Incipient magnetic order in $CeCu_6$

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Low-field (0.8 Oe), low-temperature (60 mK–2 K) static magnetic susceptibility (χ) measurements on a series of $Ce(Cu_{1-x}Ag_x)_6$ compounds with $x \leq 0.20$ reveal magnetic transitions characterized by maxima in χ at well-defined temperatures for the $x=0.05$ and 0.10 samples. All samples show marked differences between the magnetic field-cooled and zero-field-cooled data. A sharp anomaly in the specific heat for the $x=0.10$ sample at nearly the same temperature as the maximum in χ points toward an antiferromagnetic transition, whereas magnetization data for the $x=0.15$ and 0.20 samples are indicative of ferrimagnetic or ferromagnetic order. The data indicate a change from antiferromagnetic to ferrimagnetic or ferromagnetic order with increasing Ag concentration. The dependence of the magnetic ordering temperature on concentration x reveals that extremely small (~ 1.3 at. %) amounts of Ag impurity are sufficient to induce magnetic order in $CeCu_6$. The relevance of these results to the properties of $CeCu_6$ is discussed.

INTRODUCTION

To further understand the development of heavy-fermion (HF) behavior in $CeCu_6$, characterized by unusually large values of the electronic specific-heat coefficient $\gamma(0\text{ K})=1.6$ J/mole K^2 (Ref. 1) and a Pauli-like low-temperature susceptibility $\chi(0\text{ K})$, we have recently initiated alloying experiments[2] by Ag substitution at the Cu sites. The effect of such alloying is found to have a marked influence on the hybridization of the Ce $4f$ electrons with the valence electrons, which in turn considerably reduces the value of the characteristic temperature T^*. In fact, the replacement of 10 at. % of Cu by Ag induces a twofold decrease in T^* and a corresponding increase in both $\gamma(0\text{ K})$ (from 1.6 to 2.8 J/mole K^2) and $\chi(0\text{ K})$, as derived mainly from susceptibility and specific-heat measurements down to 2.4 K and 600 mK, respectively.[2] This, of course, left open the possibility of the development of long-range order (magnetic or superconducting) at still lower temperatures, as well as the effect of any such possible order on the extremely high values of γ and χ. To address this question, we have extended the temperature range of the previous specific-heat measurements on the 10 at. % Ag doped sample down to 40 mK and the dc susceptibility measurements down to about 60 mK. In addition, susceptibility measurements have also been carried out on a number of additional $Ce(Cu_{1-x}Ag_x)_6$ samples with $x \leq 0.2$, the results of which will be reported in the following sections.

RESULTS OF EXPERIMENT

The details of the sample preparation and subsequent heat treatment techniques have been reported earlier.[2] X-ray powder diffraction confirmed the single-phase nature of all the samples; however, the diffraction lines for the $x=0.20$ sample are considerably broadened and some of the lower intensity lines could not be detected. The dc susceptibility in the temperature interval 60 mK $< T <$ 2.5 K was measured using a SQUID magnetometer with a superconducting inductance bridge, the details of which can be found elsewhere.[3] The specific heat for 20 mK $< T <$ 2.5 K was measured using the semiadiabatic heat pulse technique; a brief account of the relevant thermometry has been published.[4]

Before presenting the susceptibility data for the present low-temperature measurements on the $Ce(Cu_{1-x}Ag_x)_6$ compounds, it is relevant to mention that earlier high-temperature (2.5 K $< T <$ 300 K) measurements[2] on the same system with $x=0$, 0.02, 0.05, and 0.10 show Curie-Weiss behavior $\chi=C/(T+T^*)$ above about 60 K with essentially a constant value of the Curie constant C corresponding to that of trivalent Ce. On the other hand, the paramagnetic Curie temperature T^* decreases continuously with increasing x. Recent measurements on the $x=0.15$ and $x=0.20$ samples also show similar behavior, but with somewhat reduced values of C and T^* ($p_{\text{eff}}=2.48$ and 2.31, respectively, for the $x=0.15$ and $x=0.20$ samples, compared to $p_{\text{eff}}=2.56$ for the parent compound with $x=0$). The reduction in T^* for the $x=0.15$ and 0.20 samples is consistent with the earlier results, whereas that in C (or p_{eff}) is slightly anomalous and requires further investigation.

The results of our present studies of the dc magnetic susceptibility on the $x=0.05$, 0.10, 0.15, and 0.20 samples in small fields (0.8 Oe) below 2.5 K are shown in Figs. 1(a)–1(c). Here ZFC (zero-field-cooled) refers to the set of data points taken during warming up after cooling the sample in zero field ($H \leq 3$ mOe) and applying the field at the lowest temperature, whereas FC (field-cooled) refers to data taken upon cooling with the field applied above 2.5 K. The most important observation in Figs. 1(a)–1(c) is the existence of a maximum in χ for the $x=0.05$ and 0.10 samples, observed both under FC and ZFC conditions, whereas for $x=0.15$ and 0.20 such maxima are observed only under ZFC condition. The position of the maximum $T_{\max}$ shifts gradually to higher temperatures with increasing Ag concentration. The next

important point is the quantitative, as well as qualitative, difference in the data under FC and ZFC conditions. Finally, the two orders of magnitude higher value of χ for the $x=0.15$ [Fig.1(b)] and $x=0.20$ [Fig. 1(c)] samples compared to those for $x=0.05$ and 0.10 is noteworthy.

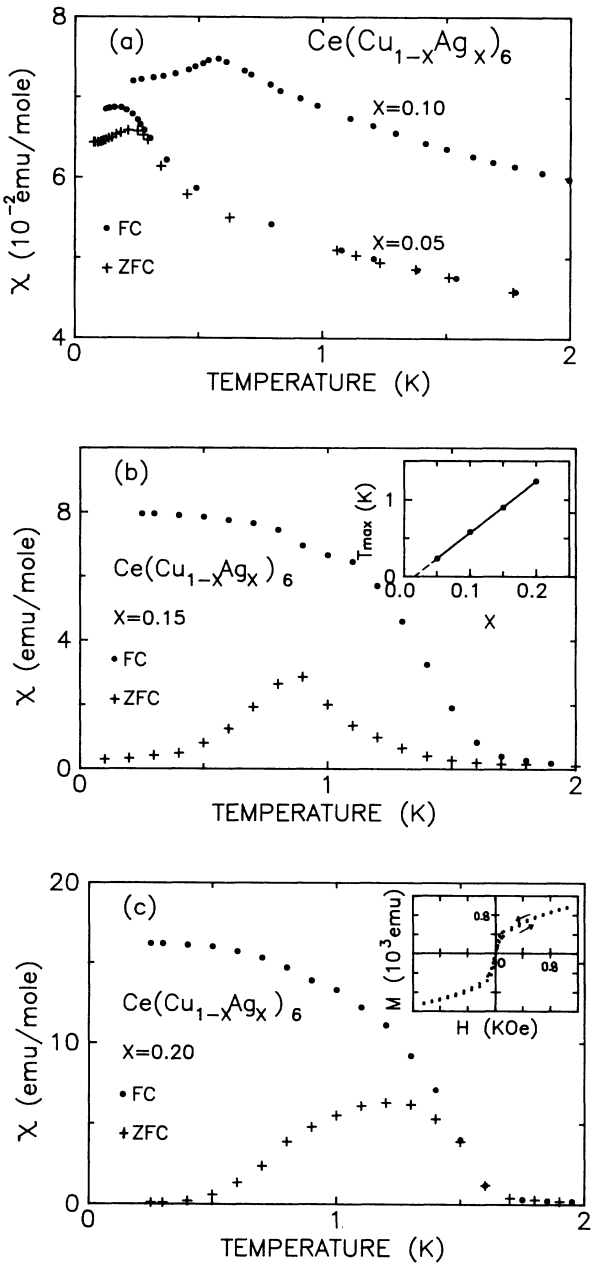

FIG. 1. (a) The low-temperature low-field dc susceptibility χ for $Ce(Cu_{1-x}Ag_x)_6$ samples for $x=0.05$ and $x=0.10$ in a field of 0.8 Oe. Notable are the maxima in χ at $T_{max}=0.23$ and 0.58 K, respectively, and the irreversibility of the data under field cooling (FC) and zero-field-cooling (ZFC) conditions. (b) The same as (a) but for $x=0.15$. Note the two orders of magnitude larger scale used than in (a). The inset shows the variation of T_{max} with x. The straight line is a guide to the eye. (c) The same as in (a) and (b) but for $x=0.20$. The inset shows the magnetic hysteresis curve for $x=0.20$ at 1.4 K, with H plotted in kOe and M in 10^3 emu/mole.

It should be mentioned in this connection that earlier ac susceptibility measurements[2] on the $x=0.10$ sample in powder form failed to show any anomaly in χ down to 120 mK, probably because of oxidation and/or strain induced in the sample during the powdering process.

Before speculating on the nature of this magnetic anomaly, it is important to establish the intrinsic nature of the observed effects. First of all, in our present measurements (not shown) the parent compound $CeCu_6$ does not show any magnetic irreversibility or transition, in agreement with the results of earlier studies.[5] Second, our powder x-ray data on the $Ce(Cu_{1-x}Ag_x)_6$ compounds do not reveal the presence of any impurity phase; in addition, none of the known impurity phases (e.g., $CeCu_5$, $CeCu_2$, CeAg, $CeAg_3$, etc.) show magnetic ordering in the observed temperature region. Finally, if we make the assumption that T_{max} in the ZFC data ($T_{max}=0.23$, 0.58, 0.90, and 1.24 K for $x=0.05$, 0.10, 0.15, and 0.20 samples, respectively) signifies the magnetic ordering temperature, then T_{max} follows a linear relationship with x, where $dT_{max}/dx=+66$ mK/at. % of Ag [see inset in Fig. 1(b)]. Such systematics speak against the possibility that an impurity phase is responsible for the observed behavior.

In light of the above observations, we will now try to understand the nature of the magnetic anomaly. A magnetic transition in the present system is not altogether unexpected if one remembers that addition of Ag causes a decrease in the characteristic temperature T^*, and such a decrease in T^* is likely to favor magnetic ordering in a system with competing (Kondo plus exchange) interactions, as suggested by the Kondo lattice model.[6] Furthermore, antiferromagnetic correlations between nearest-neighbor Ce atoms in the parent compound $CeCu_6$, as revealed by polarized neutron scattering experiments,[7] would suggest a possible antiferromagnetic order in the present system. In fact, the nature of the anomaly in χ for the $x=0.05$ and $x=0.10$ samples very much resembles those of antiferromagnetic transitions. However, the associated thermomagnetic hysteresis, manifested as a difference between the ZFC and FC data, would point to a spin-glass-like transition. Here we would like to mention that the slight mismatch in the ZFC and FC data for the $x=0.05$ sample above T_{max} is an experimental artifact, whereas the difference in the two sets of data below T_{max} is real [Fig. 1(a)]. Since a spin-glass transition is considerably broadened with increasing applied field, experiments at higher fields might have helped distinguish between the two pictures. Unfortunately, the present experimental setup is not suitable for generating fields higher than a few Oe; in such fields no significant broadening could be observed.

Compared to the $x=0.05$ and 0.10 samples, the two orders of magnitude higher values of χ for the $x=0.15$ and $x=0.20$ samples [Figs. 1(b) and 1(c)] imply a different kind of magnetic ordering in the latter two samples. The FC curves of the $x=0.15$ and $x=0.20$ samples resemble those of a ferromagnetic or ferrimagnetic transition which is somewhat broadened by sample inhomogeneity; further evidence along this direction comes from the M versus H curve for the $x=0.20$ sample as mea-

sured in a vibrating sample magnetometer which shows a small hysteresis at 1.4 K [inset of Fig. 1(c)]. Experimental limitations prevented us from obtaining similar data at still lower temperatures (far below the ordering temperature), which otherwise would have enabled us to obtain the moment per Ce atom taking part in the ordering. According to the above picture, the maximum in χ under ZFC could find a suitable explanation in terms of domains which are not oriented by the small applied field at low temperatures, but become progressively soft as the ordering temperature is approached from below in a fashion similar to that observed in hard ferromagnets. However, in such a situation the ordering temperature will not be the temperature where χ shows a maximum under ZFC (termed T_{max}) but will be located at a temperature somewhat higher than T_{max} for the $x=0.15$ and 0.20 samples. In this case the corresponding points in the inset of Fig. 1(b) would be shifted up on the temperature scale.

Since the present magnetization data are not yet completely conclusive in deciding the nature of the magnetic transition, additional information was obtained from the specific-heat measurement of one sample ($x=0.10$, for which the data above 600 mK already exist[2]) near and below the temperature of the magnetic transition. In Fig. 2 is plotted C versus T for the $x=0.10$ sample in the temperature interval 40 mK $< T <$ 2 K (dots) together with the earlier data[2] (crosses) above 600 mK. The two sets of data, taken in two different apparatus and on two different sample pieces from the same batch, are seen to match well. The most interesting feature of these data is a clear-cut anomaly in the specific heat in the same temperature region where the susceptibility shows a maximum ($T_{max}=580$ mK). These results speak in favor of a cooperative magnetic transition (probably antiferromagnetic) instead of a spin-glass-like transition. Usually the specific-heat anomaly associated with the spin-glass transition in both insulating[8] and metallic[9] spin-glass system is neither so sharp nor takes place at the same temperature where the cusp in the susceptibility (T_{max}) is observed; in fact, the broad maximum in the specific heat always lies at temperatures higher than T_{max}.

From entropy considerations, one expects below T_{max} an excess entropy release of $R\ln 2=5.76$ J/mole K for the complete removal of the twofold spin degeneracy of the crystal field ground state (as in $CeCu_6$). However, the observed entropy release below T_{max} is only about 20% of this expected value. In principle, this can happen if (1) the magnetic transition involves itinerant electrons, in which case the magnetic entropy would increase to its saturation value over a larger temperature range (up to the degeneracy temperature, or here, the characteristic temperature T^*), or (2) if the transition is driven by a charge- or spin-density wave instability resulting in the opening of a gap over only a portion of the Fermi surface. The second possibility, however, does not find any support from the excess specific heat, $\Delta C = C_{total} - C_{lattice} - C_{electrons}$, below T_{max} which should follow an activation law of the type $\Delta C = A\exp(-A/T)$, provided the gap extends over regions larger than lines or points on the Fermi surface.

To check for the first possibility, we have calculated the magnetic specific heat up to 6 K, i.e., up to the temperature where the upturn in the C/T versus T^2 plot occurs. Although as a first approximation one could subtract the specific heat of $LaCu_6$, the nonmagnetic analog of $CeCu_6$, from the present data to calculate the magnetic specific heat, such an analysis is incorrect, since the C/T versus T^2 plot for the present compound above 6 K gives a much higher value for β ($\simeq 1.62$ mJ/mole K^4), where $C/T=\gamma+\beta T^2$, than in $CeCu_6$ ($\beta=0.84$ mJ/mole K^4),[10] presumably reflecting the change in the Debye temperature due to the addition of Ag. Hence as a better approximation we have calculated

$$C_m = C_{measured} - \beta T^3$$

with $\beta=1.62$ mJ/mole K^4 derived from the C/T versus T^2 plot in the 8 K $< T <$ 12 K temperature interval where

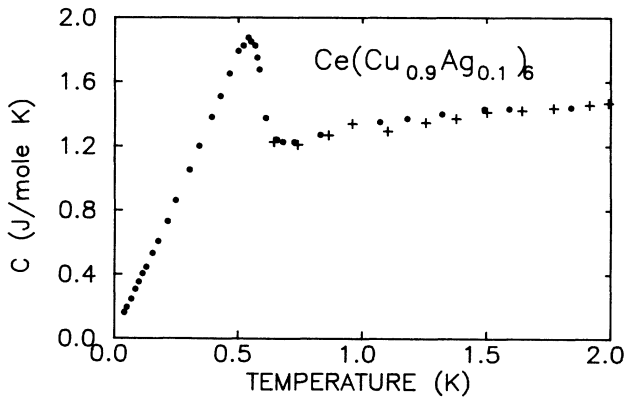

FIG. 2. The specific heat of $Ce(Cu_{0.9}Ag_{0.1})_6$ vs temperature below 2 K showing a sharp anomaly at the temperature of the maximum in χ [see Fig. 1(a)]. The dots (●) represent data from the present work whereas the plus signs (+) are taken from Ref. 2.

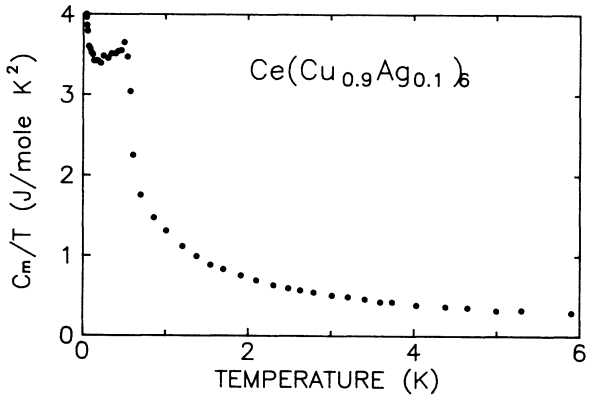

FIG. 3. The magnetic specific heat C_m after subtraction of the lattice part from the total specific heat (for details see the text) in C_m/T vs T representation. The area under the curve below 6 K gives a magnetic entropy of 5.3 J/mole K. Note the extremely large value of $(C/T)_{T\to 0\,K}=3.4$ J/mole K^2 below the magnetic transition.

γ is more or less temperature independent. Figure 3 shows a C_m/T versus T plot derived from the above analysis up to 6 K; the area under the curve gives the magnetic entropy as 5.3 J/mole K which is more than 90% of the total expected entropy of $R\ln 2$ (5.76 J/mole K). The remaining small fraction of entropy indicates that some correlation exists between the Ce $4f$ moments even above 6 K.

We now focus on several other interesting points reflected in Fig. 3. First of all, the ratio C/T shows a very small decrease below the transition temperature T_{max} followed by another upturn below about 150 mK. This upturn could be the high-temperature tail of a Schottky-type anomaly arising from the electron quadrupole or from Zeeman splitting of the nuclear levels of Cu in the presence of a hyperfine field transferred to the Cu nucleus from the ordered $4f$ moments. Generally, a nuclear Schottky anomaly is reflected by an additional contribution $C_N \sim T^{-2}$ at sufficiently low temperatures. Since the electronic and/or magnetic part of the specific heat is so large in this system, any "nuclear" upturn in C versus T data would appear only at very low temperatures, probably well below the lowest temperature of the present measurements. Assuming that the low temperature upturn in C/T is a manifestation of the high-temperature tail of a nuclear Schottky anomaly, we have tried to fit the data below about 150 mK to a $C = AT^{-2} + \gamma T$ equation. Indeed, such an analysis results in a reasonably good fit with $A \simeq 0.04$ mJ K/mole and $\gamma(T \to 0\ \text{K}) \simeq 3.4$ J/mole K^2. The coefficient A is more than one order of magnitude higher than what one would expect from the quadrupole splitting of the Cu nucleus observed from pure quadrupole resonance (PQR) experiments in $CeCu_6$.[11] Hence we conclude that this term originates from the magnetic splitting of the nuclear levels of Cu and the corresponding transferred hyperfine field is ~ 1.4 T.

On the other hand, $\gamma(T \to 0\ \text{K})$ is, by any standard, extremely large in a paramagnetic or magnetically ordered HF system and is close to the value of 2.8 J/mole K^2 deduced[2] from the extrapolation to 0 K of our earlier data above 600 mK, where we assumed the absence of any magnetic ordering at lower temperature. The only system with a comparably large value of $\gamma(\simeq 3.9$ J/mole K$^2)$ is $CePd_3B$.[12] Although the magnetization data in $CePd_3B$ also show thermomagnetic history effects below the transition temperature, the absence of any sharp anomaly in the corresponding specific-heat data in the same temperature region stands in contrast to the present results. Since in $Ce(Cu_{0.9}Ag_{0.1})_6$ γ at temperatures above 6 K is already quite large (260 mJ/mole K^2), it is reasonable to believe that the same heavy electrons are involved in the magnetic transition. However, to what extent the low-temperature value of γ is a result of the HF behavior and to what extent it is influenced by the magnetic transition still remains to be decided. Measurements of the specific heat in magnetic fields large enough to suppress the magnetic transition would be an important experiment in this direction. Such studies are currently in progress.

In summary, the present work shows that the replacement of small amounts of Cu by Ag in the HF system $CeCu_6$ can give rise to magnetic transitions, probably to an antiferromagnetically ordered state for $x \lesssim 0.10$ followed by a gradual evolution towards ferromagnetic or ferrimagnetic ordering with increasing x. The observation of thermomagnetic history effects in the ordered state points to a mixed and glassy nature of these two phases. In this connection, we point out that similar thermomagnetic history effects have been recently observed in the antiferromagnetically ordered state of a completely different type of system, namely the oxide La_2CuO_4.[13] In the dilute Ising antiferromagnetic compound $Fe_{0.70}Mg_{0.30}Cl_2$ hysteretic behavior in ZFC and FC has been observed in neutron scattering experiments,[14] although the susceptibility data[15] would describe it as a normal antiferromagnet.

It remains to be seen whether the present compound has anything in common with the systems discussed above. A first logical step in this direction would be to carry out neutron scattering experiments to establish the precise nature of the magnetic order. Among other things, microscopic inhomogeneity caused by the random substitution of Cu by Ag could be a key to understanding the glassy behavior, provided the magnetic state of Ce ions depends sensitively on the proximity of Cu or Ag.

Although the study of the nature of the magnetic state is itself quite interesting and remains a topic for future study, the most important finding of the present work is in proving the magnetic instability of the pure $CeCu_6$ system. The linear extrapolation of T_{max} versus x in Fig. 1(b) shows that even as little as 1.3 at. % Ag substitution (the small ambiguity in the determination of the ordering temperature for $x = 0.15$ and 0.20 samples does not seriously affect this estimate) is sufficient to induce magnetic instability in $CeCu_6$. This result raises the obvious question as to what extent the high value of γ in $CeCu_6$, often cited as the highest among the paramagnetic HF systems, is a signature of the HF state itself and to what extent it is due to the inherent magnetic instability (in other words the *incipient* nature of the magnetism) of the system. Other than the present results, evidence in favor of terming $CeCu_6$ an incipient magnetic system comes from the observation of a strong reduction of γ in the presence of a magnetic field.[1] Although the explanation for such a strong field dependence of $\gamma(H)$ is generally given in terms of the Kondo lattice model, a rethinking in terms of the magnetic picture would seem justified.

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