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Heat capacity of $Ce_{1-x}La_xCu_4Al$ Kondo alloys

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ABSTRACT

The temperature dependence of the specific heat $C_p(T)$, for $Ce_{1-x}La_xCu_4Al$ alloys has been studied. The specific heat has been analyzed considering the electronic, phonon and Schottky contributions. In comparison to $CeCu_4Al$, the substitution of Ce by La reduces the electronic specific heat coefficient γ values. At low temperatures γ value depends strongly on the temperature range used for the extrapolation and on the magnetic field. The scheme of the energy levels created by the crystal electric field (CEF) splitting has been determined from the Schottky anomaly. The values obtained for the energy of the levels are similar for all the compositions.

1. Introduction

The intermediate valence, Kondo behaviour, spin fluctuations, heavy fermions and quantum critical point are most often observed in the Ce-based compounds. It is a direct consequence of the tendency of the Ce 4*f* states to hybridize strongly with the conduction electrons.

The $CeCu_5$ compound was identified as a Kondo lattice compound exhibiting antiferromagnetism below 4 K and a high γ value ($100\,mJ\,mol^{-1}\,K^{-2}$) of the specific heat [1]. The substitution of Cu by Al and Ga increases the average electron density per atom and therefore, a significant change of the Kondo lattice behaviour is expected [2–7]. $CeCu_4Al$ is a heavy fermion compound and it is the derivate of $CeCu_5$. It is paramagnetic and follows the Curie–Weiss law with the effective magnetic moment $\mu_{eff} = 2.53\,\mu_B$/f.u. and the paramagnetic Curie temperature $\theta_p = -10\,K$ [2]. The estimated value of the electronic coefficient γ is about $2.2\,J\,mol^{-1}\,K^{-2}$.

Recently the effect of La dilution in $CeCu_4Al$ was investigated, mainly in relation to the electrical resistivity and magnetic susceptibility properties [8,9]. In all of the alloys studied, no evidence of a phase transition was observed down to the lowest measuring temperature of 2 K [8]. Susceptibility measurements give effective magnetic moments close to the Ce^{3+} ion value. The analysis of the magnetic resistivity at low temperatures revealed that only $CeCu_4Al$ and $Ce_{0.95}La_{0.05}Cu_4Al$ show a typical of the Kondo lattice maximum in $\rho(T)$ [8]. This behaviour is associated with the interplay of the dilution effects and the volume effects upon alloying. For all the Ce-containing alloys in this series $\rho_m(T) \sim -\ln T$ for temperature increase above 2 K, as is expected in the case of the incoherent Kondo scattering. In the low temperature region, magnetoresistivity exhibits a negative magnetic field dependence due to the Kondo effect. Magnetoresistivity measurements on the $Ce_{1-x}La_xCu_4Al$ alloys has been analyzed basing on the calculations by Schlottmann for the Bethe-*ansatz* in the frames of the Coqblin–Schrieffer model [9]. Kondo temperature T_K is decreasing with the content of La, which is probably due to the unit cell volume increase.

In this paper we present the specific heat results for the $Ce_{1-x}La_xCu_4Al$ compounds that are analyzed in terms of the different contributions.

2. Experimental details

The preparation of the polycrystalline samples of the solid solutions $Ce_{1-x}La_xCu_4Al$ ($0.0 \le x \le 1$) was described in the previous paper [8]. The hexagonal $CeCu_5$-type structure was confirmed by the powder x-ray diffraction technique. The unit cell volume V of $Ce_{1-x}La_xCu_4Al$ increases with the increase of the La concentration [8].

Heat capacity measurements were carried out by the PPMS commercial device (Quantum Design) in the temperature range 1.9–300 K by the relaxation method using the two-τ model. The thermometers have been calibrated in various magnetic fields, including the fields used in the present studies.

3. Results and discussion

Heat capacity of the studied compounds can be defined in a general way as a sum of the respective contributions:

$$C_p = C_{el} + C_{ph} + C_{mag} \quad (1)$$

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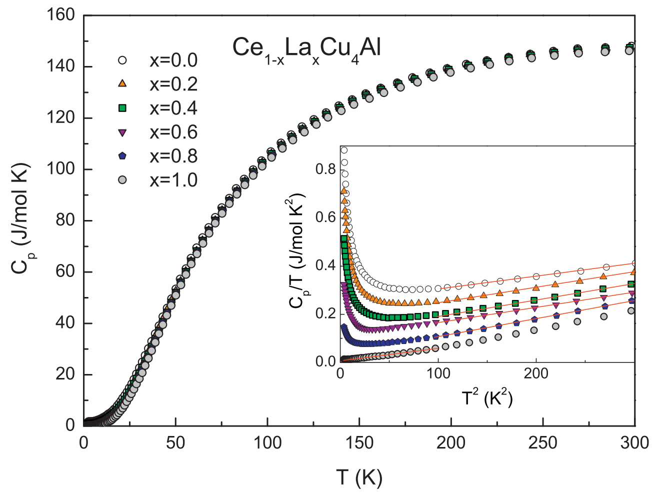

Fig. 1. Temperature dependence of the heat capacity of the studied compounds up to 300 K in zero magnetic field. The inset displays the heat capacity data at the low temperature of the C_p/T vs. T^2 dependence for $Ce_{1-x}La_xCu_4Al$ as a function of x used to determine the electronic specific heat coefficient γ.

The first term represents the electronic contribution in the form $C_{el} = \gamma T$, where γ is the Sommerfeld coefficient that is proportional to the density of states at the Fermi level. Second term describes the lattice contribution due to the lattice vibrations and plays a significant role at higher temperatures. A good description of the phonon spectrum can be obtained in the frames of the Debye and Einstein models. The last term corresponds to the magnetic part of $C_p(T)$ and is connected with the split of the ground state of the magnetic ions to the energy levels by the crystalline electric field (CEF). The thermal population of the energy levels leads to a maximum in the specific heat known as the Schottky anomaly.

Fig. 1 shows the temperature dependence of the heat capacity $C_p(T)$ of $Ce_{1-x}La_xCu_4Al$ in the temperature range 1.9–300 K in zero magnetic field. This measurement does not show any real sign of the magnetic order down to 1.9 K. The electronic part of the specific heat is expressed in a linear way as $C_{el} = \gamma T$ and at adequately low temperatures ($T \ll \Theta_D$), when the lattice contribution of optic branches is negligible the Debye model can be written in simplified form as $C_p(T) = \gamma T + \beta T^3$, where β is related to the Debye temperature by $\Theta_D = (12\pi^4 Rn/5\beta)^{1/3}$. The value of the electronic coefficient of the specific heat γ has been taken as the extrapolation of the linear part of the C_p/T vs. T^2 curves at low temperatures (inset in Fig. 1). The upturn in C_p/T observed at low temperatures is characteristic of many heavy fermion and moderate heavy fermion compounds. The substitution of Ce by La reduces the electronic heat capacity coefficient γ values from 254 mJ/mol K^2 for $CeCu_4Al$ to 9.2 mJ/mol K^2 for $LaCu_4Al$ (Table 1). The value of γ for $LaCu_4Al$ is similar to the value obtained by Bauer at al. [7] (11 mJ/mol K^2) and Toliński et al. [3] for YCu_4Al (9.13 mJ/mol K^2). Since γ is proportional to the density of states at the Fermi level, a reduction in the value of γ for $Ce_{1-x}La_xCu_4Al$ indicates a decrease in the density of states. As the values of the atomic mass of La and Ce are nearly

Table 1
Parameters obtained from specific heat analysis: electronic specific heat coefficients γ, Debye temperatures Θ_D and the values of the parameters of the formula $C_p/T = \gamma_0 \ln(T_0/T)$.

x	γ (mJ/mol K^2)	Θ_D (K)	γ_0 (J/mol K^2)	T_0 (K)
0.0	254	285	0.777	6.10
0.2	190	270	0.579	6.35
0.4	135	267	0.431	6.57
0.6	106	262	0.260	6.69
0.8	36	257	0.111	7.12

the same, the Debye temperatures Θ_D are expected to be similar. Therefore, $LaCu_4Al$ is a good candidate for the non-magnetic analog of $CeCu_4Al$. The values of Θ_D obtained from the simplified Debye model are approximating for all the investigated compounds (Table 1).

Heat capacity in the whole temperature range can be expressed by the standard Debye formula with the addition of the electronic part:

$$C_p(T) = \gamma T + 9NR\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \tag{2}$$

where $N = 6$ is the number of the atoms in the formula unit, R is the gas constant and $x = h\omega/k_B T$. However, this approach cannot fully describe the specific heat data of $LaCu_4Al$ due to the lack of the optical modes which are significant in higher temperatures. The most realistic description of the phonon part of the specific heat, especially at low temperatures has been achieved by considering the splitting of the phonon spectrum into the acoustic and optical branches. The optical modes are given by the Einstein formula:

$$C_{Ei}(T) = R\sum_{i=1}^{15}\left(\frac{\Theta_{Ei}}{T}\right)^2 \frac{e^{\Theta_{Ei}/T}}{(e^{\Theta_{Ei}/T} - 1)^2} \tag{3}$$

where Θ_{Ei} is the characteristic Einstein temperature for each optical branch.

For nonmagnetic $LaCu_4Al$ the phonon spectrum consists of 3-acoustic branches which are described by the Debye model and 15-optical branches attributed to the Einstein model. The optical branches were divided to three groups with different degeneracy n_{Ei}: (5–9–1). The isobaric specific heat of $LaCu_4Al$ was fitted using both the Debye and Einstein models together with their anharmonic correction coefficients α_D and α_{Ei}, which accounts for the discrepancy between the isobaric and the isochoric specific heat [10,11]:

$$C_p(T) = \gamma T + R\left\{\frac{9}{1 - a_D T}\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}\right\} + R\left\{\sum_{i=1}^{15}\frac{1}{1 - a_{Ei} T}\left(\frac{\Theta_{Ei}}{T}\right)^2 \frac{e^{\Theta_{Ei}/T}}{(e^{\Theta_{Ei}/T} - 1)^2}\right\} \tag{4}$$

The best fit has been obtained with the following parameters: $\Theta_D = 244$ K and $\Theta_{Ei} = 116$ K, 253 K, 420 K, with their anharmonic coefficients: $\alpha_D = 1.3 \times 10^{-4}$ and $\alpha_{Ei} = 1.6 \times 10^{-5}$, 1×10^{-5}, 1.1×10^{-5}, respectively. The experimental heat capacity data in the $C_p(T)$ representation together with the calculated contributions C_e and C_{ph} are shown in Fig. 2 and the same data in $C_p/T(T)$ representation together with the fitting parameters are presented in Fig. 3.

To analyze the magnetic part of the specific heat of $Ce_{1-x}La_xCu_4Al$ we used the specific heat of the nonmagnetic $LaCu_4Al$ analog to get information about the electronic and phonon contributions. The magnetic contribution to the specific heat of the $CeCu_4Al$ sample is depicted in Fig. 4. C_{mag}/T consists of two main contributions. The first one is the hump at about 20 K, which is a consequence of the crystal electric field effects (CEF). The second one is the steep increase at the lowest temperatures, which is probably developed by the Kondo interactions. With the increase of the La concentration this specific heat anomalies remain roughly at the same position. The hexagonal symmetry splits the sixfold degenerate state of Ce^{3+} with $J = 5/2$ into three doublets with the energy gaps Δ_1 and Δ_2 from the ground state. The contribution to the magnetic specific heat, connected with the CEF effects was fitted