagonal structure and a orthorhombic structure.¹⁹ The discrepancy in the transition behavior is probably affected by kinetic conditions such as compression rate and the initial

state of the sample. Therefore, further experiments with a reduced compression rate are required, as are those at higher-pressure regions.

In order to clarify the structure changes for clathrate hydrate, it is necessary to pursue not only the fundamental structure (the framework built up by cages) but also the vibration state of the guest molecules. For this purpose, it is required for the specimens to be characterized by x-ray diffractometry and Raman spectroscopy. The Raman spectrum resulting from the totally symmetric stretching vibration, ν_1 , of enclathrated methane can be used as a probe for their cage size and the occupancy.²⁰⁻²² In this study, both *in situ* observations of x-ray diffractometry (XRD) and Raman spectroscopy were carried out for the same samples, and three high-pressure structures, a hexagonal structure (str.A) and two orthorhombic structures (str.B and str.C) were found at higher pressure. As well, the fundamental structure of the str.A was examined.

II. EXPERIMENT

A lever and spring-type DAC was used in the high-pressure experiments. In order to control pressures lower than 2 GPa and the compression rate, several pairs of soft springs were used. Pressure measurements were made by the ruby fluorescence method. The accuracy of the present measurement system is 0.1 GPa, taking the resolution of the spectrometer and the analytical procedure into account. The pressure measurements were carried out several times, and an average of three reasonable values among them was

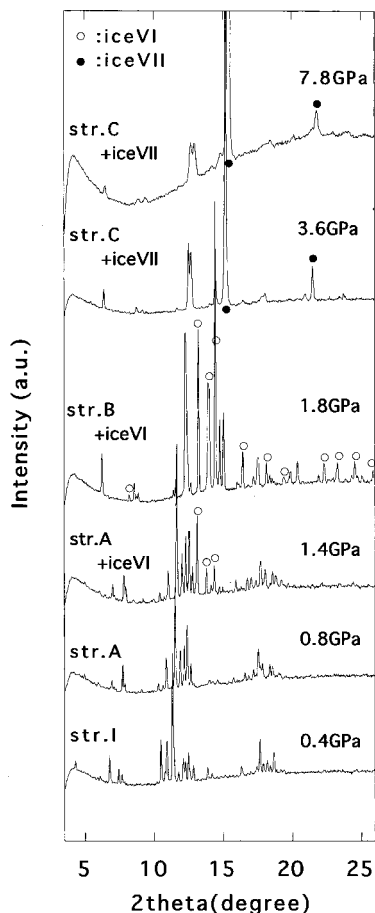


FIG. 1. XRD patterns observed with pressure changes. At 0.4 GPa, typical XRD of the str.I is shown. At 0.8 GPa, the str.A is observed as a crystalline phase. At 1.4 GPa, the str.A and ice VI (marked by open circles) are observed. At 1.8 GPa, the str.B and ice VI are observed. At 3.6 GPa, the str.C and ice VII (marked by solid circles) are observed. At 7.8 GPa, the str.C is still observed.

adopted. The XRD experiment was performed using synchrotron radiation (SR) on a BL-18C at Photon Factory, High Energy Accelerator Research Organization (KEK). The monochromatized beam with a wavelength of 0.6198 Å was used. Methane hydrate powder prepared using a conventional ice-gas interface method under the conditions of 15 MPa and -3°C was used as the initial material. This powder consisted of almost pure methane hydrate and contained a maximum of a few vol % of ice I_h according to a combustion analysis. The sample powder was put into a gasket hole in a vessel cooled by liquid nitrogen to prevent decomposition of the sample. The sample was sealed by loading the anvils slightly up to 0.2–0.3 GPa at the low temperature. Then the DAC was placed under room temperature. The sample was held as solid state during the procedure. All measurements were conducted at room temperature. Particular attention was paid to reducing the rates of compression or decompression. The mean rate was approximately 0.1 GPa per 10 mins. Raman spectroscopy was performed by using the 488 nm line of an argon ion laser with incident power of 400 mW at tube. A single monochromator and CCD-detector were used in the optical system. The calibration of wave number was carried out by using ten Ne emission lines in the

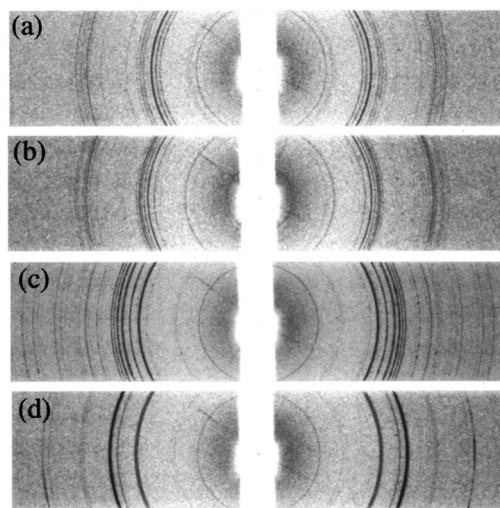


FIG. 2. Representative XRD patterns. (a) The str.I at 0.4 GPa; (b) the str.A at 0.8 GPa; (c) the str.B and ice VI (spotty rings) at 1.8 GPa; and (d) the str.C and ice VII at 3.6 GPa.

range from 1000 cm^{-1} to 3500 cm^{-1} , and by fitting the deviations between the standard and the observed values with third order polynomial.

III. RESULTS

Figure 1 shows XRD patterns observed with changes in pressure. At 0.4 GPa, a typical XRD pattern of the str.I was observed. The XRD pattern represented clear powder rings [Fig. 2(a)]. The d -values and relative intensities agreed with those of the established crystal structure I.⁶ At 0.8 GPa, a hexagonal structure (str.A) was observed in the XRD pattern. Under an optical microscope, relatively larger crystals and thin fluid layer between the crystals were observed. The XRD pattern of the str.A was spotty at this time, suggesting grain growth in the fluid. At 1.4 GPa, ice VI (marked by open circles) appeared besides the str.A, and the fluid disappeared. At 1.6 GPa, the str.A transformed into the str.B. At 2.1 GPa, the str.B further transformed into the str.C, and ice VI transformed into ice VII (marked by solid circles). At 7.8 GPa, the str.C still remained, although the diffraction intensities were rather weakened. Solid methane, phase I or phase A, were not observed in the pressure region examined.²³ The structural changes of methane hydrate occurring with increasing pressure were observed reversibly with decreasing pressure. The representative XRD patterns of the str.I, str.A, str.B, and str.C were given in Fig. 2. The XRD patterns of the str.A reverted from the str.B represented relatively homogeneous rings [Fig. 2(b)] than those observed at the decomposition from the str.I.

The changes in fundamental structure were clarified by the XRD data mentioned above. In order to examine changes in the state of the guest methane molecule along with the structural change, the Raman spectrum resulting from the totally symmetric stretching vibration (ν_1) of enclathrated methane was measured. Figure 3 shows Raman spectra observed with changes in pressure. For the str.I, a typical doublet peak was observed at 2904 cm^{-1} and 2919 cm^{-1} at 0.4

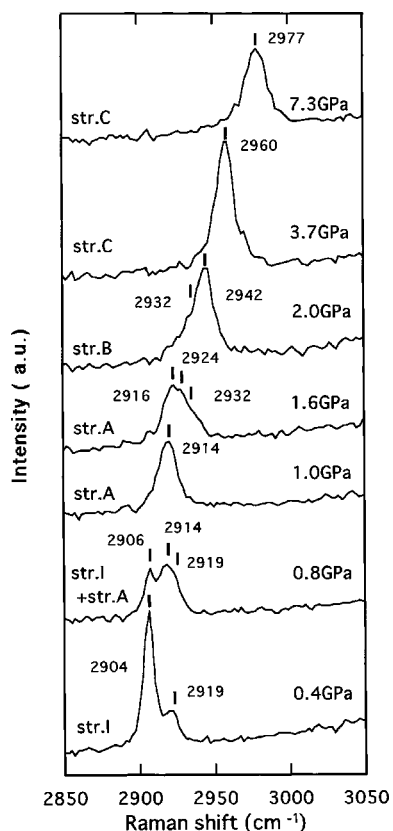


FIG. 3. Raman spectra from ν_1 of methane molecule along with the structural change.

GPa (Fig. 3). The intensity ratio of the former to the latter peak was 2.9 as an average within the measurements. The former peak, 2904 cm^{-1} , was coincident with those reported previously; on the other hand, the latter one, 2919 cm^{-1} , was a little higher than those reported, $2914\text{--}2915\text{ cm}^{-1}$.^{20,21,18} The previously reported data were obtained at ambient pressure^{20,21} or at 0.125 GPa ,¹⁸ while the present data were obtained at higher than 0.4 GPa . A certain pressure effect might occur,²² although the reason for the shift is not clear at the present time. At the transition from the str.I to str.A, the peak for the str.A began to appear between the doublet peak of the str.I at 0.8 GPa (Fig. 3). After the transition, an apparent single peak for the str.A was observed at 2914 cm^{-1} at 1.0 GPa (Fig. 3). With increasing pressure, the peak of the str.A split into two or three peaks at 1.6 GPa (Fig. 3). At 2.0 GPa , a peak for the str.B was observed at 2942 cm^{-1} . An apparent single peak for the str.C shifted to 2977 cm^{-1} at 7.3 GPa . The observed changes of ν_1 vibration of the methane molecule in the Raman spectra corresponded to the structural changes observed in the XRD patterns (Fig. 1).

The variations in volume ratios (V/V_0) with pressure for the str.I, str.A, and str.C were obtained. Fitting by Birch–Murnaghan's equation of state as $K'_0=4$, the bulk moduli, K_0 , were calculated for the str.I, str.A, and str.C to be 7.4 GPa , 9.8 GPa , and 25.0 GPa , respectively (Fig. 4). There is a smaller difference between the str.I and the str.A, suggesting that the fundamental structure of the str.A is composed of cages while the bulk modulus for the str.C is much larger which is comparable to that of ice VII. This implies that the

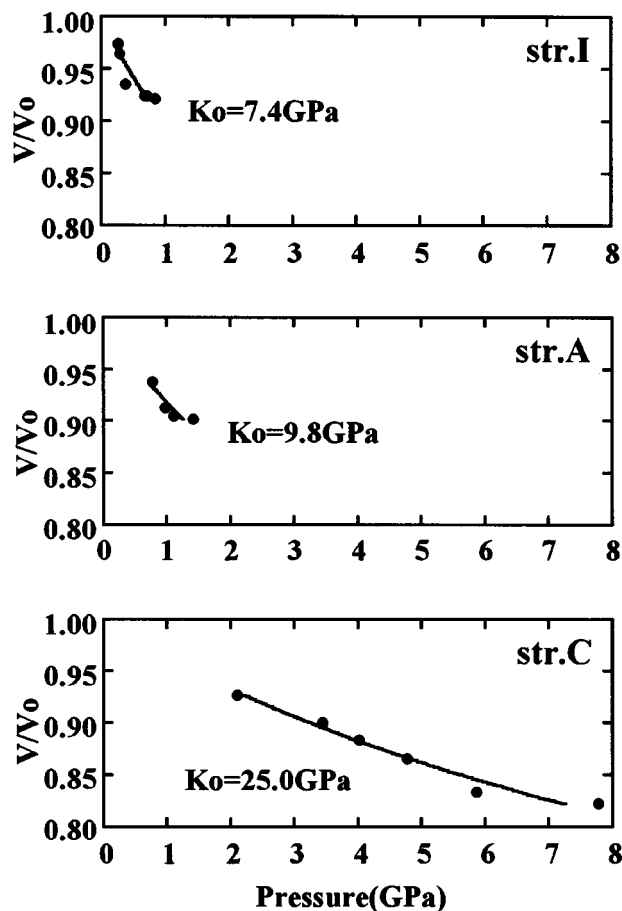


FIG. 4. Variations in the volume ratio with pressure for the str.I, str.A, and str.C.

str.C is different from those of cage structure. The bulk modulus for the str.B was not calculated because there was insufficient data for fitting due to the narrow pressure range.

IV. DISCUSSION

In the previous study by the present authors,¹⁷ where the compression rate was rather higher, methane hydrate decomposed into ice VII and solid methane (phase I) at 2.3 GPa . While, in the present study, three high-pressure structures were clearly found. The transition behavior is thought to be considerably affected by the compression rate and the starting material. The study by other authors¹⁸ reported that the str.I transformed into the structure II at 0.1 GPa , and the structure II transformed into a hexagonal structure at 0.6 GPa . The structure II was not observed within the present experiments performed. The other study¹⁹ described that at 0.9 GPa the str.I transformed to a hexagonal structure, and that at 2.0 GPa the hexagonal structure transformed to an orthorhombic structure. These hexagonal and orthorhombic structures (named as MH-II and MH-III) are thought to correspond to the present str.A and str.C, respectively, on the basis of the same unit cell parameters, the indexing, and the pressure range of existence. While the str.B was not found in that study. The str.B, in the present study, existed only in a narrow pressure range from 1.6 GPa to 2.1 GPa , but this structure was observed in good reproducibility with increas-

TABLE I. The observed and calculated d -values for the str.A at 0.8 GPa. The observed unit cell parameters: $a=12.004$ Å, $c=10.046$ Å.

hkl	d -obs. (Å)	d -calc. (Å)	Dev.	hkl	d -obs. (Å)	d -calc. (Å)	Dev.
1 0 0	10.226	10.337	-0.011	2 0 4	2.249	2.246	0.001
0 0 1	9.932	9.975	-0.004	2 2 3		2.221	
1 0 1	7.133	7.178	-0.006	4 1 1	2.205	2.200	0.002
1 1 0	5.952	5.968	-0.003	3 2 2	2.143	2.142	0.000
1 1 1	5.109	5.121	-0.002	2 1 4	2.107	2.102	0.002
0 0 2	4.988	4.988	0.000	5 0 0	2.073	2.067	0.003
2 0 1	4.575	4.589	-0.003	5 0 1		2.024	
1 0 2	4.478	4.492	-0.003	3 0 4	2.025	2.020	0.002
2 1 0	3.900	3.907	-0.002	0 0 5		1.995	
2 1 1		3.638		3 3 0	1.993	1.989	0.002
2 0 2	3.585	3.589	-0.001	4 2 0	1.956	1.953	0.002
3 0 0	3.446	3.446	0.000	3 3 1		1.951	
0 0 3	3.328	3.325	0.001	3 2 3	1.933	1.931	0.001
3 0 1	3.257	3.257	0.000	4 2 1		1.917	
1 0 3		3.165		2 2 4		1.913	
2 1 2	3.080	3.076	0.001	5 0 2	1.914	1.910	0.002
2 2 0	2.987	2.984	0.001	1 1 5		1.892	
1 1 3	2.907	2.905	0.001	3 1 4		1.882	
3 1 0	2.861	2.867	-0.002	4 1 3	1.868	1.867	0.001
2 2 1		2.859		5 1 0		1.857	
2 0 3	2.802	2.796	0.002	3 3 2		1.848	
3 1 1		2.755		4 2 2		1.819	
2 1 3	2.536	2.532	0.002	4 0 4	1.783	1.794	-0.004
3 1 2		2.486		2 1 5	1.781	1.777	0.002
1 0 4	2.436	2.424	0.005				
3 2 0	2.373	2.371	0.001				
4 0 2		2.294					

ing and decreasing pressure. And the XRD pattern was clearly distinguished from those of the str.A and str.C (Fig. 2). The str.B is certainly present as a high-pressure structure of methane hydrate. The discrepancy among these studies might be affected mainly by compression rate and the initial state of the sample.

The diffraction lines observed in the str.A were indexed by a primitive hexagonal lattice (Table I) with the unit cell parameters of $a=12.004$ Å and $c=10.046$ Å at 0.8 GPa. A hexagonal clathrate hydrates with a space group of $P6/mmm$ have been previously reported at ambient pressure, which accommodate a large guest molecule, methyl cyclohexane- d_4 in the large 20-hedra cage and small help gas, H_2S .⁸ And a structural refinement of the hexagonal structure accommodating a large 2,2-dimethylpentane molecule was performed.²⁴ The framework of these clathrate hydrates is the same as that of dodecasil 1H,^{25,26} which is a clathrate compound of silica. The dodecasil 1H also accommodates a large guest molecule of piperidine. The framework of the hexagonal structure is composed of three different cages, one 20-hedra cage [$5^{12}6^8$] (X-cage), three 12-hedra cages [5^{12}] (Y-cage), and two modified 12-hedra cages [$4^35^66^3$] (Z-cage)^{5,25} within a unit cell. The ideal composition of the structure is $1X3Y2Z/34H_2O$, when one guest molecule is contained in each cage. The number of the guest molecules is 6 for 34 water in this case. Table I shows the observed d -values and the calculated ones using crystal parameters of dodecasil 1H. Both d -values exhibit good agreement, which indicates that the fundamental structure of the present str.A is

similar to those of the low-pressure hexagonal structure reported.^{8,24,25} The recent high-pressure study¹⁸ of methane hydrate also reported that the hexagonal structure observed in that study was similar to the low-pressure one. The low-pressure hexagonal structures reported are stabilized by accommodating the large guest molecule in their large 20-hedra cage. In order to stabilize the structure only by small methane molecules, it is expected that two or more methane molecules are accommodated in the 20-hedra. According to Udachin *et al.*,²⁴ the dimensions of a free ellipsoid in the 20-hedra are 6.84, 6.84, and 8.59 Å, while the van der Waals diameter of methane molecule is 4.1 to 4.3 Å. Thus two methane molecules can be easily accommodated in the 20-hedra with sufficient intermolecular distance and also distance from the cage. On the other hand, it seems rather difficult for three methane molecules to be accommodated without superimposing each other. A preliminary structural analysis based on the low-pressure hexagonal structure suggested that the fundamental structure of the str.A might not totally be the same as that of the hexagonal structure but may be somewhat modified. A detailed refinement of the str.A should be the subject for future research.

As for two orthorhombic structures, the str.B and str.C, the unit cell parameters tentatively determined were $a=4.806$, $b=8.140$, $c=7.935$ at 1.80 GPa and $a=4.644$, $b=7.967$, $c=7.572$ at 4.80 GPa, respectively. Although these orthorhombic structures have similar unit cell parameters, they exhibit clearly different XRD patterns described above. The str.B might be a related structure of the str.A

consisting of cages, because the transition from the str.A to str.B was not clearly distinguished under the optical microscope. The str.C corresponded to the body-centered orthorhombic structure reported¹⁹ because of the same unit cell parameters and the body-center indexing. The str.C survived above 7.8 GPa. The bulk modulus is comparable to that of ice VII. These suggest that the str.C is probably a denser structure such as H₂-H₂O clathrate¹⁴ rather than other structures consisting of cages.

The present work, employing a combination of x-ray diffraction with Raman spectroscopy, has developed an understanding of the behavior of methane hydrate under high pressure. The results suggest that further new materials in the water-methane system might be present under higher pressure, and that methane hydrate might exist on the outer planets and their satellites.

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