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# Electronic structure of $\text{Nd}_3\text{Co}_{11}\text{B}_4$

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**Abstract.** The electronic structure of  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  and corresponding x-ray photoemission spectra (XPS) are presented. The band structure is calculated by the spin-polarized tight binding linear muffin tin orbital (TB LMTO) method. The XPS valence bands are compared with the calculated electronic density of states.  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  is ferromagnetic with a calculated total magnetic moment  $M = 16.10 \mu_B \text{ fu}^{-1}$  and the local magnetic moments on Nd and Co atoms are parallel.

## 1. Introduction

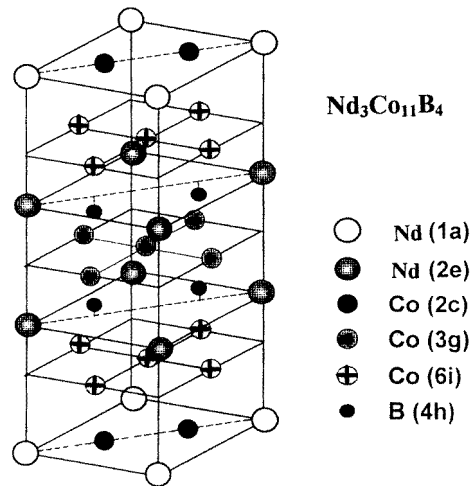
The  $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$  ( $\text{R}$  = rare earth) type compounds are an important and physically interesting class of materials. Compounds in this series are known to exist for  $n = 0$  ( $\text{RCO}_5$ ),  $n = 1$  ( $\text{RCO}_4\text{B}$ ),  $n = 2$  ( $\text{R}_3\text{Co}_{11}\text{B}_4$ ),  $n = 3$  ( $\text{R}_2\text{Co}_7\text{B}$ ) and for  $n \rightarrow \infty$  ( $\text{RCO}_3\text{B}_2$ ). These structures are based on the well known  $\text{CaCu}_5$  structure [1].

The electronic and magnetic properties of such ternary compounds have been studied intensively in the past [2–14]. Smit *et al* [2] determined the crystal-field parameters by measuring Mössbauer spectra of  $\text{Gd}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$  compounds. The strength of the individual contributions to the magnetic anisotropy and magnetic moments of the non-equivalent Co sites in these compounds was studied using nuclear magnetic resonance (NMR) [3], neutron diffraction [4] and theoretical calculations [5]. The intersublattice exchange interaction has a tendency to decrease with increasing atomic number of the rare-earth component in  $\text{R}_3\text{Co}_{11}\text{B}_4$  compounds [6].

The  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  borides crystallize in a hexagonal structure of  $\text{Ce}_3\text{Co}_{11}\text{B}_4$  type, space group  $P6/mmm$ . In this structure (figure 1), the rare-earth atoms are distributed over two different crystallographic sites (1a, 2e); the cobalt atoms occupy three different positions (2c, 3g, 6i); however the boron is located on one type of site only. The unit cell is formed by the alternate stacking of one layer of  $\text{RCO}_5$  and two layers of  $\text{RCO}_3\text{B}_2$  unit cells. The electrical resistivity at low temperatures shows a  $T^2$  dependence, implying that the electron-spin wave scattering is dominant in this temperature range [14]. At higher temperatures ( $T \geq 100$  K), the resistivity is due to s–d interaction [14]. In this paper we present x-ray photoemission spectra of  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  and the band structure calculated by the spin-polarized TB LMTO method [15].

## 2. Experimental details

The  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  sample was prepared by induction melting of stoichiometric amounts of the constituent elements in a water-cooled boat, under an argon atmosphere. The ingots were



**Figure 1.** Crystal structure of Nd<sub>3</sub>Co<sub>11</sub>B<sub>4</sub>.

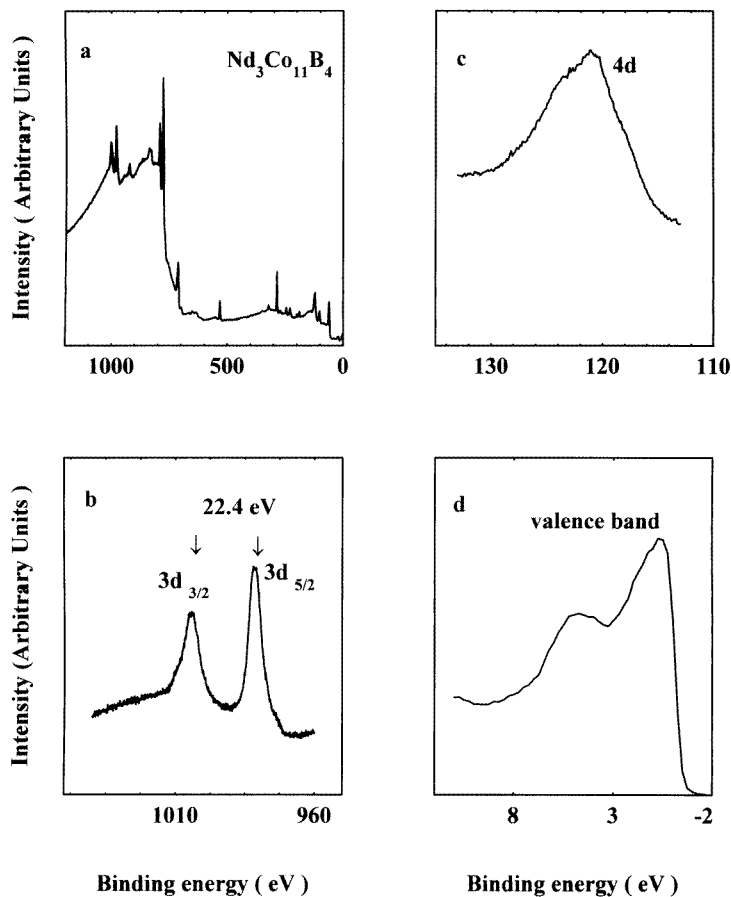
inverted and melted several times to insure homogeneity. The sample was then heat-treated at 1000 °C for two weeks. The crystal structure was established by a powder x-ray diffraction technique using Cu K $\alpha$  radiation. The room temperature x-ray powder diffraction pattern revealed the Nd<sub>3</sub>Co<sub>11</sub>B<sub>4</sub> compound to be single phase-material with the lattice constants  $a = b = 5.12 \text{ \AA}$  and  $c = 9.81 \text{ \AA}$ .

Magnetic measurements [14] were carried out using a vibrating sample magnetometer in a field up to 4 T. The Curie temperature ( $T_C$ ) was determined by the temperature dependence of magnetization ( $M$ ) in a weak external field. The value of  $T_C$  was estimated in Nd<sub>3</sub>Co<sub>11</sub>B<sub>4</sub> as  $T_C = 392 \text{ K}$  and the saturation moment  $M_s = 12.20 \mu_B \text{ fu}^{-1}$  at  $T = 4.2 \text{ K}$ .

The XPS spectra were obtained with monochromatized Al K $\alpha$  radiation ( $h\omega = 1486.6 \text{ eV}$ ) at room temperature using a Perkin Elmer PHI 5600 ci ESCA spectrometer. The energy spectra were analysed with a hemispherical mirror analyser with an energy resolution of 0.4 eV. The spectra were measured in vacua below  $6 \times 10^{-10} \text{ Torr}$ . Calibration of the spectra were performed according to Baer *et al* [16]. The binding energies were referenced to the Fermi level at  $E_F = 0 \text{ eV}$ . The 4f levels of gold were situated at 84.0 eV. Figures 2(a)–(d) present the Nd<sub>3</sub>Co<sub>11</sub>B<sub>4</sub> XPS spectra in various regions of the binding energy. In figure 2(a) the XPS spectrum in the region  $1000 < E < 0 \text{ eV}$  is presented. The positions of peaks are similar to those observed in pure neodymium [17]. Two peaks located near  $E = 1000 \text{ eV}$  show 3d<sub>3/2</sub> and 3d<sub>5/2</sub> (figure 2(b)). The spin-orbit splitting of 3d<sub>5/2</sub> and 3d<sub>3/2</sub> was found to be 22.4 eV and is close to 22.6 eV for pure Nd. The positions of the 3d peaks are in a good agreement with those shown in [17]. The position of the Nd 4d peak is presented in figure 2(c). The maximum of the Nd 4d is located at 121 eV, similarly as in [17]. The 4s peak is located at  $E = 320 \text{ eV}$ ; however 4p<sub>1/2</sub> and 4p<sub>3/2</sub> peaks are at 245 and 230 eV, respectively. The valence band of Nd<sub>3</sub>Co<sub>11</sub>B<sub>4</sub> is plotted in figure 2(d). The main peak located at 1 eV is due to the Co 3d states and the smaller one at 5 eV gives the contribution from Nd 4f<sup>3</sup>H<sub>4</sub> states [18].

### 3. The electronic structure and the photoemission spectra

The electronic structure and the magnetic moment were calculated by the spin-polarized tight binding linear muffin tin orbital (TB LMTO) method [15], within the framework

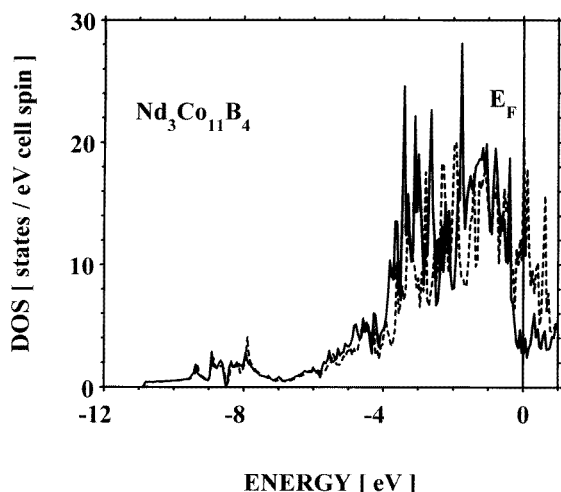


**Figure 2.** The measured x-ray photoemission spectra for  $\text{Nd}_3\text{Co}_{11}\text{B}_4$ . The Fermi level is located at  $E = 0$  eV. (a) The total XPS spectra. (b) The Nd 3d XPS spectra; the difference in position of  $3d_{5/2}$  and  $3d_{3/2}$  peaks gives the spin-orbit splitting  $\Delta = 22.4$  eV. (c) The Nd 4d XPS spectra with the maximum at  $E = 121$  eV. (d) The XPS valence band.

**Table 1.** Position of atoms in the  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  unit cell.

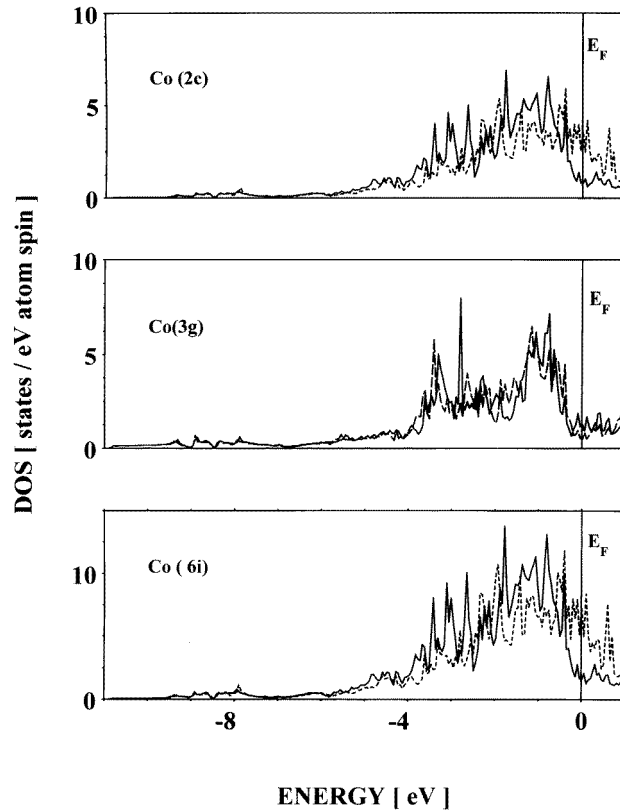
	$x$	$y$	$z$
Nd(1a)	0	0	0
Nd(2e)	0	0	1/3
Co(2c)	1/3	2/3	0
Co(3g)	1/2	0	1/2
Co(6i)	1/2	0	0.20
B(4h)	1/3	2/3	0.35

of the local spin density (LSD) approximation. The atomic sphere approximation (ASA) was employed and the standard combined corrections [15] for overlapping were used. We have applied the scheme proposed by Brooks *et al* [19] in which the 4f states of Nd are treated as open core states. In this way the 4f states of neodymium did not hybridize with the conduction electron states and the number of 4f electrons of Nd was fixed to



**Figure 3.** Total density of states for  $\text{Nd}_3\text{Co}_{11}\text{B}_4$ . The broken and solid curves denote the DOS for minority and majority spin bands, respectively. The Fermi level is located at  $E = 0$  eV.

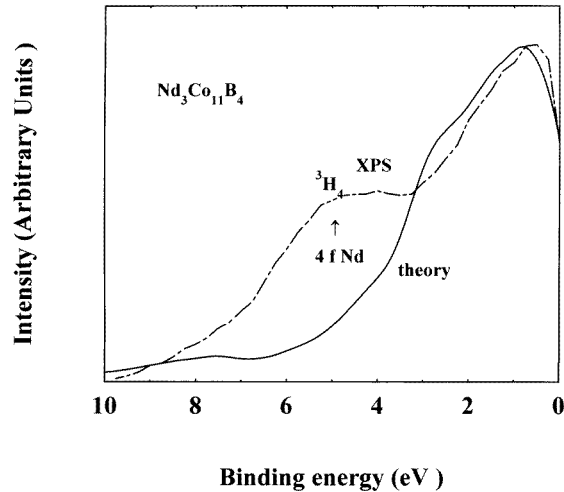
three. The motivations to use such a model are the difficulties with the band structure treatment of the localized 4f electrons of rare-earth metal and the itinerant magnetism of spd conduction electrons. Such a model was applied by Brooks *et al* [19] to different rare earth–transition metal intermetallic compounds. The self-consistent spin polarized band calculations were performed for the experimental lattice parameters. The self-consistent band calculations were carried out for 270  $k$ -points in the irreducible wedge of the Brillouin zone. The values of the atomic sphere radii were taken in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. The exchange–correlation potential was assumed in the form of von Barth and Hedin [20] and non-local corrections were also used [21]. The self-consistent LMTO calculations were performed without spin–orbit and including the spin–orbit (S–O) interaction [22] in the valence electrons. The shape of the density of states did not change drastically when we included the spin–orbit interaction. The band calculations were performed for the following values of the atomic sphere ratio:  $S_{\text{Nd}}/S_{\text{av}} = 1.3$ ,  $S_{\text{Co}(2\text{c})}/S_{\text{av}} = 1.03$ ,  $S_{\text{Co}(3\text{g})}/S_{\text{av}} = 0.925$ ,  $S_{\text{Co}(6\text{i})}/S_{\text{av}} = 0.925$ ,  $S_{\text{B}}/S_{\text{av}} = 0.767$ , where  $S_{\text{av}}$  is the average Wigner–Seitz radius. For such atomic sphere radii the values of the atomic potentials on the sphere boundary were similar and the overlapping of the spheres was less than 10%. The calculated total magnetic moment in  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  is  $16.10 \mu_{\text{B}} \text{ fu}^{-1}$  ( $15.855 \mu_{\text{B}} \text{ fu}^{-1}$  without S–O) and the local spin magnetic moments on each type of atom are  $m_{\text{Nd}}(1\text{a}) = 2.899$  ( $2.903$ )  $\mu_{\text{B}}$ ,  $m_{\text{Nd}}(2\text{e}) = 2.986$  ( $2.990$ )  $\mu_{\text{B}}$ ,  $m_{\text{Co}}(2\text{c}) = 1.750$  ( $1.768$ )  $\mu_{\text{B}}$ ,  $m_{\text{Co}}(3\text{g}) = 0.033$  ( $0.027$ )  $\mu_{\text{B}}$ ,  $m_{\text{Co}}(6\text{i}_1) = 0.624$  ( $0.576$ )  $\mu_{\text{B}}$ ,  $m_{\text{B}}(4\text{h}) = -0.029$  ( $0.027$ )  $\mu_{\text{B}}$ . The values in brackets denote the magnetic moments without S–O. The different values of the magnetic moment on the cobalt atoms are connected to the various local environments of each atom. The cobalt atom in position 2c has three Nd and nine Co atoms as the nearest neighbours. The cobalt at position 6i has four Nd and seven Co atoms in the first shell. The cobalt at 3g has four Nd and six Co atoms as the nearest neighbours. Our calculations indicate that Co in position 3g is almost non-magnetic. The density of states at the Fermi level is  $23 \text{ states eV}^{-1} \text{ fu}^{-1}$  for both spin directions. The total density of states for the ferromagnetic  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  is presented in figure 3. The broken curve presents the DOS for minority spin bands and the solid curve for majority spin bands.



**Figure 4.** Local density of states on cobalt atoms in 2c, 3g and 6i positions. The solid and broken curves correspond to minority and majority spin bands.

At the Fermi level the main contribution to the density of states is due to the majority band of Co (6i) and (2c). In figure 4 we plot the local density of states for the cobalt atoms at 2c, 3g and 6i positions. Co(2c) and Co(6i) give the large contribution to the density of states at the Fermi level. In both cases the main contribution is from majority (broken curve) spin bands. The density of states at the Fermi level for the cobalt atom at position 3g is small for minority and majority spin bands. The shapes of the DOS for minority and majority spin bands are similar and hence the cobalt atom at position 3g is almost paramagnetic. Recently Kowalczyk and Jezierski [14] studied the electron-transport properties of  $\text{Nd}_3\text{Co}_{11}\text{B}_4$ . The temperature variation of the resistivity was well described by the model in which we used the density of states calculated for the ground state. This fact indicated that the density of states did not change drastically with the increasing of temperature.

In figure 5 we present the density of states convoluted by a Lorentzian of half-width 0.4 eV and multiplied by the cross sections [23] for the partial states on each atom. The agreement of the theoretical calculations and the XPS spectra in the region  $4 \text{ eV} < E < 0$  is good. The peak in the XPS spectrum located at  $E = 5 \text{ eV}$  is due to Nd 4f states [18]. In our self-consistent band calculations we included the 4f states in the core and hence we can not observe the peak near  $E = 5 \text{ eV}$ . The valence band contains mainly the contribution from the cobalt atoms.



**Figure 5.** The measured XPS valence band spectra corrected by substraction of the background for  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  (broken curve). The solid curve presents the density of states convoluted by Lorentzians of half-width 0.4 eV and multiplied by cross sections [23].

#### 4. Concluding remarks

Our spin-polarized self-consistent LMTO band calculations show that  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  is ferromagnetic with the total magnetic moment  $m_t = 16.1 \mu_B$ . The main magnetic contribution is from the Co atom in the 2c position. The magnetic moments on cobalt and neodymium atoms have the same direction and the total value is close to the experimental one [14]. This is accordance with our recent analysis of electron-transport properties in  $\text{Nd}_3\text{Co}_{11}\text{B}_4$  using the information from our band structure calculations where we have also obtained a good agreement with the experimental measurements [14].

The convolution of the total density of states by a Lorentzian of half-width 0.4 eV and multiplied by cross sections gives a shape of the theoretical photoemission spectrum close to the experimental result.

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