XPS and thermomagnetic characterization of the CeNi₄Cr compound

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ABSTRACT

The magnetic, thermodynamic and electronic structure properties are discussed for the CeNi₄Cr compound. The X-ray photoemission spectra (XPS) provide an evidence of a mixed valence behavior with the occupancy of the f states $n_f = 0.89$ and their hybridization with the conduction electrons $\Delta = 30\,meV$. These values reproduce well the magnetic susceptibility $\chi(T = 0)$, which is enhanced compared to similar CeNi₄M (M = Al, B, Cu) compounds. In combination with a slightly increased electronic specific heat coefficient (up to $100\,mJ\,mol^{-1}\,K^{-2}$), this compound can be classified as being on the border of the heavy fermion and mixed valence behavior. Using a small magnetic field in the $\chi(T)$ measurements reveals a presence of magnetically ordered impurity phase, which is easily damped by higher fields and it is shown that the contribution of this phase is minor. The question of the dependence of the electronic specific heat coefficient on the magnetic field is also addressed and the observations agree well with theoretical predictions based on the Anderson model.

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1. Introduction

Recently, Jain et al. [1] have studied the effect of partial substitution of Ni by Cr in the CeNi₅ intermetallic compound. Their study of the pressure-composition isotherms for CeNi₅₋ₓCrₓ ($x = 0, 1, 2$) have been motivated by search for hydrogen storage materials. It was shown that all the compounds crystallized in the hexagonal CaCu₅-type structure.

Murugan et al. [2] studied the structural, magnetic, and spin-dependent transport properties of the CeNi₄M series (M = Sc–Co) using first-principles density functional calculations. They have revealed that the ferromagnetic state is energetically more favorable for all the compounds except for CeNi₄Cr, which prefers the antiferromagnetic state. The magnetism of these compounds was ascribed to M atoms.

Compounds of the CaCu₅-type structure have been in the focus of our interest in recent years [3–5], mainly from the point of view of the magnetic, transport, thermodynamic, structural and electronic properties. In this paper we present a broad characterization of the CeNi₄Cr compound.

2. Experimental

The measurements were carried out on a piece of the polycrystalline CeNi₄Cr compound prepared by induction melting of the constituent elements under an argon atmosphere. The crystal structure was checked on a powdered sample by X-ray diffraction technique, using Co–Kα radiation. The CeNi₄Cr compound crystallizes in the hexagonal CaCu₅-type structure, space group P6/mmm. The lattice constants are $a = 4.931\,Å$ and $c = 4.037\,Å$. We have found traces of a small amount of Cr and/or Cr₂O₃.

Specific heat measurements were performed by PPMS commercial device (Quantum Design) in Košice, in the temperature range 2–300 K employing the relaxation method and two-τ model.

Measurements of the dc susceptibility and magnetization curves were carried out on a SQUID instrument (Quantum Design MPMS system-Košice).

The X-ray photoemission spectra (XPS) were obtained using the Al–Kα source (1487.6 eV) with a Physical Electronics PHI 5700/660 Spectrometer. All emission spectra were measured immediately after breaking the sample in a vacuum of 10^{-10} Torr. The quantitative analysis of the CeNi₄Cr XPS spectra, taking into consideration the sensitivity factors, has shown that the nominal stoichiometry of the sample is not retained at the surface, as XPS is a surface sensitive method. We have estimated that Cr2p:Ni2p:Ce3d₅/₂ at the surface is 8:68:22.

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3. X-ray photoemission

The basic question in Ce-based compounds concerns the valence state of the Ce ions. Owing to the proximity of the Ce f states to the Fermi level a dramatic change of the physical properties can be observed along with the shift of the actual f-peak position. The main mechanism governing these effects is related to the hybridization of the f states with the conduction electrons, which is equivalent to a variation in the localization level.

We have studied the electronic structure of CeNi$_4$Cr employing the XPS method. Fig. 1 shows a broad range of the binding energy below the Fermi level. The lack of the O 2s peak at the binding energy of 23.1 eV means that the sample oxidation is rather small. The inset of Fig. 1 displays an expansion of the valence band measured with increased accuracy. It is evident that the separation of the Ce 4f contribution is not possible due to the overlapping Ni 3d and Cr 3d states. A well established procedure
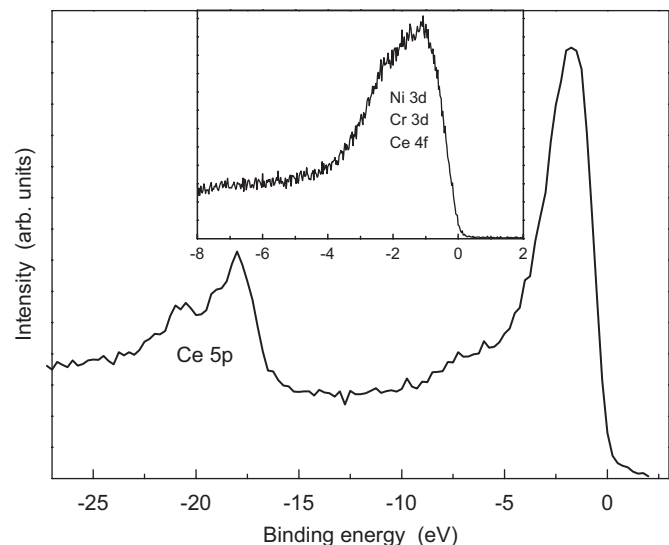
Fig. 1. Valence band region measured by XPS. Inset: energy range close to the Fermi level measured with increased accuracy.
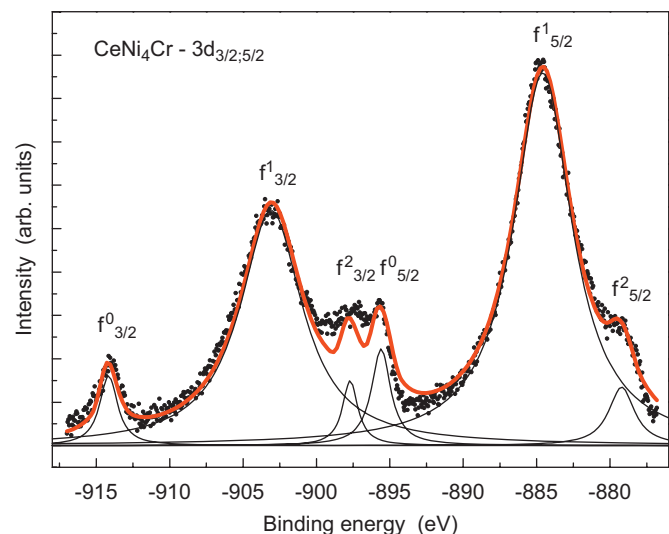
Fig. 2. XPS spectrum of the Ce 3d doublet and its satellites. A decomposition of the main fit to the components is displayed. It is performed with constraints resulting from the adequate degeneracy values.
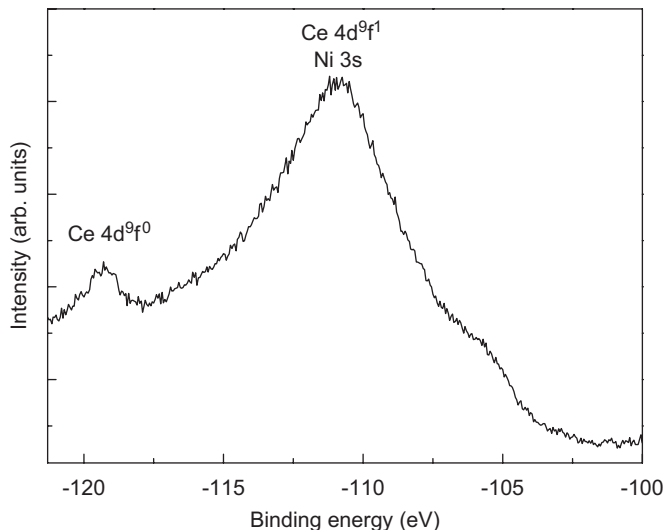
Fig. 3. XPS spectrum of the Ce 4d states. The peak close to 120 eV is a manifestation of the mixed-valence behavior.

to derive quantitatively the hybridization parameter of the f states with the conduction electrons, Δ, and the occupation of the f states, n_f, is based on the analysis of the deeper Ce 3d peaks (Fig. 2), as was proposed by Gunnarsson and Schönhammer [6,7]. The additional satellites accompanying the main spin–orbit split doublet ($3d_{3/2;5/2}$) enable to define the intensity ratios:

$$r_2 = \frac{I(f^2)}{I(f^1) + I(f^2)}, \quad r_0 = \frac{I(f^0)}{I(f^0) + I(f^1) + I(f^2)} \tag{1}$$

which provide $\Delta = 30$ meV and $n_f = 0.89$, respectively. It should be noticed that especially well resolved is the satellite at 914 eV (Fig. 2), which is related to the occupation of the f states. The tendency of the Ce ions to a mixed valence (MV) behavior in this compound is additionally corroborated by the presence of the small peak close to 120 eV in the Ce 4d XPS spectrum (Fig. 3).

4. Magnetic measurements

Within this section we discuss the results of our magnetometric studies and link them to the quantities derived from the XPS measurements. Fig. 4 shows the temperature dependence of the magnetic susceptibility $\chi(T)$. As it often occurs, the broad maximum known for MV systems like CeNi [8,9] is not visible in the temperature range studied. Besides, there was no distinct linear region observed for the reciprocal susceptibility, therefore we analyzed the data with the modified Curie–Weiss law $\chi = \chi_0 + C/(T-\theta)$ providing good fit in the entire temperature range studied. The temperature independent susceptibility $\chi_0 = 1.35 \times 10^{-3}$ emu Oe^{-1} mol^{-1}, the paramagnetic Curie temperature $\theta = -2.6$ K and the effective paramagnetic moment calculated from the constant C is $\mu_{\text{eff}} = 0.81 \mu_B$/f.u. We do not observe any sign of the magnetic ordering down to 2 K. The magnetization curve (Fig. 5) is typical of paramagnet at 300 K but shows a curvature at 2 K, which can be partly ascribed to the Brillouin function; however, impurity magnetism is also possible. One should notice that the susceptibility in Fig. 4 is measured in a magnetic field of 10 kOe, which may easily mask a tiny contribution due to a magnetic order. In Fig. 6 a result for $\chi(T)$ in $H = 50$ Oe is presented. A large hump and the irreversibility indicate that there exists a magnetic order, however, it is very weak and a larger magnetic field removes these anomalies. It is also evident from the magnetization curve at 2 K and in the region of small magnetic