Raman scattering of RB_6 (R=Ca, Ce, Dy, Gd, Pr and Yb)

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Abstract

In Raman scattering spectra of RB_6, anomalous peaks have been found below 200cm^{-1} for the $R^{+3}B_6$, except for phonons and CEF excitations. Their peak intensities decrease with decreasing temperature, and this temperature dependence correlates with that of the mean square displacement of R. Furthermore, their energies decrease with the increase of the cage size of B. This new excitation can be attributed to a local vibration of the R ion, which can be regarded as hrattlerh in the cage of B.

Key words: Rare earth Hexaboride, Raman scattering, rattling mode of rare-earth ion

1. Introduction

Rare earth hexaborides show various properties such as superconductivity (YB_6), dense Kondo systems (CeB_6), and valence fluctuating systems (SmB_6). Recent observation of multipole-ordering triggered the reinvestigation of these materials. For Raman scattering experiments of RB_6, Güntherodt group extensively studied in 1980's, however, recent development of the research lead us to the re-study of the Raman scattering experiments for RB_6, in order to clarify the microscopic origin of the various properties in the crystals. In this paper, among several excitations observed in the Raman spectra of RB_6, we focus on the peaks at about 200cm^{-1}, which was assigned as the infrared-active phonon with T_{1u} symmetry by Güntherodt group [1].

2. Experimental

The single crystals used in the present experiments were grown by a floating-zone method. The Raman scattering spectra were measured by the following multi-channel system. An Ar ion laser operated at 488.0 nm and 514.5nm, and a dye laser operated at 570-633 nm were employed as a excitation light source. The scattering geometry was nearly backward. The scattered light was analyzed by a triple spectrometer(JASCO model TRS-600/SH), and was detected by a Liq. N_2 cooled CCD detector (Princeton Instruments Inc. model LN/CCD-1100-PB).

The $Pm3m$ symmetry of the RB_6 structure gives us the following phonon numbers for each irreducible representation at Brillouin zone center; $\Gamma = A_{1g} + E_g + T_{1g} + T_{2g} + 2T_{1u} + T_{2u}$ without acoustic phonons. The Raman-active phonons are A_g, E_g, and T_{2g}. Two T_{1u} modes are infrared-active, and T_{1g} and T_{2u} are optically inactive. In this cubic symmetry, three Raman-active phonon can be observed simultaneously in the $(x+y, x+y)$ polarization geometry, where the notation of (x, y) denotes the polarization directions of incident light(x) and scattered light(y).

3. Results and Discussion

Figure 1 shows the Raman spectra of RB_6 measured at room temperature. These spectra are shifted along

the vertical direction to avoid crossing, and the order corresponds to the decrease of the lattice constants of RB_6 from the top to bottom. We summarize the obtained remarkable results of the anomalous peaks, labeled by arrows in the figure.

(i) The peaks are observed in the trivalent $R^{3+}B_6$ crystals(bottom four spectra).
(ii) The number of the peaks are two or three.
(iii) The energy systematically decreases with increasing the cage size surrounded by B_6 molecules, in spite of decrease of the lattice constant.
(iv) As shown in Fig. 2, the intensity decreases with decreasing temperature.
(v) The excitation energy dependence of the peak intensity is different from that of the phonons.
(vi) The polarization dependence does not satisfy the cubic symmetry, since a similar spectra are also observed in the (x, x) and (x, y) geometries.

Above results clearly show that the peaks are not ordinary excitations such as phonons or CEF excitations.

The inset of Fig.2 shows the intensity of peaks for GdB_6 vs. mean square displacement(MSD) of Sm ion in SmB_6, determined by neutron diffraction [2]. The linear correlation between the intensity and MSD of R ion suggests that the anomalous peak originates in thermal vibration of the R ion in RB_6, under the assumption of the similar temperature dependence of MSD to GdB_6. Furthermore, the above result (iii) indicates that the energy of the peaks are determined by the cage size surrounded by B_6 molecules. Thus, the above two results of the intensities and energies suggest that the present peaks are interpreted as "rattler" mode in the B_6 cage.

However, since the vibration of R ion is forbidden in Raman scattering for the cubic RB_6 structure, the local distortion at the R ion site is expected. Thus, to obtain the final conclusion, we need the precise diffraction measurements to determine the site symmetry at the R ion.

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References

[1] E. Zirngiebl *et al.*, J. Magn. Magn. Mater. **54-57**(1986)539.

[2] D. Yu. Chernyshov *et al.*, Physica B**234-236**(1997)146.

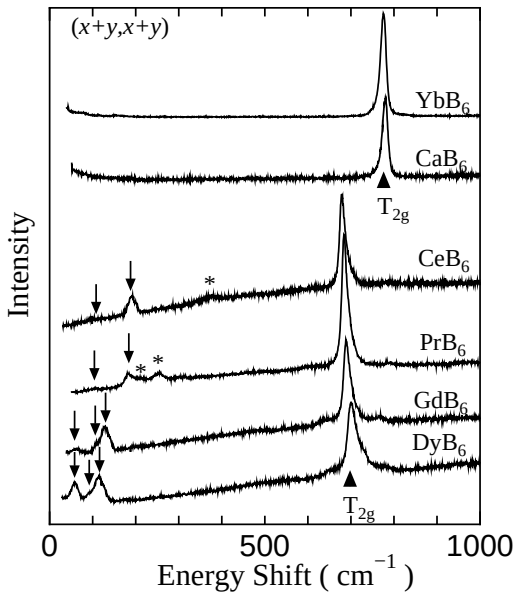

Fig. 1. Raman scattering spectra of RB_6 measured at room temperature. The anomalous peaks are labeled by arrows. The closed triangles and asterisks denote T_{2g} phonon and CEF excitations. The other A_{1g} and E_g phonons are not seen here, Their energies are $\omega(A_{1g}) \approx 1300\text{cm}^{-1}$, and $\omega(E_g) \approx 1150\text{cm}^{-1}$.

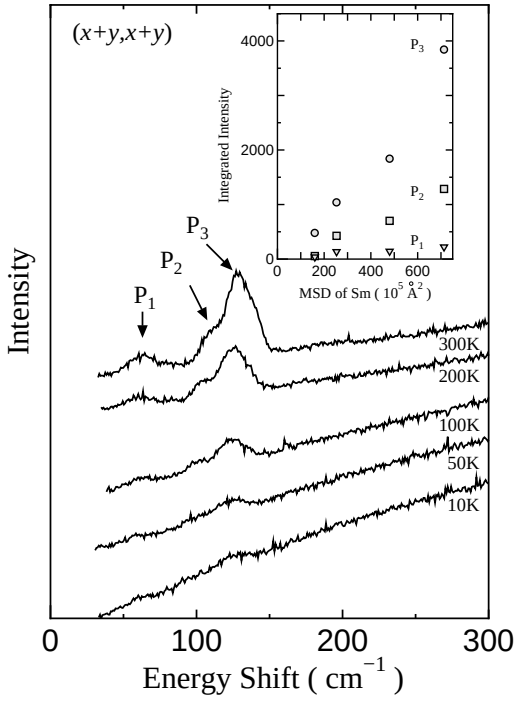

Fig. 2. Temperature dependence of Raman spectra of GdB_6. The inset is the peak intensity vs. mean square displacement(MSD) of Sm ion in SmB_6 [2].