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Phonon dispersion curves in $CeOs_4Sb_{12}$

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Abstract
Inelastic neutron scattering measurements at different temperatures were performed on single crystals of $CeOs_4Sb_{12}$. The room temperature phonon dispersion curves along principal axes [0 1 1] and [1 0 0] were obtained.

1. Introduction

Recently, the rare-earth filled skutterudite compound RT_4X_{12} (R = rare earth, T = Fe, Ru, or Os, and X = P, As or Sb), which forms in body-centred cubic structure with a space group of $Im\bar{3}$, has attracted extensive efforts not only due to a rich variety of 4f electron ground states, but also due to the high conversion efficiency for promising thermoelectric materials [1–4]. The two unusual properties, both the various electronic states, including heavy fermion semiconductor [5, 6], non-Fermi liquid [7], magnetic ordering [8], and superconducting states [9], and the distinguished lattice vibrational models, are strongly associated with the unique crystallographic structure, in which the filled rare-earth atom occupies the interstitial site of the huge cage formed by the T_4X_{12} framework. In RT_4X_{12}, the R atom can vibrate as a 'rattler' inside the oversized cage incoherently due to the weak hybridization between the R atom and the lattice. Thus the lattice thermal conductivity is dramatically reduced while the electric conductivity keeps almost the same. Such a rattling mode has a low frequency and was believed to be identified in a few series of the La filled antimonides, first in $LaFe_4Sb_{12}$ by Keppens *et al* [10], then in variant TI filled $TI_x(Fe, Co)_4(Sb, Sn)_{12}$ by Hermann [11], and currently in $La(Ce)Fe_4Sb_{12}$ [12, 13]. In addition to experiment, the vibrational behaviour of skutterudites was also studied theoretically by Feldman *et al* [12, 14–16]. The theoretical phonon density of states (DOS), as well as a sharp peak superposed on the low-lying part of the Debye response, which was believed to be the characteristic scattering from the local rattling mode, were predicted using a local density approximation (LDA) model [12]. These predictions were recently examined experimentally in $La(Ce)Fe_4Sb_{12}$ [12, 13] using inelastic neutron scattering and in $Eu^{57}Fe_4Sb_{12}$ using nuclear inelastic scattering [17]. However, in contrast to extensive studies of DOS and the incoherent local 'rattling' mode on powdered polycrystalline RT_4X_{12}, there are few experimental data about the coherent lattice excitation

Figure 1. Image of a typical single crystal grown using the Sb-flux method.
(This figure is in colour only in the electronic version)

on single crystals. In the present work, we performed inelastic neutron scattering experiments to measure the phonon dispersion relations and the data were compared with the LDA-based calculations reported by Feldman *et al*.

2. Experimental details

High quality $CeOs_4Sb_{12}$ single crystals were grown by the Sb-flux method starting from a composition of R:Os:Sb = 1:4:20 using raw elements 3N5-Ce (99.95%), 3N-Os and 6N-Sb. The detailed procedures of making crystals were described in [18]. As a typical example, figure 1 shows one image of a crystal grown by the Sb-flux method; the biggest one can reach a mass up to 13.06 g. It is clearly seen that there are blocks stacking in the surface of the crystal. Powder x-ray diffraction reveals the absence of impurity phases in crystal samples. X-ray back-reflection Laue and neutron diffraction methods indicate that the deviation angle between blocks is within 2°. Neutron diffraction measurements were performed at the triple-axis spectrometer TAS-2 installed in the reactor JRR-3M of JAERI (Japan Atomic Energy Agency) at Tokai, Japan. Crystallographic axes of single crystal samples were oriented and cut using the x-ray back-reflection Laue method. The scattering plane contains [1 0 0] and [0 1 1] crystallographic axes.

3. Results and discussion

The unusual thermoelectric properties of RT_4X_{12} compounds are strongly dependent on the lattice dynamics in the low energy region. Inelastic neutron scattering (INS) is a direct tool to study the low-lying phonon excitation quantitatively owing to the similar wavelength and energy between thermal neutrons and phonons. In this work, we performed INS measurements to study the dispersion relations. Most of the data were collected in the constant-Q mode. As an example, figure 2 shows typical INS spectra along the [0 1 1] principal direction for low frequency acoustical branches at $T = 70$ and 260 K. The peak intensity is enhanced with increasing temperature and reflects the feature of phonon scattering. The phonon line

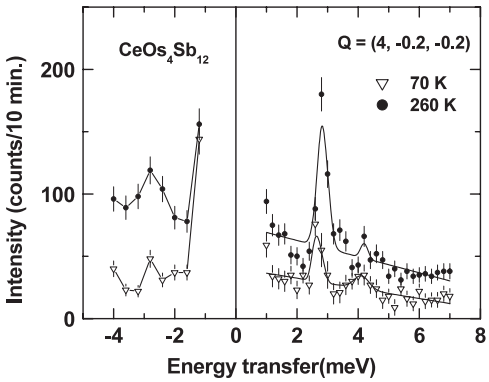

Figure 2. Typical constant-Q scans of TA phonons along [0 1 1] symmetry at $T = 70$ and 260 K for $CeOs_4Sb_{12}$. Solid lines are the fitting curves using a double Gaussian and a sloping background.

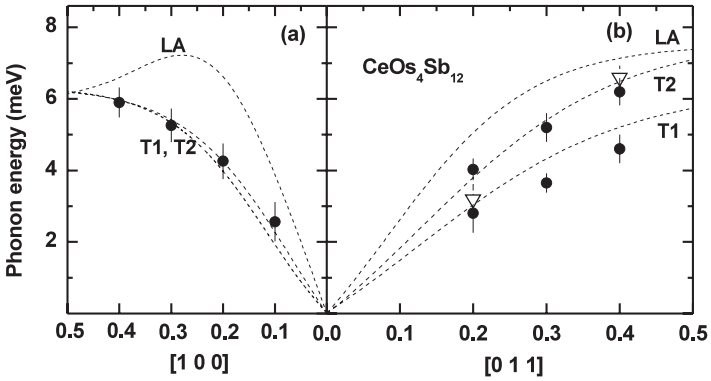

Figure 3. Measured TA phonon dispersions: (a) along [0 1 1] and (b) [1 0 0] symmetry (solid circle) at room temperature. The inverted open triangle represents the measured LA phonon. The dotted lines plot the predicted phonon dispersions calculated in [14] by Feldman *et al* using the LDA-based short-range model for $LaFe_4Sb_{12}$.

shapes were fitted with the solid curves using a double Gaussian and a linear background. The dispersion of the transverse phonon (TA) is plotted in figure 3, where the open inverse triangle symbol represents the measured data of the longitudinal mode (LA). These results may be compared with the theoretical dispersion predicted by local density approximation calculations for $LaFe_4Sb_{12}$ worked out by Feldman *et al* [12] in the case where there is no direct theoretical evaluation for $CeOs_4Sb_{12}$. In figure 3, the dashed lines present the LDA-based results of three acoustical branches. We can see that the experimental data roughly meet the theoretical data for the TA branches, while there is a considerable discrepancy for the LA component. Similarly, we also measured the phonon dispersion along [1 0 0] symmetry at room temperature (see figure 4). It is noted that there is only one peak observed in the spectrum along [1 0 0]. This fact is consistent with the calculations of the LDA-based short-range force constant model, which predicts that the two TA branches are degenerated along [1 0 0] by virtue of the cubic symmetry [12]. The dispersion of [1 0 0] was also plotted in figure 3, together with the LDA results shown as a dashed line. It can be seen that the experimental TA component along [1 0 0] also matches the theoretical results. Generally, the coherent acoustical phonon frequency

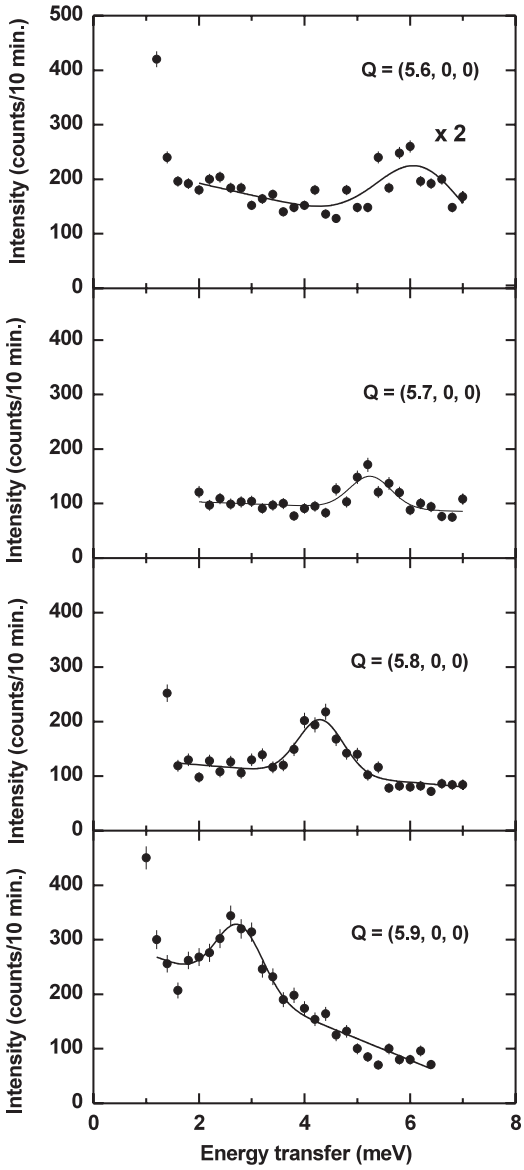

Figure 4. Several constant-Q scans of TA phonons along [1 0 0] symmetry. Note that there is only one peak observed in the spectrum.

is in inverse proportion to the square root of the total mass of the vibrating atoms. Hence it is a surprise that the phonon energy data of $CeOs_4Sb_{12}$ roughly fit the theoretical value of $LaFe_4Sb_{12}$ if one considers that the Os atom is much heavier than that of Fe (more than three times) and Os takes about 32% while Fe only 12.3% in the total weight of $CeOs_4Sb_{12}$ and $LaFe_4Sb_{12}$, respectively. Recently, a remarkable softening effect was found in the counterpart $PrOs_4Sb_{12}$, reflected by the decrease of acoustic phonon energy with decreasing temperature after neutron scattering measurements on a single crystal sample [19]. The softening can be mainly attributed to the vibration of the Pr atom, which means that the R atom, seated inside the

huge atomic cage in the skutterudite structure, dominates the feature of the acoustic phonon. Hence, it is reasonable that the phonon energy is little different between the experimental $CeOs_4Sb_{12}$ and theoretical $LaFe_4Sb_{12}$ due to the similar atomic mass between the rare earth Ce and Pr even though the mass of Os is much greater than that of Fe.

In conclusion, big $CeOs_4Sb_{12}$ crystals were obtained by using the Sb-flux method. The phonon dispersion curves of $CeOs_4Sb_{12}$ along the high-symmetry directions of [0 1 1] and [1 0 0] were measured by inelastic neutron scattering. The rattling mode of the Ce atom is not detected in this measurement.

Acknowledgments

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