Optical Conductivity Spectral Anomalies in the Off-Center Rattling System β-$Ba_8Ga_{16}Sn_{30}$

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We present optical conductivity studies of the type-I clathrate $Ba_8Ga_{16}Sn_{30}$, using a terahertz time-domain spectrometer (0.3–3.0 THz). The lowest-lying spectral peak at 0.72 THz due to the Ba(2) ion's off-center vibration in the oversized cage shows a drastic and anomalous temperature dependence. Below about 100 K, the single broad peak splits into two subpeaks, and with further lowering of the temperature, the spectral shape of this so-called rattling phonon shows non-Boltzmann broadening to the point that the linewidth becomes comparable to the peak frequency. Whereas the initial splitting can be understood by assuming a multiwell anharmonic potential, the strong linewidth broadening toward low temperature cannot, since the Boltzmann factor generally sharpens the low-temperature spectra. The observed behavior suggests strong interaction between the local anharmonic phonons and other excitations.

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Recently novel phenomena related to local anharmonic phonons observed in cagelike materials such as clathrates [1–7] have attracted much interest. In particular, the so-called rattling phonons of guest ions in polyhedral cages and how they may affect properties such as electric and thermal properties, have been studied extensively in light of their potential application in thermoelectric devices.

The type-I clathrate $Ba_8Ga_{16}Sn_{30}$ (β-BGS), which we investigate in this Letter, shows not only low thermal conductivity with a high thermoelectric figure of merit, but also glasslike temperature dependence of specific heat and thermal conductivity [6,7]. Such thermal properties are universally observed in glasses or amorphous materials [8,9], though the present material forms a regular lattice. It is thus argued that such anomalous thermal behaviors may be caused by the rattling phonons vibrating in an off-centered anharmonic potential [2–7,10,11].

The β-BGS has a cubic primitive structure containing two types of cages, isotropic dodecahedrons and broadly anisotropic tetrakaidecahedrons [12]. Each cage encapsulates a Ba atom labeled Ba(1) and Ba(2), respectively. As revealed by single crystal x-ray diffraction [6,7], the equivalent position of $Ba(2)^{2+}$ ion is split into four off-centered positions, and the large off-center displacements of $Ba(2)^{2+}$ ions are about 0.4 Å. The relation between the off-centered multiequivalent positions of guest atoms and the thermal properties have been experimentally investigated [6,7,13]. Theoretical approaches have been proposed, which have raised general interest on quantum tunneling behaviors of the rattler in a multiwell anharmonic potential [10], their effects on glasslike thermal behavior [11], and the nonmagnetic Kondo effect [14,15] caused by an electron-rattler interaction.

Investigations of dynamical properties of the rattler are crucial to understanding the microscopic mechanisms of various phenomena caused by the rattling phonon. For type-I $Ba_8Ga_{16}Ge_{30}$ (BGG) which shows quasi-on-center rattling of the $Ba(2)^{2+}$ ion, the phonon dynamics have been under intense study regarding the nature of its anharmonic vibrations, e.g., far-infrared spectroscopy [16], Raman scattering [17], and inelastic neutron scattering [18]. In our previous paper [16], we reported the optical conductivity of p-type BGG and discussed the softening and sharpening of the local anharmonic phonon toward low temperature using a one-dimensional anharmonic potential (AP) model [19]. Those characteristic behaviors are explained by nonequivalent energy level spacings resultant from the flat-bottom shape of the on-center anharmonic potential, plus the Boltzmann factor. For off-center rattling phonon systems the optical conductivity spectra has not been reported, only Raman scattering which has shown evidence of the off-center rattling behavior [13]. According to theoretical predictions [19], off-center rattling phonon spectra should show totally different structure

and temperature dependence from those of on-center anharmonic phonons, and the softening of the local phonon mode is no longer a fingerprint of anharmonic phonon behavior.

In this Letter, we report the first observation of the infrared-active off-center rattling phonon in the optical conductivity of β-BGS by the terahertz time-domain spectroscopy (THz-TDS), and discuss the observed results based on the AP model [19]. The observed rattling phonon spectra not only show a line splitting predicted in the model, but also reveal an unexpected, drastic linewidth broadening towards low temperature, which is quite opposite from conventional thermal behavior.

The single crystals used for this work were of β-BGS, self-doped with n-type carriers, grown by a self-flux method [6,7]. To obtain sufficient transmitting signals through the conductive sample, a single crystal disk of about 3 mm in diameter attached with adhesive on a sapphire substrate was polished down to 13 μm in thickness by using diamond abrasive films. THz-TDS measurements covering a frequency range of 0.3–3.0 THz were carried out with the commercial spectrometer (RT-20000, Tochigi Nikon Co., Ltd) which uses a standard technique for the transmission configuration and the temperature range from 7 K to room temperature [16,20].

Figure 1 shows the real part $\sigma_1(\omega)$ of the complex conductivity. As previously found in isostructural BGG [16], the data demonstrate four broad peaks superimposed on almost frequency-independent Drude-like contributions [see horizontal dotted lines in (b) and (c)] due to charge carriers. The latter contribution monotonically increases with decreasing temperature. This metallic behavior is contrary to the semiconducting behavior of p-type BGG in the terahertz frequency region [16].

The observed four peaks are assigned as six independent modes (ν_1-ν_6) by first-principle calculations for the infrared-active optical modes of T_{1u} symmetry [13]. To reproduce each spectral shape, we define the fitting curve as

$$\sigma_{1,\mathrm{fit}}(\omega) = \sigma_0 + \sum_i \frac{(2/\pi) S_i \omega^2 \Gamma_i}{(\omega_{0,i}^2 - \omega^2)^2 + (\omega\Gamma_i)^2}, \qquad (1)$$

where the first term σ_0 is the dc conductivity ($\omega = 0$) of the carrier contribution, and the second term sums the Lorentz-type conductivities of the phonon modes ν_i. For each mode, S_i, $\omega_{0,i}$, and Γ_i are the spectral weight, resonant angular frequency, and relaxation rate (or damping factor), respectively. Fitting results of this equation to all the data at room temperature and 7 K are demonstrated in Figs. 1(b) and 1(c). Fitting parameters are listed in Table I, and analyzed as follows.

First, the lowest peak (labeled ν_1) is assigned as the lowest energy mode of $Ba(2)^{2+}$ ions in the oversized tetrakaidecahedral cage. In order to reproduce the experimental line shape, this peak is best fitted by superposing two Lorentzian curves, L_{1A} and L_{1B}. The peak frequency of $\omega_{0,1}$ in Table I is defined as the peak position of the superposed Lorentzian curves [see the arrows in Fig. 1(c)]. The relaxation rate Γ_1 of ν_1 is evaluated from the full-width-of-the-half-maximum (FWHM) value for the curves. The ν_1 mode corresponds to the *in plane* vibration, perpendicular to the fourfold inversion axis, i.e., the off-center rattling phonon mode in the oversized cage.

The following small peak around 1.3 THz (ν_2) is also assigned as a Ba(2) mode in the oversized tetrakaidecahedra

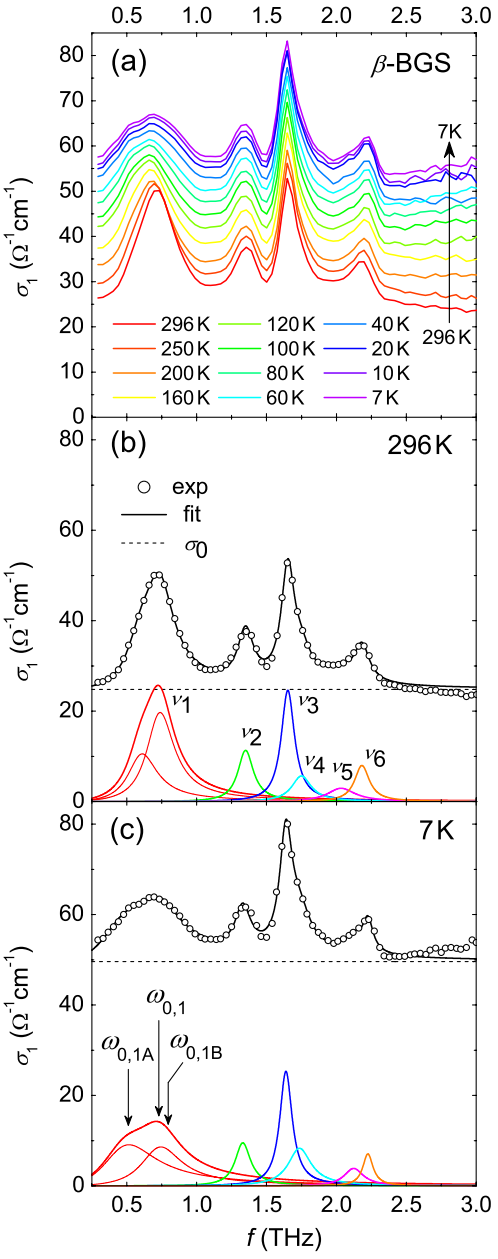


FIG. 1 (color online). (a) Temperature-dependent real part of complex conductivity spectra $\sigma_1(\omega)$ of β-BGS. Note the horizontal axis is frequency ($= \omega/2\pi$) in THz. (b) and (c) Experimental data (open circles) and fitting results (lines) at room temperature and 7 K. Details are described in text. For convenience: 1 THz = 33.3 cm^{-1} = 48 K = 4.14 meV.

TABLE I. Fitting parameters at 296 K (7 K) of β-BGS. The guest ions in the smaller ($2a$) and oversized ($6d$) cages are defined as Ba(1) and Ba(2), respectively. The definitions of $\omega_{0,1}$ and Γ_1 are described in text.

Label	Atom	$\omega_{0,i}$ (THz)	Γ_i (THz)	$S_i \times 10^{-13}$ (Ω^{-1} cm^{-1} s^{-1})
ν_1	Ba(2)	0.72 (0.71)	0.32 (0.57)	7.75 (7.27)
ν_2	Ba(2)	1.35 (1.33)	0.14 (0.13)	2.40 (2.00)
ν_3	Ba(1)	1.65 (1.64)	0.19 (0.11)	3.00 (2.76)
ν_4	Cage	1.75 (1.74)	0.15 (0.21)	0.82 (1.76)
ν_5	Cage	1.98 (2.12)	0.31 (0.18)	0.93 (0.74)
ν_6	Cage	2.18 (2.23)	0.16 (0.09)	1.40 (0.65)

cage, corresponding to the vibration along the fourfold inversion axis.

The third spectrum peak around 1.7 THz is reproduced by superposing two Lorentzian curves: a larger one (ν_3) assigned as the single Ba(1) mode in the smaller isotropic dodecahedral cage and a smaller one (ν_4) as the lowest energy cage mode.

Finally, the peak around 2.2 THz is also fitted by superposition of two Lorentzian curves, both assigned as cage modes (labeled ν_5 and ν_6). It is noteworthy that the spectral weight S_i for all these modes is independent of temperature within experimental error.

As can be seen in Fig. 1(a), all the spectral shapes (ν_2-ν_6) except the lowest ν_1 peak show little dependence on temperature. As temperature decreases, the peak frequency for ν_2 softens by 1.5% and for the ν_3 mode it also softens very slightly, while the other higher (cage) modes harden or remain constant. These behaviors are essentially similar to those in BGG [16].

Hereafter we will focus on the ν_1 mode of the rattling phonon that is drastically temperature dependent. As seen from Fig. 1(a) and also shown by circles in Fig. 2(a), with decreasing temperature the ν_1 peak frequency $\omega_{0,1}$ softens by 7% down to 100 K, then reverts and hardens toward lower temperatures. This tendency was never observed in the on-center type rattling phonons of BGG [16]. The linewidth Γ_1 indicated by marked diamonds in Fig. 2(b) increases almost by a factor of 2 from 0.3 THz at room temperature to 0.6 THz at 7 K. At this temperature the spectrum is well reproduced by assuming double peaks at about 0.5 and 0.7 THz.

Based on an analysis using a 1D-AP model, the splitting at low temperature is well understood using the calculated vibrational levels in a double-well potential $V(x) = \frac{1}{2}kx^2 + \frac{1}{4}\lambda x^4$ (Fig. 3) representing neighboring minima pairs of the fourfold, 2D potential. The parameters are fixed to reproduce the frequencies, $\omega_{0,1A} = 0.52$ THz and $\omega_{0,1B} = 0.74$ THz for the double peaks. Using the Ba atomic mass, the 1D potential parameters are uniquely determined as $k = -2.9$ [kg s^{-2}] and $\lambda = 3.7 \times 10^{21}$ [m^{-2} kg s^{-2}]. The obtained 1D potential has off-centered minima displacement of 0.28 Å so its extension into 2D implies a diagonal displacement from cage center of $\sqrt{2} \times 0.28 \approx 0.4$ Å, being in good agreement with x-ray diffraction refinements [6,7]. The features of the calculated levels are as follows. First, the $n = 0$ and 1 levels of are quasidegenerate with a tiny energy difference $\hbar\omega_{10} = 0.059$ meV. Second, the $n = 2$ and 3 levels are well separated due to the moderately deep potential well. These four characteristic low-lying levels produce double peaks at low temperature as follows. At sufficiently low temperatures, phonons are condensed in the quasidegenerate doublet, and the optical transitions occur mainly from $n = 0$ to 3 and from $n = 1$ to 2 due to

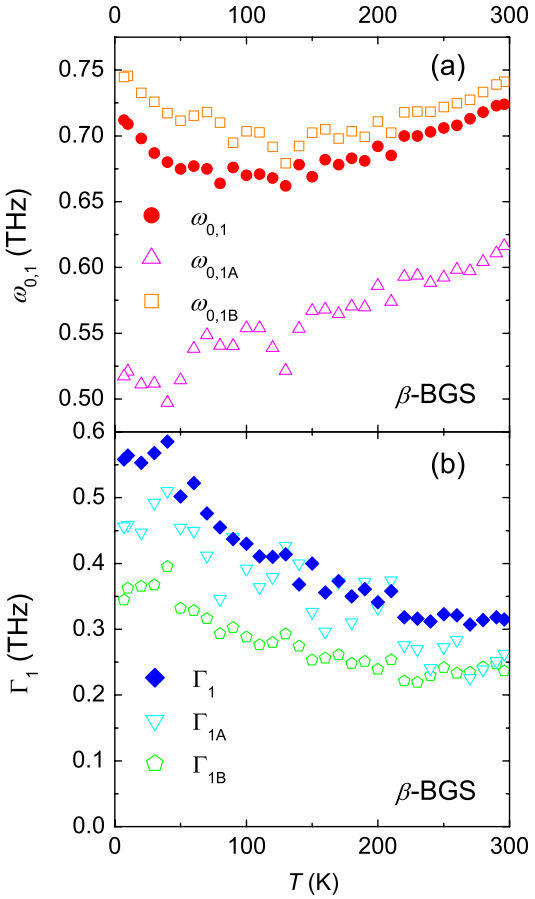
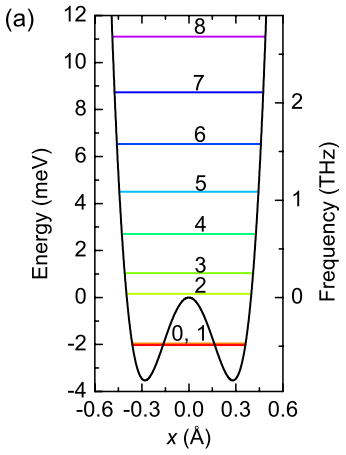


FIG. 2 (color online). Temperature dependence of (a) the peak frequency $\omega_{0,1}$ (circles) and (b) linewidth Γ_1 (diamonds) for the ν_1 mode of β-BGS. The resonant frequencies [$\omega_{0,1A}$ (open triangles) and $\omega_{0,1B}$ (open squares)] and the relaxation rates [Γ_{1A} (open inverted triangles) and Γ_{1B} (open pentagons)] are evaluated from the fitting of the ν_1 mode.



(b)

n	E (meV)
8	11.10
7	8.74
6	6.53
5	4.50
4	2.70
3	1.03
2	0.15
1	-1.96
0	-2.02

FIG. 3 (color online). (a) Calculated potential shape $V(x)$ (black line) and eigenvalues (horizontal bars) with respective level numbers, for $V(x) = \frac{1}{2}kx^2 + \frac{1}{4}\lambda x^4$ where $k = -2.9$ [kg s^{-2}] and $\lambda = 3.7 \times 10^{21}$ [m^{-2} kg s^{-2}]. Note that levels 0 and 1 are quasidegenerate. (b) Calculated eigenlevel energies for $n = 0$ to 8.

parity requirement of the wave function. Therefore these transitions result in double peaks with excitation energies $\omega_{21} \approx \omega_{20} = 0.52$ THz and $\omega_{30} = 0.74$ THz. With these excitations and the Lorentzian curve [Eq. (1)], the data in Fig. 1(c) are fitted, leading to $\Gamma_{1A} = 0.46$ THz and $\Gamma_{1B} = 0.32$ THz, respectively, corresponding to Γ_{30} and Γ_{21}.

However, the significant broadening observed in the rattling phonon spectra toward low temperature cannot be reproduced by our calculations based on the 1D-AP model or its extension to more realistic potentials of higher order and dimension (details will be published elsewhere). In the local potential model with a constant relaxation rate [19], the FWHM monotonically decreases toward low temperature due to the decrease in the number of the levels contributing to the optical transition. Thus we reach the conclusion that the observed linewidth broadening must be caused by the temperature and transition dependent relaxation rate $\Gamma_{ij}(T)$. Because of the Boltzmann factor, the contributing level transitions shift to those among low-lying levels as temperature is lowered. As a result, the low-temperature linewidth broadening suggests enhancement of the individual relaxation rates $\Gamma_{ij}(T)$ of transitions between low-lying levels.

The origin of this anomalous broadening will require further investigation, but one can consider several candidate mechanisms, such as the formation of coherent rattling domains due to dipole-dipole interaction between neighboring rattling ions [10,11] or the coupling with acoustic phonons propagating along the cage network. Interaction with the charge carriers has also been discussed [21]. It should be noted that the observed broad linewidth value is comparable to the ν_1 peak frequency and is consistent with the peak broadening in specific heat C/T^3, which cannot be reproduced by a single Einstein oscillator model [7]. Furthermore, it is reminiscent of the boson peak in true glassy materials [9,11].

In conclusion, we measured the optical conductivity of the off-center rattling phonon in the type-I clathrate β-BGS using THz-TDS. The rattling phonon spectra has shown splitting and anomalous broadening toward low temperature. From the discussion based on 1D-AP analysis, the origin of the splitting of the spectra is the characteristic depth of the off-center potential. On the other hand, the large linewidth broadening toward low temperature is quite contradictory to usual thermal behavior. We expect these results to help incite further experimental and theoretical studies to delineate how the off-center rattlers may be interacting with other excitations.

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[1] G. A. Slack, in *CRC Handbook of Thermoelectrics*, edited by M. Rowe (CRC Press, Boca Raton, FL, 1995), p. 407.
[2] G. S. Nolas *et al.*, Appl. Phys. Lett. **73**, 178 (1998).
[3] J. L. Cohn *et al.*, Phys. Rev. Lett. **82**, 779 (1999).
[4] B. C. Sales *et al.*, Phys. Rev. B **63**, 245113 (2001).
[5] S. Paschen *et al.*, Phys. Rev. B **64**, 214404 (2001).
[6] M. A. Avila *et al.*, Appl. Phys. Lett. **92**, 041901 (2008).
[7] K. Suekuni *et al.*, Phys. Rev. B **77**, 235119 (2008).
[8] R. C. Zellar and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).
[9] *Amorphous Solids: Low-Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).
[10] T. Nakayama and E. Kaneshita, Europhys. Lett. **84**, 66001 (2008).
[11] E. Kaneshita and T. Nakayama, Europhys. Lett. **86**, 56004 (2009).
[12] J. S. Kasper *et al.*, Science **150**, 1713 (1965).
[13] K. Suekuni *et al.*, Phys. Rev. B **81**, 205207 (2010); (private communication).
[14] J. Kondo, Physica (Amsterdam) **84B+C**, 40 (1976); **84B +C**, 207 (1976).
[15] T. Hotta, J. Phys. Soc. Jpn. **78**, 073707 (2009).
[16] T. Mori *et al.*, Phys. Rev. B **79**, 212301 (2009).
[17] Y. Takasu *et al.*, Phys. Rev. B **74**, 174303 (2006).
[18] M. Christensen *et al.*, Nature Mater. **7**, 811 (2008).
[19] H. Matsumoto *et al.*, Phys. Rev. B **79**, 214306 (2009).
[20] T. Mori *et al.*, Phys. Rev. B **77**, 174515 (2008).
[21] M. Takechi and K. Ueda, J. Phys. Soc. Jpn. **78**, 024604 (2009).