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$Ce(Cu_{0.9}Ag_{0.1})_6$: Highest electronic specific-heat coefficient of the heavy-fermion systems

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We have measured the static magnetic susceptibility χ of the compound $Ce(Cu_{1-x}Ag_x)_6$ for $x \leq 0.1$ from 2.4 to 300 K and the specific heat of one sample ($x=0.1$) from 0.6 to 30 K. The effect of Ag substitution is to markedly increase both χ and the Sommerfeld constant γ at low temperatures. γ for the $x=0.1$ sample is temperature dependent and reaches the value 2.1 J/mole K^2 at 0.6 K, extrapolating to approximately 2.8 J/mole K^2 at $T=0$ K. These results can be analyzed in terms of a twofold decrease in the value of the Kondo temperature T_K with 10% Ag substitution.

In recent years a new class of compounds, popularly known as heavy-fermion (HF) systems, characterized by unusually large electronic specific-heat coefficients γ (equivalently, high effective mass of the conduction electrons) and highly enhanced paramagnetic susceptibilities χ at low temperatures, has been extensively investigated. Tremendous effort[1-3] has been directed toward understanding (i) the nature of the unusual superconductivity observed in some Ce- and U-based compounds, (ii) the criteria that determine the low-temperature ground state of these systems (superconducting, magnetic, or absence of any long-range order), and (iii) the development of the HF state itself with decreasing temperature, including the onset of coherence at the lowest temperatures. In pursuit of the third goal, $CeCu_6$ and $CeAl_3$ have received the most attention since both compounds remain paramagnetic, avoiding the development of any long-range magnetic or superconducting order down to the lowest temperature of measurement ($\sim$10 mK). $CeCu_6$ crystallizes in the orthorhombic structure[4] with a Ce-Ce spacing of 4.83 Å, undergoing a small monoclinic distortion below 220 K.[5] From transport,[6-8] magnetic,[9,10] and thermodynamic measurements[6,7,11] on polycrystalline as well as on single-crystal samples, $CeCu_6$ is characterized as a dense Kondo system with the Kondo temperature in the range of 2–4 K.[11] The most interesting feature of the data is an extremely large value of the electronic specific-heat parameter [$\gamma(T=0\text{K}) \simeq 1.5$ J/mole K^2] (Refs. 7 and 11) which places it, together with $CeAl_3$,[12] as the heaviest of all known HF systems. In the framework of the "Kondo-lattice" model, such large values of both γ and the coefficient of the quadratic term A in the electrical resistivity [$\rho(T)=\rho(0)+AT^2$ at temperatures below 100 mK] find a qualitative explanation in terms of a small characteristic Kondo temperature T_K. That the HF state in $CeCu_6$ is in a delicate state of balance is amply borne out by the fact that both γ (Refs. 6 and 11) and A (Ref. 8) are strongly suppressed in high magnetic fields. This, along with the observation of Stewart[1] that $CeCu_6$, as indicated by its Wilson ratio, is nearly at the borderline between HF paramagnetic and HF superconducting behavior, provides ample stimulus for attempting alloying or high-pressure experiments on this system. Alloying experiments have been carried out by Sumiyama *et al.*[13] and by Onuki and Komatsubara[14] by substituting La for Ce, and have contributed to the understanding of the development of the dense coherent Kondo state from the dilute single-impurity Kondo limit. However, any report on the effect of substitution at the Cu site is still lacking. Such experiments would be important since the hybridization of the $4f$ electrons with the conduction electrons is of basic importance in the formation of the HF state;[15] in addition, any substitution at the Cu site is very likely to change the hybridization strength and, hence, the HF state, without seriously affecting the Ce sublattice. With the above ideas in mind, we have measured both the static magnetic susceptibility χ down to 2.4 K and the specific heat in the temperature interval 0.6 to 30 K.

Polycrystalline samples of $Ce(Cu_{1-x}Ag_x)_6$ for $x \leq 0.2$ were prepared by repeated induction melting of the starting materials of Ce (99.9% purity, zone refined), Cu (99.999% purity), and Ag (99.999% purity) in the stoichiometric ratio on a water-cooled copper cold finger. The single-phase character of all samples under investigation was confirmed by x-ray powder diffraction; the $CeCu_6$ orthorhombic structure is retained for $x \leq 0.1$.

The dc magnetic susceptibility was measured in the temperature interval 2.4 to 350 K using a sensitive Faraday-balance system with superconducting coils; experimental details can be found elsewhere.[16] In Fig. 1 we plot the inverse susceptibility (χ^{-1}) as a function of temperature (T) for both $CeCu_6$ and $Ce(Cu_{0.9}Ag_{0.1})_6$. For the sake of clarity, data for the other samples have been left out. All the samples show good Curie-Weiss behavior $\chi=C/(T+T^*)$, where C is the Curie constant, over a temperature region down to about 60 K which extends to lower temperatures with increasing Ag concentration. From the present measurements on the reference sample $CeCu_6$ the effective moment per Ce atom (μ_{eff}) is $2.56\mu_B$ and the paramagnetic Curie temperature (T^*) is 46 K;

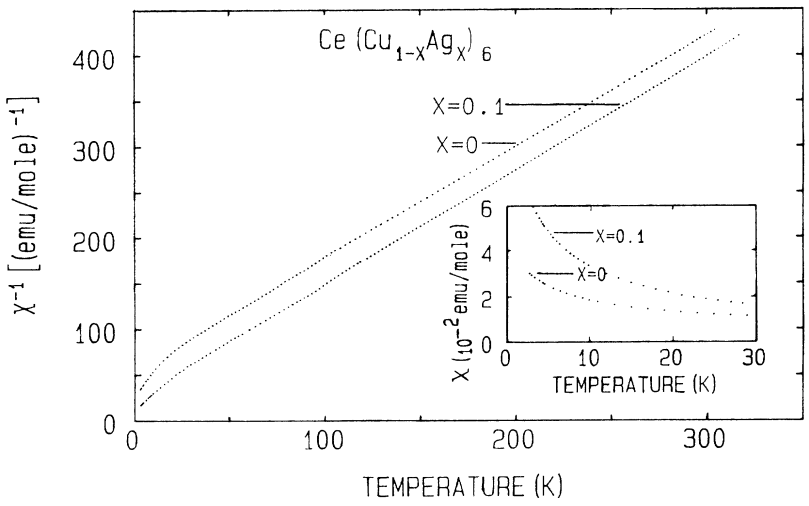

FIG. 1. Inverse of the static magnetic susceptibility as a function of temperature for polycrystalline $CeCu_6$ and $Ce(Cu_{0.9}Ag_{0.1})_6$ exhibiting the Curie-Weiss behavior. Inset shows the factor of 2 increase in χ for the 10-at.% Ag-doped sample over that of $CeCu_6$ at the lowest temperature (2.4 K). In the inset, χ is given in units of 10^{-2} emu/mole.

both values are in good agreement with those from earlier studies on polycrystalline[6] as well as on single-crystalline samples[9,10] [the later data are normalized to those from polycrystalline materials using the relation $\chi_{poly} = (\chi_{\|a} + \chi_{\|b} + \chi_{\|c})/3$].

As seen in Fig. 1, the data on our Ag-doped samples show quite a number of interesting features. First of all, $\chi(T)$ shows an increase with Ag concentration, with no sign of long-range magnetic order down to 2.4 K. This point is more clearly made by the χ vs T plot at low temperatures (see the inset in Fig. 1). Second, a slight bump is seen in the χ^{-1} vs T plot around 30 K which has been attributed[9,10] to crystalline-field effects and is more prominent in the single-crystal data of $CeCu_6$ along the a and b axes than in our polycrystal data. The decrease in the size of this anomaly for $Ce(Cu_{0.9}Ag_{0.1})_6$ indicates that the crystal-field levels are reorganized as a result of the lattice expansion caused by the Ag substitution; this fact, on the other hand, extends the temperature interval for the Curie-Weiss behavior to lower temperatures.

The values of μ_{eff} determined from the Curie constant for the Ag-substituted compounds have been found to be $2.56\mu_B$, $2.54\mu_B$, and $2.54\mu_B$, respectively, for the 2-, 5-, and 10-at.% Ag-substituted compounds. The most interesting result is the gradual decrease of T^* with the addition of Ag. $T^* = 46$ K for the parent compound $CeCu_6$ decreases to 36, 26, and 21 K, respectively, for 2-, 5-, and 10-at.% Ag substitution. This result stands in contrast to that of other studies[13] where the substitution of La for Ce causes hardly any change in T^*. Although the properties of a dense Kondo system at the lowest temperatures (below the coherence temperature T_{coh}) are believed to be determined by the coherent scattering of the conduction electrons by the Ce ions in a periodic lattice, at much higher temperatures ($T \gg T_K$), and also to some extent even in the intermediate temperature range ($T_{coh} < T \leq T_K$), the Ce ions behave as isolated impurities, similar to the dilute single-ion Kondo impurity case.[1-3] In the single-ion Kondo picture,[17] and also quite often in the case of concentrated Kondo systems,[18] T^* is taken as proportional to the characteristic Kondo temperature T_K. Thus the above variation in T^* implies a twofold *decrease* in the value of T_K with 10-at.% Ag substitution at the Cu site. This estimate is supported by the fact that at the lowest temperature of measurement (2.4 K) the susceptibility for $x = 0.1$ is approximately twice as large as that for $CeCu_6$; for the single-impurity problem in the low-temperature limit $\chi(0\text{ K}) \propto T_K^{-1}$.[19] This decrease in the value of T_K is consistent with the fact that substituting Ag for Cu causes an expansion of the lattice; it is well documented[20] that in dilute Ce Kondo systems compressing the lattice by applying high pressure leads to an increase in T_K. From these studies[20] we estimate that in the present case for $CeCu_6$, where $T_K \simeq 2$–4 K,[11] the logarithmic volume derivative of T_K takes on the value $\partial \ln T_K / \partial \ln V \simeq -40$. Since the substitution of 10-at.% Ag for Cu leads to a volume expansion of 0.5%, a 20% decrease in T_K would be anticipated. This is more than a factor of 2 smaller than the 54% decrease in T^* observed in the present experiments. Resistivity data on $CeCu_6$ under pressure[21,22] have shown that the temperature of the resistivity maximum $T_m \simeq 15$ K increases rapidly under pressure $\partial T_m / \partial P \simeq +2.1$ K/kbar.[21] If one assumes T_m and T_K are proportional,[21,22] an assumption which has yet to be confirmed,[23] one obtains, using the value 900 kbar for the bulk modulus,[22] $\partial \ln T_K / \partial \ln V \simeq -124$. Thus a volume expansion of 0.5% would be expected to cause a 62% decrease in T_K, in reasonable agreement with the 54% decrease in T^* observed here. We note, however, that one neither anticipates nor finds quantitative agreement between the effects of lattice-parameter changes in high-pressure and alloy-substitution experiments.[20,24] Substituting Ag for Cu not only expands the lattice, but, among other things, also changes the character of the conduction electrons at the Fermi energy.

Now turning our attention to the renormalization-group

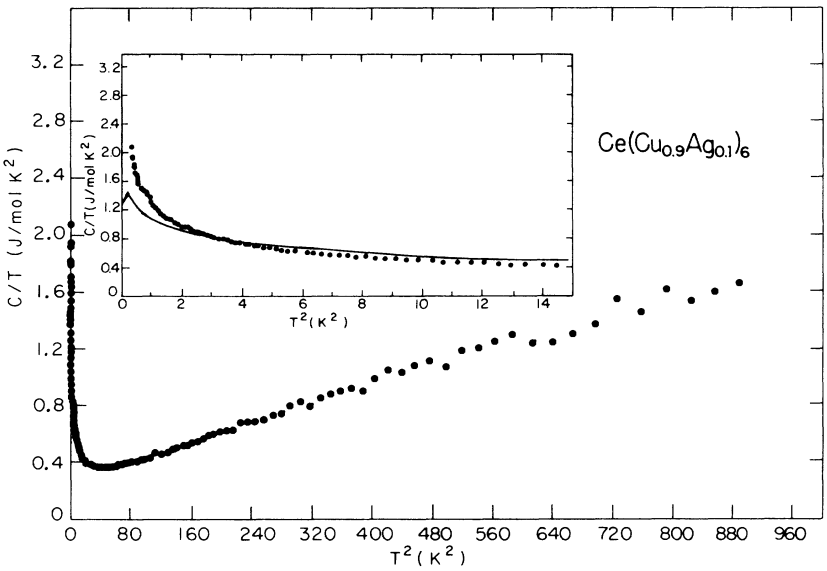

FIG. 2. The specific heat of polycrystalline $Ce(Cu_{0.9}Ag_{0.1})_6$ in the temperature range 0.6 K $< T <$ 30 K, plotted as C/T vs T^2. Remarkable is the large increase in the electronic specific-heat coefficient $\gamma(=C/T)$ for $T < 6$ K. Inset shows the enhancement of γ in the present sample (filled circles) over that in $CeCu_6$ (solid curve, single-crystal data from Ref. 11).

calculations[25] of the single-impurity Kondo problem, we observe that for $T \ll T_K$, the magnetic susceptibility $\chi(T=0$ K), the electronic specific-heat coefficient $\gamma(T=0$ K), and the coefficient of the T^2-term in the low-temperature resistivity A, are all expected to scale with a single parameter $T_K(\chi, \gamma, A \propto T_K^{-1})$. Such trends have found experimental support not only in very dilute but also in some dense Kondo systems.[26] Thus, from the present susceptibility data, we would anticipate more than a factor of 2 increase in the low-temperature value of γ for the 10-at.% Ag-doped compound. To check this prediction, we have carried out specific-heat measurements on this sample in the temperature interval 0.6 to 30 K, using a semiadiabatic heat-pulse technique (for details see Ref. 27). The results are displayed in Fig. 2 in the form of a plot of C/T vs T^2; the inset shows the same data over a smaller temperature interval along with the relevant single-crystal data for the $CeCu_6$ reference compound.[11] The most striking result is the very large upturn in $C/T[=\gamma(T)]$ for $T < 6$ K down to the lowest temperature of measurement (0.6 K) with no sign of any long-range order. γ(0.62 K) here takes on the value 2.1 J/mole K^2 compared to the value 1.2 J/mole K^2 for $CeCu_6$ at the same temperature. From extrapolation of the data below 1 K, we arrive at a conservative estimate of $\gamma(T=0$ K$)=2.8$ J/mole K^2. This value is roughly a factor of 2 larger than that for $CeCu_6$ (Ref. 11) and is, to our knowledge, the highest value of γ observed so far. Thus, $Ce(Cu_{0.9}Ag_{0.1})_6$ can be called the heaviest of the HF compounds. We attribute this increase in γ to the lowering of the Kondo temperature by roughly a factor of 2 due to the Ag addition, as discussed earlier. We would also like to point out that the upturn in C/T for the present system begins at a temperature ($\sim$6 K) which is roughly half of that observed for $CeCu_6$ (Ref. 11) ($\sim$11 K) and is consistent with the above picture.

Finally, it would be interesting to extend the present measurements to still lower temperatures to see whether the ground state remains paramagnetic or turns into an ordered (magnetic or superconducting) state. Work along this direction is in progress.

Note added in proof. Recent ac susceptibility studies on $Ce(Cu_{0.9}Ag_{0.1})_6$ show that neither magnetic ordering nor superconductivity occur down to temperatures as low as 120 mK.

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