CeNi₄Cr compound and its thermodynamic properties

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Abstract. CeNi₅ as a mother compound is well known as a Stoner enhanced paramagnet characterized by the spin fluctuation contribution on its transport properties. Previous work on CeNi₄Cr compound showed typical features of mixed valence systems with indication of tendency to heavy fermion behavior [1]. The theoretically predicted phase transition into antiferromagnetic order wasn’t observed down to 2 K. In this work we present the effect of spin fluctuations of the CeNi₄Cr compound focused on its thermodynamic properties.

1. Introduction

In previous works, Jain et al. [1] have studied the effect of partial substitution of Ni by Cr in the CeNi₅ intermetallic compound to search materials for hydrogen storage. The mother compound CeNi₅ crystallizes in the hexagonal CaCu₅ type, and it results to be a Stoner enhanced paramagnet characterized by a spin fluctuation (SF) contribution on its transport properties [2]. Murugan et al. [3] have revealed using first-principles density functional calculations that CeNi₄Cr prefers the antiferromagnetic state. In our previous work [4] we have found that CeNi₄Cr shows typical features of mixed valence systems with indication of tendency to heavy fermion behavior. The lack of a strong evidence of theoretically predicted phase transition into antiferromagnetic order may be due to Kondo screening of the magnetic moment. In order to study instability of the compound CeNi₄Cr we have provided further investigation and analysis of heat capacity measurements with possible spin fluctuations contribution.

The measurements were carried out on a piece of the polycrystalline CeNi₄Cr compound prepared by induction melting of the constituent element under argon atmosphere. The CeNi₄Cr compound crystallizes in the hexagonal CaCu₅-type structure, space group P6/mmm. The lattice constants are a = 4.931Å and c = 4.037Å. Heat capacity measurements were performed in Kosice, Slovakia by a Physical Property Measurement System (PPMS) commercial device (Quantum Design) in the temperature range 2-300 K using the two-τ model of the relaxation method in applied magnetic field up to 9 T.

2. Heat capacity

The temperature dependence of heat capacity of CeNi₄Cr doesn’t show any sign of transition into magnetically ordered state in contradiction with predictions calculated by [3] – see Fig. 1. Moreover no influence of magnetic field on heat capacity dependence is evident [Fig.1]. In order to study spin fluctuation effect on heat capacity we used the formula (1)

$$ C_p(T) = \gamma T + A' T^3 \ln \left( T/T_{sf} \right) + \frac{24.9416 + 0.05313 x_D^2 + 9.8510^{-4} x_D^4 + 4.810^{-7} x_D^6}{1 + 0.0521 x_D^2 + 4.7110^{-4} x_D^4 + 4.5610^{-6} x_D^6 + 2.10^{-8} x_D^8} $$

(1)
where first term corresponds to electronic contribution with Sommerfeld coefficient $\gamma$, second term corresponds to spin fluctuation contribution with coefficient $A*$ and characteristic spin fluctuation temperature $T_{sf}$ [5]. The third term is an expression of phonon contribution to heat capacity with $x_D = \theta_D/T$, $\theta_D$ is the Debye temperature, used by numerical analysis [6] and very good fits experimental data. The example of such fitting for compound CeNi$_4$Cr is shown in Fig. 2. It is visible that fitting with included spin fluctuation term sets better (pink curve) than without it (dark blue – represents the curve with fixed parameters obtained from pink curve).

![Fig. 1. Heat capacity dependences of CeNi$_4$Cr compound in different applied magnetic field.](image1)

![Fig. 2. Temperature dependence of heat capacity of CeNi$_4$Cr compound, pink curve represents the fitting function (1) with the free parameters $\gamma$, $\theta_D$, $A*$, $T_{sf}$, dark blue curve represents the fitting function with SF contribution with the fixed values $\gamma$, $\theta_D$ obtained from pink curve.](image2)
Magnetic contribution to heat capacity was obtained by extraction of heat capacity dependence of isostructural LaNi₅ crystallizing in CaCu₅ type of structure, space group P₆₃/mmm. We analysed the magnetic contribution by means of Schottky effect using formula (2)

\[
C_{\text{mag}}(T)/T = A^*T^2 \ln\left(\frac{T}{T_{sf}}\right) + \frac{R}{3} \left[ \frac{\sum_{\ell=0}^{n-1} \Delta_i e^{-\Delta_i/T}}{\sum_{\ell=0}^{n-1} e^{-\Delta_i/T}} - \left(\frac{\sum_{\ell=0}^{n-1} \Delta_i e^{-\Delta_i/T}}{\sum_{\ell=0}^{n-1} e^{-\Delta_i/T}}\right)^2 \right]
\] (2)

where R is gas constant, \( n \) denotes to the number of energy levels and \( \Delta 0 = 0 \). In the hexagonal symmetry the crystal field splits the Ce³⁺ (\( J = 5/2 \)) multiplet into 3 dublets (\( n = 3 \)). Magnetic contributions to heat capacity of CeNi₄Cr is shown in Fig. 3 (symbols). Fitting of Schottky using (2) without term of \( A^*T^2 ln(T/T_{sf}) \) corresponding to SF contribution is represented by blue curve. The cyan curve represents fitting of Schottky contribution using (2). One can see that the fitting including spin fluctuation contributions fits better than separate Schottky effect.

Fig. 3. Magnetic contribution to heat capacity as a function of temperature of CeNi₄Cr (pink symbols). Cyan curve represents fitting using (2) with SF term, blue curve represents fitting using standard formula by means of (2) without SF term.

The obtained values of energy levels of CEF are in good agreement with theoretically expected values in [7] and with the values of similar compound CeNi₄Si [8]. The coefficients \( A^* \) and \( T_{sf} \) determined from magnetic contribution to heat capacity are in good agreement with the values determined from the total heat capacity. On the basis of [5] and classification of spin fluctuators therein we assigned CeNi₄Cr compound to type 3 of spin fluctuators.

3. Conclusions
The temperature dependence of heat capacity of CeNi₄Cr confirms no sign of transition into magnetically ordered state in agreement with [4]. Analysis \( C \) vs. \( T \) using formula with electronic, phonon and spin fluctuation contributions shows influence of spin fluctuation on the heat capacity dependence. Further analysing of magnetic contribution in means of Schottky effect and inclusion of spin fluctuation term has confirmed that spin fluctuation effect is not negligible. The level scheme of crystal electric field splitting is in good agreement with the scheme obtained in CeNi₄Si [8].
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