

X-Ray Magnetic Circular Dichroism Studies on CeNi₄B

T. TOLIŃSKI^a, J.C. CEZAR^b, H. WENDE^c, A. KOWALCZYK^a AND K. BABERSCHKE^d

^aInstitute of Molecular Physics, Polish Academy of Sciences

M. Smoluchowskiego 17, 60-179 Poznań, Poland

^bE.S.R.F., 6 rue Jules Horowitz, 38043 Grenoble Cedex, France

^cUniversität Duisburg-Essen Fachbereich Physik

Lotharstr. 1, 47048 Duisburg, Germany

^dInstitut für Experimentalphysik, Freie Universität Berlin

Arnimallee 14, D-14195 Berlin-Dahlem, Germany

The CeNi₄B compound is a mixed-valence system. It is a paramagnet with $\mu_{\text{eff}} = 0.52 \mu_{\text{B}}/\text{f.u.}$ and the paramagnetic Curie temperature $\theta = -10.7$ K. In the present research we complete our previous magnetic susceptibility and X-ray photoemission measurements with new studies by the X-ray magnetic circular dichroism method. The observation of the Ce $M_{4,5}$ edges carried out with X-ray magnetic circular dichroism confirms the mixed-valence state deduced previously from X-ray photoemission spectroscopy. Moreover, we report on the measurements of the Ni $L_{2,3}$ edges, which enable verification of the Ni contribution to the magnetism of this compound.

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1. Introduction

Compounds based both on the lanthanides dominated by the $4f$ levels and on the transition elements governed by the $3d$ states are often a source of controversy if the magnetism of one of the elements tends to be damped [1–3]. The point is to decide if the magnetic properties of such compounds can be satisfactorily described by considering only either the $4f$ or $3d$ contribution. A good example of such a compound is CeNi₄B belonging to the series RNi₄B (R = rare earth). For this series of compounds it is usually assumed that the magnetism of nickel is negligible owing to the filling of the $3d$ states. We have chosen the CeNi₄B compound to be studied in more details by the X-ray magnetic circular dichroism (XMCD) method, as it is a paramagnetic material.

From literature and our previous investigations [2, 4] we know that CeNi₄B is characterized by $\mu_{\text{eff}} = 0.52 \mu_{\text{B}}/\text{f.u.}$ and the paramagnetic Curie temperature $\theta = -10.7$ K, as obtained from the modified Curie–Weiss law, i.e. by including the temperature independent Pauli paramagnetism.

The X-ray photoemission spectroscopy (XPS) revealed a mixed-valence behavior of the Ce ions in the CeNi₄B compound. The occupation of the f -states $n_f = 0.83$, which has been obtained from the analysis of the core Ce $3d$ doublet [5] is in excellent agreement with the value derived by Mazumdar et al. [6] by the X-ray absorption near-edge structure (XANES) studies.

Both the literature and our previous studies do not finally decide about the role of the Ni atoms in the mag-

netic properties of the RNi₄B compounds. Our theoretical calculations [1] for the ferromagnetic GdNi₄B compound using the spin-polarized tight binding linear muffin tin orbital (TB LMTO) method have indicated that the Ni magnetic moment is negligible ($\mu_{\text{Ni}} \approx 0.018 \mu_{\text{B}}$) and is antiparallel to the rare-earth magnetic moment.

2. Experimental

The polycrystalline CeNi₄B compound was synthesized by the induction melting under an argon atmosphere. As the ingot the stoichiometric amounts of Ce, Ni and B were used. This compound crystallizes in the hexagonal CeCo₄B structure, which can be derived from RNi₅ by replacing the two Ni atoms at the 2c sites in every second layer by B atoms. In the CeCo₄B structure the Ni atoms occupy 2c and 6i sites, the rare earth atoms are located in the 1a and 1b sites, and the boron atoms occupy one position, 2d [7]. The unit cell is illustrated in Fig. 1. The lattice parameters derived by fitting of the X-ray diffraction pattern with the program FullProf in the space group $P6/mmm$ are $a = 5.00$ Å and $c = 6.99$ Å.

The XMCD measurements were done on the high field magnet end station, at ID08, ESRF. The samples were filled with a diamond file under a base pressure of about 10^{-8} mbar and transferred immediately to the magnet for measurements at a pressure of about 5×10^{-10} mbar. The spectra were obtained in the total electron yield (TEY) mode, i.e. the drain current in the sample was

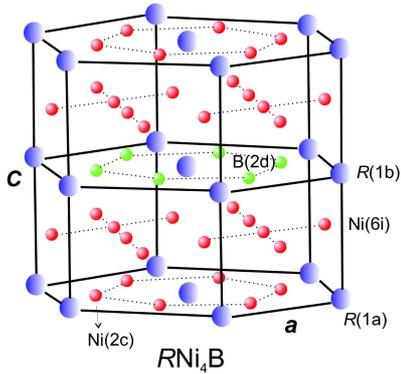


Fig. 1. Unit cell of the RNi_4B compounds. The lines are only a guide to the eye.

measured. The spectra are normalized by the incident beam intensity. The XMCD signal was determined by reversing both the ellipticity of the beam between circular left and right, and the applied magnetic field between +4 T and -4 T.

3. Results and discussion

The starting point of the discussion is if one can expect a significant XMCD signal from cerium and, perhaps, from nickel in the case of the CeNi_4B compound. First information is provided by the magnetic susceptibility measurements. As it has been mentioned in the introduction, this compound appeared to be paramagnetic, at least down to 2 K, and there has not been a wide linear region in the reciprocal magnetic susceptibility $\chi^{-1}(T)$ [2, 4]. Instead, $\chi(T)$ can be well fitted in the full temperature range using the modified Curie-Weiss law, $\chi(T) = \chi_0 + C/(T - \theta)$, where χ_0 is a temperature independent term and $\mu_{\text{eff}} = 0.52 \mu_{\text{B}}/\text{f.u.}$, $\theta = -10.7$ K. However, in the temperature range between 230–300 K, $\chi^{-1}(T)$ is linear and can be fitted with the full effective magnetic moment $\mu_{\text{eff}} = 2.54 \mu_{\text{B}}/\text{f.u.}$ and θ as large as -955 K. In the frames of the single ion Kondo model [8] this value of the paramagnetic Curie temperature implies a Kondo temperature $T_{\text{K}} = |\theta/2| = 477$ K. Such a large value means that the Ce ions are in a mixed-valence state in the compound studied. The fully demonstrated effective magnetic moment of Ce means that the paramagnetic behavior can be described without considering the contribution of the Ni atoms.

The mixed valence state has been directly corroborated by the XPS measurements of the core Ce 3d peaks [5]. Due to a finite probability of the excitation of the f^0 and f^2 states, leading to a different screening of the core hole, additional satellites can appear on the shoulders of the main Ce 3d peaks. The analysis according to the Gunnarsson and Schönhammer model [9] provided the f -occupancy $n_f = 0.83$ and the hybridization between the f states and the conduction electrons $\Delta = 85$ meV, which implies a strong mixed valence behavior [5].

The X-ray absorption spectrum (XAS) measurement is one of the best methods to study the valence state. The high energy satellites visible in Fig. 2 at about 887.5 eV and 905 eV for the Ce $M_{4,5}$ edges are characteristic of the mixed valence compounds with strong hybridization between the f states and the conduction electrons [6, 10]. The Ni $L_{2,3}$ edges for CeNi_4B are also displayed in Fig. 2.

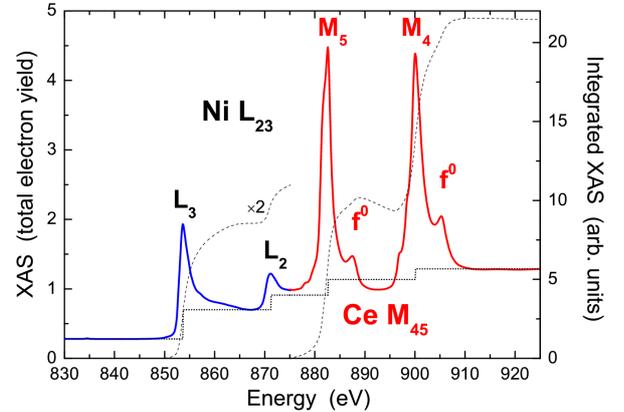


Fig. 2. XAS spectrum of the Ce $M_{4,5}$ and Ni $L_{2,3}$ edges. The dotted line represents the step function describing the non-resonant absorption. The dashed line is the integral of the XMCD spectrum (right axes).

We have shown that the magnetic susceptibility, XPS and XAS measurements demonstrate consistently that Ce is in the intermediate valence state accompanied by a strong $4f$ -conduction electrons hybridization in CeNi_4B . In spite of these observations the dichroic signal (Fig. 3), i.e. the difference between XAS of the two opposite beam polarizations, reveals that both Ce and Ni possess a small but measurable magnetic contribution. The shape of the spectra is in agreement with other Ce-based compounds [10] but an important observation concerns the mutual orientation of the Ce and Ni magnetic moments. It stems from Fig. 3 that these two contributions are antiparallel.

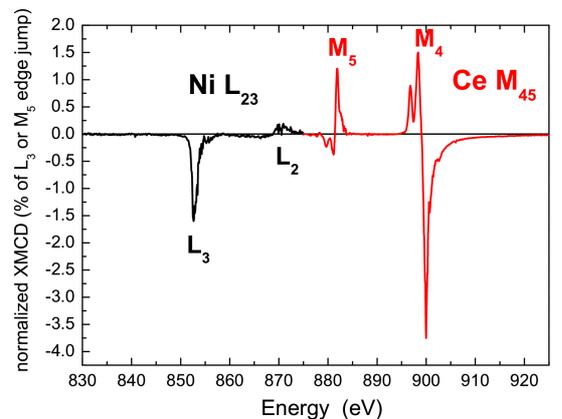


Fig. 3. XMCD signal for the Ce $M_{4,5}$ and Ni $L_{2,3}$ edges.

It is possible to estimate both the orbital and the spin contribution of the magnetic moment employing the standard analysis of the XAS and XMCD spectra [11, 12]. The orbital and the spin sum rules provide the mean value of the z component of the orbital momentum operator

$$\langle L_z \rangle = -l n_h \frac{2 \int_{J^+ + J^-} (I^{-1} - I^1) dE}{3 \int_{J^+ + J^-} (I^1 + I^{-1}) dE} \quad (1)$$

and the average value of the z component of the spin operator

$$\langle S_z \rangle = -n_h \times \frac{\int_{J^+} (I^{-1} - I^1) dE - \frac{l}{l-1} \int_{J^-} (I^{-1} - I^1) dE}{\int_{J^+ + J^-} (I^1 + I^{-1}) dE}, \quad (2)$$

where I^{-1} and I^1 denote the absorption coefficients for the right and left polarized photons. The integration is over the respective J edges and n_h corresponds to the number of holes in the l shell. It is assumed that the magnetic dipole operator $\langle T_z \rangle$ is negligible, which is reasonable in the case of polycrystalline samples.

The continuum contribution (the non-resonant absorption) is introduced by a step function (Fig. 2) with steps height determined by the degeneracy of the core hole. The dashed line in Fig. 2 shows the integral of the Ni $L_{2,3}$ and Ce $M_{4,5}$ XAS (denominator in Eqs. (1) and (2)). The other integrals involved in the equations are obtained from the integration of the XMCD spectrum.

For Ni we assume $n_h = 1.5$ (bulk value) and $l = 2$. We get the orbital magnetic moment $m_{\text{orb}}^{\text{Ni}} = 0.0039 \mu_B$ and the spin magnetic moment $m_{\text{spin}}^{\text{Ni}} = 2 \times \langle S_z \rangle = 0.0087 \mu_B$. These tiny values confirm the small contribution of Ni in magnetism of the CeNi₄B compound. One can also see that the spin and the orbital components are parallel. The ratio $m_{\text{orb}}^{\text{Ni}}/m_{\text{spin}}^{\text{Ni}}$ being 0.45 is in good agreement with the value of 0.46 found by Mizumaki et al. [13] for GdNi₂ but significantly enhanced compared to Ni metal (0.095) [14].

For Ce we put $n_h = 13.17$, based on the previous XPS studies [5] and $l = 3$. We get the orbital magnetic moment $m_{\text{orb}}^{\text{Ce}} = 0.161 \mu_B$ and the spin magnetic moment $m_{\text{spin}}^{\text{Ce}} = 2 \times \langle S_z \rangle = -0.186 \mu_B$. In the calculation of the spin component we have divided Eq. (2) by 1.6, which is a correction resulting from the off-diagonal term of the $3d-4f$ exchange interaction limiting the applicability of the spin sum rule for rare earths (for details see [15]).

The spin and the orbital components are antiparallel. The ratio $m_{\text{orb}}^{\text{Ce}}/m_{\text{spin}}^{\text{Ce}}$ is -0.86 . It is much smaller than -4 expected theoretically for $J = 5/2$ results probably from the delocalization of the $4f$ electron.

4. Conclusions

We have shown that the X-ray absorption measurements confirm the mixed valence state and strong

$4f$ -conduction electrons hybridization of the Ce ions in the CeNi₄B compound. Ni exhibits a very small but measurable magnetic signal in the X-ray magnetic circular dichroism. We have obtained $m_{\text{orb}}^{\text{Ni}} = 0.0039 \mu_B$ and $m_{\text{spin}}^{\text{Ni}} = 0.0087 \mu_B$. XMCD of the Ce $M_{4,5}$ edges have provided $m_{\text{orb}}^{\text{Ce}} = 0.161 \mu_B$ and $m_{\text{spin}}^{\text{Ce}} = -0.186 \mu_B$. The XMCD spectrum indicates that the Ce and Ni magnetic moments are antiparallel.

Acknowledgments

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