Observation of Rattling Vibrations in Clathrate under High Pressure and Low Temperature

K. Funahashi1, I. Yajima1, T. Kume†, S. Sasaki1, H. Shimizu1, T. Takabatake2
1Department of Materials Science and Technology, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan
2Graduate School of Sci. and Eng., Hiroshima Univ., Higashi Hiroshima, Hiroshima 739-0046, Japan
E-mail: kume@gifu-u.ac.jp

Abstract. An experimental system for low-frequency Raman measurements at low temperatures and high pressures was constructed in order to research low frequency vibrations of guest atoms in guest-host materials such as semiconductor clathrates. Raman measurements in the range to 10 cm\(^{-1}\) were attained under low temperature and high pressure by arranging a diamond anvil cell fixed on a cryostat in a quasi-back-scattering geometry. Raman spectra of a clathrate compound Eu\(_8\)Ga\(_{16}\)Ge\(_{30}\) were measured using this experimental system. The low frequency Eu vibration so called the rattling vibration located at ~20 cm\(^{-1}\) was clearly observed under high pressures and low temperatures.

1. Introduction

Group-14 elements are known to form clathrate compounds which consist of polyhedron cages encapsulating guest atoms (M) such as Na, Ba [1-3]. These clathrates are expected to be potential materials for thermoelectric devices because these have low thermal conductivity despite high electrical conductivity. The low thermal conductivity has been considered to result from rattling vibrations of the guest atoms, which are like an Einstein mode with large amplitude. Since the frequencies of the guest rattling are significantly low, these phonon dispersions anti-cross the acoustic phonon ones, leading to retardation of the thermal propagation [4]. Such the properties of the rattling modes arise from the weak guest-host interaction. The rattling vibration frequencies depend on the size of the cage; the larger cage induces a shift of the guest toward off-centre position and causes the more distinct rattling nature. In addition, the rattling frequency shows an anomalous change with temperature decreasing, which was interpreted with high unharmonicity. Thus, it is important to measure the rattling vibrations as a function of temperature for various case sizes controlled with pressure.

Previously, we investigated the guest vibrations of various types of clathrate compounds by Raman experiments under high pressure [5-9]. However, the experimental conditions have been restricted to room temperature and a frequency region higher than ~25 cm\(^{-1}\). The rattling vibrational frequencies of our interesting sample, i.e. Eu\(_8\)Ga\(_{16}\)Ge\(_{30}\) are at about 20 cm\(^{-1}\)[10,11], and thus, in order to investigate

† To whom any correspondence should be addressed.

Published under licence by IOP Publishing Ltd
these rattling vibrations, it is required to extend the experimental conditions to lower temperatures and lower frequencies.

In this work, we constructed an experimental system for low-frequency (LF) Raman measurements at low temperatures (LT) and high pressures (HP). Using the constructed LF-LT-HP Raman system, we successfully observed the rattling vibrations of Eu in a clathrate (Eu$_8$Ga$_{16}$Ge$_{30}$) at about 20 cm$^{-1}$ under low temperatures and high pressures.

2. Experimental

Figure 1 schematically shows an experimental system which was constructed for LF Raman measurements under LT and HP. A diamond anvil cell (DAC) and a helium flow cryostat were used for HP and LT experiments. Because our Raman measurements are carried by using a microscopic optical system, the stability of the sample position is very important. Therefore, we adopted a gas flow type cryostat which is free from vibration. The pressure of the sample was controlled under low temperature by a gas driven membrane. In Fig. 2, we indicated details around the DAC. The DAC was mounted on a cold head of the cryostat. The temperatures were measured by thermocouples which were fixed on the cold head and on a DAC surface which is the opposite side of the cold head. We estimate approximately the temperature of the sample by taking the average of the temperatures measured at these two places. Pressure is determined by a ruby fluorescence method, taking into account the shift of the fluorescence wavelength with temperature [12,13].

For low frequency Raman measurements, we adopt a quasi-back scattering geometry as shown in Fig. 2. It should be noted that the excitation light is incident on the sample in DAC with an oblique direction. The light scattered in direction vertical to the culet is collected by a microscopic objective lens, and then introduced to a spectrometer equipped with a CCD detector. Radiation of 532 nm from a solid-state laser was incident with a power of 5 mW. The resolution of the spectra is about 1.5 cm$^{-1}$. The use of the pseudo-back scattering geometry and a polished plate-like sample effectively decreases in the Rayleigh signal. As a result, it became possible to detect the Raman signals in frequency range as low as about 10 cm$^{-1}$ under low temperature and high pressure.

Using the constructed system for the LT-HP-LF Raman measurement, we attempted to make experiments on a single crystal of Eu$_8$Ga$_{16}$Ge$_{30}$. Details of synthesis of the sample were described.
The single crystal Eu$_8$Ga$_{16}$Ge$_{30}$ was cut and polished into ~50 μm in size with ~20 μm in thickness. The small plate sample was placed into the sample chamber made on a rhenium gasket, and Ar pressure medium filled the sample chamber.

3. Results and discussion

Figure 3 shows Raman spectra of Eu$_8$Ga$_{16}$Ge$_{30}$ which were measured at high pressures (0.7, 4.1, 6.8 GPa) and room temperature (RT) and at high pressures and low temperatures (4.1 GPa and 250 K, and 6.7 GPa and 202 K). We successfully observed clear signals of the rattling vibration of Eu guest atoms occurring around 20-30 cm$^{-1}$ under HP-LT conditions. The obtained signals were well consistent with the previous Raman data measured at ambient pressure [11]. As pressure increases to 4 GPa at RT, the guest rattling frequency shifted to higher frequencies. However, this shift is not observed in 4-7 GPa. On the other hand, for the host vibration at 175 cm$^{-1}$ (which was observed at 174 cm$^{-1}$ under 1 atm and assigned as A$_{1g}$ symmetry [10]), the high-frequency shift was observed up to 7 GPa. Changing of the temperature did not largely affect the Raman spectra, and the frequency of each peak position remained almost the same. This means that the volume contraction on cooling is very small under high pressures above 4 GPa.

According to the previous result reported under ambient pressure [11], the line width of the guest atom located at off-centre position shows broadening as temperature decreases, because the split of the guest peak becomes more obvious. The present spectrum of guest vibration at 4 GPa seems to become slightly broader at 250 K than RT. On the other hand, the width of the spectrum measured around 7 GPa was less sensitive to the temperature, implying that the guest atoms are located near the centre of the cage at 7GPa.
If we perform the LF Raman measurements for various pressures under low temperature, we will clarify the properties of the rattling vibration for various conditions of guest off centre or on centre. Moreover, LT-HP XRD measurements of $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ are planned to determine a guest position as a function of pressure. Such the Raman and XRD experiments will be much informative for understanding of the rattling vibration of the clathrate compounds.

4. Summary
We developed, in the present work, an experimental system for low-frequency (LF) Raman measurements at low temperatures (LT) and high pressures (HP). The use of the quasi-back scattering geometry allowed us to make the Raman measurements to 10 cm$^{-1}$ under high pressure. Temperature and pressure are controlled using the gas-driven membrane system and the He cryostat. Using the developed LT-HP-LF Raman system, we successfully observed the rattling vibrations of Eu in a clathrate ($\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$) at 20-30 cm$^{-1}$ under low temperatures and high pressures. In near future, the rattling vibration will be clarified under low temperature as a function of pressure (cage size), and the results will be published elsewhere.

Acknowledgments
This work has been supported by KAKENHI (Grant-in-Aid for Scientific Research) on the Priority Areas “New Materials Science Using Regulated Nano Spaces-Strategy in Ubiquitous Elements” from the Ministry of Education, Culture, Sports, Science and Technology of Japan.
References

[1] Kasper J S, Hagenmuller P, Pouchard M, Cros C 1965 Science 150 1713
[2] Bobev S, Sevo S C 2000 J. Solid State Chem. 153 92
[3] Kovnir K A, Shevelkov A V 2004 Rus. Chem. Rev. 73 923
[4] Christensen M, Abrahamsen A B, Christensen N B, Juranyi F, Andersen N H, Lefmann K, Andersen J, Bahl C R H and Ifersen B B 2008 Nature Materials 7 811
[5] Kume T, Fukuoka H, Koda T, Sasaki S, Shimizu H and Yamanaka S 2003 Phys. Rev. Lett. 90 155503
[6] Kume T, Koda T, Sasaki S, Shimizu H and Tse J S 2004 Phys. Rev. B 70 052101
[7] Tse J S, Itaka T, T. Kume, H. Shimizu, K. Parlinski, H. Fukuoka, and S. Yamanaka 2005 Phys. Rev. B 72 155441
[8] H. Shimizu, T. Imai, Kume T, Sasaki S, Kaltzoglou A and Fässler T F 2008 Chem. Phys. Lett. 464 54
[9] Kume T, Ohno S, Sasaki S, Shimizu H, Ohishi Y, Okamoto N L, Kishida K, Tanaka K, and Inui H 2010 J. Appl. Phys. 107 013517
[10] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K, Ishii I, Suzuki T and Takabatake T 2006 Phys. Rev. B 74 174303
[11] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K and Takabatake T 2008 Phys. Rev. Lett. 100 165503
[12] Mao H K, Bell P M, Shaner J W and Steinberg D J 1978 J. Appl. Phys. 49 3276
[13] Ragan D D, Gustavsen R and Schiferl D, 1992 J. Appl. Phys. 72 5539