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Authors
Beyermann, WP
Hundley, MF
Canfield, PC
et al.

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Antiferromagnetism and enhanced specific heat in CeM_2Sn_2 (M = Ni, Ir, Cu, Rh, Pd and Pt)

W.P. Beyermann[a], M.F. Hundley[a], P.C. Canfield[a], C. Godart[b], M. Selsane[b], Z. Fisk[a], J.L. Smith[a] and J.D. Thompson[a]

[a]*Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[b]*C.N.R.S., UPR 209, Place A. Briand, F92190, Meudon, France*

Specific heat, DC susceptibility, and resistivity measurements on annealed, polycrystalline samples of CeM_2Sn_2, where M = Ni, Ir, Cu, Rh, Pd, or Pt, indicate that each of these compounds orders antiferromagnetically with transition temperatures ranging from $T_N = 4.1$ to ≈ 0.5 K. All these materials have significant enhancements of the specific heat just before the transition, which can be as large as ~ 3.5 J/mol K^2 in some cases. Provided the enhanced heat capacities above T_N are associated with large effective masses, the anomalously low ordering temperature and the very large C/T suggest that T_N and the Kondo temperature T_K are comparable, making these materials particularly attractive for studying the interplay between these competing interactions. The susceptibility for each member of the series except M = Ir follows a Curie–Weiss behavior with a high-temperature effective moment $\mu_{eff} \sim 2.5\mu_B$/Ce and a small negative paramagnetic Curie temperature.

1. Introduction

Of the cerium-based antiferromagnets, remarkably few [1] have appreciably enhanced electronic specific heats (i.e., $\gamma > 100$ mJ/mol K^2) above their Néel temperatures T_N, which are typically close to 10 K. Generally, the explanation [2–4] of this observation is that the internal magnetic field produced by antiferromagnetic order suppresses the development of the many-body interaction (Kondo-spin fluctuations) responsible for the large γ. Among the magnets studied most extensively are those in the series CeM_2Si_2, where M is either a 4d or 5d transition element. Physical properties such as the Néel temperature [5–6], the temperature dependent resistivity [7, 8], and the neutron quasi-elastic line width [5, 9] vary with M and the unit-cell volume, and appear to be qualitatively interpretable in terms of Doniach's Kondo-necklace model [10, 11], which examines the competition between Kondo and Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions.

2. Results and discussion

Recently, a new series CeM_2Sn_2, where M = Ni, Ir, Cu, Rh, Pd, or Pt, was reported by Selsane et al. [12]. This new compound crystallizes in the tetragonal $CaBe_2Ge_2$-type structure, which is closely related to the structure formed by the CeM_2Si_2 series. The lattice parameters and unit-cell volumes of unannealed arc-melted samples are given in table 1, and the nearest-neighbor Ce–Ce distance is equivalent to the a axis length. Initially, the measured resistivities were practically independent of temperature, which is indicative of substantial crystallographic disorder. Consequently, all the samples where wrapped in Ta foil, sealed under vacuum in a quartz tube, and annealed at 800°C for three days before being measured. Two representative temperature-dependent resistivities are shown in fig. 1. Both the Ir and Ni compounds exhibit a low-temperature maximum, typical of Ce-based heavy-electron systems; whereas, the resistivities of the others monotoni-

Table 1.
The structure of unannealed CeM_2Sn_2, where M = Ni, Ir, Cu, Rh, Pd, or Pt, is the primitive tetragonal $CaBe_2Ge_2$-type with lattice constants and unit-cell volumes listed in the table. The nearest-neighbor Ce–Ce spacing is equivalent to a.

	a (Å)	c (Å)	volume (Å^3)
$CeNi_2Sn_2$	4.409	10.110	196.53
$CeIr_2Sn_2$	4.499	10.044	203.30
$CeCu_2Sn_2$	4.433	10.355	203.49
$CeRh_2Sn_2$	4.472	10.561	211.21
$CePd_2Sn_2$	4.554	10.483	217.41
$CePt_2Sn_2$	4.581	10.385	217.94

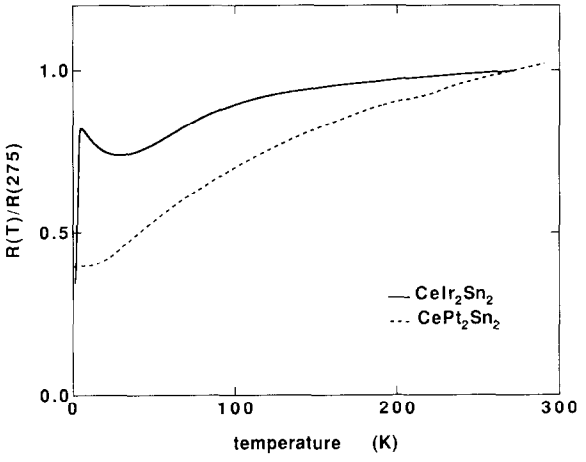

Fig. 1. The 4-probe resistivity vs. temperature for $CeIr_2Sn_2$ and $CePt_2Sn_2$. The data are normalized to the value at $T = 275$ K. $CeIr_2Sn_2$ shows a low-temperature maximum similar to $CeNi_2Sn_2$ followed by a sharp drop associated with the magnetic transition. The Cu, Pd, and Rh analogs have temperature dependent resistivities more characteristic of that displayed for $CePt_2Sn_2$.

cally decrease with decreasing temperature. Determining absolute values for the resistivity was not possible because of geometric irregularities in the samples, but the magnitudes at room temperature are estimated to be of the order of a few 100 μΩ cm. The sharp drop at low temperatures in $CeIr_2Sn_2$ is probably due to a loss of magnetic scattering. This is the only member of the series where a resistive anomaly coincides with the magnetic phase transition found in the specific heat. Since the rest of the series orders magnetically at lower temperatures, these features may be masked by disorder not removed by the annealing process.

Measurements of the DC magnetic susceptibility were made in a field of 0.1 T for temperatures between 2 and 350 K. All the compounds in the series, except Ir, show Curie–Weiss behavior at high temperatures with an effective moment μ_{eff} close to the Hund's rule value for Ce^{3+} and a small negative paramagnetic Curie temperature Θ. These parameters are listed in table 2. At low temperatures a reduced moment is observed, suggesting low-lying crystal fields are present. The inverse susceptibility of $CeIr_2Sn_2$ is concave downward over the entire temperature range, which contrasts with the Curie–Weiss behavior found in an unannealed sample.

The specific heat was measured on samples weighing only a few milligrams. A thermal relaxation technique [13] was employed to acquire the data from $T = 0.32$ K to 20 K, and τ_2 effects resulting from a significant thermal resistance between the sample and the addenda were corrected before presenting the results in figs. 2 and 3. Displayed as C/T versus temperature (note the different scales), each sample shows a low-temperature anomaly which is interpreted as an antiferromagnetic transition because measurements of the AC and DC susceptibilities find a broad maximum in this temperature range. Also, the character of these anomalies varies somewhat for the different compounds. As the temperature is lowered for the Pt and Ir materials,

Table 2.
The magnetic properties of annealed CeM_2Sn_2, where M = Ni, Ir, Cu, Rh, Pd, or Pt. Listed below are the Néel temperature, T_N, the high-temperature effective moment, μ_{eff}, and the high-temperature paramagnetic Curie temperature. The final column lists the electron configuration of the bare M atom.

	T_N (K)	μ_{eff} (μ_B/Ce)	Θ (K)	Electron config.
$CeNi_2Sn_2$	1.8	2.64	−58.4	$3d^8 4s^2$
$CeIr_2Sn_2$	4.1	–	–	$4f^{14} 5d^7 6s^2$
$CeCu_2Sn_2$	1.6	2.49	−13.7	$3d^{10} 4s^1$
$CeRh_2Sn_2$	0.47	2.53	−13.2	$4d^8 5s^1$
$CePd_2Sn_2$	0.50	2.50	−6.0	$4d^{10}$
$CePt_2Sn_2$	0.88	2.59	−25.1	$4f^{14} 5d^9 6s^1$

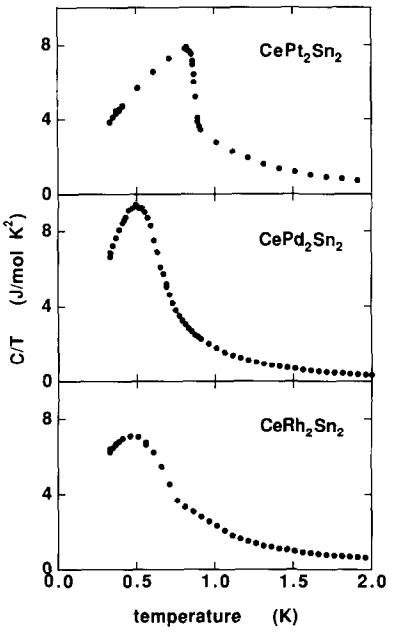

Fig. 2. The temperature dependence of C/T from $T = 0.32$ to 2.0 K for $CePt_2Sn_2$, $CePd_2Sn_2$, and $CeRh_2Sn_2$. The data are normalized per mole of Ce. The large peak in C/T, which occurs below 1 K in these three members of the series, signals an antiferromagnetic phase transition. Notice that for Pd and Rh the transitions are very rounded.

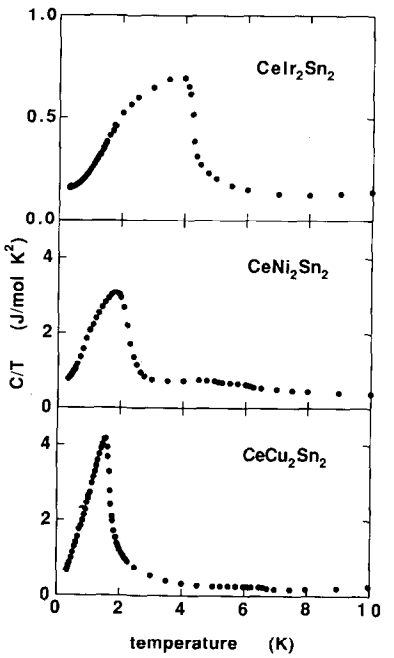

Fig. 3. C/T vs. temperature from $T = 0.32$ to 10 K for $CeIr_2Sn_2$, $CeNi_2Sn_2$, and $CeCu_2Sn_2$. The data are normalized per mole of Ce. Antiferromagnetic phase transitions are responsible for the large features occurring between 4.2 and 1.5 K in the three materials. The smaller anomalies at higher temperatures in $CeNi_2Sn_2$ and $CeCu_2Sn_2$ are probably associated with a small ferromagnetic impurity phase detected in magnetization measurements. Notice the smaller vertical scale for $CeIr_2Sn_2$.

there is a rather precipitous increase in C/T, which we define as T_N, followed by a gradual decline. This feature is very reminiscent of a mean-field second-order phase transition where critical-point fluctuations are not very important. Qualitatively different from this anomaly is the very rounded transition in the Pd and Rh compounds, and perhaps crystallographic disorder is the source of this dissimilarity. The broad nature of the feature in the second two examples makes a precise determination of the transition temperature impossible, so we choose to define T_N as the maximum in C/T. Finally, exhibiting intermediate characteristics, are the compounds $CeNi_2Sn_2$ and $CeCu_2Sn_2$. Below the transition, the specific heats of the Cu, Pt, and Pd materials seem to extrapolate to zero in the zero temperature limit, while the Ir and Ni members of the series appear to have finite intercepts. It is difficult to predict what occurs in $CeRh_2Sn_2$ because of the smeared low-temperature transition.

We list the Néel temperatures for the whole series in table 2, and notice that there is no strong correlation between T_N and the unit cell volume.

Quite evident is the pronounced increase in C/T as the temperature is decreased from above the transition. For $CePt_2Sn_2$, the electronic specific heat coefficient γ is strongly temperature dependent in this range and approximately equal to 3.5 J/mol K^2 just above T_N. Critical point fluctuations [14] could potentially explain the enhancements in C/T; however, a rudimentary analysis of the temperature dependence close to T_N, along with an estimate of the size of the critical region based on the Ginzburg criterion, seem to indicate that this explanation is less likely than a density of states effect. If a large electronic effective mass proves responsible for

the increased heat capacity, these materials would be among the heaviest ever observed. From considering both where C/T rises and the single-ion Kondo relation $\gamma T_K = R \ln 2$, we estimate that the Kondo temperature T_K and T_N are comparable.

Provided the interpretation that the large low-temperature upturn in C/T is a result of a Kondo renormalized effective mass, several interesting conclusions can be drawn from our observations. First, it seems as though T_K and T_N are comparable, and the magnitude of these quantities varies in the different materials. Secondly, these characteristic temperatures are very low, implying that $|J|\rho$, where J is the f moment conduction–electron exchange constant and ρ is the density of states, is also small. In this limit, one would expect RKKY interactions to dominate and quench the development of a heavy-mass state at low temperatures. Together, these conclusions point to the inadequacy of Doniach's model in fully explaining the competition between RKKY interactions and Kondo-spin fluctuations in CeM_2Sn_2. We suggest that the CeM_2Sn_2 series may be an ideal example for studying and understanding this competition, and these materials could be the first example of a Ce analog to the U-based heavy-electron antiferromagnets where T_K and T_N are also comparable, but an order of magnitude larger than in the CeM_2Sn_2 system.

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