EXAFS Study of Filled Skutterudites $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$

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Abstract. We present the results of EXAFS measurements of two filled skutterudites compounds, $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$. We found that the Pr(La)-Os and Pr(La)-Sb atomic pairs have larger Debye-Waller factors than that of the Os-Sb atomic pair. We analyzed the temperature dependence of the third order cumulant C_3. Consistent with the theoretical study of an asymmetric double-well potential model, C_3 shows a maximum point in the function of temperature. This study shows the maximum point of C_3 at the temperature corresponding to the energy of the potential barrier of the Pr ion in the cage of $PrOs_4Sb_{12}$.

Keywords: EXAFS, Debye-Waller factor, double-well potential, skutterudites, $PrOs_4Sb_{12}$, $LaOs_4Sb_{12}$, rattling
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INTRODUCTION

The filled skutterudite $PrOs_4Sb_{12}$ is well known to be the first Pr compound that shows heavy fermion superconductivity. The superconductivity of this material does not belong to the *s*-wave type but is expected to be a new anisotropic type of superconductivity. This interesting phenomenon is known to come from rattling motion of Pr ions in the Os_4Sb_{12} cage, suggested by ultrasonic measurements [1]. They claimed that the Pr ion is moving six off-center position. Cao *et al*. have presented XAFS results for this compound [2]. They reported that the Debye-Waller factor for the Pr-Sb atomic pair is larger than that for the Os-Sb atomic pair in the cage. They discussed the relation between rattling motion and low Einstein temperature obtained from the Einstein model fitting of Debye-Waller factors. In the rattling motion, the Pr ion can be considered to be located in the double-well potential.

Recently, the temperature dependence of XAFS cumulants (or Debye-Waller factor) was successfully calculated for the symmetric and asymmetric double-well potential based on the path-integral approach [3].

In this paper, we carried out EXAFS measurements for $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$ to compare the motion of the center atom in the cage and analyze the experimental data for both compounds using the theoretical result based on the model of a double-well potential.

EXPERIMENTAL AND DATA ANALYSIS

Single crystals of the filled skutterudite $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$ were grown by the Sb-flux method [4]. Pr L_{III}- (5.96 keV), La L_{III}- (5.48 keV) and Os L_{III}- (10.9 keV) edge X-ray absorption spectra for the powder sample prepared from the single crystals were obtained at BL9C and BL12C (Si(111) monochrometer) at the Photon Factory (KEK). The measurements were carried out in transmission mode with ionization chamber detectors at the temperature range from 25K to 300K.

Figure 1 shows (a) $\chi(k)$ and (b) their Fourier transform (|FT|) of Pr L_{III}- edge EXAFS for $PrOs_4Sb_{12}$. The *k*-range for the |FT| is $2-10$ Å^{-1} because of the L_{III}-edge analysis, which is not enough to separate |FT| peaks for Pr-Sb multi-shells. The amplitude of $\chi(k)$ and the height of the |FT| peaks show thermally damping as the temperature increase. The EXAFS analyses were performed using the XANADU code [5]. In order to obtain the structural parameters, non-linear-least-square-fitting was applied to the experimental data by fitting the following equation,

$$\chi(k) = \sum_j \frac{S_0^2 N_j}{kr_j^2} f_j(k,r_j)\exp(-2C_2k^2)\exp(-2r_j/\lambda(k)) \times \sin\left[2kr_j+\phi_j(k)-\tfrac{4}{3}C_3k^3\right] \quad (1)$$

where r_j, N_j, C_2 and C_3 are interatomic distance, coordination number, second order cumulant (or Debye-Waller factor) and third order cumulant, respectively, for each atomic pair. Phase shift $\phi_j(k)$, backscattering amplitude $f_j(k,r_j)$ and electron mean free path $\lambda(k)$ were obtained from FEFF8.1 calculations [6]. The energy shift from the

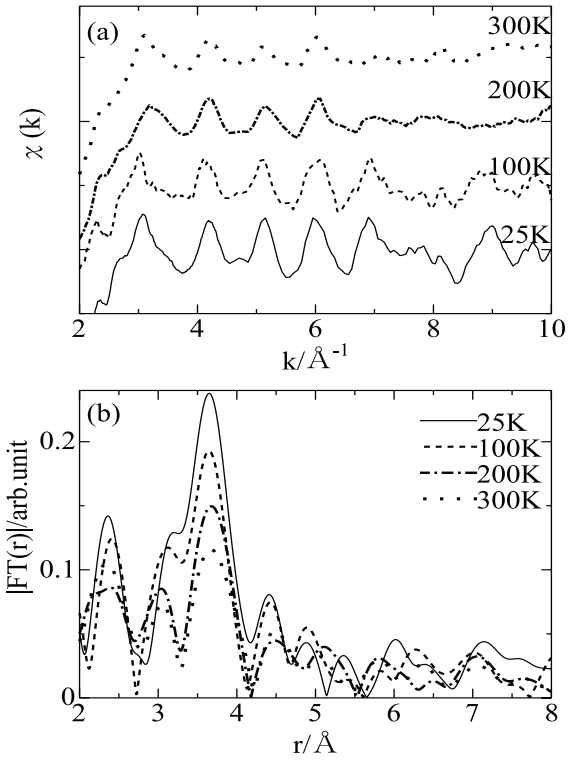

FIGURE 1. (a) $\chi(k)$ spectra and (b) their Fourier transform (|FT|) of Pr L_{III}- edge EXAFS for $PrOs_4Sb_{12}$ at various temperatures.

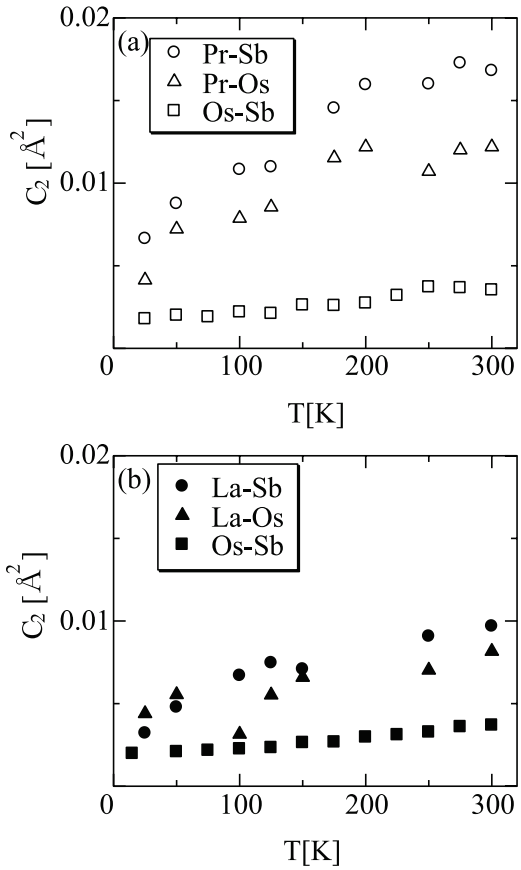

FIGURE 2. Temperature dependence of C_2 for $PrOs_4Sb_{12}$ (a) and $LaOs_4Sb_{12}$ (b).

edge jump are determined to 11.32 eV for Pr L_{III}- and 16.24 eV for Os L_{III}- edge in $PrOs_4Sb_{12}$, and 12.04 eV for La L_{III}- and 18.51 eV for Os L_{III}- edge in $LaOs_4Sb_{12}$. From the theoretical study [3], the cumulant expansion is valid in order to describe the double-well potential for relatively low temperature and low k-range.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of C_2 for (a) $PrOs_4Sb_{12}$ and (b) $LaOs_4Sb_{12}$. Cao *et al*. have presented similar EXAFS results for $PrOs_4Sb_{12}$ [2]. They reported that the Debye-Waller factors for the Pr-Sb atomic pair is larger than that for Os-Sb in the cage. We confirmed that the atomic pair contained center-atom (Pr or La) had larger C_2 values than the cage (Os-Sb) atomic pair even for $LaOs_4Sb_{12}$. Moreover, Fig. 2 shows that Pr-Os and Pr-Sb atomic pairs have larger C_2 values than La-Os and La-Sb atomic pairs. This is consistent with the existence of the rattling mechanism in $PrOs_4Sb_{12}$ pointed by the ultrasonic measurement [1]. The Pr-Sb atomic pair has larger static distortion than the other atomic pairs because C_2 for Pr-Sb is larger at T$\rightarrow$ 0, which can be an another proof of off-center mode. It should be noted that the temperature dependence of C_2 cannot be reproduced by a simple Einstein model, but it seems to coincide with the function in which the central atom (Pr) is driven into a double-well potential [3].

Figure 3 shows the temperature dependence of C_3 for $PrOs_4Sb_{12}$. A theoretical study indicates that C_3 reflects the degree of asymmetry [3]. The value of C_3 is almost zero for the cage atomic pair (Os-Sb), indicating an almost symmetric potential. The fact that the atomic pairs of Pr-Sb and Pr-Os have non-zero value of C_3 indicates that they have asymmetric potentials. The presence of a maximum in C_3 around 170 K for Pr-Sb and Pr-Os is a characteristic feature of asymmetric double-well potentials [3]. From the theoretical study [3], diatomic systems which have asymmetric double-well interatomic potentials show such a behavior and the maximum temperature depends on the height of its potential barrier. The temperature at the maximum of C_3 ($\sim$ 170 K) in the present EXAFS study is quite close to the activation energy obtained from the ultrasonic study ($\sim$ 169 K) [1].

Figure 4 shows the comparison between experimental and theoretical results for C_2 and C_3 of the Pr-Sb atomic pair. The calculation was carried out using quantum path-

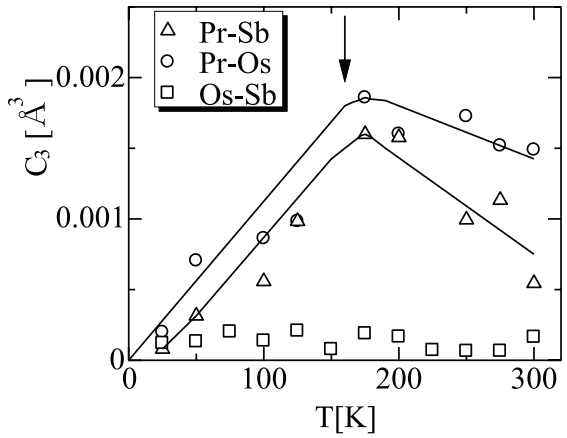

FIGURE 3. Temperature dependence of C_3 for $PrOs_4Sb_{12}$. The solid line shows guide for eyes.

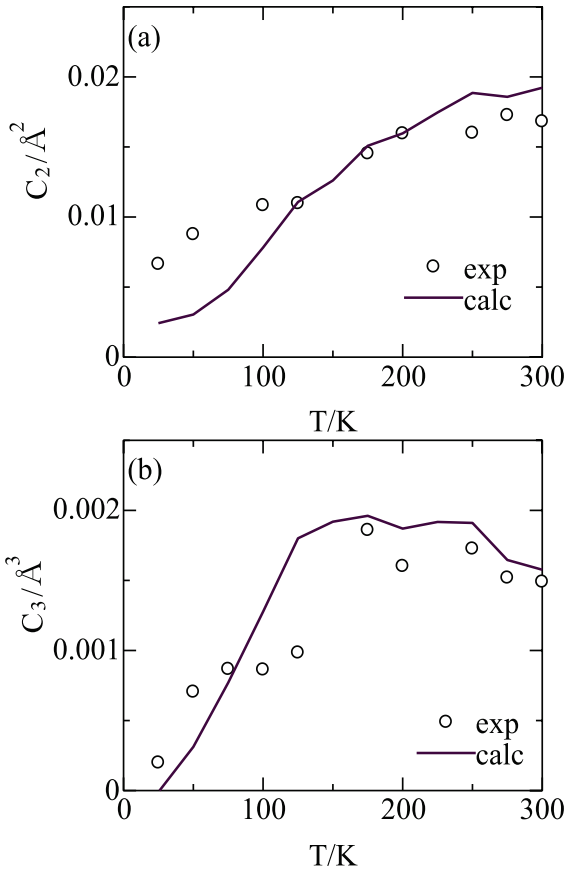

FIGURE 4. Comparison between experimental and theoretical calculation of (a) C_2 and (b) C_3 for Pr-Sb atomic pair in $PrOs_4Sb_{12}$ as a function of temperature.

integral effective potential method [3]. The behavior of C_2 is well reproduced above $T = 125$ K. The charasteristic feature of C_3 obtained from the same potential parameters also agree with the experimental results. From these comparisons, we could estimate the width between the two bottoms of the double-well potential as ~ 0.32 Å. If the off-center position of Pr atom is 0.4 Å obtained by ultrasonic measurement [1], the distance between the potential minima should be larger than 0.32 Å. This result suggests that the Pr off-center position is smaller than 0.4 Å which is consistent with results of a neutron diffraction experiment [7]. More detailed determination of the double-well potential parameters is interesting future work.

CONCLUSION

We measured Pr L_{III}-, La L_{III}- and Os L_{III}- edge EXAFS and obtained parameters of r, N, C_2 and C_3. The Debye-Waller factor (C_2) is largest for the Pr-Sb atomic pair in all temperature regions and its behavior cannot be reproduced by the Einstein model. The large C_2 value in the low temperature region for the Pr-Sb atomic pair is consistent with that the Pr ion is located in off-center positions. The third order cumulant (C_3) shows characteristic behavior for asymmetric double-well potentials in the case of the Pr-Sb, Pr-Os atomic pairs. From the comparison between experiment and theoretical calculation, we have obtained the parameters of the double-well interatomic potential of the Pr-Sb atomic pair.

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