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$UPt_{5-x}Au_x$: A heavy-fermion system with a selectable m^*

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Measurements of the resistivity, susceptibility, and specific heat on $UPt_{5-x}Au_x$ ($x \leq 3$) and related compounds are reported. The reported heavy-fermion behavior in UPt_4Au is confirmed by high-field measurements of the magnetization and specific heat. The high γ (~ 800 mJ/mol K^2) for UPt_4Au is found to be extremely composition dependent, decreasing by 40% for a 2% change in the non-f-atom site occupation. The $AuBe_5$ structure of UPt_5 is found to be preserved up to UPt_2Au_3. For $x > 1$, the Wilson ratio climbs dramatically and the materials enter into a spin-glass-like magnetic state around 4 K.

INTRODUCTION

Since the discovery[1] of superconductivity in high ($\sim 200\ m_{\text{electron}}$)-effective-mass, m^*, electrons in $CeCu_2Si_2$ [so-called "heavy-fermion" superconductivity (HFS)], many researchers have searched for other examples of such behavior. UBe_{13} (Ref. 2) and UPt_3 (Ref. 3) are the only[4] other examples of HFS since it was discovered. A recent report[5] of a large specific heat γ ($\propto m^*$) in UPt_4Au with a Wilson ratio ($\equiv \chi/\mu_{\text{eff}}^2\gamma$) near to that[6] for the three known examples of HFS, but with no superconductivity found down to 0.15 K, raised some interesting questions. Foremost, of course, is the question of superconductivity. In UPt_5 ($AuBe_5$ structure), with $d_{U-U} = 5.25$ Å, there exist two inequivalent Pt sites, with four Pt atoms on one type of site and one on the other. It is the supposition of Ref. 5 that superconductivity might occur if there were more perfect ordering of the one Au atom in UPt_4Au on this second inequivalent Pt site. Thus, long-term annealing and slight stoichiometry variations might be possible ways to achieve HFS in UPt_4Au.

A second question of interest is why Au is particularly effective in forming a heavy-fermion ground state, in comparison to Pt. Are band-structure effects dominant (a possibility suggested in Ref. 5), or are hybridization effects[7] more critical?

A third question raised is that of properties as a function of stoichiometry. Obviously, if UPt_4Au is single phase, then less Au substitution will also form this structure. Will more Au go into the $AuBe_5$ structure? What is the behavior of the specific heat γ, the magnetic susceptibility χ, the Wilson ratio $\propto \chi/\gamma$, and the resistivity with Au content? We report here on such measurements on $UPt_{5-x}Au_x$ for x as large as 3, as well as on UPt_4Ir, UPt_4Os, and UPt_4Pd.

EXPERIMENT

Samples were prepared by arc melting together in a purified Ar atmosphere 99.9% pure depleted U metal from Los Alamos National Laboratory, 99.9985% pure Pt metal and 99.9999% pure Au from Johnson Matthey, and 99.99% pure Ir and Os from Colonial Metals. The significant impurity present was 180 ppm Fe in the depleted U. Samples were melted together and turned before the next melting a total of four times. Diffraction patterns were taken on a Phillips diffractometer, model no. APD3720. The samples were all single phase except for the Os sample and the UPt_2Au_3 sample. The UPt_2Au_3 diffraction pattern indicated the presence of 5–10% second phase. The lattice parameter (see Table I and Fig. 1) also indicated that $UPt_{5-x}Au_x$ remains single phase up to approximately $x = 3$. $UPtAu_4$ was prepared, but the x-ray characterization as well as the magnetic susceptibility indicate that the additional Au merely increases the amount of second phase. The high angle x-ray diffraction linewidths were much broader (factor of at least 2 at $2\theta = 100°$) for $x = 3$ than for $x = 1$, where $\alpha_1 - \alpha_2$ doublets were easily resolvable in the latter. Annealing the $x = 3$ samples at 900 °C for over a month did not noticeably sharpen the diffraction lines.

Absolute resistivity measurements were taken on samples which were arc-cast with a cross-sectional area of $(0.8\ \text{mm})^2$. Magnetic susceptibility measurements as a function of field to 5.5 T between 1.7 and 400 K were taken using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Specific heat measurements in fields to 12 T were taken using a small sample calorimeter described in detail elsewhere.[8] Magnetization measurements to 20 T were taken at the Francis Bitter National Magnet Laboratory.

RESULTS AND DISCUSSION

Consider the fact that we are able to prepare UPt_2Au_3 as almost single-phase material. This does not indicate strongly that the one inequivalent Pt site in this structure is energetically more favorable for Au substitution than the other four available sites, since approximately half of these other sites can also be occupied by Au atoms before this phase becomes unstable. However, as we will demonstrate, $x = 1$ is an exceedingly special concentration, with $x = 0.9$ or 1.25 giving significantly different behavior in the specific heat, while the magnetic susceptibil-

TABLE I. Properties of $UPt_{5-x}Au_x$ and $UPt_4(Ir,Os)$.

x	$\gamma\left[\frac{\text{mJ}}{\text{mol K}^2}\right]$ at $T=1.1$ K	$\chi(\times10^{-3}$ emu/mol) at $T=1.7$ K	μ_{eff} (intercept) (in K)	($\mu\Omega-$cm) at $T=1.4$ K	a_0(Å)	$218.7\frac{\chi}{\mu_{\text{eff}}^2\gamma}$
0	85	4.2	2.87		7.417	1.3
0.5	205	4–5	3.16($-$295)	48.6	7.438	
0.9	515	8.1 (unannealed) 10.4 (annealed)			7.477	$\sim$0.47
1.0	710	12.9	3.09($-$125)	81	7.474	0.42
1.25	350	31	2.98	101	7.489	2.2
2	60	52	2.83	155	7.512	23.7
2.5		68	3.02($-$22)		7.550	
3	235	69	3.04($-$21)		7.599 Less than 10% 2nd phase	6.9
Ir=1	50	2.32	No Curie-Weiss region			
Os=1	2nd phase	6.1	2.97			
Pd=1		4.0	3.3			

ity rises sharply for $x > 1$.

The resistivity for $UPt_{5-x}Au_x$ for $0.5 \le x \le 2$ is shown in Fig. 2. A standard method for examining ordering on a particular lattice site is to look for a dip in the residual resistivity ρ_0 [$\sim x(1-x)$ + other terms] (see Table I) at that composition. The residual resistivity for the UPt_4Au sample is slightly ($\sim$3.5%) lower than the trend established by the values for the $x=0.5$, 1.25, and 2.0 samples, but within our geometrical factor error bar of ±5%. It is also noteworthy that our sample of UPt_4Au has a higher residual resistivity than that reported in Ref. 5, as well as a lower ratio of $\rho(300\text{ K})/\rho(1.4\text{ K})$—two in the present work versus three in Ref. 5. The resistivity data in Ref. 5 for UPt_5 also disagree with those of Ref. 9, with the data of Ref. 5 (again) being lower than those of Ref. 9 at low temperature.

The magnetic susceptibility data at 1.7 K for the $UPt_{5-x}Au_x$ ($x \le 3$) and $UPt_4(Ir,Os)_1$ samples are shown in Table I and Fig. 3. These data for our sample of UPt_4Au agree well with the results of Ref. 5. As is clear from Table I and Fig. 3, as Au is added to the UPt_5 structure, a very sharp increase in χ ($T\rightarrow0$) is observed for $x > 1$ until at the limit of phase stability, UPt_2Au_3, a factor of 5 increase is observed compared to the $x=1$ value. This large increase in magnetic behavior up to the phase boundary will be discussed below in conjunction with the

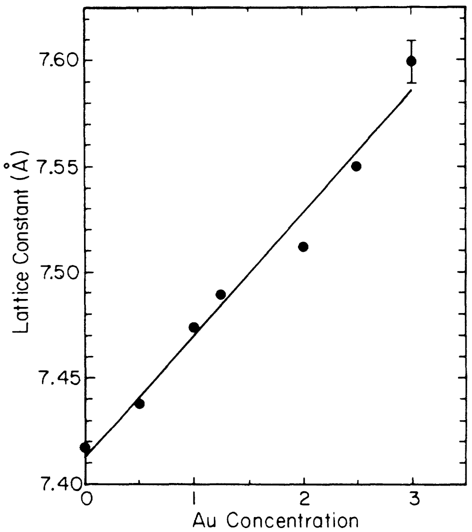

FIG. 1. Lattice parameter vs Au concentration, x, $UPt_{5-x}Au_x$. Although minor second phase lines do appear in the x-ray diffraction pattern for UPt_2Au_3, the approximately linear increase (Vegard's law) of the lattice constant up to $x=3$ indicates that $UPt_{5-x}Au_x$ is single phase almost up to $x=3$.

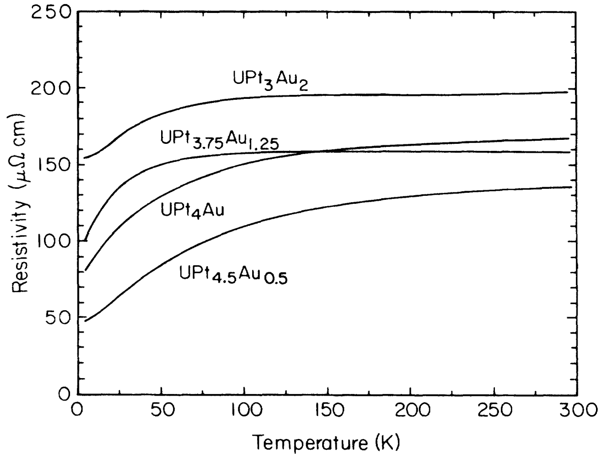

FIG. 2. Resistivity in $\mu\Omega$ cm vs temperature for $UPt_{5-x}Au_x$, $x \le 2$. Note that for $x > 1$, the resistivity remains temperature independent down to about 100 K.

specific heat data.

For all the Au-substituted samples, the magnitude of the χ data starts to grow faster than a Curie-Weiss law below some characteristic temperature, with this increase beginning at a lower temperature for the smaller Au concentrations. As seen from Table I, the effective moment derived from the high-temperature Curie-Weiss behavior of the χ data is almost constant, independent of Au concentration. Thus, the variation of the Wilson ratio ($\equiv \chi/\mu_{\mathrm{eff}}^2\gamma$) with x comes solely from changes in the ratio χ/γ.

For the Os and Pd substitutions (see Table I), the effective moment is likewise approximately the same as for Au substitution, with the major difference being the much smaller low-temperature susceptibility values in comparison with UPt_4Au. These values are comparable to those for UPt_5. What is the cause of this unique efficacy of Au to enhance χ (and, as will be discussed, C as well) in UPt_4M_1? If the effect were one of band structure, and filling the available electronic density of states up to a Fermi level, then one might expect substituting Ir ($5d^7 6s^2$) for Au ($5d^{10} 6s^1$) for $x > 1$ to give the same χ (12.9×10^{-3} emu/mol) as found for UPt_4Au. Instead, χ measurements on $UPt_{3.25}Ir_{0.25}Au_{1.5}$, $UPt_3Ir_{0.5}Au_{1.5}$, UPt_3IrAu, and $UPt_{3.5}Ir_{0.5}Au$ indicate a complex behavior, where χ does not behave monotonically with either number of d electrons or total number of electrons. Thus, site occupation and/or hybridization must play important roles.[10] The behavior of these materials will be investigated further in a later study.

The specific heat data for the $UPt_{5-x}Au_x$ samples show a number of interesting features. As is seen in Table I, the value of the specific heat divided by temperature, $C/T \equiv \gamma$, at 1.1 K sharply peaks at $x = 1$. Specific heat data between 1 and 18 K for $x \leq 1.25$ are shown in Fig. 4. Let us first focus on $x = 1$ before we consider this sharp variation with Au composition.

The extrapolated C/T at $T = 0$ for our unannealed UPt_4Au sample is ~800 mJ/molK^2 versus 725 found in Ref. 5. Annealing at 900 °C for 25 d leaves the γ value unchanged (to within 2%). It is interesting to note that our higher value of γ ($T \rightarrow 0$) *and* higher value of ρ ($T \rightarrow 0$) is inconsistent with ordering of Au on the inequivalent site creating the large γ. The upturn in C/T for UPt_4Au occurs only below about 6 K (see Fig. 4), a lower temperature for the formation of the heavy-fermion ground state than found[6] in other heavy-fermion compounds. We have therefore investigated the high-field behavior of both the magnetization (at 4.2 K) and the low-temperature specific heat, in order to verify that the upturn observed in C/T is truly a temperature-dependent formation of a large m^* ground state and not associated with some broadened magnetic anomaly, which would give strongly field-dependent properties. The magnetization at 4.2 K versus field deviates downward from linear behavior by ~16% at 20 T. The specific heat decreases in 12 T by only ~10% at 1.7 K. Both these results confirm that the upturn in C/T observed for UPt_4Au is indeed due to the formation of heavy fermions below 6 K, since such weak field dependence of M and C/T is characteristic[6] of U heavy-fermion systems.

What is more central to our present investigation is the variation in γ ($\equiv C/T$) at low temperatures with Au concentration in $UPt_{5-x}Au_x$. As may be seen from Table I and Fig. 4, the variation of γ with x is extremely rapid, with the maximum γ at $x = 1.0$. This is consistent with preferential occupation of the one inequivalent Pt site in the crystal structure by Au occurring. This rapid variation in γ with composition, reported for the first time here, is not observed in any other known heavy-fermion system. This behavior, that γ varies by a factor of 40% for a 2% change in the non-f-atom site occupation (i.e., between $UPt_{4.1}Au_{0.9}$ and UPt_4Au_1), is [coupled with our U(PtIrAu) results] strong evidence that hybridization of the Pt site atom with the U $5f$ electrons, rather than band filling, is crucial to the formation of the

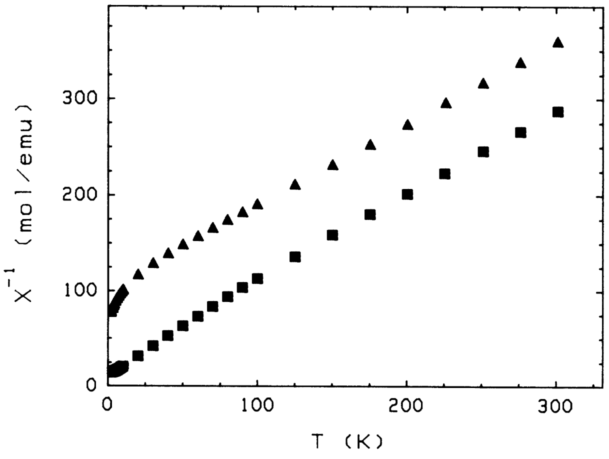

FIG. 3. Inverse magnetic susceptibility measured at 0.5 T vs temperature for UPt_4Au (triangles) and UPt_2Au_3 (squares). Note the decrease in χ at the lowest temperatures in UPt_2Au_3, below the 4 K transition seen in the specific heat.

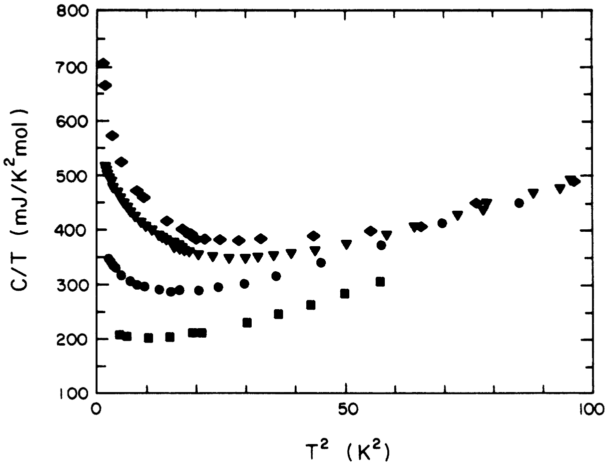

FIG. 4. Specific heat divided by temperature vs temperature squared for $UPt_{5-x}Au_x$, $x \leq 1.25$. ($x = 1.25$, circles; $x = 1$, diamonds; $x = 0.9$, triangles; $x = 0.5$, squares.) The upturns do not obey a spin fluctuation temperature dependence ($T^3 \ln T$). Data above 10 K (not shown) show that the higher temperature data is independent of x in this regime to better than 10%.

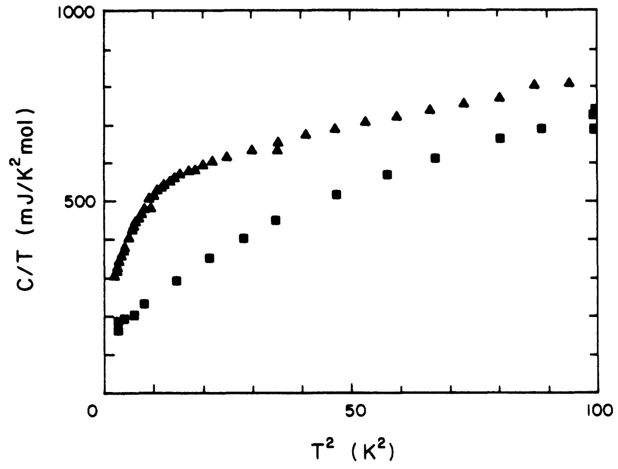

FIG. 5. Low-temperature specific heat for UPt_2Au_3 in 0 (squares) and 12 T (triangles) applied field. Note the suppression of the anomaly at 4 K and the decrease of γ with applied field. Therefore, the true value for γ without any increase from the magnetic anomaly at 4 K may be significantly lower than the zero field value of 235 mJ/mol K^2.

heavy-fermion ground state in $UPt_{5-x}Au_x$.

From the rapid increase in the susceptibility data for $x > 1$ presented above, and from specific heat data for UPt_3Au_2 and UPt_2Au_3 to be presented at this point, it is clear that beyond $x = 1$ in $UPt_{5-x}Au_x$ the samples approach quite closely, and perhaps even attain, some sort of magnetically ordered ground state, with an increase in the Wilson ratio of a factor of 16 between $x = 1$ and 3. Thus, $UPt_{5-x}Au_x$ is a further example of the closeness of the heavy-fermion ground state to magnetism, similar to UPt_3,[3,11] U ($Pt_{3-x}Pd_x$),[12,13] and $(U_{1-x}Th_x)Pt_3$.[13,14]

From Table I, we see that the fall in γ for $x > 1$ continues to $x = 2$, where γ is only 60 mJ/mol K^2. However, as the χ value at low temperature continues to rise with increasing x, γ rises from 60 at $x = 2$ to 235 mJ/mol K^2 at $x = 3$, essentially the limit of phase stability. The zero field and 12 T specific heat data for this UPt_2Au_3 sample are shown in Fig. 5. Clearly, some kind of broad anomaly exists around 4 K, which by the field dependence of the specific heat seems magnetic in nature. The low-temperature magnetic susceptibility is also field dependent, with a 25% decrease upon increasing the field from 0.5 to 5.5 T (another way of saying that M versus H bends over 25% from a linear extrapolation from low field by 5.5 T). At the present time, this anomaly appears to be spin-glass like. Measurements of the frequency dependence of the ac susceptibility are underway to check this hypothesis.

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