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Guest vibrations and resulting cage distortions in cage compounds

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Dynamics of atoms weakly bound in a cage structure has attracted attention as a new mechanism to realize interesting electronic states. In this issue, it is believed that an important condition is large amplitude of the *guest* vibrations. Such large amplitude of thermal vibration has been shown by X-ray and neutron diffraction experiments for many cage compounds. Furthermore, as a result of the large amplitude vibrations, large anharmonic effect on the guest vibrations has been also observed as an increasing energy with increasing temperature.

Large amplitude of vibrations can be found in a framework of harmonic lattice dynamics, when vibration energies of the guests concentrate on a low energy region. To satisfy the condition, we can think a material that has a hard network structure and atoms not incorporated in the network. On the other hand, to affect electronic states, the guest vibration must have a large interaction with electrons near the Fermi surface. If the guest is a cation bonding to other atoms weakly, it is impossible to expect a large interaction for a displacement of the guest. Therefore, we need to consider a condition that the interaction becomes large.

One possibility is that electrons on the guests contribute to low-energy states. It is expected when the guests are rare earth and Kondo state is realized. Another possibility is that a displacement of the guest distorts the network structure. In this case, the displacement can affect electronic states through distortion of the network structure.

Along with this latter consideration, we investigate lattice dynamics from first-principles calculations of interatomic interactions. Calculated compounds are La-filled skutterudites, Ga-Ge clathrate compounds $A_8Ga_{16}Ge_{30}$ (A=Sr, Ba), and hexaborides RB_6 (R = Ca, La). The hexaborides have also a hard network of boron and weakly bonding cations. For these compounds, the interatomic force constants are calculated from density-functional theory, and then all phonon displacements are obtained using the force constants. We can examine a distortion of the network structure in the guest vibrations through the obtained displacements.

Since lattice vibrations are eigen vectors of equation of motion, norm of the displacement $u_{i\alpha}(q)$ of atom i with wavevector q can be normalized to unity, such as $\sum_{i,\alpha} M_i|u_{i\alpha}(q)|^2 = 1$, where M_i is the mass of atom i. Using this normalized displacement, we can see a fraction of the guest in the guest vibrations by taking the summation only for the guest atoms.

The calculated fractions of La atoms in a La vibration at a Brillouin zone boundary are tabulated in Table 1. As seen for LaB_6, the La vibration at a Brillouin zone boundary is completely described by only La displacement. This is expected for hard network compounds. On the other hands, skutterudites show relatively small fractions for P and As compounds. Furthermore, for Sb skutterudites the fraction becomes lower than 0.9. This means that in the Sb skutterudites the La vibrations distort largely because of relatively soft network of Sb.

$LaFe_4P_{12}$	$LaRu_4P_{12}$	$LaOs_4P_{12}$	$LaRu_4As_{12}$	$LaFe_4Sb_{12}$	$LaRu_4Sb_{12}$	$LaOs_4Sb_{12}$	LaB_6
0.948	0.967	0.956	0.926	0.761	0.866	0.873	0.999

Table 1: Fraction of La atom in a displacements of a La vibration. The wavevector of the vibration is P (0.5 0.5 0.5) for skutterudites and X (0.5 0.0 0.0) for LaB_6.