Raman scattering of rare earth hexaborides

Norio Ogita¹, Takumi Hasegawa¹, Masayuki Udagawa¹, Fumitoshi Iga² and Satoru Kunii³

¹ Graduate School of Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima-shi, Hiroshima 739-8521, Japan
² Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima-shi, Hiroshima 739-8530, Japan
³ Department of Physics, Tohoku University, Sendai 980-8578, Japan

E-mail: nogita@hiroshima-u.ac.jp

Abstract. Raman scattering spectra were measured for the rare-earth hexaborides RB₆ (R = Ce, Gd, or Dy). All Raman-active phonons due to B₆ vibrations were observed in the range 600 - 1400 cm⁻¹. Anomalous peaks were detected below 200 cm⁻¹, which correspond to vibrations of rare-earth ion excited by second-order Raman scattering process. The intensity and energy of the rare-earth mode decrease with decreasing temperature. This suggests that the rare-earth ion vibrates in a shallow and anharmonic potential due to the boron cage. Using the reported values of mean square displacement of rare-earth ion, we estimated the anharmonic contribution for the rare-earth vibrations.

1. Introduction

Rare-earth hexaborides, RB₆, have a CsCl type structure with Pm₃m symmetry, where rare-earth ion is located at Cs site and octahedral B₆ molecule occupies the Cl place. The isostructural compounds of RB₆ exhibit interesting physical properties, such as superconductivity in YB₆ [1], dense Kondo behavior in CeB₆ [2], and intermediate valence state in SmB₆ [3]. DyB₆ exhibits successive phase transitions accompanied by the ferroquadrupolar ordering at 30K and the antiferromagnetic transition at 25 K. GdB₆ shows magnetic structure change at two successive phase transitions (15 K and 8 K). Because the interactions between any adjacent borons are extremely strong, the boron network stabilizes the structure and can be regarded as a cage; the rare-earth ion weakly interacts with the cage. This lattice dynamical behavior is observed in the specific heat [4] and the phonon dispersion curve [5]. In our previous Raman scattering study [6], we found that the rare-earth motion is excited by a second-order Raman scattering process. The caged compounds are expected to be high-performance thermoelectric materials, because the cage structure has a possibility to reduce the phonon thermal conductivity by a rattling motion of the guest atoms. One of the key properties of the rattling motion is anharmonicity. In order to clarify the anharmonicity of rare-earth motion in the hexaborides, we measured Raman scattering spectra of RB₆ (R = Ce, Gd, or Dy).

2. Experimental setup

Single crystals of RB₆ were synthesized with a floating zone method [7]. Raman scattering was measured in a quasi-backscattering geometry. An Ar ion laser operated at 488.0 nm or a dye
laser operated at 589 nm were employed as an excitation light with the output power of 10 mW at the specimen. The scattered light was analyzed by a triple-grating spectrometer and detected by a liquid nitrogen cooled CCD. Three phonons, $\Gamma_R = A_{1g} + E_g + T_{2g}$, "Raman-active phonons”, are allowed in the first-order Raman scattering. These phonons can be selected by their polarization dependence in the following geometries: $A_{1g}$ appears in the $(x,x)$, $E_g$ in $(x,x) \text{ and } (x+y,x-y)$, and $T_{2g}$ in $(x,y)$ geometry. In this $(\alpha,\beta)$ notation, $\alpha$ and $\beta$ are the polarization directions of incident and scattered light, respectively.

3. Results and discussion

Figure 1. Polarization dependence of Raman spectra in GdB$_6$, excited by 488 nm light at room temperature.

Figure 2. Temperature dependence of $(x,x)$ Raman spectra in GdB$_6$ excited by 589 nm light. The intensities of the spectra at lower energy side are doubled.

Figure 1 shows representative polarization dependence of Raman scattering spectra in GdB$_6$, excited by 488 nm light at room temperature. Raman-active phonons are marked by arrows. These phonons satisfy the polarization selection rules mentioned above. This dependence is also observed in the other hexaborides. On the other hand, the small peaks at around 100 cm$^{-1}$ have weak polarization dependence. These low-energy peaks correspond to rare-earth vibrations due to the second-order Raman scattering process [6]. Hereafter, we name this vibration as the rare-earth mode. The rare-earth modes are clearly observed in trivalent hexaborides R$^{3+}$B$_6$, and their energies and intensities are well scaled by a cage space $\delta r = a - 2r_R$, which is a available space for the rare earth ion in the boron cage; $a$ and $r_R$ are the lattice parameter and ionic radius of rare-earth ion, respectively. The intensities of rare-earth modes strongly depend on the wavelength (energy) of incident light, and increase for longer wavelength of incident light [6].

Figure 2 shows temperature dependence of $(x,x)$ Raman spectra of GdB$_6$ excited by 589 nm light. Three peaks labeled $P_1 \sim P_3$ are clearly observed as the rare-earth modes in GdB$_6$. Three rare-earth modes are also present in DyB$_6$, but only one ($P_1$) in CeB$_6$. With decreasing temperature, the intensity of the rare-earth mode decreases monotonically, in spite of the increase of the intensity for Raman-active phonons. In the classical picture, the Raman scattering intensity is proportional to the mean square displacement (MSD) of the vibration. Therefore, the displacement of the rare-earth mode in the cage decreases with decreasing temperature. GdB$_6$ shows an antiferromagnetic transition at $T_N=15.4$ K, but figure 2 reveals little change in the phonon spectra at this temperature.
Figure 3. Temperature dependence of the position of the rare-earth mode.

Figure 4. Square of the energy of rare-earth mode vs. mean square displacement.

Figure 3 shows the temperature dependence of the energy of the rare-earth modes $P_1 \sim P_3$. With decreasing temperature, the decrease of the energy is clearly observed for DyB$_6$. Since the cage space of these samples is $\delta r_{Dy} > \delta r_{Gd} > \delta r_{Ce}$, the larger cage space corresponds to the larger energy decrease, as shown in figure 3. Usually, the phonon energy increases due to the thermal shrinkage with decreasing temperature. This opposite to the ordinary phonon behavior is well understood as an anharmonic vibration [8].

To estimate the contribution of anharmonicity, we assume the simplified potential for the guest atom vibration in the cage

$$V(u) = \frac{m\omega_0^2}{2} u^2 + \frac{mk_4}{4} u^4,$$

where $m$, $\omega_0$, and $u$ are the atomic mass, the vibration energy for harmonic oscillation, and the atomic displacement from the center of the cage, respectively. The second term denotes the anharmonic potential. In this potential, the energy is derived as

$$\omega^2 = \omega_0^2 + k_4 < u^2 >.$$

$< u^2 >$ corresponds to MSD of the rare-earth mode. In this model, the third order effect of $u$ is renormalized into $\omega_0$. In the case of hexaboride, we assume $\omega_0$ as constant, because the lattice constant of GdB$_6$ decreases by about 0.1% from 300 to 10 K [9], and the energies of the Raman-active phonons increase by 1% from 300 to 10 K. Thus, the energy increment is estimated as less than 0.5 cm$^{-1}$ for the rare-earth mode. In the second equation, the anharmonic potential contributes to the phonon energy through MSD $< u^2 >$. Among many reports concerning the temperature dependence of the MSD for rare-earth ions in RB$_6$, we use the MSD data of ref. [10]. The square of $\omega$ as a function of MSD for each rare-earth ion is plotted in figure 4: $\omega$ is a half of the observed rare earth mode, because this mode corresponds to a two-phonon excitation. As shown in the figure, the fitted lines reproduce the measured data.

Figure 5 presents the temperature dependence of the ratio of anharmonic contribution $k_4 < u^2 > /\omega_0^2$. The middle peak P$_2$ shows the largest anharmonicity among three modes for GdB$_6$ and DyB$_6$. The three peaks correspond to the longitudinal or transverse phonons traveling to the X, M, or R point in the Brillouin zone [11]. Therefore, the obtained results
suggest the anharmonicity of the rare-earth mode is anisotropic, that is, it depends on the vibrating and traveling directions of the rare-earth mode in DyB$_6$ and GdB$_6$. Because the energies for CeB$_6$ are degenerate, the anharmonic contribution in CeB$_6$ seems to be isotropic. Therefore, the anisotropy is enhanced for the larger cage space.

4. Concluding remark
Here we comment on the reported MSD values. Temperature dependence of the MSD for rare-earth ion is well described by a Debye model or an Einstein model. On the other hand, the present analysis gives us the important information on the anharmonicity. The anisotropic potential in GdB$_6$ and DyB$_6$ suggests us that the directional dependence of MSD is necessary for further understanding of the dynamical properties of rare-earth ion.

Acknowledgments
This work was partially supported by the Grant-in-Aid for Scientific Research Priority Area of "Strategy in Ubiquitous Elements" and "Skutterudite" from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by a research grant from the Mazda Foundation. The low-temperature experiments have been supported by N-BARD and IAMR of Hiroshima University.

[1] Kunii S, Kasuya T, Kadowaki K, Date M and Woods S B 1984 Solid State Commun. 52 659
[2] Komatsubara T, Sato N, Kunii S, Oguro I, Furukawa Y, Ōnuki Y and Kasuya T 1983 J. Magn. Magn. Mat. 31-34 368
[3] Kasuya T, Kasaya M, Takegahara K, Fujita T, Goto T, Tamaki A, Takigawa M, Yasuoka H et al., J. Magn. Magn. Mat. 31-34, 447 (1983).
[4] Mandrus D, Sales B C and Jin R 2001 Phys. Rev. B 64 012302-1
[5] Smith H G, Dolling G, Kunii S, Kasaya M, Liu B, Takegahara K, Kasuya T and Goto T 1985 Solid State Commun. 53 15
[6] Ogita N, Nagai S, Okamoto N, Udagawa M, Iga F, Sera M, Akimitsu J and Kunii S 2003 Phys. Rev. B 68 224305
[7] Kunii S 1988 J. Phys. Soc. Jpn. 57 361
[8] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K, Takabatake T and Takasu Y 2008 Phys. Rev. Lett. 100 165503
[9] Takahashi Y, Fujimoto M, Tsuchiko M and Ohshima K 2001 J. Appl. Crystallogr. 34 208
[10] Novikov V V 2003 Phys. Solid State 45 1543
[11] Kohgi M, Kuwahara K, Ogita N, Udagawa M and Iga F 2006 J. Phys. Soc. Jpn. 75 085003