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Magnetic Properties of the RCo$_4$B Compounds (R = Y, Pr, Nd, Sm, Gd, Tb)

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The RCo$_4$B (R = rare earth) compounds crystallize with the CeCo$_4$B-type structure. They are obtained by an ordered substitution of cobalt by boron in every second layer of the CaCu$_5$ structure. We report on a study of the structural and magnetic properties of the RCo$_4$B with different rare-earth elements (R = Y, Pr, Nd, Sm, Gd, Tb). The *c* lattice parameter of the hexagonal structure remains almost constant, while the *a* parameter goes up when the atomic radius of the rare-earth element increases. The compounds with R = Y, Pr, and Nd are ferromagnetically ordered, whereas the compounds with Gd and Tb are ferrimagnetic. We also present the evolution of the easy magnetization direction depending on R at room temperature. The ordering temperatures are presented and the saturation magnetization at both temperatures 5 and 300 K are discussed for each compound. © 2000 Academic Press

Key Words: **intermetallic compounds, rare-earth, boron, alloys, magnetic properties.**

INTRODUCTION

Among all the intermetallic compounds based on a rare-earth element (R) and a transition metal, the RCo$_5$ series is one of the most intensively studied. Due to the combination of their high Curie temperature (T_c) and a large magnetocrystalline anisotropy, they have been widely used as permanent magnet materials. In 1974, Kuz'ma *et al.* (1) have shown that a limited substitution of boron for cobalt is possible in the RCo$_5$ structure, leading to a series of compounds with formula R_{n+1}Co$_{3n+5}$B$_{2n}$ ($n = 0$ (RCo$_5$), $n = 1$ (RCo$_4$B), $n = 2$ (R_3Co$_{11}$B$_4$), $n = 3$ (R_2Co$_7$B$_3$), and $n = \infty$ (RCo$_3$B$_2$)). This family of compounds represents a unique possibility for understanding the mechanism involved in the physical properties of the ternary boron intermetallics.

The investigation of the RCo$_4$B compounds is the first step in the knowledge of the properties of the R_{n+1}Co$_{3n+5}$B$_{2n}$ phases. Despite the decrease of T_c and of the saturation magnetization (M_s) upon the B for Co substitution, the SmCo$_4$B compound still possesses excellent magnetic properties and is promising for permanent magnet applications (2). This study deals with the evolution of the crystal and magnetic properties of the RCo$_4$B compounds depending upon the nature of R.

EXPERIMENTAL

The RCo$_4$B compounds (R = Y, Pr, Nd, Sm, Gd, and Tb) were prepared by melting the stoechiometric quantities of the elements (purity of at least 99.9%) in an arc furnace. The ingots were remelted in a high-frequency furnace to improve homogeneity. For SmCo$_4$B, a suitable quantity of Sm was added to compensate for the samarium loss during the synthesis. The samples were wrapped in Ta foil and annealed for 10 days at 1173 K in an evacuated quartz tube. The phase purity of the samples was checked by means of X-ray diffractometry using a $\theta/2\theta$ diffractometer and the Fe$K\alpha$ radiation. Inspection of the X-ray diagrams reveals that all the synthesized compounds were more or less single-phase materials. Field-oriented samples were prepared by solidifying the mixture of epoxy resin and the powdered specimen (≤ 50 μm) in a magnetic field of 1 T at room temperature.

The Curie temperature was measured using a Faraday-type balance with a heating and cooling rate of 5 K per minute. Magnetization curves were recorded at 5 and 300 K using the extraction method in a continuous field up to 7 T.

A possible spin reorientation temperature was determined from the anomaly in a.c. susceptibility ($\chi_{\text{a.c.}}$) versus temperature curve.

RESULTS AND DISCUSSION

The RCo$_4$B phases crystallize in the hexagonal CeCo$_4$B type of structure (space group *P*6/*mmm*) which is a derivative of the RCo$_5$ type of structure (1) by a regular substitution of Co by B in every second layer of the CaCu$_5$ structure (2c site). A schematic description of the structure is given in Fig. 1. It shows that the R atoms occupy the 1a and 1b sites, the Co atoms are in the 2c and 6i sites, and the B atoms reside in the 2d site. The evolution of the cell parameters

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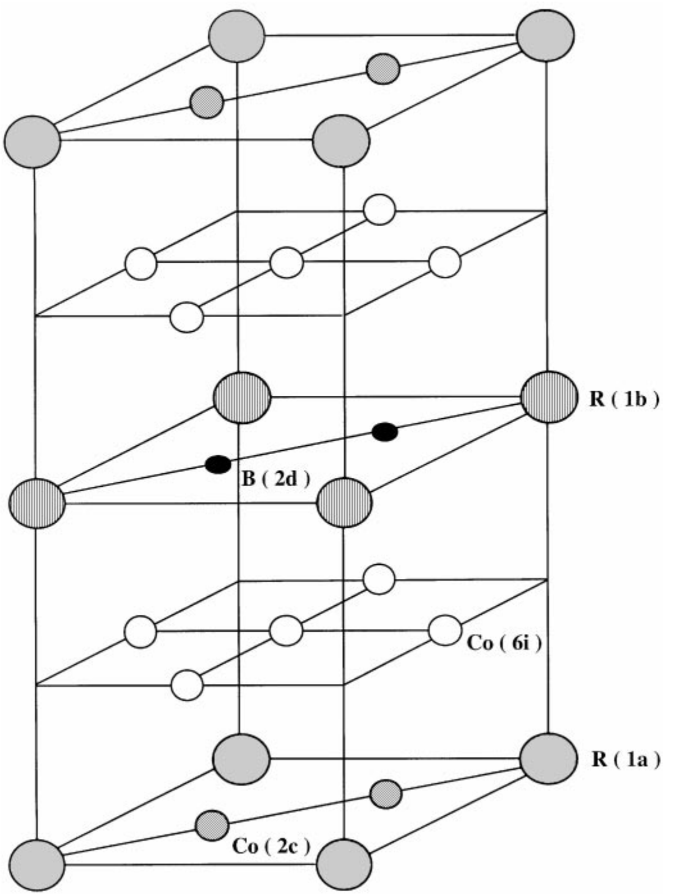

FIG. 1. Crystal structure of the RCo$_4$B compounds.

with the nature of the rare-earth element is given in Table 1. The c parameter remains constant whatever the R element alloyed is, while a significant change of the a parameter is observed. The analysis of the crystal structure and of the different interatomic distances allows us to conclude that the c parameter is determined by the two following distances: Co(2c)–Co(6i) and Co(6i)–B(2d). The nature of the rare-earth element modifies significantly the interatomic distances between R(1a)–Co(2c) and R(1b)–B atoms located in the same (u, v, 0) plane of the structure. Table 1 gives the calculated metallic radius of the R element in a cobalt-rich environment (3). It is to be noticed that the a parameter (and the unit cell volume) increases when the metallic radius of the rare earth increases.

TABLE 1
Lattice Parameters, Unit Cell Volume, and Curie Temperature of the RCo$_4$B Compounds

Compound	a (nm)	c (nm)	Metallic (3) radius of R (nm)	V (nm^3)	T_c (K)
PrCo$_4$B	0.5118(2)	0.6892(2)	0.1828	0.1564	459
NdCo$_4$B	0.5109(1)	0.6888(1)	0.1822	0.1557	468
SmCo$_4$B	0.5077(4)	0.6888(3)	0.1802	0.1538	501
GdCo$_4$B	0.5058(3)	0.6892(3)	0.180	0.1527	503
TbCo$_4$B	0.5037(2)	0.6886(7)	0.1783	0.1513	458
YCo$_4$B	0.5020(2)	0.6891(2)	0.1772	0.1504	378

Like in many R–M binary systems, the influence of the rare-earth element on the magnetic properties is important. The magnetic couplings in RCo$_4$B are similar to those observed in R_2M_{14}B (M = Co, Fe) (4). For the studied R elements, the compounds with R = Pr, Nd, and Sm are ferromagnetic and the compounds with R = Gd and Tb are ferrimagnetic (5). The different T_c of the RCo$_4$B compounds are listed in Table 1. These results show that T_c is affected by the nature of the rare-earth element. In particular, a serious difference is found between YCo$_4$B (T_c = 378 K) and the other compounds (T_c = 503 K for GdCo$_4$B for example) (6). It evidences that the Co–Co exchange interactions give rise to the largest contribution (≈378 K) to the Curie temperature and that the R–Co exchange interaction (≈100 K) contributes significantly but as a second order.

The evolution of the easy magnetization direction with the nature of R has been studied. As shown in Fig. 2, an external magnetic field applied on the powdered samples causes a change of the X-ray diffraction pattern, which might allow us to determine the easy magnetization direction at room temperature. In the case of the PrCo$_4$B, the effects of the orientation by a magnetic field on the X-ray patterns are an increase of the Bragg peaks intensity corresponding to (h, k, l) planes with index l = 0. The disappearance of the Bragg peaks with l indices different from 0 is also observed. This feature shows that the applied field induces a magnetic orientation of the powder in the basal plane. Two different types of behaviors are observed: for R = Y, Sm and Gd, the magnetic moments are aligned along the

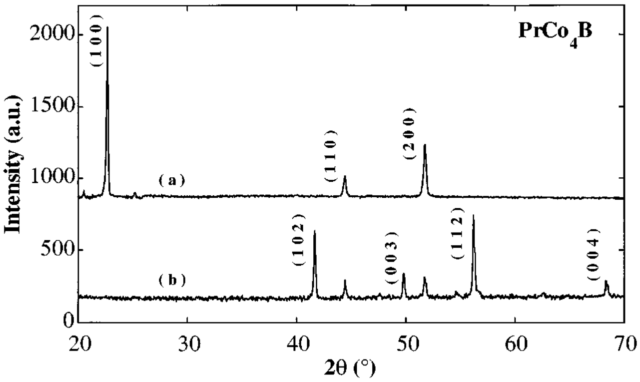

FIG. 2. Oriented (a) and free (b) X-ray powder diffraction pattern of PrCo$_4$B compound recorded after alignment of the powder in the magnetic field (a) compared to a conventional X-ray diffractogram (b).

c axis of the structure whereas for R = Pr, Nd, and Tb the magnetization lies within the basal plane. The results observed for the YCo_4B compound demonstrate that the Co sublattice favors an easy *c* axis magnetization at room temperature. The fact that the $GdCo_4B$ has also its magnetic orientation in the *c* axis direction confirms this conclusion because Gd has a half filled 4*f* shell and consequently does not influence the easy magnetization direction. The same easy magnetization direction has been already observed in the RCo_5 (7) and the $R_2Co_{14}B$ compounds (4). For the other R elements (except R and Y), a competition occurs between the R and the Co sublattice anisotropy to impose the magnetic orientation. Our study confirms that Sm has a magnetocrystalline anisotropy contrary to that of Pr and Nd. This is in good agreement with the opposite sign of their first-order Steven's coefficient, which is a pure atomic parameter (8).

The influence of the rare-earth element is also very sensitive to the saturation magnetization measurement. The M_s values were obtained by an extrapolation to zero field of the M versus B (magnetic field) curve at temperatures 5 and 300 K using powder free to rotate in the sample holder (Fig. 3). For the non magnetic R atoms (such as YCo_4B), the difference in magnetization between 5 and 300 K is explained by the proximity of the 300 K measurements to the T_c and denotes the evolution of the Co sublattice magnetization. As a consequence, the magnetic moment carried by the rare-earth atoms are largely higher at 5 K than at 300 K. A good agreement is found between the obtained value on the YCo_4B compound and those of previous studies (9, 10). The results on YCo_4B allow us to estimate the magnetization contribution of the Co sublattice in the RCo_4B compound (3 μ_B/f.u. at 5 K). Thus, we can evaluate that the mean magnetic moment carried by the Co atoms is $\langle \mu_{Co} \rangle = 0.75\ \mu_B$. After correction of the Co sublattice magnetization (subtraction or addition, for ferromagnets or ferrimagnets respectively), we can deduce the magnetic moments of the R element. Table 2 gives a comparison between the deduced R sublattice magnetization in the RCo_4B compounds and the value of the R magnetic moment in the free trivalent ion state. The obtained values for the R magnetic moment in RCo_4B are close to those of the R considered as a free ion but the value obtained from RCo_4B magnetic measurements are slightly smaller, from 0.5 in Nd to 1 μ_B in Tb. The difference between both values may come from two different origins: On the one hand, the strong boron hybridization (especially for the R(1b) site) occurring between R and B may influence the magnetic moment carried by the R atoms. On the other hand, the presence of a magnetic rare-earth atom can induce an additive magnetic polarization on the Co atoms. Consequently, slight change in the magnetization of the Co sublattice should happen. We have to keep in mind that the R magnetic moment deduced from the magnetization measurements is an indirect estimation. A precise determination of the magnetic moment carried by each atom is required to confirm these expectations. This will be done by neutron scattering.

These measurements can also help us to investigate the phenomenon of spin reorientation occurring in the YCo_4B compound (11). Two opposite terms are contributing to the Co sublattice anisotropy because of the two different crystallographic sites observed in this structure. It leads to a possible spin reorientation of the magnetization occurring at low temperature (T = 140 K). As an example, the a.c. susceptibility versus temperature is given in Fig. 4 the shape is indicating the spin reorientation in YCo_4B. At high temperature, the magnetization is aligned along the *c* axis, whereas at low temperature the magnetization is lying within the basal plane. The observed difference in the easy magnetization direction with R shows that the spin reorientation is sensitive to the R element nature. Our preliminary

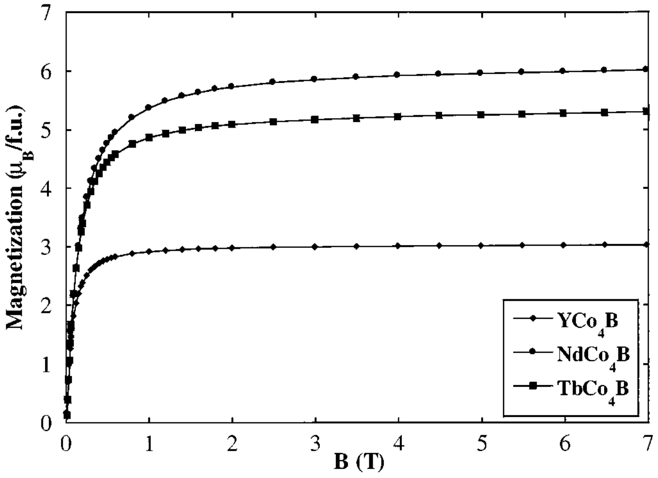

FIG. 3. Magnetization curves of YCo_4B, $NdCo_4B$, and $TbCo_4B$ measured at 5 K.

TABLE 2

Saturation Magnetization (M_s) of the RCo_4B Compounds and Magnetic Moment Carried by R (M_R) Elements in These Compounds

	M_s(μ_B/f.u.)		M_R(μ_B) at 5 K	
Compound	5 K	300 K	Free ion	RCo_4B[a]
$PrCo_4B$	5.4	3.6	3.2	2.4
$NdCo_4B$	5.8	3.7	3.3	2.8
$SmCo_4B$	3.0	2.9	0.7	0
$GdCo_4B$	3.2	0.9	7.0	6.2
$TbCo_4B$	5.0	1.1	9.0	8.0
YCo_4B	3.0	2.2	—	—

[a] In the ferromagnetic compounds, the Co sublattice contribution, 3μ_B/f.u., is subtracted; for ferrimagnetic compounds, it is added.

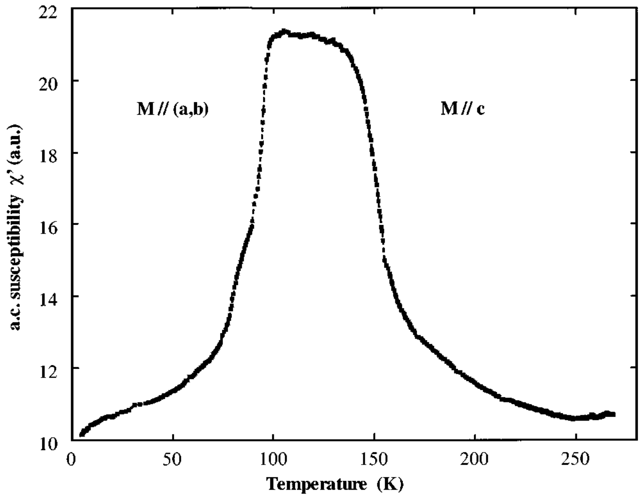

FIG. 4. a.c. susceptibility versus temperature measurements in YCo$_4$B.

study on the NdCo$_4$B compound proves that this phenomenon has disappeared. The thermal evolution of the magnetization direction with the other rare-earth elements is still to be observed and explained.

CONCLUSION

The structural and magnetic investigations on the RCo$_4$B phases show that the physical properties of these compounds are very sensitive to the nature of the rare-earth element. From the structural aspect, a significant influence of R on the lattice parameter a is revealed. The c axis is insensitive to the R nature, showing that the c parameter in this structure is determined by the B–Co interatomic distances. The magnetic properties of this series of compounds are also affected by the nature of R. We have found large differences in the T_c values and two possible (c axis or basal plane) directions of easy magnetization regarding the nature of R. We have also evidenced important modifications of the saturation magnetization. The knowledge of the magnetic moment carried by each magnetic sublattice is necessary to explain the evolution of M_s with the nature of R. Neutron diffraction experiments are planned in the near future to determine the individual magnetic moments on each crystallographic site.

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