Magnetic order and moment reduction in Ce$_{1-x}$Th$_x$Al$_2$

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The magnetic-ordering temperature versus concentration (x) in the Ce$_{1-x}$Th$_x$Al$_2$ system has been determined for $x \leq 0.4$ via thermal-expansion measurements. Our results are discussed in terms of the suppression of spin fluctuations with increasing $x$ and of magnetic dilution.

CeAl$_2$ is an intermetallic compound with a local moment magnetically ordered ground state$^{1-3}$ at ambient pressure and with a volume collapsed nonmagnetic ground state above 40–70 kbar.$^{4,5}$ The magnetic-nonmagnetic instability which must logically occur between these two states has only begun to be examined experimentally.$^6$ The first indicator of this instability is a partial demagnetization of Ce at low temperatures in CeAl$_2$.$^{3,6}$ The view of these ambient pressure “Kondo-like” effects are the precursors of the high-pressure nonmagnetic state is supported by moderate pressure$^{7,8}$ and ternary compound studies.$^9,10$ These studies indicate that the degree of moment reduction increases continuously with compression of the lattice in this system.

In the ternary system Ce$_{1-x}$Th$_x$Al$_2$ we propose that increasing $x$ carries one away from the nonmagnetic state. Our results support the premises (i) that the ordering temperature of CeAl$_2$ is suppressed by moment reduction due to nonmagnetic effects; and (ii) that nonmagnetic effects in CeAl$_2$ are rapidly quenched by the Th substitution.

I. EXPERIMENTAL

The samples were prepared in an argon arc furnace from stoichiometric amounts of the constituent metals. X-ray-diffractometry analysis revealed all samples were well formed in the MgCu$_2$ cubic Laves structure. The lattice constant, $a$, of the compound increased slightly with increasing $x$ according to $a = a_0 + \beta x$, where $a_0 = 8.054 \pm 0.002$, and $\beta = 0.008 \pm 0.004$. In accordance with the literature the hexagonal ThAl$_2$-type structure was not observed for $x \leq 0.4$; however, an $x = 0.5$ sample did show this second phase.$^{11}$

Inclusions of the hexagonal ThAl$_2$ structure$^{12}$ at levels up to 5% were also identified from the diffraction patterns. This is despite the standard 7-d 800°C anneal procedure followed for all samples. Work in our lab indicates that such inclusions are very difficult to avoid.

The details of the capacitive-dilatometric-length measurement, thermal-expansion-coefficient calculation, and thermometry, are identical to those reported previously for CeAl$_2$.$^{1,2}$

II. RESULTS

In Fig. 1 we show the critical anomaly in the thermal-expansion coefficients, $\alpha = L_0^{-1} dL/dT$ where $L_0$ is the length at 273 K, of several samples in the Ce$_{1-x}$Th$_x$Al$_2$ system. Based on results for CeAl$_2$ we identify the negative peak in $\alpha$ as the antiferromagnetic (AF) transition temperature $T_N$. The AF phase boundary in the temperature-concentration plane, as determined from such thermal expansion measurements, is shown in Fig. 2. There are two

![FIG. 1. Thermal-expansion coefficient vs temperature for several samples in the Ce$_{1-x}$Th$_x$Al$_2$ system. The normalizing length, $L_0$, is the length at 273 K. The peaks in the thermal-expansion coefficient mark the magnetic-ordering temperature.](image)
distinctive features to note in Fig. 2: (i) a slow fall off in $T_N$ for $x > 0.2$; and (ii) a rapid rise in $T_N$ for $0 \leq x < 0.2$ (see Ref. 11). We will discuss these two features below.

III. DISCUSSION

A. $x > 0.2$ behavior

As indicated in Fig. 2, the $x > 0.2$ ordering temperature versus concentration curve, $T_N(x)$, approaches the dashed line given by the linear relation $T_N^0(1-Dx)$ with $T_N^0 = 7$ K and $D = 0.66$. A mean-field treatment of simple magnetic dilution would yield a linear fall in $T_N(x)$ but with a slope of unity (not 0.66) and with an $x = 0$ intercept at 3.85 K (not 7 K). The high value of the $x = 0$ intercept will be discussed below in terms of moment reduction. The too large value of $D$ [a too-slow falloff in $T_N(x)$] we attribute to a strengthening of AF exchange upon Th substitution. This conclusion is supported by the anomalously rapid suppression of the ferromagnetic (FM) ordering temperature of Gd$_{1-x}$Th$_x$Al$_2$ with increasing $x$. In the Ce ternary, strengthened AF exchange enhances the energy of the AF ground state, whereas in the Gd ternary, it contributes to frustration in the FM ground state.

It should be noted that the spin-density wave of CeAl$_2$ (Ref. 14) and the proposed electronic origin for the crystallographic distortion at $x = 0.45$ in Ce$_{1-x}$Th$_x$Al$_2$ suggest that nonspherical (nested) Fermi-surface effects could be important in these systems.

B. $x < 0.2$ behavior

The dominant structure in the $T_N(x)$ curve is of course the rapid low-concentration enhancement of the ordering temperature. As pointed out in the preceding paragraph, an anomalous concentration dependence of the conduction-electron properties is a distinct possibility in this system and could possibly account for the low-$x$ behavior of $T_N(x)$. The absence of an analogous nonlinearity in the FM ordering temperature curve, $T_c(x)$, in the Gd$_{1-x}$Th$_x$Al$_2$ system, however, argues against this explanation.

We prefer the explanation that Th substitution acts to rapidly restore full moment behavior to the partially reduced moments of CeAl$_2$. We first present a phenomenological model aimed at estimating the influence of moment reduction on the magnetic-ordering temperatures of these ternary compounds. Then, we will discuss specific modifications in the system which we propose are caused by the Th substitution.

C. Phenomenological model for $T_N(x)$

In discussing the initial pressure dependence of the magnetic-ordering temperature, $T_N$, of CeAl$_2$, Croft et al. (Ref. 8) have assumed that $T_N$ can be expressed

$$T_N = T_N^0 F,$$

(1)

where $T_N^0$ is the full moment-ordering temperature and $F$ is a number less than or equal to 1. Here $F$ is intended to be a measure of the degree of reduction in the square of the effective Ce moment. In that discussion the decrease of $F$ was concluded to dominate the initial-pressure change of $T_N$.

In the Ce$_{1-x}$Th$_x$Al$_2$ system the suggestion that full moment behavior is restored for $x > 0.2$ corresponds to $F = 1$ for $x = 0.2$. Extrapolating the observed behavior of $T_N$ for $x > 0.2$ back to $x = 0$ (dashed line in Fig. 2) therefore yields estimates for pure CeAl$_2$ of the hypothetical full moment-ordering temperature $T_N^0 \sim 7$ K and the degree of reduction in the square of the magnetic moments $F = 0.55$. These estimates appear to be consistent with other experiments on pure CeAl$_2$.

Reference 8 provides us a crude estimate of $F$ in the approximate form

$$F \approx \frac{1}{1 + T_F/T_N^0}, \quad T_F \ll T_N^0,$$

(2)

where $T_F$ is the spin-fluctuation (Kondo) temperature. The dependence of $F$ on the ratio $T_F/T_N^0$ reflects the assumption that the degree of moment reduction
is determined by the competition of magnetic interactions with spin fluctuations.

This same phenomenology can be used to fit the observed $T_N(x)$ behavior shown in Fig. 2. By adjusting $x_D$ in the equation $T_f(x) = 5.7\exp(-x/x_0)$ and $D$ in the equation $T_f(x) = 7(1-Dx)$ the solid line passing through the data in Fig. 2 can be obtained. The authors wish to emphasize only one qualitative point in fitting this phenomenological model to the data: The rapid rise in $T_N(x)$ for $x < 0.2$ is, within this model, caused by the exponential decrease of the spin-fluctuation temperature, $T_f(x)$, from about 5.7 K at $x = 0$ to about 0.3 K at $x = 0.2$. The underlying cause for such an exponential relaxation in the energy scale for spin fluctuations will now be addressed.

D. $T_f(x)$ variation

Some years ago Buschow and van Daal first proposed such an exponential decay of the spin-fluctuation temperature in the Ce$_{1-x}$Th$_x$Al$_2$ system. Empirically they were motivated by their resistivity results. Theoretically they based their argument on the s-d Hamiltonian expression for the spin-fluctuation (Kondo) temperature

$$T_f = T_D e^{-|E/\Delta|},$$  \hspace{1cm} (3)

where $n$ is the density of conduction-band states, $T_D$ is the conduction-electron bandwidth and $j$ is the Kondo s-d exchange constant. They proposed that the density of states $n$ decreased with increasing $x$ thereby causing an exponential decrease in $T_f$ in the Ce$_{1-x}$Th$_x$Al$_2$ system.

Our discussion is based on the single-impurity Anderson model (with infinite correlation energy) expression for the spin-fluctuation temperature,

$$T_f = T_D e^{-|E/\Delta|},$$  \hspace{1cm} (4)

where $E$ is the energy of the local level relative to the Fermi level, and $\Delta$ is the Friedel width of the local level. The two expressions for $T_f$ and the Hamiltonians from which they are derived, have been shown to be equivalent provided $|E/\Delta| > 1$.

To motivate our argument we wish to consider the relative change in the 4f-level energy, $E$, between CeAl$_2$ and Ce$_{0.5}$Th$_{0.5}$Al$_2$. Using the density of states $n=0.5$ states/eV atom for LaAl$_2$, and the rigid-band assumption that each Th$^{4+}$ atom substituted for a Ce$^{4+}$ atom contributes one extra conduction electron, one finds that $|E|$ increases by about 700 K between $x = 0$ and 0.1. In general, for Ce compounds with a strong Kondo effect and for CeAl$_2$ in particular, $|E|$ is estimated to be in the hundreds of degrees$^{14}$.

Therefore $|E|$ can potentially more than double between $x = 0$ and 0.1. We believe that it is this band-filling increase in $|E|$ that causes an exponential decrease of $T_f$ in this system.

The mechanism of Buschow and van Daal may also be involved in this system because the Friedel width $\Delta$ is proportional to the density of states $n$. Nevertheless, the magnitude of the effect due to band filling and its potential for generalization to other systems make it the more attractive to the authors. Indeed there is evidence that our arguments can be applied directly to the Ce$_{1-x}$Th$_x$Al$_2$ system.

Finally, the authors would like to point out that our empirical value of $x_D = 0.066$ in the relation $T_f(x) = T_f(0) \exp(-x/x_0)$ is nearly an order of magnitude larger than would be estimated using a rigid-band model. Either a failure of the simple rigid-band approximation or an effective Th band contribution of less than four electrons could cause this discrepancy. Another explanation, consistent with recent photoemission experiments on similar Ce systems, is that the 4f-level—Fermi-energy separation ($|E|$) is not of the order 0.1 eV but is of the order 1 eV$^{19}$.

IV. SUMMARY AND CONCLUSION

We have reported a rapid rise and subsequent slow fall off in the ordering temperature $T_N$ of the Ce$_{1-x}$Th$_x$Al$_2$ system with increasing $x$. We have attributed the rise in $T_N$ to an exponential suppression of the spin-fluctuation energy scale, $T_f$, and the fall-off in $T_N$ to magnetic dilution. We have proposed that conduction-band filling caused the exponential suppression of $T_f$ consistent with ideas from the single-impurity Anderson model. Finally, it is interesting to note that the effect of Th substitution in CeAl$_2$ appears to be exactly opposite in its effect on elemental Ce, where Th substitution is an $\alpha$-state stabilizer.$^{20}$

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