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Invited Paper

RARE-EARTH TRANSITION METAL COMPOUNDS: EXCHANGE INTERACTIONS AND TRANSITION METAL MOMENTS

E. Burzo[*], L. Chioncel[a]

Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania
[a]Department of Physics, University of Nijmegen, 6500 GL, Nijmegen, The Netherlands

Magnetic measurements and band structure calculations were performed on $Gd(Co_xNi_{1-x})_2$, $Gd(Co_xAl_{1-x})_2$, $(Gd_xY_{1-x})Co_2$, $YCo_{4-x}Ni_xB$ and $(Gd_xY_{1-x})Ni_5$ compounds. The band structure calculations performed on $Gd(Co_xNi_{1-x})_2$ system show that the cobalt moments are little dependent on composition. The critical fields for the appearance of induced cobalt and nickel moments were determined. The R5d band polarizations in R–Co and R–Ni compounds where R is a magnetic rare–earth are the result of both local 4d–5d and 5d–3d short range exchange interactions. Both 5d and 4d band polarizations resulting from short range interactions show a linear dependence on the magnetizations of nearest neighbour transition metals atoms.

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1. Introduction

The exchange interactions in RM_x compounds, where R is a rare–earth and M a transition metal (M = Fe, Co, Ni) has been a subject of debate. Experimentally, has been shown that in case of light rare–earths, there is a parallel coupling of R and M moments, while in case of heavy rare–earths, the alignment is antiparallel [1]. Since 4f shell of rare–earths is well localized, in earlier studies, the magnetic interactions between R and M atoms have been assumed to be of RKKY type, through conduction electrons [2]. Some works have been performed in order to change the orientation of heavy rare–earth moments as compared to M ones, by varying the electron concentrations or distances between magnetic atoms. No effect on the magnetic coupling has been shown [3]. A phenomenological model in which the 4f electrons of rare–earths polarize their 5d bands and there are 5d–3d short range interactions with transition metals was proposed [4]. The local 4f–5d exchange interactions are positive and thus the 5d band polarizations are parallely oriented to 4f moments. Details concerning the 4f–5d–3d interactions were reported. Brooks et al [5] described the 4f–5d exchange interactions by the Hamiltonian $H_{4f\text{-}5d} = -2 J_{4f\text{-}5d}S_{4f}S_{5d}$, where $J_{4f\text{-}5d}$ depends upon the 4f–5d overlap densities and is positive. As the 4f shell contracts, the region of the overlap between the outher part of the 4f density and the inner part of the 5d density, decreases. As result, a decrease of the 4f–5d exchange integrals across the given lanthanide series of compounds was expected. According to Li et la [6], in addition to $J_{4f\text{-}5d}$ local exchange, there are also exchange interactions with p and s electrons described by the $J_{4f\text{-}6s}$ and $J_{4f\text{-}6p}$ exchange integrals. All the above exchange integrals decrease across the lanthanide series, although the $J_{4f\text{-}5d}$ one dominates. Beloritzky et al [7] suggested that the decrease of $J_{4f\text{-}5d}$ along the lanthanide series is related to r_{5d}–r_{4f} variations. By r_{5d} and r_{4f} are denoted the radii of 5d and 4f shells, respectively. Fähnle et al [8] reported that the intersublattice exchange parameter is determined mainly by $J_{4f\text{-}5d}$ and there is no major contributions from $J_{3d\text{-}5d}$. We also proposed a model [9] in which the 5d band polarization is

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[*] Corresponding author: burzo@phys.ubbcluj.ro

the result of two contributions. The first one is due to local 4f–5d exchange, while the second one is the result of the 5d–3d short range exchange interactions.

In this paper we analyse the effect of exchange interactions on transition metal moments in RM_2, RM_5 and RM_4B (M = Co,Ni)–based compounds as well as on R5d and Y4d bands polarizations. Previously [10], we proposed a model in which the cobalt moment is induced at a critical exchange field. Then, the M_{Co} values increase nearly linearly with the internal field and finally saturate. The experimental data [11,12,13] confirmed the above model. In the following, as on going study on this matter [10,11,13], we analyse the induced cobalt and nickel moments in correlation with the exchange interactions in hexagonal and cubic structures. For this purpose, in addition to magnetic measurements, band structure calculations were also performed.

2. Experimental and computing data

The samples were prepared by melting the constituent elements in arc furnace. The compounds were thermally treated, at 1000 K, for one week. The crystal structures were analysed by X–ray diffraction. The compounds were shown to have only one phase. If it is present, the impurity content is smaller than 1 %.

The $Gd(Co_xNi_{1-x})_2$ compounds crystallize in a cubic $MgCu_2$-type structure. The Gd occupies $\bar{4}3m$ sites while Co and Ni are distributed in $\bar{3}m$ positions. The RCo_5 and RNi_5 compounds crystallize in a hexagonal type structure. The R atoms are situated in 1a site while Co and Ni occupy 2c and 3g positions. The RCo_4B compounds crystallize in a $CeCo_4B$ type structure [14]. The structure is derived from $CaCu_5$ one by substituting Co in 2c sites, by B, in every second layer. Consequently, the R atoms occupy two sites R1a and R1b, the first one in the plane containing B atoms. The cobalt atoms are located in 2c and 6i sites. For $YCo_{4-x}Ni_xB$ system, Ni atoms can occupy both 6i and 2c positions as shown in RNi_4B compounds [15]. Since of greater number of 6i sites, there is a higher probability for Ni to be distributed on these sites, for samples having relatively high cobalt content.

Magnetic measurements were performed in the temperature range 4.2–1000 K and fields up to 9 T. The band structure calculations were performed by using the TB–LMTO method [16] within LDA and LDA+U approaches [17]. The LDA+U scheme is based on the Anderson impurity model in mean field (Hartree–Fock) approximation that analyses the s and p electrons as non–correlated, described by an orbital independent potential and d electrons are described by an orbital dependent potential [18].

3. Critical fields

As mentioned already, the M = Co,Ni atoms in RM_x compounds show a wide range of magnetic behaviours covering the situation when there is a well defined moment, up to paramagnetic state, crossing the region when it is a collapse (or onset) of the moment. The above behaviour is strongly correlated with variation of exchange interactions in the system. These changes can be made both by substitutions at M and R sites. In this way the M3d–M3d and R4f–5d–M3d exchange interactions, respectively can be modified. As result of substitutions it is possible to analyse the variations of M magnetizations and to estimate the critical exchange fields for the appearance (or loss) of their moments. In the following we analyse this matter for compounds having cubic and hexagonal type structures, whose compositions were gradually changed.

The $Gd(Co_xNi_{1-x})_2$ system shows interest for this analysis since Co has a magnetic moment at 4.2 K in $GdCo_2$, while Ni atoms show a very weak or null magnetic contribution in $GdNi_2$. The magnetization of $GdCo_2$ at 4.2 K is 4.95 μ_B/f.u. [1]. Supposing that the magnetic moment of Gd is given by $g_J J$ value, a Co magnetic contribution of 1.03 μ_B/atom was obtained by magnetic measurements. We performed also band structure calculations. The band structures of $GdCo_2$ and GdCoNi are plotted in Fig. 1.

The determined magnetic moment per formula unit for $GdCo_2$ is close to above, namely 5.14 μ_B/f.u.. Difference as compared to magnetic measurements can be seen for Gd and Co moments, (M_{Gd} = 7.62 μ_B/atom and M_{Co} = -1.24 μ_B/atom), since the computed M_{Gd} includes also 5d band polarization. Band structure calculations performed on $GdNi_2$ show that there is a very small magnetic moment on Ni, namely ≅ 0.12 μ_B/atom. By magnetic measurements a null nickel moment is suggested [1]. Thus, when replacing Co by Ni, the exchange interactions are modified considerably.

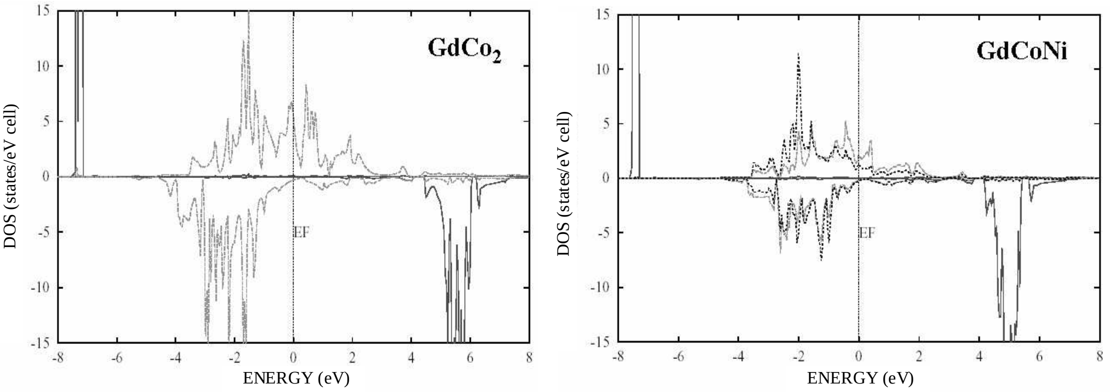

Fig. 1. Band structures of $GdCo_2$ and GdCoNi compounds. Partial densities of states: Gd4f–solid line; Co–long dashed line; Ni – short dashed line.

The composition dependence of the reduced transition metal magnetizations M(x)/M(1) in $Gd(Co_xNi_{1-x})_2$ series is plotted in Fig.2. The substitution of Co and Ni decreases strongly the transition metal moments, particularly for $x \geq 0.6$. The observed behaviour can be due to the diminution of Co moments or to the loss of magnetic moment of some Co atoms having, in nearest neighbour, a greater number of Ni. To decide on the possible mechanism involved in the variation of transition metal moments, band structure calculations were performed on GdCoNi alloy – Fig. 1. The cobalt moment in this compound is only little changed as compared to the value determined in $GdCo_2$, being 1.10 μ_B/atom. The determined Ni moments is also small, 0.18 μ_B/atom, close to the value obtained in $GdNi_2$. Thus, in the first approximation we admit that the cobalt moments are nearly constant along series and nickel magnetic contributions are rather small and can be neglected. As a result, the observed behaviour for M(x)/M(1) can be analysed in the local environment model. In this model, the mean magnetic moment, for a composition x, can be described by [19]:

$$\langle M_{Co} \rangle = \sum_{n>n_c} M_{Co}(x) P_n(x) \tag{1}$$

We denoted by $P_n(x)$, the probability for a cobalt atom to have n nearest neighbours (NN) similar atoms. Considering a random distribution of Co and Ni on $\bar{3}m$ sites we have:

$$P_n(x) = \frac{6!\, x^n (1-x)^{6-n}}{(6-n)!\, n!} \tag{2}$$

The computed moments according to the relation (1), describe well the experimental data, – Fig. 2 – supposing that cobalt has a magnetic contribution $M_{Co}(1)$, if there are a number $n \geq 3$ of Co atoms as NN and is nil if this number is smaller than $n_c = 3$.

The critical exchange field can be estimated analyzing the exchange interactions between cobalt atoms and supposing these as additive. We note that the exchange interactions due to presence of Gd are supposed to be not changed along series since the Gd content is not modified. From paramagnetic measurements we estimated the molecular field coefficient characterizing the interactions between cobalt atoms. A value $J_{CoCo} = 3.3 \cdot 10^{-22}$ J was obtained. This corresponds to a critical field $H_c \cong 70$ T for appearance of a cobalt moment, when considering the interactions in a cluster of three atoms.

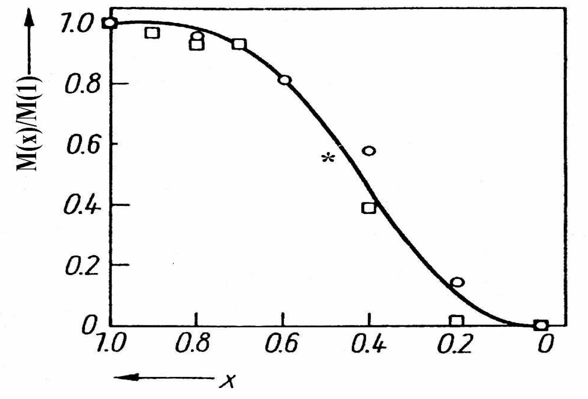

Fig. 2. Composition dependence of the transition metal magnetizations in $Gd(Co_xNi_{1-x})_2$ compounds. By O, are marked the results of magnetic measurements and by * computed values. By solid line is plotted the prediction of the relation (1).

The critical field for the appearance of Co moment can be analysed also in $Gd_xY_{1-x}Co_2$ compounds [20]. In the above system the cobalt moment is a function on Gd content, decreasing as Gd is substituted by Y. In YCo_2, at 4.2 K, the cobalt shows an exchange enhanced paramagnetism [2]. In $(Gd_xY_{1-x})Co_2$ series we estimated the exchange fields acting on cobalt, in the molecular filed approximation. The cobalt moments as function of exchange fields are plotted in Fig. 3 together with the data obtained by magnetic measurements on $Gd(Co_xAl_{1-x})_2$ and $Gd(Co_xNi_{1-x})_2$ systems.

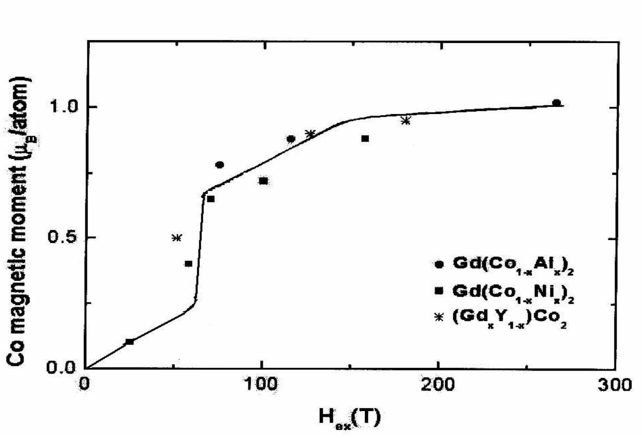

Fig. 3. The dependence of cobalt moments on exchange fields in cubic compounds.

A transition from nonmagnetic to magnetic state of cobalt can be seen at ≅ 70 T, similar value as determined in $Gd(Co_xNi_{1-x})_2$ system. The cobalt moment increases as function of internal filed and above ≅ 150 T it becomes saturated.

We analysed the critical field for the appearance of magnetic moment on nickel atoms in $Gd_xY_{1-x}Ni_5$ compounds. A magnetic moments of $\cong 0.20\ \mu_B$/atom was determined in $GdNi_5$ by magnetic measurements [22]. The $LaNi_5$, at 4.2 K, shows an exchange enhanced magnetic susceptibility. In order to estimated the H_c value, we use the data obtained from band structure calculations. A typical band structure for $GdNi_5$ is shown in Fig. 4.

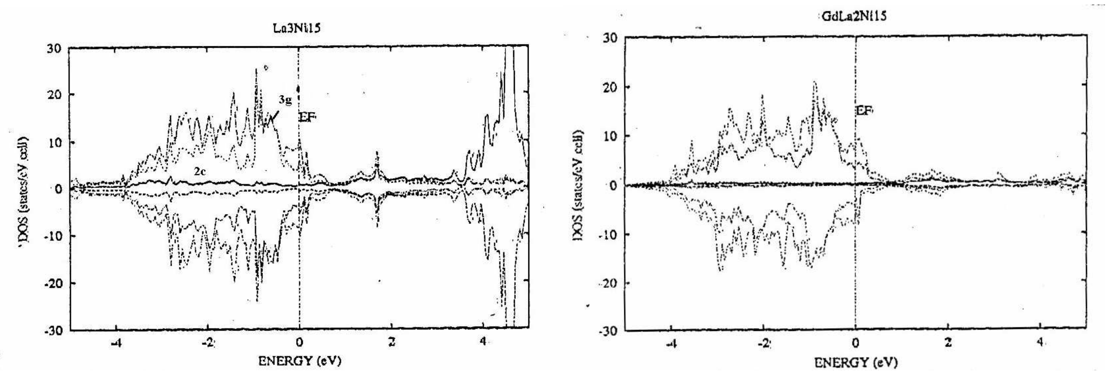

Fig. 4. Band structure of $GdNi_5$ and $Gd_{0.33}La_{0.67}Ni_5$.

The Ni magnetic moments at 2c sites are higher than at 3g ones. The 2c site in RNi_5 lattice has 6Ni(3g) and 3Ni(2c), as well as 3R as nearest neighbours, while the 3g sites have 4Ni(2c), 4Ni(3g) and 4R as nearest neighbours. The strength of interactions between nickel and gadolinium atoms is more important than between nickel atoms, whose magnetic moments are very low. The nickel moments are essentially induced by exchange interactions involving mainly gadolinium. Thus, the exchange splitting of Ni(2c) 3d band will be greater than that for Ni(3g) sites since of higher number of Gd nearest neighbours. The dependence of the Ni moments at 2c and 3g sites as function of exchange fields, determined from computed exchange splittings of 3d bands is shown in Fig. 5.

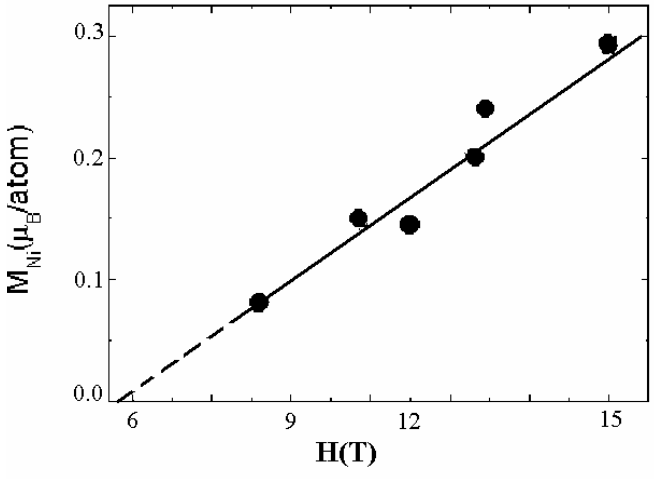

Fig. 5. The dependence of nickel moments at 2c and 3g sites in $Gd_xY_{1-x}Ni_5$ system as function of exchange field.

The extrapolation of computed values to $M_{Ni} = 0$, gives a critical field $H_c \cong 50$ T. This value is somewhat higher than that determined from magnetic measurements considering a mean value of the nickel moments, in molecular field approximation, namely $H_c \cong 35$ T.

The effect of exchange interactions on the Co and Ni moments can be also analysed in more complex system such as $YCo_{4-x}Ni_xB$. The YNi_4B compound, at T<12 K, shows a superconducting behaviour, due to the presence of small content of superconducting phase. Above 12 K, a paramagnetic behaviour was observed [23,24]. The band structures for YCo_4B and YCo_2Ni_2B compounds are plotted in Fig. 6.

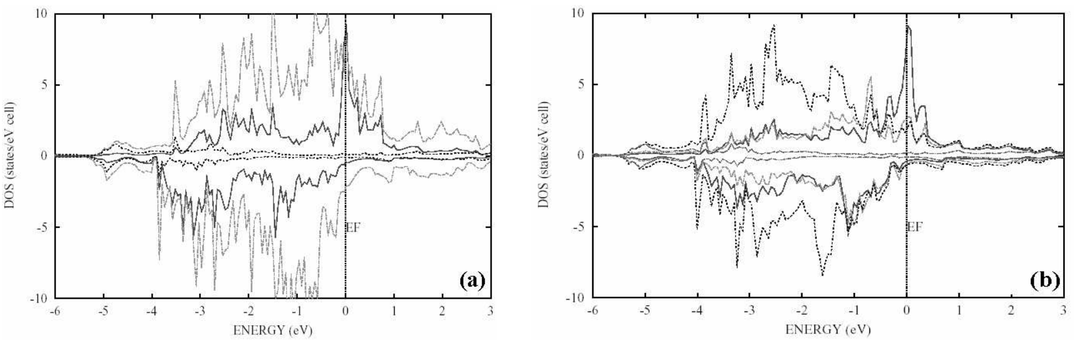

Fig. 6. Band structures of YCo_4B (a) and YCo_2Ni_2B (b) compounds. Solid lines are partial densities of states for Co 2c, dashed lines for 3g, B by points and Ni6i by long dashed lines.

In YCo_4B, the cobalt moments at 2c and 6i sites are 1.44 μ_B and 0.61 μ_B, respectively, as determined from band structure calculations. The composition dependences of Co and Ni moments in $YCo_{4-x}Ni_xB$ are given in Fig. 7.

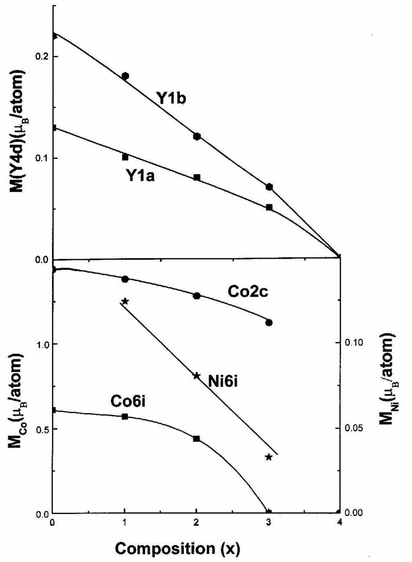

Fig. 7. Composition dependences of the cobalt moments at 2c, 6i sites and Ni 6i sites as well as of Y1a and Y1b band polarizations.

The nickel was supposed to occupies 6i sites. Due to Co-Ni short range exchange interactions a small magnetic moment is induced on Ni atoms for a composition x = 3. The nickel moments increase when the number of cobalt atoms in the nearest neighbour increases. Also, the M_{Co}, at 2c sites, shows a high increase in the composition range $3 \le x \le 4$, while for 6i sites this variation is higher in the range $2 \le x \le 3$. These variations are due to the increase of internal filed acting on Co or Ni as results of short range interactions with neighbouring atoms.

4. Y4d and R5d band polarizations

The Y4d band polarizations are also analysed. In $YCo_{4-x}Ni_xB$ system, the 4d band polarizations are different for Y1a and Y1b sites. This behaviour can be correlated with their different local environments. The Y1b sites has 6Co2c and 12Co6i atoms as NN, while Y1a site has 12Co6i and 6B2p atoms as nearest neighbours. Thus, the 5d–3d exchange interactions involving Y1b sites are higher than those at Y1a ones and can be correlated with the number of magnetic atoms, n_i and their magnetic moments, M_i situated in first coordination shell. In Fig. 8 we plotted the Y4d band polarizations as function of $\sum n_i M_i$.

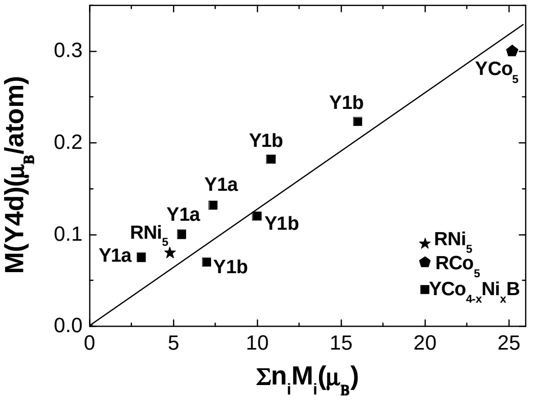

Fig. 8. The 4d band polarizations at Y1a ad Y1b sites as well as $M_{5d}(0)$ values determined in RCo_5 and RNi_5 compounds.

A linear relation is shown, suggesting that essentially the Y4d band polarizations are the result of 4d–3d short range exchange interactions.

The R5d band polarizations in magnetic heavy rare-earth compounds having $CaCu_5$–type structure, as function of DeGennes factor, $G = (g_J - 1)^2 J(J+1)$ are plotted in Fig. 9.

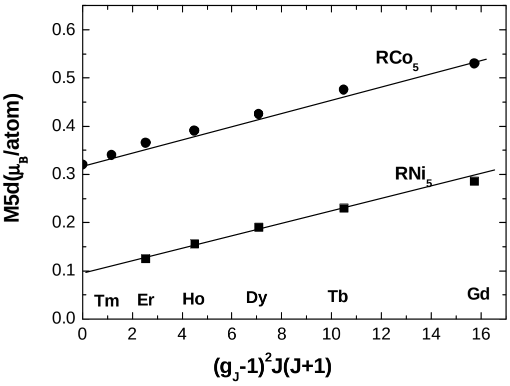

Fig. 9. The 5d band polarizations computed in RCo_5 and RNi_5 compounds.

There are linear variations and can be described by a relation [25]:

$$M_{5d} = M_{5d}(0) + \alpha G \tag{3}$$

The slope, $\alpha = 1.4 \times 10^{-2}\ \mu_B$, is the same for both RCo_5 and RNi_5, compounds. The analyses of the data plotted in Fig. 9 show that there are two contributions. The first one, αG, is due to local 4f–5d exchange interactions and the second one, $M_{5d}(0)$, can be attributed to 3d–5d short range exchange interactions. If the $M_{5d}(0)$ and Y4d values in RCo_5 and RNi_5 compounds are plotted as function of $\sum n_i M_i$, the data are situated on the same curve as that evidenced in $YCo_{4-x}Ni_xB$ system – Fig. 8. The above behaviour can be correlated with the fact that the $CaCu_5$ and $CeCo_4B$–type structures, are strongly related, as already discussed. In addition, the same behaviour can be shown for both 4d and 5d bands polarizations.

The exchange interactions of 4f–5d–3d type influence both 3d moments, through local 4f–5d and short range 5d–3d exchange interactions, and in addition there is an induced polarization at 5d or 4d bands. In case of Y-based compounds, where Y is nonmagnetic, there is only 4d band polarization induced by 3d–4d short range exchange interactions.

5. Conclusions

Band structure calculations performed on rare-earth and yttrium compounds with M = Co and Ni show a rather good agreement between computed and experimentally determined magnetizations. The cobalt and nickel moments are sensitive to the exchange interactions. For a critical field of 70 T and 40–50 T, a transition from nonmagnetic to magnetic state was shown for Co and Ni, respectively. The R5d band polarizations in compounds with magnetic rare-earths are due both to local 4d–5d and 5d–3d short range exchange interactions. Both 5d and 4d band polarizations resulting from short-range interactions follow the same trend as function of the number of neighbouring M atoms ad their magnetic moments.

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