

# Effect of Stoichiometry of Fe and Co on the Temperature Stability of the Magnetic Anisotropy in Pr–Dy–Fe–Co–B Alloys

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**Abstract**—An increase in the cobalt concentration in Pr–Dy–Fe–Co–B alloys leads to the substitution of Co atoms for Fe atoms in the atomic positions, which are the nearest neighbors with the rare-earth metal atoms, and to the formation of a significant number of boron-rich phases. At the highest (limiting) cobalt concentrations, boron can be substituted for the transition metals. As a result, the exchange interaction between magnetic sublattices of the rare-earth and transition metals is weakened. In turn, this leads to a decrease in the contribution from the rare-earth ions to the magnetic anisotropy, the temperature stability of which increases.

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## 1. INTRODUCTION

The magnetic properties of RE–TM–B alloys (RE are rare-earth metals, and TM are transition metals) are unique in magnetization energy and magnetic anisotropy [1]. Wide possibilities of replacing the types of rare-earth and transition metals and also varying their concentrations discovered in the 1980s new possibilities of understanding physical principles of the formation of the magnetic anisotropy and the exchange interaction in metals. The hard-magnetic phase with the tetragonal structure  $A = \text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  studied in this work attracts attention due to their wide application for designing various devices. The temperature stability of such magnets is very important for the stable operation of measuring and other devices [2]. In this work, it is shown that the doping of the alloys with cobalt or heavy rare-earth metals, e.g., Dy, can be used to decrease the temperature sensitivity of the magnetization of the compounds. The magnetic moment of  $\text{Dy}^{3+}$  is  $10\mu_{\text{B}}$  ( $\mu_{\text{B}}$  is the Bohr magneton) and it is ordered oppositely to the co-directed magnetic moments of Fe ( $2.2\mu_{\text{B}}$ ) and Co ( $1.4\mu_{\text{B}}$ ) [1]; because of this, the Co-doping is more preferable. Although intermetallic compounds  $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  (Nd–Fe–B, etc.) are studied in sufficient detail in the entire range of cobalt concentrations, hard-magnetic materials based on them are quite new being fairly different from available Nd–Fe–B magnets only in that they fall in the RE–Co–B phase diagram [3]. The substitution of Co for Fe in them changes the temperature depen-

dences of the saturation magnetization ( $I_{\text{S}}$ ) of both the whole material and its magnetic sublattices. Because of this, it is important to know which of the sites of the unit cell of  $A = \text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  are occupied by Co atoms. In our work, the answer to this question is given by nuclear gamma-resonance (Mössbauer) spectroscopy.

Another drastic difference of the  $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  system from the Nd–Fe–B system is a great fraction of the phase with high boron content such as  $\text{RE}(\text{Fe},\text{Co})_4\text{B}$ , the existence of which leads to the boron diffusion between the  $\text{RE}(\text{Fe},\text{Co})_4\text{B}$  phase and phase  $A$  and explains the decrease in coercive force  $H_{\text{c}}$  to zero at high Co contents [5]. However, there are no available data on studies of the role of boron diffusion in systems, such as  $(\text{Pr},\text{Dy})_x-(\text{Fe}_x\text{Co}_{1-x})-\text{B}$ , although anomalous diffusion mobility of boron in FeCoB alloys used in spintronics is reliably known [6, 7]. According to available data [1], it can be expected that high cobalt concentrations in our series of samples will favor the presence of additional phases with high boron concentration in the sample. In turn, this will lead to the interface diffusion of boron and its embedding in sites of the TM sublattice of the main magnetic phase  $(\text{Pr},\text{Dy})_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  with nearest neighboring rare-earth ions [1]. The process described above can lead to the breaking of the exchange between the TM and RE sublattices of a ferrimagnet and stabilization of the magnetic anisotropy.

Chemical compositions and occupancies of atomic positions with Fe ions in TM sublattices

Sample no.	Composition of sintered material, at %	Composition of phase A $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$ , at %	Occupancy of sites of compound $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$ with Fe ions, %					
			16k <sub>1</sub>	16k <sub>2</sub>	8j <sub>1</sub>	8j <sub>2</sub>	4e	4c
1	(Nd <sub>0.01</sub> Pr <sub>0.99</sub> ) <sub>14.5</sub> (Fe <sub>0.13</sub> Co <sub>0.87</sub> ) <sub>80.0</sub> B <sub>5.5</sub>	Pr <sub>2</sub> (Fe <sub>0.17</sub> Co <sub>0.83</sub> ) <sub>14</sub> B	19.6	16.1	4.8	32.1	14.9	12.5
2	(Pr <sub>0.70</sub> Dy <sub>0.30</sub> ) <sub>15.3</sub> (Fe <sub>0.48</sub> Co <sub>0.52</sub> ) <sub>79.7</sub> B <sub>14.0</sub>	(Pr <sub>0.66</sub> Dy <sub>0.34</sub> ) <sub>2</sub> (Fe <sub>0.51</sub> Co <sub>0.49</sub> ) <sub>14</sub> B	25.9	27.5	13.0	17.8	1.6	14.2
3	(Pr <sub>0.72</sub> Dy <sub>0.28</sub> ) <sub>14.5</sub> (Fe <sub>0.5</sub> Co <sub>0.5</sub> ) <sub>74.3</sub> B <sub>11.2</sub>	(Pr <sub>0.68</sub> Dy <sub>0.32</sub> ) <sub>2</sub> (Fe <sub>0.53</sub> Co <sub>0.47</sub> ) <sub>14</sub> B	30.6	27.7	9.7	15.3	11.0	5.6
4	(Pr <sub>0.76</sub> Dy <sub>0.24</sub> ) <sub>12.9</sub> (Fe <sub>0.53</sub> Co <sub>0.47</sub> ) <sub>81.6</sub> B <sub>5.5</sub>	(Pr <sub>0.72</sub> Dy <sub>0.28</sub> ) <sub>2</sub> (Fe <sub>0.56</sub> Co <sub>0.44</sub> ) <sub>14</sub> B	26.8	28.1	13.4	18.3	4.9	8.5
5	(Nd <sub>0.03</sub> Pr <sub>0.55</sub> Dy <sub>0.26</sub> Ce <sub>0.16</sub> ) <sub>12.8</sub> (Fe <sub>0.55</sub> Co <sub>0.45</sub> ) <sub>81.3</sub> B <sub>6.0</sub>	(Pr <sub>0.58</sub> Dy <sub>0.30</sub> Co <sub>0.12</sub> ) <sub>2</sub> (Fe <sub>0.58</sub> Co <sub>0.42</sub> ) <sub>14</sub> B	33.7	23.2	16.9	11.5	7.3	7.3
6	(Nd <sub>0.22</sub> Pr <sub>0.22</sub> Dy <sub>0.38</sub> Ce <sub>0.18</sub> ) <sub>15.1</sub> (Fe <sub>0.68</sub> Co <sub>0.32</sub> ) <sub>77.6</sub> B <sub>7.3</sub>	(Nd <sub>0.22</sub> Pr <sub>0.22</sub> Dy <sub>0.43</sub> Ce <sub>0.13</sub> ) <sub>2</sub> (Fe <sub>0.69</sub> Co <sub>0.31</sub> ) <sub>14</sub> B	35.4	27.0	10.3	16.0	9.1	2.2
7	(Pr <sub>0.42</sub> Dy <sub>0.38</sub> Gd <sub>0.2</sub> ) <sub>12.9</sub> (Fe <sub>0.7</sub> Co <sub>0.3</sub> ) <sub>81.3</sub> B <sub>5.8</sub>	(Pr <sub>0.39</sub> Dy <sub>0.41</sub> Gd <sub>0.20</sub> ) <sub>2</sub> (Fe <sub>0.69</sub> Co <sub>0.31</sub> ) <sub>14</sub> B	33.0	24.8	13.4	13.4	9.2	6.3

The aims of this work are to study the occupancy of the sites with iron atoms in the sublattice of the transition metals in the Pr–Dy–Fe–Co–B alloys over wide range of the cobalt concentrations up to extremely high concentrations and also to reveal accompanying changes in the magnetic anisotropy and its temperature stability.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

We studied sintered (Pr,Dy)–(Fe<sub>x</sub>Co<sub>1-x</sub>)<sub>1-x</sub>–B materials prepared by powder technology. The preparation technology is described in [8, 9]. The chemical compositions of the samples studied are given in table. The Mössbauer spectra were measured on the powder samples distributed in a layer with a density of ~10 mg/cm<sup>2</sup> at room temperature, using an MS-1104Em spectrometer with the Co<sup>57</sup>(Cr) source. The spectrum was interpreted by constructing a model spectrum and its subsequent fitting to the experimental spectrum by varying a set of the hyperfine-splitting parameters. The isomer chemical shift ( $I_S$ ) is given relatively to  $\alpha$ -Fe. The magnetic measurements were performed on a Quantum Design PPMS-6000

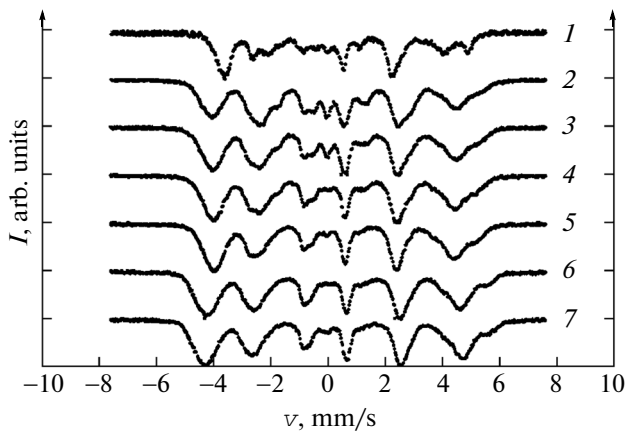


Fig. 1. Mössbauer spectra of samples 1–7 (numbers of the samples are given in the table) measured at 300 K.

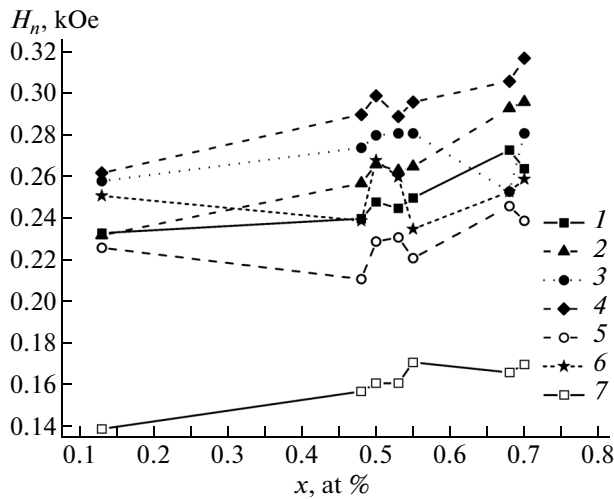
SQUID magnetometer in the temperature range of 4.2–300 K in fields to 90 kOe on the spherical-shaped sintered samples.

## 3. EXPERIMENTAL RESULTS

The Mössbauer spectra shown in Fig. 1 are superpositions of six sextets according to the number of the crystallographic nonequivalent sites characteristic of intermetallic compounds  $\text{RE}_2\text{Fe}_{14}\text{B}$  [10]. It should be underlined that six nonequivalent sites are characteristic of compounds  $\text{RE}_2\text{Fe}_{14}\text{B}$  independent of the type of RE and the cobalt doping level. When fitting the model spectrum to the experimental spectrum, it was necessary to introduce additional sextet with a low hyperfine field  $H_n$  that is likely to correspond to the impurity  $\text{RE}(\text{Fe},\text{Co})_4\text{B}$  phase [9, 11], and also a low-intense quadrupole doublet characterizing the paramagnetic impurity. The parameters obtained from the approximation of the spectra are given in the table. It is clearly seen that, as the cobalt concentration increases, the occupancies of sites 16k<sub>1</sub>, 16k<sub>2</sub>, and 8j<sub>1</sub> markedly decrease due to the increase in the occupancy of sites 8j<sub>2</sub>, 4e, and 4c neighboring to the rare-earth ions.

Figure 2 shows variations of hyperfine field  $H_n$  at the iron nuclei (in their different six positions), and also  $H_n$  in phase  $\text{RE}(\text{Fe},\text{Co})_4\text{B}$  as the iron concentration increases and, correspondingly, the cobalt concentration decreases. We observe the tendency to the increase in the hyperfine field for all types of the iron sites, with the exception for sites 4e and 4c for which  $H_n$  demonstrates a small jump only at very high Fe concentrations.

Figure 3 shows the magnetic-field dependences of the magnetization measured in the directions parallel and perpendicular to the texture at temperatures 4.2–300 K in the series of the samples under study. The magnetization curves were extrapolated to the region of their intersection, and the value of anisotropy field  $H_A$  was found in the point of intersecting the corresponding curves measured in the directions parallel and perpendicular to the texture. Temperature depen-



**Fig. 2.** Dependences of the hyperfine field at Fe nuclei in six nonequivalent positions in the  $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  phase on the iron content in the sintered materials measured at  $T = 300$  K: (1)  $16k_1$ , (2)  $16k_2$ , (3)  $8j_1$ , (4)  $8j_2$ , (5)  $4e$ , (6)  $4c$ , and (7) the hyperfine field at a nucleus in the  $(\text{Pr,Dy})(\text{Fe,Co})_4\text{B}$  phase.

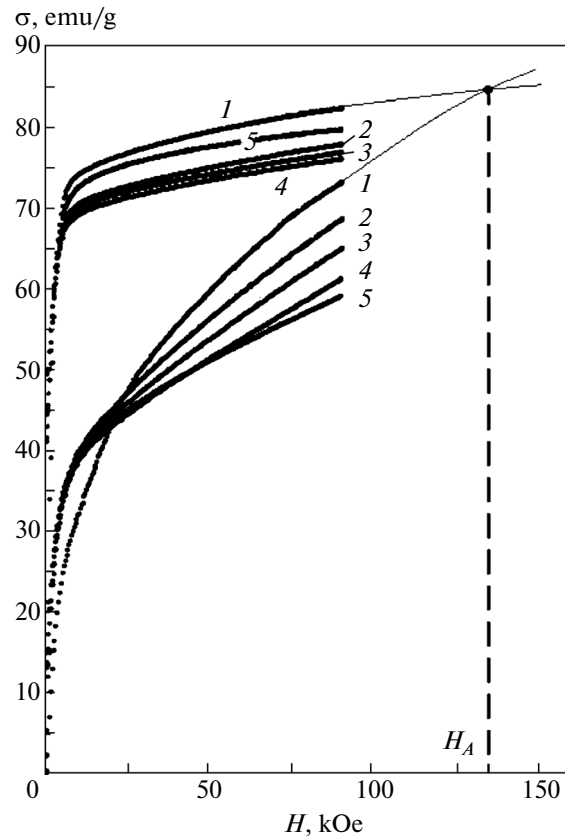
dences of the field  $H_A(T)$  obtained as is described above for the two alloys with different cobalt contents are shown in Fig. 4. As is seen from Fig. 4, in the temperature range of 4.2–300 K,  $H_A$  decreases by  $45 \pm 2\%$  in the  $(\text{Pr}_{0.70}\text{Dy}_{0.30})_{15.3}(\text{Fe}_{0.48}\text{Co}_{0.52})_{79.7}\text{B}_{14.0}$  sample and by  $32 \pm 2\%$  in the  $(\text{Pr}_{0.85}\text{Dy}_{0.15})_{16.5}(\text{Fe}_{0.17}\text{Co}_{0.83})_{69.4}\text{B}_{14.1}$  sample. Thus, the temperature dependence of the anisotropy field decreases as the cobalt concentration increases.

#### 4. DISCUSSION

If the rare-earth ion in the  $\text{RE}_2\text{Fe}_{14}\text{B}$  compounds is chosen so that its orbital moment is zero ( $\text{RE} = \text{Ce}^{4+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{La}^{3+}$ ), field  $H_A$  is almost independent of temperature in the range of 4.2–300 K. On the other hand, if we choose the ion with a non-zero magnetic moment, e.g.,  $\text{Pr}^{3+}$ , the value of  $H_A$  decreases by a factor of five on heating from 4.2 to 300 K [12, 13]. This fact demonstrates that it is the contribution of the magnetic sublattice of rare-earth ions that controls the value of the magnetic anisotropy and its temperature sensitivity. For compounds  $\text{RE}_2\text{TM}_{14}\text{B}$ , the anisotropy constant ( $K_1^S$ ) can be written as [14]

$$K_1^S = K_1^{\text{RE}} + K_1^{\text{TM}}.$$

Here,  $K_1^{\text{RE}}$  and  $K_1^{\text{TM}}$  are the first-order anisotropy constants of corresponding RE and TM sublattices [14].

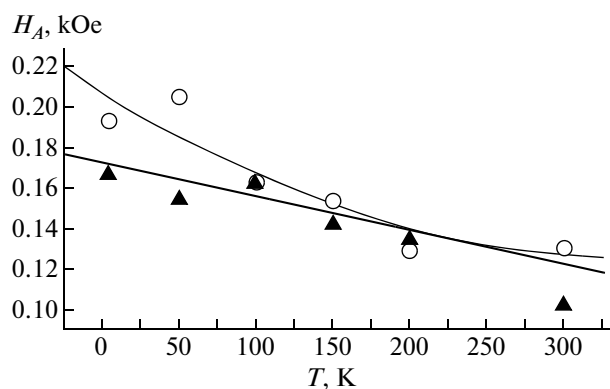


**Fig. 3.** Field dependences of the magnetization of the  $(\text{Pr}_{0.70}\text{Dy}_{0.30})_{15.3}(\text{Fe}_{0.48}\text{Co}_{0.52})_{79.7}\text{B}_{14.0}$  material measured at different temperatures in the directions parallel (upper group of curves) and perpendicular (lower group of curves) to the texture at (1) 300, (2) 200, (3) 150, (4) 100, (5) 50, and (6) 4.2 K. The solid lines show the extrapolation of the field dependences to the region of their intersection for determining the anisotropy field  $H_A$ .

Contribution  $K_1^{\text{RE}}$  to  $K_1^S$  (at  $T = 300$  K) is 86% for Pr, 95% for Dy, and 81% for Nd [14].

The replacement of nearest Fe ions bound with Pr and Dy ions by exchange interaction with cobalt ions weakens the exchange coupling between the RE and TM sublattices. Conversely, Co increases the exchange interaction and the magnetic anisotropy. However, it contradicts our results.

Because of this, a more reliable version is that, in the materials with high cobalt content (where there is a significant number of phases with high boron contents [1, 5]), the boron diffusion between the phases and inside the phases leads to the substitution of boron for Fe and Co in the nearest environment of the RE ion of the main magnetic phase  $(\text{Pr,Dy})_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$ . In this case, the exchange coupling between the sublattices of rare-earth and transition metals also should have been weakened, leading to the weakening of the temperature dependence of the anisotropy field.



**Fig. 4.** Temperature dependences of the anisotropy field of the sintered materials: (1)  $(\text{Pr}_{0.70}\text{Dy}_{0.30})_{15.3}(\text{Fe}_{0.48}\text{Co}_{0.52})_{70.7}\text{B}_{14.0}$  and (2)  $(\text{Pr}_{0.85}\text{Dy}_{0.15})_{16.5}(\text{Fe}_{0.17}\text{Co}_{0.83})_{69.4}\text{B}_{14.1}$ .

## 5. CONCLUSIONS

Thus, we determined that the crystallographically nonequivalent sites of the main  $\text{RE}_2(\text{Fe}_x\text{Co}_{1-x})_{14}\text{B}$  phase in sintered Pr–Dy–Fe–Co–B materials with the extremely high cobalt content are occupied with Fe ions and found the temperature dependences of the occupancies as a function of the cobalt concentration. This leads to an increase in the concentrations of phases with high boron content and to the possibility of substituting boron for transition metals. The substitution weakens the exchange coupling between the rare-earth sublattice and the sublattice of transition metals, which increases the temperature stability of the anisotropy field in the range of 4.2–300 K.

## REFERENCES

1. J. F. Herbst, *Rev. Mod. Phys.* **63**, 819 (1991).
2. E. N. Kablov, V. P. Piskorskii, and R. A. Valeev, *Russ. Metall.* **2014** (3), 199 (2014).
3. C. N. Christodoulou, T. B. Massalski, and W. E. Wallace, *J. Phase Equilib.* **14** (1), 31 (1993).
4. M. Rani and R. Kamal, *J. Magn. Magn. Mater.* **66**, 379 (1987).
5. E. N. Kablov, V. P. Piskorskii, R. A. Valeev, O. G. Ospennikova, I. I. Rezhikova, and N. S. Moiseeva, *Russ. Metall.* **2014** (9), 718 (2014).
6. G. V. Swamy, H. Pandey, A. K. Srivastava, M. K. Dalai, K. K. Maurya, A. Rashmi, and R. K. Rakshit, *AIP Adv.* **3**, 072129 (2013).
7. H. Kurt, K. Rode, K. Oguz, M. Boese, C. C. Faulkner, and J. M. D. Coey, *Appl. Phys. Lett.* **96**, 262501 (2010).
8. A. F. Petrakov, V. P. Piskorskii, G. S. Burkhanov, M. V. Repina, and S. I. Ivanov, *Metalloved. Term. Obrab. Met.* **7**, 3 (2012).
9. V. P. Piskorskii, G. S. Burkhanov, O. G. Ospennikova, R. A. Valeev, I. S. Tereshina, and E. A. Davydova, *Russ. Metall.* **2010** (1), 53 (2010).
10. J. F. Herbst, J. J. Croat, F. E. Pinkerton, and W. B. Yelon, *Phys. Rev. B: Condens. Matter* **29**, 4176 (1984).
11. Y. Gros, F. Hartmann-Boutron, C. Meyer, M. A. Fremy, and P. Tenaud, *J. Magn. Magn. Mater.* **74**, 319 (1988).
12. R. Grossinger, X. K. Sun, R. Eibler, K. H. J. Buschow, and H. R. Kirchmayr, *J. Magn. Magn. Mater.* **58**, 55 (1986).
13. C. Abache and H. Oesterreicher, *J. Appl. Phys.* **57**, 4112 (1985).
14. R. J. Radwanski and J. J. M. Franse, *Phys. Rev. B: Condens. Matter* **36**, 8616 (1987).

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