

Highly anisotropic $\text{Nd}_{5-x}\text{Fe}_{25+3x}\text{B}_3$ magnetic materials and new magnetically hard materials made from them

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The basic magnetic and structural properties of single crystals of the compound $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ are reported for the first time. Permanent magnets with a high magnetic energy have been produced from this compound.

Croat *et al.*¹ have reported synthesizing a thin ribbon through a rapid quenching of an Nd-Fe-B melt on a rotating disk. From this ribbon they synthesized permanent magnets with a coercive force $H_c = 15$ kOe and a maximum energy product¹⁾ $(BH)_m = 14.1$ MG Oe. In the present letter we report the first synthesis of single crystals of the compound $\text{Nd}_5\text{Fe}_{25}\text{B}_3$, which is the basic phase in these new permanent magnets. We report the magnetic characteristics of the single crystals and of sintered magnets with values of $(BH)_m$ above 30 MG Oe.

Alloys of Nd (99.8% pure), Fe (99.9%), and B (99.6%) of various chemical compositions were smelted in an induction furnace in a helium atmosphere. Metallurgical and x-ray diffraction analysis revealed that the alloys with the general formula $\text{Nd}_{5-x}\text{Fe}_{25+3x}\text{B}_3$ ($0 \leq x \leq 1$) correspond to an essentially single-phase state. The compounds with compositions in this region have a tetragonal crystal lattice whose constants depend weakly on x ($a = 8.80$ Å and $c = 12.20$ Å at $x = 0$ and $a = 8.81$ Å and $c = 12.19$ Å at $x = 1$). The Laue diffraction patterns of the single crystals are of Laue class $4/mmm$. The unit cell contains two formula units. The x-ray density calculated from the data ($\rho = 7.56$ g/cm³ at $x = 0$ and 7.63 g/cm³ at $x = 1$) agrees well with that measured by hydrostatic weighing. The results also demonstrate the existence of the isostructural compound $\text{Y}_5\text{Fe}_{25}\text{B}_3$ with nonmagnetic Y ($a = 8.74$ Å, $c = 12.05$ Å). We were able to obtain some grains from the alloy $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ ($x = 0$) from which we prepared single-crystal samples for magnetic and x-ray-diffraction measurements over the temperature range 4.2–800 K.

Figure 1 shows the temperature dependence of the specific magnetization σ along the c axis, the magnetic-anisotropy field $H_a = 2K_1/\sigma_s$ (K_1 is the first anisotropy constant, and σ_s is the spontaneous specific magnetization), determined from the $\sigma(H)$ curves along and across the c axis in field up to 25 kOe, and the angle (θ) between the c axis and the easy axis. The angle θ was determined from torque curves. We see that as the temperature is lowered from $T_c = 600$ K to $T_s = 140$ K the value of σ along the c axis increases monotonically. In this temperature range the compound is magnetically uniaxial (easy axis parallel to the c axis), and we have $\sigma = \sigma_s$. Below T_s , σ decreases, because the easy axis deviates an angle θ from the c axis; at $T = 4.2$ K, this deviation is 33° . From the curves of $H_a(T)$ we see that K_1 changes sign at T_s . Analysis of the curves of the magnetization in the hard direction shows that K_2 is positive in $\text{Nd}_5\text{Fe}_{25}\text{B}_3$. This

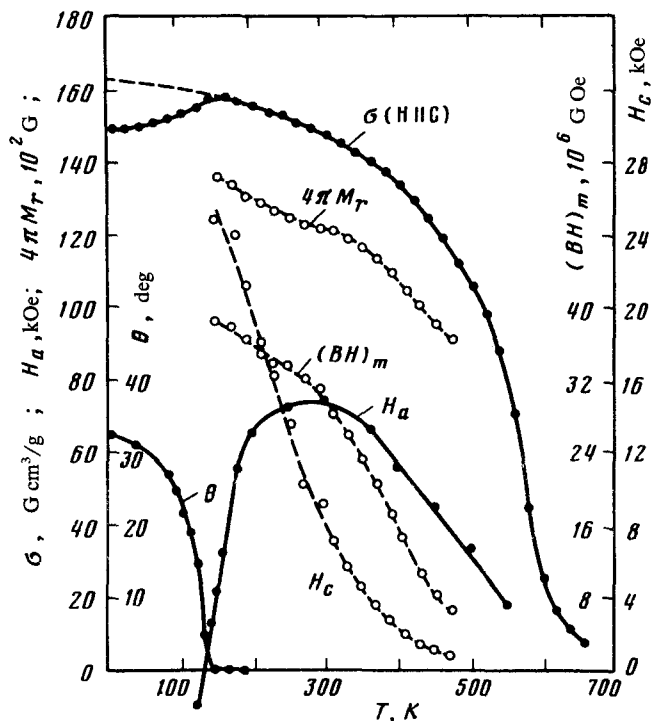


FIG. 1. Temperature dependence of the specific magnetization σ in a field $H = 20$ kOe along the c axis; the magnetic-anisotropy field H_a ; the angle θ , which is the angle between the c axis and the easy axis of the $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ single crystals; the coercive force H_c ; the remanent induction $4\pi M_r$; and the maximum energy product, $(BH)_m$, of a magnet of the alloy $\text{Nd}_5\text{Fe}_{25}\text{B}_3 + 4$ wt.%Nd.

combination of anisotropy constants (with K_1 changing sign and $K_2 > 0$) should result in a second-order spin-orientation phase transition,³ and in fact this is what we observed experimentally. Furthermore, below T_s there is a significant anisotropy in the basis plane of the crystal.

The compound $\text{Y}_5\text{Fe}_{25}\text{B}_3$, in which the anisotropy is due exclusively to the iron, is also uniaxial, with $H_a \approx 30$ kOe at room temperature. The apparent reason for such a pronounced anisotropy of the iron sublattice is a partial "thawing" of the orbital angular momentum of the iron. Comparison with the value $H_a = 74$ kOe in $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ shows that the two magnetic sublattices (Nd and Fe) have K_1 values of the same sign at room temperature. The orientational transition thus cannot be attributed to a competition between the anisotropies of the Nd and Fe subsystems. The magnetic anisotropy of the neodymium ions in nonequivalent crystallographic positions apparently has different signs and different temperature dependences, and at low temperatures the contribution of neodymium ions with a "planar" anisotropy becomes important.

In $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ and in other (4f-Fe) intermetallic compounds with light rare-earth metals, the magnetic moment of the neodymium ions is parallel to μ_{Fe} . If we assume

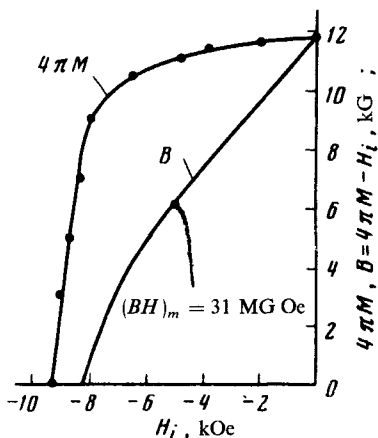


FIG. 2. Edges of the hysteresis loop in terms of the magnetization ($4\pi M$) and in terms of the induction (B) of a magnet of the alloy $\text{Nd}_3\text{Fe}_{25}\text{B}_3 + 4 \text{ wt.}\% \text{Nd}$.

that the neodymium ions are in the state Nd^{3+} , and if we use the value $\mu_{\text{Nd}} = 3.28\mu_{\text{B}}$, then from σ_s in the limit $T \rightarrow 0$ we find $\mu_{\text{Fe}} = 1.9\mu_{\text{B}}$, in approximate agreement with the value of μ_{Fe} in $\text{Y}_5\text{Fe}_{25}\text{B}_3$, in R_2Fe_{17} , and in pure Fe [$(2.0-2.2)\mu_{\text{B}}$]. Measurements of the temperature dependence of the lattice constants show that the large value of μ_{Fe} in $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ leads to pronounced spontaneous deformations of the crystal upon magnetic ordering. The thermal expansion below T_c is of an Invar nature, particularly obviously in the basis plane. The spontaneous bulk magnetostriction ω_s was determined from the difference between the experimental unit-cell volume and that extrapolated from the paramagnetic region; at $T = 4.2 \text{ K}$ it was found to reach a huge value ($+2 \times 10^{-2}$), which is nearly twice the maximum value of ω_s in the R-Fe compounds (1.2×10^{-2} in R_2Fe_{17}). The spin reorientation is also accompanied by a large bulk effect ($\Delta\omega_s = -1 \times 10^{-3}$): a compression of the lattice in all directions, apparently due to a decrease in μ_{Fe} as the easy axis deviates from the c axis.

At room temperature the compound $\text{Nd}_5\text{Fe}_{25}\text{B}_3$ has a very fortunate combination of fundamental magnetic characteristics: $4\pi M_s = 14 \text{ kG}$, $H_a = 74 \text{ kOe}$, and a theoretical limit $(BH)_{m1} = 49 \text{ MG Oe}$ for high-energy-density permanent magnets made from this material. To fabricate some permanent magnets we crushed the alloy, compacted it in a magnetic field, sintered it, and subjected it to a further annealing. Figure 2 shows edges of the hysteresis loop of the resulting magnet; Fig. 1 shows the temperature dependence of its H_c , of the remanent induction $4\pi M_r$, and $(BH)_m$. At room temperature the magnet has $H_c = 9.3 \text{ kOe}$, $BH_c = 8.2 \text{ kOe}$, $4\pi M_r = 11.8 \text{ kG}$, $\rho = 7.2 \text{ g/cm}^3$, and $(BH)_m = 31 \text{ MG Oe}$. Comparison of the initial magnetization curve with the descending branch of the hysteresis loop leads to the conclusion that the high value of H_c of this magnet is caused by the difficulty in the appearance and development of the domain structure upon magnetization reversal. The values of $(BH)_m$ of the new magnetically hard materials made from the Nd-Fe-B alloys are higher than those of SmCo_5 and Sm-Co-Fe-Cu-Zr , and they do not contain the scarce and expensive Sm and Co. There is reason to believe that the neodymium in these magnets could be

replaced by another light rare-earth metal, in particular, praseodymium, or even by an inexpensive cerium-rich mixture of metals.

Analysis of the results shows that the characteristics of the magnets reported here and in Ref. 4 could be improved substantially ($BH_m \geq 40$ MG Oe) through a further optimization of the technological parameters and chemical composition of the original alloy. The relatively high temperature coefficient (0.08%/K) of the remanent induction could be reduced by partially replacing the Nd or other light rare-earth metals by heavy rare-earth metals and by doping the alloy with components that would raise T_c . We can confidently assert that these new permanent magnets of alloys of a rare earth, iron, and boron hold promise and will find widespread use in a variety of technological fields.

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¹The high value of H_c for the Nd-Fe alloy was first reported by some Soviet scientists: R. I. Yanus and V. I. Drozhzhina back in 1935.²

²After this paper had been prepared for publication, Sagawa *et al.* published a paper⁴ reporting the use of the same technique and the alloy $\text{Nd}_3\text{Fe}_{25}\text{B}_3$ to fabricate magnets with $(BH)_m = 36$ MG Oe. The higher properties can be credited to better conditions during the texturing and compaction of the powder. As a result, the values $\rho = 7.4$ g/cm³ and $4\pi M_r = 12.3$ kG were reached in Ref. 4. The procedure for fabricating the magnets is described in detail in Ref. 4, so we have simply listed the operations here.

¹J. J. Croat, J. F. Herbst, R. W. Lee, and F. E. Pinkerton, Appl. Phys. Lett. **44**, 148 (1984).

²R. I. Yanus and V. I. Drozhzhina, Nature **36**, 175 (1935).

³K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and R. A. Levitin, Usp. Fiz. Nauk **119**, 447 (1976) [Sov. Phys. Usp. **19**, 574 (1976)].

⁴M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, J. Appl. Phys. **55**, 2083 (1984).

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