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Magnetism and its connection to non-Fermi-liquid-like behavior

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While conducting doping experiments on the recently discovered enhanced effective mass, coexistent antiferromagnetic-superconducting system UNi_2Al_3, we have discovered several examples, in samples in which doping has suppressed the magnetic transition at 4.6 K, of unusual temperature dependences of properties consistent with non-Fermi-liquid behavior. Since the other systems discovered to date [$U_{0.2}Y_{0.8}Pd_3$, $UCu_{3.5}Pd_{1.5}$, and possibly $U(Pt_{0.94}Pd_{0.06})_3$] with similar properties have similar (relatively weak) magnetic behavior, this may be an important clue for understanding, as well as for searching for other systems. Several such systems are discussed, and preliminary results on doped UPd_2Al_3 and URu_2Si_2 are discussed.

INTRODUCTION

Recently, Geibel *et al.*[1] reported the discovery that UNi_2Al_3 is weakly antiferromagnetic at $T_N=4.6$ K and superconducting at $T_c=1$ K, with a specific heat $\gamma(\propto m^*$, the electron effective mass) of 120 mJ/mole K^2. Although this γ value is small in comparison with many heavy-fermion systems (e.g., UBe_{13} has $\gamma=1000$ mJ/mole K^2 while $U_{0.97}Th_{0.03}Be_{13}$ has[2] $\gamma=2300$ mJ/mole K^2), the coexistence of antiferromagnetism and superconductivity, coupled with the non-negligible γ, make this an interesting system to further characterize. Two other[3,4] coexistent, enhanced-γ systems, URu_2Si_2 ($\gamma\simeq 70$ mJ/mole K^2, $T_N=17.5$ K, $T_c\sim 1.4$ K) and UPd_2Al_3 ($\gamma=150$ mJ/mole mole K^2, $T_N=14$ K, $T_c=2$ K), where γ is quoted for just above T_c, are also known. Since coexistent magnetism and superconductivity has recently been found[5] in a large $\gamma=1000$ mJ/mole K^2 ("heavy-fermion") system, $Ce_{1-x}Th_xCu_2Si_2$ ($0.1\leq x\leq 0.25$), this coexistent behavior must be considered a central issue in understanding the potentially unconventional superconductivity in heavy-fermion systems, with the smaller γ systems serving as important examples of continuum behavior characteristic of heavy-fermion systems in general.

Thus, following our recent studies[2,5,6] of heavy-fermion systems via doping studies, where we were able to separate single-ion from correlation effects, we doped UNi_2Al_3 on the U site with Ce, La, Y, Th, and Pr in order to vary the observed behavior. Encouraged by our results, we have also begun similar doping experiments in the related UPd_2Al_3 and URu_2Si_2 compounds, preliminary results of which are presented here for comparison.

RESULTS AND DISCUSSION

Samples were prepared via arc melting together the starting elements, followed by (with the exception of the first sample, discussed below) annealing for one week at 900 °C. All samples maintained the $PrNi_2Al_3$ structure, with the lattice parameters measured shown in Table I. Y and Pr caused the least lattice-parameter change, and Ce the most.

The dc magnetic susceptibility was measured for all samples. The value obtained at 1.8 K for our first sample of pure UNi_2Al_3 was about 8% less than that found in the discovery work by Geibel *et al.*[1] In addition, Geibel *et al.* saw a small ($\sim$6%) peak at 4.8 K in χ, whereas our data for sample 1 (see Fig. 1) are, within 2%, featureless in this region. As will be developed below more thoroughly, the sample dependence of the magnetic transition ($T_N=4.6$ K) is an important point. Thus we prepared three additional samples of pure UNi_2Al_3, whose susceptibilities (see Fig. 1) and specific heats (discussed below) were measured. Since there is significant ($\sim$20–30 %) orientation dependence for χ (1.8 K) in these samples, we focus on the relative magnitudes of the peak in χ observed (Fig. 1) in the subsequent three samples at $T\sim 5$ K vs the rounded peak in χ centered at 100 K. Samples 2 and 4 have the peak at T_N smaller than that at 100 K, sample 1 has no peak in χ at T_N, and sample 3 shows a peak at T_N *larger* than the peak in χ at 100 K. Sample 1 was prepared exactly as were 2, 3, and 4 (via arc melting together the constituent pure elements, and remelting three times), except for the annealing procedure afterwards. Sample 1 was annealed at 1000 °C for six days, while the subsequent samples were annealed in a different furnace at 900 °C for seven days. Unless the fur-

TABLE I. Parameters for $U_{0.9}M_{0.1}Ni_2Al_3$.

	a_0 (Å)	c_0 (Å)	χ (1.8 K) (memu/formula unit)
Pure UNi_2Al_3	5.184	4.023	4.55, 3.3, 3.95, 3.5
M = La	5.200	4.023	4.2
M = Y	5.184	4.024	3.9
M = Ce	5.188	4.030	4.2
M = Th	5.182	4.032	5.2
M = Pr	5.184	4.027	8.3

nace used for sample 1 was defective, this variation in χ (and, as discussed below, in C) based on so slight a change in annealing conditions seems unusual. At present, we consider the explanation for our anomalous first sample as still open. We will come back to the necessity of discussing sample variation (for the doped samples in particular) again below.

Upon doping on the U site, the low-temperature values of χ vary as detailed in Table I. The low-temperature χ results, $1.8 \leq T \leq 9$ K, for $x = 0.1$ Th and Pr obey $\chi \propto \sqrt{T}$ (see Fig. 2), as predicted[7] by two-channel quadrupolar Kondo theory, one of the current approaches to understanding non-Fermi-liquid (nFl) behavior. In order to check for sample dependence, a second sample of $U_{0.9}Th_{0.1}Ni_2Al_3$ was prepared and measured. The data also show $\sqrt{T}$ temperature dependence. As will be discussed below, as far as we are aware this is only the second example of $\chi \propto \sqrt{T}$ behavior observed in a system whose specific heat follows the nFl-indicative $C/T \propto \log_{10}[T$ (K)] [The first example[8] is $U(Pt_{0.94}Pd_{0.06})_3$.]

In order to be complete, it should also be mentioned that a recent theory[9] on the Kondo effect in disordered systems also purports to explain this type of anomalous temperature dependence, with specific mention of $U_{0.2}Y_{0.8}Pd_3$. Certainly our present studies do introduce disorder (with one exception to be discussed below); thus we present these measurements in a rapidly evolving (both experimentally and theoretically) field without claiming any fixed interpretation.

The resistivity data for $U_{0.9}Th_{0.1}Ni_2Al_3$, not shown, obey $\rho = aT$ between 1.2 and 20 K, with a positive-"a" coefficient. This temperature dependence was also reported[10] for $U_{0.2}Y_{0.8}Pd_3$, the first system reported with non-Fermi-liquid behavior, with, however, a negative "a."

The specific-heat data for $U_{0.9}M_{0.1}Ni_2Al_3$ (M = Y, Th, Pr, and La) are shown in Fig. 3, and our data for all four pure UNi_2Al_3 samples and $U_{0.9}Ce_{0.1}Ni_2Al_3$ are shown in Fig. 4. All data are normalized per mole of the formula unit, *not* per U mole. The $\Delta C/T \sim 50$ mJ/mole K^2 anomaly observed[1] by Geibel *et al.* in the specific heat of their UNi_2Al_3 sample is not observed at all in our data for sample 1, while samples 2, 3, and 4 show significant (25%) variations in the anomaly's height. Note that, although sample 3 has the most distinct peak in χ at T_N as compared with the peak in χ at 100 K, the peak in C is most pronounced in sample 2.

What can be seen quite distinctly in Fig. 3 is an upturn

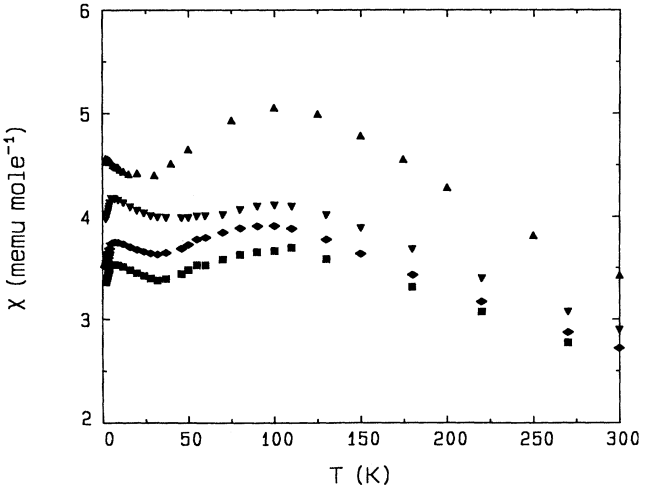

FIG. 1. The magnetic susceptibility between 1.8 and 300 K for four samples of UNi_2Al_3. As discussed in the text, sample 1 (triangles) shows no peak in χ at low temperatures, while samples 2 (squares), 3 (inverted triangles), and 4 (diamonds) do. The difference in magnitude of the susceptibility between the samples is not necessarily significant, due to uncontrollable growth (of varying degree) in preferential orientation as the individual buttons cool between T_{melt} on the copper hearth after arc melting.

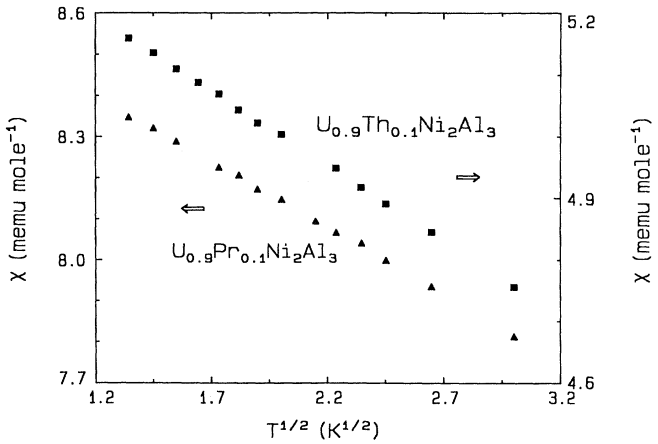

FIG. 2. The low-temperature magnetic susceptibility of $U_{0.9}Th_{0.1}Ni_2Al_3$ and $U_{0.9}Pr_{0.1}Ni_2Al_3$ plotted vs $\sqrt{T}$. Data for a second sample of $U_{0.9}Th_{0.1}Ni_2Al_3$ (not shown) show similar behavior. Above 9 K, the data begin to deviate from the $\sqrt{T}$ behavior. No background subtraction from the data is made.

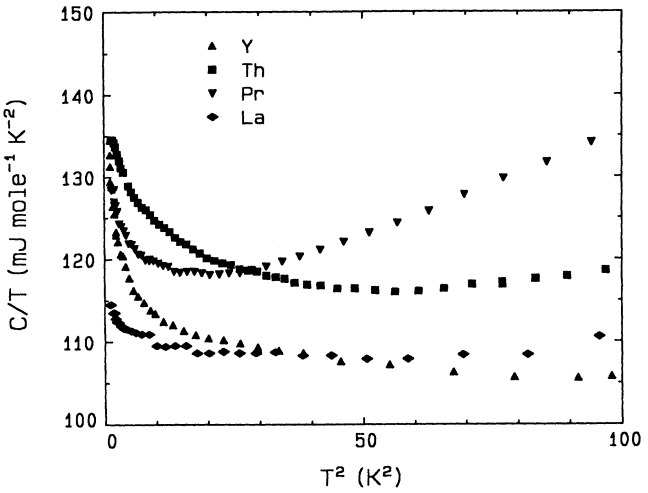

FIG. 3. The specific heat C divided by temperature T vs T^2 for $U_{0.9}M_{0.1}Ni_2Al_3$ for M=Y, Th, Pr, and La. The absolute error of the specific-heat data is ±3%, based on measurements of a standard. Note the upturn in C/T at low temperatures for Y, Th, Pr, and—to a lesser extent—for La.

in the C/T data for $U_{0.9}M_{0.1}Ni_2Al_3$ for M=Y, Th, and Pr starting below $T \simeq 7$, 7, and 5 K, respectively. However, just as the χ data for $U_{0.9}Y_{0.1}Ni_2Al_3$ do not follow the predicted[7] behavior ($\sqrt{T}$) over a significant temperature range, neither do the C/T data for $U_{0.9}Y_{0.1}Ni_2Al_3$ obey the unusual behavior of $\log_{10}[T\ (\mathrm{K})]$. In contrast, both $U_{0.9}Th_{0.1}Ni_2Al_3$ and $U_{0.9}Pr_{0.1}Ni_2Al_3$ obey both $\chi \propto \sqrt{T}$ and $C/T \propto \log_{10}[T\ (\mathrm{K})]$, the latter being shown in Fig. 5. The region over which $\log_{10}[T\ (\mathrm{K})]$ is obeyed is 0.7–7.6 K for $U_{0.9}Th_{0.1}Ni_2Al_3$ and 0.3–5 K for $U_{0.9}Pr_{0.1}Ni_2Al_3$. This quicker deviation from $\log_{10}[T\ (\mathrm{K})]$ behavior at the high-temperature end for the Pr-doped material is of course visible already in Fig. 3, since the upturn for Pr vs Th doping is weaker and starts at lower temperatures.

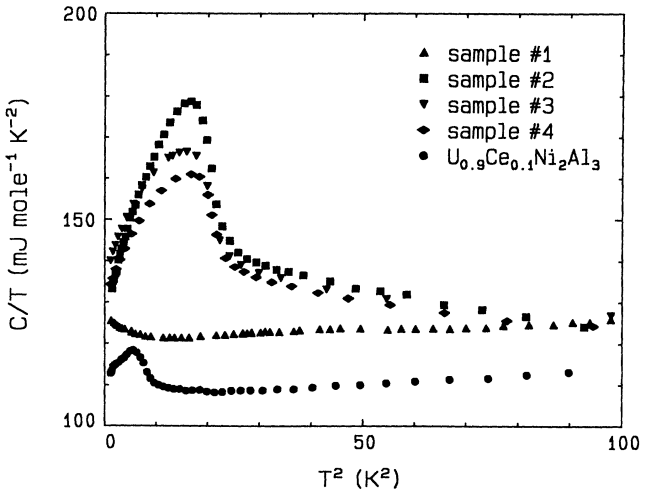

FIG. 4. C/T vs T^2 for four samples of pure UNi_2Al_3 and $U_{0.9}Ce_{0.1}Ni_2Al_3$. Note the small peak at 2.5 K in the data for the Ce-doped sample and the varying magnitude of the peak in the samples of UNi_2Al_3.

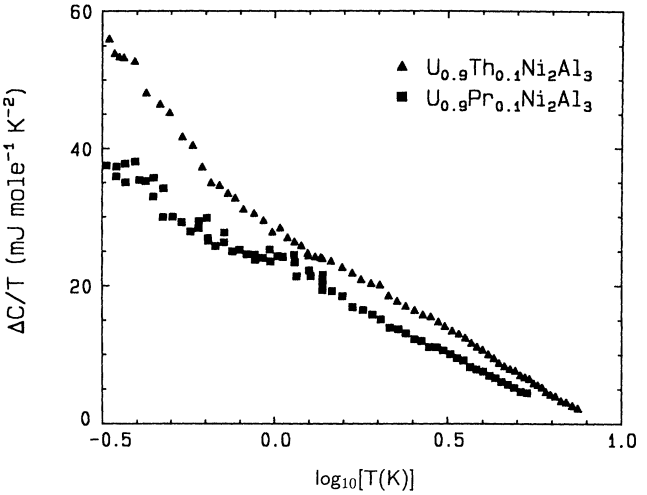

FIG. 5. C/T measured for $U_{0.9}Th_{0.1}Ni_2Al_3$ and $U_{0.9}Pr_{0.1}Ni_2Al_3$ is plotted vs $\log_{10}[T\ (\mathrm{K})]$ with a subtracted background consisting simply of a two-term ($C/T=\gamma+\beta T^2$) fit to the data above the upturn. The $\log_{10}[T\ (\mathrm{K})]$ behavior displayed in this figure is not sensitive to the background fit used.

(The upturn in the lowest temperature C/T data above a straight $\log_{10}[T\ (\mathrm{K})]$ dependence seen in Fig. 5 for the 10% Th sample is also observed[10,11] in $U_{0.2}Y_{0.8}Pd_3$.)

The question immediately arises, how does this unusual behavior behave upon further doping? The temperature range over which this $\log_{10}T$ behavior is observable shrinks upon increasing Th content, to 3.2 K for 20% Th and to 2.2 K for 30% Th, i.e., over much too limited a temperature range to be given any significant credence. As seen in Fig. 6, using Th doping as a representative example, the temperature at which the upturn in C/T be-

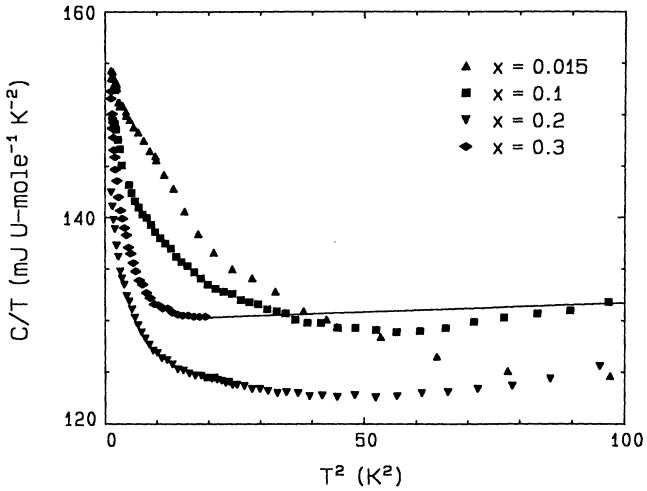

FIG. 6. C/T vs T^2 for $U_{1-x}Th_xNi_2Al_3$, x=0.015, 0.1, 0.2, and 0.3, normalized per U mole. The data for x=0.03 (not shown) agree with those for x=0.015 within our error bar of ±3%. Note that although the low temperature γ is essentially U-concentration independent, the point at which the upturn in C/T begins is strongly stoichiometry dependent, with higher Th concentrations monotonically suppressing T_{upturn}.

gins is depressed with more and more doping. This shrinking of the temperature range where $C/T \propto \log_{10}[T\ (\mathrm{K})]$ is observed is also seen upon further U doping in $U_{0.2}Y_{0.8}Pd_3$. In $UCu_{3.5}Pd_{1.5}$, varying the Pd to UCu_4Pd_1 totally destroys[12] the $\log_{10}[T\ (\mathrm{K})]$ dependence; instead, $C/T \propto T^{-0.32}$ from 1 to 10 K.

Another question to consider is, how rapidly is the antiferromagnetic transition at 4.6 K depressed with doping? This is addressed in Fig. 7, where specific-heat data for $U_{1-x}Th_xNi_2Al_3$ ($x=0.0025$, 0.005, and 0.015) are shown compared to UNi_2Al_3. As may be seen, the magnetic transition temperature, as measured by the position of the maximum in the specific-heat anomaly, decreases with increasing doping at the approximate rate of 2 K/% Th, while the size of the anomaly, ΔC, decreases by 40% for $x=0.005$. Magnetic-susceptibility measurements of these low-doped samples show a maximum in χ at ~ 4.2 K (3.7 K) for $x=0.0025$ (0.005). Thus it is clear that at the higher doping levels ($x \geq 0.1$) of Th, T_N is completely suppressed. Similar behavior for the other dopants, based on the similar properties of the doped samples we have presented here, is a reasonable first assumption.

In summary of the data presented so far, there evidently exists a region of stoichiometry in $U_{1-x}M_xNi_2Al_3$, where dilution of the U causes a suppression of T_N to lower temperatures, leaving unusual temperature dependences of χ, ρ, and C in the system at the lowest temperatures. Such dependences have been interpreted[8,10,12] variously to be either consistent with non-Fermi-liquid behavior (i.e., some scattering mechanism at low temperatures inhibits the normal Fermi-liquid increase in the quasiparticle lifetime) or due to disorder.[9] It is this *crossover region* between (weakly) magnetic and nonordering where we are finding the unusual temperature dependences of ρ, χ, and C in the $U_{1-x}M_xNi_2Al_3$ system and others. What appears to be crucial, based on our early results on $U_{1-x}M_xPd_2Al_3$, is that the magnetism must be weak and quickly suppressible in order for this behavior to be observable over a significant temperature range. In $U_{1-x}M_xPd_2Al_3$, $T_N=14$ K for $x=0$ and the antiferromagnetism is only slowly suppressed upon doping (see Fig. 8). We find in our preliminary work that the specific heat of $U_{1-x}Th_xPd_2Al_3$ follows a power law (and definitely *not* $C/T \propto \log_{10}[T\ (\mathrm{K})]$) $C \propto T^n$ between $T=1.4$ and 8 K, where $n=0.58$ ($x=0.2$), 0.72 ($x=0.3$), 0.64 ($x=0.4$), and 0.64 ($x=0.5$), when the remanent magnetic anomaly is subtracted from the data. This procedure is detailed in Fig. 9 for $U_{0.6}Th_{0.4}Pd_2Al_3$. As may be seen in Fig. 8, Y and La suppress magnetism in $U_{1-x}M_xPd_2Al_3$ even more slowly than Th. However, following the same procedure as outlined for $U_{1-x}Th_xPd_2Al_3$ (see Fig. 9), one also arrives at $C \propto T^n$, $n \sim 0.7$, for Y ($x=0.3$, 0.4, and 0.5) and La ($x=0.2$ and 0.3), with, however, a variation of ± 0.15 due to the larger anomaly subtraction necessary.

This power-law dependence in $U_{1-x}M_xPd_2Al_3$ is also consistent with nFl behavior, although not in agreement with the predictions of Ref. 7, as well as the disorder

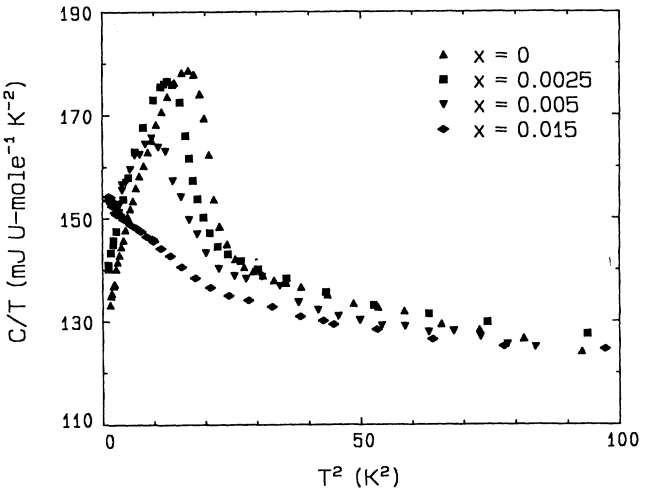

FIG. 7. C/T vs T^2 for $U_{1-x}Th_xNi_2Al_3$, $x=0$, 0.0025, 0.005, and 0.015. Here the suppression of magnetism is clearly seen to be achieved with extremely small doping levels. Note that the divergence as $T \to 0$ in C/T is already present in the undoped compound, i.e., the broad upturn above T_N observed in UNi_2Al_3 is *not* simply a broadened magnetic transition with entropy spread out to higher temperatures due to sample inhomogeneity. Instead, we see here that the magnetic transition stays relatively unbroadened as it is suppressed to lower temperature, while the C/T upturn above the anomaly is, within 5%, the same for $x=0.0025$, 0.005, 0.015, and 0.03. If the suppression of the magnetic transition were linear with doping, one would expect $T_{\mathrm{peak}} \simeq 1$ K for $x=0.015$. Instead, data down to 0.3 K show no anomaly other than the change in slope seen at ~ 3 K, which may be a sign of sample inhomogeneity but is not a bulk transition.

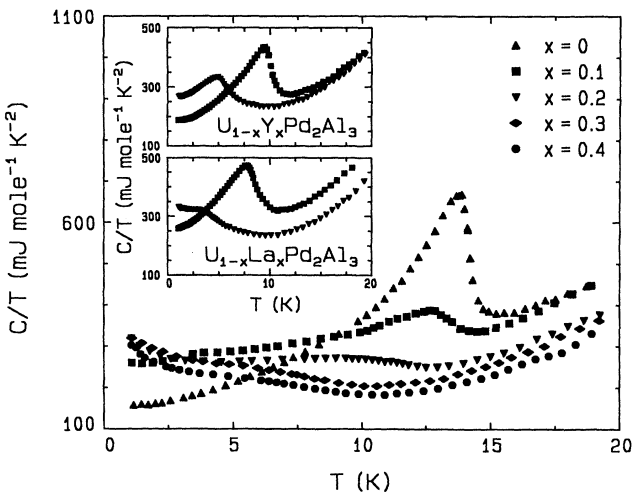

FIG. 8. The low-temperature specific heat divided by temperature of $U_{1-x}Th_xPd_2Al_3$. Note that a peak in C/T is still easily visible for $x=0.2$, with rounded features still discernible for $x=0.3$ and 0.4. Shown in the inset are data for Y and La doping as well, where the anomaly at T_N remains even more distinct upon doping. Data for Ce doping are similar to that shown for La, while doping by Pt on the Pd site ($UPd_{1.5}Pt_{0.5}Al_3$) raises T_N by about 2 K.

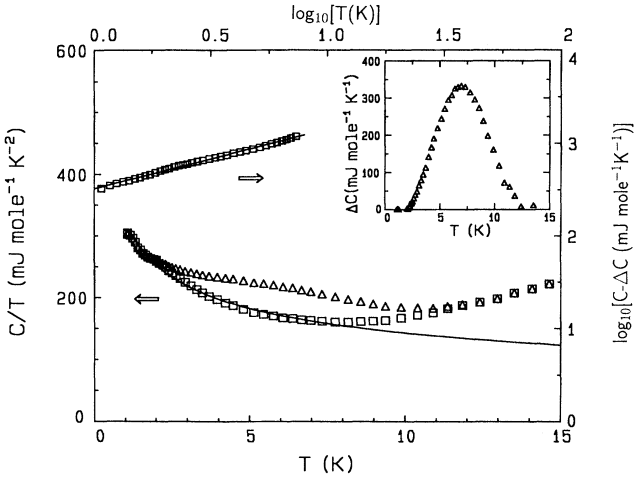

FIG. 9. Expanded view of C/T vs T^2 for $U_{0.6}Th_{0.4}Pd_2Al_3$. In order to separate off the magnetic anomaly (the shoulder in the data at 6.4 K), fits are made to the data above and below the anomaly, resulting in the ΔC shown in the inset. ΔC and T_{peak} for $U_{1-x}Th_xPd_2Al_3$ are then determined to be 1050 mJ/mole K, 9.4 K; 335 mJ/mole K, 7.5 K; 330 mJ/mole K, 7.0 K; 200 mJ/mole K, 7.2 K for $x=0.2$, 0.3, 0.4, 0.5, respectively. With this ΔC subtracted, the data are then shown plotted as $\log_{10}[(\Delta C \text{ (mJ mole}^{-1}\text{K}^{-})]$ and show (as shown here for $x=0.4$) for all four Th compositions a rather startingly constant power-law behavior. (The solid line through the squares is the power-law fit.) Work is underway to extend the temperature range of measurement down to 0.3 K. If an *ad hoc* assumption is made to estimate the phonon contribution to the specific heat ($\theta_D \simeq 200$ K) to allow its subtraction, due to the size of the electronic term here we find less than a 10% decrease in the exponent n, $C \propto T^n$, and the same excellent pure power-law behavior. (As an example, for $x=0.4$, n changes from 0.64 to 0.61.)

theory of Ref. 9. It should be mentioned that the data for, e.g., $U_{0.9}Th_{0.1}Ni_2Al_3$ which fit well $C/T \propto \log_{10}[T\text{ (K)}]$—see Fig. 5—do not fit a power law at all. Thus our data seem to indicate *distinct* kinds of unusual behavior.

In our preliminary work on $U_{1-x}M_xRu_2Si_2$, both Th and Y doping suppress the size of the specific-heat anomaly at T_N; however, T_N remains fixed at ~ 17 K even up to $x=0.3$. The entropy S from the depressed anomaly is then shifted to lower temperatures such that S (20 K) for pure URu_2Si_2 is approximately 3300 mJ/mole K and 2900 (3100) mJ/mole K for $U_{0.8}Y_{0.2}(Th_{0.2})Ru_2Si_2$. Normalized per U mole, these latter two numbers are then 10–15 % higher than for pure URu_2Si_2. There is no upturn in C/T for the Th-doped samples ($x \leq 0.3$), while the upturn for Y-doped samples—though suggestive—is too gradual to distinguish with any certainty a ΔC (with the tail of the magnetic anomaly subtracted from the measured data) and its temperature dependence.

Thus the fact that $C/T \propto \log_{10}[T\text{ (K)}]$ in $U_{1-x}M_xNi_2Al_3$ (where T_N is suppressed 2 K per percent Th doping), while $C/T \propto T^{-0.36}$ in $U_{1-x}M_xPd_2Al_3$ (for a wide range of dopings in a system where T_N is suppressed 10 times more slowly with doping), and no upturn in C/T is observable in $U_{1-x}M_xRu_2Si_2$ (where T_N remains constant with doping), argues that a low magnetic ordering temperature which can quickly be suppressed by doping is a fruitful route for studying such unusual behavior of at least two distinct kinds. Despite this seeming diversity of behavior, it should be stressed that $C/T \propto T^{-0.32}$ was also found[12] in $UCu_{3.5}Pd_{1.5}$, another system where nearness to magnetism appears to be the key to finding a divergence in C/T at low temperatures. It is also interesting to note that the upturn in C/T observed at low temperatures in $U_{1-x}M_xNi_2Al_3$ is already present above T_N in the pure compound, as seen in Fig. 7, and is apparently not due simply to a broadened magnetic transition. This fact tends to argue against the disorder interpretation,[9] since for weak disorder—as one would expect for the pure compound—the theory predicts[9] unusual temperature dependences only at ultralow temperatures. However, explanations other than non-Fermi-liquid behavior may still offer important insights and ideas for further measurement, and in the end be proven correct.

ACKNOWLEDGMENT

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