Raman scattering study of filled skutterudite compounds

N Ogita¹, R Kojima¹, T Hasegawa¹, Y Takasu¹, M Udagawa¹, T Kondo², N Takeda³, T Ikeno⁴, K Ishikawa⁴, H Sugawara⁵, D Kikuchi⁶, H Sato⁷, C Sekine⁷ and I Shirotani⁷

¹Graduate School of Integrated Arts and Sci., Hiroshima Univ., Hiroshima 739-8521, Japan
²Venture Business Laboratory, Hiroshima Univ., Higashi-Hiroshima, 739-8527, Japan
³Faculty of Engineering, Niigata Univ., Niigata 950-2181, Japan
⁴Faculty of Science, Toyama Univ., 3190 Gofuku, Toyama 930-8555, Japan
⁵Faculty of Integrated Arts and Sci., The Univ. of Tokushima, Tokushima 770-8502, Japan
⁶Department of Physics, Tokyo Metropolitan Univ., Tokyo 192-0397, Japan
⁷Faculty of Engineering, Muroran Institute of Technology, Muroran 050-8585, Japan

E-mail: nogita@hiroshima-u.ac.jp

Abstract. Raman scattering of skutterudite compounds RT₄X₁₂ (R=rare earth; T=Fe, Ru, and Os; X=pnicogen) have been measured. All first-order Raman active phonons are observed and are assigned as the pnicogen vibrations. At the low energy region, the second-order phonons, due to the vibration of the rare earth ions with a flat phonon dispersion, are observed in the spectra of RRu₄P₁₂ (R=La and Sm) and ROs₄Sb₁₂ (R=La, Ce, Pr, Nd, and Sm). The appearance of the second-order phonons in the spectra is caused by an anharmonic vibrations of rare earth ions in large cage space and a large density of state due to the flat phonon dispersion. However, in spite of the similar cage space, the 2nd-order phonons are hardly observed for RFₑ₄Sb₁₂ and RRu₄Sb₁₂. Thus, these results suggest that the dynamics of the rare earth ion is closely related to not only the cage size but also the electronic state due to the transition metals. Raman spectra of PrRu₄P₁₂ show the drastic spectral change due to the metal-insulator transition. The phonon spectra and crystal field excitations due to the structural change have been assigned above and below the transition temperature.

1. Introduction
Ternary compounds of filled skutterudite RT₄X₁₂ (R=rare earth; T=Fe, Ru, and Os; X=pnicogen) have attracted much attention, because of their various physical properties such as a metal-insulator (MI) transition in PrRu₄P₁₂ (T_{MI} ≃60K) [1], heavy fermion superconductivity in PrOs₄Sb₁₂ (T_{C}=1.85K) [2]. These properties might be caused by a strong hybridization between 4f electrons and conduction electrons. On the other hand, these compounds are expected to be a good thermoelectric material [3], because the anharmonic vibrations of the filled rare-earth ions in the oversized cage, called as "rattler" or "off-centered motion", reduce the thermal conductivity [4]. These features are originated from a unique body centered cubic structure, that is, the icosahedral cages constructed by the twelve pnicogens form the bcc configuration, and the transition metals are located at (1/4,1/4,1/4) site to connect the icosahedra. The rare-earth ion is on the center of the cage [3].
Therefore, it is important to clarify lattice dynamics of the unique structure for understanding of their physical properties. We have measured Raman scattering spectra of filled skutterudite $RT_4X_{12}$ ($R=$La, Ce, Pr, Nd, Sm, Yb; $T=$Fe, Ru, Os; $X=$P, Sb).

The details of the experimental procedure for the Raman scattering measurement were described in our previous report[5]. Single crystal samples of P-based $RT_4P_{12}$ and Sb-based $RT_4Sb_{12}$ were synthesized by Sn-flux and Sb-flux method, respectively. Eight phonons, $\Gamma_R = 2A_g + 2E_g + 4T_g$ as pnicogen vibrations, are Raman active phonons in the crystallographic symmetry $Im\bar{3}$ of the skutterudite compounds. The $A_g$, $E_g$, and $T_g$ phonons can be selectively observed by polarization dependence of incident and scattered light as following polarization geometries: $A_g$ phonons appear for the $(x,x)$ geometry, $E_g$ in $(x,x)$ and $(x+y,x−y)$, and $T_g$ in $(x,y)$. In the notation of $(\alpha, \beta)$, $\alpha$ and $\beta$ are the polarization directions of incident and scattered light, respectively.

2. Results and Discussions

Figure 1 shows the $(x+y,x−y)$ Raman spectra of $RFe_4P_{12}$, $RRu_4P_{12}$ and $ROs_4Sb_{12}$ ($R=$La, Pr, Sm) at room temperature. In this polarization geometry, two $E_g$ phonons are clearly observed in every spectra at around 400 cm$^{-1}$ for P-based skutterudites and 150 cm$^{-1}$ for Sb-based one, as shown in figure 1. The spectra are presented in the sequence of the lattice constant approximately, that is, $RFe_4P_{12}$ compounds have the shortest lattice constant and $ROs_4Sb_{12}$ are largest. The lattice constant of the skutterudite roughly depends on the ionic radius of the pnicogen. Thus, the phonon energy of P- and Sb-based skutterudites roughly depends on the lattice constant. However, as shown in the figure, the energy of $E_g$ phonons of $RRu_4P_{12}$ is slightly higher than that of $RFe_4P_{12}$, in spite of the larger lattice constant of $RRu_4P_{12}$. Since two $E_g$ phonons can be regarded as breathing and deformational inplane-motion of $P_4$ ring, the
shorter P-P distance in P₄ rings of RRu₄P₁₂ makes the $E_g$ phonon energy higher.

Except for the $E_g$ phonons, the crystal field(CF) excitations($\nabla$) in PrRu₄P₁₂ and the 2nd-order phonons($\downarrow$) in RRu₄P₁₂( R=La, Sm) and RO₈Sb₁₂ have been observed. These 2nd-order phonons correspond to the excitation of the rare earth vibration in the large icosahedral cage. Although the vibrations of rare earth ions are inactive in 1st-order Raman scattering process, the reason why the vibrations are observable as the second-order Raman process is the following. Since the rare earth is weakly bonded to the icosahedral cage, the phonon dispersion shows a low energy flat-band in the vicinity of the Brillouin zone boundary, which is a characteristic dispersion for the caged crystals. In fact, the first principle calculation shows the existence of the flat band, and the observation of the flat band has been reported by X-ray and neutron inelastic scattering [6, 7]. The good energy agreement between the 2nd-order phonons and the twice of the flat-band energy($\Delta$) by the first principle calculation for La-skutterudite and the X-ray scattering for Sm-one have been obtained.

On the other hand, we have not observed the similar 2nd-order phonons in RF₄P₁₂, in spite of the observable in the P-cage of RRu₄P₁₂. As mentioned above, the P-P bond in P₄-ring of RRu₄P₁₂ is shorter than that of RF₄P₁₂. That is, the R-P bond of RF₄P₁₂ is shorter than that of RRu₄P₁₂. The movable space of rare earth ions in the cage is narrower for RF₄P₁₂. This can be considered as a reason for the absence of 2nd-order phonons. Thus, the rare earth vibration with large amplitude in large cage makes scattered intensity of the 2nd order phonons strong. Consequently, anharmonic effect is enhanced by the large vibrations of rare earth ions. The peak intensity decreases with decreasing temperature and vanish at low temperature. The phenomena also can be explained as the anharmonic effect. The similar results have been already reported for RB₅ crystals [8]. It can be concluded that the 2nd order phonons correlates with the rattling motion of rare-earth ion.

Figure 2 shows the $(x+y, x-y)$ Raman spectra of Sb-skutterudite RT₄Sb₁₂ (R=La, Pr, T=Fe, Ru, Os) at room temperature. The lattice constants of RF₄Sb₁₂ and RRu₄Sb₁₂ are somewhat shorter than that of RO₈Sb₁₂($a \approx 9.30\text{Å}$) about 0.15 and 0.03Å, respectively. The pnicogen position, $(0, u, v)$, for RT₄Sb₁₂ (T=Fe, Ru) is not reported systematically so far, but the cage size of Sb-skutterudites seems to be similar. In fact, the similar cage size is obtained from the reported $u$ and $v$ values. Therefore, we can expect to observe the 2nd-order phonons in the Raman spectra of RT₄Sb₁₂ (T=Fe, Ru). As shown in figure 2, the expected 2nd-order phonons

Figure 3. $E_g$ Temperature dependence of Raman scattering spectra of PrRu₄P₁₂ for the energy region (a) 0-200 cm⁻¹ and (b) 200-460 cm⁻¹.
are hardly observed except for ROs$_4$Sb$_{12}$. This suggests that the observation of the 2nd-order phonon is related to the electronic state due to the transition metal. In fact, the intensity of 2nd order phonons shows resonance effect in excitation energy dependence. The lower energy excitation induces the strong scattering intensity of 2nd-order phonons. The correlation between the behavior of 2nd-order phonons and the electronic state is not clear yet.

Figure 3 shows temperature dependence Raman spectra of PRu$_4$P$_{12}$ for the energy region (a) 0-200cm$^{-1}$ and (b) 200-460 cm$^{-1}$. The spectra in figure 3(a) is expanded by 3 times along the vertical axis. The energy region in (b) displays the spectra due to phonons and in (a) that of the crystal field excitations. The spectra shown in the both energy region are drastically changed across the $T_{MI}$.

In the energy region above 200cm$^{-1}$ for figure 3(b), two additional peaks(↓) besides two $E_g$ phonons of $Im\bar{3}$ are observed below $T_{MI}$. The polarization dependence of these spectra suggests that the cubic symmetry is kept below $T_{MI}$, and the number of additional phonons are $1A_g + 2E_g + 4T_g$. Therefore, the crystal symmetry can be evaluated as $Pm\bar{3}$ below $T_{MI}$.

Below 200cm$^{-1}$ shown in figure 3(a), two very broad peaks for $T > T_{MI}$ split into several sharp peaks for $T < T_{MI}$. The peak energies at T=5K agree with the CF excitation energy determined by neutron experiment [9]. The poor polarization dependence can be also explained as the CF excitations. Below $T_{MI}$, the site symmetries of Pr at corner (Pr1) and body-center (Pr2) become inequivalent due to the structural change. Therefore, the CF excitations also split each CF levels for Pr1 and Pr2. With increasing temperature below $T_{MI}$, the CF levels for Pr1 and Pr2 coincide to that for an equivalent Pr site at $T_{MI}$. Two broad peaks observed at room temperature can be assigned as the CF excitations of Pr ion, and the temperature dependence of a part of the CF levels can be estimated from the peak energy. At this stage, the observed peaks below 200cm$^{-1}$ are assigned as CF excitation, but the phonons due to structural change are expected because the Ru motion becomes Raman active for $Pm\bar{3}$ symmetry.

Finally, we summarize the Raman spectra of filled skutterudite compounds. All Raman active phonons due to pnicogen vibrations and 2nd-order phonons due to the rare earth vibrations have been observed. The observation of the 2nd-order phonons is caused by the anharmonic vibrations of rare earth ions in large cage. In the spectra of PRu$_4$P$_{12}$, drastic spectral change due to the MI transition is observed. From the number of additional peaks and their energy, the crystal symmetry below $T_{MI}$ and CF levels are estimated.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research Priority Area “Skutterudite” (No. 15072205) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The low temperature experiments have been supported by N-BARD and IAMR of Hiroshima University.

References

[1] Sekine C, Uchiumi T, Shirotani I and Yagi T 1997 Phys. Rev. Lett. 79 3218
[2] Bauer E D, Frederick N A, Ho P -C, Zaspf V S and Maple M B 2002 Phys. Rev. B 65 100506
[3] Jeitschko W and Braun D 1977 Acta Crystallogr. Sect. B 33 340
[4] Slack G A 1995 CRC Handbook of Thermoelectrics, ed D M Rowe and Boca Raton FL (Chemical Rubber) p407
[5] Ogita N, Yamamoto K, Saha S R, Sugawara H, Sato H, Sekine C, Shirotani I and Udagawa M 2005 Physica B 359-361 847
[6] Tsutsumi T to be published
[7] Lee C H, Hase I, Sugawara H, Yoshizawa H and Sato H 2006 J. Phys. Soc. Jpn. 75 123602
[8] Ogita N, Nagai S, Okamoto N, Udagawa M, Iga F, Sera M, Akimitsu J and Kunii S 2003 Phys. Rev. B 68 224305
[9] Iwasa K, Hao L, Kuwahara K, Kohgi M, Saha S R, Sugawara H, Aoki Y and Sato H 2005 Phys. Rev. B 72 024114