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Evolution of the electronic specific heat of (La 1−x Ce x) 3 Al

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The specific heat of $(La_{1-x}Ce_x)_3Al$ was measured in the temperature range from 2 to 30 K as function of the Ce concentration. The electronic specific heat for small x is close to the normal metal value (14 mJ/K^2 mol f.u.), increasing to a maximum of 410 mJ/K^2 mol Ce for $x \sim 0.4$, characterizing a heavy-fermion behavior around this concentration. Above this critical concentration, the electronic specific heat decreases to 140 mJ/K^2 mol Ce for $x = 1$. From the fitting of the experimental data to Debye and Schottky type Kondo and crystal field contributions we estimated the Kondo temperature, θ_D, Δ_1, and Δ_2. T_K was found to increase with Ce concentration. Our results are interpreted in view of the competition between Kondo effect and Ruderman–Kittel–Kasuya–Yosida interaction. © *1997 American Institute of Physics.* [S0021-8979(97)70808-9]

I. INTRODUCTION

Many Ce based compounds have been used to study the very interesting properties attributed to the $4f$ electrons. In many cases the concentration of a transition element is changed[1] to promote variation of the exchange parameter J and density of states ρ because these parameters are critical for the physical properties under investigation. In particular, the competition between the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction and the Kondo effect have motivated many studies with this class of compounds.

A very appropriate technique for this study is the specific heat measurement because it is sensitive to magnetic ordering, Kondo effect and crystal field (CF) contributions. Under this aspect we believe that α-Ce$_3$Al is particularly interesting to be analyzed due to its characteristics. α-Ce$_3$Al has the Ni$_3$Sn hexagonal structure exhibiting a well defined minimum in the resistivity at 20 K, CF splitting to the first exited state close to 65 K and order antiferromagnetically at $T_N = 2.8$ K.[2,3] It is possible then to determine the contributions of the Kondo effect and CF to the specific heat of this material for temperatures in the range between 2 and 40 K. Substitution of the ligand in this case is complicated because of changes in the crystalline structure (for example, Ce$_3$In is cubic). Therefore, to get different ρJ values we substitute Ce by La since La$_3$Al is also hexagonal, and the series of compounds $(La_{1-x}Ce_x)_3Al$ was measured.

In this paper we present specific heat results for these compounds that are analyzed in terms of the different contributions. From these data we can obtain the behavior of the Kondo temperature as function of the Ce concentration.

II. EXPERIMENT

The samples were prepared from high purity materials in an arc-furnace in argon atmosphere. All samples were first submitted to a thermal treatment at 500 °C for at least three weeks. For $x > 0.2$ an additional period of two weeks at 200 °C was required to eliminate the cubic phase. X-ray and metallographic analysis indicate the formation of the hexagonal phase in the Ce rich side. For La$_3$Al and for small x, the results indicate the presence of eutectic phases in minor quantities. The x-ray results for La$_3$Al indicate hexagonal structure with lattice parameters $a = 7.25$ A, $c = 5.65$ A, which agree with the results reported by Buschow.[4] For Ce$_3$Al the lattice parameters are $a = 7.00$ A and $c = 5.42$ A.

The specific heat was measured using the thermal relaxation method using ~ 10 mg samples. The samples with 200 μm thickness were cut from the buttons using a diamond saw and polished prior to the thermal treatment.

III. RESULTS AND DISCUSSION

The specific heat for some Ce concentrations is shown in Fig. 1. For La$_3$Al a superconducting transition is found at $T_c \simeq 6$ K and this transition can be followed up to $x = 0.04$. A peak around 30 K can also be observed for $x = 0.7$ that corresponds to the first-order transition[2] found at $T_S = 100$ K for $x = 1$ (this transition is attributed to a change in the lattice parameters and was studied in details by Sakurai *et al.*[2]). For Ce$_3$Al the antiferromagnetic transition is clearly seen at
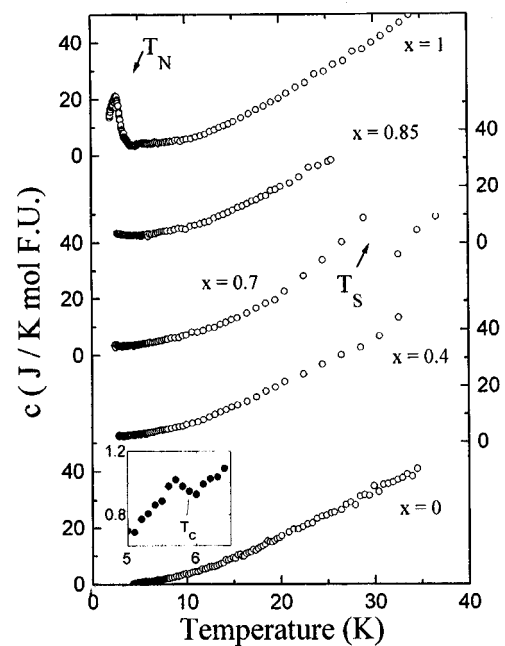

FIG. 1. $(La_{1-x}Ce_x)_3Al$ specific heat for several concentrations. For La$_3$Al the superconducting transition is shown in the inset. For $x = 0.7$ the first order transition is found close to $T_s = 30$ K and for Ce$_3$Al the antiferromagnetic transition is observed at $T_N = 2.8$ K.

TABLE I. Specific heat parameters as function of Ce concentration γ_{eff} and θ_{Deff} are obtained from the fit to $\gamma T + \beta T^3$. The remaining parameters results from a fit including Kondo, CF, and Debye contributions.

Concentr. (% of Ce)	γ_{eff} (mJ/K^2 mol Ce) (±10%)	θ_{Deff} (K) (±40 K)	γ (mJ/K^2 mol Ce) (±20%)	θ_D (K) (±20%)	Δ_1 (K) (±20 K)	Δ_2 (K) (±40 K)	T_k (K)
0	14[a]	123					
10	260	135	250	150	50	130	1(±2)
20	300	165	308	180	65	130	1(±1)
40	413	175	417	238	74	76	1.8(±1)
50	353	183	338	270	74	90	2.1(±1)
70	271	182	277	216	97	174	2.2(±0.5)
85	171	175	142	238	73	137	2.5(±0.5)
100	137	166	140	226	85	183	2.8(±0.5)

[a]γ_{eff} for La$_3$Al in mJ/K^2 mol f.u.

$T_N = 2.8$ K and for smaller concentrations this transition[2] is below 2 K, consequently out of our temperature range. Therefore, the increase on the specific heat at low temperature is not related to the magnetic transition but is certainly associated to the $4f$ electron. As is usually done we obtained the effective electronic specific heat γ from the fitting to $\gamma T + \beta T^3$ in the temperature range where c/T is linear (10 $< T < 20$ K for the Ce rich side). The results are in Table I and the behavior of γ_{eff} is shown in Fig. 2, starting at ≈ 50 mJ/K^2 mol Ce for $x = 0.03$ and reaching ≈ 140 mJ/K^2 mol Ce for $x = 1$ after passing through a maximum around 410 mJ/K^2 mol Ce at $x = 0.4$.

Usually the high values found for the low temperature γ are characteristic for Kondo systems[5] and are due to the reso-

nant peak at the Fermi level.[6] Using this model, the specific heat for a single impurity $S = 1/2$ Kondo system was calculated and the relation $\gamma \approx 1/T_K$ was obtained.[7] This calculation explains well the experimental results for some classic compounds such as CeAl$_3$, CeCu$_6$, etc.,[6] where γ can reach values of the order of 1.5 J/K^2 mol. However, for compounds where magnetic ordering is present, γ is much smaller (≈ 200 mJ/K^2 mol) as for CeAl$_2$, although T_K remains basically the same. A similar behavior of the results of Fig. 2 was observed for other systems such as Ce(Pd, Ni), Ce(Pt, Ni)[1,8] where, for a given range of Ni concentration the $\gamma \approx 1/T_K$ relation is not obeyed. The observation of a γ_{max} has been explained by a transfer of the entropy of the magnetic state to the heavy-fermion state as temperature and concentration are changed[8] or equivalently using a mean field theory to obtain $\gamma \approx T_k/(T_K^2 + E^2)$, where E is the Zeeman energy of the molecular field.[9] In other words, there are situations where γ, obtained from the linear fit of c/T vs T^2 for $T > T_N$, and T_K are increasing.

It is a common practice to subtract the specific heat of the reference compound to obtain the magnetic specific heat c_{mag}, which allows the determination of the Kondo and CF contributions. However, this procedure assumes that the Debye contribution is the same for all compounds, what is not our case (see Table I). It is necessary then to fit the data to a sum of Kondo,[7] CF and Debye contributions. Except for $x = 1$ and 0.85, the fit was poor unless a linear term γT was added. The results obtained with this fit are shown in Table I, where γ is the coefficient of the extra term, Δ_1 and Δ_2 are the CF splitting to the excited doublets and $T_K = \Delta$, the half-width of the Lorentzian shaped resonant peak. The obtained curves for a few concentrations are shown in Fig. 3. The Kondo contribution can be clearly observed in the c/T plots specially for $x < 0.85$ where $T_N < 2$ K.

From Table I we find that T_K is increasing with Ce concentration. Also, in going from La to Ce, the volume of the unit cell is reduced what will cause ρJ to increase and is, consequently, in agreement with the behavior of T_K shown in Fig. 2. We can check our T_K evaluation using ΔC_{mag} at T_N^1. For Ce$_3$Al we have $\Delta C_{\text{mag}} \cong 6$ J/K mol Ce and using Ref. 1 calculations we get $T_K/T_N \approx 0.9$, leading to $T_K = 2.5$ K, that is in good agreement with our result. The values found for γ and θ_D shown in Table I are in good agreement and exhibit
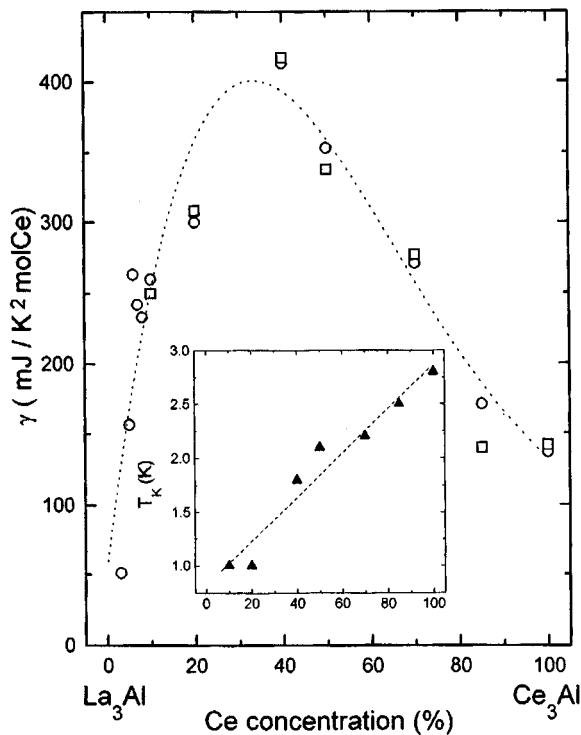

FIG. 2. Electronic specific heat γ as function of Ce concentration. (◯) are for γ_{eff} obtained from the fit to $\gamma T + \beta T^3$ and (☐) are for the fit considering Debye, CF, and Kondo contributions. The inset shows the Kondo temperature T_K obtained from the specific heat. The dashed lines are just a guide.
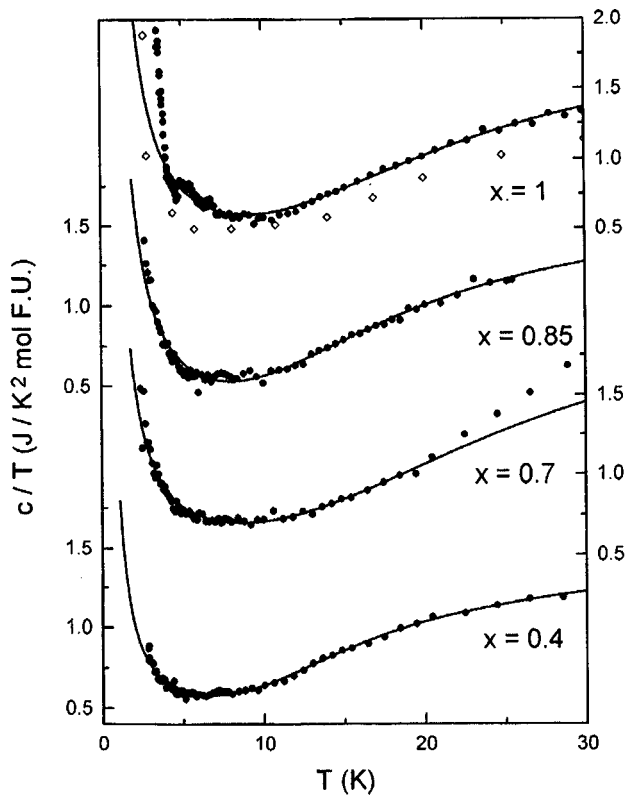
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FIG. 3. c/T vs T for several Ce concentrations. The diamonds are data from Ref. 2. The solid line is the adjusted curve including Debye, CF, Kondo, and γT.

large when compared to other Kondo systems with magnetic ordering. This is evidence of a very strong hybridization of the $4f$ and conduction electrons. Since $T_N \approx T_K$ then the Kondo effect competes with the formation of magnetic state. The fact that γ increases with Ce concentration in the small x region suggests that the magnetic state is dominant. On the other hand, for $x > 0.4$, the situation is reversed, although T_N is also increasing. This situation differs from that depicted in Refs. 1 and 8 only to the extent that for $x > x_{max}$, the Kondo effect does not fully cancel magnetic ordering.

The Kondo temperature behavior was determined by fitting Kondo, CE, Debye, and a linear term contributions to the experimental specific heat data. We found that T_K increases with Ce concentration associated to a reduction on the unit cell volume, with the consequent increase in ρJ. According to the Doniach diagram,[5] we are in a region where $\rho J < (\rho J) < (\rho J)_c$, where both T_K and T_N increase. So, if we use Y instead of La a further reduction on the unit cell volume can be obtained and it should be possible to get $\rho J > (\rho J)_c$. In this region it is expected T_N to reach a maximum, reducing afterwards.

the same behavior. Since the fitting is not particularly sensitive to Δ_2, within the experimental temperature range, the values listed in Table I are just an estimate for this parameter. Although the experimental error bar for T_K is quite large for small x, T_K clearly increases with Ce concentration. This is in disagreement with the results reported by Suzuki et al.,[2] where T_K increases from 3 K at $x = 100$ to 8 K for $x = 67\%$.

IV. CONCLUSIONS

The electronic specific heat for $(La_{1-x}Ce_x)_3Al$ exhibits a maximum of 410 mJ/K^2 mol Ce for $x = 0.4$, which is quite

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