Evidence for Non-Fermi-Liquid Behavior in the Kondo Alloy $Y_{1-x}U_xPd_3$

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We present measurements of electrical resistivity $\rho(T)$, specific heat $C(T)$, entropy $S(T)$, and magnetic susceptibility $\chi(T)$ as functions of temperature T for the alloy system $Y_{1-x}U_xPd_3$. For $x=0.2$, $\rho(T)/\rho(0)$ is almost linear in T for $0.2 \leq T \leq 20$ K, and $C(T)/T \sim -\ln(\alpha T)$ for $0.6 < T < 16$ K. Also, the added molar entropy per U, $\Delta S(T)-\Delta S(0)$ appears to saturate to $(R/2)\ln(2)$, suggesting that $\Delta S(0) \approx (R/2)\ln(2)$. We argue that our data provide comprehensive evidence in a dilute alloy for the two-channel quadrupolar Kondo effect ($T_K \approx 42$ K) with concomitant "marginal Fermi liquid" phenomenology.

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Strongly correlated electronic materials, especially the heavy-fermion systems and cuprate high-temperature superconductors, have been the focus of intense investigation over the past several years [1,2]. For the heavy-fermion materials, progress has been made in understanding the origin of the hundredfold or thousandfold enhancement of the effective mass in the normal state as we shall describe below. However, there is still little consensus as to the origin of the "Luttinger liquid" [3] or "marginal Fermi liquid" [4] phenomenology in the normal state of the cuprates.

In this Letter we present data on the Kondo alloy system $Y_{1-x}U_xPd_3$ which displays a variety of behaviors ranging from apparent localized quadrupolar order as $x \rightarrow 1$ through possible spin-glass behavior for $0.3 \leq x \leq 0.5$. We will mainly discuss the composition $x=0.2$, for which the resistivity $\rho(T)$ (Fig. 1), specific heat $\Delta C(T)$ (Fig. 2), and entropy $\Delta S(T)-\Delta S(0)$ (Fig. 3) provide compelling evidence for a two-channel Kondo effect [5]. The two-channel Kondo model is known to have the character of a "local marginal Fermi liquid" [6,7] for which $\Delta C/T \sim -\ln(\alpha T)$ [8-10], $\rho(T)/\rho(0) \sim 1 - AT$ [7], and $\Delta S(0)$ has the unusual value of $(R/2)\ln(2)$ [8-10]. Empirical arguments which indicate nominal tetravalence of the uranium ions favor interpretation of our data in terms of the two-channel quadrupolar Kondo effect of a cubic Γ_3 doublet [6,7].

It is generally accepted that in cerium- (Ce-) based systems heavy fermions arise from the Kondo effect, which is well understood in the dilute limit [1]. In this case the Kondo effect derives from antiferromagnetic coupling of one unit (or channel) of conduction electron magnetic moment to an effective spin-$\frac{1}{2}$ local magnetic moment on the Ce sites. The ground state of this model is a many-body singlet. The excitation spectrum is that of a local Fermi liquid: The added specific heat $\Delta C(T)/T$ and susceptibility $\Delta\chi(T)$ per impurity tend to $\sim 1/T_K$ at low temperatures, with the effective degeneracy temperature being the Kondo scale $T_K \sim E_F \exp(-E_F/|J|)$, where J is the antiferromagnetic exchange coupling and E_F the Fermi energy. Since usually $|J|/E_F \ll 1$, T_K is typically small, and hence the effective mass is large. That this picture extends to concentrated Ce-based compounds has considerable theoretical support [1,11] and strong empirical backing from alloying studies of $La_{1-x}Ce_xPb_3$ [12].

The origin of heavy fermions in the uranium- (U-) based intermetallics is more controversial. The greater extent of the $5f$ orbitals has led to debate over itinerant versus localized treatments [13,14]. In the localized limit it is unclear whether to take the U ions as nominally tetravalent ($5f^2$) [6,7,15] or trivalent ($5f^3$) [16], and it has been questioned whether crystal-field excitations are at all relevant [13]. There is little debate for UPd_3: This intermetallic compound possesses sharp crystal-field excitations with a first excited state at 35 meV compatible with U^{4+} [17].

Given the evidence for localized $5f^2$ states in UPd_3 [17,18], work was commenced to dilute this system by substituting U with Y to form $Y_{1-x}U_xPd_3$. This system was initially studied by photoemission spectroscopy (PES) which showed an increase in the binding energy $E_{5f}-E_F$ of the apparent $5f^2 \rightarrow 5f^1$ peak with increasing x [18]. Since the magnitude of the negative Schrieffer-Wolff exchange integral J varies with $1/|E_{5f}-E_F|$, T_K should decrease with increasing x. These considerations motivated the present study of the transport, magnetic, and thermal properties of $Y_{1-x}U_xPd_3$.

Polycrystalline specimens of $Y_{1-x}U_xPd_3$ with various U concentrations in the range $0 \le x \le 1$ were prepared by arc melting in an argon atmosphere. Powder x-ray-diffraction patterns revealed no impurity phases, indicating that these samples are single phase with the cubic Cu_3Au-type crystal structure for $0 \le x \le 0.5$ and the hexagonal Ni_3Ti-type structure for $0.9 \le x \le 1$. In the concentration regime $0.6 \le x \le 0.8$, the samples are mixed phase. For the cubic samples, the lattice parameter a increases with x from 4.072 ± 0.002 Å ($x=0$) to 4.087 ± 0.002 Å ($x=0.5$). This small rate of increase is consistent with U ions that are tetravalent, U^{4+} being more comparable in size to Y^{3+} than U^{3+}.

Despite the mixed phase regime and structural change, all properties evolve smoothly as a function of x and correlate with the PES results [19]. For $x < 0.3$ our data are consistent with a Kondo ground state for which T_K [as measured roughly by where $\rho(T)/\rho(0)=0.5$] falls with increasing x. For larger $x \gtrsim 0.3$, we observe cooperative behavior which we interpret as spin-glass freezing given the irreversible behavior of $\chi(T)$ below a freezing temperature T_{SG} which increases monotonically with x.

Figure 1 displays ρ vs $\ln T$ below 300 K for a sample with $x=0.2$. Note that $\rho(T)$ is linear in $-\ln T$ above 80 K, consistent with single-ion Kondo scattering of conduction states off localized U $5f$ states. The background contribution of YPd_3 is negligible below 100 K. In order to determine the low-temperature power-law behavior, we have plotted the data as $\ln[1-\rho/\rho(0)]$ vs $\ln T$ which yields a straight line below ~ 20 K using $\rho(0) = 357.70 \pm 0.05$ $\mu\Omega$ cm (see inset). The uncertainty in the absolute value of $\rho(0)$ is somewhat larger due to uncertainty in the geometrical factor. Subsequent linear least-squares fits for $0.2 \le T \le 20$ K yielded power-law behavior $\rho/\rho(0) = 1-(T/T_0)^n$, where $n=1.13 \pm 0.04$ and $T_0 = 180 \pm 20$ K. The best fit is represented as the straight line in the inset of Fig. 1. In contrast, if one assumed the midpoint of the logarithmic rise at $T \approx 200$ K in $\rho(T)$ to be T_K (which ignores crystal-field effects) one would expect exclusively T^2 resistivity saturation below 20 K for a single-channel, spin-$\frac{1}{2}$ magnetic Kondo effect.

The added specific heat per U site, $\Delta C/T$, is shown in Fig. 2. ΔC was obtained by subtracting an estimated phonon background term βT^3, with β obtained by scaling the value of YPd_3 ($\beta_0 = 0.256$ mJ/mol K^4) [20] by the average formula-unit molecular weight for a given x. Extrapolation of this result to $x=1$ gives $\beta = 0.41$ mJ/mol K^4, to be compared with isostructural (to UPd_3) $ThPd_3$ which has $\beta = 0.5$ mJ/mol K^4 [21]. The phonon contribution could not be determined directly due to the

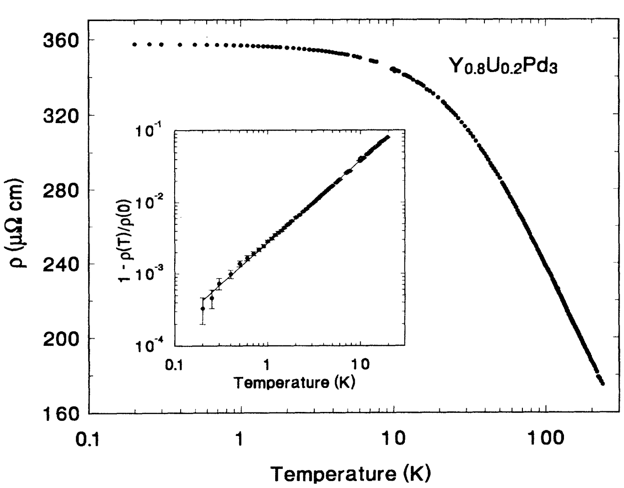

FIG. 1. Temperature dependence of the electrical resistivity $\rho(T)$ of $Y_{0.8}U_{0.2}Pd_3$. The data follow $-\ln T$ behavior, indicative of the Kondo effect, above about 80 K and saturate below ~ 20 K (inset) with power-law behavior $\rho/\rho(0) = 1-(T/T_0)^n$, with best fit using $\rho(0) = 357.7$ $\mu\Omega$ cm, $n=1.13$, and $T_0 = 180$ K.

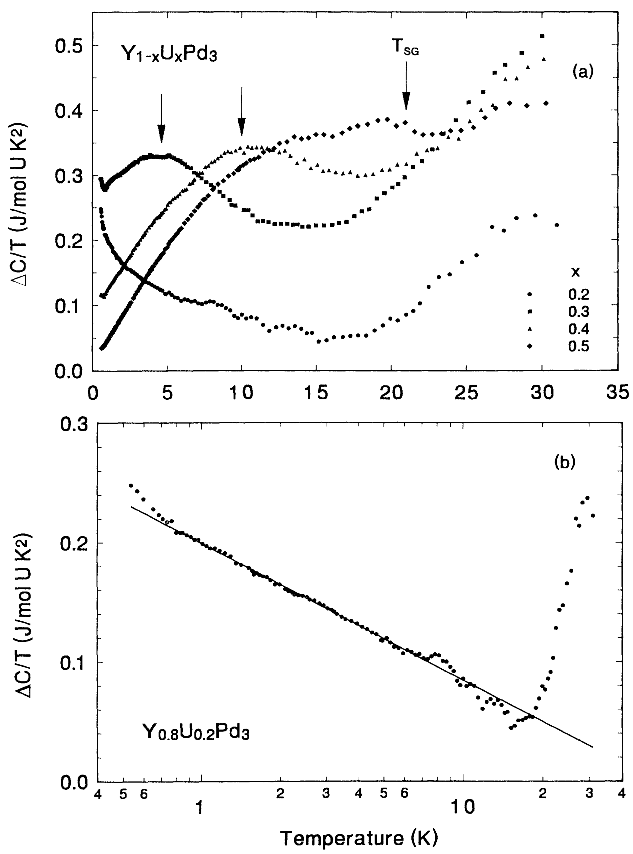

FIG. 2. (a) Temperature dependence of the electronic specific heat per U, $\Delta C(T)/T$ vs T, for $Y_{1-x}U_xPd_3$, $0.2 \le x \le 0.5$. T_{SG} is the peak position of $\Delta C(T)/T$ associated with apparent spin-glass freezing; $\chi(T)$ shows an onset to irreversibility at the same temperature. Note (i) the lack of a peak for $x=0.2$, and (ii) the upturn near 20 K due to an apparent excited-state Schottky anomaly. (b) $\Delta C(T)/T$ vs $\ln T$ for $Y_{0.8}U_{0.2}Pd_3$. The solid line represents a least-squares fit of the data by the form $-(0.25/T_K)\ln(T/0.41T_K)+b$ [9]. From the slope we obtain $T_K = 42$ K, and the background coefficient b is 61 mJ/mol K^2, which likely arises from an excited-state Schottky anomaly.

apparent Schottky anomaly, visible as an upturn in Fig. 2 above about 20 K. However, the low-temperature data are insensitive to β. For $0.3 \leq x \leq 0.5$, broad anomalies we ascribe to spin-glass freezing appear in the data [see Fig. 2(a)]; the peak positions agree well with T_{SG} determined from irreversibility in static magnetic-susceptibility measurements.

Note that there is no peak in $\Delta C(T)/T$ for $x=0.2$. The data are clearly linear in $-\ln(T)$ from about 0.8 to 20 K, as seen in Fig. 2(b). The solid line represents a linear least-squares fit of the $\Delta C(T)/T$ vs $\ln(T)$ data, which gives a slope of $-0.0500(2)$ J/(mol U) K^2 and an intercept of about 55 K. Below 0.8 K, the samples exhibit an upturn whose magnitude decreases with decreasing x; this upturn may also be responsible for the deviation from $\ln(T)$ behavior below 0.8 K in Fig. 2(b).

The entropy $\Delta S(T) - \Delta S(0)$ vs T is displayed in Fig. 3. Direct integration was used to obtain the entropy for $T \geq 0.5$ K. For $0.3 \leq x \leq 0.5$, linear extrapolation of $\Delta C(T)$ was used to obtain the entropy below 0.5 K. For $x=0.2$, we extrapolated $\Delta C/T$ below 0.8 K following the $-\ln(T)$ form discussed in the previous paragraph. We note the following: (i) for $0.3 \leq x \leq 0.5$, the $\Delta S(T) - \Delta S(0)$ curves converge for entropy values $\gtrsim R\ln(2)$ and temperatures $\gtrsim 20$ K, above T_{SG} in each case. This suggests that the spin-glass freezing removes entropy from doublet ground states. We attribute the rise above 20 K to a Schottky anomaly arising from excited crystal-field levels. (ii) For $x=0.2$, $\Delta S(T) - \Delta S(0)$ has a manifestly different character than the higher-concentration data. The entropy below 20 K is substantially lower than

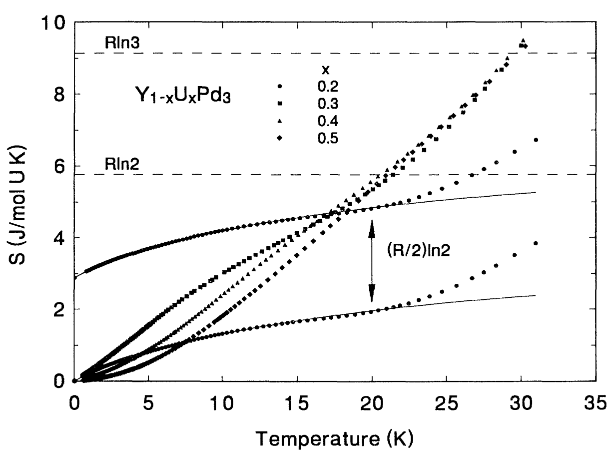

FIG. 3. Temperature dependence of the added electronic entropy per U, $\Delta S(T) - \Delta S(0)$, vs T for $Y_{1-x}U_xPd_3$ derived from the data of Fig. 2. While $\Delta S(T)$ for $0.3 \leq x \leq 0.5$ converges to $\sim R\ln(2)$ near ~ 20 K, suggestive of freezing out of a doublet ground state, $\Delta S(T) - \Delta S(0)$ is greatly reduced for $x=0.2$ with apparent saturation to $(R/2)\ln(2)$, suggestive of a ground-state entropy of the same value (offset curve). The upturn above 20 K is likely due to an excited-state Schottky anomaly. The solid line through the $x=0.2$ data is obtained from the fit of Fig. 2(b).

$R\ln(2)$, suggesting that the ground-state degeneracy is not completely lifted. Adding $\Delta S(0) = (R/2)\ln(2)$ produces the offset curve in Fig. 3 which yields an entropy at 20 K which is close to the values of the other samples. The solid line through the $x=0.2$ data represents the integrated fit of the $\Delta C(T)/T$ data plus $(R/2)\ln(2)$ for the offset curve; we observe that the extrapolated curve appears to saturate to $R\ln(2)$.

We believe the most likely possibility for explaining the $R\ln(2)$ entropy apparent in our low-temperature data is that it arises from a non-Kramer's Γ_3 ground-state doublet. This doublet derives from crystal-field splitting of the $J=4$ Hund's-rule ground multiplet at a site of cubic symmetry. To support this assignment, we note the following: (i) The nominal tetravalent behavior of the U ions here is strongly suggested by the Fermi-level-tuning interpretation of the PES data [18], supported by the evolution of T_K with x from our measurements [19]; the small increase in the cubic lattice parameter a with x; and the neutron-scattering data for UPd_3 [17], as previously mentioned. (ii) Given tetravalence, the only doublet state possible in cubic symmetry is Γ_3—the other crystal-field states are Γ_4, Γ_5 triplets and a Γ_1 singlet [22]. (iii) The cubic compound UPd_4 also has the Cu_3Au structure [23] and shows evidence (from neutron scattering and magnetization) for a Γ_3 ground state and excited Γ_5, Γ_4, and Γ_1 levels at 5, 80, and 200 meV, respectively [24]. (iv) The connection to UPd_4 is strengthened by extrapolation of our measured T_{SG} values to higher x where they pass close to the Néel temperature $T_N \approx 30$ K of UPd_4 [23]. We now interpret our results in terms of the two-channel quadrupolar Kondo effect associated with this doublet state [6,7].

The m-channel Kondo Hamiltonian [5] consists of m identical conduction bands antiferromagnetically coupled via Heisenberg exchange to an impurity spin S_I. For $m > 2S_I$, the model possesses a $T=0$ critical point [5,8–10]. A previous claim for a nontrivial number of scattering channels in a very dilute (32 ppm) Au-V alloy was made by Geens, Labro, and Mordijck, based strictly on magnetization measurements [25]. Their data are consistent with $m=5$, $S_I = \frac{3}{2}$, and $T_K = 60$ K. For the case $m=2$, $S_I = \frac{1}{2}$, the model produces a local-marginal-Fermi-liquid excitation spectrum, with logarithmically divergent $\Delta C(T)/T$ and $\Delta\chi(T)$ [8–10], a resistivity which saturates linearly as $T \to 0$ [7], and a residual ground-state entropy of $(R/2)\ln(2)$ [8–10].

Clearly, the data for $x=0.2$ are consistent with the properties of a two-channel, $S_I = \frac{1}{2}$ Kondo model. First, calculations of $\Delta C/T$ show that the low-temperature slope with respect to $\ln T$ has the universal value [9] $(1/R)d(\Delta C/T)d\ln T = -0.251/T_K$. Application of this to the logarithmic region in Fig. 2(b) yields $T_K = 42$ K. An auxiliary check is provided by the temperature T_x where the logarithmic line intersects the temperature axis which is expected to be $T_x = 1.13T_K/e = 0.41T_K$. Our data yield $T_x = 1.31T_K$, which we believe arises from the apparent Schottky anomaly: A background term in $\Delta C/T \approx 61$ mJ/mol K^2 of the form R/T_{exc} would not change the T_K estimate derived above, but would raise T_x above $0.41 T_K$. The low-temperature power-law behavior of the resistivity of Fig. 1 has the form $\rho(T)/\rho(0) = 1 - [T/(4.3 \pm 0.5)T_K]^{1.13 \pm 0.04}$ given the T_K above. A heuristic argument leads to a low-temperature resistivity of the form [7] $\rho(T)/\rho(0) \approx \{1 - [1 + \ln(2)]T/8T_K\} = 1 - T/4.7T_K$.

On rigorous group-theoretical grounds, the quadrupolar Kondo effect is the only way to realize an $m=2$, $S_I = \frac{1}{2}$ Kondo model for U^{4+} ions in cubic or tetragonal symmetry. This is described as a quadrupolar Kondo effect because the Γ_3 doublet has vanishing magnetic dipole ($\mathbf{J}$) matrix elements, but nonvanishing electric quadrupole matrix elements of $Y_{2m}(\mathbf{J})$. The local quadrupolar degrees of freedom can be described by an effective isotropic spin $\frac{1}{2}$. The orbital motion of conduction states couples "antiferromagnetically" to this local quadrupolar "spin" to quench it. The orbital quadrupolar moments are invariant under time reversal, so that two channels of conduction quadrupolar pseudospin couple to the U site.

A pure two-channel model with any magnetic character would yield a low-temperature magnetic susceptibility $\Delta\chi(T) \sim -\ln(T)$ as in $\Delta C(T)/T$ [8-10]. The situation is complicated by large van Vleck susceptibilities which are believed to give $\Delta\chi(T) \sim A - BT^{1/2}$ [7]. While our $\Delta\chi(T)$ data follow $T^{1/2}$ between 1.6 and 4.0 K, they rise somewhat more steeply than $-\ln(T)$ below $T = 1.0$ K, which may be inconsistent with the Γ_3-doublet possibility. However, the Γ_3 assignment is strengthened by new magnetic-field-dependent specific-heat data which show a crossover characteristic of coupling to the channel spin [26], a small negative magnetoresistance [19,26], and preliminary magnetic neutron-scattering data which show no pronounced quasielastic scattering intensity [27]. While the magnetic susceptibility and magnetoresistance results await complete understanding, it is clear that a magnetic Kondo effect would produce a spin-dependent crossover of the specific heat in field, strong negative magnetoresistance, and quasielastic magnetic scattering, in contrast to the data.

Furthermore, data on $Y_{0.9}U_{0.1}Pd_3$ show behavior similar to $Y_{0.8}U_{0.2}Pd_3$, but with a larger $T_K \sim 100$ K, consistent with Fermi-level tuning: $\rho(T)$ is approximately linear in T below 100 K and $\Delta C(T)/T$ shows a $-\ln T$ divergence below 7 K [19].

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