Transport and calorimetric studies on CeNi$_2$Al$_3$

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Abstract. Transport and calorimetric properties of Kondo lattice system CeNi$_2$Al$_3$ are reported. CeNi$_2$Al$_3$ shows good agreement with Grand Kadowaki-Woods relation with degeneracy of the quasi-particle N=6. The nonmagnetic nature of CeNi$_2$Al$_3$ is evident from resistivity measurement even though magnetic elements Ce and Ni are present. Three signatures, deviation from the normal metallic behaviour in resistivity above 140 K, relatively low charge carrier concentration (10$^{21}$ cm$^{-3}$) and energy gap $E_g$~11.6 meV obtained from two band model shed light on the most basic notions related to the semimetal nature of CeNi$_2$Al$_3$.

1. Introduction
Intermetallic compounds are being well studied for exhibiting different ground states because of the hybridization of the 4f electrons with the conduction electrons. Ce based systems may fall under the category of heavy fermions (HF) or intermediate valence or delocalised state which causes the enhancement of physical quantities like electronic specific heat coefficient $\gamma$, effective mass $m^*$, thermopower $S$ as the strength of the c-f hybridization increases [1].

CeNi$_2$Al$_3$ is a Kondo lattice system with $T_K=370$ K [2]. Investigation of physical properties like magnetic susceptibility $\chi$, resistivity, specific heat $C_p$, and X-ray photo emission spectroscopy revealed intermediate valent character of Ce [3] and nonmagnetic, moderately HF metallic like behaviour [4, 5]. Upon Cu doping at Ni site it shows simultaneous optimization of thermoelectric parameters [6, 2].

In this paper, we discuss the structural, transport and calorimetric properties of CeNi$_2$Al$_3$. Nonmagnetic nature of CeNi$_2$Al$_3$ is evident from its resistivity, despite of constituting magnetic elements Ce and Ni. The universal behaviour of CeNi$_2$Al$_3$ to follow Grand Kadowaki-Woods (KW) relation and probable consideration of its semimetal behaviour is discussed.

2. Experimental techniques
Polycrystalline CeNi$_2$Al$_3$ was prepared by arc melting in high purity Argon atmosphere. X-ray pattern was collected using Bruker D8 Advanced X-ray diffractometer. $C_p$ was carried out by relaxation time method using 14T/2.0K PPMS (QD-USA) from 2 K-300 K. Thermopower measurements were done by differential sandwich method using homemade setup coupled to 4 K Closed Cycle Refrigerator.
3. Results and discussion

3.1. Structural Characterization

Obtained Chi2 from the Reitveld refinement is 2.72. Earlier investigations have been done on x=0.0–0.6 on Ce(Ni_{1-x}Cu_{x})_2Al_3 series were prepared by arc melting, also observed impurity peaks [2, 5, 6].

3.2. Transport and Calorimetric properties

Figure 2 shows \( \rho(T) \) of CeNi\(_2\)Al\(_3\). It is examined under the light of two band model (TBM) to understand the conduction in CeNi\(_2\)Al\(_3\). Conductivity of metal and a semiconductor are \((\rho_0 + A T^2)^{-1}\) and \(\sigma_0 \exp(-E_g/2k_b T)\), respectively. For the case, \(1/\rho = (1/\rho_1 + 1/\rho_2)\)

\[
\rho = \left(\sigma_{01}^{-1} + A T^{-2}\right)^{-1} + \sigma_{02} \exp\left(-E_g/2k_b T\right)^{-1}
\]

The fit to the data using equation (1) is shown in figure 2. Obtained \(E_g\) in Kelvins is 135.3 K. \(d\rho/dT\) and \(dS(T)/dT\) show a broad hump around 140 K, in figure 3, which agrees with the \(E_g\) obtained from TBM. It implies the mixture of metallic as well as narrow gap semiconducting like behaviours. In order to understand better, we have estimated charge carrier concentration ‘n’ by using the following relation [8].

\[
\rho = \left(\sigma_{01}^{-1} + A T^{-2}\right)^{-1} + \sigma_{02} \exp\left(-E_g/2k_b T\right)^{-1}
\]
\[ n = \frac{2E_F D(E_F)}{3} \]  

where \( D(E_F) \) is the density of states and \( E_F \) is the Fermi energy [8-10].

\[ \gamma = \frac{2\pi k_B^2}{3} D(E_F), \quad S/T = B = \frac{2\pi k_B^2 e^2}{2eE_F} \]  

The Sommerfeld coefficient \( \gamma \) is estimated from the fit of \( C_\rho/T = \gamma + \beta T^2 \), figure 3. The obtained \( \gamma = 32.27 \text{ mJ.mol}^{-1}.\text{K}^{-2} \) is at par with those reported in literature [2, 6]. Debye temperature \( \theta_D = 350 \text{ K} \) is estimated using \( \theta_D(K) = \sqrt[3]{1944p/\beta} \), where \( p \) is the number of atoms in the formula unit. The peak at low temperature is due to antiferromagnetic nature of CeAl\(_2\) secondary phase [11, 12] as is shown in XRD. The obtained diffusion thermopower constant \( B = 0.418 \mu\text{V.K}^{-2} \) as \( T \to 0 \), figure 3. The calculated Fermi energy \( E_F \) and \( D(E_F) \) from equation (2) are 87.6 meV and \( 2.43 \times 10^{12} \text{ eV}^{-1}.\text{cm}^{-3} \). From equation (1), we get \( n = 1.4 \times 10^{13} \text{ cm}^{-3} \). Therefore the order of \( n \), hump in resistivity and energy gap \( E_g \), conclusively support the semimetal nature of CeNi\(_2\)Al\(_3\).

### 3. 2.1. Grand Kadowaki-Woods relation:

KW relation \( A/\gamma^2 = 1 \times 10^{-5} \mu\Omega \text{ cm (K.mol.mJ)}^{-1} \) is usually applicable to the Fermi liquids (FL). A \( \alpha \text{ m}^2 \) and \( \gamma \alpha \text{ m} \) are related to the electrical resistivity as \( \rho = AT^2 \) and \( C_\rho = \gamma T \), respectively [13]. Systematic and significant deviation from the KW relation is observed for Yb based intermediate valent systems and Ce based compounds even though they show FL behaviour at low temperature [14, 15].

**Figure 4.** Plot of \( A \) vs \( \gamma \) for different HF based on degeneracy of the quasi-particle \( N = 2, 4, 6 \) and 8. CeNi\(_2\)Al\(_3\) (\( N = 6 \)) is represented with \( A = 224 \times 10^{-3} \mu\Omega \text{ cm. K}^{-2} \) and \( \gamma = 32.27 \text{ mJ.mol}^{-1}.\text{K}^{-2} \).

**Figure 5.** Plot of \( \tilde{A} \) vs \( \tilde{\gamma} \) of HF systems. Universal line represents grand KW relation. CeNi\(_2\)Al\(_3\) is represented with \( \tilde{A} = 23.5 \times 10^{-3} \mu\Omega \text{ cm. K}^{-2} \) and \( \tilde{\gamma} = 2.15 \text{ mJ.mol}^{-1}.\text{K}^{-2} \).

A primary report on different HF systems revealed the deviation of \( A/\gamma^2 \) for different degeneracies, \( N = 2\text{J} + 1 \) [14]. Later on, the theoretical work on FL theory also found out the same, mentioning that \( A/\gamma^2 \) ratio would be independent of HF materials but depends on degeneracy \( N \) [16]. In CeNi\(_2\)Al\(_3\), Ce in +3 state having angular momentum \( J = 5/2 \) with \( N = 6 \). The obtained values for CeNi\(_2\)Al\(_3\), \( A = 354 \times 10^{-3} \mu\Omega \text{ cm.K}^{-2} \) and \( \gamma = 32.27 \text{ mJ.mol}^{-1}.\text{K}^{-2} \). According to Ref. [14], CeNi\(_2\)Al\(_3\), is plotted in figure 4. However, the normalized coefficients of \( A \) and \( \gamma \) by absorbing the degeneracy are given as
Using the above normalised coefficients $\tilde{A}$ and $\tilde{\gamma}$ the new relation $\tilde{A}/\tilde{\gamma}^2 = 1 \times 10^{-5}$ $\mu\Omega$ cm (K.mol.mJ$^{-1}$)$^2$ is derived and called as Grand-KW relation. This unique value is independent of materials and degeneracy of quasi-particles [17]. The estimated $\tilde{A} = 23.5 \times 10^{-5}$ $\mu\Omega$ cm. $K^{-2}$ and $\tilde{\gamma} = 2.15$ mJ.mol$^{-1}$.K$^{-2}$ for CeNi$_2$Al$_3$ with N=6 gives $\tilde{A}/\tilde{\gamma}^2 = 4.9 \times 10^{-5}$ $\mu\Omega$ cm(K mol.mJ$^{-1}$)$^2$ as is shown in the figure 5, which follows the Grand KW relation along with many other HF systems.

4. Conclusions
In summary, the experimental investigation of moderately HF system CeNi$_2$Al$_3$ by means of transport, calorimetric and structural characterization is reported. It falls on the universal line of Grand Kadowaki-Woods relation with the estimated normalised coefficients $\tilde{A} = 23.5 \times 10^{-5}$ $\mu\Omega$ cm and $\tilde{\gamma} = 2.15$ mJ.mol$^{-1}$.K$^{-2}$. Nonmagnetic nature evident from resistivity indicates that there is strong hybridization between conduction and Ce-4$f$ electrons. It shows hump like behaviour above 140 K. The estimated energy gap by implementing two band model, $E_g$ is about 140 K and the order of charge carrier concentration $n$ is $1.4 \times 10^{21}$ cm$^{-3}$. The Fermi energy as estimated from the diffusion thermopower coefficient is $E_F = 87.6$ meV. These three, conclusively, shed light on conduction behaviour of CeNi$_2$Al$_3$ and support semimetal character.

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