Softening of the Longitudinal Phonon Mode along the [100] Direction in GdB_6

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We have investigated the phonon of GdB_6, which exhibits antiferromagnetic and structural first-order phase transition by using the inelastic x-ray scattering technique. The dispersion relation curve of the longitudinal acoustic mode propagating along the simple cubic [100] axis shows the maximum energy around the wave vector $\mathbf{q} = \xi, 0, 0), \xi = 0.2 - 0.3$, and it bends down with approaching the Brillouin zone boundary. The lower-energy zone-boundary mode at $\mathbf{q_1} = (1/2, 0, 0)$ corresponds to the structural modulation in the ordered phase. The energy of this mode is 75% of the maximum value on the branch at 300 K and further decreases by 10% with decreasing temperature down to the transition temperature $T_{\rm N} = 16$ K so that this phonon mode softens considerably far above the transition temperature. On the other hand, the reference material YbB_6 that is considered to have no localized magnetic moments does not show such softening in the inelastic neutron scattering measurement. The observation indicates a strong electron-phonon coupling in GdB_6, which is expected to be magnetoelastic-type interaction between $4f$ states and displacement of Gd ions.

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I. INTRODUCTION

Recently, motions of atoms filled inside a cage lattice and their role on physical properties have become topics of condensed matter physics. For example, the low-energy anharmonic motion of filled atoms in clathrate compounds [1, 2] and rare-earth-filled skutterudites [3, 4] are considered to contribute in reducing thermal conductivity. It also expected to give rise new physical states by coupling with electronic degrees of freedom. Rare-earth boride compounds are also candidates for studying physical properties given by the motion of filled atoms inside cage structures. Boron atoms form a frame by strong bonding between each other, and the rare-earth ions are expected to be loosely connected with the boron frame. Among them, GdB_6 exhibits physical properties that have been a long-standing issue. This material crystallizes in a simple cubic structure, and it undergoes simultaneous structural and antiferromagnetic phase transitions at $T_{\mathrm{N}} = 16$ K and $T^* = 9$ K [5, 6]. The magnetic wave vector below T_{N} is $\mathbf{q_M} = (1/2, 1/4, 1/4)$ [7, 8]. Thermal vibration amplitude of Gd ions is much larger than that of boron forming the cage lattice and those observed in other rare-earth hexaborides [9]. A structural modulation with $\mathbf{q_1} = (1/2, 0, 0)$ also appears below T_{N}. The successive phase transitions and the atomic displacement patterns were discussed by Amara *et al.* in terms of exchange-displacement waves or magnetoelastic distortions, which are due to the coupling between the localized f electrons of Gd ions and their displacements [10]. The authors suggested that the superlattice with $\mathbf{q_1}$ originates from the energy gain associated with the quadratic term of the Fourier components ($\mathbf{q_M}$ and its star) of the magnetic moment arrangement. Below T^*, the superlattice structure with $\mathbf{q_1}$ is suppressed suddenly and those with $\mathbf{q_M}$ as well as $\mathbf{q_2} = (1/2, 1/2, 0)$ dominate. The switch of the structural distortion has not yet been fully understood. The dynamical property of crystal lattice of GdB_6 that has never been investigated so far is a key to get further insight into the first-order phase transition due to the strong interplay between magnetic state and crystal lattice. Hereafter, we present some scattering experiment results for investigating the dynamical properties of the crystal structure of GdB_6.

II. EXPERIMENTAL

We investigated the lattice dynamics of GdB_6 and that of the nonmetallic YbB_6 [11, 12] for reference purposes. Single crystalline samples of both these compounds were synthesized by a floating-zone method. We succeeded in observing phonon dispersion relations of GdB_6 by using the inelastic x-ray scattering spectrometer installed at BL35XU, SPring-8 [13, 14]. The x-ray energy was 21.747 keV given by a Si (11 11 11) with back scattering geometry and the set of twelve analyzer mirrors are used. The energy resolution is about 1.5 meV. The typical resolution in the reciprocal space is $\Delta\mathbf{Q} = (0.06, 0.04, 0.05)$ for the measurement at the scattering vector $\mathbf{Q} = (5.5, 0, 0)$. The phonons of YbB_6 were measured on the triple-axis thermal-neutron spectrometer TOPAN installed at the beam hole 6G of the JRR-3 reactor, JAEA. The monochromator and analyzer are pyrolytic graphite crystals. The incident energy was changed, and the final neutron energy was fixed at 30.5 meV during the measurements. The energy resolution at the elastic condition is 2.0 meV evaluated from the incoherent scattering profile. The resolution widths in the reciprocal space are estimated as 0.065 r.l.u. and 0.15 r.l.u. within the horizontal scattering plane and along the vertical direction, respectively. Conventional x-ray diffraction measurements were also carried out for GdB_6 in order to study diffuse scattering. For this experiment, we used a four-circle diffractometer equipped with a Mo rotating-anode x-ray source installed in Tohoku University.

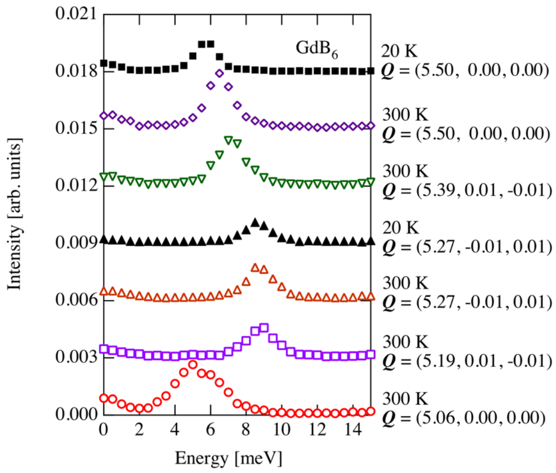

FIG. 1: Inelastic x-ray scattering spectra for the longitudinal mode propagating along the [100] axis of GdB_6. The top and fourth spectra are the results for $\mathbf{q_1} = (0.5, 0, 0)$ and $\mathbf{q} = (0.27, 0, 0)$, respectively, measured at 20 K. Others are measured at 300 K.

III. RESULTS

Figure 1 depicts the inelastic x-ray scattering spectra measured at the scattering vectors $\mathbf{Q} = (5 + \xi, 0, 0)$ of GdB_6. The data at $\xi = 0.5$ corresponds to the lattice distortion with $\mathbf{q_1}$. Peaks located between 5 and 10 meV are assigned to longitudinal acoustic phonons propagating along the [100] axis of the simple cubic lattice. Up to $\xi = 0.2$, the phonon dispersion relation takes a steep variation that is consistent with the elastic constant determined by ultrasonic measurements [15]. The excitation energy takes the maximum around $\xi = 0.2 - 0.3$, and decreases with approaching the Brillouin zone boundary even though the temperature of 300 K lies well above T_N. The circles in Fig. 3 depict the experimentally determined dispersion curves of GdB_6 for the longitudinal phonon modes propagating along the cubic [100] axis at room temperature. The mode at the zone boundary $\mathbf{Q} = (5.50, 0.00, 0.00)$ takes an anomalously low frequency that is about 75% of the maximum value of this dispersion curve. The longitudinal acoustic mode of GdB_6 near the zone boundary exhibits also strong softening as a function of temperature. The top spectrum in Fig. 1 is the measured result at 20 K for the zone boundary mode, and the peak position 5.74 meV is apparently lower than 6.51 meV at 300 K. The energy of this anomalous mode of GdB_6 is gradually reduced by about 10% from 300 K to T_N. The longitudinal mode with $\mathbf{q_1}$ of GdB_6 is considered to be a strongly softened one with decreasing temperature from far above T_N. On the other hand, as shown in the fourth and fifth data in Fig. 1, the phonon peak positions at $\mathbf{Q} = (5.27, -0.01, 0.01)$ measured at 20 K and 300 K are close to each other. The phonon modes with around $\xi = 0.2$–0.3 depend less on temperature than those near the zone boundary. These experimental results imply that the crystal lattice of GdB_6 exhibits anharmonic behaviors closely related with magnetic

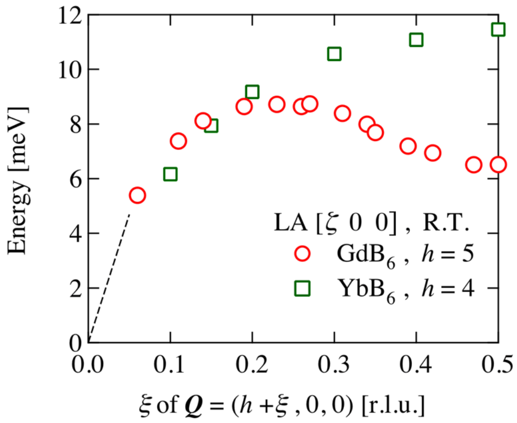

FIG. 2: Dispersion relations for the longitudinal mode propagating along the [100] axis of GdB_6 and YbB_6.at room temperature. The dotted line is calculated from the elastic constants of GdB_6 determined by the ultrasonic measurement [15].

ordering.

We measured the same phonon mode in YbB_6 by using the inelastic neutron scattering technique. This material behaves as a nonmetallic system and Yb ions are suggested to take divalent state without magnetic moments. Thus, we consider YbB_6 being a reference system for examining the magnetic effect on the crystal lattice of GdB_6. Figure 3 shows the measured spectra at $\mathbf{Q} = (4 + \xi, 0, 0)$ of YbB_6 corresponding to the same propagation vectors as in the measurement of GdB_6 shown in Fig. 1. Longitudinal acoustic phonon peak for $\xi = 0.1$ appears at 6 meV, and the peak position shifts toward the high-energy side monotonically up to 11 meV near the zone boundary. Such normal dispersion relations were seen also in other rare-earth hexaboride compounds [16]. Note that the slightly broader peaks around 7 meV can be attributed to other phonon modes that were detected due to the course resolution obtained with the vertically focusing monochromator and analyzer devices. The dispersion curve of YbB_6 is also plotted by squares in Fig. 2. It clearly shows the different behaviors between these two systems near the zone boundary for the structural modulation wave vector $\mathbf{q_1}$. Therefore, the distinct bending down of the dispersion relation for the longitudinal modes with $\mathbf{q_1}$, in contrast with those of YbB_6 and other rare-earth hexaborides, is a characteristic feature of GdB_6.

We also detected diffuse scattering intensities around $\mathbf{q_1}$ of GdB_6 by means of a conventional x-ray diffraction method. Figure 4 shows the profiles measured across the zone boundary $\mathbf{Q} = (4.5, 0, 0)$. Broad responses centering near the zone boundary were detected, and the scattering intensity shows a clear temperature dependence. This diffuse x-ray scattering originates from the lower-energy phonon mode around $\mathbf{q_1}$ as a result of integration over the excitation energy in the conventional x-ray diffraction method, as discussed later.

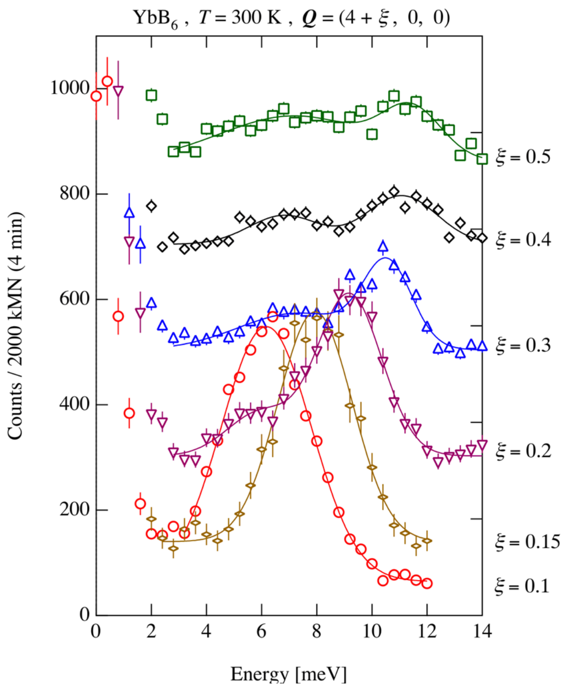

FIG. 3: Inelastic neutron scattering spectra for the longitudinal mode propagating along the [100] axis of YbB_6 at 300 K.

IV. DISCUSSION

We report two main observations: the soft mode with the wave vector $\mathbf{q_1}$, detected by the inelastic measurement, and diffuse scattering intensity detected around $\mathbf{q_1}$ by the conventional diffraction. The experimentally determined x-ray diffuse scattering intensity at $\mathbf{Q} = (4.5, 0, 0)$ is plotted by square symbols in Fig. 5, which are obtained by subtracting background intensity evaluated from the lowest counting level in the data at 15 K. The diffuse scattering intensity is given by the following formula based on integration of x-ray energy transfer for phonon excitation process [17].

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{diffuse}} \propto \sum_j \frac{1}{E_j} \coth\left(\frac{E_j}{2k_B T}\right) |F_j(\mathbf{Q})|^2 ,$$

where E_j and $F_j(\mathbf{Q})$ are the energy and the dynamical structure factor of the j-th phonon mode, respectively. On the other hand, the inelastic scattering cross section for the one phonon creation process is expressed as

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inelastic}} \propto \sum_j \frac{1}{E_j}(n_j + 1)|F_j(\mathbf{Q})|^2 \delta(E - E_j),$$

where n_j is the Bose-Einstein distribution function for the j-th mode. Therefore, the integrated intensity of inelastic x-ray scattering spectrum can give the squared dynamical

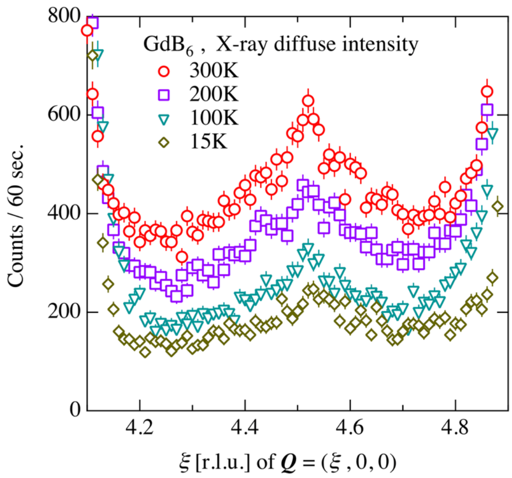

FIG. 4: X-ray diffuse scattering profiles along the longitudinal line through $\mathbf{Q} = (4.5, 0, 0)$ of GdB_6.

structure factor divided by the excitation energy, and it is used in the calculation of the diffuse scattering. We calculated the diffuse intensity shown by the solid line in Fig. 5 with an arbitrarily scale factor. It reproduces the experimental result well so that these two experimental results are consistent with each other.

From the x-ray scattering results, we conclude that GdB_6 shows the anomalous softening of the longitudinal mode with $\mathbf{q_1}$. This mode is considered to be a precursor phenomenon to the structural modulation, which results from the magnetoelastic effect proposed by Amara *et al.* [10]. They discussed that the exchange energy of the ordered structure with the magnetic Fourier components represented by the wave vector $\mathbf{q_M}$ and its star gains with the longitudinal Gd displacement wave with $\mathbf{q_1}$. The low frequency of the phonon mode with $\mathbf{q_1}$ above the transition temperature may be given by such interaction between the localized f moments and the Gd-ion motion. In previous studies on the phonon of rare-earth hexaboride compounds, the modes locating at 5–10 meV with the flat dispersion relations are suggested to be dominated by the motion of rare-earth atoms [18–20]. Then, it is natural to consider that the Gd ions; see the potential inside the boron cage modified by the inter-site interaction of their magnetic moments. The softening behavior indicates anharmonic or shallow potential for Gd ions. In contrast to such anomalous behavior of the $\mathbf{q_1}$ mode, we have confirmed that there is no peculiar lowering of energy for the modes with $\mathbf{q_2}$ and $\mathbf{q_M}$ characterizing the structural superlattice in the lowest-temperature magnetically ordered phase. The switching of structural modulation vectors at T^* remains an open question.

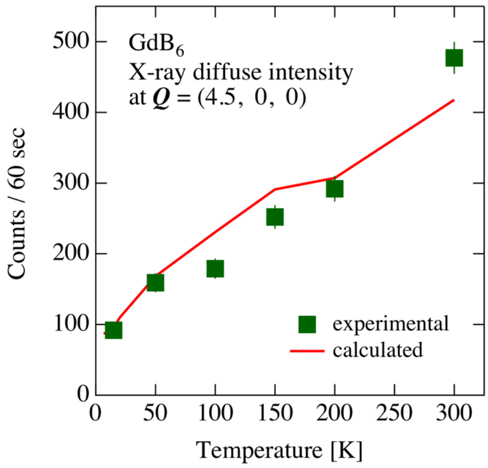

FIG. 5: Square symbols represent the experimentally observed x-ray diffuse scattering intensity at $\mathbf{Q} = (4.5, 0, 0)$. The solid line is the calculated ones based on taking into account the softening longitudinal phonon with $\mathbf{q_1}$ in GdB_6.

V. CONCLUSIONS

In GdB_6, a longitudinal phonon mode with $\mathbf{q_1}$ dominated by the Gd motion gradually softens as the temperature decreases from 300 K. The softening behavior with decrease in the temperature indicates an anharmonic potential for the Gd-ion sites and can be viewed as a precursor to the magnetic and structural transition at T_N. The characteristic properties of phonon are expected to be due to a strong coupling between the localized f electron magnetic moments and the atomic motion of Gd. On the other hand, since Yb ions in nonmetallic YbB_6 are suggested to take a divalent state without localized magnetic moments, no anomaly due to the magnetic effect is expected on the crystal lattice of YbB_6. Therefore, the interaction between $4f$ electrons and atomic motions of Gd ions is important to understand the crystal-lattice instability on the first-order magnetic and structural phase transition.

Acknowledgments

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