Raman scattering of type-I clathrate compounds: A$_8$Ga$_{16}$Ge$_{30}$ (A = Eu, Sr, Ba) and Sr$_8$Ga$_{16}$Si$_{30-x}$Ge$_x$

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Abstract. Dynamical motions of a guest ion in type-I clathrate compounds have been studied by Raman scattering measurements. The anomalous temperature dependence of the guest phonon energy has been found not only for A$_8$Ga$_{16}$Ge$_{30}$ (A = Ba, Sr, Eu), but also for A$_8$Ga$_{16}$Si$_{30-x}$Ge$_x$ (A = Ba, Sr). It has been found that the 4th order anharmonic potential is important to the guest ion motion. For Sr$_8$Ga$_{16}$Si$_{30-x}$Ge$_x$, the off-center rattling arises with the increase of Ge concentration, and it is confirmed that the off-center rattling plays an important role to the suppression of the lattice thermal conductivity.

1. Introduction

Recently, cage-structured compounds have widely attracted many researchers for the interesting lattice dynamical properties as well as the thermoelectric application. The efficiency of the thermoelectric materials can be evaluated by the dimensionless figure of merit $ZT = S^2T/\rho(\kappa_\text{el} + \kappa_L)$, where $T$, $S$, $\rho$, $\kappa_\text{el}$ and $\kappa_L$ are a operation temperature, Seebeck coefficient, electric resistivity, electric thermal conductivity and lattice thermal conductivity, respectively. Type-I clathrate compounds are the famous cage-structured compounds, whose structure is constructed by 12-hedrons (2$a$-site) and 14-hedrons (6$d$-site) that enclose guest ions. The motion of the guest ions, so-called rattling, is important role to achieve high-performance thermoelectric materials because the heat carrying acoustic phonon might be scattered by the rattling, yielding the low lattice thermal conductivity $\kappa_L$. For the type-I clathrate compounds: A$_8$Ga$_{16}$Ge$_{30}$ (A = Eu, Sr, Ba), the neutron diffraction studies have reported that the guest ion at 2$a$-site with small cage size locates at center, while that at 6$d$-site with large cage space locates at the off-center for A = Eu and Sr [1]. The temperature dependence of $\kappa_L$ of Ba$_8$Ga$_{16}$Ge$_{30}$ (BGG) is normal behavior that shows the crystalline peak at low temperature, but for Sr$_8$Ga$_{16}$Ge$_{30}$ (SGG) and Eu$_8$Ga$_{16}$Ge$_{30}$ (EGG), anomalous glass-like plateau at low temperature has been observed [1]. It has been considered that the off-center rattling affects on the suppression of $\kappa_L$, but this is not fully clarified by the experimental studies in the microscopic point of view.

Raman scattering is one of the powerful tools to investigate the dynamical motions of the guest ion. It is noticed that the motion of the guest ion at the 6$d$-site is Raman active, while one at 2$a$-site is not Raman active. Hereafter, we discuss the motions of guest ion at the 6$d$-site, and not one at the 2$a$-site. We already reported the dynamical properties of the guest ion for
A_{8}Ga_{16}Ge_{30} (A = Eu, Sr, Ba) [2, 3]. For SGG and EGG, the energy of the tangential movement of the guest ion is different between along [1,0,0] and [1,1,0]. It has been concluded that the guest ion motion is the off-center rattling. While, for n-type BGG, the two energies are almost the same. In addition, the anomalous energy decrease has been observed with the decrease of temperature. This temperature dependence of the guest modes is originated from the 4th order anharmonic potential of the cage. Recently similar energy anomaly has been found not only in type-I clathrate, but also in other cage-structured compounds: β-pyrochlore [3], skutterudite [4], and La_{3}Pd_{20}Ge_{6} [3, 5]. Therefore, this anomalous temperature dependence is recognized as the universal property for the cage-structured compounds with the large cage space.

It has been reported that the temperature dependence of κ_{L} of Ba clathrate (BGG [1] and Ba_{8}Ga_{16}Si_{30} (BGS) [6]) has a crystalline peak at low temperature. Recently, Suekuni et al. showed that the thermal conductivity changes from crystalline-like to glass-like by the Ge-doping for Sr_{8}Ga_{16}Si_{30-x}Ge_{x} (x = 0 (SGS), 20 (SGSG) and 30(SGG)) [7]. In order to clarify the cage-size correlation between κ_{L} and rattling, the additional Raman scattering experiments on BGS, SGS, and SGSG has been carried out.

2. Experimental

All measurements in this study were performed using single crystals. Raman spectra were measured by a triple monochromator (JASCO NR-1800) and a liquid N_{2} cooled CCD detector (Princeton Instruments Inc. LN/CCD-1100PB). The excitation light was 514.5 nm wavelength Ar ion laser with a power of 10 mW at the specimen.

The symmetry of the sample in this study is Pm\bar{3}n. The Raman active modes are given by the group theory analysis as 3A_{1g} + 7E_{g} + 8T_{2g} for the cage and E_{g} + T_{2g} for the guest at the 6d-site under the assumption of on-center position. These phonons with each irreducible representation have been determined by the polarization dependence measurements. The polarization geometry is given by a symbol of (α, β), where α and β denote the polarization directions of incident and scattered light, respectively. In this study, we employed three different geometries of (x, x), (x, y) and (x + y, x − y), where x and y correspond to [1,0,0] and [0,1,0] axes, respectively. The phonon with A_{1g} symmetry appears in (x, x), E_{g} in both (x, x) and (x + y, x − y), and T_{2g} in (x, y). The measurement temperature range was from 4 K to 300 K for all samples. Sample preparation was reported a previous paper [2, 8].

3. Results and Discussion

We focus the guest ion motion in the plane perpendicular to the fourfold axis at the 6d-site. If the site symmetry at the 6d-site was the original symmetry of 42m, the mode with tangential movement along [1,1,0] would be forbidden. However, even in the BGG, where Ba locates at the center according to neutron experiment, this movement is clearly observed. This shows that the site symmetry at the 6d-site becomes the lower symmetry of point group m due to the random configuration of Ga and Ge. The tangential movement along [1,0,0] in the (x, y) geometry and along [1,1,0] in the (x + y, x − y) geometry belongs to the same symmetry of A′ in the point group of m. We note that the allowed E_{g} mode is completely different vibration, since the guest ion moves along the fourfold axis. For convenience, we name the tangential movement of the guest ion along [1,0,0] and [1,1,0] as T_{2g}(1) and E_{g}(A), respectively. If the guest ion locates at the cage center, the potential energy at the center can be recognized as the same for the [1,0,0] and [1,1,0] direction. Thus, the energy difference between T_{2g}(1) and E_{g}(A) is the experimental evidence of the off-center position.

The temperature dependence of the energy of the guest modes is shown in Fig. 1. The energies of the guest modes decrease with decreasing temperature. This anomalous energy decrease does not depend on the guest ion position and its origin is explained by the large 4th order anharmonic potential for the motion of the guest ion [2]. For BGS, the both energies
change slightly within the measurement accuracy, but obvious increasing is not observed. This
means that the 4th order anharmonic potential clearly affects the motion of Ba ion in GaSi-cage.
The anomalous energy decrease has been observed not only for type-I clathrate but also in \(\beta\)-pyrochlore [3], skutterudite [4], and La\(_3\)Pd\(_{20}\)Ge\(_6\) [3, 5], where the guest ion locates at center of the cage. We note for the small cage that such energy decreases does not occur [2, 3]. Therefore, we concluded that this energy decrease is universal phenomena for the guest ion motion with the large 4th order anharmonic potential. Finally, we will discuss about the relationship between

![Figure 1](image1)

**Figure 1.** Temperature dependence of the energy of guest mode of (a) Ba\(_8\)Ga\(_{16}\)Si\(_{30}\) (BGS) and Ba\(_8\)Ga\(_{16}\)Ge\(_{30}\) (BGG), (b) Sr\(_8\)Ga\(_{16}\)Si\(_{30}\) (SGS), Sr\(_8\)Ga\(_{16}\)Si\(_{10}\)Ge\(_{20}\) (SGSG) and Sr\(_8\)Ga\(_{16}\)Ge\(_{30}\) (SGG) at room temperature. Lines are guide to eye.

off-center rattling and the lattice thermal conductivity. The temperature dependence of the lattice thermal conductivity of Sr clathrates is shown in Fig. 2, which is re-formed from ref. [7]. The Ge-doping of the Sr clathrate decreases the lattice thermal conductivity. On the other hand, for Ba clathrate, the temperature dependence of the lattice thermal conductivity has a crystalline-like peak at low temperature that is independent to the cage-size [1, 6], and there is no evidence of a remarkable off-center rattling. So, it is concluded that the off-center rattling plays an important role to suppress the lattice thermal conductivity.

![Figure 2](image2)

**Figure 2.** Temperature dependence of the lattice thermal conductivity of Sr clathrates.
4. Conclusion
In this study, we discussed about the off-center rattling of Sr ion by the results of the Raman scattering measurements. The energy of the guest phonon shows anomalous decreasing with decreasing temperature, where the 4th order anharmonic potential is dominant. This property is universal for cage-structured compounds with large anharmonicity. For the Sr clathrate, the chemical pressure, which is caused by a change in the cage composition, yields the off-center rattling. The measurement of the physical-pressure dependence of the guest mode remains as the future work.

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