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ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF CeTIn (T=Ni, Au) COMPOUNDS*

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Magnetic properties and electronic structure of CeTIn (T=Au, Ni) compounds with the hexagonal ZrNiAl-type structure have been investigated. CeAuIn is an antiferromagnet ($T_{\rm N}$ = 6.2 K) while CeNiIn was found to exhibit mixed valence and no magnetic ordering above 1.8 K. XPS measurements show that in CeNiIn the Ni 3*d* and Ce 4*f* states are both near the Fermi level. In CeAuIn only the Ce 4*f* state is near the Fermi level while the Au 5*d* band is represented by two peaks in the region between 3 and 7 eV below the Fermi level. The interpretation of Ce 3*d* XPS spectra in terms of the Gunnarsson–Schönhammer theory indicate that the hybridization energy Δ between the Ce 4*f* and conduction band is equal to 144 meV for CeAuIn and 205 meV for CeNiIn.

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X-ray data confirm that the CeTIn (T=Au, Ni) compounds crystallize in the hexagonal ZrNiAl-type structure [1,2]. Magnetic data indicates that the CeNiIn compound is a valence fluctuating system with Kondo-like behavior [3]. Magnetic properties of CeAuIn have not been investigated yet.

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This work reports the results of magnetization and magnetic susceptibility (a vibrating sample magnetometer, fields up to 50 Oe; SQUID magnetometer, fields up to 100 Oe; temperature range 1.8–400 K) as well as X-ray photoelectron spectroscopy (Leybold LHS10 XPS spectrometer, K_α radiation source, $hv = 1253.6$ eV, energy resolution about 0.75 eV for Ag $3d$; room temperature). In the case of CeAuIn the temperature dependence of magnetization in low magnetic field shows the main maximum at 6.2 K and an increase at low temperatures. This maximum is also observed in the temperature dependence of magnetic susceptibility (Fig. 1). For CeNiIn no maxima but only an increase in the magnetic susceptibility at low temperatures is observed. At high temperatures the reciprocal magnetic susceptibility of CeAuIn fulfills the Curie–Weiss law with a negative values of the paramagnetic Curie temperature ($\Theta = -20$ K) and the effective magnetic moment equal to the free Ce^{3+} ion value (2.54 μ_B). For CeNiIn the reciprocal magnetic susceptibility obeys the Curie-Weiss law above 150 K with ($\Theta = -270$ K) and the effective magnetic moment equal to 2.9 μ_B. Magnetization curve for CeAuIn shows metamagnetic character with the critical field H_C equal to 27 kOe while for CeNiIn, after sharp increase in low field, a slow increase with increasing magnetic field is observed. The XPS valence band spectra are compared with *ab-initio* electronic structure calculated by the *Tight-Binding Linear Muffin-Tin Orbital* method (TB LMTO) [4]. Fig. 2 shows the XPS valence bands of the investigated compounds between the Fermi level, located at $E = 0$ eV, and the binding energy of about 11 eV. The experimental results are compared with the calculated ones. The detailed analysis gives the following informations: for CeAuIn $(5d6s)^3$ and the Ce $4f$ bands are located below the Fermi level. Between 3 and 7 eV two peaks corresponding to the Au $5d_{5/2}$ and $5d_{3/2}$ states are observed. A maximum at 7.9 eV corresponds to the In $5p$ state,for CeNiIn below the Fermi level

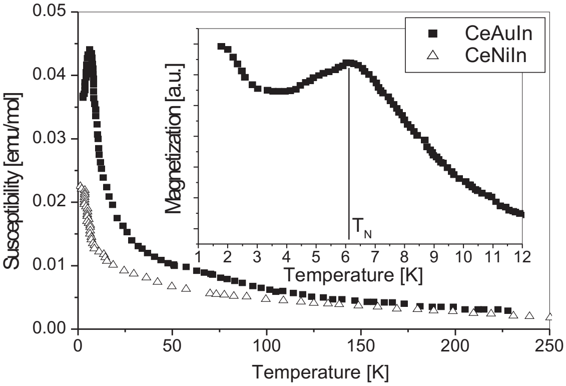

Fig. 1. Magnetic susceptibility and magnetization of the CeNiIn and CeAuIn.

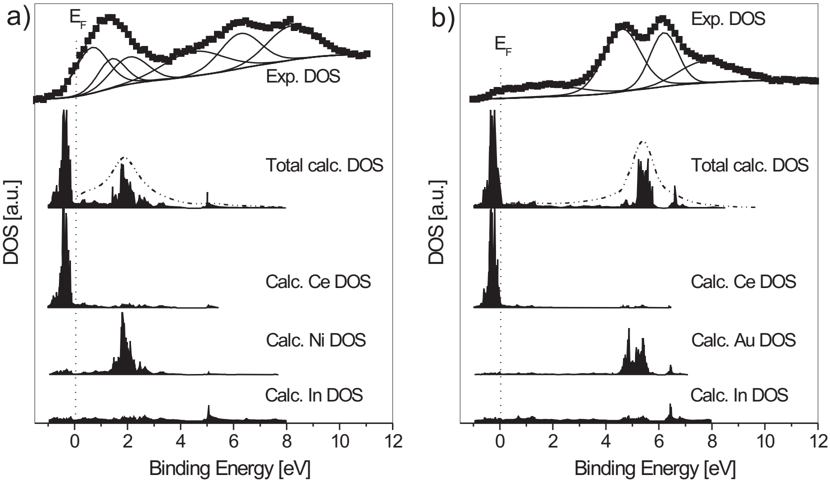

Fig. 2. Calculated and experimental valence band DOS for: (a) CeNiIn, (b) CeAuIn.

broad peaks connected with the Ni 3d, Ce 4f states and $(5d6s)^3$ band are observed. This indicates strong hybridization of Ce 4f and Ni 3d states. In the region between 5 and 9 eV a broad peaks connected with In 5s and 5p states are detected.The core level states data for In $4d_{5/2},\ _{3/2}$, In $3p_{3/2},\ _{1/2}$, Ni $3p_{3/2},\ _{1/2}$ and Au $4f_{7/2},\ _{5/2}$ are similar to the pure elements spectra. The XPS spectra of Ce 3d core levels give more information about the 4f shell configurations and hybridization. Intensity of the Ce 3d lines in the Ce intermetallic compounds show different final state depending on the occupation of the f shell [5,6]. Figure 3 presents the Ce 3d XPS spectra of both investigated compounds. Three final state contributions f^0, f^1 and f^2 are observed and the spin–orbit splitting $\Delta_{\rm SO}$=18.6 eV can be extracted. The

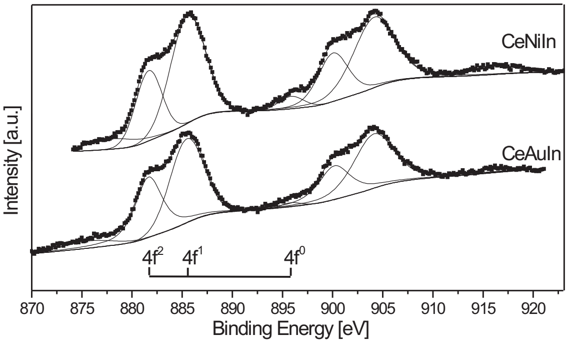

Fig. 3. Comparison of Ce 3d band for CeNiIn and CeAuIn.

appearance of the f^0 component is a clear evidence of mixed valence. Basing on the Gunnarsson–Schönhammer theoretical model [5, 6], the intensity ratio $r_1 = I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$, which should be directly related to the f-occupation probability in the final state, determines the f-occupation number $n_f = 1 - r_1$ equal to 0.95 for CeAuIn and 0.90 for CeNiIn. The f^2 state located at low-binding-energy side of f^1 state in the Ce $3d$ spectra (Fig. 3) is attributed to the hybridization between the f states and the conduction band [5]. The separation of the peaks, based on the Doniach–Šunjić theory [7], gives the intensity ratio $r = I(f^2)/[I(f^1)+I(f^2)]$. It was possible to determine the coupling parameter Δ using the measured intensity ratio r as a function of the previously published Δ values [6]. The coupling parameter Δ is defined as $\pi V^2 \rho_{\max}$, where $\rho_{\max}$ is the maximum of the density of conduction states and V is the hybridization. The r values are equal to 0.29 for CeAuIn and 0.38 for CeNiIn which corresponds to the hybridization energies of 144 meV and 205 meV respectively. The above results indicate that hybridization between the Ce $4f$ state and conduction band is larger for CeNiIn than for CeAuIn. The Ce atoms in CeAuIn, are trivalent while the Ce atoms in CeNiIn (similarly to CeNiSn [8]) are in a mixed valence state with the valence very close to $3+ \ (n_f)$, which is also mainly caused by the hybridization between the Ce $4f$ orbitals and the conduction band.

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