Magnetoresistance of heavy fermion-like compound Ce(Ni$_{1-x}$Cu$_x$)$_2$Al$_3$

Sankararao Yadam, Durgesh Singh, D. Venkateshwarlu, Mohan Gangrade, S. Shanmukharao Samatham, V. Ganesan

Low Temperature Laboratory, UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, M.P. India

*Corresponding author. Tel: (+91) 731243913; E-mail: vganesan@csr.res.in

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ABSTRACT

CeNi$_2$Al$_3$ system is a potential candidate for low temperature thermoelectrics. Substitution studies, especially at the Ni site are considered to be of importance due to the drastic tuning of its physical properties. Resistivity in magnetic fields and thermoelectric power measurements of Cu doped CeNi$_2$Al$_3$ ($x=0.0$ to 0.4) system is reported in this investigation. This dense Kondo lattice system is investigated with an aim of understanding its basic transport mechanism. Negative magnetoresistance is seen for $x=0.3$ and 0.4 in the magnetic field up to 14 T. Deviation from the Kondo behavior occurs at temperatures close to 2 K with a down turn in resistivity. The nature of resistivity at low temperatures is investigated in view of the possible evidence for Fermi liquid behavior and also the formation of heavy Fermion in correlation with specific heat studies. Doping dependence of linear diffusion coefficient and Sommerfeld coefficient of specific heat are analyzed and discussed in connection with the heavy Fermion formation. The results obtained show a promising trend in tuning these materials by way of Kondo route as well as by the substitution especially at the Ni site in the present system. Copyright © 2015 VBRI Press.

Keywords: Magnetoresistance; kondo effect; fermi liquid; heavy fermion.

Introduction

Thermo Electric Power (TEP) is considered to be a property of prime interest in materials science especially in the scenario of energy conversion. Recently a variety of novel phenomena are associated as reasons for high figure of merit seen in thermoelectric materials. Examples include Topological Insulator behavior in Bi$_2$Te$_3$ based systems, resonant charge relaxation as a source of high TEP in a Kondo Insulator type FeSi, resonant distortion of electronic density of states in Sm doped Zn$_2$Sb$_3$ and the possible rattling motion of rare earth (RE) atoms in doped Skutterudites. In addition, Ce based compounds that exhibit unusual ground states and novel phenomena such as heavy Fermion behavior and non-Fermi liquid behavior are considered to be of potential candidate in this arena [1-4]. Presence of strong hybridization between localized 4f electrons and conduction electrons is responsible for the above phenomena. Competition between Kondo and RKKY interactions are responsible for several magnetic ground states.

The parent compound, CeNi$_2$Al$_3$, is one of the compounds with strong c-f hybridization regime. It crystallizes in the hexagonal PrNi$_2$Al$_3$-type structure with space group P6/mmm and exhibits metallic behavior [5]. Enhancement in the unit cell volume, conduction electrons, thermoelectric power and specific heat were reported upon increasing Cu concentration as well as the system undergoes a transition from Pauli paramagnetic to Curie-Weiss type paramagnetic state at 40% doping in Ce(Ni$_{1-x}$Cu$_x$)$_2$Al$_3$ [6]. Upon further increasing in Cu concentration, the system undergoes antiferromagnetic ordered state [7]. Like other Ce- and Eu-based heavy Fermion systems, Ce(Pb$_{1-x}$Sn$_x$)$_3$, Ce(Pt$_{1-x}$Ni$_x$), and EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$, the present system has also been shown to have a proportionality between the initial slope of TEP S(T) curve and the electronic specific heat coefficient as $T\rightarrow$0K limit [8]. From the thermoelectric measurements, parameters obtained from the two band model fit, it was observed that an evolution from a simple compensated metal ($x=0.0$) to a paramagnetic one ($x=0.4$) in this series Ce(Ni$_{1-x}$Cu$_x$)$_2$Al$_3$ [9]. The change of transport properties with concentration doping under the effect of magnetic fields, is not yet studied. In this communication, we report on the magnetotransport as well as a note on the enhancement of carrier concentration with Cu doping. The
title compound is investigated in view of the possible evidence for Fermi liquid behavior and also the formation of heavy quasi particles in corroboration with specific heat. An attempt has been made to show indirectly that enhancement in the charge carrier concentration using specific heat and thermoelectric measurements as $T \rightarrow 0$ K. A deeper insight is obtained by investigating the system under magnetic fields that corroborates the formation of heavy quasi particles. Such a study establishes the contribution of Kondo type route in enhancing the thermo electric power and the corresponding manifestation in the physical properties.

**Experimental**

**Materials**

Polycrystalline Ce(Ni$_{1-x}$Cu$_x$)$_2$Al$_3$ with $x=0.0,0.1,0.3,0.4$ have been prepared by taking constituent elements, Ce (99.9%), Ni (99.995%) supplied by Leico from USA and Mateck from Germany respectively. Cu (99.9%) and Al (99%) are supplied by Cerac from USA. Stoichiometric amounts were arc melted in high purity Argon atmosphere. For phase homogeneity flipping was done three times and finally rods of few centimeters were prepared.

**Method**

The Phase purity was checked on unannealed powder specimens with the Bruker D8 Advanced X-ray diffractometer using Cu-Kα radiation. Resistivity measurements were carried out using four probe technique with the 14T/2K PPMS, (QD-USA) temperature down to 2K and magnetic field up to 14T. Thermoelectric power measurements were done by the differential method (Chromel/Au+0.07% Fe thermocouple as detector) using a homemade setup [10].

**Results and discussion**

Fig. 1 shows resistivity vs temperature of Ce(Ni$_{1-x}$Cu$_x$)$_2$Al$_3$ with $x=0.0-0.4$ in the magnetic field up to 14 T. Sample $x=0.0$ shows metallic behavior [5], whereas $x=0.1$ shows broad hump at high temperature. This feature is gradually enhanced and shifted towards low temperature with doping concentration. The broad hump around 150 K and low temperature rise is shown for $x=0.4$ is due to crystalline electric field effect on Ce$^{4+}$ [11]. Apart from $x=0.4$, $x=0.3$ also shows a clear rise (for clarity refer to figure 2) at low temperatures. Positive magnetoresistance (PMR) is observed for the samples $x=0.0$ and 0.1 as can be observed in insets of Figure 1. Since these samples show Pauli paramagnetic and metallic behavior [6] one can expect the above said PMR. From the literature, for $x=0.3$ the magnetic susceptibility ($\chi$) values are improved compared to $x=0.0$ and $1/\chi$ apparently approached towards a linear dependence [6]. Interestingly above ~15K $x=0.3$, shows PMR, indicating dominant character of Pauli paramagnetism. However, crossover of magnetoresistance from negative to positive happens at ~15 K. Further, for 40% Cu doping, the system exhibits negative magnetoresistance throughout the temperature range measured because of Curie-Weiss type paramagnetism [6] and is as expected.

$$\rho = \rho_0 - b \ln(T)$$  \hspace{1cm} (1)

where $\rho_0$ and $b$ are constants (shown in the Fig. 4).

Fig. 2 and 3 shows magnetic field effect on the $\rho(T)$. At low temperature $−\ln T$ (Kondo effect) rise of resistivity with decreasing the temperature is observed and is fitting to the equation 1.

![Resistivity vs Temperature](image1)

![Resistivity vs Temperature](image2)

Fig. 4 shows the fitting parameters $\rho_0$ and $b$ from the Equation 1 which is fitted to the $x=0.3$ (Fig. 2) and 0.4 (Fig. 3). The decreasing trend of $\rho_0$ and $b$ indicates weakening of spin flip scattering between conduction electrons and Ce-4f electrons while increasing the applied magnetic field strength. Commonly, for $x=0.3$ and 0.4, the low temperature resistivity takes a downturn after an initial rise in presence of higher magnetic fields at ~6 T ($x=0.3$) and ~8 T ($x=0.4$), respectively. The temperature at which down-turn ($T_{down-turn}$) occurs, is gradually shifted towards high temperatures upon increasing the magnetic field.
strength. Such a behavior can be understood in the following manner. In general, this down turn is a common feature of heavy Fermion compounds (based on Kondo route) [12-16] which show Fermi liquid behavior. The external magnetic field gradually shifts the \( T_{\text{down-turn}} \) to high temperatures. It suggests that compounds with \( x=0.3 \) and 0.4 have heavy Fermion like character. In order to see this sharp fall of resistance at zero field one has to extend measurements below 2 K.

\[ \rho (\mu \Omega \text{cm}) \]

**Fig. 3.** Resistivity vs temperature of \( x=0.4 \) at low temperatures in the magnetic field up to 14 T are fitted to the kondo model with Equation 1.

\[ H(T) \]

\[ \rho (\mu \Omega \text{cm}) \]

**Fig. 4.** \( \rho_0 \) and \( b \) vs \( H \) of Ce(Ni\(_{1-x}\)Cu\(_x\))\(_2\)Al\(_3\) with \( x=0.3 \) (red) and 0.4 (black) using equation 1.

Linear temperature coefficient of thermoelectric power which is obtained from the linear fit to the data (as shown in **Fig. 5**) is plotted in **Fig. 6**. The \( \gamma_0 \), the enhanced electronic specific heat coefficient, is estimated by extrapolating the low temperature rise of \( C_p/T \) vs \( T^2 \) down to 0K. The plots have been reported in our earlier communication [9]. Obtained \( \gamma_0 \) values are in agreement with literature [6, 8]. Such enhancement of \( \gamma_0 \) up to 269 mJ/mole-K\(^2\) suggests Ce(Ni\(_{1-x}\)Cu\(_x\))\(_2\)Al\(_3\) compound to be heavy Fermion-like character.

\[ \frac{S}{T} = \frac{C/T}{ne} \] (2)

\[ n = \frac{\gamma}{(S/T)e} \] (3)

At low temperatures, as the temperature decreases TEP decreases linearly which is shown in figure 6. The linear fit to the temperature dependent thermoelectric power below about \( \sim 11 \) K is shown in figure 6. Obtained fit parameters along with \( \gamma \) are shown in **Table 1**.

\[ (\mu \Omega \text{cm}) \]

**Fig. 5.** Seebeck coefficient vs temperature of Ce(Ni\(_{1-x}\)Cu\(_x\))\(_2\)Al\(_3\) with \( x=0.0-0.4 \) below 11 K, which is fitted with linear equation.

\[ \mu \text{cm/K} \]

**Fig. 6.** Slope of \( S(T) \) and electronic specific heat coefficient (\( \gamma_0 \)) vs doping concentration (\( x \)) of Ce(Ni\(_{1-x}\)Cu\(_x\))\(_2\)Al\(_3\) with \( x=0.0-0.4 \).
From the Table 1 it is clear that the carrier concentration ‘n’ increases with increasing Cu doping at Ni site and it falls in between common metals and semiconductors. Especially this region of concentration is suitable for obtaining the figure of merit. The suggested ‘n’ value for achieving high figure of merit (ZT) is between 10^19 and 10^21 carriers per cm^3 [18].

Table 1. Sommerfeld coefficient γ and linear temperature coefficient of the thermoelectric power S/T of Ce(Ni1-xCux)2Al3 with x=0.0-0.4 are obtained from the our earlier report [9] and linear fit from Fig. 5 respectively.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>γ (J/moleK^2)</th>
<th>S/T (µV/K)</th>
<th>n (permgr)</th>
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<tr>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.418</td>
<td>1.2x10^10</td>
</tr>
<tr>
<td>0.1</td>
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<td>0.870</td>
<td>2.0x10^10</td>
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<td>4.9x10^10</td>
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