Evolution from a localized to an intermediate valence regime in Ce$_2$Cu$_{2-x}$Ni$_x$In

A P Pikul and D Kaczorowski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P Nr 1410, 50–590 Wroclaw 2, Poland

E-mail: A.Pikul@int.pan.wroc.pl

Received 8 August 2011
Published 28 October 2011
Online at stacks.iop.org/JPhysCM/23/456002

Abstract
Polycrystalline samples of the solid solution Ce$_2$Cu$_{2-x}$Ni$_x$In were studied by means of x-ray powder diffraction, magnetic susceptibility and electrical resistivity measurements performed in a wide temperature range. Partial substitution of copper atoms by nickel atoms results in a quasi-linear decrease of the lattice parameters and the unit cell volume of the system. The lattice compression leads to an increase in the exchange integral and yields a reversal in the order of the magnetic 4f$^1$ and nonmagnetic 4f$^0$ states, being in line with the Doniach phase diagram. In the localized regime, where an interplay of the Kondo scattering and the crystalline electric field effect occurs, the rise in the hybridization strength is accompanied by a relative reduction in the scattering conduction electrons on excited crystal field levels.

(Some figures may appear in colour only in the online journal)

1. Introduction

Ternary intermetallics Ce$_2$Cu$_2$In and Ce$_2$Ni$_2$In crystallize in a primitive tetragonal structure of the Mo$_2$FeB$_2$ type (space group P4/mmbm) with the lattice parameters $a = 7.7368(6)$ Å, $c = 3.9240(3)$ Å for the former phase and $a = 7.5305(3)$ Å, $c = 3.7223(2)$ Å for the latter one [1]. The physical properties of Ce$_2$Cu$_2$In indicate well localized magnetism due to the presence of stable Ce$^{3+}$ ions. The compound orders antiferromagnetically at the Néel temperature $T_N = 5.5$ K, and its electrical resistivity is dominated by an interplay of strong Kondo and crystalline electric field interactions. In contrast, the Ce$_2$Ni$_2$In compound exhibits features characteristic of intermediate valence systems, with partly delocalized 4f electrons of cerium [1, 2].

Since both compounds are isostructural, the qualitative difference in their ground states results exclusively from swapping copper atoms for nickel atoms. This fact motivated us to perform alloying studies of Ce$_2$Cu$_{2-x}$Ni$_x$In as a unique opportunity to investigate the evolution of a 4f system from a fully localized regime to a well defined intermediate valence state that is predicted by the Doniach diagram [3]. It is worth noting that systematic studies of such evolution are often difficult (or even impossible) due to either a relatively small difference between the ground states of two isostructural parent compounds or different crystal structures of the two terminal phases. In other words, such experimental studies usually cover only part of the Doniach diagram, e.g. the quantum critical region.

In this paper we present the results of magnetic and electrical transport measurements of the solid solution Ce$_2$Cu$_{2-x}$Ni$_x$In, performed in a wide temperature range, using polycrystalline samples. We demonstrate the prominent evolution of the main physical characteristics of the system with increasing nickel content, and interpret the experimental data in terms of some theoretical models developed for localized and intermediate valence states. We argue that Cu/Ni substitution leads to an increase in the exchange integral, which yields a reversal in the order of the magnetic 4f$^1$ and nonmagnetic 4f$^0$ states. Moreover, the rise in the exchange integral brings about a diminishing influence of excited crystal field levels on the electrical transport in the system studied.

2. Experimental details

Polycrystalline samples of Ce$_2$Cu$_{2-x}$Ni$_x$In were prepared by arc melting stoichiometric amounts of the elemental...
components in a titanium-gettered argon atmosphere. The pellets were turned over and remelted several times to ensure good homogeneity. No further heat treatment was given to the as-cast ingots.

The quality of the products was verified by x-ray powder diffraction (Stoe diffractometer with Cu $K \alpha_1$ radiation) and energy dispersive x-ray spectroscopy (Phillips 515 scanning electron microscope equipped with an EDAX PV 9800 spectrometer). All the diffractograms were easily indexed within the expected primitive tetragonal structure. The microprobe analysis showed that the samples are nearly single phase (with minor traces of unidentified impurities) and their compositions are close to the nominal ones.

The magnetic properties were studied at temperatures of 1.7–400 K and in magnetic fields up to 5 T using a commercial Quantum Design SQUID magnetometer. Electrical resistivity was measured on bar-shaped samples in zero field from 4.2 K up to room temperature, using a home-made setup.

3. Results and discussion

3.1. Crystal structure

Analysis of the x-ray diffraction patterns (not given here) confirmed that substitution of copper atoms by nickel atoms does not change the crystal structure of the system. It also revealed that the lattice parameters and the unit cell volume of the Ce$_2$Cu$_{2-x}$Ni$_x$In alloys systematically decrease (in a quasi-linear manner) with increasing nickel content from $a = 7.7368(6)$ Å, $c = 3.9240(3)$ Å and $V = 234.88$ Å$^3$ for Ce$_2$Cu$_2$In to $a = 7.5305(3)$ Å, $c = 3.7223(2)$ Å and $V = 211.09$ Å$^3$ for Ce$_2$Cu$_2$In [1] (see figure 1).

3.2. Magnetic properties

Figure 2(a) presents the temperature dependences of the inverse magnetic susceptibility of the alloys studied. As seen, $\chi^{-1}(T)$ measured for the Cu-rich alloys (i.e., for $x \leq 1.00$) exhibit a linear behaviour above about 100 K given by the conventional Curie–Weiss law:

$$\chi(T) = \frac{\mu_{\text{eff}}^2}{8(T - \theta_p)},$$

where $\mu_{\text{eff}}$ is the effective magnetic moment and $\theta_p$ stands for the paramagnetic Curie temperature. Least squares fittings

![Figure 1. Lattice parameters $a$ and $c$ and unit cell volume $V$ of selected alloys Ce$_{2}$Cu$_{2-x}$Ni$_{x}$In as a function of the nominal nickel content $x$.](image1)

![Figure 2. (a) Inverse magnetic susceptibility $\chi^{-1}$ of selected alloys Ce$_{2}$Cu$_{2-x}$Ni$_{x}$In as a function of temperature $T$. Straight solid lines represent Curie–Weiss fittings; results for $0.00 < x < 1.00$ are omitted for the sake of clarity. Dashed lines are fittings of the ICF model (equation (6)). (b) Magnetic susceptibility $\chi$ of Ce$_{2}$Cu$_{2-x}$Ni$_{x}$In with $x \leq 0.45$ versus $T$. Solid curves serve as guides for the eye and the arrows mark the Néel temperature $T_N$. $x$ is the nominal composition.](image2)
of (1) to the experimental data collected for the alloys with \( x \leq 1.00 \) (see the solid lines in figure 2(a)) yielded nearly constant \( \mu_{\text{eff}} \) of about 2.5–2.6 \( \mu_B \) and \( \theta_0 \), decreasing monotonically from about \( -16 \) K for \( \text{Ce}_2\text{Cu}_2\text{In} \) (in agreement with [11]) to \( -51 \) K for \( \text{Ce}_2\text{Cu}_{1.0}\text{Ni}_{1.0}\text{In} \). The obtained values of the effective magnetic moments are close to the theoretical one calculated for free \( \text{Ce}^{3+} \) ions (i.e. 2.54 \( \mu_B \)) and point at the presence of well localized 4f electrons of cerium. The increase in the absolute value of the paramagnetic Curie temperature can be ascribed to the enhancement of the hybridization strength between conduction electrons and 4f shells, expected for increasing Ni content.

The latter hypothesis is in line with further evolution of \( \chi^{-1}(T) \), that is observed for the alloys with \( x > 1 \). Along with increasing the nickel content, the inverse magnetic susceptibility deviates more and more from the Curie–Weiss behaviour, suggesting progressive delocalization of the 4f electrons (i.e. evolution from the state 4f\(^1\) to the configuration 4f\(^0\)).

According to the interconfiguration fluctuation (ICF) model developed by Sales and Wohleben [4], the magnetic susceptibility of the 4f electron component can be described as a sum of susceptibilities of two states, 4f\(^0\) and 4f\(^1\). Respectively, the states are characterized by well defined angular momenta \( J_n \) and \( J_{n-1} \), degeneracies \( 2J_n + 1 \) and \( 2J_{n-1} + 1 \), Hund’s-rule effective magnetic moments \( \mu_n \) and \( \mu_{n-1} \), and energies \( E_n \) and \( E_{n-1} \). The total magnetic susceptibility \( \chi(T) \) of such a system can be expressed as

\[
\chi(T) = \frac{1}{8} \left( \frac{v(T)\mu_n^2}{T + T_{sf}} + \frac{1}{8} \left[ 1 - v(T) \right] \frac{\mu_{n-1}^2}{T + T_{sf}} \right),
\]

with the fractional occupation \( v(T) \) of the 4f\(^0\) state

\[
v(T) = \frac{(2J_n + 1)}{(2J_n + 1) + (2J_{n-1} + 1)} \exp[-E^*/(T + T_{sf})],
\]

where \( T_{sf} \) is the spin fluctuation temperature related to the transition rate \( \omega_n \) between the two electron configurations involved (\( k_BT_{sf} = \hbar\omega_n \)), and \( E^* \) is the energy difference between the two 4f states \( (E^* = E_{n-1} - E_n) \), expressed in kelvin.

In cerium compounds, there are two possible configurations of the 4f shell: 4f\(^1\) (with \( J_1 = \frac{5}{2} \) and \( \mu_1 = 2.54 \mu_B \)) and 4f\(^0\) (with \( J_0 = 0 \) and \( \mu_0 = 0 \)). Hence, (2) and (3) take the form, respectively,

\[
\chi(T) = \frac{1}{8} \frac{v(T)(2.54 \mu_B)^2}{T + T_{sf}},
\]

and

\[
v(T) = \frac{6}{6 + \exp[-E^*/(T + T_{sf})]},
\]

with \( E^* = E_0 - E_1 \). According to this notation, in systems with the magnetic ground state 4f\(^1\) (e.g. magnetically ordered compounds, Kondo and heavy fermion systems) \( E^* \) is positive, while in intermediate valence systems, in which the 4f\(^1\) configuration is the excited state, \( E^* \) is negative. For \( E^* \geq 0 \), the fractional occupation \( v \) of the ground 4f\(^1\) state is weakly dependent on temperature and decreases from 1 (for \( E^* \to +\infty \)) to 6/7 (for \( E^* = 0 \)), and the associated magnetic moment changes from 2.54 \( \mu_B \) to 2.35 \( \mu_B \), respectively. Thus, the system exhibits features characteristic of localized magnetism, and (4) is a good approximation of the Curie–Weiss law. In turn, for \( E^* < 0 \), a characteristic maximum in \( \chi(T) \) develops with increasing \( |E^*| \), yet Curie–Weiss behaviour can still be observed at high enough temperatures (\( T \gg |E^*| \)).

The magnetic susceptibility of the alloys \( \text{Ce}_2\text{Cu}_{2-x}\text{Ni}_x\text{In} \) seems to nicely follow the predictions of the ICF model. The experimental data can be described at elevated temperatures by (4) modified by adding a constant term \( \chi_0 \), which accounts for possible temperature independent paramagnetic and diamagnetic contributions to the total magnetic susceptibility (cf [1, 5]), i.e.

\[
\chi(T) = \frac{1}{8} \frac{v(T)(2.54 \mu_B)^2}{T + T_{sf}} + \chi_0.
\]

Least squares fittings of (6) to the experimental data (see the dashed lines in figure 2(a) and the fitting parameters in figure 3) yielded \( E^* \) decreasing monotonically from +169(18) K for \( \text{Ce}_2\text{Cu}_2\text{In} \) to \( -882(9) \) K for \( \text{Ce}_2\text{Ni}_2\text{In} \) (in agreement with the value of \( -884 \) K, reported previously [1]). The parameter \( T_{sf} \) was found to increase from +11(1) K to 93(4) K, respectively, in a non-linear manner with a local maximum of 147(5) K for \( \text{Ce}_2\text{Cu}_{0.4}\text{Ni}_{1.6}\text{In} \). In turn, the temperature independent term was found to be nearly constant in the whole series of alloys and equal to \( \chi_0 \sim 10^{-4} \) emu mol\(^{-1} \).

As is apparent from figure 2(a), at low temperatures the experimental \( \chi^{-1}(T) \) variations measured for strongly intermediate valence alloys significantly deviate from the predictions of the ICF model (note Curie-like tails \( \chi \sim 1/T \)). Such a behaviour is often observed in the intermediate valence systems and can be ascribed to the presence of paramagnetic impurities (cf [1]). While in the localized regime the latter contribution is negligible, in the intermediate valence state (exhibiting relatively weak magnetism) it becomes significant and thus strongly modifies the expected ICF curvature of \( \chi^{-1}(T) \).

The change of \( E^* \) with increasing nickel content (figure 3) is in line with the observed evolution of the magnetic properties of the system \( \text{Ce}_2\text{Cu}_{2-x}\text{Ni}_x\text{In} \). One should note,
however, that the ICF model does not take into account *inter alia* the crystal electric field effect and magnetic correlations, which are also expected to have some role in the alloys studied (cf [1]). Therefore, the derived absolute values of $E^*$ can differ from the actual energy difference between the $4f^4$ and $4f^0$ configurations, especially in the localized regime.

Figure 2(b) displays the temperature dependences of the magnetic susceptibility $\chi(T)$ for the alloys with $x \leq 0.45$, which exhibit well localized magnetic moments. Clearly, the compound Ce$_2$Cu$_2$In orders antiferromagnetically at the Néel temperature $T_N = 5.5$ K, in agreement with the previous finding [1]. With increasing $x$, $T_N$ (defined as a maximum on the $\chi(T)$ curve) rapidly decreases. For $x = 0.45$, hardly any anomaly is visible in $\chi(T)$, at least in the temperature range studied. Extrapolation of the dependence $T_N(x)$ to zero temperature (see the dashed line in figure 3) yields the critical concentration $x_c$ of about 0.4. In parallel with the suppression of $T_N$, one observes gradual broadening of the maximum in $\chi(T)$ that manifests the antiferromagnetic phase transition. This finding suggests that the quantum critical phase transition smears out and hence no quantum critical state could be reached, as concluded also, for example, in CePd$_{1−x}$Rh$_x$ [6–8].

3.3. Electric properties

The temperature variations of the electrical resistivity of Ce$_2$Cu$_{1−x}$Ni$_x$In and the nonmagnetic reference La$_2$Cu$_2$In (normalized to room temperature values) are presented in figure 4. While the $\rho(T)$ curve obtained for the La sample is characteristic of simple metals, the resistivity of the parent compound Ce$_2$Cu$_2$In exhibits features of a magnetically ordered dense Kondo system. In the paramagnetic region, $\rho(T)$ forms a broad hump at about 100 K and exhibits a negative logarithmic slope below about 20 K, both manifesting the Kondo scattering of conduction electrons on crystalline electric field $4f^4$ sublevels (cf [1]). A drop of the resistivity at about 6 K results from the antiferromagnetic phase transition. For the alloys with $x > 0$, the magnetic phase transition could not be evidenced because of the temperature limit of our resistivity measurements ($\approx 4$ K). With increasing nickel content, the low temperature $-\log T$ contribution becomes dominant and for $x = 0.4$ it entirely merges with the hump at elevated temperatures. Over an extended temperature range $\rho(T)$ this alloy exhibits a single nearly logarithmic slope (figure 4(a)). For higher $x$, the low temperature resistivity evolves into a $T^2$ dependence (see dashed curve in figure 4(b)) that signals the intermediate valence behaviour.

In order to shed more light on the observed evolution of $\rho(T)$ of the alloys Ce$_2$Cu$_{1−x}$Ni$_x$In with $x \leq 0.4$, we derived the magnetic contribution $\rho_{\text{mag}}$ to their total resistivity by subtracting the phonon contribution to $\rho(T)$ of La$_2$Cu$_2$In (cf [1]). The $\rho_{\text{mag}}(T)$ curve obtained for Ce$_2$Cu$_2$In revealed that the hump in $\rho(T)$ results from the presence of a distinct maximum in $\rho_{\text{mag}}$ followed by another $-\log T$ dependence at high temperatures (figure 5(a)). Moreover, two logarithmic slopes are also visible in the other Cu-rich alloys, in which the maximum at 100 K is somewhat obscured by the low temperature $-\log T$ dependence.

According to the Cornut–Coqblin model [9], in the localized regime with the magnetic ground state the interplay of the Kondo effect and the crystalline electric field (CEF) results in the magnetic contribution to the total resistivity, which can be expressed as

$$
\rho_i(T) = aD_i^2 \frac{\lambda_i^2 - 1}{\lambda_i(2J_i + 1)} + 2aN(E_F)I_i^2 \frac{\lambda_i^2 - 1}{(2J_i + 1)} \log \frac{T}{D_i},
$$

(7)
where $J_1 = 5/2$, $\lambda_i$ denotes the effective degeneracy of the $4f^i$ state, $J_{ex}$ is the negative exchange integral, $N(E_F)$ is the density of states at the Fermi level, $D$ is the cutoff parameter, and $a$ is a constant. In the case of Ce$^{3+}$ ions experiencing a tetragonal crystal electric field potential, the sixfold degenerate $4f^1$ multiplet splits into three doublets located at the energies $\Delta_1 = 0$, $\Delta_2 = 50$ K and $\Delta_3 = 100$ K. Population of these levels depends on the temperature, so the effective degeneracy of the $4f^1$ state increases with increasing $T$ from $\lambda_1 = 2$ (ground doublet) at absolute zero temperature, to $\lambda_2 = 4$ (pseudo-quartet) at elevated $T$, to $\lambda_3 = 6$ (pseudo-sextet) at high temperatures. From (7) it becomes clear that the slope and the magnitude of $\rho_i(T)$ depend on $\lambda_i$, so for well separated doublets one can observe up to three $-\log T$ slopes in the magnetic contribution to the resistivity.

However, from the point of view of the present study, it is more important to note that the relative magnitudes of the particular $\rho_i(T)$ contributions (equation (7)) may also vary with $J_{ex}$, making the observation of the separated Kondo slopes difficult (cf [9]). Assuming Boltzmann-like thermal excitations of the crystalline electric field doublets (in line with the Cornu–Coqblin approach [9]), the Kondo contribution $\rho_{mag}$ to the electrical resistivity can be expressed as

$$\rho_{mag}(T) = \rho_1 + (\rho_2 - \rho_1) \exp\left(-\frac{\Delta_2}{T}\right) + (\rho_3 - \rho_2) \exp\left(-\frac{\Delta_3}{T}\right).$$

Note, that the contributions $\rho_2$ and $\rho_3$ already include $\rho_1$ and $\rho_2$, respectively. In order to avoid their multiplication, two corrections, i.e. $-\rho_1 \exp(-\Delta_2/T)$ and $-\rho_2 \exp(-\Delta_3/T)$, were added. In order to check the influence of magnetic exchange on the overall character of $\rho_{mag}(T)$, we made a few simulations using a fixed crystal electric field scheme (2:2:2 exchange on the overall character of $\rho_{mag}(T)$) calculated for different values of $J_{ex}$. The assumed CEF splitting scheme is $\Delta_1 = 0$ K, $\Delta_2 = 50$ K and $\Delta_3 = 100$ K. The dashed lines represent the individual $\rho_i$ contributions (equation (7)) for fully populated crystal field levels.

![Figure 5](image-url)  

**Figure 5.** (a) Temperature dependences of a Kondo contribution $\rho_{mag}$ to the electrical resistivity of Ce$_2$Cu$_{2-x}$Ni$_x$. $x$ is the nominal nickel content and the arrow marks the Néel temperature $T_N$. Panels (b)–(d) display theoretical $\rho_{mag}(T)$ of a Ce$^{3+}$-based system and tetragonal CEF potential (equation (8)), calculated for different values of $J_{ex}$. The assumed CEF splitting scheme is $\Delta_1 = 0$ K, $\Delta_2 = 50$ K and $\Delta_3 = 100$ K. The dashed lines represent the individual $\rho_i$ contributions (equation (7)) for fully populated crystal field levels.

### 4. Summary and conclusions

The partial substitution of Cu by Ni in the antiferromagnetically ordered compound Ce$_2$Cu$_2$In results in a monotonic compression of its unit cell (up to 10%), accompanied by...
a drastic change of the physical properties of the system. In particular, magnetic measurements of Ce$_2$Cu$_{2-x}$Ni$_x$In revealed continuous evolution from the localized magnetic moments regime for $x \lesssim 0.6$ to the fluctuating valence state for $x \gtrsim 1.6$. Detailed analysis of the inverse magnetic susceptibility data within the ICF model yielded reversal of the order of the magnetic 4f$^1$ and nonmagnetic 4f$^0$ levels in the alloys with $0.6 \lesssim x \lesssim 1.6$. In other words, the 4f$^1$ level, being the ground state in the Cu-rich alloys and lying below the Fermi level (equivalent to the 4f$^0$ configuration), becomes an excited state in the Ni-rich alloys, lying above the Fermi level.

Deep in the localized regime, the Ce magnetic moments order antiferromagnetically, and the Néel temperature decreases quasi-linearly with increasing nickel content from 5.5 K in Ce$_2$CuIn down to 2.7 K in Ce$_2$Cu$_{1.2}$Ni$_{0.8}$In. Simultaneous significant broadening of the maximum in $\chi(T)$ at $T_N$ indicates possible smearing of the phase transition at temperatures approaching absolute zero. Analysis of the temperature dependences of the electrical resistivity of the Ce$_2$Cu$_{2-x}$Ni$_x$In series revealed an evolution of the system from the dense Kondo lattice regime towards the nonmagnetic metal regime, controlled mainly by the increase in the exchange integral.

All the presented findings are in line with the Doniach picture of Kondo systems, which predicts a change in the character of the ground state from long range magnetic order to intermediate valence. This transformation is induced by an increase in the value of the exchange integral $J_{\text{ex}}$ that measures the hybridization strength. For Ce$_2$Cu$_{2-x}$Ni$_x$In, the increase of $J_{\text{ex}}$ with increasing $x$ is probably a consequence of the observed compression of the unit cell volume. Simultaneous reduction in a number of the 3d electrons, which could probably lead to some decrease in $J_{\text{ex}}$, seems to have a less significant influence on the physical properties of the system.

To verify our hypothesis detailed spectroscopic studies of the Ce$_2$Cu$_{2-x}$Ni$_x$In series are indispensable.

**Acknowledgments**

This work was supported by the Polish Ministry of Science and Higher Education within research grant no. N N202 102338.

**References**

[1] Kaczorowski D, Rogl P and Hiebl K 1996 Phys. Rev. B **54** 9891
[2] Hauser H, Michor H, Bauer E, Hilscher G and Kaczorowski D 1997 Physica B **230–232** 211
[3] Doniach S 1977 *Valence Instabilities and Related Narrow Band Phenomena* ed R D Parks (New York: Plenum) p 169
[4] Sales B B and Wohlleben D K 1975 Phys. Rev. Lett. **18** 1240
[5] Pecharsky V K, Gschneidner J K A and Miller L L 1991 Phys. Rev. B **43** 10906
[6] Sereni J G, Westerkamp T, Küchler R, Caroca-Canales N, Gegenwart P and Geibel C 2007 Phys. Rev. B **75** 024432
[7] Pikul A P, Caroca-Canales N, Deppe M, Gegenwart P, Sereni J G, Geibel C and Steglich F 2006 J. Phys.: Condens. Matter **18** L535
[8] Westerkamp T, Deppe M, Küchler R, Brando M, Geibel C, Gegenwart P, Pikul A P and Steglich F 2009 Phys. Rev. Lett. **102** 206404
[9] Cornut D and Coqblin B 1972 Phys. Rev. B **5** 4541