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Gd interactions in (Ce,Gd)Al_3

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The susceptibility of $Ce_{1-x}Gd_xAl_3$ for $0.08 \leq x \leq 0.9$ has an anomaly which resembles that associated with a spin-glass transition. For x greater than the percolation threshold concentration for antiferromagnetism at $x \approx 0.5$, the size of the susceptibility anomaly decreases two orders of magnitude and a resistivity anomaly appears.

When Gd is added to a nonmagnetic host such as La-Au or Ag, the Gd moments interact via the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction. Because the sign of this interaction oscillates as a function of the separation between the moments, any Gd moment in general has both ferromagnetic and antiferromagnetic exchange interactions with its neighboring Gd atoms. These competing interactions can give rise to a spin-glass transition.[1]

Here we discuss adding Gd to a special kind of magnetic host, a heavy-fermion (HF) system[2] $CeAl_3$. The original motivation of an earlier study[3] of $Ce_{1-x}Gd_xAl_3$ was an interest in determining whether replacing Ce with Gd added ferromagnetic interactions that might affect the magnetostriction. Here we report some of our susceptibility, resistivity, magnetization, and specific-heat measurements on this system for $0.08 \leq x \leq 0.9$ which show that the interactions between the Gd moments are surprisingly strong in this host. Further, we have observed several new phenomena connected with heavy fermions, spin glasses, and percolation.

Because the host is unusual it is worthwhile to briefly describe its properties. At high temperatures the Ce atoms in $CeAl_3$ are magnetic and have approximately the expected Hund's-rule moment. At low temperatures the system goes into a Kondo singlet ground state.[4-9] It is less clear how the Gd moments will interact in this host. For $0.08 \leq x \leq 0.9$, we observe susceptibility anomalies (see Fig. 1) which resemble spin-glass transitions. For $x \leq 0.50$, these anomalies are cusps while for $x = 0.635$ and 0.77 we only observed step increases. We denote the temperature at which these anomalies occur as T_m. The phenomena due to the interacting Gd moments occur in two composition ranges.

(1) For $0.05 \leq x \leq 0.4$ and $T = 2$ K, the spontaneous magnetization M_s is approximately 10% of the value possible from just the Gd moments (see Fig. 2), i.e., this property scales with x. For $x \leq 0.23$, the system is still a HF system as determined by specific-heat measurements.

(2) For $x > 0.4$, the amplitude of the susceptibility maximum peaks as one approaches (from below) the percolation threshold for antiferromagnetism at $x \equiv x_c \approx 0.5$. For $x = 0.5$, M_s is approximately 40% of the value possible from just the Gd moments (see Fig. 2). For $x > x_c$, T_m does not change abruptly but the amplitude of the susceptibility at the maxima decreases by more than two orders of magnitude (see inset of Fig. 1). A resistivity anomaly occurs at T_m for $x > x_c$ but not for $x < x_c$.[10] The Ce atoms are apparently responsible for the high values of T_m and the strong Gd-Gd interactions in this host. These values, approximately 100 K for $x \cong 0.5$, are surprisingly high since the ordering temperatures[11] of all the rare-earth trialuminides are less that 25 K. An indication that both the Ce and Gd are necessary for the high values of T_m is provided by the facts that no spin-glass transition was found[12] in (La,Ce)Al_3 and in our measurements on $La_{1-x}Gd_xAl_3$ with $x = 0.2$, 0.4, 0.6, and 0.8 for $5 \leq T \leq 300$ K.

We investigated arc-melted, polycrystalline samples[13] that had been annealed for two weeks at 980 °C. X-ray diffraction analysis shows that the lattice parameters of this system, which has the hexagonal DO_{19} structure (space group $P6_3/mmc$), varied approximately linearly as

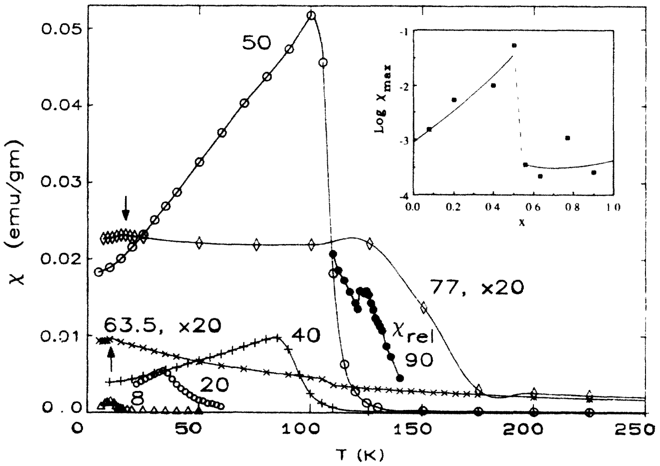

FIG. 1. χ of $Ce_{1-x}Gd_xAl_3$ vs T. The values for $x = 0.635$ and 0.77 have been multiplied by a factor of 20. The arrows indicate the antiferromagnetic transition in the $x = 0.635$ and 0.77 samples. The peak in χ_{rel} for $x = 0.9$ is 2% above the background. The inset shows the logarithm (base 10) of the susceptibility maxima (in emu/g) at T_m vs x.

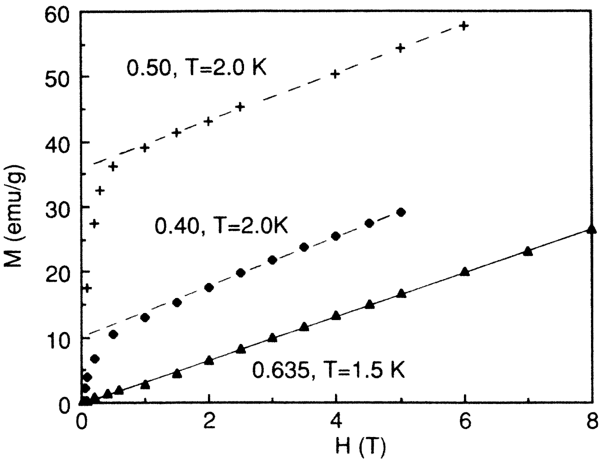

FIG. 2. Magnetization M at low temperatures vs field H for $x=0.40$, 0.50, and 0.635.

a function of Gd concentration. Because of the inherent difficulty of preparing single-phase samples, we present the following evidence that the transition at T_m is due to the (Ce,Gd)Al_3 phase.

(1) *Evidence against the dialuminide phase being responsible.* A few samples which exhibited two transitions had one at T_m and the other at the Curie temperature[14] of (Ce,Gd)Al_2, the dialuminide phase. The magnitude of the susceptibility at T_m correlated with the amount of trialuminide and inversely correlated with the amount of dialuminide as determined by x-ray diffraction. Less careful annealing caused the transition at T_m to disappear but not the dialuminide transition. None of our conclusions depend upon data taken on these samples exhibiting two transitions.

(2) *Evidence against the 3:11 phase being responsible.* No transition was observed at T_m in $(Ce_{0.55}Gd_{0.45})_3Al_{11}$. The drastic change we observe for $x>0.5$ is not connected with the disappearance of the 3:11 phase since we have found that this phase persists up to at least 65 at.% Gd.

(3) *Evidence against either the dialuminide or the 3:11 phase being responsible.* It is difficult to understand how the presence of the dialuminide or the 3:11 phase could give rise the appearance of a resistivity anomaly for $x>x_c$ but not for $x<x_c$.

The susceptibility measurements were made in low fields (three to several tens of Oe) using superconducting quantum interference device (SQUID) magnetometry. Most measurements were performed with increasing temperature after the sample had been cooled in the lowest available field, 1-5 Oe. Figure 1 is a plot of the susceptibility χ vs T for several samples. One sees that for $x\leq 0.50$ there is a cusp, which resembles that at the freezing temperature of a spin glass,[1] at the temperature T_m. Additional support for associating T_m with a spin-glass transition temperature at low Gd concentrations, is given by other observations on the $x=0.08$ sample. (1) We observed[10] the usual difference between initial cooling in "zero" field or in a field. (2) After cooling in "zero" field and then applying a field we observed a slow small upward drift in the susceptibility. Further, comparison of the specific heat C for $x=0.08$ with that for $CeAl_3$ on an expanded scale shows the existence of a broad shoulder near 8 K, consistent with a spin-glass transition at $T_m=11$ K.

Fitting the inverse susceptibility data above T_m for all the samples other than $x=0.50$ to a Curies-Weiss form $T-\Theta$, one obtains a very small value for the intercept Θ ($\Theta \ll T_m$). This is the usual behavior of a spin-glass system. For $x=0.50$, Θ is large and positive. This is consistent with considerable ferromagnetic coupling.

The amplitude of the susceptibility anomalies shown in Fig. 1 is a strong function of x. This is illustrated more clearly in the inset of Fig. 1 where we plot the *logarithm* of the susceptibility maximum at T_m as a function of x. The amplitude of the susceptibility at T_m *decreases two orders of magnitude* between $x=0.5$ and 0.56. We now show that this decrease correlates with the onset of antiferromagnetism.

For $x=0.635$, 0.77, and 0.90 (not shown), in addition to the anomaly at T_m, there is also a low-temperature anomaly[15] below 20 K (shown by an arrow). We associate the latter with an antiferromagnetic transition because of the following. (1) $GdAl_3$ is an antiferromagnet[11] with $T_N=17$ K. (2) The specific heat of $Ce_{0.23}Gd_{0.77}Al_3$ shows characteristics of an antiferromagnetic transition.[10] There is a cusp at 13.7 K, and for $0.32\leq T\leq 1.0$ K, $C=20.5T+98T^3$ (mJ/mol K). The T^3 coefficient is approximately 100 times greater than a typical lattice contribution and is of the form expected for antiferromagnetic spin waves.[16]

Measurements of the low-temperature magnetization M shown in part in Fig. 2, provide further evidence that the magnetic character of the system changes for $x>0.5$. (Measurements[3] of M for $x=0.05$ and 0.20 are omitted for clarity.) For $x\leq 0.50$ and $T<T_m$, a linear extrapolation of the high-field part of M gives a finite $H=0$ intercept M_s. For $x\leq 0.40$, $M_s \propto x$. For $x=0.5$, M_s is approximately four times larger than for $x=0.4$. Apparently M_s increases at a faster rate between 0.4 and 0.5. This result suggests that the fraction of spins that are correlated increases as x approaches 0.5 from below. By contrast, no portion of M saturates at low fields for $x=0.635$. For $x=0.635$, $M\propto H$ up to our highest fields, 8 T.[17] Such a linear field dependence is associated with antiferromagnetic interactions. These data suggest that ferromagnetic interactions dominate for $x\leq 0.5$ and antiferromagnetic interactions dominate for $x\geq 0.635$.

Specific-heat measurements[10] have determined the range in x for which the system exhibits HF behavior. The $T=0$ intercepts of C/T, γ, are 1.20, 1.24, 0.41, 0.048, and 0.021 J/mol K^2 for $x=0$, 0.08, 0.23, 0.50, and 0.77, respectively. Using Stewart's criterion[2] $Ce_{1-x}Gd_xAl_3$ is a HF system for $x\leq 0.23$.

As one would expect the HF contribution to γ, γ_{HF}, is reduced by dilution since $\gamma_{HF}\propto(1-x)/T_K$. In addition, the presence of a spin-glass state would give rise to two competing effects. The low-temperature portion of the spin-glass specific-heat anomaly increases γ, but the HF contribution to γ is decreased by the effective internal field of the spin-glass state. To be more quantitative about this we employ a type of resonant level model

(RLM) to interpret the specific heat of the $x=0.23$ sample. Previously we applied [18] a RLM, which included the crystal-field contribution, to $CeAl_3$. We now also include the distribution of an effective internal field H_{eff} of a spin-glass state.[19] We assume the following. (1) The Ce atoms give rise to a Lorentzian density of states peak which, in zero field, is centered at the Fermi energy. We take for the width of the Lorentzian the same value as we used[18] for $CeAl_3$, 4.5 K (the Kondo temperature T_K of $CeAl_3$). (2) A magnetic field (either applied or internal) rigidly shifts the up and down spins density of states in different directions relative to the Fermi energy. (3) The values of H_{eff} in the c-axis direction have a Gaussian probability distribution centered at H_0. The component of H_{eff} perpendicular to the c axis is taken to be zero because its contribution is small.[18] We have chosen $\mu=\frac{6}{7}\times\frac{3}{2}\mu_B$, $H_0=6$ T and considered two values for the Gaussian's half width, 2 and 6 T.

Experimental and calculated values of C/T for $x=0.23$ are shown in Fig. 3. The curves of the calculated values have the correct general shape at high temperatures but do not reproduce the large decrease that occurs below 1 K. This decrease may be due to spin fluctuations. Doniach[20] has shown that spin-density-wave fluctuations can be the source of the peak in C/T of $CeAl_3$ and it was demonstrated [7] that a temperature-dependent width in the RLM can also be used to obtain this temperature dependence.[21] To not introduce additional parameters in the present calculation, we have used a temperature-independent width.

The values calculated above represent only the heavy-fermion contribution to C/T. One should add to these values the contribution from the low-temperature portion of the spin-glass specific-heat anomaly. This contribution is of the form for $\gamma_{SG}T$ for $T \ll T_m$. Using our specific-heat data for the $x=0.08$ sample, we estimate $\gamma_{SG}\sim 0.08$ J/mol K^2. One can also use the model to show that there is a γ_{SG} contribution to C/T by assuming the H_{eff} acts on the Gd moments. Unfortunately the values one calculates for γ_{SG} are very sensitive to the choice of the width of the Gaussian.

Using our data we have constructed the tentative phase diagram shown in Fig. 4. Some of the boundaries are not clearly delineated either because there is not a sharp transition or because of insufficient data. We have arbitrarily taken the temperature on the HF "boundary" as the highest temperature for which the experimental values of C/T are greater than 0.40 J/mol K^2. The value on the antiferromagnetic boundary for $GdAl_3$ was taken from Ref. 11, but also corresponds to that derived from our measurement of C. Except for these cases, the values plotted in Fig. 4 are the temperatures of the susceptibility maxima or, if there is no maximum, a temperature just below the step increase in the susceptibility. Our susceptibility data permit us to determine that $0.5 \lesssim x_c < 0.635$. The fact that we were able to qualitatively fit the specific-heat data for $x=0.23$ by incorporating an effective field of a spin-glass state suggests that the HF state and the spin-glass state may coexist at low temperatures.

Though the values of T_m appear to lie near a smooth curve, which does not change slope at x_c, our data indicate that there is at least a change in the character of the transition at x_c. For $x > x_c$ there is a decrease in the susceptibility anomaly, the appearance of the resistivity anomaly at T_m, and the qualitative change in the magnetization. We wish to emphasize that the state below T_m at high Gd concentrations may be quite different from the usual spin-glass state. Nevertheless, because we have no evidence that it is different and for want of a better name, we will call the state for both $x \le x_c$ and $x > x_c$ a spin-glass-like state.

Let us summarize our results. We have correlated the large decrease in the high-temperature susceptibility maximum, the qualitative change in M, and the appearance of

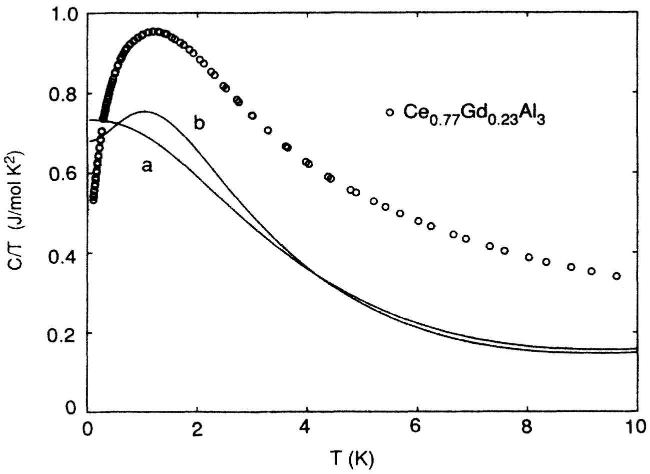

FIG. 3. Comparison of experimental and calculated values of C/T vs T for $Ce_{0.77}Gd_{0.23}Al_3$. The two curves are the values calculated from the model for $H_0=6$ T for a half-width at half maximum of 6 T (curve labeled a) and for a half-width at half maximum of 2 T (curve labeled b).

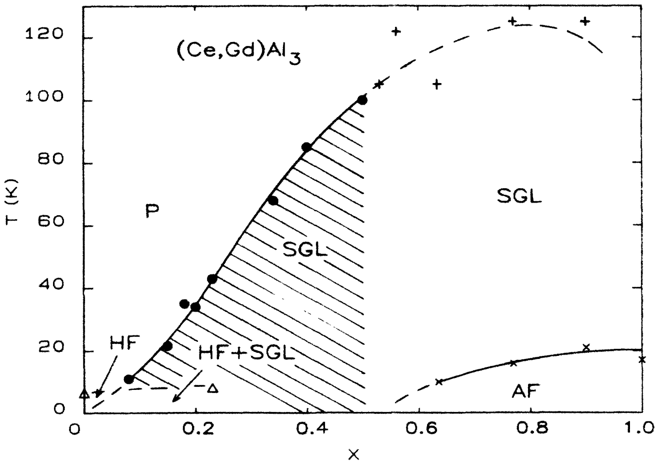

FIG. 4. Tentative phase diagram. The symbols AF, HF, P, and SGL represent the antiferromagnetic, heavy-fermion, paramagnetic, and spin-glass-like phases, respectively. The dashed curve representing a transition from a paramagnetic state into a spin-glass-like state curves down at large x since T_m has to go to zero at $x=1$.

a resistivity anomaly with the onset of antiferromagnetism at x_c. Both the distribution of the interactions and the change in topology at x_c probably play a role. The increase in M_s between $x = 0.4$ and 0.5 suggests that the fraction of the Gd atoms participating in the spin-glass-like transition increases rapidly as one approaches $x_c \cong 0.5$ from below. For $x < x_c$ ferromagnetic interactions appear to dominate, while for $x > x_c$ antiferromagnetic interactions appear to dominate even at temperatures as high as 100 K. ($M \propto H$ for $x = 0.635$ even near T_m and a linear field dependence is suggestive of antiferromagnetic interactions.) Nearly all the spins, including the Ce, may become correlated for $x > x_c$. This is suggested by two facts: (1) the curvature exhibited by the magnetization of CeAl$_3$ as a function of field at low temperatures, and (2) $M \propto H$ for $x = 0.635$ at $T = 2.0$ K.

The high values of T_m relative to the ordering temperature of other rare-earth trialuminides, and the absence of a spin-glass-like transition in the isostructural series (La,Gd)Al$_3$, point to the important role of the Ce atoms.[22]

The large γ values observed in HF systems are thought to be an indication of many-body peaks (one for each spin direction) in the density of states at the Fermi energy. Such peaks played a central role in both the model used[17] to fit CeAl$_3$ data and the generalized model employed here to interpret the specific-heat data for $x = 0.23$. The generalized model incorporates an internal field of the spin-glass state which acts on the peaks in the density of states in this HF system. Thus our work provides some insight into both spin-glass and HF systems.

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