Low-lying optical modes in filled skutterudites using inelastic x-ray scattering techniques

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Abstract. We have carried out high resolution inelastic x-ray scattering and 149Sm nuclear resonant inelastic scattering of a skutterudite SmRu4P12. The inelastic x-ray scattering spectra and dispersion show q-dependence and zone-dependence except for the modes lying at 9 meV. The dispersionless modes, which are zone-independent, are observed at 9 meV. The energy of this mode agrees with that obtained by 149Sm nuclear resonant inelastic scattering. The dispersion suggests the presence of strong hybridization between low-lying optical mode at 9 meV and acoustic ones.

1. Introduction

Skutterudites attract the interests both as materials in strongly correlated electron systems and as candidates of thermoelectric materials experimentally and theoretically [1]. The expectation of the localized modes is one of common features in these compounds, because these are a member of clathrates. The discussion of the presence of a localized mode has been discussed by many experimental results [2-7]. Recently, the direct observation of the low-lying dispersionless modes has been reported by inelastic neutron scattering, nuclear resonant inelastic scattering (NRIS) and inelastic x-ray scattering (IXS) [3, 6-8]. Among the phonon measurements such as inelastic x-ray and neutron scattering, nuclear resonant inelastic scattering is a powerful tool as an element-specific measurement.

In spite of many experimental results, the coupling or decoupling between atomic motion in the cage (guest mode) and atomic motion of the cage atoms (host mode) has not clarified yet as common feature in skutterudites. An anticrossing dispersion in skutterudite was reported by Lee et al. [7] This result suggests the hybridization between the dispersionless and acoustic modes. However, it has not been clarified whether the dispersionless modes are harmonic or anharmonic experimentally. The
recent Raman scattering of type-I clathrate proposed that the off-centered low-lying optical mode is essential to realize good thermoelectricity [9]. Sm-filled skutterudites are one of the interesting materials in strongly correlated electron system. SmRu₄P₁₂ is one of most interesting materials among them. This compound shows a metal-insulator transition at 16 K [10]. At the same temperature, an octupolar ordering is proposed by an ultrasound measurement [11]. On the aspects of the similarity to a metal-insulator transition material PrRu₄P₁₂, the lattice instability due to the Fermi surface nesting has also been discussed in SmRu₄P₁₂ [12]. In the present work, we have investigated the q-dependence of the phonon dispersion along the longitudinal (100) direction in SmRu₄P₁₂ to discuss the q-dependence of the low-lying modes observed by the ¹⁴⁹Sm nuclear resonant inelastic scattering and the hybridization with the low-lying Sm modes and acoustic modes.

2. Experimental procedure
The experiments were carried out at BL35XU for IXS and at BL09XU for ¹⁴⁹Sm NRIS in SPring-8. The Si(11 11 11) backscattering geometry was chosen in the IXS experiments. The energy resolution is about 1.6 meV, slightly depending on the analyzer crystals. The sample measured is a single crystal one with about 1 mm³. The optics related to the NRIS is shown in Ref. 13. The energy resolution of the setup is 1.5 meV in ¹⁴⁹Sm nuclear resonance of 22.494 keV. The sample measured is a powdered one.

3. Experimental results and discussion
We have measured the IXS spectra along the longitudinal (1 0 0) direction at 25 K in SmRu₄P₁₂. We have investigated the zone dependence of the IXS spectra. Figs. 1 and 2 show typical IXS spectra along the longitudinal (1 0 0) direction in SmRu₄P₁₂. The former are the spectra at the middle of zone, and the latter are those at the zone boundaries. The excitations at 9 meV are either independent of q value or zone. The mode at 9 meV is mostly correlated with Sm atoms, judging from the ¹⁴⁹Sm nuclear resonant inelastic scattering as shown in Fig. 3 [14, 15]. Since the Sm atoms stay in the cage of twelve P atoms, this was originally proposed as an Einstein mode in a metallic material [2]. Our recent work has clarified that this mode is an anharmonic low-lying optical mode [8]. A strong contrast is observed in the IXS spectra between the middle of the zone and the zone boundary. In the middle of the zone, a strong contrast was observed in the spectra around 15 meV. Since the intensity of the Bragg peak is stronger at (10 0 0) than that in (6 0 0), this difference is caused by the one of the

![Figure 1.](image1.png)  ![Figure 2.](image2.png)

**Figure 1.** IXS spectra of SmRu₄P₁₂ in the middle of zone at 25 K. The solid lines are a fitting curve.

**Figure 2.** IXS spectra of SmRu₄P₁₂ in zone boundaries at 25 K. The solid lines are a fitting curve.
acoustic contribution. However, the spectra at the zone boundary at (0.06 7.00 0.03) is similar to that at (0.09 11.00 0.04). There are basically two possibilities in the contrasts due to q-dependence: One is the q-dependence of the intensity in acoustic contribution; the other is strongly hybridization with the other modes. In fact, the phonon dispersion based on the ab initio calculation in LaRu4P12 using ABNIT shows the presence of many optical modes between 10 and 30 meV as shown in Fig. 4 [16]. The calculated result also demonstrates that the pure longitudinal acoustic-like modes are absent close to the zone boundaries because of the hybridization among the acoustic and some optical modes which includes the dispersionless mode due to the La motion [8].

Figure 4 shows the calculated phonon dispersion in the (100) direction of LaRu4P12, isostructural with SmRu4P12. The bold line shows the La mode in the longitudinal contribution. This indicates that the rare-earth atomic motions are contributed to the acoustic mode in low energy region and low-lying dispersionless mode. This also agrees with the zone-dependent IXS spectra as shown in Figs. 1 and 2. Judging from the intensities of the Bragg peaks at (6 0 0) and (10 0 0), the acoustic contribution at (0.03 10.42 0.01) is stronger than that at (0.02 6.42 0.01). The longitudinal acoustic mode hybridized with the dispersionless mode approaches 30 meV at the zone boundary as shown in Fig. 4. Besides weakening the acoustic contribution towards the zone boundary, however, an optical mode is lying at the same energy at the zone boundary. This is one of the reasons why the small contrast of IXS spectra was obtained at the zone boundary.

We have also investigated the phonon dispersion of SmRu4P12 at 25 K along the longitudinal (100) direction. Fig. 5 is the phonon dispersion in the zone of (0 6+k 0), and Fig. 6 is in that of (0 10+k 0).

**Figure 3.** $^{149}$Sm nuclear resonant inelastic scattering spectrum of SmRu4P12 at 25 K.

**Figure 4.** Calculated phonon dispersion along the (100) direction in LaRu4P12. The bold solid line shows the longitudinal mode correlated with La atomic motion. The bold dotted line shows the modes with nearly pure longitudinal contribution.

**Figure 5.** Phonon dispersion in the zone of (0 6+k 0) of SmRu4P12 at 25 K. Error bars shows line width of every excitation. The dotted lines are a guide for eyes.

**Figure 6.** Phonon dispersion in the zone of (0 10+k 0) of SmRu4P12 at 25 K. Error bars shows line width of every excitation. The dotted lines are a guide for eyes.
The obtained dispersion agrees with the calculation in \( \text{LaRu}_4\text{P}_{12} \) as shown in Fig. 4. The differences in the dispersion are caused by the contribution of the dynamical structure factor mostly to the acoustic modes. The former is relatively difficult to see the acoustic modes and the latter is relatively easy to see the acoustic modes. Nearly dispersionless modes at 9 meV are observed in both zones. The anticrossings in both zones also suggest that the dispersionless modes are hybridized with the acoustic modes.

4. Summary
We have investigated the zone dependence of the inelastic x-ray scattering spectra and the phonon dispersion in \( \text{SmRu}_4\text{P}_{12} \) at 25 K. We observed significant zone dependence except for the dispersionless mode at 9 meV. The energy and intensity are independent of zone at the equivalent q-position in inelastic x-ray scattering spectra. Since the dispersionless modes are anharmonic [8], the strong hybridization between dispersionless and acoustic modes suggests the possible reduction of the thermal conductivity in the phonon contribution.

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