

## Noninteger Ce Valency in $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$

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It has been claimed earlier (*J. Alloys Comp.* **186**, 223 (1992)) that  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  is ferromagnetic at room temperature. In this paper it is shown, with magnetic susceptibility and electrical resistivity measurements, that no ferromagnetic order exists in our  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  sample down to 1.7 K. Moreover, the temperature dependencies of both magnetic susceptibility and electrical resistivity agree well with the existing theoretical models for intermediate valence fluctuating compounds. This agreement together with X-ray absorption spectroscopy data obtained at two fixed temperatures, 10 and 300 K, clearly give evidence for a nonintegral valence state of Ce in  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ . © 2001

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**Key Words:**  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ ; noninteger Ce-valency; magnetic susceptibility; electrical resistivity;  $L_{\text{III}}$ -X-ray absorption spectroscopy.

### INTRODUCTION

Our general interest in the magneto-electrical properties of compounds containing rare earth elements prone to valence instabilities (cerium, ytterbium, and europium) and the interesting interplay with magnetic ordering and/or superconductivity (1–4) prompted us toward a closer inspection of the physical properties of intermetallic Ce-based alloys  $\text{Ce}_2\text{Ni}_{22}\text{C}_{3-x}$ , where  $x = 0$  and 0.25.

$\text{Ce}_2\text{Ni}_{22}\text{C}_3$  was first identified in an isothermal section at 400°C as a ternary phase without homogeneity range in equilibrium together with (C), (Ni),  $\text{CeNi}_{15}\text{C}_{14}$  and  $\text{CeNi}_5$  (5). The unique crystal structure of this compound was derived from X-ray single-crystal data (6) to be orthorhombic with two independent crystallographic sites for the cerium atoms. The crystal structure was redetermined (7) at somewhat higher levels of accuracy; however, symmetry, structure, and particularly the short distances  $d_{\text{Ce-Ni}}$  of

about 0.2762 nm (6) were all confirmed, although these short distances were argued to be unreliable in a paper by Putyatin (8) on compounds labeled  $\text{RENi}_{18}\text{C}_{12}$  instead of  $\text{RE}_2\text{Ni}_{22}\text{C}_{3-x}$ . The refinement (7) indicated a small deficiency in one of the carbon sites, yielding the overall formula  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ . Furthermore,  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  was claimed to be metallic with a temperature-independent resistivity in the range from 2 to 300 K and this feature was believed to correspond to an intermediate or mixed Ce valency (7). In addition, the compound was said to be ferromagnetic at room temperature (7).

This interesting, although rather rare, interplay between ferromagnetism and intermediate/mixed valency stimulated our interest. The present paper therefore deals with a detailed inspection of the physical properties of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  to obtain deeper insight into the electron interaction mechanism.

### EXPERIMENTAL

Samples, each of about 2 g, were prepared by repeated arc-melting of the high-purity elements together in a Ti-gettered argon atmosphere. Weight losses due to the arc-melting process were insignificant (less than 0.2 mass%). The following starting materials were used: Ce (ingot, m3N, Auer-Remy, Germany); Ni (powder, m3N Goodfellow, England), and C (powder (compacted together with Ni), reactor grade with impurities <140 ppm, Carbone Lorraine, France). After melting, the reguli were packed in molybdenum or tantalum foil, sealed in evacuated silica tubes, and heat-treated for at least 140 h at 850°C in a wire-wound power-controlled tubular furnace calibrated against a Pt/PtRh thermocouple. After annealing, the samples were quenched by casting the silica tubes into cold water.

Precise lattice parameters and standard deviations were obtained by a least-squares refinement of room-temperature Guinier-Huber X-ray powder data ( $\text{CuK}\alpha_1$ ), employing an internal standard of 99.9999 mass% pure Ge ( $a_{\text{Ge}} = 0.5657906$  nm). Rietveld refinements were performed

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on X-ray powder intensity data collected from flat specimens in a Siemens D5000 diffractometer ( $\text{CuK}\alpha$ ).

Magnetic measurements were performed in the temperature range 1.7–400 K in magnetic fields up to 5.5 T using a Quantum Design MPMS-5 SQUID magnetometer. Electrical resistivity was measured in the range 4.2–300 K employing a conventional dc four-point technique. In these measurements the specimens were cuboid-shaped polycrystals with the Au electrical leads attached by silver-epoxy paste.

X-ray absorption spectroscopy (XAS) measurements were performed at the French synchrotron radiation facility of LURE using the X-ray beam delivered by the DCI storage ring, working at 1.85 GeV and 320 mA, on the EXAFS 2 station. Experiments were made on powdered samples in the range [5660–5840 eV] around the  $L_{\text{III}}$  edge of Ce at two fixed temperatures, at 10 and 300 K. To avoid third-order harmonics, a two-mirror device was adjusted to cutoff energies higher than 9 keV. Further experimental details and the  $L_{\text{III}}$ -edge deconvolution technique were already described in one of our previous papers (1) as well as by (9).

## RESULTS AND DISCUSSION

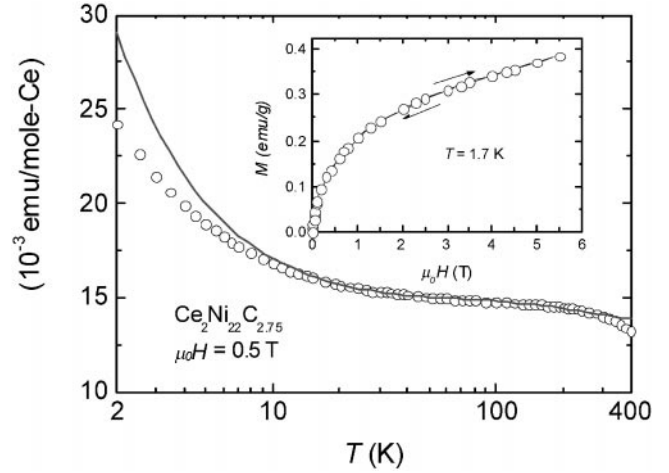
### a. Crystal Structure of $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$

Powder X-ray diffraction data of the alloy  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  were consistent with the intensities calculated from the atom parameters for a standardized setting of the unit cell, as given by Parthé *et al.* (10). The results confirm isotypism with the  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  type (6, 7). A comparison of the lattice parameters obtained from our refinement with those reported in a literature is presented in Table 1. It reveals close correspondence of our data with those reported in (7, 8), while data given by Bodak *et al.* (6) seem to be significantly higher. In this context it is interesting to note that an almost linear dependency of the unit cell volumes was observed for the isotypic La-, Ce-, and Pr-containing compounds (6), whereas a pronounced “dip” is seen for the cerium compound in the corresponding dependency re-

**TABLE 1**  
Crystallographic Data for  $\text{Ce}_2\text{Ni}_{22}\text{C}_{3-x}$  and Comparison with Data from Literature

Lattice parameters (nm)				Comments	Refs.
$a$	$b$	$c$	$V$ (nm <sup>3</sup> )		
1.1384(3)	1.5024(7)	1.4671(5)	2.5092	$\text{Ce}_2\text{Ni}_{22}\text{C}_3$	(6)
1.1380	1.5027	1.4639	2.5051	$\text{CeNi}_{-8}\text{C}_{-2}$	(8)
1.1373(2)	1.5004(3)	1.4625(4)	2.4956	$\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$	(7)
1.1375(3)	1.5001(5)	1.4613(5)	2.4935	$\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$	This work

Note. Space group:  $Cmca$ , No. 64; two inequivalent Ce sites: Ce(1) in  $8e$  and Ce(2) in  $8f$ .



**FIG. 1.** Temperature dependence of magnetic susceptibility of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  measured in the field of 0.5 T. Solid line represents a least-squares fit to the experimental data according to Eq. [1]. Inset shows magnetization at 1.7 K as a function of magnetic field.

ported by (7, 8). Such a “dip” is generally a straightforward indication for a valency of cerium higher than 3 as for the neighboring rare earth elements in the Periodic Chart.

### b. Magnetism, Electric Resistivity, and X-Ray Absorption Spectroscopy

The temperature dependence of the molar magnetic susceptibility in a field of 0.5 T is shown in Fig. 1. Above 300 K, the susceptibility,  $\chi(T)$ , follows a Curie–Weiss law with a large (negative) paramagnetic Curie temperature. The remarkable feature, however, is the presence of a wide temperature range, i.e., 50 to 300 K, where much less temperature-dependent behavior of  $\chi$  is observed. Such a feature is indicative of the intermediate valence (IV) phenomena. It furthermore can be seen that the susceptibility below about 30 K rapidly increases with decreasing temperature. Instead of interpretation in terms of ferromagnetic impurities, we attribute this  $\chi$ -upturn to the contribution of a fraction of paramagnetic  $\text{Ce}^{3+}$  ions. Indeed, the inset of Fig. 1 shows neither spontaneous magnetization nor hysteresis at 1.7 K in fields up to 5.5 T. It is obvious that the magnetization is strongly curvilinear and no saturation is achieved. Let us emphasize that the magnetization at 5.5 T of our compound amounts to only a tiny fraction of the saturation moment of  $\text{Ce}^{3+}$  ( $gJ = 2.14 \mu_B$ ). Quenched moment phenomena are common for cerium-based compounds, but in our case a significant reduction in the magnetic moment value is a hint for an intermediate valence state of Ce ions.

To account for the susceptibility behavior in the overall temperature range, we have considered an ionic two-inter-configurational fluctuation (ICF) model proposed by Sales and Wohllaben (11). Within the scope of this model, the

magnetic susceptibility of IV compounds,  $\chi_{\text{IV}}(T)$ , follows from fluctuations between the magnetic and the nonmagnetic configuration. For cerium-based compounds,  $\chi_{\text{IV}}(T)$  is given by

$$\chi_{\text{IV}}(T) = \frac{N_{\text{A}}\mu_{\text{eff}}^2(1 - v(T))}{3k_{\text{B}}(T + T_{\text{sf}})},$$

with

$$v(T) = \frac{1}{1 + 6 \exp(-E_{\text{ex}}/k_{\text{B}}(T + T_{\text{sf}}))}.$$

In those equations,  $E_{\text{ex}}$  is the energy difference of the  $4f^1$  and the  $4f^0$  state, while  $T_{\text{sf}}$  is a characteristic temperature describing fluctuations between those states. For temperatures between 12 and 315 K, our experimental data are then fitted by the equation

$$\chi(T) = \chi_0 + n \frac{C}{T} + \chi_{\text{IV}}(T), \quad [1]$$

with the temperature-independent Pauli contribution,  $\chi_0 = 0.0126(5)$  emu/mol, the amount of  $\text{Ce}^{3+}$  moments,  $n = 0.037(3)$ ,  $E_{\text{ex}} = 384(11)$  K, and  $T_{\text{sf}} = 115(5)$  K. The result of fit is illustrated as a solid line in Fig. 1. It should be noted that these values are typical for cerium-based (IV) compounds. The valence of Ce in our compound can be deduced from the  $E_{\text{ex}}$  and  $T_{\text{sf}}$  parameters to be 3.29 at room temperature.

The electrical resistivity of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  is shown in Fig. 2. The room-temperature (RT) resistivity is estimated to be about  $120 \mu\Omega\text{-cm}$ , which is of the same order of

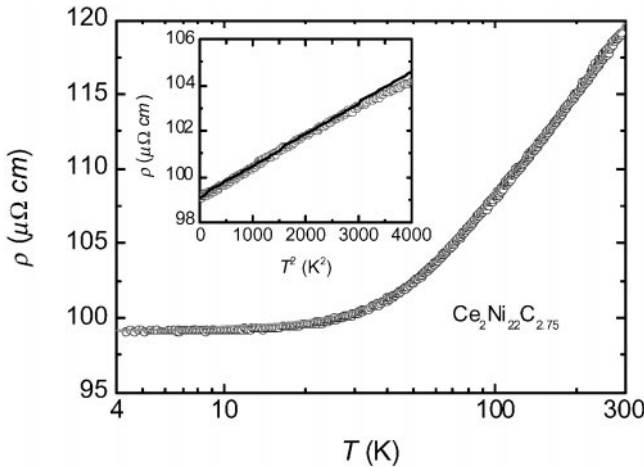


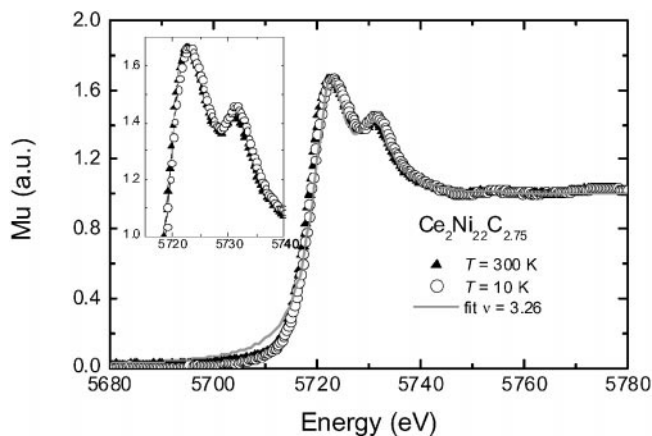
FIG. 2. Temperature dependence of electrical resistivity of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ . Solid line represents a least-squares fit to the experimental data according to Eq. [2]. Inset shows  $T^2$  plot of the low-temperature resistivity.

magnitude as reported for this compound (7). Similar to previous data (7), our compound also has a rather low residual resistance ratio,  $\rho(\text{RT})/\rho(4\text{K})$ , of 1.21. However, the important result of our measurements is that  $\rho(T)$  exhibits an  $AT^2$  dependence below 35 K with  $A = 0.0014 \mu\Omega\text{-cm}/\text{K}^2$  (see inset of Fig. 2). Furthermore, the resistivity follows a linear variation between 40 and 80 K and then shows  $\ln T$  behavior at high temperatures. According to the theory of Kaiser and Doniach (13), the temperature where transition from  $T^2$  to a  $T$  law occurs correlates with  $T_{\text{sf}}$  by the relation  $T_{\text{sf}}/4$ . It means that in our case this transition should appear around 29 K, in fine agreement with our observation. A similar temperature dependence of the resistivity is observed in intermediate valence compounds (12). Therefore, the  $\rho(T)$  dependence can be analyzed in terms of a model given by Freimuth for the case of Ce and Yb compounds with unstable  $4f$  shells (14). In this approach, the dominant contribution to the resistivity value arises from the scattering between the electrons in the broad  $sd$ -conduction band and those in the narrow Lorentzian-shaped  $4f$  band. This contribution, therefore, is proportional to the density of states  $W(T)/[T_0^2 + W(T)^2]$ , where  $W(T) = T_{\text{sf}} * \exp(-T_{\text{sf}}/T)$  is the effective energy width for scattering, and  $T_0$  represents the position of the center of the  $4f$  band with respect to the Fermi energy. Thus, the total resistivity could be expressed as (14)

$$\rho(T) = \rho_0 + aT + \frac{bJ_{\text{sf}}^2 W(T)}{T_0^2 + W(T)^2}; \quad [2]$$

$\rho_0$  is the temperature-independent residual resistivity,  $a$  is a coefficient indicating the strength of the nonmagnetic phonon term, and  $bJ_{\text{sf}}^2$  is a parameter which relates to the strength of the  $sd$ - $f$  hybridization. A least-squares fit to the experimental data gave  $\rho_0 = 99 \mu\Omega\text{-cm}$ ,  $a = 0.041(5) \mu\Omega\text{-cm}/\text{K}$ ,  $T_{\text{sf}} = 131(5)$  K, and  $T_0 = 112(8)$  K. The result of fitting is shown as a solid line in Fig. 2. Taking  $b = m * k_{\text{B}}/ne^2\hbar = 0.1 \mu\Omega\text{-cm}/\text{K}$  as in (14), one obtains  $J_{\text{sf}} = 1650$  K. Such values are comparable with those of known (IV) compounds (14). We wish to note that the  $T_{\text{sf}}$  value derived from resistivity data is consistent with that found in the magnetic measurement, indicating that Freimuth's model can explain qualitatively the resistivity behavior of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ .

$L_{\text{III}}$ -absorption-edge spectra at 300 and 10 K are shown in Fig. 3. Both show a double peak at around 5723 and 5730 eV, corresponding to Ce in trivalent and tetravalent states. The inset shows that the relative intensity of the two peaks slightly evolves versus temperature, the  $\text{Ce}^{4+}$  peak increasing at the lower temperature. This temperature dependence is characteristic of intermediate (fluctuating) valence material. Using a classical decomposition of the spectra in a sum of two Lorentzian and two arc-tangent



**FIG. 3.**  $L_{\text{III}}$  absorption spectra of  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  at 300 and 10 K and fit with a valence of 3.26(3). Inset shows that the  $\text{Ce}^{4+}$  component slightly increases at 10 K.

components, we derive a value of the average valence of 3.26(3). We should note that the technique gives a mean value of the valence irrelevant of the Ce site. This value is of the order of that observed in some other strongly intermediate valence systems, for instance, 3.30 in  $\text{CeNi}_4\text{B}$  or  $\text{CeNi}_5$  (15), and in agreement with the magnetic and transport data reported above.

### CONCLUSION

We have synthesized and investigated a single-phase polycrystalline sample  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ . The powder X-ray diffraction data confirm its crystal structure to be unique ( $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  type). The lattice parameters of our sample reveal close correspondence with those reported earlier (7, 8). By means of XAS, we have measured directly the valence of the Ce ion in  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$ . We have observed in the  $L_{\text{III}}$ -absorption spectra a clear double-peak structure, which would plead for an intermediate Ce valence of the average value  $\nu = 3.26(3)$ . The magnetic susceptibility and electrical resistivity measurements both also show evidence of a valence fluctuating state for the Ce ion. The  $\chi(T)$  dependence, analyzed in terms of the ICF model, which at room temperature yields a Ce valence of 3.29, is in fine agreement with that deduced from XAS data. Furthermore, the curvilinear

behavior of  $\rho(T)$  can be explained on the basis of the Freimuth model. Owing to the relatively low value of  $T_0$ , it is interesting to speculate that the  $4f$  level is very close to the Fermi level and therefore one expects rather unusual behavior of Ce atoms in this compound. Finally, we would like to recall that the two crystallographically independent Ce atoms in the unit cell have different environments. Therefore, future investigations of the  $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$  compound and its solid solutions containing a metal with stable valence should shed more light into the problem of local (IV) changes.

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