Neutron scattering study of phonon dynamics on type-I Clathrate Ba$_8$Ga$_{16}$Ge$_{30}$

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Abstract. Phonon dynamics of type-I clathrates Ba$_8$Ga$_{16}$Ge$_{30}$ has been studied at room temperature by inelastic neutron scattering for energy less than 9 meV. Optical phonons associated with large vibrations of Ba atoms filled in large tetrakaidecahedral cages are observed around $E = 4.5$ meV. Analysis based on a Born-Von Kármán force model shows that the longitudinal force constants between the Ba atoms and the oversized cages has a relatively small value of 0.011 ∼ 0.014 mdyn/Å. The results indicate that the Ba atoms are very loosely bound to the surrounding oversized cages that consist of Ga and Ge atoms.

1. Introduction

A large vibration of an atom in an oversized atomic cage, so called rattling, has attracted great interest since it can be the origin of exotic physical properties. For example, filled skutterudites, RM$_4$X$_{12}$ (R = rare-earth; M = Fe, Ru or Os; X = P, As or Sb), which are known to be a good thermoelectric material, are one of those compounds that have large cages filled with rare-earth atoms [1, 2, 3, 4]. Remarkably, in the filled skutterudite antimonides, lattice thermal conductivity is as small as a glass although they show well-defined crystalline structure [5]. It is considered that rattling can play an important role in suppressing the thermal conductivity. Rattling can also influence the electronic properties via electron-phonon coupling. It has been suggested that rattling assists the occurrence of superconductivity in the $\beta$-pyrochlore compound KOs$_2$O$_6$ [6] and in the type-I silicon clathrate Ba$_8$Si$_{46}$ [7].

To clarify the effect of the rattling motion on exotic physical properties in materials having oversized atomic cages, it is essential to study the nature of the rattling. Inelastic neutron scattering using a single crystal is a useful method for studying the dynamics of atomic vibrations, since it can measure both the energy and momentum dependences of phonon spectra. Previously, the phonon dynamics of CeRu$_4$Sb$_{12}$ were investigated by inelastic neutron scattering [8]. The result suggests that the rattling motion is a coherent optical phonon and that the suppression of the lattice thermal conductivity can be ascribed to an increase in Umklapp scattering caused by the presence of low-lying optical phonons.

Although valuable information regarding rattling in CeRu$_4$Sb$_{12}$ has already been obtained, it is still important to study the rattling motions of other compounds that have similar oversized
cages. In particular, the universal features of rattling need to be clarified by further studies. Type-I clathrate \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) is one of compounds that have large Ga and Ge atomic cages filled with Ba guest atoms \[9\]. In \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \), there are two kinds of cage, \( \text{Ba(Ga,Ge)}_{24} \) tetrakaidecahedral cages and \( \text{Ba(Ga,Ge)}_{20} \) dodecahedral cages. The \( \text{Ba(Ga,Ge)}_{24} \) cages are oversized compared to the size of Ba atoms. It is considered that the Ba atoms in the \( \text{Ba(Ga,Ge)}_{24} \) cages behave as rattlers. In this study, we examined the nature of the rattling motion in \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) by inelastic neutron scattering using single crystals.

2. Experimental details

A single crystal of \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) was grown by a self-flux method using excess Ga, which is described in detail elsewhere \[10, 11\]. The composition of the grown single crystal was found to be \( \text{Ba}_8\text{Ga}_{15.98}\text{Ge}_{30.02} \) using an electron probe microanalyzer. The single crystal has n-type charge carriers. Two single crystals cut from the same batch were used for the neutron scattering measurements. The total volume of samples was about 1 cc.

Neutron scattering measurements were carried out using a triple-axis spectrometer, HQR, at the JRR-3 reactor of JAEA at Tokai. The initial neutron energy was fixed at \( E_i = 13.5 \) meV using a pyrolytic graphite (PG) monochromator. A PG filter was inserted before the sample to remove higher order neutrons. The sequence of horizontal collimators was 12'-open-S-60'-60', where S denotes the sample position. The measurements were conducted at room temperature.

To estimate the interatomic force constants, we performed calculations based on the Born-von Kármán atomic force model. The longitudinal force constants of the fifteen closest atomic pairs were chosen as fitting parameters (see Table 1), and the calculated intensities of the phonon spectra as well as the energies were fitted to the observed data. Since we only measured phonons below \( E = 9 \) meV, fitting of phonon energies above \( E = 9 \) meV was conducted using data observed by Raman measurements \[12\]. In the analysis, the atomic coordinates were taken from ref \[9\].

3. Results and discussion

Figure 1 shows energy spectra of transverse modes with the propagation vector \([100]\) below \( E = 9 \) meV. The solid lines depict the results of Gaussian fits. At \( Q = (0.35,3,3) \), a well-defined acoustic phonon is observed around \( E = 3 \) meV with optical phonons at a higher energy. Since the linewidth of the optical phonon around \( E = 4.7 \) meV is larger than the instrumental energy resolution, several phonon branches can be included in the peak. As the wave vector \( q \) increases, the scattering intensity of the acoustic phonon decreases drastically and becomes comparable to optical phonons beyond \( Q = (0.4,3,3) \). At \( Q = (0.45,3,3) \), a double peak structure is still observed around \( E = 5 \) meV, but neither peak has a sharp linewidth in contrast with the spectra obtained below \( Q = (0.4,3,3) \). On the other hand, at the zone boundary \( Q = (0.5,3,3) \), a relatively sharp peak reappears at \( E = 6 \) meV.

Figure 2 shows the obtained phonon dispersion of \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) with propagation vector of \([100]\). The filled circles depict the peak positions of the observed phonons. The vertical lines drawn through each data point above \( E = 3.9 \) meV indicate the full width at half maximum (FWHM) of each phonon profile. The solid lines depict results of a fit based on the Born-von Kármán force model, and the contour maps show the calculated scattering function for the transverse phonon modes at \( (\xi,3,3) \). As the figure shows, the calculated lines reproduce the observed data reasonably well. We also confirmed that the calculated phonon energies of \( A_{1g} \), \( E_g \) and \( T_{2g} \) modes above \( E = 9 \) meV agree with those observed by Raman measurements \[12\] to an accuracy of \( \Delta E = 1.7 \) meV only with one exception for an \( E_g \) mode that differs by \( \Delta E = 4.9 \) meV. Almost all of them agree within \( \Delta E = 1.0 \) meV.

According to the analysis, the optical phonon modes observed around \( E = 4.5 \) meV correspond to guest modes, in which Ba atoms filled in the large \( \text{Ba(Ga,Ge)}_{24} \) cages vibrate.
Figure 1. Energy spectra of transverse acoustic and optical phonons with propagation vector [100] in Ba$_{8}$Ga$_{16}$Ge$_{30}$. The solid lines are the results of Gaussian fits.

With large amplitudes. These guest modes around $E = 4.5$ meV have a variety of symmetries. Among them, the energy of the guest mode having $T_u$ symmetry at the zone center increases in the vicinity of the zone boundary, exhibiting anticrossing behavior with an acoustic phonon mode around $q = (0.45,0,0)$. This anticrossing behavior indicates that the guest mode mixes strongly with the acoustic mode. The dashed lines demonstrate phonon dispersion curves when they do not show anticrossing, assuming a linear curve for the acoustic mode. As shown, these dashed lines deviate from the observed data, suggesting that the data cannot be reproduced by a crossing picture. The energy of the guest modes found in this study at $E = 4.5$ meV is smaller than the previously reported guest mode energy in CeRu$_4$Sb$_{12}$, which is about $E = 6$ meV [8]. Since the Ba atom is lighter than the Ce atom, a smaller guest mode energy in Ba$_{8}$Ga$_{16}$Ge$_{30}$ suggests that the guest atoms in Ba$_{8}$Ga$_{16}$Ge$_{30}$ are more weakly bound to the surrounding cage atoms than those in CeRu$_4$Sb$_{12}$.

The force constants obtained by the analysis are summarized in Table 1. As shown, the force constants of Ba2-(Ga,Ge) pairs are very small, with a value of 0.011 $\sim$ 0.014 mdyn/Å, indicating that the Ba2 atoms in the large Ba(Ga,Ge)$_{24}$ cages are bound loosely to the surrounding atoms. This result shows that the Ba2 atoms can vibrate with large amplitudes, which is consistent with previous expectation for guest atoms filled in oversized atomic cages. On the other hand, the force constants of Ba1-(Ga,Ge) pairs are comparable with those of (Ga,Ge)-(Ga,Ge) pairs, indicating that Ba1 atoms in the smaller Ba(Ga,Ge)$_{20}$ cages are bound rigidly.
Table 1. Interatomic force constants obtained from analysis based on the Born-von Kármán model. G depicts Ga or Ge atoms. The atomic coordinates of Ba1, Ba2, G1, G2, G3 are taken to be 2a (0, 0, 0), 6d (0, 1/4, 1/2), 6c (1/4, 0, 1/2), 16i (0.1844, 0.1844, 0.1844) and 24k (0, 0.3083, 0.1181), respectively [9].

| Pair     | bond length (Å) | Force constants (mdyn/Å) | Pair     | bond length (Å) | Force constants (mdyn/Å) |
|----------|-----------------|--------------------------|----------|-----------------|--------------------------|
| G2-G2    | 2.45            | 0.80                     | G2-G2    | 3.98            | 0.05                     |
| G2-G3    | 2.50            | 0.80                     | Ba2-G2   | 4.01            | 0.011                    |
| G1-G3    | 2.51            | 0.68                     | G1-G2    | 4.01            | 0.05                     |
| G3-G3    | 2.55            | 0.60                     | G2-G3    | 4.02            | 0.05                     |
| Ba1-G2   | 3.44            | 0.80                     | G3-G3    | 4.05            | 0.05                     |
| Ba1-G3   | 3.56            | 0.60                     | Ba2-G3   | 4.08            | 0.10                     |
| Ba2-G3   | 3.63            | 0.014                    | G3-G3    | 4.11            | 0.02                     |
| Ba2-G1   | 3.81            | 0.013                    |          |                 |                          |

to the surrounding atoms. Although the guest atoms in the Ba(Ga,Ge)_{24} cages are bound very weakly, the anticrossing behavior indicates that a guest mode can interact with an acoustic mode, which is consistent with the findings of a previous report on CeRu_{4}Sb_{12} [8].

4. Conclusion
Phonon dynamics of Ba_{8}Ga_{16}Ge_{30} have been studied by inelastic neutron scattering. It has been found that guest modes where Ba atoms vibrate with large amplitudes in oversized Ba(Ga,Ge)_{24} cages lie at relatively low energy of E ∼ 4.5 meV. Analysis based on a Born-Von Kármán force model has clarified that the Ba atoms in oversized Ba(Ga,Ge)_{24} cages are bound very weakly to surrounding atoms, with a value of 0.011 ∼ 0.014 mdyn/Å.

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