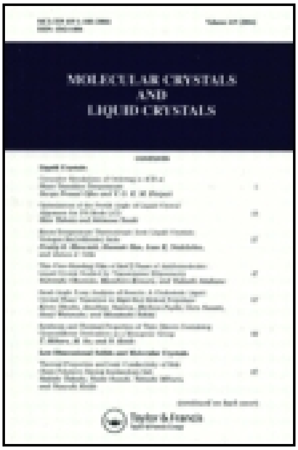

Molecular Crystals and Liquid Crystals

Rare-Earth Based Materials: Electronic Structures and Magnetic Properties

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Version of record first published: 18 Oct 2010

To cite this article: Burzo* (2004): Rare-Earth Based Materials: Electronic Structures and Magnetic Properties, Molecular Crystals and Liquid Crystals, 417:1, 7-28

To link to this article: http://dx.doi.org/10.1080/15421400490478489

Mol. Cryst. Liq. Cryst., Vol. 417, pp. 7/[491]–28/[512], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478489

RARE-EARTH BASED MATERIALS: ELECTRONIC STRUCTURES AND MAGNETIC PROPERTIES

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The electronic structures and magnetic properties of some rare-earth-transition metal compounds having technical interest is analyzed. The exchange interactions of 4f-5d-3d type is discussed in correlation with crystal structure and transition metal partner. The contributions to 5d band polarization due to local 4f-5d and short-range 5d-3d exchange interactions are estimated. Finally we analyze the magnetic behaviour of transition metals in rare-earth compounds.

1. INTRODUCTION

The rare-earth (R)-transition metal (M) compounds form an interesting group of magnetic materials with large technical applications [1]. The 4f electrons of rare-earths have a small spatial extent and generally one can assume that they are localized. On the other hand, there are 3d electrons of transition metals which give rise to typical itinerant magnetism with a wide range of magnetic behaviours. As function of crystal structure and composition, these cover the situation in which M atoms show a well defined magnetism or are in nonmagnetic state crossing the region of onset/collapse of magnetism. Well defined magnetism of 3d metals can be evidenced in compounds which are used for manufacturing permanent magnets (R_2Co_{17}, RCo_5) or magnetostrictive devices (RFe_2). The high Curie temperatures of these compounds are mainly determined by the magnetic interactions involving cobalt and iron. The magnetic coupling between magnetizations of 3d elements and rare-earths allows that a significant fraction of the anisotropy or magnetostriction, characteristic of R ions at low temperatures, to be preserved at room temperatures, determining their technical use.

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The RNi_5 compounds can be used as hydrogen storage materials. In these compounds nickel is nonmagnetic, as in $LaNi_5$, or has a very weak moment as in compounds with magnetic rare-earths [1]. In this case, the transition of nickel from nonmagnetic to magnetic state can be studied. This type of analysis for cobalt magnetism may be made on $R_{n+1}Co_{3n+5}B_{2n}$ series, having the compositions: $n = 0$ (RCo_5), $n = 1$ (RCo_4B), $n = 2$ ($R_3Co_{11}B_4$), $n = 3$ ($R_2Co_7B_3$) and $n = \infty$ (RCo_3B_2).

The RM_5 compounds crystallize in a hexagonal $CaCu_5$-type structure (P6/mmm space group). In this structure R atoms occupy only one type of site (1a) and M atoms are situated in 2c and 3g sites. The R_2M_{17} compounds crystallize both in a hexagonal structure having $P6_3/mmc$ – space group or in a rhombohedral structure of $R\overline{3}m$ space group. The crystal structures of $R_{n+1}Co_{3n+5}B_{2n}$ compounds can be considered as being build up by alternative stacking of one layer of RCo_5 and n layers of RCo_3B_2 unit cells. All these compounds have P6/mmm space group. In these structures, R, Co and B atoms are distributed on different crystallographic sites having different number and nature of nearest neighbours. The M atoms situated in different positions are expected to have different magnetic contributions. By magnetic measurements, only the mean values of M moments may be obtained. Experimentally, only neutron diffraction studies may give information between correlation of magnetic moments and their environments. Band structure calculations also can give the values of the magnetic moments in various lattice sites.

The RM_2 compounds crystallize in a cubic $MgCu_2$-type structure in which both R and M atoms occupy each only one type of site. For this reason the above system is more suitable for theoretical analysis of the magnetic behaviour.

The magnetic moments of R and M atoms are parallely coupled in light rare-earth – and antiparallel in heavy rare-earth-compounds. Some models have been developed in order to describe the magnetic interactions between R and M atoms. In earlier reports, the magnetic interactions between R and M atoms have been assumed to be of RKKY-type [1]. Some works have been done in order to reverse the antiparallel R-M coupling in heavy rare-earth compounds by changing the electron concentration and the distances between magnetic atoms [3]. No effects on the magnetic coupling has been reported. Campbell [4] proposed a phenomenological model in which the 4f electrons of rare-earths polarize their 5d band by local interactions and there are short-range 5d-3d interactions of R with neighbouring transition metal atoms. The Campbell [4] and RKKY [3] models describe two extreme types of exchange interactions. The first one, takes into account short-range exchange interactions while the second one is of long-range and oscillatory type. The RKKY model seems to be incompatible with the antiparallel coupling between

4f and 3d spins but this coupling can be well described in terms of 3d-5d hybridization.

In this paper we present, comparatively, the experimentally determined magnetic moments of heavy rare-earth transition metal compounds and those obtained from band structure calculations. The local 4f-5d as well as the short range 5d-3d exchange interactions are analyzed. The peculiar case, when the cerium 4f states are in band, is also presented. The effect of exchange interactions on transition metal moments will be analyzed in $Gd_xY_{1-x}Co_{3n+5}B_{2n}$ and $(Gd_xLa_{1-x})Ni_5$ compounds. Finally, the magnetic behaviour of transition metals in rare-earth compounds is discussed.

2. EXPERIMENTAL AND COMPUTING METHOD

The compounds were prepared in an induction furnace in purified argon atmosphere. The cobalt and iron compounds were thermally treated in vacuum, at 1000°C, and the nickel ones at 950°C, for one weak. The X-ray analyses show the presence of only one phase having crystal structures previously reported [1].

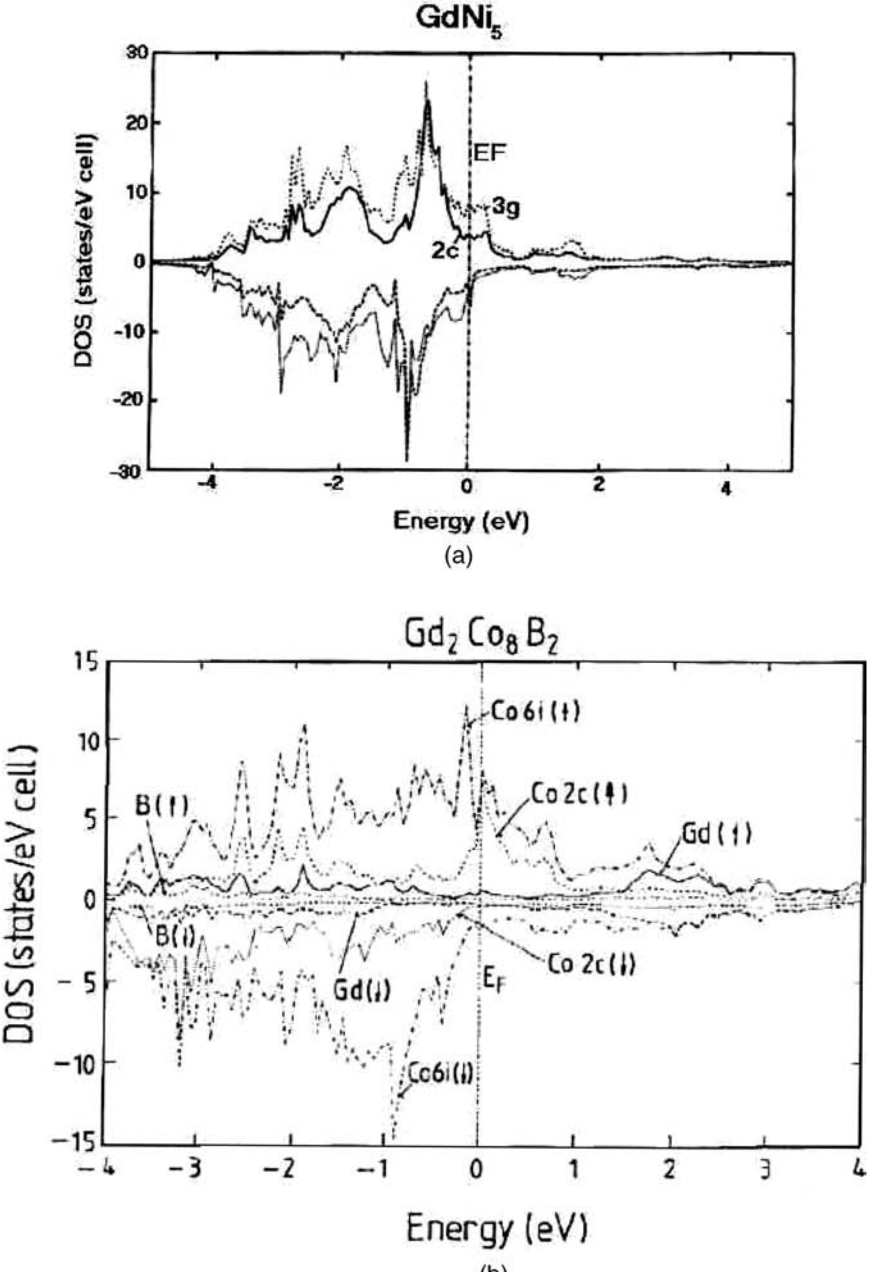
Magnetic measurements were performed in the temperature range 1.7(4.2) – 1000 K and fields up to 9 T. Because of high anisotropy of compounds with non-S state rare-earths, the saturation magnetizations, M_s, were obtained according to approach to saturation law $M = M_s(1 - a/H)$, by extrapolating the measured values M to $H^{-1} \to 0$. By a we denoted the magnetic hardness coefficient. The magnetic behaviour of the compounds were studied also in the paramagnetic range.

Band structure calculations were carried out by using the ab initio tight-binding linear muffin tin orbital method in the atomic sphere approximation. The detailed procedure of calculation was described elsewhere [5]. In the framework of the local density approximation (LDA) the total electronic potential is the sum of external, coulomb and exchange correlation potentials [6]. The functional form of the exchange correlation energy used in the present work was the free electron parametrization of Von-Barth and Hedin [7]. Relativistic correlations were included. All the calculations were performed by using the experimental lattice constants. Some computed band structures are plotted in Figure 1.

3. ELECTRONIC STRUCTURES AND MAGNETIC PROPERTIES

3.1. Magnetic Moments

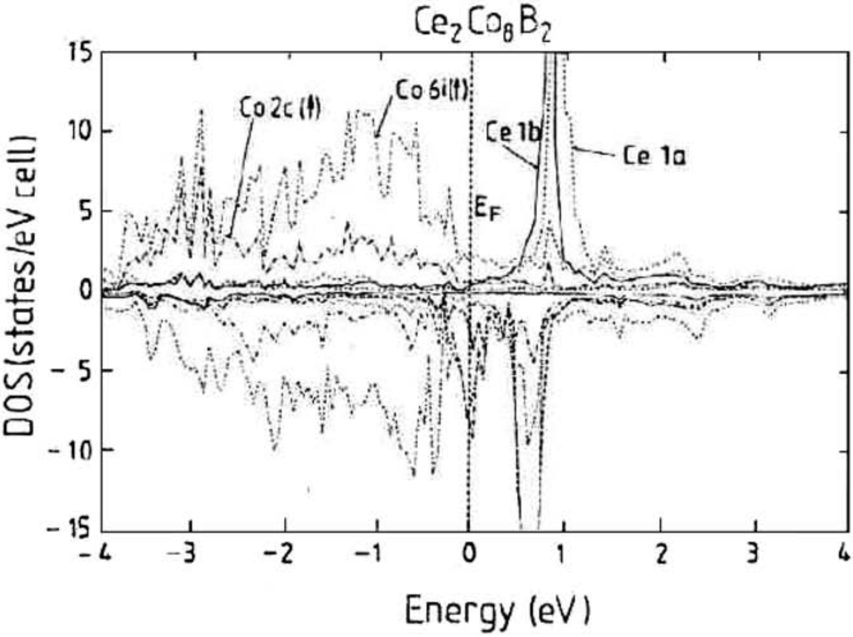
The composition dependences, of the saturation magnetic moments per formula unit in R_2Co_{17}, R_2Ni_{17}, RFe_2 and RCo_2 where R is a heavy



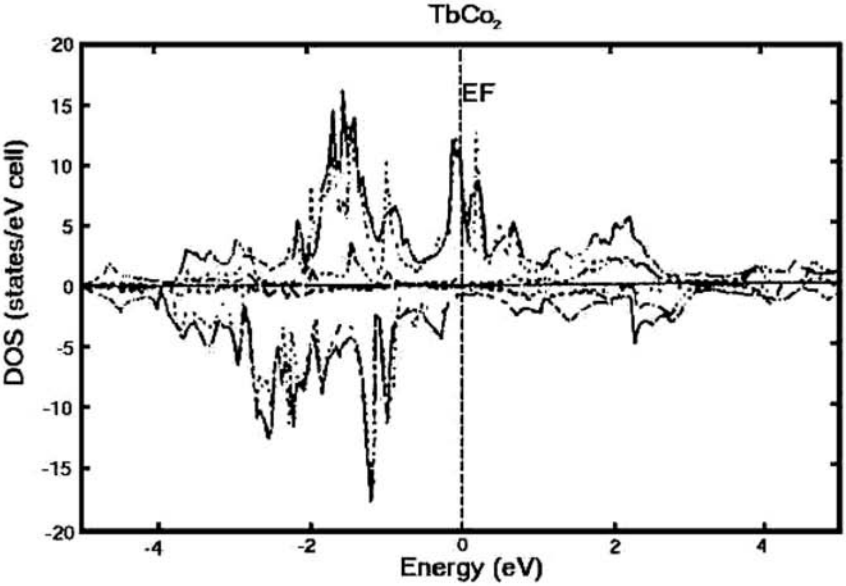
(a)

(b)

FIGURE 1 The density of states for $GdNi_5$ (a), $GdCo_4B$ (b), $CeCo_4B$ (c) and $TbCo_2$ (d).



(c)



(d)

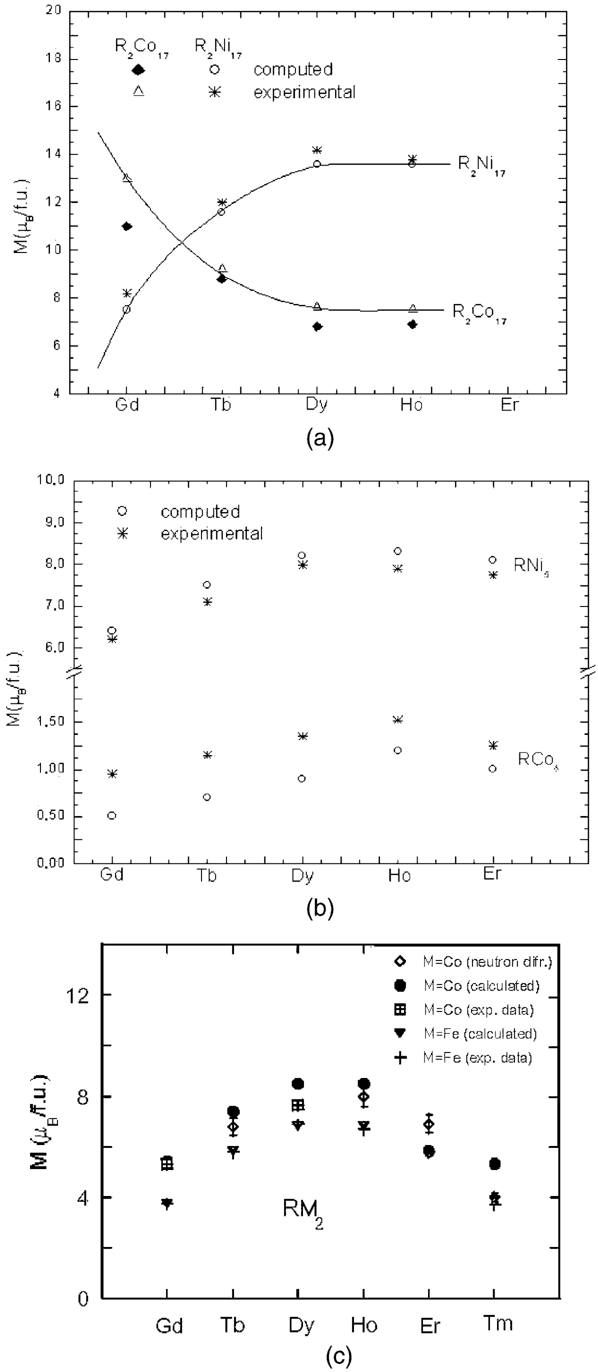
FIGURE 1 Continued.

rare-earth are plotted in Figure 2. On the same figures are given the magnetizations obtained by band structure calculations. There is a good agreement between the two sets of data showing that the calculated values describe well the real situation.

The cobalt moments, M_{Co}, in various sites, in case of R_2Co_{17} and RCo_5 systems are practically not dependent on the rare-earth partner. The M_{Co} values in these compounds show a rather localized behaviour. The variations of nickel moments in rhombohedral R_2Ni_{17} and hexagonal RNi_5 [8] compounds are shown in Figure 3. These values can be correlated with their local environments, exemplified for RNi_5 compounds. The magnetic moments of Ni(3g) sites are higher than in Ni(2c) sites. The 2c site in RNi_5 has 6Ni(3g) and 3Ni(2c) atoms as well as 3R ones, while the 3g sites have 4Ni(2c), 4Ni(3g) and 4R as nearest neighbours. The strength of exchange interactions between nickel and gadolinium are more important than between nickel atoms. The nickel moments are essentially induced by the exchange interactions due to presence of magnetic rare-earths. Thus, the exchange splitting of Ni(2c) 3d band is greater than for Ni(3g) sites since of higher number of magnetic R nearest neighbours. For a given lattice site, the variation of nickel moments are of the order of 8% in $ErNi_5$ as compared to $GdNi_5$. We note that $LaNi_5$ is paramagnetic in all temperature range.

The magnetic moments of atoms in various lattice sites, in case of $R_{n+1}Co_{3n+5}B_{2n}$ compounds with R = Gd or Y, are listed in Table 1. From these data can be seen that the cobalt moments, for a given rare-earth or yttrium compound, decrease as boron content increase. Also, in Gd compounds the cobalt moments are higher than in yttrium ones. This fact may be attributed to the increase of exchange interactions when replacing nonmagnetic Y by magnetic Gd [9].

The magnitude of cobalt moment for a given compound may be analyzed by extending a mixing model proposed by Kanamori [10]. As example, we discuss the case of $Gd_3Co_{11}B_4$. In Figure 4 we plotted the relative positions of the centers of gravity for Gd5d, Co3d and B2p states. The Co(6i) atomic layer is located between the ones containing B(4h) and Co(2c) atoms. Due to the mixing of 3d(6i) states with B2p and Gd5d (1e, 2e) states the center of gravity for local DOS shift to the lower energy for Gd5d (1a, 2e) and Co3d (6i, 3g) and to higher energy for B2p. Mixing of Co3d(2c) with Gd5d (1a, 2e) and Co3d (6i, 3g) states shifts the center of gravity for local DOS to lower energy for Gd (1a, 2e) and Co3d (6i, 3g) and to higher energy for Co3d(2c) states. Since of characteristic sites of B atoms, as above mentioned, the electrons "flow" into Co(6i) and Co(3g) from neighbouring B atoms because B2p states shift to higher energy. Since the majority spin band is full, the minority spin band occupation increase and the difference between the populations of majority spin band and the minority one



(a)

(b)

(c)

FIGURE 2 Composition dependences of the saturation magnetic moments per formula unit in heavy rare-earth compounds R_2Co_{17}, R_2Ni_{17} (a), RCo_5, RNi_5 (b), RFe_2 and RCo_2 (c).

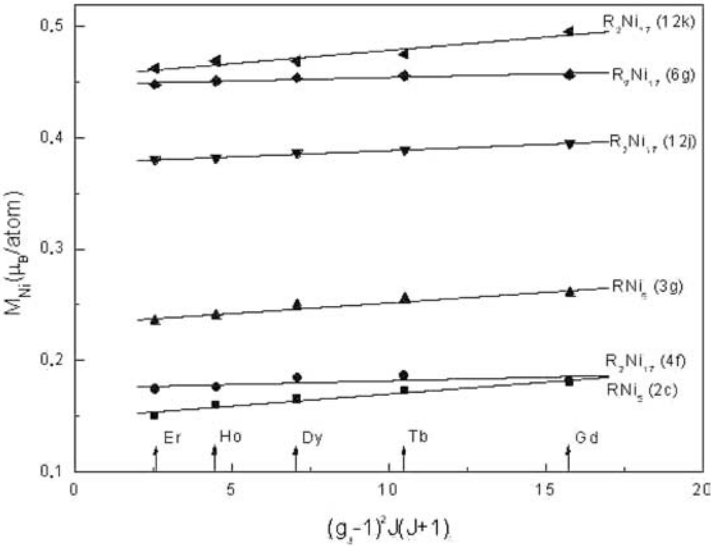


FIGURE 3 The nickel moments as function of De Gennes factor in R_2Ni_{17} (rhombohedral) and RNi_5 (hexagonal) compounds.

diminishes and the magnetic moments of Co(6i) atoms becomes smaller. The local moments of Co(2c) site in compounds with $n \geq 1$ is larger than that in case of $GdCo_5$ compound. As mentioned above, the center of gravity for Co(2c) sites shifts toward higher energy. Some electrons of Co(2c) sites

TABLE 1 Magnetic Moments of Cobalt in Gd and Y Compounds and the Gd5d and Y(4d) Band Polarizations

	M_{5d} or M_{4d} (μ_B)			M_{Co} (μ_B/atom)				
Compound	1a	1b	2e	2c	3g	6i	$6i_1$	$6i_2$
$GdCo_5$	−0.53			1.51	1.46			
YCo_5	−0.29			1.40	1.39			
$GdCo_4B$	−0.49	−0.38		1.63		0.77		
YCo_4B	−0.23	−0.13		1.43		0.60		
$CeCo_4B$	−0.53	−0.42		1.35		0.44		
$Gd_3Co_{11}B_4$	−0.41	−0.34		1.71	0.14	0.65		
$Y_3Co_{11}B_4$	−0.15	−0.11		1.63	0.09	0.52		
$Gd_2Co_7B_3$	−0.39	−0.23	−0.32	1.71			0.61	0.14
$Y_2Co_7B_3$	−0.11	0	−0.08	1.61			0.47	0.06
$GdCo_3B_2$	−0.20				0.1			

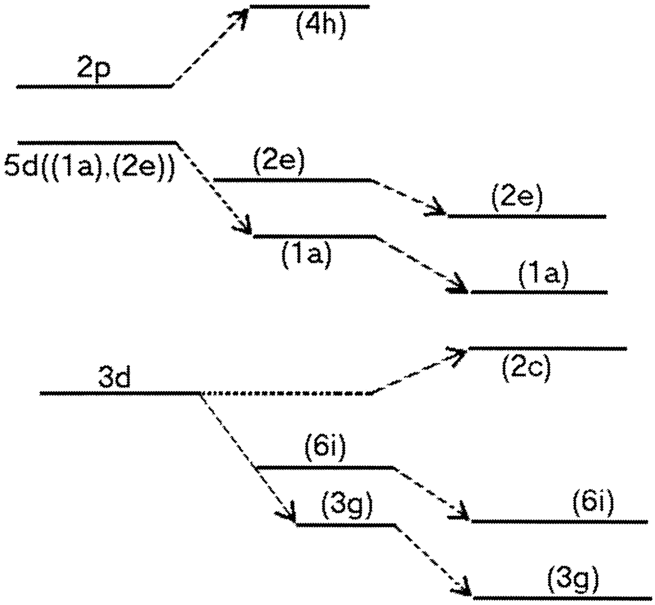


FIGURE 4 Schematic representation of mixing between Co3d, Gd(5d) and B2p states in $Gd_3Co_{11}B_4$ compound.

flow out decreasing the number of electrons with minority spin (majority spin band being full). Therefore, the magnetic moments of Co(2c) sites in compounds with n = 1 will become larger compared to that in $GdCo_5$.

The dependences of Fe, Co and Ni computed moments in RM_2 compounds, as function of De Gennes factor, are plotted in Figure 5. In these systems nickel moments are nil.

3.2. R5d Band Polarization

The R5d band polarizations as function of De Gennes factor, for R_2Ni_{17}, RCo_5 and RNi_5 where R is a heavy rare-earth are given in Figure 6, and those computed in case of RM_2 compounds are plotted in Figure 7. There are linear variations which can be described by the relation:

$$M_{5d} = M_{5d}(0) + \alpha G \tag{1}$$

where G is the De Gennes factor $G = (g_J - 1)^2 J(J+1)$.

For a given series of compounds, as R_2M_{17} with M = Fe, Co, Ni, RM_2 (M = Fe, Co, Ni) systems or RM_5 (R = Co, Ni) compounds, the polarizations as function of De Gennes factor, are described by the same α

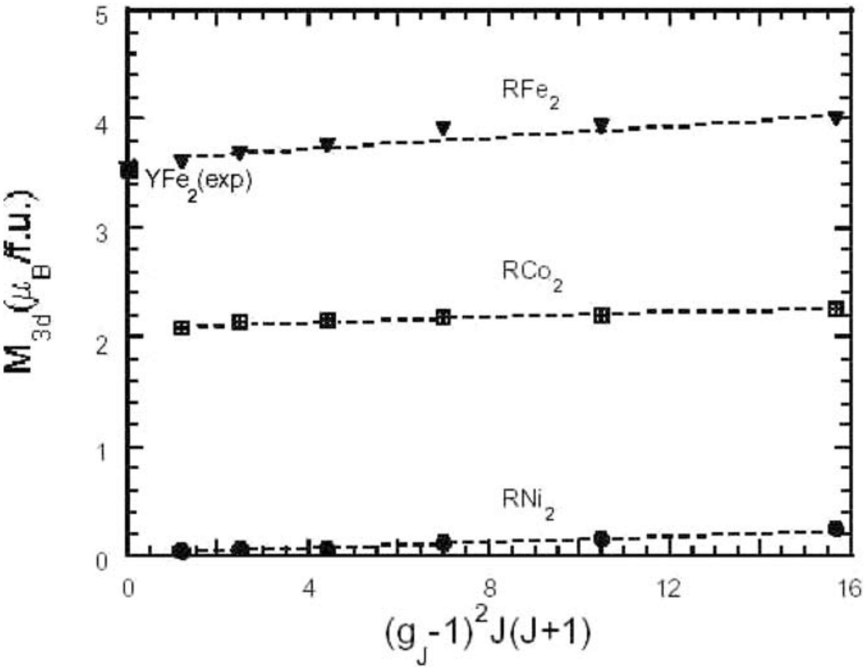


FIGURE 5 The dependence of Fe, Co and Ni computed moments in RM_2 compounds on the De Gennes factor.

slope. Values $\alpha = 2.1 \cdot 10^{-2}$ μ_B, $1.4 \cdot 10^{-2}$ μ_B and $1 \cdot 10^{-2}$ μ_B were evidenced in RM_2, RM_5 and R_2M_{17} compounds, respectively.

The analysis of the above data suggests the presence of two contributions to the 5d band polarization. The first one may be attributed to a local 4f-5d exchange. This contribution is identical for a given rare-earth, in the same structure-type. The second one $M_{5d}(0)$ is dependent on the magnetic contribution of M partner and can be evidenced in compounds with non-magnetic rare-earth, as for example $LaCo_5$. As seen in Figure 6 the $M_{5d}(0)$ value for $LaCo_5$ is the same as that obtained by extrapolation of observed trend to G = 0. It is interesting to note, that for a given series, the ratio $m = M_{5d}(0)/M_M$ where the M_M is the magnetization of transition metals corresponding to one R atom depends on crystal structure. The n values are 0.12, 0.04 and 0.025 for RM_2, RM_5 and R_2M_{17} compounds.

The $M_{5d}(0)$ band polarizations for different R sites, as example in $R_{n+1}Co_{3n+5}B_{2n}$ compounds are different. This behaviour may be correlated with short range exchange interactions of 5d-3d or 5d-5d types with next neighbourings atoms to a given site. In order to analyze the $M_{5d}(0)$

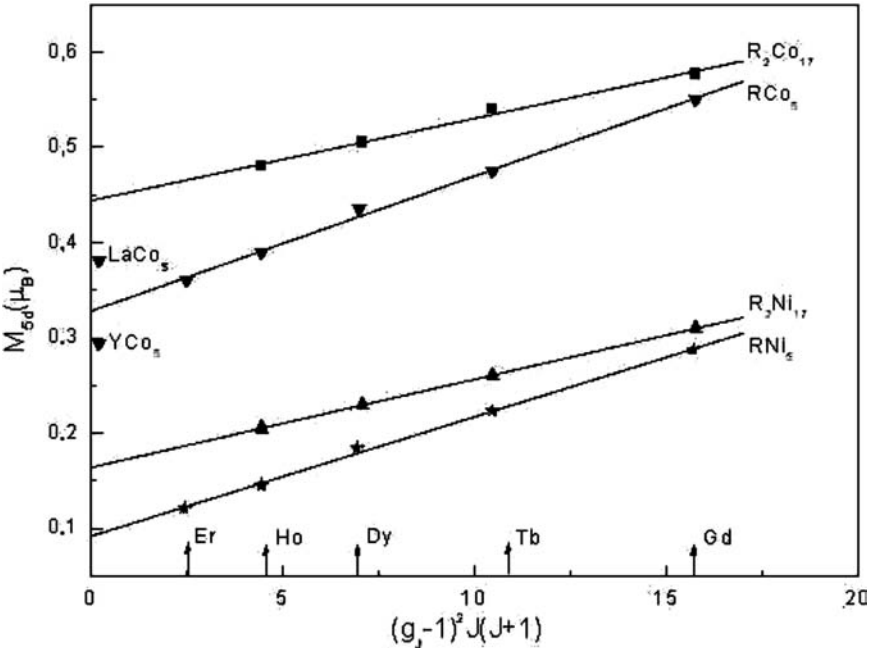


FIGURE 6 The R5d polarizations in RNi_5 and R_2Ni_{17} heavy rare-earth compounds as function of De Gennes factor.

contributions, as result of short-range exchange interactions, we consider the Hamiltonian:

$$\mathcal{H} = 2\sum_{i} J_{3d_i-5d}S_{5d}(0)\sum_{n_i} S_{3d_i,n_i} - J_{5d-5d}S_{5d}(0)\sum_{j} S_{5d_j}(0) \tag{2}$$

We denoted by i the number of sites occupied by M atoms, n_i is the number of neigbouring M atoms to a given R site and j is the number of R neigbouring atoms to a given R.

The 3d-5d and 5d-5d exchange interactions act as an internal field, H_{exch} and increase the 5d band polarization [11]. In the molecular field approximation, the exchange field can be written as $H_{exch} = N_{5d\text{-}3d}M_{3d} + N_{5d\text{-}5d}M_{5d}$, where $N_{5d\text{-}3d}$ and $N_{5d\text{-}5d}$ are the molecular field coefficients describing the R_{5d}-M_{3d} and R_{5d}-R_{5d} exchange interactions. For cobalt compounds we have $N_{5d\text{-}3d} > N_{5d\text{-}5d}$ and $M_{3d} \gg M_{5d}$. As a result, the second term in the expression of exchange field can be neglected. For nickel compounds $N_{5d\text{-}3d} \cong N_{5d\text{-}5d}$. Thus, in both cases, the exchange field can be written $H_{exch} = \alpha M_d$, where $M_d = M_{3d} + M_{5d}$ is the total d magnetization per formula unit. As seen from Figure 8, there is a linear dependence of $M_{5d}(0)$

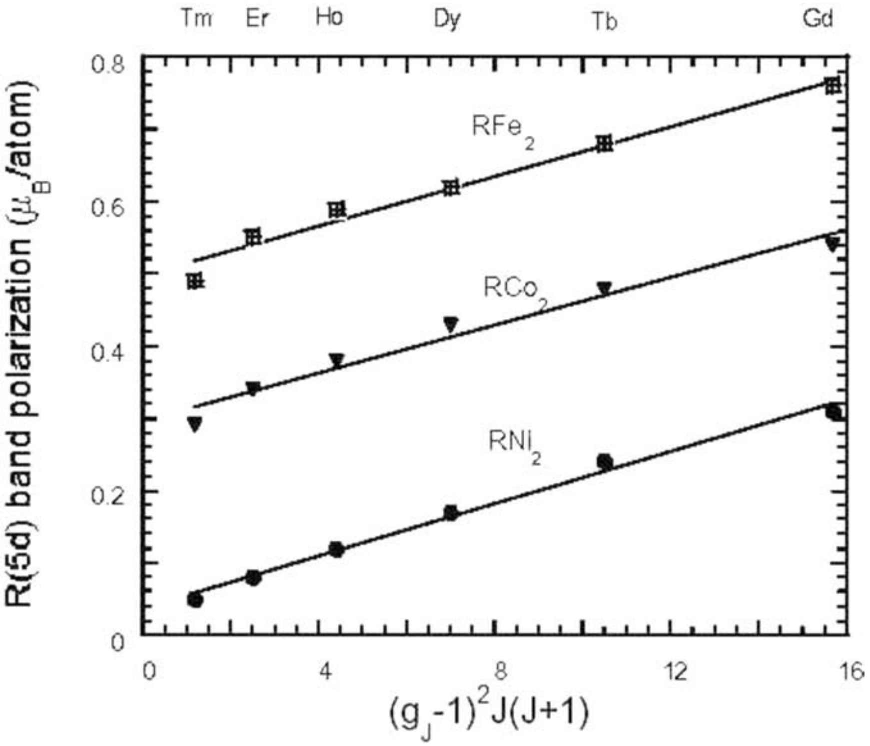


FIGURE 7 The R5d band polarizations in RM_2 compounds as function of De Gennes factor.

on M_d in one of RM_5 and their derivative structure RCo_4B with a slope $\alpha \cong 0.04$. This slope is close to that given by the ratio between $M_{5d}(0)$ and $M_{3d}(0)$ evidenced in RM_5 compounds. This shows that the different contributions to polarizations, $M_{5d}(0)$ induced by short-range exchange interactions, are close related to the number and nature of atoms situated in next neighbourhood of a given R site.

A peculiar case of 5d and 4f bands polarizations can be observed in $CeCo_4B$ compound [12]. In this case the Ce4f states are in band – Figure 1. The computed cerium moments at 1a and 1b sites are antiparallel oriented to the cobalt ones and depends a lattice sites. The difference between the polarizations of Ce1a and Ce1b is $\sim 0.11\,\mu_B$, the same as that evidenced for the corresponding Gd sites in $GdCo_4B$ – Table 1. The induced polarization on Ce site is antiparallel oriented to cobalt moments, differing from the general rule that light-rare earth-transition metal compounds are ferromagnetic. The presence of an additional 4f

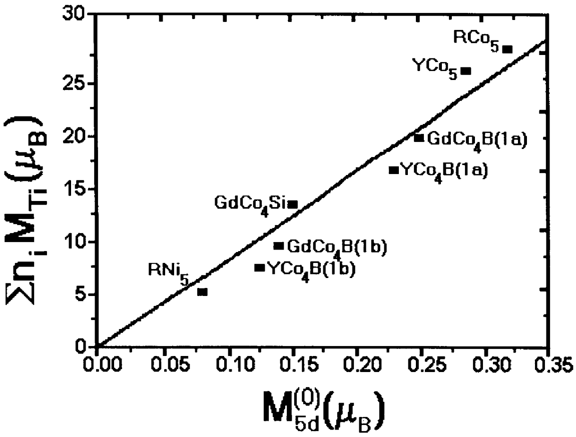


FIGURE 8 The $M_{5d}(0)$ contributions to 5d band polarization due to 5d-3d short range exchange interactions as function of the $\sum_i n_i M_{M_i}$ where n_i is the number of neighbouring atoms having M_{M_i} magnetic moments.

polarization leads to Ce(4f + 5d) induced polarizations higher than that on Gd(5d) in RCo_4B type structure, although the nearest neighbour Co atoms to R site have smaller magnetic contributions.

3.3 Band Structure and Bonding

The band structures and bonding in RNi_5 compounds were analyzed in terms of projection of the bands onto orthogonal orbitals [13]. The "fat" band representation was considered. A local coordinate system was used in which for Ni(2c), Ni(3g) and La, Gd(1a) the z axis is parallel to **c**-axis. For Ni(2c) the x-axis is along the shortest Ni(2c)-Ni(2c) distance and for Ni(3g) the y-axis is parallel to **a**-axis [14]. In Figure 9 the band structures are projected onto the orthogonal LMTO's [5] or equivalently, partial waves normalized to unity in their respective spheres. The zero of the energy is taken at the Fermi level. In such a "fat" band structure, each band is given a width proportional to the (sum of the) weight (s) of the corresponding orthonormal orbital (s).

In case of La site, in $LaNi_5$, the dominant 5d-5d hybridization are between $d_{3z^2\text{-}1}$ orbitals with lobes pointing along **c**-axis, which leads to decorated (fat) bands. The bands are strongly dispensed in K-Γ and Γ-A directions. Important interactions are between almost all the projected orbitals of nickel. As example for Ni 2c site in $LaNi_5$, d_{xy} orbitals create "fat" bands at –1 eV below the Fermi level. In $GdNi_5$ "fat" bands are created at the Fermi level for $d_{3z^2-1} \downarrow$ orbitals and for $d_{3z^2\text{-}1} \uparrow$ orbitals at 0.4 eV above the Fermi level along A-L direction.

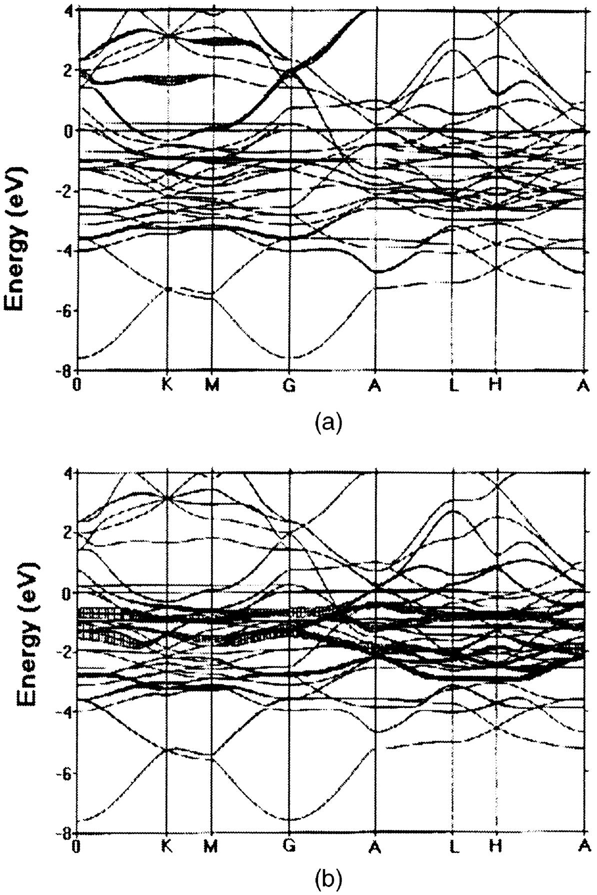


FIGURE 9 Energy bands of $LaNi_5$ and $GdNi_5$ decorated with orthogonal orbital character: (a) $La5d_{3z^2\text{-}1}$, (b) Ni(2c) in $LaNi_5(d_{xy})$; (c, d) Ni(3g) in $GdNi_5$ d_{3z^2-1} ↓, d_{3z^21} ↑

3.4 Induced Transition Metal Moments

The M = Fe, Co and Ni moments in rare-earth compounds are dependent on crystal structure, composition and rare-earth partner. In order to analyze the correlation between M magnetic moments and the exchange interactions, determined by the above mentioned reasons, we used the molecular field approximation. Generally, we considered for heavy rare-earth compounds a ferrimagnetic type ordering, the R and M moments being antiparallel oriented. A mean magnetic moment was considered for both magnetic sublattices. The molecular field coefficients N_{ij} characteri-

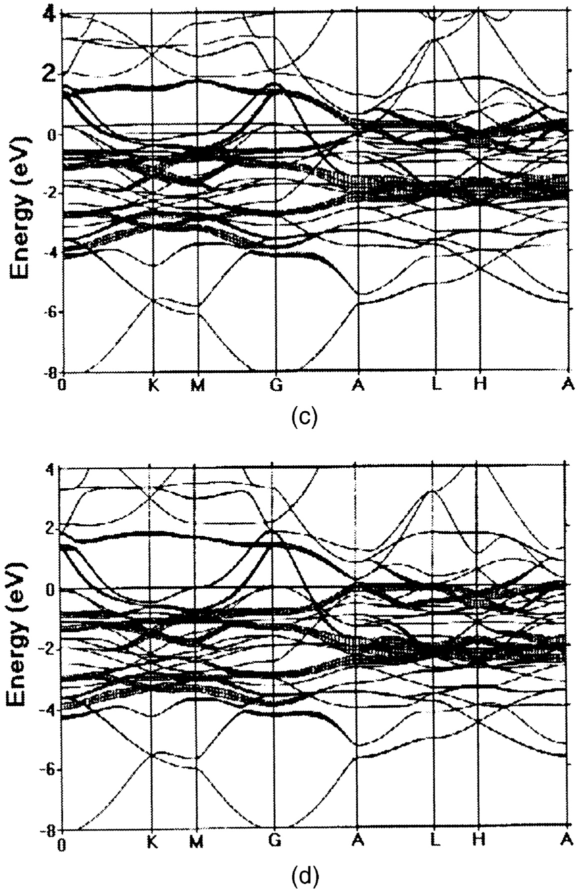


FIGURE 9 Continued.

zing the exchange interactions inside and between magnetic sublattices were evaluated from temperature dependences of magnetizations and of magnetic susceptibilities. By using the N_{ij} values, we computed the exchange field acting on transition metal atoms. The magnetic rare-earth were replaced by nonmagnetic Y or La in order to change the strength of the exchange interactions.

The iron moments, at 4.2 K, increase only little when replacing Y by Gd in $(Gd_xY_{1-x})Fe_n$ compounds with $n = 2$, 3 and 8.5 or $(Gd_xY_{1-x})_2Fe_1B$ system. The induced iron moments, ΔM_M, can be described by relation [15].

$$\Delta M_M = \beta \Delta H_{exch} \tag{3}$$

where ΔH_{exch} is the variation of exchange field and $\beta = (1/18)10^{-6}$ μ_B/Oe. This shows a weak sensitivity of iron moments to exchange interactions.

The cobalt, unlike iron, shows a wide range of magnetic behaviours in rare-earth compounds. Rather localized Co moments can be seen in RCo_5 and R_2Co_{17} compounds. In these systems the cobalt moments are little dependent on the exchange interactions. In case of RCo_2 or $R_{n+1}Co_{3n+5}B_{2n}$ compounds, as function of R partner and/or composition, a transition from nonmagnetic to magnetic state can be observed [16]. The mean moments at 4.2 K, as for example in $(Gd_xY_{1-x})_{n+1}Co_{3n+5}B_{2n}$ compounds, are plotted in Figure 10. There are significant differences between M_{Co} values in Y and Gd compounds. YCo_3B_2 is nonmagnetic, while a cobalt moment was observed in $GdCo_3B_2$.

The mean cobalt moments, M_{Co} as function of exchange fields are plotted in Figure 11. There is a small increase of M_{Co} values up to a field $\mu_o H_{cr} \cong 70$ T, when a sudden increase is observed. Then, the cobalt moments depend linearly on the exchange field, according to relation (3) with $V_{Co} = (1/3)10^{-6}$ μ_B/Oe and finally saturate. The observed trend

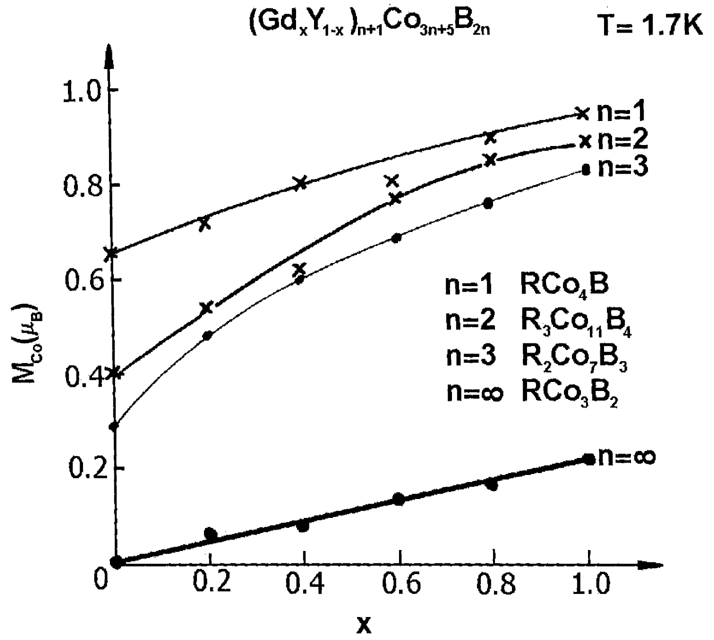


FIGURE 10 Composition dependences of the cobalt moments at 1.7 K in $(Gd_xY_{1-x})_{n+1}Co_{2n+5}B_{2n}$ compounds.

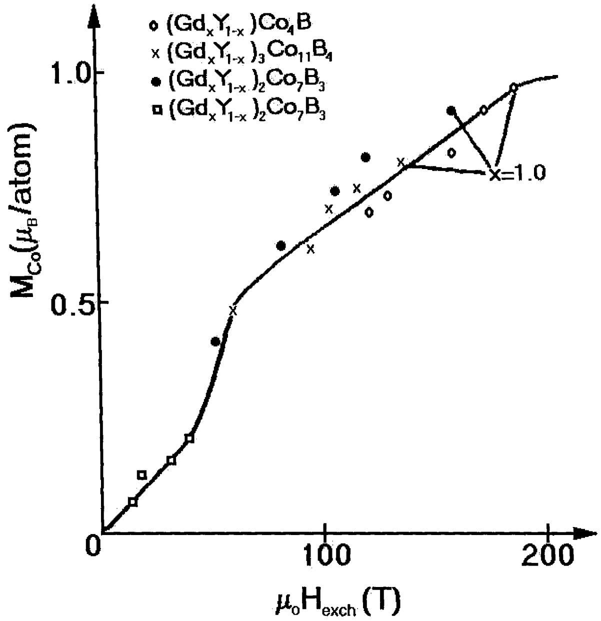


FIGURE 11 Mean cobalt moments in $(Gd_xY_{1-x})_{n+1}Co_{2n+5}B_{2n}$ compounds as function of the exchange fields.

was called itinerant electron metamagnetism [18] or induced magnetism [19]. The observed behaviour was related to the appearance of the cobalt moments as result of a sudden splitting of Co3d states for a critical exchange field value. Then a gradually increase of splitting energy, proportional to the exchange field is suggested by band structure calculation. The same type of behaviour can be observed in $(Gd_xLa_{1-x})Ni_5$ compounds, where the correlation between Ni moments and exchange splitting energies of 3d band, at 2c and 3g sites are plotted – Figure 12. As for cobalt, there seems to be a critical value of the exchange splitting energy $E_{ex} \cong 0.005$ eV at which a nickel moment will appear. Then a linear increase of Ni moments can be observed. The above critical exchange splitting energy corresponds to critical field of $\mu_oH_{exch} = 50 - 60$ T, somewhat smaller than in case of cobalt compounds. The same analysis performed in molecular field approximation, by considering a mean nickel moment, shows a linear dependence of M_{Ni} vs H_{exch}, above a critical value $\mu_oH_{exch} \cong 30$ T. The difference for H_{exch} values in the above analyses may be attributed to the fact that in first case, the local moments at 2c and 3g sites, determined by band structure calculations, were take into account and in the second one mean values were considered. Also, there can be

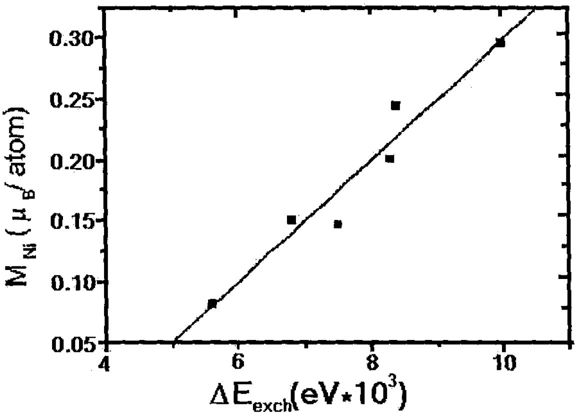


FIGURE 12 The correlation between computed Ni magnetic moments at 2c and 3 g sites in $Gd_xLa_{1-x}Ni_5$ and exchange splitting energy of their 3d bands.

some errors in evaluating the molecular field coefficients from experimental data. In spite of these approximations the two sets of data are in reasonable agreement.

We performed also paramagnetic measurements on a greater number of compounds. In compounds which show an exchange enhanced paramagnetism, the magnetic susceptibilities follow, at low temperatures, a T^2 dependence. This trend changes, above a characteristic temperature T^*, to a Curie-Weiss-type behaviour. The effective moments, determined from Curie constants depends on the exchange enhancement factor as evidenced in $Y(Co_xA_{1-x})_2$ systems with A = Ni, Si [20] or $La(Ni_xA_{1-x})_5$ with A = Cu, Al [21]. For magnetic rare-earth transition metal compounds, the effective 3d moments are higher than the moments determined at 4.2 K. As example, in Figure 13 we plotted the composition dependence of the effective cobalt moments, $M_{eff}(Co)$ in $(Gd_xY_{1-x})_{2n}Co_{3n+5}B_{2n}$. The $M_{eff}(Co)$ values, for a given series, are little dependent on composition. Values $M_{Co} = 2.50(10)$ μ_B $(n = 1)$, $2.30(20)$ μ_B $(n = 2,\ 3)$ and 1.32 μ_s $(n = \infty)$ were obtained.

Previously [22], was shown that the ratio between the number of spins, S_p, determined from effective M moments and S_o determined from saturation data is dependent on the Curie temperature and was considered as a measure of itinerancy. In Figure 14 we plotted the $r = S_p/S_o$, values as function of reciprocal exchange fields for a number of cobalt, nickel and iron compounds. In the range of exchange field $05 \cdot 10^2$ T $\leq H_{exch} \leq 3 \cdot 10^2$, the r values show a linear dependence on the exchange field. This fact evidence a strong correlation between the degree of itinerancy of transition metal atoms and the exchange fields.

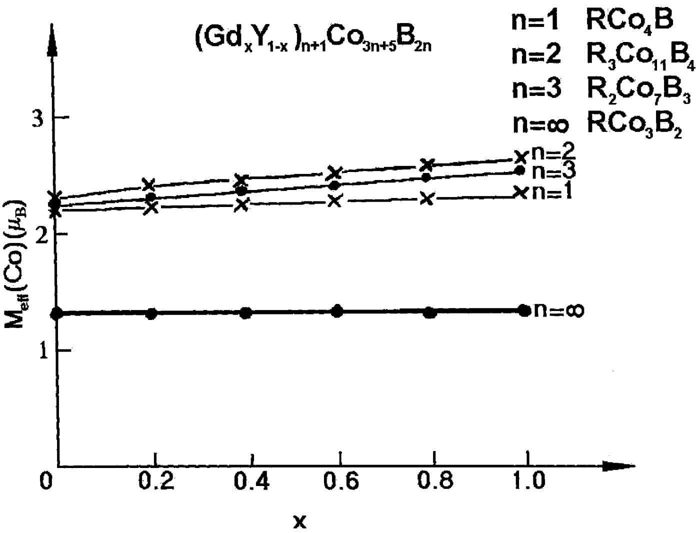


FIGURE 13 Composition dependences of the effective cobalt moments in $(Gd_xY_{1-x})_{n+1}Co_{3n+5}B_{2n}$ compounds.

The magnetic behaviour of transition metals in rare-earth compound may be analyzed by considering models that take into account the electron correlation effects in d band as a spin fluctuation model [23] or dynamical mean field theory [24]. These models reconcile the dual character of the electron which, as a particle, requires a real space description and as a wave, a momentum space description. The spin fluctuation model considers the balance between the frequencies of longitudinal spin fluctuation, which are determined by their lifetime and of transverse fluctuations that are of thermal origin. These effects lead to the concept of temperature induced moments. For a weakly or nearly ferromagnet, as Co or Ni in rare-earth compounds, the wave number dependent susceptibility χ_q has a large enhancement due to electron-electron interaction for small q values. The χ_q shows a significant temperature dependence only for q values close to zero. The average amplitude of spin fluctuations $\langle S_{loc}^2 \rangle = 3k_B T \sum_q \chi_q$ increases with the temperature and reaches an upper limit at a temperature T*. For $T > T^*$, a Curie-Weiss behaviour is predicted, similar to a system having local moments. These moments are localized in a q space.

The spin fluctuations can be gradually quenched by internal field when the exchange interactions increase [25]. The nearly constant effective cobalt moments for a given series, as for example in

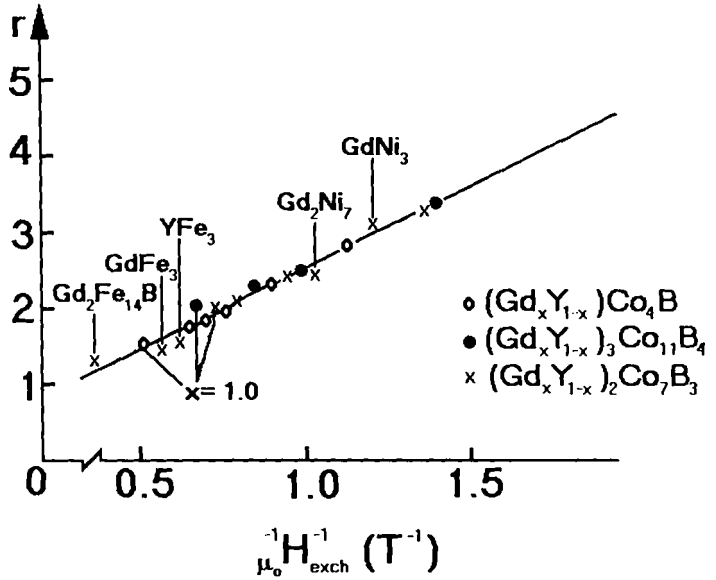


FIGURE 14 The ratio $r = S_p/S_o$ in some intermetallic compounds as function of exchange field.

$(Gd_xY_{1-x})_{n+1}Co_{3n+5}B_{2n}$ compounds, may be the result of two opposite mechanisms. The first is a gradual quenching of spin fluctuations by internal field when Gd content increases. This behaviour was reported in RCo_2 compounds and is evidenced by a decrease of the effective cobalt moments when increasing the exchange field [25]. For compounds with high Gd content there is also an additional exchange splitting of Co(3d) band which may increase the cobalt moment. This tendency seems to be counterbalanced by gradual quenching of spin fluctuations. Consequently, it is expected only small variations of the effective cobalt moments along the series.

The magnetic behaviour of transition metals in rare-earth compounds may also be analyzed in the dynamical mean field theory (DMFT) combined with standard LDA band calculation (LDA + DMFT) [24,26]. In a strongly correlated system, leading Curie-Weiss behaviour, at high temperatures, is predicted. For an itinerant electron system, the time dependence of the correlation function results in a temperature dependence of $\langle S_{loc}^2 \rangle$. Fluctuating moments and atomic like configurations are large at short time scales. The moment is reduced at longer time scales, corresponding to a more band like less correlated electronic structure near the Fermi level.

4. CONCLUSIONS

Band structure calculations were performed on a large number of rare-earth transition metal compounds. The experimentally determined magnetizations are well described by the computed values. The local moments at various crystallographic sites can be well correlated with their local environments. The polarizations of R5d bands were shown to be due to local 4f-5d exchange as well as to short-range 5d-3d and 5d-5d exchange interactions. The first one is proportional to De Gennes factor while the second contribution is dependent on the number of nearest-neighbour atoms as well as their magnetic contributions. The delocalized 4f states in $CeCo_4B$, similar as for 5d bands, have a negative polarization as compared to cobalt, determining the presence of a ferrimagnetic type ordering.

The contributions of various orbitals to the exchange interactions were evaluated in RNi_5 compounds. The dominant 5d-5d hybridizations are between d_{3z^2-1} orbitals with lobes pointing along **c**-axis. Important interactions are between almost all the projected orbitals of nickel.

The iron in rare-earth compounds shows a rather localized behaviour. In compounds with low Curie temperatures, a transition of Co and Ni from nonmagnetic to magnetic state was shown when a nonmagnetic rare-earth or yttrium is substituted by a magnetic rare-earth. This behaviour was correlated with the exchange field acting on transition metal atoms. Finally, we concluded that the magnetic behaviour of transition metals in rare-earth compounds can be described in models that take into account the electron correlation effects in d bands.

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