Heavy-fermion behavior of the ferrimagnetic compound UCu_5Sn

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We have measured ac-magnetic susceptibility, magnetization, electrical resistivity, magnetoresistance, and specific heat on the polycrystalline sample UCu_5Sn. The specific heat over temperature shows a strong increase at low temperatures. The electronic specific heat coefficient γ of 330 mJ/K^{2}mol determined by extrapolation to $T=0$ K classifies this compound as a moderate heavy-fermion system. The other measurements together with neutron diffraction reveal that this compound orders ferrimagnetically at $T_C=53.5$ K. The temperature dependence of the magnetic resistivity of UCu_5Sn indicates a behavior consistent with Kondo-type interactions with $T_K=15$ K in the presence of crystalline electric field effects. [S0163-1829(99)06731-4]

I. INTRODUCTION

Heavy-fermion (HF) materials continue to attract considerable interest due to a puzzled transformation observed at low temperatures from the localized to itinerant behavior. This phenomenon, despite numerous studies in the past, still requires many theoretical and experimental attempts to be explained. One of the most crucial aspects of heavy fermions is their relationship to magnetism and magnetic order. Magnetism is a more robust aspect of HF systems than initially envisioned when they were classified into nonmagnetic and magnetic types. Careful microscopic studies continue to provide evidence for some kind of usually weak antiferromagnetic order occurring in most, if not all, HF's. Thus a classification scheme and a framework for understanding the mutual relationship between the HF state and magnetic order has emerged. This framework recognizes two scenarios:[1] (i) magnetism arising among strongly interacting heavy quasiparticles, or (ii) competition between on-site Kondo screening and intersite Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions as implied by Kondo-lattice models. These two scenarios can be schematically described by two relevant energy scales T_K and T_M, where T_K is a Kondo scale or the effective degeneracy of the Kondo electron band, and T_M represents the strength of magnetic interactions. T_K is measured by the electronic specific heat coefficient while T_M is the temperature of the magnetic order. The first scenario corresponds to $T_M < T_K$; the second scenario implies $T_M \approx T_K$. Here we present the results of thermodynamic, magnetic, and transport measurements on UCu_5Sn, a moderately heavy fermion system, which defies this phenomenological description of HF's. As is shown below, the magnetic order is of ferrimagnetic type and $T_M \gg T_K$.

UCu_5Sn belongs to a recently discovered family of UCu_5M compounds, where M stands for Al, In, or Sn. The crystal structures of these compounds are different and only that for UCu_5In relates to the $CeCu_5Au$ type.[2] Those for Al (Ref. 3) and Sn (this work) are tetragonal and hexagonal, respectively. As found in our previous studies, the first two compounds order antiferromagnetically with $T_N=18$ K for Al and 23 K for In ternaries.[3,4] Their corresponding linear specific heat coefficients are also alike, 180 mJ/K^{2}mol for UCu_5Al and 170 mJ/K^{2}mol for UCu_5In.[3,4] The low-temperature state for both these compounds can be then understood in the second scenario of competing RKKY and on-site Kondo interactions for which $T_N \approx T_K$.

II. EXPERIMENT

Samples UCu_5Sn and $ThCu_5Sn$ were prepared by arc melting the constituent elements (U: 99.95 at.%; Th: 99.9 at.%; Cu: 99.999 at.%, and Sn: 99.999 at.%) on a water-cooled copper hearth under a high purity argon gas. The weight loss of samples during the arc melting was smaller than 0.5%. In the case of UCu_5Sn, two separately synthesized samples were used in our study. Sample no. 1 was not annealed, while sample no. 2 was vacuum annealed at 800 °C for three days. The annealing slightly increased the value of the resistivity, but did not affect any other data, particularly the magnetization. The data presented here were obtained on sample no. 2. X-ray analysis reveals that the investigated samples were single phase with a hexagonal structure. The room-temperature lattice parameters were determined by a least-squares fitting to experimental data. They are $a=498.3$ (1) and $c=2029.5$ (4) pm for UCu_5Sn, and $a=498.8$ (1) and $c=2028.6$ (5) pm for $ThCu_5Sn$. As a very recent x-ray refinement of a single crystal of UCu_5Sn has revealed, the crystal structure of this ternary stannide is of $CeNi_5Sn$ type.[5]

III. RESULTS AND DISCUSSION

In Fig. 1 we present results of ac-magnetic susceptibility, χ_{ac}, measurements in the temperature range 4–100 K performed with a Lake Shore susceptometer (series 7000). Both in-phase (χ') and out-of-phase (χ'') components of χ_{ac} have pronounced maxima. The characteristic peak in χ' at $T_C=53.5$ K indicates a magnetic phase transition. The pres-

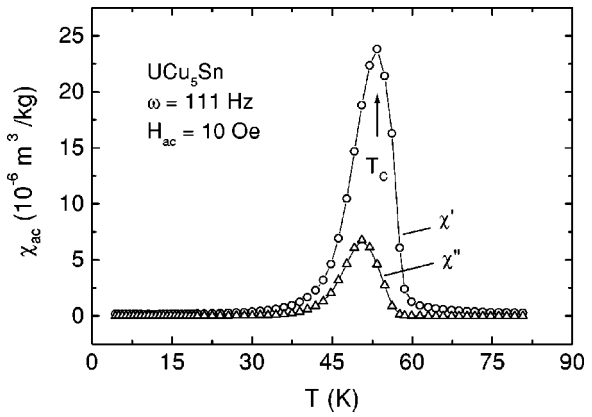

FIG. 1. The temperature dependence of ac-magnetic susceptibility, χ_{ac}, for UCu_5Sn. The solid lines are guides to the eye.

ence of a pronounced maximum in χ'' at a temperature slightly lower than T_C indicates a ferromagnetic contribution to the magnetically ordered state. An ordinary antiferromagnetic ordering (AF) should not give rise to the χ'' anomaly.

Further arguments for the existence of the ferromagnetic component in the ordered state of UCu_5Sn are provided by dc susceptibility and magnetization measurements. These measurements were performed using either the Faraday balance or superconducting quantum interference device (SQUID) magnetometer (quantum design MPMS-5 type). For these measurements, the samples were first powdered and then potted into a cylindrical cell. This procedure effectively eliminates any preferential orientation of arc-melted material and leads to direction-averaged properties. Figure 2 shows the inverse of dc susceptibility (χ_{dc}^{-1}) as a function of temperature between 1.7–1000 K. This χ_{dc} is defined as magnetization (M) obtained in the field (B) of 0.5 T divided by this field. At temperatures larger than 200 K, χ_{dc} follows a Curie-Weiss law with an effective moment $\mu_{eff} = 3.11(5)$ μ_B/U and a paramagnetic Curie temperature $\Theta_p = -63(2)$ K. Below 200 K, the χ_{dc}^{-1} versus T dependence shows a strong downward deviation from a straight line and marked curvature at temperatures near T_C, reminiscent of ferrimagnetic materials. Usually, the inflection point of the magnetization (minimum of derivative of the magnetization $dM(T)/dT$) taken at the lowest magnetic field defines an ordering temperature T_C. This point for UCu_5Sn is close to that determined from the χ_{ac} curve and is equal to 53.9 K. Below T_C, the M_{FC}(T) dependence demonstrates a clear ferromagneticlike character of the sample, while M_{ZFC}(T) shows a broad maximum at about 30 K. A marked difference between ZFC and FC magnetization curves implies the presence of a large magnetocrystalline anisotropy in the investigated material.

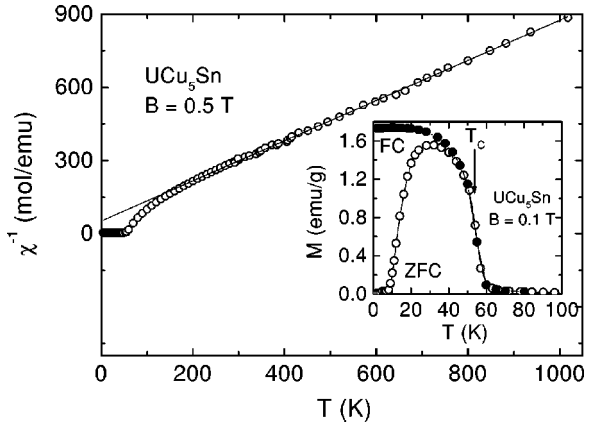

FIG. 2. UCu_5Sn as a function of temperature. The solid line is a fit to the experimental data. The inset shows the low-temperature magnetization taken on zero-field cooled (ZFC) and on field cooled (FC) samples at $B = 0.1$ T. The solid lines in the inset are guides to the eye.

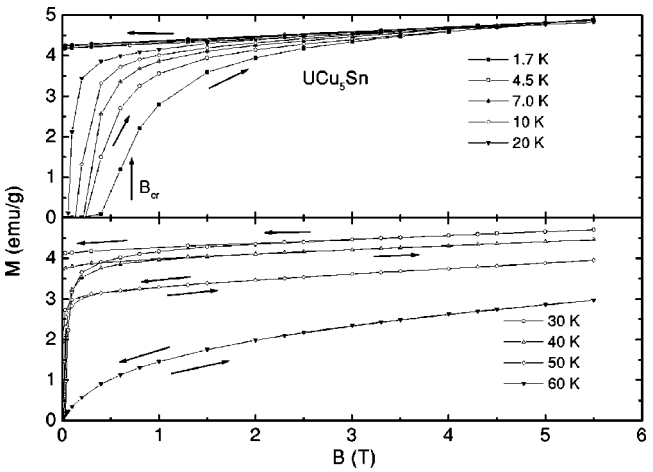

FIG. 3. Magnetization of UCu_5Sn measured in fields up to 5.5 T and at selected temperatures between 1.7–60 K. The solid lines are guides to the eye.

The magnetization versus field curves $M(B)$, taken at selected temperatures are shown in Fig. 3. These curves exhibit typical hysteretic behavior of ferromagnetic materials with a strong crystalline anisotropy. At 1.7 K, the magnetization initially increases almost linearly with field, then suddenly increases and exhibits saturation effects in still higher fields. This sudden jump in magnetization is due to overcoming of the magnetocrystalline anisotropy. We accept the field corresponding to the inflection point, B_{cr}, as the measure of anisotropy energy. B_{cr} is about 0.7 T for $T = 1.7$ K and decreases at higher temperature becoming 0 T at about 50 K. The striking feature of these data is the rather low averaged magnetic moment $M = 0.6$ μ_B/at.U, reached for a powdered sample in a maximum applied field of 5.5 T. At first glance, this behavior indicates that either the two different U sublattices in the unit cell of the $CeNi_5Sn$ type, with antiferromagnetically coupled moments are not completely compensated or there exists some canting of magnetic moments. In order to further explain these magnetization data we have initiated collaborative efforts to study the magnetic structure of this compound via neutron diffraction. From the recently performed neutron scattering measurements we have found a ferrimagnetic structure with a propagation vector $k = (0,0,0)$. In this structure the alignment of U magnetic moments is along the hexagonal c axis. This structure is also characterized by ferromagnetic planes with the $(+-)$ stacking sequence. The size of the U moments lying in the (0,0,0) plane, formed by the sites $(2a)$, is about 10 times larger than those in the adjacent (0, 0, 1/4) plane formed by the sites $2(d)$. The atomic ratio of both these sites in the unit cell is

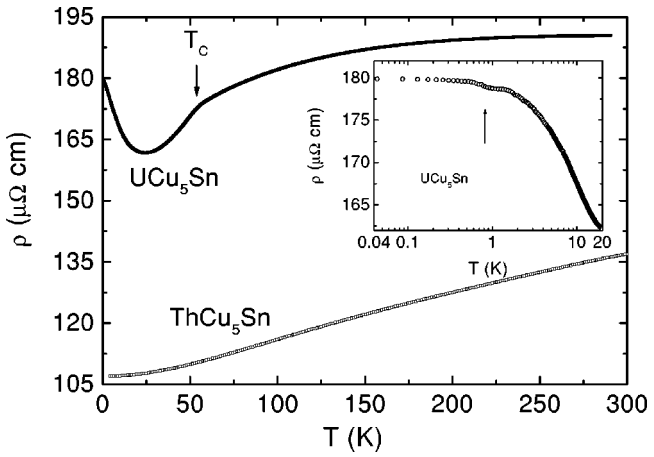

FIG. 4. The electrical resistivity of UCu_5Sn and $ThCu_5Sn$ between 4 and 300 K. The inset shows the resistivity of UCu_5Sn versus ln$T$ at temperatures below 4 K.

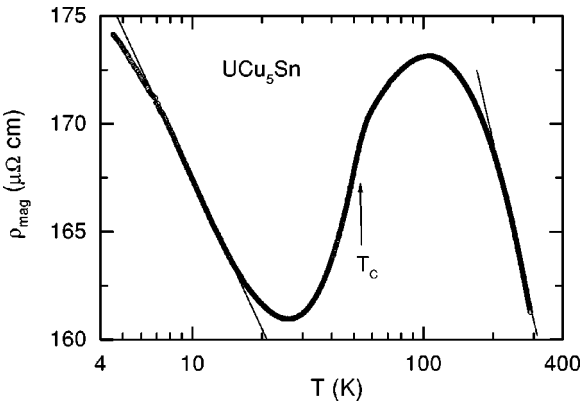

FIG. 5. The magnetic contribution to the resistivity, ρ_{mag}, of UCu_5Sn as a function of ln$T$. The solid lines illustrate a Kondo temperature dependence of resistivity $\rho \propto \ln T$.

1:1 and this difference in the magnitudes of the moments leads to a net moment of uranium atoms. More detailed neutron diffraction data will be published elsewhere.[6] These results explain the relatively small value of the ordered magnetic moment and the sign of the paramagnetic Curie-Weiss temperature. This sign, as opposed to normal ferromagnets, is negative, implying predominance of negative, antiferromagnetic exchange interactions.

The electrical resistivity, discussed next, is also not typical of ferromagnetic compounds. The electrical resistivity $\rho(T)$, measured using a standard dc four-probe method, is shown in Fig. 4 for temperatures between 40 mK and 300 K. Upon cooling from room temperature, the resistivity initially decreases slightly and then near $T=54$ K, $\rho(T)$ drops markedly due to the onset of the magnetic order. Furthermore, at $T=27$ K, $\rho(T)$ goes through a deep minimum and then increases steeply when the temperature is lowered. As shown in the inset to Fig. 4, $\rho(T)$ shows a small keen anomaly at $T=0.8$ K, saturating at a constant value below this temperature.

In order to estimate the phonon contribution to the resistivity of UCu_5Sn, the resistivity of nonmagnetic, isostructural homologue $ThCu_5Sn$ has been measured. As it is shown in Fig. 4, $\rho(T)$ of this compound has a typical metallic temperature dependence. The magnetic, $5f$-electron contribution to the resistivity of UCu_5Sn has been obtained from the following subtraction: $\rho(UCu_5Sn)-\rho(ThCu_5Sn)$. The result is presented in the form of ρ_{mag} versus ln$T$ in Fig. 5. This curve is strikingly similar to those for Ce-Kondo lattice compounds and mimics the theoretical behavior predicted for Kondo systems with crystal-field effects. According to the theory of Cornut and Coqblin,[7] the broad maximum, observed for UCu_5Sn at temperatures slightly above 100 K, would correspond to the overall crystal-field (CF) splitting Δ_{CF}. For Ce materials showing no magnetic ordering, the slopes of ρ_{mag} versus ln$T$ at lower and higher temperatures are just related to the effective crystal-field degeneracy of the ground state and higher excited CF states, respectively. However, the low-temperature slope of ρ_{mag} in our case is a result of the competition between the dropping tendency of spin-disorder resistivity with decreasing temperature due to the onset of magnetic order on the one hand, and on the other the rising resistivity values due to the Kondo interaction with the CF ground state. Hence, any comparison of the UCu_5Sn case to the situation found in a number of nonmagnetic Ce compounds at low temperatures cannot be considered here. However, the temperature of the broad maximum in $\rho_{mag}(T)$ of UCu_5Sn T_{max} happens to be considerably higher than T_C and therefore can be attributed to Δ_{CF}.

According to the Suhl-Nagaoka theory,[8,9] the inflection point of the ρ_{mag} versus lnT corresponds to the Kondo temperature. This value for UCu_5Sn would be roughly 15 K (see the inset of Fig. 4). At this point it is worth recalling that the measured paramagnetic Curie-Weiss temperature, $\Theta_p = -63$ K, is also consistent with the Kondo temperature of order 15 K. Various theoretical approaches relate Θ_p to T_K by $T_K=|\Theta_p|/n$, where n is usually between 2 and 4.[10]

We have searched for additional signatures of the Kondo character of this compound by performing magnetoresistance (MR) measurements, $\Delta\rho/\rho=[\rho(B)-\rho(0)]/\rho(0)$, for several temperatures and magnetic fields. The UCu_5Sn sample was first cooled down to 4.2 K in a zero field (ZFC) and then data were taken first in increasing fields (up to 8 T) followed by a decrease of field at constant intervals. For temperatures higher than 4.2 K, the sample was initially heated to the respective temperature in zero field and the data were recorded in the same manner as that for 4.2 K. The obtained MR against magnetic field curves are shown in Fig. 6. This magnetoresistance is negative, as it is expected for both the Kondo effect and ferro- or ferrimagnetic ordering. Due to the latter effect, the magnetoresistance also shows large hysteretic features clearly visible for temperatures lower than 35 K. Similar hysteretic behavior has been previously found for UPdIn,[11] and UCu_2Ge_2.[12] Ferrimagnetic ordering (uncompensated spins) was established for the first compound, while a possible canting of ferromagnetically aligned spins was found in the second compound. The low-field magnetoresistance isotherms of UCu_5Sn have a field dependence that can be mistakenly assigned to pure Kondo behavior. Note that the characteristic magnetic field, B_c, corresponding to the inflection point of the magnetoresistance (Fig. 6) has a temperature dependence opposite to that for a characteristic field of the Kondo model, B^*. B_c, as opposed to B^*, decreases with an increase of the temperature, i.e., it has a similar temperature dependence to B_{cr}, which we related to the an-

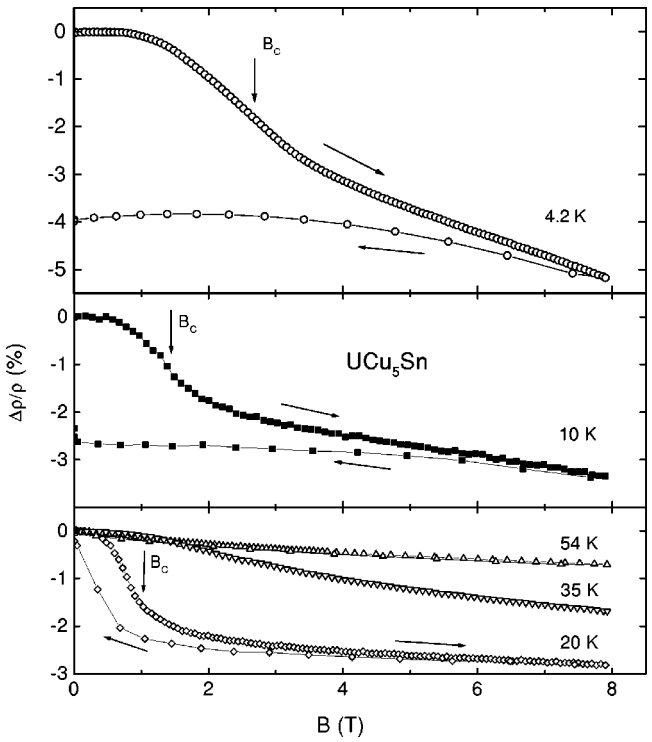

FIG. 6. Magnetoresistance $\Delta\rho/\rho$ versus field at various temperatures between 4.2 and 54 K for UCu_5Sn. The solid lines are guides to the eye.

isotropy field (Fig. 3). However, B_c values are markedly larger than those for B_{cr} at the same temperature. The origin of this discrepancy is probably caused by different sizes and shapes of polycrystalline samples studied. Furthermore, in Fig. 7 we display the plots of MR versus temperature obtained in two different ways of measurements. First, the sample was cooled in zero field down to 4.2 K and we then measured the virgin ZFC resistivity, whilst slowly warming the sample up to 75 K. Then the sample was cooled in zero field down to 4.2 K and the resistivity was remeasured in a field of 8 T, as indicated above. Based on these two results we have calculated MR and its temperature dependence, which in Fig. 7 is marked as ZFC. One sees from these

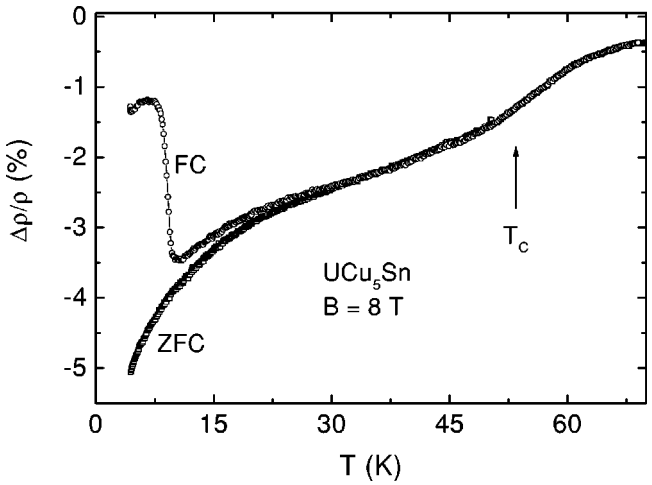

FIG. 7. Magnetoresistance $\Delta\rho/\rho$ of UCu_5Sn as a function of temperature.

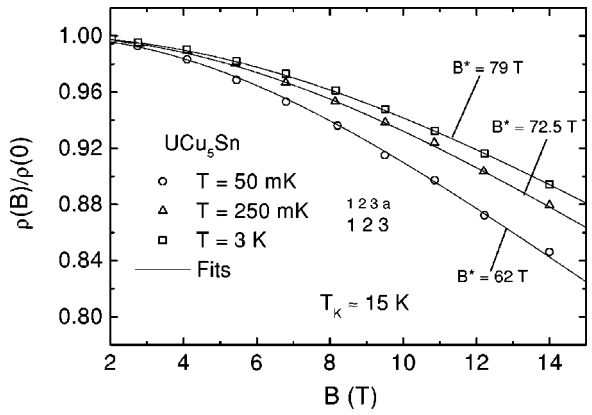

FIG. 8. Field-dependence magnetoresistance $\rho(B)/\rho(0)$ of UCu_5Sn at different temperature below 4.2 K. The solid lines are fits to the experimental data.

measurements that in contrast to typical ferro- or ferrimagnetic materials the largest MR is found not at the T_C but at the lowest temperature measured. Hence, this finding strongly suggests that the decrease in the resistivity under high-magnetic fields is due to the reduction of the Kondo scattering by fields in the incoherent state.

In the second run, marked in Fig. 7 as FC, we referred the high-field resistivity to zero-field resistivity, but determined after cooling the sample under 8 T down to 4.2 K and then warming up at this field. As can be seen in Fig. 7, the difference between the ZFC and FC magnetoresistance results are only significant below 20 K. Especially, at 10 K, the FC-MR exhibits a jump and a tendency to saturation with further decreasing temperature. At present, this irreversibility effect is not clear, and may arise from a competition between Kondo and magnetic order interactions or from a reorientation of spins. A similar effect was observed in our study of $URu_{0.2}Pd_{0.8}Ga$ material,[13] for which ferrimagnetic ordering with two magnetic propagation vectors $k_1=(0,0,0)$ and $k_2=(0,0,0.2)$ were observed below $T_C=52$ K.[14]

On the other hand, the magnetoresistance of UCu_5Sn previously measured at 50 mK, 0.25 K, 3 K and in fields up to 14 T,[15] but only with increasing magnetic fields, do not show an S-type shape. In these temperatures and in fields above 2 T, where coherence effect is thought to be absent (see Ref. 15), MR shows a negative curvature depending nearly quadratically on B, indicating the dominant Kondo-type behavior of UCu_5Sn. Therefore, it seems that these high-field and very low-temperature magnetoresistance data taken from Ref. 15 can also be analyzed in terms of the $S=1/2$ Coqblin-Schrieffer model.[16] The solid lines in Fig. 8 represent a fit to this model. As seen, all experimental points can be satisfactorily described by a function of B/B^*.[17] This model also predicts that $B^*(T)$ is proportional to temperature, $B^*(T)=\mu_K/k_B(T+T_K)$; where T_K is the Kondo temperature. By forcing a straight line fit of B^* versus T we arrive at $T_K\approx 15$ K and $\mu_K\approx 0.43\mu_B$. Since the three points used in the fit do not fall on the straight line, these values can be used as very rough approximations only. Nevertheless, this T_K is consistent with the value based on the zero-field resistivity and magnetic susceptibility data. We should also have in mind the fact that the above procedure has been applied in the magnetically ordered state, though the spin disorder or

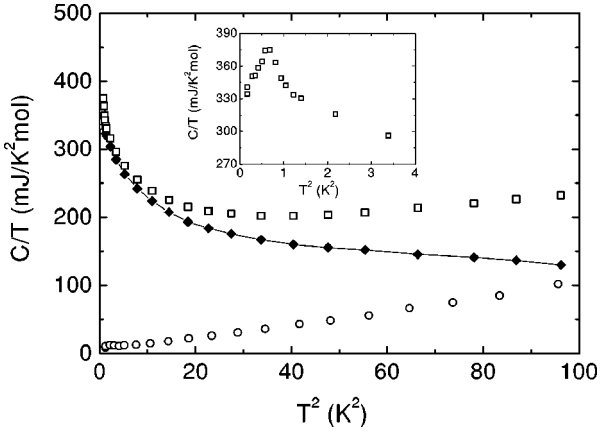

FIG. 9. The specific heat plotted as C/T versus T^2 for UCu_5Sn (open squares), $ThCu_5Sn$ (open circles), and their difference (solid diamonds). The inset shows the low-temperature behavior of C/T for UCu_5Sn.

contribution to the total resistivity at these lowest temperatures should be quite marginal.

The distinct Kondo-like signature of the resistivity below T_C suggests the possibility of a heavy-fermion state at low temperatures. Specific heat results, discussed next, provide some evidence for the heavy-fermion state of UCu_5Sn. The specific heat (C), between 0.4 and 10 K for UCu_5Sn, and between 1 and 10 K for $ThCu_5Sn$, has been measured by the relaxation method. The results for UCu_5Sn and for the nonmagnetic reference sample, $ThCu_5Sn$, are shown in Fig. 9 in the form of C/T versus T^2. For UCu_5Sn, an increase of C/T, characteristic of a heavy-fermion state, is observed below about 7 K. C/T reaches a maximum value of about 375 mJ/K^2mol at 0.8 K before it starts to decrease (see the inset to Fig. 9). Recall that we have found a corresponding anomaly in the resistivity, also at about 0.8 K. Despite the fact that the origin of this anomaly is currently unclear, however, we think that its influence on the final $\gamma(0)$ value may be negligible. The support of this argument lies in the measured C/T for solid solutions $U_{1-x}Th_xCu_5Sn$, where the $\gamma(0)$ value per uranium mole reaches the same order of magnitude as that for pure UCu_5Sn. Moreover, these compositions have not shown any anomaly in their C/T versus T as well as in ρ versus T dependences down to very low temperatures. More systematic studies of the magnetic properties of the solid solutions $U_{1-x}Th_xCu_5Sn$ will be published elsewhere.

The $\gamma(0)$ value of UCu_5Sn, determined by the extrapolation to $T=0$ K of the lowest temperature values of C/T, is then about 330 mJ/K^2 mol. This value which, however, may be influenced by the observed maximum in C/T at 0.8 K, is again well in line with the Kondo temperature approximated from the magnetic susceptibility, resistivity or magnetoresistance.

IV. CONCLUSION

We have presented experimental results of the magnetic, transport, and thermal properties of UCu_5Sn. The following conclusions are remarkable.

(i) The bulk and neutron powder diffraction measurements point to a ferrimagnetic order below $T_C=53.5$ K.

(ii) The electrical resistivity behavior can be qualitatively explained in terms of the Kondo interaction and crystalline field splitting. The dc-magnetic susceptibility, electrical resistivity, magnetoresistance, and specific heat data also indicate an existence of the Kondo effect, which is characterized by the Kondo temperature of order 15 K.

(iii) The specific heat data imply that UCu_5Sn is a moderate heavy fermion. It is unique in the sense that the heavy-fermion state is formed in the ferrimagnetic state. Particularly, the heavy-fermion characteristics are found in this compound despite the fact that the magnetic energy scale is much larger than the Kondo scale, i.e., $T_C \gg T_K$.

(iv) Both the electrical resistivity and specific heat display an anomaly at $T=0.8$ K, which may suggest some additional transition, if its appearance is not caused by extrinsic reasons. Additional microscopic measurements at very low temperatures are required to further probe the behavior of this interesting compound.

ACKNOWLEDGMENTS

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