

Dedicated to Academician Aureliu Săndulescu's 80th Anniversary

ELECTRONIC STRUCTURES AND EXCHANGE INTERACTIONS IN RT_5
AND R_2T_{17} COMPOUNDS, WHERE R IS A RARE-EARTH OR YTTRIUM
AND T = Co OR Ni

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Received November 11, 2011

Band structure calculations and magnetic measurements were performed on rare-earth and yttrium (R)–transition metal (T) compounds having 1:5 and 2:17 type structures. The transition metal moments were shown to be linearly correlated with 3d band exchange splittings and internal fields, respectively. The R5d–T3d exchange interactions and R5d(Y4d) band polarizations were also analysed. The magnetic behavior of cobalt and nickel has been discussed in spin fluctuations model.

Key words: band structure, magnetic properties, spin fluctuations.

1. INTRODUCTION

The rare-earth (R)–transition metal (T) compounds have been investigated both for their interesting magnetic properties as well as in correlation with possible technical applications [1, 2]. The rare-earths in the above compounds, possess a well localized magnetic moments. As function of composition, cobalt and nickel were shown to have a wide range of magnetic behaviors, extending from non magnetic to a rather localized moment [1].

The exchange interactions between rare-earths and transition metals can be described by 4f–5d–3d model [3]. The 4f electrons of rare-earths polarize their 5d bands and there are also direct 5d–3d exchange interactions with transition metal atoms. The local 4f–5d exchange interactions are positive. The 4f moments and 5d band polarizations will align parallelly in heavy rare-earth compounds, but antiparallely to transition metal moments [4]. The exchange interactions between transition metal atoms are of short range, while those between rare-earths take place by means of conduction electrons or/and 5d–5d types [5].

The rare-earth-transition metal compounds, generally have a complex crystalline structure in which transition metals occupy different lattice positions, their magnetic contributions being dependent on the site location. In case of hexagonal systems, having $CaCu_5$ -type structure, the transition metals are located in 2c and 3g sites, while the R atoms in 1a type positions. By magnetic measurements only their mean values can be determined. The magnetic contributions of T atoms, at a given site, can be obtained experimentally by neutron diffraction studies or theoretically by band structure calculations. By latter type analysis, the R5d band polarizations can be also determined.

In this paper we present the results of band structure calculations on some compounds having hexagonal structure, derived from RT_5 -type as well as on R_2T_{17} ones, in correlation with magnetic measurements. A linear dependence of cobalt and nickel moments on their 3d bands splittings was shown. This behavior was correlated also with the exchange field acting on transition metal atoms.

2. EXPERIMENTAL AND COMPUTING METHOD

The YCo_4M ($M = Al, Si, Co$), $(Gd_xY_{1-x})Co_4Si$ and $(Gd_xLa_{1-x})Ni_5$ compounds were prepared by arc melting the constituent elements in a purified argon atmosphere. The samples were remelted several times to ensure a good homogeneity. A small excess of rare-earth or yttrium was added to starting compositions, as compared with stoichiometric ones, in order to compensate their loss during melting. In this way, the formation of phases with higher Curie temperatures, can be avoided. This fact is important in order to obtain reliable magnetic data in the paramagnetic range. The samples were thermally treated at $1000^\circ C$ for one week. The X-ray analyses evidenced the presence of only one phase.

Magnetic measurements were performed in the temperature range 1.5 (4.2) – 900 K and fields up to 10 T. In the paramagnetic range, the magnetic susceptibilities, χ , were determined from magnetization isotherms, according to Honda–Arrott plot [6]: $\chi_m = \chi + dM_s H^{-1}$, by extrapolating the measured values, χ_m , in high fields at $H^{-1} \rightarrow 0$. By d is denoted a presumed impurity content and M_s is their saturation magnetization. By this method, any possible alteration of χ values due to possible presence of small quantity of magnetic ordered phase can be avoided.

The band structure calculations were carried out by using the *ab initio* tight binding linear muffin–tin orbital method in the atomic sphere approximation, together with the coherent potential approximation [7]. The local spin density approximation was used for the exchange–correlation potential within Vosko–Vilk–Nusair parameterization [8].

The band structure calculations of $RCo_{5-x}M_x$ ($x \leq 1$) were performed admitting that M elements are located in 3g sites. We showed already [9], by energy considerations, that $M = Al$ can be located exclusively in 3g sites. In case of $M = Ga$ and Si , the minimum energy corresponds to a fraction of atoms $x \cong 0.9$, situated in 3g sites.

3. EXPERIMENTAL AND COMPUTING RESULTS

The band structure of GdNi_5 is shown in Fig.1, while in Fig. 2 are plotted the decomposed densities of states for YCo_4Si compound. Similar band structures, as for YCo_4Si were obtained in YCo_4M ($M = \text{Al, Ga, Co}$) and pseudothernary $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{Si}$ compounds. In all cases the Fermi level is situated in a peak of states density of Co3d spin up subband both for 3g and 2c sites. The corresponding densities of states for the spin down subbands are rather low.

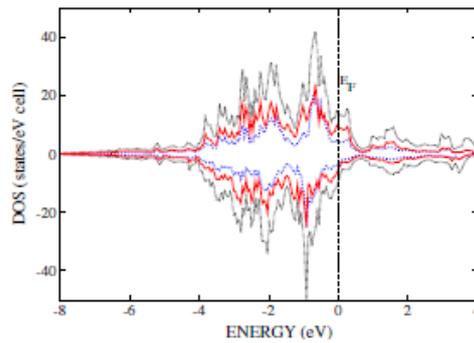


Fig. 1 – Band structure of GdNi_5 compound.

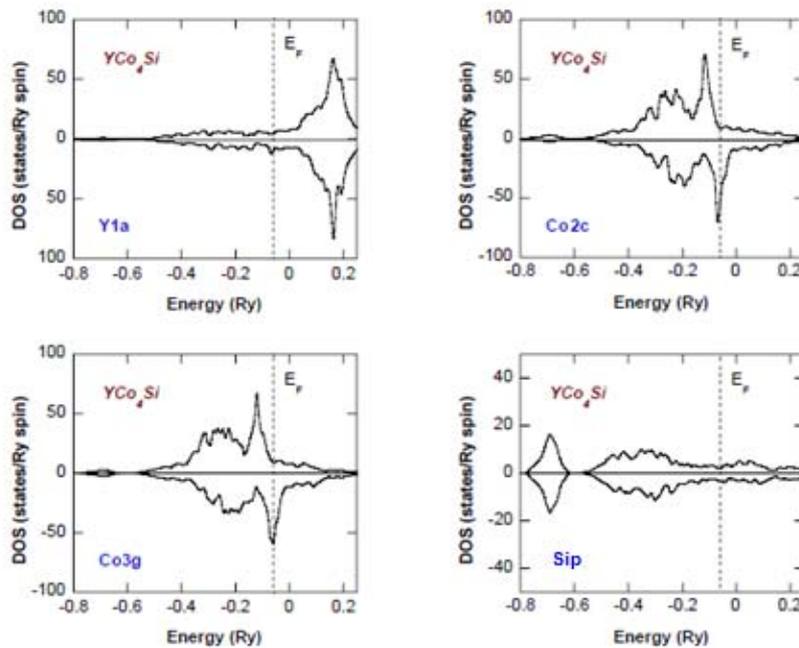


Fig. 2 – The densities of states of Co2c, Co3g, Y1a and Sip in YCo_4Si compound.

The dependence of cobalt moments, at the 2c and 3g sites, as function of silicon content for $x \leq 1$, is shown in Fig. 3. High variations can be shown as function of composition. Thus, even for small deviations from the stoichiometry as compared to that of YCo_4Si , significant changes in the cobalt moments can be shown. The small deviations from expected silicon content cannot be evidenced by X-ray analyses and consequently in all cases the YCo_4Si composition was considered. In this way can be explained the differences in the saturation magnetizations reported by various authors.

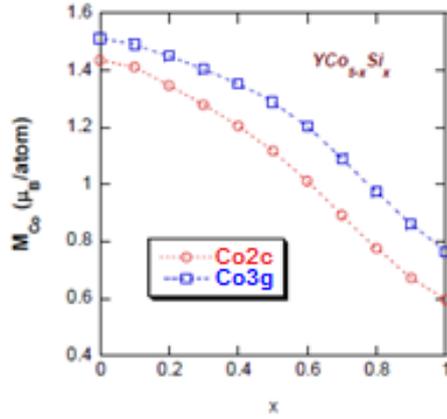


Fig. 3 – The variations of cobalt moments at 2c and 3g sites in $YCo_{5-x}Si_x$ compounds.

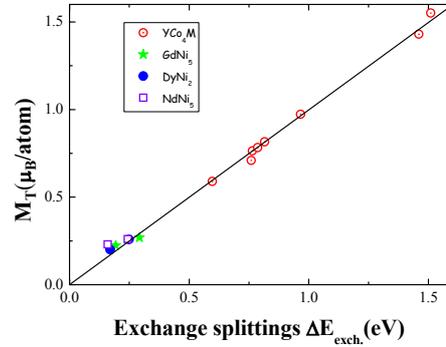


Fig. 4 – The correlation between transition metal moments and exchange splittings of 3d bands.

The centers of gravity of the spin up Co3d density of states are shifted toward the Fermi level, in YCo_4M compounds relative to their positions in YCo_5 , in a greater extent than those of the spin down subbands, particularly for 2c sites. As a result there is a higher diminution of cobalt moments at 2c sites as compared to 3g ones. The neutron diffraction studies confirmed the above behaviour [10, 11].

The computed cobalt and nickel moments at 2c and 3g sites, as function of 3d band splittings are plotted in Fig. 4. A linear variation is shown with a slope $s = 0.95 \text{ eV}/\mu_B$. This is in good agreement with that obtained from band structure calculations on $Zr-T$ ($T = Fe, Co, Ni$) amorphous alloys [12] or crystalline compounds [9, 12]. The s value seems to be not influenced by the valence state of transition metal partner (Zr^{4+}, Y^{3+}, R^{3+}) or by crystallinity degree of the samples.

The $LaNi_5$ is an exchange enhanced paramagnet [13]. The substitution of nonmagnetic Y by Gd in $(Gd_xY_{1-x})Ni_5$ polarizes the nickel 3d band by the resulting internal field, H_{exch} . The exchange field splits the Ni3d bands, the splittings being proportional with H_{exch} values. In case of YCo_4M ($M = Al, Si, Ga$), there are hybridization effects of Co3d and p states of substituting elements, which also shift the centers of gravity of the subbands. These result in changes of the cobalt

moments as well as of Curie temperatures and consequently the exchange fields. Thus, both mechanisms involving the modifications of exchange splitting of transition metal subbands, finally, can be correlated with the of internal fields.

The computed magnetic moments per formula unit, are in rather good agreement with experimentally determined values – Fig. 5. In case of YCo_4Si , we mentioned on the figure, on the figure, the range of values reported by various authors. The somewhat, smaller experimental values than theoretical ones, can be attributed to difficulty in saturation the magnetization. The above data confirmed the reliability of computed magnetizations. The experimental data are well described by those obtained from band structure calculations also in $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{B}$ compounds.

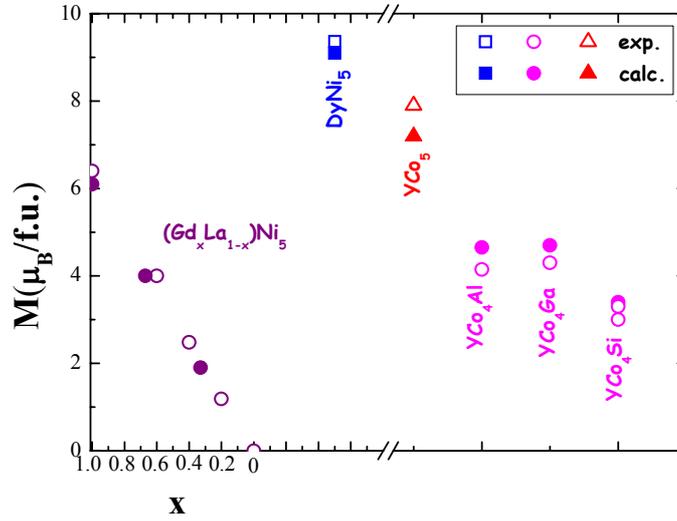


Fig. 5 – Computed and experimentally determined moments per formula unit in $(\text{Gd}_x\text{La}_{1-x})\text{Ni}_5$, DyNi_5 and YCo_4M ($\text{M}=\text{Al}, \text{Ga}, \text{Si}, \text{Co}$) compounds.

As already mentioned, the exchange interactions between rare-earths and transition metals, in R–T compounds, involved the presence of R5d band polarization. The part played by the R5d polarization, in analysing the exchange interactions, is a fundamental question. The dependence of the R5d band polarizations on De Gennes factor, $G=(g_J-1)^2J(J+1)$, for heavy rare earth RT_5 [4] and R_2T_{17} ($\text{T}=\text{Co}, \text{Ni}$) compounds are plotted in Fig. 6. As in case of RT_2 systems [4], polarizations can be described by the relation:

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

By $M_{5d}(d)$ is denoted the induced polarization due to hybridization effects, as result of 5d–3d short range exchange interactions and $M_{5d}(f)=\alpha G$ is due to local 4f–5d exchange.

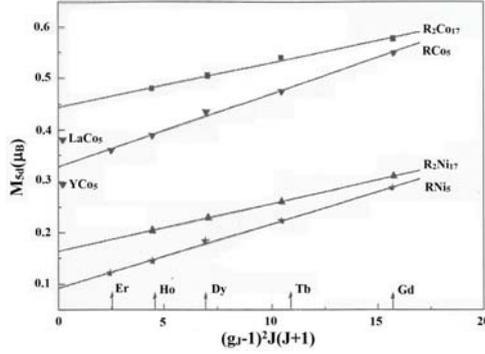


Fig. 6 – The band polarizations M_{5d} in RT_5 and R_2T_{17} ($T=Co, Ni$) compounds as function of De Gennes factor $G=(g_J-1)^2J(J+1)$.

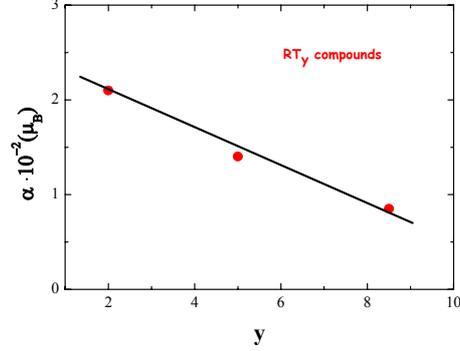


Fig. 7 – The slopes α as function of composition in RT_2 , RT_5 and $RT_{8.5}$ heavy rare-earths compounds.

The magnetic moments of T atoms, in heavy rare earth compounds, are little dependent on R partner and thus, the $M_{5d}(d)$ values, for a given series and T partner, can be obtained by extrapolation at $G = 0$. These are not dependent on the involved rare-earth.

The slopes α , depend on the crystal structure, and transition metal partner, respectively. Nearly linear variation on the T content, was shown when changing their content (Fig. 7).

There is also an induced Y4d band polarization as result of the 4d–3d hybridization effects (Fig. 2). The Y4d band polarizations are antiparallely oriented to transition metal moments. For YCo_4M compounds, values of $0.18 \mu_B$ ($M = Si$), $0.24 \mu_B$ ($M = Al$), $0.25 \mu_B$ ($M = Ga$) and $0.43 \mu_B$ ($M = Co$) were determined. Small polarizations were induced also on p states of M atoms, also antiparallely oriented to transition metal moments. For YCo_4M compounds these values are of $0.04 \mu_B$ ($M = Al, Ga$) and $0.02 \mu_B$ ($T = Si$).

The temperature dependences of the magnetic susceptibilities, χ , for $(Gd_xLa_{1-x})Ni_5$ compounds are shown in Fig. 8, while those determined in YCo_4M ($M = Si, Al$) compounds are plotted in Fig. 9. Non linear variations of χ vs T^{-1} , typical for ferrimagnetic compounds are shown in $(Gd_xNa_{1-x})Ni_5$ system, where small nickel moments are antiparallely oriented to those of gadolinium. The interactions between gadolinium atoms of 5d–5d type seems to play a major role. As a result, the deviations from nonlinearity of χ^{-1} vs T , are rather small. In the temperature range $T > 150$ K, linear dependences are shown, allowing the determination of the Curie constants. According to additional law of magnetic susceptibilities, the contributions of nickel atoms to the Curie constants and effective nickel moments, respectively were determined (Fig. 10). As the gadolinium content, exchange interactions, respectively are higher, the effective nickel moments diminish.

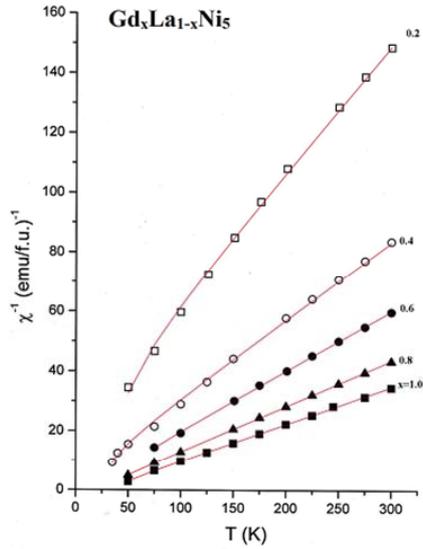


Fig. 8 – Thermal variations of reciprocal susceptibilities for $(\text{Gd}_x\text{La}_{1-x})\text{Ni}_5$ compounds.

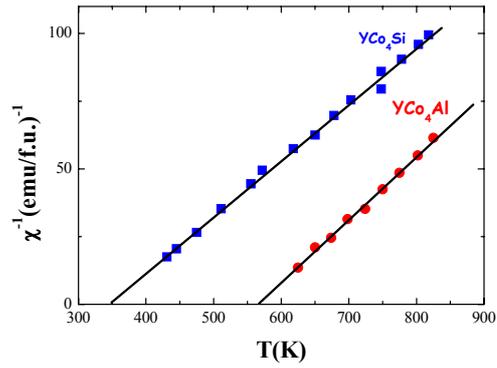


Fig. 9 – Thermal variations of reciprocal susceptibilities for YCo_4M ($\text{M}=\text{Si},\text{Al}$) compounds.

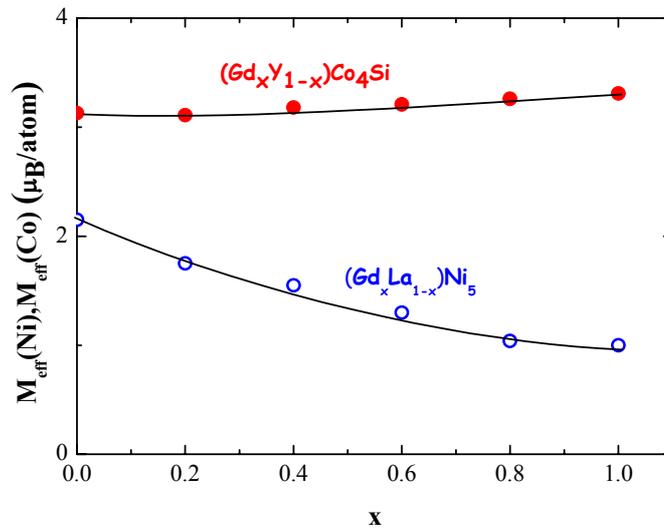


Fig. 10 – Effective nickel and cobalt moments determined in $(\text{Gd}_x\text{La}_{1-x})\text{Ni}_5$ and $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{Si}$ systems.

In case of YCo_4M ($\text{M}=\text{Si},\text{Al}$) compounds, the reciprocal susceptibilities show linear variations, as previously reported in yttrium-based compounds [15, 16]. The effective cobalt moments are around $3 \mu_{\text{B}}/\text{atom}$.

4. DISCUSSION

Starting from experimental data, by using the molecular field model, the exchange (internal) fields, H_{exch} , acting on transition metal atoms were evaluated. Their estimation involved some approximations. These were connected mainly with the considerations of mean values for transition metal moments as well as of the molecular field coefficients describing the interactions inside and between magnetic sublattices [17]. Linear dependences of mean cobalt and nickel moments were shown, when plotted as function of H_{exch} values.

The mean magnetic cobalt moments in $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{Si}$ increase from $0.73 \mu_B$ ($x = 0$) to $1.25 \mu_B$ ($x = 1$) [5]. Their dependence on exchange field has a slope $a = 2.5 \cdot 10^2 \text{T}/\mu_B$. The above value agrees well with those previously determined in R–Co–B compounds, under the action of exchange fields [17,18] or external field [19]. The effect of field used in measurements has been neglected in cobalt compounds since it is no higher than 4 % from exchange field. We note that the YCo_2 exchange enhanced paramagnet, in field of 70 T, jumps the magnetization from 0 up to $0.44 \mu_B$ [20]. The external field necessary to induce a magnetic moment of $1 \mu_B$ corresponds to a value $a \cong 3.1 \cdot 10^2 \text{T}/\mu_B$, close to that above estimated.

The external fields used for measurements on $(\text{Gd}_x\text{La}_{1-x})\text{Ni}_5$, as well as on others nickel-heavy rare-earth compounds, is of the same order of magnitude as the exchange fields and consequently cannot be neglected in estimating the a values. Thus, if only internal field is considered, a value $a \cong 1.5 \cdot 10^2 \text{T}/\mu_B$ was obtained. When the internal fields were added to exchange ones, the a slope was of $\cong 2.2 \cdot 10^2 \text{T}/\mu_B$, close to that obtained in cobalt compounds.

Since there are similar dependences and with the same slope, both for cobalt and nickel moments on exchange (external) fields, it follows that the exchange splittings can be correlated in the same way with both Co and Ni moments in agreement with the trend evidenced by band structure calculations (Fig. 4).

The magnetic behaviour of cobalt and nickel in the studied compounds can be analysed in spin fluctuations model [21]. The effective cobalt moments in $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{Si}$ alloys are little dependent on composition, while the saturation ones increase gradually as the gadolinium content, exchange interactions, respectively are higher. As a result, the ratio r between the number of spins determined from effective cobalt moments and saturation ones changes from $r \cong 3.2$ in YCo_4M ($\text{M}=\text{Si},\text{Al}$) to $r = 1.9$ in GdCo_4Si compound. This trend suggests an increase in the degree of localization of cobalt moments. The nearly constant $M_{\text{eff}}(\text{Co})$ values, along series, can be attributed to partial quenching of spin fluctuations.

The temperature dependence of the magnetic susceptibilities in LaNi_5 changes from a T^2 law, at low temperatures, to a Curie–Weiss type at $T > 180 \text{K}$, behaviour characteristic for a spin fluctuations system [14]. The determined

effective nickel moment is $M_{\text{eff}}(\text{Ni})=2.15 \mu_{\text{B}}$ [13]. A value $r \rightarrow \infty$ is suggested in this case. The effective nickel moments in $(\text{Gd}_x\text{La}_{1-x})\text{Ni}_5$ system decreased as the gadolinium content is higher, while those determined at 1.5 K increased. As a result, the r ratio decreased gradually when La was substituted by Gd and a value $r \cong 2$ was shown in GdNi_5 . This behaviour can be also attributed to gradual quenching of spin fluctuations by internal (external) fields. Similar behaviour was already evidenced in RCO_2 -type compounds with heavy rare-earths or yttrium [22, 23]. In YCo_2 and LuCo_2 , the electronic specific heat coefficients decreased by 4–10 % under the action of a field of 10 T [23]. In addition, magnetic measurements [22] evidenced a gradually decreases of the effective cobalt moments along series, from $3.87 \mu_{\text{B}}$ determined in TmCo_2 , to $2.70 \mu_{\text{B}}$ in GdCo_2 , as result of the increase of exchange interactions. The above behaviour is similar to that evidenced in Fig. 6, suggesting the presence of the same mechanism.

The spin fluctuations model suggests that the Curie constants are not dependent on saturation moment, at $T = 0$, but only on the band structures around the Fermi energy. The analysis of the band structures of $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_4\text{Si}$ and YCo_4M compounds evidenced rather similar Co partial density of states, although the Curie temperatures (exchange interactions) and Co saturation moments are dependent on composition. In additions, no sensitive changes in effective cobalt moments are shown – Fig. 10 – in agreement with spin fluctuations model.

The exchange fields can influence both saturation and effective Co and Ni moments but the involved mechanisms are different. At low temperatures, there is a change of 3d saturation moments when the exchange splittings are modified by internal (external) fields. Above the Curie temperatures, a mechanism involving quenching of spin fluctuations can be invoked to take into account the behaviour of effective moments.

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