Off-Center Rattling and Anisotropic Expansion of Type-I Clathrates Studied by Raman Scattering

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Dynamical motions of the guest ions in type-I clathrates $Sr_8Ga_{16}Si_{30-x}Ge_x$ and $Ba_8Ga_{16}Si_{30-x}Ge_x$ have been studied by Raman scattering spectroscopy, to clarify the role of guest vibration modes in these systems with unusual thermal transport behaviors. An anomalous decrease of the guest energies with decreasing temperature is observed for both systems. The Ge-doping expands the cage surrounding the 6*d* site anisotropically for $Sr_8Ga_{16}Si_{30-x}Ge_x$, but isotropically for $Ba_8Ga_{16}Si_{30-x}Ge_x$. Especially for $Sr_8Ga_{16}Si_{30-x}Ge_x$, off-center rattling arises simultaneously with the anisotropic expansion, and it is confirmed that these anomalies play a crucial role to suppress lattice thermal conductivity in these systems.

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Guest-ion rattling, especially the "off-center" rattling, is a key concept to understanding the thermal transport behavior of thermoelectric materials based on cage structures. It has been suggested that the rattling phonons play a crucial role in improving their thermoelectric properties, since the rattling phonon can interfere with the heat-carrying acoustic phonon flow effectively, resulting in suppression of the lattice thermal conductivity κ_L [1–14]. This is one of the most promising new approaches to achieving high-performance thermoelectric conversion devices, since the thermoelectric figure of merit depends inversely on the thermal conductivity. For example, filled skutterudite antimonides show a dramatic suppression of κ_L compared to their unfilled counterparts, and it has been believed that this suppression is due to the rattling motion of the guest ion [2–6]. However, in general, the randomly disordered system shows a glasslike temperature dependence of κ_L, since the disordered lattice should disturb the heat conduction. In fact, the temperature dependence of κ_L changes from crystallinelike to glasslike behavior by the doping of 4th and 5th components for a ternary filled skutterudite [5].

From the microscopic point of view, the off-center rattling itself is important for the thermoelectric behavior of the type-I clathrates, which are also promising high-performance thermoelectric materials [8–14]. This family's basic structure has cubic symmetry and the chemical formula A_8X_{46}, where X forms a host cage that is constructed by 12-hedrons and 14-hedrons in which the guest ions A are inserted (2*a* and 6*d* sites, respectively). The low-temperature κ_L of $A_8Ga_{16}Ge_{30}$ (A = Eu, Sr, Ba), which are the typical type-I clathrates, shows a strong guest-ion dependence [15,16]. The value of κ_L at room temperature decreases in order of A = Ba (BGG), A = Sr (SGG), and A = Eu (EGG). In the low-temperature region, the κ_L of SGG and EGG is strongly suppressed, showing an anomalous glasslike plateau, while that of BGG has a normal crystalline peak. Neutron diffraction studies have reported that the guest ion at the 2*a* site is located at the small cage center, while the 6*d* site guest ion in the large cage is actually located at the off center for EGG [17] and SGG, but almost on center for BGG [16,18–20]. These experimental results indicate that the off-center rattling would be the fundamental concept to explain the thermoelectric properties when the cage randomness is not so large. Thus, the dynamical properties of the off-center rattling from the microscopic standpoint warrants detailed experimental clarification.

Recently, Suekuni and coworkers have reported that the temperature dependence of κ_L [$\kappa_L(T)$] of $Sr_8Ga_{16}Si_{30-x}Ge_x$ changes from crystallinelike to glasslike behavior with increasing Ge concentration [21]. On the other hand, it has been reported that $\kappa_L(T)$ of $Ba_8Ga_{16}Si_{30-x}Ge_x$ [$x = 0$ (BGS) and 30 (BGG)] has a normal crystalline peak without relation to the cage composition [13,16]. Therefore the $A_8Ga_{16}Si_{30-x}Ge_x$ systems (A = Sr and Ba) are appropriate to investigating the guest free space dependence of κ_L, since the cage size of these clathrates increases linearly with increasing Ge fraction x.

In this Letter, we report the Raman scattering measurements on the single-crystalline Sr clathrates $Sr_8Ga_{16}Si_{30-x}Ge_x$ [$x = 0$ (SGS), 20 (SGSG), and 30 (SGG)] and the Ba clathrate (BGS and BGG), and demonstrate the cage-size dependence of the off-center rattling. Raman scattering is one of the most powerful techniques for investigating the dynamical properties of the guest ion from the microscopic viewpoint [22–26]. The cage-size dependence of the guest energies for the Sr clathrates reveals that the location of the guest ion at the 6*d* site changes from almost on center to off center with the

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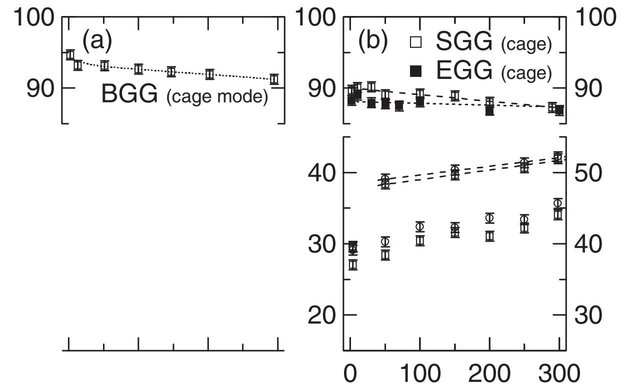
cage size and increases monotonically with the increase of the Ge concentration [21], Fig. 2(a) indicates the cage-size dependence of both guest energies. The energy difference between $T_{2g}(1)$ and $E_g(A)$ is small for the Ba clathrates, while it becomes increasingly large with the Ge doping for the $Sr_8Ga_{16}Si_{30-x}Ge_x$. If the position of the guest ion were centered at the cage, the potential energy of the cage would be recognized as the same for the [100] and [110] directions. This means that the large energy difference between $T_{2g}(1)$ and $E_g(A)$ is an experimental demonstration of the off-center location of the guest ion. Thus, the position of the Sr ion changes from nearly on center to off center with the increase of the cage size, while that of Ba ion remains almost on center independently of the cage size in these compounds. The energy of $T_{2g}(1)$ is smaller than that of $E_g(A)$ for the case in SGSG and SGG. This result indicates that the potential energy distribution is highly anisotropic and that a potential minimum exists toward the [100] direction, consistent with neutron diffraction measurements [16]. For SGS and the Ba clathrates, the potential is essentially isotropic, since both energies are almost the same.

The similarity in the slopes of $E_g(A)$ for the Sr and Ba compounds clearly shows that the expansion of the Sr clathrate along [110] by Ge doping is similar to that of the Ba case, but the different slope of $T_{2g}(1)$ suggests that the expansion along [100] is different. The stronger decrease of $T_{2g}(1)$ than $E_g(A)$ suggests that the effect of the higher order potential is enhanced. This means that the movable space for the Sr ion expands toward the [100] direction, resulting in off-center rattling which in turn may affect the cage modes. Figure 2(b) shows the Raman spectra of the T_{2g} mode of BGG, SGG, and EGG measured at room temperature. The cage-mode energies at about 90 cm^{-1} of SGG and EGG marked by filled triangles in Fig. 2(b) are smaller than that of BGG. This mode corresponds to the collective motion of the cage. Thus, the off-center rattling decreases the atomic interaction strength at the cage, which is experimental evidence that the larger off-center rattling expands the 14-hedron.

Figure 3 shows the temperature dependence of the collective cage mode, which corresponds to the mode marked by filled triangles shown in Fig. 2(b), and the guest mode. The energy of the cage mode shows normal temperature dependence, while that of the guest mode shows an anomalous one that the energy decreases with decreasing temperature. Even for BGS, both energies decrease slightly within the measurement accuracy. 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 guest-ion motion [27]. This anomaly is a common property of type-I clathrate compounds, which has a large cage size for the guest ion and has a weak interaction between guest and cage. More recently, a similar anomalous energy decrease has been observed not only



on type-I clathrates but also on β-pyrochlore [28], skutterudites [29], and $La_3Pd_{20}Ge_6$ [28,30], in which the guest ions are located at the center of the cage. Therefore, we conclude that this energy decrease is a universal phenomenon for the guest-ion motion with large 4th order anharmonic potential.

Finally, the relationship between the off-center rattling and κ_L is discussed. The $\kappa_L(T)$ of the Sr clathrates from Ref. [21] is shown in Fig. 4. The κ_L changes from crystallinelike to glasslike behavior and the value of κ_L decreases with the Ge doping in $Sr_8Ga_{16}Si_{30-x}Ge_x$. As we showed in Fig. 2(a), the Ge doping increases the off-center rattling. For the Ba there is no evidence of off-center rattling, κ_L maintains a crystalline peak at low temperature [13,16] independently of the cage size, and the values of κ_L are larger than those of SGG and SGSG. Thus, it is concluded that the off-center rattling plays a crucial role in suppressing κ_L in the case that the cage randomness is small.

In summary, we have investigated the off-center rattling of the Sr ion in $Sr_8Ga_{16}Si_{30-x}Ge_x$ clathrates by Raman scattering. The guest energy shows an anomalous decrease with decreasing temperature, where the 4th order anharmonic potential is dominant for the guest-ion motion. This anomaly is a universal phenomenon for cage-structured compounds with large cage space for the guest and weak interaction between guest and cage. The cage-size dependence of the guest energies for Sr and Ba clathrates reveals that an anisotropic expansion as well as the appearance of off-center rattling occurs simultaneously with the release of chemical pressure by changing the cage composition. We have demonstrated the importance of the relationship between the anisotropic expansion and the off-center rattling. Measurement of the physical-pressure dependence of the guest mode remains as a future work that may help clarify this issue. We also demonstrate that the off-center rattling plays an important role in suppressing the lattice thermal conductivity. This result solidifies the initial hypotheses [7,9]. It is desirable that the relationship between the anisotropic expansion, the off-center rattling, and the suppression of the lattice thermal conductivity be clarified, to better establish this route as a guideline for thermoelectric material research.

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