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Band structure and magnetic properties of RNi_4B compounds with R=Gd, Tb, Dy, Ho and Er

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The RNi_4B compounds (R=Gd, Tb, Dy, Ho and Er) crystallize in a hexagonal type structure having P6/mmm space group. Band structure calculations show that small magnetic moments are induced on the Ni(2c) and Ni(3g) atoms. The R(5d) band polarizations are linearly dependent on the De Gennes factor. The contribution from local 4f-5d and short range 5d-3d exchange interactions to R(5d) band polarization were determined. The Curie temperatures are linearly dependent on the De Gennes factor. Above Curie temperatures, the magnetic susceptibilities follow a Curie-Weiss behavior. The effective nickel moments are $\cong 1.8\ \mu_B$/atom. The magnetic behavior of nickel is analyzed in the spin fluctuation model.

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1. Introduction

The RNi_4B compounds crystallize in a hexagonal structure of $CeCo_4B$ type having the P6/mmm space group [1]. This structure is obtained from that of $CaCu_5$ one, in which crystallize the RNi_5 compounds, by substituting every two layers Ni (2c) atoms by B. In the $CeCo_4B$-type structure the R atoms occupy two different crystallographic positions: (1a) and (1b), the Ni atoms occupy the (2c) and (6i) sites and the boron atoms are located on the (2d) positions. The analysis of the magnetic properties of the RNi_4B compounds suggested that the nickel is not magnetic [2-4]. Band structure calculations performed on the $ErNi_4B$ compound showed the presence of a small nickel magnetic moment at 0 K [5].

Previously, we reported that in $RNi_{5-x}M_x$ compounds (R=Dy, Ho and M=Al, Cu), at low temperatures, the nickel has a small magnetic moment of the order of 0.2 μ_B/atom [6-8]. Also, in the paramagnetic domain, an effective nickel magnetic moment of 2.2 μ_B/atom was evidenced. This behavior was analyzed in models that take into account the electron correlations effects in the d band [9, 10].

In this paper we analyze the magnetic properties of the RNi_4B compounds in order to obtain more information of the above mention trend. In addition to the magnetic measurements, band structure calculations were also performed.

2. Experimental methods and computational details

The RNi_4B (R=Gd, Tb, Dy, Ho and Er) compounds were prepared in an induction furnace in a purified argon atmosphere. The samples were thermally treated in vacuum, at $\approx$ 900 ^oC, for ten days. The X-ray analyses show the presence of only one phase of $CeCo_4B$-type structure. Magnetic measurements were performed in the temperature range 4.2-900 K an in magnetic fields up to 10 T. Above Curie temperatures, the magnetic susceptibilities were determined by using a Faraday type balance in fields up to 1 T. The band structure calculations were carried out by using the ab-initio tight-binding linear muffin-tin method (TB-LMTO) in its atomic sphere approximation (ASA). The detailed procedure of calculations were described elsewhere [11,12]. In the framework of the local density approximation (LDA), the total electronic potential is the sum of the external, Coulomb and exchange correlation potentials [13]. The functional form of the exchange correlation energy used in the present work was the free electron gas parameterization of von Barth and Hedin [14]. Relativistic corrections were also included.

3. Band structure

The total and l-decomposed Ni-3d density of states (DOS) in some of studied RNi_4B compounds are plotted in Fig. 1 and Fig. 2. The calculated Ni magnetic moments are rather small and antiparallel coupled to the R moments. The Ni moments decrease linearly as a function of De Gennes factor, $G=(g_J-1)^2J(J+1)$, of the rare earths (Fig. 3). The Ni (2c) contribution is higher than that of atoms located at (6i) sites. This behavior can be analyzed considering the center of gravity of local DOS for various sites in correlation with local environment. The Ni (6i) states are located between the layers containing the B (2d) and Ni (2c) atoms. The mixing of Ni (6i) states with 2p states of boron and respectively, with 5d states of R atoms shifts to lower energy the R(5d) (1a, 1b) and Ni(3d) (6i) bands and at higher energy B(2p) states. Also, the mixing of Ni(3d) (2c) with R(5d) (1a, 1b) and with B(2p) states will shift the local DOS to lower energy. This shift is smaller than in case of Ni (6i) states. The electrons from

B(2p) states will flow into the Ni(3d) states and thus sensitively reducing the Ni moments, particularly on the (6i) sites. The dependencies of R(5d) band polarization (M_{5d}) on the De Gennes factor is plotted in the Fig. 3. The M_{5d} values for both R (1a) and R (1b) sites follow the same type of variation: $M_{5d}=M_{5d}^{0}+bG$, with b=4×10^{-3} μ_B and M_{5d}^{0} =0.06 μ_B for R (1b) and respectively 0.03 μ_B for R (1a). The first term may be attributed to the short-range exchange interactions of R(5d) with the neighboring atoms while the second term is due to the local 4f-5d exchange interactions.

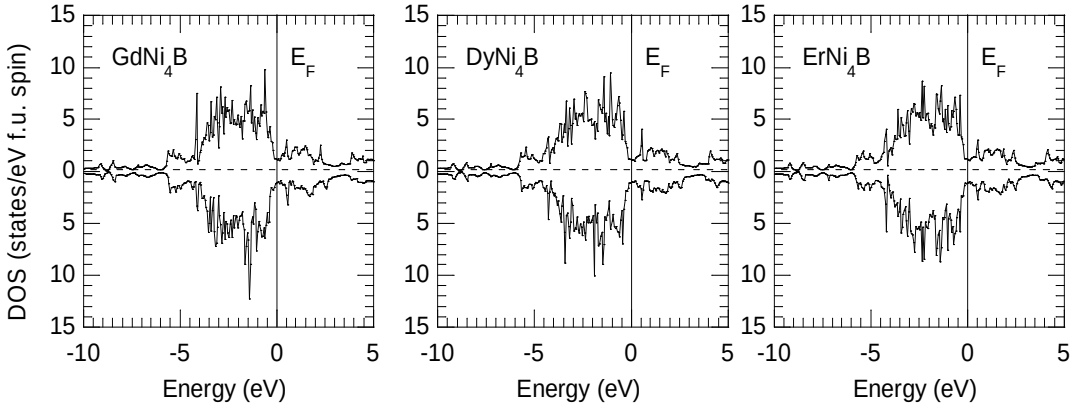

Fig. 1. Total DOS for RNi_4B compounds (R=Gd, Dy and Er).

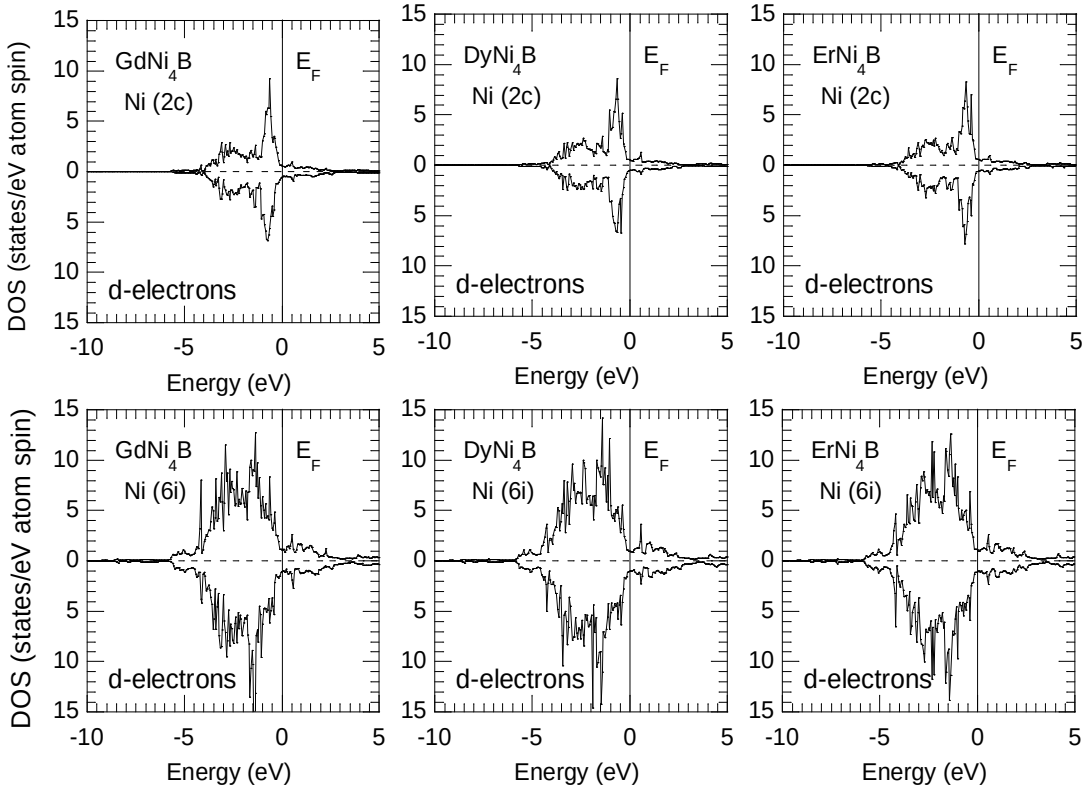

Fig. 2. Ni-3d DOS atoms in RNi_4B compounds (R=Gd, Dy and Er).

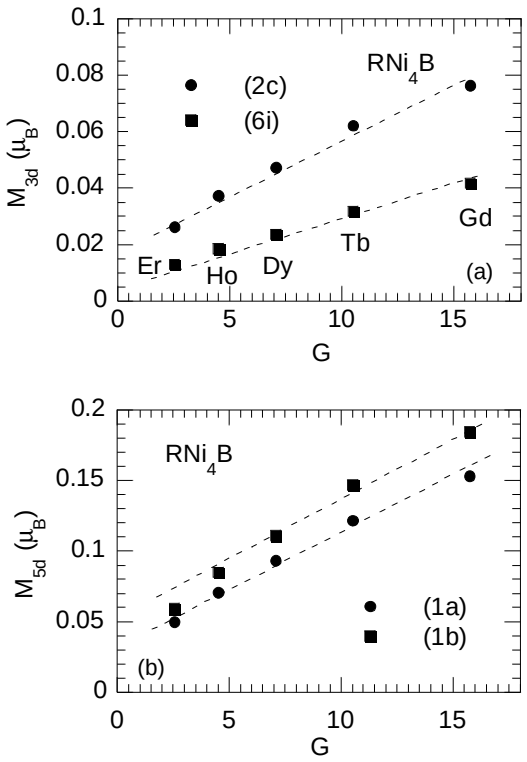

Fig. 3. The dependence of the Ni magnetic moments (a) and R-5d band polarizations (b) as function of De Gennes factor.

The obtained b value is closed to that evidenced in RM_x compounds [15]. The M_{5d}^0 polarizations for R (1b) sites are higher than that at the R (1a) sites. This fact may be correlated with a higher number of Ni atoms situated in the first shell of coordination. The M_{5d}^0 value can be evaluated by considering the exchange interaction hamiltonian [6]:

$$H_{ex} = -2\sum_i J_{3d_i-5d_i} S_{5d_i}^0 \sum_{n_i} S_{3d_{i,n_i}}^0 - 2J_{5d-5d} S_{5d}^0 \sum_j S_{5d_j}^0 \quad (1)$$

where i refers to the number of sites occupied by Ni atoms, n_i is the number of atoms occupying a given site and j is the number of R atoms situated along c-axis. The 3d-5d and 5d-5d exchange interactions act as an internal field, H_{ex}, and increase the 5d band polarization. In the molecular field approximation, the exchange field can be written as $H_{ex}=N_{5d\text{-}3d}M_{Ni}+N_{5d\text{-}5d}M_{5d}^0$ where the $N_{5d\text{-}3d}$ and $N_{5d\text{-}5d}$ are the molecular field coefficients describing the interactions between R_{5d}-Ni_{3d} and R_{5d}-R_{5d} atoms. In the assumption that $N_{5d\text{-}3d} \cong N_{5d\text{-}5d}$, we have $H_{ex} \propto M_d$, where $M_d=M_{3d}+M_{5d}$ is the total magnetization. We compute $\sum_{i,j} n_{ij} M_{ij}$ values for the atoms situated in the first coordination shell. The M_{5d} band polarizations are plotted in Fig. 4 as a function of $\sum n_i M_i$. The values follow the trend previously showed in the case of RM_5 (M=Co, Ni) [15] and RCo_4B compounds [16].

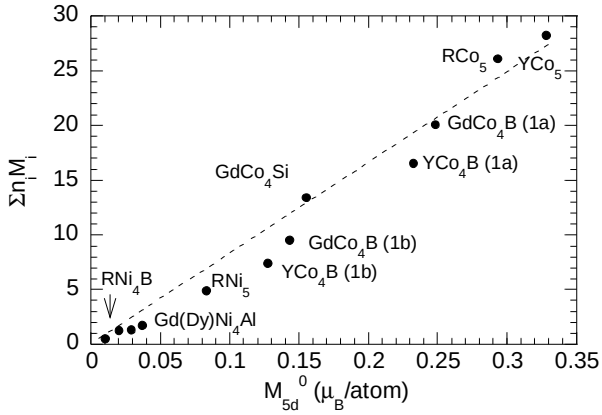

Fig. 4. The 5d band polarization as function of $\Sigma n_i M_i$.

The nickel moments presents a linear dependence on the 3d exchange splitting energy, Fig. 5. From the above data we estimated a value of the critical exchange field, H_c=38 T, for inducing a nickel moment.

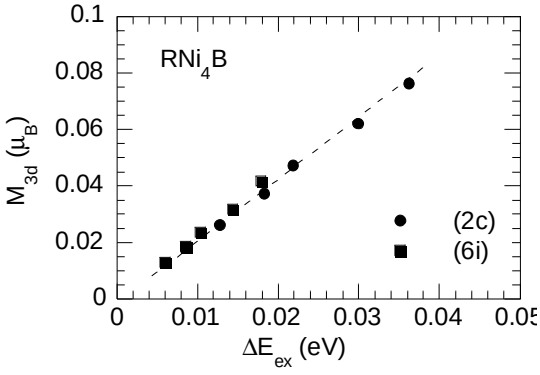

Fig. 5. Ni-3d moments as function of exchange splitting energy.

4. Magnetic properties

The saturation magnetization of RNi_4B (R=Tb, Dy, Ho, Er) compounds were previously reported. In case of $GdNi_4B$ compound a value of 7.00 μ_B was obtained at 4.2 K. Taking into account the magnetic moments determined from band structure calculations we obtained 7.04 μ_B/f.u., the same as experimentally determined. The saturation magnetizations at 4.2 K for non-S state rare earth compounds are smaller than g_iJ values. This behavior was attributed to the crystal field effect. The dependence of Curie temperatures on the De Gennes factor is plotted in Fig. 6. A linear dependence is shown, suggesting that the magnetic interactions between rare earths are dominants. The magnetic susceptibilities above T_C, show a Curie-Weiss dependence described by the relation: $\chi=C(T-\theta)^{-1}$. We denoted by C the Curie constant and by θ the

paramagnetic Curie temperature. The C values are higher than those of R^{3+} ions. This suggests the presence of the nickel contribution, C_{Ni}, to the Curie constant. According to the additional law of the magnetic susceptibilities we determined the C_{Ni} and $M_{eff}(Ni)$ values. The effective nickel moments are nearly constant and close to 1.8 μ_B/atom.

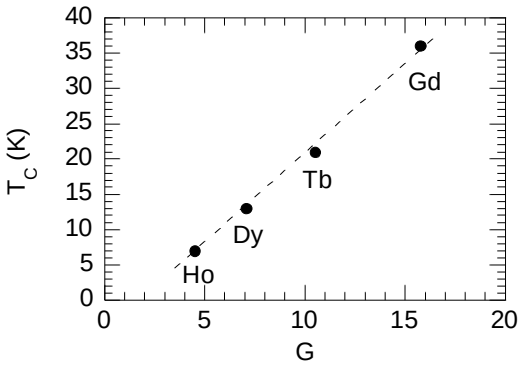

Fig. 6. Curie temperatures as function of De Gennes factor.

5. Conclusions

The nickel in RNi_4B compounds, at low temperatures, has a very small magnetic moment. The M_{Ni} values corresponding to the (2c) sites are somewhat higher than those from (6i) sites. This can be related to their local environments. Above the Curie temperatures, an effective nickel moment $M_{eff}(Ni) \cong 1.8\ \mu_B$/atom was obtained. The above behavior may be analyzed in the spin fluctuation model [9]. The model consider the balance between frequencies of longitudinal spin fluctuations which are determined by their life time and of transverse spin fluctuations which are of thermal origin. For a weak ferromagnet, as Ni in RNi_4B compounds, the wave number dependent susceptibility, χ_q, shows significant temperature dependence. As a result, the average spin fluctuation amplitude $\langle S_{loc}^2 \rangle = 3k_B T \sum_q \chi_q$ increases with the temperature, in a narrow range above T_C, and reaches an upper limit determined by the charge neutrality condition. Then, the magnetic susceptibilities show a Curie-Weiss behavior, similar as in systems having local moments. The moments are localized in q space. Due to the Ni(3d) – B(2p) hybridization, the saturated effective nickel moments are smaller than the Ni^{2+} free ion value (2.83 μ_B/atom).

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