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Magnetic behavior of $Ce(Cu_{1-x}Ag_x)_6$

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We have investigated doped $CeCu_6$ via x-ray diffraction, dc and ac susceptibility, and specific heat in zero and applied magnetic field with a primary focus on the magnetic behavior caused by Ag doping. We present evidence from bulk specific heat and metallography data that the limit of Ag solubility in $Ce(Cu_{1-x}Ag_x)_6$ is $x \sim 0.1$. Data below the magnetic ordering temperature may be fit to an exponential temperature dependence, implying a weak-coupled energy gap of $\Delta = 0.58$ K, contradicting an earlier report the C behaves linearly with temperature with a γ over 3 J/mol K^2 in the ordered state. Comparisons to magnetically ordered, doped UPt_3 are made.

I. INTRODUCTION

Doping in heavy-fermion systems has a history of producing new results that are interesting in their own right but, more importantly, shed light on the heavy-fermion behavior of the parent compound. Thus, the recent finding[1] that UPt_3 has an ordered magnetic moment at nonzero frequency of $0.02 \pm 0.01 \mu_B$ at 6 K in addition to its known spin-fluctuation behavior[2,3] was presaged by the earlier discoveries[4-7] that small doping levels [either $(UPt_{3-x}Pd_x)$ or $(U_{1-x}Th_x)Pt_3$] in UPt_3 created antiferromagnetism at 6 K, albeit with[7] a larger ordered moment ($0.65\mu_B$). In UBe_{13}, as is well known, Th doping evidently causes an additional magnetic transition below the superconducting T_c, with this lower magnetic transition T_2 having the intriguing property that it increases the slope of H_{c1} below T_2.

Recently, work on $CeCu_6$ doped by Ag has, after some initial confusion,[8] established[9] the existence of an apparently antiferromagnetic transition in the vicinity of 0.7 K whose temperature is composition dependent.

Further investigation of the magnetic behavior of $Ce(Cu_{1-x}Ag_x)_6$ over a wide range of doping concentrations, as well as in applied magnetic fields, is necessary in order to properly clarify the intrinsic behavior of this system, and the implications for heavy-fermion systems in general. We report here on zero- and high-field low-temperature specific heat, C, and ac susceptibility results on $Ce(Cu_{1-x}Ag)_6$ for $x = 0.07$, 0.08, 0.10, 0.15, and 0.20 that (1) imply the existence of *two* low-temperature magnetic transitions for $x > 0.1$, and (2) call into question the interpretation[9] of the C/T data below T_N as being indicative of a record high (3.4 J/mole K^2) specific heat γ for this material.

II. RESULTS

In this rather complex $Ce(Cu_{1-x}M_x)_6$ system, we focus here on M=Ag. Reference 9 reports specific-heat data for the composition $x = 0.1$ Ag, while Ref. 10 also reports χ and C data for Au-doped $CeCu_6$. We find that doping with Pd, Pt, Zn, and Ga produces a second phase. Our specific-heat data for Ag, with $x = 0.07$, 0.08, 0.10, 0.15, and 0.20 are shown in Fig. 1. Table I lists the onset and peak temperatures for each concentration. Table I also lists the peak temperature in the susceptibility both from our ac susceptibility data and those of Ref. 9. The increase observed at low temperatures ($T \geq 1.8$ K) in χ measured in our SQUID susceptometer for $Ce(Cu_{1-x}Ag_x)_6$ shifts to lower temperatures with increasing field, implying antiferromagneticlike behavior for all the Ag-doped samples. (This will be further evidenced in the following in the discussion of the low-temperature specific heat as a function of applied magnetic field.)

Before a discussion of our nonzero-field results, let us consider the data in Fig. 1 and in Table I. Clearly, the antiferromagnetic transition observed via susceptibility in Ref. 9 upon doping with Ag in $CeCu_6$ has a more complex behavior in the bulk with composition than inferred from their $T^{\chi}_{\max} = \text{const} \times (\text{at.}\ \%\ \text{Ag})$ linear relation. Although $T^{\chi}_{\max}$ rises linearly with % Ag doping, the maximum in C we observe at the anomaly saturates both in temperature and magnitude (see Table I and Fig. 2 for a plot thereof) above $x = 0.10$. At and below $x = 0.10$, an extrapolation of $T^{C}_{\max}$ to $T^{C}_{\max} = 0$ yields $x = 0.015$ for an onset of magnetism in Ag-doped $CeCu_6$ in good agreement with the $x = 1.3\%$ value inferred from the dc susceptibility data of Ref. 9. (Due to the sharpness of the peak in C, extrapolating $T^{C}_{\max}$ to 0 gives a more reliable estimate. However, extrapolating T^{C}_{onset} gives essentially the same answer.)

An indication of this added complexity was already present in the susceptibility results for $Ce(Cu_{1-x}Ag_x)_6$ of Ref. 9, where it was found that (1) field cooling versus zero-field cooling made a difference in the shape of χ for $x = 0.15$ and 0.20, but not for $x = 0.05$ and 0.10; (2) χ for $x = 0.15$ and 0.20 was two orders of magnitude larger than for $x = 0.05$ and 0.10; (3) a small hysteresis in M versus H for $x = 0.20$ at 1.4 K was observed. These results led the authors of Ref. 9 to propose that an antiferromagnetic transition present for $x = 0.05$ and 0.10 becomes ferrimagnetic or ferromagnetic for $x \geq 0.15$. In this latter case, they note that the true ordering temperature would be larger than that inferred from using $T^{\chi}_{\max}$ for $x=0.15$ and 0.20, not smaller as we observe via bulk specific heat measurements (Fig. 2).

Instead of a single transition that changes character for $x>0.1$ in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$, the data of the present work suggest that a second transition comes into existence above $x=0.1$. The data supporting this view are (1) the aforementioned two orders of magnitude difference[9] in the value of χ for $x>0.1$; (2) the widening separation (see Fig. 2) between T^{χ}_{peak} and T^{C}_{peak} in the data of this work [performed on the *same* sample for both sets (χ and C) of measurements] as Ag content increases; (3) the saturation of the anomaly in C above $x=0.1$ (i.e., $C^{\max}$ as well as $C^{\max}/T^{\max}$ is approximately constant for $x>0.1$) while $T^{\chi}_{\max}$ is still rising. Finally, although difficult to discern in the zero-field data (see arrow, Fig. 3), there does appear to be a second, very minute specific-heat anomaly at $T\sim1.4$ K for $x=0.2$, which might be connected with the hysteretic magnetic behavior observed[9] at 1.4 K. This small specific-heat anomaly appears broadened and strengthened in the field data; see Fig. 4.

What is puzzling about this interpretation is the shear coincidence that a second phase appears in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ for $x>0.1$ with a magnetic transition whose temperature dependence with Ag concentration is so like that of $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$. (In our χ data, the slope of $T^{\chi}_{\max}$ for $x=0.15$ and 0.20 is somewhat higher, by $\sim50\%$, perhaps due to sample variation, than that reported at lower x in Ref. 9.) Although it is true[9] that no known second phase has a magnetic transition in the 1.4 K temperature region, it is at least plausible, in this complicated Ce-Cu-Ag ternary system, that such a second phase exists in the phase $\mathrm{Ce(Cu_{1-x}Ag_x)_5}$. Since the discovery[11] of antiferromagnetism at 3.8 K in $\mathrm{CeCu_5}$ it has been found[12] that doping by Al[$\mathrm{Ce(Cu_{0.8}Al_{0.2})_5}$]

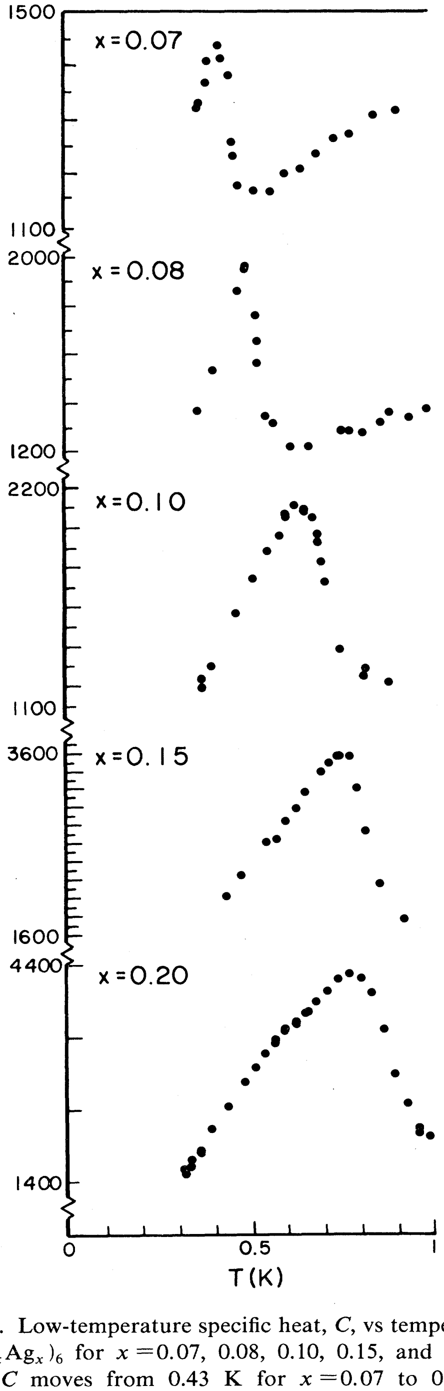

FIG. 1. Low-temperature specific heat, C, vs temperature for $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ for $x=0.07$, 0.08, 0.10, 0.15, and 0.20. The peak in C moves from 0.43 K for $x=0.07$ to 0.76 K for $x=0.15$. The peak for $x=0.20$ is at essentially the same temperature (0.77 K) within our error limits as for $x=0.15$. The data for $x=0.1$ may be compared with those of Ref. 9 on nominally the same composition, where $T_{\mathrm{peak}}=0.58$ and $C_{\mathrm{peak}}\sim1.9$ J/mole K. These differences are perhaps due to the sample in this work being more homogeneous.

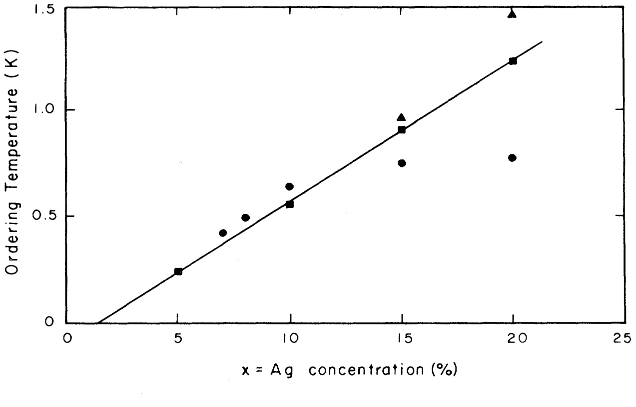

FIG. 2. Ordering temperature determined via peak in χ_{ac} (triangles), dc χ (Ref. 9, squares), and the peak in the specific heat (circles) vs Ag concentration in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$. These data make it apparent that the bulk specific-heat antiferromagnetic transition does not change its location in temperature above some Ag concentration between $x=0.1$ and $x=0.15$, while the location of the susceptibility anomaly continues to move to higher temperature with increasing x. Due to the many x-ray lines, it is difficult to state with certainty that second phase peaks are visible in the x-ray pattern up to $x=0.2$, i.e., at least 5% second phase would not be distinguished from the diffractometer trace. For $x=0.4$, many second-phase lines are visible.

TABLE I. Parameters for $Ce(Cu_{1-x}Ag_x)_6$.

Composition	T onset, C (K)	T peak, C (K)	T peak, χ (K) This work/ Ref. 9	C at peak (mJ/mole K)	C/T peak	Peak position (K)/field (T)	Lattice parameters[a] a_0 (Å)	b_0 (Å)	c_0 (Å)
Ag, 0.05			/0.23						
0.07	0.50	0.43		1445	3360				
0.08	0.54	0.50		1950	3900				
0.10	0.81	0.65 (0.580 from Ref. 9)	/0.58	2080	3200		8.164	5.072	10.231
0.15	0.89	0.76	0.96/0.90	3700	4900		8.271	5.072	10.342
0.20	0.94	0.77	1.45/1.24	4000	5200	$0.77/H=0$ $0.70/H=1$ $0.60/H=1.4$ $0.52/H=1.8$ $0.49/H=2.0$	8.256	5.074	10.351

[a] We find 8.041, 5.076, and 10.061 Å, respectively, for pure $CeCu_6$. b_0 appears ~ constant with Ag doping.

suppresses T_N below 150 mK. Work is underway to investigate the effects of Ag doping in $CeCu_5$.

The possibility that the existence of two transitions in $Ce(Cu_{1-x}Ag_x)_6$ is intrinsic to single-phase material can best be addressed by careful lattice parameter measurements in the doped orthorhombic system, combined with metallography. Although the multitude of x-ray lines produced by this structure make analysis somewhat difficult, our analysis of the lattice parameters for the doped systems (see Table I) indicates a possible saturation of the change of a_0 and c_0 with increasing Ag above $x=0.10$, while b_0 is apparently independent of Ag content. Further work with a more precise diffractometer is needed to verify these results, which are only approximate.

To complement the lattice parameter determination, we have prepared polished specimens of the $x=0.1$ and

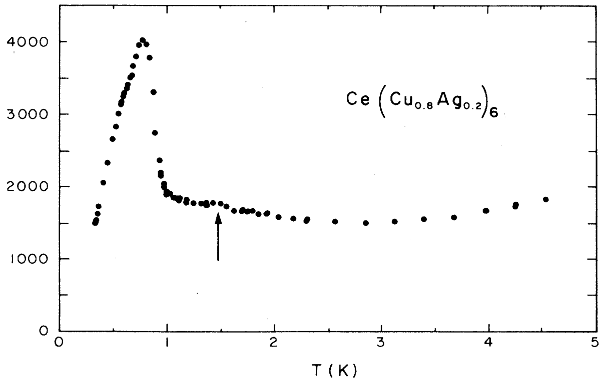

FIG. 3. Low-temperature specific heat vs temperature of $Ce(Cu_{0.8}Ag_{0.2})_6$, with the antiferromagnetic ordering peak at $T \sim 0.77$ K. Within our error, the position and height of this peak is the same as seen in Fig. 1 for $Ce(Cu_{0.85}Ag_{0.15})_6$. A feature (see discussion in text) in C is seen here at 1.4 K and indicated by an arrow.

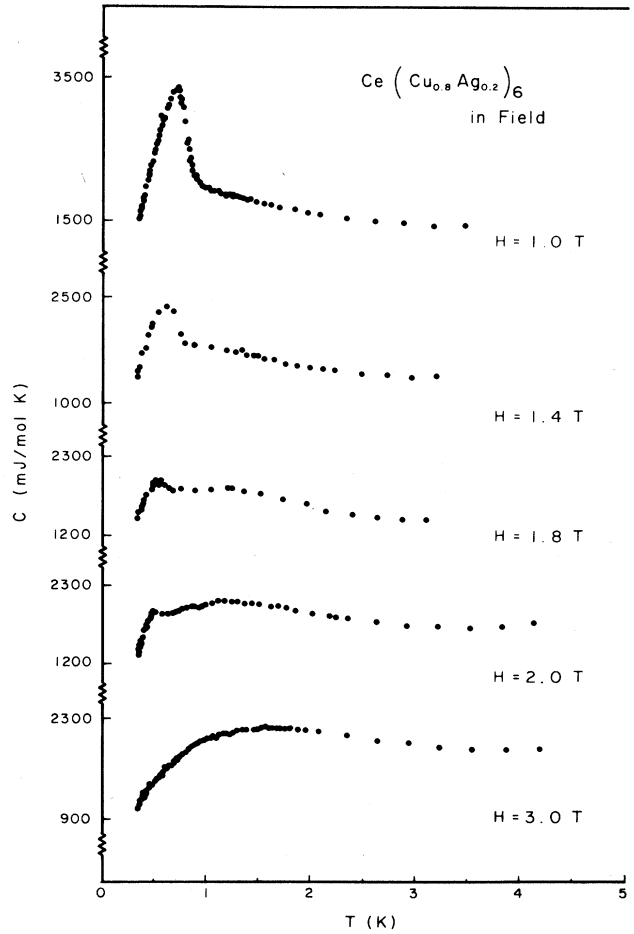

FIG. 4. Low-temperature specific heat vs temperature as a function of magnetic field for $Ce(Cu_{0.8}Ag_{0.2})_6$. Note the suppression of the peak both to lower temperature and in magnitude by the applied field. The feature at ~1.4 K is most apparent in the 1.8- and 3-T data.

0.2 samples and examined the surfaces at magnifications of 1000 and 2000 on a JEOL model 733 super probe. Using selected area energy dispersive spectroscopy, we have identified a second phase in the $x=0.2$ sample that is not present in the $x=0.1$ sample. This second phase is Ce deficient compared to the majority phase, with approximately the same Ag/Cu ration.

A second piece of evidence that contradicts the proposal[9] that the character of the majority-phase transition in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ changes from antiferromagnetic to ferrimagnetic or ferromagnetic for $x>0.1$ can be obtained by examining C as a function of field. $C(H)$ data for our $x=0.2$ sample are shown in Fig. 4. Two features are worth noting. The transition peak temperature moves *down* in temperature monotonically with increasing field (see also Table I). This is not consistent with ferrimagnetic or ferromagnetic ordering for $x>0.1$. Second, the slight bump in the zero-field data at 1.4 K (see Fig. 3) becomes more visible as the large, lower-temperature anomaly is suppressed by the applied field (Fig. 4). Apparently, there exists a large, rounded anomaly in C versus T which is clearly visible in the 1.8-T data, Fig. 4, with the lower T increase in C caused by the bulk, intrinsic antiferromagnetic transition suppressed. As the lower T increase in C becomes larger and larger with lower field, the anomaly at 1.4 K is effectively masked: the high-temperature-side increase in C for this anomaly is masked as a precursor effect for the low-T anomaly and the low-T-side falloff in C for the the 1.4 K anomaly seen in the 1.8-T data is swamped by the large increase in C caused by the onset of antiferromagnetic order for the low-T transition.

Thus, our specific-heat data in field for $\mathrm{Ce(Cu_{0.8}Ag_{0.2})_6}$ establish that the bulk anomaly observed at 0.77 K at $H=0$ is suppressed with increasing field and that a second, smaller anomaly at 1.4 K becomes visible as the precursor specific-heat increase above the 0.77-K transition is suppressed by applied field. This result, coupled with our zero-field specific-heat and x-ray and microprobe analysis imply that a second phase is the probable explanation for the 1.4-K anomaly and that there is no further rise in temperature with doping of the antiferromagnetic anomaly in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ above about $x=0.115$, the limit of phase stability determined from the behavior of T^C_{peak} with x.

Considering now the very low-temperature, $T<T_N$, behavior of the specific heat, what is the specific heat $\gamma(\equiv C/T)$, proportional to the effective mass m^* in the ordered state? Above T_N in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$, the value of C/T (away from the upturn that presages the antiferromagnetic transition and above our inferred 1.4-K anomaly) at 2 K is 700 mJ/mole K^2, approximately independent of x, compared to $\sim$900 mJ/mole K^2 for pure $\mathrm{CeCu_6}$. A difficulty arises, however, in determining γ in $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ below T_N due to the low value of T_N not providing much of a temperature range below the transition in which to sort out the linear temperature dependence, or γ, of the specific heat. Below 0.150 K, the specific-heat data of Ref. 9 for $\mathrm{Ce(Cu_{0.9}Ag_{0.1})_6}$ show a nuclear Schottky anomaly. Although our specific-heat data for, e.g., $\mathrm{Ce(Cu_{0.8}Ag_{0.2})_6}$ appear quasilinear with temperature (see Fig. 3) implying a γ over 3 J/mole K^2, a careful analysis of these 16 data points between 0.33 and 0.775 K shows that they do not at all fit a $C\sim\gamma T$ behavior over even this limited temperature range. (It should be noted that the lattice contribution below 1 K is negligible, $<0.05\%$ of C_{tot}). However, a plot of all the data points on a natural log C versus $1/T$ plot, shown in Fig. 5, clearly shows that the temperature dependence of these data obeys $C\sim Ae^{-\Delta/T}$. The standard deviation,

$$\sigma\left[\equiv\left[\sum_{i=1}^{N}(\text{fit}-\text{measured }C_i)^2\right]^{1/2}\Big/\sqrt{N-1}\right],$$

of this exponential fit is more than four times smaller (29 versus 128) than that of the best power-law fit ($\propto T^{1.175}$) of the same N data points. The Δ obtained from the exponential fit, 0.58 K, gives a corresponding value of Δ/T_{peak} (0.75) which implies much weaker coupling than observed[6] in Th doped $\mathrm{UPt_3}$, where Δ/T_{peak} is 4.0. (A similar plot, not shown, of our $x=0.10$ data gives $\Delta=0.50$ K.)

Thus, a picture emerges from our results for $\mathrm{Ce(Cu_{1-x}Ag_x)_6}$ with implications for the nearness to

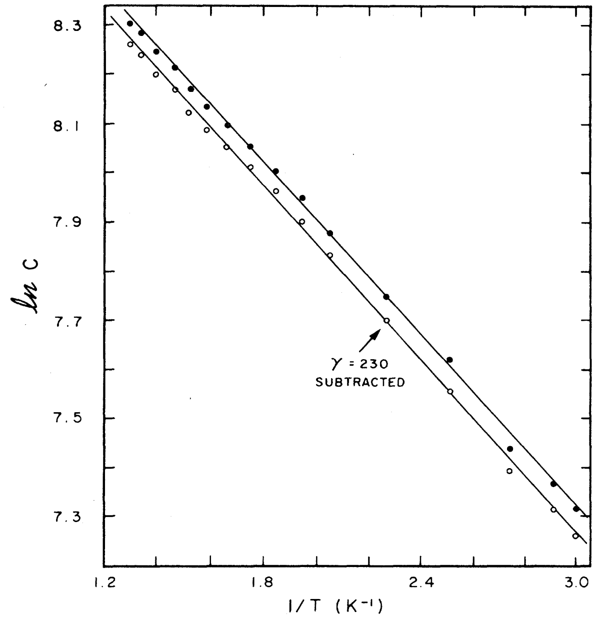

FIG. 5. Shown here in the upper set of data (solid circles) is the natural logarithm of the specific heat vs $1/T$. The lattice contribution is negligible. Also shown (lower set of data) is $\ln(C-\gamma T)$, with $\gamma=230$ as an estimate (Ref. 13) for the nonmagnetic electronic contribution to show that a residual term in the specific heat linear in temperature does not materially alter the fit (both visually and in the standard deviation σ) to an exponential temperature dependence. (A γ of 700 rather than 230 has the same lack of effect.) Although these data only extend over $\sim$0.45 K, such a plot plus the relatively low standard deviation of the fit show that the correct temperature dependence below the ordering peak is exponential with $1/T$, i.e., a gap is formed.

magnetism of the parent heavy-fermion compound $CeCu_6$ as compared to UPt_3. In $(U_{1-x}Th_x)Pt_3$ and $U(Pt_{1-x}Pd_x)_3$, levels of doping similar in proportion to that for $Ce(Cu_{0.9}Ag_{0.1})_6$ cause an antiferromagnetic, or spin-density wave, transition already at 6 K in UPt_3, compared to a factor of 10 less in $CeCu_6$. The coupling strength of the magnetic ordering, as measured by Δ/T_N, is a factor of 5 weaker in doped $CeCu_6$ compared to doped UPt_3. In $Ce(Cu_{0.8}Ag_{0.2})_6$, T_N falls in an applied magnetic field at a rate of 0.14 K/T versus 0.2 K/T in $(U_{0.8}Th_{0.2})Pt_3$. Another important difference in the magnetic behavior of the two doped heavy-fermion systems is the behavior of the ordering temperature with doping. In $CeCu_6$ doped with Ag, T_N rises smoothly, albeit slowly, with increasing Ag ($x \leq 0.1$). In UPt_3, T_N springs up very rapidly and nonlinearly with much lower concentrations of either Th or Pd.

Thus, even though $CeCu_6$ has a much larger γ than UPt_3 (which implies a higher degree of electron-electron correlations), as well as a higher magnetic susceptibility, doped $CeCu_6$ is a much weaker magnet than doped UPt_3, with its strong spin fluctuations already present in the undoped state.

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