Effects of hydrogen doping on UPd_2Al_3

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We have succeeded in doping hydrogen into the "semiheavy" UPd_2Al_3 up to a stable concentration of $UPd_2Al_3H_{1.3}$. Magnetism is depressed in $UPd_2Al_3H_x$: T_N falls from 14.5 K with an initial slope of about 55 mK/%H, χ(1.8 K) initially remains relatively constant but rises substantially for $x>0.34$ to 21.4 memu/mole at $x=1.30$, while the effective moment inferred from the Curie-Weiss behavior in the susceptibility above 100 K falls monotonically with hydrogen doping from $3.39\mu_B$ for $x=0$ to $2.82\mu_B$ for $x=1.30$. Superconductivity is totally suppressed by approximately $x=0.5$. At the same time as the antiferromagnetic peak in the specific heat is being depressed to lower temperatures with increasing x, the specific heat divided by temperature data show more and more of an upturn below 10 K, reminiscent of the behavior seen in heavy fermion systems like $CeCu_2Si_2$. Whether or not this upturn in C/T is magnetic in character was checked via measurements of the magnetization at 1.8 K, which showed no signs of saturation up to 5.5 T, and of the field dependence of the low-temperature ($0.3\ \mathrm{K} \le T < 1.5\ \mathrm{K}$) specific heat in 14 T, which showed approximately a 25% decrease. Such a decrease in the specific heat with field is significantly smaller than that seen in, e.g., $CeCu_6$ (65% suppression in 14.5 T) where magnetic correlations are thought to be strong, and is similar to the size effect seen in nonsuperconducting samples of $CeCu_2Si_2$ (35% suppression in 10 T). However, whether this upturn in C/T in $UPd_2Al_3H_{1.3}$ is indicative of an electron effective mass increased by a factor of 4 vs pure UPd_2Al_3, or due to magnetic correlations/short-range magnetic order remains an open question.

I. INTRODUCTION

A number of interesting results[1-8] in the study of heavy fermion systems have been achieved via doping, e.g., in $U_{1-x}Th_xBe_{13}$ (Ref. 1) and $UPt_{5-x}Au_x$.[5,6] One drawback of such studies, of course, is that the host lattice is strongly disturbed, with one or the other sublattices being occupied by "foreign" atoms. It has been conclusively shown[4] in UBe_{13}, for example, that 60% of the large low-temperature electron effect mass, $m^*(\propto\gamma=C/T$ as $T\to 0)$ comes from interaction effects between the U atoms which are destroyed by substitutions on the U sublattice. These correlation or coherence effects are not well understood.

One possibility for studying heavy fermion systems where the occupation of the sublattice would remain undisturbed is that of hydrogen doping. This method has been used extensively in other materials to further understanding of the electronic properties, e.g., in[9] V_3GaH_x where the behavior of the superconductivity and the low-temperature specific heat as a function of hydrogen uptake were studied.

We report here on $UPd_2Al_3H_x$, $0\le x\le 1.30$, where the hydrogen remains stable in the lattice under ambient pressure. A number of other heavy fermion materials were checked for hydrogen uptake, but so far only UPd_2Al_3 and (work in progress) the companion compound UNi_2Al_3 retain the hydrogen. UPd_2Al_3 was discovered by Geibel *et al.*[10] to be a "semiheavy" system, with the specific heat $\gamma(\propto m^*)=150$ mJ/mole K^2, which combines antiferromagnetism at 14.5 K with superconductivity at 2 K. The behavior of the coexistent superconductivity and magnetism upon hydrogen doping (where the hydrogen proton goes into the lattice interstitially and the electron goes into the Fermi sea) provides a particularly rich complement of effects for this report[11] on the effect of hydrogen doping in this field of research.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Samples were hydrided in a Parr pressure vessel, with pressures monitored by pressure transducers from Data Instruments with a precision of ± 1 psi. Hydrogen uptake in UPd_2Al_3 required repeated (20–30) application and removal of the hydrogen gas, using pressures of 2000 psi and temperatures up to 450 °C. Also, unlike the more readily hydridable materials, e.g., $LaNi_5$, we found that hydrogen uptake in a bulk chunk of material was ineffective; thus, we powdered our samples before loading them in the pressure vessel. This grinding was found to affect the properties of the unhydrided material, as has already been seen[12] in $U_{1-x}Th_xPt_3$, $UPt_{3-x}Pd_x$, and UPt_3 itself.[13] Thus, T_c onset (as determined by ac susceptibility) is depressed 0.19 K, dH_{c2}/dT at T_c is depressed a factor of 4, and the antiferromagnetic anomaly in the specific heat is made 30% smaller and broadened by grinding. (All of these results were taken on the same sample to rule out sample-dependent effects.)

As expected, hydrogen uptake in UPd_2Al_3 led to a slight lattice expansion, with the hexagonal lattice parameter a increased by 0.52% and c decreased by 0.31% as a result of the maximum doping we were able to achieve, $UPd_2Al_3H_{1.30}$. This results in a unit-cell volume $((3\sqrt{3}/2)a^2c)$ increase of 0.75%.

In order to determine the hydrogen content of the various samples prepared, the rough, initial determination used the weight gain of the powder in the pressure vessel, where the accuracy was limited by our ability to gather all of the powder after hydriding. After all measurements were finished, each sample (the powders were pressed into pellets for ease of handling and for improved thermal contact for low-temperature measurements) was dehydrided by heating, using a weak hydrogen flame, in an evacuated quartz tube hooked to a pumping plenum. The temperature where hydrogen begins to come out of the lattice, determined by heating in a sand bath, is about 225 °C. Samples of stoichiometry intermediate between $x=0$ and 1.3 were prepared by partially dehydriding material with a higher hydrogen content using controlled heating in the quartz tube-plenum arrangement, while watching the pressure rise. In this fashion, we prepared $x=1.09$, 0.77, 0.64, 0.34, 0.20, 0.17, and 0.13. Although we have no direct method to measure the homogeneity of the hydrogen in the lattice, we estimate the homogeneity to be ±25%.

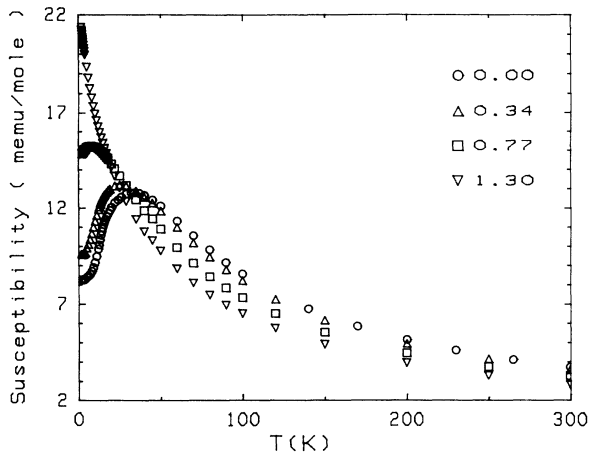

FIG. 1. Low-temperature, $T \leq 300$ K, magnetic susceptibility of representative concentrations of $UPd_2Al_3H_x$, $x=0$, 0.34, 0.77, and 1.30. Note the shift to lower temperatures and gradual decrease in size with increasing x of the anomaly at 35 K.

A. Normal state

The magnetic susceptibility of $UPd_2Al_3H_x$, $0 \leq x \leq 1.30$, is shown in Fig. 1 and summarized numerically in Table I. The feature in χ at 35 K, Fig. 1, is depressed to lower temperatures with increasing x, see also Table I. Although the position of this feature has been described[14] as due to crystal-field splitting of the uranium $5f$ levels in pure UPd_2Al_3, it is unlikely that such a simple description is valid for the hydrogen-doped samples, especially since the maximum is suppressed to 7 K by $x=0.77$. More useful information on the influence of hydrogen doping on the magnetic behavior can be gleaned from the behavior of the higher temperature, Curie-Weiss effective moment, μ_{eff}, and the magnitude of the low-temperature magnetic susceptibility (see Table I). As may be seen, the effective moment falls monotonically with increasing x, while χ (1.8 K) first remains relatively constant, then rises for $x > 0.34$. A further parameter which we have measured is the magnetization as a function of field. In pure UPd_2Al_3, there exists[14] an inflection point in the M vs H curve near $H=2$ T, where M rises more rapidly than linearly with H over a small region of H, which has been explained[14] as a rearrangement of the spins in the basal plane. Hydrogen doping for $x > 1.0$ destroys this inflection point, at least up to our maximum field of 5.5 T, giving a linear M vs H behavior.

In order to more completely discuss magnetism in $UPd_2Al_3H_x$, we need also to consider the behavior of T_N, which is visible as an inflection point at 14.5 K in χ vs T (Fig. 1), but is much more readily apparent in the low-temperature specific heat. Considering these data, shown in Fig. 2, we see that the peak position (see also Table I) shifts downward in temperature rather quickly with hydrogen doping, and is already below 5 K for

TABLE I. Parameters for hydrogen doped $UPd_2Al_3H_x$.

$x=$	0	0.13	0.17	0.20	0.34	0.64	0.77	1.09	1.30
$T_\chi^{\max}$ (K)	35	32	30	29	26	13	7		
$\mu_{\text{eff}}(\mu_B)$	3.39	3.21	3.23	3.21	3.19	3.14	3.08	2.96	2.82
$\chi(1.8\text{ K})\left[\frac{\text{memu}}{\text{mole}}\right]$	8.3	8.2	8.6	8.8	9.6	12.7	14.8	18.2	21.4
$T(C_{\max}/T)$ (K)	13.6	12.6	12.7	12.2	10.8	4.9			
$C/T(T\to 0)$ (mJ/mole K^2)	155[a]		180[a]		220[b]	380	425	610	740
$\chi(1.8\text{ K})/[C/T(T\to 0)]$ (memu K^2/mJ)	0.054		0.048		0.044	0.033	0.035	0.030	0.029
$S(17\text{ K})$(mJ/mole K)	5600		5600		5800	6100	6100	6200	6100
T_c^{onset} from χ_{ac} (K)	1.78[c]	1.73	1.37	1.33					
$H_c(0)(G)$[d]	450	300	430	230					
$-(dH_{c2}/dT)_{T_c}(T/\text{K})$	0.47	0.23	0.45	0.48					

[a]Sample is superconducting, value given is C/T at 2 K.

[b]Since this sample shows a slight superconducting anomaly in C, $C/T(T\to 0)$ is somewhat smaller than it otherwise would be.

[c]This value, as well as those for all the hydrided samples, is measured on ground powder. For a nonground sample, $T_c^{\text{onset}}=1.97$ K.

[d]As discussed in, e.g., Ref. 19, $H_c(0)$ is found from $\int_0^{T_c}[S_n(T)-S_s(T)]dt = VH_c(0)^2/8\pi$, where $S_n(S_s)$ is the normal (superconducting) state entropy.

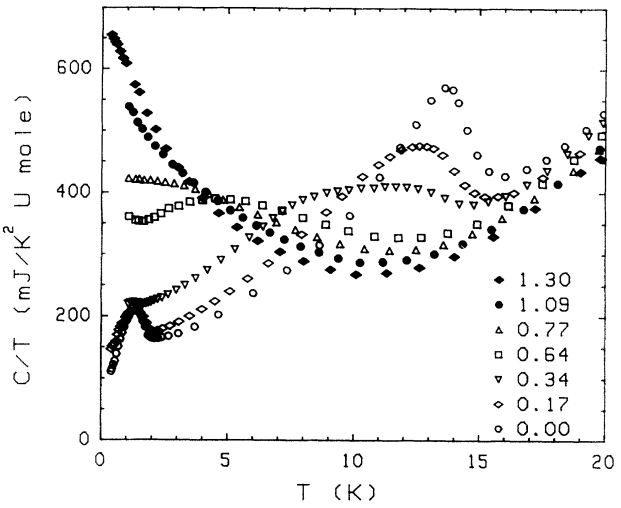

FIG. 2. Low-temperature specific heat C divided by temperature vs temperature for $UPd_2Al_3H_x$, $0 \le x \le 1.30$. For clarity, data for $x = 0.13$ and 0.20 are not shown. Note the superconducting transition at 2 K for $x = 0$, and the magnetic transitions that are depressed to lower temperatures with increasing x. These specific-heat data show that the apparent inhomogeneity of the doped samples, based on the transition width, is rather large, e.g., T_N^{onset}, or where the peak in C begins for the $x = 0.34$ sample is 14 K, while T_N^{peak} is 11 K. Some of this broadness in the anomaly is due to the grinding-induced effects (our undoped powder has $(T_{\max} - T_{\text{onset}}) \simeq 2$ K, whereas bulk material has $\Delta T_N \simeq 1$K), and some is due to inhomogeneity in the local hydrogen concentration in the lattice.

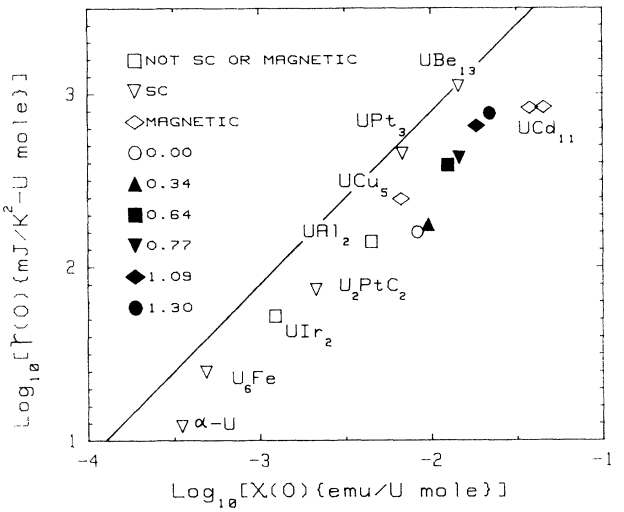

FIG. 3. $\gamma (\equiv C/T \text{ as } T \to 0)$ vs χ for a number of heavy and "semiheavy" systems. The line corresponds to superconductivity and the maximum γ possible for a given χ. Note that $UPd_2Al_3H_x$ with increasing x tends to parallel this line, consistent with both χ and γ in $UPd_2Al_3H_x$ being due to a m^* that increases with x.

$UPd_2Al_3H_{0.64}$. Thus, these specific-heat data combined with the magnetic-susceptibility and magnetization data present a consistent picture of the effect on UPd_2Al_3 of hydrogen doping: the magnetism, as judged by the size of χ (1.8 K), μ_{eff}, and T_N, is suppressed and becomes weaker with increasing x. This effect is consistent with the added electrons in the Fermi sea increasing hybridization and lowering the effective $5f$ local moment.

One inconsistency in this picture is the increase of χ (1.8 K) for $x > 0.34$. Also unexplained is the upturn at low temperatures observed in C/T, see Fig. 2, for the very same samples where χ (1.8 K) shows an increase, i.e., for $x > 0.34$. Thus, below the magnetic anomaly in C/T for $x = 0.34$ and 0.64, we see an upturn in C/T, while for $x \ge 0.77$ the magnetic anomaly is gone and this upturn in C/T is itself the dominant feature. (Data to 0.3 K for $x = 1.30$, see Fig. 2, show no sign of an anomaly down to our lowest temperature of measurement.) In fact, one can already observe, in $UPd_2Al_3H_{0.17}$ that C/T between T_c and T_N is larger than for $x = 0$, a trend that accelerates for $x \ge 0.34$.

One possible explanation for these data is that these increasing values of C/T $(T \to 0)$, Fig. 2 and Table I, for $x \ge 0.34$ are coupled to the increasing low-temperature magnetic susceptibility values through the Wilson ratio χ/γ, i.e., both the increase in χ (1.8 K) and C/T $(T \to 0)$ are due to an increased effective mass m^*. This χ/γ ratio is shown in Table I, and shown graphically in Fig. 3 in a Fisk plot of γ as a function of χ. It is apparent from these data that the values we observe for $UPd_2Al_3H_x$ approach nicely the Sommerfeld free-electron line shown in Fig. 3, i.e., are consistent with an m^* increasing with x interpretation.

When one considers the low-temperature entropies S of the samples in Table I, we see that all samples have S (17 K) = 5900±5% mJ/mole K, or about R ln2. For the smaller $x UPd_2Al_3H_x$ samples, this entropy (simply the area under the data in Fig. 2) contains a large contribution from the magnetic anomaly and a small contribution from the $\gamma (\equiv C/T \text{ as } T \to 0)$ term in the specific heat. As the magnetic anomaly is suppressed, the upturn in C/T begins and contributes a growing share of the (essentially) constant entropy. Thus, this consideration of shifting entropy from magnetism to creating a large γ would support the idea that χ/γ remaining approximately constant as x increases is due to an increasing m^* simultaneously enhancing χ and γ.

In order to try to distinguish if the upturn in C/T, Fig. 2, for our higher doped $UPd_2Al_3H_x$ samples is due to magnetic effects or m^* formation, we have measured the low-temperature specific heat, 0.3 K $< T \le 1.4$ K, in 14 T of our $UPd_2Al_3H_{1.30}$ sample. What we observe is a uniform shift downward by ~20–25 % of the data with applied field, with C/T (14 T) as $T \to 0$ equal to 590 mJ/mole K^2. This result is consistent with results for other known heavy fermion systems like nonsuperconducting $CeCu_2Si_2$,[15] but is larger than the change observed[15] in, e.g., UBe_{13}. A system where it is now believed[16] that magnetic correlations make a significant contribution to C/T at low temperatures, $CeCu_6$, has[17] a much larger (65%) decrease in C/T $(T \to 0)$ in 14.5 T.

Another possible interpretation of our data is that the hydrogen goes into the lattice inhomogeneously and simply first broadens out the magnetic anomaly and then, with increasing x, destroys long-range order—leaving

behind short-range magnetic correlations. Thus, the entropy remains constant, the anomaly in M vs H is washed out by disorder, χ (1.8 K) is enhanced by the correlations, and C/T at low temperatures is due to correlations that are, in comparison to $CeCu_6$, not very strongly affected by an applied field. This latter interpretation does not explain the distinct, although small, upturn in C/T below 2 K for $x=0.64$ shown in Fig. 2, which is separate from the higher-temperature, broadened magnetic anomaly.

Neutron-scattering experiments would be an excellent method of resolving whether $UPd_2Al_3H_{1.3}$ is a material with a large effective mass corresponding to a $\gamma > 700 \text{mJ/mole K}$ or a system whose properties are dominated by short-range magnetic correlations.

B. Superconductivity

As may be seen in Fig. 2, some superconductivity remains in $UPd_2Al_3H_{0.34}$, but only a very faint anomaly is visible in the specific heat. A more sensitive measurement technique (one which, however, measures T_c onset and is not a bulk measurement) is that of ac susceptibility. Superconducting onset transition temperatures so determined are shown in Table I, where the data $T_c^{\text{onset}}=1.73$ K for the $x=0.13$ sample, 1.37 K for $x=0.17$, and 1.33 K for $x=0.20$ show a good deal of scatter. This scatter carries over into our determination of other superconducting parameters, see the thermodynamic critical field, $H_c(0)$, data and the critical field slope at T_c data in Table I.

Thus, we can roughly say that hydrogen depresses T_c by 20 mK/%H, but the scatter in this value is appreciable. The $H_c(0)$ values fall with increasing hydrogen doping as the superconducting anomaly in the specific heat is depressed. The critical field slope determined via measurement of χ_{ac} in a magnetic field remains relatively constant; this is presumably a sign that the superconductor goes towards the dirty limit where H'_{c2} is proportional to[18] the specific heat γ times the electrical resistivity ρ.

More exact determinations of these and related parameters such as ξ_0 must await achieving a more monotonic set of behaviors as a function of x for low doping levels. Although annealing of the ground powder before hydriding will make some improvement, the real key to narrower superconducting transitions and lower scatter in the measured superconducting parameters probably lies in the method of hydriding. Dehydriding samples from $x=1.30$ down to $x=0.13$ will intrinsically cause inhomogeneity. Hydriding at lower pressures, and remaining for a long period at one pressure on the x vs P slope, even though it is very steep, should lead to better homogeneity.

III. CONCLUSIONS

We have hydrided a heavy fermion related system, UPd_2Al_3, up to a hydrogen content of over one hydrogen atom per unit cell. The antiferromagnetism and the superconductivity are both suppressed, with an accompanying increase in the low-temperature specific heat. This increase in C may be due to an increasing electron effective mass as the $5f$-electron entropy shifts out of the magnetic transition. Measurements of magnetic neutron scattering are planned to help resolve the question.

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