Exchange interactions and magnetic properties of hexagonal rare-earth-cobalt compounds

E. Burzo
Romanian Academy, Cluj-Napoca Branch, Romania
emil.burzo@phys.ubbcluj.ro

Abstract. The magnetic properties of some Gd\(_{x}\)Y\(_{1-x}\)Co\(_4\)A compounds with A = Co, Si or B are analysed including the pressure effects. Isomorphous structure transitions, parallelly with changes of cobalt moments from high spin states to low spin states, were shown as pressure increases. The magnetic data, obtained from band structures, were compared with those predicted by the mean field model.

1. Introduction

The magnetic properties of RCo\(_5\)-based compounds, where R is a rare earth or yttrium, were intensively investigated both from scientific reasons as well as in connection with their technical uses, as permanent magnets [1, 2]. These compounds crystallize in a CaCu\(_5\)-type structure, space group P6/mmm. In this lattice, the R atoms are located in 1a site and cobalt at 2c and 3g positions [1]. The RCo\(_4\)B compounds have a hexagonal structure, derived from CaCu\(_5\) one, by replacing every two layers Co2c atoms by boron. There are two sites for R(1a, 1b) and Co(2c,6i) atoms and one for boron (2d) [3]. When R is a magnetic heavy rare-earth the above compounds are ferrimagnetically ordered, while for light rare earths, a parallel alignment of R and Co moments is shown. The easy axis of magnetization, for RCo\(_5\) compounds with R = Y or Gd, is the c-axis, as imposed by the local uniaxial anisotropy of the 2c sites, higher than the planar one favoured by 3g atoms [4]. YCo\(_4\)B shows also uniaxial anisotropy, at ambient temperature, which changes to planar one, at T\(_{\text{SR}}\) = 159 K [5].

The exchange interactions between magnetic rare-earths and cobalt are mediated by R5d band polarization, as suggested by the 4f-5d-3d model [6, 7]. The above polarization is the result of both local 4f-5d exchange as well as due to R5d-Co3d short range interactions, hybridization effects, respectively. The exchange interactions between cobalt atoms are of short range as well as those between R5d-R5d orbitals, in addition to those by means of conduction electrons (RKKY-type) [8].

In this paper, we analyse the exchange interactions in Gd\(_{x}\)Y\(_{1-x}\)Co\(_4\)A series with A = Co, Si, B in the framework of mean field model [9], as well as based on the data obtained from their band structures. The pressure dependences of the cobalt moments, for end series compounds, are theoretically investigated. A linear dependence of cobalt moments on the exchange splitting energy of their 3d bands was shown.

2. Experimental and computing method

The samples were prepared from high purity elements, in an induction furnace or by arc melting. An excess of rare earth (yttrium) of (2-4)% was added in order to compensate their losses during the melting. The samples were annealed at temperatures 900 °C ≤ T ≤ 1000 °C, in vacuum for one week. The X-rays
analysis, at ambient temperature, evidenced the presence of only one phase. Some samples were already prepared [10, 11]. Magnetic measurements were performed in the temperature range 4.2 – 1000 K, and fields up to 70 kOe.

The ground state electronic structures and magnetic properties have been determined in the scalar-relativistic limit, i.e. without spin-orbit coupling, by using the tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic sphere approximation (ASA) [12, 13]. The local density approximation (LSDA) has been employed for the exchange and correlation potential of the electron gas, assuming Von Barth and Hedin parameterization [14]. The valence basis consists of s-, p-, and d-electrons. All $k$-space integrations were carried out with a $16 \times 16 \times 16$ $k$-point mesh with an accuracy of $10^{-2}$ meV. The silicon was located in 3g sites, as previously reported [15].

3. Results

The partial density of states (DOS) of Co2c and Co6i atoms in YCo$_4$B, at ambient pressure, $v/v_0 = 1$, as well as at $v/v_0 = 0.88$ are plotted in Fig.1. The Fermi level, $E_F$, when $v/v_0=1$ is situated in a peak, or nearly on a peak in the density of states in spin-up cobalt sub bands at 2c and 6i sites, respectively. In the spin down sub-bands, the $E_F$ is located in a deep in DOS. As effect of pressure, relative volumes reduction, respectively, there is a shift of the spin-up sub-bands to lower energy and of the spin down ones, at higher energy. As a result, there is a decrease of DOS at $E_F$ in spin up sub band and an increase in spin down one. When cobalt in nonmagnetic, the densities of states for spin up and spin down sub bands are near identical, in a mirror-plane. The evolution with pressure of the centres of gravity, on the energy scale, for cobalt sub-bands were determined, the exchange splitting energy of Co3d bands, $\Delta E_s$, respectively. A linear dependence of cobalt moments, at both sites, on the exchange splitting energy was shown, with a rate $\Delta E_s/M_{Co}=0.94$ eV/$\mu_B$, close to the previous reported values [10, 16, 17].

![Figure 1](image1.png)  

**Figure 1.** Partial densities of states for Co2c and Co6i atoms in YCo$_4$B compound, at $v/v_0=1.0$ and 0.88.

The pressure, relative volume dependences, respectively of the cobalt moments at 2c and 3g/6i sites in GdCo$_5$, YCo$_4$Si and YCo$_4$B are given in Fig.2. At relative low pressures, corresponding to reduced
volumes 0.965 $\delta v/v_0 \delta 1.0$, there is a nearly linear decrease of cobalt moments, the corresponding rates $\Delta M/M$ being higher, as the initial cobalt moments are smaller. This behaviour can be correlated with their itinerancy degree – Fig.3. At a characteristic pressure, relative volume, respectively, a collapse of the cobalt moments from high spin state to low spin one is evidenced. When the initial cobalt moments are small, as example at 6i site in YCo$_4$B, a direct transition to nonmagnetic state is evidenced. The magnetic anomaly develops parallelly with a sudden decrease of a c/a ratio, an isomorphous phase transition, respectively. Similar behaviour has been already evidenced in YCo$_5$ compound and attributed [18] to a first order Lifshitz transition [19] or to a spin reorientation transition [20]. The transition develops, parallelly with the change of the Fermi surface topology. A change of anisotropy from uniaxial to planar, in YCo$_5$, has been previously suggested in connection with the diminution of cobalt moments [21-25]. The anisotropy of YCo$_4$B, at ambient pressure, changes from uniaxial to planar one, at $T_{sr} = 159$ K [5]. As effect of pressure, the $T_{sr}$ temperature decreases with a rate of 22 K/GPa [26] and thus, at pressures estimated for the isomorphous structure transition (p > 7 GPa), the uniaxial anisotropy is still present, and consequently, a possible spin reorientation to planar anisotropy.

![Figure 2](image2.png)

**Figure 2.** The dependence of the cobalt moments, at 2c and 3g/6i sites, on relative volumes, describing the pressure effects for GdCo$_5$, YCo$_5$Si and YCo$_4$B compounds.

![Figure 3](image3.png)

**Figure 3.** The rate of variations of cobalt moments at 2c and 3g/6i sites, in hexagonal compounds in the range $0.965 \leq v/v_0 \leq 1.0$, as function of their values at $v/v_0=1$.

The Gd5d and Y5d band polarizations follow, as function of pressure, a similar trend as the cobalt moments. The induced polarization by 4f-5d exchange is of $\approx 0.19 \mu_B$, as determined in GdCo$_5$, at relative volume (pressure), $v/v_0 = 0.7$, when the cobalt magnetic moment is nil. The induced polarizations, $M_{sd}(d)$ and $M_{sd}$, by 5d(4d)-3d short range exchange interactions are proportional to the number of magnetic
atoms situated in the first coordination shell to an R site, \( z_i \) and their magnetic moments, \( M_i \). The ratio \( |M_{5d}(d)/M_{4d}| \sum z_i M_i = 1.25 \times 10^{-2} \). The same value has been already evidenced in \( RM_5 \) (\( M = \text{Co, Ni} \)), compounds [7, 10], being a characteristic feature of all hexagonal \( R\text{Co}_5 \)-based compounds. The exchange interactions, at the level of unit cell, are mediated by \( R5d/Y4d \) band polarizations. The changes of magnetic behaviour, of R and Co sublattices, as well as the implied exchange interactions, are mirrored by the \( R5d/Y4d \) band polarizations. This is also confirmed by linear dependence of the Curie temperatures on \( R5d/Y4d \) band polarizations of \( R\text{Co}_5 \)-based samples with different substitutions both at R or Co sites – Fig. 4.

The magnetic properties of ferrimagnetic \( \text{Gd}_x\text{Y}_{1-x}\text{Co}_4 \)A with \( A = \text{Si or B} \) are analysed also by using a two sublattices mean field model and the average cobalt moments compared with those obtained from band structures. The magnetizations of gadolinium and cobalt sublattices, at 4 K, compensate at \( x = 0.57 \) for \( A=\text{Si} \) and \( x = 0.43 \) when \( A = \text{B} \) – Fig. 5. Assuming that gadolinium moment is \( 7 \mu_B \), the mean cobalt moments were determined as well the parameters characterizing the interactions inside and between magnetic sublattices.

A linear dependence of mean cobalt moments on the exchange field, \( H_{\text{exch}} \), is evidenced – Fig. 6 – with a rate \( \Delta M_{\text{Co}}/\Delta H_{\text{exch}} \approx (3 \times 10^6)^{-1} \mu_B/\text{Oe} \), similar as that reported in \( \text{RCO}_2 \) based compounds [27]. The mean induced cobalt moments in the composition range \( 0 \leq x \leq 1.0 \) are of \( \approx 0.52 \mu_B \) (\( A = \text{Si} \)), \( 0.2 \mu_B \) (\( A = \text{B} \)) and of \( 0.1 \mu_B \) when \( A = \text{Co} \). These values are close to those determined from band structure, when considering the mean cobalt moments at 2c and 3g/6i sites: \((0.57, 0.44 \mu_B) \) for \( A = \text{Si} \), \((0.2, 0.17 \mu_B) \) for \( A = \text{B} \).
when A = B and (0.17, 0.06 \mu_B) if A = Co. These data indicate that the exchange splitting of Co3d bands is nearly proportional to the internal field intensities.

As effect of pressure, or through the variations of the internal fields, the exchange splitting energies of Co3d bands and the related cobalt moments are modified. The mean field model, gives only the general trend on the evolution of cobalt moments, the band structure calculations allowing a more accurate description of magnetic moments and exchange interactions in connection with the considered cobalt sites.

The exchange interactions, in RCo5 based compounds, at the level of the unit cell, are mediated by R5d band polarizations. The Y4d band polarizations mirror all changes in the cobalt sublattice magnetizations. Thus, the M_{5d} and M_{4d} values are key points in describing the exchange interactions in a considered system, as also confirmed by their linear trend when plotting with respect to Curie temperatures.

4. Conclusions
The pressure dependences of the cobalt moments in hexagonal compounds, evidence the presence of a first order isomorphous structure transitions, parallelly with the cobalt moment collapse from high spin state to low spin one. The Fermi surface topology, at the transition, is also changed. The R5d and Y4d band polarizations mirror the changes in the magnetic properties as effect of substitutions both at R and Co sites, mediating also the exchange interactions. The mean field model can describe only the general features of the magnetic properties of the hexagonal compounds, but not at the atomic level particularly when non-equivalent sites are present in the considered structure.

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