Competing interactions in the heavy-electron antiferromagnets CeM_2Sn_2 (M = Ni, Ir, Cu, Rh, Pd, and Pt)

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(Received 26 December 1990)

Specific-heat, magnetic-susceptibility, and resistivity measurements on annealed polycrystalline samples of CeM_2Sn_2, with M = Ni, Ir, Cu, Rh, Pd, and Pt, indicate that each of these compounds orders antiferromagnetically at Néel temperatures T_N between ~ 0.5 and 4.2 K. Just above T_N, all these materials have a significant enhancement of their electronic specific heat, which can be as large as 3–4 J/mol K^2. We discuss the role of critical fluctuations on the specific heat and argue that the enhancement is associated with a large effective mass and not fluctuations. The anomalously low ordering temperatures and very large electronic specific heat suggest that T_N and the Kondo temperature T_K are comparable, making these materials particularly attractive for studying the competition between Kondo and Ruderman-Kittel-Kasuya-Yosida interactions. Measurements of the pressure dependence of T_N in $CeIr_2Sn_2$ were performed to explore this competition, which is discussed in terms of Doniach's Kondo-necklace model.

INTRODUCTION

Of the cerium-based antiferromagnets, remarkably few 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. The lack of heavy-electron behavior, characterized by low-temperature γ values approaching 1000 mJ/mol K^2, in these antiferromagnets may be explained by observing that the very large electronic specific heat in heavy-electron systems only begins to develop typically at temperatures below about 10 K and in these magnets the internal magnetic field produced by antiferromagnetic order suppresses the development of the many-body interaction (Kondo spin fluctuations) responsible for the large γ.[1] 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, the temperature dependent resistivity, their pressure dependence,[2] and the neutron quasielastic linewidth[3,4] vary with M and the unit cell volume, and appear to be qualitatively interpretable in terms of Doniach's Kondo-necklace model,[5] which examines the competition between Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions.

Recently, a series given by CeM_2Sn_2, where M is Ni, Ir, Cu, Rh, Pd, or Pt, was reported by Selsane *et al.*[6] As-prepared compounds crystallize in the tetragonal $CaBe_2Ge_2$-type structure which is closely related to the structure formed by the CeM_2Si_2 series. Although both structures are tetragonal, the $CaBe_2Ge_2$ type is primitive ($P4/nmm$), whereas the $ThCr_2Si_2$ type, in which all but one of the CeM_2Si_2 compounds form,[7] is body centered ($I4/mmm$). Compared to the CeM_2Si_2 compounds, relatively little is known about the physical properties of the CeM_2Sn_2 series. CeL_{III} x-ray absorption measurements on polycrystalline samples, as prepared[6] or annealed for periods of two to three days at 800 °C in the case of Ni,[8] show that Ce is trivalent or nearly so in the whole series, consistent with the reported[6] effective magnetic moments that are close to those for Ce^{3+} ($\mu_{eff} = 2.54\mu_B$/Ce). Only $CeNi_2Sn_2$ has been studied in greater detail. Magnetic susceptibility and resistivity measurements on single crystals of $CeNi_2Sn_2$ show that both properties are anisotropic,[9] as expected from the structure. The anisotropic susceptibility can be fit to a Curie-Weiss form, provided that the $J = 5/2$ manifold is crystal-field split into a ground state doublet and higher lying doublets at 17.2 and 218 K above the ground state. The temperature dependent resistivities parallel and perpendicular to the tetragonal c axis are similar, being approximately linear in T above ~ 50 K, with a maximum near 7 K and a sharp decrease at 2.1 K, signaling the onset of antiferromagnetic order at $T_N = 1.8$ K determined by specific heat measurements on a polycrystalline sample. Above T_N, the electronic contribution to the specific heat is rather large, $\gamma \equiv C/T \sim 0.6$ J/mol K^2, indicating that $CeNi_2Sn_2$ is a heavy-electron antiferromagnet.[9] To investigate the generality of behavior shown by $CeNi_2Sn_2$, we have measured the specific heat, magnetic susceptibility and electrical resistance across the CeM_2Sn_2 series. We find that all order antiferromagnetically at low temperatures and

have substantially enhanced C/T, making these interesting candidates for studying the competition between Kondo and RKKY interactions.

EXPERIMENTAL

Polycrystalline samples were prepared by arc melting on a water-cooled copper hearth in an argon atmosphere. Less than 1% weight loss occurred during the melting process. Metallographic, x-ray and microprobe investigations confirmed the samples to be single phase and close to stoichiometry, with evidence for a general slight substoichiometry in the M element by $\sim 2.5\%$. Details of the structural parameters of unannealed samples are given in Ref. 6 and their unit cell volumes are listed in Table I. Four-probe ac resistance measurements on as-prepared samples gave resistivities that were essentially temperature independent for all compounds, indicating substantial crystallographic disorder. Consequently, all samples were wrapped in Ta foil, sealed under vacuum in a quartz tube and annealed at 800 °C for three days. Annealing increased the resistance ratio between room temperature and 4 K from about unity to around 2.5 Re-examination of annealed $CePt_2Sn_2$ and $LaPt_2Sn_2$ by x-ray analysis revealed a slight monoclinic distortion of the $CaBe_2Ge_2$ structure and evidence for superlattice lines at twice the unit cell parameters, which was verified by transmission electron microscopy. We believe that this arises from a glide of atom-planes and/or ordering of M-atom vacancies between two basic neighboring cells. X-ray line profile examination before and after annealing shows evidence of the proximity of as-prepared samples to this structural change which could be at least partially responsible for their resistance ratio being close to one. We also note that evidence for a monoclinic distortion of $CeNi_2Sn_2$ annealed at 700 °C has been reported,[9] so that this is probably a general characteristic of CeM_2Sn_2 compounds; although, further work is needed to confirm this speculation.

Specific heat was determined on milligram quantities of annealed samples using a thermal relaxation technique over the temperature range of 0.32 to 20 K. In some cases, a second relaxation time τ_2, arising from thermal resistance between the sample and its platform, was detected. In all cases, τ_2 effects were corrected for in calculating the specific heat. The dc magnetic susceptibility was measured between 2 and 350 K using a Quantum Design SQUID magnetometer with an applied field of 1 kOe. Between 0.35 and 1 K, the susceptibility was determined with a conventional ac bridge technique.

TABLE I. The unit cell volume V, Néel temperature T_N, as defined in the text, and entropy S calculated from the area under a smooth extrapolation of C/T vs T from T_N to zero temperature for the CeM_2Sn_2 series.

M	V (Å^3)	T_N (K)	$S(Rln2)$
Ni	196.53	1.8	0.56
Ir	203.30	4.1	0.33
Cu	203.49	1.6	0.57
Rh	211.21	0.47	0.42
Pd	217.41	0.50	0.46
Pt	217.94	0.88	0.68

RESULTS

We show in Figs. 1 and 2 the low-temperature specific heat divided by temperature versus temperature for the six compounds in this series. Each sample shows an anomaly associated with antiferromagnetic order, which is inferred from a maximum in the magnetic susceptibility in the same temperature range as the anomaly. The character of these anomalies varies among the different compounds. As the temperature is lowered for the Pt and Ir materials, there is a rather precipitous increase in C/T, which we define as T_N, followed by a gradual decline. This feature in 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 residual 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 arbitrarily define T_N as the maximum in C/T. Finally, exhibiting intermediate characteristics are the compounds $CeNi_2Sn_2$ and $CeCu_2Sn_2$.

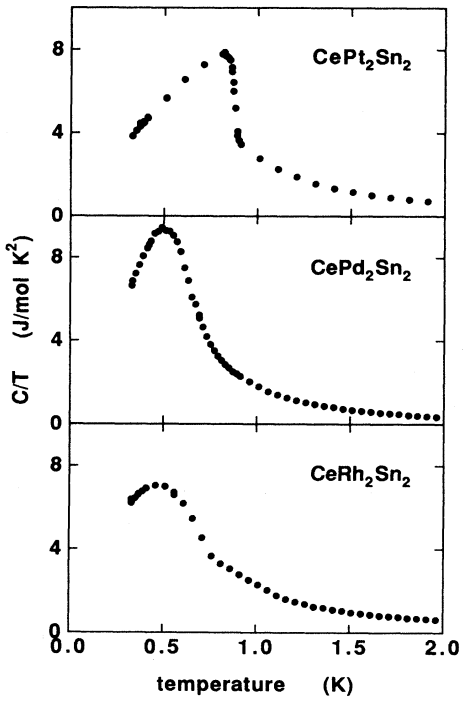

FIG. 1. The temperature dependence of C/T from $T=0.32$ K to 2.0 K for $CePt_2Sn_2$, $CePd_2Sn_2$, and $CeRh_2Sn_2$. The data are normalized per mole of Ce. The large peak in C/T, which occurs below 1 K in these three members of the series, signals an antiferromagnetic phase transition. Notice that for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

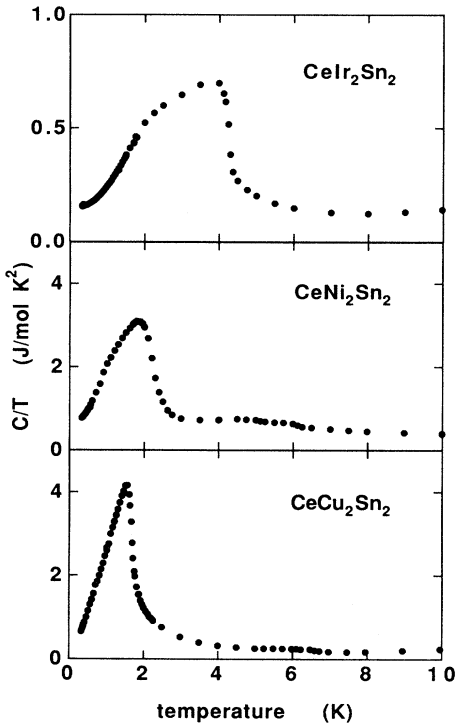

FIG. 2. C/T versus temperature from $T=0.32$ K to 10 K for $CeIr_2Sn_2$, $CeNi_2Sn_2$, and $CeCu_2Sn_2$. The data are normalized per mole of Ce. Antiferromagnetic phase transitions are responsible for the large features occurring between 4.2 and 1.5 K in the three materials. The smaller anomalies at 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 $CeIr_2Sn_2$.

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 transition. We list the Néel temperatures, defined as mentioned above, and entropy generated up to T_N for the whole series in Table I, and notice that there is no strong correlation between T_N and the unit cell volume; although, caution is advised in a quantitative comparison because of the arbitrariness in defining T_N and because cell volumes are those for the tetragonal as-prepared compounds. (The cell volume of a three-day annealed Pt sample is $\lesssim 1\%$ larger than given in Table I.)

Quite evident in these data is the pronounced increase in C/T as the temperature is decreased toward the transition. For $CePt_2Sn_2$, the electronic specific heat coefficient γ is strongly temperature dependent in this range and approximately 3.5 J/mol K^2 just above T_N. As shall be argued, we believe on the basis of both theory and experiment that this very large value of γ arises from a many-body mass renormalization and is not influenced significantly by critical fluctuations out of the antiferromagnetic state.

Not shown in Figs. 1 and 2 is the specific heat at higher temperatures. In all cases except $M=$Ir, C/T deviates from a T^2 dependence for $T \gtrsim 10$ K. For Ir, C/T is linear in T^2 to 20 K, and from this slope we infer a Debye temperature of 205 K, which is $\sim 10\%$ less than that found for $LaPt_2Sn_2$ (Ref. 10) at temperatures below 3 K. In the other cases, C/T either approaches saturation or shows a broad maximum above 15 K. Such behavior could be associated with a Schottky anomaly arising from transitions between the ground state and a low-lying crystal-field level, with a splitting on the order of 60–80 K. We also point out very weak anomalies in C/T that appear in the $CeNi_2Sn_2$ and $CeCu_2Sn_2$ data near 6 and 6.5 K, respectively. Magnetization versus field measurements indicate the presence of trace amounts of unidentified ferromagnetic second phases that have Curie temperatures corresponding to the temperatures of these anomalies.

The inverse magnetic susceptibility χ^{-1} from $T=350$ to 2 K is displayed in Fig. 3 for $CeIr_2Sn_2$ and $CePt_2Sn_2$. 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. Figure 4 shows an expanded view of χ^{-1} at low temperatures, where a reduced moment is observed, suggesting low-lying crystal fields may be present. The definite curvature of the inverse susceptibility for $CeIr_2Sn_2$ is markedly different from the behavior in the other compounds and will be discussed later. Also, this is the only one in the series whose susceptibility is drastically altered by the annealing process, being Curie-Weiss-like before annealing. To summarize our observations, both the high and low temperature μ_{eff} and Θ are listed in Table II; the low-temperature values were obtained from χ^{-1} data at temperatures less than 6 K and only for those samples not showing magnetic second phases.

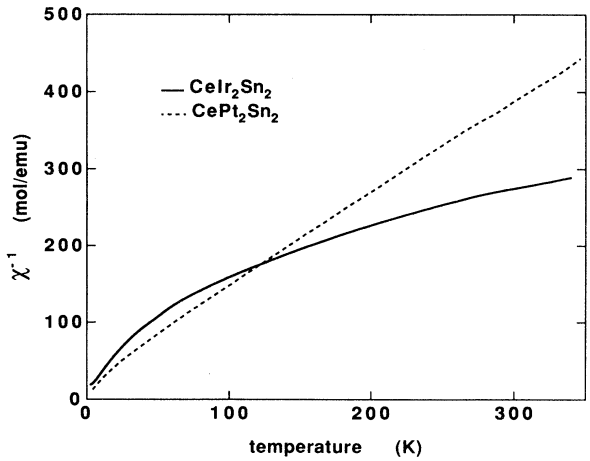

FIG. 3. Inverse magnetic susceptibility $1/\chi$ as a function of temperature for $CePt_2Sn_2$ and $CeIr_2Sn_2$. The behavior shown by $CePt_2Sn_2$ is typical of all other compounds in the series, as well as $CeIr_2Sn_2$ before it was annealed.

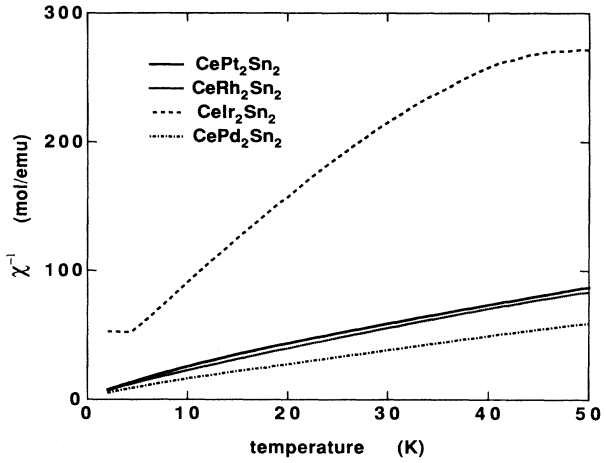

FIG. 4. View of the inverse magnetic susceptibility versus temperature for some CeM_2Sn_2 compounds below 50 K. Data for $CeCu_2Sn_2$ and $CeNi_2Sn_2$ are excluded from this figure because $1/\chi$ at low temperatures is distorted by the presence of ferromagnetic second phases in these samples.

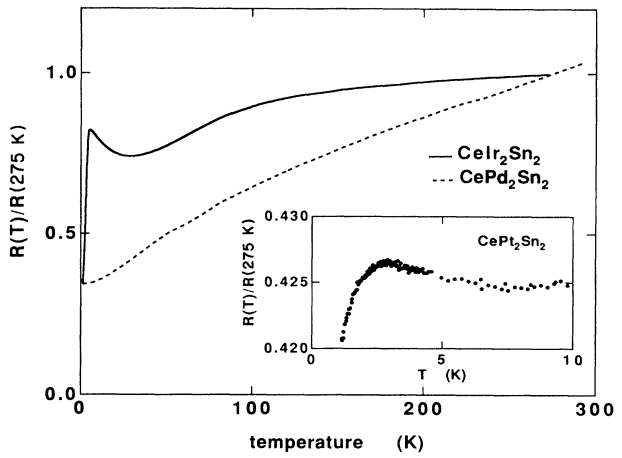

FIG. 5. The four-probe resistance versus temperature for $CeIr_2Sn_2$ and $CePd_2Sn_2$. The data are normalized to the resistance at $T=275$ K. $CeIr_2Sn_2$ shows a low-temperature maximum, similar to $CeNi_2Sn_2$, followed by a sharp drop associated with the magnetic transition. The Cu, Pt, and Rh analogs have temperature-dependent resistivities more characteristic of that displayed for $CePd_2Sn_2$. The inset shows low-temperature resistance for a $CePt_2Sn_2$ sample annealed for three weeks at 800 °C.

Finally, two characteristic temperature-dependent resistivities were measured in CeM_2Sn_2 compounds. Examples of each, as represented by $CeIr_2Sn_2$ and $CePd_2Sn_2$, are shown in Fig. 5. Both the Ir and Ni compounds annealed for three days and a Pt sample annealed for three weeks exhibit a low-temperature maximum characteristic of the onset of coherence in the electronic scattering of Ce-based heavy-electron systems. The resistivities of the others monotonically decrease with decreasing temperature. The sharp drop in resistance near 4 K in $CeIr_2Sn_2$ is due to a loss of magnetic scattering; this is the only example in the series where a clear resistive anomaly is observed that coincides with the magnetic phase transition. We believe that some residual disorder scattering masks both coherence and magnetic signatures expected in the resistivity. Weak resistive anomalies were observed, however, at low temperatures in a few of the compounds, most notably $CeCu_2Sn_2$; these are believed to not represent bulk properties, but rather they are more likely a consequence of small impurity phases, as suggested from magnetization studies mentioned above.

TABLE II. Effective moment μ_{eff} and paramagnetic Curie temperature Θ obtained at high and low (L) temperatures as described in the text for CeM_2Sn_2 compounds.

M	μ_{eff}/μ_B	Θ (K)	μ_{eff}^L/μ_B	Θ^L (K)
Ni	2.64	−58.4		
Ir				
Cu	2.49	−13.7		
Rh	2.53	−13.2	1.96	−2.0
Pd	2.50	−6.0	2.32	−1.6
Pt	2.59	−25.1	1.85	−1.2

DISCUSSION

First, we consider the origin of the enhanced C/T found just above T_N. Such an enhancement could originate from a many-body renormalization of the effective electronic mass, characteristic of heavy-electron systems, or from magnetic fluctuations out of the ordered ground state. We concentrate on the case of $CePt_2Sn_2$ because it exhibits one of the largest enhancements and its specific heat anomaly at T_N is most similar to that of a second-order phase transition.

Within the Gaussian approximation, Ginzburg-Landau theory[11] of a second-order phase transition predicts a fluctuation-driven power-law divergence of the specific heat, i.e., $C=C_0t^{-\alpha}$, where $t=T/T_N-1$ is the reduced temperature. The exponent α is often less than 1/2 expected for a mean-field transition and occasionally a logarithmic divergence is observed,[12] which is predicted for a two-dimensional Ising model. To look for these dependencies, we plot in Fig. 6 C vs log t and log C vs log t, where T_N is taken as the midpoint of the nearly vertical rise in C/T for $CePt_2Sn_2$. Between $T_N=0.88$ K and $T\sim1.2$ K, $C\propto t^{-0.1}$ which is consistent with fluctuations. Small changes in the choice of T_N do not affect this behavior qualitatively. However, above 1.2 K the temperature dependence is more nearly logarithmic. Even though a log dependence can be associated with fluctuations, Rajan[13] has shown that the single-impurity Kondo effect also produces a temperature-dependent specific heat that is approximately logarithmic over one decade in reduced temperature above the Kondo temperature.

We can estimate the temperature range over which

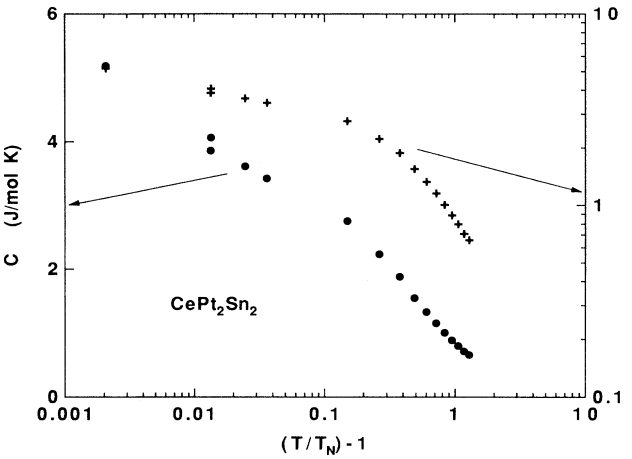

FIG. 6. Specific heat C as a function of Log t and Log C vs Log t, (double-logarithmic scale) where t is the reduced temperature T/T_N-1 and T_N is defined as the midpoint of the nearly vertical rise in C/T for $CePt_2Sn_2$.

critical fluctuations should be important using the Ginzburg criterion[11] in three dimensions: $T_G=T_N[k_B/(2\pi\xi_0)^3\Delta C]$, where ΔC is the specific heat jump at T_N and ξ_0 is the zero temperature correlation length. 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 estimates for T_G were low by an order of magnitude, critical fluctuations are probably still not important.

Although these arguments suggest that fluctuations are not important, the most convincing support comes from experiment. Specific heat measurements[10] on three-day annealed $Ce_{0.8}La_{0.2}Pt_2Sn_2$, which has a T_N depressed by 0.25 K relative to three-day annealed $CePt_2Sn_2$, has within experimental uncertainty an identical C/T, normalized per mole of Ce, at $T\geq 0.9$ K, as does $CePt_2Sn_2$ that was annealed for three weeks at 800 °C. Thus, we conclude that most of the enhanced C/T above T_N, at least in $CePt_2Sn_2$ and presumably in the other compounds of the CeM_2Sn_2 series, arises because a heavy-electron state develops that typically is attributed[14] to an Abrikosov-Suhl resonance produced in the electronic density of states by the Kondo effect.

Taking this point of view, we can estimate the Kondo temperature T_K from the single-ion relationship[15] $T_K\gamma=0.68R$, where R is the gas constant and γ is C/T just above T_N. This gives values of T_K that range from as low as ~ 1.5 K for $CePt_2Sn_2$ to ~ 10 K for $CeNi_2Sn_2$, the latter value agreeing closely with T_K inferred from resistivity measurements on a single crystal.[9] (The rapid increase in C/T around a few Kelvin also implies values of T_K in this range.) For $CeIr_2Sn_2$, which has the smallest C/T above T_N, we estimate $T_K\sim 28$ K. In all cases except $CeIr_2Sn_2$, the estimated T_K is small and comparable (within about a factor of 2) to T_N. That $T_K>T_N$ in all cases is consistent with the entropy (Table I) being less than R ln2 below T_N since a fraction (approximately 1/2) of the magnetic entropy is consumed in developing the heavy-electron ground state. Thus, in CeM_2Sn_2 there is an intimate competition between local moment magnetism, presumably mediated by RKKY interactions, and the tendency to form a magnetic singlet by Kondo interactions.

It is interesting to consider where these compounds fall within Doniach's model[5] of a Kondo necklace, which considers exactly this competition. For a single Kondo impurity, T_K is given by $T_K=T_F\exp(-1/\rho|J|)$, where T_F is the unrenormalized Fermi temperature, ρ is the conduction band density of electronic states and J is the exchange parameter characterizing the s-f interaction. Assuming a typical $T_F\simeq 10^4$ K and the values of T_K estimated from C/T, we find that $\rho|J|$ varies from as small as 0.11 for $CePt_2Sn_2$ to as large as 0.17 for $CeIr_2Sn_2$. These relatively small values of $\rho|J|$ are consistent with the low T_N's in the CeM_2Sn_2 series, since the strength of RKKY interactions is proportional to ρJ^2, and place these compounds in the weak-coupling limit of Doniach's phase diagram. In this limit, RKKY interactions should dominate because they increase geometrically with $\rho|J|$, whereas Kondo spin fluctuations increase exponentially. Consequently, we would expect from this naive analysis that $T_N>T_K$ and that antiferromagnetic order would quench the development of a heavy-mass state, neither of which is consistent with our observations.

Aspects of Doniach's model, however, are qualitatively consistent with the data. Because it is difficult to determine in most CeM_2Sn_2 compounds precisely where the increase in C/T ceases to be dominated by many-body effects and begins to be affected strongly by the onset of long-range magnetic order, we consider two of the clearer examples, $CePt_2Sn_2$ and $CeIr_2Sn_2$. For these, the ratio T_K/T_N is ~ 1.7 and ~ 6.8, respectively. Consequently, we would expect substantially less entropy below T_N in $CeIr_2Sn_2$, which is indeed the case. Further, we might expect that the application of pressure, which generally enhances $\rho|J|$ in Ce-based heavy-electron compounds,[16] would depress T_N in $CeIr_2Sn_2$. To check this, we have studied the effect of hydrostatic pressure on the electrical resistance of $CeIr_2Sn_2$, which as mentioned is the only one in the CeM_2Sn_2 series showing a clear electrical signature at T_N. Figure 7 shows the temperature derivative of the resistance of $CeIr_2Sn_2$ at selected pressures. The sharp rise in dR/dT reflects the resistive signature for T_N, which clearly is depressed with increasing pressure. Thus, the behavior anticipated from the large T_K/T_N ratio is confirmed. However, neither the large ratio nor this pressure dependence is expected within Doniach's model for the value of $\rho|J|$ estimated for $CeIr_2Sn_2$, but both would be expected if $\rho|J|$ were closer to to 0.5. This suggests that perhaps Doniach's model contains the essential physics of the competition between Kondo and RKKY interactions but that the single-ion expression for estimating $\rho|J|$ is inadequate. Such a discrepancy may be explained if the wave-vector dependence of J were prop-

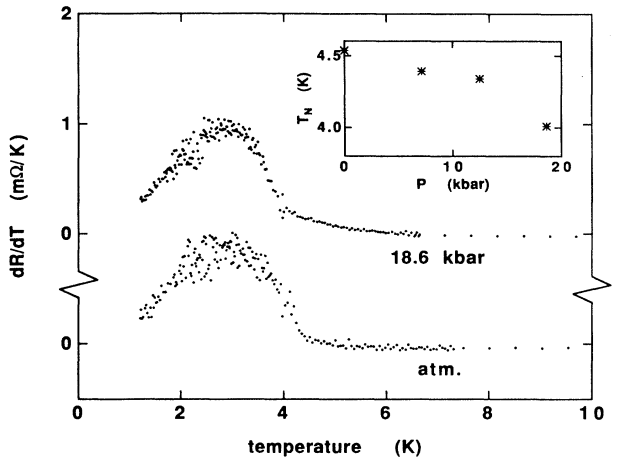

FIG. 7. Temperature derivative of the resistance dR/dT versus temperature for $CeIr_2Sn_2$ under various hydrostatic pressures. The sharp rise in dR/dT signals the Néel temperature. The inset shows the pressure dependence of T_N derived from these data.

erly taken into account, as suggested from pressure studies on other heavy-electron systems.[17]

Finally, we comment on the temperature dependence of the inverse susceptibility for these compounds. As indicated, all CeM_2Sn_2 compounds except $CeIr_2Sn_2$ exhibit Curie-Weiss behavior with full moment at high temperatures and reduced moment at lower temperatures, suggesting the presence of crystal-field effects that also may be manifested in the specific heat in some cases. Such behavior is typical of Ce-based heavy-electron systems.[18] The inverse susceptibility of $CeIr_2Sn_2$ is non-Curie-Weiss-like over the entire temperature range and the specific heat to 20 K shows no evidence for a Schottky anomaly. Together, these facts suggest that $CeIr_2Sn_2$ may be mixed valent; however, this is not seen by L_{III} edge measurements and the compound does order magnetically. Further, the entropy below T_N is consistent with ordering in a doublet ground state having a relatively high T_K inferred from C/T just above T_N. An alternative to the mixed valence interpretation is that the non-Curie-Weiss temperature dependence results from the combination of magnetic anisotropy and a crystal-field scheme unlike that in other compounds in the series. We note that as-prepared $CeIr_2Sn_2$ did show a Curie-Weiss susceptibility, so that annealing may have introduced a slightly different monoclinic distortion that produces the above effects. This difference, however, should not affect appreciably the specific heat near T_N or the arguments given above for the pressure dependence of T_N.

CONCLUSIONS

We have argued that the very large values of C/T observed in the CeM_2Sn_2 series at $T \geq T_N$ is dominated by a many-body renormalization of the effective electronic mass. This makes these materials, particularly $CePt_2Sn_2$, among the heaviest electron systems known. What is especially intriguing about these systems is that the heavy-mass state develops in the presence of RKKY interactions that are only slightly weaker than Kondo interactions. Thus, these materials are ideal candidates for studying the competition between these two effects. We also have noted that it is difficult to understand how these materials fit into Doniach's Kondo-necklace model when their physical properties are analyzed using simple Kondo-impurity relationships. Although we believe Doniach's model embodies the essential physics that describes the competing interactions, clearly improvements can be made that would allow more complete reconciliation of experiments with theory. Additional experiments on these materials may clarify in part the discrepancy between theory and experiments. Determination of the neutron quasielastic linewidth, which measures T_K directly, and crystal field splitting by inelastic neutron scattering would be most valuable, as would be measurements of the temperature-dependent electrical resistivity and magnetic susceptibility on high quality single crystals. Finally, establishing the pressure dependence of T_N across the series would further our understanding of the interplay between Kondo and RKKY interactions.

Note added in proof. Very careful reexamination of $CeNi_2Sn_2$ shows that as-prepared and annealed (21 days at 750 °C) samples belong to the same monoclinic $P2_1$ space group. For both samples the monoclinic distortion is very weak. Neutron diffraction to 1.5 K does not reveal any structural change.

ACKNOWLEDGMENTS

Work at Los Alamos was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences.

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