Crossing of the crystalline-electric-field and rattling-phonon excitation energies in the filled skutterudite superconductor Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$

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Abstract. By specific heat measurements on Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, we have studied the $x$-dependences of the 4f-electron crystalline-electric-field first excitation energy and the rattling energy of the Pr ion. The former increases monotonically from $\sim 10$ K to $\sim 85$ K, while the latter of $\sim 45$ K does not change much resulting in a crossing of the two energy levels at $x \approx 0.6$. The reported minimum in the superconducting transition temperature $T_c$ at $x \approx 0.6$ could be associated with the level crossing.

1. Introduction

Filled skutterudite compound PrOs$_4$Sb$_{12}$ exhibits unconventional properties in the superconducting state [1] (for a review, see Ref. [2]), for example, heavy fermion (HF) superconductivity with relatively high superconducting transition temperature $T_c = 1.85$ K, possible existence of multiple superconducting phases [3], time reversal symmetry breaking [4] and multiband nature of the superconductivity [5].

In the realization of the unconventional superconducting state in PrOs$_4$Sb$_{12}$, it is considered that the low energy 4f-electron crystalline-electric-field (CEF) excitations of Pr ions play an important role. In the filled skutterudite crystal structure, the $J = 4$ multiplet of Pr$^{3+}$ ions splits into four sublevels, i.e., a singlet $\Gamma_1$, a non-Kramers nonmagnetic $\Gamma_{23}$, and two triplets $\Gamma^{(1)}_4$ and $\Gamma^{(2)}_4$ by the CEF effect with the $T_h$ site symmetry [6]. At low temperatures, the CEF excitations dominate from the $\Gamma_1$ ground state to the $\Gamma^{(2)}_4$ first excited state with the excitation energy $\Delta_1 \sim 8$ K [7,8]. As originally discussed by P. Fulde et al. [9], inelastic quadrupolar Coulomb scattering of conduction electrons can enhance $T_c$ as well as the quasiparticle mass. The variations of $T_c$ in alloyed (Pr,La)Os$_4$Sb$_{12}$ [10,11] and PrT$_4$X$_{12}$ series [12] are consistent with this theoretical idea.

In comparison, PrRu$_4$Sb$_{12}$ with a larger CEF singlet-triplet energy separation $\Delta_1 \sim 65$ K exhibits a conventional BCS-type superconductivity with $T_c = 0.9$ K [13,14]. In alloy series of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, superconductivity appears for all the Ru content $0 \leq x \leq 1$ showing a minimum in $T_c$ at $x \approx 0.6$ [15]. Based on this observation, possible switching of...
two competing different superconducting phases at this concentration has been pointed out, although experimental confirmation has not been made yet.

In this paper, we report specific heat measurement on the alloy series Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ for the purpose to investigate the Ru-content dependence of the 4f-electron CEF level scheme of Pr ions in the normal state. In the specific heat data, contribution from anharmonic local vibrations of Pr ions in the Os$_4$Sb$_{12}$ cage (so-called “rattling”) also appears. The rattling rare-earth ions in the cage is another feature of the filled skutterudite structure [16] and possible relevance to the superconductivity through strong electron-phonon coupling has been discussed [17, 18]. From the specific heat data, the characteristic energy of the rattling, which can be represented by the Einstein temperature of the corresponding Einstein phonon mode, is obtained and is compared with the CEF excitations.

2. Experimental method

Single crystalline samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ as well as LaOs$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$ (no 4f-electron references) have been prepared by Sb self-flux method. The cubic-shaped single crystals with the size of ~ 1mm and the mass of ~ 10mg were used for specific heat measurement using a Quantum Design PPMS in zero magnetic field and the temperature range of 2 ~ 50K.

3. Results and discussion

The low-temperature specific heat of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ (represented hereafter by $C_{\text{Pr}}(T, x)$) can be described as

$$C_{\text{Pr}}(T, x) = C_{\text{cond}}^{\text{Pr}}(T, x) + C_{\text{ph}}(T, \Theta_D^{\text{Pr}}(x)) + C_{\text{ratt}}(T, \Theta_E^{\text{Pr}}(x)) + C_{4f}(T, x),$$

where $C_{\text{cond}}^{\text{Pr}} \approx \gamma_{\text{Pr}}(x)T$, $C_{\text{ph}}$, $C_{\text{ratt}}$ and $C_{4f}$ are the contributions from conduction electrons, ordinary acoustic phonons (represented by the Debye model), rattling phonons (represented by the Einstein model) and the CEF thermal excitations of the 4f-electrons, respectively, and $\gamma_{\text{Pr}}(x)$, $\Theta_D^{\text{Pr}}(x)$ and $\Theta_E^{\text{Pr}}(x)$ represent Sommerfeld coefficient, Debye temperature and Einstein temperature of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$. Note that the nuclear contribution is completely negligible in $T > 2K$. In a similar manner, specific heat of La(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ can be described as

$$C_{\text{La}}(T, x) = C_{\text{cond}}^{\text{La}}(T, x) + C_{\text{ph}}(T, \Theta_D^{\text{La}}(x)) + C_{\text{ratt}}(T, \Theta_E^{\text{La}}(x)).$$

Using specific heat data of LaOs$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$, $C_{\text{La}}$ is obtained as $C_{\text{La}} = (1 - x)C_{[\text{LaOs}_4\text{Sb}_{12}]} + xC_{[\text{LaRu}_4\text{Sb}_{12}]}$.

![Figure 1. $\Delta C$ vs $T$ for Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ with $0 \leq x \leq 1$. For $x = 0$, $\Delta C$ has two broad peaks appearing at $\sim 3$ K and $\sim 10$ K. With increasing $x$, the 3K peak shifts to higher temperatures resulting in a broad peak for $x$ above 0.4.](image-url)

Using the experimental data, we have obtained $\Delta C(T, x) \equiv C_{\text{Pr}}(T, x) - C_{\text{La}}(T, x)$, which are shown in Fig.1. As will be demonstrated later, the dominant contributions to $\Delta C(T, x)$ are $C_{4f}(T, x)$ and $\Delta C_{\text{ratt}}(T, x) = C_{\text{ratt}}(T, \Theta_D^{\text{Pr}}(x)) - C_{\text{ratt}}(T, \Theta_E^{\text{La}}(x))$; note that $C_{\text{ph}}(T, \Theta_D^{\text{Pr}}(x)) - $
C_{ph}(T, \Theta_L^\text{La}(x)) and C_{\text{cond}}^{\text{Pr}} - C_{\text{cond}}^\text{La} have minor contributions. For \( x = 0 \), \( \Delta C(T, x) \) has two broad peaks appearing at \( \sim 3 \) K and \( \sim 10 \) K. The former peak corresponds to the CEF singlet-triplet \( (\Gamma_1 - \Gamma_4^{(2)}) \) excitation. The peak height (6.70 J/Kmol) is strongly suppressed compared to 8.51 J/Kmol expected for a simple singlet-triplet Schottky contribution. This suppression is attributable to the dispersion of the \( \Gamma_1 - \Gamma_4^{(2)} \) excitations in the wavevector space and the temperature dependence of the excitation energy observed by inelastic neutron scattering [19]. Tentatively, we introduce a rectangular-shaped distribution (with the width \( \delta \)) to the density-of-states of the \( \Gamma_1 - \Gamma_4^{(2)} \) excitations. As shown in Fig.2, the 3K peak for \( x = 0 \) can be nicely reproduced by the CEF model. Note that the thermal excitations to the higher excited states \( \Gamma_1^{(1)} \) and \( \Gamma_{23}^{(1)} \) [8] become visible above \( \sim 20 \) K as shown in Fig.2 and therefore those excitation energies cannot be determined accurately by the present low-temperature study.

The other broad peak appearing around 10K, which cannot be explained by \( C_{4f}(T) \), is most probably due to the rattling contribution \( \Delta C_{\text{ratt}}(T) \). The height and the maximum temperature of the broad peak depend on the difference between \( \Theta_L^\text{Pr} \) and \( \Theta_L^\text{La} \). By the least squares fitting, \( \Theta_L^\text{Pr} \) has been determined to be 43.5 K, which is consistent with that obtained from Raman scattering data [20].

\[
\Delta C(T) = C_{4f}(T) + \Delta C_{\text{ratt}}(T)
\]

For samples with \( x > 0 \), similar analysis has been made and it has been found that the \( \Delta C \) data can be well reproduced by \( C_{4f} + \Delta C_{\text{ratt}} \) as demonstrated in Fig.2. Thus obtained three parameters, i.e., the CEF excitation energy \( \Delta_1 \), the width of the excitation \( \delta \) and rattling Einstein temperature \( \Theta_E^\text{Pr} \), are plotted in Fig.3 as a function of \( x \).

\( \Delta_1 \) increases monotonically with increasing \( x \). The \( x \)-dependence of \( \Delta_1 \) is visible in Fig.1 as the shift of the 3K peak to higher temperatures with increasing \( x \). On the other hand, \( \Theta_E^\text{Pr} \) stays at around 45 K for all \( x \) values without significant change. A remarkable finding here is that a level crossing appears between \( \Delta_1 \) and \( \Theta_E^\text{Pr} \) around \( x \sim 0.6 \). In Fig.2, this crossing is reflected in the development of the broad peak height for \( x \) above 0.6 at high temperatures.

In Pr(Os_{1-x}Ru_x)_{4}Sb_{12}, it is probable that \( T_c \) is controlled by inelastic aspherical charge scattering process [9] associated with 4f quadrupole moments in the low-energy \( \Gamma_1 - \Gamma_4^{(2)} \) sublevels. At \( x \sim 0.6 \), since \( \Delta_1 \) has almost the same energy as \( \Theta_E^\text{Pr} \), a bound state of the
two excitations could be formed by magnetoelastic coupling effect, as discussed for CeAl$_2$ [21]. By the resulting modification of the 4f-electron excitations, the conduction electron scattering process could be disturbed, possibly resulting in a suppression of superconductivity. In this manner, the experimentally observed minimum in $T_c$ at $x \simeq 0.6$ [15] can be attributed to this effect.

4. Summary

By specific heat measurements on filled skutterudite superconductor Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, we have determined the $x$-dependences of the CEF singlet-triplet excitation energy and the rattling energy of the Pr ion. The former increases monotonically while the latter does not change much resulting in a crossing at $x \sim 0.6$. The observed minimum in $T_c$ around $x = 0.6$ can be attributed to this level crossing, since, by the formation of a bound state of the two excitations, the inelastic quadrupolar Coulomb scattering responsible for the Cooper pairing could be suppressed.

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