Electrical-resistance anomalies in a Ce-Ru-Sn phase

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We present the results of electrical-resistivity, ρ (1.4–300 K), and magnetic-susceptibility, χ (4.2–300 K), measurements on a ternary Ce-Ru-Sn alloy with the starting composition $CeRu_4Sn_6$. It is found that this alloy exhibits characteristics of dense Kondo systems. The total resistivity of this alloy mimics the behavior of ρ in some Ce compounds exhibiting a hybridization-induced energy gap.

Though the ground state of a vast majority of mixed-valent and heavy-fermion compounds are known to be metallic, there are a few cases such as SmB_6 (Ref. 1) and YbB_{12} (Refs. 2–4) exhibiting semiconducting behavior. In particular, the identification of the compounds showing an energy gap because of $4f$ hybridization among Ce systems has picked up momentum in the current literature in order to find a requisite condition for gap opening. Thus, the hybridization-induced energy gap seems to form in CeNiSn,[5] $CeFe_4P_{12}$,[6] $Ce_3Bi_4Pt_3$,[7] and possibly in $Ce_3Pt_3Sb_4$ (Ref. 8) and CeRhSb.[9] Here we report the results of electrical-resistivity, ρ (1.4–300 K), and magnetic-susceptibility, χ (4.2–300 K), measurements on a Ce-Ru-Sn phase with the starting composition $CeRu_4Sn_6$. For the sake of comparison, we also investigated YRu_4Sn_6,[10] $LaRu_4Sn_6$, and $GdRu_4Sn_6$. The total resistivity above 125 K seems to show activated behavior, similar to that noted for $Ce_3Bi_4Pt_3$,[7] while at low temperatures, Kondo lattice characteristics are observed.

The motivation behind the investigation of this alloy system with the formula $CeRu_4Sn_6$ is based on the identification of a tetragonal Y-Ru-Sn system with the above composition by Venturini *et al.*[10] For this crystal structure, possible reflections in the x-ray diffraction were reported to obey the condition $h+k+l=2n$. The crystal structure could be considered as a ternary derivative of YSn_3 ($AuCu_3$ type) where half of the Y atoms are replaced by the Ru_4 clusters. The Ru atoms are surrounded by 6 Sn which form a strongly deformed octahedron. Other crystallographic details can be obtained from Ref. 10. In the present work, we report on the existence of analogous rare-earth containing specimens.

The samples, $R Ru_4Sn_6$ (R = La, Ce, Gd, and Y), were prepared by arc melting several times stoichiometric amounts of constituent elements. The weight loss during melting was negligible. In the case of Ce, we made a few more specimens, with the excess of Ce (about 15 at. %) in one of the specimens (called C). All the ingots were annealed at 1123 K for 5 days. The x-ray-diffraction patterns (Cu K_α) look very similar in all the cases, though we have observed a few diffraction lines (at $2\theta=33.7°$ and 34.6°, $<15\%$) not obeying the condition[10] $h+k+l=2n$, even for YRu_4Sn_6. We have analyzed the specimens by energy dispersive analysis of x rays and the compositions correspond very closely to the starting ones and hence we tend to believe that most of the results reported here are representative of $R Ru_4Sn_6$ phase. It may be remarked that several ternary phases are known to exist.[11] Electrical resistivity, ρ, measurements were performed in the temperature interval 1.4–300 K by a conventional four-probe method. Magnetic susceptibility, χ, data were taken (4.2–300 K) by the Faraday method employing a magnetic field of 4 kOe.

The results of electrical resistivity, ρ, measurements are shown in the Fig. 1 for all the alloys. We discuss first the results on Ce systems. For all the specimens, the ρ-vs-T plots look qualitatively similar above 10 K for all the specimens in the sense that ρ increases with decreasing temperature. Though the value of ρ above 150 K is the same for all the specimens, it is sample dependent below 150 K even for the two specimens (A and B) at the ideal stoichiometry. At low temperatures, however, the behavior of ρ is qualitatively different. There is a peak in

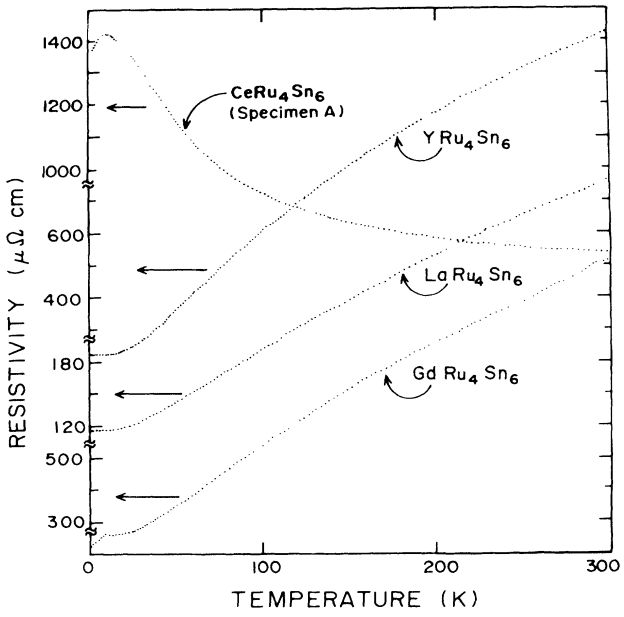

FIG. 1. Electrical resistivity as a function of temperature for the alloys, $R Ru_4Sn_6$ (R = La, Ce, Gd, Y).

ρ at about 10 K for specimen A, as expected for Kondo lattices, while for B, ρ appears to be nearly temperature independent below 10 K; interestingly, below 5 K, there is a weak rise for the specimen C (containing excess Ce) in addition to a shoulder at about 10 K (Fig. 2). It is not clear whether this rise is intrinsic to the $CeRu_4Sn_6$ phase or due to an impurity phase (particularly when there is excess Ce). If it is characteristic of the proper phase of the above formula, then this feature can be attributed to the formation of an extremely narrow energy gap (<0.1 K) at the Fermi level due to the periodicity of the Kondo centers. Though such a rise could be attributed to the incoherent Kondo lattice behavior,[12] the shoulder at 10 K is typical of coherent Kondo lattices only. If the existence of a gap is proved, then the absence of the rise in specimen A may indicate the destruction of the periodicity of the Ce sublattice caused by a minor undetectable level of deficiency of Ce concentration due to evaporation while arc melting.

An interesting observation we have noted is that, while the ρ, in all cases, undergoes logarithmic variation in the temperature interval 20–100 K typical of the Kondo effect (see Fig. 3) as expected, there is a deviation from this behavior above 100 K. Though this deviation can be attributed to the modification of the Kondo interaction, we are prompted to describe it in terms of an activated variation at high temperatures in view of similar analysis for two other systems, $Ce_3Bi_4Pt_3$ (Ref. 7) and $Ce_3Au_3Sb_4$.[8] Such an analysis for the data above 125 K by the activation law, $\rho(T) \propto \exp(E_g/kT)$ yields $E_g/k \simeq 30$ K. The proposed high-temperature activated behavior and Kondo effect in the intermediate-temperature range, common

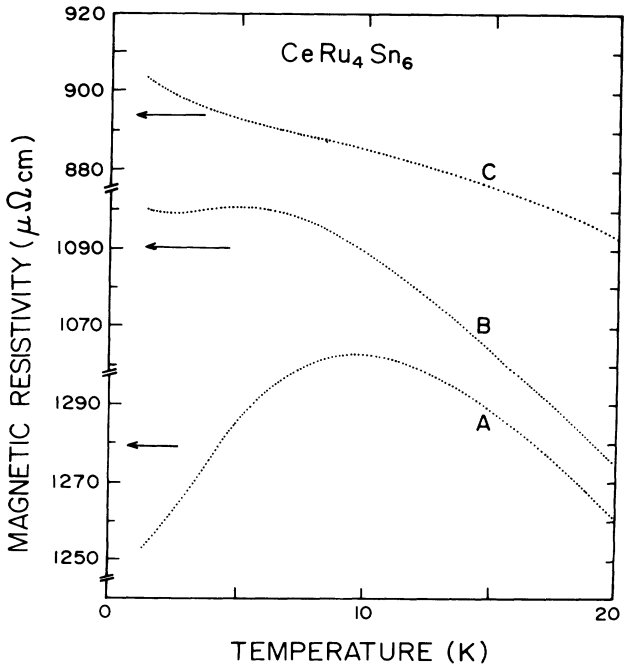

FIG. 2. Low-temperature magnetic resistivity behavior of various $CeRu_4Sn_6$ specimens. The curve C corresponds to a specimen containing about 15% excess Ce.

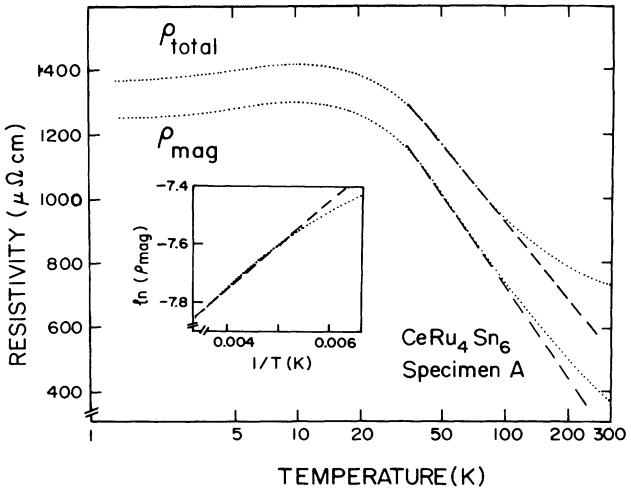

FIG. 3. The total resistivity ρ and the magnetic contribution to resistivity ρ_{mag} are plotted in a logarithmic scale for $CeRu_4Sn_6$. The high-temperature data are plotted in the form of $\ln\rho_{mag}$ vs $1/T$ in order to highlight the activated behavior (inset); the lines are drawn through the linear region.

to these three systems, need special attention. It is also possible that the deviation observed from the logarithmic variation for $T > 125$ K is due to the tendency of the phonon contribution to ρ to dominate. Though it is rather difficult to determine precisely the lattice contribution, particularly in strongly hybridized systems, it may be assumed that the values of the La analog represent this contribution. The magnetic contribution to resistivity, ρ_{mag}, obtained by subtracting the measured ρ of the La compound from that of Ce alloy, is also shown in Fig. 3 and it appears that the above deviation still persists. In order to look for the activated behavior in ρ_{mag}, we have plotted $\ln(\rho_{mag})$ versus $1/T$ in the inset of Fig. 3. The plot appears to be linear in the temperature interval 200–300 K and the activation energy (E_g) obtained from this plot turns out to be higher (160 K) than that obtained from total ρ. Though E_g derived from the high-temperature data, being less than or comparable to T, cannot be normally relied upon, it appears that one can place faith on the value of E_g thus obtained, as Seebeck and Hall coefficients for $Ce_3Bi_4Pt_3$ (Ref. 7) confirm such a value. It is also possible that below about 125 K the gap is reduced to very low values due to the anomalous thermal contraction effects, as a result of which the logarithmic variation due to the Kondo effect dominates in the temperature interval 20–100 K.

In order to show that the observed anomalies for this Ce-Ru-Sn phase are related to $4f$ hybridization, we have also measured ρ-vs-T behavior for $LaRu_4Sn_6$, YRu_4Sn_6, and $GdRu_4Sn_6$ (Fig. 1). ρ-vs-T behavior noted by us for YRu_4Sn_6 is similar to those of Venturini *et al.*[10] It is obvious that, in all these compounds, ρ does not show any increase with decreasing temperature, in contrast to the observation for the Ce specimens. The ρ of $GdRu_4Sn_6$ shows a drop at 9 K, showing thereby the existence of a long-range magnetic ordering of Gd ions: the presence of a cusp in χ at 9 K (Fig. 4 inset) may indicate some kind of

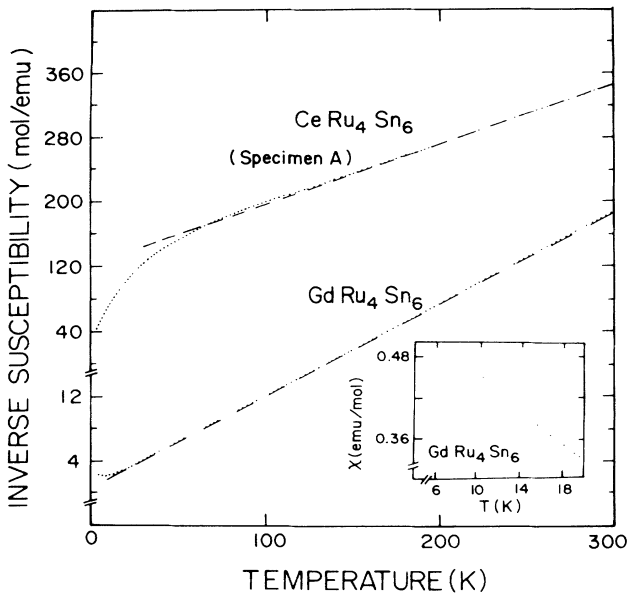

FIG. 4. Inverse susceptibility as a function of temperature for $CeRu_4Sn_6$ and $GdRu_4Sn_6$ alloys. The dashed lines are drawn to highlight the linear region. The inset shows the χ data for $GdRu_4Sn_6$ below 20 K.

antiferromagnetic interaction. Neutron-diffraction studies would be useful to elucidate the exact nature of the magnetic ordering.

Magnetic-susceptibility data (Fig. 4) for $CeRu_4Sn_6$ do not show any distinct anomaly due to magnetic ordering in the temperature interval 4.2–300 K. However, it seems that χ continues to increase strongly with decreasing temperature below 25 K, suggesting some degree of enhancement of magnetic correlation among $4f$ electrons or the heavy-fermion behavior at low temperatures. Curie-Weiss behavior is observed above 100 K and the effective moment ($\sim 2.7\mu_B$) obtained from the slope of χ^{-1}-vs-T plot above 100 K indicates that the Ce ions are essentially trivalent. The value of the paramagnetic Curie temperature (Θ_p) is of the order of -150 K for all the three Ce specimens, and this magnitude is significantly larger than that for $GdRu_4Sn_6$ (-10 K), indicating that this Ce-based alloy is a dense Kondo system. The deviation observed from the Curie-Weiss behavior below 80 K is attributed to crystal-field effects.

To conclude, the alloy $CeRu_4Sn_6$ is a concentrated Kondo system with no evidence for magnetic ordering in the temperature range of investigation. Since the identification of Ce intermetallics with an energy gap is of current interest, we bring out possible existence of an energy-gap in a Ce-Ru-Sn phase. We call for further detailed investigations to see whether the resistive anomalies, particularly at low temperatures, truly represent the $CeRu_4Sn_6$ phase. It should be interesting to initiate studies on other ternary phases in order to look for possible interference from such phases. There is a need for additional measurements like NMR relaxation time, Hall effect, thermopower, etc. It may be noted that the transport properties could also be a sensitive function of stoichiometry as demonstrated, for instance, in $CeRuSn_3$,[13] and hence we must exercise caution in attributing the observed behavior to the stoichiometric compound. Finally, there is no evidence for superconductivity in any of the specimens in the temperature range of investigation.

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[1]J. W. Allen, B. Batlogg, and P. Wachter, Phys. Rev. B **20**, 4807 (1979).

[2]M. Kasaya, F. Iga, K. Negishi, S. Nakai, and T. Kasuya, J. Magn. Magn. Mater. **31-34**, 437 (1983).

[3]M. Kasaya, F. Iga, M. Takigawa, and T. Kasuya, J. Magn. Magn. Mater. **47&48**, 429 (1985).

[4]F. Iga, M. Kasaya, and T. Kasuya, J. Magn. Magn. Mater. **76&77**, 156 (1988).

[5]T. Takabatake, Y. Nakazawa, and M. Ishikawa, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 547 (1987); T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, J. Sakurai, and D. Jaccord, Phys. Rev. B **41**, 9607 (1990).

[6]G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, and R. P. Guertin, J. Appl. Phys. **57**, 3073 (1985).

[7]M. F. Hundley, P. C. Canfield, J. D. Thompson, Z. Fisk, and J. M. Lawrence, Phys. Rev. B **42**, 6842 (1990).

[8]M. Kasaya, K. Katoh, and K. Takegahara, Solid State Commun. **78**, 797 (1991).

[9]S. K. Malik and D. T. Adroja, Phys. Rev. B **43**, 6277 (1991).

[10]G. Venturini, B. Chafik El Idrissi, J. F. Marechè, and B. Malaman, Mater. Res. Bull. **25**, 1541 (1990).

[11]See several articles in *Superconductivity in Ternary Compounds–II,* edited by M. B. Maple and O. Fischer (Springer-Verlag, Berlin, 1982), Vol. 34.

[12]I. Das, E. V. Sampathkumaran, E. Bauer, and N. Pillmayr, J. Magn. Magn. Mater. **108**, 82 (1992).

[13]T. Fukuhara, I. Sakamot, and H. Sato, J. Phys. Condens. Matter **3**, 8917 (1991).