Valence dependence of interatomic interactions in RB\textsubscript{6}

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Abstract. Previous Raman measurements of phonon in hexaborides have shown that bandwidth of low-frequency vibrations of R in divalent hexaborides is very broad in comparison with that in trivalent ones. To investigate this valence dependence, we have calculated interatomic force constants (IFC) from first principles for RB\textsubscript{6} (R=Ca, Sr, Ba, Y, and La). The calculated phonon dispersion curves reproduce the valence dependence. From the investigation of calculated IFC, we conclude that the different bandwidth is originated from the flatness of the dispersion curve of R ion vibration produced by IFC between R ions. Thus, the dispersion curve is highly dispersive for the divalent case. Since the IFC in divalent hexaborides are similar to those of dipole-dipole interactions, we suggest that an origin of the difference of IFC is the screening effect of the dipole field by conduction electrons in metallic trivalent hexaborides.

1. Introduction
Atomic vibration in a cage structure has attracted much interest because of its possibility to improve thermoelectric properties [1], or to realize superconductivity [2, 3] and heavy fermion state [4, 5] through interactions with electronic states. For the relatively large cage size compared with that of guest atom trapped in the cage, its vibration has large amplitude and low frequencies. Therefore, the dynamical properties of the guest atoms with low frequency are very important for the cage structural compounds.

Many compounds, constructed by boron and metallic atoms, reveal the cage structure, because very hard network structure is constructed by boron and metallic ions locate in the interspaces of the network. Therefore, we can recognize the metallic atoms as the guests in the context of cage compounds. However, in boron compounds, amplitude of the guest vibrations might not be so large to affect electronic states because of not so large interspaces for most metallic ions. Nevertheless, boron compounds will be useful to investigate the dynamics of the guest atoms, because their structures are relatively simple in comparison with other cage compounds. In this paper, we have focused on hexaborides, RB\textsubscript{6}, which is one of the simplest compounds among the cage compounds.

Our previous Raman scattering investigation [6] of divalent and trivalent hexaborides have clarified two results with the valence dependence of R ion. One is the frequency of T\textsubscript{2g} mode, which takes about 700 cm\textsuperscript{-1} or 800 cm\textsuperscript{-1} for trivalent or divalent hexaborides, respectively. The other is spectrum of second-order scattering from low-frequency vibrations of R (LFV). In trivalent hexaborides, this spectrum is sharp and its intensity largely depends on temperature. On the other hand, in divalent hexaborides, the spectrum is broad and weak. Its intensity is
Figure 1. Calculated phonon dispersion curves at a low-energy region for CaB$_6$ (left), BaB$_6$ (center), and LaB$_6$ (right).

almost independent of temperature. These two facts indicate that the interatomic interactions are strongly affected by electronic state. The spectrum width of the second-order scattering reflects dispersion of LFV band. The observed feature means the small dispersion for trivalent R$^{3+}$ and large one for divalent R$^{2+}$. This behavior of the dispersion has been also confirmed by inelastic neutron scattering [7]. In this paper, to quantitatively clarify the latter result, we have calculated the interatomic force constants (IFC) using first principles calculations.

2. Calculation method

Calculations have been performed with ABINIT package [8]. The package relies on density functional theory with local density approximation (LDA) and plane-wave basis together with norm-conserved pseudopotential. For exchange-correlation energy functional, the LDA potential presented by Perdew and Wang [9] was used. The Troullier-Martins type [10] pseudopotentials have been obtained using FPI98PP [11] and the pseudopotentials of R include semi-core states, except for Y. Cut-off energy for the plane-wave basis was from 34 Ry for Ba to 54 Ry for La, where 1 Ry = 13.6 eV. For an integration of the Brillouin zone, special points [12, 13] on $8 \times 8 \times 8$ $\mathbf{k}$-point grids with a smearing width 0.02 Ry were employed. Calculations of lattice dynamics were proceeded by density functional perturbation theory [14, 15]. To obtain IFC and phonon dispersion curves, the Fourier interpolation method was used on $4 \times 4 \times 4$ grids. Lattice constants and parameter $x$ of boron position have been optimized. Then, IFC was calculated for the obtained structure. As the results, the calculated lattice constants are smaller than the experimental ones by about 0.10 Å, and the calculated phonon frequencies are larger than the experimental results by $30 \sim 50$ cm$^{-1}$ for three Raman active modes.

3. Result and discussion

Calculated results of phonon dispersion curves in a low-energy region are shown in figure 1 for CaB$_6$, BaB$_6$, and LaB$_6$. The calculated phonon dispersions are similar to the reported results of first principles calculations [16]. The relatively flat phonon bands around 100 cm$^{-1}$ correspond to LFV. Their widths are determined by variation of force constant $k(q)$ at wavevector $q$, and frequency of the vibration is expressed by $\sqrt{k(q)/M}$, where $M$ is the mass of R. From this expression, the width is narrow for heavy R and also for small R ion because of weak IFC. Therefore, the result in figure 1 is inevitable at first sight. However, as shown below, the IFC are different between divalent and trivalent hexaborides, especially between Ca$^{2+}$ and La$^{3+}$. Since the ionic radii of Ca$^{2+}$ and La$^{3+}$ are close, the difference of force constants between them are originated from the different electronic states.

The IFC $D_{\alpha j\beta}$ is defined by force $f_{i\alpha}$ acted on atom $i$, when atom $j$ move by $u_{j\beta}$, as $f_{i\alpha} = \sum_{\beta} D_{\alpha j\beta} u_{j\beta}$. Since it is very cumbersome to treat all components of $D_{\alpha j\beta}$, we define a
Figure 2. Norm $D_{ij}$ of IFC from R at (0 0 0) to B at (x 0.5 0.5) (top), R at (1 0 0) (middle), and R at (1 1 0) (bottom), for divalent (triangle) and trivalent (square) hexaborides.

The norm $D_{ij}$ by following formula.

$$D_{ij}^2 = \frac{1}{4\pi} \int_{-1}^{1} d\cos\theta \int_{0}^{2\pi} d\phi \sum_{\alpha} \sum_{\beta} D_{i\alpha j\beta}(\theta, \phi) \left(\sum_{\beta} D_{i\alpha j\beta}(\theta, \phi)\right)^2 = \frac{1}{3} \sum_{\alpha\beta} D_{i\alpha j\beta}^2,$$

where $e_{\beta}(\theta, \phi)$ is a unit vector in polar coordinate. $D_{ij}$ from R at (0 0 0) to B (x 0.5 0.5), R (1 0 0), and R (1 1 0) are shown in figure 2. As seen in figure 2, the IFC between R atoms are quite different between divalent and trivalent hexaborides, while the difference for IFC between R and B is small. From this result, we can conclude that the IFC between R atoms are important for the difference of bandwidth of LFV. This conclusion can be easily confirmed by calculating phonon dispersion using IFC, where IFC between Ca ions are set to 0 and the others are same as those obtained for CaB$_6$.

Figure 3. Phonon dispersion curve calculated using IFC, where IFC between Ca ions are set to 0 and the other IFC are same as those obtained for CaB$_6$.

The figure clearly demonstrates that the bandwidth is caused by IFC between R atoms and that the difference of the width is due to a difference of IFC between R atoms.

Roughly speaking, in the hexaboride system, the nearest neighbor IFC between R and B organizes the bottom of LFV band, and the IFC between R atoms determine the width of the band. This gives good contrast to the skutterudite system, where IFC between guest atoms are very small, and width of guest vibration band is determined by hardness of cage structure [17]. Since the guest atom motion causes a cage distortion with wavevector dependence, the variation of distortion produces the bandwidth in skutterudites. In the hexaboride case, the boron network is very hard and is not deformed by R ion motion. Therefore, the origin of the bandwidth of guest vibrations is quite different between hexaborides and skutterudites.

Now, we discuss an origin of the valence dependence of IFC. One possibility is difference of screening ability of dipole electric field by conduction electrons as discussed in the previous paper [6]. It must be examined from first principle results, but it is difficult to divide the IFC to dipole interaction part and the other part in metallic compounds. Unfortunately, our calculations produce metallic states even for divalent hexaborides. This fault is perhaps due to the use of LDA which tends to underestimate the band gap. Nevertheless, as shown in figure 2, different norm of the IFC gives us a hint to discuss the problem. If the large IFC in divalent hexaborides are dominated by dipole interactions between R$^{2+}$, directions of forces acting on R$^{2+}$ are similar to those of dipole electronic field. Figure 4 shows forces acting on neighbor R ions in CaB$_6$ and LaB$_6$ due to the displacement of the center ion. As clearly seen, the directions...
of forces are quite similar to those of dipole field for CaB\(_6\) and different for LaB\(_6\). Therefore, we suggest that the large IFC between R are due to dipole-dipole interactions between R\(^{2+}\) in divalent hexaborides, and that the small IFC in trivalent hexaborides are due to the screening effect by conduction electrons.

4. Conclusion
We have calculated IFC using first principles method for CaB\(_6\), SrB\(_6\), BaB\(_6\), YB\(_6\), and LaB\(_6\). The calculated result of phonon dispersion curves shows valence dependence of bandwidth of LFV as observed. From the calculated IFC, we conclude that the difference of the bandwidth is due to difference of IFC between R. In the hexaboride case, the bandwidth is determined by the IFC between R, and large bandwidth in divalent hexaborides is caused by large IFC between R. The large IFC in divalent hexaborides are similar to those of dipole-dipole interactions. Therefore, we suggest that the small bandwidth in trivalent hexaborides is due to the screening effect of the dipole field by conduction electrons.

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