**Microscopic observation and in situ Raman scattering studies on high-pressure phase transformations of a synthetic nitrogen hydrate.**

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Visual observations through a microscope and in situ Raman scattering measurements of a synthesized nitrogen hydrate have been performed at pressures up to 6 GPa and 296 K. High-pressure transformations have been found at 0.85 and 1.45 GPa. The cubic structure II (sII) of nitrogen hydrate initially transforms to the hexagonal structure (sH) at 0.85 GPa and finally forms the orthorhombic diphosphate (sO) above 1.45 GPa. The sO phase of nitrogen hydrate exists up to at least 6 GPa. A variety of Raman spectra composed of three peaks have been sometimes observed in sH phase below 0.50 GPa, which implies that the guest nitrogen molecules doubly occupy the large hexakaidecahedron cages. Two Raman bands of the guest nitrogen vibrations with nearly equal intensities appearing in sH phase suggest that five nitrogen species are filling in extra large icosahedron cages. **2003 American Institute of Physics. [DOI: 10.1063/1.1636300]**

**I. INTRODUCTION**

Gas hydrates are a special class of inclusion compounds in which the water molecules form a hydrogen-bonded cage framework. In order to stabilize it, the guest molecules occupy some minimum amount of the voids inside the cages. At low pressures, it is well known that there are two cubic hydrate structures I and II, and one hexagonal structure (sH). Which of these structures is found depends on the size of the guest molecules. In the case of nitrogen hydrate, small-size nitrogen molecules (N2) primarily fill in small pentagonal dodecahedron cages (sC) to form sII hydrate (Fd3m) accompanied by large hexakaidecahedron cages (L cage). The unit cell of sII contains 136 water molecules forming 16 cages and 8 L cages.

Much attention has been focused on the double occupancy in host water cages since the pressure-dependent high resolution neutron diffraction study on sII nitrogen hydrate revealed that the L cages are partially occupied by two N2 molecules. Klaerken et al. have performed molecular dynamics simulations of sII nitrogen hydrate with varying N2 cage occupancies and at different conditions, and show that nitrogen hydrate remains stable even for the case of a full double occupancy of L cages. These results support the double occupancy determined by the above neutron diffraction measurements. Klaerken et al. also calculated the vibrational frequencies for sII nitrogen hydrate, in which the three N-S stretching peak frequencies for the single occupied cage and the double occupied L cages, and single occupied L cages. Although a number of Raman experiments for the N-N stretching vibrations in natural synthetic hydrates have been performed, there is evidence for the double occupancy.

The high-pressure Raman spectroscopic study on synthetic nitrogen hydrates at 295 K has been carried out by Y. Hisamitsu et al. In their experiments up to 1.8 GPa, the spectra of sII hydrate is under hydrostatic condition because the surrounding nitrogen around nitrogen-hydrate crystals is fluid up to 2.5 GPa. They found the free high-pressure phase which exists from 0.84 to 1.84 GPa by the splitting of the N-N stretching vibrations at 0.84 GPa. On the other hand, Dyadin et al. present there are threehydrate phases, which was determined from the deconvolution curve in the nitrogen–water system without structural determination of two high-pressure phases. They proposed the similarity between the nitrogen–water system and the Ar–Kr–water systems. Very recently, Lovdock et al. have carried out a synchrotron X–ray and neutron diffractive measurements of nitrogen hydrate at pressures up to 2 GPa and at room temperature. According to their results, the nitrogen hydrate initially transforms to sH at 0.84 GPa.

**II. EXPERIMENT**

Visual observation through a microscope and in situ Raman experiments of nitrogen hydrates have been performed with a DAC. A high-pressure vessel was employed to load the compressed guest gas and host water into a sample chamber of the DAC. Prior to the loading of N2 gas, distilled water and a ruby chip for pressure calibration were put into the small sample chamber (0.3 mm in diameter, 0.3 mm in depth). The DAC was set in the high-pressure vessel and the air inside the vessel was replaced by nitrogen gas in order to avoid the contamination by impurities. When the appropriate guest-gas pressure was applied, the sample chamber was sealed by the remote control. After the loading of sample into the DAC, liquid water and fluid nitrogen as droplets are separate in the sample chamber [see Fig. 1(a)]. The sII nitrogen hydrate crystallized in three phase equilibrium among water, fluid nitrogen, and crystalline nitrogen hydrate at about 1.15 GPa and 296 K. This three-phase coexistence pressure is consistent with the P–T projection of the phase diagram for nitrogen–water systems. The applied pressure is estimated by using the ruby fluorescence method. Its uncertainty is within 0.02 GPa.

All Raman scattering measurements of nitrogen hydrate have been carried out in a backscattering geometry at 296 K. The sample was excited by a 514.5 nm line of an Ar ion laser and the spectra were obtained by a spectrometer (JASCO, HR1800) equipped with a triple monochromator and a liquid-nitrogen-cooled charge-coupled device (CCD) detector. Since a very small part (within 5 μm in diameter) of the specimen is illuminated by laser, we can precisely measure in situ Raman spectrum from a single phase even if two or three phases coexist.

**III. RESULTS AND DISCUSSION**

A. Microscopic observation of a crystalline nitrogen hydrate at high pressures

Microscopic observation of crystalline nitrogen hydrates provides the direct information on phase transformations. At pressure of about 0.15 GPa, water and fluid nitrogen transformed into the sII nitrogen hydrate named NH-I. We grew a single crystal of NH-I in three phase equilibrium by controlling pressure and temperature as shown in Fig. 1(b). This crystal shows a transparent octahedron-like shape resulting from the transformation around 1.3 GPa to the trapezoidal structure (sT) found by Kurnosov et al. At 1.6 GPa this nitrogen hydrate eventually forms the orthorhombic diphosphate (sO) which is the same structure as NH-III phase of methane hydrate. Therefore, the phase changes and the multiple occupancies of L cages of sII nitrogen hydrate at these pressures and higher pressure regions. In this paper, we present the visual observations of crystalline nitrogen hydrates in a diamond anvil cell (DAC) and the in situ high-pressure Raman spectroscopy of guest N2 molecules at pressures up to 6 GPa.

FIG. 1. Photographs of nitrogen hydrate in a DAC at 296 K. (a) A picture just after the loading of nitrogen gas and water into a sample chamber (300 μm in diameter, 300 μm in depth of the DAC). Bubbles and the surrounding fluid are nitrogen and water. (b) A single crystalline nitrogen hydrate in all phase, named NH-I, in pressure of 0.24 GPa. The surrounding water (c) A number of fine brown patches appeared in a single crystalline nitrogen hydrate above 0.50 GPa, (d) NH-I crystal at 0.92 GPa. Some grains of NH-II are clearly observed. (e) NH-II crystal surrounded by ice-VI at 1.22 GPa, (f) NH-III crystal at 1.48 GPa. A great many of very fine patches appeared at 1.45 GPa. (g) NH-III crystal surrounded by ice-VII at 2.13 and 3.04 GPa, respectively. No phase transformation of nitrogen hydrate was observed at pressures between 1.45 and 6 GPa.

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from the cubic structure for sII phase. The surrounding is water and a small ruby chip is beside the hydrate crystal. An oval on the single crystal NH-I is not fluid nitrogen but an ordinary pit generated during crystal growth, which could be distinguished by their characteristic Raman spectra. With increasing pressure, we found two phase transformations at 0.85 and 1.45 GPa. Their high-pressure hexagonal phases are named NH-II and NH-III, respectively. At about 0.50 GPa, a single-crystalline NH-I turned reddish brown, retaining the outward form as shown in Fig. 1(c). Subsequently, NH-I clearly transformed to NH-II at 0.85 GPa as shown in Fig. 1(d). The reddish-brown crystal became transparent again, and many grains appeared in the part of crystalline NH-II. By way of the phase transition of surrounding water to ice-VI at 1.0 GPa [Fig. 1(e)], NH-II eventually transformed to NH-III and became black because of the appearance of a great number of fine grains as shown in Fig. 1(f). Whereas the surrounding ice-VI underwent the phase transition to ice-VII at about 2.0 GPa, no phase transformation was confirmed above 1.45 GPa by the visual observation as shown in Figs. 1(g) and 1(h). Two Raman phase transformations at 0.85 and 1.45 GPa probably correspond to the sII–sH and the sH–sT transitions at 0.84 and 1.3 GPa determined by the synchrotron x-ray and neutron diffraction measurements.25

24.5 GPa 2.45 GPa 1.22 GPa 0.51 GPa 0.24 GPa

NITROGEN HYDRATE

N-H IV: VIBRATIONAL MODE

NH-III

5.12 GPa 3.69 GPa 2.45 GPa 1.48 GPa 0.92 GPa

FIG. 2. Raman spectra for N–N vibrational modes of the guest N₂ molecules in nitrogen hydrate at various pressures up to 6 GPa and at 296 K.

2.38 cm⁻¹ 2.63 cm⁻¹

Wavenumber (cm⁻¹)

Pressure (GPa)

5.12 GPa

3.69 GPa

2.45 GPa

1.48 GPa

0.92 GPa

0.51 GPa

0.24 GPa

FIG. 3. Pressure dependence of Raman peak frequencies for N–N vibrational modes of the guest N₂ molecules in nitrogen hydrate at 296 K. The experimental data are plotted by open circles. Vertical broken lines indicate the phase transitions of NH-I (sII–sH), NH-IId (sH–sIII), and sIII (sO) phases and the pressure dependence of their peak frequencies, respectively. From these results, one can see the obvious changes in response to the phase transformations at 0.85 and 1.45 GPa.

B. High-pressure Raman scattering measurements of nitrogen hydrates

Raman scattering experiments for the N–N stretching vibrational mode of nitrogen hydrates are very useful for investigating the state of guest N₂ molecules in host water cages, since the interactions between the guest molecule and the host cage molecule manifest itself directly as a change in the vibrational frequency of the guest molecule. Figures 2 and 3 present the Raman spectra for the N–N stretching vibrations corresponding to NH-I (sII–sH), sH–sIII, and sIII (sO) phases and the pressure dependence of their peak frequencies, respectively. From these results, one can see the obvious changes in response to the phase transformations at 0.85 and 1.45 GPa.

In NH-I (sII phase), the Raman spectrum for the N–N stretching vibrational mode generally shows a slightly broad single peak (see Fig. 2) around 232.4 cm⁻¹, in spite of the existence of two sorts of cages and of nitrogen double occupancy. According to the neutron diffraction study in the sII nitrogen hydrate, the number of double occupied L-cages exceeds at least 25% of the whole number of L cages at 0.24 GPa and 273 K. Therefore, it is plausible that the unresolved broad Raman spectrum in NH-I (sII) phase consists of three N–N vibrational peaks of guest N₂ molecules in the single occupied S cages, the double occupied L cages, and the single occupied L cages. Moreover, we sometimes observed the asymmetric Raman spectra clearly composed of three peaks below 0.50 GPa. In these cases, a single peak of NH-I (sII) was grown in three phase equilibrium at about 280 K. However, this crystal is not transient formation such as the sI nitrogen hydrate reported by Kuo et al. because the corresponding spectra retained its shape over the period of a few weeks at 296 K. One typical example from these spectra is shown in Fig. 4. This spectrum evidently has the extra peak at low frequency side around 232 cm⁻¹ in comparison with that shown in Fig. 2. The reason why this complex spectrum with three distinct components appeared should be the occurrence of nitrogen hydrate L cages of all nitrogen hydrate. As the filling of L cages of sI nitrogen hydrate strongly depends on pressure and probably on temperature, the crystalline sI nitrogen hydrate grown at about 280 K may have a different occupancy from those made at 296 K. Thus, we could fortuitously observe the Raman spectra for the N–N vibrations composed of three distinct peaks. In order to investigate the complex spectrum shown in Fig. 4, we analyzed it into three peaks with frequencies of 232.0, 232.5, and 232.1 cm⁻¹ indicated by broken curves using the least-squares fitting method, which allows us to discuss the intrinsic properties of three distinct peaks. Incidentally, this complex spectrum could not be analyzed into two peaks. Recently, Klavenor et al. have measured the high-pressure Raman spectra of NH-I (sII–sH) and sII nitrogen hydrate with lattice constant 17 A at 273 K on the assumption that the L cages are doubly occupied in part by guest N₂ molecules. They showed three characteristic peaks with frequencies of 233.0, 232.5, and 232.5 cm⁻¹ in response to the single occupied L cages, the double occupied L cages, and the single occupied S cages, respectively. Although their calculation is obviously different from the present experimental results because of the different conditions between their calculation and the experiments, the qualitative comparison between them is valuable for deducing the origin of Raman signals. On the other hand, our results can temporarily assign the low, middle, and high frequency peaks to the guest N₂ vibrations in the single occupied L cages, the double occupied L cages, and the single occupied S cages, respectively. This assignment, namely, the extra peak around 232 cm⁻¹ corresponding to the single occupied L cages indicates that the number of the doubly occupied L cages in NH-I (sII) grown at about 280 K is less than that in NH-I (sII) grown at 296 K. In other words, most of the L cages are doubly occupied in NH-I (sII) grown at 296 K and both the L cages and the S cages accommodate the same number of the guest N₂ molecules in a unit cell. Consequently, the slightly broad single peak in NH-I (sII) is mainly composed of two peaks with some intensities and small frequency separation of 1.5 cm⁻¹. Any spectrum obtained below 0.50 GPa eventually becomes a slightly broad single peak at pressures above 0.50 GPa. From the above-mentioned speculation, it is thought that this spectral change is due to the variation of the occupancies of each cage in sII and that the rate of double occupied L cages becomes constant above 0.5 GPa.

In the NH-II (sh) phase, the N–N vibrational peak obviously splits into two peaks having nearly equal intensities as seen in Fig. 2. The sh is composed of three S cages, two S’ cages (dodecahedron with four tetragonal, six pentagonal, and three hexagonal faces), and one LL cage (icosahedron with twelve pentagonal and eight hexagonal faces) per unit cell. Matsumura et al. have reported that the phase II of argon hydrate has the sh with five argon atoms in LL cages.26 In addition to that, Lovern et al. indicated that the sh of methane hydrate (MH-II) having larger guest CH₄ molecules than Ar and R₂ accept the same structure as the phase II of argon hydrate.27 Therefore, it is reasonable to accept that five nitrogen molecules are included in LL cages of NH-II. Based on the assumption that NH-II is the same state as MH-II of methane hydrate and phase II of Ar hydrate for its structure and the occupancy, the following interpretation for the spectral shape is possible and plausible. Since S and S’ cages have almost the same radii (3.9 Å for S cage, 4.06 Å for S’ cage) and encage at most one guest molecule in each cage, two N–N vibrational peaks corresponding to five N₂ molecules in three S and two S’ cages and five molecules in one LL cage are expected to appear with nearly equal intensities. These estimations seem to be consistent with the present Raman spectra appearing in NH-II phase. Consequently, the NH-II phase probably has the sh with five nitrogen molecules in LL cages. In the present experiments, it is difficult to determine which of the two nitrogen hydrates appearing in NH-II phase are assigned to the N–N vibrations of guest N₂ molecules in the LL cages of sh. However, we can speculate that the higher N–N vibrational frequency with steep slopes against pressure means the shorter intermolecular distance between the guest–guest or guest–host molecules. If this intermolecular distance in LL cages is surprisingly short like the case of MH-II,22 the higher N–N vibrational peak around 232.5 cm⁻¹ at 0.85 GPa may result from the N₂ molecules in LL cages. On the other hand, the lower peak around 232.4 cm⁻¹ at 0.85 GPa in NH-II (sh) phase, which is close to the guest N₂ in S cages vibrational frequency of 232.0 cm⁻¹ at 0.85 GPa, can be attributed to the N–N vibration of N₂ molecules in S and S’ cages.

Van Hinsberg et al. have carried out the high-pressure Raman scattering measurements in many phases of equilibrium between nitrogen hydrate and liquid nitrogen up to 1.8 GPa at 295 K and have found that the new high-pressure phase, namely, NH-II exists from 0.84 to at least 1.8 GPa.28 The present Raman spectra of the N–N vibration
NH and NH-II are in good agreement with their results. Nevertheless, NH-II transformed into NH-III at 1.45 GPa in the present study. Moreover, Loveday et al. have shown that the $g$ hyperfine nitrogen exists up to 1.3 GPa, which is close in the present results. As Loveday et al. and we have performed the experiments for NH-II ($g$) in equilibrium between nitrogen hydrate and water or ice-VI and nitrogen, influences the phase transformation of $g$ hyperfine nitrogen. Therefore, it turns out that the above disagreement is basically caused by the difference in equilibrium state. To clarify this disagreement, further experiments will be required for the phase stability of nitrogen hydrate with respect to the difference in the state of equilibrium.

When NH-II transformed into NH-III at 1.45 GPa, two peaks in NH-II ($g$) phase became a single peak with a small shoulder at low frequency side. The Raman frequencies of the $N_2$ molecules in NH-II are almost the same as those of liquid nitrogen. If the NH-II decomposed into liquid nitrogen and ice-VI at 1.45 GPa, the Raman spectra of nitrogen would show the small jump of 2 cm$^{-1}$ at the liquid to $g$ phase transition pressure of 2.5 GPa and split into two peaks (2335.9 and 2345.5 cm$^{-1}$ at 4.6 GPa) at the $g$ phase transition pressure of 4.5 GPa. However, the Raman spectra of the $N_2$ molecules in NH-III remains a single peak up to 6 GPa, as shown in Figs. 2 and 3. Thus, NH-III phase is known to be one of the nitrogen hydrate phases. Moreover, a part of NH-II often decomposed into ice-VII and solid nitrogen $g$ phase above 3.0 GPa (or at $g$ phase above 4.5 GPa) because of the pressure strain, and the corresponding peaks of solid nitrogen appeared in addition to that of nitrogen hydrate. Excepting this partial decomposition, no spectral variation about the nitrogen hydrate was found up to 6 GPa.

The pressure dependence of the $N$-N vibration in NH-III phase shows no discontinuity at around 1.6 GPa as shown in Fig. 3. Loveday et al. found that nitrogen hydrate has two phases above 1.3 GPa, the $t$ phase with two tetradecahedrons (with two tetragonal, eight pentagonal, and four hexagonal faces) per unit cell in the pressure range between 1.3 and 1.6 GPa and the $g$ phase (dihydrate) without cage-like structure above 1.6 GPa. Considering that the $t$ phase has one sort of tetradecahedron cage and that the $g$ phase of methane hydrate shows the only one guest $g$-scheme symmetrical Raman peak, both $t$ and $g$ phases of the nitrogen hydrate should yield a single peak of the $N$-N vibration. Therefore, we could not judge the existence of the $t$ phase only from the present $N$-N vibrational Raman spectra above 1.45 GPa, but the NH-III at least above 1.6 GPa is thought to be the $g$ phase.

Figures 5 and 6 show the Raman spectra at various pressures and the pressure-dependent peak frequencies of lattice and $O$-$H$ stretching vibrations for host water cages of nitrogen hydrate, respectively. With increasing pressure the peak frequencies of the $O$-$H$ lattice and $O$-$H$ vibration marks by open triangles in Fig. 5, are monotonously increasing and decreasing, respectively, with showing small jumps at 1.31 to 1.15 GPa. The negative slopes for the $O$-$H$ vibrational frequencies is the characteristic of the hydrogen phase transformation of $N$-II ($g$) phase into NH-III phase with water. The observed spectra were deconvoluted with a Gaussian function and, the best fits were obtained with two or three peaks. Figure 6 shows the nitrogen hydrate spectra, which are typical for nitrogen hydrate and which show the characteristic bands of nitrogen hydrate and water. The spectra are deconvoluted with a Gaussian function and, the best fits were obtained with two or three peaks. Figure 6 shows the nitrogen hydrate spectra, which are typical for nitrogen hydrate and which show the characteristic bands of nitrogen hydrate and water. The spectra are deconvoluted with a Gaussian function and, the best fits were obtained with two or three peaks.

A. CONCLUSION

Microscopic observations and in situ Raman scattering measurements on a synthesized nitrogen hydrogen have been performed at high pressures up to 6 GPa and 296 K. The NH-III phase is only transformed into NH-II ($g$) phase at 0.5 GPa and finally changed to NH-III ($g$) phase at 1.45 GPa. No phase transformation occurs at pressures above 1.45 GPa and the NH-III ($g$) phase exists up to at least 6 GPa. In response to those, Raman peaks for guest $N_2$ molecules clearly changed. Two signals with nearly equal intensities appearing in NH-II ($g$) phase reveal that five nitrogen molecules occupy each cavity. A comparison of three spectra were sometimes observed at pressures below 0.50 GPa in NH-III phase, which implies that guest nitrogen molecules doubly occupy the L cages. Moreover, the spectral change around 1.45 GPa is seen as the variation of the occupancies of the cages in NH-III in which the rate of double occupied L cage becomes constant. The $g$ phase found by Loveday et al. at pressures between 1.3 and 1.6 GPa was not confirmed in the present work.