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EXCHANGE ENHANCED PARAMAGNETS: TEMPERATURE INDUCED TRANSITION METAL MOMENTS[1]

E. Burzo

Faculty of Physics, Babes-Bolyai University Cluj-Napoca, Romania

Abstract
The exchange enhanced paramagnets based on $LaNi_5$-, YCo_2- and Y-Co-B compounds show a transition from a T^2 dependence of the magnetic susceptibilities, to a Curie-Weiss behavior, as temperature increases. The band structure calculations were used to describe the low temperature magnetic susceptibilities as well as their temperature dependences. The magnetic behavior of Co and Ni, in the above systems, were analysed in spin fluctuation model.

1. Introduction

The study of the magnetic behavior of R-M- and R-M-B-based compounds, where R is a rare-earth or yttrium and M = Co or Ni is useful for understanding the magnetic phenomena. The 3d electrons of Co and Ni, as function of composition, show a diversity of magnetic behaviors, from well established magnetism, crossing the situation when this collapse, up to exchange enhanced paramagnetism [1]. In this paper we analyse the magnetic behavior of exchange enhanced paramagnets of R-M- and R-M-B-based compounds where R is a nonmagnetic rare-earth or yttrium and M=Co or Ni. The magnetic properties of the exchanged paramagnets are difficult to be studied. The presence of small quantities of magnetic ordered impurities can modify the real magnetic susceptibilities. Thus, a careful preparation of the compounds as well as the analysis of the data, in ordered to eliminate the contributions to susceptibilities from magnetic ordered phases, is necessary.

In previous papers [2-7] we showed interesting properties of exchange enhanced paramagnets based on YCo_2- and $LaNi_5$- compounds. In high temperature range there is a change in their magnetic behavior, the systems showing a similar behavior as for those characterized by local moments. As an on-going work, we present in this paper the magnetic

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behavior both in low and high temperature range of some exchange enhanced paramagnets. In addition band structure calculations were performed.

2. Experimental and Computing Method

The $YCo_{2-x}M_x$ with M = Si, Cr, Cu and Ni [5], $LaNi_{5-x}M_x$ with M = Al, Cu [2,3], $Y_2Co_{7-x}Ni_xB_3$, and $YCo_{3-x}Ni_xB$ compounds were prepared in induction furnace or in arc furnace in purified argon atmosphere. The samples were thermally treated in vacuum between 900 and 1000^0C for one weak. The X-ray analyses show that the $YCo_{2-x}M_x$ form solid solutions having cubic $MgCu_2$-type structure for $x \leq 0.25$ (Ti), $x \leq 0.40$ (Cr), $x \leq 0.2$ (Cu) and $x \leq 0.3$ (Si). When M = Ni, solid solutions are formed in all the composition range. $LaNi_{5-x}M_x$ with M = Cu or Al, forms solid solutions having hexagonal $CaCu_5$-type structure for $x \leq 2$. The $YCo_{3-x}Ni_xB$ with $x \leq 2$ and $YCo_{7-x}Ni_xB_3$ compounds with $x \leq 4$ crystallize in a hexagonal structure having P6/mmm space group.

Magnetic measurements were performed in the temperature range 1.7 – 800 K. The magnetic susceptibilities, χ, were determined from their field dependences according to the relation $\chi_m = \chi + cM_sH^{-1}$, by extrapolating the measured values χ_m to $H^{-1} \rightarrow 0$. We denoted by c a presumed magnetic ordered impurity content and M_s is their saturation magnetization. By this method any possible alteration of the magnetic susceptibilities, due to presence of small quantities of magnetic ordered phase is avoided.

Band structure calculations were performed by using the ab intio tight binding linear muffin tin orbital method (LMTO) in atomic sphere approximation [8-10]. In the framework of local density approximation (LDA), the total electronic potential in the sum of the external, Coulomb and exchange correlation potential [11]. The frozen core approximation was employed in the generation of the potential and parameterization of Von-Barth and Hedin [12] was used for the exchange correlation part of the effective one electron potential, obtained within the local spin density approximation of the density functional theory.

3. Experimental results

The thermal variations of reciprocal susceptibilities of $YCo_{2-x}Si_x$, $YCo_{2-x}Ni_x$, $YCo_{3-x}Ni_xB$, $Y_2Co_3Ni_4B_3$ and $LaNi_{5-x}Cu_x$ compounds are plotted in Fig.1. The magnetic susceptibilities increase up to a temperature, T_{max}, and then decrease. Above a characteristic temperature, T*, a Curie-Weiss type behaviour was shown.

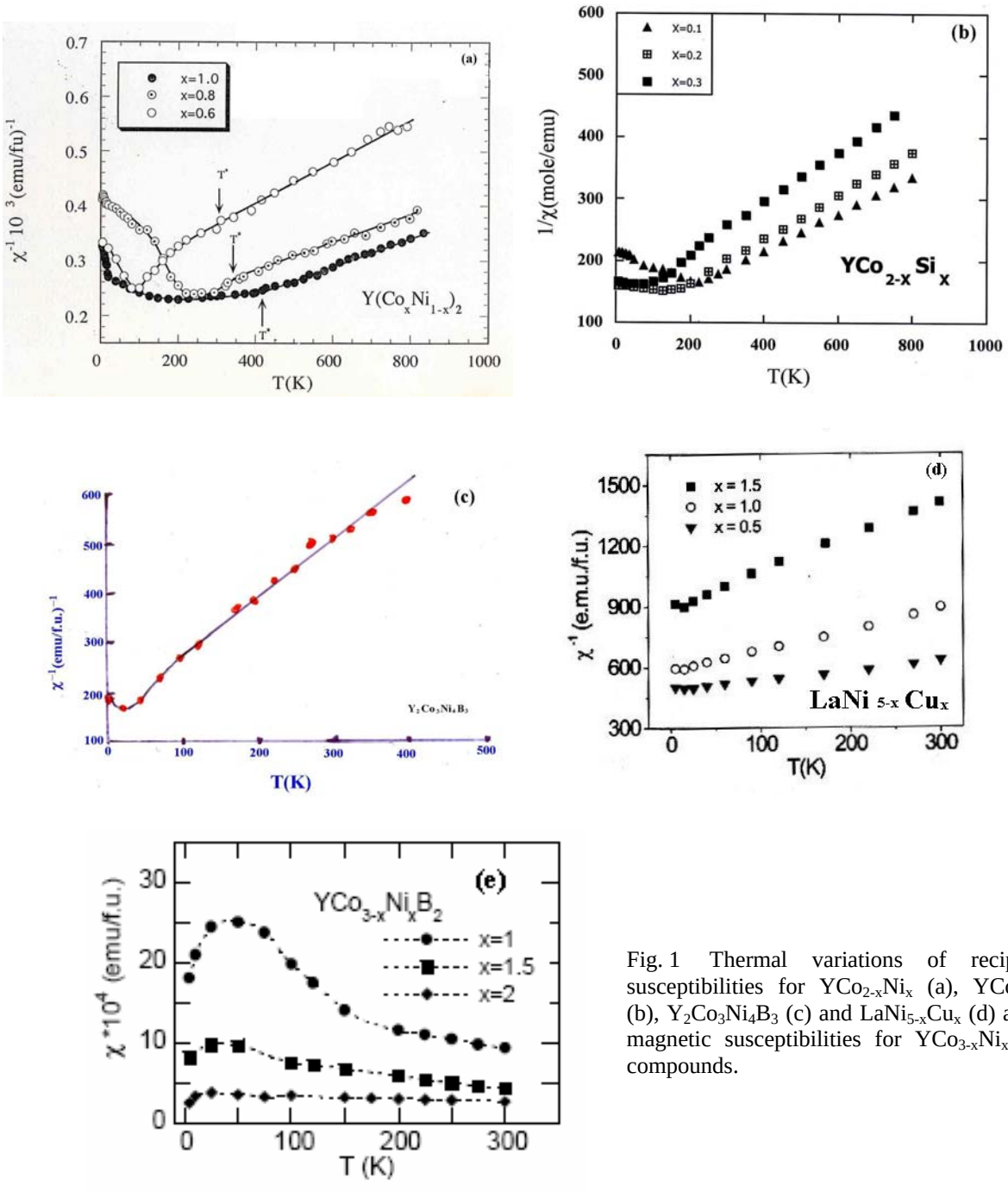


Fig. 1 Thermal variations of reciprocal susceptibilities for $YCo_{2-x}Ni_x$ (a), $YCo_{2-x}Si_x$ (b), $Y_2Co_3Ni_4B_3$ (c) and $LaNi_{5-x}Cu_x$ (d) and of magnetic susceptibilities for $YCo_{3-x}Ni_xB$ (e) compounds.

In the low temperature range, the magnetic susceptibilities follow a variation which can be described by a T^2 dependence – Fig. 2.

$$\chi = \chi_0(1+aT^2) \qquad (1)$$

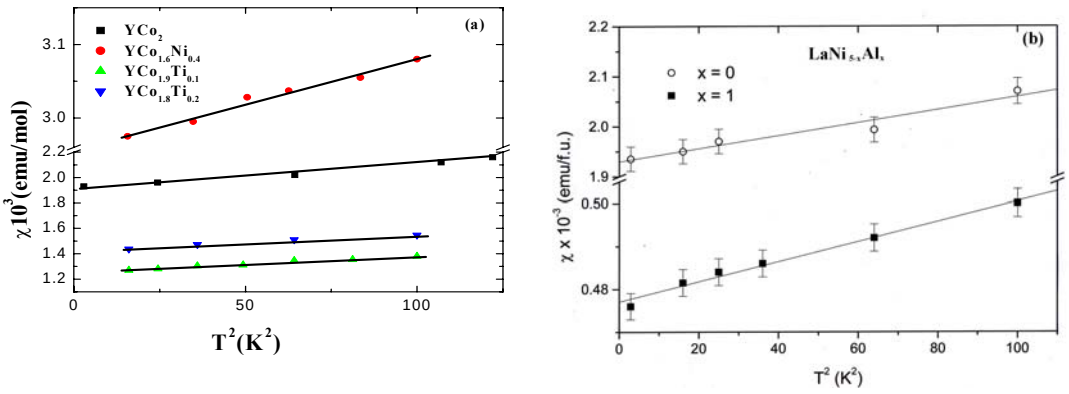


Fig.2 Temperature dependences of the magnetic susceptibilities, for $YCo_{2-x}M_x$ (M=Ni,Ti) (a) and $LaNi_{5-x}Al_x$ (b) compounds at T < 10 K.

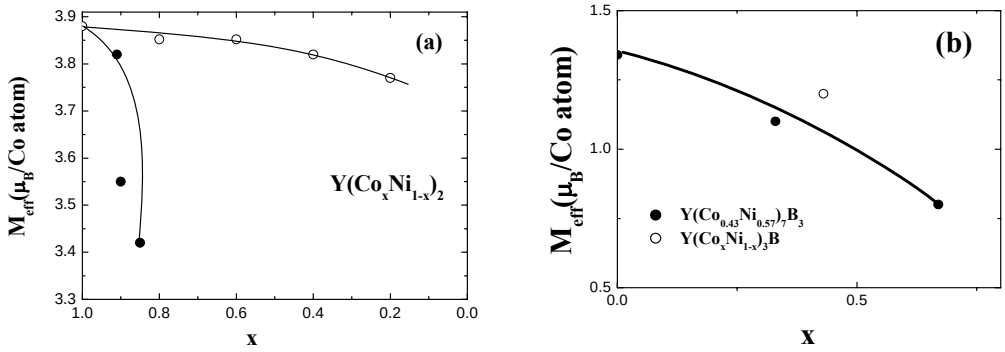


Fig. 3 The effective cobalt moments in $YCo_{2-x}M_x$ (M = Co,Si) (a) and $YCo_{3-x}Ni_xB$ and $Y_2Co_3Ni_4B_3$ (b) compounds.

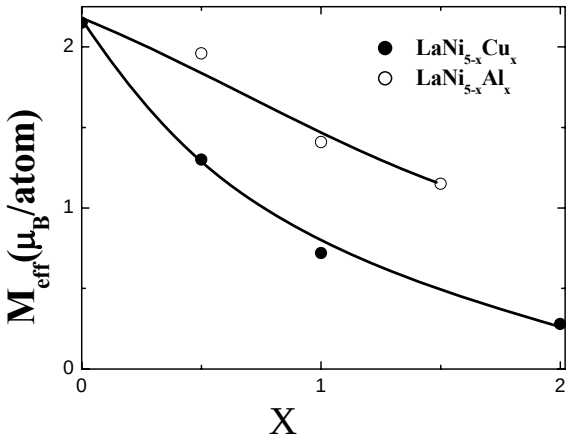


Fig. 4 The effective nickel moments in $LaNi_{5-x}M_x$ (M = Cu,Al).

Above the temperature T*, there is a change in magnetic behavior; the χ^{-1} vs T for all the systems follows linear dependences – Fig.1. The effective magnetic moments of cobalt, M_{eff}(Co), in $YCo_{2-x}Ni_x$ and $YCo_{2-x}Si_x$, $YCo_{3-x}Ni_xB$ and $Y_2Co_3Ni_4B_3$ are plotted in Fig.3. In Fig. 4 the effective nickel moments in $LaNi_{5-x}M_x$ with M = Cu, Al are plotted. The effective cobalt moments in $YCo_{2-x}Ni_x$ are little dependent on composition, while in case of $YCo_{2-x}Si_x$,

$YCo_{3-x}Ni_xB$ and $Y_2Co_3Ni_4B_3$ systems, the M_{eff}(Co) decrease rather rapidly when increasing silicon content. A decrease of effective nickel moments can be shown in nickel based compounds, when nickel is substituted by Cu or Al.

In order to obtain more information on the above behaviour, band structure calculations were performed.

The total density of states as well as of Co3d ones for YCo_2, $YCo_{1.7}Si_{0.3}$, $YCo_{1.625}Ni_{0.375}$ are plotted in Fig.5 and the total density of states in case of $LaNi_5$, $LaNi_4Cu$ and $LaNi_4Al$ compounds are given in Fig.6. From the above data, we computed the magnetic susceptibilities at 0 K. The values thus obtained, in $LaNi_{5-x}M_x$ systems, as well as those experimentally determined are given in Fig.7. There is a rather good agreement. The high decrease of the χ values in $LaNi_{5-x}Al_x$ can be attributed to hybridization effects of Ni3d and Al3p states. This is not observed in copper substituted system where separate Cu and Ni bands were shown as evidenced in Fig.6. The effect of hybridization may be better observed in $YCo_{2-x}Si_x$ system -Fig.5. In YCo_2 the Fermi level is situated above the characteristic double sharp peak structure of the local DOS of cobalt d states. The double peak structure of Co d states decrease in intensity and is broadened by p-d hybridization and in addition the Co3d band is shifted to lower energies. In this way can be explained the rather high decrease of the cobalt moment in silicon doped compounds. No much changes can be observed in the band structures $YCo_{2-x}Ni_x$ compounds.

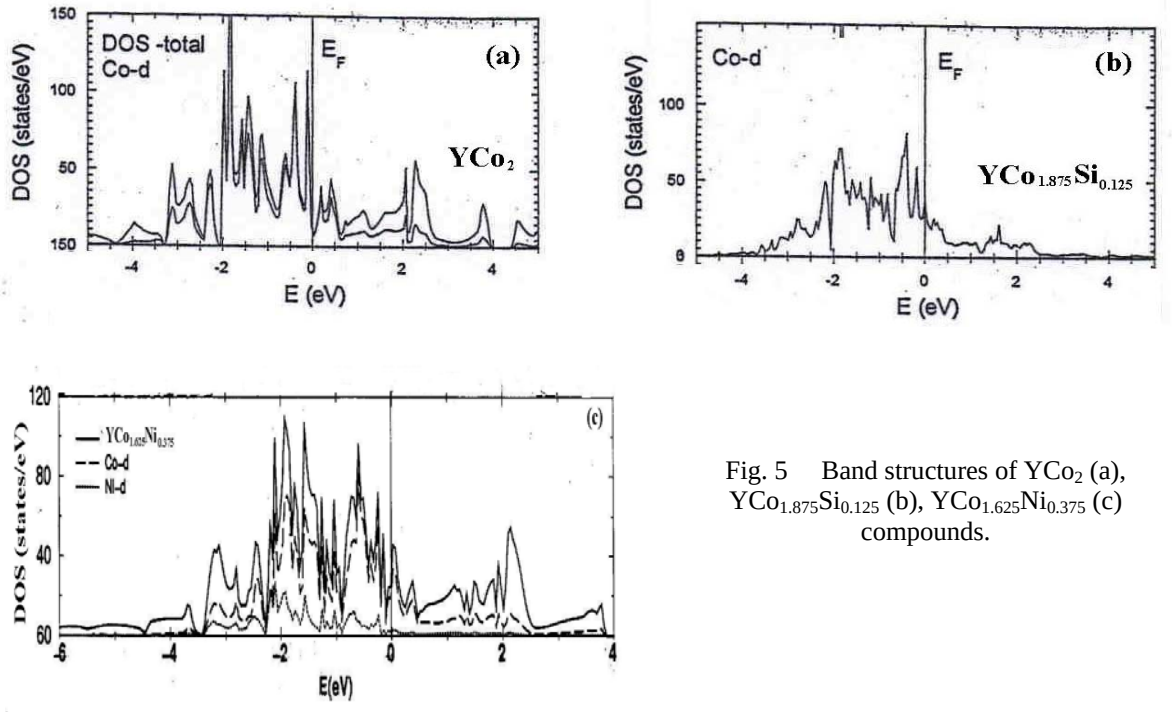
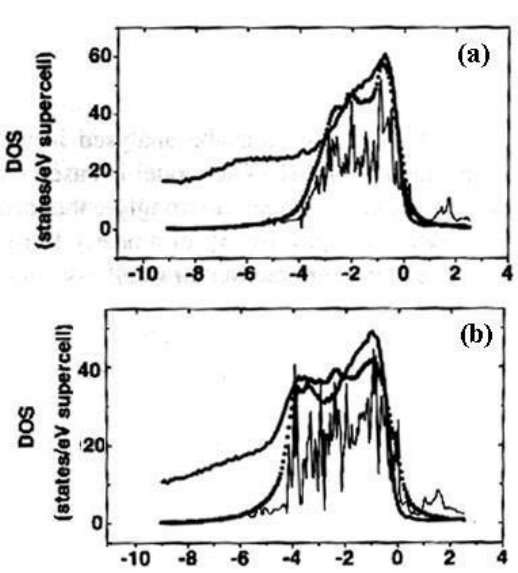


Fig. 5 Band structures of YCo_2 (a), $YCo_{1.875}Si_{0.125}$ (b), $YCo_{1.625}Ni_{0.375}$ (c) compounds.



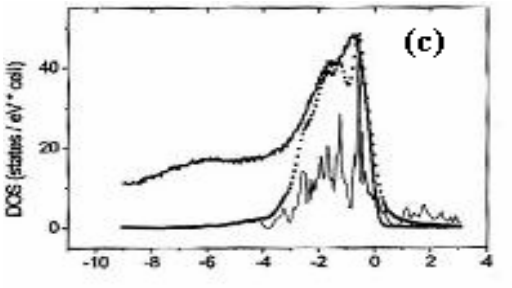


Fig.6 Band structures for $LaNi_5$ (a), $LaNi_4Cu$ (b) and $LaNi_4Al$ (c). On the same figures the measured XPS valence bands (thick solid curves) and the convoluted DOS (with Lorentzian's of half width 0.4 eV and taking into account appropriate cross-sections for partial bands with different l-symmetry, dotted curve) are plotted.

The coefficients, a, describing the slope of χ^{-1} vs T^2, as mentioned in relation (1) were calculated by considering a paramagnon model [13,14]. In this model the a term is given by:

$$a = \frac{\pi^2}{6}\left(2\frac{\eta''}{\eta} - 1.2\frac{\eta'^2}{\eta^2}\right)_{E_F} s^2 \qquad (2)$$

We denoted by η, η' and η" the state density at the Fermi level and their first and second of their derivatives and by s the exchange enhancement factor. From band structures we determined the $\eta(E_F)$, $\eta'(E_F)$ and $\eta''(E_F)$ and thus the a values. As seen in Table 1 there is a rather good agreement between the computed and experimentally determined values.

Table 1: The experimentally determined and computed a parameters

Compound	$a \cdot 10^{-3}$ (K^{-2})	
	experimental	theoretical
$LaNi_5$	1.30	1.22
$LaNi_4Al$	0.23	0.17
$LaNi_4Cu$	1.00	0.94
YCo_2	1.80	2.06
$YCo_{1.6}Ni_{0.4}$	1.30	1.52
$YCo_{1.9}Ti_{0.1}$	1.068	
$YCo_{1.875}Ti_{0.125}$		0.996
$YCo_{1.8}Ti_{0.2}$	0.91	
$YCo_{1.75}Ti_{0.25}$		0.895

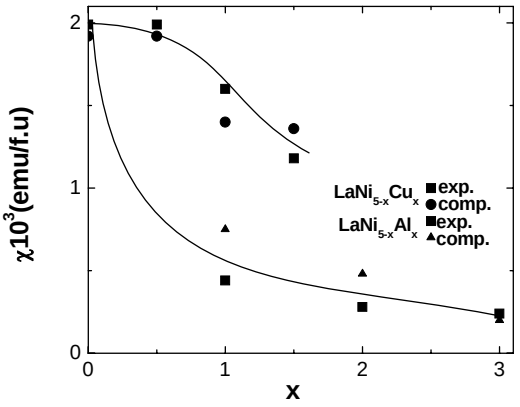


Fig.7 The computed susceptibilities from band structure calculations and the experimentally determined values, at 1.7 K, for $LaNi_{5-x}M_x$ with M = Al and Cu.

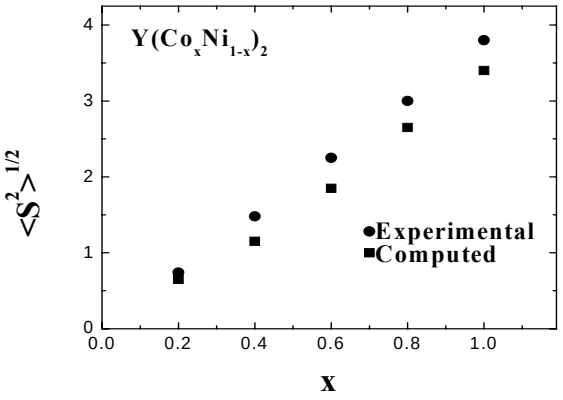


Fig.8 The experimental determined $<S^2>^{1/2}$ values and those computed in $Y(Co_xNi_{1-x})_2$ compounds

As already evidenced, there is a transition from a T^2 dependence of the magnetic susceptibilities, characteristic to a Pauli-type paramagnetism, to a Curie-Weiss behavior typical for localized moments. This behavior can be analysed in the spin fluctuation model [15]. The model is based on the concept of temperature induced moments for systems having a strongly enhanced paramagnetic susceptibility. In this model, the wave number dependent susceptibility, χ_q, for a nearly ferromagnetic alloy has a large enhancement due to electron-electron interaction for small q values. The χ_q shows significant temperature dependence only for q values close to zero. The average amplitude of spin fluctuations $<S^2> = 3\ k_B T\ \Sigma\ \chi_q$ increases with temperature and reaches an upper limit at a temperature T*. For T > T* a Curie-Weiss type behaviour is predicted, similar as in systems having local moments. The moments are localized in q space. The spin fluctuations are saturated only for samples having high enhancement factor, as YCo_2, where s ≅ 10. In $LaNi_5$-based systems, the exchange enhancement factor s ≅ 5-6 and thus the spin fluctuations are not saturated. In first case the effective moments are close to that of free Co^{2+} ions, white in second one these are smaller than that of free Ni^{2+} ion. We analysed the temperature dependences of the magnetic susceptibilities in $YCo_{2-x}Ni_x$ system, in which the spin fluctuations seem to be saturated in high temperature range [4]. The contributions of spin fluctuations were considered to obey a classical gaussian statistics [16,17]. In this model, it is possible to estimate quantitatively the contributions to the susceptibilities, χ_s, from the spin fluctuations, in terms of a realistic density of states as [16-19]:

$$\chi_s^{-1} = a_1 - \alpha + \frac{5}{3} a_3 < S^2 > + \frac{35}{9} a_5 < S^2 >^2 + \frac{35}{3} a_7 < S^2 >^3 + \ldots\ldots \quad (3)$$

where the mean square value of the fluctuating magnetization, $<S^2>$, is given by:

$$< S^2 >= \frac{3}{2\pi^2} k_B T q_m A^{-1} \left(\frac{1 - tg^{-1}(q_m \sqrt{A\chi}}{q_m \sqrt{A\chi}} \right) \qquad (4)$$

We denoted by a_1, a_3, a_5 and a_7 the expansion coefficients of the free energy with respect to the square of the magnetization density and α, q_m and A denote the molecular field coefficient, the cut-off wave vector of spin fluctuations and the exchange stiffness constant, respectively.

In the following, the series expansion development up to terms in $<S^2>$ was considered. The explicit expressions for a_i coefficients were given as [18,19]:

$$a_1 = \frac{2}{g^2 \mu_B^2 N} \left\{ 1 + \frac{1}{6} (\pi k_B T)^2 \left[\left(\frac{\eta'}{\eta} \right)^2 - \frac{\eta''}{\eta} \right] + ... \right\} \qquad (5)$$

$$a_3 = \frac{g^2 \mu_B^2}{2^2 3!} \cdot a_1^3 \left\{ 3\left(\frac{\eta'}{\eta} \right)^2 - \frac{\eta''}{\eta} + \frac{1}{6} (\pi k_B T)^2 \left[6\left(\frac{\eta'}{\eta} \right)^4 - 13 \frac{\eta'' \eta'^2}{\eta^3} + \left(\frac{\eta''}{\eta} \right)^2 + 7\left(\frac{\eta''' \eta'}{\eta^2} \right) - \frac{\eta''''}{\eta} \right] + .. \right\} \qquad (6)$$

As previously, η''' and η'''' are the derivative of three and fourth order, respectively, of the state density. The temperature dependences of $<S^2>$ values were determined, according to the above relations, in $YCo_{2-x}Ni_x$ system up to temperature of 800 K. The values thus obtained close to saturation ($T \cong$ 800 K) are given in Fig.7 together with those experimentally determined. The computed values are only little smaller than the experimental ones. The differences can be attributed to limitation of the number of terms in series development of χ values as well as to the fact that $<S^2>$ values were computed only up to 800 K. We evaluated also the exchange stiffness constants A. These values decrease gradually when the nickel content increase. This is in agreement with the decrease of the exchange enhancement factor, as evidenced from susceptibilities data in $YCo_{2-x}Ni_x$ compounds.

4. Conclusions

The exchange enhanced paramagnets show a spin fluctuations behavior. A transition from a T^2 dependence of the magnetic susceptibilities, to a Curie-Weiss behavior was shown, as temperature increases.

The magnetic susceptibilities of Y-Co, Y-Co-B and La-Ni- based systems show a transition from a T^2 dependence to a Curie-Weiss behavior as temperature increases. The above data can be analysed in spin fluctuations model. The model reconciles the dual character of electron, which as particle requires a real space description and as a wave, a

momentum space description. The spin fluctuations model considers the balance between the frequencies of longitudinal spin fluctuations, which are determined by their lifetime and of transverse fluctuations, which are of thermal origin. These effects lead to the concept of temperature-induced magnetic moment. The XPS studies performed on the studied systems show that the 3d band of Ni and Co, at 300K, are not filled, in agreement with the magnetic measurements.

The low temperature magnetic susceptibilities are well described in paramagnon model, by using the densities of states determined from band structure calculations.

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