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Electronic structure and magnetic properties of the compound CeCuIn

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Abstract

Magnetization, magnetic susceptibility, electrical resistivity, thermoelectric power and X-ray photoemission measurements were performed on a polycrystalline sample of CeCuIn. This compound crystallizes in a hexagonal structure of the ZrNiAl type. The magnetic data indicate that CeCuIn remains paramagnetic down to 1.9 K with a paramagnetic Curie temperature of -13 K and an effective magnetic moment equal to $2.5 \mu_B$. The electrical resistivity has metallic character, yet in the entire temperature range studied here, it is a strongly nonlinear function of temperature. The temperature dependence of the thermoelectric power is dominated by a small positive maximum near 76 K and a deep negative minimum at about 16 K. Above 150 K the thermopower exhibits a Mott's type behavior. The positive sign of the Seebeck coefficient in this temperature region indicates that the holes are dominant charge and heat carriers. The structure of Ce $3d_{5/2}$ and Ce $3d_{3/2}$ XPS spectra has been interpreted in terms of the Gunnarsson-Schönhammer theory. Three final-state contributions f^0 , f^1 and f^2 are clearly observed, which exhibit a spin-orbit splitting $\Delta_{SO} \approx 18.7$ eV. The appearance of the $3d^9f^0$ component is a clear evidence of the intermediate valence behavior of Ce. From the intensity ratio $I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$ the 4f-occupation number is estimated to be 0.95. In turn, the ratio $I(f^2)/[I(f^1) + I(f^2)] = 0.08$ yields a measure of the hybridization energy that is equal to 45 meV.

Keywords: Cerium intermetallic compounds; Magnetic properties; Transport properties; Electronic structure

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1. Introduction

Cerium ternary intermetallic compounds have attracted considerable attention due to their anomalous properties, such as valence fluctuation phenomena, Kondo effect, heavy fermion behavior, superconductivity etc. [1-3]. These anomalous properties are associated with the instability of the 4f states. The magnetic properties result from a competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, crystal electric field (CEF) and Kondo interactions [4]. The long-range exchange RKKY interactions mediated by conduction electrons favor magnetic ordering. The Kondo interactions tend to prevent the formation of local magnetic moments and lead to a variety of correlated electronic ground states observed in cerium compounds.

CeTX compounds, where T is an nd-electron element and X a p-electron element, form in a few different crystal structures. Our recent investigations concentrate on the CeTIn phases that crystallize in the hexagonal ZrNiAl type, and exhibit various properties [5-8], e.g. CeNiIn and CeRhIn are valence fluctuating systems, CePtIn is a non-magnetic heavy fermion compound, while CePdIn and CeAuIn order antiferromagnetically at low temperatures.

In this paper we present the results of magnetization, electrical resistivity, thermoelectric power and XPS measurements performed on a polycrystalline sample of CeCuIn. This compound was reported in the literature to crystallize either in a ZrNiAl-type structure [9,10] or a CaIn₂-type structure [11]. Published magnetic and resistivity data indicate that it is paramagnetic down to 4.2 K [11].

2. Experimental details

Polycrystalline samples of CeCuIn and LuCuIn were obtained by arc melting stoichiometric amounts of the constituents (Merck AG; purity: Ce and Lu 99.9 wt.%, Cu and In 99.99 wt.%) under high-purity argon atmosphere on a water-cooled copper hearth, using a titanium-zirconium alloy as a getter. Subsequently, the buttons were annealed in evacuated quartz tubes at 800°C for a week. The quality of the products was checked by X-ray powder diffraction at room temperature. The X-ray data were analyzed by the program FULLPROF [12].

The magnetic properties were studied in the temperature range 1.9–300 K and in external magnetic fields up to 5 T using a commercial SQUID magnetometer (Quantum Design MPMS-5). The electrical resistivity was measured over the temperature interval 4.2–280 K employing a standard dc four-probe technique. The current contacts were made using silver paste and the voltage contacts were made by ultrasonic welding. The Seebeck coefficient was measured in the temperature range 5–300 K by a differential method with copper as reference material.

The XPS spectra were obtained at room temperature in a vacuum of about 10^{-9} mbar using a Multipurpose Electron Spectrometer PHI 5700/660 with AlK_{α} monochromatized radiation ($h\nu = 1486.6$ eV) and a Leybold LHS10 electron photoemission spectrometer with MgK_{α} ($h\nu = 1253.6$ eV) and AlK_{α} ($h\nu = 1486.6$ eV) radiation. The total energy resolution of the spectrometer with a hemispherical energy analyzer was about 0.3 eV for the PHI 5700/660 spectrometer and 0.75 eV for the LHS10 spectrometer for Ag 3d. Binding energies were referred to the Fermi level ($E_F = 0$). The spectrometer was calibrated using the Cu $2p_{3/2}$ (932.5 eV), Ag $3d_{5/2}$ (368.1 eV) and Au $4f_{7/2}$ (84.0 eV) core-level photoemission spectra. The surface of the sample was mechanically cleaned by scraping with a diamond file in a preparation chamber under high vacuum (10^{-9} mbar) and the sample was then immediately moved into the analysis chamber. This procedure was repeated until the C 1s and O 1s core-level peaks were negligibly small or were not changed after further scrapings. Such a cleaning procedure was performed before each XPS measurement. The Shirley method [13] was used to subtract the background. The experimental spectra were numerically fitted using an 80% Gaussian and 20% Lorentzian model.

3. Results

The powder X-ray diffraction data revealed that the investigated sample of CeCuIn crystallizes in a hexagonal ZrNiAl-type structure (space group No 189), in agreement with [9,10]. The refined lattice parameters are equal to $a = 7.4915(6)$ Å and $c = 4.2452(5)$ Å and are in agreement with earlier results [9,10]. In the unit cell the atoms are located as follows:

Ce at 3(g) site: $x_{Ce}, 0, \frac{1}{2}$ with $x_{Ce} = 0.5832(4)$;

Cu1 at 1(b) site: $0, 0, \frac{1}{2}$;

Cu2 at 2(c) site: $\frac{1}{3}, \frac{2}{3}, 0$;

In at 3(f) site: $x_{In}, 0, 0$ with $x_{In} = 0.2486(5)$.

As shown in Fig. 1, above about 40 K the reciprocal magnetic susceptibility of CeCuIn follows the Curie-Weiss law with an effective magnetic moment μ_{eff} of $2.50 \mu_B$ (i.e. close to $\mu_{eff} = 2.54 \mu_B$ expected for a free Ce^{3+} ion) and a strongly negative paramagnetic Curie temperature θ_p being equal to -15 K. Some deviation from the Curie-Weiss behavior is observed below 40 K, presumably due to crystal field effects. These results are in good agreement with those reported in [11]. The cerium moments do not order magnetically down to 1.9 K. The magnetization curve recorded at this temperature has a paramagnetic character (see the inset in Fig. 1). The Ce magnetic moment measured at 1.9 K in a field of 5 T amounts to $0.66 \mu_B$.

The electrical resistivity of CeCuIn is presented in Fig. 2(a). The $\rho(T)$ dependence is strongly non-linear in the entire temperature range, yet the resistivity increases with rising temperature, as

expected for a metal. This resistivity curve differs from that reported in [11] because the latter shows a straight-line behavior from room temperature down to 100 K, followed by some curvature at lower temperatures only.

The value of the residual resistivity of our sample equals $36.7 \mu\Omega \text{ cm}$, i.e. it is smaller than that observed in [11] ($56.2 \mu\Omega \text{ cm}$), which indicates that our sample is of better quality. The resistivity of CeCuIn is also quite different from the $\rho(T)$ behavior of LuCuIn (see Fig. 2(a)), which is a non-magnetic isostructural counterpart to the Ce-based compound studied here. As shown in the figure by a thin solid line, the resistivity of the latter can be well described by the standard Bloch-Grüneisen (BG) formula

$$\rho(T) = \rho_0 + 4RT \left(\frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})},$$

which accounts for scattering the conduction electrons on lattice imperfections and phonons. The fit parameters found by the least-squares method are the residual resistivity $\rho_0 = 25.1 \mu\Omega \text{ cm}$, the BG coefficient $R = 0.105 \mu\Omega \cdot \text{cm/K}$ and the Debye temperature $\Theta_D = 183 \text{ K}$.

Assuming that the electron-phonon scattering in CeCuIn is similar to that in LuCuIn the magnetic contribution to the resistivity of the Ce compound may be derived:

$$\rho_m(T)[\text{CeCuIn}] = \{\rho(T)[\text{CeCuIn}] - \rho_0[\text{CeCuIn}]\} - \{\rho(T)[\text{LuCuIn}] - \rho_0[\text{LuCuIn}]\}.$$

The thick solid line in Fig. 2(a) represents the so-obtained magnetic resistivity (enlarged by the residual resistivity). Apparently, ρ_m of CeCuIn is strongly temperature-dependent in the whole temperature range, presumably because of the interplay of crystal field interactions (see above) and spin fluctuations. It is worthwhile noting that the $\rho_m(T)$ graph does not provide any indication of Kondo effect in CeCuIn.

Fig. 2(b) shows the temperature dependence of the thermoelectric power of CeCuIn. At low temperatures a deep negative minimum occurs at about 16 K with a sign reversal in the vicinity of 25 K. At 76 K a broad maximum is observed, which may be due to a phonon drag effect [14] or caused by inelastic scattering of carriers by acoustic phonons [15]. The positive sign of the Seebeck coefficient at ambient temperatures possibly indicates that holes are dominant charge and heat carriers [15].

Fig. 3 shows the XPS spectrum of CeCuIn collected in a wide 0–1200 eV binding energy range. The binding energies are referred to the Fermi level ($E_F = 0 \text{ eV}$). The XPS valence band spectrum of CeCuIn, extending from the Fermi level energy to a binding energy of about 12.5 eV, is presented in Fig. 4. Near the Fermi level there is a peak at 1.9 eV that corresponds to the Ce 4f and Ce 5d s^2 states. At 4.0 eV a peak occurs due to the Cu 3d state, and then at 6.3 and 8.9 eV the peaks of In 5s and In 5p states are observed. In turn, the In 4d $_{5/2}$ and In 4d $_{3/2}$ states manifest themselves as

peaks occurring at 16.85 and 17.75 eV, respectively. Their spin-orbit splitting amounts to 0.9 eV, while the literature value is 0.8 eV [16].

The Ce 3d spectrum is displayed in Fig. 5. The Ce 3d_{5/2} and Ce 3d_{3/2} states spin-split of $\Delta_{SO} \approx 18.7$ eV are clearly seen. Both peaks have three final state contributions, f^0 , f^1 and f^2 , which can be analyzed in terms of the Gunnarsson-Schönhammer theory [17]. For this purpose the spectrum was separated into particular components using an approach based on the Doniach-Šunjić theory [18]. The appearance of the f^0 contribution is a clear evidence of a mixed valence state. The intensity ratio $r_1 = I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$ provides an estimate for the occupation of the final f states $n^{XPS} = 1 - r_1$ being equal to 0.95. The f^2 components located at the low-binding energy side of the f^1 components in the Ce XPS spectrum may be attributed within the Gunnarsson-Schönhammer model to the hybridization between the f states and the conduction band states. The hybridization energy Δ is defined as $\pi V^2 \rho_{max}$, where ρ_{max} is the maximum of the density of states of the conduction band and V is the hybridization matrix element. Since the intensity ratio $r_2 = I(f^2)/[I(f^1) + I(f^2)]$ had been calculated for Ce in [19] as a function of Δ , it is possible to determine the strength of the hybridization interactions. From the calculated value $r_2 = 0.08$, the hybridization energy in CeCuIn is estimated to be 45 meV. This value is considerably lower than that reported for the isostructural compound CeNiIn (140 meV) [16].

The Cu 2p_{3/2} and Cu 2p_{1/2} peaks are located at 933.1 and 952.9 eV, respectively, which yields the spin-orbit splitting $\Delta_{SO} = 19.1$ eV. Similarly, the In 3d_{5/2} and In 3d_{3/2} states, which occur at 443.8 and 451.4 eV, respectively (see Fig. 3), are spin-split by $\Delta_{SO} = 7.6$ eV. The two latter values of Δ_{SO} are in good agreement with the literature data [16].

4. Discussion

The reported investigations aimed at determining the magnetic and electrical transport properties as well as the electronic structure of CeCuIn. The obtained magnetic data seem to indicate that the cerium magnetic moments are fairly well localized. In the paramagnetic state the effective magnetic moment is close to the free Ce³⁺ ion value, and at the lowest temperatures some manifestation of crystalline electrical field is observed. However, the Ce moments do not order magnetically down to 1.9 K, and nevertheless the paramagnetic Curie temperature is strongly negative. From this behavior one might infer that Kondo interactions play an important role. Such a presumption is, however, not compatible with the electrical behavior of CeCuIn, which does not provide any hint at the latter effect.

Actually, in the isostructural series CeTIn, where T = Ni, Rh, Pd and Au, Kondo screening interactions have been found to govern the ground state properties, which range from valence

fluctuations to long-range magnetic order. Qualitatively these properties can be explained based on the Doniach phase diagram [20]. In this model the key parameter is the coupling constant J_{cf} , which represents the interaction between 4f and conduction electrons. The indirect magnetic exchange between local moments via conduction electrons polarization, the so-called RKKY interaction, is characterized by a temperature defined as $T_{RKKY} \sim J_{cf}^2 N(E_F)$, where $N(E_F)$ is the density of states at the Fermi level, whereas the Kondo effect, which tends to compensate for the local moment and leads to the formation of a nonmagnetic ground state, is given by the temperature $T_K \sim \exp\left[\frac{1}{N(E_F)J_{cf}}\right]$. The ground-state behavior of a given compound results from a competition/interplay of these two mechanisms. Fig. 6 shows the Kondo and Néel temperatures of the CeTIn compounds, plotted as a function of the unit cell volumes. Apparently, the RKKY interactions take over in the compounds having large unit cell volumes, so that antiferromagnetic ordering is found, as for CeAuIn and CePdIn. In contrast, for small unit cell volumes the Kondo effect is the dominant interaction and hence no long-range order is observed. Here, the prominent examples are the valence fluctuation systems CeNiIn and CeRhIn. The compound CeCuIn, investigated in the present work, lies in the intermediate region between these two regions, and is somewhat similar to the heavy fermion paramagnet CePtIn.

More advanced discussion is possible based on the experimentally determined electronic structures of the CeTIn compounds. From the XPS data obtained for CeNiIn [21] it is clear that Ce 4f and Ni 3d are mutually hybridized, which brings about the non-magnetic state. On the contrary, the analysis of the XPS valence band spectra of CeAuIn [21] confirms the well localized character of the Ce 4f state. In the case of CeCuIn the XPS spectra of Ce 3d states hint at little hybridization of the 4f states with the conduction band states. It is remarkable that the hybridization strength in CeCuIn derived from the XPS data (45 meV) is much lower than that reported for CeNiIn (140 meV).

Acknowledgements

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Figure captions

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of CeCuIn. The solid line represents the Curie-Weiss fit. The inset displays the field-dependent magnetization measured at 1.9 K with increasing (full symbols) and decreasing (open symbols) magnetic field.

Fig. 2. Temperature dependencies of (a) electrical resistivity of CeCuIn and LuCuIn and (b) thermoelectric power of CeCuIn.

Fig. 3. XPS spectrum of CeCuIn collected for the 0-1100 eV binding energy range.

Fig. 4. XPS valence band spectrum of CeCuIn of its deconvolution into components.

Fig. 5. Ce 3d XPS spectrum of CeCuIn of its deconvolution into components.

Fig. 6. Kondo ($\circ$) and Néel (Δ) temperatures vs. the unit cell volume for several CeTIn compounds.

Fig. 1

Fig. 2a

Fig. 2b

Fig. 4

Fig. 5

Fig. 6