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Collective heavy-fermion state and superconductivity in $Pr_{1-x}La_xOs_4Sb_{12}$: A specific heat study

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We report the low-temperature susceptibility and specific heat for single crystals of $Pr_{1-x}La_xOs_4Sb_{12}$ ($0 \leq x \leq 1$). The ionic properties of the material, characterized by the energy spectrum of crystalline electric field (CEF) levels of Pr, are unchanged by La doping. The average T_c is only weakly affected by La substitution and varies approximately linearly between the end compounds. The discontinuity in the specific heat divided by temperature C/T at T_c is drastically reduced from about 800 mJ/K^2 mol for $x=0$ to the value of $LaOs_4Sb_{12}$ near $x=0.3$. This behavior of a superconducting transition implies a collective origin of the heavy-fermion state in $PrOs_4Sb_{12}$. We suggest that fluctuations of the anti-ferro-quadrupolar order parameter are responsible for this heavy-fermion state.

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$PrOs_4Sb_{12}$ is a rare-earth-based superconducting heavy-fermion compound[1] in which the crystalline electric fields (CEFs) do not support straightforward magnetism.[2–4] Yet, it shows heavy-fermion behavior in simultaneously enhanced specific heat and susceptibility. It also undergoes a superconducting transition where the superconducting carriers are the heavy electrons. Currently, the only experimentally verified and established theory of heavy fermions is based on the magnetic Kondo effect. The non-Kramers configuration of Pr (two f electrons) provides for possibly novel ground states and novel physics.

In addition to the intrinsic merits, understanding $PrOs_4Sb_{12}$ and other Pr-based heavy-fermions offers an opportunity to get new insight into the origin of unusual properties of U-based materials. These materials have been a source of many important discoveries, over more than a quarter of a century, stimulating developments of new theoretical models of condensed matter. Despite enormous experimental and theoretical efforts, the understanding of U and other actinide systems remains limited at best. A major obstacle is that the ionic configuration of U in these systems is not known. Both f^2 and f^3 configurations have been suggested by thermodynamic and magnetic investigations. However, the only somewhat successful studies of CEF's directly by inelastic neutron scattering[5,6] are more consistent with the f^2 configuration, allowing for a similar CEF scheme as that for Pr.

Thus, the nature of the electron mass enhancement in $PrOs_4Sb_{12}$ remains an outstanding and unsolved problem, with important consequences for the entire heavy-fermion physics. Mechanisms that have been considered range from single-ion models, such as the quadrupolar Kondo effect[1,7] or virtual CEF excitations,[3,8] to cooperative models invoking proximity to a long-range order. The main goal of our study was to differentiate between these models by performing systematic investigation on single-crystalline alloys in which Pr is partially substituted by non-f-electron analog La. We show that relevant single ion properties, such as the CEF eigenstates and energies of Pr and the local environment of Pr, are unchanged, while heavy-fermion characteristics show a dramatic dependence on La concentration. In addition, we discuss the relationship between the heavy-fermion characteristics and superconductivity.

There are strong indications, from a wide range of transport, thermodynamic, and magnetic measurements, that the superconductivity in $PrOs_4Sb_{12}$ is unconventional. Two superconducting transitions in the specific heat have been reported by several research groups.[9–12] There is still no consensus as to whether these two transitions are due to spatial inhomogeneities or whether they are signatures of unconventional superconductivity in a homogeneous medium. How these two anomalies respond to alloying was one of the specific goals of our study.

All single-crystalline samples used in this investigation were synthesized by the Sb-flux method.[13] La and Pr were premelted and flipped over several times in an arc melter to improve the homogeneity of samples. The results of the x-ray powder diffraction analysis[14] were consistent with single phase materials. We have detected a linear (within the scattering), but very small, increase of the lattice constant with the La content. These very small changes (0.04% between the end compounds; on the border of sensitivity of our technique) are in agreement with previously reported[15] an almost nonexistent lanthanide contraction in ternary skutterudites containing Sb, of a general form LnT_4Sb_{12}; where T and Ln are transition element and light lanthanide, respectively. These extremely small changes of the lattice constant in $Pr_{1-x}La_xOs_4Sb_{12}$ provide a unique opportunity for the alloying study of superconductivity and other phenomena that are strongly influenced by microscopic inhomogeneities associated with the lattice constants' mismatch. Furthermore, very small changes of the lattice constant across the system argue for very small variation of the hybridization between f and ligand states.

For all concentrations studied, we have performed measurements, both specific heat and susceptibility, on at least two different crystals with masses 1–5 mg. For the specific heat of $LaOs_4Sb_{12}$ a large single crystal, about 40 mg was grown. Within the uncertainty of these measurements we have observed good reproducibility for crystals from the same batch. On the other hand, we found some discrepancies between crystals from different batches with the same nominal concentration and corresponding to small doping levels

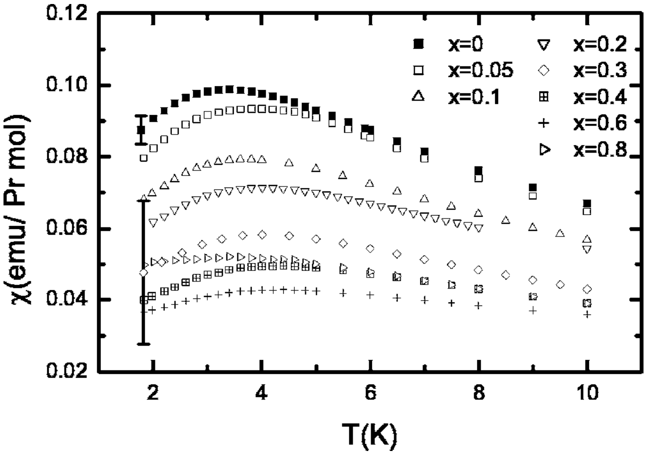

FIG. 1. Magnetic susceptibility of $Pr_{1-x}La_xOs_4Sb_{12}$ between 1.8 and 10 K, measured in the field of 0.5 T. The absolute error for $x=0$ is consistent with the size of the symbol and it increases approximately linearly with x. It is ±0.02 emu/Pr mol for $x=0.8$.

($x \leqslant 0.05$). We believe these discrepancies are due to a small variation in the actual composition, in agreement with our high precision ac-susceptibility measurements near T_c and, as it will be discussed, a strong concentration dependence of the specific heat near $x=0$. These differences have no bearing on the conclusions of our investigation.

Figure 1 shows the susceptibility for $Pr_{1-x}La_xOs_4Sb_{12}$ crystals at temperatures 1.85 to 10 K obtained in the field of 0.5 T and normalized to a mole of Pr. The specific heat discussed next is also for the same single crystals. Because of a small size of crystals, samples' magnetization was comparable to the background (sample holder) below 10 K and was much smaller than the background at room temperature, especially for strongly dilute samples. Therefore, additional susceptibility measurements, to 300 K, were performed for concentrations with sufficient amount of material available to obtain reliable results ($x=0$, 0.05, 0.3, 0.8, and 0.95). In these measurements, material was pressed in between two long concentric tubes such that no background subtraction was needed. All these additional measurements yielded a Curie-Weiss temperature variation above 150 K, corresponding to an effective magnetic moment of $3.2-3.6\mu_B$/Pr atom. This moment is within the range of values reported for the undoped compound[1,16] and supports the notion of an essentially trivalent state of Pr in all alloys.

All low-temperature susceptibility curves show a broad maximum 3–5 K which is believed to be due to excitations between the lowest CEF states. Measurements performed on assemblies of crystals using the method discussed above, confirmed these maxima at about 4 K, for all concentrations including our most dilute alloy of $x=0.95$. Previous studies have established that the CEF ground state is a Γ_1 singlet separated by about 8 K from the first excited Γ_5 triplet.[2–4] Thus very small variation in the position of these maxima in χ implies very small, if any, changes in CEF energies. Recently, we have performed additional investigation of CEF energies of $Pr_{1-x}La_xOs_4Sb_{12}$ via specific heat in magnetic fields.[17] These measurements provided an additional confirmation of essentially unchanged CEF energies upon La substitution.

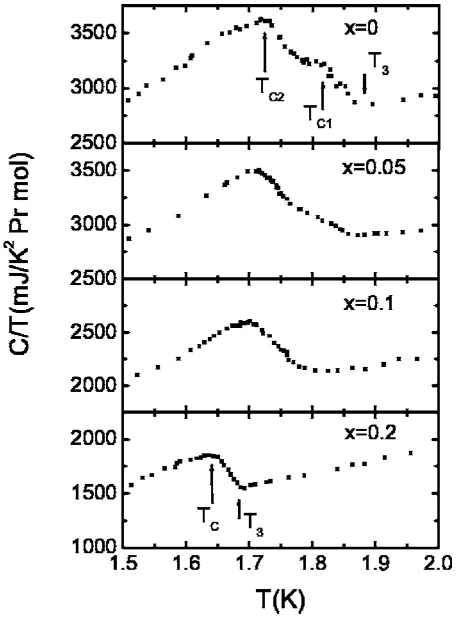

FIG. 2. C/T versus T near T_c for $Pr_{1-x}La_xOs_4Sb_{12}$, where $x=0$, 0.05, 0.1, and 0.2. Arrows indicate our scheme of determining transition temperatures and the width of the transition. See text for details.

Another interesting aspect of the susceptibility is a strong initial reduction of the low-temperature values (normalized to a mole of Pr) by La. The reduction of the maximum susceptibility from approximately 100 for $x=0$ to about 50 memu/Pr mol for $x=0.4$ is clearly outside the error bar. The aforementioned measurements on assemblies of crystals for $x=0.8$ and 0.95 also resulted in a 4 K value of about 50±5 memu/Pr mol for both compositions. Some broadening and decrease in magnitude of the CEF susceptibility are expected in mixed alloys due to increased atomic disorder. However, the very large initial drop in the susceptibility and lack of variation above $x=0.4$ might indicate that some characteristic electronic energy (analogous to a Kondo temperature) increases sharply upon substituting La for Pr. A similar suppression of the corresponding maximum is observed in the specific heat discussed next.

The specific heat (Figs. 2 and 3) was measured by a standard relaxation technique. The absolute uncertainty of the measured specific heat was about 10%, mainly due to uncertainty in addenda and weak link conductance. To minimize the effect of systematic errors, all measurements were performed with a single calorimeter. The specific heat in the form of C/T (specific heat divided by temperature) versus T shown in Figs. 2 and 3 is normalized to a mole of Pr, after subtracting phonon and normal electrons contribution assumed to be identical to that for $LaOs_4Sb_{12}$. Since two previous reports[1,18] on $LaOs_4Sb_{12}$ had somewhat different low-temperature C/T values we have performed a measurement on a single crystal grown in an identical manner as all mixed alloys. Total C/T between 1 and 10 K can be expressed as $C/T=59+1.03T^2+0.058T^4-1.705\times 10^{-4}\,T^6$, where C/T is in mJ/K^2 mol and T in K. A C/T discontinuity at T_c (0.74) is 86 mJ/K^2 mol.

Arrows in the upper and lower panels of Fig. 2 demon-

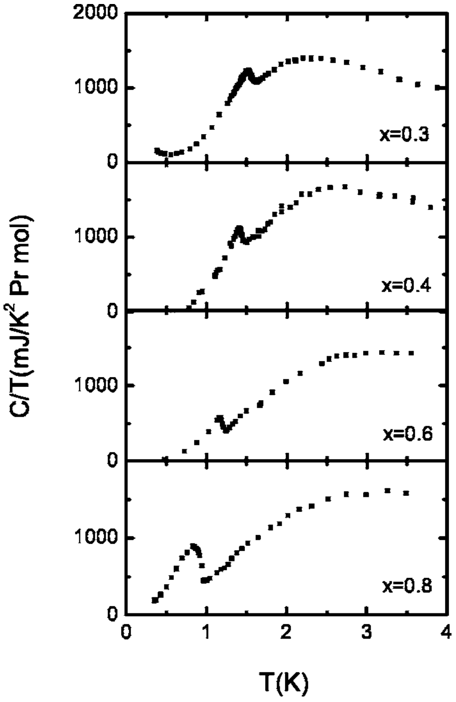

FIG. 3. C/T versus T for $\mathrm{Pr}_{1-x}\mathrm{La}_x\mathrm{Os}_4\mathrm{Sb}_{12}$; $x \geqslant 0.3$.

strate our method of determining transition temperatures (T_{c1} and T_{c2}) (shown in Fig. 4) and the width of the transition $T_3 - T_{c2}$ (or $T_3 - T_c$ if two transitions could not be resolved). The discontinuity in C/T $[\Delta(C/T)]$ is defined as a difference between C/T at T_{c2} (or T_c) and $C/T(T_3)$. All measured crystals of the pure compound showed two distinct anomalies with an average $\Delta(C/T)$ of about 800 mJ/K^2 mol. Also, the $x=0.02$ (not shown) and 0.05 compositions have shoulders that seem to correspond to the anomaly at T_{c1} for $x=0$. On the other hand, only a single superconducting transition is observed in $x=0.2$. There is also a single superconducting transition for all alloys with $x \geqslant 0.2$. Figure 3 shows C/T for alloys with $x \geqslant 0.4$. There are a number of interesting differences between alloys showing two anomalies ($x=0$, 0.02, and 0.05) and those corresponding to $x \geqslant 0.2$. First, the width of the transition defined above is drastically reduced for the latter group of compositions. Obviously, some reduction of the width is expected if T_c itself is decreased. However, a similar reduction takes place for the width normalized to T_c. Thus, it is probable that alloys corresponding to $x \geqslant 0.2$ exhibit only a single transition as opposed to alloys with $x \leqslant 0.05$ that can show two anomalies. The width of the transition for $x=0.1$ is in between those for $x=0$ and 0.2. Second, there is a drastic decrease of $\Delta(C/T)$ from about an average 800 for $x=0$ to 280 for $x=0.2$ and further to about 160 mJ/K^2 Pr mol for $x=0.3$. In BCS-type superconductors $\Delta C/T_c$ is simply related to the electronic specific heat coefficient γ. In general, the ratio of $\Delta C/T_c$ and γ is also affected by the coupling strength of Cooper pairs and can vary by a factor of order of 2–3. In fact, the very large $\Delta C/T_c$ in $\mathrm{PrOs}_4\mathrm{Sb}_{12}$ was the first, and still the strongest, indication of the heavy-fermion state. A broad Schottky-like anomaly centered just above T_c (see Fig. 3) obscures a direct measurement of γ. Moreover, strong hybridization effects make a straightforward subtraction of this Schottky-like maximum difficult and unreliable. Therefore, for lack of any other reliable measure of γ, we propose to use $\Delta(C/T)$ as a rough estimate of the electronic specific heat coefficient. Note that $\Delta(C/T)$ as inferred from Figs. 2 and 3 is normalized to a mole of Pr. Since $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ itself is superconducting, this normalization for fairly dilute Pr alloys has no obvious meaning. Instead, in Fig. 5 we display $\Delta(C/T)$ per formula unit, called further total $\Delta(C/T)$. The total $\Delta(C/T)$ is more than sevenfold reduced between $x=0$ and 0.3. Its value for alloys with $x \geqslant 0.3$ is approximately constant and about equal to that of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$, which is an ordinary superconductor. These results imply that the electronic specific heat coefficient of $\mathrm{PrOs}_4\mathrm{Sb}_{12}$ is greatly suppressed by La and the heavy-fermion character is lost somewhere near $x=0.3$.

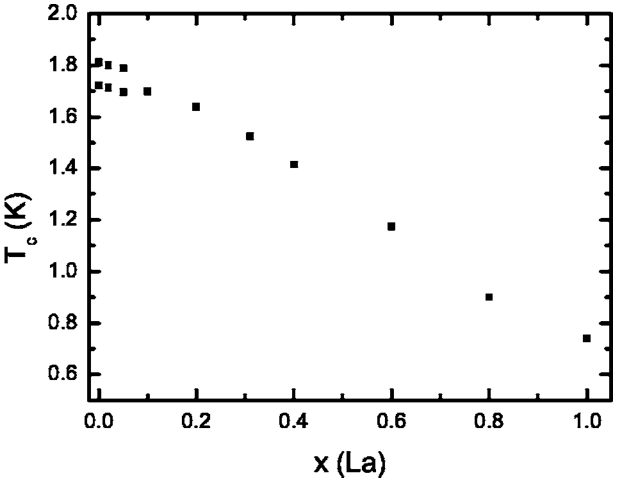

FIG. 4. Superconducting transition temperature T_c of $\mathrm{Pr}_{1-x}\mathrm{La}_x\mathrm{Os}_4\mathrm{Sb}_{12}$ versus x.

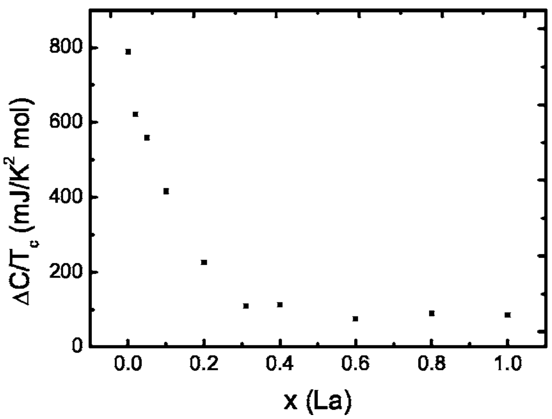

FIG. 5. Total C/T discontinuity at T_c versus concentration x for $\mathrm{Pr}_{1-x}\mathrm{La}_x\mathrm{Os}_4\mathrm{Sb}_{12}$, where $0 \leqslant x \leqslant 1$. See text for definitions.

Obviously, there is a question on the meaning of $\Delta(C/T)$ in the case of two superconducting transitions, such as those in the pure compound. If the two transitions correspond to different regions of the sample entering the superconducting state, the combined $\Delta(C/T)$ (such as that shown in Fig. 5) is a good measure of the average γ of the material. However, if the lower transition is between two superconducting states, γ

deduced from such a combined $\Delta(C/T)$ might be overestimated. In fact, the largest reported ratios of $\Delta(C/T)$ and γ are for systems exhibiting two superconducting anomalies such as UBe_{13} and its alloys.[19] Vollmer *et al.*[10] suggest that the two discontinuities in $PrOs_4Sb_{12}$ are of approximately equal magnitudes, which is in agreement with other results including our data. Thus, if we assume that the C/T discontinuity due to the transition between normal and superconducting states is only 50% of the total $\Delta(C/T)$ for $x=0$, this still leaves an enhanced γ for $x=0$ that decreases rapidly with x to an approximate value of $LaOs_4Sb_{12}$ around $x=0.3$.

As it can be inferred from Figs. 2–4, T_c itself is only moderately suppressed by the La substitution. La impurities, which do not have f electrons, are not strong pair breakers and there is a smooth evolution between the superconducting states of $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$. This approximately linear variation of T_c on x in $Pr_{1-x}La_xOs_4Sb_{12}$ is unusual for heavy-fermion alloys. For instance, UBe_{13} that shows a number of striking similarities to $PrOs_4Sb_{12}$ has its superconductivity completely suppressed by just 3% of La.[20] The very different sensitivity of T_c on La impurities between $PrOs_4Sb_{12}$ and canonical heavy-fermion superconductors cannot be accounted for by vastly different coherence lengths. In fact, the coherence lengths of the UBe_{13} and $PrOs_4Sb_{12}$ are almost identical, 140 (Ref. 21) and 120 Å (Ref. 1), respectively. A somewhat stronger suppression of T_c in $PrOs_4Sb_{12}$ was found for Ru impurities replacing Os.[22] However, even in this case the rate of the reduction of T_c is small in comparison with the majority of Ce- and U-based heavy fermions and considering very different paramagnetic states of $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$. $PrRu_4Sb_{12}$ is an ordinary metal[23] with relevant CEF energies much larger than those for $PrOs_4Sb_{12}$.

Thus, there seems to be a lack of strong correlation between the heavy-fermion character as measured by $\Delta C/T_c$ and the average T_c. It is then likely that different mechanisms are responsible for the electronic mass enhancement (m^*) and the enhancement of the transition temperature in $PrOs_4Sb_{12}$.

There is an emerging consensus[3,12] that the origin of the heavy-fermion mass in $PrOs_4Sb_{12}$ is the scattering of conduction electrons on excited CEF levels, the mechanism proposed initially for elemental Pr.[8] The essential parameters of this model are CEF eigenstates and eigenvalues, and conduction electron density at the Fermi level. As discussed above, these parameters are expected to be constant across $Pr_{1-x}La_xOs_4Sb_{12}$ while m^* is clearly reduced with x. Furthermore, our work indicates that any single-ion type model of heavy fermions is most probably inapplicable to $PrOs_4Sb_{12}$. An obvious candidate for collective-type mechanism is the fluctuations of the anti-ferro-quadrupolar order parameter. $PrOs_4Sb_{12}$ exhibits an anti-ferro-quadrupolar order in fields between about 5 and 13 T.[11] Thus, the magnetic field response of m^* might shed further light on the heavy-fermion mechanism. Does m^* increase when approaching the long-range order boundary? A direct measurement of m^* in fields by specific heat is unreliable due to the strong contribution of excited CEF levels and nuclear specific heat. For fields 5–13 T the two lowest CEF levels are sufficiently close to form a pseudoublet with quadrupolar and magnetic degrees of freedom, resulting in a long range order. On the other hand, our initial magnetoresistance measurements are promising in this respect.[24] They indicate that $m*$ initially increases with fields smaller than 10 T followed by a decrease by fields stronger than 14 T. Summarizing, the presented results demonstrate that the heavy-fermion state in $PrOs_4Sb_{12}$, or at least a large fraction of m^* enhancement, is due to collective excitations involving Pr lattice.

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