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New spin-fluctuation system: $U_{0.5}Th_{0.5}Al_3$

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Low-temperature measurements show a $T^3(\ln T/T_{SF})$ term in the specific heat of the pseudobinary compound $U_{0.5}Th_{0.5}Al_3$. This is considered strong evidence for long-range ferromagnetic spin fluctuations. The specific heat γ is 360 mJ/[(mole U) K^2] and $\chi(T\rightarrow 0)=9.6\times 10^{-3}$ emu/(mole U). Except for a much less rapid decrease in resistance below 50 K than in UPt_3, the resistance, susceptibility, and specific-heat data for the $D0_{19}$ structure $U_{0.5}Th_{0.5}Al_3$ are very similar to those of the isostructural heavy-fermion superconductor UPt_3. In addition to the poorer resistivity ratio, $U_{0.5}Th_{0.5}Al_3$ has a significantly larger ($\sim$50%) Wilson ratio than UPt_3, explaining the lack of superconductivity down to 0.020 K.

I. INTRODUCTION

Of the eight known heavy-fermion materials,[1] two occur with the hexagonal $D0_{19}$ structure: $CeAl_3$ and UPt_3. The interest in $CeAl_3$, which is neither magnetic nor superconducting, is of long standing. Andres *et al.*[2] showed in 1975 that the specific heat γ, proportional to the dressed electronic density of states of the Fermi energy, was 1620 mJ/mole K,[2] a record large value that may still stand.[3] This first discovered large effect mass ($\Longleftrightarrow$ large γ), or "heavy-fermion," system has the same structure as the most recently discovered[4] large-γ, heavy-fermion system—UPt_3. The finding[5] of superconductivity in UPt_3, along with the existence of evidence[5,6] for spin fluctuations, has led to speculation[5,7] that UPt_3 may not be a usual BCS-type superconductor, but might be the first example of a *p*-wave superconductor. Although some experimental evidence[8–10] has been found to support this speculation, UPt_3 may be[1,11] just an unusual *s*-wave superconductor.

We have found that the pseudobinary compound $U_{0.5}Th_{0.5}Al_3$, which occurs in the $D0_{19}$ structure with $d_{U\text{-}U}=4.354$ Å (versus $d_{U\text{-}U}=4.132$ Å in UPt_3), has low-temperature properties very similar to those of UPt_3 without, however, a transition into the superconducting state above 0.020 K. Additionally, we have measured the specific heat of $U_{0.2}Th_{0.8}Al_3$, $ThAl_3$, and $Ce_{0.5}Th_{0.5}Al_3$ for comparison purposes.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The various compounds ($U_{0.5}Th_{0.5}Al_3$, $U_{0.2}Th_{0.8}Al_3$, $Ce_{0.5}Th_{0.5}Al_3$, and $ThAl_3$) were prepared from crystal bar Th, ^{238}U, Al (99.999% purity), and Ce (99.9% purity) by arc melting under a purified argon atmosphere. For the $ThAl_3$ composition, proper weights of the two metals were melted to form the desired composition and the melting was repeated four times with the button turned over between meltings to insure homogeneity. The preparation of the pseudobinary compositions of (Th,U)Al_3 and (Ce,Th)Al_3 was carried out in two steps. Alloys of Th plus U and of Th plus Ce were first prepared by repeated arc melting as described above. The proper weight of Al was then added to each of the alloys and the pseudobinary compounds prepared by repeated arc melting. The weight loss in all cases was below 0.2% so the compositions reported correspond to the starting weights.

Room-temperature x-ray diffraction patterns of the finely powdered arc-cast materials were taken with a General Electric XRD-6 diffractometer using Cu radiation and lattice parameters of the $D0_{19}$ phase were determined. These are listed in Table I. The x-ray diffraction pattern for the arc-cast $U_{0.5}Th_{0.5}Al_3$ showed the presence of a small amount (approximately 5%) of a second phase identified as UAl_3. To determine the effect of annealing, a portion of the arc-cast sample was heated inductively under vacuum at 1050 °C to 90 h. This treatment was found to cause an increase in the amount of the second phase and also an increase in the lattice parameters of the $D0_{19}$ phase. These results suggest that the arc-cast composition contains the upper U-concentration limit for the $U_{1-x}Th_xAl_3$ pseudobinary system so the heat capacity, susceptibility, and resistivity measurements were carried out on the arc-cast materials.

III. RESULTS AND DISCUSSION

The resistivity between 1.4 and 300 K for $U_{0.5}Th_{0.5}Al_3$ is shown in Fig. 1. The resistivity ratio of this alloy is seen to be only 1.8, whereas values of $R(300\ K)/R(1.4\ K)$ for UPt_3 as high as 90 have been observed.[12] However, it

TABLE I. Lattice parameters for various compositions.

Compositions	a_0 (Å)	c_0 (Å)	c/a
$U_{0.5}Th_{0.5}Al_3$	6.399	4.606	0.72
$U_{0.2}Th_{0.8}Al_3$	6.450	4.609	0.72
$Ce_{0.5}Th_{0.5}Al_3$	6.518	4.619	0.71
$ThAl_3$	6.495	4.622	0.71
$CeAl_3$	6.545	4.609	0.70

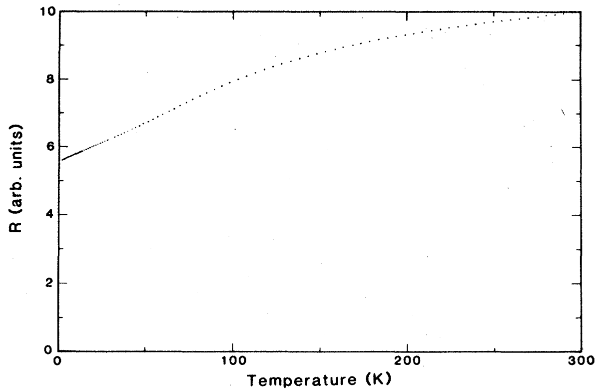

FIG. 1. Resistance versus temperature of $U_{0.5}Th_{0.5}Al_3$ between 1.4 and 300 K. A decrease in R below 1 K (not shown here) is, as discussed in the text, thought to be due to a small amount of an (unknown) second phase.

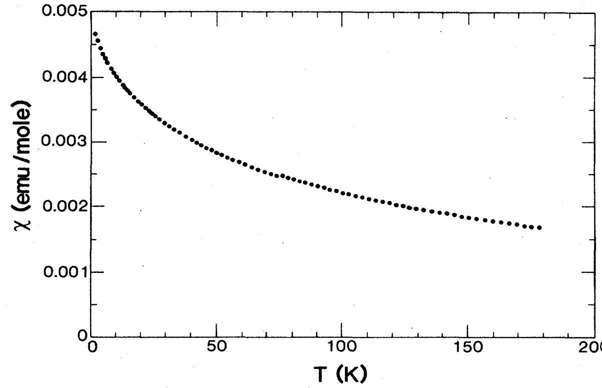

FIG. 2. Magnetic susceptibility of $U_{0.5}Th_{0.5}Al_3$ per mole of the formula unit, i.e., per $\frac{1}{2}$ mole of U. The slight anomaly around liquid-nitrogen temperature is of instrumental origin.

should be stressed that between 50 and 300 K, $U_{0.5}Th_{0.5}Al_3$ and UPt_3 have almost exactly the same temperature dependence, i.e., $R(300\text{ K})/R(50\text{ K})$ is the same for both materials. Below 50 K, the resistivity of UPt_3 falls precipitously, while in $U_{0.5}Th_{0.5}Al_3$ it continues to decrease in a gradual, linear fashion. This enhanced low-temperature scattering compared to UPt_3 is presumably due to the disordered nature of the pseudobinary alloy.

Below 1 K, the resistivity falls by a factor of 3, in stark contrast to the relatively flat behavior above 1 K. An applied magnetic field of 30 Oe essentially destroys this abrupt decrease in R below 1 K, leading to the conclusion that the falloff is due to a small amount of the superconducting second phase. Such a low critical field is totally inconsistent with any sort of bulk effect, since an estimate for $\rho(T\rightarrow 0)\sim 100\ \mu\Omega\,\text{cm}$ and the measured γ discussed below would lead[13] to a critical-field slope of at least 1 T/K.

The magnetic susceptibility of $U_{0.5}Th_{0.5}Al_3$ between 1.4 and 180 K is shown in Fig. 2. Since, as we will see below, the Th makes very little contribution to the electronic density of states, it is sensible to normalize the susceptibility per mole of U, rather than per mole of $U_{0.5}Th_{0.5}Al_3$ as shown in Fig. 2. Thus, for comparison to UPt_3, the susceptibility of $U_{0.4}Th_{0.5}Al_3$ as $T\rightarrow 0$ is ~ 0.0096 emu/(mole U), or 17% higher than that[4] of UPt_3, 0.0082 emu/(mole U). Both these values may be considered strongly enhanced over those for normal metals since even for Pd, $\chi(T\rightarrow 0)$ is only 0.1 of these $D0_{19}$ structure values.

Although crystal-field effects may still be shaping χ at 180 K, the susceptibility data above 100 K in Fig. 2 may be fit to be Curie-Weiss law, giving $\mu_{\text{eff}}=3.0\mu_B$, exactly the same as for[4] UPt_3.

The specific heat of $U_{0.5}Th_{0.5}Al_3$ is shown in Fig. 3. Just as for the susceptibility, these data may also be normalized per mole U, which would give $\gamma\simeq 360$ mJ/[(mole U) K^2], with γ just the intercept on the C/T plot shown. The important feature of the specific-heat data shown in Fig. 3 is the upturn occurring below 10 K, or $T^2=100\ K^2$. For long-range ferromagnetic spin fluctuations, Doniach and Engelberg[14] predicted that C/T would go as

$$C/T=\gamma+\beta T^2+\delta T^2\ln(T/T_{\text{SF}}) \qquad (1)$$

or

$$C/T=\gamma+\beta' T^2+\delta T^2\ln T\ ,$$

where $\beta'=\beta-\delta\ln T_{\text{SF}}$, βT^2 is just the normal lattice specific heat and the last term is due to long-range ferromagnetic spin fluctuations.[15] Such a term has been observed in UAl_2,[16,17] $TiBe_2$,[18,19] UPt_3,[5,6] and of course in ^3He.[20] Care must be taken to achieve a good fit of data to Eq. (1), which appears like the solid line in Fig. 3 qualitatively, since some materials show a similar upturn in C/T at low temperatures due to impurities. The solid line shown in Fig. 3 is a least-squares computer fit of the data to Eq. (1), giving $\gamma=184$ mJ/Mol K^2. As is evident, Eq. (1) is a good fit to the specific-heat data over the whole temperature range, similar in accuracy to such a fit for the other spin-fluctuation systems just mentioned. Also, an applied magnetic field of 11 T does not alter the specific heat below 4 K to within $\pm 3\%$,[21] eliminating the possibility of any sort of magnetic-impurity-caused upturn in C/T. (This lack of field dependence of C also rules out

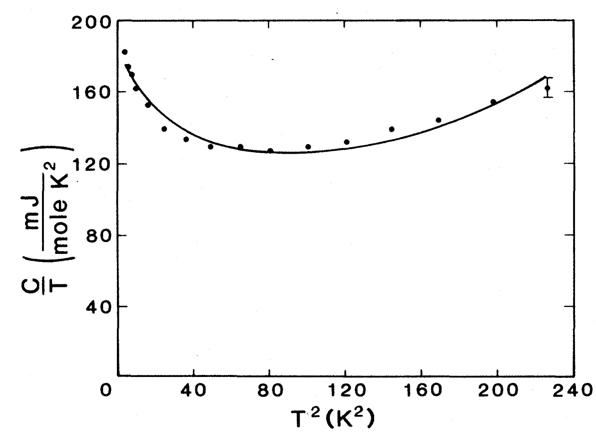

FIG. 3. Specific heat of $U_{0.5}Th_{0.5}Al_3$ per formula-unit mole, just as in Fig. 2. The solid line is a fit of Eq. (1) to the data, see text. The upturn in C/T, and its agreement with a $T^3\ln(T/T_{\text{SF}})$ dependence, is a strong indication of ferromagnetic spin fluctuations.

the possibility that the large γ value observed is caused by a narrow feature in the density of states at the Fermi energy as proposed for UBe_{13},[22] since an 11-T field would significantly broaden any such sharp feature.) It should be stressed that Eq. (1) is a three-term polynominal fit. A fourth term, e.g., ξT^5, could be added to take into account non-Debye-like behavior of the lattice. In this case, using a four-term fit to the data, the fit is extremely good with all points lying within $\pm 1\%$ of the fitted curve. However, a four-term fit does not significantly change γ, β, or δ from the result using Eq. (1) and we believe the accuracy of the three-term fit is more convincing evidence for a $T^3 \ln T$ term. A three-term fit with either a $1/T$ or $1/T^2$ (spin-glass or Schottky behavior, respectively) dependence for C replacing the $T^3 \ln T$ term does not fit the data shown in Fig. 3 well at all. Systematic deviations of over $\pm 10\%$ result. Therefore, we believe there is strong evidence for spin fluctuations in $U_{0.5}Th_{0.5}Al_3$, i.e., a $T^3 \ln T$ term in the low-temperature specific heat.

For comparison, we also measured the heats of isostructural $U_{0.2}Th_{0.8}Al_3$, $Ce_{0.5}Th_{0.5}Al_3$, and $ThAl_3$. The specific heat of $U_{0.2}Th_{0.8}Al_3$, per mole U, is quite similar to the data shown in Fig. 3 for the more concentrated alloy, with the coefficient γ, per mole U, the same within 5%. The main difference in the two sets of data is the shifting of the minimum in C/T observed in Fig. 3 from 9 K for $U_{0.5}Th_{0.5}Al_3$ down to 6 K in $U_{0.2}Th_{0.8}Al_3$. The specific heat of the Ce alloy analogous to $U_{0.5}Th_{0.5}Al_3$, $Ce_{0.5}Th_{0.5}Al_3$, shows a local-moment magnetic (perhaps ferromagnetic) transition starting at 7 K, with $R\ln 2$ of entropy increase per mole Ce, which corresponds to a sharp fall in the resistivity at a similar temperature as reported in Ref. 23 for $Ce_{0.5}Th_{0.5}Al_3$. The specific heat of $ThAl_3$, in the absence of f electrons, is very similar to that of a normal metal, with $\gamma = 8$ mJ/mole K^2 and a Debye temperature of 330 K. Thus, Ce may be considered more magnetic than U in $M_{0.5}Th_{0.5}Al_3$, just as $CeAl_2$, antiferromagnetic at 4 K, is more magnetic than UAl_2.

The question of why $U_{0.5}Th_{0.5}Al_3$ is not superconducting, while UPt_3 is, may be answered in two ways. First, a large resistivity ratio has been found[5] which is very important for superconductivity in UPt_3, with T_c only 0.27 K for $R(300\text{ K})/R(T_c^+) = 43$ versus $T_c = 0.54$ K for $R(300\text{ K})/R(T_c^+) = 145$. Thus, the extra scattering in $U_{0.5}Th_{0.5}Al_3$ below 50 K compared to that found in UPt_3 may be considered as destroying the rather delicate interaction in $U_{0.5}Th_{0.5}Al_3$ that leads to superconductivity in UPt_3. Second, a recent review of heavy-fermion systems has pointed out the importance of the "Wilson ratio" R, where, in units of 10^{-3} emu/mole for χ and mJ/mole K^2 for γ and where μ_{eff} is dimensionless,

$$R = \frac{\pi^2 k^2 \chi(T=0)}{g^2 \mu_B^2 \gamma^J (J+1)} = 218.7 \chi / \mu_{\text{eff}}^2 \gamma \quad (2)$$

for determining if a given system will become superconducting or not, with smaller R values being found in the superconducting materials. Since μ_{eff} is the same for UPt_3 and $U_{0.5}Th_{0.5}Al_3$, while χ for the latter is 17% higher and γ is 20% lower, R is almost 50% bigger for $U_{0.5}Th_{0.5}Al_3$ than for UPt_3 (0.65 versus 0.44). To put this in perspective,[1] $R = 0.59$ for $CeCu_6$ and 0.70 for $CeAl_3$, both nonsuperconducting heavy-fermion systems, while $R = 0.16$ to 0.52 for various superconducting $CeCu_2Si_2$ samples and $R = 0.31$ for superconducting UBe_{13}. Thus, the value of R for $U_{0.5}Th_{0.5}Al_3$ of 0.65 agrees with the correlation between the Wilson ratio and occurrence of superconductivity in heavy-fermion systems noted in Ref. 1.

IV. CONCLUSIONS

We have discovered a new f-atom system that displays a $T^3 \ln T$ upturn in the low-temperature specific heat, characteristic of ferromagnetic spin fluctuations. This pseudobinary alloy, $U_{0.5}Th_{0.5}Al_3$, occurs in the hexagonal $D0_{19}$ structure, just as do UPt_3 and $CeAl_3$—two other heavy-fermion systems. The low-temperature γ for $U_{0.5}Th_{0.5}Al_3$, 360 mJ/[(mole U) K^2], and χ, 9.6×10^{-3} emu/(mole U), are similar to values found for UPt_3, while the resistivity below 50 K for $U_{0.5}Th_{0.5}Al_3$ decreases only slightly, in contrast to UPt_3. Both the increased low-temperature scattering as seen in resistivity and the almost 50% larger Wilson ratio are possible causes of the lack of superconductivity in $U_{0.5}Th_{0.5}Al_3$ as compared to UPt_3.

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Engelsberg, Ref. 14, was for a spherical Fermi surface and ^{3}He. Thus, the existence of a $T^3\ln(T/T_{SF})$ term in an f-electron system is a strong indication, but not proof, of long-range ferromagnetic spin fluctuations.

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