

Heavy-Fermion Behavior and the Single-Ion Kondo Model

C. L. Lin, A. Wallash, J. E. Crow, T. Mihalisin, and P. Schlottmann
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122
 (Received 28 July 1986)

Measurements of the temperature and concentration dependence of the specific heat, magnetic susceptibility, and electrical resistivity for $Ce_{1-x}La_xPb_3$ are presented. The data scale with the concentration of Ce ions over surprisingly large intervals of x and T . The low-temperature specific heat per Ce ion agrees quantitatively with that of an $S = \frac{1}{2}$ Kondo impurity of $T_K \cong 3.3$ K. These results strongly suggest that intersite correlations do not play the expected important role and that the high specific heat γ reported for $CePb_3$ is mainly a manifestation of the single-ion Kondo resonance.

PACS numbers: 72.15.Qm, 75.20.Hr, 75.50.Ee

Within condensed matter physics, one of the most exciting problems to have emerged during the last several years has been to understand the perplexing properties of heavy-fermion (HF) systems¹⁻³ and their relation to the broader issue of magnetic-moment formation. Characteristic of heavy fermions is an unusually large electronic specific heat at low temperatures, $C = \gamma T$, where γ corresponds to a very high density of states at the Fermi level or equivalently to an effective electron mass of 10^2 - 10^3 times that of the free-electron mass. As a consequence of the large density of states these systems typically have a large Pauli susceptibility. The temperature dependence of C and χ can be explained in terms of narrow resonant levels or a narrow band with a typical width of a few millielectronvolts or less. This narrow peak in the density of states has been attributed^{2,3} to a Kondo resonance, to hybridization effects and to Fermi-liquid properties, and its formation is still to be understood. Heavy-fermion behavior occurs in a variety of Ce-, Np-, U-, or Yb-based (concentrated or dilute) alloys and stoichiometric compounds.

The low-temperature transport properties of stoichiometric HF compounds differ from those of alloys, while at high T , they are very similar. In compounds, the resistivity initially increases as one lowers T (which can be attributed to the Kondo effect), then goes through a large maximum and shows a sharp decrease at very low T . Both features, the existence of a maximum and the high resistivity at this maximum, are uncommon to normal metals. The rapid decrease of $\rho(T)$ at low T is caused by a transition from incoherent to coherent scattering of the conduction electrons by the rare-earth (actinide) ions.¹⁻³ In alloys, on the other hand, the low-temperature low-energy excitations are not coherent and $\rho(T)$ remains at its high value as $T \rightarrow 0$.

Compounds may become antiferromagnetic or superconducting at low T as a consequence of the coherence of the low-energy excitation spectrum. Anomalous superconductivity has been discovered in some U compounds with highly unusual properties which may be due to triplet pairing.^{4,5} The parameters or interactions determin-

ing the low- T phase, i.e., superconducting, magnetically ordered or a Pauli paramagnet, are still to be understood, as well as the mechanism leading to superconductivity.

At high temperature, the conduction electrons are incoherently scattered by the rare-earth ions and the properties, when scaled by the concentration, are then expected to be similar to isolated impurities and can be described by the Anderson or Coqblin-Schrieffer models with appropriate crystal fields (for exact and approximate solutions, see Refs. 2, 3, Rajan,⁶ and Andrei, Furuya, and Lowenstein⁷). When the temperature is lowered, the impurity spin is gradually compensated by the conduction electrons to form a singlet state. At $T=0$ the spin of an isolated impurity is screened within a sphere of radius⁸ $\xi \sim \chi/k_F T_K$, where D is the bandwidth, k_F is the Fermi momentum and T_K is the Kondo temperature. This length is much larger than interatomic distances and is expected to decrease when the screening becomes incomplete with increasing T . In a concentrated system, these spheres overlap at low T and the screening can no longer be regarded as that of individual ions.⁹ The interference between different rare-earth (actinide) sites should modify the properties of the system. Furthermore, in concentrated systems the number of available conduction electrons may not be sufficient to screen the rare-earth ions individually and a collective screening¹⁰ giving rise to antiferromagnetic fluctuations has been invoked. The above arguments are valid for stoichiometric compounds as well as for concentrated alloys.

Although some limiting cases of the above HF picture are well understood, it is still not clearly established to what extent the local single-ion features survive at intermediate temperatures. For the "lighter" HF compounds $YbCuAl$ and $CeSn_3$ a surprisingly good agreement for χ , C , magnetization and neutron-scattering linewidth with the single-impurity theory has been found¹¹ down to very low T . Such a study is difficult in the "heavier" HF compounds, because of the small characteristic energy scale and large crystal-field effects. In such systems, the

role of the site-to-site correlations of the f electrons is more conveniently probed by alloying studies. In several studies¹² Ce ions have been gradually replaced by La, e.g., (Ce,La)Al₃,¹³ (Ce,La)Cu₂Si₂,¹⁴ (Ce,La)Ge₂,¹⁵ and (Ce,La)B₆,¹⁶ or by Th, e.g., (Ce,Th)Pd₃.¹⁷ Unfortunately, alloying in these systems (unlike the one reported here) changes the degree of valence mixing or Kondo temperature as well as the crystal-field splittings, complicating the analysis, such that only a qualitative comparison is possible.

Within this Letter, we present measurements of the electrical resistivity, $\rho(T)$, specific heat, $C(T)$, and susceptibility, $\chi(T)$, for Ce_{1-x}La_xPb₃. This system has the fortuitous and (so far) *unique* property that the relevant parameters (T_K and crystal-field splitting) are concentration independent. This permits one (for the first time) to appraise quantitatively the effect of the intersite correlations of the f electrons for the entire concentration range $0 \leq x < 1$ and as a function of T . The $x=0$ end point corresponds to CePb₃ which is a HF antiferromagnet displaying coherent behavior with unusual high-field magnetoresistance.¹⁸

The polycrystalline (Ce,La)Pb₃ samples were prepared in an inert atmosphere arc furnace with appropriate care taken to compensate for the weight loss of the more volatile constituent, Pb. The samples were annealed under high vacuum at 600°C for one week. Powered x-ray diffraction studies revealed that all samples were single phase and the diffraction pattern is indexable to a face-centered-cubic structure. The concentration dependence of the lattice constant followed a linear behavior across the series without any indication of a valence change. The electrical resistivity, $\rho(T)$, was measured using a conventional four-probe dc technique. The specific heat $C(T)$ was measured using both a quasiadiabatic method for $1.5 < T < 20$ K and a low-mass thermal-relaxation method for $0.4 < T \leq 4$ K. The magnetic susceptibility $\chi(T)$ was measured for $1.8 < T < 300$ K by use of a commercial vibrating sample magnetometer.

Shown in Fig. 1 is the temperature dependence of the magnetic contribution to the electrical resistivity, $\rho_m(T)$, defined to be equal to $\rho(T)$ for (Ce,La)Pb₃ minus the temperature-dependent resistivity of LaPb₃ (the non-magnetic, isomorphic, analog of CePb₃). In Fig. 1(a), $\rho_m(T)$ for $T < 20$ K and $x \leq 0.15$ is displayed. Clearly shown in this figure is the onset of coherence, considerably above $T_N = 1.1$ K, for the strongly correlated pure CePb₃ sample ($x=0$). That is, ρ_m begins to decrease markedly below 2.5 K for the $x=0$ sample. This coherence is rapidly suppressed upon dilution and by $x=0.2$, there is no evidence of coherence to the lowest temperature measured, $T=0.4$ K. In Fig. 1(b), the temperature dependence of $\rho_m(T)$ over an extended range of La-concentration is displayed. If the measured $\rho_m(T)$ is normalized by the Ce concentration, i.e., $\rho_m(T)/(1-x)$, the data collapse onto a single curve for all $x \geq 0.2$ with

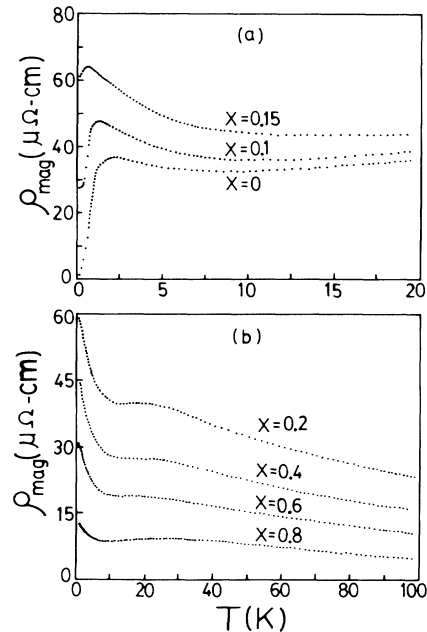


FIG. 1. Magnetic resistivity ρ_m vs temperature for Ce_{1-x}La_xPb₃ samples. Here ρ_m is defined as the total resistivity minus the temperature-dependent resistivity of LaPb₃. (a) $x=0, 0.1$, and 0.15 up to $T=20$ K. (b) $x=0.2$ to 0.8 up to $T=100$ K.

a slight spread in the data of about 5% (the shoulder for $x=0.8$ is somewhat more pronounced, but within the 5% spread). The $\rho_m(T)/(1-x)$ data are qualitatively consistent with a recent calculation by Maekawa and co-workers¹⁹ of the resistivity of a Coqblin-Schrieffer impurity with $J = \frac{5}{2}$ (Ce³⁺) with appropriate crystal-field splitting, Δ . The resistivity shows a peak or shoulder due to the gradual freezing out of the crystal-field states. The peak is broadened as a result of relaxation and at low T a peak due to the Kondo resonance arises. The crystal-field peak (shoulder) appears at a temperature of about $1/3$ to $1/2.5$ of the splitting if Δ is large compared to T_K . Neutron studies²⁰ have shown that the $J = \frac{5}{2}$ Ce³⁺ Hund's-rule ground state is split by the cubic crystalline electric field (CEF) into a Γ_7 -doublet ground state and an excited Γ_8 quartet with a CEF splitting $\cong 66$ K.¹⁹ Hence, the CEF shoulder should appear at about 25 K in the resistivity, in agreement with the findings for all x . Thus, for $x \geq 0.2$, $\rho_m(T)/(1-x)$ is independent of x , suggesting that T_K and CEF splitting are also independent of x .

Figure 2 shows $\chi(T)$ per mole Ce versus T . As with $\rho_m(T)$ [and as we will see below for the excess specific heat, $\Delta C(T)$], $\chi(T)$ per mole Ce is independent of concentration. For $T > 20$ K, the $\chi(T)$ per Ce can be fitted to a modified Curie-Weiss law, i.e., $\chi(T) = C/(T+T^*)$ with $T^* = 18$ K and an effective paramagnetic moment of $2.5\mu_B$. These results are consistent with those recently

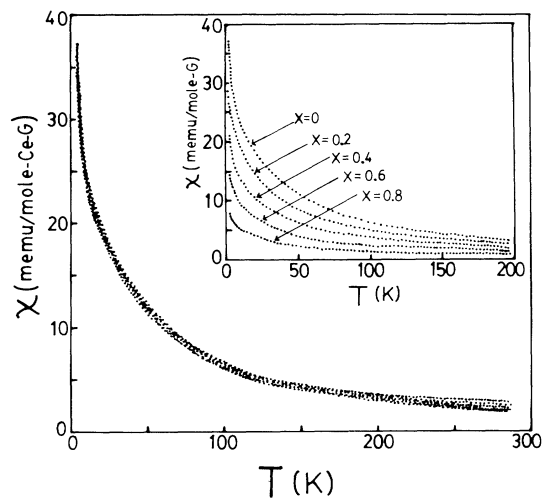


FIG. 2. Magnetic susceptibility per mole Ce vs T for $Ce_{1-x}La_xPb_3$ samples, $x=0, 0.2, 0.4, 0.6,$ and 0.8 . Inset: Magnetic susceptibility per mole (not per Ce mole) vs T for the same samples.

published by Durkop *et al.*²¹ Durkop *et al.*²¹ have measured $\chi(T)$ and for the low-temperature data (i.e., $T_N < T < 4$ K), the data were fitted by a modified Curie-Weiss behavior. For this low-temperature region, they obtained $\mu_{eff} = 1.6\mu_B$ and $T^* = 7.5$ K. This T^* value is consistent with a low T_K obtained from specific-heat results to be presented next.

Shown in the inset of Fig. 3 is $C(T)/T$ per mole Ce versus T^2 for $(Ce,La)Pb_3$ at $T \geq 1.5$ K. Note that

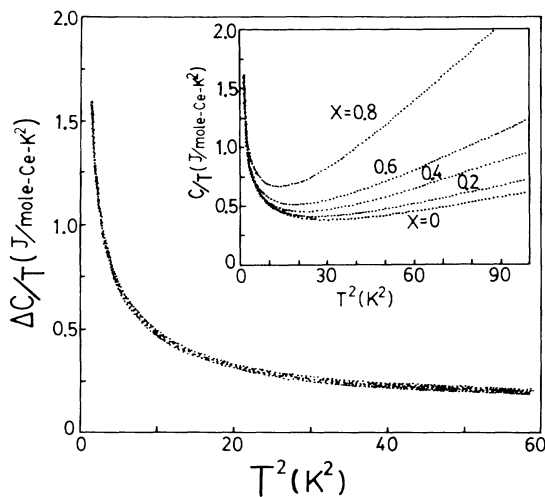


FIG. 3. The excess specific heat per mole Ce divided by temperature, $\Delta C/T$ vs T^2 for $Ce_{1-x}La_xPb_3$ samples, $x=0, 0.2, 0.4, 0.6,$ and 0.8 . For a definition of $\Delta C/T$ see the text. Inset: Total specific heat divided by T , C/T vs T^2 , for the same samples.

$C(T)/T$ data for $T \cong 1.5$ K approach a common limit independent of x . Shown in Fig. 3 is $\Delta C(T)/T$ per mole Ce versus T^2 , where $\Delta C(T)$ is $C(T)$ minus the βT^3 obtained from a fit of $C(T) = \gamma T + \beta T^3$ for $8 < T < 20$ K. The subtracted contribution is due to the lattice. There was only a slight variation of β across the alloy series obtained from this analysis, i.e., for $CePb_3$ $\beta = 4.09$ mJ/mole K^4 and for $LaPb_3$ $\beta = 4.33$ mJ/mole K^4 . The amazing result displayed in Fig. 3 is that $\Delta C(T)/T$ versus data for all samples collapse onto a single curve for $1.5 < T < 8$ K as did the $\chi(T)$ curves of Fig. 2. This also indicates that T_K is independent of concentration. Hence, the extremely enhanced $\gamma = C(T)/T$ previously reported for $CePb_3$ (which orders antiferromagnetically at $T_N = 1.1$ K) cannot be dismissed as simply a precursor to a magnetic transition since as little as 20% La ($x = 0.2$) appears to drive T_N to zero and $\Delta C/T$ per mole Ce is independent of Ce concentration.

Shown in Fig. 4 is $\Delta C(T)$ per mole Ce versus $\log(T/T_K)$ for three samples of widely varying Ce content (60%, 40%, and 4%) which do not order magnetically. Plots of $\Delta C(T)$ versus $\ln(T)$ have a maximum at 2.3 K which is again independent of Ce concentration. Since exact calculations of $C(T)$ vs T for a single-ion Kondo model⁶ predict a maximum in $C(T)$ at $T \cong 0.7T_K$ we find $T_K = 3.3$ K for all three samples. When one considers that there are no theoretical parameters other than T_K , i.e., the magnitude and temperature dependence of $C(T)$ vs T is completely specified, the excellent agreement of theory (solid curve of Fig. 4) and data for 4%,

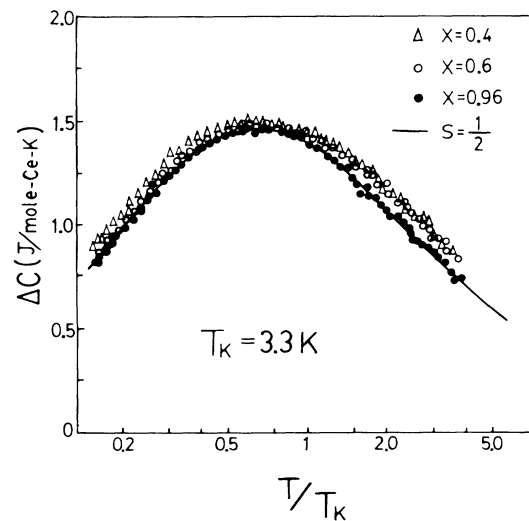


FIG. 4. The excess specific heat per mole Ce, ΔC vs $\log(T/T_K)$ for $Ce_{1-x}La_xPb_3$ samples with $x=0.4, 0.6,$ and 0.96 . Here T_K is the Kondo temperature (3.3 K for all three samples) and ΔC is defined in the text. The solid curve is the theoretical fit involving no adjustable parameters other than T_K as discussed in the text.

40%, and 60% Ce is quite remarkable. For $x < 0.4$ (more than 60% Ce) a slight upswing is seen below $T/T_K \cong 0.4$ because of magnetic correlations which eventually lead to magnetic ordering for the very Ce-rich alloys. However, the large γ observed for CePb₃ down to $T = 1.5$ K (i.e., 0.4 K above $T_K = 1.1$ K) appears to be totally attributable to an enhanced density of states due to the single-ion Kondo resonance at the Fermi energy.

In summary, we found that for Ce_{1-x}La_xPb₃ the relevant parameters, e.g., T_K and the crystal-field scheme, are independent of the concentration. The resistivity, $\rho_m(T)$, the susceptibility, $\chi(T)$, and the specific heat, $\Delta C(T)$, scale with the concentration of Ce ions over a surprisingly large interval of x . Exceptions to this scaling are the antiferromagnetic order (and precursing fluctuations) and the onset of coherence in the resistivity for $x \leq 0.15$ at low T . At intermediate temperatures and $x \leq 0.15$, $\rho_m(T)$ shows minor deviations from scaling which may be a precursor to coherence and/or due to a small renormalization of T_K . Furthermore, we have shown that the scaled specific heat agrees quantitatively with that of an $S = \frac{1}{2}$ Kondo impurity⁶ and the scaled resistivity is qualitatively in accord with the theoretical prediction¹⁹ for a Ce ion.

In conclusion, the interference effects between different Ce sites in (Ce,La)Pb₃ are surprisingly small. The impurity picture is valid over a larger temperature interval than expected, even for Ce-rich samples. The high γ value of CePb₃ is to be attributable to the Kondo resonance, rather than to other Fermi-liquid corrections. Although our experimental findings quantify the interaction effects between Ce ions, the key question⁹ as to how a concentrated Kondo system with almost noninterfering sites can exist remains unanswered.

This work was supported by the National Science Foundation Grant No. DMR-82-19782.

¹G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984), and references therein.

²P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Condens. Matter Phys. **12**, 98 (1986).

³Articles in *Theory of Heavy Fermions and Valence Fluctuations*, edited by T. Kasuyo and T. Saso (Springer-Verlag, Berlin, 1985).

⁴H. R. Ott, H. Rudigier, T. M. Rice, K. Ueda, Z. Fisk, and J. L. Smith, Phys. Rev. **52**, 1915 (1984).

⁵P. W. Anderson, Phys. Rev. **B 30**, 1549 (1984).

⁶V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

⁷N. Andrei, K. Furuya, and J. H. Lowenstein, Rev. Mod. Phys. **55**, 331 (1983).

⁸P. Nozières, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Otaniemi, Finland, 1975*, edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975), Vol. 5, p. 339.

⁹P. Nozières, Ann. Phys. (Paris) **10**, 19 (1985).

¹⁰R. Jullien, J. Fields, and S. Doniach, Phys. Rev. Lett. **38**, 1500 (1977); C. Lacroix and M. Cyrot, Phys. Rev. **B 20**, 1969 (1979).

¹¹A. C. Hewson *et al.*, in Ref. 3; P. Schlottmann, J. Appl. Phys. **57**, 3155 (1985), and Z. Phys. **B 57**, 23 (1984); D. L. Cox, N. E. Bickers, and J. W. Wilkins, J. Appl. Phys. **57**, 3166 (1985).

¹²N. B. Brandt and V. V. Moschalkov, Adv. Phys. **33**, 373 (1984), and references therein.

¹³R. E. Majewski, A. S. Edelstein, and A. E. Dwight, Solid State Commun. **31**, 315 (1979).

¹⁴F. G. Aliev, N. B. Brandt, V. V. Molschalkov, and S. M. Chundinov, J. Low Temp. Phys. **57**, 61 (1984).

¹⁵M. Mori, H. Yashima, and Nobuga Sato, J. Low Temp. Phys. **58**, 513 (1985).

¹⁶N. Sato, S. Kunii, I. Oguro, T. Komatsubara, and T. Kasuya, J. Phys. Soc. Jpn. **54**, 1923 (1985).

¹⁷R. Selim and T. Mihalisin, Solid State Commun. **59**, 785 (1986).

¹⁸C. L. Lin, J. Teter, J. E. Crow, T. Mihalisin, J. Brooks, A. I. Abou-Aly, and G. R. Stewart, Phys. Rev. Lett. **54**, 2541 (1985).

¹⁹S. Kashiba, S. Maekawa, S. Takahashi, and M. Tachiki, J. Phys. Soc. Jpn. **55**, 1341 (1986); S. Maekawa, S. Kashiba, S. Takahashi, and M. Tachicki, in Ref. 3, p. 90.

²⁰C. Vettier, P. Morin, and J. Flouquet, Phys. Rev. Lett. **56**, 1981 (1986).

²¹D. Durkop, E. Braun, B. Politt, H. Schmidt, B. Roden, and D. Wohlleben, Z. Phys. **B 63**, 55 (1986).