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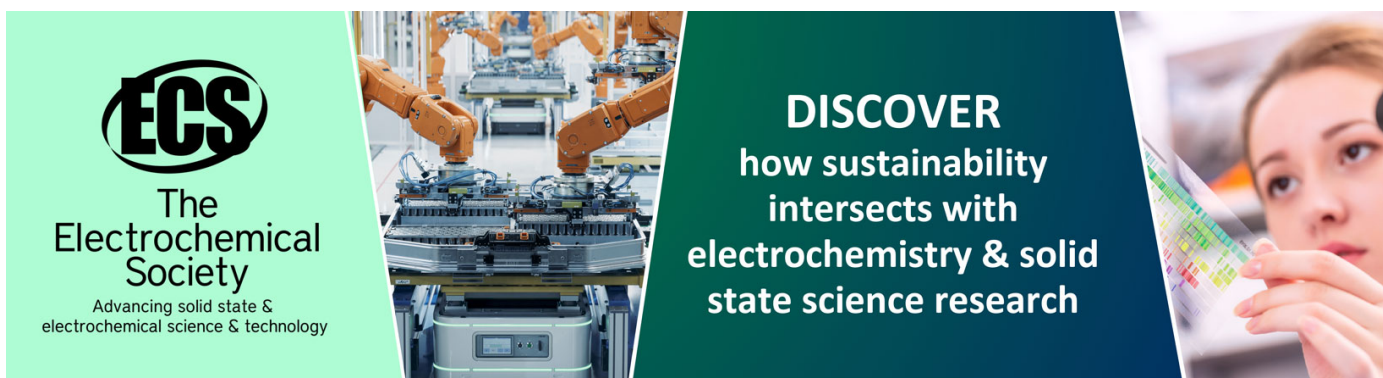
Phase changes induced by guest orientational ordering of filled ice I_h methane hydrate under high pressure and low temperature

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Phase changes induced by guest orientational ordering of filled ice I_h methane hydrate under high pressure and low temperature

H Hirai¹, T Tanaka¹, T Matsuoka², Y Ohishi³, T Yagi¹, M Ohtake⁴
and Y Yamamoto⁴

¹Geodynamics Research Center, Ehime University, Matsuyama, Ehime 790-8577, Japan

²KYOKUGEN, Osaka University, Toyonaka, Osaka 560-8531, Japan

³Japan Synchrotron Radiation Research Institute, Harima 679-5198, Japan

⁴The National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan

E-mail: hirai@sci.ehime-u.ac.jp

Abstract. Low-temperature and high-pressure experiments were performed with filled ice I_h structure of methane hydrate under pressure and temperature conditions of 2.0 to 77.0 GPa and 30 to 300 K, respectively, using diamond anvil cells and a helium-refrigeration cryostat. Distinct changes in the axial ratios of the host framework were revealed by *In-situ* X-ray diffractometry. Splitting in the CH vibration modes of the guest methane molecules, which was previously explained by the orientational ordering of the guest molecules, was observed by Raman spectroscopy. The pressure and temperature conditions at the split of the vibration modes agreed well with those of the axial ratio changes. The results indicated that orientational ordering of the guest methane molecules from orientational disordered-state occurred at high pressures and low temperatures, and that this guest ordering led to the axial ratio changes in the host framework. Existing regions of the guest disordered-phase and the guest ordered-phase were roughly estimated by the X-ray data. In addition, above the pressure of the guest-ordered phase, another high pressure phase was developed at a low-temperature region. The deuterated-water host samples were also examined and isotopic effects on the guest ordering and phase changes were observed.

1. Introduction

Methane hydrate, called burning ice, is expected as a clean and fruitful energy resource, while methane is a greenhouse gas even more potent than carbon dioxide at causing global warming. Gas hydrates containing methane hydrate take several structures accommodating a wide variety of guest gas species under high pressures. Gas hydrates exhibit clathrate structures at relatively low pressures, which are composed of host cages formed by hydrogen-bonded water molecules with guest species accommodated in the cages, see pages 45 to 111 in [1]. At higher pressures, several gas hydrates change to filled ice structures [2, 3]. The filled ice structures consist of a host ice framework and the guest species filled in the voids of the framework [4]. Comprehensive studies of gas hydrates at room temperature and high pressure had been performed. Yet, there were only a few studies of hydrogen hydrates and methane hydrate at low temperature and high pressure [5-8].



Methane hydrate exists in cubic structure, sI, at room temperature and low pressures. It transforms to a hexagonal clathrate structure, sH, at 1 GPa, and further transforms to a filled ice Ih structure (hereafter referred as MH-FI) at 2 GPa [2, 3, 9]. The host framework of MH-FI resembles ice Ih and the guest methane molecules are filled in the tunnel-like voids of the framework [4]. The previous studies by the present authors reported that the fundamental structure of MH-FI survived at least up to 90 GPa at room temperature with phase changes occurred at 40 GPa and 15 to 20 GPa [10, 11]. The phase change at 40 GPa detected by the X-ray diffraction (XRD) patterns was inferred to be related to the symmetrization of hydrogen bonds of the host framework. The other phase change at 15 to 20 GPa was detected by Raman spectroscopy, and the splitting of CH vibration modes of methane molecules was explained to be caused by orientational ordering of the guest methane molecules [12]. In the present paper, orientational ordering refers to a phenomenon where the random rotation of guest molecules is fixed at a certain orientation by pressure and/or low temperature. Guest molecules in such state are in orientational ordered-state [13]. At lower pressure and higher temperature conditions, guest molecules rotate randomly with spherical symmetry in the structure. Molecules in such state are in orientational disordered-state [13]. Orientational ordering of methane hydrate has been explained by Machida et al [12]. The CH stretching modes ν_3 and ν_1 of methane molecules began to split at 15 and 20 GPa, respectively. At that pressures, the intermolecular distances between the methane molecules in the MH-FI [14] attained the distance for the transformation from phase A (methane molecules are in orientational disordered-state) to phase B (ones are in an orientational ordered-state) in the solid methane [15]. During the transformation from phase A to phase B the CH vibration modes showed splits similar to those of the MH-FI [16, 13]. In this way, orientational ordering in the MH-FI was explained. A Raman spectroscopy study also observed changes in lattice vibration modes at about 15 GPa for MH-FI [17], however, the structural change due to the guest ordering at around 20 GPa and other phase changes at low temperatures and high pressures have not yet been explored by XRD study.

In this study, in order to clarify the phase change of MH-FI under high pressure, and low and room temperature conditions, the lattice parameters of the host framework and the vibration modes of the guest were examined by XRD and Raman spectroscopy. Moreover, substituting host water molecules by deuterated water, isotope effects are expected to occur on phase changes and guest ordering, which may help to understand the nature of the phases. Therefore, to study possible isotopic effects, deuterated-water host samples (referred as MD-FI) were also examined.

2. Experimental procedure

Clamp-type diamond anvil cells (DAC) and a helium refrigeration cryostat were used to generate high pressure and low temperature conditions. Rhenium gaskets were used. The pressure and temperature ranges were 2.0 to 77.0 GPa and 30 to 300 K, respectively. Pressure was measured via ruby fluorescence method and diamond Raman method. Temperature was measured by a silicon semiconductor thermometer and chromel-alumel thermocouples. The initial samples of MH-FI were

synthesized by the conventional ice-gas interface method, and those of MD-FI were by two methods. The first method was the ice-gas interface method in which powder ice of deuterated water was used. The second method was the gas-loading method (figure 1). The samples were characterized by XRD using synchrotron radiation at BL-10XU at SPring-8 and BL-18C at the Photon Factory of High Energy Accelerator Research Organization (KEK). A monochromatized X-ray with wavelengths of 0.04163 nm and 0.06198 nm was used. The XRD patterns were detected using an imaging plate. The

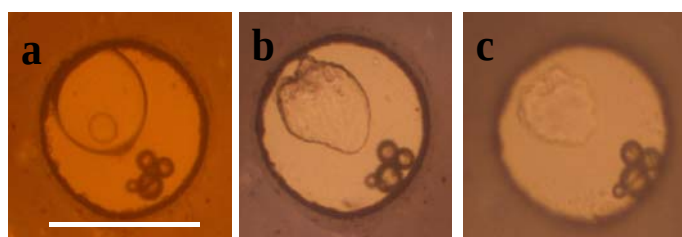


Figure 1. Photomicrographs of MD samples. a: after gas loading at 0.3 GPa, b: after 1 day, c: after 2 days. Methane molecules diffused to form sI around methane fluid. Bar scale is 100 μm .

diffraction peaks were fitted with fitting software FITYK. Raman spectroscopy was performed at high pressures and room to low temperatures by a liquid nitrogen cooling system. Sixteen experimental paths for ten MH-FI samples and six paths for four MD-FI samples were examined.

3. Results

The crystal structure of MH-FI was previously determined by neutron and XRD studies, and Imcm space group with a proton-disordered structure was proposed [4]. The diffraction lines of the XRD pattern at 2.6 GPa and 300 K were indexed as 011, 110, 002, 121, 112, 013, 200, 211, 132, 123, 003, 222, 114, 213, 143, 321, and 125 of MH-FI. At around 15 to 20 GPa no change in XRD patterns was observed. A diffraction line from solid methane was never observed, showing that the decomposition of MH-FI did not occur. Above 40 GPa, new diffraction lines that were not explained by Imcm appeared near the 002, 112, 202, 132, 123, and 213 reflections of MH-FI. These results were consistent with the previous studies, which reported these new lines at above 40 GPa and at room temperature [10, 11]. This phase was referred as a high pressure phase (HP-phase) [10, 11]. The XRD patterns presently observed at above 40 GPa were the same as those of the HP-phase. The HP-phase reverted to the MH-FI with decreasing pressure. Details about the HP-phase will be discussed later. At 100 K and below 51.8 GPa, the diffraction lines were same as those in MH-FI and ice VIII, and above 56.9 GPa the HP-phase appeared. The HP-phase was observed in a wide range of low temperature in this study. For the MD-FI samples, almost similar changes in the XRD patterns were observed at 300 K, 200 K, and 100 K, but the HP-phase appeared at very low pressure of 28 GPa at 300K.

The variations of lattice parameters with pressure at 300K and 100 K for MH-FI and MD-FI were obtained. The lattice parameters decreased monotonically with increasing pressure, and gap or sharp change in slope was not observed for all four cases. On the other hand, if one takes the axial ratio from the lattice parameters, distinct changes in slope were observed. The changes in axial ratios, a/b , b/c , and c/a at 300 K for MH-FI are shown in figure 2a (indicated by blue marks). The slopes of b/c and c/a clearly changed at about 15-20 GPa, while that of a/b remained almost unchanged. These features indicated that c-axis became relatively incompressible above the pressure. The pressure at which the axial ratio changed agreed with that at orientational ordering of methane molecules observed by a previous Raman study [12]. The changes in the axial ratio reverted reversibly with decreasing pressure. Figure 2b shows changes in axial ratios at 100 K for MH-FI (blue marks). Similar changes were found, but the pressure at which the change in slope occurred shifted to a higher pressure of 25 GPa. Pink marks show variations of axial ratios for MD-FI superimposed on those of MH-FI (blue circles). Both ratios almost coincided at 300 K, while at 100 K the MD-FI's change of axial ratio shifted to further high pressure of 40 GPa. This could be the isotopic effect on the change in axial ratio especially at low temperature.

In a previous Raman study performed at room temperature, splits of CH vibration modes due to orientational ordering were observed at 15 to 20 GPa [12]. In the present study at the same pressure distinct change in axial ratios was

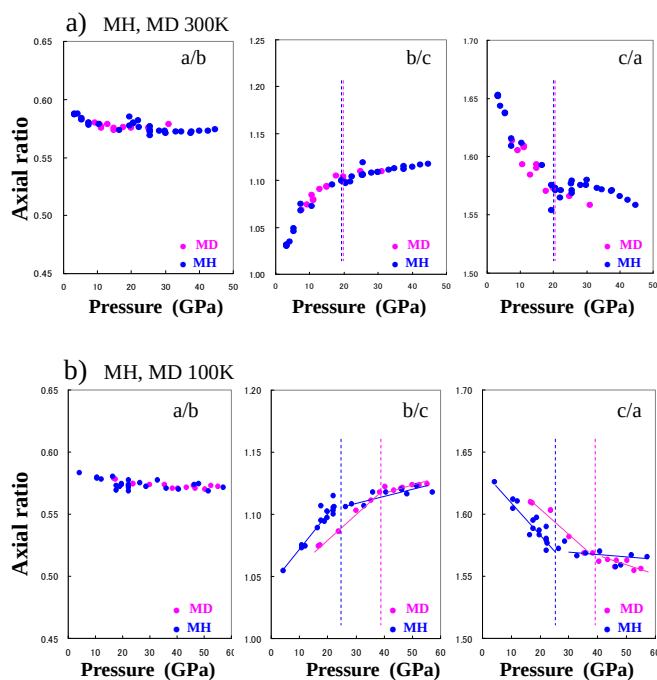


Figure 2. Axial ratio changes with pressure.

observed at room temperature, and such axial ratio changes were also observed at low temperatures. Thus, in order to examine if the splits of the vibration modes continued at low temperature region, Raman study was performed at room temperature and low temperatures. At room temperature with increasing pressure the ν_3 began to split at above 13.6 GPa, and ν_1 began to show asymmetric shape at 20.7 GPa (figure 3). This was consistent with the previous study. When the temperature decreased from room temperature, the splits were observed until about 160 K at 21 GPa. Similar changes in the Raman spectra were observed in other several measurement paths.

4. Discussion

In the present study, the changes in the axial ratios were observed at high pressures and low temperatures for MH-FI and MD-FI. Also, the splits of CH vibration modes were found at room temperature and low temperatures for MH-FI samples. The temperature and pressure conditions of the splits almost agreed with those of the change in axial ratios. The splits of vibration mode were related to the orientational ordering of the guest molecules as described above [12]. Therefore, the experimental results suggested that orientational ordering occurred in a wide temperature and pressure range. In addition, it could be interpreted that orientational ordering of the guest molecules induced anisotropic contraction of the host framework that changed the axial ratios within the same fundamental structure.

Orientational ordering of constituent molecules from disordered state is a well-known phenomenon under high pressure and low temperature in molecular crystals, and it is regarded as a phase change [13]. In the present study, the states characterized by different axial ratios can also be regarded as different phases because they have different guest ordering manners. All phase changes observed by the XRD study are summarized in figure 4. Both MH and MD samples possess three phases: the original FI with guest disordered-state (blue rhombuses), the phase with guest ordered-state (green ones, and labelled as GOS-phase in figure 4), and the HP-phase (red ones) developed in low temperature and high pressure region above 2 GPa. The grey belts in figure 4 denote the boundaries between phases that were roughly estimated from the distribution of the individual phases. For the MD samples, the boundaries shift towards higher pressure region.

For filled ice Ic hydrogen hydrate, orientational ordering of guest hydrogen molecules induced at low temperature and high pressure conditions led to the structural change from cubic to tetragonal [5, 6]. At the guest orientational ordering, the hydrogen molecules should change from spherical to lowered symmetry such as ellipsoidal. This results in elongation of one of the cubic axes, and the original cubic structure changes to a tetragonal structure. For MH-FI, the original structure is orthorhombic. Although anisotropic contraction was caused by guest ordering, the fundamental orthorhombic structure was maintained. In any case, guest molecules in gas hydrate structures have been known to be rotating freely under low pressure and room temperature, but the common behaviour of hydrogen and methane hydrates involves that the random rotation of the guest molecules is suppressed to be fixed to some orientations in the host framework at high pressure and low temperature.

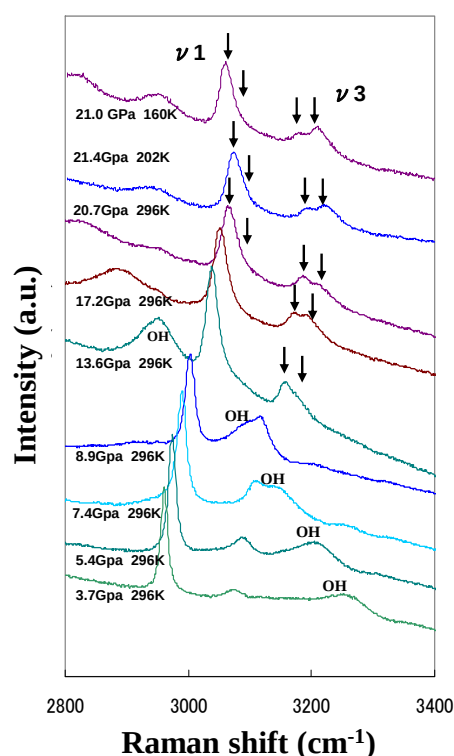


Figure 3. Raman spectra of C-H vibration modes, ν_1 and ν_3 , of methane molecules.

The HP-phase was observed above 40 GPa at 300 K and above 57 GPa at 100 K for MH samples, and above 28 GPa at 300 K for MD samples. A possible explanation of the HP-phase might be related to the symmetrization of hydrogen bond in the host water molecules [10]. In the present study of MD samples, however, the HP-phase was observed above a very low pressure of 28 GPa at 300 K. Oxygen-oxygen distance at 28 GPa may be longer than that expected for the symmetrization of hydrogen bond [18]. A theoretical study of MH-FI predicted that symmetrization of hydrogen bond occurs at a higher pressure of 70 GPa at room temperature [14]. Thus, another possible explanation is inferred that the HP-phase might be produced by a different manner of orientation of the guest molecules.

Comparing the distributions of phases between MH and MD samples, a significant influence of isotopic effect on the orientational ordering and on the phase change was observed. For the influence of the isotopic effect, the mass and quantum effects should be considered. For the mass effect, when the host water is substituted by deuterated water, the frequency of the intramolecular O–D vibration mode drops significantly because of the larger mass. Subsequently, the host–guest interaction may change to allow free rotation of the guests until higher pressures. The quantum effect influences the phonons of the material, and thus, a change of phonons affects the phase-transformation behaviour. The quantum effect usually becomes obvious at low

temperatures, whereas it is rather difficult to detect at higher temperatures because of thermal disturbance. In fact, the transformation pressures for the HP phase for MD samples were higher than those of the MH samples at low temperature, which suggests that some quantum effect is present. Moreover, the difference in the axial ratio between the MD and MH samples was distinct at 100 K, whereas it was not clear at 300 K (figure 2). Such differences depending on temperature suggest that quantum effects also have an influence on axial ratio change, namely guest-orientational ordering. As described above, it is speculated that both the mass and quantum effects might have influenced the isotopic effect. Aside from the above possibilities, the isotopic effect hints that a different manner of guest orientation may occur at even higher pressures. A detailed explanation for the isotopic effect and its relationship to host–guest interactions has not yet been clarified. Thus, further experimental and theoretical studies should be done to understand the isotopic effects and the nature of the HP-phase.

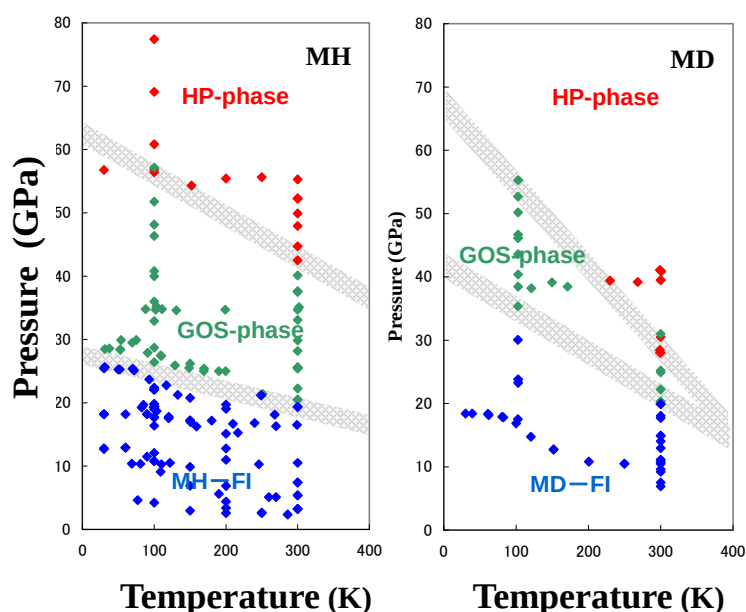


Figure 4. Summary of phase changes for MH and MD.

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