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Competing anisotropies on 3d sub-lattice of $\text{YNi}_{4-x}\text{Co}_x\text{B}$ compounds

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The magnetic anisotropy of 3d sub-lattices has an important rule on the overall magnetic properties of hard magnets. Intermetallics alloys with boron (R-Co/Ni-B, for instance) belong to those hard magnets family and are useful objects to help to understand the magnetic behavior of 3d sub-lattice, specially when the rare earth ions R do not have magnetic nature, like YCo_4B ferromagnetic material. Interestingly, YNi_4B is a paramagnetic material and Ni ions do not contribute to the magnetic anisotropy. We focused therefore our attention to $\text{YNi}_{4-x}\text{Co}_x\text{B}$ series, with $x = 0, 1, 2, 3$, and 4. The magnetic anisotropy of these compounds is deeper described using statistical and preferential models of Co occupation among the possible Wyckoff positions into the CeCo_4B type hexagonal structure. We found that the preferential model is the most suitable to explain the magnetization experimental data. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Since the 1970s researchers have studied intermetallic compounds with boron additions, such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Ref. 1) and SmCo_4B .² The goals have been to define and understand the permanent magnetic properties of these compounds. Some of these materials were inspired by SmCo_5 ,³ from the substitution of Co by B into the $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ family (R = rare earth), with $n = 1, 2, 3$, and ∞ .⁴⁻⁶ It is well known that the magnetic anisotropy is an important property that rules the magnetic hardness of the material; specially the anisotropy from the 3d sub-lattice.

The aim of this effort is therefore to provide further knowledge on the 3d magnetic anisotropy of intermetallics alloys with boron. To this purpose, we consider a non-magnetic rare-earth (yttrium), in order to be sure the magnetic contributions are only due to the 3d sub-lattice. In addition, we considered two transition metals: Ni and Co. From one side, Ni ions do not contribute to the magnetic anisotropy,⁷ while Co ions are extremely anisotropic.⁸

Thus, we prepare $\text{YNi}_{4-x}\text{Co}_x\text{B}$ alloys, with $x = 0, 1, 2, 3$, and 4. YNi_4B ($x = 0$) is a paramagnetic material and does not present signatures of anisotropy,⁹ while YCo_4B ($x = 4$) has its Curie temperature at 380 K and spin reorientation (due to a strong anisotropy competition), at 150 K.¹⁰⁻¹² It is therefore straightforward to suggest the anisotropy of $\text{YNi}_{4-x}\text{Co}_x\text{B}$ alloys depends on Co/Ni substitution.

To explore these features, we thus develop a statistical model of Co occupation among the Wyckoff sites (2c, with axial anisotropy and 6i, with planar anisotropy¹¹), in which predicts a strong competing anisotropy among these two sites and then spin reorientation for all of the samples of the series. On the other hand, a preferential model, in which Co ions go into a preferential position into Wyckoff sites, is developed and predicts that only $x = 2$ and $x = 4$ samples

would have strong competing anisotropies with spin reorientation. Experimental measurements of magnetization on those samples verify that this last model exactly describes the nature of 3d magnetic anisotropy of this family. This preferential occupation of Co into 3d sites has a simple physical meaning: maximization of Co-Co distances. Indeed, this kind of approach was already experimentally verified with neutrons diffraction measurements in other samples, like $\text{PrNi}_{5-x}\text{Co}_x$ (Ref. 13) and $\text{YCo}_{4-x}\text{Fe}_x\text{B}$.¹⁴

II. EXPERIMENTAL DETAILS

The polycrystalline samples were prepared in an arc furnace under argon atmosphere with appropriate amounts of cobalt, nickel, boron, and yttrium. To ensure the samples are in single phase, we added 7% of yttrium to compensate evaporation during melting. This additional amount was found measuring separately the mass of yttrium before and after the melting. The ingots were wrapped in tantalum foils, sealed in a silica tube filled with argon and annealed for 10 days at 1323 K with subsequent quench in water.

X-ray powder diffraction data were obtained at UFF and at room temperature using a Bruker AXS D8 Advance diffractometer with Cu-K_α radiation ($\lambda = 1.54056 \text{ \AA}$). The magnetic measurements were carried out using a commercial vibrating sample magnetometer (VSM) and a commercial superconducting quantum interference device (SQUID) at Unicamp, in temperature range between 4 K to 320 K and magnetic field between 0 and 70 kOe. In order to determine composition and topology of the samples, we carried out scanning electron microscopy (SEM) measurements at IF Sudeste MG.

III. CRYSTALLOGRAPHY

$\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ structures with $n = 1, 2, 3, \dots, \infty$ are possible due to the replacement of Co by B in every second layer

of RCo_5 ($n=0$).⁴⁻⁶ More precisely, RCo_4B ($n=1$) compounds consist of two crystallographic sites for rare-earth: $1a$ and $1b$; two crystallographic sites for Co (or $3d$ ions): $2c$ and $6i$; and only one site for B ions: $2d$.¹⁵ This can be seen in Figure 1, where the RCo_5 ($n=0$) case is also shown for the sake of comparison.

These compounds have the CeCo_4B type structure, with space group $\text{P6}/\text{mmm}$ (ICSD $n^\circ 191$).¹⁶ The first YNi_4B alloy was reported by Niihara¹⁷ with the same structure as above. Later, Kuz'ma and Khaburskaya¹⁵ reported a superstructure with lattice constant $a = 3a_0$ and $c = c_0$, where a_0 and c_0 are the lattice constant of the original structure found by Nihara. This superstructure was also found on $\text{YNi}_{4-x}\text{Co}_x\text{B}$ series by Isnard and co-workers.¹⁸⁻²⁰

X-ray diffraction and SEM measurements on our samples show that all those crystallize in a single phase, similar to CeCo_4B structure, without extra lines associated to the superstructure reported by Isnard *et al.*²⁰ (see Figure 2 for further analysis). The lattice parameters were determined using the standard pattern matching method of the Powder Cell software;²¹ and these change almost linearly as a function of Co content, as can be seen in Figure 3. A similar behavior was found by Chacon on $\text{YNi}_{4-x}\text{Co}_x\text{B}$ (Ref. 19) and Ağıl *et al.* on $\text{PrNi}_{4-x}\text{Co}_x\text{B}$.²²

IV. COMPETING ANISOTROPIES ON 3D SUB-LATTICE

The magnetic anisotropy of $\text{YNi}_{4-x}\text{Co}_x\text{B}$ compounds is due to the presence of Co ions, since Ni ions do not contribute to the anisotropy.⁹ To understand the anisotropy of these compounds we need first to know, from the crystallographic point of view, the mechanism of Ni/Co substitution. Let us first consider YCo_4B compound, where $2c$ and $6i$ sites are fully filled of Co. The anisotropy/ion for each site, at 0 K, are known¹⁰ $\epsilon_{2c} = 34.53$ K/ion and $\epsilon_{6i} = -11.58$ K/ion; and therefore the total anisotropy for each site reads as:

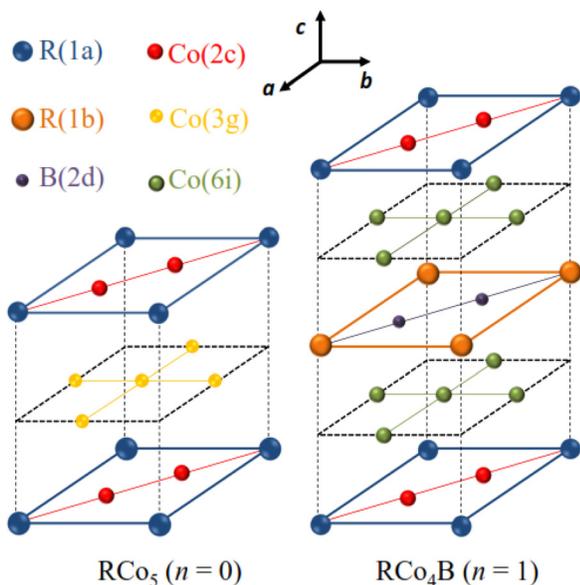


FIG. 1. Crystal structure of (left) RCo_5 ($n=0$) and (right) RCo_4B ($n=1$). Note the crystal structure on the left has one unit formula (RCo_5), while the right structure has two unit formulas ($\text{R}_2\text{Co}_8\text{B}_2$).

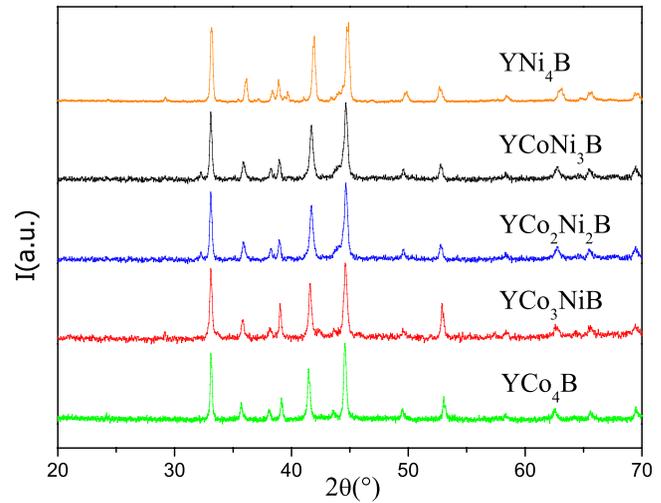


FIG. 2. Powder XRD pattern for $\text{YNi}_{4-x}\text{Co}_x\text{B}$ alloys.

$E_{2c} = 1\epsilon_{2c} = 34.53$ K and $E_{6i} = 3\epsilon_{6i} = -34.74$ K. Note the pre-factor are the corresponding occupation factor of the Wyckoff sites ($3/4$ for $6i$ and $1/4$ for $2c$), and we are considering only one formula unit, i.e., YCo_4B . On the other hand, $2c$ site has its magnetic moment with axial anisotropy, while $6i$ site has planar anisotropy (result from Mossbauer measurement¹¹). These facts leads therefore to a strong competition of anisotropies, since the magnitude of those two contributions are the same, but the directions are different. The consequence is simple: a minor energy addition to the system (either thermal or magnetic, for instance), is able to unbalance this fragile equilibrium; and indeed it occurs: a spin reorientation at 150 K, from the plane to the axis with temperature increasing. Note this competing anisotropies make almost zero the overall anisotropy energy $E_a = E_{2c} + E_{6i}$.

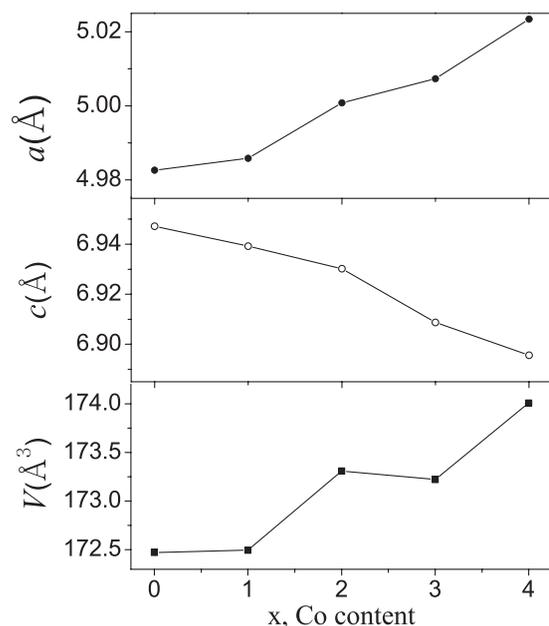


FIG. 3. Lattice constant and volume of the cell as a function of Co content. This behavior is similar to other R-M-B compounds.^{19,22}

To understand the magnetic anisotropy of the proposed series, we need thus to understand the mechanism of Ni/Co substitution. Thus, for a given compound of the $\text{YNi}_{4-x}\text{Co}_x\text{B}$ series let us consider

$$P_k(x) = \frac{x!}{k!(x-k)!} p^k (1-p)^{x-k}, \quad (1)$$

as the probability to find k Co ions into the $6i$ site, for a given Co content x . It simply considers this problem as an addicted game, since $6i$ site has a weight of $p = 3/4$, due to its bigger size. Based on this distribution probability, let us focus on two different models: one with statistical distribution, in which all of the distribution probabilities are taken into account; and a second model, in which only the most probable distribution is considered. This last represents a preferential site occupancy on the Ni/Co substitution and was already seen on $\text{PrNi}_{5-x}\text{Co}_x$ (Ref. 13) and $\text{YCo}_{4-x}\text{Fe}_x\text{B}$.¹⁴

The first model considers all possibilities of occupancy to obtain the anisotropy energy for each site. Thus, it is straightforward to write

$$E_{6i} = \sum_{k=0}^x P_k(x) k \epsilon_{6i}, \quad (2)$$

$$E_{2c} = \sum_{k=0}^x P_k(x) (x-k) \epsilon_{2c}. \quad (3)$$

Evaluation of the above energies leads to the result shown in Figure 4 (top). This model then predicts that the anisotropy energy of $2c$ and $6i$ sites are the same in magnitude for all of

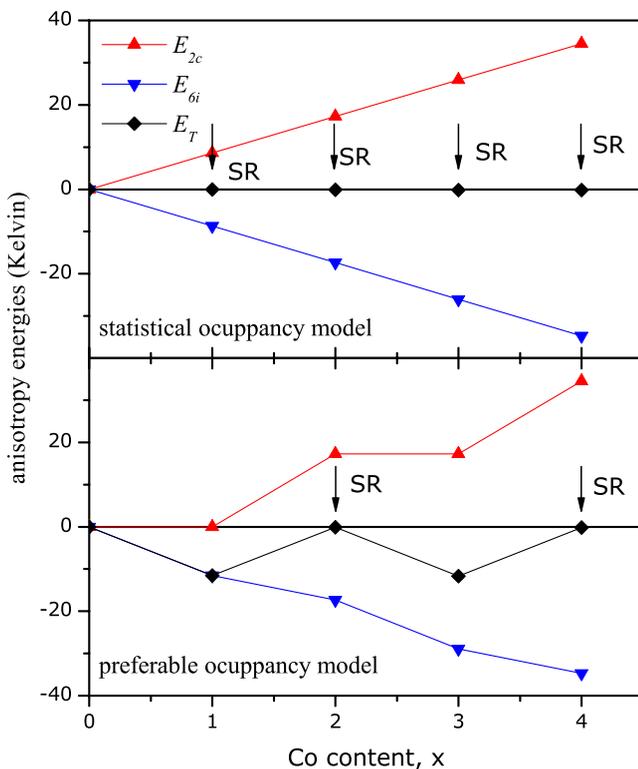


FIG. 4. Anisotropy energies for those two considered models: statistical (top) and preferential (bottom) occupancy. SR means Spin Reorientation. Note the model on the top panel predicts SR for all concentrations with Co, while the model on the bottom panel predicts SR for only $x = 2$ and 4 , in accordance with the experimental magnetization data (see Sec. V).

the samples—and therefore a strong anisotropy competition would be observed with further spin reorientation on all of those samples.

In a different fashion as before, the preferential occupation model considers that Co ions are distributed among those two Wyckoff sites in a preferential fashion. To evaluate this idea, we considered only the most probable element of the set $\{P_k(x)\}$ and save its corresponding k value, named as k_{max} , i.e.: $P_{k_{max}} = \max\{P_k(x)\}$. Thus, the anisotropy energy of each site can be written as

$$E_{6i} = k_{max} \epsilon_{6i} \quad (4)$$

and

$$E_{2c} = (x - k_{max}) \epsilon_{2c}. \quad (5)$$

The most probable distributions, for each value of Co content, x , are shown in Table I. Note the physical meaning of this preferential occupation model: Co ions try to keep the maximum distance of each other.

TABLE I. $\text{YNi}_{4-x}\text{Co}_x\text{B}$ compounds prepared for the present effort and the corresponding $3d$ site anisotropy energies and crystallographic preferential distribution among the Wyckoff sites. ● represents Ni and ○ represents Co. Note E_{2c} and E_{6i} are theoretical values, while T_{SR} and T_c are experimental.

	Sub-lattice 3d	E_{2c} (K)	E_{6i} (K)	T_{SR} (K)	T_c (K)
YNi_4B		0	0	No	No
YNi_3CoB		0	-11.58	No	180
$\text{YNi}_2\text{Co}_2\text{B}$		17.27	-17.37	150	307
YNiCo_3B		-28.95	-11.69	No	314
YCo_4B		34.53	-34.74	150	380

Figure 4 (bottom) summarizes the results of this last model. For $x = 1$, it predicts that the anisotropy energy of the $2c$ site is zero (there is no Co ions into this site for this Co concentration), while the anisotropy energy of $6i$ site is finite. As a consequence, there is not a competing anisotropy and the magnetic moment of the $6i$ site keeps on the basal plane. Obviously, without anisotropy competition there is no spin reorientation. This analysis is (almost) the same for $x = 3$ sample, i.e., there is neither anisotropy competition nor spin reorientation. The scenario is different for the samples $x = 2$ and $x = 4$. For these two samples, the anisotropy energy of each site is comparable leading therefore to a strong anisotropy competition that, on its turns, leads to a spin reorientation phenomena. Summarizing, the present model considers a preferential occupation into the Wyckoff sites, given by the most probable value on the distribution considered in Eq. (1). The physical roots of this model, interestingly, is to maximize the Co-Co distances. As a consequence, we found magnetic anisotropies for all of the samples of the series, however, competing anisotropies with a consequent spin reorientation we found only for samples with $x = 2$ and $x = 4$. It is important to stress that this kind of model was already experimentally verified on similar materials: $\text{PrNi}_{5-x}\text{Co}_x$ (Ref. 13) and $\text{YCo}_{4-x}\text{Fe}_x\text{B}$.¹⁴

V. MAGNETISM

Nagarajan²³ studied YNi_4B compound and observed paramagnetic behavior from room temperature down to 12 K; and below this threshold temperature, they found a superconducting behavior. Later,^{24–26} this superconducting behavior was ascribed to be from an additional phase containing carbon. On the other hand, YCo_4B is a ferromagnetic material with $T_c = 380$ K, exhibiting spin reorientation at 150 K due to the competition among the two crystallographic sites of Co.¹² The magnetic properties of the $\text{RNi}_{4-x}\text{Co}_x\text{B}$ compounds were studied in materials with Sm,²⁷ Pr,²² Nd,²⁸ and La.²⁹ For these, the increasing of Co content increases monotonically the saturation magnetization (M_s) and Curie temperature (T_c). In short, these are the known results.

In what concerns our samples, we measured magnetization as a function of magnetic field at 4 K (see Figure 5(a)). YNi_4B sample has no hysteresis and, in addition, quite small value of magnetization. Increasing Co content increases the hysteresis width, with a maximum width at $x = 2$. This fact is in accordance with both proposed models, since the anisotropy energy of each Wyckoff site promotes this hysteresis. Note also the saturation value of magnetization for these samples increases by increasing Co content.

Temperature dependence of the magnetization was also measured and is presented in Figure 5(b). YNi_4B is indeed paramagnetic with a possible superconducting behavior below c.a. 20 K, in accordance with references.^{24–26} Considering a monotonic increasing of the Curie temperature, as expected and shown by Isnard,²⁰ the sample with $x = 1$ has a ferro-paramagnetic phase transition at $T_c = 180$ K, *without* thus a spin reorientation phenomena. Further increasing of Co content, at $x = 2$, we assigned the strong drop of magnetization at 150 K as a spin reorientation,

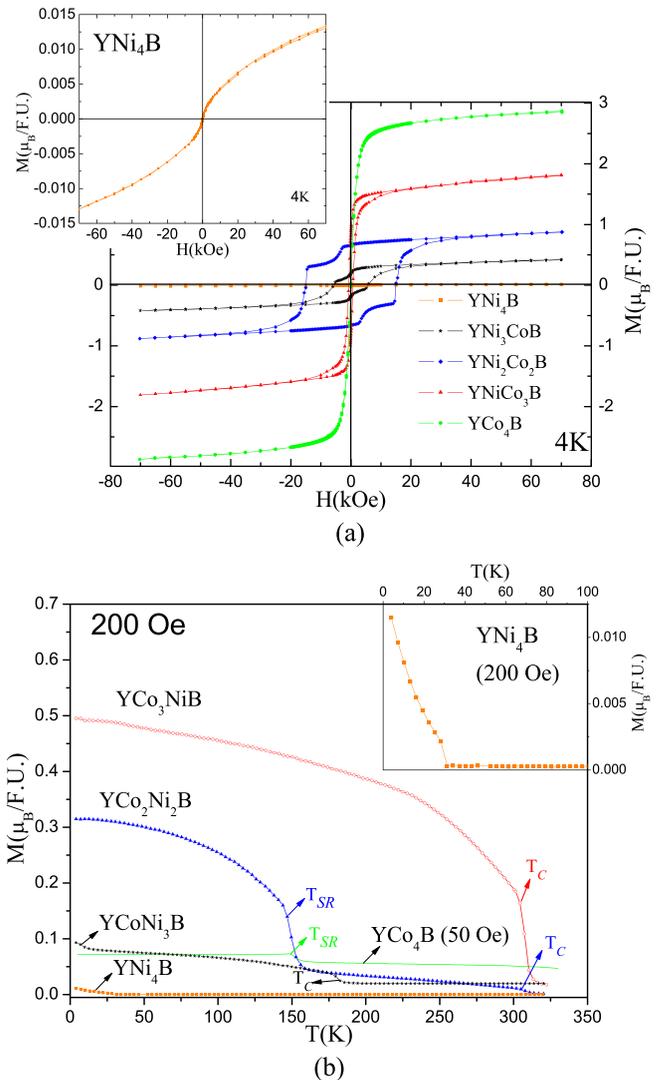


FIG. 5. Magnetization as a function of (a) external magnetic field and (b) temperature. The inset magnifies the YNi_4B result, since it was hidden when presenting the result of all samples together.

justified by the monotonic increasing of the Curie temperature increasing Co content. We then expect a ferro-paramagnetic phase transition for this sample and it occurs at c.a. 310 K. This series is able to receive more Co ions and then, for $x = 3$ sample, we observe the Curie temperature at c.a. 307 K, in accordance with Ref. 20. Finally, the last sample of our series is well known from literature^{10–12} and a spin reorientation occurs at 150 K and the para-ferromagnetic Curie temperature at 380 K. These remarkable temperatures are shown in Table I.

It is worth to note that the present experimental result is in absolute agreement with the proposed model of preferential occupancy, in which predicted spin reorientation for only the samples with $x = 2$ and $x = 4$ (see Figure 4 and Table I).

VI. CONCLUSIONS

The present effort proposes two possible occupation models for Co ions into the $3d$ sub-lattice of the $\text{YNi}_{4-x}\text{Co}_x\text{B}$ samples. One model considers a statistical distribution of Co/Ni ions, while the other considers a preferential

occupation under Co/Ni substitution. The former predicts strong anisotropy competition among the two $3d$ possible Wyckoff sites ($2c$ and $6i$) with spin reorientation for all of the samples considered, while the second model predicts that both sites have strong anisotropies, however, the competition ($|E_{2c}| = |E_{6i}|$) and spin reorientation arise only to $x=2$ and $x=4$. The experimental data of magnetization as a function of magnetic field and temperature show indeed that only these two last compositions have spin reorientation. This experimental result indicates that our model of preferential occupation fits the physical mechanism that rules the $3d$ magnetic anisotropies on this Y-Co-B system; and, indeed, was already verified for similar compounds.^{13,14} From the physical point view, this preferential occupation model interestingly mimics the case in which Co-Co distances are maximized. Thus, this result provides further knowledge to the area of hard magnets.

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