(P1-18)

Raman scattering of type-I clathrate compounds $X_8Ga_{16}Ge_{30}$ (X = Eu, Sr, Ba)

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Lattice dynamical properties, especially dynamical motion of guest ions, of type-I clathrate compounds $X_8Ga_{16}Ge_{30}$ (X = Eu, Sr, Ba) have been investigated by Raman scattering. Raman active phonons of this cage-like framework are given by group theory as $3A_g + 8E_g + 9T_{2g}$, and of guest ions at 6*d*-site as $E_g + T_{2g}$, where the position of the guest ion is center of the cage. The Raman active modes are fully assigned by the polarized Raman scattering on single crystalline $X_8Ga_{16}Ge_{30}$ and the first principles calculations for the precise phonon mode assignment. The guest modes can be distinguished from the cage modes. Moreover, we found the additional mode on $A_{1g} + E_g$ and E_g spectra due to the off-centered position.

To clarify the properties of Raman active phonon modes, the temperature dependence measurements are carried out. The energy of the cage modes shows normal behavior between 2 K and 500 K, where the energy increases upon cooling. On the other hand, the guest modes on E_g and T_{2g} exhibit an opposite dependence, and this anomalous dependence has been the common characteristic that does not depend on a guest ion (see Fig. 1(a)). We can represent that this anomaly is explained by the quartic anharmonic potential, and the effect of anharmonicity can be estimate by this measurement using the reported thermal factor[1] for $Ba_8Ga_{16}Ge_{30}$ (see Fig. 1(b)).

Moreover, we presented the temperature dependence of the additional A_{1g} mode, especially on $Eu_8Ga_{16}Ge_{30}$. The energy shift of additional A_{1g} upon cooling is larger than that of cage modes. The temperature dependence are well fitted by the function $a\sqrt{T_0 - T}$. This softening means that above T_0, the position of Eu ion should be on-center. We can describe this change as a new type transition, because the correlation between the guest ions is very weak due to the shielding of carriers on the cage. Thus, the new type transition may be identified as an incoherent transition since the phonon dispersion of the guest ion is flat reported by the present first principles calculations and a recent study[2].

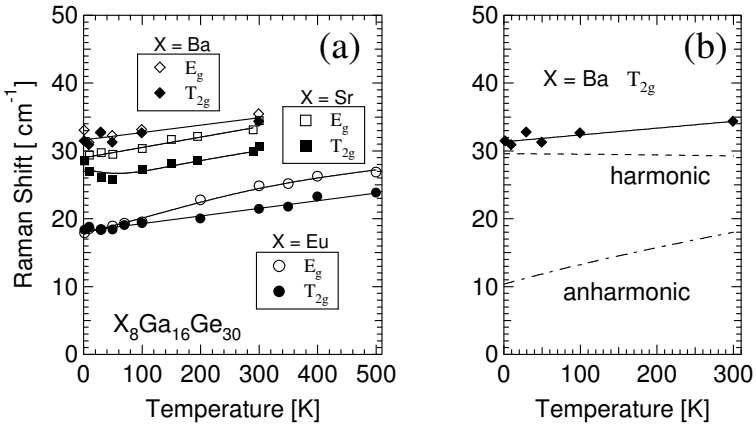

Figure 1: (a) Temperature dependence of the guest modes, (b) Estimation of the harmonic and anharmonic energy for X = Ba.

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[2] G. K. H. Madsen and G. Santi, Phys. Rev. B **72**, 220301(R) (2005).