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Magnetic properties and electronic structure of $Y_2Co_{7-x}Fe_xB$ compounds

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The $Y_2Co_{7-x}Fe_xB_3$ compounds form solid solutions in the composition range x≤2. Magnetic measurements were performed in the temperature range 4.2 – 800 K. The compounds are ferromagnetically ordered. Both Curie temperatures and saturation magnetizations increase when cobalt is substituted by iron. Band structure calculations on $Y_2Co_7B_3$ show that cobalt moments are sensitive to their local environments. A negative polarization is induced on Y4d bands. The mean cobalt moments, at 4.2 K, vary from 0.3 μ_B (x=0) to 0.7 μ_B (x=2), while iron shows a more localized behaviour. The effective cobalt and iron moments seems to be only little dependent on composition.

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1. Introduction

The $R_2Co_7B_3$ compounds, where R is a rare–earth or yttrium, crystallize in a hexagonal structure having P6/mmm space group [1]. In this lattice the rare–earth (yttrium) and cobalt are located in three types of sites and boron in two positions.

The magnetic properties of $(Gd_xY_{1-x})_2Co_7B_3$ were previously reported [2,3]. It was shown that the cobalt magnetic moments, at 4.2 K, are strongly dependent on the exchange interactions. Thus, the mean cobalt moments increase from 0.30 μ_B up to 0.82 μ_B when yttrium is replaced by gadolinium.

The $R_2Co_7B_3$ compounds were also studied in connection with their possible use as permanent magnets. For this purpose, the cobalt has been replaced by iron. Thus, he magnetic properties of $R_2(Co_{1-x}Fe_x)_7B_3$ compounds with R=Sm [4]. Nd [5] and Pr [6] were studied. Band structure calculations were also performed on $R_2Co_7B_3$ compounds[7,8].

As an on going work on the $R_2Co_7B_3$–based compounds we reported in this paper the crystal structure and magnetic properties of $Y_2Co_{7-x}Fe_xB_3$ system. Band structure calculations were also performed.

2. Experimental and computing method

The $Y_2Co_{7-x}Fe_xB_3$ compounds with x≤2 were prepared by melting the constituents elements in an arc furnace, in purified argon atmosphere. A small excess of yttrium was added to offset their loss due to evaporation. In this way the presence of impurities having higher transition metal content in avoided. The samples were thermally treated under vacuum at 1000 °C for six days.

The X–ray analyses show the presence only the $Co_2Co_7B_3$–type structure, of P6/mmm type, in the composition range x ≤ 2. The lattice parameters increase as cobalt is substituted by iron–Fig.1. This behaviour can be correlated with greater ionic radius of iron as compared to the cobalt one.

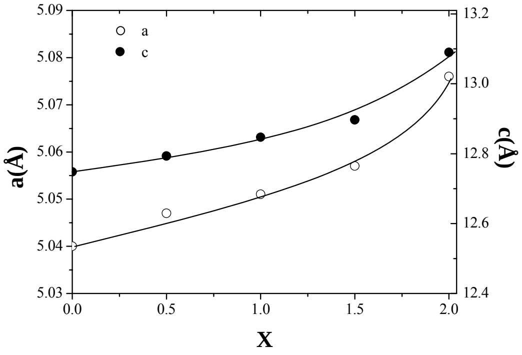

Fig. 1. Composition dependences of the lattice parameters.

Magnetic measurements were performed in the temperature range 4.2–800 K and external fields up to 9 T. The spontaneous magnetizations, M_s, were obtained from magnetization isotherms, according to approach to saturation law, $M=M_s(1-a/H)+\chi_0'H$. We denoted by χ_0' a field independent susceptibility and a is the coefficient of magnetic hardness. Above the Curie points, T_C, the magnetic susceptibilities χ, were determined from Honda–Arrott plots, according to the relation $\chi_m=\chi+cM_s'/H$, by extrapolation to $H^{-1}\to 0$. By c is denoted a presumed impurity content having M_s' saturation magnetization. By this method any possible alteration of the magnetic susceptibilities, at T>T_C, is avoided. The analysis of the above plots showed that the content of other phases were smaller than 1 %.

Band structure calculations were also performed by using ab initio tight binding linear muffin–thin orbital method in the atomic sphere approximation (TB–LMTO–ASA) [9]. In the form of local density approximation (LDA), the total electronic potential is the sum of external, Coulomb and exchange correlation potential [10]. The functional form of the exchange correlation energy was the free electron gas parameterization [11].

3. Magnetic properties

The temperature dependencies of the spontaneous magnetizations are plotted in Fig. 2. The presence of ferromagnetic–type ordering is suggested. Both the Curie temperatures and saturation magnetizations increase when cobalt is replaced by iron–Fig. 3.

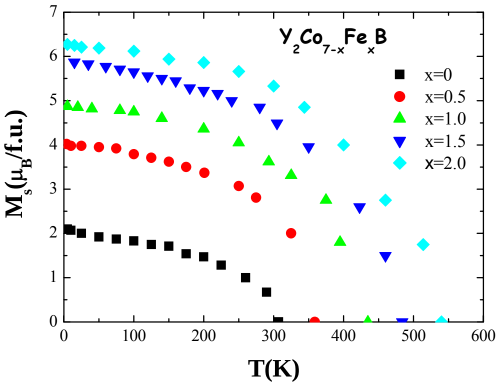

Fig. 2. Thermal variations of spontaneous magnetizations.

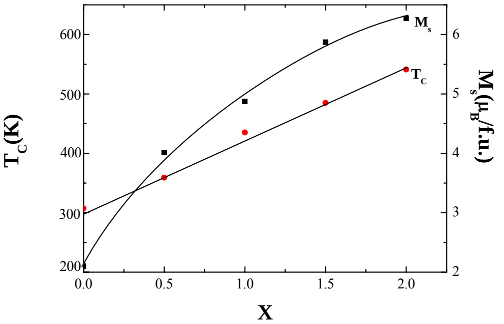

Fig. 3. Composition dependences of the saturation magnetization and Curie temperatures in $Y_2Co_{7-x}Fe_xB_3$ system.

The total density of states for $Y_2Co_7B_3$ is plotted in Fig.4. The determined magnetic moments are listed in Table 1. The higher cobalt moment is associated with Co(2c) site. This site has, as nearest neighbours, the greater number of cobalt atoms, namely six Co($6i_1$). The magnetic moment of Co($6i_2$) is the smallest one. This site has as nearest neighbours two B(2d) atoms. A magnetic polarization, M_{4d}, is induced on Y4d band which is antiparallely oriented to cobalt moments. The M_{4d} values were attributed to Co3d–Y4d band hybridization. The higher band polarization is induced on Y(1a) site which has six Co(2c) atoms as nearest neighbours, while the Y(1b) polarization is nearly nil since of the presence of six B(4h) in the first coordination shell. The Y4d band polarization increases nearly linearly as function of the $\sum n_i M_{Coi}$, the total magnetic moments of n_i cobalt atoms situated in their nearest neighbour–Fig.5. A small polarization is also induced on boron sites as result of Co3d–B2p band hybridization.

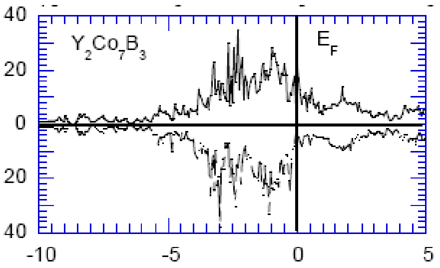

Fig. 4. Total density of states in $Y_2Co_7B_3$ compound.

Table 1. Magnetic data obtained from band structure calculations of $Y_2Co_7B_3$ compound.

Atom	Magnetic moment (μ_B)	Magnetic moment (μ_B/f.u.)	
		computed	experimentally determined
Y(1a)	-0.11		
Y(1b)	-0.03		
Y(2e)	-0.07		
Co(2c)	1.611	3.04	2.12
Co($6i_1$)	0.474		
Co($6i_2$)	0.061		
B(2d)	-0.010		
B(4h)	-0.015		

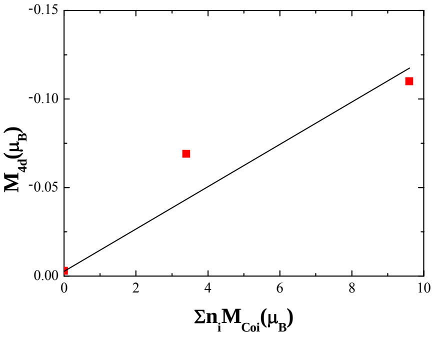

Fig. 5. The Y4d band polarization as function of $\sum n_i M_{Coi}$.

The computed magnetization per formula unit is 3.04 μ_B higher than the experimentally determined value of 2.12 μ_B. The discrepancy may be correlated with the fact that the magnetization has been not fully saturated in the studied external fields. We note that the computed magnetization is somewhat smaller than that reported previously, of 3.643 μ_B/f.u. [7].

There is a difficult matter to analyse the distinct magnetic behaviour of cobalt and iron only from magnetic measurements. Information of the magnetic behaviour of iron can be obtained from Mössbauer effect measurements, at ^{57}Fe nucleus. A correlation between the iron moment and ^{57}Fe hyperfine field value, B_{eff}, was reported previously in rare–earth (yttrium) –iron intermetallic compounds [12]. A relation $B_{eff}=AM_{Fe}$ with $A=147\pm2$ kG/μ_B was shown.

The ^{57}Fe Mössbauer spectra at, 78 K, of $Y_2Co_{7\text{-}x}Fe_xB$ ($x \leq 2$) are rather complex. We evaluated preliminarily, a mean hyperfine field at ^{57}Fe nucleus, B_{eff}=190 kG. This seems to change only little as function of composition. Taking the above into account we estimated a mean iron moment of $\cong$ 1.3 μ_B/atom. This value is only little smaller than that determined in $LuFe_4B$ compound, namely of 1.40 μ_B/Fe atom[13]. When admitting that the M_{Fe} is nearly constant along the series, the mean cobalt moments can be estimated. The M_{Co} values increase form 0.3 μ_B (x=0) up to 0.7 μ_B (x=). This behaviour can be attributed to the increase of the exchange interactions as the iron content is higher. Really, in the above composition range the Curie temperatures increase form 315 K (x=0) to 543 K(x=2) reflecting the increase of the exchange interactions.

The magnetic behaviour of cobalt in this system is similar to that determined in $(Gd_xY_{1\text{-}x})_2Co_7B_3$ compounds, where the cobalt moment increase from 0.30 μ_B/atom to 0.82 μ_B/atom as yttrium is substituted by gadolinium.

The thermal variations of reciprocal susceptibilities, χ^{-1}, follow a Curie–Weiss behaviour–Fig.6– in agreement with the ferromagnetic–type ordering suggested by magnetic measurements, at $T<T_C$. The paramagnetic Curie temperatures, θ, are higher than the ferromagnetic ones, the ratio $(\theta\text{-}T_C)T_c^{-1}$ being of $\cong$ 16%. Probably that small magnetic clusters are present, in limited temperature range, above T_C.

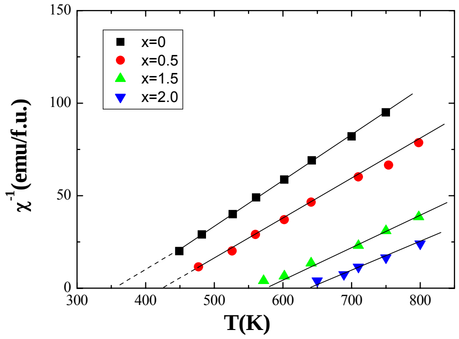

Fig. 6. Thermal variations of reciprocal susceptibilities.

The Curie constants increase as result of cobalt substitution by iron. Previously, we showed that the effective cobalt moments in $R_{n+1}Co_{3n+5}B_{2n}$ compounds are little dependent on composition for a given n series [14]. In case of $(Gd_xY_{1\text{-}x})_2Co_7B_3$ system, a mean effective cobalt moment of $\cong$2.30 μ_B/atom was determined. Admitting that this statement is valid also for $Y_2Co_{7\text{-}x}Fe_xB_3$, system, from additional law of magnetic susceptibilities, we determined the contributions of iron to the Curie constant and the effective iron moments, M_{eff}(Fe), respectively Values around 4.3 μ_B/Fe atom were obtained which little changes with composition. These values are close to that determined in $Y_2Fe_{14}B$ compound where an effective iron moment of 4.00 μ_B was obtained [15,16].

4. Conclusions

The $Y_2Co_{7\text{-}x}Fe_xB_3$ compounds form solid solutions in the composition range $x\leq2$, having $Ce_2Co_7B_3$–type structure. The compounds are ferromagnetically ordered. Both the Curie temperatures and saturation magnetizations increase when cobalt is substituted by iron. Band structure calculations on $Y_2Co_7B_3$ showed a good correlation of local cobalt moments and Y5d band polarizations, for a given site, with their local environments. The mean cobalt moments, at 4.2 K, are sensitive to exchange interactions, while iron shows a more localized behaviour. The effective cobalt and iron moments are little dependent on composition.

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