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Calculated magnetic moments and electronic structures of the compounds $R_{n+1}Co_{3n+5}B_{2n}$, R = Gd, Tb, n = 0, 1, 2, 3, and ∞

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The compounds of the $R_{n+1}Co_{3n+5}B_{2n}$ family crystallize in a hexagonal structure with the *P6/mmm* space group. *Ab initio* spin-polarized band structure calculations have been performed based on the tight-binding linear muffin-tin orbitals method (TB LMTO) for the following five representatives: RCo_5, RCo_4B, $R_3Co_{11}B_4$, $R_2Co_7B_3$, and RCo_3B_2, where R = Gd or Tb. The cobalt atoms in these compounds occupy distinct sites having different types and numbers of neighbouring atoms, and as a consequence their magnetic moments are different. The calculated values are compared with bulk measurements.

Key words: rare earth compounds; electronic structure; magnetic moments

1. Introduction

Lanthanide compounds $R_{n+1}Co_{3n+5}B_{2n}$ are interesting as they allow systematic studies of the dependence of magnetic moments on local environment, not to mention their relevance to the search for high performance permanent magnets. The compounds crystallize in a hexagonal $CaCu_5$-type structure, belonging to the *P6/mmm* space group. Their structure is generated from RCo_5 (n = 0) by replacing Co atoms by B atoms, until saturation (n = ∞) is reached in RCo_3B_2 [1]. Systematic studies of electronic structure have been performed for the series $Y_{n+1}Co_{3n+5}B_{2n}$ [2–4]. Some calculations have been done for the representatives of the Gd series [5–11]. In the present paper, the results of systematic studies of the band structure for R = Gd and Tb are given.

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2. Computational details

Band 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) [12, 13]. The overlap volumes of the muffin-tin spheres for both structures are in the range 7.7–8.7%. The standard [12] combined corrections for overlapping were used to compensate for errors due to the ASA. Spin-orbit interactions were taken into account in the form proposed by Min and Jang [14]. The Perdew–Wang [15] exchange-correlation potential with non-local corrections was used. The input electronic configurations were taken as: core(Xe + $4f^7$) + $5d^16s^2$ for Gd, core(Xe + $4f^8$) + $5d^16s^2$ for Tb, core(Ar) + $3d^74s^2$ for Co, and core (He) + $2s^22p^1$ for the B atom. Due to difficulties related to the band structure treatment of the localized 4f electrons of rare-earth metals and the itinerant magnetism of spd conduction electrons, the scheme proposed by Brooks et al. [16] was used. In this approach, the 4f states of Gd and Tb are treated as open core states that do not hybridise with conduction electron states. The number of 4f electrons of Gd was fixed to seven and to eight for Tb, and experimental values of lattice constants [1] were used in the calculations. Self-consistent calculations were carried out for 259 k-points in the irreducible wedge (1/24) of the Brillouin zone. For integration over the Brillouin zone, the tetrahedron method was used [17]. Iterations were repeated until the total energies of the consecutive iteration steps were the same within an error of 0.01 mRy.

3. Results

The results of the band structure calculations are summarized in Fig. 1 as the total densities of electronic states for up and down spins. The shift of the up valence band with respect to the down band is an indication of the ferromagnetic ground state of the studied compounds. The shift is the largest for $n = 0$ (i.e., for RCo_5), decreases for increasing n, and at $n = \infty$ (i.e. for RCo_3B_2) is quite small.

The calculated saturation magnetic moments are collected in Table 1. The large moments on Gd and Tb obviously come from the core 4f states. The calculated moments, however, are higher than the values from Hund's rule for the free ions Gd^{3+} and Tb^{3+} – $7\mu_B$ and $9\mu_B$, respectively. A plausible explanation of this difference can be the contribution of the valence d-electrons of Gd or Tb. The magnetic moments on Co atoms are sensitive to the number of cobalt ions in the local environment and vary from $\sim 1.8\mu_B$ to $\sim 0.1\mu_B$. As is typical of rare earth compounds with transition metals, the calculated magnetic moments on Gd and Tb are antiparallel to the ones on Co. For the Tb compounds, the calculated magnetic moments can be compared with experimental data available from neutron scattering [18], quoted (in the 5th and 10th columns) in Table 1. Except for $n = 3$, at least qualitative agreement with measurements [18] can be claimed.

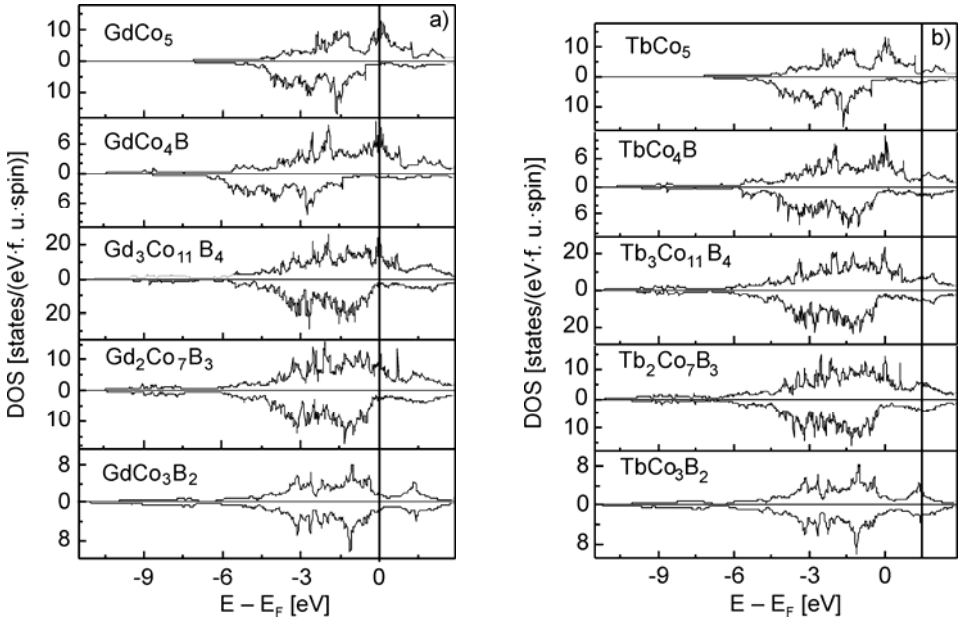

Fig. 1. The densities of states (DOS) of RCo_5, RCo_4B, $R_3Co_{11}B_4$, $R_2Co_7B_3$, and RCo_3B_2 compounds, where R = Gd (a) or Tb (b)

Table 1. The calculated and measured [18] local magnetic moments of $R_{n+1}Co_{3n+5}B_{2n}$ compounds, where n = 0, 1, 2, 3, and ∞, and R = Gd or Tb. For n = 3, only the "raw" data from [18] are quoted, not the ones from a specific refinement procedure

Compound	Atoms	m [μ_B/atom]			Compound	Atoms	m [μ_B/atom]		
		R = Gd	R = Tb	R = Tb [4]			R = Gd	R = Tb	R = Tb [4]
n = 0	R (1a)	–7.580	–9.530	–8.35(55)	n = 3	R (1a)	–7.457	–9.423	–11(4)
RCo_5	Co (2c)	1.514	1.575	1.55(20)	$R_2Co_7B_3$	R (1b)	–7.236	–9.219	–6(3)
	Co (3g)	1.517	1.519	1.7(1)		R (2*e*)	–7.366	–9.309	–10(3)
	R (1a)	–7.442	–9.394	–7(1)		Co (2c)	1.776	1.760	–0.5(10)
n = 1	R (1b)	–7.556	–9.508	–7.3(7)		Co (6i$_1$)	0.795	0.744	1.6(7)
RCo_4B	Co (2c)	1.521	1.619	1.6(3)		Co (6i$_2$)	0.164	0.184	–0.4(8)
	Co (6i)	0.778	0.863	0.6(1)		B (2*d*)	–0.014	–0.016	0
	B (2*d*)	–0.048	–0.056	0		B (4h)	–0.034	–0.031	0
	R (1a)	–7.500	–9.439	–8.5(7)					
	R (2*e*)	–7.377	–9.349	–7.9(7)					
n = 2	Co (2c)	1.648	1.749	1.3(5)					
$R_3Co_{11}B_4$	Co (3g)	0.171	0.126	0.5(4)	n = ∞	R (1a)	–7.227	–9.183	–5.4(2)
	Co (6i)	0.792	0.787	0.5(2)	RCo_3B_2	Co (2c)	0.106	0.086	–0.13(7)
	B (4h)	–0.035	–0.032	0		B (3g)	–0.005	–0.003	0

The densities of states at the Fermi level are predominantly due to d-electrons, as is evident from Table 2.

Table 2. Spin projected (↑, ↓) densities of electronic states at the Fermi energy, DOS (E_F) in states/(eV × spin formula unit). The numbers in parentheses are the partial contributions from d-electrons, DOS_d (E_F)

Compound	R = Gd		R = Tb	
	↑	↓	↑	↓
RCo_5	13.98 (13.63)	1.14 (1.10)	11.95 (11.57)	1.22 (0.76)
RCo_4B	3.38 (3.24)	0.46 (0.34)	3.53 (3.40)	0.52 (0.38)
$R_3Co_{11}B_4$	22.82 (21.76)	2.66 (2.04)	20.53 (19.53)	2.53 (1.96)
$R_2Co_7B_3$	5.05 (4.73)	1.09 (0.84)	5.90 (5.50)	1.32 (1.06)
RCo_3B_2	1.86 (1.59)	1.76 (1.39)	1.84 (1.84)	1.70 (1.38)

The following conclusions can be drawn from the calculations: the magnetic moments on Gd and Tb are antiparallel to Co moments, the moments on Co are sensitive to the type of the crystallographic site, i.e. to the symmetry of the environment, the band structure near the Fermi energy is dominated by d-electrons.

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