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Electronic and magnetic properties of $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$

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The compounds $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$ were manufactured as promising systems suitable for the fabrication of permanent magnets. They belong to the $R_{m+n}Co_{5m+3n}B_{2n}$ family and have the *P6/mmm* space group. Band structure calculations are performed by the tight binding version of the linear muffin-tin orbital method in the atomic sphere approximation (TB-LMTO ASA). The calculated magnetic moments on Co atoms depend on their local environment. The calculated values are compared with bulk measurements.

Key words: *rare earth compounds; electronic structure; magnetic moment*

1. Introduction

Boron substitution for Co in RCo_5 Haucke compounds (R = rare earth element) leads to the formation of a series of systems expressed by the general formula $R_{1+n}Co_{5+3n}B_{2n}$, n = 0, 1, 2, .., ∞ [1]. Unit cells of these systems have an interesting crystallographic regularity (see Fig. 1 in [2]); they are formed by the alternate stacking of one layer of RCo_5 and n layers of RCo_3B_2. A partial substitution of Co atoms by boron in the $R_{1+n}Co_{5+3n}B_{2n}$ system causes a decrease in the Curie temperature (T_C), saturation magnetization (M_S), and effective inter-sublattice exchange interaction ([3] and references therein). Although the systems have uniaxial symmetry, their T_C and M_S are too low to be suitable for permanent magnet applications [4–6]. In order to overcome this drawback, a new series of compounds, $R_{m+1}Co_{5m+3}B_2$, with high Co content, was proposed [7–9]. The above-mentioned two homologous series can be expressed by the general formula $R_{m+n}Co_{5m+3n}B_{2n}$.

It has been shown that the magnetic moments of Co atoms depend on their local environment in $R_{1+n}Co_{5+3n}B_{2n}$. This observation was confirmed by *ab initio* calculations [2, 10–12] as well as by neutron diffraction measurements [13, 14]. In this pa-

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per, a study of the electronic structure of hexagonal $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$ systems is presented.

2. Method of calculations and results

The electronic structures and magnetic moments were calculated using the spin-polarized tight-binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [15, 16], where the unit cell is filled by Wigner–Seitz spheres with the same total volumes

$$\frac{4\pi}{3}\sum_{j=1}^{N_A} S_j^3 = V$$

where j is the index of the atom in the unit cell, N_A is number of atoms in the cell, S_j is the Wigner–Seitz radius of the j-type atom, and V is the volume of the unit cell. In our case, the unit cells contain one formula unit each (N_A = 30 for $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$). The structures of the unit cells of the considered compounds are presented in Fig. 1.

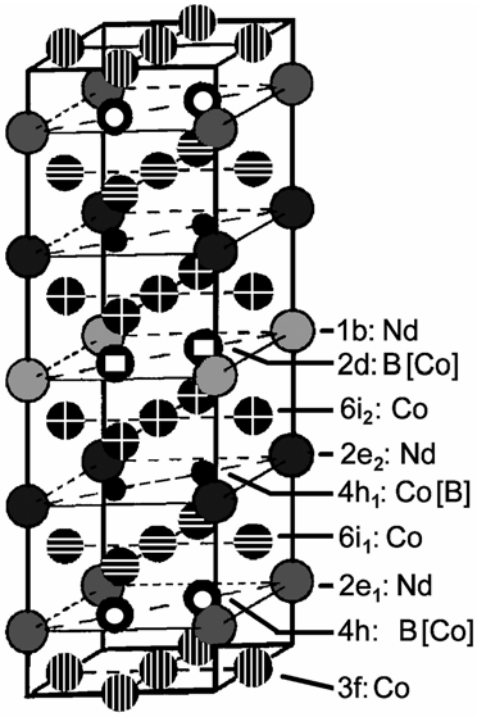

Fig. 1. Crystal structure of $Nd_5Co_{19}B_6$ [$Nd_5Co_{21}B_4$]

The overlap volumes of the muffin-tin spheres for both structures are about 7.3%. The standard combined corrections [15] for overlapping were used to compensate for errors due to the ASA. The experimental values of the lattice constants [8, 9] were used in the calculations. Spin-orbit interactions were taken into account in the form proposed by Min and Jang [17]. The Perdew–Wang [18] potential with non-local corrections was used. The input electronic configurations were taken as: core ($Xe+4f^3$) + $5d^16s^2$ for Nd, core(Ar) + $3d^74s^2$ for Co, and core(He) + $2s^22p^1$ for B atom. Due to difficulties with the band structure treatment of the localized 4f electrons of rare-earth metal and the itinerant magnetism of spd conduction electrons, the scheme proposed by Brooks et al. [19] was used.

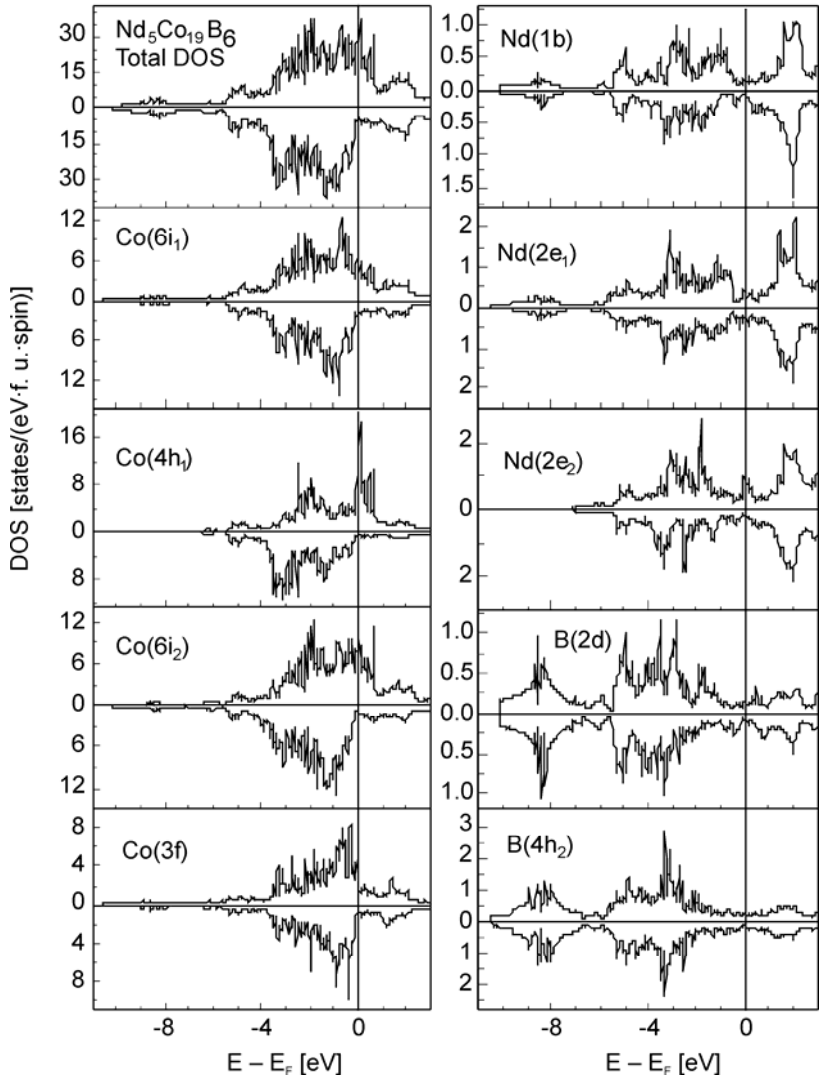

Fig. 2. Total and local DOS functions for the Nd, Co, and B atoms of $Nd_5Co_{19}B_6$

In this approach, the 4f states of Nd are treated as open core states that do not hybridise with conduction electron states. The number of *4f* electrons in Nd was fixed to three. Self-consistent calculations were carried out for 259 *k*-points in the irreducible wedge (1/24) of the Brillouin zone. The tetrahedron method was used to integrate over the Brillouin zone [20]. Iterations were repeated until the total energies of the consecutive iteration steps were the same within an error of 0.01 mRy.

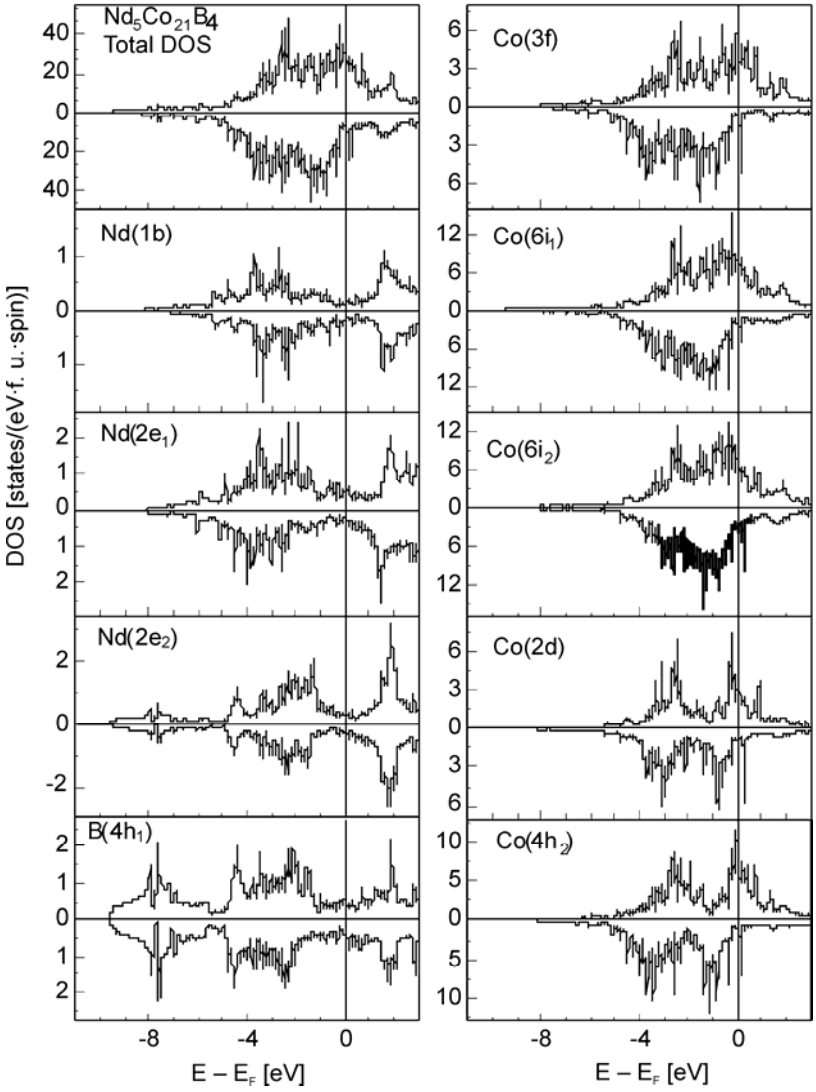

Fig. 3. Total and local DOS functions for the Nd, Co, and B atoms of $Nd_5Co_{21}B_4$

The densities of states (DOS) are presented in Fig. 2 for $Nd_5Co_{19}B_6$ and in Fig. 3 for $Nd_5Co_{21}B_4$. In both cases, the widths of the valence bands are similar. The bottoms

of the valence bands are formed foremost by s-type electrons, localized mainly on B atoms and their neighbours: (1b), ($2e_2$) for Nd and ($6i_1$), ($6i_2$) for Co in $Nd_5Co_{21}B_4$, and (1b), ($2e_1$) for Nd and ($6i_1$), ($6i_2$), (3f) for Co in $Nd_5Co_{19}B_6$. The rest of the atoms provide essential contributions to the DOS above 3.5 eV from the bottom of the valence band. The main contribution to the DOS at the Fermi level (E_F) is provided by Co atoms, especially d-type electrons localized close to the E_F (above 90% of the contributions to the total DOS on Co atoms, see Table I). The values of the total DOS at the Fermi level are 36.60 and 5.00 states/(eV·spin·f. u.) for $Nd_5Co_{19}B_6$ with spin up and down, respectively. The corresponding values for $Nd_5Co_{21}B_4$ are: 27.58 and 7.69 states/(eV·spin·f. u.).

Table 1. Spin projected (↑, ↓) densities of electronic states (DOS [states/(eV·spin·f. u.)]) at the Fermi level and calculated local magnetic moments (m [μ_B/atom]) for $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$

Compound	Atoms	DOS ↑	DOS ↓	m	Compound	Atoms	DOS ↑	DOS ↓	m
$Nd_5Co_{19}B_6$	Nd(1b)	0.152	0.070	2.92	$Nd_5Co_{21}B_4$	Nd(1b)	0.189	0.212	2.98
	Nd($2e_1$)	0.550	0.279	3.07		Nd($2e_1$)	0.431	0.333	2.84
	Nd($2e_2$)	0.901	0.184	2.98		Nd($2e_2$)	0.287	0.321	2.93
	Co($6i_1$)	5.288	1.702	0.40		Co($6i_1$)	7.198	1.613	0.88
	Co($6i_2$)	9.468	0.908	0.80		Co($6i_2$)	6.303	2.632	0.46
	Co($4h_1$)	16.647	0.651	1.65		Co($4h_2$)	5.488	0.827	1.18
	Co(3f)	3.180	0.956	0.21		Co(3f)	4.379	0.570	0.63
	B(2d)	0.177	0.078	–0.05		Co(2d)	2.877	0.765	1.17
	B($4h_2$)	0.235	0.175	–0.02		B($4h_1$)	0.432	0.412	–0.08

The magnetic moments of Co atoms are strongly dependent on local environment. Their values vary between 0.2 and 1.65μ_B/atom (Table 1). The mean magnetic moment calculated per Co atom is slightly larger for $Nd_5Co_{21}B_4$ (0.81μ_B/Co atom) than for $Nd_5Co_{19}B_6$ (0.79μ_B/Co atom). This results in a larger magnetic moment per formula unit. The experimental values of saturation magnetization μ_s are 23.7μ_B/f. u. and 31.1μ_B/f. u. for $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$, respectively [13, 14]. The corresponding calculated values are equal to 29.46 and 31.53μ_B/f. u.

3. Conclusions

In this paper, the electronic structures of $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$ have been calculated by the TB-LMTO method. The results were compared with experimental bulk measurements of saturation magnetization. Electronic structure calculations showed that $Nd_5Co_{19}B_6$ and $Nd_5Co_{21}B_4$ are ferromagnetically ordered. The Co bands dominate the densities of states near the Fermi level. Nd and B atoms provide very small contributions to the DOS at the Fermi level. The values of magnetic moments on Co atoms are strongly dependent on the local environment. The largest magnetic moments of Co

atoms were found for the ($4h_1$) site of $Nd_5Co_{19}B_6$ ($1.65\mu_B$/atom) and for the ($4h_2$) and (2d) sites of $Nd_5Co_{21}B_4$ (1.18 and $1.17\mu_B$/atom, respectively).

References

[1] KUZ'MA Y.B., BILONIZHKO N.S., Kristallografiya, 18 (1973), 710.
[2] SZAJEK A., J. Magn. Magn. Mat., 185 (1998), 322.
[3] KOWALCZYK A., J. Magn. Magn. Mat., 175 (1997), 279.
[4] PEDZIWIATR A.T., JIANG S.Y., WALLECE W.E., BURZO E., POP V., J. Magn. Magn. Mat., 66 (1987), 69.
[5] TETEAN R., BURZO E., J. Magn. Magn. Mat., 157/158 (1996), 633.
[6] ITO T., ASANO H., IDO H., YAMADA M., J. Appl. Phys., 79 (1996), 5507.
[7] CHEN Y., LIU Q.L., LIANG J.K., CHEN X.L., SHEN B.G., HUANG F., Appl. Phys. Lett., 74 (1999), 856.
[8] CHEN Y., LIANG J.K., CHEN X.L., LIU Q.L., SHEN B.G., SHEN Y.P., J. Phys. Cond. Matter, 11 (1999), 8251.
[9] CHU W.G., RAO G.H., YANG H.F., LIU G.Y., LIANG J.K., J. Appl. Phys., 90 (2001), 1931.
[10] JEZIERSKI A., KOWALCZYK A., MAEHL S., NEUMANN M., BORSTEL G., J. Phys. Cond. Matter, 10 (1998), 6277.
[11] KOWALCZYK A., SZAJEK A., CHEŁKOWSKA G., TOLIŃSKI T., Solid State Commun., 132 (2004), 225.
[12] SZAJEK A., KOWALCZYK A., Czech. J. Phys., 54, Suppl. D (2004), D343.
[13] CASPI E.N., PINTO H., KUZNIETZ M., ETTEDGUI H., MELAMUD M., FELNER I., SHAKED H., J. Appl. Phys., 83 (1998), 6733.
[14] CASPI E.N., PINTO H., MELAMUD M., J. Appl. Phys., 87 (2000), 416.
[15] ANDERSEN O.K., JEPSEN O., ŠOB M., [in:] *Electronic Structure and Its Applications*, M.S. Yussouff (Ed.), Springer-Verlag, Berlin, 1987, p.2.
[16] KRIER G., JEPSEN O., BURKHARDT A., ANDERSEN O.K., The TB-LMTO-ASA program, source code, version 4.7, available upon request from the authors of the program.
[17] MIN B.I., JANG Y.-R., J. Phys. Cond. Matter, 3 (1991), 5131.
[18] PERDEW J.P., CHEVARY J.A., VOSKO S.H., JACKSON K.A., PEDERSON M.R., SINGH D.J., FIOLHAIS C., Phys. Rev. B, 46 (1992), 6671.
[19] BROOKS M.S.S., NORDSTROM L., JOHANSSON B., Physica B, 172 (1991), 95.
[20] BLÖCHL P., JEPSEN O., ANDERSEN O.K., Phys. Rev. B, 49 (1994), 16223.

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