Low-temperature heat capacity of $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$: Tunneling states and electron-phonon interaction in clathrates

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(Received 26 July 2010; published 23 August 2010)

Tunneling states of $Sr_8Ga_{16}Ge_{30}$ (SGG) and $Ba_8Ga_{16}Ge_{30}$ (BGG) are studied in detail using single crystals with a variety of carrier concentrations from the view point of heat capacity (C_p). An important excessive contribution αT due to the tunneling states is found besides $\gamma_e T$ of the conduction electrons. The value of α is accurately deduced to be 10.1 ± 1.5 mJ/mol K^2 for SGG while such a value is as small as 0.8 ± 0.4 mJ/mol K^2 for BGG. From the temperature evolution of C_p as a function of carrier concentration, the effective masses, one of the most important physical parameters for evaluating electron-phonon interactions $\lambda_{e\text{-}ph}$, are accurately estimated to be $1.68m_0$ and $1.01m_0$ for SGG and BGG, respectively. The $\lambda_{e\text{-}ph}$ seems to be enhanced when the anharmonic rattling modes are involved.

DOI: 10.1103/PhysRevB.82.085206 PACS number(s): 63.20.kd, 63.20.Ry, 65.40.Ba

I. INTRODUCTION

Clathrate compounds have a cage structure and can accommodate alkali and alkaline-earth elements. In the case of the type-I clathrates, the guest atoms reside in the two dodechedra (2a site) and six tetrakaidecahedra (6d site) cages as shown in Fig. 1. Large freedom especially in the tetrakaidecahedral cages makes clathrates one of the most suitable candidates for the phonon glass electron crystal concept.[1] In Ge-based clathrates, when the guest atom is changed from Ba (1.60 Å) to Sr (1.44 Å) or Eu (1.35 Å), thermal conductivity is greatly suppressed and changes from a crystallike to glasslike behavior.[2] The Sr atoms are suggested to be off-centered in $Sr_8Ga_{16}Ge_{30}$ (SGG) while in $Ba_8Ga_{16}Ge_{30}$ (BGG) the Ba atoms are placed almost at the on-centered site.[2] In addition, extended x-ray-absorption fine structure and x-ray photoemission spectroscopy experiments show that 75% Sr atoms are displaced away from the center whereas the other 25% Sr are centered.[3,4]

Quantum tunneling of guest atoms has been a very important issue to understand the physical properties of clathrates.[5–10] For Eu clathrates, quantum tunneling at ~450 MHz frequency among the four equivalent sites was discussed from the viewpoint of Mössbauer experiments.[5] The mixed state of thermal rattling and tunneling are argued using raman spectroscopy in the Ge clathrate family.[6] The presence of tunneling states in SGG was corroborated by the T^3 dependence of ultrasonic attenuation[7] and the T^2 behavior of thermal conductivity below 1 K.[8–10] These behaviors are considered to be associated with a two-level system introduced by Anderson *et al.*[11] in order to explain the anomalies observed in glasses. A generic two-well soft potential model[12] has also been proposed.

A T-linear contribution (αT) to the heat capacity due to the tunneling between two local minima has previously been suggested to be present for SGG.[10] An αT term was also reported for $Ba_8Ga_{16}Sn_{30}$ (BGS), where the γ obtained from heat-capacity analyses ($C_p/T = \gamma + AT^2$) is a factor of ten times larger than the expected electronic Sommerfeld γ_e considering the carrier concentration.[13] Although an exact evaluation of the αT term is very important for accurately evaluating curious electron-phonon interactions in this system from the effective-mass enhancement, no accurate examination has been reported so far. This is because the T-linear dependence simultaneously involves both tunneling αT and electron $\gamma_e T$ terms. Here we perform detailed heat-capacity studies using single crystals of $Ae_8Ga_{16}Ge_{30}$ (Ae=Ba and Sr). We will determine the intrinsic γ_e as well as α values accurately by employing samples with a large variety of carrier concentrations.

II. EXPERIMENTAL

SGG and BGG single crystals were synthesized by a self-flux method using stoichiometric amounts of Sr/Ba and Ge under excessive amount of Ga.[4,14] The sample quality was checked by single-crystal x-ray diffraction with a Rigaku Saturn charge coupled device area detector with graphite monochromated Mo $K\alpha$ radiation (λ=0.71070 Å). The samples were polished into thin pieces for Hall coefficient measurements, and the size was controlled to be smallest possible for heat-capacity measurements. The carrier type and concentration were determined by Hall coefficient measurements with a Quantum Design physical properties measurement system (PPMS). Heat-capacity measurements were also carried out in the range of 0.4–50 K with PPMS equipped with a He-3 cryostat. The same specimen was used for both measurements to minimize any errors from inhomogeneity. Many efforts were also made to widen the carrier concentration variation, but the carrier concentration for BGG and SGG is somehow restricted in a limited range.[15]

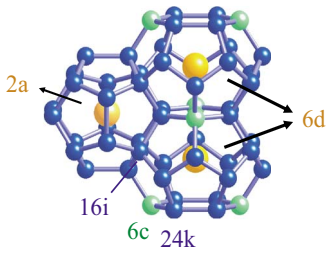

FIG. 1. (Color online) Structure of type-I clathrate.

III. RESULTS AND DISCUSSION

C_p/T vs T^2 data of SGG and BGG in the low-temperature regime are shown in Fig. 2. Although the C_p/T curves of all BGG samples show a T^2 dependence, those of SGG exhibit a strong deviation from the conventional T^2 dependence. One of the most plausible reasons is the anharmonicity of the phonons. An anharmonic potential model[12] was previously reported and has been successfully used for interpretation of clathrates.[10,13] According to this model, the potential is given by

$$V(x) = W\left[D_1\left(\frac{x}{d}\right) + D_2\left(\frac{x}{d}\right)^2 + \left(\frac{x}{d}\right)^4\right], \tag{1}$$

where D_1 and D_2 are the coefficients of the asymmetry, harmonic-potential terms and W is the characteristic energy of the potential. As argued in earlier papers,[12] the phonon density of states (PDOS) should be the sum of a constant density of tunneling states, a ν^2 density of sound waves and a ν^4 density of soft vibrational modes.

$$g(\nu) = c + a\nu^2 + b\nu^4. \tag{2}$$

According to this PDOS, heat capacity can be calculated and simplified at low temperatures as

$$C_{ph} = \alpha T + AT^3 + BT^5. \tag{3}$$

For harmonic potentials $[V(x) = W(x/d)^2]$, Debye and Einstein models are generally applied.

In $Ae_8Ga_{16}Ge_{30}$, the host structure is covalent and C_p is thought to be well described by the Debye model. Phonons associated with the guest atoms can be categorized as the Einstein model or the soft potential model.[10,15] The total heat capacity can be written as

$$C_p = C_{elec} + C_{host} + C_{guest} = \gamma_e T + AT^3 + C_{guest}, \tag{4}$$

where C_{elec}, C_{host}, and C_{guest} are the contributions of electrons, host structure, and guest atoms, respectively, and γ_e is the Sommerfeld coefficient. For SGG, the soft vibration term indicates an obvious anharmonic potential of the guest atoms. The low-temperature Debye behavior indicates that the anharmonicity of Ba is very small in BGG, which is consistent with its small off-centered displacement reported by Christensen, *et al.*[16]

Up to now, only an apparent experimental evidence showing the existence of αT has been reported for the BGS system because $\gamma = \alpha + \gamma_e$ is ten times larger than the expected

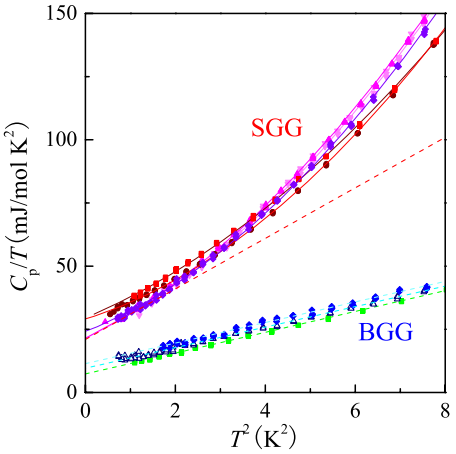

FIG. 2. (Color online) Temperature dependence of the heat capacity C_p of $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ with different carrier concentrations, presented as C_p/T vs T^2. The dashed lines were fitted using a standard Debye model. The solid lines were fitted using another soft vibration T^4 term.

Sommerfeld coefficient γ_e.[13] Actually, it is generally difficult to differentiate the contributions of αT and $\gamma_e T$ since both are linearly dependent on T. Here it should be noted that γ_e is related to the carrier concentration n and the density of state effective mass m^* in the framework of the effective-mass approximations

$$\gamma_e = \frac{k_B^2}{3\hbar^2} m^* \left(3\pi^2 \frac{N_0}{V}\right)^{1/3} = cm^* n^{1/3}, \tag{5}$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, m^* is the effective mass of electrons, N_0 is the total electron number, and V is the volume. The value of m^* for clathrates is known to be almost independent of n as long as the similar structures are considered.[17] Therefore, α and γ_e can be separated from each other through experiments carried out by changing the carrier concentration. In addition, the m^* can also be accurately obtained, as described later.

$$\gamma = \alpha + \gamma_e = \alpha + cm^* n^{1/3}. \tag{6}$$

The carrier type and the concentration of the samples have been determined by Hall coefficient measurements using a common single-carrier assumption as used in previous papers.[2,18–28] All SGG and BGG crystals are n type, which is nearly independent of temperature. The carrier concentrations of the prepared samples cover almost the largest possible range under the present situation.[15] We have also tried to make samples with lower carrier concentrations, but the inhomogeneity became worse not to be sufficient for accurate studies. Low-temperature carrier concentrations, listed in Table I, was used for Eq. (6). The relationships between γ and $n^{1/3}$ for SGG and BGG samples are plotted in Fig. 3. The α value of 10.1 ± 1.5 mJ/mol K^2 for SGG is larger than that of 0.8 ± 0.4 mJ/mol K^2 for BGG. The effective mass can be obtained from the slopes. The value of m^* is deduced to be $\approx 1.68m_0$ for SGG as compared to $m^* \approx 1.01m_0$ for BGG, where m_0 is the free-electron mass.

TABLE I. Carrier type and concentration n at 2 K, T-linear factor from heat capacity γ of BGG and SGG crystals.

Sample	Type	n ($\times 10^{20}$ cm^{-3})	γ [mJ/(mol K^2)]
BGG1	n	1.85	7.53
BGG2	n	3.02	9.03
BGG3	n	6.28	11.03
SGG1	n	11.34	29.55
SGG2	n	6.64	29.04
SGG3	n	4.14	24.21
SGG4	n	2.20	21.85
SGG5	n	3.77	24.56

A T-linear dependence of heat capacity at low temperatures was first found in an amorphous system, and a two-level system with continuous random potentials was proposed for describing a tunneling model.[11,12] The degree of disorder is estimated by comparing the α value with that of amorphous silica, which has been reported to be 2.7 J/m^3 K^2.[12] The values for SGG and BGG evaluated in the present paper after unit conversion are about 13.9 J/m^3 K^2 and 1.1 J/m^3 K^2, respectively. The α value of SGG is larger than that of silica and the one for BGG is on the same order magnitude. These results suggest the existence of large disorder in clathrates, which may come from the random displacement of Ga and Ge in the host framework. The present experiments show that this disorder is much larger in SGG than that in BGG.

For SGG, the tunneling contribution to C_p can be calculated to be about 20 mJ/mol K at 2 K from the α value. This is very small as compared to the thermal rattling contribution of about 35 mJ/mol K estimated from the soft vibration T^5 term at the same temperature. The small tunneling contribution described in the present paper is consistent with the previous arguments.[2]

Values of m^* were previously reported for polycrystalline samples using Seebeck (S) measurements by several researchers. The m^*/m_0 values of 1.2–2.0 have often been reported for polycrystalline BGG samples,[18–21] although there are a few reports of values in the range of 0.3–1.0.[22,23] The values for polycrystalline samples of SGG have been 2.9–3.1, except for one in the early study, where a value of 0.1 was reported.[24–26] The scattered data are considered to be due to the polycrystalline nature of the samples. The reported values using single crystals determined by S still vary depending on the reports. A value of 2.6 was reported for BGG whereas 1.28 was reported for SGG.[27,28] The same value of 3.0 was also reported for all SGG, BGG, and EGG.[2] The reported variations even in single crystals are considered to be caused by the inhomogeneity of the carrier distribution.[14] In the present studies, we have used the smallest possible single-crystal specimen in order to minimize the inhomogeneity and estimated the values from C_p. Our estimated value of 1.01 for BGG is nearly the same as m_0, and this is very small compared to many earlier estimates. Furthermore, we have determined the effective mass of $1.68m_0$ for SGG, which is also different from the earlier studies.

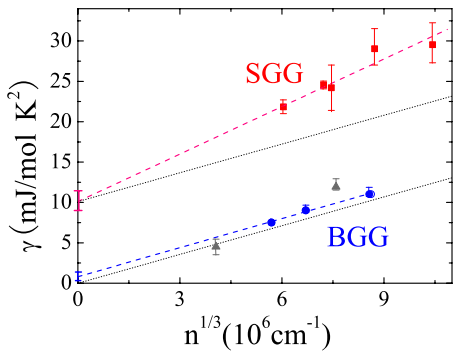

FIG. 3. (Color online) T-linear factor γ plotted as a function of the carrier concentration $n^{1/3}$. Red squares and blue circles are SGG and n-type BGG, respectively. Two points for p-type BGG are also plotted using dark gray triangles. Error bars come from different fit ranges in the heat-capacity data. Dashed lines are fits to the results while dotted lines are calculations using the free-electron mass.

The regions of the samples with small carrier concentrations greatly contribute to the S measurements, and this may cause errors in the evaluation of m^*. On the other hand in the case of C_p, these problems can be minimized using the smallest possible sample since γ_e is scaled by $n^{1/3}$ and a good estimate can be possible when the electronic and the tunneling parts can successfully be separated from each other. Consequently, we believe that the estimated m^* in the present work is reasonably accurate, making it valuable in discussing the electron-phonon interactions as described in the next paragraph.

The observed enhancement of m^* can be interpreted in terms of electron-phonon interactions, since electron correlations are not important in this system. The value of m^* can be described as

$$m^* = m_0(1 + \lambda_{e\text{-}ph} + \lambda_s), \tag{7}$$

where $\lambda_{e\text{-}ph}$ is the electron-phonon term and λ_s is the spin fluctuation one contributing to the quasiparticle mass enhancement.[29] The last term is considered to be less important in SGG and BGG and then $\lambda_{e\text{-}ph}$ can be estimated to be 0.68 for SGG and 0.01 for BGG. The small deviation in m^* of BGG from that of a free electron indicates that the electron-phonon interactions in this system are not large as far as the harmonic phonons are concerned. However, $\lambda_{e\text{-}ph} = 0.68$ for SGG seems to be greatly enhanced and this would most probably be due to the anharmonic motions of the guest atoms associated with rattling phonons. To date, the contribution of the rattling phonons to the electronic properties has been an important topic of debate. Our present experiments clearly show that the electron-phonon interactions can be enhanced when the rattling mode is involved. Therefore, superconductivity with a higher T_c can be expected when a sufficient DOS at the Fermi level is given. Since many clathrate families do not have sufficient DOS values, superconductivity does not generally occur. In addition, the local Jahn-Teller distortion leading to instability of the Fermi surface some

times prevents the occurrence in superconductivity.[30,31] If both high DOS and stability in the host framework can be satisfied, a relatively higher T_c can be anticipated. Recently reported superconductivity in K pyrochlore may be a good example of this.[32,33]

IV. CONCLUSIONS

In summary, low-temperature heat capacities of SGG and BGG were studied over a wide range of energy scale. A glasslike T-linear contribution of C_{TLS} was observed for SGG and its α was 10.1 ± 1.5 mJ/mol K^2 while a small $\alpha(0.8 \pm 0.4$ mJ/mol K^2) was observed for BGG. The large α as compared to that of amorphous silica indicates the existence of large disorder in the clathrates, most likely originating from the random displacement of Ga and Ge atoms in the host framework. In SGG, m^* is enhanced due to the anharmonic rattling modes and the electron-phonon interactions $\lambda_{e\text{-}ph}$, one of the most important physical parameters, was accurately estimated to be 0.68. If good inelastic neutron diffraction were available, the electron-phonon interactions could also be estimated from the viewpoint of broadening of the phonon peaks. It is very curious to see such a kind of studies in the future and compare the results to the present study.

ACKNOWLEDGMENTS

We would like to thank Pierre Richard and Zhe Qu for useful discussions. This work was supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, Grants No. 18204030, No. 19014001, No. 18651075, and No. 18204032 and a Grant-in-Aid for Scientific Research on Priority Areas (New Materials Science Using Regulated Nano Spaces-Strategy in Ubiquitous Elements) from the MEXT of Japan. In addition, the present work was partially supported by the Tohoku University GCOE program: Particle-Matter Hierarchy.

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