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Spin fluctuations in cobalt and nickel-rare-earth (yttrium) exchange enhanced paramagnets

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The temperature dependences of the magnetic susceptibilities of cobalt and nickel-rare-earth (yttrium) exchange enhanced paramagnets were analyzed. As the temperature increases there is a change from a T^2 dependence, to a Curie-Weiss behavior. The experimental data were analyzed in spin fluctuations model by using a classical Gaussian statistics. The quenching of spin fluctuation by internal fields, when nonmagnetic rare-earth (yttrium) is replaced by a magnetic one, was discussed. The decrease of the effective cobalt and nickel moments is linearly dependent on the exchange field.

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1. Introduction

The transition metals, cobalt and nickel, in rare-earth or yttrium compounds show a diversity of magnetic behaviors, from well established magnetism, in compounds having high ordering temperatures, to paramagnetism by crossing the situation in which their magnetic ordered moments, at 0 K, collapse [1]. A large number of compounds are paramagnetic, at low temperatures. In earlier papers these were considered to be normal paramagnets, although in some cases maxima in temperature dependences of their magnetic susceptibilities were shown.

Generally, it is difficult to determine accurate values of the magnetic susceptibilities since of the presence of magnetic ordered impurities. Even in small quantities, these influence considerably the magnetic data. Accurate values can be obtained by analyzing the field dependences of the magnetic susceptibilities and eliminating the contributions of magnetic impurities according to Honda-Arrott plot [2]: $\chi_m=\chi+cM_s\cdot H^{-1}$, by extrapolating the measured values to $H^{-1} \rightarrow 0$. We denoted by c a presumed content of magnetic ordered impurity and M_s is their saturation magnetization.

By using this method, accurate values of the magnetic susceptibilities of RCo_2 (R=Lu,Y,Sc and Hf) compounds were obtained [2]. As function of temperature, the susceptibilities change from a behavior characteristic to a Pauli type paramagnetism to a Curie-Weiss type dependence.

In this paper we analyze the temperature dependences of the magnetic susceptibilities of some pseudo binary and ternary exchange enhanced paramagnets. We selected samples crystallizing in cubic $MgCu_2$-type structure and hexagonal structures. In addition to magnetic measurements, band structure calculations were performed. It was shown that the behavior evidenced in RCo_2 (R=Y,Lu,Sc,Hf) is generally characteristic for paramagnetic systems having high enhanced magnetic susceptibilities. Finally, we analyze the effect of the exchange field on the magnetic properties of the exchange enhanced paramagnets.

2. Experimental and computing method

The $Y(Co_{1-x}M_x)_2$ with M = Ni, Ti, Si, YCo_3B_2, $Y_3Co_3Ni_8B_4$, RNi_5 with R = La, Y and $Gd_xLa_{1-x}Ni_5$ systems were studied. The samples were prepared by melting the constituent elements in an induction furnace. The samples were heat treated at temperatures between 800 and 900^0C, depending on composition [3-7]. A small excess of Y or rare-earth was used in order to compensate for the weight loss during melting and to avoid the formation of magnetic ordered phases. The X-ray analyses showed, in all cases, the presence of a single phase. The $(YCo_{1-x}M_x)_2$ compounds, in the studied composition range, crystallize in cubic $MgCu_2$ type structure, the RNi_5 in hexagonal $CaCu_5$ type structure and YCo_3B_2 and $Y_3Co_3Ni_8B_4$ in hexagonal structures.

The magnetic measurements were performed in a large temperature range, from 1.7 K and in fields up to 9 T. For each temperature, the susceptibilities were determined according to Honda-Arott plot. The content of magnetic impurities, if existed, was estimated to be smaller than 0.3 %.

Band structure calculations were carried out by using the ab initio tight binding linear muffin thin orbital method in the atomic sphere approximation (TB-LMTO). The detailed procedure of calculation was described else where [8]. In the framework of the local density approximation (LDA), the total electronic potential is the sum of external, Coulomb and exchange correlation potentials [9]. The functional form of the exchange correlation energy, used in the present work, was the free electron gas parameterization of Von Barth and Hedin [10]. Relativistic correlations were included.

3. Experimental results and computing data

3.1 Cobalt based compounds

The temperature dependences of the reciprocal susceptibilities for some $Y(Co_{1-x}M_x)_2$ compounds with M = Ni, Si and Ti are shown in Fig. 1.

The magnetic susceptibilities increase up to a characteristic temperature, T_{max}, and then decrease. The T_{max} values are shifted to lower temperatures as the cobalt is replaced by M elements [4,5]. Maxima in the temperature dependences of the magnetic susceptibilities of YCo_3B_2 and $Y_3Co_3Ni_8B_4$ compounds were also shown – Fig. 2.

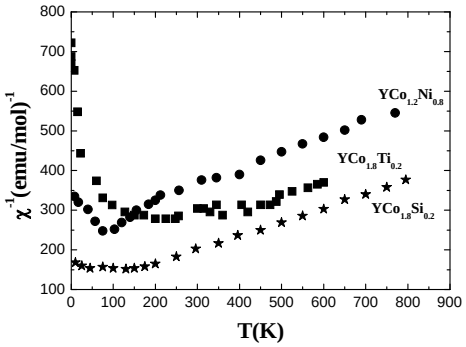

Fig. 1. Thermal variations of reciprocal susceptibilities for $YCo_{1.2}Ni_{0.8}$, $YCo_{1.8}Si_{0.2}$ and $YCo_{1.8}Ti_{0.2}$ compounds.

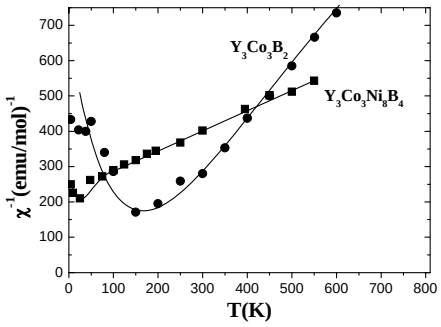

Fig. 2. Thermal variations of reciprocal susceptibilities for YCo_3B_2 and $Y_3Co_3Ni_8B_4$ compounds.

In the low temperature range, –Fig.3– the magnetic susceptibilities follow a T^2 dependence described by the relation:

$$\chi=\chi_0(1+\beta T^2) \quad (1)$$

The slopes, β of these dependences are listed in Table 1.

At temperatures higher than a characteristic value, T*, the reciprocal susceptibilities follow linear dependences described by a Curie-Weiss law:

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

We denoted by C the Curie constant and θ is an asymptotic temperature. The θ values are negative.

The effective cobalt moments, $M_{eff}(Co)$, determined from the Curie constants are given in Fig. 4. For YCo_2 the effective cobalt moment is close to that of free Co^{2+} ion considering only spin contribution. When cobalt is substituted by Ni or Ti, there are small variations in $M_{eff}(Co)$ values. A higher decrease of the effective cobalt moments was shown when cobalt is replaced gradually by silicon.

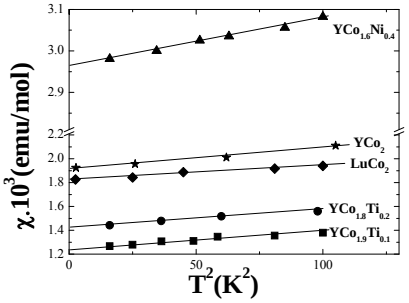

Fig. 3. Thermal variations of magnetic susceptibilities at $T \leq 10$ K, for YCo_2, $LuCo_2$, $YCo_{1.6}Ni_{0.4}$, $YCo_{1.9}Si_{0.1}$, $YCo_{1.8}Ti_{0.2}$ alloys.

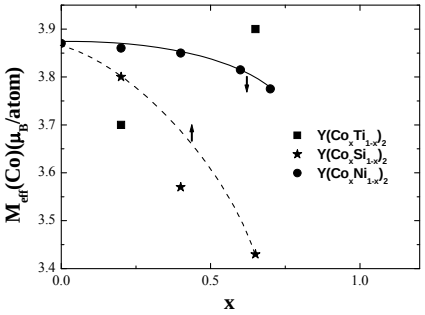

Fig. 4. Effective cobalt moments in $Y(Co_{1-x}Ni_x)_2$, $Y(Co_{1-x}Si_x)_2$ and $Y(Co_{1-x}Ti_x)_2$ compounds.

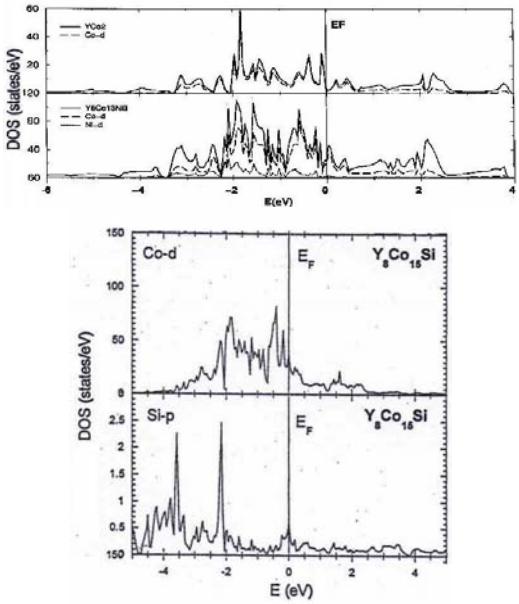

Fig. 5. Band structures of YCo_2, $YCo_{1.6}Ni_{0.4}$, and $YCo_{1.875}Si_{0.125}$ compounds.

Table 1. Magnetic susceptibilities at 1.7 K and β values experimentally determined and computed from band structures

Compound	$\chi \cdot 10^3$ (emu/mol)		$\beta \cdot 10^3$ (K^{-2})	
	experimental	computed	experimental	computed
YCo_2	1.92	2.15	1.8	1.7
$YCo_{1.6}Ni_{0.4}$	2.92			
$YCo_{1.9}Ti_{0.1}$	1.27		1.17	
$YCo_{1.875}Si_{0.125}$	1.75	1.80		1.00
$LuCo_2$	1.83	2.50	1.05	1.15
$LaNi_5$	1.93	1.88	1.30	1.22
YNi_5	2.50	3.25	3.00	3.50

The band structures of YCo_2, $YCo_{1.6}Ni_{0.4}$ and $YCo_{1.875}Si_{0.125}$ are plotted in Fig. 5. The Fermi level in YCo_2 is situated above a characteristic double sharp peak structure of local DOS of cobalt d states. When Co is replaced by Ni or Ti there is a shift of density of states at the Fermi level toward lower energies. The double peak is still present. The double peak of Co3d states decreases in intensity when silicon content increases and is broadened by p-d hybridization. The density of the d states, at the Fermi level decreases. The computed magnetic susceptibilities starting from band structures agree rather well with experimentally determined values – Table 1.

The temperature factor, β, of the low temperature susceptibility from relation (1) was computed according to [11]:

$$\beta=\frac{\pi^2}{6}\left[\left(2\frac{\eta''}{\eta}-1.2\frac{\eta'^2}{\eta^2}\right)_{E_F}\right]s^2 \qquad (3)$$

where s is the Stoner exchange enhancement factor and η, η' and η" are the state densities at the Fermi level and its first and second derivatives. The computed β values describe reasonably the experimental values.

The experimental data on the above exchange enhanced paramagnets are in agreement with the prediction of spin fluctuation model [12]. The model is based on the concept of temperature induced moments for systems which have a strongly enhanced magnetic susceptibility with high Stoner enhancement factors, as in RCo_2 (R=Y,Lu) compounds, where s=8-10. At low temperatures, the frequency of longitudinal spin fluctuations is higher than of transverse ones and we have the approximation for non-magnetic state. At high temperatures the situation is reversed and the temperature dependences of the susceptibilities are similar to that of a system as having local moments. In our case, the moments are localized in q space.

The temperature dependences of the magnetic susceptibilities of $Y(Co_{1-x}M_x)_2$ compounds with M = Ni, Si were calculated from the computed density of states and taking into account the effects of spin fluctuations [13,14]. The contribution of spin fluctuations, for the general model of itinerant electron paramagnetism, can be analyzed in the classical Gaussian statistics. By limiting the series expansion development up to terms in $\langle S^2\rangle$ we have

$$\chi=a_1-\alpha+\frac{5}{3}a_3\langle S^2\rangle+\ldots \qquad (4)$$

where the mean square value of the spin fluctuating magnetization $\langle S^2\rangle$ is given by

$$\langle S^2\rangle=\frac{3}{2\pi^2}k_B T q_m A^{-1}\left(1-\frac{tg^{-1}(q_m\sqrt{A\chi})}{q_m\sqrt{A\chi}}\right) \qquad (5)$$

The a_1 and a_3 are the expansion coefficients of free energy with respect to square of magnetization density, given by [13] 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.

The temperature dependences of $\langle S^2\rangle$ values in $Y(Co_{1-x}Ni_x)_2$ compounds are shown in Fig. 6 [13]. The $\langle S^2\rangle$ values are not fully saturated even at 750 K. The S values thus determined, at 750 K, are somewhat smaller than those experimentally obtained–Fig.7. This behavior can be correlated with the limitation of the number of terms in series expansion, only up to $\langle S^2\rangle$.

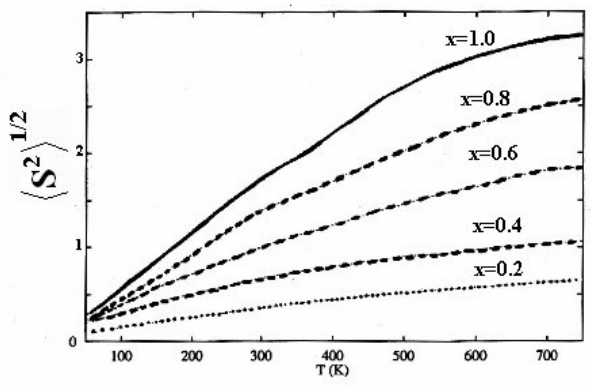

Fig. 6. Thermal variations of mean square amplitude of spin fluctuations $\langle S^2\rangle$ in $Y(Co_{1-x}Ni_x)_2$ compounds

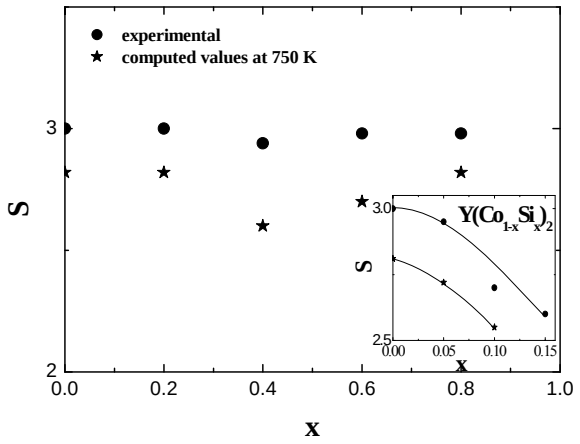

Fig. 7. The number of the spins of cobalt atoms determined from Curie constants and those theoretically obtained at 750 K.

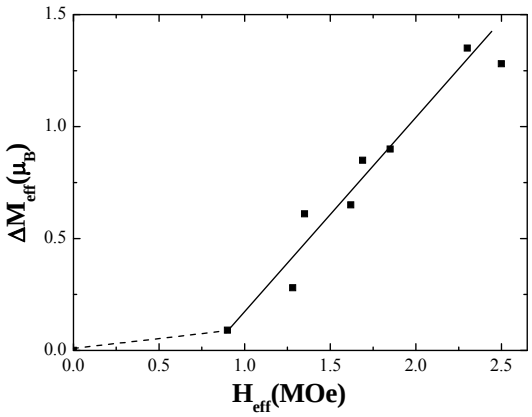

Fig. 8. The decrease of the effective cobalt moments, ΔM_{eff}(Co), in RCo_2 compounds with magnetic R elements as compared to those of YCo_2 or $LuCo_2$, as function of exchange field .

We analyzed also the effect of internal field on the effective cobalt moments, as result of substitution of yttrium or non-magnetic rare-earth by magnetic ones. There is a decrease of cobalt effective moments in RCo_2 compounds as the Curie temperatures, exchange interactions, respectively increase [3]. This behavior was attributed to the quenching of spin fluctuations. The quenching of spin fluctuations by external field has been previously discussed. According to Brinkman and Engelsberg [15], a magnetic field, $H_{eff} = k_B T_s/\mu_B s^{1/2}$, where T_s is the spin fluctuation temperature, is required to quench the spin fluctuations enhancement. If the magnetic field is sufficiently large so that the Zeeman splitting energy of opposite spin states is comparable to or larger than the characteristic spin fluctuation energy, then the paramagnet no longer has sufficient energy to flip spins and therefore the inelastic spin-flip scattering is quenched. According to Beal-Monod et al [16], the decrease of heat capacity, at 0K, for a nearly ferromagnetic liquid Fermi, is proportional to H^2. Hertel [17] stated that the electronic contribution to the heat capacity would be depressed by a few percent, at 0.1 MOe, if the Stoner enhancement and the mass enhancement factors due to spin fluctuations are large and also the spin fluctuation temperature is small. Experimentally, was shown a reduction of the electronic specific heat coefficient by 4 % and 10 % in YCo_2 and $LuCo_2$, respectively in a field of 0.1 MOe [18]. The decrease of the effective cobalt moments in RCo_2 compounds, as compared to the value determined in $LuCo_2$, ΔM_{eff}, as function of the exchange field, is plotted in Fig. 8. Above a characteristic field, the ΔM_{eff} values follow linear variation.

The YCo_3B_2 and $Y_3Co_3Ni_8B_4$ as well as other Y-Co-B exchange enhancement paramagnets – Fig. 2 –show similar temperature dependences of the magnetic susceptibilities as for pseudo binary R-Co ones. In the high temperature range a Curie-Weiss behavior was shown. When Y is replaced gradually by Gd, in YCo_3B_2, cobalt magnetic moments are induced, at 1.7 K, and there is an increase of the exchange field acting on cobalt atoms. The highest Curie temperature, of ≅ 49 K, was shown in $GdCo_3B_2$ [19]. In this system, in limit of experimental errors, of ± 0,2 μ_B, the effective cobalt moments, M_{eff}(Co)=1.34 μ_B, are not dependent on the exchange field. In the composition range $0 \le x \le 1$, the exchange interactions increase only little and the effective fields are not sufficient to induce a significant decrease of the effective cobalt moments. The situation is similar to that observed in $TmCo_2$ having T_c ≅ 33 K– Fig.8, where effective cobalt moment is close to the value determined in YCo_2. As above, no significant increase in the exchange field was expected in this case in order to influence the effective moment.

3.2 Nickel based compounds

The thermal variation of reciprocal susceptibility in $LaNi_5$ compound is plotted in Fig.9. Similar behavior was reported in $LaNi_{5-x}M_x$ with M=Al or Cu or $YNi_{5-x}Al_x$ compounds [7,20]. In the low temperature range, T ≤ 10 K, a T^2 dependence of the magnetic susceptibilities was shown. The β values are listed for Table 1. Above a characteristic temperature, T*, a Curie-Weiss behavior was evidenced. An effective nickel moment of ≅ 2.15 μ_B was determined in $LaNi_5$ and ≅ 1.7 μ_B in YNi_5. These values are smaller than that characteristic for Ni^{2+} free ion, considering only spin contribution (2.83 μ_B). In the above systems the Stoner enhancement factor, s = 6-7, is smaller than in the RCo_2 systems and consequently the M_{eff}(Ni) values are not saturated. This behavior was confirmed by analyzing $LaNi_{5-x}Cu_x$ system in which XPS studies showed that

separate Ni and Cu bands were formed [7]. Consequently, there are no hybridization effects and thus only the decrease of the exchange enhancement factors can be considered for the diminution of the effective nickel moments.

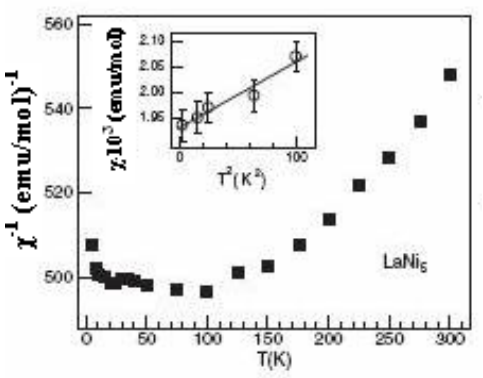

Fig. 9. Thermal variation of reciprocal susceptibility for $LaNi_5$ compound. In inset the low temperature variation of susceptibilities is shown.

When substituting La by Gd in $La_{1-x}Gd_xNi_5$ system, the effective nickel moments decrease. This behavior is similar to that observed in RCo_2 compounds. The decrease of the nickel moments, $\Delta M_{eff}(Ni)$, as function of exchange field, is plotted in Fig.10. Above a field of ≅ 0.35 MOe a linear dependence was shown. The slope of the curve is the same as that evidenced in RCo_2 compounds – Fig.8.

The XPS $Ni2p_{3/2}$, $2p_{1/2}$ and $La3d_{3/2}$ core lines of $LaNi_5$ and metallic Ni are plotted in Fig.11a and their XPS valence bands, at room temperature, are given in Fig.11b. The computed density of states of $LaNi_5$ is also included in the Fig.11b. Reasonable agreement between valence band spectra and computed density of states is shown. There is a similarity of Ni3d band of pure nickel and that of $LaNi_5$. This suggests that the $LaNi_5$ XPS spectra are mainly derived from the Ni3d ones. The structure at ≅ 6 eV binding energy in XPS spectra shows that there are holes in Ni3d band of $LaNi_5$ as suggested by magnetic measurements.

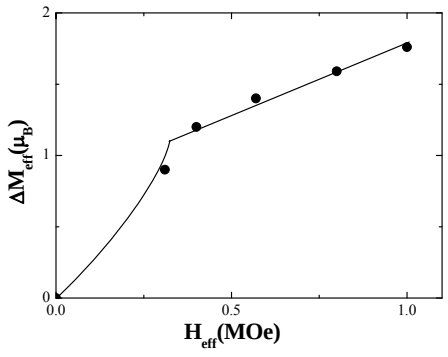

Fig. 10. The decrease of the effective nickel moments, $\Delta M_{eff}(Ni)$, in $Gd_xLa_{1-x}Ni_5$ compounds as function of exchange field

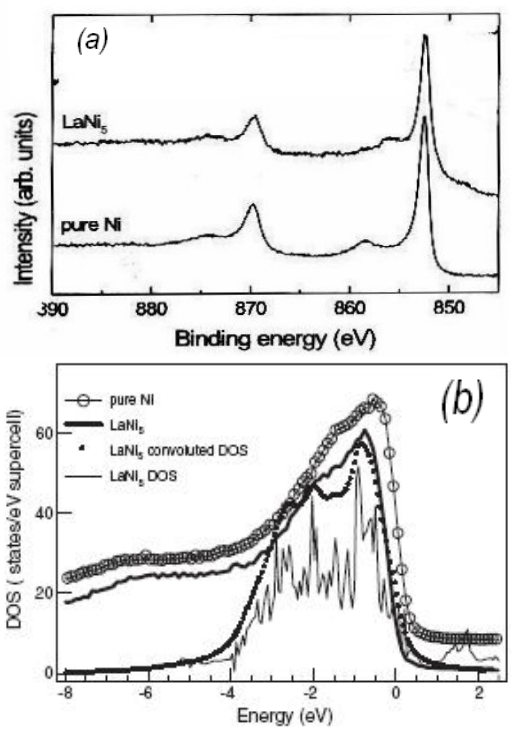

Fig. 11. The $Ni2p_{3/2}$, $2p_{1/2}$ and $La3d_{5/2}$ core lines of $LaNi_5$ (a) and comparison of the measured XPS valence band (thick solid line) and convoluted DOS (by Lorentzian of half width of 0.4 eV taking into account proper cross sections for partial bands with different l symmetry, dashed line) for $LaNi_5$ (b). The XPS spectra of Ni are also plotted in above figures.

4. Conclusions

The temperature dependences of the magnetic susceptibilities of R-Co or R-Ni (R = La,Y,Lu) exchange enhanced paramagnets change from T^2 dependence to a Curie-Weiss behavior as temperature increase. This behavior seems to be a characteristic trend for rare-earth (yttrium)–cobalt (nickel) exchange enhanced paramagnets. The experimental results are well described in the spin fluctuations model. The computed data, for susceptibilities and their temperature variations, from band structures, agree reasonable with those experimentally determined.

The spin fluctuations are gradually quenched by internal field when nonmagnetic R elements or Y are replaced by a magnetic rare-earth. The effective Co and Ni moments decrease linearly when internal field increases. There seems to be a characteristic field from which the above dependence is shown. This seems to be connected with the critical field, H_{cr}, for the appearance of induced moments of Co or Ni at 0 K. Values of critical field of 0.7 MOe, determined in RCo_2 compounds [21] or at 0.3-0.4 MOe for nickel compounds [22] correlate well with the onset of changes in the effective moments as plotted in Figs.8 and 10.

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