

Effect of Copper on the Properties of Pr–Dy–Fe–Co–B Sintered Magnets

E. N. Kablov^a, V. P. Piskorskii^a, R. A. Valeev^a, N. V. Volkov^b, E. A. Davydova^a,
K. A. Shaikhutdinov^b, D. A. Balaev^b, and S. V. Semenov^b

^aAll-Russia Scientific Research Institute of Aviation Materials, ul. Radio 17, Moscow, 105005 Russia

e-mail: admin@viam.ru

^bKirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok 50, bld. 38, Krasnoyarsk, 660036 Russia

Received June 26, 2013

Abstract—The effect of copper on the properties of magnets $(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{80.3-x}\text{Cu}_x\text{B}_{6.7}$ ($x = 0-10$) has been studied. Alloying with copper is shown to decrease the sintering temperature and to increase the content of the principal $(\text{Pr,Dy})_2(\text{Fe,Co})_{14}\text{B}$ magnetic phase. For compositions with $x = 1.3-3.3$, copper is found to affect the value and sign of the temperature induction coefficient (TIC). It is shown that the effect of copper on the TIC is determined by the substitution of copper ions for iron ions in lattice sites, which are coupled via an antiferromagnetic exchange interaction.

DOI: 10.1134/S0036029514010078

INTRODUCTION

The development of high-energy thermal stable hard magnetic materials for aircraft devices is a challenging problem [1, 2]. We have shown in a number of works that the alloying of the $R\text{--Fe--B}$ system (with $R = \text{Pr, Nd}$) with dysprosium and cobalt can substantially increase the temperature stability of the material up to the zero temperature induction coefficient (TCI) [3, 4]. However, alloying with only dysprosium and cobalt was found to have a substantial disadvantage, since residual inductance B_r at $\text{TIC} \approx 0$ decreases (this also follows from calculations [3, 5]). Partial substitution of gadolinium for dysprosium (the magnetic moment of gadolinium is lower than that of dysprosium) does not improve residual inductance B_r , since its slight increase is accompanied by an increase in the TIC; i.e., the thermal stability of material decreases [5, 6]. In other words, the alloying system that allows one not only to decrease the TIC but also to change the behavior of the temperature dependence of magnetization of the principal magnetic phase $R_2F_{14}\text{B}$ (with $R = \text{Pr} + \text{Dy}$, $F = \text{Fe} + \text{Co}$; phase A) without a substantial decrease in B_r is necessary. As an alloying element, we chose copper.

EXPERIMENTAL

We have studied materials having the compositions (at %) $(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{80.3-x}\text{Cu}_x\text{B}_{6.7}$ ($x = 0-10$). Alloys were prepared by a traditional technique using a vacuum induction furnace [3, 4]. Ingots were crushed in an inert atmosphere and subsequently milled into particles less than 630 μm in size. Fine

milling was performed in a trifluorotrchloroethan medium using a centrifugal planetary mill. Magnets blanks in the form of prisms were compacted by “wet” pressing in a transverse magnetic field of 800 kA/m. Copper was made a component of material at the stage of powder processing. Sintering and heat treatment were performed at temperatures of 1080–1160°C using an SNVE-1.3.1/16-IZ vacuum furnace. The temperature characteristics were measured using a SQUID magnetometer (superconducting quantum Josephson interferometer) and spherical samples. The local chemical compositions of phases were studied by quantitative and qualitative electron microprobe analysis (EMA) using a Superprobe-733 (JCMA-733) (JEOL, Japan) analyzer. The analysis locality and depth was 1 μm^2 and 1 μm , respectively.

RESULTS

Figure 1 shows coercive force H_{ci} of the sintered materials with different copper contents versus sintering temperature T_{sin} . It follows from the data in Fig. 2 that, for copper contents of 0–3.3 at %, the dependence exhibits a maximum, which is sufficiently abrupt at a copper content of 2 at %. The subsequent increase in the copper content leads to an abrupt decrease in H_{ci} of the magnetic material. We note also some increase (no more than 5%) in H_{ci} for the material after annealing at 1000°C for 1 h. Figure 3 shows the dependences of the contents of phase A components (Fe, Co, Cu) on the copper content in the magnetic material. It is seen from the dependences that copper substitutes for iron in phase A; the cobalt con-

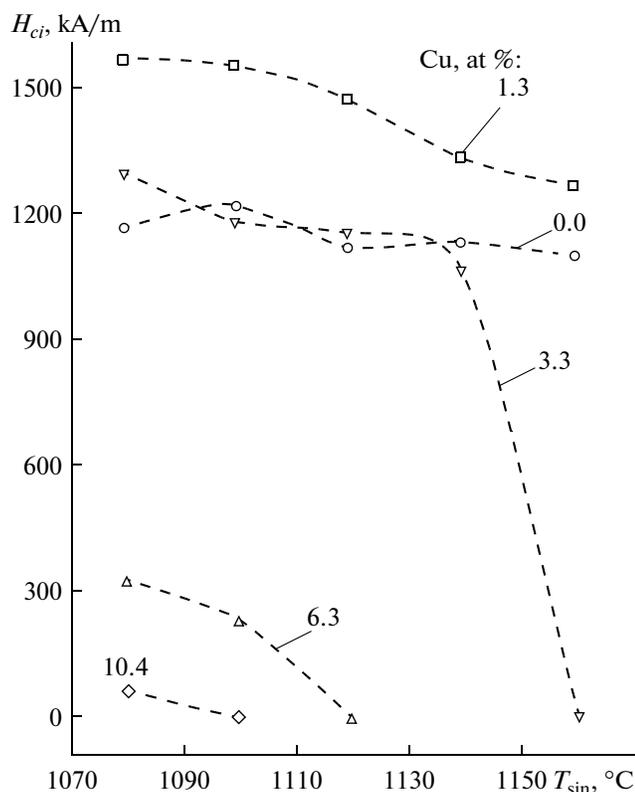


Fig. 1. Coercive force H_{ci} for the $(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{80.3-x}\text{Cu}_x\text{B}_{6.7}$ materials with various copper contents (numerals at the curves) as a function of the sintering temperature.

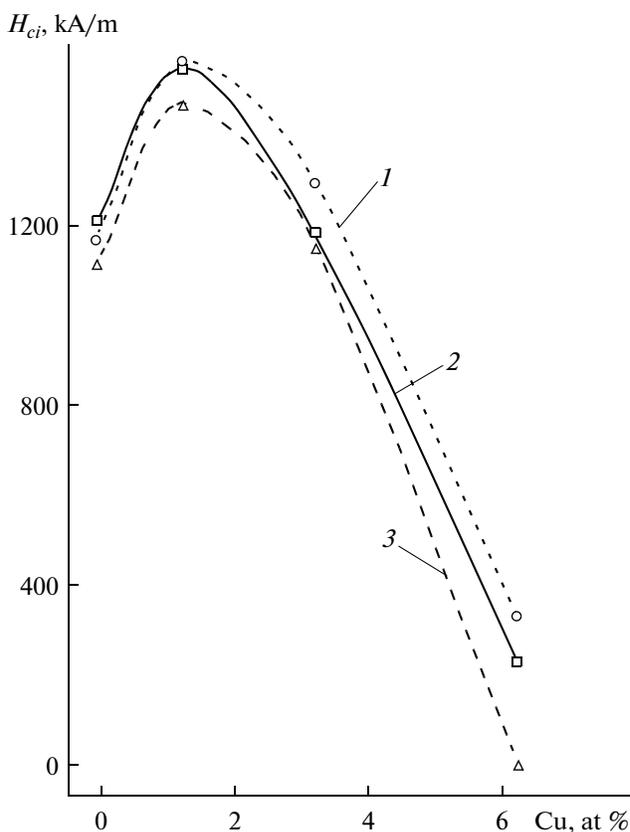


Fig. 2. H_{ci} of the $(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{80.3-x}\text{Cu}_x\text{B}_{6.7}$ materials vs. the copper content sintered at a temperature of $T_{\text{sin}} = (1) 1080$, $(2) 1100$, and $(3) 1120^\circ\text{C}$.

content remains unchanged. Figure 4 shows the temperature dependence of the magnetization measured in zero external field $H = 0$. It is seen that, as the copper content increases, the behavior of the temperature dependence changes and the TIC alternates the sign (Table 1). As was shown by EMA, the dysprosium and cobalt contents in phase A remain unchanged for this range of copper contents. Figure 5 shows the dependence of the volume contents of individual phases on the copper content in the material. It is seen that, as the copper content increases, the amount of the principal magnetic A phase increases; the maximum con-

tent of the RF_4B phase corresponds to 2 at % copper in a magnet.

DISCUSSION OF RESULTS

It was shown in [6] that, in the course of sintering of magnets with a high cobalt content, the main components of the liquid phase are $(\text{Pr}, \text{Dy})(\text{Fe}, \text{Co})_2$, $(\text{Pr}, \text{Dy})(\text{Fe}, \text{Co})_2\text{B}_2$, $(\text{Pr}, \text{Dy})(\text{Fe}, \text{Co})_4\text{B}$, $(\text{Pr}, \text{Dy})(\text{Fe}, \text{Co})_3\text{B}_2$, and $(\text{Pr}, \text{Dy})(\text{Fe}, \text{Co})_3$. It is likely that copper always decreases the melting point of these compounds [7] and results in a decrease in the sintering temperature (see Fig. 1). The $R_2F_{14}B$ phase can have a variable composition in boron [8]; as a result, boron transfers from this phase into other boron-containing phases during annealing in a certain temperature range. In this case, the structure of the near-surface region of this phase becomes distorted; this leads to the nucleation of reverse magnetization domains and to an experimentally observed decrease in H_{ci} [9]. The sufficiently abrupt maximum in the dependence of H_{ci} on the copper content (see Fig. 2) is likely to be caused by changes in the magnet structure, since this range corresponds to the maximum content of the RF_4B phase, as is seen from Fig. 4. We can assume that this is related to a change in the melting temperature

Table 1. TIC vs. the copper content in magnetic materials in the temperature range from -60 to $+80^\circ\text{C}$

Material*	TIC ($-60 \dots +80^\circ\text{C}$), $5\%/^\circ\text{C}$
$(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{79}\text{Cu}_{1.9}\text{B}_{6.7}$	-0.00150
$(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{78.2}\text{Cu}_{2.1}\text{B}_{6.7}$	-0.00062
$(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{77}\text{Cu}_{3.3}\text{B}_{6.7}$	$+0.09000$

* Composition is given in at %.

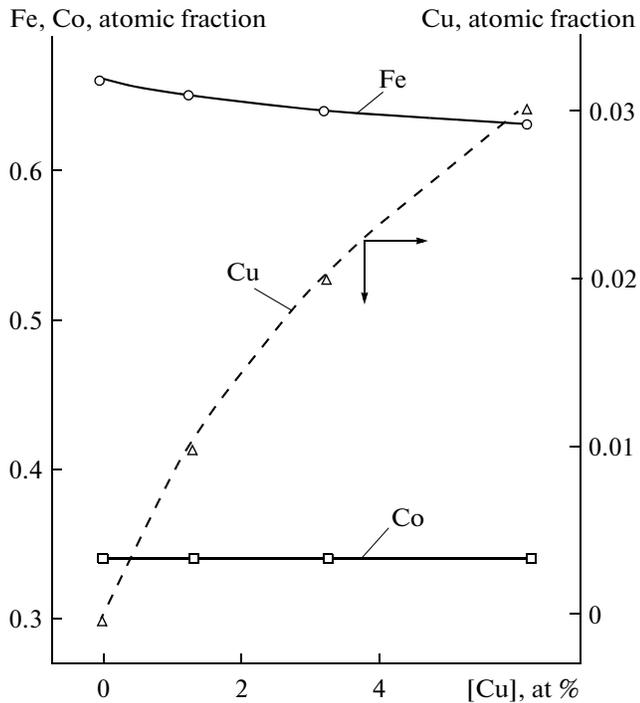


Fig. 3. Phase A component (Cu, Fe, Co) content vs. the copper content in a magnetic material.

of liquid during sintering. As is seen from Fig. 3, copper does substitute for iron in phase A and does not affect the cobalt content. It is known that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ intermetallic has the following six crystallographically nonequivalent atomic positions in the $3d$ sublattice: $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, and $4e$ [10]. Using Mössbauer spectroscopy, it was shown for the $\text{Nd}_2(\text{Fe}_{0.87}\text{Co}_{0.13})_{14}$ compound [11] that each of these six groups of atoms exhibits individual behavior of the temperature dependence of magnetization J , i.e., is characterized by a specific TIC magnitude. The total TIC of the entire material is the algebraic sum of the TICs of all sites. The temperature dependence of magnetization for each site is determined by the signs of the exchange interaction between the nearest neighbors. In particular, when the distance between atoms in the $3d$ lattice is ≤ 0.25 nm, the sign of exchange interaction becomes negative (antiferromagnetic interaction) [10]. When nonmagnetic atoms in $R_2F_{14}B$ substitute for iron in $3d$ sites, some interactions can be “switched off”; therefore, the temperature dependence of magnetization can change. It is known that alloying-element atoms incorporated into the $\text{Nd}_2\text{Fe}_{14}\text{B}$ lattice substitute for iron at different sites; this is related to both their ion radius and the Wigner–Seitz cell volume. For example, copper atoms substitute for iron at the $16k_2$ and $8j_1$ sites [12], whereas cobalt atoms substitute for iron atoms at the $16k_2$ and $16k_1$ sites [13]. Data on the nearest environment of all iron sites in phase A with $r < 0.4$ nm are available in [10]. The results of our analysis are given in Table 2,

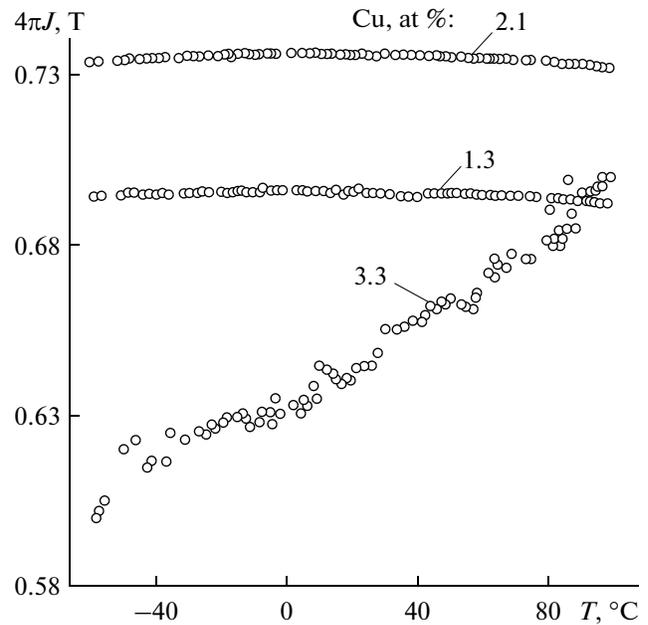


Fig. 4. Temperature dependences of the magnetization of spherical samples $(\text{Pr}_{0.52}\text{Dy}_{0.48})_{13}(\text{Fe}_{0.65}\text{Co}_{0.35})_{80.3-x}\text{Cu}_xB_{6.7}$ in the absence of applied field.

which gives the interatomic distances between a given cell site in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ lattice and sites k_2 and j_1 from the nearest environment of this site and the TICs measured at different iron sites in the $\text{Nd}_2(\text{Fe}_{0.87}\text{Co}_{0.13})_{14}\text{B}$ compound in a temperature range from -23 to $+77^\circ\text{C}$ by Mössbauer spectroscopy [9, 10]. Table 2 (third column) also presents the number of the nearest sites and the distances to them for $r \leq 0.25$ nm. As is seen from Table 2, the $16k_2$ site has a single j_1 site ($r = 0.239$ nm) in the nearest environment. All other sites have either longer distances or cannot be occupied with copper atoms. A similar situation also takes place for the

Table 2. Interatomic distances between a given site in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound cell and sites k_2 and j_1 in the nearest environment of the site and the values of TIC measured by Mössbauer spectroscopy

Site	TIC, %/°C	Number of nearest sites (distance to them, nm)
$16k_1$	−0.052	$1k_2$ (0.246)
$16k_2$	−0.125	$1j_1$ (0.239)
$8j_1$	−0.038	$1j_1$ (0.244), $2k_2$ (0.239)
$8j_2$	−0.025	− (≤ 0.250)
$4e$	−0.370	− (≤ 0.250)
$4c$	−0.420	$4k_2$ (0.250)

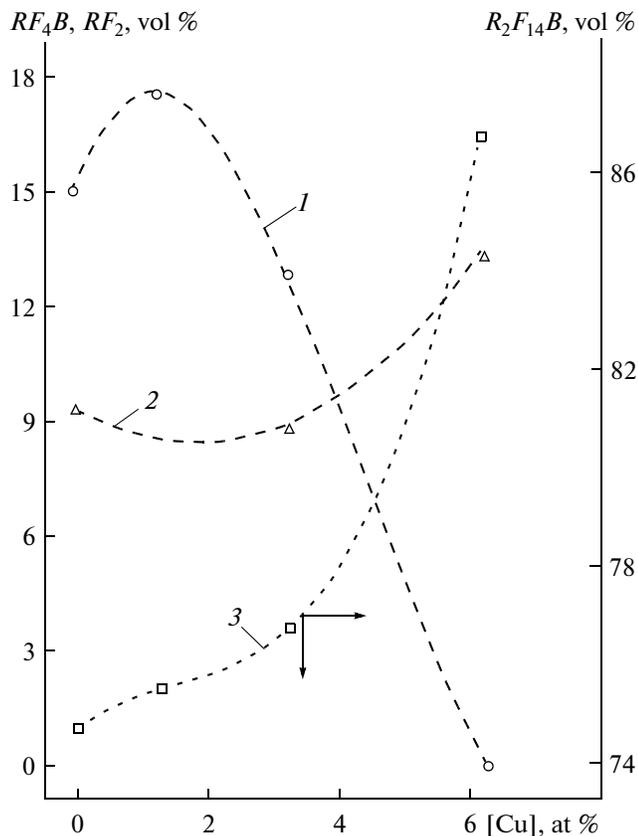


Fig. 5. Volume contents of the (1) RF_4B , (2) RF_2 , and (3) $R_2F_{14}B$ phases vs. the copper content in a magnetic material.

4c site. It has four nearest sites k_2 ($r = 0.25$ nm), and the substitution of copper for iron atoms should lead to a decrease in TIC for the 4c site. The $8j_1$ site has a single j_1 site ($r = 0.244$ nm) and two k_2 nearest sites ($r = 0.239$ nm). The substitution of copper for iron atoms in these sites also should lead to a decrease in the TICs for these sites. Thus, the decrease in the TIC of the copper-alloyed material can be explained qualitatively. However, it should be noted that the data given in Table 2 are related to the $Nd_2(Fe_{0.87}Co_{0.13})_{14}B$ system. In our case, the material composition is $(Pr_{0.52}Dy_{0.48})_{13}(Fe_{0.65}Co_{0.35})_{80.3-x}Cu_xB_{6.7}$ (with $x = 1.3, 2.1, 3.3$). The average composition of phase A in the $(Pr_{0.52}Dy_{0.48})_{13}(Fe_{0.65}Co_{0.35})_{77}Cu_{3.3}B_{6.7}$ material is $(Pr_{0.48}Dy_{0.52})_2(Fe_{0.64}Cu_{0.01}Co_{0.35})_{14}B$. In this case, the calculated TIC magnitude (range from -60 to $+80$) is $+0.0069\%/^{\circ}C$ [14], which is substantially lower than the experimental value (see Table 1). However, our calculation is incorrect, since the real distribution of iron, cobalt and copper atoms in sites was not taken into account. The calculation is based on the change of the Curie temperature $\Delta\theta_C$ of the material with different copper contents [3, 5, 14]. For the $Nd_2(Fe_{1-x}Cu_x)_{14}B$ material with $x = 0-0.05$ (limiting

copper solubility), the change in θ_C is only 2 K [15]. Thus, the effect of copper on TIC in this case is not related to a change in the Curie temperature of phase A.

CONCLUSIONS

(1) An increase in the copper content in the sintered material $(Pr_{0.52}Dy_{0.48})_{13}(Fe_{0.65}Co_{0.35})_{80.3-x}Cu_xB_{6.7}$ leads to a decrease in the sintering temperature and an abrupt decrease in H_{ci} . The coercive force is maximum in the copper content range 0–3.3 at %.

(2) As the copper content increases, the content of the $(Pr,Dy)(Fe,Co)_4B$ phase decreases (up to zero) and the content of the principal A phase increases progressively. Copper atoms substitute for iron atoms in phase A and do not change the cobalt content.

(3) In the copper contents range 1.3–3.3 at %, TIC varies from -0.0015 to $+0.090\%/^{\circ}C$ in the range from -60 to $+80$. In this case, the dysprosium and cobalt contents in phase A are unchanged. The effect of copper on TIC is explained by the substitution of copper for iron atoms in the $16k_2$ and $8j_1$ sites of crystal lattice.

REFERENCES

1. *Aviation Materials and Technologies*, Ed. by E. N. Kablov (VIAM, Moscow, 2012).
2. E. N. Kablov, "Strategic directions in developing materials and their processing technologies up to 2030," in *Aviation Materials and Technologies: Jubilee Scientific and Technical Collection, Supplement* (VIAM, Moscow, 2012), pp. 7–17.
3. E. N. Kablov, A. F. Petrakov, V. P. Piskorskii, R. A. Valeev, and N. V. Nazarova, "Effect of dysprosium and cobalt on the temperature dependence of the magnetization and phase composition of a material of the Nd–Dy–Fe–Co–B system," *Metall. Obrab. Met.*, No. 4, 3–10 (2007).
4. V. P. Piskorskii, R. A. Valeev, I. S. Tereshina, M. B. Bronfin, E. B. Chabina, E. A. Davydova, and A. V. Buzenkov, "Magnetic properties and phase composition of Pr–Dy–Fe–Co–B materials," *Perspectivnye Materialy*, No. 3, 16–19 (2007).
5. V. P. Piskorskii, G. S. Burkhanov, O. G. Ospennikova, R. A. Valeev, I. S. Tereshina, E. A. Davydova, "Calculation of the temperature induction coefficient of nanostructured hard magnetic Pr–Dy–Gd–Fe–Co– materials using the molecular-field approximation," *Russian Metallurgy*, No. 1, 53–56 (2010).
6. A. F. Petrakov, V. P. Piskorskii, G. S. Burkhanov, M. V. Repina, and S. I. Ivanov, "Peculiarities of sintering of Nd(Pr)–Dy–Fe–Co–B magnets with a high copper content," *Metall. Obrab. Met.*, No. 7, 3–9 (2012).
7. N. I. Ganina, A. M. Zakharov, V. G. Olenicheva, and L. A. Petrova, *Phase Diagrams of Metallic Systems Published in 1987* (VINITI, Moscow, 1988), Vyp. 32.
8. G. S. Burkhanov, V. P. Piskorskii, I. S. Tereshina, N. S. Moiseeva, E. A. Davydova, and R. A. Valeev, "The existence of a homogeneity range with respect to

- iron for the 2-14-1 hard-magnetic phase,” Dokl. Ross. Akad. Nauk **447** (3), 1–3 (2012).
9. V. P. Piskorskii, G. S. Burkhanov, O. G. Ospennikova, R. A. Valeev, I. S. Tereshina, and E. A. Davydova, “Effect of heat treatment on the properties of nano-structured magnetically hard Pr–Dy–Fe–Co–B materials,” Russian Metallurgy, No. 5, 442–447 (2010).
 10. J. F. Herbst, “ $R_2\text{Fe}_{14}\text{B}$ materials: intrinsic properties and technological aspects,” Rev. Modern Phys. **63** (4), 819–898 (1991).
 11. M. Rani and R. Kamal, “Mössbauer spectroscopy study of $\text{Nd}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{B}$ at $x = 0.13$ between 100 K and 700 K,” J. Less-Com. Met. **128**, 343–350 (1987).
 12. E. Burzo and N. Plugary, “Magnetic properties of $R_2\text{Fe}_{14-x}\text{Cu}_x\text{B}$ compounds with $R = \text{Nd}$ or Er ,” J. Magn. Magn. Mater. **86**, 97–101 (1990).
 13. H. Honma and H. Ino, “Preferential site occupation of Fe and Co atoms in $\text{Nd}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{B}$,” IEEE Trans. Magn. **23** (5), 3116–3118 (1987).
 14. V. P. Piskorskii, R. A. Valeev, E. A. Davydova, and V. A. Belousova, “Calculation of the temperature induction coefficient of Pr–Dy–Fe–Co–B materials in the molecular field approximation,” Perspektivnye Materialy, March, 329–331 (2008).
 15. S. K. Chen, J. G. Duh, and H. C. Ku, “Structural and magnetic properties of pseudoternary $\text{Nd}_2(\text{Fe}_{1-x}\text{Cu}_x)_{14}\text{B}$ compounds,” J. Appl. Phys. **63**, 2739–2741 (1988).

Translated by N. Kolchugina