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Raman scattering of caged compounds

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Recently guest ion motion in the cage is extensively studied for the thermoelectric applications. As one of the possible mechanisms to decrease the phonon thermal conductivity, rattling motion of the guest ion has been pointed out. This mode is understood as the individual (Einstein) vibration with the flat phonon dispersion relation. The rattling mode is usually evaluated by the large thermal factor and specific heat measurement. Here we note the results of the ultrasonic experiments measured by Goto et al for $PrOs_4Sb_{12}$ and $La_3Pd_{20}Ge_6$[1]. They found the elastic dispersion and also found the softening of the elastic constant at low temperature. These anomalies have been explained by the thermal rattling for the former and a quantum tunneling for the latter. Thus, in order to understand the dynamical properties of the guest ion motion, Raman scattering was performed for the following caged compounds; $A_8Ga_{16}Ge_{30}$ (A=Sr,Ba,Eu), $La_3Pd_{20}Ge_6$, RB_6, and RT_4X_{12}. In this presentation, we summarize the recent studies of the above compounds. Among them, the guest ions position in the cage deviates by ~ 0.4Å from the center position at the cage for the first compounds of $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$. However the guest ion locates at the center for the remaining three compounds. In Raman scattering, we have found two types of spectra due to thermal rattling; one phonon and two phonon processes.

1st order (one phonon) Raman precess in $A_8Ga_{16}Ge_{30}$ (A=Sr,Ba,Eu) and $La_3Pd_{20}Ge_6$

The off-center position of the guest ion decreases the site symmetry at 6*d* site in $A_8Ga_{16}Ge_{30}$ (A=Sr,Ba,Eu). In fact the precise mode assignment gives the additional phonons due to the cage ion at 6*d* site. The energies of the additional modes with T_{2g} and E_g decreases with decreasing temperature. It has been found that the contribution of the 4th order anharmonic potentials is relatively large for the energy decrease in $Ba_8Ga_{16}Ge_{30}$. In addition, the spectral shape of T_{2g} and E_g changes from the single peak to the flat response below 10K in $Eu_8Ga_{16}Ge_{30}$. We believe that this spectral change is originated by the change from thermal ratting to quantum tunneling. In $La_3Pd_{20}Ge_6$, the energy of the Raman active guest mode also slightly decreases with decreasing temperature. In spite of few experimental evidences, we think this energy decrease is the universal property for the thermal rattling. The detailed reports will be presented at the posters of P1-17 and 18 in this meeting.

2nd order (two phonon) Raman process in RB_6, and RT_4X_{12}

For the 2nd order Raman scattering, we have found the clear correlation of the energy and intensity of the guest ion motion with the cage size and also the correlation between their intensity and mean square displacement of the guest ion due to thermal fluctuation in RB_6. For the thermal rattling, the existence of the carriers on the cage is necessary to change from the ordinary phonon to the individual Einstein modes.

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