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RESISTIVITY, SUSCEPTIBILITY AND SPECIFIC HEAT OF $(Y_{1-x}U_x)B_4$

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An anomalous magnetic phase diagram for dilutions of UB_4 with YB_4 had been previously established. The $(Y_{1-x}U_x)B_4$ system is paramagnetic for $x > 0.6$, ferromagnetic for $0.1 < x < 0.6$ and paramagnetic for $x < 0.1$. Measurements of the resistivity and magnetic susceptibility for $1 \text{ K} < T < 300 \text{ K}$ and the low temperature specific heat are presented. The observed behavior is suggestive of a localization of the 5f electrons upon dilution of UB_4 by YB_4 due to the reduction of the 5f–5f overlap.

1. Introduction

During the last few years, a high level of experimental and theoretical activity has been focused on the magnetic–nonmagnetic transition seen in many Ce based systems [1]. These studies have stimulated a broader interest in understanding the features associated with magnetic moment formation. A particularly interesting area of study is the nonmagnetic–magnetic behavior seen in Actinide (Ac) materials; partially because they display many of the features seen in Ce systems. The transition from magnetic to nonmagnetic behavior in Ac systems is associated with the delocalization of the 5f electrons due to increased f–f overlap and/or f–spd hybridization. A dramatic demonstration of the importance of f–f overlap in these systems is the establishment of a critical spacing between Ac ions and Ce ions below which long range magnetic behavior does not exist [2]. Those systems with an Ac–Ac spacing in the vicinity of this critical spacing should show the most dramatic manifestations of f–f overlap on their magnetic properties.

One such system is UB_4 , which does not magnetically order but does have a U–U spacing (i.e. $\approx 3.7 \text{ \AA}$) slightly larger than the upper limit of the critical spacing

(i.e. $\approx 3.6 \text{ \AA}$) separating the nonmagnetic and magnetic U-systems [2,3]. Upon dilution of UB_4 with YB_4 , the average U–U separation is increased and an anomalous magnetic phase diagram is obtained [3]. Giorgi et al. [3] has shown that the $(Y_{1-x}U_x)B_4$ system is paramagnetic for $x > 0.6$, ferromagnetic for $0.1 < x < 0.6$ and paramagnetic for $x < 0.1$. It was also established that upon substitution of U for Y in YB_4 , the lattice parameter initially follows Vegard's law for $x < 0.4$ and deviated from this linear dependence for $x > 0.4$ [4]. The lattice parameter data could be explained assuming that the f–f overlap is reduced upon dilution of UB_4 and the 5f electrons become localized and magnetic, if the number of U nearest neighbors is 4 or less. A similar analysis was successfully applied to an NMR study of this system [5]. Because of the extremely anomalous phase diagram obtained for the $(Y, U)B_4$ system and the profound interest in localization–delocalization phenomena, we have measured the magnetic susceptibility, $\chi(T)$, the specific heat, $C(T)$, and the electrical resistivity, $\rho(T)$, in this system. These results are presented below along with a comparison to the two site theory for the U-ions and spin fluctuation theories.

2. Experimental

The samples were prepared in an inert atmosphere arc furnace and annealed at 1100°C for 5 days. Both

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UB₄ and YB₄ crystallize in the tetragonal ThB₄ structure, and crystal structure determination using powder X-ray diffraction methods indicated that all of the (Y, U)B₄ samples were single phase. The $\rho(T)$ samples were pressure cast into (1 mm² × 1 cm) bars and $\rho(T)$ was measured using a standard 4-probe dc method. The $C(T)$ was measured using the adiabatic method and $\chi(T)$ was measured using a vibrating sample magnetometer.

3. Results

The reciprocal of the magnetic susceptibility for (Y, U)B₄ versus T is shown in fig. 1 for $x = 0.3, 0.6, 0.8$ and 1.0. The data for UB₄ does not show the same temperature dependence as previously published by Chechernikov et al. [6] where a rather pronounced maximum was reported near 120 K and $\chi(T)$ appears to be Curie–Weiss like at higher temperatures. Our data for UB₄ is consistent with unpublished data obtained at Bell Laboratories, Inc. [7]. Note that (Y_{0.7}U_{0.3})B₄ becomes ferromagnetic with a $T_c \approx 17$ K and (Y_{0.4}U_{0.6})B₄ appears to be very near the magnetic phase boundary. These results are consistent with the previously reported magnetic phase boundary. [3] We have analyzed our $\chi(T)$ data using the two site model previously proposed to explain the x -dependence of the lattice parameters [3] and NMR results [5]. In refs. [3,5], the two site model assumed that the U-ions with more than 4 U nearest neighbors were nonmagnetic and those with 4 or less U nearest neighbors were magnetic. Consistent with their analysis, we assumed that all U-ions with greater than 4 U nearest neighbors would remain nonmagnetic and would have a $\chi(T)$ as given by UB₄ and those U-ions with 4 or less U nearest neighbors would be magnetic and have a Curie–Weiss susceptibility. Application of

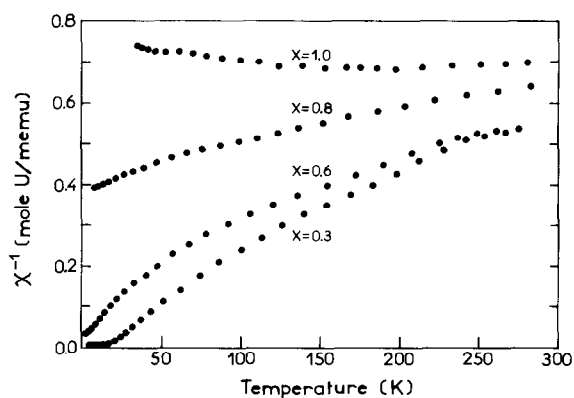


Fig. 1. The inverse magnetic susceptibility versus temperature for Y_{1-x}U_xB₄.

Table 1.
 $\chi(0)$ and γ for (Y_{1-x}U_x)B₄.

x	$\chi(0)$ (memu/mol U)	γ (mJ/mol UK ²)
1.0	1.9	33.5
0.8	2.6	60.5
0.7	5.9	86.5
0.6	33.0	116.3

this simple model to all the Y doped samples in fig. 1 yields a Curie–Weiss law for the magnetic U-ions with a Curie constant equivalent to an effective moment of $(2.6 \pm 0.2)\mu_B$. Considering the simplicity of this model, this value compares favorably with the predicted highly localized 5f electron values of $\mu_{\text{eff}} = 3.5\mu_B$ for 5f² and $\mu_{\text{eff}} = 3.62\mu_B$ for 5f³. For samples in the paramagnetic region, $\chi(T)$ approaches a constant value, $\chi(0)$ as $T \rightarrow 0$. Extrapolated values for $\chi(0)$ within this region are given in table 1.

We have measured the magnetization below T_c for (Y_{0.7}U_{0.3})B₄ and an Arrott plot analysis yields a saturation moment of $0.32\mu_B$. This result seems not to be consistent with the above localized description. Further analysis including possible crystal field effects is required.

Shown in fig. 2 is the low temperature dependence of $C(T)/T$ versus T^2 for (Y, U)B₄ samples in the paramagnetic region. The data show a marked enhancement of the low temperature $C(T)$ as the 5f overlap is reduced upon dilution of UB₄ and the magnetic instability is approached. It is not clear what is the most appropriate model to apply to these results. The two site model may explain the observed behavior if a distribution of T_c 's exists due to statistical clustering of magnetic U ions. However the data also resembles that

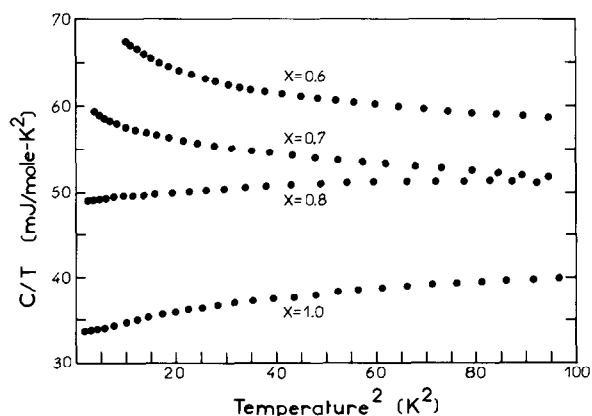


Fig. 2. The specific heat divided by temperature versus the temperature squared for Y_{1-x}U_xB₄.

predicted by spin fluctuation models as the magnetic instability is approached [8]. In such a model the low temperature up-turn in $C(T)/T$ versus T^2 is due to a spin fluctuation contribution and this contribution should be enhanced as the system approaches a magnetic instability. Using such a model, extrapolated values for γ , the electronic coefficient of the specific heat, are given in table 1. The relative importance of the contributions to $C(T)$ due to the two models mentioned above may be determined from the analysis of the entropy removal and magnetic field dependence of $C(T)$. Such measurements are now being conducted. Another feature not totally apparent in the $C(T)$ data shown in fig. 2 but seen in $C(T)$ at high temperatures, is the large decrease in the relative contribution to $C(T)$ due to the phonons as compared to the electronic contribution. This decrease is indicative of a substantial increase in the Debye temperature from UB₄ to YB₄. This increase is consistent with their relative melting temperatures [9].

The $\rho(T)$ versus T for several (Y, U)B₄ samples is shown in fig. 3. As Y is substituted for U in UB₄, there is a significant increase in the resistivity at all temperatures, with $\rho(300)$ roughly following a Nordheim dependence, i.e. $\rho(300)$ peaks in the vicinity of $x = 0.5$. However, $\rho(0)$ does not behave in this way but peaks in the vicinity of $x = 0.3$ which is mid-range in the ferromagnetic region. A more appropriate way to display the concentration dependence of $\rho(T)$ is to examine the resistivity per U-ion. Plotted in fig. 4 is the $\rho(0)/x$ versus x , the U-concentration. The $\rho(0)/\text{U-ion}$ is dramatically enhanced as the f-f overlap is reduced. Both the temperature and concentration dependence of $\rho(T)$ for (Y, U)B₄ seems to be inconsistent with the predictions of existing theoretical models such as spin fluctuation and Kondo theories; thus a more quantitative analysis is not possible at this time. For UB₄, $\rho(T)$ has a T^2 -dependence as $T \rightarrow 0$ and using a simple spin

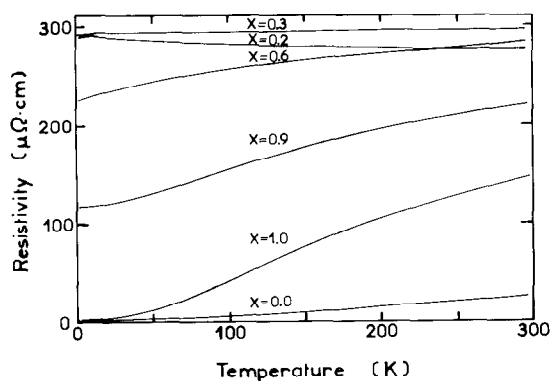


Fig. 3. Electrical resistivity versus temperature for Y_{1-x}U_xB₄.

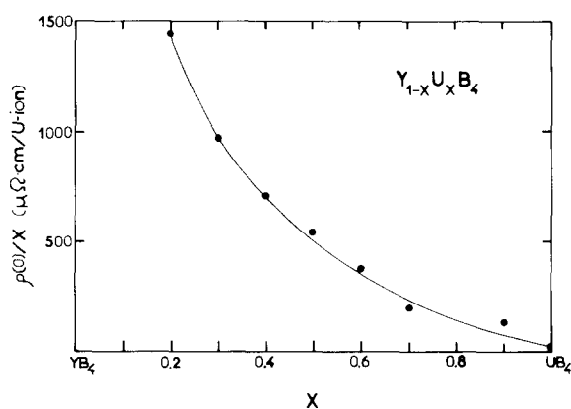


Fig. 4. The electrical resistivity at $T = 0$ per U-ion versus U concentration in Y_{1-x}U_xB₄.

fluctuation argument indicates a $T_{sf} \approx 18$ K. However, this estimate of T_{sf} is inconsistent with spin fluctuation analysis of $C(T)$ and $\chi(T)$ for UB₄ which indicates a much larger T_{sf} (i.e. $T_{sf} \approx 300$ – 1000 K). A more complete discussion of our analysis will be presented in a future publication.

Summarizing, the measurements of $\chi(T)$ versus T for (Y, U)B₄ are consistent with a previously published determination of the magnetic phase boundary and the two site model. The effective moment indicates that there is an increased localization of the 5f electrons due to the reduction of f-f overlap as UB₄ is diluted with YB₄. $C(T)$ versus T and $\rho(0)/\text{U-ion}$ shows an enhancement as the magnetically ordered region is approached.

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