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Magnetic behavior of Co and Ni in pseudoternary boron compounds

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Abstract

The magnetic properties of $YA_{4-x}M_xB$ with A = cobalt (Co) or nickel (Ni) and M = Al or Cu were analyzed. Solid solutions are formed for $x \leqslant 1.5$ when M = Cu and $x \leqslant 2$ for M = Al. The magnetizations and Curie temperatures decrease as result of substitutions. The YCo_2Al_2B compound is paramagnetic. Band structure calculations were performed on the above systems. Finally, the magnetic behaviors of Co and Ni in $YA_{4-x}M_xB$ compounds is analyzed.

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Keywords: Yttrium compounds; Magnetic measurements; Band structures

The RM_4B compounds where R is a rare earth or yttrium and M = cobalt (Co) or nickel (Ni), except YNi_4B, crystallize in a $CeCo_4B$ type structure [1]. YNi_4B shows a superstructure with $a = 3a_o(CeCo_4B)$ [2]. At low temperatures, YNi_4B is superconductor [3]. In $CeCo_4B$ type structure the R atoms are located in 1a and 1b sites, Co in 2c and 6i sites and boron atoms in 2d positions. The magnetic measurements performed on RCo_4B compounds show that the cobalt mean moment is strongly dependent on R partner. As example, in YCo_4B a value of 0.70 μ_B/Co atom was shown, while in case of $GdCo_4B$ it is of 0.96 μ_B/Co atom [4]. This shows a highly sensitivity of Co moments to the exchange interactions. In RNi_4B compounds, Ni, at low temperatures, is nonmagnetic [5,6].

The effect of Co or Ni substitutions in YM_4B-type compounds, by Cu or Al, on the crystal structure and magnetic properties will be analyzed. The induced Ni moment in $YCo_{4-x}Ni_xB$ system will be also reported. In addition to magnetic studies, band structure calculations were also performed.

The samples were prepared by arc melting the constituent elements in a purified argon atmosphere and remelted several times to ensure a good homogeneity. The X-ray analyses show that $YCo_{4-x}Cu_xB$ system crystallizes in a $CeCo_4B$—type structure up to $x = 1.5$. In $YCo_{3.5}Cu_{1.5}B$ sample, a small amount of $CaCu_5$-type structure was also present. The $CeCo_4B$ type structure was shown for $YCo_{4-x}Al_xB$ with $x \leqslant 2$ and in $YCo_{4-x}Ni_xB$, for $x \leqslant 3$ compounds.

Magnetic measurements were performed in the temperature range 4.2(1.7)−800 K and fields up to 9 T. In paramagnetic range, the magnetic susceptibilities have been determined from magnetization isotherms, according to the relation $\chi_m = \chi + aM_sH^{-1}$, by extrapolating the measured values χ_m to $H^{-1} \to 0$. By a is denoted a presumed content of magnetic ordered impurity and M_s is their saturation magnetization.

Band structure calculations were performed using the *ab initio* tight binding linear muffin tin orbital method in the atomic sphere approximation [7], within local density approximation [8]. In case of RCo_5-based systems, the atoms having smaller radius than Co occupy 3g sites, while the greater ones are distributed in 2c sites [9]. Since the RCo_4B-type structure is derived from RCo_5 one, by replacing every second layer the cobalt atoms in 2c sites by boron, we assumed the same site distribution. Thus, the Al was assumed to replace Co in 6i and Cu in Co2c sites.

The thermal variations of spontaneous magnetizations of $YCo_{4-x}Cu_xB$ compounds are plotted in Fig. 1. The

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compounds are ferromagnetically ordered. Both the magnetizations and Curie temperatures decrease, as the copper content is higher. The experimentally determined moments are listed in Table 1.

In paramagnetic range, a Curie–Weiss behavior was shown. The magnetizations of $YCo_{4-x}Al_xB$ compounds decrease more rapidly than in case of Cu-substituted systems. The YCo_2Al_2B is paramagnetic at 4.2 K. The susceptibilities increase as function of temperature and show a maximum at $\cong 50$ K and, for $T > 100$ K, a Curie–Weiss behavior was shown, Fig. 2.

The Ni is not magnetic, at low temperatures, in RNi_4B compounds [6,10]. The Curie constants, determined at $T > T_c$ are higher than those of the R^{3+} ions, suggesting the presence of a contribution from Ni atoms. An effective Ni moment of $\cong 1.80\,\mu_B$/Ni atom was determined. This is close to the value evidenced in $LaNi_5$ of $\cong 2.15\,\mu_B$/Ni atom [11]. In case of YNi_4B, the susceptibility is temperature dependent. An effective moment of $0.34\,\mu_B$/Ni atom was obtained from Curie constant [4]. The present results confirm the above behavior with somewhat higher effective moment of $\cong 0.50\,\mu_B$/Ni atom. We studied also the magnetic behavior of YNi_3CuB. The susceptibility, at 4.2 K is 2.1×10^{-4} emu/f.u. The χ versus T curve has a maximum at $T_m = 40$ K. At $T > 80$ K, the reciprocal susceptibilities as function of temperature, shows a linear dependence—Fig. 2. An effective moment of $0.50\,\mu_B$/Ni atom was determined. This suggests that, at high temperatures, Ni has a magnetic moment. The above statement was confirmed by X-ray photoelectron spectroscopy, (XPS), measurements on YNi_4B, at 300 K. The Ni $2p_{3/2}$, $2p_{1/2}$ core-level lines of YNi_4B are situated at nearly the same binding energies as in pure Ni. There is a diminution of the intensity of the 6 eV satellite. The valence band of YNi_4B is mainly determined from Ni3d contribution. But, the density of the states at the Fermi level decreased and the maximum in the valence band is situated at 1.40 eV higher binding energy as compared to pure nickel. Similar shifts were observed in $LaNi_{5-x}Al_x$ compounds [11]. The 6 eV satellite line, in valence band spectrum, as in Ni 2p core

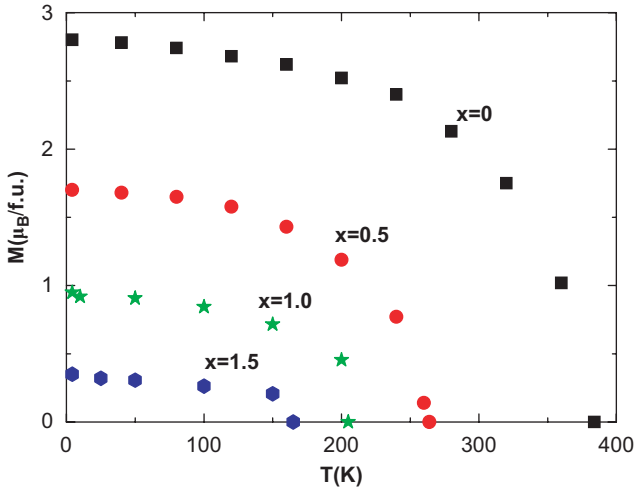

Fig. 1. Thermal variations of magnetizations in $YCo_{4-x}Cu_xB$ compounds.

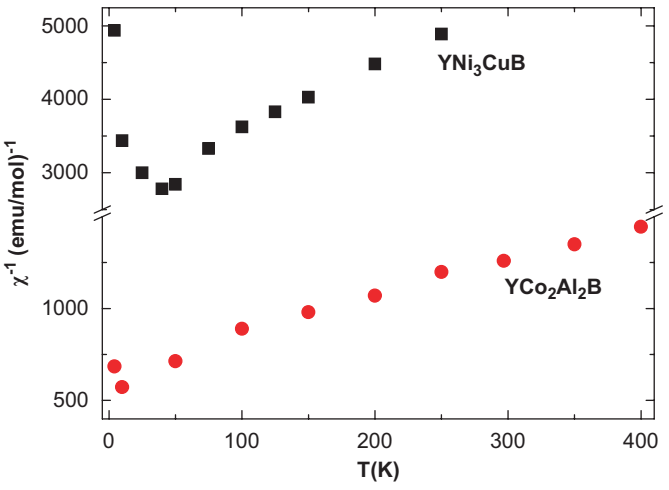

Fig. 2. Thermal variations of reciprocal susceptibilities for YCo_2Al_2B and YNi_3CuB compounds.

Table 1
Magnetic properties computed and experimentally determined

Compound	Magnetic moments (μ_B/atom) (calc.)							Magnetic moments (μ_B/f.u.)		$\chi \times 10^3$ (emu/mol) at 4.2 K		M_{eff} (μ_B/atom)
	Y(1a)	Y(1b)	Co(2c)	Co(6i)	B	Ni(2c)	Ni(6i)	Calc.	Exp.	Calc.	Exp.	
YCo_4B	−0.06	−0.12	1.71	0.55	−0.03			3.23	2.82			2.20(Co)
$YCo_{3.5}Cu_{0.5}B$	−0.10	−0.13	1.24	0.43	−0.03			2.01	1.75			
YCo_3CuB(6i)	−0.07	−0.12	1.31	0.33	−0.02			1.85	0.96			1.90(Co)
YCo_3CuB(2c)	−0.08	−0.14	—	0.43	−0.02			1.16	0.96			
$YCo_{2.5}Cu_{1.5}B$	−0.07	−0.11	1.41	0.37	−0.02			1.25	0.40			
YCo_3NiB(2c)	−0.16	−0.28	—	0.80	−0.07	0.32		2.40	1.70			
YCo_3NiB(6i)	−0.16	−0.25	1.54	0.76	−0.05		0.10	2.90	1.70			
YCo_3AlB(6i)	−0.03	−0.04	1.15	0.24	—			1.63				1.50 (Co)
YCo_2Al_2B										1.95	1.50	1.42 (Co)
YNi_4B												0.50 (Ni)
YNi_3CuB										0.20	0.21	0.50 (Ni)

level one, is strongly diminished as compared to that of pure Ni. Thus, the XPS data suggest a strong diminution of the number of holes in Ni 3d band as compared to Ni, although still exists.

Band structures for YCo_4B, YCo_3CuB and YCo_2Al_2B compounds are plotted in Fig. 3. The M_{Co}(2c) moments are higher than for Co(6i) sites. This may be correlated with a higher number of Co atoms in the first coordination shell of a 2c site. Thus, the increased exchange interactions involving 2c sites induce and additional Co moment. The susceptibilities, computed from state densities at the Fermi level, in case of YCo_2Al_2B and YNi_3CuB compounds agree rather well with the experimental determined values as seen in Table 1.

The Y4d bands are polarized, a small magnetic moment being induced by 4d–3d hybridization. This is antiparallel oriented to cobalt moments (see Table 1). The Y4d polarization is also dependent on the number of magnetic atoms situated in the Y environment, as well as on their moments, as previously stated [11].

The computed moments per formula units are higher than those experimentally determined. This is commonly observed in case of rare-earth intermetallic compounds. The saturation is not fully attained in fields up to 9 T. In addition, a random distribution of substituted atoms in both 2c and 6i sites are also possible, influencing the values of computed moments.

Although Ni, at 1.7 K, is not magnetic in RNi_4B compounds, a magnetic moment is induced when it replaced cobalt in $YCo_{4-x}Ni_xB$ system. The exchange interactions involving Ni are higher when it substitutes the 2c sites than 6i ones. As a result, a higher magnetic moment can be seen when Ni is located in 2c positions—Table 1.

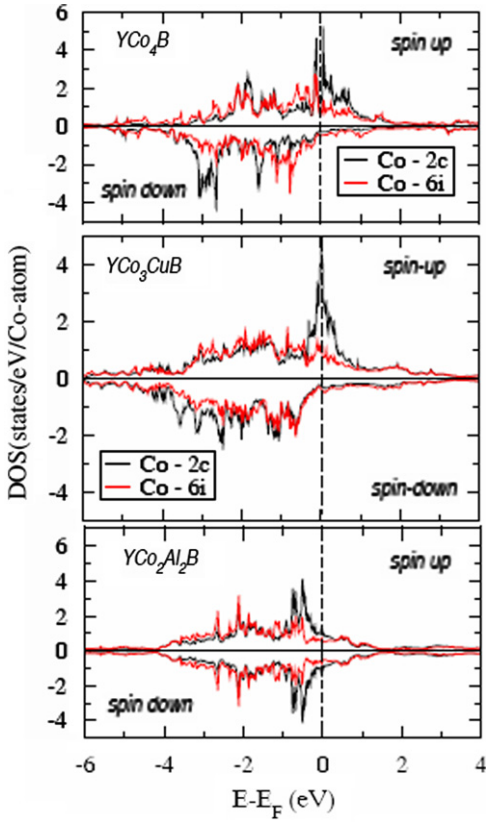

Fig. 3. Band structures of YCo_4B, YCo_3CuB and YCo_2Al_2B compounds.

The Ni and Co in the studied systems show, at low temperatures, a weak ferromagnetism or are not magnetic. For systems, which are magnetic, as $YCo_{4-x}Cu_xB$ compounds, the ratio between the mean number of Co spins determined from Curie constant and saturation magnetization is $\cong 2$. This shows a rather high degree of itinerancy.

The compounds that are paramagnetic at 4.2 K, show at higher temperatures, a temperature dependence of susceptibilities typical for localized moments. The above behavior may be analyzed in models, which take into account the electron correlations effects in d bands. These models reconcile the dual character of the electron, which as a particle, requires a real space description and as a wave, a momentum space description. The spin fluctuation model [12] considers the balance between the frequencies of longitudinal spin fluctuations, which are determined by their lifetime and of transverse fluctuations that are of thermal origin. At low temperatures, the frequency of longitudinal spin fluctuations are higher than of the transverse ones, and there is the approximation for non-magnetic or weak ferromagnetic state.

At higher temperatures, an effective magnetic moment can be shown, since the frequency of transverse spin fluctuations are higher than those of longitudinal ones. For exchange-enhanced paramagnets, these effects lead to the concept of temperature-induced moment. The average amplitude of spin fluctuations increases and at temperature higher than a characteristic value T^* reaches the saturation value. A Curie–Weiss type dependence is expected as in systems having local moments. This type of dependence is experimentally observed in $YCo_{4-x}Al_x$ with $x>1$, YNi_4B or YNi_3CuB. In this case the moments are localized in q-space. The effective moments are smaller than those expected for spin only contributions of Co^{2+} or Ni^{2+} ions. This decrease may be attributed to hybridization effects. The effective Co moment in YCo_4B of 2.20 μ_B/atom, is also smaller due to Co(3d)-Y(4d) and Co(3d)-B(2p) hybridization. The presence of Al determined a hybridization of Co(3p) and Al(2p) states as evidenced by band structure calculations, which lead to a relatively high decrease of the effective Co moment. A similar mechanism may describe the magnetic behavior of Ni in YNi_4B and YNi_3CuB compounds, where $M_{eff}(Ni)\cong 0.50\,\mu_B$/atom, are smaller than the value characteristic for Ni^{2+} ion.

The magnetic behavior of Co and Ni in the studied systems, can be also analyzed in the dynamical mean field theory [13] combined with standard LDA band calculations [14]. In a strongly correlated system, leading Curie–Weiss behavior, at high temperatures, is predicted. For an itinerant electron system, the time dependence of the correlation function results in temperature dependence of the $\langle S^2_{loc}\rangle$. Fluctuating moments and atomic-like configurations are large at short time scales. The moment

is reduced at longer time scales corresponding to a more band-like less correlated electronic structure near Fermi level.

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