Title

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Journal

Physical Review Letters, 66(25)

ISSN

0031-9007

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Publication Date

1991-06-24

DOI

10.1103/physrevlett.66.3289

Peer reviewed

Heavy-Electron Antiferromagnetism in CePt2Sn2

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(Received 6 August 1990)

We have measured specific heat, magnetic susceptibility, and resistivity on the cerium-intermetallic compound CePt2Sn2. The heat capacity shows a strong increase below a few kelvin, typical of a large many-body enhancement of the density of states or equivalently of the effective electronic mass. Just before the material orders antiferromagnetically at $T_N = 0.88$ K, the linear temperature coefficient of the specific heat γ is approximately 3.5 J/mole K^2, making this material one of the heaviest electron systems known. The low Néel temperature and huge specific heat imply similarly low energy scales for competing RKKY and Kondo-like interactions.

The competition between Kondo-spin fluctuations and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in cerium intermetallics is an intriguing question that has been the subject of experimental and theoretical investigations.[1-4] In these materials, the RKKY interaction between localized f moments, which is mediated by the conduction electrons, can eventually produce magnetic order, provided Kondo-like interactions do not compensate the localized moments. In the process of compensating these moments, the Kondo effect also generates a quasibound state characterized by an Abrikosov-Suhl resonance close to the Fermi level. Both the specific heat and the magnetic susceptibility are enhanced by the presence of these many-body interactions. Depending on which of these two interactions (Kondo or RKKY) is stronger, a material can be either an ordinary magnetically ordered 4f metal or a nonmagnetic Kondo lattice with moderately enhanced thermodynamic properties.[5,6] We report specific heat, magnetic susceptibility, and resistivity measurements indicating that CePt2Sn2 is a material lying between these two extremes. The Sommerfeld coefficient becomes very large in CePt2Sn2 before it orders antiferromagnetically at $T_N = 0.88$ K. Critical fluctuations, though present at the transition, do not dominate the specific heat in this region, but instead the large Sommerfeld coefficient probably arises from a strong many-body enhancement of the effective electronic mass, which develops on a temperature scale comparable to T_N.

The material was prepared by arc melting Ce (99.9%), Pt (99.99%), and Sn (99.999%) together on a water-cooled copper hearth in an argon atmosphere. X-ray powder diffraction, x-ray diffraction using a fourfold-axis goniometer on small single crystals, and microprobe analysis confirmed the polycrystalline samples to be single phase with the primitive tetragonal CaBe2Ge2-type structure. The unit-cell volume is 217.94 Å^3, making it the largest of the isostructural series CeM2Sn2 (M = Ni, Cu,Rh,Pd,Ir,Pt).[7]

As-prepared samples had a resistance ratio R(300 K)/R(4 K) of 1 or less, indicating substantial disorder.

Consequently, the samples were wrapped in Ta foil, sealed under vacuum in a quartz tube, and annealed for three days at 800°C. An important effect of annealing is to introduce a weak monoclinic distortion.[7] After annealing, the room-temperature resistivity was approximately 140 $\mu\Omega$ cm (accurate only to within a factor of 2 because of the uncertainties in the contact geometry), and from there the resistivity monotonically decreased with decreasing temperature until ~10 K below which it was essentially constant at ~55 $\mu\Omega$ cm. When the sample was annealed for three weeks at 800°C, a small maximum appeared in the resistivity around $T_{\max} \sim 3$ K that is believed to reflect the onset of correlations that produce a coherent Bloch state in Kondo-lattice compounds at temperatures much less than $T_{\max}$.[8] These data are displayed in Fig. 1(a). Longer annealing times did not affect any other measurements, in particular, specific heat. The data discussed in this paper were taken on samples annealed for three days.

The magnetic susceptibility was measured between 2.0 and 300 K in an applied magnetic field of 0.1 T with a SQUID magnetometer, and the temperature dependence of the reciprocal susceptibility χ^{-1} is shown in Fig. 1(b). Above ≈ 50 K, the curve closely follows a Curie-Weiss law incorporating an effective moment of $\mu_{\text{eff}} = 2.59 \mu_B$/Ce, consistent with the full (Hund's rule) degeneracy of Ce^{3+} (i.e., 2.54μ_B/Ce), and a paramagnetic Curie temperature of $\Theta = -25$ K. The downward curvature of χ^{-1} at low-temperatures indicates a reduced effective moment which would be expected from the lifting of degeneracy by crystal fields. In the temperature region from 2 to 5 K, the Curie-Weiss behavior is characterized by an effective moment $\mu_{\text{eff}}^l = 1.85\mu_B$/Ce and a low-temperature $\Theta^l = -1.2$ K.

To explore the low-temperature behavior of this compound, the specific heat C was measured on milligram samples in the temperature range from 0.32 to 20 K using a thermal-relaxation technique.[9] A second short-time relaxation was observed in the thermal decay at lower temperatures and is attributed to τ_2 effects, which are a consequence of a thermal impedance between the
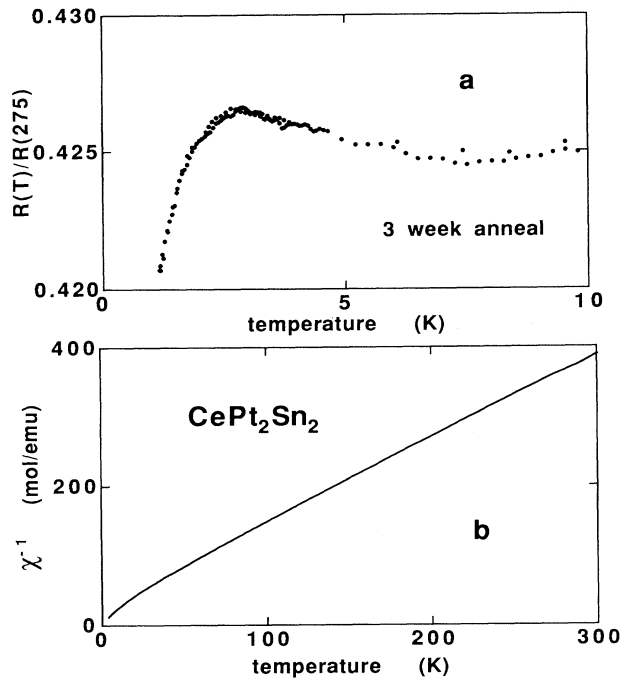
FIG. 1. (a) The four-probe resistivity, which is normalized to $T = 275$ K, vs temperature for $CePt_2Sn_2$ after a 3-week anneal. (b) The inverse magnetic susceptibility χ^{-1} as a function of temperature for $CePt_2Sn_2$. The high-temperature results yield an effective moment of $2.59\mu_B$/Ce, consistent with Ce^{3+}, and a paramagnetic Curie temperature of $\Theta = -25$ K. Below ~ 5 K, the effective moment is $1.85\mu_B$/Ce and $\Theta' = -1.2$ K.

FIG. 2. The temperature dependence of C/T for $CePt_2Sn_2$ and $Ce_{0.8}La_{0.2}Pt_2Sn_2$. The data are normalized per mole of Ce atoms. The precipitous rise at $T_N = 0.88$ K signals a phase transition to an antiferromagnetic ground state in $CePt_2Sn_2$. Substituting La for Ce suppresses the transition, leaving a heavy-electron state.

sample and the addenda. Based on calculations with the expressions in Ref. 9, these effects reduce the measured heat capacity by approximately 24% at the lowest temperature and gradually disappear with increasing temperature. τ_2 corrections were included in the data displayed in this paper. Plotted as C/T vs T in Fig. 2, the results below 2.0 K for $CePt_2Sn_2$ show a fairly steep upturn as the temperature is lowered to 0.88 K where there is a precipitous jump in C/T followed by a gradual decline—reminiscent of a mean-field second-order phase transition at this temperature. ac susceptibility measurements in this temperature range reveal a maximum centered near 0.9 K, indicating that the C/T jump is due to antiferromagnetic order. Integrating C/T from $T = 0$ K to $T_N = 0.88$ K gives an entropy for the transition of 4.0 J/mole K $= 0.70 R \ln(2)$, which is 30% less than expected for magnetic ordering within a doubly degenerate ground state having no Kondo compensation of the local moment.

Most notable in these data is the very large increase of C/T (approaching 3.5 J/mole K^2) just above the phase transition. Either critical fluctuations out of the antiferromagnetic state or a many-body (Kondo) renormalization of the effective mass might explain such a huge specific heat and an entropy less than $R \ln(2)$. Inspection of the data between T_N and ~ 1.2 K shows that the
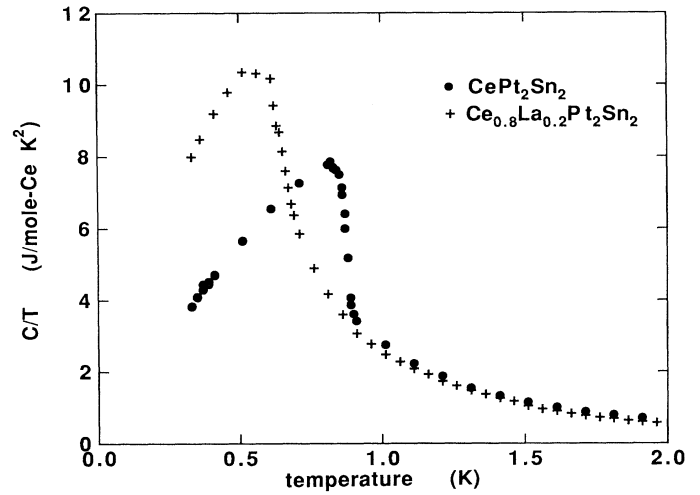
specific heat tends to diverge approximately as $C = C_0 |T - T_N|^{-0.1}$ which is characteristic of fluctuations in simple magnetic systems.[10] A Ginzburg-Landau treatment of critical phenomena incorporating the Gaussian approximation predicts a power-law divergence of C with the same power both above and below the transition. A divergence below T_N was not observed in $CePt_2Sn_2$. Furthermore, an estimate of the temperature range T_G over which critical fluctuations are important is provided by the Ginzburg criterion in this theory.[10] For a three-dimensional phase transition, $T_G = T_N [k_B/(2\pi\xi_0)^3 \Delta C]^2$, where ΔC is the specific-heat discontinuity, ξ_0 is the zero-temperature correlation length, and k_B is Boltzmann's constant. An upper limit for T_G is found by choosing the smallest reasonable value for ξ_0. Setting ξ_0 equal to the nearest-neighbor Ce-Ce distance of 4.581 Å, we find $T_G \sim 0.4$ mK for $\Delta C = 3.0 \times 10^{-2}$ J/cm^3 K. This value is so small that even if our estimate for T_G were low by an order of magnitude, critical fluctuations are probably still not important.

On the other hand, a low-temperature increase of C/T is typical for heavy-electron behavior. Above $T \sim 1.2$ K, the temperature dependence in $CePt_2Sn_2$ looks more logarithmic, and this continues up to ~ 3.8 K where a broad upturn in C starts to interfere. Even though a logarithmic singularity can be associated with critical phenomena, Rajan[11] demonstrated that the specific heat for a single Kondo impurity has an approximately logarithmic dependence over one decade of reduced temperature above T_K. Kondo-spin fluctuations above the transition also reduce the expected entropy below T_N by partially transforming the magnetic entropy into that of a heavy-mass state.[1]

The strongest evidence supporting a Kondo-enhanced specific heat is obtained when La is substituted for Ce, thereby suppressing the magnetic transition. Specific heat for $Ce_{0.8}La_{0.2}Pt_2Sn_2$ is also displayed in Fig. 2, and when C/T is normalized per mole Ce (the concentration of Ce was determined from the Curie constant), there is no significant change in C/T above $T \sim 0.9$ K, despite a reduction in T_N from 0.88 K to ~ 0.6 K.

Hence, C/T approaches 3.5 J/mole K^2 just above the phase transition, and despite the possible presence of critical fluctuations, most of the enhanced specific heat occurs because a heavy-electron state develops. From the rapid rise in the electronic contribution of the specific heat below 5 K, we estimate the Kondo temperature T_K to be on the order of 1 K. Evaluated at T_N, the single-impurity relation[5] $T_K\gamma = 0.68R$, where R is the gas constant, yields $T_K = 1.6$ K. The thermodynamic enhancement in this material is significantly larger than in the prototypical heavy-electron compounds $CeAl_3$ and $CeCu_6$ (Ref. 1) or in $CeCu_4Ga$,[12] which is also a Kondo-lattice antiferromagnet with $T_N = 0.7$ K and an enhanced C/T; to our knowledge, $CePt_2Sn_2$ is the heaviest electron system known. A smooth extrapolation of C/T from above T_N would yield a zero-temperature value equal to or greater than 10 J/mole K^2 if the ground-state symmetry were not broken. Magnetic transitions typically reduce the enhanced heat capacity because internal magnetic fields produced by the local-moment order partially suppress the Kondo resonance.[1] Evidence for this effect is seen in $CePt_2Sn_2$ where an extrapolation to zero temperature from below the transition gives a value close to zero, typical of cerium-based Kondo-lattice magnets.

Extrapolating χ^{-1} to $T \geq T_N$ gives $\chi(0.9$ K$) = 0.20$ emu/mole. The relative importance of many-body interactions on the susceptibility and the specific heat is reflected in the Wilson ratio[4] $R_W = (\pi^2 k_B^2/\mu_{\text{eff}}^2)\chi(0)/\gamma(0)$, where both the susceptibility χ and linear specific-heat coefficient γ are taken in the zero-temperature limit. To avoid the uncertainty introduced by magnetic order, we evaluated this ratio at $T = 0.9$ K $\sim T_N$ and find $R_W = 3.6$ for $\mu_{\text{eff}} = 1.85\mu_B$/Ce. If instead $\mu_{\text{eff}} = 2.59\mu_B$/Ce is used, then $R_W = 1.8$. These values of R_W are in the range of those found in U-based heavy-electron antiferromagnets where magnetic interactions enhance χ somewhat more than γ.

Because phonon contributions are important at higher temperatures, the specific heat of nonmagnetic $LaPt_2Sn_2$ (shown in the inset of Fig. 3) was also measured and subtracted from the high-temperature data for $CePt_2Sn_2$. The La analog should not contain any magnetic, enhanced electron, or crystal-field contributions to the heat capacity. Displayed in the main body of Fig. 3, a broad maximum is present in the subtracted data at $T \approx 18$ K which is qualitatively similar to a Schottky anomaly with a level splitting of ≈ 60 K. Even though quantitative fits with a two-level model[13] are poor, com-
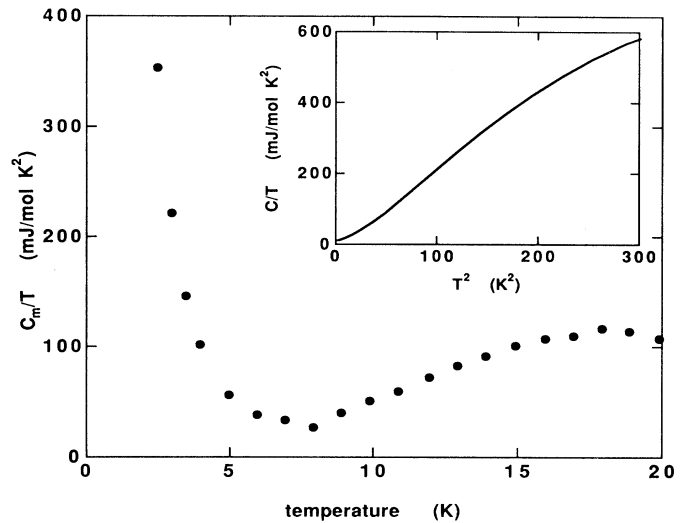

FIG. 3. Inset: C/T vs T^2 for $LaPt_2Sn_2$. Below 3 K, C/T is linear in T^2, but at higher temperatures, the dependence is no longer Debye-like. Similar curvature in C/T vs T^2 is found in the raw data for $CePt_2Sn_2$. The specific heat for $LaPt_2Sn_2$, which is dominated by phonons, was subtracted from the high-temperature results for $CePt_2Sn_2$ and plotted in the main body of the figure vs temperature.

plicated crystal-field effects, possibly combined with a Kondo effect on the first excited level[14] and some crystallographic disorder, may be responsible for this feature. At temperatures below a few degrees, the phonon-subtracted entropy builds up fairly quickly to a value of $\sim R \ln(2)$. Above $T \sim 4$ K, the entropy levels off somewhat, and it is $1.12R \ln(2)$ at $T = 8$ K (the minimum in C_m/T), implying that the system is in the lowest crystal-field doublet when the heavy-mass state develops. Eventually, the entropy begins to increase again in the region of the broad maximum in C_m/T; the additional 12% above $R \ln(2)$ at $T = 8$ K could easily be the low-temperature contribution from the $T \sim 18$ K Schottky anomaly.

The vibrational excitations for both the Ce and La analogs may also be unusual. A plot of C/T vs T^2 for $LaPt_2Sn_2$ is linear below $T \approx 3$ K. From the intercept and slope, we find $\gamma = 10$ mJ/mole K^2 and a Debye temperature of $T_D = 230$ K for $LaPt_2Sn_2$. As illustrated in the inset of Fig. 3, the specific heat no longer has a cubic temperature dependence at higher temperatures implying a non-Debye-like phonon spectrum. In terms of the Debye model, the deviations from $C \propto T^3$ are inconsistent with the low-temperature determination of T_D. Curvature is also seen in the data for $CePt_2Sn_2$ before the subtraction.

The rapid rise of C/T below ~ 5 K, the very large specific heat at $T \geq T_N$, and $\Theta' \geq T_N$ all imply that $T_K \sim T_N \sim 1$ K in $CePt_2Sn_2$. From the single-ion expression for the Kondo temperature $T_K = T_F \exp(-1/\rho|J|)$, where ρ is the density of states and J is the f-moment–conduction-electron exchange parameter, we

estimate the product $\rho|J|$ using the above value for T_K. Assuming a typical Fermi temperature of $T_F = 10^4$ K, we find $\rho|J| \sim 0.1$, suggesting that $CePt_2Sn_2$ falls in the weak-coupling limit of Doniach's Kondo-necklace phase diagram.[6] This relatively small value of $\rho|J|$ is compatible with a large unit-cell volume and a low T_N, since the strength of the RKKY interaction is proportional to ρJ^2. Although the Kondo-necklace model seems applicable to several CeM_2Si_2 antiferromagnets,[3,15] there is difficulty with this interpretation for $CePt_2Sn_2$. At small $\rho|J|$, RKKY interactions should dominate because they increase geometrically with $\rho|J|$, whereas Kondo-spin fluctuations increase exponentially. Thus, antiferromagnetic order should quench the development of a low-temperature heavy-mass state with T_N substantially larger than T_K. Even though this is generally the case with other Ce-based antiferromagnets, the observation of $T_K \sim T_N$ in $CePt_2Sn_2$ contradicts this fact. The very large thermodynamic enhancement in $CePt_2Sn_2$ is only possible if a Kondo ground state is at least partially established before magnetism ensues. It appears as though $CePt_2Sn_2$ is substantively different from previously studied Ce-based antiferromagnets, and it may be an extreme example of U-based heavy-fermion antiferromagnets where T_N is also $\sim T_K$, but with the energy scales for U compounds approximately 1 order of magnitude larger. A consistent theoretical interpretation of the magnetic ground state and its influence on the enhanced thermodynamic properties over the whole range of exchange parameters at finite temperature is lacking and would be very beneficial in understanding our results.

In summary, we find that even though $CePt_2Sn_2$ orders antiferromagnetically at $T_N \approx 0.88$ K, it still has the largest low-temperature specific heat of any known heavy-electron compound. A simple interpretation of our data suggests that both T_K and T_N are comparable, making $CePt_2Sn_2$ an ideal candidate for studying the complex competition between Kondo-spin fluctuations and RKKY interactions, including their role in producing heavy-electron ground states. Preliminary measurements indicate that other members of the CeM_2Sn_2 series exhibit similar properties, with most of them ordering magnetically below 2 K and possessing enhanced low-temperature specific heat.

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