

Exchange interactions in heavy rare-earths RCo₂ compounds

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Abstract. The magnetic behaviour of RCo₂ (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 $\cong 7\text{\AA}$, 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 RCo₂ 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 RCo₂ compounds, where R is a magnetic heavy rare-earth (R = Gd to Tm) are ferrimagnetically ordered, the rare earth and cobalt moments being antiparallely 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, χ^{-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 RCo₂ 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 antiparallely to parallelly oriented to Tm one was shown in TmCo₂, 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, $H_c \cong 75\text{ T}$ [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 RCo₂ compounds with non-magnetic [13, 14] and magnetic rare-earths [15, 16].

The following studies, performed on ErCo₂ 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 $\cong 7\text{\AA}$ [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 RCo₂ (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 $\cong 7.2\text{\AA}$. No magnetic ordered phase, of the Griffiths-type, can be shown, at $T > T_c$, in RCO_2 ($R = \text{Tb, Ho, Er, Tm}$) compounds.

2. Exchange interactions in RCO_2 compounds

The exchange interactions in 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 RM_2 ($M = \text{Fe, Co, Ni}$) compounds with heavy rare-earths [26]. The R5d band polarizations, M_{5d} , in RCO_2 compounds, as function of De Gennes factor, G , are plotted in Fig.1. These are antiparallely 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 $\alpha = 2.1 \cdot 10^{-2} \mu_B$.

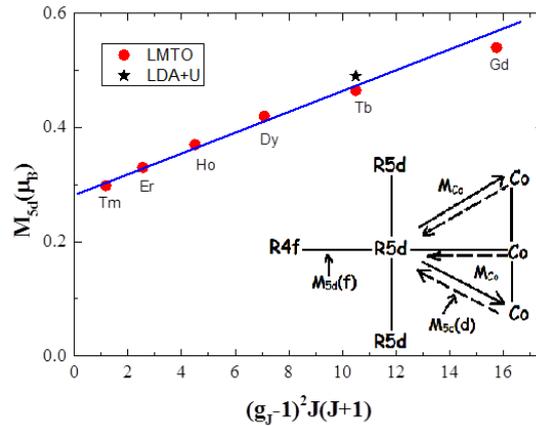


Figure 1. The R5d band polarizations in heavy rare-earths RCO_2 compounds. In the inset, the exchange interactions at the level of unit cell are schematically presented.

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 $\sum_i z_i M_i$ [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 RCO_2 based compounds as evidenced in Fig.2. The slope of this dependence, $|M_{5d}(d)| / \sum_i z_i M_i \cong 2 \cdot 10^{-2}$, is the same as that evidenced in RM_2 ($M = \text{Fe, Ni}$) – based compounds, having similar crystal structures as 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 RCO_2 compounds is a fundamental question [26].

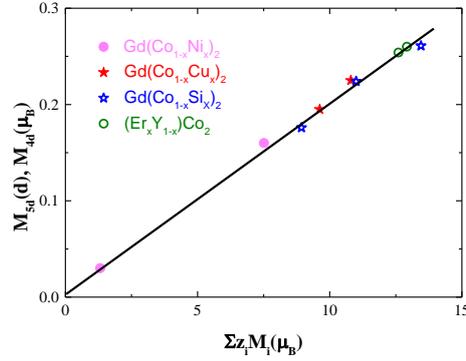


Figure 2. The $M_{5d(d)}$ components of R5d band polarizations, in RCo_2 -based compounds, as function of $\sum_i z_i M_i$.

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 $(Gd_xY_{1-x})Co_2$ [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, χ_q , has a large enhancement due to electron-electron interactions for small q values. The average amplitude of spin fluctuations $\langle S_{loc}^2 \rangle = k_B T \sum \chi_q$ 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 $\langle S_{loc}^2 \rangle$ 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 $\langle S_{loc}^2 \rangle$ values, at temperatures $T > 550$ K, where a linear χ^{-1} 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 μ_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 $R\text{Co}_2$ compounds ($T > 550$ K), the χ^{-1} vs T shows linear dependences. The determined effective cobalt moments decrease little with increasing Curie temperatures, from 3.85 μ_B (TmCo_2) to 3.65 μ_B (ErCo_2) and 3.25 μ_B (HoCo_2). These variations were attributed to partial quenching of spin fluctuations by the internal field [13]. The ratio $r = S_p/S_0$ between the number of spins determined from the effective cobalt moment, S_p , and the saturation one, S_0 , follows in $R\text{Co}_2$ compounds, a $T_c^{-2/3}$ dependence [36]. This type of behaviour is really predicted by the spin fluctuations model [37].

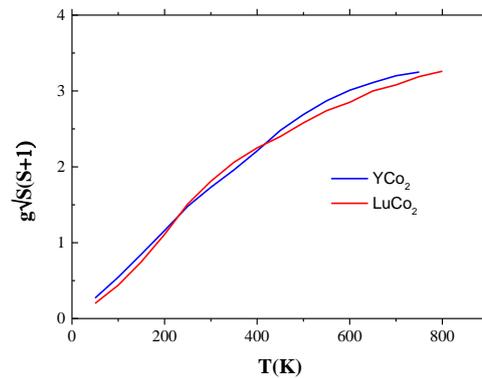


Figure 3. The temperature dependence of the mean square root amplitude $g\sqrt{S(S+1)}$, of the fluctuating cobalt moments, in $R\text{Co}_2$ ($R = \text{Lu}, \text{Y}$) compounds.

4. Magnetic behaviour of heavy rare earth $R\text{Co}_2$ compounds in the paramagnetic range

Magnetic measurements were made on ErCo_2 compound at temperatures where the Griffiths 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 $T > T_c$.

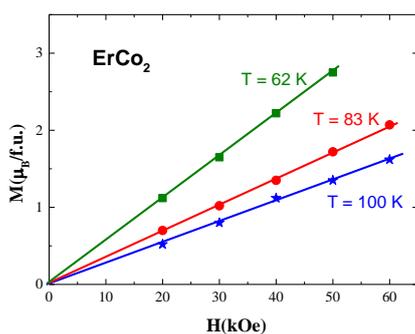


Figure 4. The field dependences of magnetizations in ErCo_2 , at some temperatures above, T_c .

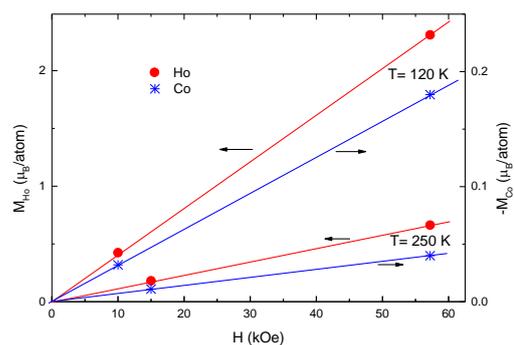


Figure 5. The field dependences of cobalt and holmium moments in HoCo_2 as determined by a neutron diffraction study [6].

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 Griffiths 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 ($40 \text{ K} \leq T \leq 300 \text{ K}$) and external fields ($10 \text{ kOe} \leq H \leq 57.2 \text{ kOe}$). 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 $a \cong 0.041$ value, as determined by polarized neutron on ErCo_2 single crystal at $T = 40 \text{ K}$ [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 La5d-Co3d magnetic coupling was also shown in paramagnetic LuCo_2 single crystal, at $T = 100 \text{ K}$ and field $H = 57.2 \text{ kOe}$, 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 $|M_{5d}/\sum_i z_i M_i| \cong (3.5 \pm 2.5) \cdot 10^{-2}$ being, in the limit of experimental errors, the same as that determined in magnetic ordered RCo_2 compounds, in fundamental state ($2 \cdot 10^{-2}$).

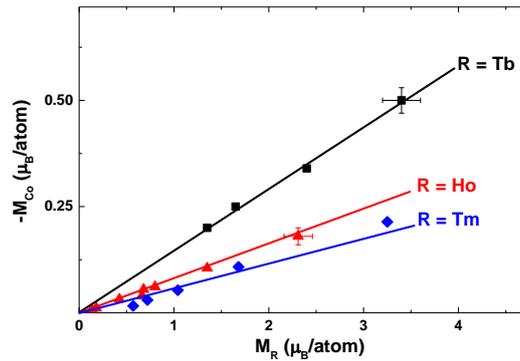


Figure 6. The cobalt magnetic moments in RCo_2 ($R = \text{Tb}, \text{Ho}, \text{Tm}$) compounds, at $T > T_c$, as function of rare-earths ones.

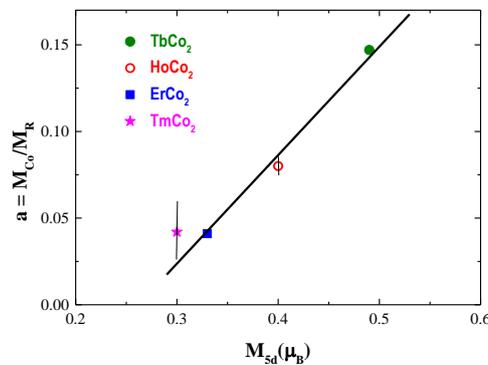


Figure 7. The relation between $a = M_{Co}/M_R$ parameters and the M_{5d} band polarizations.

5. Discussions

The present analysis suggests that the “ferrimagnetic correlations”, at $T > T_c$, as evidenced by SANS experiments, having correlation length of $\cong 7\text{-}8 \text{ \AA}$ can be associated with those in the $R\text{Co}_2$ 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_1 . 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 R5d-Co3d interactions characteristic for a given $R\text{Co}_2$ 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.

Analysing the magnetic properties of the clusters evidenced by SANS measurements in ErCo_2 , an effective moment $M_{\text{eff}}(\text{cell}) \cong 20 \mu_B$ 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_{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 $M_{\text{eff}}(\text{cell}) \cong 27 \mu_B$, 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 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 $R\text{Co}_2$ above the Curie temperatures will be further presented [41].

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