Electronic Structure of DyCo$_5$
and DyCo$_3$B$_2$ Compounds

A. Jezierski and A. Kowalczyk*

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

We study the electronic structure of the hexagonal DyCo$_5$ and DyCo$_3$B$_2$ compounds. The magnetic moments and the band structures were calculated by *ab initio* self-consistent tight binding linear muffin-tin orbital method within the atomic sphere approximation. These compounds crystallize in a hexagonal structure having the $P6/mmm$ space group. The substitution of cobalt by boron atoms changes the local environment of remaining Co atoms and leads to the decrease in the local magnetic moments as well as in the Curie temperature.

PACS numbers: 71.20.–b, 72.15.Eb

1. Introduction

Rare earth (R)–transition metal (T) intermetallic compounds attract a great deal of interest not only because of their potential application as permanent magnet materials but also because of the opportunities they offer for extended studies of the magnetic properties of the $4f$ and $3d$ elements.

The DyCo$_5$ and DyCo$_3$B$_2$ compounds crystallize in a hexagonal structure having the $P6/mmm$ space group [1]. The compounds belong to R$_{n+1}$Co$_{3n+5}$B$_{2n}$ (or R(Co$_{1-x}$B$_x$)$_5$) family. The crystal structure of these compounds with $n = 1$ (RCo$_4$B), $n = 2$ (R$_3$Co$_{11}$B$_4$), $n = 3$ (R$_2$Co$_7$B$_3$) and $n \to \infty$ (RCo$_3$B$_2$) can be imagined as being built up by ordered substitutions of B atoms onto the Co sites in the RCo$_5$-type structure. The unit cells are formed by alternative stacking of one layer of RCo$_5$ and n layers of RCo$_3$B$_2$. The lattice parameters obey the relationships $a = a_{RCo_5}$; $c = c_{RCo_5} + nc_{RCo_3B_2}$. The partial replacement of the Co atoms by boron in Nd(Co$_{1-x}$B$_x$)$_5$ system causes the decrease in the Curie temperature T_C, Co magnetic moment M_{Co}, and effective intersublattice exchange interactions J_{RCo} [2].

*corresponding author

On the theoretical side, Malik et al. [3] performed spin-polarized band structure calculation on YCo_5 to study its local magnetic moments at each crystallographically inequivalent sites. By considering the spin–orbit coupling and orbital polarization effects, Nordström et al. [4, 5] studied the orbital magnetism and magnetocrystalline anisotropy (MCA) of YCo_5. Kitagawa et al. [6] have investigated the dependence of the magnetic moments of YCo_5. It has been found that Co moments decrease abruptly at a critical constant. Szajek [7], based on *ab initio* linear muffin-tin orbital (LMTO) band structure calculations, showed the dependence of the magnetic moments of Co atoms on the local environment in $Y_{n+1}Co_{3n+5}B_{2n}$. The atomic moment was decreased strongly by the neighbouring B atoms.

In this paper, we present the *ab initio* spin-polarized self-consistent tight binding-LMTO (TB-LMTO) [8] calculations of the electronic structure of $DyCo_5$ and $DyCo_3B_2$ hexagonal compounds. We pay our attention on the change of the local density of states and the local magnetic moment on cobalt atom at (3g) position.

2. The method of calculation

The electronic density of states (DOS) and the local magnetic moments of $DyCo_5$ and $DyCo_3B_2$ were calculated by the spin-polarized self-consistent TB-LMTO in the atomic sphere approximation (ASA) [8] for the experimental lattice parameters listed in Table. The scalar-relativistic approximation for band electrons and the fully-relativistic treatment of the frozen core electrons were applied. 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

TABLE

Position of atoms in the $DyCo_5$ and $DyCo_3B_2$ unit cells.

$DyCo_5$	$a = 4.933$ Å		$c = 3.983$ Å
	x	y	z
Dy (1a)	0	0	0
Co (2c)	1/3	2/3	0
Co (3g)	1/2	0	1/2
$DyCo_3B_2$	$a = 5.02$ Å		$c = 3.02$ Å
	x	y	z
Dy (1a)	0	0	0
Co (3g)	1/2	0	1/2
B (2c)	1/3	1/3	0

exchange correlation potential was assumed in form of von Barth and Hedin [9] and non-local corrections were also used [10]. In the band calculations the initial atomic configurations were taken according to the periodic table of elements. The self-consistent spin-polarized band calculations were performed for 270 k points in the irreducible wedge of the Brillouin zone. In the band calculations we included the full hybridization between s, p, d, and f electrons of dysprosium, cobalt, and boron atoms. We have also performed the self-consistent calculations for the scheme proposed by Brooks et al. [11] in which the $4f$ states of Dy were treated as open core states. In such model the number of $4f$ electrons of Dy was fixed to 9 and the localized magnetic moment on dysprosium was $5\mu_B$.

3. Results and discussion

The DyCo$_5$ compound is ferrimagnet with a Curie temperature equal to 998 K and saturation moment of 1.71 μ_B/f.u. at $T = 4.2$ K. The value of T_C was estimated in DyCo$_3$B$_2$ as $T_C = 22$ K and the saturation moment $M_s = 8.3$ μ_B/f.u. at $T = 4.2$ K [12]. The electrical resistivity of DyCo$_3$B$_3$ at low temperatures shows a T^2 dependence, implying the electron–spin wave scattering is dominant in this temperature range. At higher temperatures ($T \geq 80$ K), the resistivity is due to $s-d$ interaction [12].

Experimentally, the Curie temperature T_C decreases on replacing Co atoms in Dy(Co$_{1-x}$B$_x$)$_5$ by B atoms [3]. This reduction in T_C presumably results from weakened Co–Co exchange interactions due to the replacement of Co by B at the (2c) sites. The cobalt's moments calculated from the saturation magnetization under assumption that the rare earth is saturated at all boron concentrations, decrease with increasing boron concentration. These results suggested that the Co atomic moment decreased strongly due to the neighbouring B atoms, which means that the valence electrons of B atom transferred to the neighbouring Co d band hole. The decrease in T_C and M_{Co} is also observed in Nd(Co$_{1-x}$B$_x$)$_5$ [2]. A decrease in J_{RCo} with increasing Co concentration is observed. According to Brooks et al. [13] the $3d-5d$ hybridization strongly governs the interatomic $3d-5d$ interaction.

DyCo$_5$ crystallizes in a hexagonal CaCu$_5$ structure. The CaCu$_5$-type structure contains one Dy atom at (1a), five Co atoms at (2c) and (3g) sites. The DyCo$_3$B$_2$ compound crystallizes in the CeCo$_3$B$_2$ type of structure which is derived from the CaCu$_5$ type by replacing Co atoms at the (2c) site by boron atoms. The main structural difference is in the local environment of cobalt atoms. The number of the nearest neighbours for Co (3g) decreases from 8 in DyCo$_5$ to 4 in DyCo$_3$B$_2$. The second effect is the low distance between Co planes. Such structural effect leads to the change of the local magnetic moment on the cobalt atoms.

In DyCo$_5$ there are two non-equivalent cobalt atoms with the different magnetic moments: Co at position (2c) has the local magnetic moment $m_{Co}(2c) = 1.61\mu_B$ and the magnetic moment at Co (3g) is lower i.e. $m_{Co}(3g) = 1.50\mu_B$. The

different values of the magnetic moment on the Co atoms are connected to the various local environments of each atom. The cobalt atom in position (2c) has 3 Dy and 11 Co atoms as the nearest neighbours. The Co atom at position (3g) has 4 Dy and 8 Co atoms in the first shell. These results are similar as those calculated on YCo_5 by Nordström et al. [5], Kitagawa et al. [6], and by Szajek [7]. By the neutron diffraction measurements, magnetic moments of Co atoms on 3g and 2c sites are observed as $1.72\mu_B$ and $1.77\mu_B$, respectively [14].

The local magnetic moment of Co (3g) in $DyCo_3B_2$ is small, $m_{Co}(3g) = 0.20\mu_B$. Such effect is connected with the change of the local environment of cobalt atom in $DyCo_3B_2$. The Co atom at (3g) position has 4 Dy, 4 B, and 4 Co atoms as the nearest neighbours. Our calculations indicate that B in position (2c) is non-magnetic. The magnetic study [15], NMR measurements [16], and theoretical calculations [7] indicate that YCo_3B_2 is Pauli paramagnetic. In both compounds the magnetic moments on cobalt atoms are antiparallel to the magnetic moment of Dy. Yamada et al. [17] has previously shown that the effect of B in rare-earth–cobalt–boron system can be explained by the mixing model between $3d$ states of Co and $2p$ states of B. The importance of mixing between them in $Y_2Co_{14}B$ is also emphasized by Coehoorn [18].

In Figs. 1 and 2 we presented the electronic density of states (DOS) for $DyCo_5$ and $DyCo_3B_2$ compounds. The upper plot presents the total DOS for minority (broken curve) and majority (solid curve) spin band. In both compounds the minority $4f$ peak from Dy is located near $E = -3.9$ eV which is in a good agreement with the XPS measurements [19]. The $3d$ cobalt bands are located mainly below the Fermi level. Near the Fermi energy ($E = 0$) we observe the strong hybridization between $4f$ majority spin band of Dy and $3d$ Co states. In $DyCo_3B_2$, contribution to the density of states at the Fermi level from cobalt atoms is smaller than in $DyCo_5$. The values of the density of states at the Fermi energy are 23.1 and 20.3 (states/eV f.u.) for $DyCo_5$ and $DyCo_3B_2$, respectively. The spin magnetic moment on Dy atoms consists of $4f$ contribution (4.72 and $4.79\mu_B$) and the spd contributions (-0.24 and $0.05\mu_B$) in $DyCo_5$ and $DyCo_3B_2$, respectively. The self-consistent calculations for the case in which the $4f$ electrons of Dy were treated as open core states gave the similar values of the local magnetic moments [12]. The local magnetic moment on Dy was 4.77 and $5.13\mu_B$ in $DyCo_5$ and $DyCo_3B_2$, respectively. The main contribution to the DOS at the Fermi level is given by the Dy atoms. In $DyCo_3B_2$ the DOS at the Fermi level for the Co 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 Co atom at position (3g) is almost paramagnetic. Recently, Kowalczyk and Jezierski [12] have studied the transport properties of $DyCo_3B_2$ compound. 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 DOS did not change drastically with the increase in temperature.
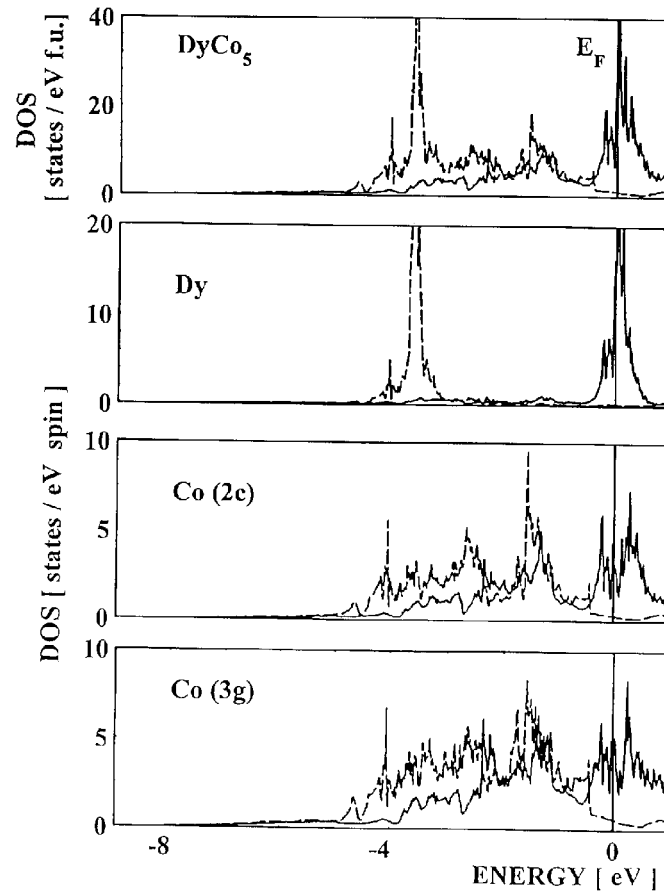
Fig. 1. The total density of states (for spin up and down) and the local contributions from Dy and Co for the DyCo₅ compound. The solid line shows the positions of the Fermi energy.

The influence of boron atoms on the electronic and magnetic properties of $R_3Co_{11}B_4$ for R = Nd and Gd, was recently studied by Jezierski et al. [20] and Kowalczyk et al. [21]. In both systems the shape of the local density of states was quite similar and the contribution to the density of states at the Fermi level was small. The value of the local magnetic moment on a Co atom at the (2c) sites in $Nd_3Co_{11}B_4$ ($m_{Co}(2c) = 1.75\mu_B$) [20] is larger than that in DyCo₅. On the other hand, the magnetic moments on a Co atom at the (6i) and (3g) sites (the sites in $R_3Co_{11}B_4$ are crystallographically equivalent to the (3g) site in RCo₅) are smaller than that at the (3g) in DyCo₅. The value of the magnetic moment on cobalt atom at (3g) position increased with the increase in the atomic number of rare-earth atom ($m_{Co}(3g) = 0.03$, 0.10, and $0.20\mu_B$, for R = Nd, Gd, and Dy, respectively).
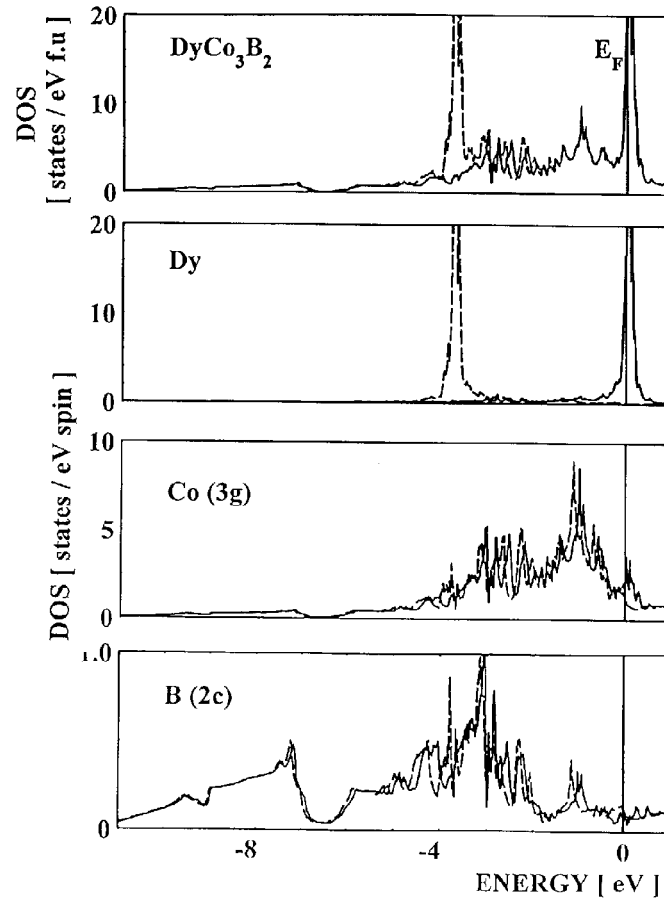
Fig. 2. The total density of states (for spin up and down) and the local contributions from Dy, Co, and B for the $DyCo_3B_2$ compound. The solid line shows the positions of the Fermi energy.

4. Conclusions

In this paper we discussed the influence of the local environment effect on the electronic properties of rare-earth–cobalt intermetallic compounds with the $CaCu_5$ based structure.

The main results are summarized as follows:

1) In $DyCo_5$ and $DyCo_3B_2$ compounds the magnetic moments on Co atoms are antiparallel to the magnetic moment of Dy and the values of the magnetic moments on Co atoms strongly depend on the local environment and distances between Co planes.

2) In $DyCo_3B_2$ the DOS at the Fermi level for the Co 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 Co atom at position (3g) is almost paramagnetic.

3) In DyCo$_5$ the magnetic moments and the shapes of local DOS on the two crystallographically different positions (2c) and (3g) are very similar. The local moments of Co atoms on the (2c) and (3g) are 1.61μ_B and 1.50μ_B, respectively. The density of states at the Fermi level contains the contribution from 4f states of dysprosium and 3d states of cobalt atoms.

4) The shape of the local DOS of Co at (3g) position is quite similar in the similar R-Co intermetallic compounds based on CaCu$_5$ type structure. The local magnetic moment on cobalt atom is small and it has a tendency to increase with the increase in the atomic number of rare-earth atoms.

Acknowledgments

References

[1] Y.B. Kuz'ma, N.S. Bilonizhko, *Kristallografiya* **18**, 710 (1973).

[2] A. Kowalczyk, L. Smardz, *Acta Phys. Pol. A* **92**, 285 (1998).

[3] S.K. Malik, F.J. Arlinhaus, W.E. Wallace, *Phys. Rev.* **16**, 1242 (1977).

[4] L. Nordström, M.S.S. Brooks, B. Johansson, *J. Phys., Condens. Matter* **4**, 3241 (1992).

[5] L. Nordström, O. Eriksson, M.S.S. Brooks, B. Johansson, *Phys. Rev. B* **41**, 9111 (1990).

[6] I. Kitagawa, K. Terao, M. Aoki, H. Yamada, *J. Phys., Condens. Matter* **9**, 231 (1997).

[7] A. Szajek, *J. Magn. Magn. Mater.* **185**, 322 (1998).

[8] O.K. Andersen, O. Jepsen, M. Sob, in: *Electronic Structure and its Applications*, Ed. M. Yussouff, Springer, Berlin 1987, p. 2.

[9] U. von Barth, L. Hedin, *J. Phys. C, Solid State Phys.* **5**, 1629 (1972).

[10] D. Hu, D.C. Langreth, *Phys. Scr.* **32**, 391 (1985).

[11] M.S.S. Brooks, B. Johansson, in: *Ferromagnetic Materials*, Vol. 7, Ed. K.H.J. Buschow, North-Holland, Amsterdam 1993, p. 139.

[12] A. Kowalczyk, A. Jezierski, *J. Magn. Magn. Mater.* **188**, 361 (1998).

[13] M.S.S. Brooks, L. Nordström, B. Johansson, *Physica B* **172**, 95 (1991).

[14] J. Schweizer, F. Tasset, *J. Phys. F, Metal Phys.* **10**, 2799 (1980).

[15] H. Ido, M. Nanjo, M. Yamada, *J. Appl. Phys.* **75**, 7140 (1994).

[16] Cz. Kapusta, M. Rosenberg, K.H.J. Buschow, *J. Alloys Comp.* **187**, 409 (1992).

[17] H. Yamada, K. Terao, H. Nakazawa, I. Kitagawa, N. Suzuki, H. Ido, *J. Magn. Magn. Mater.* **183**, 94 (1998).

[18] R. Coehoorn, *J. Magn. Magn. Mater.* **99,** 55 (1991).

[19] J.K. Lang, Y. Baer, P.A. Cox, *J. Phys., Metal Phys.* **11,** 121 (1981).

[20] A. Jezierski, A. Kowalczyk, S. Mahl, M. Neumann, G. Borstel, *J. Phys., Condens. Matter* **10,** 6277 (1998).

[21] A. Kowalczyk, L. Smardz, A. Jezierski, *J. Magn. Magn. Mater.* **190,** 205 (1998).