Title
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Publication Date
1986-05-01

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Materials & Molecular Research Division

Presented at the International Conference on Anomalous Rare Earths and Actinides, Grenoble, France, July 7-11, 1986; and to be published in Journal of Magnetism and Magnetic Materials

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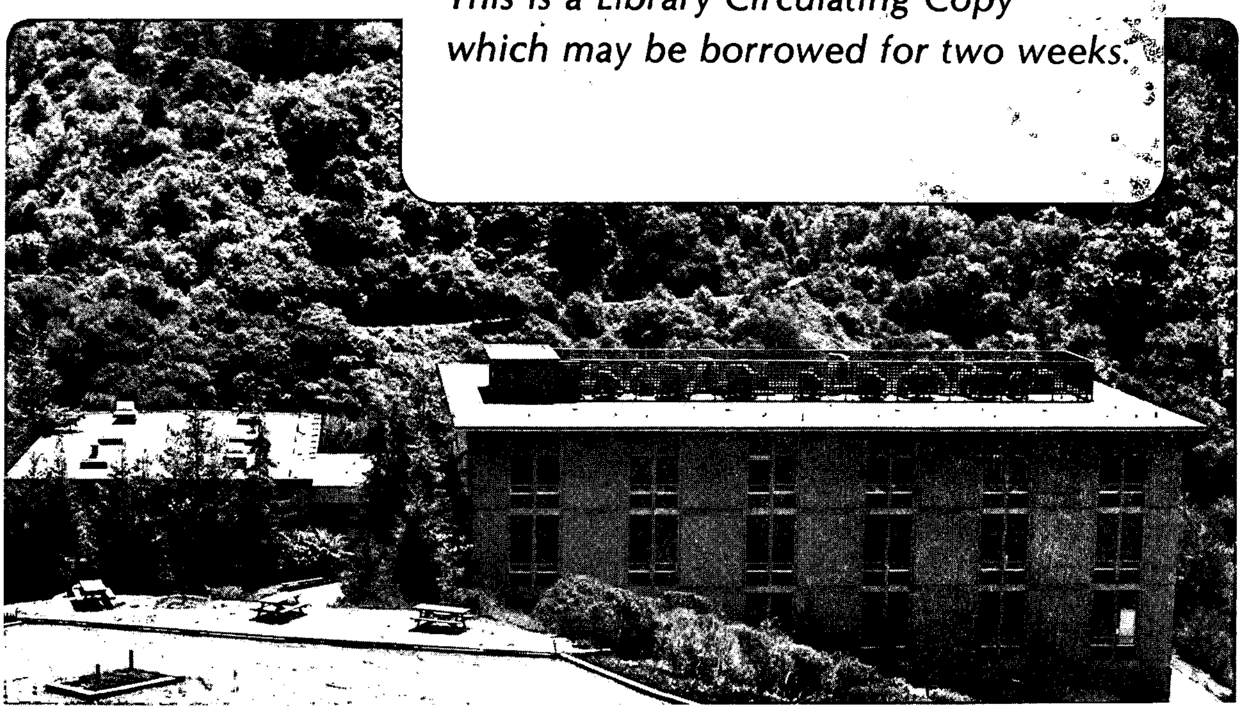

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Heavy-Fermion, Kondo, Spin Glass-like, and Antiferromagnetic Behavior in (Ce,Gd)Al_3

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We have found that $Ce_{1-x}Gd_xAl_3$ with x=0.23 is a heavy-fermion system which undergoes a spin glass transition. The amplitude of the peak in the susceptibility that characterizes the spin glass transition passes through a sharp maximum at x=0.5. For x=0.635 and 0.77 the system undergoes a spin glass-like transition at $T \approx 100$ K and an antiferromagnetic transition at $T \approx 20$ K.

PACS numbers: 75.20.Hr, 75.30.-m, 75.30.Kz, 75.20.En

Abreviated running title: Heavy-Fermion, Spin-Glass, Antiferromagnetic (Ce,Gd)Al_3

Key words: heavy-fermion, spin-glass, antiferromagnetism

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The definition[1] of a heavy-fermion system as one for which $\gamma \geq 400$ mJ/mole-K^2 (where γ is the $T \rightarrow 0$ ratio of the low temperature specific heat C to the temperature T) is arbitrary, but useful and frequently adopted. Some heavy-fermion systems undergo a superconducting transition[2-4] or order antiferromagnetically[5,6] while others do not undergo either transition.[1]

Here, we present susceptibility data[7] which demonstrate that $Ce_{1-x}Gd_xAl_3$ with x=0.23 undergoes a spin glass transition with a freezing temperature, T_m, of 43 K and specific heat data which shows that it has a large enough low temperature γ value (410 mJ/mole-K^2) to be characterized as a heavy-fermion system. Several points should be emphasized. First, we find this transition persists to high concentrations. Second, the Ce atoms, which are responsible for the heavy-fermion character of the system, are also necessary for the large value of T_m. Third, the spin glass transition occurs at a much higher temperature than the temperature region where the heavy-fermion nature of the system was established. Because of this, one might expect the system as a whole to be altered by the spin glass transition. The data indicates that the two phenomena affect one another. The spin glass transition would probably not occur at these high temperatures if the system were not a heavy-fermion system. On the other hand, the specific heat and hence the heavy-fermion character of the system appears to be modified by the spin glass transition.

Another highly unusual result that we have obtained is that, for x=0.635 and x=0.77 there is both a spin glass-like transition near 120 K and an antiferromagnetic transition near 20 K. For $0.635 \leq x \leq 0.9$ and T<20 K the spin glass-like and antiferromagnetic states probably coexist.

Though most studies on spin glasses have been confined to nonmagnetic hosts, we have employed a rather special magnetic host, the heavy-fermion compound[8-11] $CeAl_3$. $CeAl_3$ exhibits local moment behavior at high temperatures, but at low temperatures, instead of magnetically ordering, it goes into a Kondo singlet ground state. The nature of the host is clearly important for the formation of spin glass order, since in the present work, we did not observe a spin glass transition in $La_{1-x}Gd_xAl_3$ for x=0.2 and 0.4, $5 \leq T \leq 50$ K. Thus the spin glass behavior reported here provides evidence that the Ce atoms assist the interaction between the Gd atoms.

Other unusual features we have observed in $Ce_{1-x}Gd_xAl_3$ are: 1) The amplitude of the anomaly in the susceptibility that occurs at the transition peaks sharply at x=0.50. 2)The values of T_m, which are greater than 100 K for x>0.5, are surprisingly high considering that the magnetic ordering temperatures of all the rare earth trialuminides[12] are less than 25 K. 3) The occurrence of the transition is sensitive to sample quality.

Our investigations were performed on arc melted, polycrystalline samples which had been annealed for two weeks at 980 ^{0}C. X-ray diffraction analysis indicates that all the samples had the correct DO_{19} structure and that the lattice parameters varied smoothly as a function of Gd concentration. Some of the samples show the presence of small amounts of a second phase with the Ce_3Al_{11} structure.

Figure 1 is a plot of low field susceptibility χ versus T for x=0.08. One sees that, similar to what is observed in a spin glass freezing transition, there is a cusp in the susceptibility if the sample is cooled in zero field, but the cusp is no longer present if the sample is cooled in a field of 10 Oe. Most measurements were performed with increasing temperature after the sample had been cooled in "zero" field. Measurements made on samples with x=0.15, 0.18, 0.20, 0.34, 0.40 and 0.50 show similar spin glass-like cusps. Also, another similarity to a spin glass transition, is the fact that the temperature at which the cusp occurs, T_m, increases roughly proportional to x. The amplitude of the anomaly increases as a function x up to x=0.50. For x>0.5 there is still a high-temperature anomaly in the susceptibility, but the amplitude of the susceptibility maximum decreases approximately two orders of magnitude in going from x=0.5 to 0.635. We have observed this high-temperature anomaly for x=0.635, 0.77, and 0.90. The temperatures at which the high-temperature anomaly occurs for x>0.5 falls on a smooth curve which is an extension of the curve for x≤0.5. In addition for x>0.5 there is a second maximum in the susceptibility which occurs at T≈ 20. Because $GdAl_3$ is an antiferromagnet with a Neel temperature of 17 K and from the specific heat data presented below, we identify the low temperature transition as an antiferromagnetic transition.

Some of our samples for which we deviated in our sample preparation procedure failed to exhibit a spin glass transition. Sensitivity to sample quality was observed[13] in the magnetic ordering of the heavy-fermion U_2Zn_{17}.

Specific heat data on $Ce_{.77}Gd_{.23}Al_3$ and $Ce_{.23}Gd_{.77}Al_3$ are compared with data[10] on $CeAl_3$ in Fig. 2 where C/T versus T is plotted. From the T=0 intercept, one sees that $Ce_{.77}Gd_{.23}Al_3$ (γ= 410 mJ/mole-K^2) is a heavy-fermion system but that $Ce_{.23}Gd_{.77}Al_3$ (γ=20.5 mJ/mole-K^2) is not. The general shape of the curves is similar for $CeAl_3$ and $Ce_{.77}Gd_{.23}Al_3$ except that the peak in C/T occurs at a higher temperature in the case of $Ce_{.77}Gd_{.23}Al_3$. The entropy per mole at 10 K found by integrating C/T is approximately the same for $Ce_{.77}Gd_{.23}Al_3$ and $CeAl_3$. Since the spin glass transition is absent in (La,Gd)Al_3, the Ce atoms must be playing a role in the spin glass transition in $Ce_{.77}Gd_{.23}Al_3$. Despite this, the entropy comparison seems to indicate that below the spin glass-like freezing temperature T_m nearly all the Ce atoms are contributing to the heavy-fermion character of the system. The insert shows the antiferromagnetic transition in $Ce_{.23}Gd_{.77}Al_3$. For $0.32 \leq T \leq 1.0$ K this data can be fitted to $C=20.5T+98T^3$ (mJ/mole-K). The T^3 coefficient is approximately 100 times greater than a typical lattice contribution and is like one expects for antiferromagnetic spin waves. A similar T^3 contribution was observed[5] for heavy-fermion antiferromagnetic U_2Zn_{17}.

In general the resistivity resembles[14] that of (Ce,M)Al_3 for M= La, Y, and Th. Figure 3 shows a plot of the resistivity for x=0.635 as a function of both increasing and decreasing temperature. We attribute the difference between these two cases to difficulty in making ideal contact to the sample. The resistivity for T<100 K, is similar to the resistivity of other concentrated Kondo systems, and can be interpreted in terms of crystal field and interference effects. However, for T=125 K there is an additional, unusual anomaly which was not observed in the measurements[14] on (Ce,M)Al_3. Because this additional resistivity anomaly occurs at the same temperature as the high-temperature susceptibility anomaly, it is likely that they are signatures of the same transition. This resistivity anomaly is absent for $x \leq 0.5$. One only expects to observe a resistance anomaly if the range of the order is at least as large as the mean free path. Thus we tentatively conclude from the existence of the resistance anomaly when x is greater than the threshold for antiferromagnetic percolation that the range of the ordering at T_m is at least comparable to the mean free path.

Using our data we have constructed the tentative phase diagram shown in Fig. 4. We have arbitrarily taken the temperature at the heavy-fermion phase boundary as the highest temperature for which $C/T \geq 400$ mJ/mole-K^2. The value on the antiferromagnetic boundary for $GdAl_3$ was taken from Ref. 12. Except for these cases, the values plotted in Fig. 4 are the temperatures of susceptibility maxima. One sees there is a concentration range, $x \leq 0.23$, where there is a spin glass transition and the system is still a heavy-fermion system. For $0.635 \leq x \leq 0.90$ there is a spin glass-like transition followed by an antiferromagnetic transition at lower temperatures. Because of the high temperatures of the spin glass-like transitions, it is likely that the alignment of the spins involved is not affected very much by the antiferromagnetic transition. Thus we suggest that these two phases may coexist. Wong et al. have reported[15] the coexistence of the spin glass and antiferromagnetic states in $Fe_{.55}Mg_{.45}Cl_2$. In contrast to the present case, for $Fe_{.55}Mg_{.45}Cl_2$ the antiferromagnetic transition (T_N=7.0 K) is above the spin glass transition (T_f=3.0 K).

Two facts suggest that the Ce atoms play a very important role. First, the values of T_m for x>0.3 are so much larger than the ordering temperatures of the rare earth trialuminides. Secondly, our measurements on the isostructural series $(La,Gd)Al_3$ fail to show a spin glass transition. Since apparently both the Ce and Gd atoms play a role in the transition, it is reasonable to suppose that local regions containing both Ce and Gd atoms are involved. These may be regions in which the Gd atoms primarily have Ce nearest neighbors and Gd second nearest neighbors. Recent theory [16] is consistent with the possibility that the second nearest neighbor coupling, mediated by an intervening Ce atom, is quite different from the the usual RKKY interaction and stronger than the nearest neighbor coupling. A simple alternative explanation for this increase in coupling is that it is due an increase in the density of states. The fact that the magnitude of the susceptibility peaks strongly at x=0.5 suggests that the ferromagnetic coupling is maximized when these regions contain a nearly equal number of Ce and Gd atoms. For x>0.5 the number of Gd spins that are not affected by the Ce atoms,and which interact with weaker antiferromagnetic interactions, increases rapidly with increasing x. These rapid changes with concentration may be due to a type of magnetic percolation of ferromagnetic and antiferromagnetic regions.

In conclusion, in $Ce_{1-x}Gd_xAl_3$, for x=0.23 we have observed a spin glass transition in a heavy-fermion system while for x=0.635, 0.77 we have observed both spin glass-like and antiferromagnetic transitions. Both the Ce and Gd atoms are involved in the spin glass and spin glass-like transitions.

We wish to thank Prof. Chia-Ling Chien for the hospitality extended to us during our measurements at Johns Hopkins University. The work at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Figure Captions

1. Susceptibility of $Ce_{.92}Gd_{.08}Al_3$ versus increasing temperature after the sample was first cooled in zero field and in decreasing temperature in a field of 10 Oe.

2. The specific heat C divided by the temperature T for $CeAl_3$, $Ce_{.77}Gd_{.23}Al_3$ and $Ce_{.23}Gd_{.77}Al_3$. The specific heat of $Ce_{.77}Gd_{.23}Al_3$ is plotted in the insert.

3. Resistivity of $Ce_{.365}Gd_{.635}Al_3$ versus T.

4. Tentative phase diagram. The symbols AF, HF, P,and SGL represent the antiferromagnetic, heavy-fermion, paramagnetic, and spin glass-like phases. The text describes how the values were chosen.

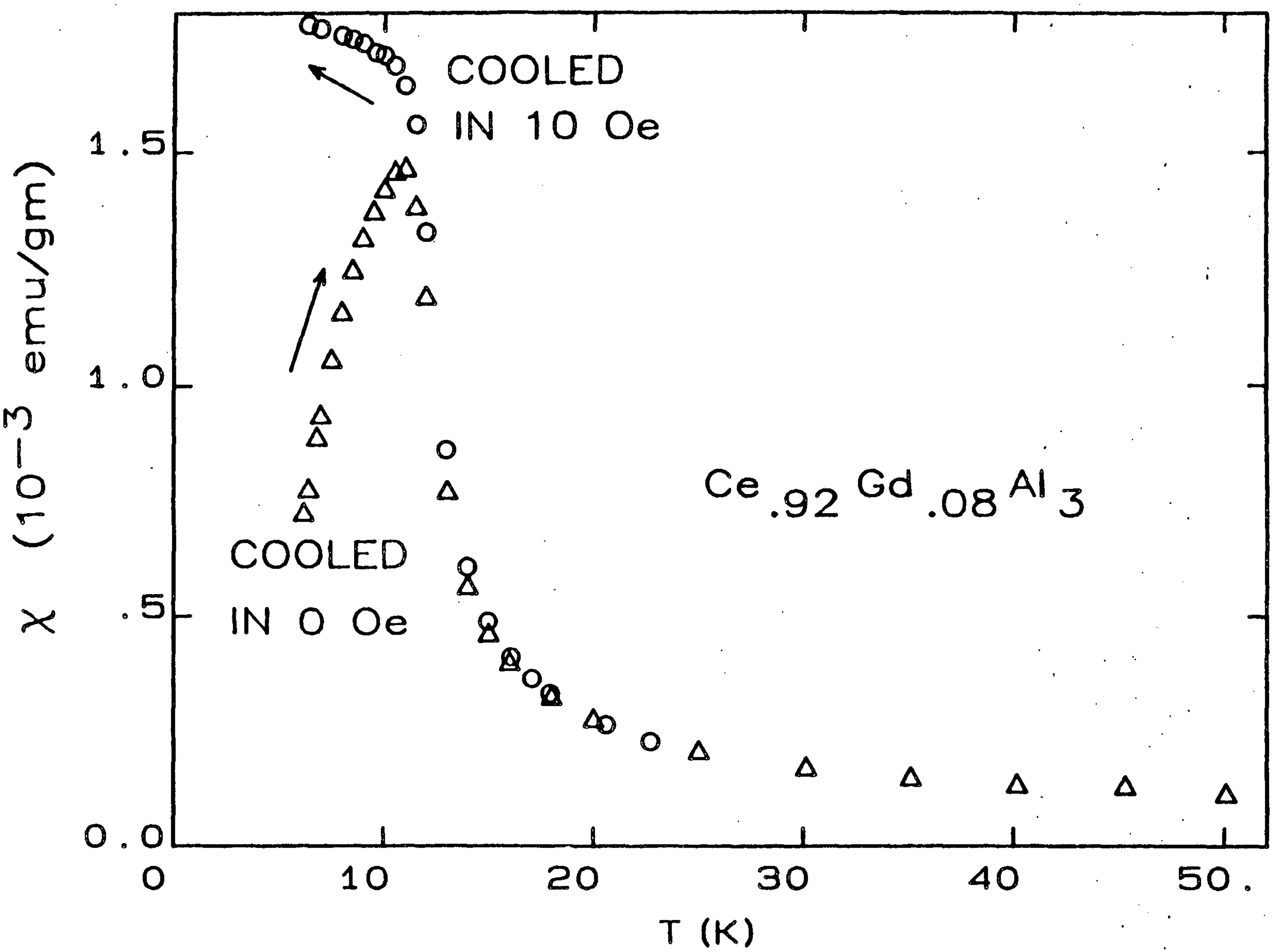
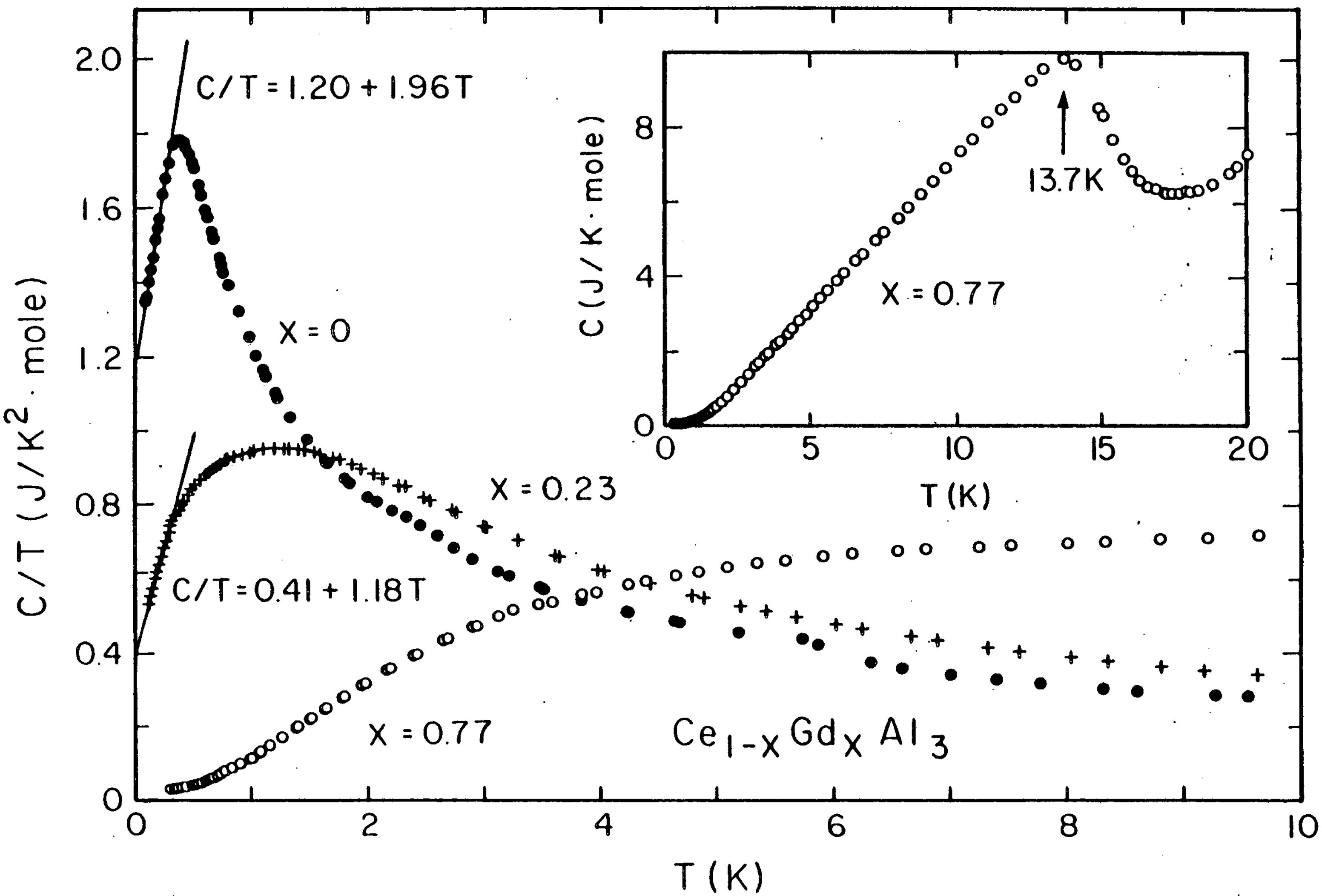

COOLED
IN 10 Oe
COOLED
IN 0 Oe
Ce .92 Gd .08 Al 3
χ (10^-3 emu/gm)
1.5
1.0
.5
0.0
0
10
20
30
40
50.
T (K)

Fig. 1



XBL 861-345A

Fig. 2

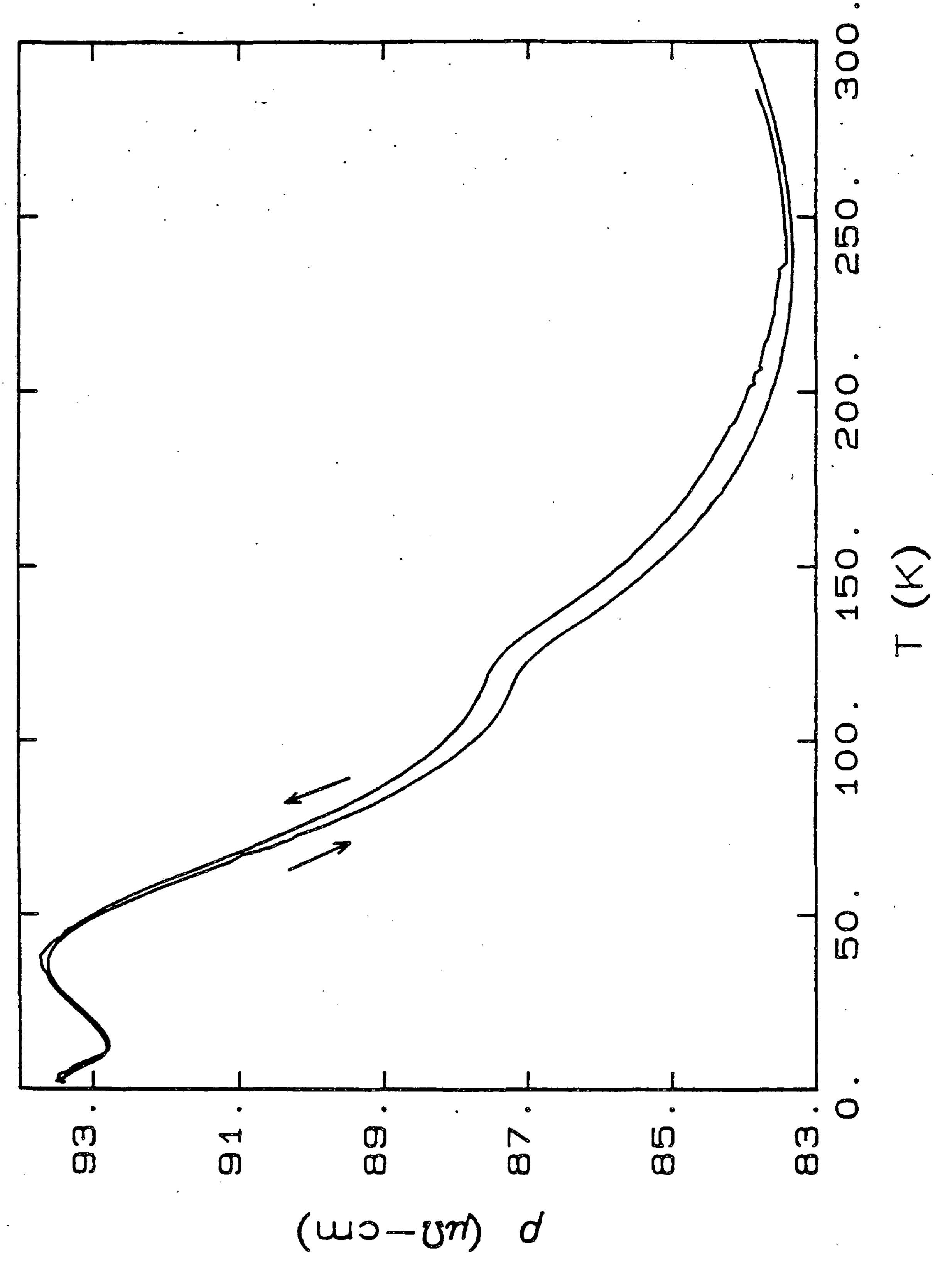


Fig. 3

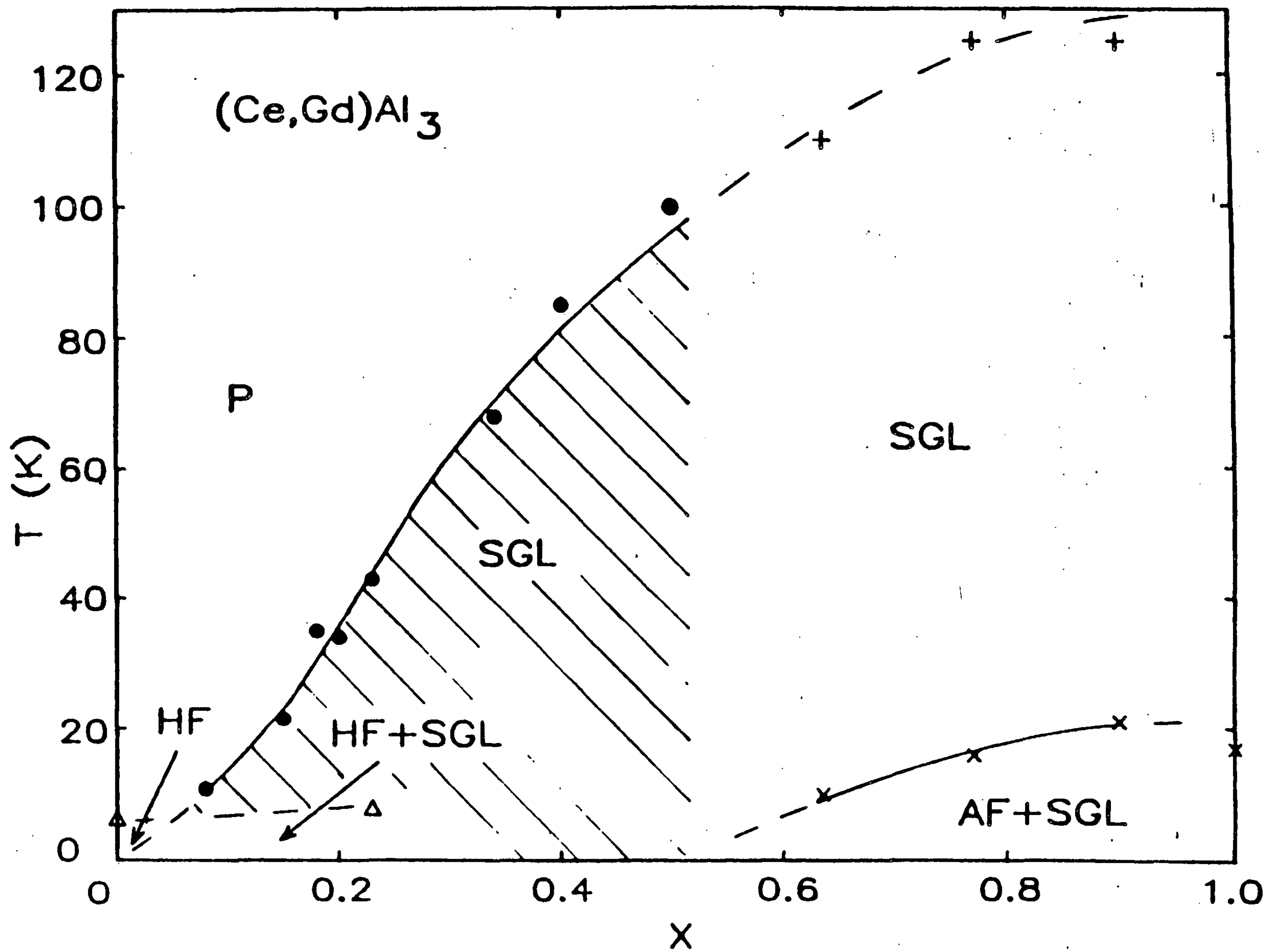

(Ce,Gd)Al3
T (K)
X
P
SGL
HF
HF+SGL
AF+SGL
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1.0

Fig. 4