Dynamical properties of guest ions in the type-I clathrate compounds $X_8Ga_{16}Ge_{30}$ (X=Eu,Sr,Ba) investigated by Raman scattering

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Raman active phonons in the type-I clathrate compounds of $X_8Ga_{16}Ge_{30}$ (X=Eu,Sr,Ba) have been fully assigned by the combination of polarized Raman scattering and first principles calculations. The dynamical motions of guest ions in the $6d$-site cage have been clearly identified. The energy of the modes, related to a rattling motion, decreases with decreasing temperature. The energy-decrease at low temperatures is a common property for thermal rattling in $X_8Ga_{16}Ge_{30}$. The anomalous decreases are originated from the quartic anharmonic potential, and its contribution has been experimentally determined. A mixed state between thermal rattling and quantum tunneling has been observed below 10 K. A soft mode due to the guest ion motion has been observed, but the transition due to this soft mode is somewhat different from the ordinary structural transition because of the shielding by carriers. In addition, it is found that the elastic dispersion of $Sr_8Ga_{16}Ge_{30}$ is caused by the interference with the rattling motion of the guest ion in the cage, and that the rattling at the off-center location plays an important role to suppress a lattice thermal conductivity and to achieve the phonon-glass state in $X_8Ga_{16}Ge_{30}$.

I. INTRODUCTION

Recently, clathrate compounds and filled skutterudites known as cagelike compounds have been extensively studied by many groups for not only thermoelectric application but also their interesting lattice-dynamical properties.[1–12] Especially, the motions of guest ions in the cage, so-called "rattling motions," have attracted much attention based on the concept of "phonon glass and electron crystal" (PGEC).[13] In order to achieve the phonon glass, it has been believed that the thermal conductivity of acoustic phonons should be decreased by the anharmonic vibrations of the guest ions. Thus, the rattling motions of the guest ions must be anharmonic vibrations and have a suitable energy range that leads to significant interaction or scattering of the heat carrying phonons of the overall crystal lattice. The first prediction of the concept of PGEC was reported by Nolas *et al.* for the Ge clathrates.[14] The assignments of the rattling mode at the low-energy region have been done by Raman scattering and theoretical calculations.[4–7] Unfortunately, the full assignment of the observed Raman modes and also the precise dynamical properties of the rattling modes have not been established, since all measurements were done using polycrystals. Thus, the characteristic property of the rattling motion is still unclear and Raman scattering measurements using single crystals are necessary. On the other hand, for type-I $X_8Ga_{16}Ge_{30}$, the important results concerning the guest ions have been obtained by the studies of neutron diffraction[9–11] and extended x-ray-absorption fine structure (EXAFS).[12] These studies have reported that the guest ion is on-center for the $2a$-site cage (12-hedron), but off-center for the $6d$-site cage (14-hedron). Furthermore, the length deviated from the cage center has been reported as almost zero for Ba, 0.4 Å for Sr, and 0.44 Å for Eu.[12] These results suggest that the Raman

modes of the guest ion at the $6d$ site appear as the first ordered Raman scattering process due to the lowered local symmetry in $X_8Ga_{16}Ge_{30}$. To clarify the dynamical properties of the guest ion motion, we have measured the Raman scattering spectra of single crystalline $X_8Ga_{16}Ge_{30}$, and we have also employed first-principles calculations for the precise phonon mode assignment. To our knowledge, this is the first report of the detailed dynamical properties of the guest ions in the cages, especially the rattling motions.

II. EXPERIMENTAL

Single crystals were grown by the self-flux method (excess Ga) using a starting proportion of 8:26:30.[15,16] The high-purity elements (99.95% or better) were sealed in carbonized quartz ampoules under partial argon atmosphere. The ampoule was placed in a box furnace, soaked at 1150 °C for 2 h, then cooled over 100 h between 720 and 620 °C, at which point it was quickly removed and the molten flux separated by centrifuging.

In the Raman scattering measurements, the 514.5 nm excitation of an Ar-ion laser (Spectra Physics, Stabilite 2017) was used with a power of less than 10 mW at the specimen. The backscattered light was analyzed by a triple monochromator (JASCO, NR-1800) and the analyzed light was detected by a liquid nitrogen cooled CCD multichannel detector (Princeton Instruments, LN/CCD-1100-PB).

The symmetry of $X_8Ga_{16}Ge_{30}$ (X=Eu,Sr,Ba) is $Pm\bar{3}n$. The Raman-active modes are given by group theory as $3A_{1g}+7E_g+8T_{2g}$ for the cage ions and E_g+T_{2g} for the guest ion at the $6d$ site, respectively, under the assumption of the on-center location at the $6d$ site. We note that movements of the guest ion at the $2a$ site are not Raman-active. The
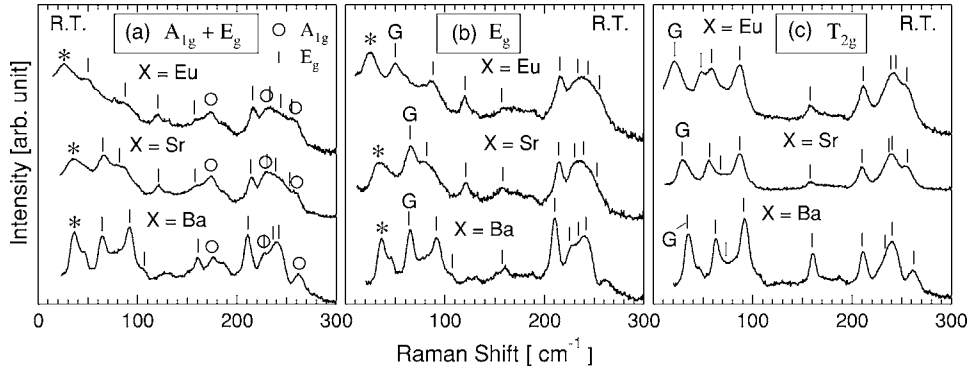
FIG. 1. Polarization dependence of Raman spectra for $X_8Ga_{16}Ge_{30}$ at room temperature. The "G" is the symmetry-allowed Raman active phonons, and bars and open circles denote the assigned peak. The peaks marked by * are the additional modes.

phonons with each irreducible representation have been determined by the polarization dependence. 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 ranged from 2 to 300 K, except for $Eu_8Ga_{16}Ge_{30}$ between 2 and 500 K.

The first-principles calculations of phonon energy at wave vector $q=0$ were made for $Ba_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ using the ABINIT code,[17,18] which is based on *ab initio* pseudopotentials and a plane-wave basis set in the framework of the density-functional formalism. The Troullier-Martins type[19] pseudopotentials were generated using the FHI98PP code.[20] The ground-state and response-function calculations were performed with the local-density approximation parametrized by Perdew and Wang[21] and with the Brillouin zone sampling of a Monkhorst-Pack[22] $2 \times 2 \times 2$ mesh of the special q points. The cutoff kinetic energies were 34 Ry for $Ba_8Ga_{16}Ge_{30}$ and 40 Ry for $Sr_8Ga_{16}Ge_{30}$, where 1 Ry$=13.605$ eV. The phonon energy was calculated using the density-functional perturbation theory, whose technical details on the computation of responses to atomic displacements and homogeneous electric fields are described in Refs. 23 and 24. This calculation was done for the on-center position of the guest ion at the $6d$ site.

III. RESULTS AND DISCUSSION

The polarization dependence measured at room temperature is shown in Fig. 1, where (a), (b), and (c) are the spectra of $A_{1g}+E_g[(x,x)]$, $E_g[(x+y,x-y)]$, and $T_{2g}[(x,y)]$, respectively. The phonons with the E_g and T_{2g} symmetries are directly assigned from the $(x+y,x-y)$ and (x,y) spectra, respectively. For the A_{1g} symmetry modes, the comparison between (x,x) and $(x+y,x-y)$ gives us the different-energy peaks, as shown in Fig. 1 and Table I. Table I summarizes both energies determined by the experiment and by the first-principles calculation. The energies between the experiments and the calculations are in good agreement, especially for $X=$Ba. The imaginary energy of $T_{2g}(1)$ for the $X=$Sr indicates that the center is not the minimum energy position, as

was reported in Ref. 25. The peaks at 64 cm^{-1} of $E_g(1)$ and 34 cm^{-1} of $T_{2g}(1)$ for $X=$Ba are the allowed vibrations of the guest ions even for the on-center position at the $6d$ site and they are marked by "G" in Fig. 1. The Ba displacements parallel and perpendicular to the fourfold axis are the base vectors for E_g and T_{2g}, respectively. Thus, all symmetry-allowed phonons are fully assigned for $Ba_8Ga_{16}Ge_{30}$. The assigned peaks are depicted by open circles for A_{1g} and by bars for E_g and T_{2g} in Fig. 1.

Next, we describe the mode assignments for $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$, referring to the results of $Ba_8Ga_{16}Ge_{30}$. The phonons of these crystals can be roughly classified into two kinds of vibrations: Vibrations due to the guest ion below 70 cm^{-1} (guest mode) and those due to cage ions above 70 cm^{-1} (cage mode). Since the observed spectra due to the cage ions above 70 cm^{-1} are very similar between three compounds, the phonon modes of the cage ions are fully assigned for the three compounds at room temperature, in spite of the worse peak's separation of the E_g spectrum at 230 cm^{-1} for $X=$Eu.

In addition to the symmetry-allowed phonons, there are two additional peaks, marked by asterisks in Fig. 1, at the low-energy region in the $A_{1g}+E_g$ and E_g spectra. In order to assign the symmetry, the A_{1g} spectra have been obtained by the subtraction of the E_g spectra from the $A_{1g}+E_g$ one. The temperature dependence of individual symmetry for $Eu_8Ga_{16}Ge_{30}$ is shown in Fig. 2. The symmetries of the additional modes are A_{1g} and E_g, which are the vibrations of the guest atom at the $6d$ site, since that at the $2a$ site does not produce a Raman-active mode. According to the neutron-diffraction report,[10] the equilibrium position of the guest atom at the $6d$ site deviates along the [1,0,0] direction, which is perpendicular to the fourfold axis. This deviation lowers the $6d$ site symmetry from $\bar{4}2m$ to m, where the normal direction of the mirror plane is perpendicular to both fourfold and [1,0,0] axes. This lowered symmetry does not affect the symmetry-allowed guest modes $E_g(1)$ and $T_{2g}(1)$, but the ionic displacement along the [1,0,0] axis becomes Raman-active and corresponds to the $A_{1g}(A)$ mode. Thus, the remaining problem is the origin of the additional $E_g(A)$ mode, since there remains no additional degrees of freedom for the off-centered guest ion at the $6d$ site. If the guest ion stays at one of four possible positions, the $E_g(A)$ mode should not be Raman-active. The existence of this $E_g(A)$ mode clearly shows that the guest ion moves rotationally between the four possible positions by hopping or tunneling. Because the tan-

TABLE I. Phonon energy of $X_8Ga_{16}Ge_{30}$ (X=Ba, Sr, Eu) at room temperature. The energy unit is cm^{-1}. Observed and calculated phonon energies are presented in *obs.* and *cal.* columns, respectively. The value in the parentheses denotes the observed energy at 2 K.

	Peak label		*X*=Ba obs.	*X*=Ba cal.	*X*=Sr obs.	*X*=Sr cal.	*X*=Eu obs.
Allowed modes	A_{1g}	(1)	175	174	174	174	174
		(2)	227	226	229	237	230
		(3)	263	267	261	264	259
	E_g	(1)	64(64)	65	65(66)	63	50(48)
		(2)	91	85	82	79	88
		(3)	108	120	121	119	120
		(4)	158	154	158	159	157
		(5)	210	208	214	212	216
		(6)	226	225	230	227	233
		(7)	234	234	239	243	244
		(8)	242	246	253	255	255
	T_{2g}	(1)	34(31)	26	30(29)	8i	21(18)
		(2)	62	59	56	52	48
		(3)	73	80	68	73	59
		(4)	91	89	87	86	87
		(5)	160	154	158	151	158
		(6)	210	211	211	211	211
		(7)	233	241	237	240	239
		(8)	241	244	241	246	244
		(9)	262	267	256	262	255
Additional modes	A_{1g}	(A)			48(49)		36(40)
	E_g	(A)	35(33)		33(29)		25(18)

gential fluctuation to [1,1,0] corresponds to E_g(A), this E_g(A) mode should be the same as the T_{2g}(1) guest mode. To confirm this, a discussion based on the temperature dependence is given below.

The cage modes do not show any anomalous behaviors between 2 and 500 K as shown in Fig. 2, where their energy normally increases with decreasing temperature. This is the same manner for X=Ba and X=Sr. However, the guest modes exhibit an opposite dependence, as shown Fig. 3(a). The energy of T_{2g}(1) and E_g(A) decreases with decreasing temperature. Both energies coincide for X=Ba, but they are different at high temperature for X=Sr and X=Eu. At 2 K, their energies for X=Sr and X=Eu merge. The energy difference at high temperature can be understood by the aniso-
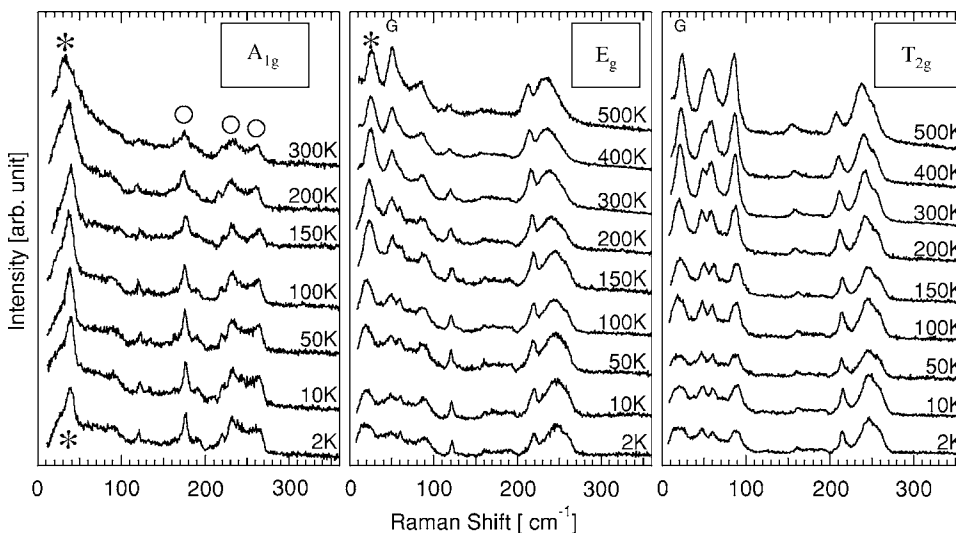

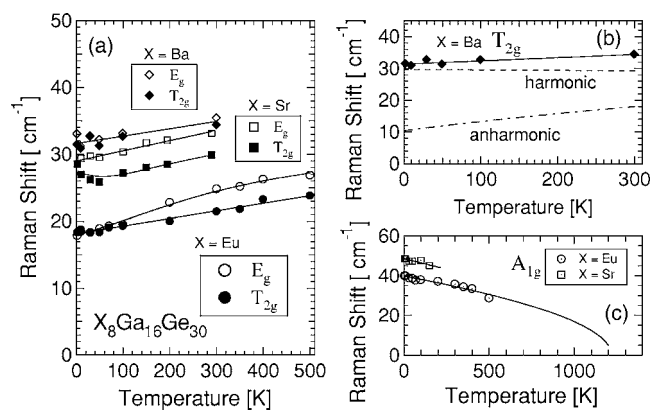FIG. 2. Temperature dependence of Raman spectra of $Eu_8Ga_{16}Ge_{30}$.

FIG. 3. Temperature dependence of the vibrational energy of the guest modes. (a) $T_{2g}(1)$ and $E_g(A)$, (b) $T_{2g}(1)$ for X=Ba with harmonic and anharmonic energy, (c) $A_{1g}(A)$ for X=Eu and X=Sr.

tropic potential energy. Since the ionic displacements of $T_{2g}(1)$ and $E_g(A)$ are the tangential movement to [1,0,0] and [1,1,0], respectively, the potential energy at [1,1,0] is larger by 5 cm^{-1} (7 K) than that at [1,0,0]. In fact, this energy difference drastically changes the spectral shape for X=Sr and X=Eu below 10 K, where both energies merge. In contrast, the Ba compound energy is isotropic, since the Ba ion is located near the center of the cage.

The anomalous energy decrease upon cooling can be explained by the quartic anharmonic potential. The phonon energy ω can be written by the equation of $\omega^2 = \omega_0^2 + k_4 \langle u^2 \rangle$, where ω_0, k_4, and $\langle u^2 \rangle$ are the harmonic energy, the coefficient of quartic anharmonic potential, and the square of the guest ion thermal displacement, respectively. Here, we evaluate the second term for the Ba case, since this equation becomes complicated for the off-center motion. Two terms are separately obtained from two sets of data at different temperatures and the reported thermal factor.[10] The results are shown in Fig. 3(b), where the harmonic energy is depicted by the dashed line and the quartic contribution is plotted by the dot-dashed line. This result emphasizes the importance of the quartic anharmonic potential for not only temperature dependence but also the thermal rattling. Furthermore, the energies of the guest modes decrease in the sequence of Ba, Sr, and Eu. This order cannot be explained by a simple mass effect, since the mass of Ba is much heavier than that of Sr.

The energy of $E_g(1)$ with the displacement along the fourfold axis is temperature-independent as shown in Table I. However, the linewidth for X=Eu increases with decreasing temperature below 100 K, whereas such a change has not been observed for X=Sr and X=Ba.

The temperature dependence of the energy of the additional $A_{1g}(A)$ is shown in Fig. 3(c). We note that the appearance of $A_{1g}(A)$ is related to the distance deviated from the center, since there is no clear A_{1g} peak even at low temperature for X=Ba and the intensity of X=Eu is stronger than that of X=Sr. The decrease of the energy of $A_{1g}(A)$ is more than 25% between 2 and 500 K, but that of the cage modes is less than 5%. Thus, this remarkable decrease suggests that $A_{1g}(A)$ is recognized as the soft mode related to the distance deviated from the center, since this mode is the radial vibra-

tion along [1,0,0]. The solid curve for X=Eu in Fig. 3(c) is a fitted curve by the function of $a\sqrt{T_0-T}$, where a, T_0, and T are frequency, transition temperature, and absolute temperature, respectively. The presented curve is the result with T_0 =1200 K and a=1.14 cm$^{-1}(K^{1/2})$. A similar decrease has also been observed for X=Sr, as shown in Fig. 3(c). Above T_0, the equilibrium position should become the center. This phase transition is different from the ordinary cooperative phase transition, since the correlation between the guest ions is very weak due to the shielding of carriers on the cage. Thus, we may call this new type of phase transition of the off-centered compounds the incoherent phase transition, since the phonon dispersion of the guest ion is flat in the whole Brillouin zone calculated by our first-principles calculation and a recent report.[25]

We discuss the thermal rattling and quantum tunneling. For the caged compounds of $La_3Pd_{20}M_6$, the elastic dispersion due to rattling motion has been observed for M=Ge,[26] but not for M=Si.[27] With decreasing temperature, we have observed an anomalous energy decrease of the guest mode for the former, but an ordinary increase for the latter.[28] Thus, it can be concluded that the energy decrease of the guest mode is the common property for the rattling. For $X_8Ga_{16}Ge_{30}$ with X=Sr and X=Eu, the spectral shape of $T_{2g}(1)$ and $E_g(A)$ changes below 10 K. Thereby, the guest ion motion seems to change from thermal rattling to quantum tunneling, considering the potential-energy difference of 7 K between [1,0,0] and [1,0,0]. However, the quantum tunneling is not the dominant process even at 2 K, since the energy difference between the ground state and the first excited state has been reported as small as 0.04 meV (0.46 K).[25] Thus, the guest ion motion at 2 K is a mixed state of thermal rattling and quantum tunneling. In order to investigate the full quantum tunneling, we should extend the temperature range below 0.5 K.

Finally, we discuss the relationship between the thermal rattling mode and the observed other physical quantities. Recently in the Sr clathrate, the elastic dispersion of C_{44} has been observed in the temperature range of 25–60 K by two of the authors,[29] and this temperature range corresponds to the energy range of 17–42 cm^{-1}. The largest elastic dispersion occurs at about 45 K (31 cm^{-1}), which coincides with the energy of the $T_{2g}(1)$ mode of the Sr clathrate. Very recently, Lee has found the anticrossing of the C_{44} acoustic phonon and the rattling $T_{2g}(1)$ mode by inelastic-neutron scattering for Sr and Ba clathrates.[30] Thus, these results conclude that the origin of the elastic dispersion in the clathrates is originated from the interference with the thermal rattling mode. This conclusion agrees with the previous predictions.[5,31,32]

In the thermal conductivity, the propagating wave is an acoustic phonon. We do not know which acoustic phonon plays an important role. However, the lattice thermal conductivity of Ba clathrate has a normal temperature dependence as with the usual crystalline behavior, while that of Eu and Sr clathrates shows an anomalous dependence having the glasslike plateau, and the value of the thermal conductivity of Sr and Eu clathrates is much smaller than that of the Ba one.[11] The present Raman study shows that the thermal rattling

occurs in the Ba, Sr, and Eu clathrates. However, the position of the Ba ion in the cage is almost center, while that of Sr and Eu ions is off-center. Thus, these facts show that the existence of the thermal rattling at the off-center position is very important to suppress the thermal conductivity. The present conclusion, derived by the experimental facts, is consistent with the theoretical suggestions.[33]

IV. CONCLUSION

The Raman-active phonons in type I clathrate compounds $X_8Ga_{16}Ge_{30}$ (X=Eu,Sr,Ba) have been fully assigned. Dynamical properties of the guest ion in the cage at the $6d$ site have been studied, and the rattling motions of the guest ion have been determined by the E_g(A) and T_{2g}(1) modes. The energy of rattling modes anomalously decreases with decreasing temperature. This anomalous decrease is explained by the quartic anharmonic potential in $X_8Ga_{16}Ge_{30}$, and is the common feature of the cagelike compounds. The A_{1g}(A) mode, which was observed in Eu and Sr clathrates, corresponds to the radial vibration. The existence of the A_{1g} mode is strong evidence that the guest ion is located at the off-center position. Thus, it is concluded that the Eu and Sr ions are located at off-center and the Ba ion at almost on-center. The behavior of the A_{1g} mode of Eu and Sr clathrates against temperature suggests the new type of transition with the incoherent interaction of guest ions. Furthermore, it is found that the elastic dispersion in the clathrate originates from the coupling of the acoustic phonon and the rattling mode, and also that the rattling at the off-center position is very important to suppress the phonon thermal conductivity and to achieve the phonon glass.

The following problems remain in the research of clathrate compounds. The first problem is why the off-center position is stable for Sr and Eu. This is a completely open question. The second one is the experimental clarification of the quantum tunneling of the guest ion at the lower temperature.

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