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Anomalous low-temperature state of a possible Kondo semimetal $CeOs_4Sb_{12}$: Magnetic field and La impurity study

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Specific heat in magnetic fields to 14 T, magnetic susceptibility and electrical resistivity for single crystalline samples of $Ce_{1-x}La_xOs_4Sb_{12}$ ($x=0, 0.02, 0.1$) are reported. The results of the magnetic susceptibility and electrical resistivity are consistent with a formation of the hybridization gap below 100 K in all investigated alloys. We argue for the intrinsic origin of a large electronic specific heat coefficient and 1.1 K anomaly. The low temperature state is very sensitive to the La alloying. On the other hand, the Kondo temperature and energy gap, extracted from susceptibility and resistance measurements, are unaffected by the alloying. The magnetic phase diagram of the pure compound is presented.

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I. INTRODUCTION

Filled skutterudites with a chemical formula RT_4X_{12}, where R is a rare earth, T is a transition metal, and X=P, As, or Sb, lately have been of great interest due to their broad spectrum of exotic properties related to the unique crystal structure. Among them, $PrOs_4Sb_{12}$ is the first heavy fermion superconductor based on Pr.[1] $PrFe_4P_{12}$ is a field induced heavy fermion compound.[2] $CeRu_4Sb_{12}$ is a semimetallic non-Fermi liquid system.[3] $CeOs_4Sb_{12}$, a subject of this investigation, is a possible Kondo insulator.[4] Low temperature properties of this material are not fully understood and their interpretation remains controversial.

The resistivity of $CeOs_4Sb_{12}$ is metallic at room temperature, but shows behavior typical of an insulator, i.e., increases strongly with a decrease of temperature, below 50 K. The resistivity does not strictly follow an activation-type temperature variation. At temperatures lower than 10 K, the rate of the resistivity increase is smaller than that expected from the energy gap of about 10 K.[4] A recent study of optical conductivity spectra[5] shows a strong temperature dependence and a gap of 30 meV below 60 K. In addition, a structure observed at 70 meV was interpreted in terms of the hybridization gap peak. These transport properties are quite consistent with a Kondo insulator or hybridizataion gap semiconductor.[6]

On the other hand, the two reported values of the electronic specific heat coefficient, γ, are 90 (Ref. 4) and 180 mJ/K^2 mol,[7] hardly consistent with the presence of an energy gap. The specific heat also exhibits a peak near 1.1 K. Because of a very small entropy associated with this peak (about 2% of $R \ln 2$ only) the initial study has suggested a possibility of some impurity phase being responsible for the 1.1 K anomaly.[4] Subsequent investigations, particularly by specific heat in magnetic fields,[7,8] provided strong arguments for the intrinsic origin of the anomaly.

To shed more light on the nature of the ground state in $CeOs_4Sb_{12}$, we have extended the specific heat measurements to fields as large as 14 T and introduced La impurities on Ce sites. The La-doped samples were also investigated by magnetic susceptibility and electrical resistivity.

II. EXPERIMENTAL AND RESULTS

Single crystalline samples of $Ce_{1-x}La_xOs_4Sb_{12}$, with $x=0$, 0.02, and 0.1, were obtained by the Sb self-flux method described elsewhere.[4] For mixed alloys, Ce and La were premelted first to assure the homogeneity of samples. X-ray diffraction measurements were performed on powdered single crystals using a Philips APD 3720 diffractometer. All spectra were indexed by the BCC ($Im\bar{3}$) crystal structure. No external phases were detected. The change of the lattice constants between the end compounds, $CeOs_4Sb_{12}$ and $LaOs_4Sb_{12}$, is very small and on the edge of our experimental resolution. These lattice constants are, 9.304(2) and 9.309(2) Å, respectively. On the other hand, any variation of the lattice constant between $x=0$ and 0.1 is too small to be reliably resolved by this technique. This insensitivity of the lattice constant of ROs_4Sb_{12} to the atomic size of R is a unique property of this crystal structure.[4,9] A Ce ion in $CeOs_4Sb_{12}$ is surrounded by an oversized icosahedral cage formed by 12 Sb ions. Thus, only small variations of the hybridization parameters upon La doping are expected.

The results of the specific heat study of the pure compound in zero and applied magnetic fields are shown in Figs. 1 and 2. The comparison of all up-to-date specific heat measurements indicates strong sample dependency. Our C/T (specific heat divided by temperature) obtained on a single crystal of $CeOs_4Sb_{12}$, exhibits a peak at $T_m=1.1$ K (Fig. 1), thus at a temperature identical to that reported by Bauer *et al.*,[4] Namiki *et al.*,[7] on the other hand, found this peak at 0.9 K. Furthermore, the height of the peak in C/T is approximately 220, 510, and 380 $mJ/mol\,K^2$ according to Bauer *et al.*, Namiki *et al.*, and our data, respectively. There is also a large discrepancy in C/T results above the anomaly. Our data above 3 K are in better agreement with those of Namiki *et al.*, i.e., are consistent with the electronic specific heat coefficient of 180 $mJ/mol\,K^2$. However, since this coefficient was obtained using a narrow temperature range below 5 K, we have performed additional measurements between 1.6 and 14 K on an assembly of single crystals. The result is demonstrated in Fig. 2. C/T is approximately linear in T^2 between 4 and 8 K. The least square fit yields the

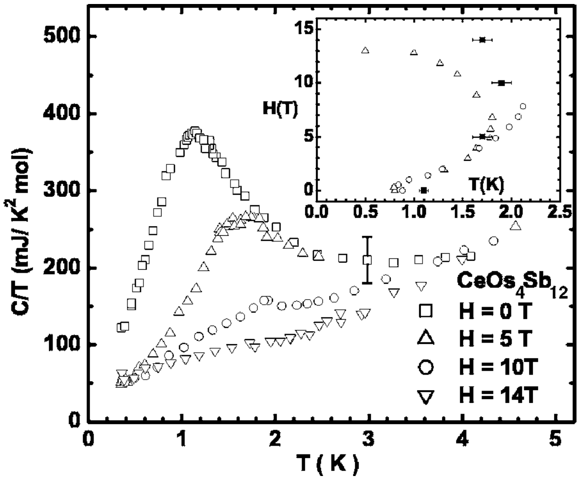

FIG. 1. C/T versus T for CeOs$_4$Sb$_{12}$ in H=0, 5, 10, and 14 T. The magnetic field was applied along the (100) direction. The inset shows the H-T phase diagram. The transition temperatures were identified by the maximum values of C/T (filled squares). Open dots represents the phase diagram according to the of Namiki *et al.* (Ref. 7), open triangles are according to the resistivity measurements of Sugawara *et al.* (Ref. 14).

high temperature electronic specific heat coefficient γ 160±10 mJ/mol K^2 and a rather small Debye temperature Θ_D of approximately 160 K. For comparison, Θ_D for LaOs$_4$Sb$_{12}$, also measured by the specific heat, is approximately 320 K.[10,11] This large difference could be due to nonphonon degrees of freedom (not identified) contributing to the slope of C/T versus T^2 at low temperatures. On the other hand, Vollmer *et al.*[12] proposed a somewhat similar Θ_D of 165 K for the isostructural PrOs$_4$Sb$_{12}$. This high temperature γ in CeOs$_4$Sb$_{12}$ is reduced by the 1.1 K transition (Fig. 1). Strictly speaking, the low temperature γ cannot be reliably determined from our data above 0.4 K since the character of the 1 K transition and hence the expected temperature dependence of the specific heat at the lowest temperature are unknown. However, the value of C/T at 0.4 K is about 115 mJ/mol K^2, thus significantly smaller than the proposed high temperature γ of 160 mJ/mol K^2. An extrapolation of our lowest temperature C/T data to T=0 implies that this low temperature γ is much smaller than 100 mJ/mol K^2. Note that the results presented in Fig. 1 exclude a nuclear contribution. This nuclear contribution can be separated from the electronic one in the relaxation-method calorimetry, if the two characteristic time constants entering the measurement, τ characterizing the coupling between electronic degrees of freedom and the heat reservoir and the nuclear spin-lattice relaxation time T_1, determining the coupling between nuclear and electronic degrees of freedom, differ substantially.[13] Because of a small mass of the single crystal (about 5 mg), this first time constant ($\tau \sim 0.1$ s) was more than an order of magnitude smaller than T_1.

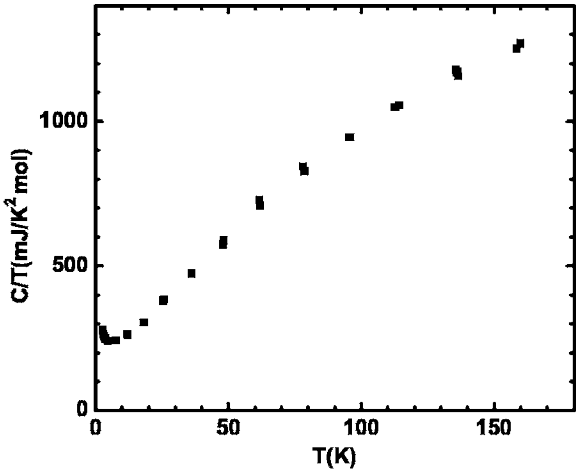

FIG. 2. C/T versus T^2 for CeOs$_4$Sb$_{12}$ between 1.6 and 14 K. The measurement was performed on an assembly of single crystals.

This strong impact of the transition on the linear specific heat coefficient is an obvious indication that either the transition itself is intrinsic to CeOs$_4$Sb$_{12}$ or that both the anomaly and large high temperature γ are due to an extrinsic phase. This second scenario is unlikely since this extrinsic phase would have to be a much larger fraction of the sample than initially assumed.[4] A similar conclusion was reached by Namiki *et al.*, using the specific heat data at 4 T and a similar argument of the reduction of γ at T_m.

In agreement with the previous specific heat study,[7] we find that a moderately strong magnetic field of 5 T, applied along the (100) crystallographic direction, shifts the anomaly to a higher temperature, but at the same time, the magnitude of the peak is reduced. At the lowest temperatures just below 0.4 K, C/T values in magnetic fields of 5, 10, and 14 T are approximately the same, about 50 mJ/mol K^2, i.e., much smaller than the proposed high temperature γ for the zero field. We do not expect the high temperature γ to be significantly reduced by a magnetic field of order 5 T. In fact, the 4 T data of Namiki *et al.*,[7] imply a slight increase of the high temperature γ. Thus, again, these high magnetic field data strongly suggest an intrinsic origin of the 1.1 K transition.

The inset to Fig. 1 presents the magnetic phase diagram obtained from our specific heat measurements and compares it with that obtained from the specific heat study of Namiki *et al.*[7] and electrical resitance study of Sugawara *et al.*[14] All three sets of data imply a similar trend for T_m versus H. T_m clearly increases with H below 5 T followed by a decrease above 10 T. Sugawara *et al.* suggest a sample misalignment as a possible source of discrepancies between these results. Our specific heat platform, oriented at room temperature, can be misaligned by 10°–15° upon cooling and applying the magnetic field. Thus, a possible strong magnetic anisotropy in this cubic system should be investigated.

This low temperature state of CeOs$_4$Sb$_{12}$ is extremely sensitive to La impurities. Just 2% of La introduced for Ce suppresses the anomaly to temperatures lower than 0.4 K (Fig. 3). There is an increase of C/T below 1 K, possibly related to this transition taking place at much lower temperatures or some non-Fermi liquid effects. There is also a relatively large decrease of the electronic specific heat in the paramagnetic state, as evidenced by a large reduction of C/T values at temperatures 3–4 K. In order to confirm this result we have measured two different crystals with different masses. These samples were approximately 7 mg (#1) and

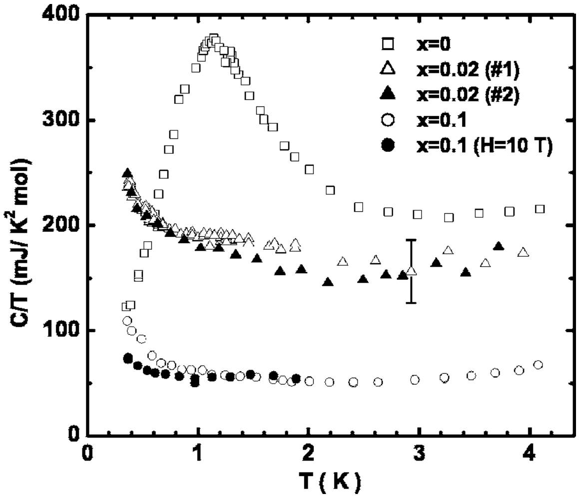

FIG. 3. C/T versus T for $Ce_{1-x}La_xOs_4Sb_{12}$, where $x=0$, 0.02, and 0.1 ($H=0$ and 10 T).

2 mg (#2). Large scattering was due to a combination of a short time constant (τ), large background contribution, and a lack of averaging several measurements at the same temperature. Nevertheless, there is a good agreement between the two sets of data for $x=0.02$, demonstrating that our addenda subtraction is accurate. Moreover, this addenda is almost identical for all measured samples, thus it cannot explain a large drop in C/T between $x=0$ and 0.02. Further substitution of La for Ce results in additional reduction of the specific heat. This reduction, say at 3 K, is by more than 70% for just 10% of La. The 10 T magnetic field applied along the (100) direction suppresses the lowest temperature C/T.

A disappearance of the 1.1 K peak in the La-doped samples provides complementary evidence for the intrinsic origin of this peak. La is chemically similar to Ce but carries no f electrons. The substitution of La for Ce leads to some randomness on f-electron sites. The low temperature structure seems to be characteristic of undoped, high quality samples only.

A similarly critical dependence on chemical disorder on the f-ion site was previously reported for $CeAl_3$ (Ref. 15) and $CeRu_4Sb_{12}$.[16] In $CeAl_3$, however, La induces bulk magnetism, as opposed to the case of $CeOs_4Sb_{12}$. In the case of the related $CeRu_4Sb_{12}$ system, 2% of La reduces C/T at 1 K by about 40%. We will return to this and other similarities between the two compounds throughout the paper.

The magnetic phase diagram of $CeOs_4Sb_{12}$ shown in the inset to Fig. 1 is atypical of a Ce based Kondo insulator or a Kondo-lattice system. A positive sign of dT_m/dH is inconsistent with antiferromagnetism. The temperature variation of the susceptibility indicates a predominance of aniferromagnetic-type interactions rather than ferromagnetic.[4] A recent NQR and NMR investigation finds strong AFM QCP fluctuations below 25 K and suggests that the 1 K order is unconventional SDW or CDW type.[17] Namiki *et al.*,[7] on the other hand, noticed that the magnetic phase diagram is reminiscent of CeB_6 (Ref. 18) [or La-doped (Ref. 19) CeB_6], which undergoes antiferroquadrupolar ordering. However, this type of order is inconsistent with small entropy released below T_m and with the proposed[4] crystalline electric field (CEF) configuration of Ce in $CeOs_4Sb_{12}$. This CEF scheme, however, was extracted from rather indirect measurements, from the magnetic susceptibility and carries large uncertainty. In particular, the magnetic susceptibility below 25 K shows an approximate Curie law temperature dependence with an effective moment closer to the expected value for the Γ_7 doublet than for Γ_8 quartet. However, it was concluded that the low temperature susceptibility is affected by some impurity contribution leading to a nonlinear dependence of the magnetization on the field. Furthermore, a recent inelastic neutron scattering experiment[20] has not found crystal field excitations implied by the susceptibility analysis. To get some insight into the nature of the low temperature tail in the susceptibility and possibly the CEF scheme we have performed magnetic susceptibility measurements for $x=0$, 0.02, and 0.1.

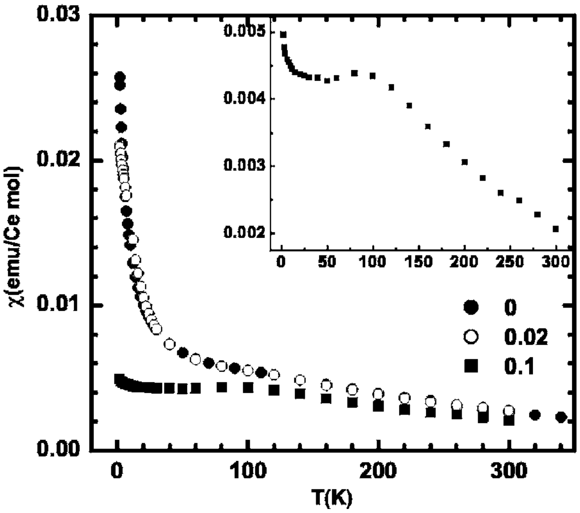

FIG. 4. Magnetic susceptibility of $Ce_{1-x}La_xOs_4Sb_{12}$; $x=0$, 0.02, and 0.1, measured at 0.5 T. The inset shows the susceptibility of $Ce_{0.9}La_{0.1}Os_4Sb_{12}$.

The susceptibility shown in Fig. 4 is defined as the ratio of the magnetization per Ce mole and magnetic field H. The magnetization measurements were performed on single crystals (6–10 mg) using a commercial SQUID magnetometer from Quantum Design. Crystals were placed snuggly in between two homogeneous and concentric tubes such that no holder subtraction was needed. In agreement with the previous magnetization report,[1] we find that the magnetization is strongly nonlinear with the applied field. However, this effect becomes smaller in La-doped samples. Hence, it is difficult to explain the nonlinear magnetization and low temperature tails for $x=0$ and 0.02 by extrinsic effects since all three compositions were synthesized simultaneously using the same starting components. The $x=0.1$ composition shows a Curie-Weiss temperature dependence above 140 K corresponding to the effective moment of 2.54 μ_B/Ce, consistent with a trivalent Ce, and negative paramagnetic Curie-Weiss temperature of 65 K. On the other hand such fits for $x=0$ and 0.02 were quite sensitive to the temperature range used yielding effective moment between 2.5 and 2.8 μ_B/Ce. Interestingly, the $x=0.1$ sample (inset to Fig. 4) shows a

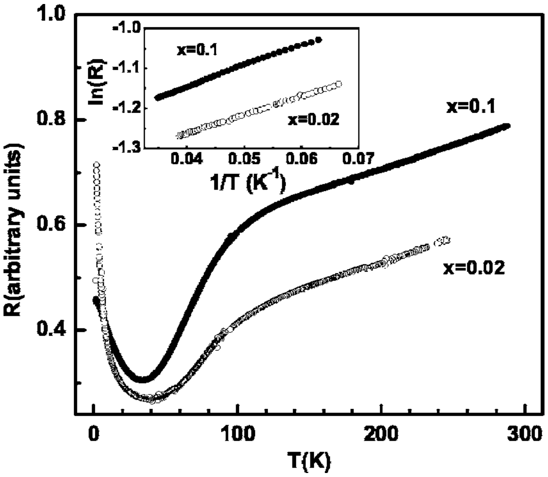

FIG. 5. Electrical resistance of $Ce_{1-x}La_xOs_4Sb_{12}$; $x=0.02$ and 0.1. The inset shows $\ln(R)$ versus $1/T$ for temperatures where $\ln(R)$ is linear in $1/T$.

broad anomaly at about 80–100 K. No such structure has been seen in undoped $CeOs_4Sb_{12}$. We find this structure to be related to the features in the electrical resistivity, discussed next.

The resistance versus temperature for $x=0.02$ and 0.2 is presented in Fig. 5. Because of the small size of these crystals we have not attempted to calculate the resistivity. The normalization factors were chosen to have approximately parallel resistance curves at high temperatures. At these high temperatures we expect the resistivity to be dominated by the electron-phonon scattering that should lead to similar slopes of the resistivity versus temperature for both alloys. Although this assumption might not be completely correct it has no bearing on our discussion. The residual resistivity ratio (RRR) defined as $R(300\text{ K})/R(1.6\text{ K})$ is about 0.7 for $x=0.02$, thus within the range of values reported for the pure compound, 0.25 to 1. On the other hand, RRR for $x=0.1$ is significantly larger, about 2.2, indicating a more metallic character of the resistivity. A faint knee observed in $CeOs_4Sb_{12}$ near 80–100 K becomes more pronounced in mixed samples, particularly in $x=0.1$.

A sharp decrease of the resistivity below 100 K coincides with the already discussed broad anomaly in the susceptibility. The $x=0.1$ composition has a susceptibility and resistivity very similar to that of the aforementioned already, $CeRu_4Sb_{12}$. This latter compound shows a broad maximum in the susceptibility at 80–90 K (T^*), a knee in the resistivity also at 80–90 K, and a rapid decrease of the resistivity below this temperature.[3] The maximum in the susceptibility of $CeRu_4Sb_{12}$ has been explained by the mixed-valent character of Ce. More recently, it has been postulated[21] that $T^*=80$ K is a coherence Kondo lattice temperature of $CeRu_4Sb_{12}$. Below T^*, the electronic density of states at E_F is gradually reduced. Ultrahigh resolution photoemission measurements demonstrated that this reduction is roughly proportional to temperature.[21]

The inset to Fig. 5 demonstrates that the resistivity of $x=0.02$ and 0.1 alloys can be described by the activated temperature dependence, but only over a limited range of temperatures, between 15 and 25 K. Surprisingly, the energy gap extracted from the resistance seems to be independent on the La content and in the range of values reported for the undoped compound, 6–7 K. On the other hand, the $T^{-1/2}$ temperature variation found[14] in the resistivity of $CeOs_4Sb_{12}$ and suggested to be due to a combination of antiferromagnetic spin fluctuations and temperature dependent carrier density can describe the low temperature resistivity data of the $x=0.02$ over a limited temperature range but fails for $x=0.1$. Below 10 K and down to 1.5 K, the lowest temperature of the resistance measurement, the resistivity can also be approximated by a logarithmic temperature variation, characteristic of some non-Fermi liquid systems.

III. CONCLUSIONS

Our results provide new experimental evidences on a close relationship between $CeRu_4Sb_{12}$ and $CeOs_4Sb_{12}$, first suggested by Sugawara *et al.*,[14] based on the Hall effect measurements. $Ce_{0.9}La_{0.1}Os_4Sb_{12}$, similarly to $CeRu_4Sb_{12}$, exhibits a broad maximum in the susceptibility at 80–100 K and a sharp decrease of the resistivity below 100 K. Such a maximum in the susceptibility is expected for a Kondo insulator (or Kondo semimetal). Below 100 K, the number of carriers gradually decreases leading initially to a steep reduction of the resistivity followed by an increase at lower temperatures. Electrical resistivities of $(Ce,La)Os_4Sb_{12}$ alloys display activated temperature variation but only over a small range of temperatures. The activation energy extracted from the resistivity is about 6–7 K and does not depend on the La concentration. The temperature of the maximum in the susceptibility can be associated with the Kondo temperature (T_K). Since this susceptibility maximum and knee in the resistivity occur at the same temperature for $x=0.1$ and because the resistivity knee is at the same temperature in undoped and La-doped samples, we believe that the T_K is also insensitive to the La doping. Recently, we have performed additional susceptibility measurements on a relatively dilute alloy, $Ce_{0.2}La_{0.8}Os_4Sb_{12}$ (not shown). This latter composition also exhibits a broad maximum in the susceptibility at 80 K, in agreement with our hypothesis of T_K having no dependence on x. Interestingly, this latter alloy has no low temperature tail in the susceptibility down to at least 2 K.

The unusually strong sensitivity of $CeOs_4Sb_{12}$ to La doping is puzzling. An explanation already considered is that there is an extrinsic phase leading to strong tails in the susceptibility and a small anomaly in the specific heat. However, our results for the undoped compound imply that this extrinsic phase would have to be a large fraction of crystals, detectable in x-ray diffraction measurements. Moreover, it would be difficult to explain why substitution of La for Ce would result in better quality samples, considering also that all studied compositions, in the form of single crystals, were synthesized in identical manner, using the same starting materials. Instead, our results strongly suggest electron correlations in this low carrier concentration system leading to a development of a low temperature state with a characteristic energy much smaller than T_K. This low temperature state is affected by impurities or imperfections. Magnetic ordering, probably of itinerant character, is suppressed by 2% La impurities. This 2% sample has C/T and electrical resistivity approximately proportional to a logarithm of temperature at the lowest temperatures of our investigation. Such a behavior is characteristic of non-Fermi liquids. Thus, extension of the specific heat and electrical resistivity study to much lower temperatures on this and other compositions with small amounts of La impurities is highly desirable.

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