Electrical and thermal transport properties of the alloy system \((\text{Ce}_{1-x}\text{La}_x)\text{Cu}_4\text{In}\)

Aiman K Bashir\(^1\), Moise B Tchoula Tchokont\(^{	ext{è}}\)\(^1\), Douglas Britz\(^2\), B M Sondezi\(^3\), André M Strydom\(^2\) Dariusz Kaczorowski\(^3\)

\(^1\)Department of Physics, University of the Western Cape, Private Bag X 17, Bellville 7535, South Africa
\(^2\)Highly Correlated Matter Research Group, Department of Physics, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa
\(^3\)Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50 - 950 Wroc\’law, Poland

E-mail: mtchokonte@uwc.ac.za (M B Tchoula Tchokont\(^{	ext{è}}\))

Abstract. The studies of electrical resistivity, \(\rho(T)\), magnetoresistivity, MR, thermoelectric power, \(S(T)\) and thermal conductivity, \(\lambda(T)\), of the alloy system \((\text{Ce}_{1-x} \text{La}_x)\text{Cu}_4\text{In}\) \((0 \leq x \leq 1)\) are reported. The room temperature powder X-ray diffraction studies confirm the orthorhombic \(\text{CeCu}_4\text{In}_1\) - type crystal structure with space group \(P\,\overline{nnm}\) (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

\(\text{CeCu}_5\) 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 \(\text{CeCu}_5\) leading to a non magnetic heavy -Fermion (HF) ground state in \(\text{CeCu}_4\text{M}\) \([2, 3, 4]\). Several experimental investigations were reported on the series \(\text{CeCu}_4\text{M}\), \((M = \text{Al, Ga, In})\) \([2, 3, 4, 5, 6]\). Transport, magnetic and thermodynamic properties studies of the \(\text{CeCu}_4\text{M}\) 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 \(\text{CeCu}_4\text{In}\) compound in particular \([6, 7]\), indicate paramagnetic behaviour down to 2 K that follows the Curie - Weiss law with effective magnetic moment 2.40 \(\mu_B\) and paramagnetic Weiss temperature \(\theta_p = -27\) K. Heat capacity studies confirm the HF character for this compound with the electronic heat capacity coefficient
$\gamma = 235 \text{ mJ}/\text{mole.K}^2$, $\rho(T)$ 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 $(\text{Ce}_{1-x}\text{La}_x)\text{Cu}_4\text{In}$.

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 ($\lambda = 1.5406 \text{ Å}$). 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$_4$In 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](image1.png)

**Figure 1.** Lattice parameters $a$, $b$ and $c$ and unit cell volume $V$ as a function of La content $x$ of $(\text{Ce}_{1-x}\text{La}_x)\text{Cu}_4\text{In}$.

![Figure 2](image2.png)

**Figure 2.** (color online) $\rho(T)$ for the $(\text{Ce}_{1-x}\text{La}_x)\text{Cu}_4\text{In}$ 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 $(\text{Ce}_{1-x}\text{La}_x)\text{Cu}_4\text{In}$ 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 $T_{\text{m}}^\rho$ as indicated in table 1 to incoherent single-ion Kondo behaviour for alloys with $x \geq 0.4$. It is observed that $T_{\text{m}}^\rho$ 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$_4$In departs from linearity at high temperatures and is described by the Bloch - Gr"uneissen - Mott formula:

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

where all the parameters have their usual meaning. Least-squares (LSQ) fit of Eq.(1) to the experimental $\rho(T)$ for the LaCu$_4$In (solid line in figure 2) gives $\rho_0 = 5.95 \mu\Omega\text{cm}$, $\kappa = 2000 \mu\Omega\text{cmK}$, $\theta_R = 132 \text{K}$ and $\alpha = 0.31 \times 10^{-8} \mu\Omega\text{cmK}^{-3}$. $\rho(T)$ curves for all compositions where incoherent Kondo scattering is observed are described by

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

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 $\alpha[10^{-8} \mu\Omega\text{cmK}^{-3}] = 4.3(3)$ 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$_4$In 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

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

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]

$$
B^*(T) = B^*(0) + \frac{k_BT}{g\mu_K} = k_B \frac{T_{K\text{MR}} + T}{g\mu_K},
$$

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 $T_{K\text{MR}}$ and $\mu_K$ are listed in table 1. The values of $\mu_K$ decrease with increase in La content. Similarly to $T_{\text{m}}^\rho$, it is also observed that $T_{K\text{MR}}$ 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 $T_{K\text{MR}}$ and $\mu_K$ 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.

Table 1. Electrical and thermal transport data for the (Ce$_{1-x}$La$_x$)Cu$_4$In 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  |
|------|------|------|------|------|------|------|------|------|
| $\rho_0$ [$\mu\Omega\cdot cm$] | 336(4) | 227(3) | 216(2) | 158(1) | 139.7(2) | 115.4(2) | 63.2(2) | 31.1(1) |
| $b$ [$10^{-3} \mu\Omega\cdot cm/K$] | 210(8) | 124(7) | 133(3) | 98(3) | 99(4) | 142(3) | 82(7) | 118(2) |
| $C_K$ [$\mu\Omega\cdot cm$] | 56(1) | 33(1) | 31.7(5) | 20.5(4) | 17.9(1) | 16.4(1) | 6.5(1) | 3.03(4) |
| $T_{\rho_{max}}$ [$K$] | 34.0(1) | 27.9(1) | 17.8(1) | 13.4(1) |  |
| $T_{MR}$ [$K$] | 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) |  |
| $T_{CEF}$ [$K$] | 21.8(7) | 17.3(6) | 14.9(7) | 10.7(4) |  |
| $a$ [$\mu V/K^2$] | 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$_4$In 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

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

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

**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 $ZT$. 
$S(T)$ data give the parameters listed in table 1. The behaviour of $T_K^S$ with La content is similar to that of $T_{\text{max}}^\rho$ and $T_K^{MR}$. The resulting parameters obtained for our parent compound CeCu$_4$In 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$_4$In. The thermal conductivity of metals originates from two contributions: an electron component $\lambda_e(T)$ and a lattice component $\lambda_p(T)$ 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 $L_0 = 2.45 \times 10^{-8}$ $\text{W}\cdot\text{K}^{-2}$. 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 $T_{\text{max}}$ 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 $T_{\text{max}}$. 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 $T_{\text{max}}$ observed for our parent compound CeCu$_4$In is in agreement with the value of 16 K reported in Ref.[7].

Figure 6B presents values of the dimensionless figure of merit $ZT = S^2T/\chi\rho$, which determines the efficiency of the thermoelectric material. A commonly used thermoelectric material in power generation or refrigeration is Bi$_2$Te$_3$ 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$_4$In is about 0.06 at $T = 48$ K and $ZT$ takes the value of $12.5 \times 10^{-3}$ 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 $Pmnm$. $\rho(T)$ evolves from coherent to incoherent single - ion Kondo scattering. 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 $T_{\text{max}}^MR$, $T_K^{MR}$ 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
Support is acknowledged from the NRF through grants No.: 81296, 81804 and 91683. AMS thanks the SA-NRF (78832), and the Faculty of Science and URC of UJ for financial assistance.
References

[1] Bauer E et al. 1987 J. Magn. Magn. Mater. 69 158.
[2] Eichler A et al. 1995 Physica B 206 - 207 258.
[3] Andraka B et al. 1991 Phys. Rev. B 44 4371.
[4] Bauer E et al. 1987 Solid State Commun. 62 271.
[5] Kowalczyk A et al. 2009 J. Phys.: Condens. Matter 20 255252.
[6] Kowalczyk A et al. 2009 J. Alloys Compd. 481 40.
[7] Tolinski T et al. 2010 J. Alloys Compd. 490 15.
[8] Falkowski E et al. 1987 Intermetallics 19 433.
[9] Baraniak M et al. 1991 Izvestiya AN SSSR. Neorgan. Materialy 27 1235.
[10] Tchoula Tchokonte M B et al. 2004 J. Phys.: Condens. Matter 16 1981.
[11] Andrei N 1982 Phys. Lett. A 87 299.
[12] Schlottmann P 1983 Z. Phys. B 51 223.
[13] Batlogg B et al. 1987 J. Magn. Magn. Mater. 63-64 441.
[14] Lavagna M et al. 1983 J. Phys. F: Metal Phys. 13 1007.
[15] Gottwich U et al. 1985 J. Magn. Magn. Mater. 47-48 536.
[16] Bauer E et al. 1991 J. Phys.: Condens. Matter 3 7641.
[17] Duck Y C et al. 1997 XVI ICT 97. Proceedings ICT 97 459.
[18] Tolinski T et al. 2011 Eur. Phys. J. B 84 177.