Rare-earth Atom Motions in $ROs_4Sb_{12}$ ($R = \text{La, Pr, Nd, Sm}$)

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Abstract. High-resolution inelastic x-ray scattering (IXS) was carried out in the filled-skutterudites $ROs_4Sb_{12}$ ($R = \text{La, Pr, Nd, Sm}$). Low-energy rare-earth modes were found in these compounds. They show significant rare-earth dependence, suggesting a correlation with lanthanide contraction. We discuss the relation between the present IXS measurements and reported other experiments.

1. Introduction
The series of filled skutterudites is an interesting type of strongly correlated electron system. Their crystal structure may cause these materials to demonstrate heavy fermion (HF) behaviour, metal-insulator transition and other unusual properties [1]. The crystal structure includes a cage consisting of twelve pnictogen atoms, containing a rare-earth ($R$) atom. This may result in strong hybridization between 4f- and conduction electrons in rare-earth filled skutterudites because the $R$ atoms are surrounded by the many p-electrons of the pnictogen atoms. In addition, they have an Einstein-like phonon mode which may affect the electronic states through electron-phonon coupling [2-4]. In general, the investigation of crystal electric field schemes is one of the indispensable conditions of discussion of the electronic states in $R$ compounds. Usually, the specific heat of $\text{La}$ compounds is subtracted from that of other $R$ compounds to estimate the electronic part of the specific heat.
However, Matsuhira et al. pointed out that this approach is not adequate in SmOs$_4$Sb$_{12}$ because of the significant $R$ dependence of an Einstein-like low-lying mode [5]. Possible $R$ dependence of an Einstein-like low-lying mode is also reported by Raman scattering [6].

Lattice dynamics of the atoms inserted into the pnictogen cages in filled skutterudites were investigated by inelastic neutron and x-ray scattering techniques. At the beginning of these researches, measurements of phonon density of states (DOS) were performed using polycrystalline samples [7-12]. Broad excitations were observed in the antimonides whose cage size is larger than that in the phosphides. Partial DOS associated the atoms consisting of the cages seems to be independent of the inserted atoms like a localized mode [9, 12]. However, recently, phonon dispersion relations were elucidated using single-crystalline samples of filled skutterudites by both neutron and x-ray techniques [13, 14]. The observation of the anticrossings in the dispersion relation demonstrates that the motion of the inserted atoms is not a purely localized mode, but a dispersionless or nearly dispersionless optical mode.

The comparison of the dispersion relations between unfilled skutterudite IrSb$_3$ and filled skutterudite LaOs$_4$Sb$_{12}$ displays the presence of an additional low-lying mode due to the La atomic motion [4]. The dispersion relations obtained experimentally [15] also agree with the calculation using the ABINIT code [16, 17]. However, the phonon calculation including f-electrons has not been confirmed yet. Therefore, $R$-dependence of the high resolution inelastic x-ray scattering (IXS) spectra is useful to assign the $R$ atomic motion in a series of ROs$_4$Sb$_{12}$. We have carried out IXS of a series of ROs$_4$Sb$_{12}$ materials to elucidate their $R$ atomic motions.

2. Experimental Setups

IXS measurements were carried out at BL35XU in SPring-8 [18, 19]. We chose the Si(111 11 11) backscattering setup whose energy resolution is about 1.5 meV, depending slightly on the analyzer crystal. The IXS spectra of ROs$_4$Sb$_{12}$ ($R = \text{La, Pr, Nd and Sm}$) were measured at room temperature.

![Figure 1. IXS spectra of ROs$_4$Sb$_{12}$ ($R = \text{La, Pr, Nd and Sm}$) at room temperature. Arrowed excitations show the phonon modes associated with $R$ atoms’ motion in the icosahedral Sb cage.](image-url)
The measured samples were single crystals prepared by the Sb self-flux method with the typical size less than 1 mm$^3$. The rocking curve width of each sample is about 0.02 degrees.

3. Experimental Results and Discussion

Figure 1 shows IXS spectra filled skutterudites $RO_{\text{s}}Sb_{12}$ ($R = \text{La, Pr, Nd and Sm}$) around $(1100)$, a zone boundary (ZB) along the longitudinal $(100)$ direction, at room temperature. Phonon excitations at less than about 5 meV were observed in a series of $RO_{\text{s}}Sb_{12}$, whereas no low-energy excitation was observed in IrSb$_3$ [15]. This demonstrates that the mode at less than 5 meV correlates with $R$ atomic motion. The phonon energy significantly decreases with the increase of the atomic number of $R$ atoms.

Figure 2 shows the plot of the phonon energy associated with $R$ atomic motion as a function of the number of f-electrons in $R$ atoms. The open circles indicate the phonon energy at the zone boundary along the longitudinal $(100)$ direction and the closed ones indicate those at the zone boundary along the transverse $(011)$ direction. Note that direction-dependent phonon energy of the $R$ mode was smaller in filled skutterudite phosphides than in filled skutterudite antimonides [20]. The difference may be ascribed to the fact that the Sb cage of $RO_{\text{s}}Sb_{12}$ is large compared with the $R$ atoms. In addition, Fig. 2 demonstrates that the phonon energy correlates with the $R$ atoms’ ionic radii rather than their valence state. Since the Sm valence state at 300 K was determined as 2.83, not a pure trivalent state, by x-ray absorption spectroscopy [21], a negative deviation at Sm from the linear correlation in Fig. 2 would have suggested a correlation of the phonon energy and valence state. However, the energy of the Sm motion shows positive deviation from the linear correlation estimated from the phonon energies in other $RO_{\text{s}}Sb_{12}$ materials. This fact indicates that one of the crucial factors determining the $R$ mode energy is the free space of the $R$ atoms in the icosahedral Sb cages.

The presence of the low-lying dispersionless modes like an Einstein mode contribute to the specific heat at low temperature, which is especially associated with the estimation of the electronic contribution in the specific heat measurements as mentioned above. The dispersion relation obtained experimentally in LaOs$_4$Sb$_{12}$ demonstrates the presence of the La low-lying dispersionless mode [15]. Therefore, the present results mean that the low-lying $R$ modes exist in the $RO_{\text{s}}Sb_{12}$ series. When electron-phonon coupling is present between the $R$ modes and conduction electrons, possible HF behavior induced by an Einstein-like phonon is realized in these compounds [2-4]. The energy of the $R$ modes, corresponding to the Kondo temperature in conventional HF materials, is low enough to realize this model.

Figure 2 also shows direction dependence of the $R$ modes in the series of $RO_{\text{s}}Sb_{12}$. The $ab$ initio calculation suggests that the excitation energy in the longitudinal $(100)$ direction is the highest and that in the transverse $(110)$ direction is the lowest associated with the La atomic motions in LaOs$_4$Sb$_{12}$ [16]. The difference between the highest and lowest is broader than that in the skutterudite
phosphides because of the difference of the highest phonon mode energy between the phosphides and antimonides [16, 22]. In addition, the $R$ modes in filled skutterudites are low-lying optical ones, not Einstein modes as localized motions in the cage structure, while these modes are treated as an Einstein mode in the analyses of the specific heat coefficient, atomic displacement factor and so on. One of the evidence is Brillouin zone dependence, suggesting the hybridization between $R$ modes and acoustic ones, of the measured dynamical structure factor in a filled skutterudite [13, 20, 22]. The presence of the dispersionless or nearly dispersionless modes associated with the $R$ atoms’ motion make it possible to treat the $R$ modes in filled skutterudites as an Einstein mode in the aspects on phonon DOS treatments.

Finally, the correlation of the present result and the reported second-order Raman scattering is mentioned. Ogita et al. reported the observation of the low-energy broad excitation as the second-order Raman scattering signals in $ROs_{4}Sb_{12}$ [6]. The results of the second-order Raman scattering agrees with the energy of the $R$ modes observed by IXS. The present IXS result shows the significant energy difference of the $R$ modes between the longitudinal ($100$) and transverse ($110$) modes. The broad excitations observed in the second-order signals in Raman scattering probably correlate with the energy difference depending on the directions, because main contribution of the signals comes from that of the two phonon excitations associated with $R$ atomic motion at the zone boundaries. The observed energy is the sum of the phonon energies in two different directions. The width of the second-order signals correlates with the direction dependence of the phonon energies.

4. Summary

We have successfully demonstrated significant $R$ dependence of the low-lying $R$ modes in the $ROs_{4}Sb_{12}$ series by IXS. Not only the Raman scattering but also the Einstein temperature estimated by the temperature dependence of the atomic displacement factor obtained by the diffraction experiments agree with the energy observed by IXS [23-25]. The low-energy dispersionless modes in these compounds are expected to cause HF behavior due to a novel mechanism that is theoretically free from spin degrees of freedom [2-4]. Since the electronic specific heat coefficients in these compounds are more than $100\ mJ/\ mol\ K^{2}$ [26-29], the investigation of the direct evidences for significant electron phonon coupling associated with Einstein-like phonons, which is theoretically predicted as a scenario of novel HF behaviors in these compounds [3, 4], is crucial.

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