Exchange interactions in heavy rare-earths RCo$_2$ compounds

E. Burzo
Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania
emil.burzo@phys.ubbcluj.ro

Abstract. The magnetic behaviour of RCo$_2$ (R = Tm, Er, Ho, Tb) compounds, above the Curie temperatures, $T_c$, has been analysed. The interdependent exchange interactions at the level of unit cell are discussed in correlation with R5d band polarizations. The clusters evidenced by SANS experiments in paramagnetic region, having correlation length of $\approx 7$Å, were associated with the exchange coupled atoms at the level of the unit cell. The exchange interactions are not so high to induce a magnetic ordered phase.

1. Introduction
The RCo$_2$ compounds, where R is a rare-earth or yttrium crystallize, at normal conditions in a cubic-type structure having Fd3m space group [1]. Below the Curie temperatures, $T_c$, their crystal structures are distorted due to magnetostrictive effects.

The RCo$_2$ compounds, where R is a magnetic heavy rare-earth (R = Gd to Tm) are ferrimagnetically ordered, the rare earth and cobalt moments being antiparallelly oriented. The magnetic transitions are of first order when R = Dy, Ho, Er and of second order for R = Gd, Tb, Tm. Above the Curie points, the reciprocal susceptibilities, $\chi^{-1}$, follow non-linear temperature dependences as expected for ferrimagnetic systems [2, 3]. The paramagnetic data were analysed considering that cobalt has an exchange enhanced magnetic susceptibility [4] or an effective intrinsic moment [2, 3].

The polarized neutron diffraction studies performed on RCo$_2$ compounds with R = Tb [5], Ho [6,7] or Tm [7,8], above the Curie points, in the presence of external fields, evidenced an antiparallel orientation of rare-earth and cobalt moments. A change in the direction of cobalt moment from antiparallelly to parallelly oriented to Tm one was shown in TmCo$_2$, as temperature increased [7, 8]. The paramagnetic data were analysed assuming that cobalt has an exchange enhanced magnetic susceptibility, the cobalt moment being induced by the total field acting on the cobalt atoms [5-8]. The exchange field acting on cobalt, at $T > T_c$, is smaller than the value characteristic for metamagnetic transitions, $H_c \approx 75$ T [9-12]. Thus, only an intrinsic effective cobalt moment can be present. This statement has been confirmed particularly by analysing the thermal dependences of magnetic susceptibilities for RCo$_2$ compounds with non-magnetic [13, 14] and magnetic rare-earths [15, 16].

The following studies, performed on ErCo$_2$ compound, evidenced also an antiparallel orientation of Er and Co moments at $T > T_c$ [17-19]. The presence of intrinsic cobalt moment was also shown [17]. In addition, the SANS measurements evidenced short-range correlations, having correlation length of $\approx 7$ Å [20, 21]. These were associated with the presence of Griffiths–like phase above Curie point. The same antiparallel orientation of rare-earth and cobalt moments was further reported in RCo$_2$ (R = Ho, Tm) compounds [22-24], in agreement with previous studies [6-8]. The Griffiths phase was described as “establishing a short–range order a kind of low temperature remnant magnetic order of undiluted
system” [23]. The antiparallel orientation of rare-earth and cobalt moments, in the presence of external field, at $T > T_c$, was called parimagnetism. As function of temperature and external field, different arrangements of cobalt and rare-earths moments, above $T_c$, were also shown [22-24].

In the present paper, starting from the analysis of exchange interactions as well as of cobalt magnetic behaviour at $T > T_c$, the short range order previously reported [20, 21], was associated with the exchange coupled magnetic atoms at the level of the unit cell, having dimensions of $\simeq 7.2\AA$. No magnetic ordered phase, of the Griffits-type, can be shown, at $T > T_c$, in $\text{RCO}_2$ ($R=\text{Tb, Ho, Er, Tm}$) compounds.

2. Exchange interactions in $\text{RCO}_2$ compounds

The exchange interactions in $\text{RCO}_2$ compounds, at $T < T_c$, are rather complex, essentially determining the cobalt moments. Those between R and Co atoms are described as being of 4f-5d-3d type [25, 26]. The exchange interactions between cobalt atoms are of short range. Since of high extension of R5d orbitals, short range interactions are expected to take place between R atoms [27], in addition to those by means of conduction electrons.

The band structure calculations were performed on $\text{RM}_2$ ($M=\text{Fe, Co, Ni}$) compounds with heavy rare-earths [26]. The R5d band polarizations, $M_{5d}$, in $\text{RCO}_2$ compounds, as function of De Gennes factor, G, are plotted in Fig.1. These are antiparallelly oriented to cobalt moments and can be described by the relation:

$$M_{5d} = M_{5d}(d) + \alpha G$$

where $M_{5d}(d)$ is the R5d band polarization extrapolated at $G = 0$ and $\alpha = 2.1 \cdot 10^{-2} \mu_B$.

![Figure 1.](image.png)

**Figure 1.** The R5d band polarizations in heavy rare-earths $\text{RCO}_2$ compounds. In the inset, the exchange interactions at the level of unit cell are schematically presented.

Two different contributions are present. The first one $M_{5d}(f) = \alpha G$ is due to local 4f-5d exchange, while the second one, $M_{5d}(d)$, is the result of R5d-Co3d short range exchange interactions, the corresponding hybridizations effects, respectively. The $M_{5d}(d)$ contributions to R5d band polarization were shown to be proportional to $\sum z_i M_i$ [26]. By $z_i$ is denoted the number of cobalt atoms situated in the first coordination shell to an R one and $M_i$ are their magnetic moments. This relation is followed in $\text{RCO}_2$ based compounds as evidenced in Fig.2. The slope of this dependence, $\frac{M_{5d}(d)}{\sum z_i M_i} \simeq 2 \cdot 10^{-2}$, is the same as that evidenced in $\text{RM}_2$ ($M=\text{Fe, Ni}$) – based compounds, having similar crystal structures as $\text{RCO}_2$ ones. These data show a strong correlation between the R5d band polarizations and cobalt magnetic moments. As already mentioned, the part played by R5d band polarization in analysing the interactions in $\text{RCO}_2$ compounds is a fundamental question [26].
The above data suggest also that the exchange interactions, at the level of the unit cell, are interdependent. The induced cobalt moment by 4f-5d-3d exchange path is stabilized by the Co3d-Co3d short range exchange interactions. Concomitantly with the appearance of a cobalt moment, an additional polarization, \( M_{5d}(d) \) is induced on R5d band by a reverse path, as depicted in Fig.1 inset. The cobalt moments, parallelly with R5d band polarizations, are strongly influenced by magnetic dilution effects, both at R and Co sites, as evidenced for example, in Gd(Co\(_{1-x}\)Ni\(_x\))\(_2\) [28, 29] or (Gd, Y\(_{1-x}\))Co\(_2\) [30] pseudobinary compounds. Taking into account the above complex and interdependent magnetic interactions, at the level of unit cell, this can be viewed as a “cluster” of magnetic interacting atoms. Above the Curie temperatures, the thermal energy is not enough high to compensate the exchange energy and thus the magnetic coupling evidenced in magnetic ordered state still exist. The magnetic interactions are significantly diminished as compared to those present in ordered phase and thus no magnetic ordering can appear at the level of unit cell; this keeps only a “cluster” feature.

3. Magnetic behaviour of cobalt in RCo\(_2\) compounds at T > T\(_c\)

The magnetic properties of RCo\(_2\) compounds above the Curie points are also determined by those of cobalt atoms. As mentioned in introduction, either the presence of an exchange enhanced paramagnetism [4] or an intrinsic effective moment [2, 3] were initially considered, at T > T\(_c\). Latter studies, evidenced that the cobalt magnetic behaviour, in RCo\(_2\) compounds, can be described by the spin fluctuations model [13-16]. The model [31], takes into account the balance between the frequencies of longitudinal spin fluctuations, which are determined by their lifetime and of transverse fluctuations that are of thermal origin. These phenomena lead to the concept of temperature induced moment. For a weakly or nearly ferromagnet, as cobalt in RCo\(_2\) compounds, the wave number dependent susceptibility, \( \chi_q \), has a large enhancement due to electron-electron interactions for small q values. The average amplitude of spin fluctuations \( \langle S^2_{\text{loc}} \rangle = k_B T \sum \chi_q \) increases with temperature and reaches an upper limit determined by the charge neutrality condition at a temperature T\(^*\). At T > T\(^*\), a Curie-Weiss behaviour is predicted, similar as in systems having local moments. The moments are localized in q-space.

By using the calculated density of states and taking into account the effect of spin fluctuations, the temperature dependences of \( \langle S^2_{\text{loc}} \rangle \) were calculated in YCo\(_2\) [32] and LuCo\(_2\) [33] compounds, by using the procedure previously reported [34, 35]. As can be seen in Fig.3, there is a tendency to saturate \( \langle S^2_{\text{loc}} \rangle \) values, at temperatures T > 550 K, where a linear \( \chi' \) vs T dependence has been experimentally observed. The same behaviour was already reported in YCo\(_2\) compound [35].

The presence of an intrinsic cobalt moment was shown in RCo\(_2\) compounds with R = Ho, Er and Tm by magnetic circular dichroism, at T > T\(_c\). Values of 0.2 \( \mu_B \) (ErCo\(_2\)) [17], 0.3 \( \mu_B \) (HoCo\(_2\)) and 0.4 \( \mu_B \) (TmCo\(_2\)) [24] were reported. The cobalt moment was also shown to increase with temperature [17], as predicted by spin fluctuations model. Taking into account that M\(_{Co} = gS\), the corresponding effective
cobalt moments in the above compounds, $M_{\text{eff}} = g\sqrt{S(S+1)}$, are of 0.66, 0.83 and 1.00 $\mu_B$, respectively. The effective moments increase with temperature, in a similar way as evidenced in Fig.3, up to saturation values. In the asymptotic region of RCo$_2$ compounds ($T > 550$ K), the $\chi^1$ vs $T$ shows linear dependences. The determined effective cobalt moments decrease little with increasing Curie temperatures, from 3.85 $\mu_B$ (TmCo$_2$) to 3.65 $\mu_B$ (ErCo$_2$) and 3.25 $\mu_B$ (HoCo$_2$). These variations were attributed to partial quenching of spin fluctuations by the internal field [13]. The ratio $r = S_p/S_o$ between the number of spins determined from the effective cobalt moment, $S_p$, and the saturation one, $S_o$, follows in RCo$_2$ compounds, a $T_c^{2/3}$ dependence [36]. This type of behaviour is really predicted by the spin fluctuations model [37].

Figure 3. The temperature dependence of the mean square root amplitude $g\sqrt{S(S+1)}$ of the fluctuating cobalt moments, in RCo$_2$ (R = Lu, Y) compounds.

4. Magnetic behaviour of heavy rare earth RCo$_2$ compounds in the paramagnetic range

Magnetic measurements were made on ErCo$_2$ compound at temperatures where the Griffits phase is supposed to be present. As seen in Fig. 4, linear dependences of the magnetic moments on the external field are shown. These suggest that no magnetic ordered phase exist at $T > T_c$.

Figure 4. The field dependences of magnetizations in ErCo$_2$, at some temperatures above, $T_c$.

Figure 5. The field dependences of cobalt and holmium moments in HoCo$_2$ as determined by a neutron diffraction study [6].

The magnetic ordered impurities, if exist, are below 0.1% and influence very little the magnetic data. The same behaviour can be shown in HoCo$_2$, where both Ho and Co magnetic moments are linearly dependent on the external field as evidenced by neutron diffraction studies [6, 7] – Fig.5. These data suggest that there are no magnetic ordered cobalt clusters, of a Griffits phase type. This statement is
confirmed also by the evolution with temperature of the rare-earths and cobalt moments, at \( T > T_c \), as determined by polarized neutron diffraction, in various external fields [5-8] – Fig.6. There is a linear dependence of cobalt moments on the rare earth ones in the studied temperature range (40 K \( \leq T \leq 300 \) K) and external fields (10 kOe \( \leq H \leq 57.2 \) kOe). The slopes, \( a = (M_{Co}/M_R) \), are dependent on the rare-earth partner, decreasing in the same way as the \( M_{5d} \) band polarizations as evidenced in Fig.7. On the same figure, the \( a \approx 0.041 \) value, as determined by polarized neutron on ErCo\(_2\) single crystal at \( T = 40 \) K [23] is also given. Since the small cobalt moments, as well as due to partial quenching of Tm moment, as determined by neutron diffraction, the errors in estimating the \( a \) value in TmCo\(_2\) are higher than in others RCo\(_2\) compounds.

As already mentioned [26, 38], the R5d-Co3d short range exchange interactions are important in describing the magnetic properties of rare-earth transition metal compounds which is the essential idea of the Campbell model [25]. The 4f-5d-3d exchange interactions are still present above the Curie temperatures, in a relative large temperature range, parallelly with those between cobalt atoms. The exchange couplings are not enough high to induce a magnetic ordering. The presence of Lu5d-Co3d magnetic coupling was also shown in paramagnetic LuCo\(_2\) single crystal, at \( T = 100 \) K and field \( H = 57.2 \) kOe, by a polarized neutron diffraction study [39]. A cobalt moment of 0.016 \( \mu_B \) has been determined, the corresponding form factor being similar to that of 3d electrons in cobalt metal. The Lu5d band is negatively polarized and of \( = 0.007(5) \) \( \mu_B \), the ratio \( |M_{5d}/\sum \sum_{i} z_i M_i| \approx (3.5 \pm 2.5) \cdot 10^{-2} \) being, in the limit of experimental errors, the same as that determined in magnetic ordered RCo\(_2\) compounds, in fundamental state \( (2 \cdot 10^{-2}) \).

**Figure 6.** The cobalt magnetic moments in RCo\(_2\) (R = Tb, Ho, Tm) compounds, at \( T > T_c \), as function of rare-earths ones.

**Figure 7.** The relation between \( a = M_{Co}/M_R \) parameters and the \( M_{5d} \) band polarizations.
5. Discussions
The present analysis suggests that the “ferrimagnetic correlations”, at \( T > T_c \), as evidenced by SANS experiments, having correlation length of \( \approx 7-8 \) Å can be associated with those in the \( \text{RCO}_2 \) unit cells, where the characteristic exchange interactions between all atoms in ordered phase, are still present in paramagnetic range. Their intensities are not enough to induce a magnetic ordered state. The antiparallel coupling of R and Co moments can be evidenced only in the presence of external field. From energy considerations, the higher rare-earth moment than the cobalt one, will be aligned parallelly to the external field, the 4f-5d-3d coupling, imposing an antiparallel orientation for cobalt moments, up to a characteristic temperature, \( T_c \). The thermal energy is not sufficient to induce a full disordering, in the considered temperature range, as in normal ferrimagnets. Parallel orientations of magnetic moments in external fields can be seen only at higher temperatures, their values depending on the strength of 5d-Co3d interactions characteristic for a given \( \text{RCO}_2 \) compound. The evolutions with temperature of cobalt moment and of the anisotropy field can determine a more complex magnetic arrangement of rare-earth and cobalt atoms.

Analyzing the magnetic properties of the clusters evidenced by SANS measurements in \( \text{ErCo}_2 \), an effective moment \( M_{\text{eff}}(\text{cell}) \approx 20 \mu_B \) has been reported [18]. The cluster was considered to be constituted from 60 to 100 cobalt and 30 to 50 erbium atoms. The above estimation is unrealistic and can be the result of using the values of the magnetic moments \( M = gS \) instead of the effective ones, \( M_{\text{eff}} \), in estimating the cluster composition. Really the effective moment of the unit cell containing 16 cobalt and 8 erbium atoms can fit well the above \( M_{\text{eff}}(\text{cell}) \) value. Assuming that the effective moment of erbium is given by its free ion value (9.59 \( \mu_B \)) and that of cobalt of 0.66 \( \mu_B \), as already mentioned, the corresponding effective moment of the unit cell is \( M_{\text{eff}}(\text{cell}) \approx 27 \mu_B \), supporting our conclusion. Generally, the effective moments in characterizing the systems containing atoms with different magnetic contributions has not a physical significance. The corresponding magnetic behaviour can be described better by the addition law of the magnetic susceptibilities, Curie constants, respectively than of the squares of effective moments.

In high external field, the \( T_c \) value of \( \text{ErCo}_2 \) shifts to higher values [40] and as result, deviations from the linear field dependences of magnetizations can be seen at temperatures higher than the Curie point, as evidenced in smaller fields [40].

A more detailed analysis concerning the magnetic behaviour of \( \text{RCO}_2 \) above the Curie temperatures will be further presented [41].

This work was supported by the Romanian Ministry of Education and Research (UEFISCDI), grant no. PN-II-ID-PCE-2012-4-0028.

References

[1]. E.Burzo, A.Chelkowoski, H.R. Kirchmayr, Landolt Börnstein Handbook, Springer Verlag, Vol.19d2, 1990
[2]. E.Burzo, Phys. Rev. B6, 2882 (1972)
[3]. E.Burzo, Int. J. Magn. 3, 161 (1972)
[4]. D.Bloch, R.Lemaire, Phys. Rev. B2, 2648 (1970)
[5]. D.Gignoux, F.Givord, J.Phys. F: Metal Phys. 9, 1409 (1979)
[6]. D.Gignoux, F.Givord, J.Schweizer, J.Phys. F: Metal Phys. 7, 1823 (1977)
[7]. D.Gignoux, F.Givord, W.C.Koehler, Physica, B86-88, 165 (1977)
[8]. D.Gignoux, D.Givord, F.Givord, W.C. Koehler, R.M.Moon, Phys. Rev. B14, 162 (1976)
[9]. E.Burzo, Rev. Roum. Phys. 23, 693 (1978); J. Less Common Met. 77, 251 (1981)
[10]. E.Burzo, N. Plugaru, I. Creanga, I. Ursu, J. Less Common Met. 155, 281(1989)
[11]. T.Goto, A.H.Katori, T.Sakakibara, H.Mitamura, K.Fukamichi, K.Murata, J. Appl. Phys. 76, 6682 (1991)
[12]. N.N.Duc, T.D.Hien, P.E.Brommer, J.J.Franse, J. Magn. Magn. Mater. 104-107, 1252 (1992)
[13]. E.Burzo. R. Lemaire, Solid State Commun. 84, 1145 (1992)
[14]. E.Burzo, E.Graz, V.Pop, J.Magn.Magn. Mater. 123, 159 (1993)
[15]. E.Burzo, P.Vlaic, D.P.Kozlenko, S.E.Kichanov, N.T.Dang, A.V.Rutkauskas, B.N.Savenko, J. Alloys Comp. 584, 393 (2014)
[16]. D.P.Kozlenko, E.Burzo, P.Vlaic, S.E. Kichanov, A.V.Rutkauskas, B.N.Savenko, Sci. Reports, 5, 8620 (2015)
[17]. J. Herrero-Albillos, L.M.Garcia, F.Bartolomé, A.T.Young, T.Funk, J. Magn. Magn. Mater. 316, e442 (2007)
[18]. J.Herrero-Albillos, F.Bartolomé, L.M.Garcia, A.T. Young, T.Funk, J.Campo, G.J.Cuello, Phys. Rev.B76, 094409 (2007)
[19]. J.Herrero-Albillos, F.Bartolomé, L.M.Garcia, A.T. Young, T.Funk, G.J.Cuello, J.Magn. Magn. Mater. 310, 1645 (2007)
[20]. J.Herrero-Albillos, L.M.Garcia, F.Bartolomé, J.Phys. : Condens. Matter, 21, 216004 (2009)
[21]. C.M.Bonilla, N.Marcano, J.Herrero-Albillos, A.Maisuradze, L.M.Garcia, F.Bartolome, Phys. Rev. B 84, 184425 (2011)
[22]. C.M.Bonilla, I.Calvo, J.Herrero-Albillos, A.I.Figueroa, C.Castan-Guerrero, J.Bartolome, J.A.Rodriguez-Velamazan, D.Schmitz, E.Weschke, D.Paudyal, V.K.Pecharsky, K.A.Gschneidner, F.Bartolomé, L.M.Garcia, J.Appl. Phys. 111, 07E315 (2012)
[23]. F.Bartolomé, C.M. Bonilla, J.Herrero-Albillos, I.Calvo-Almazan, C.Castan, E.Weschke, D.Schmitz, D.Paudyal, Y.Mudryk, V.Pecharsky, K.A. Gschneidner, A.Stunault, L.M.Garcia, Eur. Phys. J. B84, 489 (2013)
[24]. C.M. Bonilla, J.Herrero-Albillos, A.I.Figueroa, C.Castan-Guerrero, J.Bartolome, F.Bartolomé, J.Calvo-Almazan, D.Schmitz, E.Weschke, L.M.Garcia, J.Phys. : Condens. Matter 26, 156001 (2014)
[25]. I.A.Campbell, J. Phys. F.: Metal. Phys. 2, L47 (1972)
[26]. E.Burzo, L.Chioncel, R.Tetean, O.Isnard, J. Phys.:Condens. Matter, 23, 026001 (2011) and references
[27]. E.Burzo, L.Chioncel, L.Costina, S.G. Chiuzbaian, J. Phys.: Condens. Matter, 18, 4861 (2006)
[28]. E.Burzo, D.P. Lazar, M. Ciorascu, Phys. Stat. Solidi (b), 65, K145 (1974)
[29]. E.Burzo, L. Chioncel, J. Opt. Adv. Mater. 6, 917 (2004)
[30]. E.Burzo, D.P.Lazar, J. Solid State Chem. 16, 257 (1976)
[31]. T.Moriya, J. Magn. Magn. Mater. 14, 1(1979); 100, 261 (1991)
[32]. L.Chioncel, E.Burzo, R.Tetean, V.Pop, Mol. Cryst. Liquid Cryst. 417, 513 (2004)
[33]. E.Burzo, AIP Conf. Proc. 1694, 030001 (2015)
[34]. M. Shimizu, Phys. Letters 81A, 87 (1981); Report Progr. Phys. 44, 21 (1981)
[35]. H.Yamada, J. Inoue, K.Terao, S.Kanda, M. Shimizu, J. Phys. F: Metal Phys. 14, 1543 (1984)
[36]. E. Burzo, P. Vlaic, D.P.Kozlenko, S.E.Kichanov, N.T.Dang, E.V.Lukin, B.N.Savenko, J. Alloys Comp. 551, 702 (2013)
[37]. E.P.Wohlfarth, J. Magn. Magn. Mater., 7, 113 (1978)
[38]. H.H.Li, Y.P.Li, J.M.D.Coez, J. Magn. Magn. Mater. 104-107, 1444 (1992)
[39]. D.Gignoux, F.Givord, W.C.Koehler, R.M.Moon, J. Magn. Magn. Mater. 5, 172 (1977)
[40]. J. Woo, Y.Jo, H.C.Kim, A.Pirogov, J.G.Park, H.C.Ri, A.Podlesnyak, J.Schefer, Th. Strassle, A.Teplykh, Physica B, 329, 653 (2003)
[41]. E. Burzo, L. Chioncel, Cogent Physics (sent for publication)