Weak coupling magnetism in Ce$_4$Pt$_{12}$Sn$_{25}$: a small exchange limit in the Doniach phase diagram

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Abstract

Magnetic susceptibility, magnetization, specific heat, and electrical resistivity studies on single crystals of Ce$_4$Pt$_{12}$Sn$_{25}$ reveal an antiferromagnetic transition at $T_N = 0.19$ K, which develops from a paramagnetic state with a very large specific heat coefficient ($C/T$) of 14 J mol$^{-1}$ K$^{-2}$.Ce just above $T_N$. On the basis of its crystal structure and these measurements, we argue that a weak magnetic exchange interaction in Ce$_4$Pt$_{12}$Sn$_{25}$ is responsible for its low ordering temperature and a negligible Kondo-derived contribution to physical properties above $T_N$. The anomalous enhancement of specific heat above $T_N$ is suggested to be related, in part, to weak geometric frustration of $f$-moments in this compound.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Kondo-lattice systems have attracted interest due to the unusual and widely varying ground states that emerge from strong electronic correlations [1, 2]. The primary interactions in these systems are the Kondo coupling between a local moment and itinerant electrons [3] and the itinerant-electron mediated Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [4] between localized moments, both of which depend on the magnetic exchange $J$ between local spin and conduction electrons. The Kondo interaction, which grows exponentially with $J$, produces a non-magnetic singlet at sufficiently low temperatures, whereas, the RKKY interaction, which depends quadratically on $J$, promotes long-range magnetic order. By their natures, these two interactions compete with each other. Doniach has considered this competition as a function of $J$ for a one-dimensional Kondo necklace [5]. When $J$ is small, the intersite RKKY interaction dominates and the system orders magnetically (either antiferromagnetic or ferromagnetic ground state); but when $J$ is larger, magnetic order is suppressed and the system eventually enters a paramagnetic phase once Kondo-screening of the moments dominates. Between these extreme limits of $J$, the magnetic ordering temperature approaches zero, where non-Fermi-liquid behaviors and unconventional superconductivity often emerge [6]. Despite a variety of the ground states having been studied and a large number of different compounds having been reported to be Kondo-lattice systems, there have been few examples of the very small-$J$ limit. Here we report on the Kondo-lattice system Ce$_4$Pt$_{12}$Sn$_{25}$ that shows characteristics of weak Kondo and RKKY interactions: an antiferromagnetic transition at $\sim 0.19$ K, which is an unusually low temperature for a Ce-based Kondo lattice, and a negligible Kondo-derived contribution to specific heat or electrical resistivity above $T_N$.

2. Experimental details

Single crystals of Ce$_4$Pt$_{12}$Sn$_{25}$ were grown using excess Sn as a flux. The constituent elements were placed in an
alumina crucible and sealed in an evacuated quartz tube. The ampule was then heated to 1180°C, followed by slow cooling down to 500°C before spinning the quartz tube to separate the crystals from molten flux. Using a similar procedure, we also synthesized single crystals of the non-magnetic analog La₄Pt₁₂Sn₂₅ in order to compare it with Ce₄Pt₁₂Sn₂₅. Single crystal x-ray diffraction patterns were collected at room temperature using an R3m/V Siemens diffractometer, with Mo Ka radiation at λ = 0.71073 Å and with a graphite monochromator and a modified Enraf-Nonius low-temperature apparatus. The ψ-scan method was used to perform an empirical absorption correction. The structure was identified by direct methods and refined by the full-matrix least-squares method on F² (SHELXTL-97, Sheldrick 1990). Temperature-dependent dc magnetic susceptibility and field-dependent magnetization were measured with a Quantum Design MPMS. A standard lock-in technique was used to measure ac susceptibility from 17 mK to 2 K. Heat capacity, determined by a relaxation-time technique and heat pulse measurement, and four-probe electrical resistivity were measured to be 0.35 K in a Quantum Design PPMS and to 70 mK in a dilution refrigerator.

3. Results and discussion

Except for its crystal structure, first reported by Chafik et al [7], no physical properties of Ce₄Pt₁₂Sn₂₅ are known. Analysis of our x-ray diffraction data verifies that single crystals of Ce₄Pt₁₂Sn₂₅ form in a complex cubic structure with space group Im3, as found by Chafik et al, and no residual peaks in the refinement were present. Although the structure is cubic, Ce atoms occupy sites with three-fold point symmetry, which is expected to split the six-fold degenerate ground state of Ce⁵⁺ into three crystal-field doublets. As shown in figure 1, Ce sites, separated by a large distance of 6.14 Å, are surrounded by a cage of 6-Pt nearest neighbors (at ∼7–8 Å) and 12-Sn atoms (six at Sn2 and six at Sn3 positions), forming edge-sharing hexacapped cuboctahedral cages. At a Ce-Sn3 separation of ∼3.44 Å, the six Sn3 sites are comparable to Pt atoms in their distance from Ce. As shown by Chafik et al, thermal vibrations of the Sn3 atoms are large and anisotropic, giving rise to a static deformation with two statistically significant sites called Sn3 and Sn3', each about 50% deficient. This crystal structure has the same space group as filled skutterudites; however, the rare-earth ion in skutterudites sits at the 2a site, forming a body-centered cubic environment, but Ce in Ce₄Pt₁₂Sn₂₅ is located at the 8c site that is occupied by transition-metal atoms in the skutterudite structure. As a result, the Ce site in Ce₄Pt₁₂Sn₂₅ (T = Fe, Ru, Os; Pn = P, As, Sb) skutterudites is surrounded by 12 Pnicosahedral cages that are not shared by any other Ce atoms [8]. In Ce₄Pt₁₂Sn₂₅, 6-Pt and 12-Sn hexacapped-cuboctahedral cages are shared by other Ce atoms. Furthermore, the distance from Sn2 to Ce in Ce₄Pt₁₂Sn₂₅ is 3.776 Å, a rather large distance not favorable for strong f–p hybridization. Thus, the number of effective atoms around Ce is six per each Ce atom. Though the Ce–Ce distance in skutterudites is somewhat larger (∼7–8 Å) than in Ce₄Pt₁₂Sn₂₅, the smaller number of effective atoms around each Ce site in Ce₄Pt₁₂Sn₂₅ might be expected to lead to weaker f–p hybridization. Other materials with similarly large Ce–Ce distance (∼5.6 Å) include CeNi₃X₄ (X = Si, Ge). These compounds have strong hybridization between Ce-4f and conduction electrons from Ni and X ions, like Ce-skutterudites, where this hybridization dominates over the RKKY interaction due to large distances between Ce ions and leads to single-ion Kondo behavior [9].

The magnetic susceptibility, $\chi = M/H$, as a function of temperature, plotted in figure 2(a), appears to follow a Curie–Weiss law above 250 K with an effective moment of 2.2 $\mu_B$/Ce, which is smaller than expected (2.54 $\mu_B$/Ce) for the full Hund’s rule degeneracy of Ce⁵⁺. As discussed below, this smaller effective moment probably is the result of large crystal-field splitting of the $J = 5/2$ manifold. The Curie–Weiss temperature is negative with an absolute value of ∼6 K, suggesting weak antiferromagnetic exchange even at high temperatures. As shown in the inset of figure 2(a), the susceptibility again exhibits Curie–Weiss behavior below ∼4 K, but with a smaller effective moment (1.15 $\mu_B$/Ce) and a smaller Curie–Weiss temperature of ∼0.4 K, which indicates very weak antiferromagnetic coupling of local moments to one another and to itinerant electrons. Field-dependent magnetization data at 2 K are plotted in figure 2(b). These data have been fitted by a Brillouin function, assuming a crystal-field doublet ground state with $g|J_z|=0.675 \mu_B$, which most likely implies a $\Gamma_7$ doublet ground state assuming $g = 6/7$. To track the magnetic response below 1.8 K, ac magnetic susceptibility was measured, with results presented in figure 2(c). Although somewhat noisy, these data increase with decreasing temperature below 2 K, as expected for a Curie–Weiss paramagnetic state, and exhibit a sharp kink at 0.19 K that is followed by a decrease at lower temperatures. This drop in susceptibility below 0.19 K rules out the ferromagnetic nature of this transition, but is consistent with an antiferromagnetic transition, as also indicated from the small, negative Weiss temperature inferred from the dc susceptibility.

Specific heat measurements support conclusions drawn from magnetic susceptibility and magnetization measure-
magnets. Figure 3 shows the magnetic contribution $C_{mag}$ to the specific heat of Ce$_4$Pt$_{12}$Sn$_{25}$, obtained by subtracting the specific heat of non-magnetic La$_4$Pt$_{12}$Sn$_{25}$ from the total specific heat of Ce$_4$Pt$_{12}$Sn$_{25}$. A broad peak in $C_{mag}$ near 90 K is described reasonably well by Schottky contributions from two crystal-field doublets, separated from a ground state doublet by 199 and 247 K. The inverse susceptibility starts to deviate from linear behavior below about 250 K (see figure 2), consistent with this estimate of crystal-field excitation energies. The existence of crystal fields, as well as the high-temperature effective moment for Ce$_4$Pt$_{12}$Sn$_{25}$, suggests a well-localized Ce$^{3+}$ state.

As shown in the inset of figure 3, there is a well-defined specific heat anomaly at 0.19 K, confirming the transition observed in the ac susceptibility. The features at 0.19 K, suggesting an antiferromagnetic magnon contribution. A magnetic field-induced decrease of the temperature at which an anomaly develops (data not shown) also supports the interpretation that the 0.19 K transition is into an antiferromagnetic state. Also shown in the inset is the evolution of magnetic entropy as a function of temperature. An entropy of $R \ln 2$ is recovered at ~2 K, consistent with antiferromagnetic order in a crystal-field doublet; however, only about 50% of $R \ln 2$ appears below $T_N$, with the remaining entropy reflected in the extremely large $C/T$ that develops between ~2 K and $T_N$. Just above $T_N$, $C/T$ reaches 14 J mol$^{-1}$ K$^{-2}$, before it jumps to ~45 J mol$^{-1}$ K$^{-2}$ at 0.19 K. With the complex, three-dimensional structure of Ce$_4$Pt$_{12}$Sn$_{25}$, this large $C/T$ extending from $T_N$ to ~10$T_N$ cannot be due to critical fluctuations associated with the antiferromagnetic order. Numerical calculations for a 3D Heisenberg model, which fits reasonably well the shape of the data irrespective of the choice of $T_N$, shows that the calculated temperature dependence does not describe the data. Indeed, the theoretical form alone cannot account for the data irrespective of the choice of $T_N$ [11].

Moreover, the large specific heat above $T_N$ does not increase with increasing.

Figure 2. Magnetic susceptibility and magnetization of Ce$_4$Pt$_{12}$Sn$_{25}$. The upper panel is a plot of the dc susceptibility, measured in a field of 1 kOe, as a function of temperature. The inverse susceptibility over the whole temperature range and at low temperatures is shown in the insets. The middle panel is a plot of magnetization versus field measured at 2 K. The solid line is a fit to a Brillouin function as described in the text. The bottom panel shows ac magnetic susceptibility at low temperatures where there is a clear transition at 0.19 K.

Figure 3. Magnetic contribution to the specific heat of Ce$_4$Pt$_{12}$Sn$_{25}$ obtained by subtracting the specific heat of non-magnetic La$_4$Pt$_{12}$Sn$_{25}$. The solid curve is a fit to the Schottky contributions from crystal-field excitations, as described in the text. The inset is a plot of $C/T$ and magnetic entropy as a function of temperature. A second-order phase transition into an antiferromagnetic state is clear at 0.19 K. Below $T_N$, $C/T$ is described well by $C/T = \gamma + AT^2$, with $\gamma = 0.45$ J mol$^{-1}$ K$^{-2}$ and $A = 1430$ J mol$^{-1}$ K$^{-3}$, as discussed in the text. The dashed curve is calculated for a spin-1/2 Kondo impurity.
magnetic field until the magnetic transition is fully suppressed, which is contrary to expectations of Kondo-impurity physics.

A fit to the specific heat below \( T_N \) gives a substantial \( T \)-linear term, \( C = \gamma T \) where \( \gamma \approx 0.45(\pm 0.24) \) J mol\(^{-1}\) K\(^{-2}\). This value of \( \gamma \) is an upper limit, and its precise value is subject to some uncertainty because of experimental constraints imposed by the huge value of \( C/T \) at \( T_N \), which is at least 100 times larger. Irrespective of its precise value, from our experiments, it is not possible to determine whether this \( T \)-linear term reflects the presence of Kondo-derived heavy quasiparticles or whether it has some other origin. We return to this in a discussion of the electrical resistivity.

With a substantial role of the Kondo effect in question, we consider other sources for such a large specific heat over a protracted temperature range above \( T_N \). Intrinsic disorder from shared Sn3 and Sn3\(^{\prime}\) sites might play a role, but the sharp jump in specific heat at \( T_N \) does not support this possibility. Alternatively, it could be that the Ce moment is geometrically frustrated by the three-fold point symmetry of the Ce site. With this frustration-prone symmetry and Ce’s coordination by six nearest and 12 next nearest neighbors, the coupling between nearest and next nearest neighbors could lead to frustration that is relieved only below \( T_N \). In this scenario, however, we might expect \( T_N \) to be much less than the low-temperature Curie–Weiss scale, and the Curie–Weiss scale to be on the order of 2 K or higher (where \( C/T \) starts to grow dramatically), but neither of these conditions is observed. Yet another possibility is that the increase in \( C/T \) below 2 K is due to the development of short-range correlations among the Ce moments; however, why correlations should develop on a scale ten times \( T_N \) in this cubic compound is not obvious.

Figure 4 shows the temperature dependence of the electrical resistivity of Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\) and La\(_4\)Pt\(_{12}\)Sn\(_{25}\). The resistivity is metallic and comparable for both compounds over the entire temperature range, and the ratio of resistivities at 300 and 2 K (RRR) is about 2.5–3.8, depending on the sample. The small RRR may be a consequence of structural disorder in Sn3 sites as discussed earlier. We note a barely detectable kink in the resistivity of Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\) near 170 K, where there also is a weak anomaly in specific heat but no feature in magnetic susceptibility. We tentatively attribute this kink to a still unknown change in crystal structure.

The magnetic resistivity of Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\), obtained by subtracting the resistivity of La\(_4\)Pt\(_{12}\)Sn\(_{25}\), is presented in the lower inset of figure 4. A maximum in the magnetic resistivity near 120 K is consistent with scattering off excited crystal-field levels, possibly combined with some Kondo-like scattering in the excited levels [12], but there is no logarithmic dependence or a resistivity maximum at lower temperatures. The absence at lower temperatures of these characteristic signatures for Kondo-lattice behavior indicates that a Kondo effect, if present at low temperatures, should have a temperature scale on the order of \( T_N \) or lower. On the other hand, as shown in the upper inset of figure 4, the resistivity of Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\) below \( T_N \) is well-described by \( \rho(T) = \rho_0 + AT^2 + BT^5 \). The \( T^5 \) term is typical of scattering by antiferromagnetic spin waves, and the large \( T^2 \) coefficient, \( A = 11 \) \( \mu \)\( \Omega \) cm K\(^{-2}\), is characteristic of heavy-fermion behavior in a Kondo lattice. In the Néel state, the ratio \( A/\gamma^2 \) is \( > 5 \times 10^{-5} \) \( \mu \)\( \Omega \) cm (K mol mJ\(^{-1}\))^\(^{-2}\), a value at least five times larger than the typical Kadowaki–Woods ratio found in Ce-based heavy-fermion systems [13]. In part, an enhanced Kadowaki–Woods ratio could arise from the small Fermi momentum of Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\), discussed below, but being inconclusive, it still leaves open the question of whether A and \( \gamma \) reflect heavy-fermion character.

There is no \( T^2 \) dependence to the resistivity above \( T_N \); on the contrary, the resistivity decreases weakly and sublinearly with decreasing temperature below \( \sim 1 \) K, as shown in the upper inset of figure 4. The temperature of the onset of the decreasing resistivity correlates with the beginning of the development of the large \( C/T \) above \( T_N \). A reasonable interpretation of this relationship is that the decrease in \( \rho(T) \) reflects a decrease in spin-disorder scattering due to the development of antiferromagnetic correlations among Ce moments that, in turn, are responsible for the increasing \( C/T \) as \( T_N \) is approached. Though neither frustration, Kondo correlations, nor antiferromagnetic correlations can by itself explain all experimental observations, we suggest a combination of a small magnetic exchange between Ce moments, between Ce moments and spins of itinerant electrons, and weak frustration is responsible for the extended temperature range over which these magnetic correlations persist.

We can estimate the scale of the magnetic exchange in Ce\(_4\)Pt\(_{12}\)Sn\(_{25}\) as follows. From the discussion above, we assume that the Kondo-impurity scale is 0.26 K or less. This scale

\[
\frac{A}{\gamma^2} > 5 \times 10^{-5} \text{ mJ} \text{ K}^{-1} \text{ mol}^{-1}.
\]

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is given by \( T_k \approx \left[ 1/N_0 \right] \exp\left(-1/(2JN_0)\right) \), where \( N_0 \) is the unrenormalized density of electronic states that we obtain from the Sommerfeld coefficient \( \gamma = 5 \) mJ mol\(^{-1}\) K\(^{-2}\) of isoelectronic, non-magnetic \( \text{La}_4\text{Pt}_{12}\text{Sn}_{25} \). Assuming \( T_k = 0.26 \) K, this expression gives \( N_0J \approx 0.05 \), which, indeed, puts \( \text{Ce}_4\text{Pt}_{12}\text{Sn}_{25} \) in the very small-\( J \) limit of the Doniach model [14]. Further, a small RKKY scale, and hence \( T_N \), in \( \text{Ce}_4\text{Pt}_{12}\text{Sn}_{25} \) is due in part to its small Fermi momentum. Again using free electron relations, we estimate \( k_F \approx 0.09 \) \( \text{Å}^{-1} \) from the Sommerfeld coefficient of \( \text{La}_4\text{Pt}_{12}\text{Sn}_{25} \). With a Ce-Ce spacing of \( d = 6.14 \) \( \text{Å} \) in \( \text{Ce}_4\text{Pt}_{12}\text{Sn}_{25} \), \( 2k_Fd \) is somewhat smaller than \( \pi/2 \), where an oscillation in the RKKY interaction crosses zero. This estimate of \( 2k_Fd \) would imply that RKKY exchange in \( \text{Ce}_4\text{Pt}_{12}\text{Sn}_{25} \) is weakly ferromagnetic, but given the crudeness of our estimate, it is not inconsistent with a very small RKKY exchange and the small \( T_N \) that is observed.

We also can compare \( T_k \) estimated above with a molecular field calculation for a spin-1/2 resonant level model [15]. With the experimentally observed specific heat jump (\( \Delta C_{\text{mag}} \approx 5.2 \) J mol\(^{-1}\) K\(^{-2}\)) at \( T_N \), this model gives a ratio of \( T_k/T_N \approx 1 \), which is consistent with our previous estimates and the expectation of small Kondo and magnetic interaction energy scales.

4. Summary

In summary, \( \text{Ce}_4\text{Pt}_{12}\text{Sn}_{25} \) appears to be one of the few examples of a very small-\( J \) Kondo-lattice system. Most interesting is the very large \( C/T \) that develops above \( T_N \) and that represents 50% of \( R \ln 2 \) entropy at low temperatures. The origin of this large \( C/T \) does not have an obvious simple explanation nor is it clear that this is characteristic of all Kondo-lattices in the small-\( J \) limit. This behavior is not found in compounds with similar but non-frustrated structures, such as skutterudites. On the basis of electrical resistivity, specific heat, and magnetic susceptibility measurements, however, we suggest that it arises from the interplay among weak frustration, the development of short-range magnetic correlations, and a small magnetic exchange interaction between Ce moments and between Ce moments and spins of itinerant electrons. Neutron scattering and nuclear magnetic resonance (NMR) studies would be useful in resolving this interplay. We also find evidence for a structural transition near 170 K that might influence the interplay.

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