JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 798 - 800

Crystal structures, magnetic and electronic properties of Y-Co-Cu-B system

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The $YCo_{4-x}Cu_xB$ series form solid solutions in the composition range $x \leq 1$. The compounds are ferromagnetically ordered. Both the saturation magnetizations and Curie temperatures decrease when increasing copper content. The reciprocal susceptibilities follow a Curie-Weiss type behaviour. Band structure calculations show a parallel diminution of cobalt moments, at 2c and 6i sites, when increasing Cu content. The induced Y4d band polarizations are antiparallely oriented to cobalt moments and dependent on Y4d-Co3d short range exchange interactions. Finally, the magnetic behaviour of cobalt in analysed.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Rare-earth compounds, Band structures, Magnetic properties, Y-Co-Cu-B

1. Introduction

The RCo_4B compounds, where R is a rare-earth or yttrium crystallize in a hexagonal structure of $CeCo_4B$-type [1]. In this lattice, the R atoms are located in 1a and 1b sites, Co in 2c and 6i sites and B in 2d positions. Magnetic measurements were performed on the above compounds [2]. The mean cobalt moments, M_{Co}, were shown to be sensitive to R partner, exchange interactions respectively. The M_{Co} values increase from 0.67 μ_B for R=Y, to 0.94 μ_B for R=Gd. The exchange interactions may be also modified by substituting, in the above compounds, cobalt by a nonmagnetic element. In this way, additional information on cobalt magnetic behaviour can be obtained. Thus, in this paper we report the magnetic properties of $YCo_{4-x}Cu_xB$ compounds in a large temperature range. In addition, band structure calculations were also performed.

Table 1. Data obtained from magnetic measurements and band structure calculations.

Compound	Band structure						Experimental	
	Magnetic moment (μ_B/atom)					M_s	M_s	M_{eff}(Co)
	Y(1b)	Y(1a)	Co(2c)	Co(6i)	B	μ_B/f.u.	μ_B/f.u.	μ_B/atom
YCo_4B	-0.22	-0.13	1.44	0.61	-0.03	3.01	2.70	2.27
$YCo_{3.5}Cu_{0.5}B$	-0.15	-0.10	1.25	0.44	-0.03	1.80	1.70	1.98
YCo_3CuB	-0.12	-0.07	1.11	0.32	-0.02	1.20	0.95	1.83
$YCo_{2.5}Cu_{1.5}B$							0.35	

2. Experimental

The samples were prepared by arc melting the constituent elements in a purified argon atmosphere. These were melted several times to ensure a good homogeneity. The samples were thermally treated under vacuum, at 1000 °C, for one week. The X-ray analyses show that $YCo_{4-x}Cu_xB$ system form solid solutions in the composition range $x \leq 1$. For x = 1.5, the presence of a second phase, having $CaCu_5$-type structure was also shown.

Magnetic measurements were performed in the temperature range 4.2-500 K, in fields up to 9 T. In the paramagnetic range the magnetic susceptibilities have been determined from magnetization isotherms, according the relation $\chi_m = \chi + aM_sH^{-1}$, by extrapolating the measured values to $H^{-1} \rightarrow 0$. By a is denoted a presumed impurity content and M_s is their saturation magnetization. By this method any possible alteration of χ values, as results of the presence of small quantities of magnetic ordered phase is avoided.

Band structure calculations were carried out by using ab initio tight binding linear muffin tin orbital method in the atomic sphere approximation [3]. In the frame of local density approximation, the total electronic potential is the sum of external, Coulomb and exchange correlation potentials [4]. The functional form of the exchange correlation energy, used in the present work, was the free electron gas parametrization of von Barth and Hedin [5]. Relativistic corrections were included.

In case of RCo_5 based systems, the atoms having smaller radius than cobalt, occupy 3g sites, while the greater ones are distributed on 2c sites [6]. Since the RCo_4B type structure is derived from the RCo_5 one, by replacing the cobalt atoms in 2c sites by boron, every second layer, we assumed the same site distribution. Thus, the Cu was assumed to replace Co in 2c sites.

3. Band structures

The band structures of $YCo_{4-x}Cu_xB$ compounds with x = 0; 0.5 and 1.0 are plotted in Fig. 1. The computed magnetic moments, at various lattice sites, are listed in Table 1. The Co6i moments are sensitive smaller than the Co2c ones. This behaviour can be connected with different local environments. The Co6i sites have, in their first coordination shell, 2B, 2Co(2c) and 4Co(6i) atoms, while Co2c sites have 6Co(6i), 3Co(2c) and 3Y1a atoms. The cobalt moments, both at 2c and 6i sites, decrease linearly when the copper content increase, with the same slope of $0.32 \pm 0.02\ \mu_B$ per one copper substituted atom.

The Y4d bands are polarized. Their magnetic contributions are antiparallely oriented to cobalt moments and decrease when the copper content increases. The Y1b 5d band polarizations are higher than those of Y1a sites. This behaviour can be analysed in correlation with the exchange interactions. In $YCo_{4-x}Cu_xB$ there are both Co3d-Co3d and Y4d-Co3d short range exchange interactions, the first one being dominant. Since of relatively high spatial extent, there is a hybridization of Y4d bands with those of Co3d atoms situated in their neighborhood and a corresponding charge transfer to Y4d band. The 4f-3d short range exchange interactions may be described by the Hamiltonian [7].

$$H = -2\sum_{i,j} J_{3d_i-4d_j} S_{4d_j} \sum_{i} S_{3d_i}$$

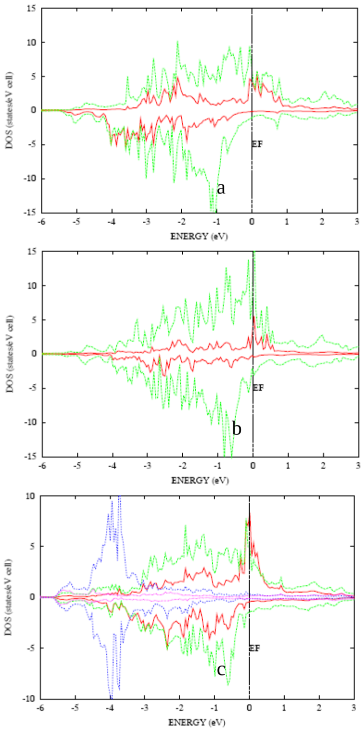

Fig. 1. Band structure of YCo_4B(a), $YCo_{3.5}Cu_{0.5}B$(b) and YCo_3CuB(c) compounds.

We denoted by i the number of Co3d atoms situated in the first coordination shell to an Y atom and j is the number of corresponding Y sites. In YCo_4B the Y1b site has 6Co(2c), 12Co(6i) as first neighbours, while Y(1a) have 6B and 12Co(6i) atoms situated in the first coordination sheel.

The 4d-3d exchange interactions act as an internal field, H_{exch}, on the 4d band and a polarization of this band is induced. The Hamiltonian (1) was analysed in molecular field approximation assuming that $J_{4d_j-3d_i}$ exchange interactions are not dependent on the lattice sites. In this case the Y4d band polarizations can be described by

$$M4d_j \propto \sum_i n_i M_{Co_i} \tag{2}$$

Where n_i is the number of cobalt atoms situated in the first coordination shell to a given Y atom and M_{Co_i} is their moment.

A linear variation of Y4d band polarizations, M_{4d}, as function of $\sum n_i M_{Co_i}$ was obtained – Fig. 2 – with a slope $\alpha \cong 1.2\times10^{-2}$ similar to that obtained for other rare-earth-transition metal compounds [8], confirming our model.

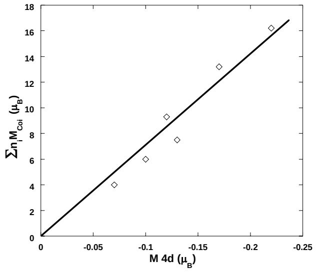

Fig. 2. The dependence of Y4d band polarizations on the $\sum n_i M_{Co_i}$ values.

There is a hybridization of Co3d band with B2p ones, particularly for atoms located in 6i sites. As a result, a polarization of – 0.03 μ_B is induced on boron sites, antiparallely oriented to cobalt moments.

4. Magnetic properties

The thermal variations of spontaneous magnetizations, M_s, are plotted in Fig. 3. The compounds are ferromagnetically ordered. The saturation magnetizations and Curie temperatures, T_C, decrease when increasing the copper content. Since T_C values are determined by the exchange interactions, the change in the magnetizations can be correlated with the diminution of exchange field acting on cobalt. A linear dependence between the M_s values, at 4.2 K, and Curie temperatures is shown – Fig. 4.

Previously [9] we showed that the variation of cobalt moments in rare earth compounds is linearly dependent on exchange fields. A similar dependence can be obtained in the present system, although the proportionality constant is somewhat lower than $(3\times10^6)^{-1}\ \mu_B$/Oe evidenced in Laves phase structures.

The saturation magnetizations are somewhat lower than the computed values. This behaviour was generally observed in rare-earth intermetallic compounds. Since of relative high anisotropy, the saturation magnetizations are difficult to be obtained in commonly used external fields.

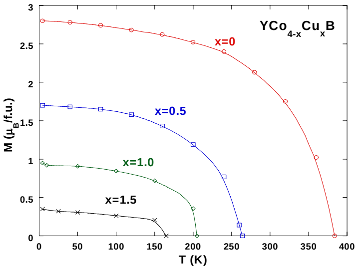

Fig. 3. Thermal variations of spontaneous magnetizations.

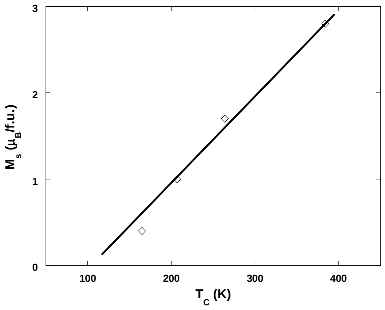

Fig. 4. The correlation between saturation magnetizations and Curie temperatures.

The temperature dependences of reciprocal susceptibilities follow a Curie-Weiss type behaviour - Fig. 5:

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

We denoted by C, the Curie constant and θ is the paramagnetic Curie temperatures.

The mean effective cobalt moments decrease from 2.20 μ_B/atom for x = 0 up to 1.80 μ_B/atom for x = 1.0.

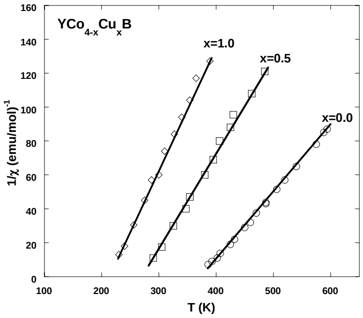

Fig. 5. Thermal variations of reciprocal susceptibilities.

4. Discussions

The band structure calculations show the importance of local environments of a given site in determining the cobalt magnetic moments or of the Y4d band polarizations. As was shown, these are essentially determined by short range exchange interactions with the atoms situated in their neighborhood.

By magnetic measurements only the mean values of the cobalt moments M_{Co} can be obtained. Neglecting the Y4d band polarizations, the M_{Co} values decrease from 0.67 μ_B (x=0) to 0.486 μ_B (x=0.5) and finally to 0.32 μ_B (x=1).

Information on the degree of itinerancy of cobalt atoms can be obtained from the ratio $r = S_p/S_o$, between the mean number of spins determined from Curie constants, S_p, and those obtained from saturation measurements, S_o. The r ratio increases from r=2.9 (x=0) to r ≅3.8 (x=1.0) showing an increase of the degree of itinerancy.

The cobalt in the present system can be characterized as a weak ferromagnet, as showed by the sensitivity to the exchange interactions as well as by the rather high difference between the number of spins determined from Curie constants and saturation measurements. The observed behaviour can be analysed in models, which take into account the electron correlation effects in d-band as dynamical mean field theory combined with standard LDA band calculations [10].

Realized under contract CEEX 19 / 2005 NANOMAG

References

[1] Y. B. Kuzma, N. S. Bilonizhko, Kristallografia **18**, 710 (1973).
[2] E. Burzo, N. Plugaru, I. Creanga, I. Ursu, J. less Common Met. **155**, 281 (1989).
[3] O. K. Anderson, O. Jepsen, Phys. Rev. **B12**, 3060 (1975) O. K. Anderson, O. Jepsen, D. Gözel, in: F. Bessani, F. Fumi, and M.P. Tosi (Eds.), Highlights of Condensed Theory, North Holland, Amsterdam, 1995.
[4] R. O. Jones and Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).
[5] U. Von Barth, L. Hedin, J. Phys. C.: Solid State **5**, 1629 (1972).
[6] E. Burzo, A. Chelkovski, H. R. Krichmayr, Landold Börnstein Handbook, Springer, Berlin, vol. 19d2, 1990.
[7] E. Burzo, L. Chioncel, I. Costina, S. G. Chiuzbaian, J. Phys.: Condens. Matter **18**, 4861 (2006).
[8] E. Burzo, Mol. Cryst. Liq. Cryst. **417**, 491 (2004).
[9] E. Burzo, J. Solid State Chem. **16**, 257 (1976); J. less Common Met. **77**, 251 (1981).
[10] Georges, G. Kothar, W. Krauth, M. J. Rosenberg, Rev, Mod. Phys. **68**, 13 (1996).

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