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Dedicated to Professor Valentin I. Vlad's 70th Anniversary

MAGNETIC PROERTIES AND BAND STRUCTURES OF $Y_2Co_{7-x}Ni_x$ COMPOUNDS

I. CREANGA

University "Politehnica" of Bucharest, Department of Physics, Splaiul Independentei 313, 060042, Bucharest Romania, E-mail: ilcreanga@yahoo.com

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Abstract. The $Y_2Co_{7-x}Ni_x$ compounds crystallize in rhombohedral $R\bar{3}m$ type structure. The lattice parameters follow a Veguard-type law. The compounds are ferromagnetic. Above the Curie temperatures, Curie-Weiss type dependences are shown. Band structure calculations evidenced a correlation between cobalt and nickel moments, at different sites and their local environments. The nickel in the above compounds shows a weak ferromagnetism, while the magnetic behaviour of cobalt can be described in spin fluctuations model.

Key words: Yttrium compounds, magnetic properties, band structures.

1. INTRODUCTION

The Y_2M_7 compounds with M = Co or Ni crystallize in a rhombohedral type lattice having $R\bar{3}m$ space group [1]. In this crystal structure, the Y atoms are distributed in two types of sites while cobalt atoms are located in five positions.

The Y_2Co_7 compound is ferromagnetic. For a lower cobalt content than the stoichiometric one, a random substitutions of some Co by Y atoms takes place [2]. It results a decrease of the magnetic correlations and the cobalt atoms situated in the neighborhood of the substitution were unstable from the magnetic point of view. A field induced transition to a state with higher magnetization has been evidenced at 240 K. Similar transitions have been observed in the temperature range 160–320 K. For temperatures higher than 320 K, the transition was covered by the effects of thermal fluctuations of magnetization. For stoichiometric Y_2Co_7 compound a normal behaviour has been found.

The Y_2Ni_7 compound shows a weak ferromagnetism. The magnetic moment per formula unit was reported to be $M_s = 0.41\mu_B$ [4] or $M_s = 0.56\ \mu_B$ [3] and Curie temperature $T_C = 54$ K [3].

In the Y_2M_7 compounds, the exchange interactions between transition metals, M3d-M3d are of short range. The same type of interactions are shown between

Y4d and M3d atoms; as a result of hybridization effects a negative polarization is induced on Y4d band.

The study performed on $Y_2Co_{7-x}Ni_x$ system evidenced a very fast decrease both of magnetizations and Curie temperatures as the cobalt is gradually substituted by nickel [5]. A similar behaviour was reported in $Gd(Co_xNi_{1-x})_2$ system [6, 7]. The local environment effects were used in order to analyse the magnetic properties of cobalt in the last system.

The crystal structures and magnetic properties of $Y_2Co_{7-x}Ni_x$ compounds will be analysed in this report. Band structure calculations on end series compounds have been also made. The cobalt in the above system shows a spin fluctuations type behaviour while nickel can better described as a very weak ferromagnet.

2. EXPERIMENTAL AND COMPUTING METHOD

The $Y_2Co_{7-x}Ni_x$ compounds with $x \leq 4$ and $x = 7$ have been prepared by arc melting the constituent elements in a purified argon atmosphere and remelted several time to ensure a good homogeneity. A small excess of yttrium was added to starting compositions in order to compensate the weight loss during melting and to avoid the formation of impurities having higher Curie temperatures than of nominal phases. The compounds were annealed one week at 1000 ^oC.

The X-ray analyses evidenced the presence of only one phase having $R\bar{3}m$ - type structure. The lattice constants of the end series compounds are in agreement with previously reported data [1]. Both *a*- and *c*- lattice parameters decrease when increasing nickel content according to an approximate Veguard law (Fig. 1).

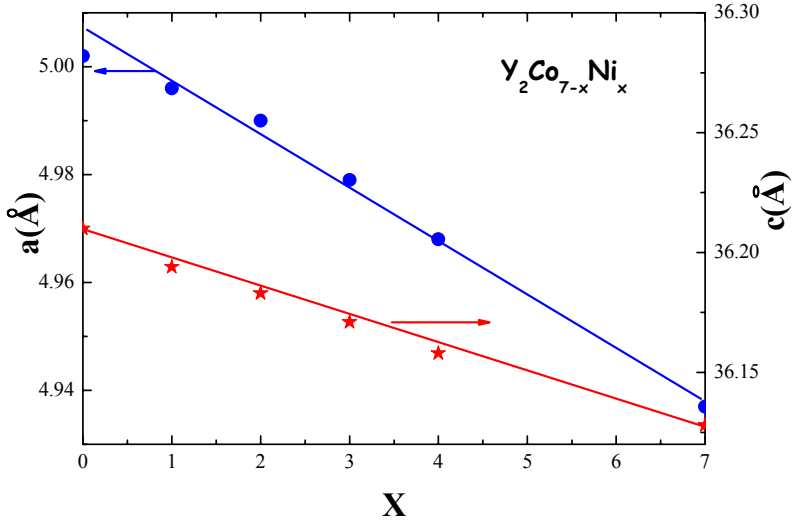


Fig. 1 – Composition dependences of lattice parameters in $Y_2Co_{7-x}Ni_x$ compounds.

Magnetic measurements were performed in the temperature range 4–1000 K and fields up to 7 T. The saturation magnetizations have been determined from magnetization isotherms, according to the approach to saturation law. The magnetic susceptibilities, above the Curie temperatures, T_C, were obtained according to Honda-Arrot plot (M/H vs $1/H$), by extrapolating the data at $H^{-1} \rightarrow 0$ [8]. Some measurements were also performed by using a Faraday type balance. Generally, no presence of magnetic impurities have been evidenced, at $T > T_C$.

The ground state electronic structure calculations of Y_2M_7 (M = Co or Ni) compounds were performed by using tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation [9]. The self consistent spin polarized calculations were performed at the experimental values of the lattice parameters and carried out for 793 **k**-points in the irreducible wedge of the Brillouin zone (BZ), corresponding to 13824 **k**-points in the full Brillouin zone. The local spin density approximation (LSDA) has been used for the exchange and correlation potential within Vosko-Wilk-Nussair parameterization [10]. Relativistic corrections were taken into account without spin-orbit coupling.

3. BAND STRUCTURES

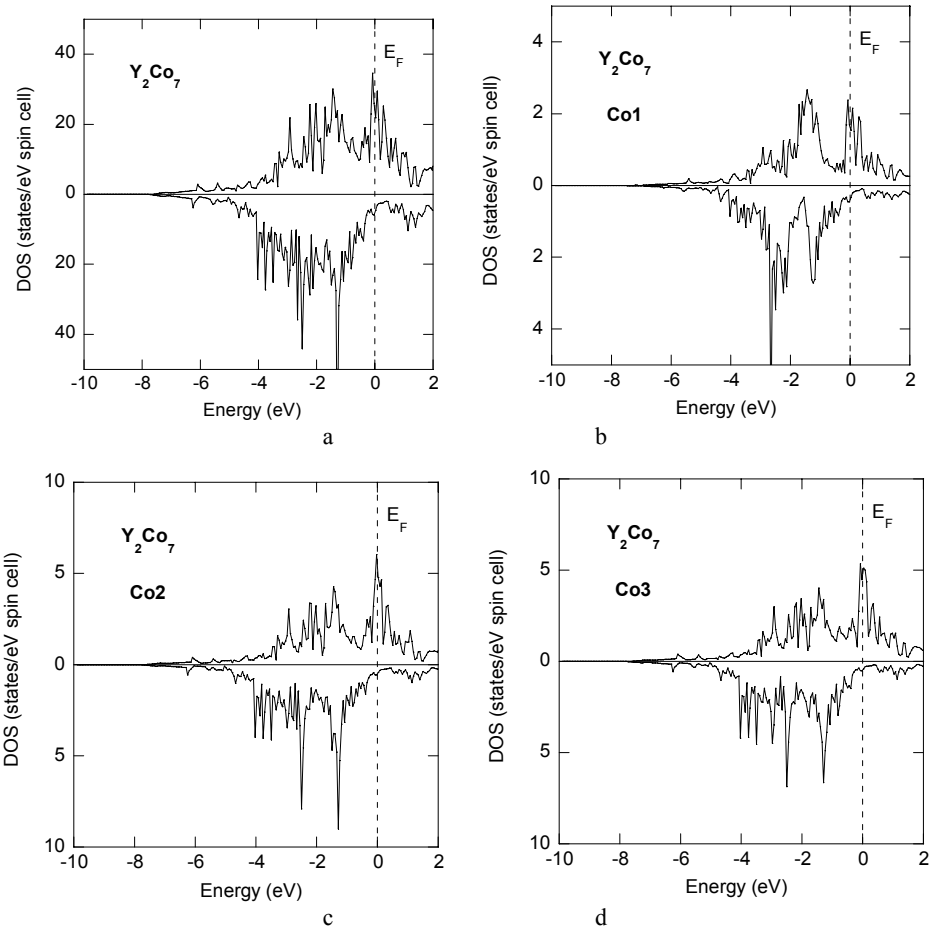
The total density of states (DOS) as well as the partial DOS for cobalt atoms located in the five sites, in Y_2Co_7 compound, are given in Fig. 2. The computed cobalt magnetic moments and the Y4d band polarizations are listed in Table 1. The computed cobalt moments can be correlated with their local environments, and the DOS at the Fermi level, E_F. The highest cobalt moments can be seen at the Co2 and Co3 sites, where there are (9Co+3Y) and (8Co+4Y) atoms in their first coordination shell. For these sites the Fermi level, in spin-up sub-bands is situated in a peak of DOS while the state densities in spin down sub-band are significantly lower. The smallest computed moments can be evidenced at Co1 and Co5 sites where in their neighborhood are located (6Co+6Y) and (7Co+5Y) atoms, respectively. In the spin up sub-bands, the Fermi level is situated near a minimum in DOS and at the small peak in spin down sub-bands, respectively. These data evidence the part played by Co3d-Co3d short range exchange interactions as well as the Co3d-Y4d hybridization effects in determining the cobalt moments. Similar effects were evidenced in $Gd(Co_xNi_{1-x})_2$ compounds, where the appearance of a cobalt moments was correlated with their local environments [6, 7].

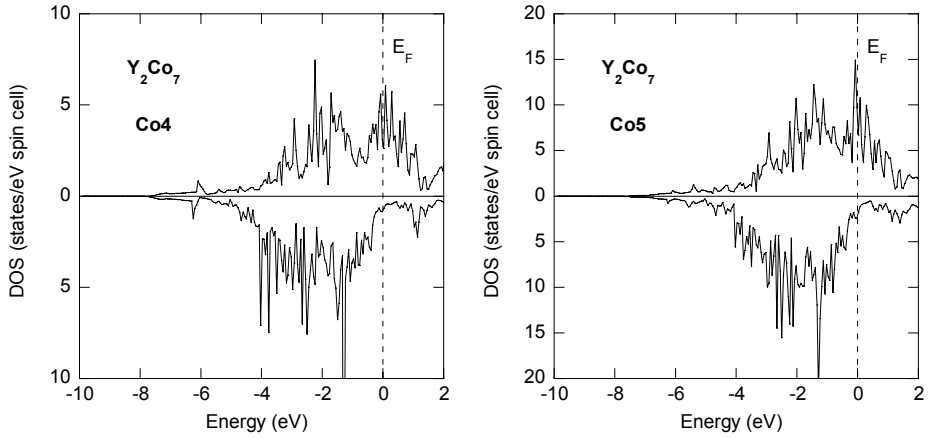
Table 1

Magnetic moments determined from band structure calculations

Y_2Co_7				Y_2Ni_7			
Atom	M (μ_B/atom)	Magnetic moments (μ_B/f.u.)		Atom	M (μ_B/atom)	Magnetic moments (μ_B/f.u.)	
		computed	experimental			computed	experimental
Y1(6c)	-0.237	8.756	9.24 [16] 9.6 [17] 7.96*	Y1(6c)	-0.039	0.456	0.41 [4] 0.56 [3] 0.5*
Y2(6c)	-0.348			Y2(6c)	-0.024		
Co1(3b)	1.232			Ni1(3b)	0.039		
Co2(6c)	1.450			Ni2(6c)	0.039		
Co3(6c)	1.446			Ni3(6c)	0.105		
Co4(9e)	1.400			Ni4(9e)	1.157		
Co5(18h)	1.244			Ni5(18h)	0.066		

* present data



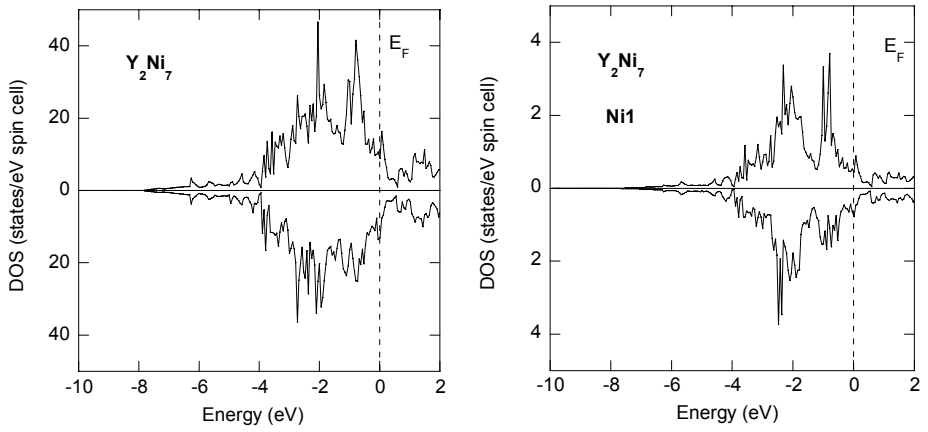


e f

Fig. 2 – Total (a) and cobalt partial (b-f) densities of states in Y_2Co_7 compound.

The cobalt magnetic moments determined by neutron diffraction in Y_2Co_7 compound [2, 11], as well as those obtained by band structure calculations [12] are in close agreement with the present data.

The total density of states as well as the partial DOS for nickel atoms in Y_2Ni_{17} compound, are presented in Fig. 3. For all nickel sites, in spin up sub-bands, the E_F is located close to a peak in DOS, while in the spin down sub-bands is situated in small peaks. The nickel moments are rather small, as expected for a weak ferromagnet. The higher nickel moments can be shown at Ni3 and Ni4 sites, evidencing, as in Y_2Co_7 compound, the importance of local environment effects.



a b

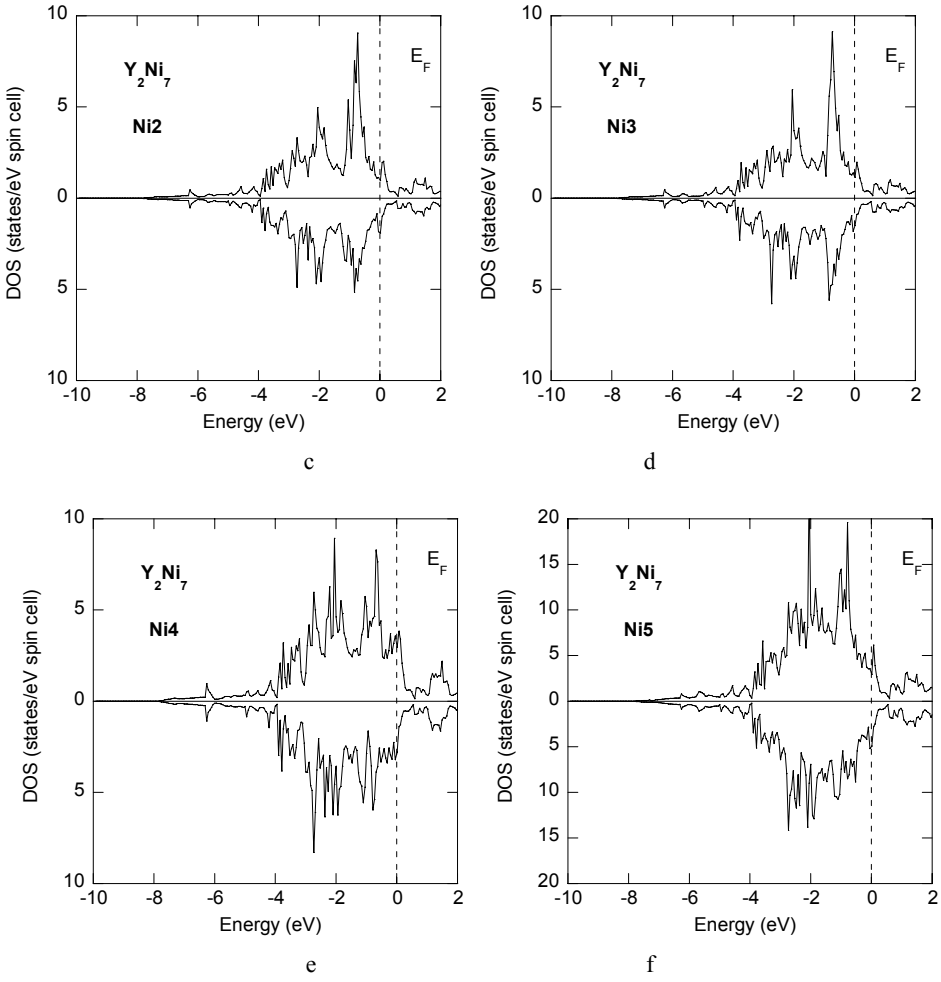


Fig. 3 – Total (a) and nickel partial (b-f) densities of states in Y_2Ni_7 compound.

As already was shown, the Y4d band polarizations, $M_Y(4d)$, are induced by Y4d-M3d short range exchange interactions, and corresponding hybridization effects respectively. In a molecular field approximation this can be described by the relation [13,14]:

$$M_Y(4d) \propto \sum_i z_i M_i, \tag{1}$$

where z_i is the number of magnetic atoms situated in the first coordination shell to a given Y and M_i are their moments.

The Y4d band polarizations in Y_2M_7 (M = Co, Ni) show a linear dependence on $\sum_i z_i M_i$ with a slope $1.85 \cdot 10^{-2}$ (Fig. 4). This value is intermediate between that determined in RCo_2-based compounds ($2.0 \cdot 10^{-2}$) and that evidenced in YCo_5-based ones, respectively ($1.3 \cdot 10^{-2}$) [15]. As a general feature, it seems to be a decrease of the slopes of the above dependences, as the content of transition metal, for a given series, is increased.

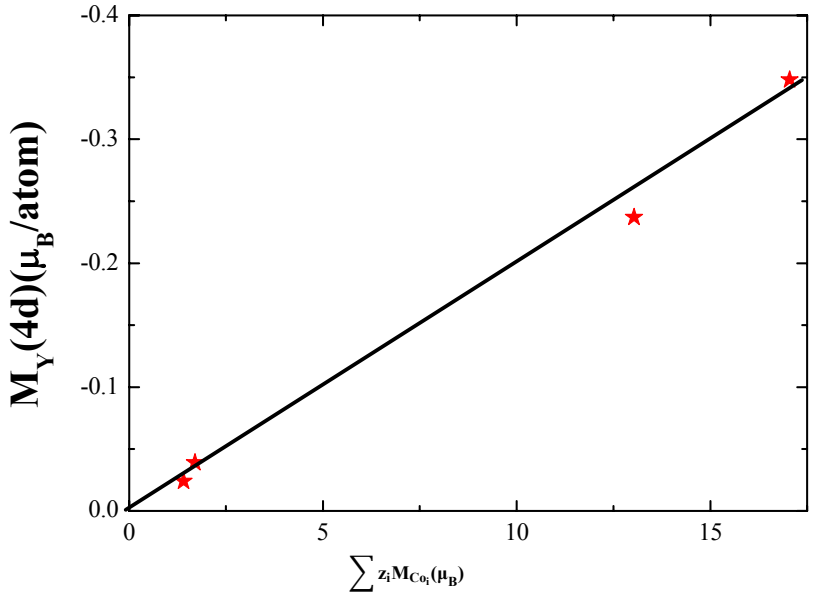


Fig. 4 – The dependence of Y4d band polarization on the number of magnetic atoms situated in the first coordination shell z_i and their moments M_{C_0}.

4. MAGNETIC PROPERTIES

The composition dependence of the saturation magnetizations, M_s, at 4K is plotted in Fig. 5. A value 7.96 μ_B has been determined in Y_2Co_7. This is little higher than that reported in nonstoichiometric compound, of 7.6 μ_B [2], but lower than those evidenced in stoichiometric samples [2, 16, 17] (Table 1). Qualitatively, the sudden magnetic transition of some cobalt atoms from low magnetic state to higher one, in nonsoichiometric compound [2] can be explained in the model of induced magnetism [18]. By adding the external field to the internal one, a critical value is obtained, in order to realize the above transition.

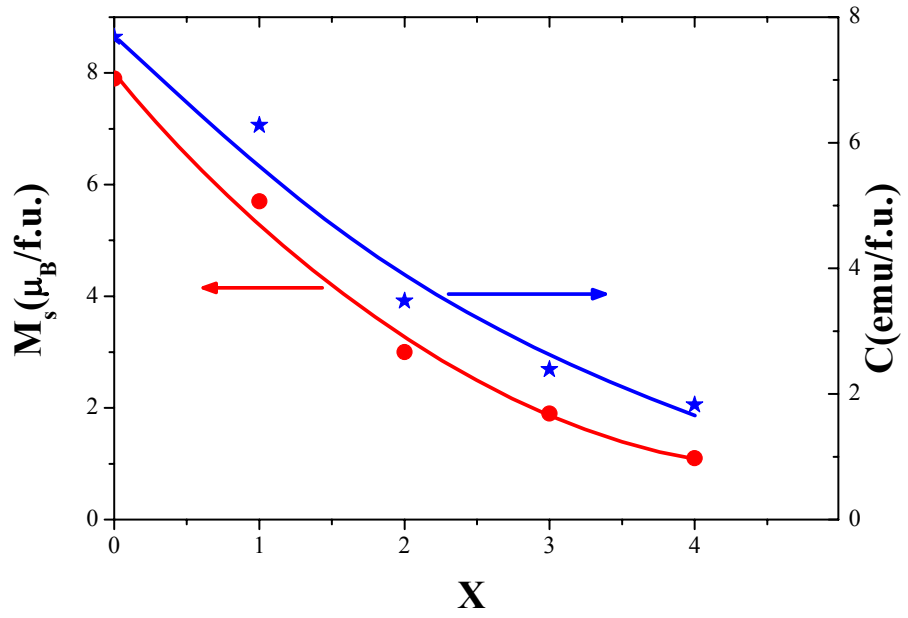


Fig. 5 – The composition dependences of the saturation magnetizations at 4K and of Curie constants in $Y_2Co_{7-x}Ni_x$ system.

The high decrease of saturation magnetizations, as the nickel content increased, can be attributed to "magnetic dilution" as suggested by the very small nickel moment.

The thermal variations of reciprocal susceptibilities are plotted in Fig. 6. The experimental data can be described by a modified Curie Weiss law:

$$\chi = \chi_0 + C(T-\theta)^{-1}, \quad (2)$$

where C is the Curie constant, θ paramagnetic Curie temperature and χ_o a paramagnetic contribution to susceptibility not dependent on temperature.

The Curie constants decrease rather quickly as the nickel content is increased (Fig. 5). A rather high decrease of Curie temperatures can be also shown, evidencing a strong diminution of the exchange interactions (Fig. 7). The paramagnetic Curie temperatures, θ, are by 12 to 43 K higher than the ferromagnetic ones.

The magnetic measurements made on Y_2Ni_7 evidenced a saturation magnetization of $\cong 0.5\mu_B$/f.u.. Also a Curie constant C = 0.58 emu/f.u. was determined in paramagnetic range, corresponding to an effective nickel moment of 0.82 μ_B/atom.

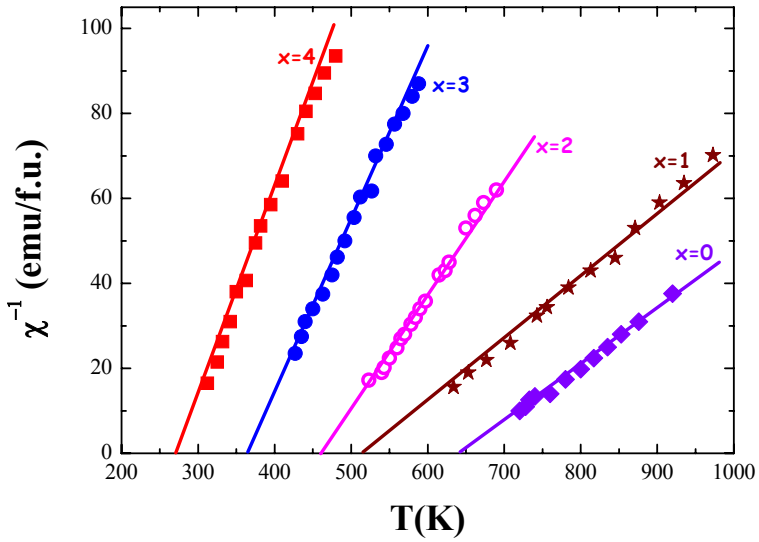


Fig. 6 – Thermal variations of the reciprocal susceptibilities in $Y_2Co_{7-x}Ni_x$, with $x \leq 4$.

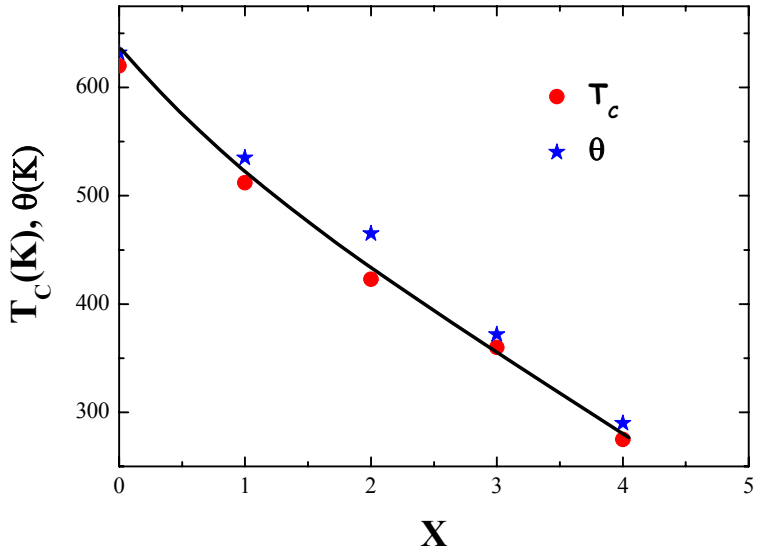


Fig. 7– Composition dependences of Curie temperatures T_C, and of the paramagnetic Curie temperatures, θ.

Preliminary band structure calculations for a sample with $x = 3$ evidenced that there is only a small increase of mean nickel moment in pseudobinary compounds, up to $\cong 0.13$ μ_B/atom. Admitting a constant mean nickel moment along the $Y_2Co_{7-x}Ni_x$ series, having the above value, the contributions of mean cobalt

moments, M_{Co}, to saturation magnetizations, were determined. The M_{Co} values decreased from 1.14 μ_B/atom (x = 0) to 0.17 μ_B/atom (x = 4). The above behaviour can be correlated with the diminution of the exchange interactions, as effect of "magnetic dilution" evidenced also by the strong decrease of T_C values.

In the supposition that the mean effective nickel moments are not strongly dependent on composition, starting from paramagnetic measurements, the contributions of cobalt to the Curie constants and the mean effective cobalt moments, M_{eff}(Co), respectively were determined. The M_{eff}(Co) values decrease from 2.86 μ_B/atom (x = 0) to 1.97 μ_B/atom (x = 4). A more slowly composition dependence that than of mean saturation moments is shown.

Information on the cobalt magnetic behaviour can be obtained from the ratios $r = S_p/S_o$, between the number of spins determined from effective moments, S_p, and from saturation data, S_o, respectively. For a localized model we have r = 1. The ratio r increases with increasing the itinerancy degree.

In the itinerant electron model of ferromagnetism, the ratio r is proportional to T_C^{-1} [19], while in spin fluctuations model the r values can be described by a $T_C^{-2/3}$ law [19,20]. The r values plotted as function of T_C^{-1} and $T_C^{-2/3}$, respectively are given in Fig. 8. In the limit of experimental errors a nearly linear variation can be shown in both cases.

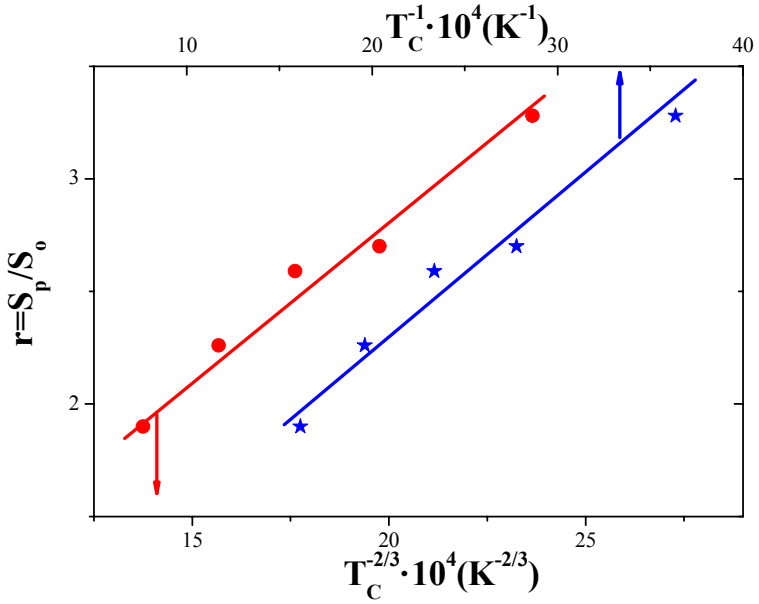


Fig. 8 – The ratio $r = S_p/S_o$ as function of $T_C^{-2/3}$ and T_C^{-1} in $Y_2Co_{7-x}Ni_x$ compounds, with $x \leq 4$.

The neutron diffraction studies performed on Y_2Co_7 compound evidenced that the cobalt moments are localized on the corresponding lattice sites [2, 11].

Thus, a model which considers both band and localized features of cobalt moments is suggested, as described by the spin fluctuations one [20]. The spin fluctuations model predicts, for ferromagnetic systems, a Curie-Weiss type dependence for magnetic susceptibility. In the itinerant electron model such dependence is difficult to be simulated. Also the Curie constants are not dependent on the saturation moment at $T = 0$, but depends on the band structure around the Fermi energy. These features are clearly evidenced in $Y_2Co_{7-x}Ni_x$ system. Thus, a $T_C^{-2/3}$ dependence of the r values is most probable, as evidenced in Fig. 8.

5. CONCLUSIONS

The $Y_2Co_{7-x}Ni_x$ compounds are ferromagnetic. Both the saturation magnetizations and Curie constants decrease when increasing the nickel content. The observed behaviour can be correlated with magnetic dilution effects, as evidenced by a high decrease of the Curie temperatures.

A correlation between the transition metal moments and their local environments was shown. The short range exchange interactions of the M3d-M3d and M3d-Y4d types are important in determining the transition metal moments. A negative polarization is induced on Y4d band which is determined by the number of magnetic atoms situated in the first coordination shell to Y one, as well as their moments. The magnetic behaviour of cobalt can be described in spin fluctuations model while nickel shows a weak ferromagnetism.

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