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Electrical and thermal transport properties of the alloy system $(Ce_{1-x}La_x)Cu_4In$

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Abstract. The studies of electrical resistivity, $\rho(T)$, magnetoresistivity, MR, thermoelectric power, $S(T)$ and thermal conductivity, $\lambda(T)$, of the alloy system $(Ce_{1-x}La_x)Cu_4In$ $(0 \leq x \leq 1)$ are reported. The room temperature powder X-ray diffraction studies confirm the orthorhombic $CeCu_{4.38}In_{1.62}$ - type crystal structure with space group $Pnnm$ (No. 58) for all investigated compositions across the series. $\rho(T)$ results indicate an evolution from coherent Kondo scattering to incoherent single - ion Kondo scattering, with increased La content x. $\rho(T)$ for each composition at high temperature is described by a $-ln(T)$ behaviour. MR measurements on Ce dilute alloys are interpreted within the single - ion Bethe ansatz description of the Coqblin - Schrieffer model. $S(T)$ results are described by the phenomenological resonance model. $\lambda(T)$ data increase linearly with temperature from low T and shows a tendency toward saturation above 300 K for dilute Ce alloys. The Lorentz number, L/L_0 and the dimensionless figure of merit, $ZT = S^2T/\lambda\rho$ increase upon cooling and exhibit maxima at low temperatures.

1. Introduction

$CeCu_5$ is well known to be an antiferromagnetic (AF) Kondo lattice compound with $T_N = 4$ K [1]. The substitutions of one Cu with elements of the p - block (M), increase the average conduction electron density, which screen the localized $4f$ moments state in $CeCu_5$ leading to a non magnetic heavy -Fermion (HF) ground state in $CeCu_4M$ [2, 3, 4]. Several experimental investigations were reported on the series $CeCu_4M$, (M = Al, Ga, In) [2, 3, 4, 5, 6]. Transport, magnetic and thermodynamic properties studies of the $CeCu_4M$ compounds have confirmed the HF state with an electronic specific heat coefficient taking huge values of the order of 2 - 3 $J.K^{-2}.mol^{-1}$. The transport properties studies indicate a Kondo temperature in the range 2 - 5 K from the $\rho(T)$ measurement [3, 5, 6], while the thermoelectric power shows positive values with large peak at a temperature in the range 20 - 30 K [4, 6].

The studies of magnetic and electronic properties of $CeCu_4In$ compound in particular [6, 7], indicate paramagnetic behaviour down to 2 K that follows the Curie - Weiss law with effective magnetic moment 2.40 μ_B and paramagnetic Weiss temperature $\theta_p = -27$ K. Heat capacity studies confirm the HF character for this compound with the electronic heat capacity coefficient

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$\gamma = 235$ mJ/mole.K^2. $\rho(T)$ behaviour is characteristic of a Kondo lattice compound with a well defined resistivity maximum at 25 K.

In the current paper, we report on the study of the electrical and thermal transport properties of the alloy system $(Ce_{1-x}La_x)Cu_4In$.

2. Results and discussion

2.1. Lattice parameters and unit - cell volume

The crystal structure was checked and confirmed by the powder X-ray diffraction technique, using the CuKα radiation ($\lambda = 1.5406$ Å). We have observed that all the compositions crystallize in the orthorhombic *Pnnm* system [No. 58] [9]. The lattice parameters and the unit cell volume obtained for the $CeCu_4In$ are in good agreement with previously reported values [6]. It is observed that the refined room - temperature lattice parameters a, b and c and the unit - cell volume V increase linearly with increased La content x (see figure 1). The observed linear increase in V confirms the Vegard's rule which suggests no sudden change in the Ce valence across the series.

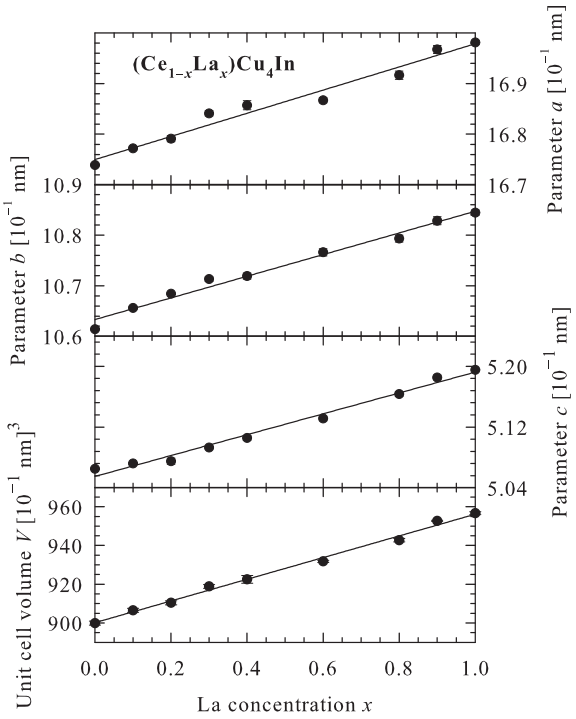

Figure 1. Lattice parameters a, b and c and unit cell volume V as a function of La content x of $(Ce_{1-x}La_x)Cu_4In$.

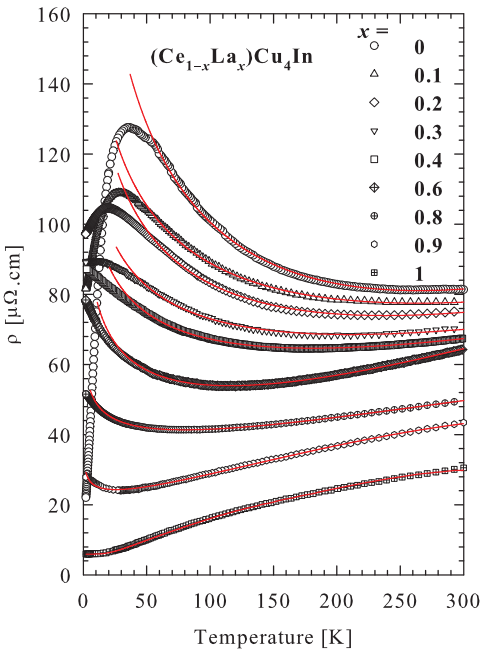

Figure 2. (color online) $\rho(T)$ for the $(Ce_{1-x}La_x)Cu_4In$ alloy system. The solid red lines are LSQ fits of Eqs.1 and 2 to the measured data.

2.2. Electrical transport

2.2.1. Electrical resistivity: The temperature dependence of the zero - field total resistivity $\rho(T)$ of alloys in the series $(Ce_{1-x}La_x)Cu_4In$ is shown in figure 2. It is observed that $\rho(T)$ evolves from coherent Kondo behaviour at low temperatures for alloys in the range $0 \leq x \leq 0.3$,

with a well defined Kondo peak at T^{ρ}_{max} as indicated in table 1 to incoherent single - ion Kondo behaviour for alloys with $x \geq 0.4$. It is observed that T^{ρ}_{max} which is a fair indication of the Kondo temperature T_K for dense Kondo alloys systems, shifts to lower temperature with increased La content x. At higher temperatures for all Ce containing alloys in the series, $\rho(T)$ follows a $-ln(T)$ as is to be expected for incoherent Kondo scattering. $\rho(T)$ of the non - magnetic counterpart $LaCu_4In$ departs from linearity at high temperatures and is described by the Bloch - Grüneissen - Mott formula:

$$\rho(T) = \rho_0 + \frac{4\kappa}{\theta_R}.(\frac{T}{\theta_R})^5 \int_0^{\theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - \alpha T^3, \quad (1)$$

where all the parameters have their usual meaning. Least - squares (LSQ) fit of Eq.(1) to the experimental $\rho(T)$ for the $LaCu_4In$ (solid line in figure 2) gives $\rho_0 = 5.95$ $\mu\Omega$.cm, $\kappa = 2000$ $\mu\Omega$.cm.K, $\theta_R = 132$ K and $\alpha = 0.31 \times 10^{-8}$ $\mu\Omega$.cm.K^{-3}. $\rho(T)$ curves for all compositions where incoherent Kondo scattering is observed are described by

$$\rho(T) = \rho_0^{'} + \rho_{ph}(T) - C_K ln(T), \quad (2)$$

where $\rho_0^{'}$ is the residual resistivity. It is observed that LSQ fits of $\rho(T)$ data to Eq. 2 for alloys with $x \leq 0.6$, the interband scattering that seems to be present for alloys with $x \geq 0.8$ is suppressed with 40% Ce doping. For this reason we include only the second term in $\rho_{ph}(T)$ in Eq.(1) and approximate it to $\rho_{ph}(T) = bT$ for compositions with $x \leq 0.8$. The Mott's term $(-\alpha T^3)$ was included only for alloys with $x = 0.8$ and 0.9. LSQ fits of Eq.(2) to $\rho(T)$ data (solid lines figure 2) yield $\rho(T)$ parameters listed in table 1 and $\alpha[10^{-8}\mu\Omega.\text{cm/K}^3] = 4.3(3)$ and 23(2) for the $x = 0.8$ and 0.9 alloys respectively.

2.2.2. Magnetoresistivity: The isothermal MR was studied on a selected number of $(Ce_{1-x}La_x)Cu_4In$ alloys for which their $\rho(T)$ curves are characteristic of incoherent Kondo scattering. The results of these studies are presented in figure 3 for two representative compositions $x = 0.6$ and 0.8. As shown in figure 3 for the investigated alloys, a negative MR has been observed at all temperatures as a result of suppression of the incoherent Kondo scattering in magnetic field. We proceed to analyze the results in terms of the Bethe - ansatz calculation of the Coqblin - Schrieffer model given by Andrei [11] and Schlottmann [12] for total angular momentum $J = 1/2$ in the integer valence limit

$$\frac{\rho(B,T)}{\rho(B=0,T)} = [\frac{1}{2J+1} sin^2(\frac{\pi n_f}{2J+1}) \sum_{\ell=0}^{2J} sin^{-2}(\pi n_\ell)]^{-1}, \quad (3)$$

where n_f is the electron occupation number. The solid lines in the main panel of figure 3 show fits of the experimental isothermal MR data according to Eq. 3 and this yields values of the characteristic Kondo field B^* which is related to the Kondo temperature T_K according to the relation [13]

$$B^*(T) = B^*(0) + \frac{k_B T}{g\mu_K} = \frac{k_B(T_K^{MR} + T)}{g\mu_K}, \quad (4)$$

where the parameters have their usual meaning. LSQ fits of Eq. 4 to these B^* values obtained at the isotherms in the main panel of figure 3 are represented by solid lines in the inset of figure 3 and the obtained values of T_K^{MR} and μ_K are listed in table 1. The values of μ_K decrease with increase in La content. Similarly to T^{ρ}_{max}, it is also observed that T_K^{MR} values decrease monotonically with increase in La content, which results from the increase in unit - cell volume which in turn weakens the on - site Kondo exchange interaction according to the compressible Kondo lattice model [14]. Similar behaviour of T_K^{MR} and μ_K was observed in many diluted Ce alloys [10]. Finally, figure 4 illustrates the excellent scaling of the MR data in accordance with the Bethe ansatz formulation of the single - ion MR by showing the collapse of MR data from all isotherms on a single curve.

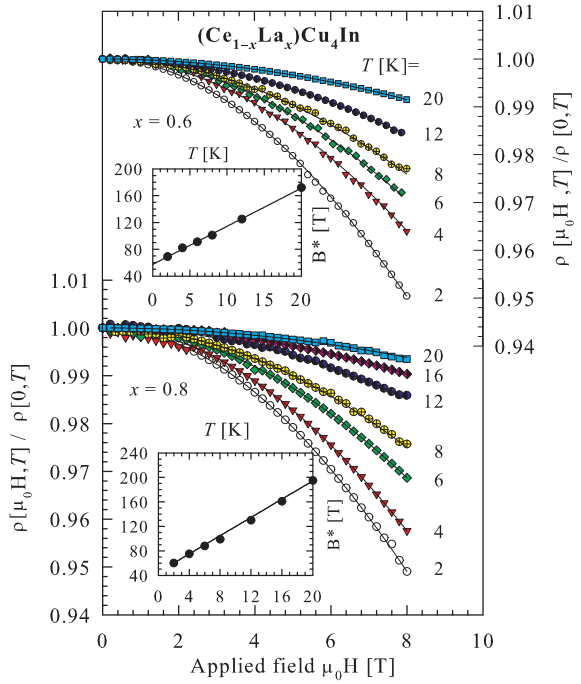

Figure 3. (color online) MR isotherms at various temperature. The solid lines in the main panel are LSQ fits of Eq. 3 to the measured data. The insets shows the temperature variation of $B^*(T)$, and the solid lines through the data points are an LSQ fit of Eq. 4 to the B^* values.

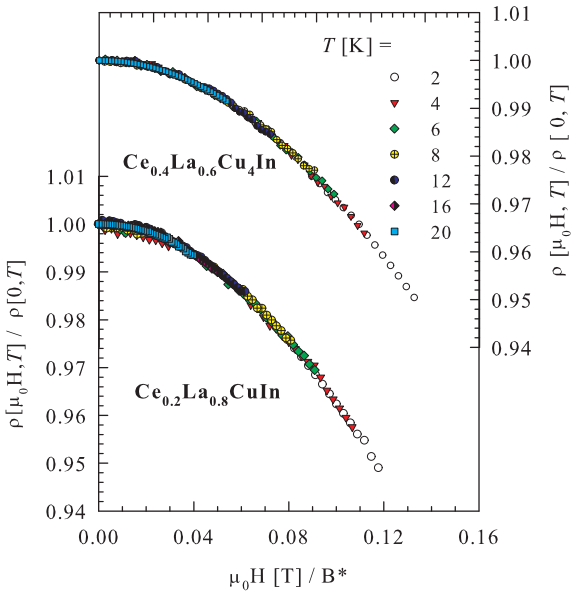

Figure 4. (color online) Scaling of MR data for different isotherms as measured in field up to 8 T and at various temperatures between 2 and 20 K.

Table 1. Electrical and thermal transport data for the $(Ce_{1-x}La_x)Cu_4In$ alloy system. These values are obtained from LSQ fits of Eqs. 1, 2, 3 4 and 5 to the measured data (see text).

x	0	0.1	0.2	0.3	0.4	0.6	0.8	0.9
$\rho_0[\mu\Omega.\text{cm}]$	336(4)	227(3)	216(2)	158(1)	139.7(2)	115.4(2)	63.2(2)	31.1(1)
$b[10^{-3}\mu\Omega.\text{cm/K}]$	210(8)	124(7)	133(3)	98(3)	99(4)	142(3)	82(7)	118(2)
$C_K[\mu\Omega.\text{cm}]$	56(1)	33(1)	31.7(5)	20.5(4)	17.9(1)	16.4(1)	6.5(1)	3.03(4)
T^{ρ}_{max}[K]	34.0(1)	27.9(1)	17.8(1)	13.4(1)				
T_K^{MR}[K]				20.1(3)	11.3(8)	10.1(2)	6.0(4)	
$\mu_K[\mu_B]$				0.412(8)	0.340(3)	0.305(5)	0.233(1)	
T_K^S[K]	21.8(7)	17.3(6)				14.9(7)	10.7(4)	
$a[\mu V/\text{K}^2]$	0.022(2)	0.029(4)				0.024(5)	0.018(3)	
T_{CEF}[K]	95(2)	94(2)				98(3)	96(2)	

2.3. Thermal transport

2.3.1. Thermoelectric power: The combined results of the TEP of selected compositions in the alloys series $(Ce_{1-x}La_x)Cu_4In$ are shown in figure 5A. The results obtained are typical of heavy

- fermion compounds characterized by one peak below room temperature and differ drastically to that of a normal metal [4]. For all investigated compositions, $S(T)$ is positive in the whole temperature range and exhibit a maximum roughly at the same temperature of 30 K. The observed $S(T)$ maximum decreases in magnitude with increased La content x. We have carried out the analysis of the measured $S(T)$ data in terms of the phenomenological resonance model [15], which describes the low temperature $S(T)$ data. This model assumes that the dominant contribution to $S(T)$ originates from the scattering of electrons from a wide conduction band into a narrow f - band approximated by a Lorentzian shape. According to the model, two parameters must be taken into account: the position of the f - electron band relative to Fermi level $(E_f - E_F)$ and the width of the resonance peak W_f. Thus, the temperature variation of $S(T)$ can then be expressed in the form

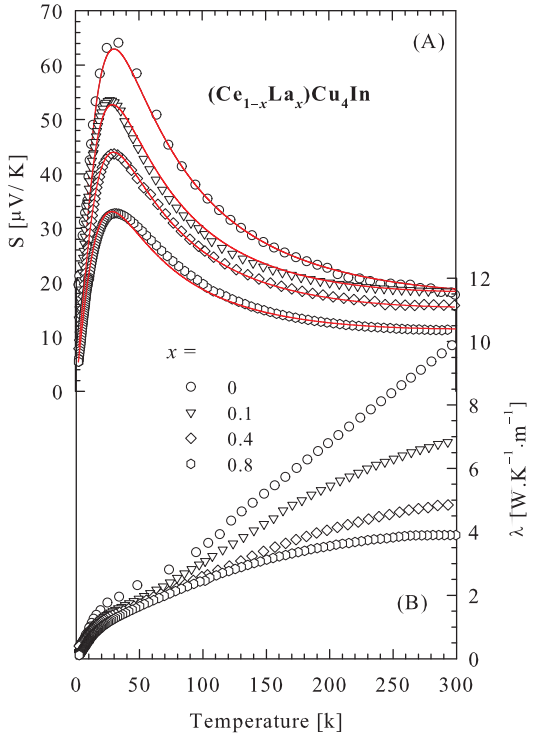

Figure 5. (color online) Temperature dependence (A) of $S(T)$ and (B) $\lambda(T)$. The solid lines in the panel (A) are LSQ fits of Eq.5 to the measured data.

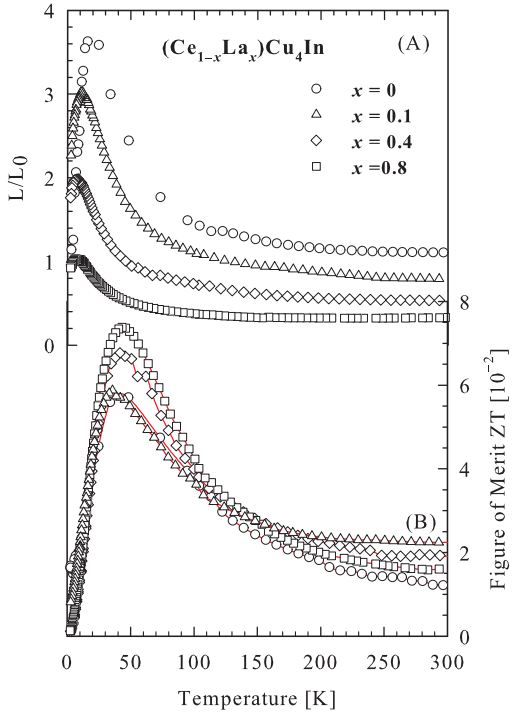

Figure 6. (color online) Temperature dependence (A) of the Lorentz number L/L_0 and (B) the Figure of merits ZT.

$$S(T) = \frac{2}{3}\frac{k_B}{|e|}\frac{\pi^2 T E_f}{(\pi^2/3)T^2 + E_f^2 + W_f^2} + S_d(T), \tag{5}$$

where $S_d(T) = aT$ is the Mott's contribution originating from the interband scattering, E_f and W_f have the unit of temperature (K). The first term in Eq.5 describes very well $S(T)$ of mixed valence system due to their high value of T_K. Therefore, to obtain a good fit shown by solid line in figure 5A we have included the Mott's term and made a similar assumption as in Ref.[7] taking $E_f = T_K^S$ and $W_f = \pi T_{CEF}/N_f$, where N_f is the orbital degeneracy $2J+1$ and T_{CEF} the characteristic temperature which is a measure of the CEF. LSQ fits of Eq.5 to the experimental

$S(T)$ data give the parameters listed in table 1. The behaviour of T_K^S with La content is similar to that of T_{max}^{ρ} and T_K^{MR}. The resulting parameters obtained for our parent compound $CeCu_4In$ are in good agreement with previously reported results [7].

2.3.2. Thermal conductivity: Figure 5B shows the results of $\lambda(T)$ of selected compositions in the alloys series $(Ce_{1-x}La_x)Cu_4In$. The thermal conductivity of metals originates from two contributions: an electron component $\lambda_e(T)$ and a lattice component $\lambda_{ph}(T)$ for which phonons are heat carriers. It is observed that the slope of the linear part of $\lambda(T)$ in the temperature range $50K \leq T \leq 150K$, is increased with decreasing La content x. At temperatures below 20 K, $\lambda(T)$ is proportional to T, which is typical for scattering of electrons on lattice imperfections. At temperatures above 150 K, $\lambda(T)$ for diluted Ce alloys deviate from linearity, with a downward curvature and a tendency toward saturation above 300 K. Such a saturation of $\lambda(T)$ follows the Wilson's law which predicts a constant value of $\lambda(T)$, typical for scattering electrons on thermally excited phonons [16]. The linear behaviour of $\lambda(T)$ for the pure Ce compound is not predicted theoretically.

Combining the results of $\lambda(T)$ and $\rho(T)$, we have plotted in figure 6A the Lorentz number $L(T) = \lambda(T)\rho(T)/T$ normalized to the value of $L_0 = 2.45 \times 10^{-8}$ W.Ω.K^{-2}. It is observed that the values of L/L_0 decrease rapidly with increasing La content x. The overall behaviour of L/L_0 for all investigated compositions is a rapid increase on cooling followed by a maximum at a temperature T_{max} which shifts slightly from 16 K to 9 K with increasing in La content x. This is followed by a sudden drop of L/L_0 below T_{max}. The observed maximum decreases in magnitude with increase in La content. The increase of L/L_0 at low temperatures deviates from the Wiedemann - Franz law which predicts $L/L_0 = 1$, and this may be attributed to an additional lattice thermal conductivity or can also arise from the energy dependent Kondo scattering process. Such a tendency was observed for several Ce compounds [7]. Our value of T_{max} observed for our parent compound $CeCu_4In$ is in agreement with the value of 16 K reported in Ref.[7].

Figure 6B presents values of the dimensionless figure of merit $ZT = S^2T/\lambda\rho$, which determines the efficiency of the thermoelectric material. A commonly used thermoelectric material in power generation or refrigeration is Bi_2Te_3 with ZT between 0.8 and 1 [17]. It is observed that ZT values for all the investigated compositions increase on cooling and exhibit a maximum at temperature between 42 and 48 K. The observed peak increases in magnitude with increasing La content, opposite to that of L/L_0. Our maximum value for $CeCu_4In$ is about 0.06 at $T = 48$ K and ZT takes the value of 12.5×10^{-3} at room temperature. These values are roughly twice larger than the values reported for the same compound in Ref.[18] at $T = 50$ K.

2.4. Conclusions

XRD studies confirm the orthorhombic $CeCu_{4.38}In_{1.62}$ - type crystal structure with space group $Pnnm$. $\rho(T)$ evolves from coherent to incoherent single - ion Kondo scatterring. A negative MR and positive $S(T)$ are observed for all investigated compositions. MR data are interpreted within the single - ion Bethe ansatz description of the Coqblin - Schrieffer model. $S(T)$ data are described by the phenomenological resonance model. The resulting values of T_{max}^{ρ}, T_K^{MR} and T_K^S decrease with increasing La content x which is consistent with the compressible Kondo lattice model. $\lambda(T)$ follows the Wilson's law near 300 K for diluted Ce alloys. L/L_0 and ZT increase rapidly upon cooling followed by a maximum at low temperature.

Acknowledgments

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