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The effects of Gd substitutions on the heavy fermion compound $CeAl_3$*

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Abstract

Results are reported of electrical resistivity, magnetic susceptibility and specific heat measurements on alloys in the series $CeAl_3$–$GdAl_3$. The general form of the probable magnetic phase diagram is indicated. For more than 20% Gd substitution a low temperature spin-glass is found, but this is replaced by long-range antiferromagnetism for more than about 50% Gd. Higher temperature susceptibility anomalies are shown to arise from traces of the ferromagnetic $CeAl_2$–$GdAl_2$ compounds.

1. Introduction

In studies of intermetallic compounds in a given alloy system, one of the most interesting features is the variation in the electronic properties with change of crystal structure and stoichiometry. Such variations are especially striking when some or all of the compounds are superconducting, as shown by Khan and Raub for the system Nb–Ir [1]. Alloys of the rare earth metals with aluminium are of interest for the variations found in the magnetic ground state. (For a compilation see Buschow [2]). The Ce–Al system is of especial interest since it contains two compounds with many of the features considered characteristic of heavy fermion systems or Kondo lattices. However, $CeAl_3$, the first reported heavy fermion compound, has been thought until recently to show no magnetic ordering, while $CeAl_2$ shows the onset of an interesting form of antiferromagnetism at 3.8 K [3, 4]. (Strangely, the compound most dilute in cerium, Ce_3Al_{11}, has a higher ferromagnetic, transition at 6 K.)

In the Gd–Al system more straightforward behaviour might have been expected, but while $GdAl_2$ is a good ferromagnetic below 170 K $GdAl_3$ does not order (antiferromagnetically) until 17 K in spite of a Curie–Weiss θ value of -190 K. This indication of strong frustration is confirmed by the electron paramagnetic resonance linewidth behaviour [5].

*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

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Since very recent work on $CeAl_3$ [6] suggests antiferromagnetic ordering of a very small cerium moment (reminiscent of UPt_3) below 1.6 K, it is of particular interest to investigate the magnetic behaviour when gadolinium is substituted on the cerium sites and to compare this with the behaviour of the $CeCu_6$–$GdCu_6$ system [7] where the pure $CeCu_6$ phase is more metallurgically friendly, but again a heavy fermion system.

The system $CeAl_3$–$GdAl_3$ forms a complete range of solid solutions in the Ni_3Sn structure, just as the $CeAl_2$–$GdAl_2$ system does in the cubic Laves phase structure, although in the latter system ferromagnetism exists for the composition range with more than 25% Gd, the antiferromagnetism of $CeAl_2$ having been suppressed [8].

While a number of investigations of the $CeAl_3$–$GdAl_3$ system have been reported [9] there has inevitably been anxiety about the possible influence of small amounts of other phases, especially $(Ce,Gd)Al_2$ since, being ferromagnetic, it would dominate the low-field magnetic response of a two-phase alloy with non-ferromagnetic $(Ce,Gd)Al_3$ even at low concentrations.

In the present work therefore, great care was taken to undertake more sensitive searches for second phases than X-ray powder diffraction, and greater weight was attached to electrical resistivity and specific heat measurements, which are much less sensitive than the susceptibility to small amounts of ferromagnetic phases.

2. Sample preparation and character

All the samples were prepared by melting weighed quantities of the pure metals together in an argon arc furnace and, after several inversions and remelts, chill casting in rods 1–5 mm in diameter and 15–40 mm in length. Melting losses were always small (less than 0.5%) and the compositions quoted are based on the masses of metals used. The resulting rods were annealed in evacuated capsules at 873 K for 1 week in an effort to produce single-phase samples in the RAl_3 structure. Since the phase purity is critical to the interpretation of the magnetic data, careful metallographic examination of the annealed samples was carried out, both in the as-polished condition, when second phases could be revealed by contrasts in colour, reflectivity and hardness, and also after etching with appropriate dilute acids. In all specimens, in addition to a few small oxide particles, small amounts of other metallic phases (less than 2% and therefore not detectable by X-rays) were observed. The magnetic data presented below suggest that these were principally of Ce_3Al_{11} ($T=6$ K) [2] (with a little substituted gadolinium) for alloys of up to 10% Gd substitution, and $(Ce,Gd)Al_2$ for alloys of more than 20% Gd ($T=25$–170 K) [8].

X-ray diffraction shows a gradual decrease across the system in lattice spacing and atomic volume of the RAl_3 phase, the a parameter going from 6.626 to 6.332 Å and the unit cell volume from 172.9 to 159.7 Å^3.

3. Experimental results

3.1. Electrical resistivity

It is well known that small isolated particles of a second phase have little effect on the resistivity of an alloy, and we believe that the results shown in Figs. 1 and 2 (where the values for pure $LaAl_3$ have been subtracted) represent the sum of the magnetic and alloy scattering for single-phase $(Ce,Gd)Al_3$ alloys. Certainly none of the high-temperature anomalies seen in the susceptibilities (see below) of the more gadolinium-rich alloys are visible. All these results are for polycrystalline material, but the possibility of preferred orientation in alloys prepared by our method may mean that they are not simple averages of a and c direction resistivities. Measurements were made by conventional four-probe methods and the absolute values (see Table 1) are somewhat uncertain because of specimen dimension uncertainty.

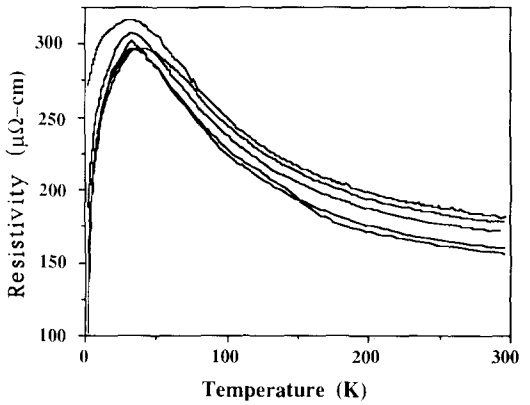

Fig. 1. Electrical resistivities of $(Ce,Gd)Al_3$ alloys with 0.0, 1.0, 2.0, 5.0 and 25% Gd substitution. The room temperature values increase slightly with gadolinium content.

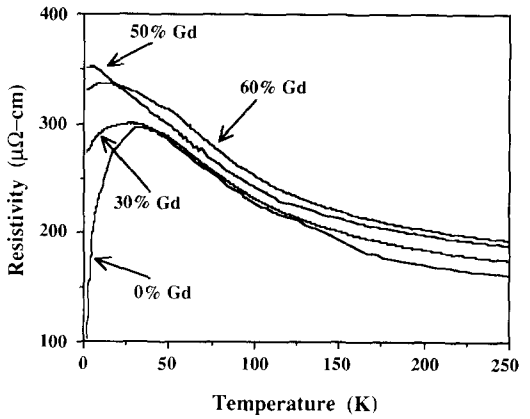

Fig. 2. Electrical resistivities of $(Ce,Gd)Al_3$ alloys showing low-temperature magnetic freezing. The curve for pure $CeAl_3$ is included for comparison.

TABLE 1

Parameters for $(Ce_{1-x}Gd_x)Al_3$ resistivity samples

x	T for ρ_{max} (K)	$\rho(4.2)$ ($\mu\Omega$-cm)	Residual resistivity ratio
0.00	33.9	180.1	0.868
0.01	32.6	196.4	0.817
0.02	47.5	198.1	0.899
0.05	32.1	222.1	0.768
0.08	34.5	225.0	0.784
0.25	31.6	280.9	0.645
0.30	28.7	280.3	0.614
0.50	4.5	351.8	0.528
0.60	12.9	333.2	0.565

At high temperatures the resistivity is dominated by magnetic scattering and the Kondo decrease has much the same character throughout. What is at first sight surprising is how slowly the low-temperature fall we associate with the folding together of crystal field effects and Kondo coherence is eliminated by gadolinium, still being visible at 30% Gd. It is not clear how much of this is crystal field originated.

Similar behaviour has, however, been observed for $(Ce,Gd)Cu_6$ [7] and the greater sensitivity in $CeCu_6$ of the onset of coherence to substitution on the copper site than to substitutions on the cerium site has been noted previously [10]. No maximum is found for 40% Gd but, as the gadolinium concentration increases, a low-temperature fall appears, which we associate with the freezing of the gadolinium moments through their mutual interactions. The transition from spin-glass freezing to long-range magnetic order is not easy to determine from these results, but the flattening out of ρ with decreasing temperature, followed by a sharper fall at 13 K, for the 60% alloy is what one might expect from short-range order above T_N in a frustrated antiferromagnet.

3.2. *Specific heat*

Specific heat measurements were made at Harwell Laboratories (courtesy of Dr. M. Mortimer and R. A. Hall). Pumping facilities were unavailable at the time so the lowest temperature achieved was around 4.2 K. The system design only allowed measurements up to 20 K. Above this, experimental uncertainties become significant.

In alloys with up to 10% Gd the value of C/T per mole of cerium was close to that of pure $CeAl_3$ (exceeding 0.8 J mol^{-1} K^{-1} at 4 K), indicating the persistence of Kondo lattice character. At higher concentrations such a term (increasingly being more like a Kondo single-ion contribution) will be accompanied by a contribution from gadolinium moment freezing, and the separation of these is not a simple matter.

However, the observation of a shallow minimum in C *vs.* T between 5 and 6 K for alloys of 25–40% Gd suggests that the gadolinium spin-freezing entropy only becomes large below those temperatures, with short-range order and heavy fermion effects both contributing to the large values of specific heat between 5 and 10 K. Measurements could not be made with the available apparatus to a low enough temperature to establish whether spin-glass character was clearly present.

3.3. Susceptibility and magnetization

Without the resistivity and specific heat data the magnetic susceptibility and magnetization would prove (as they have in previous work on this system) very difficult to interpret.

The susceptibility of pure $CeAl_3$ [11] shows a Curie–Weiss behaviour at high temperatures with an effective moment of $2.5\mu_B$ per Ce atom, as expected for trivalent cerium. At low temperatures, however, it becomes almost temperature independent and was interpreted as the enhanced Pauli susceptibility of a heavy fermion system that does not order. More recent measurements on single crystals [6] seem to suggest an interpretation in terms of a very small-moment antiferromagnetic ordering at 1.6 K.

Our measurements on pure polycrystalline $CeAl_3$ are in agreement with published data, but alloys with up to 10% Gd show (Fig. 3), in addition to the enhanced Curie–Weiss contribution due to gadolinium moments, a distinct peak at about 6 K which can be ascribed to the Ce_3Al_{11} phase in small quantities.

The nearly gadolinium-independent temperature of this peak suggests that little gadolinium is incorporated in this phase. At higher concentrations, however, a higher-temperature anomaly appears in the susceptibility at temperatures close to the Curie temperatures of the $CeAl_2$–$GdAl_2$ Laves phase pseudobinary alloys [8]. Such anomalies were found in the work of Edelstein *et al.* [9] and attributed to a spin-glass transition in $CeAl_3$–$GdAl_3$ alloys, but

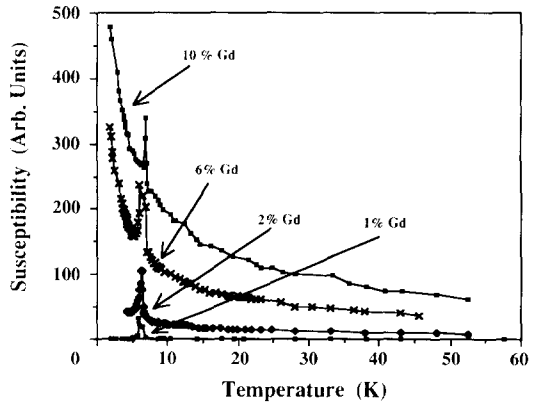

Fig. 3. Low field a.c. susceptibilities of $(Ce,Gd)Al_3$ with up to 10% Gd. The anomaly due to a trace of ferromagnetic Ce_3Al_{11} is clearly visible.

we believe that the resistivity and specific heat behaviour of our alloys strongly support our interpretation of these effects as due to small amounts of the $CeAl_2$–$GdAl_2$ material as a second phase. The data shown in Fig. 4 for the magnetization of a $Ce_{0.75}Gd_{0.25}$ Al_3 alloy in a field of 0.5 T support this interpretation, the magnetization at low temperatures (where the second-phase RAl_2 particles are saturated) being dominated by the Curie–Weiss susceptibility of the majority $Ce_{0.75}Gd_{0.25}Al_3$ phase.

Figure 5 shows the Curie temperatures reported by Iwata *et al.* [8] for the $CeAl_2$–$GdAl_2$ pseudobinary alloys together with the temperatures of the anomalies in our alloys, both as a function of percentage substitution of gadolinium for cerium. These data are powerful support for our interpretation of the origin of the high-temperature anomalies. It is interesting to note that these data indicate a slightly larger concentration of gadolinium in the impurity

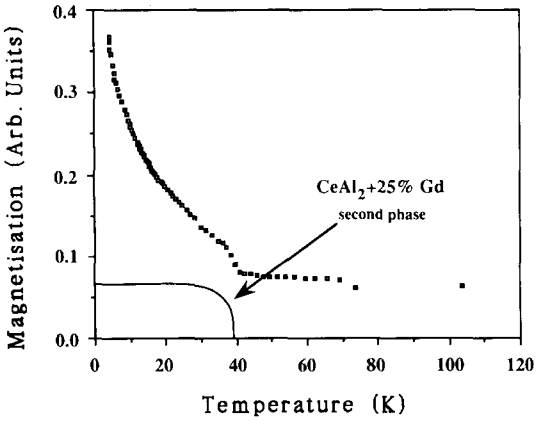

Fig. 4. The magnetization of $Ce_{0.75}$ $Gd_{0.25}$ Al_3 in 0.5 T: ——, the contribution believed to come from a trace of ferromagnetic $Ce_{0.75}$ $Gd_{0.25}$ Al_3.

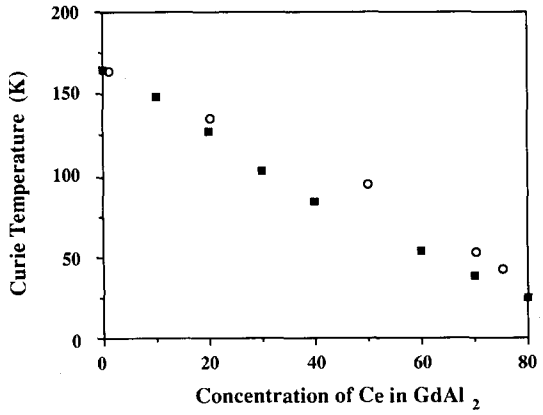

Fig. 5. The Curie temperatures reported in ref. 8 for the ferromagnetic range of $(Ce,Gd)Al_2$ (■) and the temperatures (○) of anomalies in the susceptibility of $(Ce,Gd)Al_3$.

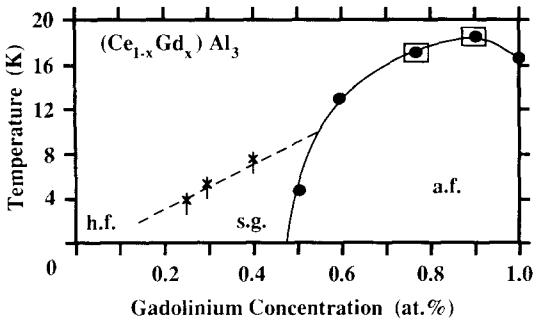

Fig. 6. A tentative magnetic phase diagram for $CeAl_3$–$GdAl_3$: ▣, values taken from ref. 9.

phase than in the alloy, suggesting that the tie-lines in the two-phase RAl_2–RAl_3 region of the ternary diagram do not (as they need not) extrapolate to the pure aluminium corner of the diagram.

4. Conclusions

We cannot claim to present a definitive magnetic phase diagram for pure single-phase $CeAl_3$–$GdAl_3$ pseudobinary alloys. Figure 6 shows what we believe its general form will prove to be, this being based on the resistivity and specific heat results. No clear information yet exists about the effects of gadolinium on the weak antiferromagnetism reported for $CeAl_3$, and the first clear signs of freezing of gadolinium moments are only found at and above 25% Gd. From the rounded maxima we observe in $d\rho/dT$ at 25 and 30% Gd it seems likely that this freezing has spin-glass character up to about 50% Gd with antiferromagnetism of $(Gd,Ce)Al_3$ type at higher concentrations. What seems certain is that susceptibility anomalies found above 30 K are associated with $CeAl_2$–$GdAl_2$ impurity phases.

For small substitutions of gadolinium for cerium the Kondo lattice behaviour of $CeAl_3$ seems to persist (as in $Ce(Gd)Cu_6$ [7]) but above 30% Gd Kondo coherence seems likely to have disappeared although effects of crystal fields can still be seen in ρ. The resistivity of 60% Gd still shows clear evidence of single-atom Kondo scattering by Ce atoms, in spite of the presence of large moments on the Gd atoms. This seems to indicate (again as in the $CeCu_6$–$GdCu_6$) that local spin-disorder scattering by Gd atoms is approximately temperature independent and does not interfere with the Kondo scattering from Ce atoms via the negative J_{sf} that arises from 4f conduction electron hybridization on the cerium sites.

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