Heavy-non-Fermi-liquid behavior in $U(Cu,Pd)_5$

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We report measurements of the lattice constant, electrical resistivity, magnetic susceptibility, and specific heat of $UCu_{5-x}Pd_x$ for $0 \le x \le 2.3$. Alloys corresponding to $x < 0.75$ are antiferromagnets, with T_N strongly concentration dependent. χ and C for $x \ge 2$ are consistent with spin-glass freezing. C/T for $UCu_{3.5}Pd_{1.5}$ diverges logarithmically as $T \to 0$ K while ρ is linear in T at the lowest temperatures. The thermodynamic properties of this alloy are inconsistent with the Fermi-liquid theory down to at least 0.32 K.

The discovery[1] of an unusual temperature dependence of the specific heat and electrical resistivity in $U_{0.2}Y_{0.8}Pd_3$ has revived an interest in a possibility of observing non-Fermi-liquid ground states in metallic systems. This discovery might also have important implications for our understanding of the low-temperature enhancement of thermodynamic and magnetic properties in some U intermetallics commonly referred to as heavy fermions.[2]

A canonical description of heavy-fermion materials is based on the existence of two temperature regimes: (1) a high-temperature regime characterized by weak interactions of local magnetic moments and conduction electrons and (2) a strongly interacting, low-temperature regime having Fermi-liquid-like character. The crossover temperature T_K also plays the role of a Fermi temperature for the low-temperature properties. The novel feature of the thermodynamic, magnetic, and transport data of $U_{0.2}Y_{0.8}Pd_3$ is the lack of a transition into the low-temperature Fermi-liquid state. The mechanism, which prevents the occurrence of this transition has recently became a subject of extended debate. Several different scenarios have been proposed: (1) nontrivial overcompensation of the $S=\frac{1}{2}$ impurities via the single-impurity two-channel (quadrupolar) Kondo effect,[1] (2) magnetic intersite interactions leading to a novel phase transition at 0 K,[3] and (3) disorder on nonmagnetic sites, possibly with effects on the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, in the proximity of a metal-insulator transition.[4]

In order to resolve this issue and to further explore the character of the ground state of $U_{0.2}Y_{0.8}Pd_3$ we have been searching for other U-based systems showing similar non-Fermi-liquid characteristics. In this communication we report a discovery of a Fermi-liquid breakdown in pseudobinary alloys of $UCu_{5-x}Pd_x$. Our studies of this system were motivated by unusual low-temperature properties of UCu_5 (Refs. 5 and 6) and by encouraging ^{4}He temperature magnetic susceptibilities and electrical resistivity results for $UCu_{5-x}Pd_x$.[7] Some of the experimental results presented here were already reported elsewhere[8] and have generated considerable interest.

The low-temperature properties of UCu_5 are difficult to reconcile with a conventional Kondo effect, on which the present microscopic understanding of heavy fermions is based. This compound develops high values of C/T at temperatures below 10 K, despite large, local-moment antiferromagnetic ordering at about 16 K. UCu_5 undergoes an additional, 1-K phase transition, presumably first order, of unknown origin, which is accompanied by a 10-fold reduction of C/T below 1 K (Ref. 6) and a large increase of the electrical resistivity.[5] The low-temperature electrical resistivity approaches an enormous, for an ordered metallic compound, value of almost 1000 $\mu\Omega$cm giving strong indication of proximity to a metal-insulator transition. An especially sharp rise of the electronic part of C/T in the 4–1 K temperature range offers a hope of observing a divergence of C/T as $T \to 0$, provided that the 1- and 16-K transitions are suppressed by appropriate alloying.

Since the end compounds UCu_5 and UPd_5 belong to different crystal structures,[9] (UCu_5 has the fcc $AuBe_5$ structure, UPd_5 can exist in two different not well-identified structures), we confined our investigation to the single-phase fcc, Cu-rich region of the phase diagram. The highest Pd content alloy prepared, UCu_2Pd_3 ($x=3$), was multiphase, while an alloy corresponding to $x=2.3$ was a single-phase material according to the x-ray-diffraction analysis. No extra diffraction lines were detected for $x=2.3$, while the measured lattice constant was consistent with the trend established by the lattice constants for $x<2.3$ (Fig. 1). It is interesting to note that the lattice constant of $UCu_{5-x}Pd_x$ increases only slightly for $x<1$, while for larger values of x the lattice constant changes more rapidly. This non-Vegard's-law behavior is probably caused by the existence of two inequivalent Cu sites in the UCu_5 structure with 20% of the Cu atoms occupying one type of site, say number 1 and the rest of the Cu atoms the number 2 sites. The UCu_4Pd would be a compound in which Cu and Pd atoms were separated on inequivalent crystallographic sites. This conjecture is partially supported by the study of $UPt_{5-x}Au_x$ of the same crystal structure. The residual resistivity analysis indicated that Au atoms, which are larger than Pt (in analogy to Pd being larger than Cu) go preferentially on the number 1 site.

Substitution of Pd for Cu strongly affects the magnetic properties of the $UCu_{5-x}Pd_x$ system (Table I and Fig. 2). The magnetic phase diagram is uncommonly rich and interesting. The magnetic susceptibility results divide the

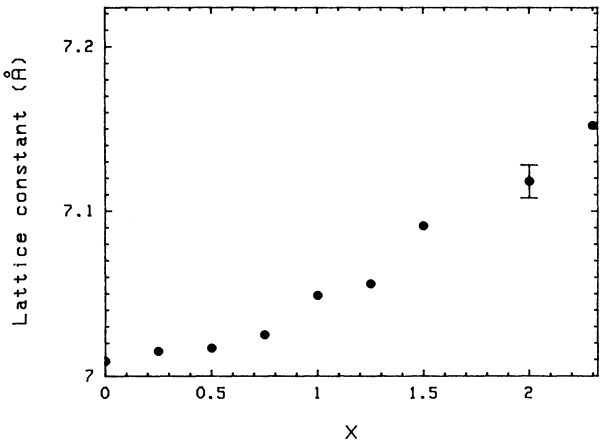

FIG. 1. Lattice constant vs x for $UCu_{5-x}Pd_x$.

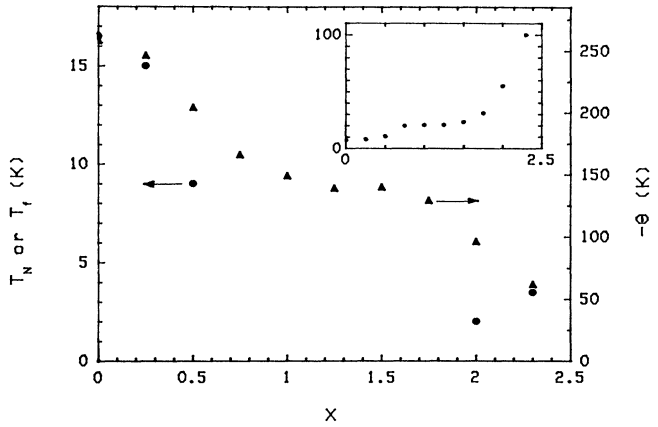

FIG. 2. T_N or T_f (dots) and $-\theta$ (triangles) vs x for $UCu_{5-x}Pd_x$. The inset shows χ_{max} (in memu/mol) vs x. All symbols as defined in the text and Table I.

whole investigated concentration range into three regions: the small Pd content range, $x \leq 0.5$, where the antiferromagnetic transition is suppressed with increasing x, the intermediate region for which no magnetic ordering was observed down to 1.8 K via dc magnetic susceptibility and down to 0.32 K via specific-heat measurements, and the high Pd content range, $x \geq 2$, characterized by a spin-glass behavior.

The maximum of the measured magnetic susceptibility χ_{max} (corresponding to $T=1.8$ K for nonordering alloys ($0.75 \leq x \leq 1.75$) or to the ordering or freezing temperatures for the other compositions) spans a large range of values from 7.2 to 100 memu/mol for $x=0$ and $x=2.3$, respectively. It is interesting to note that for $x<2$, χ_{max} anticorrelates with the ordering temperature, e.g., samples that do not order have χ_{max} 3–4 times larger than that for UCu_5.

At sufficiently high temperatures (>200 K), the magnetic susceptibilities of the $UCu_{5-x}Pd_x$ alloys obey a Curie-Weiss law with the effective moment μ_{eff} only weakly dependent on x. The values of μ_{eff}, $3.2-3.45\mu_B$, are consistent with U ions that have either five f^2 ($\mu_{eff}=3.58\mu_B$) or five f^3 ($3.62\mu_B$) configurations and exclude the five f^4 ($2.68\mu_B$) or five f^1 ($2.54\mu_B$) configurations. The negative paramagnetic Curie temperature ($-\Theta$), on the other hand, is again sensitive to x and correlates inversely with χ_{max}. It is important, for further discussion, to note in Fig. 1 the plateau region ($1 \leq x \leq 1.75$) for both χ_{max} and θ.

TABLE I. Magnetic susceptibility parameters for $UCu_{5-x}Pd_x$. The measurements were performed, down to 1.8 K, in the commercial SQUID susceptometer. T_N stands for a Néel temperature and T_f for a spin-glass-freezing temperature. See the text for explanation of other symbols.

W	χ_{max} or χ (1.8 K) [memu/mol]	$T_N(x \leq 0.5)$ $T_f(x \geq 2)$ [K]	θ [K]	μ_{eff} [μ_B]
0	7.2	16.5	−258	3.43
0.25	8.1	15	−246	3.44
0.5	10.7	9	−204	3.43
0.75	20		−166	3.34
1	20.7		−149	3.37
1.25	20.9		−139	3.33
1.5	23.3		−140	3.34
1.75	31		−129	3.33
2	55	2.0	−96	3.25
2.3	100	3.5	−62	3.21

All the specific-heat results presented below correspond to the electronic part of the specific heat only. The phonon contribution was accounted for by measuring a specific heat for several isostructural $Zr(Cu,Pd)_5$ samples and subtracted from the total specific heat for $U(Cu,Pd)_5$ after proper renormalization reflecting different molecular weights. This correction was about 3% at 4 K for the samples reported here.

It is well known that the low-temperature specific heat of UCu_5 strongly depends on preparation procedures and especially on annealing conditions.[5,6] The exact role of the annealing is not fully understood; however, this annealing seems to be of lesser importance for our Pd-doped samples. Specific-heat measurements performed on an as-prepared $UCu_{3.5}Pd_{1.5}$ sample and on the same sample annealed for two weeks at 950 °C yield identical results. The data presented in this paper, with the exception of UCu_5, were obtained on unannealed material. The low-temperature specific heat for all investigated concentrations is enhanced over that of normal or transition metals.

The 1-K phase transition of pure UCu_5 is quickly suppressed by Pd; a small specific-heat anomaly was still observed at about 0.6 K for $x=0.25$; no such anomaly was detected down to 0.32 K for $x=0.5$.

A different kind of anomaly is exhibited by specific heats corresponding to the other end of the investigated concentration range; C/T for $x=2$ and $x=2.3$ (shown in Fig. 3) alloys show broad maxima at about 2.2 and 3.8 K, respectively. Below these temperatures C/T varies linearly with T or $C=c_1T+c_2T^2$ (Fig. 3). Such a temperature dependence is characteristic of spin glasses[10] and was found for *Cu*Mn alloys.[11] Two other observations strongly support the spin-glass interpretation. The zero-

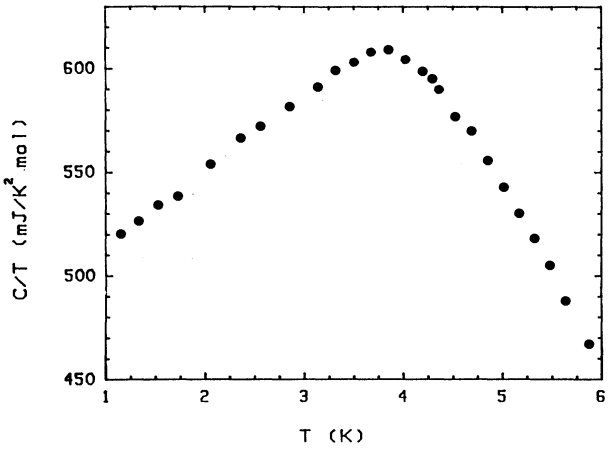

FIG. 3. Specific heat (C) vs temperature (T) for $UCu_{2.7}Pd_{2.3}$.

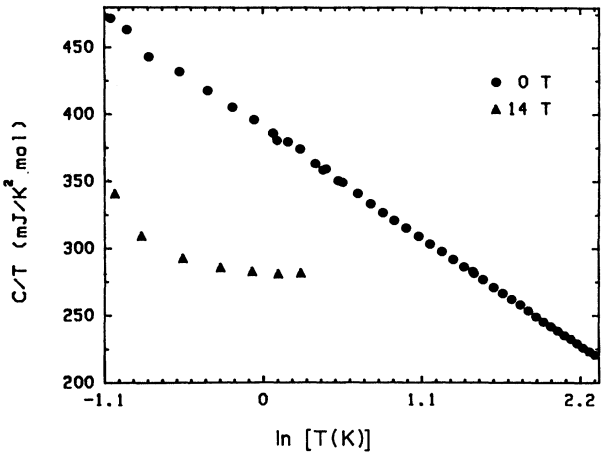

FIG. 5. C/T vs $\ln T$ for $UCu_{3.5}Pd_{1.5}$.

field-cooled static susceptibilities (Fig. 4) for these two concentrations have sharp peaks at temperatures roughly 10% lower than the temperatures corresponding to the maxima of C/T and there are marked deviations between the zero-field-cooled and the field-cooled susceptibilities below the freezing temperatures (T_f). It is remarkable that these concentrated U alloys exhibit classic handbook spin-glass behavior observed previously chiefly only for strongly diluted Mn or Fe in nonmagnetic hosts like Cu or Au.

However, the most interesting low-temperature specific heats are possessed by those compositions that do not order down to at least 0.32 K. The zero-field electronic specific-heat of $UCu_{3.5}Pd_{1.5}$ (see Fig. 5) follows the temperature dependence found previously for $U_{0.2}Y_{0.8}Pd_3$, i.e., $C/T = A \ln(T/T_x)$, where in the present work $A = 74.1 \pm 0.3$ mJ/K^2 mol and $T_x = 191 \pm 2$ K. (The errors are 1σ statistical errors derived from the least-squares fit.) This relation holds over the entire range of temperatures at which the measurements were performed, from 0.32 to 10 K, thus over 1.5 decades of temperatures. In an analysis following the two-channel Kondo model[12] we arrive at a $T_K = 28$ K and $\alpha = T_x/T_K = 6.82$. The change of the entropy between 0.3 and 10 K exceeds $0.5R$ ln2. This value is much too large to be accounted for by the model; according to the numerical calculation[13] ΔS reaches $0.5R$ ln2 at temperatures $\sim 10^3 T_K$ and is only $\sim 0.3R$ ln2 at T_K. A part of our measured entropy could be associated with excited crystal-field levels. Cox has proposed[14] that the numerical value of the α coefficient for the quadrupolar Kondo effect is 0.41. However, this value would imply an enormous crystal-field background $\gamma_0 (\equiv \Delta C/T) = 210$ mJ/K^2 mol, temperature-independent over a large range of temperatures.

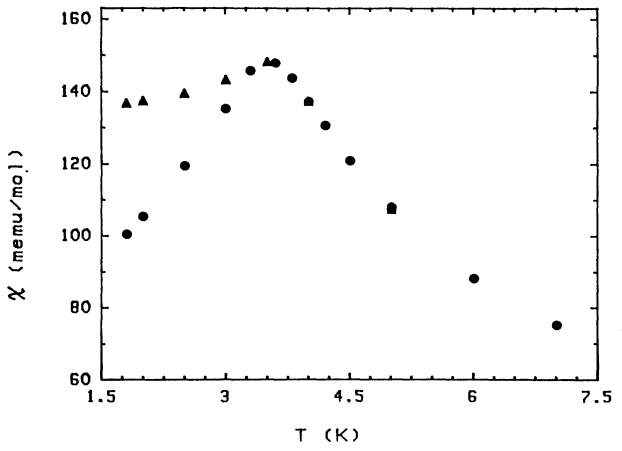

FIG. 4. Magnetic susceptibility for $UCu_{2.7}Pd_{2.3}$ measured at 100 Oe: dots, zero field cooled; triangles, field cooled.

The concentration dependence of the specific heat in this work is also inconsistent with the two-channel Kondo model, which is a single impurity model and therefore should have a trivial concentration dependence. The span of x's for which the pure logarithmic temperature variation of C/T is observed is narrow. Some deviations from this variation, which cannot be accounted for by the error of C/T or T measurements are seen already for $x = 1.25$ and 1.75, the two investigated concentrations on the phase diagram nearest to $x = 1.5$. These deviations are seen clearly for $x = 1$ (see Fig. 6). Between 1 and 10 K, the temperature variation of the electronic specific heat for UCu_4Pd can be much better represented by the power law, $C/T = \Delta T^{-\delta}$; $\Delta = 450$ mJ/K^2 mol, $\delta = 0.32$. The low-field (100-G) magnetic susceptibility of UCu_4Pd can also be approximated by $T^{-\delta}$ (from 10 K down to at least 1.8 K). Such a temperature dependence of C/T and χ is consistent with an overcompensated four-channel magnetic Kondo model,[15] although probably, this agreement is coincidental. Obviously, this temperature dependence of C/T and χ, if present at the lowest temperatures, would constitute even stronger violation of the Fermi-liquid behavior than is observed in $UCu_{3.5}Pd_{1.5}$ and $U_{0.2}Y_{0.8}Pd_3$. However, the power-law formula overestimates the lowest temperature data; the measured C/T values for $x = 1$ below 1 K fall under the curve by as much as 16% at 0.34 K (see Fig. 6).

Magnetic fields depress the low-temperature specific

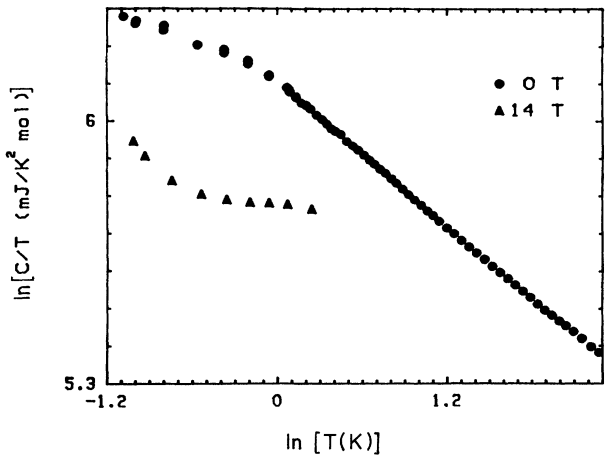

FIG. 6. $\ln C/T$ vs $\ln T$ for UCu_4Pd. C is expressed in mJ/K^2 mol and T in K.

heat for both compounds. The 14-T field reduces C/T for $x=1$ (Fig. 6) and $x=1.5$ (Fig. 5) by about 35% at 0.5 K. A sharp rise of C/T in $H=14$ T below 0.5 K is consistent with a Schottky anomaly. The magnitude of this rise agrees with the value expected for the nuclear contribution due to Cu.

The decrease of the low-temperature specific heat with the magnetic field argues against the existence of a large residual entropy at $T=0$ and $H=0$ ($\frac{1}{2}R\ln 2$ in the two-channel Kondo model). The application of a magnetic field would increase the specific heat in removing the residual degeneracy. The systematic experiments[3] in $U_{0.2}Y_{0.8}Pd_3$ showed that the specific heat monotonically decreases with H at low temperatures. Such systematic measurements were not performed in $UCu_{3.5}Pd_{1.5}$ and UCu_4Pd; however, the magnitude of C/T reduction at 14 T and the temperature dependence of C/T at 14 T for these two alloys are almost identical to those for $U_{0.2}Y_{0.8}Pd_3$.

The low-temperature electrical resistivity curves for $UCu_{3.5}Pd_{1.5}$ and UCu_4Pd are shown in Fig. 7. At high temperatures, above 60 K, the electrical resistivities for both alloys have Kondo-like appearances; they vary as $-\ln T$. At temperatures lower than 10 K, down to the lowest temperatures of the measurements, the resistivities as shown in Fig. 7 are approximately linear in T; $\rho\approx\rho_0(1-T/T_0)$, where $\rho_0=375\mu\Omega$ cm, $T_0=60$ K for UCu_4Pd, and $\rho_0=235\mu\Omega$ cm, $T_0=260$ K for $UCu_{3.5}Pd_{1.5}$. Both alloys therefore have electrical resistivities generic to that for $U_{0.2}Y_{0.8}Pd_3$. Such a linear temperature dependence of ρ substantiates further our claim for a non-Fermi-liquid ground state. It should be stressed that although part of the observed large difference in the ρ_0 values for $x=1$ and 1.5 might result from our relatively large uncertainty of ρ measurement ($\pm 20\%$, almost entirely due to a geometrical factor) the even larger observed discrepancy in T_0 values is definitely beyond our experimental error ($\pm 5\%$).

For one of the compositions, UCu_4Pd, we have also performed magnetoresistance measurements. Similarly to the case of $U_{0.2}Y_{0.8}Pd_3$, the measured magnetoresistance is negative and relatively small. The 14-T field reduces ρ by 8, 7, and 5.9% at 0.36, 1.45, and 4.2 K, respectively.

Further evidence for the same ground state for $UCu_{3.5}Pd_{1.5}$ as in $U_{0.2}Y_{0.8}Pd_3$ is furnished by magnetic measurements. The magnetic susceptibility of $UCu_{3.5}Pd_{1.5}$, as measured at 100 G, see the inset in Fig. 8, can be expressed as $\chi=\chi_0 T^{-\eta}$, where $\chi_0=28\pm 0.5$ memu/mol and $\eta=0.27\pm 0.03$. Note that exponent is within 10% of the value found for $U_{0.2}Y_{0.8}Pd_3$. Also, our magnetization data are consistent with the scaling behavior postulated for $U_{0.2}Y_{0.8}Pd_3$, i.e., all low-temperature magnetization curves can be superimposed on each other by plotting them as $M/HT^{0.27}$ vs $H/T^{1.3}$ (Fig. 8). Again the value of the magnetic-field scaling dimension (1.3 ± 0.2) implies nonsingle impurity interpretation of the low-temperature properties of $UCu_{3.5}Pd_{1.5}$.

It is customary to assign to heavy-electron systems a

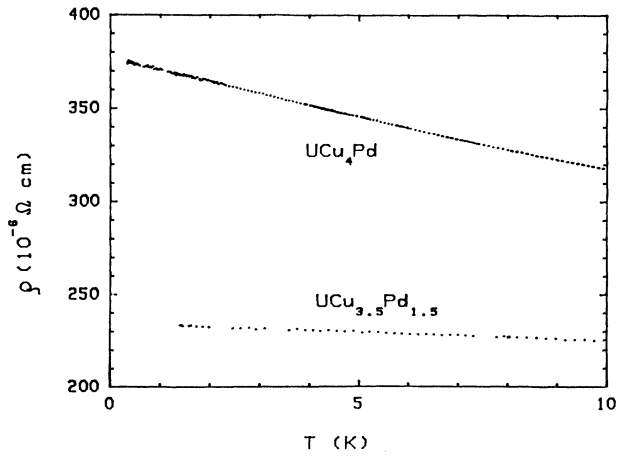

FIG. 7. Low-temperature electrical resistivity for UCu_4Pd and $UCu_{3.5}Pd_{1.5}$.

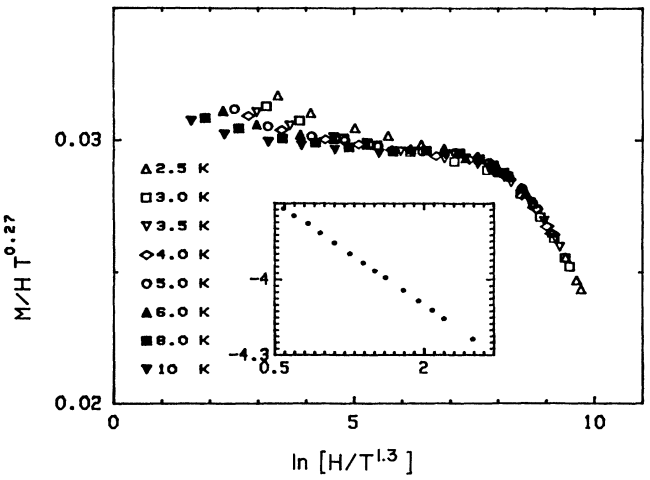

FIG. 8. Magnetization curves for $UCu_{3.5}Pd_{1.5}$ at various temperatures. M is expressed in emu/mol, H in Oe, and T in K. The inset shows $\ln\chi$ vs $\ln T$ measured at 100 Oe.

single energy scale, the Kondo temperature, which characterizes the low-temperature state. (T_K is usually derived from the lowest measured temperature value of the electronic specific heat.) Such a practice is justified by the closeness of some systems to an ideal single impurity Kondo behavior with the prime example of $Ce_{1-x}La_xPb_3$.[16] Here, we present a case for which such a procedure is inappropriate. Although the 1 K value of C/T is relatively insensitive to x (it varies by less than 20% from the average value of 420 mJ/K^2 mol over the whole investigated range of concentrations) the other measured characteristics χ_{max} and θ span a large range of values; χ_{max} varies by a factor of 14, while θ by more than 4. Therefore, different characteristics would yield different T_K values for the same concentration. This problem should be addressed in a more general context for all U-based compounds and alloys. A number of recent studies on UBe_{13}, one of the best characterized heavy-electron systems, provide clear examples of the inefficacy of a single-energy-scale viewpoint. A replacement of 20% of U by other metals can drive C/T down by as much as 60% without affecting the low-temperature magnetic susceptibility values.[17] The magnetic field response of the specific heat and electrical resistivity of UBe_{13} is beyond a single-parameter-theory explanation. Although the specific heat of UBe_{13} is essentially field independent, the resistivity is extremely sensitive to H;[18] in fact, the magnetoresistance measurements indicate $T_K \rightarrow 0$ as $T \rightarrow 0$. A similar inconsistency between magnetic-field response of thermodynamic and transport properties was observed for $U_{0.2}Y_{0.8}Pd_3$.[3] In this latter case, the specific heat is strongly suppressed by magnetic fields, while the resistivity is hardly affected by magnetic fields at all. Thus a single-energy scale is unable to account for both of these materials. Lack of a low-temperature single-energy scale in U-based heavy fermions differentiates these materials from more conventional, Kondo-like, Ce-based heavy fermions.

The central conclusion of our study is that $UCu_{3.5}Pd_{1.5}$ is another U-based alloy, which exhibits non-Fermi-liquid behavior down to the lowest measurable temperatures. The magnetic field-specific heat data for $UCu_{3.5}Pd_{1.5}$ together with the magnetic susceptibility and magnetization are consistent with the scaling postulated for $U_{0.2}Y_{0.8}Pd_3$, which is a nonsingle impurity scaling. The other composition described, UCu_4Pd, is also an excellent candidate to have a non-Fermi-liquid ground state. Both the specific heat and electrical resistivity above 1 K for this last compound exhibit even stronger non-Fermi-liquid effects than $UCu_{3.5}Pd_{1.5}$. Since χ_{max} and θ are almost identical for the two compositions, we believe that the strength of the intersite interactions cannot be solely responsible for the qualitatively different behavior of the specific heat in these alloys. On the other hand, different degrees of randomness on the nonmagnetic sites could be the source of the discrepancy. The concentration dependence of the lattice constant and the magnetic phase diagram of $UCu_{5-x}Pd_x$ imply greater disorder for the $x=1.5$ composition than for $x=1$. We are planning to study UCu_4Pd in which disorder will be induced by nonchemical means (e.g., controlled neutron irradiation). The aim of this study is to find out whether the low-temperature state of $UCu_{3.5}Pd_{1.5}$ can be achieved in UCu_4Pd via controlled increase of disorder only.

Finally, we would like to stress our previous finding[3] that the described non-Fermi-liquid behavior is a limiting case of a magnetic state. The extrapolations of the freezing temperature (T_f) vs x intercept the x axis near $UCu_{3.5}Pd_{1.5}$ and $U_{0.2}Y_{0.8}Pd_3$ concentrations ($T_f=0$) on the respective magnetic phase diagrams for $UCu_{5-x}Pd_x$ and $U_{1-x}Y_xPd_3$. On the other hand, a line drawn for the Néel temperatures (T_N) for $UCu_{5-x}Pd_x$ intercepts the x axis ($T_N=0$) in the vicinity of UCu_4Pd (Table I).

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