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Susceptibility, magnetization, and specific heat in the paramagnetic and ferromagnetic regions of $(Y_{1-x}U_x)B_4$

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An anomalous magnetic phase diagram for $(Y_{1-x}U_x)B_4$ has previously been reported. This system is paramagnetic for $x > 0.6$, ferromagnetic for $0.1 < x < 0.6$, and paramagnetic for $x < 0.1$. Measurements of the magnetic susceptibility suggest a localization of the $5f$ electrons upon alloying UB_4 with nonmagnetic YB_4 due to a reduction of f-f overlap. The temperature and x dependence of the magnetic susceptibility is consistent with a two site model. This model assumes that the $5f$ electrons associated with U ions that have four or less nearest neighbors become localized and develop a stable paramagnetic moment. From our analysis, we obtain a paramagnetic moment of $(2.6 \pm 0.2)\mu_B$. The saturation moment per U ion for $(Y_{0.7}U_{0.3})B_4$ is $(0.32 \pm 0.03)\mu_B$. The specific heat of $(Y,U)B_4$ shows a substantial enhancement as x decreases but the origin of this enhancement is not understood at this time. These results are presented and discussed in relation to the expected behavior as the system approaches the ferromagnetic instability.

INTRODUCTION

The exceptionally varied magnetic behavior seen in the lighter actinide (Ac) metals and intermetallic compounds can be attributed to the close proximity of the $5f$ states to the Fermi level and the degree of localization of these electrons. A particularly interesting example of the unusual magnetic behavior seen in these systems is the anomalous magnetic phase diagram reported for the $(Y_{1-x}U_x)B_4$ system.[1] UB_4 is weakly paramagnetic at all temperatures and YB_4 is non-magnetic. However, as shown by Giorgi *et al.*,[1] 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 $x < 0.1$. The magnetic to nonmagnetic behavior seen in Ac systems is attributed to the delocalization of the f electrons due to f-f overlap and/or f-spd hybridization. The importance of f-f overlap as a factor limiting magnetic moment formation in the lighter Ac (i.e., U, Np, and Pu) and Ce was dramatically demonstrated by H. H. Hill.[2] In these systems, f-electron magnetism does not occur if the Ac-Ac interionic spacing is below a critical value. For U systems, this critical spacing is 3.4–3.6 Å. Beyond this critical spacing, f-electron magnetism may or may not occur depending on the level of f-spd hybridization. The U-U spacing in UB_4 ($\cong 3.7$ Å) is slightly larger than the critical spacing established by Hill. Thus, the formation of a stable magnetic moment and long range magnetic ordering in UB_4 is supressed due to f-f overlap. The transition to a ferromagnetic state upon dilution of UB_4 by YB_4 can be attributed to a localization of the $5f$ electrons and an associated growth of stable magnetic moments as the average U-U spacing is increased and f-f overlap is reduced. A dramatic indication of the increased f-electron localiza-tion with the reduction in f-f overlap is seen in the variation of the lattice constants with x for this system.[3] The lattice constants for $(Y_{1-x}U_x)B_4$ initially follow Vegard's Law for $x < 0.4$ then deviate from this initial linear dependence for $x > 0.4$. This deviation in the lattice constants from Vegard's Law is similar to those seen in Ce mixed valent systems.[4] Thus, certainly much of the interest in Ac intermetallic systems, particularly U systems, centers around exploring the apparent similarities between Ce mixed valent systems and the behavior reported for many Ac systems. We have measured the magnetic susceptibility, $\chi(T)$, the specific heat $C(T)$ at low temperatures (i.e., $1.5 K \leqslant T \leqslant 20$ K), and the magnetization $M(H,T)$, in the ferromagnetic regime for selected samples of $(Y_{1-x}U_x)B_4$. The electrical resistivity was also measured for $(Y,U)B_4$ and has been reported in a previous publication.[5]

RESULTS

The samples were prepared in a conventional inert atmosphere arc furnace. A small weight loss primarily due to the evaporation of the more volatile constituents (i.e., Y and U) occurred during melting. Additional Y, U, and B was added in proportion to their relative vapor pressures and consistent with the weight losses obtained in melting the terminal compounds. Assuming these estimates were correct, the final weight of the pseudobinary alloy was within 0.4% of the expected weight for a stoichiometric ratio of the atoms. The concentrations of the constituents reported here are nominal concentrations based on the weight of the constituents added. The samples were annealed at 1100 °C for 5 days. Two samples $(Y_{0.7}U_{0.3})B_4$ and $(Y_{0.5}U_{0.5})B_4$ were further annealed at 1100 °C for four weeks. Both YB_4 and UB_4 crystallize in the tetragonal ThB_4 structure, and x-ray diffraction studies indicated that the samples appear to be single phase with lattice constants similar to those previous-
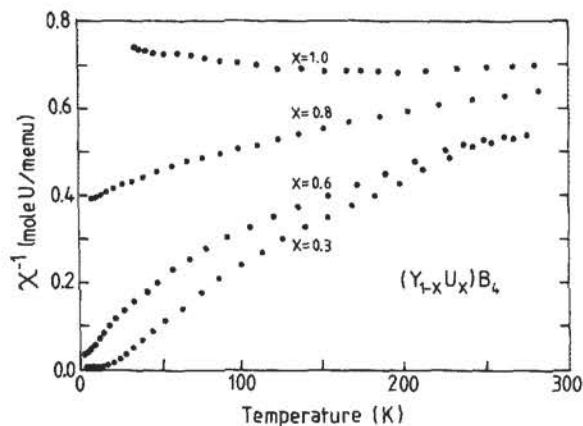
FIG. 1. The inverse magnetic susceptibility vs temperature for $(Y_{1-x}U_x)B_4$.

Fig. 3. Magnetization for $(Y_{1-x}U_x)B_4$ vs applied magnetic field.

ly reported.[3] The susceptibility and magnetization were measured with a vibrating sample magnetometer and the specific heat was measured using a standard pulsed adiabatic method.

Shown in Fig. 1 is the reciprocal of the magnetic susceptibility, $\chi^{-1}(T)$ vs T for $(Y_{1-x}U_x)B_4$ with $x = 0.3$, 0.6, 0.8, and 1.0. For $x = 1.0$ (i.e., UB_4), $\chi(T)$ is nearly temperature independent from $5 \leqslant T \leqslant 300$ K. This $\chi(T)$ dependence for UB_4 is inconsistent with the behavior reported by Chechernikov et al.[6] where $\chi(T)$ followed a Curie–Weiss dependence at high temperatures and had a pronounced maximum in the vicinity of 120 K. The $\chi(T)$ for UB_4 shown in Fig. 1 is in agreement with that obtained by B. Batlogg.[7] As Y is substituted for UB_4, $\chi(0)$ is enhanced as shown in Fig. 5. For $(Y_{0.7}U_{0.3})B_4$, $\chi^{-1}(T)$ indicates a ferromagnetic transition at $T_C \cong 15$ K.

H. H. Hill and co-workers proposed a two site model for $(Y,U)B_4$ to explain their lattice constant variation with x (Ref. 3) and NMR measurements of the hyperfine field.[8] This model assumed that the $5f$ electrons associated with U ions having 4 or less U nearest neighbors become localized with a localized magnetic moment. Furthermore, those $5f$ electrons in U ions with more than 4 U nearest neighbors remained delocalized and weakly paramagnetic. We have applied this model to the $\chi(T)^{-1}$ vs T data shown in Fig. 1. We

have assumed that the U ions with more than four nearest neighbors would have a $\chi(T)$ equal to that measured for UB_4 and that those U ions with 4 or less nearest neighbors would have a $\chi(T)$ given by a modified Curie–Weiss law [i.e., $C/(T - T^*)$]. Shown in Fig. 2 is $\Delta\chi(T)^{-1}$ vs T where $\Delta\chi(T)$ is equal to the measured $\chi(T)$ minus $\chi(T)$ for UB_4 times the statistical number of U ions with more than four nearest neighbors. As can be seen in Fig. 2, $\Delta\chi(T)^{-1}$ vs T becomes much more Curie–Weiss like. The solid lines in Fig. 2 are fits to $\Delta\chi(T) = C/(T - T^*)$. The Curie constant C is nearly constant through the series and corresponds to an effective paramagnetic moment, μ_P, of $(2.6 \pm 0.2)\mu_B$. Thus, the rather simple two site model used to explain both the lattice constants and NMR data works remarkably well for $\chi(T)$. Furthermore, our $\chi(T)$ results indicate that the $5f$ electrons become localized and give rise to a substantial paramagnetic moment as Y is substituted for U in UB_4.

Shown in Fig. 3 are some representative curves for the magnetization versus applied magnetic field for $(Y_{0.7}U_{0.3})B_4$. This sample gives a $T_C \cong 15$ K and is at the maximum in T_C vs x previously reported by Giorgi et al.[1] As seen in Fig. 3, $M(H,T)$ is linear with H well above T_C but developed a significant curvature as $T \to T_C$. For $T < T_C$, $M(H,T)$ vs H becomes hysteretic. Using an Arrott plot[9] analysis of $M(H,T)$ for this sample we obtain a saturation magnetization μ_0 as $T \to 0$ which corresponds to $(0.32 \pm 0.03)\mu_B$
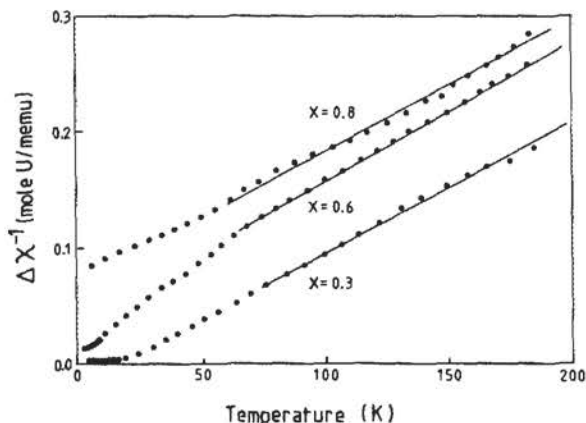

Fig. 2. The reciprocal of the magnetic susceptibility $\chi(T)$ minus $\chi(T)$ for UB_4 times the fraction of U ions with more than four U nearest neighbors, vs temperature.
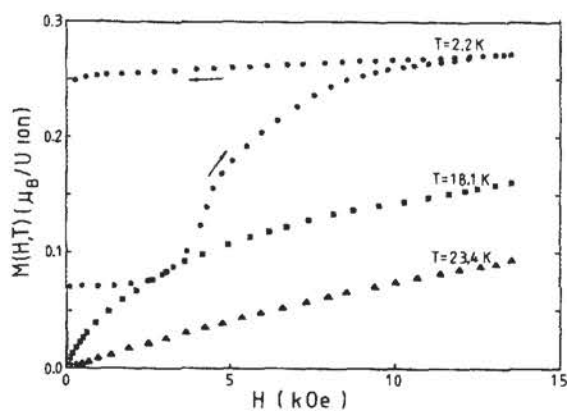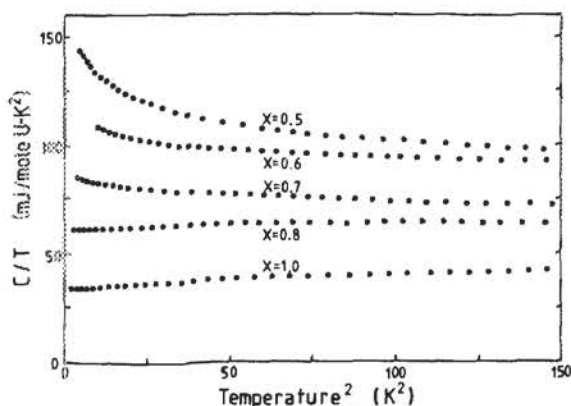

Fig. 4. The specific heat divided by temperature vs the temperature squared for $(Y_{1-x}U_x)B_4$.
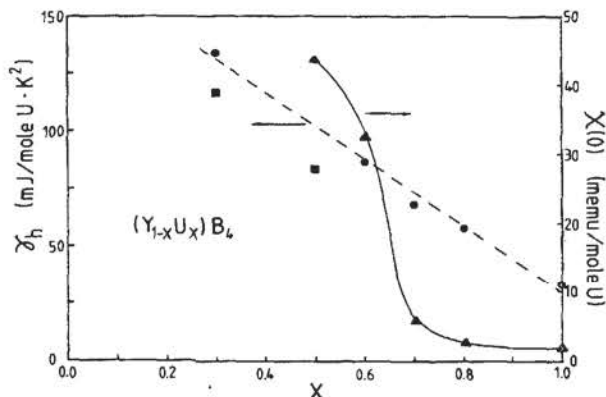
Fig. 5. The high temperature electronic specific heat coefficient γ_h and zero temperature intercept of the magnetic susceptibility $\chi(0)$ vs x for $(Y_{1-x}U_x)B_4$. ● $= (Y_{1-x}U_x)B_4$ annealed at 1100 °C for 4 days; ▨ $= (Y_{1-x}U_x)B_4$ annealed at 1100 °C for 4 weeks.

per U ion. The saturation moment of 0.32 μ_B per U ion is below the value expected for a localized $5f^4$ or $5f^3$ configuration of U in the absence of crystalline electric effects. Knowledge of the size of such interactions is lacking at this time, and thus prohibits any meaningful quantitative comparison of μ_0 to that expected from the localized two site model.

Shown in Fig. 4 is $C(T)/T$ vs T^2 for several $(Y,U)B_4$ pseudobinary alloys. There are several salient features that should be noted. Fits of $C(T)$ to $\gamma T + \beta T^3$ in the high temperature region (i.e., $15 < T < 25$ K) where the $C(T)/T$ is more linear with T^2, yields a rapidly increasing γ, the electronic specific heat coefficient, and Θ_D, the Debye temperature, with decreasing x. The variation of this high temperature γ_h with x is shown in Fig. 5. The increase in Θ_D with decreasing x is qualitatively consistent with what would be expected using the Lindemann relationship[10] and the melting temperatures of the terminal solutions. However, because of the strong enhancement of $C(T)$ as $T \rightarrow 0$ over what would be expected for a simple Fermi liquid, we doubt that these Θ_D values accurately represent the actual low temperature Θ_D. Based on the previously reported magnetic phase diagram, T_C for $(Y_{0.5}U_{0.5})B_4$ should have been 6 K. However, we do not see any evidence of a ferromagnetic transition in $C(T)$ or $\chi(T)$ for this sample. This particular sample was annealed much longer (4 weeks) than the samples used in the previous study and our other samples. There seems to be a slight decrease in γ_h for the samples that have been annealed for very long times. The origin of these effects is not clear at this time and requires further study.

Another important feature of the $C(T)$ data shown in Fig. 4 is the anomalously strong enhancement of $C(T)/T$ as $T^2 \rightarrow 0$ and x approaches the ferromagnetic regime. This enhancement is qualitatively consistent with what would be expected assuming a decrease in the spin fluctuation temperature as x decreases. We can fit our data to the expected behavior assuming spin fluctuations[11] for $T < 10$ K, but we seem to be unable to adequately fit the higher temperature data. Because of the incredible enhancement of the low temperature resistivity per U ion as x decreases,[5] we have also compared our $C(T)$ to that expected for a Kondo system without crystal electric effects [i.e., including a $T\ln(T)$ contribution to $C(T)$].[12] The data can be fitted over a wider temperature range than possible with a spin fluctuation model. However, the appropriateness of a Kondo model for this system is not clear at this time. Considerably more attention will be given to the analysis of these data in the near future.

In conclusion, our measurements of $\chi(T)$ vs T for $(Y,U)B_4$ are compatible with what would be expected using the two site model and is suggestive of an increased localization of the $5f$ electrons upon dilution of UB_4 by nonmagnetic YB_4. The specific heat versus temperature shows a significant enhancement at low temperatures, but it is not clear at this time if this enhancement is due to spin fluctuations or a Kondo effect. Further studies of the ferromagnetic regime and the paramagnetic regime with $x < 0.1$ are presently being pursued.

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