Magnetic anisotropy in the $U_xTh_{1-x}Zn_{8.5}$ system

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We have investigated the source of the anisotropic susceptibility of $UZn_{8.5}$ by preparing single crystals of $U_xTh_{1-x}Zn_{8.5}$ for small x. Preliminary indications are that anisotropic exchange, rather than crystal field effects, are responsible for the anisotropy, but possible impurity contributions to the (anisotropic) susceptibility of the $ThZn_{8.5}$ do not permit a stronger statement. Further measurements for small x show that both the electronic specific heat and the susceptibility at low temperature are strongly enhanced, and that Kondo-type resistivity minima are observed. The enhancements are somewhat reduced in the concentrated system $UZn_{8.5}$.

In the last several years, a new class of materials has been discovered that is characterized by extremely large values of the effective electron mass m^*, which are known as heavy electron or heavy fermion systems. Experimentally, very large values of the electronic specific-heat coefficient γ and magnetic susceptibility χ_0 at $T=0$ are observed. From these, a very high density of states at the Fermi energy $N(E_F)$ and consequently large m^* are inferred. These values of m^* range up to several hundred times the free electron mass m_e, hence the adjective "heavy." These compounds exhibit superconducting, normal Fermi liquid, or magnetically ordered ground states.[1] It is the latter that is of interest in the present paper. U_2Zn_{17} or $UZn_{8.5}$, which is the formula unit we employ, is a heavy electron antiferromagnet with a Neél temperature T_N of 9.8 K as determined from anomalies in the specific heat C_p, the dc susceptibility χ, and the resistivity ρ as a function of temperature T.[2] The compound $UZn_{8.5}$ forms in the rhombohedral Th_2Zn_{17} structure, which we will deal with in the usual hexagonal representation. From neutron diffraction results, the ordered moments of $0.8 \pm 0.1\mu_B$ on the uranium sites were found to lie in the basal plane and to be oriented antiparallel to the nearest neighbors within the ab plane and along the c axis.[3] Recent magnetotransport measurements show a local minimum in the Hall coefficient and a sign change in the magnetoresistivity at T_N (Ref. 4); the authors interpret the results as suggesting an independent Kondo system at high temperature, gradually transforming to a coherent one below about 18 K and then magnetically ordering at T_N.

In the present work we focus on two questions in $UZn_{8.5}$: the anisotropy in the magnetic susceptibility and the dilute Kondo regime accessed in pseudobinary compounds of $U_xTh_{1-x}Zn_{8.5}$ for small x. The source of the anisotropy can be identified by examining the anisotropy for small x, for which anisotropic exchange should be very small relative to $x=1$, whereas crystal field anisotropy should be relatively unchanged. Studying the properties of dilute uranium compounds is useful in understanding the independent Kondo system and its progression to the concentrated Kondo lattice of the heavy electron systems. To these ends, we have prepared and examined single-crystal specimens near $x=0$ and reexamined pure $UZn_{8.5}$.

Samples of $U_xTh_{1-x}Zn_{8.5}$ were prepared by placing the constituents in an outgassed BeO crucible, sealing this in a quartz tube, heating to 1050 °C, and cooling slowly. The large single crystals that resulted were oriented by x-ray diffraction using a standard Laue camera and spark-cut from the bulk for further measurement. The susceptibility was determined in either a Faraday balance magnetometer or in a SQUID susceptometer in magnetic fields from 2 to 20 kOe. The specific-heat measurements were carried out in a small sample calorimeter using the time-constant relaxation method. Resistivity measurements were performed using a standard four-terminal ac technique. The compositions stated are those of the starting materials.

Figure 1 shows the results of dc susceptibility measurements on pure $UZn_{8.5}$. The anisotropy is readily apparent near the Neél temperature T_n of 9.8 K. At 15 K the susceptibility for the applied field H perpendicular to the hexagonal c axis, $\chi_{H\perp c}$, is about 30% greater than the susceptibility for the field applied parallel to the c axis, $\chi_{H\parallel c}$. A plot of $1/\chi$ vs T for these data yields an effective paramagnetic moment p_{eff} of $3.3 \pm 0.1\mu_B$ per uranium atom and Curie–Weiss intercepts θ_{CW} of -130 ± 5 K for $H\parallel c$ and -95 ± 5 K for $H\perp c$ for a calculated powder average of -107 ± 7 K. These values are slightly different from those reported in Ref. 2, but in good agreement ($3.15 \pm 0.1\mu_B$, -120 ± 5K) with those

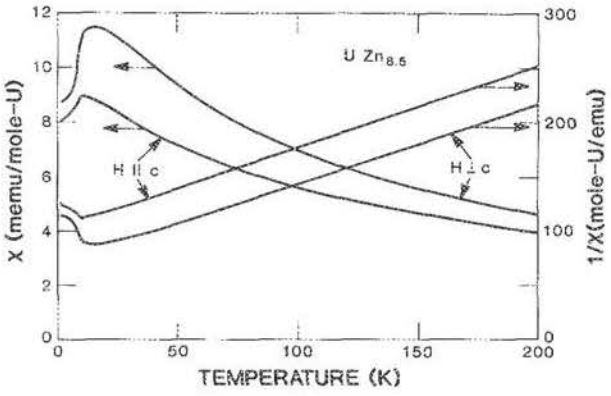

FIG. 1. The dc susceptibility and the inverse susceptibility vs temperature for $UZn_{8.5}$ for $H\parallel$ to and $H\perp$ to the c axis.

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TABLE I. Susceptibility parameters of $U_x Th_{1-x} Zn_{8.5}$ for $H \| c$ axis.

x	p_{eff} (μ_B/U atom)	θ_{CW} (K)	$\chi_0 = \chi(T=0)$ (emu/mol-U)
0.020	3.87 ± 0.1	-36.5	10×10^{-2}
0.043	3.54 ± 0.15	-33	9.2×10^{-2}
$1 (T > T_N)$	3.3 ± 0.1	-130	1.0×10^{-2}
$1 (T < T_N)$			0.8×10^{-2}

of Ref. 4. The effective moment is about 10% smaller than the U $5f^2$ or $5f^3$ configuration ($\approx 3.6 \mu_B$) as is frequently seen in other uranium compounds.

We probed the source of the anisotropy by looking at dilute concentrations of uranium in the (non-f) isostructural host $ThZn_{8.5}$. Single crystals of $x = 0$, 0.020, and 0.043 were prepared. The susceptibility was measured for $H \| c$ and $H \perp c$. Magnetization M vs H curves were practically linear to 50 kOe, showing only slight tendencies toward saturation, for $H \| c$ at 1.8 K. However, for $H \perp c$ for the $x = 0$ and 0.02 specimens, there was a much stronger tendency to saturate one component of the magnetization at fields on the order of 20–30 kOe at 1.8 K. This suggests an unusual intrinsic effect or the possibility of ferromagnetic impurities in the lattice, which would account for the anisotropic saturation behavior. We estimate that this effect would require 350 ppm of Gd (or equivalent) on Th sites in the lattice. We saw no evidence of this number of magnetic impurities in any of the starting materials; however, contamination by the crucible cannot be ruled out at present. Neglecting this unlikely impurity effect, which is small above 100 K, we then find, after subtracting the diamagnetic contribution of the $ThZn_{8.5}$, that the trend is for $\chi_{H \| c}$ to be depressed relative to $\chi_{H \| c}$ as x is increased. This preliminary result suggests that the large anisotropy in χ seen in $UZn_{8.5}$ ($\chi_{H \perp c} > \chi_{H \| c}$) is due to anisotropic exchange rather than crystal field effects; the latter would not be expected to be as sensitive to x as the former. The question of possible impurity effects in the $ThZn_{8.5}$ for $H \perp c$ must be resolved before a definitive conclusion can be reached.

Several parameters from the susceptibility data are collected in Table I for the $H \| c$ axis case from which M was always linear with H. In the dilute limit, the θ values are still substantially negative indicating some residual antiferromagnetic interactions, and the susceptibility χ_0 at $T = 0$ per mole uranium is enhanced a factor of 10 over the value for $x = 1$. The moment values are close to those for the U $5f^2$ or $5f^3$ configuration.

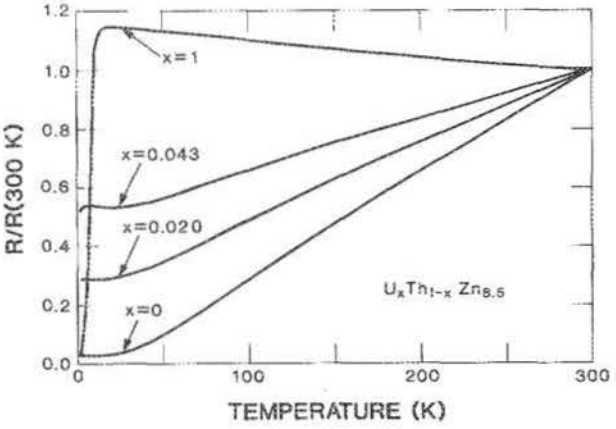

FIG. 2. The resistance of $U_x Th_{1-x} Zn_{8.5}$ normalized to the room-temperature value vs temperature for the indicated values of x.

The low-temperature specific heats C_p for $x = 0.020$ and 0.043 deviate from the value for $x = 0$ below about 7 K. For $x = 0$ the specific heat can be represented as $C_p = \gamma T + \beta T^3$, where γ is the electronic specific-heat coefficient related to the density of states at the Fermi energy, and hence to the effective electron mass m^*, and β is proportional to $\theta_D^{-1/3}$ where θ_D is the Debye temperature. For $x > 0$ there are strong enhancements to the value of $\gamma = C_p/T$ below 10 K. The measured γ value plus a calculated γ value per mole uranium are given for each x in Table II. It is clear from Table II that there are indeed manybody enhancements associated with the presence of uranium atoms for $x > 0$. Just as for χ_0, the γ values are significantly larger for the dilute ($x < 0.05$) than for the concentrated system. This suggests that, in going from the single Kondo impurity to the concentrated (Kondo lattice) system, there is a substantial decrease in the enhancement of the density of states and of m^* as reflected in the γ and χ_0 values.[5]

The temperature dependence of the resistance of $U_x Th_{1-x} Zn_{8.5}$ changes drastically as x is increased from 0 to 1; see Fig. 2. For $x = 0$ the behavior is the same as a normal metal: linear temperature dependence at high temperatures and saturation below 10 K. For $x = 0.020$ and 0.043, there appears a Kondo-type minimum in the resistance. This minimum at $T(R_{min})$ moves to higher temperatures with x, with $T(R_{min})$ apparently much greater than 300 K at $x = 1$, for which a coherent ground state begins to develop below about 17 K. Several of the resistance parameters are collected in Table III. We also observed a substantial resistance drop below 5 K for $x = 0.043$; we see no corresponding feature in

TABLE II. Specific-heat parameters of $U_x Th_{1-x} Zn_{8.5}$.

x	γ (mJ/mole-K^2)	γ_U (mJ/mole U-K^2)	θ_D (K)
0	5 ± 0.5	...	290 ± 10
0.020	18 ± 1	650 ± 50	
0.043	30 ± 1	580 ± 60	
$1 (T > T_N)$	410 ± 25	410 ± 25	
$1 (T < T_N)$	290 ± 20	290 ± 20	

TABLE III. Resistance parameters of $U_x Th_{1-x} Zn_{8.5}$.

x	$RRR \equiv \frac{R(300\,K)}{R(1.4\,K)}$	$T(R_{min})$ (K)	$T(R_{max})$ (K)
0	37	...	...
0.020	3.4	16	...
0.043	1.9	22	6
1	34	>300	17

either χ or C_p near this temperature. It is known that for $x = 0.9$ the coherent state present for $x = 1$ has already been destroyed[6] and thus would not be expected for $x = 0.043$; the nature of this feature is not currently understood.

In conclusion, we find resistivity minima and strong enhancements of the specific heat γ values and the low-temperature susceptibility χ_0 for small values of x. In the concentrated system the resistivity minimum is pushed above 300 K, and coherence develops at low temperature; the strong enhancements are reduced somewhat but are still orders of magnitude larger than seen in normal, not heavy, electron systems. We believe that these results suggest some similarities between Ce-based Kondo systems and the uranium-based compound under study here.

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