Softening phonon and relaxation mode in the filled skutterudite PrT₄Sb₁₂ (T = Ru and Os)

Kazuaki Iwasa¹, Yoshiaki Mori¹, Lijie Hao¹, Youichi Murakami¹, Masahumi Kohgi², Hitoshi Sugawara³ and Hideyuki Sato²

¹ Department of Physics, Tohoku University, 6-3 Aramaki-aza-aoba, Aoba-ku, 980-8578 Sendai, Japan
² Department of Physics, Tokyo Metropolitan University, 1-1 Minami-osawa, 192-0397 Hachioji, Japan
³ Department of Mathematics and Natural Sciences, The University of Tokushima, 1-1 Nanjo-Mishimacho, 770-8502 Tokushima, Japan

E-mail: iwasa@i2iyo.phys.tohoku.ac.jp

Abstract. Dynamics of rare-earth ions in filled skutterudite compounds PrT₄Sb₁₂ (T = Ru and Os) has been investigated by a neutron inelastic scattering technique. We found an optical mode located at extremely low energy around 4 meV exhibiting apparent softening behavior by 10 - 30% from 300 to 10 K. This softening mode is attributed to the motion of the filled Pr ions bound in anharmonic potential within the Sb cage. In addition, quasielastic responses near the Brillouin zone center indicate relaxation modes. These features can be explained in terms of a mode coupling scenario involving the motion of the filled Pr ions with huge amplitude.

1. Introduction
Motion of atoms filled in the cage structure has been extensively studied in terms of the effects on electronic properties and on crystal-lattice thermal properties. The motion of filled atoms in the cage with large amplitudes is so-called “rattling” [1]. The large fluctuation of atoms is expected to give rise to anomalous electronic properties. Kondo effect due to electron scattering accompanied by atomic motion in multi-well potential is theoretically argued [2]. The rattling motions are also focused as a scattering center against propagating phonons, resulting in reduction of thermal conductivity that is favorable for high performance of thermoelectric devices [1]. Such rattling motions have been taken into account in various compounds; superconducting clathrate Ba₂₂₄Ge₁₀₀ [3] and Ba₂₂₄Si₁₀₀ [4], superconducting β-pyrochlore AOs₂₉O₆ (A = alkaline metal) [5], and off-center atomic displacement in X₄Ge₁₆Ge₃₀ (X = Eu, Sr, Ba) [6]. Therefore, investigation of the rattling motion as functions of energy and momentum is a crucial demand in solid state physics.

Rare-earth filled skutterudites RT₄X₁₂ (R = rare earth, T = transition metal, X = pnictogen) are also categorized in the materials exhibiting the rattling motion with the cage structure [1]. These crystallize in a body-centered cubic structure with the space group Th. Twelve pnictogens form an icosahedral cage structure and a rare-earth ion is located inside of this cage. In particular case of PrOs₄Sb₁₂, the nearest neighbor distance between Pr and Sb is 3.480 Å [7] that is larger than 3.188 Å [9] of PrSb forming a rock-salt structure. Thus, the filled ions take a large thermal motion amplitude, as confirmed by evaluation of Debye-Waller factors [7]. In addition, dispersive...
elastic constants detected by the ultrasonic measurement for PrOs₄Sb₁₂ were interpreted as charge fluctuation with Γ₂₃ symmetry, which may closely related with the Pr-ion motion [8].

In the present study, we measured phonon spectra of the filled skutterudite compounds PrRu₄Sb₁₂ and PrOs₄Sb₁₂ by using neutron inelastic scattering technique, to reveal characteristic phonon properties of filled skutterudite structure. A part of the study was published so far [10].

2. Experimental procedure

Single crystalline samples of PrRu₄Sb₁₂ and PrOs₄Sb₁₂ were synthesized by Sb self-flux method, as reported in the reference [11]. Neutron inelastic scattering measurements were performed at the triple-axis spectrometers TOPAN installed at the thermal neutron beam hole 6G, HER at the cold one C1-1 and LTAS at the cold one C2-1 of JRR-3 reactor of Japan Atomic Energy Agency, Tokai, Japan. In the present paper, we will show the data by thermal neutron scattering measurement with horizontal collimators open-60°-60°-60° and with fixed scattered neutron energy of 13.5 meV selected by a pyrolytic graphite analyzer through a pyrolytic graphite filter eliminating higher-order contamination. Sample temperatures were controlled between 10 and 300 K by a helium closed-cycle refrigerator.

3. Experimental results

Figures 1 and 2 show energy spectra at 300 K for the scattering vectors \( Q = (6 - \eta - \eta) \) \( k = (0 \eta \eta) \) of PrRu₄Sb₁₂. Figure 1. Open symbols represent experimentally observed phonon scattering laws as functions of excitation energy observed at \( Q = (6 - \eta - \eta) \) \( k = (0 \eta \eta) \) of PrRu₄Sb₁₂. Broken lines are calculated one based on eq. (1).

Figure 2. Solid symbols represent experimentally observed phonon scattering laws as functions of excitation energy observed at \( Q = (6 - \eta - \eta) \) \( k = (0 \eta \eta) \) of PrOs₄Sb₁₂.
phonon branch whose energy is above 6 meV for $\eta > 0.4$. In addition to the sharp acoustic mode enhanced with approaching the Brillouin zone center, we detected intensities at the higher-energy side shoulder of the acoustic mode peaks. The observed behavior of the two modes is interpreted as an anticrossing between the anomalously low-energy flat mode and the acoustic one. Acoustic modes of PrOs$_4$Sb$_{12}$ are unclear near the zone boundary, but the feature below 4 meV is very similar to that below 6 meV of PrRu$_4$Sb$_{12}$ [12]. The anticrossing behavior was observed also in CeRu$_4$Sb$_{12}$ [13], and the dispersionless mode located at 6 meV is assigned to be predominated by the large Ce-ion motion based on the analysis taking Born-von Kármán force constant model. Therefore, the 4.2 and 3.4 meV peaks of Pr-based systems are attributed to the motion of Pr ions, corresponding to the rattling motion. The mode assignment is also supported from the fact that temperature dependence of the integrated phonon intensity follows Debye-Waller factor of Pr ions determined from x-ray diffraction multiplied by $(n(E) + 1)/E$, where $n(E)$ means the Bose-Einstein distribution function, although the data is not shown here. It is notable that the responses at $Q = (6 0 0)$ with anomalously long tails up to 5 meV were detected in the both compounds. It was also detected in cold neutron scattering experiments with higher resolution.

Figure 3 depicts temperature dependence of the spectra at $Q = (6 -0.4 -0.4)$ of PrRu$_4$Sb$_{12}$. The Pr-ion mode shows distinct softening behavior by over 10% from 300 to 10 K. The similar softening was observed in the same mode of PrOs$_4$Sb$_{12}$ as reported previously [10]. Therefore, we naturally expect anharmonic potential for the Pr ion motion in the Sb cage of the filled skutterudite structure.

4. Analysis and discussion
The observed long tail response near the zone center can be interpreted as a relaxation mode. This mode as well as the softening one are indicative of renormalization effect on phonons. In order to understand phenomenologically, we adopted the mode coupling model that explains critical behaviors of structural phase transitions [14]. Imaginary part of phonon susceptibility $\chi''(k, E)$ by taking into account coupling between a finite-frequency phonon mode and a
relaxation mode is represented by

\[ \chi''(k, E) = \frac{\tau \delta^2}{E^2 - (E^2(k) - \delta^2)^2 + E^2 \tau^2 (E^2(k) - E^2)^2}. \]  

(1)

Taking arbitrarily the bare phonon frequency \( E_0(k) \) [meV] = 3.715 − 0.925cos(2\( \eta \)) − 0.3cos(4\( \eta \)) for the reduced wavevector \( k = (0, \eta, \eta) \), calculated neutron scattering functions \( S(k, E) = \chi''(k, E)(n(E) + 1) \) with \( \tau = 0.25 \) meV\(^{-1} \) = (1.034 \times 10^{-12}) \) sec as a relaxation time constant and \( \delta = 2.3 \) meV as a renormalization frequency due to the coupling are shown by broken lines in Figure 1. The result succeeds in reproducing overall spectral feature of the relaxation mode near the zone center as well as the low-energy optical mode. The softening behavior against temperature may be interpreted by the temperature variation of \( \eta \) and \( \delta \). On the other hand, \( \chi''(k, E) \) of eq. (1) is not satisfactory to explain the peak structure at \( \eta = 0 \) of PrOs\(_4\)Sb\(_12\). Moreover, the magnitude of phonon softening of the mode at \( Q = (6 - 0.4 - 0.4) \) of PrOs\(_4\)Sb\(_12\) is 30% larger than that of PrRu\(_4\)Sb\(_12\). These facts indicate different renormalization mechanism between the two compounds.

At present it is not clear that what kind of degree of freedom gives the relaxation mode in Pr-filled skutterudites. These materials are metals and undergo superconducting phases below 2 K [15, 16]. Thus, charge density fluctuation of conduction electrons may be an origin of the relaxation mode. Another interesting point is that the relaxation mode appears near the zone center where the acoustic phonon shows strong response. Thus, the coupling of the acoustic mode with the low-energy optical one may give rise to the observed phenomenon. We have to proceed further measurements to study fine structures of phonon spectra.

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[12] In our previous report on PrOs\(_4\)Sb\(_12\) [10], we assigned the 3.4 meV peak at \( Q = (6 - 0.4 - 0.4) \) to an acoustic mode. However, it has recently found that this peak corresponds to a low-energy optical mode. The acoustic mode is expected to have small scattering cross section at this scattering vector.