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2002 J. Phys.: Condens. Matter 14 11443

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High-pressure structures of methane hydrate

H Hirai¹, Y Uchihara¹, H Fujihisa², M Sakashita², E Katoh², K Aoki²,
Y Yamamoto³, K Nagashima³ and T Yagi⁴

¹ Institute of Geoscience, University of Tsukuba, 1-1 Tennoudai, Tsukuba,
Ibaraki 305-8571, Japan

² National Institute of Advanced Industrial Science and Technology (AIST), Central 5,
1-1-1 Higashi, Tsukuba, 305-8565, Japan

³ AIST, Institute for Energy Utilization, 16-1 Onogawa Tsukuba, Ibaraki 305-8569, Japan

⁴ ISSP, Tokyo University, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

Received 24 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/11443

Abstract

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 str. A and fluid at 0.8 GPa. Str. A transformed into str. B at 1.6 GPa, and str. B further transformed into 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 bulk moduli, K_0 , for str. I, str. A, and str. C were calculated to be 7.4, 9.8, and 25.0 GPa, respectively.

1. Introduction

Methane hydrate is globally distributed in oceanic depositions, and plays important roles in the global environment and natural resources. Investigation of methane hydrate, therefore, is of great importance in relation to problems that need addressing urgently, as well as understanding basic materials science of water–methane systems. Recently, the present authors reported an *in situ* x-ray diffraction study at pressures of up to 5.5 GPa using a diamond anvil cell (DAC) [1]. This study showed that structure I (str. I) of methane hydrate survived until 2.3 GPa by changing its cage occupancy. Another high-pressure study by means of x-ray diffractometry (XRD) and Raman spectroscopy reported transformations to a hexagonal structure via structure II [2]. And other work based on neutron and XRD described the existence of a hexagonal structure and an orthorhombic structure [3]. The discrepancy in transition behaviour is probably affected by kinetic conditions such as compression rate and the initial state of the sample. In the present study, *in situ* observations by means of both XRD and Raman spectroscopy were carried out, and three high-pressure structures, a hexagonal structure (str. A), a primitive orthorhombic one (str. B), and a body-centred orthorhombic one (str. C), were found at higher pressure.

2. Experimental details

A lever and spring-type DAC was used in the high-pressure experiments. 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 adopted. The XRD experiment was performed using synchrotron radiation on a BL-18C at the Photon Factory (KEK). A 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. The sample powder was put into a gasket hole in a vessel cooled by liquid nitrogen to prevent decomposition of the sample. All measurements were conducted at room temperature. The mean compression rate was approximately 0.1 GPa per 10 min. Raman spectroscopy was performed by using the 488 nm line of an argon ion laser with output power of 400 mW at the tube. A single monochromator and CCD detector were used in the optical system. The calibration of the wavenumber was carried out by using Ne emission lines.

3. Results

At 0.4 GPa, a typical XRD pattern of str. I was observed (figure 1). The XRD pattern represented clear powder rings. The d -values and relative intensities agreed with those of the established crystal structure I. At 0.8 GPa, a hexagonal structure (str. A) was observed in the XRD pattern (figure 1). Under an optical microscope, larger crystals and a thin fluid layer between the crystals were observed. The XRD pattern of 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 str. A (figure 1), and the fluid disappeared. At 1.6 GPa, str. A transformed into str. B. At 2.1 GPa, str. B further transformed into str. C, and ice VI transformed into ice VII (marked by solid circles) (figure 1). At 7.8 GPa, str. C still remained, although the diffraction intensities were rather weakened. Solid methane, phase I or phase A, was not observed in the pressure region examined. The structural changes of methane hydrate occurring with increasing pressure were observed reversibly with decreasing pressure.

The changes in fundamental structure were clarified by means of 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 symmetric stretching vibration (ν_1) of enclathrated methane was measured. Figure 2 shows Raman spectra observed with changes in pressure. For str. I, a typical doublet peak was observed at 2904 and 2919 cm^{-1} at 0.4 GPa (figure 2). The ratio of the intensity of the former peak to that of the latter was 2.9 on 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, 2914–2915 cm^{-1} . The previously reported data were obtained at ambient pressure or at 0.125 GPa [2], while the present data were obtained at above 0.4 GPa. A certain pressure effect might occur. At the transition from str. I to str. A, the peak for str. A began to appear between the doublet peaks of str. I at 0.8 GPa (figure 2). After the transition, an apparent single peak for str. A was observed at 2914 cm^{-1} at 1.0 GPa (figure 2). With increasing pressure, the peak of str. A split into two or three peaks at 1.6 GPa (figure 2). At 2.0 GPa, a peak for str. B was observed at 2942 cm^{-1} . An apparent single peak for 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 (figure 1).

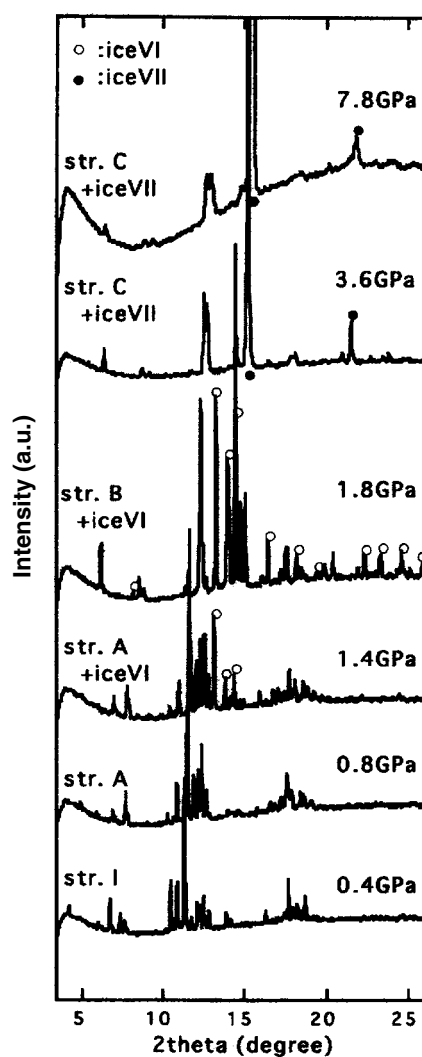


Figure 1. XRD patterns observed with pressure changes.

The variations in volume ratios (V/V_0) with pressure for str. I, str. A, and str. C were obtained. Fitting with the Birch–Murnaghan equation of state for $K'_0 = 4$, the bulk moduli, K_0 , were calculated for str. I, str. A, and str. C to be 7.4, 9.8, and 25.0 GPa, respectively (figure 3). There is a smaller difference between str. I and str. A, suggesting that the fundamental structure of str. A is composed of cages; while the bulk modulus for str. C is much larger, comparable to that of ice VII. This implies that str. C is different from the cage structure.

4. Discussion

In the previous study by the present authors, where the compression rate was rather higher, methane hydrate decomposed into ice VII and solid methane (phase I) at 2.3 GPa [1]; while in the present study, three high-pressure structures were clearly found. The transition behaviour is thought to be considerably affected by the compression rate and the starting material.

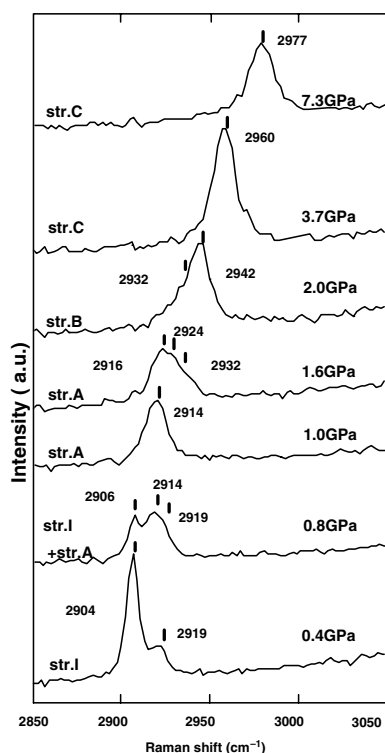


Figure 2. Raman spectra resulting from ν_1 for the methane molecule.

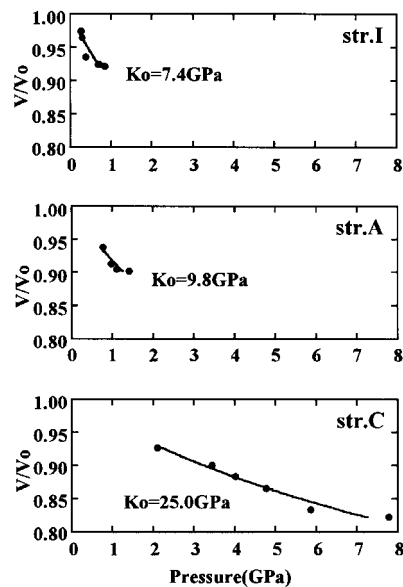


Figure 3. Variations in the volume ratio with pressure.

The diffraction lines observed for str. A were indexed to a primitive hexagonal lattice with the unit-cell parameters of $a = 12.004 \text{ \AA}$ and $c = 10.046 \text{ \AA}$ at 0.8 GPa. Two hexagonal clathrate hydrates with a space group of $P6/mmm$ have been reported at ambient pressure, which accommodate a large guest molecule in the large 20-hedra cage [4, 5]. The fundamental structure of the present str. A might be similar to the low-pressure hexagonal structures reported.

As for the two orthorhombic structures, str. B and str. C, the unit-cell parameters were $a = 8.140 \text{ \AA}$, $b = 7.935 \text{ \AA}$, $c = 4.806 \text{ \AA}$ at 1.8 GPa and $a = 7.572 \text{ \AA}$, $b = 7.967 \text{ \AA}$, $c = 4.644 \text{ \AA}$ at 4.8 GPa, respectively. Str. B could be indexed as a primitive lattice, and str. C as a body-centred lattice. Str. C corresponded to the body-centred orthorhombic structure reported [3]. Str. C survived above 7.8 GPa. The bulk modulus is comparable to that of ice VII. These findings suggest that str. C is probably a denser structure than other structures consisting of cages.

References

- [1] Hirai H *et al* 2000 *J. Phys. Chem. B* **104** 1429
- [2] Chou I-Ming *et al* 2000 *Proc. Natl Acad. Sci. USA* **97** 13 484
- [3] Loveday J S *et al* 2001 *Nature* **410** 661
- [4] Ripmeester J A *et al* 1987 *Nature* **325** 135
- [5] Udachin K A *et al* 1997 *Supramol. Chem.* **8** 173