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Exchange Enhanced Paramagnetism of Rare-Earth (Yttrium)-Transition Metal Compounds

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Abstract. The magnetic susceptibilities, χ, of R-M and R-M-B exchange enhanced paramagnets where R = Y, La, Lu and M= Co, Ni are analysed. As a general feature, there is a T^2 dependence of χ values at T < 10 K, while for T > T* a Curie-Weiss behavior is shown. The experimental data are discussed in correlation with band structure calculations. The pressure dependence of $LuCo_2$ magnetic susceptibility is also analysed.

INTRODUCTION

The rare-earth or yttrium (R)-transition metal (M) compounds are of great interest for both fundamental studies as well as for their technical uses [1]. In the above compounds iron generally shows localized magnetic features. The cobalt has a wide range of magnetic behaviors, starting from strong ferromagnetism to exchange enhanced paramagnetism, crossing the situation when cobalt moment collapses. The nickel in rare-earth (yttrium) compounds is either a weak ferromagnet or shows a paramagnetic behavior.

The earlier magnetic measurements, on R-M exchange enhanced paramagnets, were performed in a limited temperature range, commonly up to 300-400 K. Maxima in the temperature dependences of the magnetic susceptibilities of RCo_2 (R = Y, Lu) compounds were shown [1, 2]. The same behavior was evidenced in $LaNi_5$ [3]. In the above compounds, the presence of small amounts of magnetic ordered impurities can affect the experimentally determined properties. Thus, reliable data can be obtained only by analyzing the magnetization isotherms. As a result of these studies, a more complex magnetic behavior of rare-earth(yttrium)- transition metal exchange enhanced paramagnets can be shown.

In this paper, based on the present and our previously published studies [2-11],on R-M or R-M-B exchange enhanced paramagnets, common features, for a wide range of crystal structures and Stoner enhancement factors, are evidenced. The experimentally determined susceptibilities are compared with those obtained from band structure calculations. The pressure dependence of the magnetic susceptibility of $LuCo_2$is also analysed.

EXPERIMENTAL AND COMPUTING METHOD

The R-M and R-M-B based compounds with R = Y, La, Lu and M = Fe or Ni were prepared by levitation or arc melting methods. A small excess of R elements was added in order to compensate their loss during melting. The samples were thermally treated at T = 1000-1100 K. The X-ray analyses showed, in all cases, the presence of only one phase. The SEM studies evidenced only small content of other phases, commonly below 0.1 %.

The magnetic measurements were performed in the temperature range 1.7-800 K and fields up to 90 kOe. Some previously reported data were also obtained up to 900 K [2]. The magnetic susceptibilities were determined from magnetization isotherms, according to Honda-Arrott plot [12]: $\chi_m = \chi + cM_sH^{-1}$, by extrapolating the measured values χ_m to $H^{-1} \rightarrow 0$. By c is denoted a presumed magnetic ordered impurity content and M_s is their saturation magnetization. In all cases the data were obtained for a range of external fields where the magnetizations are saturated.

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Band structure calculations were carried out by using the ab initio tight binding linear muffin tin orbital (LMTO) method in the atomic sphere approximation (ASA) [13, 14]. In the framework of the local density approximation, the total electronic potential is the sum of external, Coulomb and exchange correlation potentials [15]. The functional form of the exchange correlation energy used, was the free electron gas parameterization of Von Barth and Hedin [16]. Relativistic correlations were included.

EXPERIMENTAL RESULTS AND COMPUTED DATA

The temperature dependences of the magnetic susceptibilities for some pseudo-binary YCo_2-based cubic compounds are given in Fig.1, while for hexagonal Y-Co-B ones are plotted in Fig.2a. The magnetic behavior of YNi_5- or $LaNi_5$ – based compounds are illustrated in Fig.2b. In all cases, the magnetic susceptibilities increase up to a temperature T_{max}, dependent on the given compound. Then, there is a decrease of the χ values. Above a characteristic temperature, T*, the χ^{-1} vs T curves follows a Curie-Weiss type behavior with negative paramagnetic Curie temperatures, θ. There are different ways in which substituting elements, on the end series compounds, influence the T_{max} values. In $YCo_{2-x}M_x$ compounds, for M = Ti, only little changes of T_{max} temperatures are shown, while when Co is replaced by M = Ni, Si or Cr, the T_{max} values decrease when increasing the content of substituting elements. Higher T_{max} temperatures, as compared to that determined in YCo_2, can be shown for $LuCo_2$ or $ScCo_2$ compounds. In case of $Y(Co,Ni)_3B_2$, $Y(Ni,Cu,Al)_4B$, $La(Ni,Cu,Al)_5$ or $Y(Ni,Cu,Al)_5$ compounds, there is a gradual decrease of T_{max} when the magnetic dilution is increased.

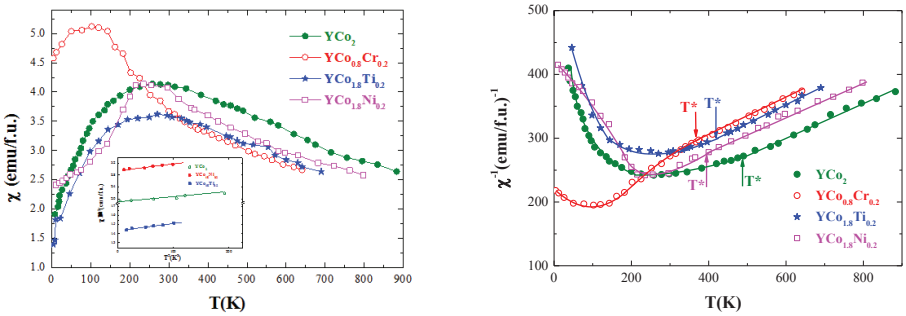
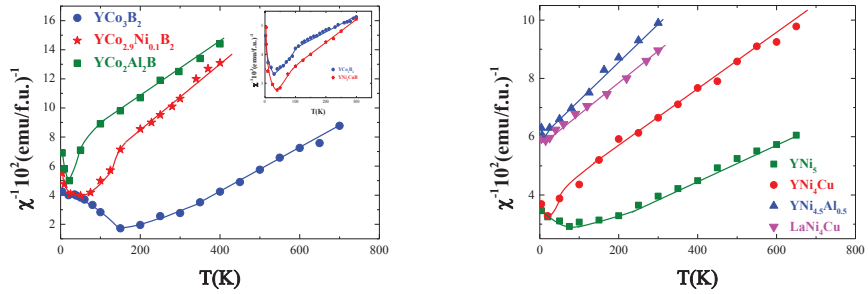


FIGURE 1. Thermal variations of magnetic susceptibilities and their reciprocal values in some $YCo_{2-x}M_x$ compounds with M = Cr, Ni, Ti.



(a) (b)

FIGURE 2. Thermal variations of reciprocal susceptibilities for some Y-Co-B (a) and $YNi_{5-x}M_x$ or $LaNi_{5-x}M_x$ with M = Cu, Al (b) compounds

At low temperatures, T < 10-15 K, the magnetic susceptibilities follow a T^2 dependence, as evidenced in Fig.1 inset:

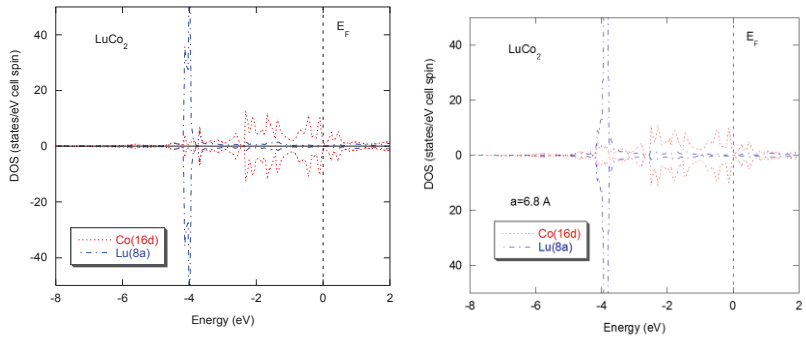
$$\chi = \chi_0(1+aT^2) \quad (1)$$

According to paramagnon model, for a general band structure, the a parameter from the relation (1) can be expressed as [17]:

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

where s is the Stoner enhancement factor and η, η' and η" are the state density at the Fermi level and their first and second derivatives, respectively.

In order to obtain more data on the studied systems, at low temperatures, band structure calculations were made. Some computed band structures are given in Figs.3 and 4. As a characteristic feature, in all cases, there is a peak in DOS at lower energies, but close to the Fermi level, E_F.



(a) (b)

FIGURE 3. Band structures of $LuCo_2$ at reduced volumes (a) $v/v_0 = 1$ and 0.96 (b).

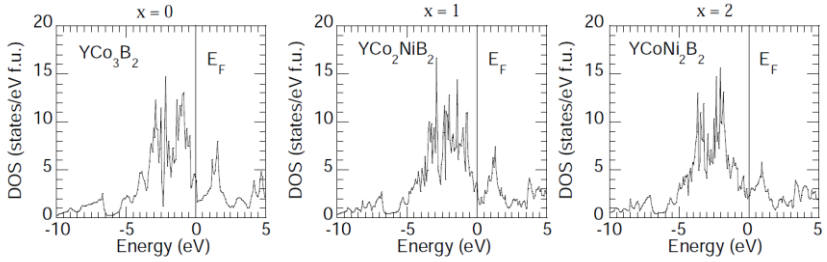


FIGURE 4. Band structures of $YCo_{3-x}Ni_xB_2$ compounds.

TABLE 1. Magnetic properties of some cobalt exchange enhanced paramagnets.

Compound	$\chi_{exp}\cdot10^{-3}$ at 2 K (emu/f.u.)	$\chi_{calc}\cdot10^{-3}$ (emu/f.u.)	T_{max} (K)	T* (K)	$a\cdot10^{-6}$		M_{eff}(Co) (μ_B/atom)
					exp.	theor.	
$LuCo_2$	1.94	2.02	370	550	0.764	0.91	4.10
$Y Co_2$	1.95	2.25	260	485	1.64	1.81	3.86
$Y Co_{1.8}Ni_{0.2}$	2.90	3.02	215	408	1.24	1.36	3.84
$Y Co_{0.9}Ti_{0.1}$	1.271		275	450	1.068		3.95
$YCo_{1.875}T_{0.125}$		1.796				0.9961	
$YCo_{1.8}Ti_{0.2}$	1.442	1.944	250	420	0.908	0.895	3.90
$Y Co_3B_2$	2.34	1.65	150	320	1.10	1.40	1.34
$Y Co_2B_2$	0.21	0.32	50	140	0.75	0.88	0.85

Starting from the density of states (DOS) at EF, the magnetic susceptibilities, at 0K, as well as the a parameters were computed. A rather good agreement between calculated values and experimental data can be shown – Table 1.

The magnetic behavior of exchange enhanced paramagnet, at T > T*, for all studied compounds, can be described by a Curie-Weiss type dependence:

$$\chi = C(T-\theta)^{-1} \qquad (3)$$

where C is the Curie constant.

The temperature dependences of the magnetic susceptibilities in the studied compounds can be described in the framework of self-consistent renormalization (SCR) theory of spin fluctuations [18]. 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 analysis considers the balance between the frequencies of longitudinal spin fluctuations, ω_l, which are determined by their lifetime and of transverse fluctuations, ω_t, which are of thermal origin. Their balance leads to the concept of temperature induced transition metal moment. For an exchange enhanced paramagnet, the wave number dependent susceptibility, χ_q, has a large enhancement due to electron-electron interactions for small q values. The mean average amplitude of spin fluctuation $\langle S^2\rangle = 3k_B T \sum_q \chi_q$ increases with temperature and reaches an upper limit, at T > T*, as determined by charge neutrality condition. In the temperature range where $\omega_t >> \omega_l$, the system behaves as having a local moment. The moment is localized in q space.

The effective cobalt moments in RCo_2 (R = Y, Lu, Sc, Hf) as well as in some of their pseudobinary compounds, where the exchange enhancement factor is s = 9-11, are close to that of Co^{2+} free ion, but decrease parallely with s values – Table 1. The effective nickel moments in $LaNi_5$ based compounds are significantly lower than that of Ni^{2+} free ion. In this case, the Stoner enhancement factors are smaller than s = 5. These data evidence a correlation between the magnetic behavior in the asymptotic region and s values.

The thermal variation of the $LuCo_2$magnetic susceptibility is analysed starting from the computed density of states and taking into account the effect of spin fluctuations [19, 20]. The contributions from spin fluctuations, for a general model of itinerant electron paramagnetism, has been considered in the classical Gaussian statistics. In the first order of the series expansion method of the free energy with respect to the square of magnetization density $\langle S^2\rangle$, this is given by :

$$\chi^{-1} = a_1 - \alpha + \frac{5}{3} a_3 \langle S^2 \rangle + \ldots\ldots\ldots\ldots \quad (4)$$

where the mean square value of the fluctuating magnetization is described by:

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

By α, q_m and A are denoted the molecular field coefficient, the cut-off wave vector of spin fluctuations and the exchange stiffness constant, respectively. The expression of a_1 coefficient is given by [19, 20]:

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

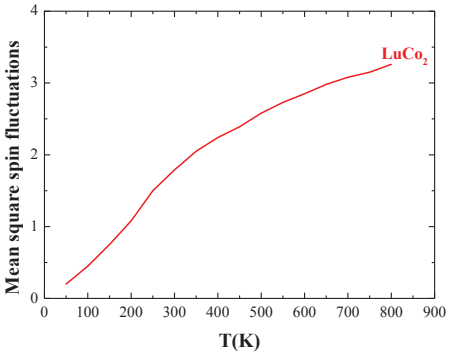
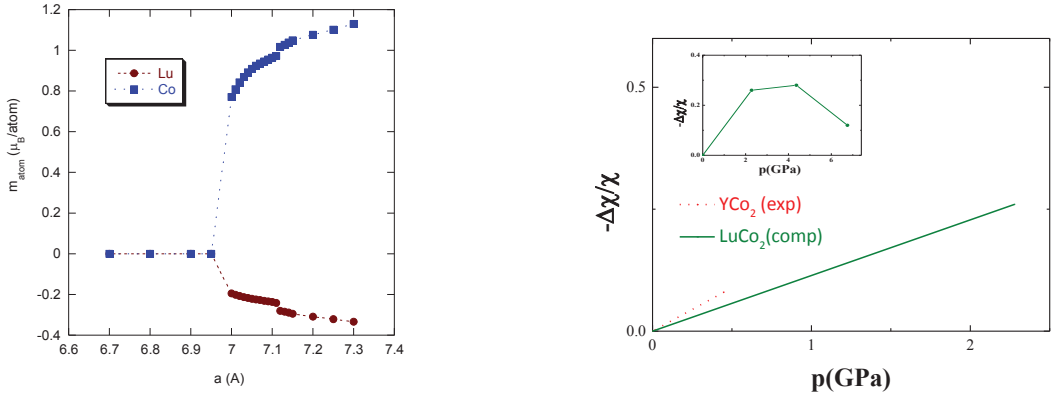


FIGURE 5. Temperature dependence of $\langle S^2\rangle$ mean square amplitude of spin fluctuations in $LuCo_2$.

The experimental χ values can be better fitted when using a = 7.1 Å, λ = 2.04, $q_m = \pi/a\lambda = 0.217$ and A = $5.8(cm^5Oe^2/erg)10^{-12}$. The temperature dependence of $\langle S^2\rangle$, as determined by fitting procedure is given in Fig.5. This is close to that previously determined in YCo_2 compound [4]. The $\langle S^2\rangle$ value of cobalt in $LuCo_2$,at 800 K, is somewhat smaller than that obtained from experimental data. The difference can be attributed, at least partially, to the limitation to one of the number of terms in the series expansion development of free energy.

The effects of volume variations, simulating the pressure effects, on the magnetic susceptibility at low temperature, has been also studied. For this purpose, the band structures of $LuCo_2$ were analysed starting from a large range of lattice parameters, volumes, respectively – Fig. 3. In the framework of L(S)DA approach, for the volume corresponding to lattice parameter, a = 7.1 Å, determined at ambient condition, the ground state is magnetic. The non-magnetic state is obtained for a volume, corresponding to equilibrium lattice constant, smaller by 4 % than the above – Fig.6a. The L(S)DA approximation, used in the present analysis, neglects Hubbard correlations beyond

the mean field and thus the magnetic tendency of strongly, Hubbard, correlated system is underestimated. More accurate description [22] can be obtained when using LSDA+ DMFT method [23]. The total density of states, at the Fermi level, has a smaller value in comparison with that found in L(S)DA calculations, as already reported in YCo_2 compound [22]. When the L(S)DA+DMFT method has been used, in analyzing the above compound, the ground state was found to be paramagnetic for experimentally determined lattice constant.



(a) (b)

FIGURE 6. The magnetic behavior of $LuCo_2$as function of lattice parameters (a) and changes in their susceptibility in various pressure ranges (b).The pressure dependence of $\Delta\chi/\chi$ values for YCo_2 [24] is also given.

Starting from the DOS at the Fermi level, at different volumes, the magnetic susceptibilities of $LuCo_2$ have been obtained – Fig.6b. In order to correlate their evolution with pressure, a compressibility value $k = 9.4 \cdot 10^{-2}$ GPa^{-1}, determined on RCo_2 compounds [2], has been used. The magnetic susceptibility decreases with pressure up to $p \cong 4$ GPa and then increases. The corresponding dependence can be approximated by linear variations in limited pressure ranges. For $p < 2.3$ GPa a value $d\log\chi/d\log v = -12.2$ has been obtained. This is close to that experimentally determined in YCo_2, of -14 ± 2, in the pressure range $p \leq 0.45$ GPa [24]. The $d\log\chi/d\log v$ values change to -1.2 at $2.3 < p < 4.4$ GPa and then increase at +6.2 for $4.4 < p < 6.8$GPa pressure range.

The pressure dependence of the magnetic susceptibility of YCo_2 has been previously analysed in correlation with the Curie temperatures of magnetic ordered RCo_2 compounds [24]. From the present data the $\chi = f(p)$ seems to be better correlated with the evolution of state density at the Fermi level.

The effect of the external field on the $LuCo_2$ magnetic properties is also of interest. Gignoux et al [25] studied by neutron diffraction a $LuCo_2$ single crystal, at 100 K, in field of 57.2 kOe. The localization of the 3d electrons was shown to be similar to that observed in cobalt metal. A cobalt moment $M_{Co} = 0.016$ μ_B/Co atom and a negative 5d band polarization of $M_{5d}(d) = -0.007 \pm 0.005\mu_B$ were reported.

The R-M exchange interactions in magnetic ordered compounds are described by 4f-5d-3d model [26, 27], through R5d band polarization. This is determined by both local 4f-5d exchange, $M_{5d}(f)$ as well as by 5d-3d short range exchange interactions, $M_{5d}(d)$. A value: $b = M_{5d}(d)/\sum_i n_i M_i = 2 \cdot 10^{-2}$ has been obtained in magnetic ordered RM_2 (M = Fe, Co, Ni) compounds. By n_i is denoted the number of magnetic atoms situated in the first coordination shell to R one and M_i are their moments. A similar ratio, as above, in the limit of experimental errors, has been obtained in $LuCo_2$ by neutron diffraction study [25], $b = (3.5\pm2.5)\cdot10^{-2}$. The above data suggest the presence of a R5d-M3d coupling also in paramagnetic state. The R5d shell has a great extension, $r_{5d} \cong 5.33$Å, for all R atoms [28]. Thus, even the short range exchange interactions between cobalt atoms, at T_c vanishes, the R5d-M3d coupling is still present. When an external field will align the R moments, at $T > T_c$, in magnetic ordered RCo_2 compounds, an induced cobalt moment is present, antiparallel oriented to R one. This effect has been previously evidenced by neutron diffraction studies on RCo_2 compounds [29].The same behavior can be evidenced by analysing the computed magnetic moments in$LuCo_2$, for lattice constants higher than a ≅ 7 Å. The ratio $b=M_{5d}(d)/\sum_i n_i M_i=(2.2\pm0.2)\cdot10^{-2}$, is the same as in other magnetic ordered RCo_2 compounds.

CONCLUSIONS

The exchange enhanced R-Co, R-Co-B and R-Ni paramagnets show, at low temperatures, a T^2dependence of the magnetic susceptibilities, while at T > T* a Curie-Weiss-type behavior is evidenced. The effective transition metal moments are strongly correlated with the Stoner's enhancement factor. The experimentally determined magnetic susceptibilities are well described by the computed values starting from their band structures. By using the spin fluctuations model, the temperature dependence of the mean square amplitude $\langle S^2 \rangle$ of spin fluctuations in $LuCo_2$ has been obtained. At T = 800 K, the $\langle S^2 \rangle$ value is smaller by ≅ 14 % as compared to that experimentally determined. The pressure dependence of $LuCo_2$ magnetic susceptibility is analysed starting from band structures. The R5d-Co3d coupling is still present in paramagnetic RCo_2 compounds as well as in magnetic ordered ones, above the Curie temperatures.

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