Bull. Mater. Sci., Vol. 39, No. 2, April 2016, pp. 537–541. © Indian Academy of Sciences.

Magneto-heat capacity study on Kondo lattice system $Ce(Ni_{1-x}Cu_x)_2Al_3$

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MS received 16 July 2015; accepted 21 September 2015

Abstract. **Heat capacity studies on the Kondo lattice system $Ce(Ni_{1-x}Cu_x)_2Al_3$, in the presence of magnetic fields, were reported for $x = 0.0-0.4$. The physical properties of the intermediate compositions like $x = 0.3$ and 0.4 were known for their enhanced thermoelectric power and hence have been analysed with an extra interest. It was also shown from the X-ray diffraction that these systems with $x = 0.3$ and 0.4 were in single phase in terms of sample purity and it stabilized the phases easily with the increase in the Cu doping in the system. The low temperature rise in C_p/T below 10 K under the influence of high magnetic fields was analysed using a multi-level Schottky effect. A gradual decrease of the total angular momentum (*J*) with the increase of applied magnetic fields indicated a scenario of screening of Ce^{3+} magnetic moment while simultaneously the system settled for the Fermi liquid state. The screening thus seen was in line with the expectations of electrical conductivity measurements on these samples.**

Keywords. **Kondo lattice system; Fermi liquid; heavy Fermion; Schottky effect.**

1. Introduction

Hybridization between localized 4f and conduction electrons are responsible for exotic states like heavy Fermion (HF) behaviour, non-Fermi liquid states, etc. in many of the intermetallic systems that include the recent times focused $CeNi_2Al_3$ system which is known for its high figure of merit in low temperature applications [1–5]. These systems show a prominent low-temperature upturn in the heat capacity that can be attributed to a variety of phenomena [6–12]. $CeNi_2Al_3$ crystallizes in the hexagonal $PrNi_2Al_3$-type structure with a space group P6/mmm and exhibits metallic behaviour [13]. The low-temperature upturn in specific heat, enhancement in the unit cell volume, carrier density and thermoelectric power were reported upon increasing Cu concentration. The system undergoes a transition from Pauli paramagnetic to Curie–Weiss-type paramagnetic state at 40% doping in $Ce(Ni_{1-x}Cu_x)_2Al_3$ [14]. Upon further increase in the Cu concentration, the system undergoes to an antiferromagnetic state [5]. Similar to Ce- and Eu-based systems like $Ce(Pb_{1-x}Sn_x)_3$, $CePt_{1-x}Ni_x$ and $EuCu_2(Ge_{1-x}Si_x)_2$, the present system $Ce(Ni_{1-x}Cu_x)_2Al_3$ does not show magnetic ordering down to the lowest temperature measured. These solid solutions also exhibit a proportionality between the initial slope of thermopower $S(T)$ and the electronic specific heat coefficient as $T \rightarrow 0$ K limit [15]. An evolution from a simple compensated metal ($x = 0.0$) to a paramagnetic one ($x = 0.4$) was observed in $Ce(Ni_{1-x}Cu_x)_2Al_3$ through the parameters obtained from the two band model fit to the thermoelectric power [16]. In recent times it has also been speculated from the resistivity under magnetic fields that the formation of a Fermi liquid-like behaviour is quite probable and is in line with the expectations of specific heat studies [17]. However, a convincing study is needed towards this and is the aim of the present investigation. In this paper, magneto-heat capacity study of polycrystalline $Ce(Ni_{1-x}Cu_x)_2Al_3$ system for $x = 0.0$–0.4 has been reported.

The Schottky analysis was used to understand low temperature rise in C_p/T and its magnetic field dependence of specific heat. If systems do not have the magnetic ordering and their excess specific heat is obtained due to local moment/cluster at low temperatures, then one can use Schottky model to analyse the systems. There are two types of Schottky effects for analysing the excess specific heat namely (i) two-level Schottky effect which is applicable if excess specific heat is due to the local moment, (ii) multi-level Schottky effect which is applicable if the excess specific heat is due to the magnetic cluster [18,19]. Here multi-level Schottky analysis is employed on specific heat of $x = 0.3$ and 0.4 samples which are in single phase conformed by X-ray diffraction (XRD). The results confirm that the system is indeed transformed to a Fermi liquid-like state accompanied by a screening of Ce^{3+} magnetic moment.

2. Experimental

Polycrystalline $Ce(Ni_{1-x}Cu_x)_2Al_3$ with $x = 0.0$, 0.1, 0.3, and 0.4 have been prepared by taking constituent elements, Ce (99.9%) from Leico, Ni (99.995%) from Matech, Cu (99.9%) and Al (99%) from Cerac Company, respectively. The stoichiometric amounts were arc melted in high-purity

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Argon atmosphere. For phase homogeneity flipping was carried out three times and finally rods of few centimetres were prepared. The phase purity was checked on unannealed powder specimens with the Bruker D8 Advanced X-ray diffractometer using Cu-Kα radiation. Heat capacity measurements were carried out using the heat relaxation technique with the 14T/2K PPMS (QD-USA).

3. Results and discussion

Figure 1 shows the XRD pattern for $x = 0.0$–0.4. Samples $x = 0.0, 0.1$ showed less than 1% of $CeAl_2$ second phase. As the doping concentration is further increased, $CeAl_2$ phase dissolves and attains its pure phase for $x = 0.3$ and 0.4. Figure 1b shows Reitveld refined for $x = 0.4$. Refinement analysis was done using Fullprof-2K Reitveld refinement program which shows that $x = 0.3$ and 0.4 are in single phase. It crystallizes in the hexagonal $PrNi_2Al_3$-type structure with a space group P6/mmm. The earlier investigations have been carried out on $Ce(Ni_{1-x}Cu_x)_2Al_3$ series and reported that impurity peaks are presented throughout the series [5,13,14]. No unaccounted peak in the above mentioned 2θ range for $x = 0.3$ and 0.4 is observed, indicating that higher doping of Cu in this system stabilizes the phases easily.

Specific heat of $Ce(Ni_{1-x}Cu_x)_2Al_3$ system for $x = 0.0$–0.4 is shown as C_p/T *vs.* T^2 plots in figure 2. It has to be noted that a pronounced peak seen in $CeNi_2Al_3$ at 6 K is attributed to the impurity phase [13,14]. Instead, in our case, at 6 K, the samples $x = 0.0$ and 0.1 show only a very tiny and broad hump like feature (inset of figure 2). Around 2.9 K another peak was observed for $x = 0.0$ and 0.1, in the present case (inset of figure 2) where as a sharp rise in C_p/T is observed around this temperaure and is attributed to the impurity spins [13]. The low-T rise of C_p/T for $x = 0.3$ and 0.4 is considered to be an intrinsic feature of phase pure samples [5,14,16]. Low-T electronic specific heat coefficient γ_0 estimated by extrapolating the data to 0 K gives a value of 141 and 269 mJ mol^{-1} K^{-2} for $x = 0.3$ and 0.4, respectively. The relatively high values suggest moderately HF like nature as is also supported in the literature [5,14], however, no indication of magnetic ordering in the present series. However, there are many reasons quoted in literature for variety of samples for the low temperature upturn below 10 K. They may have origin in characters like HF, non-Fermi liquid, spin fluctuations, spin glass or magnetic defects like clusters and localized moments [6–12]. However, in recent times magentoresistance studies at low temperature and high magentic fields (LTHM) reveals Fermi liquid like behaviour of the present system [17].

In order to have a deep insight into the system to know about the nature of the ground state and to see the expected heavy Fermion and Fermi-liquid behaviour we have performed the magnetic field dependence of specific heat. Figures 3 and 4 represent characteristic curves in the magnetic fields up to 12 T at temperatures below 15 and 20 K for $x = 0.3$ and 0.4, respectively. Above these temperatures, the heat capacity data in magnetic fields coincide with that of zero fields. Positive field effect on C_p/T *vs.* T is seen up to 4 and 5 T for $x = 0.3$ and 0.4, respectively. Further application of magnetic field results in the down turn and becomes prominent in the form of hump at 12 T as shown in the figures 3 and 4. It is observed that the maximum of the hump is shifted to higher temperatures with increasing the

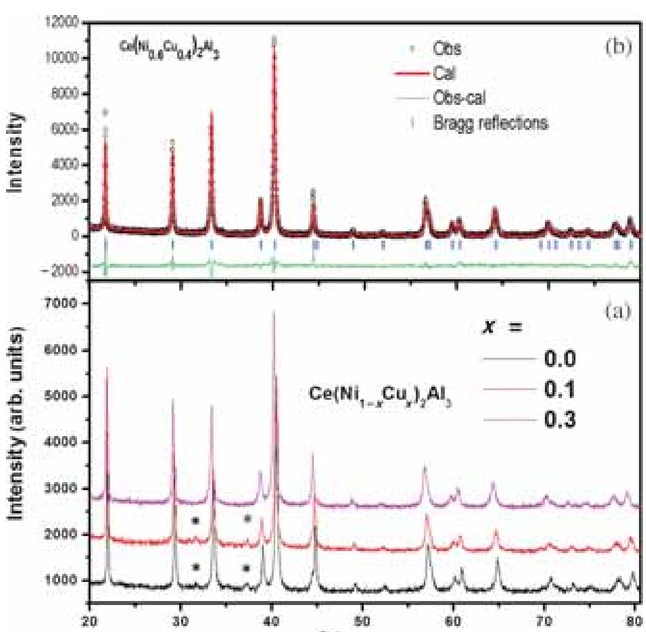

Figure 1. (**a**) X-ray diffraction pattern of $Ce(Ni_{1-x}Cu_x)_2Al_3$ with $x = 0.0$, 0.1 and 0.3. Less than 1% of $CeAl_2$ impurity phase in $x = 0.0, 0.1$ indicated with * symbol. (**b**) Reitveld refinement for $x = 0.4$.

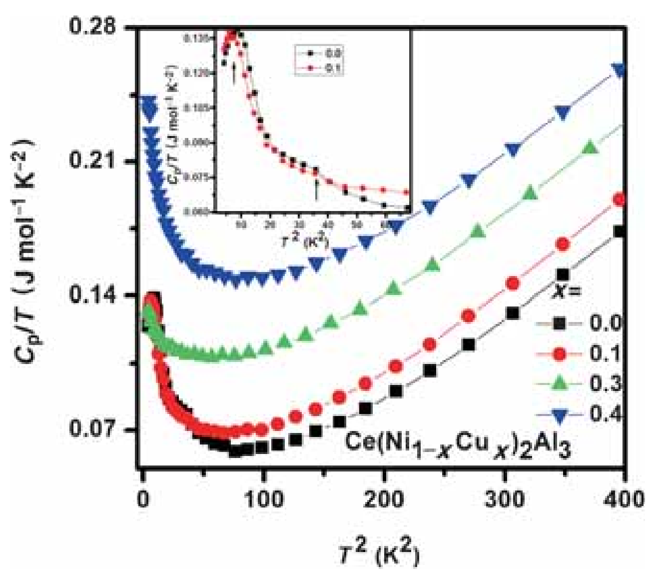

Figure 2. C_p/T *vs.* T^2 of $Ce(Ni_{1-x}Cu_x)_2Al_3$ for $x = 0.0$–0.4 below 20 K. Inset shows the low temperature anomalies due to the presence of secondary phases, shown with arrows for $x = 0.0$ and 0.1 below 10 K.

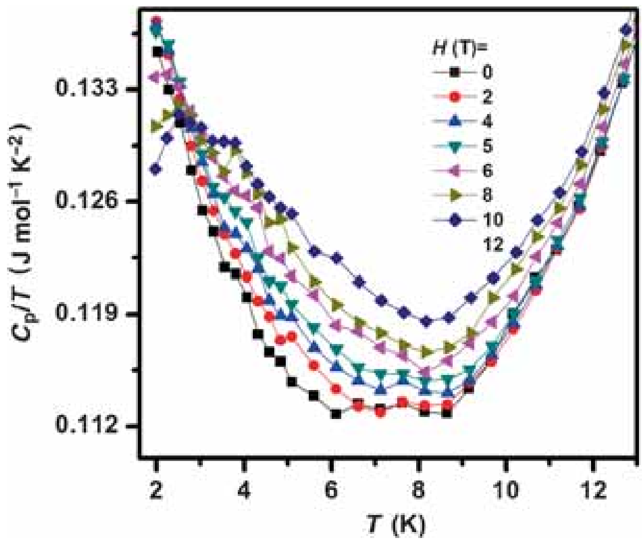

Figure 3. C_p/T *vs.* T below 15 K for the sample of $Ce(Ni_{1-x}Cu_x)_2Al_3$ with $x = 0.3$.

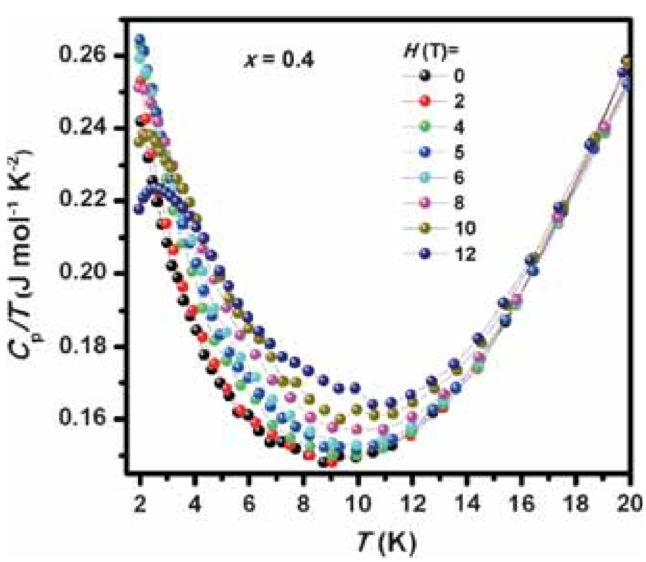

Figure 4. C_p/T *vs.* T below 20 K for the sample of $Ce(Ni_{1-x}Cu_x)_2Al_3$ with $x = 0.4$.

field strength. To have a clear insight, we have plotted excess specific heat (ΔC) defined as $\Delta C = C_p - (\gamma T + \beta T^3)$ in different external magnetic fields for $x = 0.3$ and 0.4.

$$C_{\mathrm{Sch}} = Nk_{\mathrm{B}}\left[\frac{x^2e^x}{(e^x-1)^2} - (2J+1)^2\frac{x^2e^{(2J+1)x}}{\left(e^{(2J+1)x}-1\right)^2}\right], \tag{1}$$

where

$$x = \frac{g\mu_{\mathrm{B}}H_{\mathrm{eff}}}{k_{\mathrm{B}}T} \quad \text{and} \quad H_{\mathrm{eff}} = H_{\mathrm{int}} + H_{\mathrm{appl}}.$$

Maximum of ΔC shifts to higher temperatures with increasing the magnetic field resembling Schottky behaviour (hereafter ΔC is read as ΔC_{Sch}). Figures 5 and 6 show

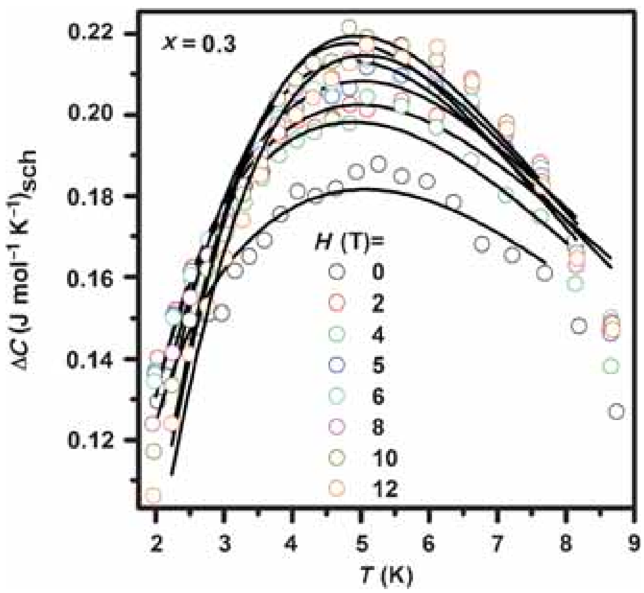

Figure 5. Temperature dependence of excess specific heat $\Delta C = C_p - (\gamma T + \beta T^3)$ for $x = 0.3$. The circles represent experimental data and the solid lines represent fitting to the multi-level Schottky function (equation (1)).

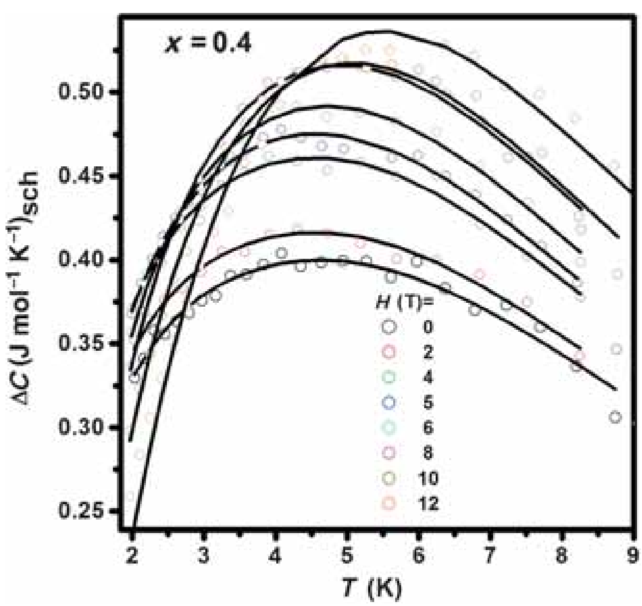

Figure 6. Temperature dependence of excess specific heat $\Delta C = C_p - (\gamma T + \beta T^3)$ for $x = 0.4$. The circles represent experimental data and the solid lines represent fitting to the multi-level Schottky function (equation (1)).

temperature variation of ΔC_{Sch} below 10 K and in fields up to 12 T. The γ and β are obtained by fitting the data at high T, $C_p/T = \gamma + \beta T^2$ where γT is the electronic contribution and βT^3 is the lattice contribution to the specific heat to each field data. Schottky contribution is given by equation (1) represents the multi-level Schottky contribution to the specific heat [18,19]. Figures 5 and 6 show the fitted curves with

Table 1. Fitting parameters total angular momentum (J) and internal magnetic field (H_{int}) obtained by fitting the data using equation (1) for samples of $x = 0.3$ and 0.4 shown in figures 5 and 6.

H (T)	$x = 0.3$, total angular momentum J ($\hbar$)	$x = 0.3$, H_{int} (T)	$x = 0.4$, total angular momentum J ($\hbar$)	$x = 0.4$, H_{int} (T)
0	3.5	8.57	5	6.32
2	3	7.26	5	4.10
4	3	5.02	4.5	2.55
5	2.5	5.35	4	2.11
6	2	5.38	3.5	1.99
8	2	5.13	3	1.13
10	1.5	2.39	2.5	0.48
12	1.5	1.69	2	0.86

solid lines along with experimental data in circles. The fitting parameters are tabulated in table 1.

A careful look into table 1 reveals the following. In the absence of magnetic field total angular momentum (J) has a value higher than that of the free ion angular moment ($J = 2.5\hbar$) of Ce^{3+} as shown in table 1 for both the samples $x = 0.3$ and 0.4. This implies that instead of simple local moment a scenario is evolved wherein local magnetic clusters might have been formed due to disorder induced carriers when Cu is doped. It is to be noted that we have already shown disorder induced effects in TEP in our earlier report [16]. Upon application of magnetic fields, J value decreases and reaches to a value lower than that of free ion moment like $1.5\hbar$ and $2\hbar$ at 12 T for $x = 0.3$ and 0.4, respectively. Such a decrement in J and H_{int} values as shown in table 1 are indicative of the magnetic moments are partially screened. The screening is slightly more for $x = 0.3$ because of its more conducting nature as compared to that of $x = 0.4$ sample. Such a physical scenario favours the system to settle ultimately at high fields to behave like a screened Fermi-liquid like state [17].

Common features observed in both magnetic field dependence of resistivity [17] and heat capacity (present study) of $Ce(Ni_{1-x}Cu_x)_2Al_3$ for $x = 0.3$ and 0.4 at LTHM are (i) low temperature rise in C_p/T and ρ with the decrease in the temperature is observed. Resistivity indicates the screening or higher scattering strength at the Kondo cloud. Specific heat indicates the increase of mass and in-turn better screening. (ii) The observed rise at low temperature decreases and develops a peak in the C_p/T of specific heat with increasing the strength of the magnetic field. Analogously broad hump is developed in magnetoresistance measurements. (iii) The hump/peak shifted to high temperature with the increase in the strength of the magnetic field in both C_p/T and ρ. As discussed above, the screening is inferred by analysing the specific heat is at one to one correspondence with that of the magnetoresistance measurements, one can conclude without hesitation the screening of Ce^{3+} moments. The present system for $x = 0.3$ and 0.4 shows moderately heavy fermion behaviour with γ_0 141 and 269 mJ mol^{-1} K^{-2} for $x = 0.3$ and 0.4, respectively, do not have magnetic ordering and fall in the category of other Ce-based heavy Fermion-Fermi liquid systems like $CeCu_6$ [20], $CeAl_3$ [21] and $CeCu_2Si_2$ [22].

4. Conclusion

The Heat capacity studies on the Kondo lattice system $Ce(Ni_{1-x}Cu_x)_2Al_3$ in the presence of magnetic fields have been reported for $x = 0.0$–0.4, with a special emphasis on $x = 0.3$ and 0.4 which are known for their enhanced thermoelectric power. The low temperature rise in C_p/T below 10 K at high magnetic fields is analysed using a multi-level Schottky phenomenon. The total angular momentum (J) has a value higher than that of free ion moment of Ce^{3+} at zero fields. This value decreases with increase of applied magnetic fields and at 1 T it is much lower than that of the free ion moment. This indicates a scenario of screening of magnetic moment of Ce^{3+} while simultaneously the system settles for a probable Fermi liquid like state. The screening thus seen is in line with the expectations of electrical conductivity measurements on these samples reported earlier.

Acknowledgements

We thank Dr A K Sinha for the support and encouragement. The in-mates of LTL and Cryogenics were thanked for their help, especially, Er P Saravanan for the supply of cryogens. DST, India, is thanked for their initial assistance in setting up of LTHM facilities.

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