Effects of alloying on the heavy fermion compound CeCu$_6$: substituion of Al

LETTER TO THE EDITOR

Effects of alloying on the heavy fermion compound CeCu$_6$: substitution of Al

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Abstract. Results of susceptibility, resistivity and specific heat measurements on Ce(Cu$_{1-x}$Al$_x$)$_6$ with x up to 0.1 can be consistently interpreted in terms of increased 4f conduction electron hybridisation, and a consequent move away from a magnetically ordered ground state. Reasons for this contrast with the effects of alloying with Au and Ag are suggested.

Among the growing number of intermetallic compounds that show heavy fermion behaviour, particular attention has sometimes been focused on those like CeCu$_6$ that can be cooled to very low temperatures without the manifestation of either a super-conducting or a magnetically ordered ground state. (Overviews of the field and lists of relevant materials can be found in recent conference proceedings: Assmus *et al* (1988), Smith (1990).) There is evidence in all such compounds, however, that the ground state can be modified by substitutions on either the f-element site or the non-f metal site. Thus in UPt$_3$ substitutions of either Th on U sites (Stewart *et al* 1986) or Pd on Pt sites (de Visser *et al* 1986) destroy superconductivity and stabilise magnetic order at higher moment values than the very weak antiferromagnetism of the pure compound (Aeppli *et al* 1988). Th substitutions in UBe$_{13}$ give complicated and widely studied effects (Ott *et al* 1985), one of which is the appearance of a double transition structure below 1 K, the lower of which has been shown to have magnetic character (Batlogg *et al* 1985, Heffner *et al* 1987).

Ce compounds also show a variety of behaviours, although the co-existence of antiferromagnetism and superconductivity has not yet been reported, and in some of these magnetic transitions can be induced by alloying. CeCu$_6$ is of special interest, since the heavy fermion ground state, although showing no phase transitions down to the lowest attainable temperature, can be radically altered by high magnetic fields (Stewart *et al* 1988), antiferromagnetic spin fluctuations have been detected by inelastic neutron scattering (Aeppli *et al* 1986) and substitutions of Au or Ag on the Cu sites have been found to produce magnetic order (Gangopadhyay *et al* 1988, Germann *et al* 1988, Lees and Coles 1988, Fraunberger *et al* 1989). Substitutions of Au or Ag leave the Ce sublattice unperturbed, and since they are iso-electronic with Cu the principal effects must be on the lattice spacing. More drastic changes might be expected for Al substitutions for

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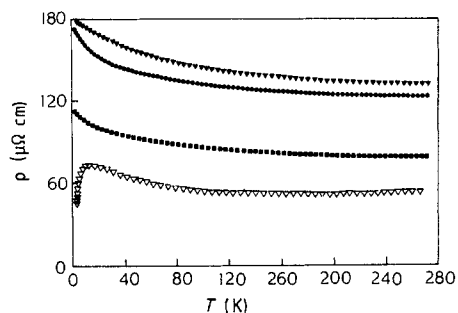
Figure 1. The resistivity as a function of temperature, T, of Ce $(Cu_{1-x}Al_x)_6$: ∇: $x = 0$; ■: $x = 0.02$; ●: $x = 0.05$; ▼: $x = 0.1$.

Cu, and we report here a study of Ce$(Cu_{1-x}Al_x)_6$ alloys by x-ray, metallographic, susceptibility, resistivity and specific heat measurements.

Alloys with 0, 2, 5 and 10% Al substitutions for Cu were prepared by argon arc melting and suction chill-casting (Stone 1974) to form square cross section rods which were annealed in vacuum for one week at temperatures between 600 and 700 °C. Since an isostructural $CeAl_6$ does not exist, care was taken to establish the limit of Al substitution, which still retains the $CeCu_6$ structure. Metallographic examination (the most sensitive technique) showed evidence for a small amount (less than 5%) of a copper rich second phase at $x = 0.1$ but not in the more dilute samples. X-ray diffraction studies on $x = 0$, 0.05 and 0.1 showed only the orthorhombic crystal structure of $CeCu_6$, so that it was not possible to identify the small amount of second phase found in our metallographic study. The lattice spacings of the $CeCu_6$ phase showed a cell volume reduction of about 0.24% for 10% Al, as compared with increases of 0.51% and 1.65% for 10% Ag and Au respectively (Lees 1989).

The resistivities of the rod shaped samples (about 10 m × 1.5 mm × 1.5 mm) were measured by a standard four-probe method between 1.5 and 280 K, and the susceptibilities were measured between 2 K and 400 K by a Quantum Design SQUID magnetometer. A well established time constant method (Bachmann *et al* 1972, Stewart 1983) was used for specific heat measurements between 1.1 and 10 K.

The resistivity data are shown in figure 1 and show a number of significant features. First, that even 2% of Al completely suppresses the low-temperature resistivity peak of $CeCu_6$ (which is often termed a Kondo coherence peak and is a characteristic of almost all the heavy fermion systems), in contrast to the persistence of that resistivity peak to at least 10% of rare earth substitutions on the Ce sites (Roy *et al* 1990). Attention has previously been drawn to the contrast, in effects on coherence, of substitutions on the two types of sites in Ce compounds (Lees and Coles 1988). Previous work on the present system (Zemirli and Barbara 1985) found that even 0.8% Al substitution suppressed the low temperature resistivity fall. Since coherence represents, in effect, the transition from independent character of Ce sites to Bloch-type wave function of hybrid 4f conduction electron character it is understandable that strong scattering of conduction electron states associated with the non-4f atoms has a serious effect on the onset of coherence. It is also significant that, while the high temperature resistance of $CeCu_6$ (dominated by the incoherent spin disorder scattering of the Ce atoms) is little changed by substitutions of Au (Lees 1989) (Au being isoelectronic with Cu), Al substitutions produce an additional atomic disorder scattering so that $\rho_{280 K}$ increases significantly (see figure 1). Since the specimens are polycrystalline the values in this figure are averages over the crystallographic directions, but they are probably significant since variations in the
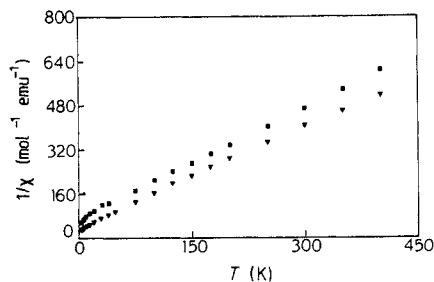
Figure 2. Inverse of susceptibility as a function of temperature, T, of Ce $(Cu_{1-x}Al_x)_6$: ▼: $x = 0$; ■: $x = 0.1$.
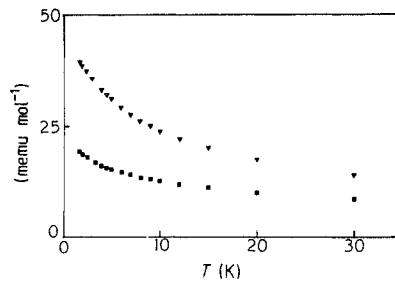
Figure 3. Susceptibility as a function of temperature, T, of Ce $(Cu_{1-x}Al_x)_6$: ▼: $x = 0$; ■: $x = 0.1$.

Table 1. Parameters for $Ce(Cu_{1-x}T_x)_6$; $T = $ Al, Au, Ag.

| Composition	χ (2 K) (memu mol^{-1})	μ_{eff}	γ (1.1 K) (mJ mol^{-1} K^2)
Al 0	39	2.54	~910
0.05	35	2.33	800
0.1	21	2.42	540
Au 0.05	55†	2.38†	
0.08	72‡		1000‡
0.1	103†	2.54†	
Ag 0.05	45§		
0.1	60§	2.51¶	1200‖

† Lees (1989).
‡ Germann *et al* (1988).
§ Gangopadhyay *et al* (1988).
‖ Fraunberger *et al* (1989).
¶ Obtained from high temperature susceptibility data of Gangopadhyay *et al* (1988).

amount of preferred orientation are unlikely to be large, all specimens having been prepared in the same way.

The inverse susceptibility $(1/\chi)$ as a function of temperature (T) and low-temperature $(2 \leqslant T \leqslant 30$ K) susceptibility (χ) for $Ce(Cu_{1-x}Al_x)_6$ with $x = 0$ and 0.1 are shown in figures 2 and 3 respectively. Data for $x = 0.05$ also exist but are not shown here for the sake of clarity. The effective moment (μ_{eff}) obtained from a linear fit in the high temperature region $(T > 150$ K) and value of the susceptibility (χ) at 2 K for the alloys with $x = 0$, 0.05 and 0.1 are collated in table 1. The susceptibility data show significant deviations from those for the Au and Ag substituted alloys (see table 1), since in the latter susceptibility increases foreshadowing the onset of magnetic order at lower temperatures $(T < 2$ K). In the Al alloys on the other hand, the low temperature $(T = 2$ K) susceptibility values show a steady decrease with increasing Al content. It should be noted that this behaviour cannot be explained simply in terms of the growth for the Ag and Au alloys of a negative θ value in the Curie–Weiss susceptibility since that would decrease χ for $T > T_N$. One is forced to conclude that the effective moment (at low
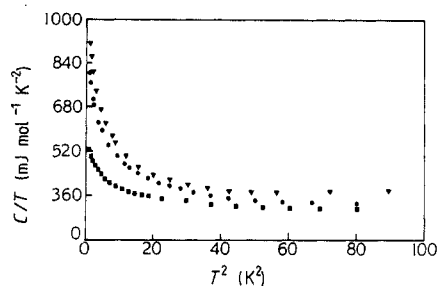
Figure 4. Specific heat/temperature as a function of temperature squared. T^2, of Ce $(Cu_{1-x}Al_x)_6$: ▼: $x = 0$; ●: $x = 0.05$; ■: $x = 0.1$.
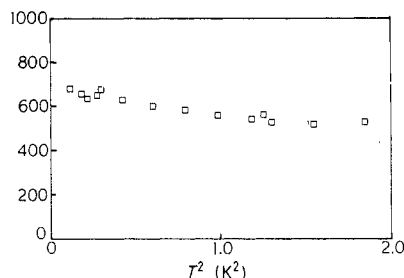
Figure 5. Specific heat/temperature as a function of temperature squared. T^2, of Ce $(Cu_{0.9}Al_{0.1})_6$ in the temperature range $0.32 < T < 1.5$ K.

temperature) of Ce (insofar as that term has meaning for hybrid 4f conduction states) is increased by Ag or Au and decreased by Al doping.

Such behaviour accords with the general indications of the Kondo lattice model (Doniach 1977, Moshchalkov and Brandt 1986). If 4f moments survive Kondo demagnetisation down to temperatures where they can be coupled by RKKY type interactions, the ground state will be magnetically ordered, and the moments coupled in it (and contributing to χ at $T_N + \delta$) will approach those of independent $4f^1$ Ce atoms. For strong 4f conduction electrons (V_{kf}) hybridisation a simple treatment of the de Gennes–Kondo–Schrieffer–Wolff projection of J_{eff} out of V_{kf} would suggest a higher magnetic ordering temperature, but this approach fails to recognise that the on-site J_{eff} leads to a reduction in the effective moments, and it is not therefore to be inserted in a simplistic way into the RKKY expression.

It is clear that for Al substitutions in CeCu$_6$ the increase in the conduction electron concentration and also perhaps the reduction in cell volume increases the hybridisation V_{kf}, decreases the effective Ce moments, and moves the system away from magnetic order.

The specific heat results provide striking support for the above views. The data are shown in figure 4 and the values of C/T at 1.1 K are collated in Table 1. The specific heat of the alloy Ce$(Cu_{0.9}Al_{0.1})_6$ (see figure 5) was measured down to 0.32 K to check for the indication of any magnetic ordering and none was found. In contrast to the effects of Ag and Au (Gangopadhyay *et al* 1988, Germann *et al* 1988, Fraunberger *et al* 1989, Lees 1989) the specific heat of CeCu$_6$ is strongly depressed by Al. The value of γ (0 K) for Ce$(Cu_{0.9}Al_{0.1})$ obtained from extrapolation of C/T values in the temperature range $0.32 \leqslant T \leqslant 1$ K is found to be about 750 mJ mol^{-1} K^{-2} which is almost half of that of CeCu$_6$ (Stewart 1984). In simple treatments of the Kondo effect $\gamma \propto 1/T_K$ and increasing V_{kf} leads to increasing T_K, but it must be borne in mind that the simple T_K–V_{kf} relation is only valid for small V_{kf}, and that the virtual bound state approach to the hybrid f

conduction band states becomes more appropriate as V_{kf} increases. However, thermal expansion data for $CeCu_6$ alloyed with Al (de Visser *et al* 1989) have also been interpreted in terms of an increase in T_K.

We conclude that a consistent approach to the effects of alloying on the behaviour of $CeCu_6$ is possible. Results which will shortly be presented on $(Ce_{1-x}R_x)Cu_6$, where R is Y, Gd and Pr, fit a similar description. These results may be usefully compared with data for $(U_{1-x}M_x)Be_{13}$ for a wide range of M elements (Kim *et al* 1990) which support the view of UBe_{13} as significantly affected by the single ion 5f character to quite low temperatures.

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