ELECTRONIC STRUCTURES AND MAGNETIC PROPERTIES OF $R_{n+1}Co_{3n+5}B_{2n}$
(n=0, 1, 2, 3 and $\infty$) COMPOUNDS WITH $R=\text{Y}$ AND Gd

P. Vlaic, E. Burzo
Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania

ABSTRACT  $R_{n+1}Co_{3n+5}B_{2n}$ compounds where $R=\text{rare earth or yttrium}$ crystallize in a hexagonal structure having P6/mmm space group. The magnetic behavior of cobalt in compounds with $R=\text{Y}$ and Gd is studied by first-principle spin polarized band calculations. The computed magnetizations are compared with those experimentally obtained. The magnetic behavior of cobalt is strongly dependent on nature of $R$ elements and on local environment.

INTRODUCTION

$R_{n+1}Co_{3n+5}B_{2n}$ compounds where $R$ is a rare earth or yttrium having $n=1$ (RCO$_4$B), $n=2$ (R$_5$Co$_{11}$B$_4$), $n=3$ (R$_7$Co$_{7}B_3$) and $n=\infty$ (RCO$_3$B$_2$) are obtained by ordered substitutions of cobalt with boron in a $\text{RCO}_5$-type structure [1]. $\text{RCO}_5$ compounds crystallize in a hexagonal structure of $\text{CaCu}_5$-type having P6/mmm space group. The crystalline structure of compounds with $n \geq 1$ can be imagined as being built up by alternative stacking of one layer of $\text{RCO}_5$ and $n$ layers of $\text{RCO}_3B_2$ unit cells (Fig. 1). All these compounds have also P6/mmm space group. In these structures $R$, Co and B atoms are distributed on different crystallographic sites (Table 1) having different number and nature of nearest-neighbors (NN). As the local environment depends on crystallographic site, the cobalt atoms from different positions are expected to have different magnetic contributions. By magnetic measurements only the mean values of cobalt moments may be obtained. The mean cobalt moments, $M_{Co}$, calculated from saturation magnetizations depend on the nature of $R$ elements and decrease with increasing concentration of boron as shown in Fig. 2a for compounds with $R=\text{Y}$ or Gd. Reliable values of the saturation moments of cobalt may be obtained only for gadolinium (S-state) or yttrium (non-magnetic element). For non-S-state rare earth compounds due to high anisotropy, the saturation is difficult to be obtained. The compounds with yttrium are ferromagnetic while in case of gadolinium system they are ferrimagnetically ordered.

Fig. 1 The crystalline structures of $R_{n+1}Co_{3n+5}B_{2n}$ compounds
Table 1 Crystallographic characteristics of $R_{n+1}Co_{3n+5}B_{2n}$ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atoms</th>
<th>Lattice constants</th>
<th>Number</th>
<th>Coordinates</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R=Y$</td>
<td>$R=Gd$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>a (Å)  c (Å) Ref.</td>
<td>a (Å)  c (Å) Ref.</td>
<td>x/a y/b z/c</td>
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<tr>
<td>$RCo_5$</td>
<td>R (1a)</td>
<td>4.928  3.992 [2]</td>
<td>4.974  3.973 [2]</td>
<td>6 (Co (2c)) 0 0 0</td>
</tr>
<tr>
<td></td>
<td>Co (2c)</td>
<td></td>
<td>6 (Co (3g))</td>
<td>1/3 2/3 0</td>
</tr>
<tr>
<td></td>
<td>Co (3g)</td>
<td></td>
<td>4 (Co (2c))</td>
<td>1/2 0 1/2</td>
</tr>
<tr>
<td></td>
<td>R (1b)</td>
<td></td>
<td>5.020  6.875 [3]</td>
<td>6 (Co (2c)) 0 0 0</td>
</tr>
<tr>
<td></td>
<td>Co (2c)</td>
<td></td>
<td>6 (Co (6i))</td>
<td>1/3 2/3 0</td>
</tr>
<tr>
<td></td>
<td>Co (6i)</td>
<td></td>
<td>2 (B (2d))</td>
<td>1/2 0 0.387</td>
</tr>
<tr>
<td></td>
<td>B (2d)</td>
<td></td>
<td>6 (Co (6i))</td>
<td>1/3 2/3 1/2</td>
</tr>
<tr>
<td>$RCo_4B$</td>
<td>R (1a)</td>
<td>5.080  9.810 [4]</td>
<td>5.070  9.840 [4]</td>
<td>6 (Co (3g, 6i)) 1/3 2/3 0.350</td>
</tr>
<tr>
<td></td>
<td>R (1b)</td>
<td></td>
<td>6 (Co (6i))</td>
<td>0 0 0.333</td>
</tr>
<tr>
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<td>R (2e)</td>
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<td>6 (Co (6i))</td>
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</tr>
<tr>
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<td>Co (2c)</td>
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<td>4 (B (4h))</td>
<td>1/2 0 1/2</td>
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<tr>
<td></td>
<td>Co (6i)</td>
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<td>2 (B (4h))</td>
<td>1/2 0 0.200</td>
</tr>
<tr>
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<td>B (4h)</td>
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<td>6 (Co (3g, 6i))</td>
<td>1/3 2/3 0.350</td>
</tr>
<tr>
<td>$R_3Co_1B_4$</td>
<td>R (1a)</td>
<td>5.045  12.88 [7]</td>
<td>5.067  12.940 [5]</td>
<td>6 (Co (2c)) 0 0 0</td>
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<tr>
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<td>R (1b)</td>
<td></td>
<td>6 (Co (6i))</td>
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</tr>
<tr>
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<td>R (2e)</td>
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<td>6 (Co (6i))</td>
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</tr>
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<td>Co (2c)</td>
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<td>2 (B (2d))</td>
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</tr>
<tr>
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<td>1/2 0 0.375</td>
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<tr>
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<td>B (2d)</td>
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<td>3 (Co (6i))</td>
<td>1/3 2/3 1/2</td>
</tr>
<tr>
<td></td>
<td>B (4h)</td>
<td></td>
<td>6 (Co (6i))</td>
<td>1/3 2/3 0.262</td>
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<td>$R_2Co_7B_3$</td>
<td>R (1a)</td>
<td>5.051  3.035 [6]</td>
<td>5.074  3.039 [6]</td>
<td>6 (B (2c)) 0 0 1/2</td>
</tr>
<tr>
<td></td>
<td>Co (3g)</td>
<td></td>
<td>4 (B (2c))</td>
<td>1/2 0 1/2</td>
</tr>
<tr>
<td></td>
<td>B (2c)</td>
<td></td>
<td>6 (Co (3g))</td>
<td>1/3 2/3 0</td>
</tr>
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</table>

Fig.2 Dependences of mean cobalt moments at 4.2 K (a) and Curie temperatures (b) on $n/[3(n+1)]$ ratio in $(Y,Gd)_{n+1}Co_{3n+5}B_{2n}$ compounds

The aim of this paper is to investigate the correlation between crystallographic and magnetic properties starting from band structure calculations and magnetic measurements.
METHOD OF CALCULATIONS AND RESULTS

The electronic structure is the key to the understanding of the materials properties like the saturation magnetization, Curie temperature and magnetic anisotropy.

The band structure calculations were performed by using the ab initio tight binding linear muffin-tin orbital method in the atomic sphere approximation (TB-LMTO-ASA) [7]. The calculations were performed by using experimental values of lattice constants. The radii of atomic spheres used in ASA were determined in such a way that the volume of a unit cell to be equal to the total volume of touching spheres centered on each atom. In the form of local density approximation (LDA) the total electronic potential is the sum of external, Coulomb and exchange–correlation potentials [8]. The functional form of the exchange–correlation energy was the free electron parameterization [9]. Relativistic corrections were included without spin–orbit coupling.

The total densities of states (DOS) obtained for (Y,Gd)n+1Co3n+5B2n compounds are presented in Fig. 3. According to actual theories [10, 11], the values of N(E_F) for majority and minority spin subbands are the crucial point that affects T_C. For both series T_C decreases with increasing r-values (Fig. 2b), N(E_F) having also similar behavior for both spin subbands. The partial DOS obtained for Co atoms occupying same crystallographic sites, for a given R element, are almost identical. These atoms have similar DOS since they have similar local environment. The cobalt atoms located on (2c) and (6i) or (6i1) positions have the main contribution to the DOS at the Fermi level. Co (3g) atoms have an important contribution to N(E_F) only in case of (Y,Gd)Co_5 compounds where there are no boron atoms. Also, Y, B and Gd atoms have only small contributions to the DOS at E=E_F.

The magnetic moments of different atoms located on various crystallographic sites, obtained from band structure calculations are presented in Table 2. The magnetic moments per formula unit agree reasonably with those experimentally determined, the difference probably being caused by the fact that the saturation has not been attained in all cases. Small magnetic moments were induced on Y 4d shells due to hybridization with Co 3d bands. The induced Y 4d moments are antiparallel oriented with the cobalt ones and decrease with increasing n in R_{n+1}Co_{3n+5}B_{2n} formula. The highest values of Y 4d moments may be associated with highest number of cobalt atoms as nearest-neighbors. For both R=Y and Gd systems, the cobalt moments are dependent on lattice sites. Co (2c) site has the highest value of magnetic moment since these atoms have in first sphere of coordination 6 Co (6i) atoms. The magnetic moments of Co (6i) atoms are lower than those of Co (2c) ones since they have in first shell of coordination 2 B atoms. The lowest values of cobalt moments in boron compounds are obtained for Co (3g) positions where in first coordination shell we have 4 boron atoms. The cobalt magnetic moments depend also on the nature of R element. We note that for a given R and for the same number of NN, the cobalt magnetic moments seem to depend also on the interatomic distances.

The first attempt to estimate the cobalt magnetic moments of unequivalent sites was made by Ogata [12]. Starting with experimental values of saturation magnetizations, the average Co moments for Y system may be expressed by relation (1), where M_{Co}(N) represents the magnetic moment of cobalt atoms

\[ M_{Co} = \frac{3(n+1)M_{Co}(2)+6M_{Co}(1)+2M_{Co}(0))}{(3n+5)} \]  

which have N boron layers just above and/or below (N=0, 1 and 2). By fitting the above equation with the experimentally observed values and assuming that the magnetic moments of Y and B atoms are equal to zero they obtained the following values: M_{Co}(0)=1.66 \mu_B, M_{Co}(1)=0.5 \mu_B and M_{Co}(2)=0 \mu_B, the agreement with our results being quite good. In case of Gd compounds our calculations gave: M_{Co}(0)=1.7 \mu_B, M_{Co}(1)=0.8 \mu_B and M_{Co}(2)=0.1 \mu_B, also in good agreement with those obtained from band structure calculations.
Fig. 3 The total DOS for (Y,Gd)$_{n+1}$Co$_{3n+5}$B$_{2n}$ compounds
Table 2  The magnetic moments of \((Y,Gd)_{n+1}Co_{3n+5}B_{2n}\) compounds (n=0, 1, 2, 3 and \(\infty\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atoms</th>
<th>(M_{\text{atom}} (\mu_B))</th>
<th>(M_{\text{total}} (\mu_B/\text{f.u.)})</th>
<th>(M_{\exp} (\mu_B/\text{f.u.)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R=\text{Y})</td>
<td>(R=Gd)</td>
<td>(R=\text{Y})</td>
<td>(R=Gd)</td>
</tr>
<tr>
<td>(\text{RCO}_5)</td>
<td>(R) (1a)</td>
<td>-0.287</td>
<td>7.531</td>
<td>6.702</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}) (3g)</td>
<td>1.399</td>
<td>-1.462</td>
<td>2.991</td>
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<tr>
<td>(\text{RCO}_4\text{B})</td>
<td>(R) (1a)</td>
<td>-0.128</td>
<td>7.386</td>
<td>6.187</td>
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<td>(R) (1b)</td>
<td>-0.233</td>
<td>7.496</td>
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<tr>
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<td>(\text{Co}) (6i)</td>
<td>0.592</td>
<td>-0.766</td>
<td>0.088</td>
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<tr>
<td></td>
<td>(\text{B}) (2d)</td>
<td>-0.034</td>
<td>0.040</td>
<td>0.019</td>
</tr>
<tr>
<td>(\text{R}<em>3\text{Co}</em>{11}\text{B}_4)</td>
<td>(R) (1a)</td>
<td>-0.149</td>
<td>7.405</td>
<td>3.040</td>
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<td>(\text{Co}) (2c)</td>
<td>1.629</td>
<td>-1.709</td>
<td>0.474</td>
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<tr>
<td></td>
<td>(\text{Co}) (3g)</td>
<td>0.088</td>
<td>-0.144</td>
<td>0.019</td>
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<td>(\text{Co}) (6i)</td>
<td>0.519</td>
<td>-0.645</td>
<td>0.019</td>
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<td>(\text{B}) (4h)</td>
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<td>0.021</td>
<td>0.019</td>
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<tr>
<td>(\text{R}_2\text{Co}_7\text{B}_3)</td>
<td>(R) (1a)</td>
<td>-0.109</td>
<td>7.387</td>
<td>3.040</td>
</tr>
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<td>(R) (2e)</td>
<td>-0.079</td>
<td>7.317</td>
<td>0.474</td>
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<tr>
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<td>(\text{Co}) (2c)</td>
<td>1.611</td>
<td>-1.707</td>
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<tr>
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<td>(\text{Co}) (6i)</td>
<td>0.474</td>
<td>-0.607</td>
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<td>(\text{B}) (2d)</td>
<td>-0.010</td>
<td>0.016</td>
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<td>(\text{B}) (4h)</td>
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<td>(\text{RCO}_2\text{B}_2)</td>
<td>(R) (1a)</td>
<td>0.000016</td>
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<td>(\text{Co}) (3g)</td>
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<td>(\text{B}) (2c)</td>
<td>-0.000023</td>
<td>0.004</td>
<td>0.00003</td>
</tr>
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</table>

CONCLUSIONS

Electronic structure calculations showed that the \((Y,Gd)_{n+1}Co_{3n+5}B_{2n}\) compounds are ferimagnetically ordered. The values of magnetic moments of cobalt atoms are strongly dependent on local atomic configurations. The highest values of Co atomic moments were obtained for (2c) positions.

The magnitude of cobalt moments may be analyzed by extending a mixing model proposed by Kanamori [24] in order to explain the effect of B in R-Fe-B system. For example in case of \(Y_3\text{Co}_{11}\text{B}_4\) compound, in Fig. 4 we plotted the relative positions of centers of gravity for Y 4d, Co 3d and B 2p states. The Co (6i) atomic layer is located between the ones containing B (4h) and Co (2c) atoms. Due to the mixing of 3d (6i) states with B 2p and Y 4d (1a, 2e) states, the center of gravity for local DOS shifts to lower energy for Y 4d (1a, 2e) and Co 3d (6i, 3g) and to higher energy for B 2p states. Mixing of Co 3d (2c) with Y 4d (1a, 2e) and Co 3d (6i, 3g) states shifts the center of gravity for local DOS to lower energy for Y (1a, 2e) and Co 3d (6i, 3g) and to higher energy for Co 3d (2c) states. Due to characteristic sites of B atoms, as above mentioned, the electrons flow into Co (6i) and Co (3g) from neighboring B atoms because B 2p states shift to higher energy. Since the majority spin band is full, the minority spin band occupation increases and the difference between the populations of majority spin band and the minority one diminishes and the magnetic moment of Co (6i) atoms becomes small.

The local moments of Co (2c) atoms in compounds with \(n \geq 1\) are larger than that in case of YCO5 compound. As mentioned above the center of gravity for Co (2c) sites shifts towards higher energy side. Some electrons of Co (2c) sites flow out decreasing the number of electrons with
minority spin (majority spin band being full). Therefore, the magnetic moments of Co (2c) sites in compounds with \( n \geq 1 \) will become larger compared with that in YCo\(_5\).

The magnetic susceptibility of YCo\(_3\)B\(_2\) compound observed experimentally at \( T \to 0 \) K is \( \chi_{\text{exp}} = 2.39 \times 10^{-3} \text{ emu/f.u.} \) [19]. The spin susceptibility at 0 K estimated from DOS at \( E_F \) is \( 1.63 \times 10^{-3} \text{ emu/f.u.} \), in good agreement with the experimental one.

Fig. 4 Schematic representation of mixing between Co 3d, Y 4d and B 2p states in Y\(_3\)Co\(_{11}\)B\(_4\) compound

REFERENCES