Raman Scattering Investigation of Skutterudite Compounds

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abstract

Raman scattering spectra of filled skutterudite RT_4X_{12} (R=La, Ce, Pr, Nd, Sm and Y, T=Fe, Ru and Os, and X=Sb and P) and unfilled skutterudite CoP_3 have been measured. All first-order Raman active phonons, which are due to the vibration of pnictogens, are observed. In addition, the crystal field excitations in $PrRu_4P_{12}$ spectra and the 2^{nd}- order phonons including rare-earth vibrations in $SmRu_4P_{12}$ and ROs_4Sb_{12} are also observed. The 2^{nd}- order phonons can be observed for the sample with the larger cage space. The peak intensity of the 2^{nd}- order phonons decreases with decreasing temperature and vanishes at low temperature. Such a temperature dependence suggests that the 2^{nd}- order phonons are thermally excited and due to independent vibrations of the rare-earth ions, that is rattler motion.

keyword

Skutterudite, Raman scattering, rattling vibration

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Ternary compounds of filled skutterudite RT_4X_{12} (R:rare-earth, T: transition metal, and X:pnictogen) have attracted much attention, because of having their various physical properties, such as metal-insulator transition in $PrRu_4P_{12}$($T_{MI} \simeq$60K)[1], heavy fermion superconductivity in $PrOs_4Sb_{12}$(T_C=1.85K)[2] and so on. For the appearance of these properties, the strong *p*-*f* hybridization between the rare-earth ions and the surrounding 12 pnictogens plays an important role. Furthermore, anharmonic and independent vibration of rare-earth ions strongly affects as well. The vibration is called as "rattling vibration" or "off-centered motion"[3]. To clarify a microscopic mechanism and relationship between the physical properties and the lattice dynamics, especially a role of the rare-earth motion, we have measured Raman spectra of the filled skutterudite of RT_4X_{12} (R=La, Ce, Pr, Nd, Sm and Y, T=Fe, Ru and Os, and X=Sb and P) and a unfilled skutterudite of CoP_3.

Single crystal samples of P-based skutterudite RX_4P_{12} and Sb-based one RX_4Sb_{12} were synthesized by Sn-flux and Sb-flux method, respectively. The detailed experimental procedure for the Raman scattering measurement of single crystals was described in our previous report[4]. Polycrystalline CoP_3 was synthesized by using a wedge-type cubic-anvil high pressure apparatus. For the polycrystalline samples composed of single crystal grains with 10μm in diameter, we employed micro-Raman system. The crystal symmetry $Im\bar{3}$ of the skutterudite compounds gives eight Raman-active phonons as $\Gamma_{\rm R} = 2A_g + 2E_g + 4T_g$, where A_g, E_g, and T_g denote the irreducible representations. These phonons correspond to the vibrations of only pnictogen atoms. The phonons in each irreducible representation are observed in the spectra of the 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 (α,β), α and β are the polarization directions of incident and scattered light, respectively. In this study, x and y correspond to the crystal axes of [1,0,0] and [0,1,0], respectively.

Figure **??** shows the E_g Raman spectra of RT_4X_{12} measured at room temperature. Two strong peaks in every spectra are the E_g phonons. The energy difference of the E_g phonons between P-based RX_4P_{12} and Sb-based RX_4Sb_{12} depends on the pnictogen mass and lattice parameter. In addition, the crystal field excitation ($\bigtriangledown$) in $PrRu_4P_{12}$ and the

2^{nd}- order phonon(▼) in $SmRu_4P_{12}$ and ROs_4Sb_{12} have been observed. The crystal field excitations in $PrRu_4P_{12}$ spectrum drastically change below T_{MI}[5].

Here, we forcus on the 2^{nd}- order phonons. The 2^{nd}- order phonons are originated from the excitation of the low energy flat-band in the phonon dispersion curves at the Brillouin zone boundary, which is a characteristic dispersion for the caged crystals [6]. In fact, the first principle calculation predicts the existence of the flat band, and the observation of the flat band has been reported by X-ray inelastic scattering [7]. The good energy agreement between the 2^{nd}-order phonons and twice of the flat-band by the first principle calculation and the X-ray scattering have been obtained. On the other hand, we have not found the similar 2^{nd}- order phonons in RFe_4P_{12} and RRu_4P_{12} (R=La and Pr).

To clarify the reason why the 2^{nd}-order phonon is observable in $SmRu_4P_{12}$ and ROs_4Sb_{12} or that is unobservable in RFe_4P_{12} and RRu_4P_{12} (R=La and Pr), we paid attention to the cage space taking into account of the ionic radii of rare-earth ions and pnictogens. The reason is because we have so far obtained a clear and systematic relationship between the peak intensity of the rare-earth vibrations and the cage space in the rare-earth hexaborides RB_6[8]. Each spectrum in Fig. **??** is depicted in the order of the increasing cage space from top to bottom. As shown in the figure, the critical cage space is around the size of $SmRu_4P_{12}$. Therefore, the larger cage space(movable space) is necessary for being observable the 2^{nd}-order phonon in the Raman spectra, . In addition, the peak intensity decreases with decreasing temperature and vanishes at low temperature. It can be concluded that this temperature dependence of the 2^{nd}- order phonons correlates with the rattling motion of rare-earth ion.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research Priority Area "Skutterudite" (No. 15072205) and for COE Research (No. 13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The low temperature experiments is supported by N-BARD of Hiroshima University.

References

[1] C. Sekine, et al., Phys. Rev. Lett. **79**, 3218(1997).

[2] E. D. Bauer, et al., Phys. Rev. **B 65**, 100506(2002).

[3] T. Goto, et al., Rev. **B 69**, 180511R(2004).

[4] N. Ogita, et al., Physica B **359-361**, 847(2005).

[5] N. Ogita, et al., Physica B, to be published.

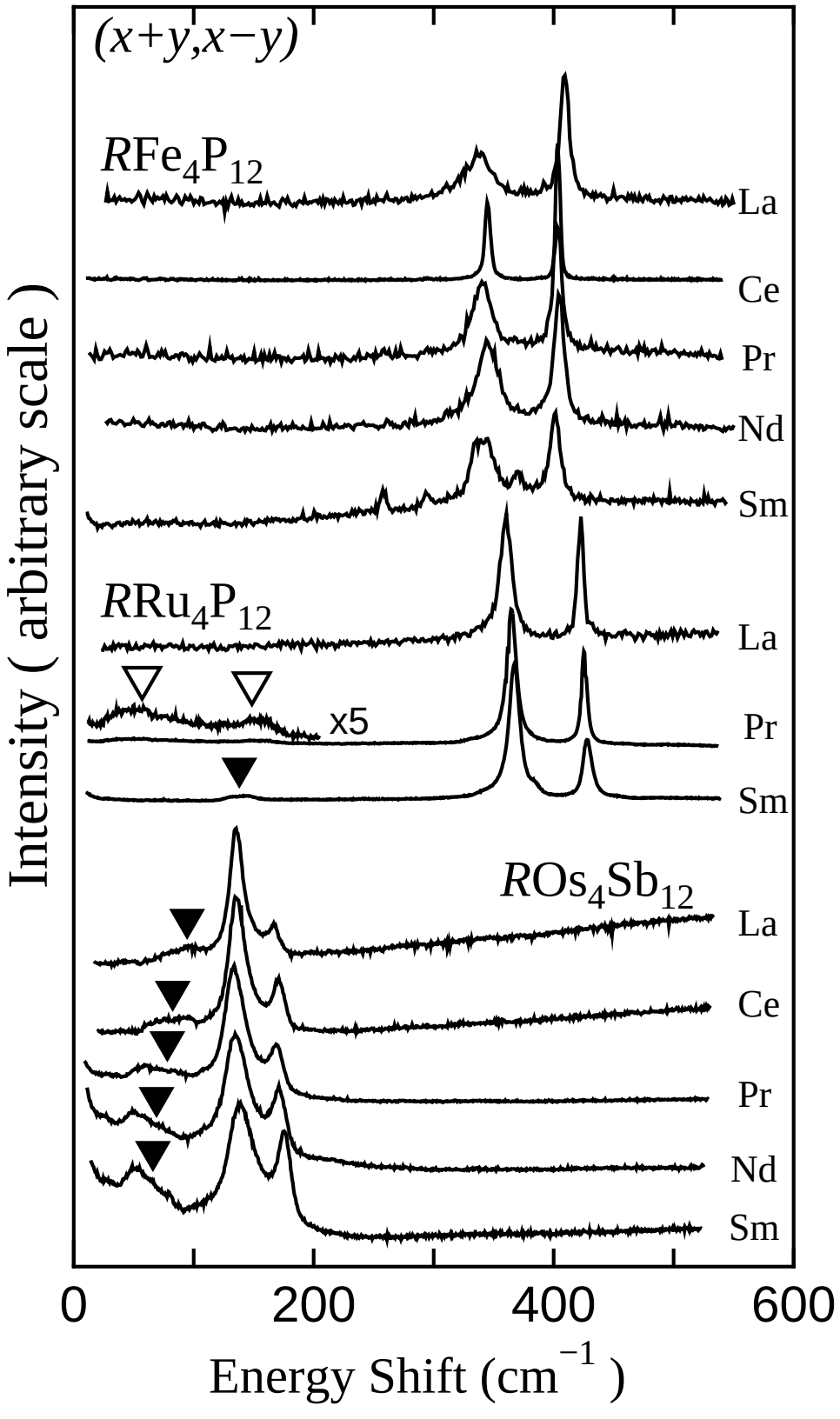
[6] S. Kunii, et al., J. Phys. Soc. Jpn. **66**, 1029(1997); K. Takegahara et al., Solid State Commun. **53**, 21(1985).

[7] S. Tsutsui, to be published

[8] N. Ogita, et al., Phys. Rev. B **68**, (2003) 224605.

Figure caption

E_g Raman scattering spectra of the filled skutterudite at room temperature.


(x+y,x−y)
RFe4P12
La
Ce
Pr
Nd
Sm
RRu4P12
La
x5
Pr
Sm
ROs4Sb12
La
Ce
Pr
Nd
Sm
Intensity (arbitrary scale)
0
200
400
600
Energy Shift (cm−1)