

# Rare-earth magnetically hard materials

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## 1. INTRODUCTION

Permanent magnets were discovered in nature even before our era and stand at the sources of development of the study of magnetism. Already in antiquity they found practical application as "floating lodestones"—marine compasses ("south-pointers")—and played an important role in the development of navigation, which in turn was responsible for the discovery of new countries. The history of the development and application of permanent magnets is set forth, for example, in the books<sup>[1]</sup>. In our time permanent magnets play an extremely important role in technology, and at present it would be difficult to name any branch of it where they are not used. Most people know about the application of permanent magnets in loudspeakers. But few are aware that there are areas of technology where the use of magnets is incomparably more important. Foremost are electric motors and generators, magnetic systems for focusing an electron beam, electrical measurement instruments, frictionless magnetic bearings, magnetic clutches for transmitting motion through an impenetrable partition, magnetic separators for cleansing friable and liquid media of ferromagnetic impurities, and switching devices of various kinds (relays). Permanent magnets are used in pickup heads, speedometers, television receivers, radio receivers, telephones, electrodynamic microphones, and door latches. On the basis of these there have been developed biasing devices in blocks of magnetically recorded information, miniature hearing aids, and entertaining childhood toys. The demand for permanent magnets increases each year; and it will perhaps not be a great exaggeration to say that the level of development of contemporary technology, including that of the home, depends to a significant degree on the level of development of permanent magnets.

In whatever magnetic system permanent magnets are used, they are primarily sources of magnetic field that cost nothing to operate. In the case of the simplest magnetic circuit—a ring-shaped magnet with a gap—the field in the gap is  $|H_g| = q\sqrt{BH V_m / V_g}$ . Here the value of the coefficient  $q$  is completely determined by the geometry of the magnetic system. It follows from this expression that a given volume of permanent magnet ( $V_m$ ) produces, in an air gap of volume  $V_g$ , the strongest field possible if the induction of the magnet ( $B$ ) corresponds to the maximum of the product  $(BH)$ .<sup>[1]</sup> Therefore the value of the maximum energy product  $(BH)_m$  is one of the most important characteristics of permanent magnets. It is proportional to the magnetic energy  $(BH)_m / 8\pi$  stored during magnetization of unit volume of the magnet, and also to the magnetic energy  $(H_g^2 / 8\pi)$  of unit volume of the gap. The method of determining  $(BH)_m$  experimentally is as follows: for each value of the internal field of the magnet  $H$  in the second quadrant of the hysteresis loop, one finds the product of the value of this field by the corresponding value of the induction ( $B = 4\pi I - H$ ), constructs the energy-product curve  $(BH) = f(H)$ , and from it determines the maximum value  $(BH)_m$ , as is shown in Fig. 1.

In order that a magnetic material may be a permanent magnet, it must possess residual induction ( $B_r = 4\pi I_r$ ) after magnetization in a magnetic field and must retain this state as long as possible (magnets must not "age"). The presence of residual magnetization in a magnetic material in general and in a permanent magnet in particular is caused by magnetic hysteresis: that is, lag of the change of magnetic induction ( $B = H + 4\pi I$ ) behind the change of magnetic field intensity ( $H$ ) during magnetization and reversal of the magnetization of the magnetic material.

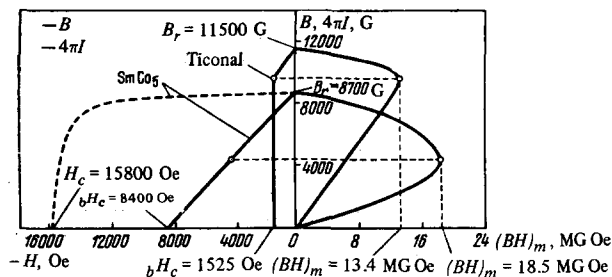


FIG. 1. Definition of magnetic characteristics of permanent magnets. By way of example and for comparison, the figure shows the best results for ticonal alloy (35.0% Fe, 34.8% Co, 14.9% Ni, 7.5% Al, 2.4% Cu, 5.4% Ti)<sup>[2]</sup> and the results of the first report on magnets of the alloy SmCo<sub>5</sub>.<sup>[3]</sup>

In recent years, the interest of physicists and engineers in permanent magnets has grown especially because of the discovery, among alloys of rare-earth metals with 3d transition metals (T), of intermetallic compounds possessing a unique (for the purpose of obtaining permanent magnets) combination of values of the magnetocrystalline anisotropy constant ( $K$ ), the saturation magnetization ( $4\pi I_s$ ), and the Curie temperature ( $T_c$ ). These are primarily compounds  $RT_5$  and  $R_2T_{17}$ , precipitation-hardened alloys  $R(T, Cu)_5$ , magnetically multiaxial compounds  $RFe_2$ , materials with extremely narrow (monatomic) domain walls for permanent magnets operating at low temperatures in cryogenic technology, etc. Permanent magnets obtained on the basis of these materials, which possess an enormous value of the coercive force ( $H_c$ ), high temperature stability of the magnetic characteristics, and a value of  $(BH)_m$  exceeding by a factor of more than two that of the best magnets obtained on the basis of metals of the iron or platinum group, have given a powerful thrust in the direction of development of new devices and apparatus, and improvement and cost reduction of the existing ones, in various areas of technology.

The present article reviews the experimental and theoretical research done in the last 10–15 years in the area of rare-earth magnetically hard materials. Principal attention is concentrated on those papers in which is demonstrated most simply and clearly the physical side of the questions considered (methods of obtaining permanent magnets, the nature of their high-coercivity state and of the magnetization-reversal processes, temperature stability of the magnetic properties, their relation to the crystal and domain structures, the nature of the magnetic anisotropy and of the magnetic moment, etc.) and from which emerge most clearly the prospects of further development of rare-earth permanent magnets. In order to show the scientific and practical significance of the successes achieved in this section of the physics of magnetic materials, the beginning of the article sets forth briefly the state of developments in the area of “pre-rare-earth” permanent magnets, and also considers the basic concepts in the area of the theory of magnetic hysteresis and of domain structure of magnets, which is often related in most direct fashion to the hysteretic properties of magnetically hard materials.

## 2. DOMAIN STRUCTURE AND MAGNETIC HYSTERESIS. GENERAL CONCEPTS

### A. Existence of domains, and the single-domain state

After cooling from the magnetic ordering temperature ( $T_p$ ), in order to lower the magnetostatic self-energy  $E_0$ , a magnet with size above a certain critical size ( $d_{cr}$ ) splits into domains<sup>[4]</sup>—regions spontaneously magnetized to saturation under the action of exchange forces of electrostatic origin (Fig. 2). Different domains are magnetized in different directions, but always along an axis of easy magnetization (AEM), in such a way that the crystal has no resultant magnetic moment. A thermodynamic theory that justifies the existence of the domains themselves and predicts the form of the domain structure (the size and shape of the domains and the orientation of the spontaneous magnetization within them), for magnetically uniaxial crystals of the cobalt type and for magnetically triaxial crystals of the iron type, was first developed by Landau and Lifshitz in 1935.<sup>[5]</sup>

In the transition from one domain to another, the change of orientation of the magnetization  $I_s$  in the majority of cases occurs by a gradual rotation of the elementary magnetic moments (spins) within a certain transitional layer (domain boundary—DB). Here the exchange energy, which is responsible for the parallel orientation of the spins, strives to increase the boundary thickness ( $\delta$ ), i. e., to change the orientation of  $I_s$  more gradually within it. The magnetic anisotropy energy acts in the opposite direction, because every deviation of  $I_s$  from the AEM increases it. As a result of the competition of these two energies, there are established an equilibrium boundary thickness  $\delta = \pi\sqrt{A/K}$ , for  $K \gg 2\pi I_s^2$ , and a corresponding boundary surface-energy density  $\gamma = 4\sqrt{AK}$ , where  $A \approx kT_c/a$  is an exchange-interaction parameter,  $k = 1.38 \cdot 10^{-16}$  erg/deg,  $a$  is the distance between magnetically active ions in the lattice, and  $K$  is the magnetic anisotropy constant.

On decrease of the size ( $d$ ) of the magnet, its magnetostatic energy  $E_0$  decreases faster than the surface

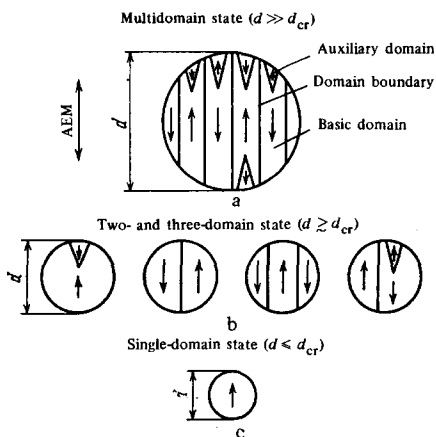


FIG. 2. Schematic domain structure (DS) of magnetically uniaxial monocrystals of various sizes. The arrows show the direction of the spontaneous magnetization in the domains.

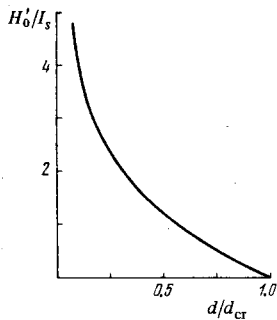


FIG. 3. Size dependence<sup>[7]</sup> of the value of the field  $H_0$  at which a two-domain state originates in a particle that is single-domain at  $H=0$ .

energy  $E_\gamma$  of the DB. Therefore in a magnet with  $d$  below a certain critical  $d_{cr}$ , no domain structure (DS) exists at  $H=0$ , and the magnet is in thermodynamic equilibrium in a single-domain state (Fig. 2).<sup>[6]</sup> For high-anisotropy magnets ( $K \gg 2\pi I_s^2$ ), the single-domain size is  $d_{cr} = 0.7\gamma/I_s^2$ . But in a magnetic field ( $H_0$ ), a multidomain state occurs even at  $d \leq d_{cr}$ . The value of this field increases with decrease of  $d$  and essentially determines the minimum value of the coercive force resulting, for given  $K$  and  $I_s$ , purely from the influence of the geometric size of the crystal (Fig. 3).<sup>[7]</sup>

## B. Causes of magnetic hysteresis

The magnetization of a multidomain magnet, on increase of a field applied along an AEM, occurs by increase of the volume of domains with the direction of  $I_s$  closest to  $H$  at the expense of the others, by displacement of the DB. Magnetization reversal may occur both by irreversible displacement of the DB and also by irreversible rotation of  $I_s$  (uniform or nonuniform) throughout the whole volume of the specimen. This irreversibility expresses itself also in magnetic hysteresis, the energy characteristic of which is the area of the hysteresis loop, which in turn is characterized by the coercive force ( $H_c$ ) and the residual magnetization ( $4\pi I_r$ ).

We may point out the four most important causes of magnetic hysteresis in real ferromagnets<sup>[8,9]</sup>:

1) *Irreversible magnetization rotation processes.* This type of hysteresis is realized in its pure form when the appearance of nuclei of the reverse magnetic phase during magnetization reversal is extremely difficult, or when the size of the magnet is so small ( $d = d_c \lesssim \delta$ ) that the existence of nuclei, with localized DB, is energetically disadvantageous because of the great increase of the energy of the crystal in consequence of the energy of the boundary layer. It leads to a residual magnetization equal to the saturation magnetization  $4\pi I_s$ , and to an  $H_c$  that varies within the limits<sup>[10,11]</sup>

$$\frac{2K}{I_s} \leq |H_c| \leq \frac{2K}{I_s} - NI_s. \quad (1)$$

The upper bound, equal to the anisotropy field ( $H_a = 2K/I_s$ ), corresponds to uniform rotation of  $I_s$ ; the lower, to the minimum possible value of  $H_c$  in nonuniform remagnetization of a perfect crystal with demagnetizing form-factor  $N$ . Intermediate values of  $H_c$  also cor-

respond to remagnetization of the crystal by nonuniform rotation of  $I_s$ , but the value depends in addition on the shape and size of the magnet. For high-anisotropy magnets ( $H_a \gg NI_s$ ), the ratio  $(H_c^{\max} - H_c^{\min})/H_c^{\max}$  is extremely small; for example, for  $\text{SmCo}_5$  ( $H_a \approx 400$  kOe,  $4\pi I_s \approx 10$  kOe), it amounts to only 2.5%. Hence follows a deduction most important in practical design: in high-anisotropy magnets, independently of their shape and dimensions, there is in principle a possibility of obtaining a coercive force close in value to the anisotropy field, with a residual magnetization equal to the saturation magnetization. In this case the magnet is a permanent magnet with a value of the maximum energy product  $(BH)_m$  equal to the maximum theoretical limit  $(BH)_{mt} = (4\pi I_s)^2/4$ .

2) *Irreversible domain-boundary displacement processes.* If, on decrease of the magnetizing field (during magnetization reversal), nuclei of the reverse magnetic phase originate easily in fields below the coercive force (in absolute value), then the magnetization reversal of a magnet with  $d > d_{cr}$  occurs by irreversible displacement of the DB, which may be impeded by obstacles of various kinds—crystal defects. This is due to the fact that in the neighborhood of defects the effective values of the fundamental magnetic characteristics, such as the magnetocrystalline anisotropy constant ( $K'$ ), the spontaneous magnetization ( $I_s'$ ), the exchange parameter ( $A'$ ), etc., differ from the corresponding quantities in a perfect part of the crystal ( $K, I_s, A$ ). This difference leads to the result that the boundary surface-energy density ( $\gamma = 4\sqrt{AK}$ ) becomes different in magnitude in the perfect and the defective parts of the crystal. The critical field value  $H_{cr}$  necessary for "breaking away" of a 180-degree DB in the direction of its normal ( $n$ ) is determined by the value of the maximum gradient of the boundary energy,<sup>[4]</sup>

$$H_{cr} = \frac{1}{2I_s} \frac{d\gamma}{dn} \quad (2)$$

and in essence determines the value of the coercive force. Thus the calculation of  $H_c$  for real magnets reduces to the calculation of  $d\gamma/dn = f(K, K', A, A', d')$  at defects (pores and nonmagnetic inclusions,<sup>[12]</sup> dislocations,<sup>[13]</sup> antiphase boundaries,<sup>[14]</sup> stacking faults,<sup>[15]</sup> point defects,<sup>[16]</sup> subboundaries, etc.), with allowance for the density ( $N_0$ ) of distribution of defects in the specimen and also for their structure, which in the simplest models is sometimes characterized by the magnetically active defect size ( $d'$ ), so that  $H_c = H_a f(K, K', A, A', I_s, I_s', N_0, d')$ . Calculations show that  $H_c^{\min}$  is bounded by the intrinsic coercivity ( $H_w$ ) of the DB, while  $H_c^{\max}$ , just as in the case of magnetization reversal by irreversible rotation of  $I_s$ , may reach values of the order of magnitude of the anisotropy field ( $H_a$ ).<sup>[12,14,17]</sup>

3) *Hysteresis of nucleus formation.* It has now been established experimentally that during the magnetization of a magnet, the DS disappears in a field  $H_s \approx NI_s$ , while during magnetization reversal nuclei of the reverse magnetic phase appear, as a rule, in a field  $H_n < H_s$ ; that is, hysteresis occurs because of the difficulty of generation of nuclei.<sup>[9]</sup> This type of hystere-

sis is particularly important in the magnetization reversal of high-anisotropy magnets, although sometimes  $\Delta h = |(H_s - H_n)/H_s| < 1$  has no effect on  $H_c$ . The minimum absolute value of  $H_n$ , and consequently of  $H_c$ , for a perfect crystal is<sup>[11,18]</sup>

$$|H_{cr}^{min}| = H_n = H_a - NI_s. \quad (3)$$

Consequently, for such magnets there is in principle a possibility, even with allowance for this type of hysteresis, of obtaining a value  $H_c \approx H_a$ . In practice this is attained only for very perfect crystals, for example filamentary crystals (whiskers) of iron,<sup>[19]</sup> perfect platelets of barium ferrite,<sup>[20]</sup> crystal films of MnBi alloy,<sup>[21]</sup> and others. In most cases the experimental values of  $H_c$  are significantly (sometimes by several orders of magnitude) below  $H_a$ . This is due to the fact that formation of nuclei occurs relatively easily in a region of crystal defects, where, as has already been mentioned, the local anisotropy field ( $H'_a = 2K'/I_s$ ) is lowered.<sup>[18]</sup> The effect of defects of various kinds on the value of the nucleation field has been treated theoretically in a number of papers.<sup>[22-26]</sup>

4) *Hysteresis due to inhibition of the growth of nuclei.* This type of hysteresis is essentially due to the fact that only after reaching a certain critical size  $r_c$  are nuclei able to increase their dimensions irreversibly in a start field  $H_{0s}$ , leading to magnetization reversal of the crystal. The theory of this hysteresis<sup>[27-30]</sup> gives the result that

$$H_c < H_{0s} = -\left(H_{cr} + \frac{b\gamma}{I_s r}\right). \quad (4)$$

where  $H_{cr}$  is determined by formula (2), and where  $b \approx 1$ . It should be mentioned that the theory predicts a qualitatively correct variation  $H_{0s} = f(r)$ , but only under specially chosen conditions.<sup>[4]</sup>

Thus from a short analysis of the basis types of magnetic hysteresis, it follows that each of them, for high-anisotropy magnets under suitable conditions, may lead to values of  $H_c$  equal approximately to the anisotropy field; that is, each provides a possibility of storing, after magnetization of such a material, a value of the magnetic-energy density equal to the theoretical limit, if  $H_a \geq 2\pi I_s$ . This is why magnets with high magnetic anisotropy are the most suitable materials for permanent magnets. It is of course important that such a magnetic material have a high value of  $4\pi I_s$ , which is an upper bound for the residual magnetization and determines an upper bound for the maximum energy product, and a high value of  $T_c$ , which determines the temperature range of application of the magnets and the parameters of temperature stability of their magnetic properties. From this point of view we shall consider below the existing magnetically hard materials and the possibilities for further improvement of their magnetic properties. Special attention will be given to the state of physical investigations and the prospects for development of materials for permanent magnets from alloys based on rare-earth metals (REM).

### 3. MATERIALS FOR PERMANENT MAGNETS

#### A. "Pre-rare-earth" magnetically hard materials and possibilities for improvement of their properties

Until 1968, the magnetically hard material with the highest value of the maximum energy product,  $(BH)_m = 13.4$  MGOe, was an alloy based on Fe-Co-Ni-Al, alloyed with Cu and Ti (Ticonal).<sup>[2,31]</sup> The record-breaking top of its hysteresis loop is shown in Fig. 1. The value of  $(BH)_m$  of commercially manufactured magnets is only slightly lower ( $\sim 10$  MGOe). Such outstanding results of physics and technology were attained at the cost of great efforts over the span of the last almost 40 years. Further increase of the  $(BH)_m$  of these alloys (to 16-18 MGOe), while still possible, involves great difficulties both of fundamental and of technological nature. In fact, this can be attained only by increase of  $H_c$  or of  $4\pi I_s$ . But  $H_c$  in an alloy of the Alnico type is determined by the value of the magnetic shape anisotropy of elongated single-domain particles of a strongly magnetic phase ( $H_c \sim \Delta NI_s$ ) located in a weakly magnetic matrix and by the magnetostatic interaction between them, and increasing it requires decreasing the packing density of the particles; and this decreases  $4\pi I_s$ . To increase  $4\pi I_s$ , it is necessary to increase the amount of the strongly magnetic phase; that is, to decrease the distance between the particles or increase their dimensions. Decrease of the distance leads to a strengthening of the magnetostatic interaction, to the occurrence of an interaction DS,<sup>[32]</sup> and consequently to a lowering of  $H_c$ . Increase of the particle size leads to a similar result in consequence of the strong dimensional dependence of  $H_c$  for elongated particles of weakly anisotropic materials ( $K \ll 2\pi I_s^2$ ).<sup>[10]</sup> Further increase of the  $(BH)_m$  of alloys is possible if conditions for obtaining and heat-treating the alloys are developed (or rather selected) under which particles would be produced that were perfect in shape, correctly distributed, uniform in size, and with a higher value of  $4\pi I_s$ .<sup>[1]</sup> But all this involves great difficulties, and a slight increase of  $(BH)_m$  leads to a great rise in the cost of magnets of Alnico-type alloys.

One of the important disadvantages of Alnico magnets is the low  $H_c$  (up to 2 kOe), which limits their application under conditions of strong demagnetizing fields (either self- or produced by external sources). Therefore great interest attaches to permanent magnets of high-anisotropy ferrites (barium, strontium, cobalt; see Table I).<sup>[18,34-36]</sup> But their  $(BH)_m$  and  $(BH)_{mt}$  are not large, and they find wide application also because of their low cost.

Great interest attaches to magnetically uniaxial alloys based on manganese, which have high values of  $H_a$  and  $H_c$  (Table I).<sup>[37-52]</sup> Magnetic hardness in them is attained by a special mode of heat treatment and of plastic deformation.<sup>[41,49]</sup> But a high  $(BH)_m$  has not yet been successfully obtained in consequence of the difficulty of

<sup>1)</sup>Fahlenbrach,<sup>33</sup> citing a private communication, indicates that magnets with  $(BH)_m \approx 15$  MGOe have been obtained from Ticonal alloys.

TABLE I. Magnetic properties of some magnetically hard materials ( $T = 20^\circ\text{C}$ ).

Material	$T_c$ , °C	$I_s$ , G	$K \cdot 10^{-6}$ , erg/cm <sup>3</sup>	Maximum theoretical values			Experimentally* obtained values			References
				$H_c = H_c$ , kOe	$bH_c = 4\pi I_s$ , kOe	$(BH)_{mT}$ , MG Oe	$H_c$ , kOe	$bH_c$ , kOe	$(BH)_{mT}$ , MG Oe	
Alnico-8	—	950	—	—	—	—	1.55	1.53	13.4	2, 34
BaOFe <sub>2</sub> O <sub>3</sub>	450	335	3.0	17	4.8	5.7	2.5	2.3	3.7	18, 34, 35
SrOFe <sub>2</sub> O <sub>3</sub>	—	380	3.4	19	4.8	5.7	2.8	2.5	4.3	35
Co <sub>9</sub> Fe <sub>2</sub> zO <sub>4</sub>	520	425	2.9	14	5.3	7.0	1.7	—	1.8	34, 36
MnBi	360	620	11.6	40	7.7	14.8	13.0	3.4	4.4	37-39
MnAl	380	560	10.4	37	7.1	12.6	6.5	2.4	4.0	40-45
MnAlGe	250	310	6.7	43	3.9	3.8	6.4	—	—	46, 47
MnGa (e')	420	320	6.0	38	4.0	4.0	8.6	2.6	1.8	48-52
MnGa (η)	370	550	9.9	39	6.9	12.0	5.9	2.0	4.0	48-52
FePd	460	1100	26-47	47	13.8	47.5	3.6	—	—	53-56
FePt	470	—	40	—	—	—	13.0	—	—	56-58
CoPt	540	800	49	120	10.1	25.5	9.0	3.9	12.5	56, 59
Co-Pt-Fe	—	—	—	—	—	—	5.0	—	15.0	60

\*The values given are the highest for laboratory specimens.

producing a perfect magnetic texture because of the crystallographic. This family of alloys has not yet found very wide practical use.

A great step forward in the area of permanent magnets was the development of magnetically hard alloys based on platinum: CaPt, FePt, Co-Fe-Pt. They have high values of  $K$ ,  $4\pi I_s$ , and  $T_c$  and consequently high values of  $H_c$ ,  $4\pi I_s$ , and  $(BH)_m$ . But the possibilities of these alloys are being exhausted. Despite the huge cost and the scarcity of noble metals, they are used quite widely in important magnetic systems, where high values of  $H_c$  and  $(BH)_m$  are necessary. In addition, these alloys are ductile and withstand mechanical working well; this is important in the manufacture of magnets of complicated shapes. Indubitably interesting are investigations of the magnetic properties of the alloy Fe-Pd, which has the highest bound for  $(BH)_{mT}$  [53-55] among this series of alloys. Unfortunately, it has not yet been possible to obtain in it an  $H_c$  larger than 3.6 kOe.

From the above short review of magnetically hard materials it is easily seen that though progress may be expected in the area of further improvement of their properties, it would not be significant. In this situation, sensational indeed was the report of Buschow and co-workers, [3, 61, 62] who in 1968-1969 obtained from powders of SmCo<sub>5</sub> alloy permanent magnets with  $(BH)_m$  about 20 MG Oe (see Fig. 1). This work by itself stimulated a new step in intensive investigation of the physical properties of magnetic materials based on inter-

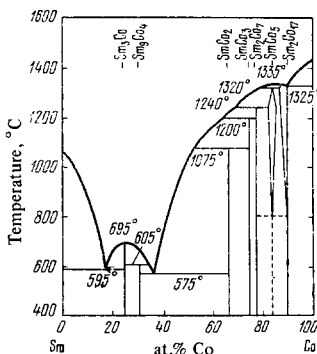


FIG. 4. Phase diagram of alloys of the system Sm-Co.

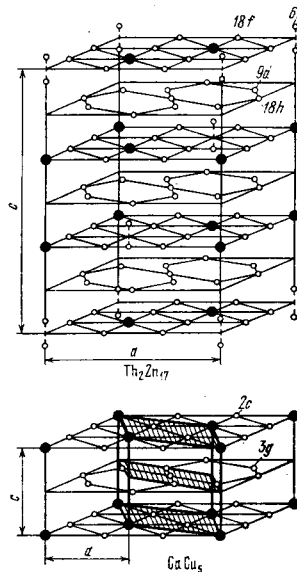


FIG. 5. Structure of Th<sub>2</sub>Zn<sub>17</sub> type and of CaCu<sub>5</sub> type. The heavy lines show the elementary cell of CaCu<sub>5</sub>. Also shown here are the various positions occupied by Co atoms; the number before the letter shows the number of such positions in an elementary cell.

metallic compounds of REM with 3d transition metals of the iron group ( $T$ ) in many magnetic laboratories of the world.

## B. Materials for rare-earth permanent magnets

1) Phase diagram of (R-T) alloys and crystal structure of RT compounds. The phase diagrams of alloys of REM with 3d metals contain a large number of intermetallic compounds. [63-66] For illustration, Fig. 4 shows the phase diagram of alloys of the system Sm-Co, since it is alloys of this system that at present are of the greatest interest for high-energy-capacity permanent magnets. As is evident, the majority of compounds are formed as a result of a peritectic reaction ( $RT_5$ ,  $R_2T_7$ ,  $RT_3$ ,  $RT_2$ ,  $R_3T_4$ ) or congruently ( $R_3T$ ,  $R_2T_{17}$ ). They all have a quite complicated crystal structure. Therefore we shall restrict ourselves, below, to those among them that are of interest for permanent magnets or that are concomitant to the obtaining of magnets.

The basis structure for the majority of RT compounds is the structure of the compound  $RT_5$ , which is related to the hexagonal type CaCu<sub>5</sub> of the space group  $P6/mmm$  (Fig. 5). It consists of two types of planes, alternating with each other along the  $c$  axis. In one of them, the Co atoms are arranged in a hexagonal grid (position 3g), at the centers of which the R atoms are located. In the other are located only Co atoms (2c), forming a less densely packed (eccentric) Kagomé net, which, generally speaking, constitutes the basic structural elements for the majority of structures of RT compounds.

The structure of the compound  $R_2T_{17}$  is obtained from the structure of  $RT_5$  by an ordered replacement along the  $c$  axis of every third R atom by a pair ("dumbbell") of Co atoms ( $3RT_5 - R + 2Co = R_2T_{17}$ ). This pair of Co atoms is arranged along the  $c$  axis on both sides of the RT layer (see Fig. 5). There are two modifications of phase of  $R_2T_{17}$ : the hexagonal (with heavy REM), of the type Th<sub>2</sub>Ni<sub>17</sub> ( $P6_3/mmc$ ), and the rhombohedral (with light REM), of the type Th<sub>2</sub>Zn<sub>17</sub> ( $P\bar{3}m$ ), which differ with

respect to the nature of the alternation of dumbbells and  $R$  atoms along the  $c$  axis. It should be mentioned that some compounds with light REM (for example, with samarium) of the type  $R_2T_{17}$  also have, at high temperatures, a hexagonal modification.

The structure of the compound  $R_2T_7$  (or  $RT_3$ ) is obtained by an ordered replacement of one of the  $Co$  atoms in the  $RT_5$  structure, arranged along the  $c$  axis, according to the formula:  $3RT_5 - T + R = 2R_2T_7$  (or  $2RT_5 - T + R = 3RT_3$ ). But the substituting  $R$  atom is not located exactly at the position of the replaced  $Co$  atom; in consequence of geometric requirements, it is located both above and below the hexagonal planes. Thus the original cell undergoes transverse rhombohedral shifts, leading to the  $R_2T_7$  (or  $RT_3$ ) structure. For compounds  $R_2T_7$  with light REM and gadolinium, there are both a rhombohedral modification of the type  $Gd_2Co_7$  of space group  $P6_3$ , and a hexagonal of the type  $Ce_2Ni_7(P6_3/mmc)$ ; with heavy REM, only the rhombohedral modification. Compounds  $RT_3$  for all REM have a rhombohedral lattice of the type  $PuNi_3(P\bar{3}m)$ . The lattice parameter  $a$  of all the structures considered above (except  $R_2T_{17}$ , where  $a_{R_2T_{17}} = \sqrt{3}a_{RT_5}$ ) are close in value to the parameter  $a$  of the  $RT_5$  structure, while the parameter  $c$  is approximately a multiple of the parameter  $c$  of the  $RT_5$  lattice.

Great interest for permanent magnets, and especially for high-magnetostriction materials, attaches to compounds  $RT_2$  ( $RT_5 - T + R = 2RT_2$ ), which have a cubic lattice of the type  $MgCu_2(Fd\bar{3}m)$ —the Laves phase. The crystal structure of the Laves phases is well known, and we shall not go into it. We remark only that intermetallic compounds of REM with  $3d$  metals, with this structure, are very abundant among  $RT$  compounds and play a most important role in a variety of physical investigations.

In conclusion, it should be said that at present the crystal structures of the majority of  $RT$  compounds are well documented, and data on the lattice parameters can be found in the appropriate literature (see, for example, [67,69]). It has been established that the lattice parameters for one or another type of compounds with different REM, as a rule, decrease with increase of the number of the REM in consequence of the decrease of the ionic radius of the REM (the law of "lanthanide compression"). Cerium compounds are an exception; their lattice parameters are smaller than is to be expected. This anomaly is due to the fact that the cerium in these compounds has a valence between  $3^+$  and  $4^+$ , in contrast to valence  $3^+$  for the other REM; this, in the opinion of some authors, is due to a partial or complete transfer of one  $4f$  electron to the conduction band.

The relation between the crystal structures of intermetallic  $RT$  compounds, and the formation of compounds through peritectic reaction, lead to the result that the alloys obtained, as a rule, are not single-phase, contain microscopic inhomogeneities of chemical composition, and require a long annealing (sometimes over a period of several months) at a high tem-

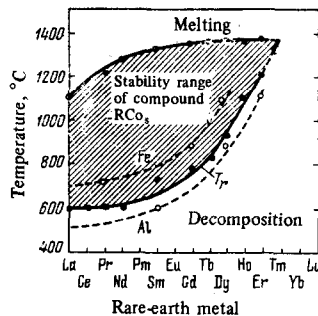


FIG. 6. Melting points and eutectoid decomposition temperatures of compounds  $RCO_5$  with the  $CaCu_5$  structure. The dashed curves show the decomposition temperature of compounds  $RCO_5$  alloyed with iron and with aluminum. [81]

perature in order to remove these inhomogeneities and produce alloys that are chemically homogeneous and single-phase not only according to x-ray and metallographic analysis but also according to more stringent criteria.

It has been established experimentally [63,67,68,229] that compounds  $RT_5$  and  $R_2T_{17}$  ( $R = Y, Ce, Sm, Gd$ ) at temperatures below a certain  $T_r$  (for example,  $\sim 800^\circ C$  for  $SmCo_5$  and  $Sm_2Co_{17}$ ) have relatively broad ranges of homogeneity (for example, from  $SmCo_{4.8}$  to  $SmCo_{5.7}$ ), which at still higher temperatures ( $\sim 1250^\circ C$  for  $SmCo_5$  and  $Sm_2Co_{17}$ ) practically close up (see Fig. 4). It may be assumed that compounds of this type with other REM also have such homogeneity ranges. In the homogeneity ranges, the lattice parameters vary linearly with the concentration of the components. This fact can be used to determine the exact chemical composition of compounds by x-ray measurements of the lattice parameters. In the homogeneity range,  $K$ ,  $4\pi I_s$ , and  $T_c$  vary in accordance with the chemical composition; and as will be shown below, this range plays an important role in the production of a high-coercivity state in permanent magnets based on  $RCO_5$  alloys. [69,70]

In relation to the operating conditions of permanent magnets, an especially important question is the room-temperature stability of the compounds, because the magnets obtained from them must be non-aging in time and thermally stable over a definite temperature range, prescribed by the operating conditions of the magnetic system. (Existing standards allow a change of the value of the residual induction of permanent magnets by only a few percent, and sometimes considerably less, over a period of 11 years!) A whole series of publications [71-82] has been devoted to the solution of this problem. In most of these it is noted that, for example, compounds  $RCO_5$  are not in thermodynamic equilibrium at a temperature below the eutectoid decomposition temperature ( $T_r$ ) and decompose into  $R_2Co_7$  and  $R_2Co_{17}$ . But the decomposition at a temperature  $T$  even inappreciably below  $T_r$  proceeds extremely slowly. The decomposition temperature coincides in value with the temperature at which the homogeneity range begins, and it increases with increase of the number of the REM [71] or alloying of the  $RCO_5$  compound by  $Cr, Pt, Mn, Fe, Au, Pd, Ag, C,$  or  $Pb$  and decreases with addition of  $Ni, Si, Ge, Ga, Cu,$  or  $Al$  (Fig. 6). [81] It should be mentioned, however, that while in the case of heavy REM there is no doubt about decomposition, for compounds with light REM, for example  $Sm$ , there has so far been no success, despite great efforts, in x-ray

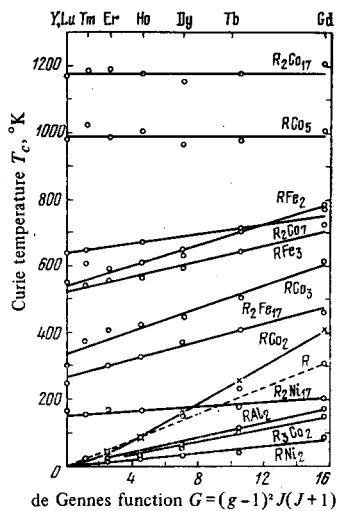


FIG. 7. Dependence of the Curie temperature of REM and of their compounds with metals of the iron group on the de Gennes function  $G = (g - 1)^2 J(J + 1)$ .

detection of the  $\text{Sm}_2\text{Co}_7$  phase, which, along with  $\text{Sm}_2\text{Co}_{17}$ , should be present in noticeable amounts in eutectoidal decomposition. In those cases in which decomposition has apparently occurred, the possibility was not excluded that the chemical composition of the compound changed because of oxidation or evaporation during the process of prolonged maintenance of quite high temperatures of the REM. On the other hand, the unsuccessful attempt to obtain the compound  $\text{SmCo}_5$  by diffusion saturation at temperature  $775^\circ\text{C}$  and its appearance in the temperature range  $820\text{--}1130^\circ\text{C}$  indicate the presence of eutectoid decomposition with  $T_r$  about  $800^\circ\text{C}$  for this compound.<sup>[76]</sup> An unambiguous resolution of this problem is extremely important both for understanding of the physics of the high-coercivity state of rare-earth permanent magnets and for further developments in this area. In particular, looking ahead, we remark that if in fact alloying changes the temperature range of stability of  $\text{RCo}_5$  compounds, then it should also change the homogeneity range. These two factors exert an important influence on change of the magnetic properties of permanent magnets as a result of structural aging; they can therefore be used for developing heat-resistant magnets of alloys based on REM.

## 2) Magnetic structure and exchange interactions.

Most intermetallic compounds of REM with 3d transition metals are collinear magnets.<sup>[83,84]</sup> Their magnetic structure consists of two magnetic sublattices. One of them is formed by the REM ions (the R sublattice). The nature of the magnetic ordering within and between the sublattices is determined by three types of exchange interaction: R-R, R-T, and T-T. The weakest among this group is the R-R interaction; that is, the interaction between the magnetic moments of the REM ions. Because of the strong localization of the 4f electrons in REM ions, this interaction is indirect and is accomplished through spin polarization of the conduction electrons.<sup>[87,89]</sup> Such a nature of the R-R exchange interaction is corroborated by the fact that in RT compounds with nonmagnetic T ions, and also with Co or Ni at high REM concentration ( $\text{RNi}_2$ ,  $\text{RCo}_2$ ,  $\text{R}_3\text{Co}$ , etc.), as also in pure REM, the magnetic-ordering temperature

of compounds with different REM varies linearly with the de Gennes function  $G = (g - 1)^2 J(J + 1)$ , as is required by the RKKY theory of indirect exchange, in which  $T_c = 0$  if  $G = 0$  (Fig. 7).

The strongest exchange interaction is the T-T interaction. This is evident, for example, from a comparison of the values of  $T_c$  for the compounds  $\text{GdFe}_2$  ( $785^\circ\text{K}$ ),  $\text{YFe}_2$  ( $545^\circ\text{K}$ ), and  $\text{GdNi}_2$  ( $85^\circ\text{K}$ ), which give estimates, respectively, of the resultant R-R, R-T, and T-T interaction, the T-T interaction, and the R-R interaction. It is usually assumed that this interaction is direct, as in pure metals of the iron group. The magnetic moment of the T ions is due to the splitting of the 3d band by the molecular field and to the different populations of the 3d bands of the electrons. The generalized band model of magnetism permits also the existence of "localized" moments on the T ions; this can be related to the spatial nonuniformity of the spin polarization.<sup>[228]</sup>

As is seen from Fig. 7 (see also Fig. 11), the value of  $T_c$  for R-Co compounds is less dependent on the kind of R ion, the higher the concentration of Co in them; and for the compounds  $\text{RCo}_5$  and  $\text{R}_2\text{Co}_{17}$  it is practically constant, and close in magnitude to the  $T_c$  ( $\sim 1400^\circ\text{K}$ ) of pure cobalt, even for compounds with nonmagnetic Y and Lu. This shows that in cobalt-rich compounds, the determining mechanism of exchange is in fact direct exchange interaction between the Co ions. The magnetic moment of these compounds is satisfactorily described by a two-sublattice model of the magnetic structure ( $\mu_{\text{R}_m\text{Co}_m} = n\mu_{\text{R}} \pm m\mu_{\text{Co}}$ , sign (+) for compounds with light REM and (-) for compounds with heavy), if we assume that the magnetic moment ( $\mu_{\text{Co}}$ ) of the Co ion in them is the same as in  $\text{YCo}_5$  ( $\text{Y}^{3+}$  is a nonmagnetic ion), i. e.,  $1.66 \mu_B$ ,<sup>[229]</sup> which is close to the value of the moment for metallic cobalt ( $1.71 \mu_B$ ).<sup>[11]</sup> But in RT compounds (T = Fe, Co, Ni) with higher and higher concentration of REM, the magnetic moment of the T ion becomes smaller and smaller. This decrease of  $\mu_T$  is explained by some authors by a partial or complete (for example, in  $\text{RNi}_5$ ) filling of the 3d band by valence electrons of R atoms.<sup>[230]</sup> The decrease of the moment of the T ion leads to a weakening of the T-T interaction, and this causes a decrease of  $T_c$ . This correlation between the values of  $\mu_T$  and of  $T_c$  shows up especially well in the series of (Y-Ni) compounds.<sup>[89]</sup> A similar effect results from increase of the electron concentration in the series of compounds  $\text{R}_{1-x}\text{Th}_x\text{Co}_5$  (R = Gd, Er, Ho, Y) with replacement of the trivalent R ion by the quadrivalent thorium.<sup>[89,231]</sup> Here the experimentally observed values  $\mu_{\text{Co}} = 0.92 \mu_B$  for  $\text{ThCo}_5$  are close to the calculated values ( $0.86 \mu_B$ ) in the rigid-band model. But the situation is directly the opposite for compounds of REM with iron. In fact,<sup>[88,232]</sup> with increase of the electron concentration in the series of compounds  $\text{R}_2\text{Fe}_{17}$ ,  $\text{RFe}_3$ , or  $\text{RFe}_2$  (R = Y, Er), the magnetic moment of the iron atom either changes slowly (from  $\sim 2$  to  $\sim 1.5 \mu_B$ ), as in the case of yttrium, or remains constant, as in the case of erbium; nevertheless  $T_c$  increases greatly (by about a factor 2). A similar result is obtained if in the compound  $\text{Y}_{1-x}\text{Ce}_x\text{Fe}_2$  one replaces the nonmagnetic trivalent yttrium by the

still nonmagnetic but quadrivalent cerium:  $T_c$  decreases from 545 °K for  $\text{YFe}_2$  to 230 °K for  $\text{CeFe}_2$ , although the magnetic moment of the iron ion remains constant ( $1.45 \mu_B$ ) up to  $x=0.8$  and thereafter decreases only insignificantly (to  $1.3 \mu_B$  at  $x=1.0$ ). The reasons for this anomalous behavior of the magnetic properties of iron compounds is not yet clear, although in [232] it was hypothesized that the reason may be a change of the coordination number, the interatomic distance, or the degree of localization of the 3d electrons when one REM is replaced by another in quasi-binary compounds. We shall not be able, within the framework of this review, to discuss in more detail these and other experiments relating to the T-T exchange interaction. But even the results already presented illustrate the great difficulties encountered in the interpretation of the magnetic properties of RT compounds, and suggest that it will still be some time before they are resolved.

The nature of the exchange interactions for an R-T pair is still more complicated, because two kinds of ion participate in them: those with localized and with delocalized magnetically active electrons. Therefore it is possible to attribute the exchange either to direct interaction between 4f and 3d electrons, or to polarization of electrons in the 3d band or of conduction electrons. But when we consider that for all compounds of REM with iron, cobalt, and nickel the value of  $T_c$  depends on the kind of rare-earth component and, relatively to the  $T_c$  of the yttrium compounds, increases in direct proportion to the de Gennes function (see Fig. 7), we may conclude that the preferred R-T exchange interaction is the indirect.

Experiment shows that the R-T interaction leads to alignment of the resultant spin moments of the R and T sublattices antiparallel to each other. As is well known, [4] in accordance with Hund's rule, in the filling of the electronic layers of atoms of light REM (from La to Gd) the total magnetic moment ( $J$ ) of an  $R^{3+}$  ion is the difference of the orbital ( $L$ ) and spin ( $S$ ) moments, i. e.  $J=L-S$ , whereas for ions of heavy REM (from Gd to Lu), on the contrary,  $J=L+S$  (Fig. 8). Hence for RT compounds with light REM, the resultant moments of the R and T sublattices ( $J_R$  and  $J_T$ ) are parallel to each other, and these compounds have a high value of the saturation magnetization  $4\pi I_s$ . In compounds with heavy REM, on the contrary, their  $4\pi I_s$  is low in absolute value. Of course all this is correct at  $T=0^\circ\text{K}$  and is less clearly expressed at room temperature.

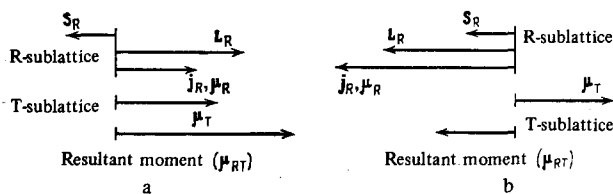


FIG. 8. Schematic magnetic structure of compounds of light (a) and heavy (b) REM with metals of the iron group, of types  $\text{RT}_5$  and  $\text{R}_2\text{T}_{17}$ .

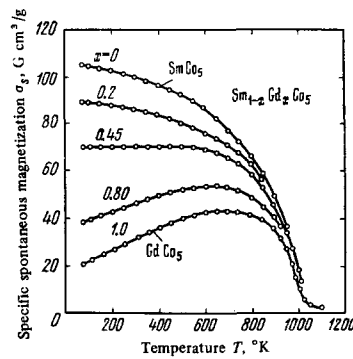


FIG. 9. Temperature dependence of specific spontaneous magnetization of monocrystals of compounds  $\text{SM}_{1-x}\text{Gd}_x\text{Co}_5$ , along the AEM. [85]

The different character (ferromagnetic or ferrimagnetic) of the mutual ordering of the resultant magnetic moment of the R sublattice with respect to the T sublattice for RT compounds with light and heavy REM leads to a qualitative difference in the temperature dependence of the spontaneous magnetization (Fig. 9). This fact, as will be shown below, has proved extremely opportune in the development of materials for permanent magnets with different values of the temperature coefficient of reversible change of the residual induction and, in particular, of magnets with high temperature stability of the magnetic characteristics. [85]

3) *Magnetocrystalline anisotropy.* Even the first investigations of the magnetic anisotropy of monocrystals of the compounds  $\text{YCo}_5$  and  $\text{Y}_2\text{Co}_{17}$  showed that compounds of REM with Co may also possess an extremely high magnetocrystalline anisotropy and, consequently, coercive force; and this class of materials is of interest for permanent magnets. [90] At present most investigators consider that, as in the case of pure REM, [91-93] the magnetic anisotropy of RT compounds is caused by interaction of the orbital moment of the 4f electron shell of the  $R^{3+}$  ion with the crystalline field of the lattice (single-ion anisotropy [94]). [88,95-110] Characteristic of the single-ion mechanism of anisotropy is a linear dependence of  $K$  on the concentration of the magnetically active ions, in the present case  $R^{3+}$ . In fact, for the compounds  $\text{Nd}_{1-x}\text{Y}_x\text{Co}_5$  such a linearity occurs (Fig. 10). Thus by changing the value of the crystalline field, by change of the environment of the REM, it is possible deliberately to change also [97] the value of  $K$ , as was found possible for the compounds  $\text{R}_2(\text{T}_{1-x}\text{T}'_x)_{17}$  [96] and  $\text{Sm}(\text{Co}_{1-x}\text{Ni}_x)_5$  [109] when one T ion is replaced by another, if the difference between their electrical charges is nonzero.

It should be mentioned, however, that this treatment

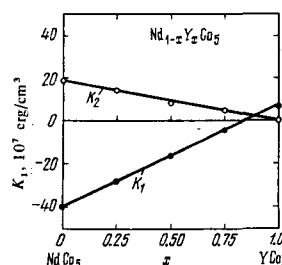


FIG. 10. Concentration dependence of magnetocrystalline anisotropy constants ( $K_1$  and  $K_2$ ) of compounds  $\text{Nd}_{1-x}\text{Y}_x\text{Co}_5$ . [107]



completely ignores the contribution of the  $T$  ions themselves to the anisotropy; this can scarcely be considered sound. In fact, the value of  $K_1$  for the alloy  $YCo_5$  ( $Y^{3+}$  is a nonmagnetic ion) is only 3.8 (at 4.2 °K) or 3.2 (at 300 °K) times smaller than  $K_1$  for one of the most highly anisotropic intermetallic compounds of the series  $RCO_5$ ,  $SmCo_5$ .<sup>[98,104]</sup> It seems that one of the reasons for the high magnetocrystalline anisotropy of  $RCO_5$  compounds is the large contribution to the anisotropy from the Co ions in consequence of the peculiar arrangement of the Co in a crystal lattice of the  $CaCu_5$  type. This suggests the possibility of obtaining other (new) compounds (and even ones without REM, like  $CoPt$ ) with high values of  $K$ , and it emphasizes the necessity for experimental and theoretical explanation of the nature of magnetic anisotropy in RT compounds (in particular, compounds  $RCO_5$ ) in which R is a nonmagnetic ion, for example Y, Ce, Lu, or Th, and for taking into account the contribution to the complete anisotropy of the RT compound from the  $T$  ions. For more complete understanding of the mechanism of anisotropy, as well as for its correct determination, it is obviously necessary also to take into account the magnetostrictive contribution to the anisotropy and the effect of a magnetic field on the magnetic structure.<sup>[108]</sup>

4. Magnetic properties of rare-earth compounds as materials for permanent magnets. 4.1) Compounds  $RT_5$ . These compounds, with a crystal lattice of the  $CaCu_5$  type (see Fig. 5), are formed only with Co and Ni and not with Fe. Compounds  $RNi_5$  have low values of  $T_c$  (down to 30 °K)<sup>[87,89]</sup> and are not of particular interest for permanent magnets, at least for ones operating near room temperature. All cobalt compounds of the type  $RCO_5$ , with the exception of  $TbCo_{5.1}$  and  $DyCo_{5.2}$ , are magnetically uniaxial at room temperature,<sup>[98,104,107]</sup> with high values of the magnetocrystalline anisotropy field  $H_a$ , the Curie temperature  $T_c$ , and the saturation magnetization  $4\pi I_s$ ; therefore they can, at least in principle, be used for permanent magnets (Figs. 11 and 12). The highest values of  $H_a$  and  $4\pi I_s$  are possessed by  $YCo_5$ ,  $NdCo_5$ ,  $PrCo_5$ , and  $SmCo_5$ . The compound  $NdCo_5$  has the lowest value of the field  $H_a$  (~30 kOe), and in addition its  $K_1$  decreases with lowering of the temperature and

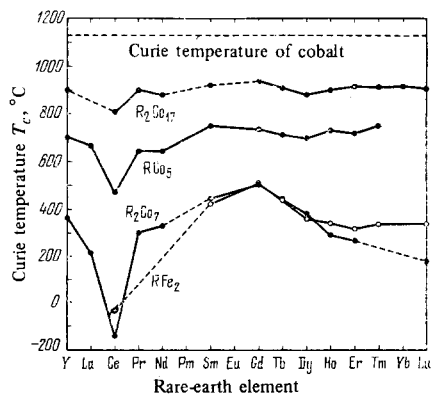


FIG. 11. Curie temperature ( $T_c$ ) of RT compounds for permanent magnets with operating temperature near room temperature.<sup>[87]</sup>

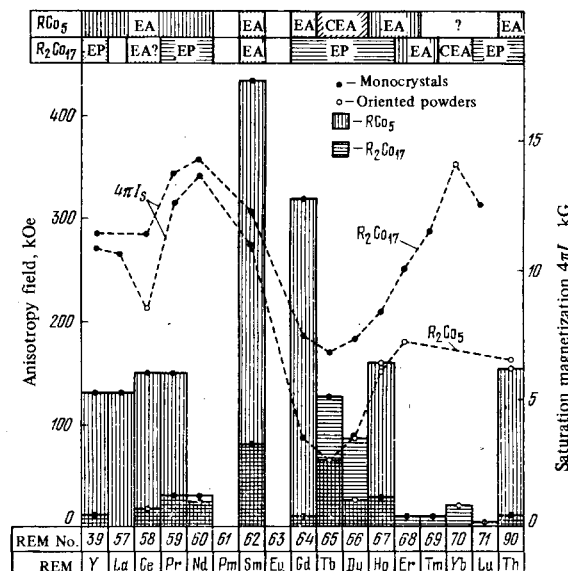


FIG. 12. Saturation magnetization ( $4\pi I_s$ ) and magnetocrystalline anisotropy field ( $H_a$ ) of compounds  $RCO_5$  and  $R_2Co_{17}$  at  $T = 20$  °C. EA, "easy" axis; CEA, cone of "easy" axes; EP, "easy" plane.

becomes negative only slightly below room temperature.<sup>[98,104,107,110]</sup> A similar situation is observed also for  $PrCo_5$ , but in the vicinity of 100 °K.<sup>[98,107]</sup> This fact prevents the application of  $NdCo_5$  and limits the application of  $PrCo_5$  for permanent magnets operating over a wide temperature range near room temperature. The compounds  $YCo_5$  and  $SmCo_5$  have approximately the same values of  $4\pi I_s$  and of the theoretical limit of the maximum energy product,  $(BH)_m$ , the anisotropy field, however, is lower by a factor 3 for  $YCo_5$  than for  $SmCo_5$ ,<sup>[104]</sup> while in return  $(BH)_{mt}$  per unit weight is larger. The alloys  $CeCo_5$ ,  $(CeMM)Co_5$ , and  $(CeMM, Sm)Co_5$  likewise do not have such great possibilities (in comparison with  $SmCo_5$ ) as materials for permanent magnets, but their economic advantages are obvious because of the low cost of cerium and of cerium alloys.

Application of binary alloys of Co with heavy REM, in consequence of their low values of the theoretical limit  $(BH)_{mt}$  of the maximum energy product, will apparently be due only to the necessity for obtaining magnetically hard materials with a high positive value of the temperature coefficient of reversible changes of the residual induction (see Fig. 9).<sup>[86]</sup>

The wide possibilities for use of various REM open up on application of quasibinary compounds, in which REM represents a combination of two or more rare-earth elements. The use of  $Sm_{1-x}Pr_xCo_5$  has already made possible the production of magnets with  $(BH)_m = 26 \cdot 10$  MGOe.<sup>[70,111]</sup> Magnets of  $Sm_{1-x}La_xCo_5$  have very high squareness of the hysteresis loop,<sup>[112]</sup> and magnets of  $(Sm, CeMM)Co_5$ , besides having a high value of  $(BH)_m = 20$  MGOe, are relatively cheap.<sup>[113]</sup> For the purpose of lowering the cost, yet without significant loss of  $(BH)_m$ , the compounds  $(Sm_{1-x}Y_x)Co_5$  are of interest.<sup>[114]</sup>

Finally, by changing the relation between light



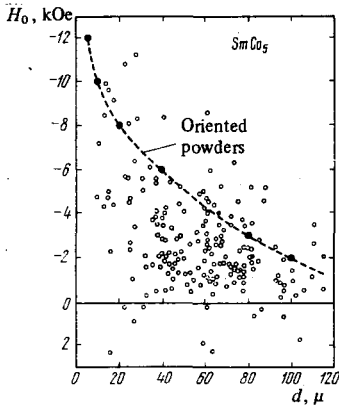


FIG. 14. Effect of the "size" of monocrystalline particles of compound  $\text{SmCo}_5$  on the value of the field  $H_0$  at which they undergo discontinuous magnetization reversal, [129,130] and on the coercive force ( $H_c$ ) of oriented powders of the same compound.

the practical use of such monocrystals. It must be remarked that the "building blocks" of commercially manufactured rare-earth magnets are just such monocrystals, of dimensions only 5–10  $\mu\text{m}$ . Consequently, in order to understand the physical nature of the magnetic properties of rare-earth permanent magnets and the principles for obtaining them, it is necessary to know the behavior of these "building blocks" under the action of various physical influences.

### B. Coercive force and phase transformations

One of the most interesting physical results basic to the methods of obtaining both monocrystalline and metallographic (baked) rare-earth magnets is the nonmonotonic dependence of the coercive force of  $\text{RCO}_5$  monocrystals on the annealing temperature (Fig. 15). [69,132] A large number of papers have been devoted to explanation of the reasons for this dependence. [16, 70, 71, 78, 136–148] This likewise is primarily due to the practical importance of the question why it is not possible to obtain for all  $\text{RCO}_5$  alloys the desired high

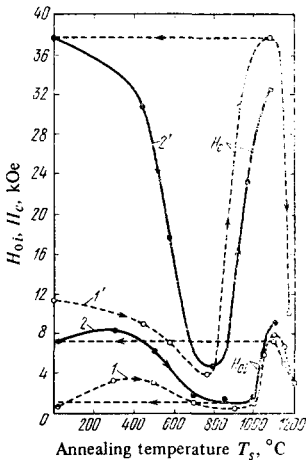


FIG. 15. Dependence on annealing temperature of the magnetization-reversal field  $H_{0t}$  of monocrystals of diameter 3 mm, and of the coercive force  $H_c$  of powders, of alloy  $\text{SmCo}_5$ ; annealing for 30 min at each temperature. 1, 1': specimens obtained from cast alloy (ingot). 2, 2': the same specimens, but annealed to maximum  $H_{0t}$  or  $H_c$  at  $T=1100$  and  $1080^\circ\text{C}$ , respectively, and reannealed at the indicated temperatures. Properties measured at room temperature. [69,132]

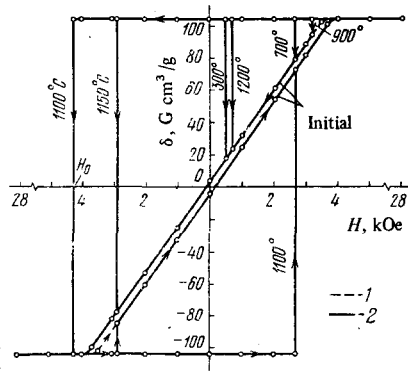


FIG. 16. Effect of annealing temperature (annealing for 30 min) on the shape of the hysteresis loop and the value of the field  $H_0$  of a monocrystal of  $\text{SmCo}_{5.3}$ . 1, before and 2, after chemical polishing of the surface.

values of  $H_c$ . We shall consider this question in somewhat greater detail for the example of a monocrystal of  $\text{SmCo}_{5+x}$ , slightly enriched with cobalt in relation to the stoichiometric ratio 1:5 (approximately 1:5.3). [132] Such monocrystals, immediately after being cut from a coarse grain of an ingot, have as a rule low  $H_{cw}$  ( $\sim 100$  Oe). Both magnetization and remagnetization of them occur by DB displacement. The hysteresis loop is an ordinary one (Fig. 16). With increase of the annealing temperature, a change occurs in it: hysteresis appears that is caused by inhibition of the generation and/or growth of nuclei of the reverse magnetic phase. After annealing at temperature  $1100^\circ\text{C}$ , the hysteresis loop becomes rectangular. Magnetization reversal occurs by a single big jump in an external magnetic field  $H_0$ , which is numerically equal to the coercive force. On further increase of the annealing temperature to  $1200^\circ\text{C}$ ,  $H_0$  decreases. But if the monocrystal is again annealed at  $1100^\circ\text{C}$ , then  $H_0$  again increases (see Fig. 15).

On repeated annealing of a monocrystal already in the high-coercivity state, the dependence of the internal field  $H_{0t} = H_0 - NI_s$  on the annealing temperature has the form shown in Fig. 15 (curve 2). A characteristic peculiarity of the  $H_{0t}(T_s)$  dependence is the minimum of the remagnetization field  $H_{0t}$  in the interval  $700$ – $1000^\circ\text{C}$  and the maximum near  $1100^\circ\text{C}$ . The  $H_{0t}(T_s)$  curve is reversible in the high-temperature range and irreversible in the low-temperature range (below  $800^\circ\text{C}$ ). [149] It is clear that these properties cannot be explained by a change of the defect structure with annealing. Most probably such behavior is due to phase transformations in a monocrystal of the  $\text{SmCo}_{5+x}$  alloy. The only phase transformation that can occur in accordance with the phase diagram of the  $\text{Sm-Co}$  system, in this temperature interval, is decomposition of the solid solution  $\text{SmCo}_{5+x}$  with segregation of the phase  $\text{Sm}_2\text{Co}_{17}$  (see Fig. 4). In order to exclude uncertainty about the microstructure of the original monocrystal, we shall consider curve 2 in Fig. 15 (repeated annealing). After annealing at  $1100^\circ\text{C}$  the monocrystal is a supersaturated solid solution  $\text{SmCo}_{5+x}$ . Upon heating of it to  $T_s = 800^\circ\text{C}$ , there occurs a segregation of the



FIG. 17. A monocrystalline magnet in the form of a sphere of weight 78 mg, of  $\text{SmCo}_5$  alloy, with  $(BH)_m = 30$  MG Oe, holds a load of weight 80 g.

rhombohedral modification of the phase  $\text{Sm}_2\text{Co}_{17}$ , because the supersaturated solid solution is not in thermodynamic equilibrium below  $800^\circ\text{C}$  (the temperature of the lower part of the homogeneity range of compound 1-5). If we assume that this phase serves as a center of easy nucleation, then  $H_{0i}$  will drop upon heating, because the number and size of  $\text{Sm}_2\text{Co}_{17}$  precipitations increases. With annealing above  $800^\circ\text{C}$  the reverse process occurs in consequence of broadening of the homogeneity range, and  $H_{0i}$  should increase, as is in fact observed experimentally. The maximum of  $H_{0i}$  at  $1100^\circ\text{C}$  apparently corresponds to an optimal structure-phase state. The structural transformations described are corroborated by data from investigations of the lattice parameters of solid solution  $\text{SmCo}_{5+x}$  and are compatible with data from measurement of its  $T_c$  after heat treatment.<sup>[137,149]</sup> The decrease of  $H_{0i}$  after annealing at  $1200^\circ\text{C}$  is less clear. It may also be caused by segregation of the phase  $\text{Sm}_2\text{Co}_{17}$ , because the homogeneity range narrows above this temperature. The possibility is not excluded, however, that here more complicated structure-phase transformations are occurring (change of the defect structure, or segregation of the hexagonal modification of  $\text{Sm}_2\text{Co}_{17}$ ). Despite the relatively simple and quite logical explanations of the  $H_{0i}(T_s)$  dependence, one serious contradiction arises: the phase  $\text{Sm}_2\text{Co}_{17}$  has  $(H_a - NI_s) \approx 70$  kOe<sup>[86]</sup> and is coherently related to  $\text{SmCo}_5$ , so that the directions of their AEM coincide (the  $c$  axis).<sup>[150,151]</sup> If the phase  $\text{Sm}_2\text{Co}_{17}$  actually serves as a center from which (or near which) nuclei of the reverse magnetic phase are formed during magnetization reversal, then the question arises why the maximum value of  $H_{0i}$  found for the monocrystals is almost an order of magnitude smaller than  $H_a$  of the phase  $\text{Sm}_2\text{Co}_{17}$ . Does the interphase boundary exert an effect on  $H_{0i}$ , and what is the role of structural defects (dislocations, packing defects, small-angle boundaries)? At any rate, it is now experimentally established that for attainment of the high-coercivity state a monocrystal must be subjected to a high-temperature heat treatment at  $1100^\circ\text{C}$ . They then have values of  $(BH)_m$  equal to the theoretical limit. For  $\text{SmCo}_{5+x}$ ,  $(BH)_m = 30-32$  MG Oe<sup>[132-135,149]</sup>; for  $\text{Sm}_{1-x}\text{Pr}_x\text{Co}_5$ , up to 40 MG Oe.<sup>[149,152]</sup> To make it easier

to describe the force of such a magnet, we point out that a monocrystalline magnet in the form of a sphere of diameter 3 mm with  $(BH)_m = 30$  MG Oe holds a load approximately 1000 times its own weight (Fig. 17). It is certain that such magnets can find application in miniature magnetic systems when it is necessary to obtain strong magnetic fields in small volumes under rigid limitations in regard to weight. A large obstacle in this direction is the fact that at present there are not sufficiently well developed methods of obtaining perfect monocrystals of compounds of the  $\text{RCO}_5$  type of large size, although the literature has contained reports of the obtaining of such monocrystals of  $\text{RCO}_5$ .<sup>[153-155]</sup>

From the above results of investigation of the magnetic properties of monocrystals of  $\text{RCO}_5$ , one gets a clear perspective of the physical aspect of another, technically simpler procedure for obtaining rare-earth permanent magnets—by high-temperature heat treatment (baking) of pseudomonocrystals, obtained by compression of a magnetic-field-oriented powder, consisting of monocrystalline particles of size  $5-10 \mu\text{m}$ . Their  $H_c$ , like that of individual monocrystals, varies nonmonotonically with annealing temperature (see Fig. 15). It was by this method that magnets of  $\text{SmCo}_5$  with  $(BH)_m \approx 20$  MG Oe were first obtained,<sup>[70,156-160]</sup> and this procedure at present forms the basis of the technological process for industrial production of rare-earth permanent magnets.

### C. Effect of substructure on the coercive force of monocrystals

Figure 18 shows the dependence of the field  $H_{0i}$  on the angle of misorientation ( $\varphi_m$ ) of the subgrains of 17  $\text{SmCo}_{5+x}$  crystals that had passed through optimal heat treatment to the high-coercivity state.<sup>[161]</sup> It is seen that the larger the angle of misorientation, i. e., the less perfect the crystal, the lower  $H_{0i}$  is. Under mechanical action (for example, shock), such monocrystals cleave, as a rule, along the subgrain boundaries with the greatest  $\varphi_m$ . The fragments obtained therefore have smaller  $\varphi_m$ , and therefore after chemical polishing of the surface, and especially after repeated high-temperature annealing, they as a rule have higher  $H_{0i}$ . Consequently it seems to us that the  $H_c$  of permanent magnets obtained by baking of a powder with mean size of the monocrystals  $5-10 \mu\text{m}$  is significantly larger than the  $H_{0i}$  of the individual monocrystals of size several millimeters.

It is so far not altogether clear by what mechanism

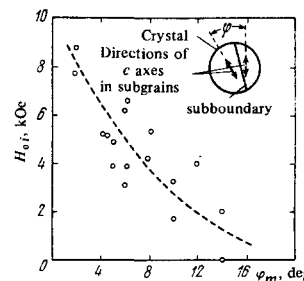


FIG. 18. Effect of maximum misorientation angle of subgrains ( $\varphi_m$ ) on the value of the magnetization-reversal field  $H_{0i}$  of seventeen  $\text{SmCo}_{5+x}$  crystals of diameter 3 mm, which had been brought by optimal heat treatment to the high-coercivity state.<sup>[161]</sup>

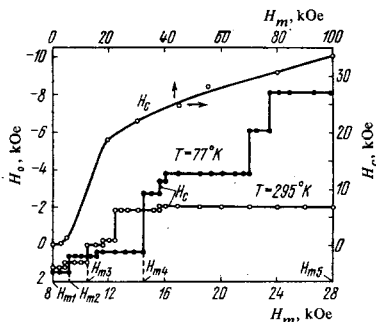


FIG. 19. Dependence of field  $H_0$  on the value of the magnetizing field ( $H_m$ ) for a monocrystal of  $\text{SmCo}_{5.3}$  at temperatures 77 and 300 °K.<sup>[169,170]</sup> Also shown here is the function<sup>[69]</sup>  $H_c(H_m)$  for a permanent magnet obtained by sintering a  $\text{SmCo}_5$  powder.

subboundaries of dislocation nature, or individual dislocations, influence the value of the field  $H_{0i}$  of high-anisotropy magnets, although there is direct evidence that they can, on the one hand, facilitate the nucleation process and, on the other hand, impede the growth of the nuclei during magnetization.<sup>[162-165]</sup> According to the existing theoretical ideas, this is possible if in the neighborhood of these defects the anisotropy field is lowered or there is a magnetic inhomogeneity of the DB type. But in order to explain the experimentally observed value of  $H_{0i}$  ( $\sim 10$  kOe) for  $\text{SmCo}_5$ , it is necessary to suppose that within a region of size about  $10^{-8}$  cm, which is reasonable for the distorted part near defects of the dislocation type, the magnetocrystalline anisotropy constant is zero or at least several orders of magnitude smaller than  $K$  for  $\text{SmCo}_5$ . Such a lowering can scarcely be caused by the magnetoelastic contribution to the anisotropy, since its value with magnetostriction of order  $10^{-3}$ – $10^{-4}$ <sup>[166,167]</sup> and with elastic stress of order  $10^{12}$  dyn/cm<sup>2</sup> amounts to  $10^{-2}$ – $10^{-4}$  of the magnetic anisotropy energy. Therefore the lowering is due rather to a change of the magnetic symmetry of the lattice near the defects<sup>[168]</sup>; that is, actually to microprecipitations of other weakly anisotropic phases. This would be logically related to the results of investigations described in the preceding section, if we were to suppose that the phase in question in the present case is  $\text{Sm}_2\text{Co}_{17}$ . But there are so far no experiments to support or refute this hypothesis.

#### D. Effect of the magnetizing field on the stability of the single-domain state of monocrystals

One of the peculiarities of rare-earth permanent magnets is the strong dependence of  $H_c$  in the field range above  $H_s$ , i. e., when technical saturation has already been attained, on the value of the magnetizing field (Fig. 19).<sup>[69]</sup> For individual monocrystals it has a steplike form<sup>[169]</sup> and is different both for different temperatures<sup>[170]</sup> and for different monocrystal specimens; it is not the same for application of the field in different directions with respect to the AEM<sup>[129,130]</sup>; it strongly depends on the previous history of the specimen; it often fails to repeat quantitatively in repeated measurements (it repeats only qualitatively).<sup>[9]</sup> Great importance is at present attached to the explanation of

the reasons for the observed effects,<sup>[129,130,169-178]</sup> because understanding of them would permit a deeper understanding of the mechanism of formation of the high-coercivity state in high-anisotropy ferromagnets and an approach to the purposeful control of their hysteretic properties. It should be mentioned that a similar dependence was observed considerably earlier in crystals of MnBi alloy,<sup>[171]</sup> orthoferrite crystals,<sup>[173-175]</sup> MnAlGe alloy,<sup>[9]</sup> etc. At the same time, this dependence is far from universal; it is absent if the crystal is very perfect or, on the contrary, very defective.<sup>[128]</sup> This indicates that the  $H_0(H_m)$  or  $H_c(H_m)$  dependence is to one degree or another due to interaction of the magnetization with crystal defects.

So far there are, in our opinion, two more or less clearly held, alternative points of view on the nature of the  $H_0(H_m)$  dependence.<sup>[130]</sup> One of these actually comes from the idea that the field  $H_0$  is due to the degree of difficulty of growth of nuclei of reverse magnetization, whose role is played by remnants of DB that persist during magnetization in the neighborhood of various structural defects and therefore have various values of the start field  $H_{0s}$  (see (4)). With increasing  $H_m$ , nuclei with larger and larger negative start fields are annihilated. This leads to a discrete  $H_0(H_m)$  dependence: each step corresponds to its own magnetically active nucleus. The  $H_0(H_m)$  dependence is also explained if we suppose that only one nucleus operates in the crystal, but that it is localized near a cluster of defects. With magnetization, in consequence of the diminution of its size, it falls into places with higher and higher DW coercivity, and its start field increases. Only the limiting value of  $H_0$  in these models can be due to inhibition of the processes of nucleation and is determined by the value of the field  $H_n$ .

The other point of view is that the value of the field  $H_0$ , even in partial cycles, is determined by processes of nucleation near defects of the crystalline or magnetic structure. In this case it is necessary only to suppose that on increase of  $H_m$  a magnetic (spin) inhomogeneity changes irreversibly from one configurational (energetic) state to another, less magnetically active in the sense of facilitating nucleation processes, or that the structures of defects change under the action of the magnetic field because of magnetostrictive forces, for example, by virtue of diffusion of point defects within them. To give preference to one or the other point of view, from the experimental data available in the literature, does not seem possible. For this purpose we still need direct observations of the behavior of the magnetization near structural defects, similar to those that are made on some transparent ferromagnets.<sup>[164,165]</sup>

#### E. Peculiarities of the temperature dependence of the coercive force of monocrystals

In the neighborhood of structural defects, the fundamental magnetic characteristics may have not only different values, but also a different temperature dependence. Since the field  $H_{0i}$  of  $\text{RCO}_5$  monocrystals is determined by the local interaction of the magnetization with defects, it is to be expected that the  $H_{0i}(T)$  de-

pendence will be determined by the temperature variation not only of the mean, but also of the local magnetic constants.<sup>[14,126]</sup> The nature of the variation of the latter will depend on the kind of defects. For illustration, Fig. 20 shows the  $H_{0i}(T)$  dependence for three monocrystals of  $\text{SmCo}_{5+x}$ .<sup>[179]</sup> There may be a very simple explanation for the observed diversity of  $H_{0i}(T)$ . We suppose that in the temperature interval under investigation only two magnetically active defects operate, with nucleation fields  $H_n^{(1)}$  and  $H_n^{(2)}$  and start fields  $H_{0s}^{(1)}$  and  $H_{0s}^{(2)}$ , and all these quantities have different temperature dependences, for simplicity linear (Fig. 21). In the magnetization reversal process at  $T > T_1$ , the first nucleus is formed at  $H_n^{(1)}$ . But  $H_n^{(1)} < H_{0s}^{(1)}$ , and magnetization reversal of the crystal in this temperature range will occur at field  $H_{0s}^{(1)}$ . Consequently  $H_{0i}$  is determined by the difficulty of growth of the first nucleus.

In the interval  $T_1$  to  $T_4$ ,  $H_n^{(1)} > H_{0s}^{(1)}$ ; magnetization reversal occurs at  $H_n^{(1)}$ ;  $H_{0i}$  is determined by the difficulty of nucleation. For  $T < T_4$ ,  $H_{0i}$  depends on  $H_{0s}^{(2)}$  of the second nucleus, which exists in  $T_3$  to  $T_4$  simultaneously with the first but has no effect on  $H_{0i}$  because of the high  $H_{0s}^{(2)}$ . In sum,  $H_{0i}(T)$  has the form of a continuous line similar to that which is observed experimentally (curve 3 in Fig. 20). Obviously by use of these simple model concepts it is possible to explain the varying form of the  $H_{0i}(T)$  dependence. It is possible to do the same thing by supposing that in different temperature intervals the dependence  $H_{0i}(T)$  of the field  $H_{0i}$  is determined by the difficulty of forming nuclei at defects that "operate," i.e., are magnetically active, only in a definite temperature range.

When  $H_m$  is small, so as to reach a limiting  $H_{0i}$  at all temperatures, a discontinuous decrease of  $H_{0i}$  is observed on lowering of  $T$ , even if the mean value of  $K$  for the whole crystal is increasing. This is clear from Fig. 19, in which  $H_0(H_m)$  is shown for a monocrystal of  $\text{SmCo}_5$  at 293 and 77°K: in the intervals 0 to  $H_{m1}$  and  $H_{m3}$  to  $H_{m4}$  the field  $H_{0i}$  will decrease, but in  $H_{m2}$  to  $H_{m3}$  and in  $H_{m4}$  to  $H_{m5}$  increase, as in Fig. 20, 3'. If the magnetization is carried out at a constant temperature corresponding to a low  $H_a$ , and if the hysteresis loop is a limiting one, but the specimen is cooled

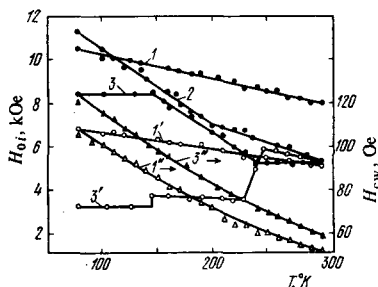


FIG. 20. Dependence on measurement temperature<sup>[179]</sup> of the field  $H_{0i}$  of three monocrystals of  $\text{SmCo}_{5+x}$  (diameter 3 mm) after magnetization of all of them in field  $H_m = 28$  kOe (curves 1–3) and of crystals 1 and 3 in  $H_m = 11$  kOe (curves 1' and 3'); and of the displacement coercive force  $H_{cw}$  of crystals 1 and 3 (curves 1'' and 3'').

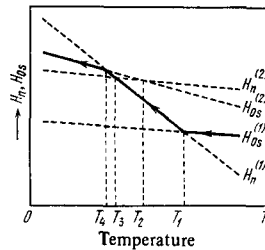


FIG. 21. Schematic explanation of the nonmonotonic temperature dependence of the magnetization-reversal field  $H_{0i}$  of  $\text{SmCo}_5$  monocrystals (see Fig. 20).

in the magnetized state, then most probably  $H_{0i}(T)$  will be a function that increases with increase of  $H_a$ .

Finally, we note that the displacement coercive force  $H_{cw}$ , measured on partial cycles of the hysteresis loop ( $H_m < NI_s$ ), changes with temperature identically in all the above-mentioned cases, because it is determined by the "cooperative" interaction of DB with a large number of defects distributed over the whole volume of the crystal.<sup>[179]</sup>

Thus it follows from the above results that it is impossible to describe the temperature variation of the field  $H_{0i}$  theoretically, if it is determined by local interaction of the magnetization with defects of the crystal lattice, without taking into account, in this theory, the temperature variations of the fundamental magnetic constants in the neighborhood of concrete magnetically active defects—as has been done so far. In this connection there opens up the interesting possibility of a deliberate change of the  $H_{0i}(T)$  of crystals by intentional introduction into the material of definite structural defects or change of the microstructure of existing volume or surface defects. For example, by change of the degree of surface oxidation of monocrystalline particles in a  $\text{PrCo}_5$  powder it is possible to change  $H_c(T)$  within wide limits and to produce such conditions that  $H_c$  becomes temperature independent over the range 77–300°C.<sup>[180]</sup> Apparently something similar can be accomplished by decoration of magnetoactive defects with impurity atoms.

## 5. TEMPERATURE STABILITY OF MAGNETIC PROPERTIES OF RARE-EARTH PERMANENT MAGNETS

### A. Temperature stability of the single-domain state

The discussion above related primarily to questions of field stability of the hysteretic properties of rare-earth permanent magnets. But in technical use of permanent magnets, not only is a high level of the magnetic characteristics important, but also their invariability (stability) during fluctuations of temperature over a definite range, for example from  $-180$  to  $+250$ °C, or, contrariwise, their change according to a definite law. For solution of these problems, it is obviously necessary to know the physical factors that determine both the reversible and the irreversible temperature changes of the magnetic properties.

It has been established experimentally<sup>[87,181–183]</sup> that after heating a magnet, the value of its residual magnetization or of the magnetization at the operating point

( $4\pi I_d$ ) decreases irreversibly, if no repeated magnetization is carried out (Fig. 22). This decrease (magnetic aging) is larger, the smaller  $H_c$  (the larger  $H_d$ ) and the worse the squareness of the hysteresis loop, i. e., the lower  $H'_{cr}$  ( $H'_{cr}$  is the  $H$  at which  $4\pi I = 0.9(4\pi I_d)$ ). Why is such a correlation observed? Figure 23 shows, by means of the Kerr effect, the change of domain structure of monocrystalline particles (grains) of a permanent magnet with  $(BH)_m \approx 18 \cdot 10^6$  GOe, obtained by isostatic compression of a powder of  $\text{SmCo}_5$  in a magnetic field.<sup>[129,130]</sup> For the investigation, a group of grains with different  $H_0$ 's was specially chosen. On heating, the grains in turn changed discontinuously from the single-domain state to the multidomain under the action of the self-demagnetizing field along ( $H_d = NI_s \approx 3.6$  kOe), each at its own temperature ( $T_{dis}^{(i)}$ ). After lowering of  $T$  from  $T_{dis}^{(i)}$  to room temperature, they remained multidomain, i. e., practically demagnetized, because their  $d > d_{cr}$  and the multidomain state at  $H = 0$  is one of thermodynamic equilibrium. (Completely analogous results were obtained also for sintered magnets.) Thus after heating, the value of the residual magnetization decreased by the amount  $\Delta = 4\pi I_s V \beta$ , where  $V$  is the total volume of the particles demagnetized by heating to a certain temperature, and where  $\beta$  describes the degree of magnetic texture. Therefore in order to remove the irreversible loss  $\Delta$ , it is necessary to decrease  $V$ . From the data obtained it is not evident how this can be done, since there is no unique relation between the  $H_0$  of a particle and  $T_{dis}$ . The absence of this uniqueness is easy to understand if we

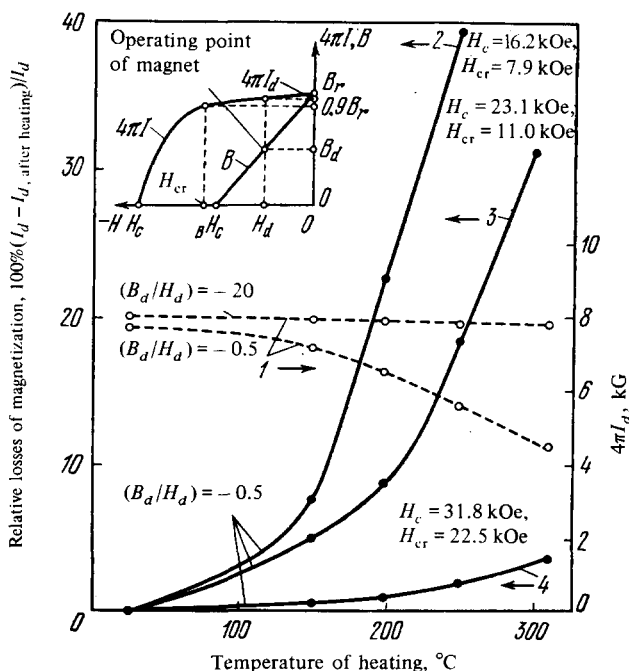


FIG. 22. Effect of heating in air for 30 min, at various temperatures, on the values of the magnetization at two different operating points of magnet 1, and on the values of the relative irreversible losses of magnetization at the operating point  $(B_d/H_d) = -0.5$  of magnets 2, 3, and 4, with various values of  $H_c$  and  $H_{cr}$ . All the magnets were obtained by baking a powder of  $\text{SmCo}_5$ . All measurements of the magnetic properties were made at room temperature.<sup>[181]</sup>

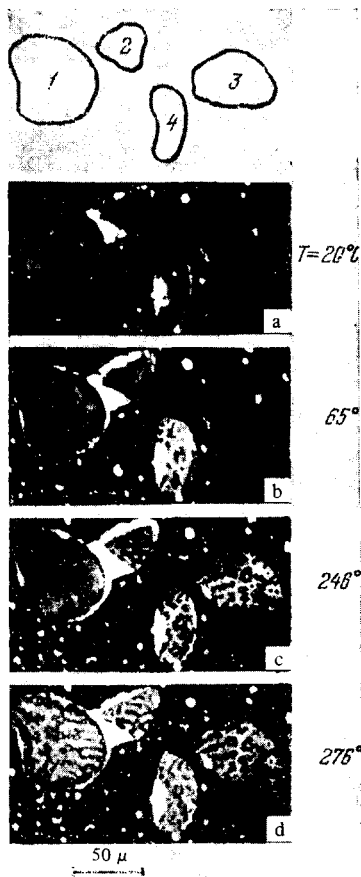


FIG. 23. Domain structure of individual particles (grains) with different values of the field  $H_0$  (1, 1740 Oe; 2, 3300 Oe; 3, 3600 Oe; 4, 2600 Oe), in a  $\text{SmCo}_5$  magnet at temperatures: a), 20°C; b), 65°C; c), 246°C; d), 276°C.<sup>130</sup>

take into account that the temperature dependence of  $H_{0i}$  is different for different monocrystal specimens (see Fig. 20). We shall assume for simplicity that it is linear for all the particles, but that the slope of the straight line  $H_{0i}(T)$  is different for different specimens (Fig. 24). Then on increase of  $T$ , the fields  $H_{0i}$  decrease for all the particles. When their values become equal to the self-demagnetizing field, the particles change discontinuously from the single-domain state to the multidomain. This will occur for different particles at different  $T_{dis}$ . Although actually  $H_{0i}(T)$  may have a more complicated form, and although the values of the demagnetizing field are different for different particles because of their difference with respect to shape and with respect to their environment of other particles, this scheme in Fig. 24 clearly illustrates why there is no unique relation between  $H_{0i}$  and  $T_{dis}$ . Fortunately, the nonuniqueness occurs only when the number of

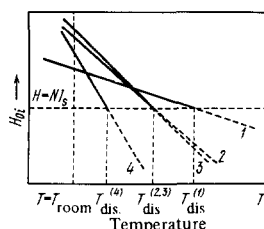


FIG. 24. Schematic explanation of the absence of a unique relation between the values of  $T_{dis}$  and of  $H_{0i}$  of individual monocrystalline particles, and also of the mechanism by which irreversible losses of magnetization occur in baked rare-earth magnets after they have been heated.

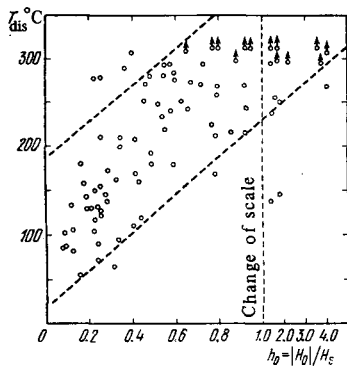


FIG. 25. Effect of the value of the magnetization-reversal field on the temperature  $T_{dis}$  at which a transition of the particle occurs from the single-domain to the multidomain state. The upward arrows show particles that had still not undergone transition to the multidomain state at the indicated temperatures.<sup>130</sup>

particles considered is small, as in the present case. In a study of a large number of particles (Fig. 25), a general trend in the change of properties is clearly evident: the larger in absolute value the field  $H_0$ , the more stable the single-domain state is with respect to thermal action, i. e., the higher  $T_{dis}$  is.<sup>[129,130]</sup> In relation to a magnet composed of an enormous number of grains, this means that the higher its  $H_c$  (the lower its  $H_d$ ), the smaller is the number of particles, and consequently also their total volume  $V$ , that are demagnetized at a given temperature; that is, the smaller will be the irreversible losses  $\Delta$  (see Fig. 22).

If the descending branch of the hysteresis loop is a straight line parallel to the  $H$  axis until a certain field  $H'_{cr}$ , this means that in the magnet there are no particles with  $H_0 < H'_{cr}$  and that the mean  $H_0 > H'_{cr}$ . Hence it follows that particles that pass from the single-domain state to the multidomain at temperatures  $T$  less than a certain  $T_{cr} = f(H'_{cr})$  either are not present at all or are very few, and consequently the losses  $\Delta$  will be small. Therefore in order to raise the operating temperature  $T_{cr}$  of the magnet for given value of the loss  $\Delta$ , it is necessary to increase  $H'_{cr}$ , i. e., to increase the squareness of the hysteresis loop; or the operating point of the magnet must be so chosen that  $(H_d/H'_{cr}) \ll 1$ , since increase of  $H_d$  effectively lowers  $H'_{cr}$  and  $H_c$  (Fig. 22). In this connection it can be shown that in a certain temperature interval magnets with low  $H_c$  but high  $H_{cr}$  will have better temperature stability than magnets with high  $H_c$  but low  $H_{cr}$ . From the above analysis it follows that the value of the irreversible losses of magnetization  $4\pi I_d$  is actually determined by the temperature behavior of  $H_0$ ; consequently, in order to change it all the methods are used that change the  $H_0(T)$  dependence (see Sec. E of Chap. 4).

## B. Structural aging and the problem of thermal stability of magnets

In a number of important devices there arises an acute need for permanent magnets that would have high-level magnetic properties and would be able to operate at elevated temperatures ( $\sim 500^\circ\text{C}$ ) in a vacuum, in air, or even in a corrosive medium. We shall consider

from the physical side the prospects for use of rare-earth permanent magnets for these cases. The temperature variations of their magnetic properties are determined principally by the temperature behavior of  $4\pi I_s$  and  $K$ , provided no structural transformations occur, since  $H_c$  is a very structure-sensitive characteristic. In the case of magnets for which all stages of production are carried out in air, the maximum operating temperature does not exceed  $100^\circ\text{C}$ .<sup>[70]</sup> This temperature increases to  $150^\circ$ <sup>[184]</sup> if the process of producing the magnets is carried out in an inert medium, and to  $250^\circ\text{C}$  for magnets obtained by baking of a powder of Sm-Co containing a surplus of Sm with respect to the stoichiometric composition 1-5.<sup>[70]</sup> At temperatures above these, an irreversible decrease occurs in the magnetic characteristics ( $4\pi I_s$ ,  $H_c$ , and  $(BH)_m$ ). It may be due to two causes: to oxidation (more generally, to corrosion), and to phase transformations that occur in the  $\text{SmCo}_5$  alloy on heating.

The first cause is not fundamental and may be removed by freeing the original components, the process for obtaining the permanent magnets, and the working medium of oxygen and other corrosive components; by creation of closed pores, as in baked magnets; or by deposition of a protective covering on the surface of the magnet.<sup>[131]</sup> To remove the second cause is enormously more complicated, because it results from the nature of the very material of the magnet, namely from its instability at temperatures below the temperature of eutectoid decomposition ( $\sim 800^\circ\text{C}$  for  $\text{SmCo}_5$ ). Obviously an increase of the thermal stability requires a retardation of the decomposition processes. Since these are diffusion processes, such as retardation requires an increase of the activation energy for migration of atoms.<sup>[185]</sup> Evidently this can be done by alloying the basic  $\text{SmCo}_5$  alloy with components that change (preferably raise) the temperature of eutectoid decomposition. This temperature can be changed as much as  $200^\circ\text{C}$  by alloying (see Fig. 6). If meanwhile the minimum of  $H_c$  on the  $H_c(T)$  shifts in corresponding fashion (see Fig. 15), then there are possibilities of retarding the structural transformations as much as  $500^\circ\text{C}$ . Of course it is necessary here to strive to make the monocrystals—the “building blocks” of the permanent magnets—as perfect as possible, in order to inhibit the formation of nuclei of new phases. Thus, it seems we have the possibility, on the basis of  $\text{RCO}_5$ , of producing permanent magnets with operating temperature up to  $500^\circ\text{C}$ , and, for short-time operation, higher.

What sort of magnetic properties may be expected at such temperatures? It is surprising that for these purposes also, the most suitable basic alloy is  $\text{SmCo}_5$ . Of all  $\text{RCO}_5$ , it has at elevated temperatures the highest value of the anisotropy field and one of the highest values of  $4\pi I_s$ . For example, at  $500^\circ\text{C}$   $H_a \approx 100$  kOe,  $4\pi I_s = 6.2$  kG.<sup>[104]</sup> Consequently there is a possibility in principle of obtaining from this alloy high-coercivity magnets with  $(BH)_m$  up to 10 MGoe. Such magnets should have an  $H_c$  at room temperature of about 100 kOe. Of course this is a complicated problem. But it



must not be forgotten that investigations in the field of rare-earth permanent magnets have been in progress for some 5 to 10 years and that the possibilities are still far from exhausted, whereas the forecasts given above are based essentially on the experimental material available at the present time, which in many respects must not be considered extensive.

### C. Rare-earth permanent magnets with high temperature stability

The preceding section considered the causes of irreversible change of induction with a rise of temperature (magnetic aging). Its value is determined, as was seen, by the level of the hysteretic magnetic characteristics of the permanent magnet. But if we give the magnetized magnets a preliminary aging by changing the temperature over a range wider than the operating temperature interval, then in the process of using the magnetic system we shall no longer notice any irreversible changes of the residual induction, provided, of course, we neglect change of the magnetic properties with time (temporal magnetic aging). Here there can be only changes of induction that are reversible with change of temperature. The rate of change of induction with temperature

$$\alpha_d = \frac{dB_d}{B_d dT} = \frac{dI_d}{I_d dT} = \frac{d\sigma_d}{\sigma_d dT}$$

at the operating point of the magnet is determined by the temperature variations of the fundamental magnetic characteristics and primarily of the saturation magnetization. In some special cases, the value of the reversible change of induction will be affected by the temperature dependence of the effective magnetic anisotropy responsible for the coercive force.

It has been found that in the case of rare-earth permanent magnets, the problem of obtaining a very low (all the way down to zero) temperature coefficient  $\alpha_d$ , or likewise a high value of it, is solved very simply with use, for the material, of multicomponent alloys of light and heavy REM with cobalt. [85,186] In fact, alloys of light REM with Co, in the temperature range below  $T_c$  ( $\sim 1000^\circ\text{K}$ ), are typical ferromagnets,  $\alpha_s < 0$ , where-

TABLE II. Magnetic properties of rare-earth permanent magnets with various degrees of temperature stability of the magnetic characteristics. [85]

Compound	$B_r$ , kG	$I^H_c$ , kOe	$b^H_c$ , kOe	$(BH)_m$ , MG Oe	$\alpha_d$ , %/deg			
					From -100 to +20°C	From +20 to +100°C	From +100 to +200°C	From -100°C to +200°C
Sm <sub>0.55</sub> Gd <sub>0.45</sub> Co <sub>5</sub> (monocrystal)	7.5	4.8	4.8	14.0	<<0.005	0.005	—	<<0.005*
Sm <sub>0.53</sub> Gd <sub>0.47</sub> Co <sub>5</sub>	6.5	25.0	6.5	10.6	<<0.005	0.005	-0.012	<<0.005
Sm <sub>0.7</sub> Tb <sub>0.3</sub> Co <sub>5</sub>	7.8	9.5	6.6	13.4	<<0.005	-0.016	-0.022	-0.014
Sm <sub>0.45</sub> Tb <sub>0.55</sub> Co <sub>5</sub>	7.4	17.2	7.2	13.3	<<0.005	-0.011	-0.019	-0.012
Sm <sub>0.7</sub> Dy <sub>0.3</sub> Co <sub>5</sub>	8.0	13.5	7.2	14.3	<<0.005	-0.014	-0.022	-0.013
Sm <sub>0.45</sub> Dy <sub>0.55</sub> Co <sub>5</sub>	7.6	20.0	7.4	14.3	<<0.005	-0.010	-0.018	-0.011
Sm <sub>0.45</sub> Er <sub>0.55</sub> Co <sub>5</sub>	8.2	23.5	7.6	16.0	-0.007	-0.013	-0.024	-0.014
SmCo <sub>5</sub>	9.2	25.0	9.2	21.0	-(0.020-0.030)	-(0.025-0.035)	-(0.030-0.045)	-(0.026-0.036)
SmCo <sub>5</sub> (monocrystal)	11.3	9.8	9.8	31.9	-0.020	-0.025	—	-0.026

$\alpha_d$  measured in the self-demagnetizing field of the magnet (a sphere of diameter  $\approx 3$  m),  $\sim 0.25 B_r$ ; the value of  $\alpha_d$  marked with an asterisk was measured over the temperature range from -100 to +120°C.

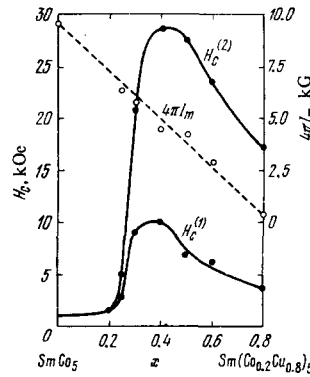


FIG. 26. Effect of copper content in the alloy (x) on magnetization  $4\pi I_m$  ( $H_m = 30.5$  kOe) and coercive force ( $H_c$ ) of  $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5$  alloy after smelting in an arc furnace ( $H_c^{(1)}$ ) and after a low-temperature tempering ( $H_c^{(2)}$ ). [190]

as for alloys with heavy REM, in consequence of the ferrimagnetic ordering of the magnetic sublattices, at low temperatures, but not below the compensation temperature,  $\alpha_s > 0$ . [86,107,187] Consequently, for quasi-binary compounds ( $\text{R}_1^{1-x}\text{R}_2^x$ )Co<sub>5</sub>,  $\alpha_s$  can vary within broad limits on change of x. When we take into account also that both  $\text{R}^1\text{Co}_5$  compounds and  $\text{R}^2\text{Co}_5$  compounds have a qualitatively different  $\alpha_s(T)$  dependence for different  $\text{R}^1$  and  $\text{R}^2$ , then, by changing the value of x and the kind of REM in multicomponent alloys, it is possible to obtain alloys with  $\alpha_s(T)$  varying with temperature according to a different law both in the same and in different temperature intervals. Thus by choosing one or another alloy for manufacture of a permanent magnet containing different combinations of REM, it is possible to vary the values of the magnetic characteristics of the permanent magnets over a wide range and in the necessary direction.

By way of example, Table II shows the parameters of permanent magnets of various ternary alloys, for the purpose of illustrating the practical possibilities of obtaining high-energy-capacity permanent magnets with high temperature stability. [85]

## 6. HIGH-COERCIVITY PRECIPITATION-HARDENED ALLOYS OF REM WITH 3d METALS

### A. Magnetic properties

It was first discovered in 1968 that alloys of the type  $\text{RCO}_5$  ( $\text{R} = \text{Sm}, \text{Ce}$ ) in which part of the cobalt has been replaced by copper, nickel, or aluminum are precipitation-hardened, and that in the cast state they have high values of  $H_c$ . [188,189] Such substitution decreases  $4\pi I_s$  and  $T_c$ , because the magnetic cobalt atoms are replaced by nonmagnetic. [109,190] (The nickel in these compounds, as has already been mentioned, has the electronic configuration  $3d^{10}$  and carries no magnetic moment.) As an example, Fig. 26 shows the concentration dependence of the magnetic properties of the alloy  $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5$ . The coercive force of specimens quenched from high temperatures varies nonmonotonically with the degree of substitution: it has a maximum near the composition  $\text{Sm}(\text{Co}_{0.6}\text{Cu}_{0.4})_5$ . [188,190,191,192] Its value increases appreciably after annealing at 300–600°C and reaches a value of about 30 kOe. [188,193] But the maximum value of  $(BH)_m$  is not large, 7.7 MG Oe for  $\text{Sm}(\text{Co}, \text{Cu})_5$  [193] and 8.0 MG Oe for  $\text{Ce}(\text{Co}, \text{Cu})_5$ . [189] Such a low  $(BH)_m$  in comparison with the  $(BH)_m$  of mag-

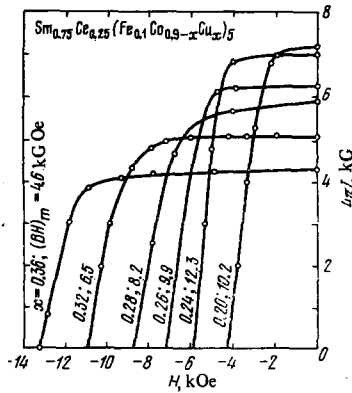


FIG. 27. Effect of copper content on magnetic properties of alloys  $\text{Sm}_{0.75}\text{Ce}_{0.25}(\text{Fe}_{0.1}\text{Co}_{0.9-x}\text{Cu}_x)_5$ .<sup>186</sup>

nets of  $\text{SmCo}_5$  alloy ( $\sim 20$  MGoe) is due primarily to the low value of  $4\pi I_s$ . In order to increase it, a part of the cobalt atoms ( $\sim 0.1$ ) are replaced by iron atoms, which have a larger value of magnetic moment,<sup>[186,194,195]</sup> The magnetic properties of alloys containing Fe, for various Cu contents, are shown in Fig. 27. As is seen  $(BH)_m$  reaches 12.3 MGoe. Use of multistage heat treatment<sup>[182]</sup> or of slow cooling<sup>[196]</sup> makes it possible to raise  $(BH)_m$  to 13–13.5 MGoe, i. e., to the value of  $(BH)_m$  for magnets of alloys based on Co–Pt. In order to increase  $4\pi I_s$  and  $(BH)_m$  further, the content of  $3d$  metal has been raised in a more general manner, primarily by increasing the content of magnetic components Co and Fe, and use has been made of a method of obtaining permanent magnets by high-temperature sintering, like that used for obtaining magnets of  $\text{SmCo}_5$  alloys. It consists of the following. An alloy of the required composition was ground after smelting, The resulting powder was oriented and compressed in a magnetic field and thereafter sintered at high temperatures (1000–1200 °C). After quenching from this temperature and subsequent low-temperature annealing (300–700 °C), magnet specimens were obtained from the alloy  $\text{Ce}(\text{Co}_{0.72}\text{Fe}_{0.14}\text{Cu}_{0.14})_5$  with  $(BH)_m = 12$  MGoe<sup>[197]</sup> and from  $\text{Sm}_{0.7}\text{Ce}_{0.3}(\text{Co}_{0.8}\text{Fe}_{0.05}\text{Cu}_{0.15})_7$  with  $(BH)_m = 18.3$  MGoe.<sup>[198]</sup> These are the highest values of  $(BH)_m$  obtained for rare-earth precipitation-hardened  $fd$  alloys.

### B. Microstructure, and nature of the high coercive force

X-ray and electron-microscope investigation<sup>[191]</sup> of the crystallographic structure and the microstructure of  $\text{R}(\text{Co}, \text{Cu})_5$  alloys has shown that after high-tempera-

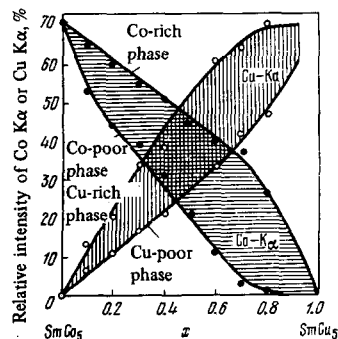


FIG. 28. Change of relative cobalt and copper contents in the Co- and Cu-rich and the Co- and Cu-poor phases on increase of the copper content in alloys  $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5$  obtained by smelting in an arc furnace.<sup>196</sup>

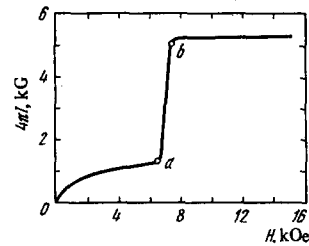


FIG. 29. Magnetization curve of a thermally demagnetized monocrystal of alloy  $\text{Ce}_{1.09}(\text{Fe}_{0.1}\text{Co}_{0.7}\text{Cu}_{0.2})_5$  along the AEM ([0001]).<sup>199</sup>

ture homogenization and fast cooling, the alloys are most homogenous but supersaturated solid solutions. In this state the coercive force, as a rule, is relatively low. But it depends very strongly on the rate of cooling. On annealing of the quenched alloy in the interval 300–600 °C, there occurs spinodal decomposition (precipitation hardening) of the supersaturated solid solution into two phases, which have the same crystal lattice, of the  $\text{CaCu}_5$  type, but different lattice parameters because of their different chemical composition. One of these is enriched in cobalt, the other in copper, as compared with the chemical composition of the supersaturated solid solution. The composition of the phases depends on the chemical composition of the original alloy (Fig. 28). If the alloy is cobalt-enriched, then copper-enriched particles precipitate in a cobalt-enriched matrix. If the alloy is copper-enriched, then it is the other way around. The particles are of elongated shape, with diameter about 100 Å and length about 1000 Å, and are coherent with the matrix. The magnetic characteristics of the phases have not so far been established.

In the thermally demagnetized state, the precipitation-hardened alloys have a multidomain structure.<sup>[199]</sup> DB displacement during magnetization and magnetization reversal is greatly hindered by the change of their surface energy on passage through precipitates. This hindrance of displacement leads also to high values of  $H_c$ . One of the peculiarities of cast precipitation-hardened alloys based on REM is a large magnetic after-effect, due to gradual displacement of DB in a magnetic field.<sup>[200,201]</sup> Unfortunately very little research has been devoted to explanation of the nature of the high-coercivity state and of the magnetic after-effect in these alloys, as is true also of detailed investigations of the microstructure. In the light of this it is not clear whether the whole magnetization of the crystal proceeds by DB displacement (to point *b*), or whether this process ends at point *a* and the further increase of  $4\pi I$  occurs by remagnetization of particles with  $I_s$  oriented unfavorably with respect to  $H$  (Fig. 29). One gets the impression that one phase (the matrix) is first magnetized by DB displacement, and then precipitates of the other phase. Since their size is close to  $d_c$ , they may by themselves have high values of  $H_c$ . It is interesting to note that the temperature dependence  $\sigma_s(T)$  undergoes no noticeable anomalies above room temperature.<sup>[182]</sup> This is possibly due to a very wide transitional (with respect to chemical composition) zone between phases. As is evident from the above, the situation here is enormously more complicated than it may appear at first glance, and more refined struc-

tural and magnetic investigations are required in order to understand the nature of the high-coercivity state in these alloys.

In conclusion we note that precipitation-hardened alloys based on REM have so far not found wide application. This is due to the relatively low level of their magnetic properties, their inferior mechanical characteristics, and their relatively poor temperature stability. The above values of  $(BH)_m$  were obtained on specimens of small dimensions ( $\sim 3$  mm). In order to obtain magnets of large size, it is still necessary to develop a procedure for obtaining a perfect magnetic texture, which is dependent on the crystallographic; that is, a procedure for oriented crystallization of ingots of large size and homogeneous in chemical composition. Specimens with an energy value  $(BH)_m = 18.3$  MGOe have been obtained by powder-metallurgy methods; therefore such magnets, in the technological sense, have no advantage over baked magnets of  $\text{RCO}_5$  alloys, although they may have a higher suitable yield. Furthermore, these alloys have values of  $T_c$  below the  $T_c$  of magnets of  $\text{RCO}_5$ , and their temperature coefficient is about twice as large. Nevertheless, these alloys are of great interest, not only as objects for academic investigations of the kinetics of formation of the high-coercivity state in high-anisotropy precipitation-hardened alloys, but as objects for study of the mechanism of spinodal precipitation. The author hopes that by alloying of R-Co-Cu alloys with various components it will be possible to improve their mechanical properties and to raise the level of their magnetic characteristics. Possibly this will facilitate the obtaining of perfect texture in large ingots. It seems that these alloys deserve closer attention than they are at present receiving.

## 7. HIGH-ANISOTROPY, MAGNETICALLY MULTIAXIAL, COMPOUNDS, BASED ON REM, FOR PERMANENT MAGNETS

### A. Magnetic properties and peculiarities of domain structure

Until recently it was supposed<sup>[202]</sup> that the most suitable materials for permanent magnets were high-anisotropy magnetically uniaxial magnets, because the available multiaxial ones (with three or four axes) had lower values of the magnetic-anisotropy constant. But recent investigations<sup>[122-124]</sup> have shown that intermetallic compounds of REM with Fe, of the type  $\text{RFe}_2$ , with the  $\text{MgCu}_2$  crystal lattice (Laves phase), have enormous values of  $K$  and of the magnetostriction ( $\lambda$ ), with quite high saturation magnetization ( $K(0^\circ\text{K}) = -7 \cdot 10^8$  and  $-5 \cdot 10^8$  erg/cm<sup>3</sup> for  $\text{TbFe}_2$  and  $\text{ErFe}_2$ ;  $K(300^\circ\text{K}) = 2 \cdot 10^7$  and  $-3.3 \cdot 10^6$  erg/cm<sup>3</sup> for  $\text{DyFe}_2$  and  $\text{ErFe}_2$ ;  $\lambda_{111}(0^\circ\text{K}) = 5 \cdot 10^{-3}$  and  $\lambda_{111}(300^\circ\text{K}) = 3 \cdot 10^{-3}$  for  $\text{TbFe}_2$  and  $\lambda_{111}(300^\circ\text{K}) = 0.3 \cdot 10^{-3}$  for  $\text{ErFe}_2$ ;  $4\pi I_s(0^\circ\text{K}) = 10.9$  kG for  $\text{TbFe}_2$ ). They have the highest values of  $T_c$  (600–700°K) among all the RT-compounds containing Fe, because of the polarizing effect of the R sublattice. Their anisotropy field reaches  $10^6$  Oe at  $0^\circ\text{K}$ . Such a high magnetocrystalline anisotropy, first observed in

intermetallic compounds with cubic symmetry,<sup>2)</sup> is caused by the strong interaction of the 4f shell of the REM ion with the crystalline field of the lattice.<sup>[122]</sup> The temperature variation of  $K$  was treated theoretically, on the basis of the single-ion-isotropy model, in Refs. 105, 122.

The large value of  $K$ , or more accurately of the ratio  $K/I_s^2$ , leads to the result that in  $\text{DyFe}_2$  and  $\text{ErFe}_2$  crystals there is observed a DS with exposed poles and unclosed magnetic flux, as in high-anisotropy magnetically uniaxial magnets.<sup>[203]</sup> The large magnetostriction is the reason for the fact that the form of the DS in these alloys is very sensitive to stresses. In particular, after mechanical polishing of the surface of an  $\text{ErFe}_2$  crystal and magnetization of the crystal, the deformed surface layer exists in a single-domain state even in negative fields, whereas the interior of the crystal breaks up into domains already in positive. Preliminary investigations of the magnetic properties of powders of this alloy, conducted in our laboratory, have shown that the surface layer is a sort of "spring" that restricts the irreversible reconstruction of the internal DS in the process of remagnetization of the powder particles and that leads to asymmetric, sometimes almost hysteresis-free partial cycles of the hysteresis loop.<sup>3)</sup>

### B. Hysteretic properties in the amorphous state

Alloys  $\text{RFe}_2$  (R = Sm, Gd, Tb, Dy, Er, Y) after a rapid quench from the liquid state are amorphous, with grain size about  $100 \text{ \AA}$ .<sup>[123]</sup> For  $\text{TbFe}_2$  and  $\text{GdFe}_2$ ,  $T_c$  in this state is about 40% lower than in the crystalline state. The value of the magnetic moment of  $\text{GdFe}_2$  at  $0^\circ\text{K}$  is the same in both states, whereas that of  $\text{TbFe}_2$  is 20% lower. No unambiguous explanation of the observed effects is so far known, but certain considerations in this connection were presented in<sup>[124]</sup>.

The coercive force in the amorphous state is very high at  $T = 4.2^\circ\text{K}$  and for  $\text{TbFe}_2$ , for example, is about 30 kOe, with  $\sigma_r \approx 100 \text{ G cm}^3/\text{g}$  and  $(BH)_m = 29$  MGOe.<sup>[123]</sup> But these values decrease rapidly with rise of temperature, so that  $H_c(300^\circ\text{K}) \approx 100$  Oe. Qualitatively similar results were obtained for  $\text{DyFe}_2$  ( $H_c(4.2^\circ\text{K}) = 32$  kOe) and  $\text{SmFe}_2$  ( $H_c(4.2^\circ\text{K}) = 21$  kOe). Such high values of the hysteretic characteristics and their abrupt changes with rise of temperature are explained if we suppose that in the amorphous state there are weakly interacting magnetically ordered regions (clusters) of volume  $100\text{--}1000 (\text{ \AA})^3$ , which during remagnetization behave like pseudosuperparamagnetic particles.<sup>[124]</sup> Therefore if we increase the relaxation time, for example by increasing the volume of the clusters, then we may expect higher values of  $H_c$  even at room temperature. This is possibly the reason for the increase of  $H_c$  from 0.1 to  $\sim 4$  kOe after a recrystallizing anneal of

<sup>2)</sup> Magnetocrystalline anisotropy of the same order of magnitude was observed earlier in certain magnetically multiaxial rare-earth iron garnets.<sup>83,233</sup>

<sup>3)</sup> These investigations were conducted by the author together with G. S. Kandaurova and A. E. Lagutin.

amorphous TbFe<sub>2</sub> (Fig. 30), when the grain size increases 1.5 times.  $(BH)_m$  after annealing is 8.7 MG Oe. This is the highest value of  $(BH)_m$  ever obtained on magnets with a cubic lattice, if we disregard the  $(BH)_m \approx 10$  MG Oe obtained experimentally for filamentary crystals ("whiskers") of iron of very small size.<sup>[19]</sup>

To emphasize the importance of the above results, we note the following. In the first place, they have demonstrated the practical possibility of obtaining a huge magnetic anisotropy ( $K(0^\circ\text{K}) \approx 10^9$  erg/cm<sup>3</sup>) in crystals with cubic symmetry based on REM, and using them for permanent magnets. In the second place, they have shown us still another technological possibility for the attainment of high values of  $H_c$  in high-anisotropy rare-earth compounds, via the amorphous state. In the third place, the values obtained for TbFe<sub>2</sub>,  $(BH)_m = 30$  MG Oe at 4.2 °K and 8.7 MG Oe at room temperature, are high enough to allow us to count on their successful practical use both at room temperature and also at cryogenic temperatures. There is still another fact that is favorable to RFe<sub>2</sub>. These are essentially polycrystalline magnets; but in consequence of their magnetic multiaxiality, they have high values of the residual magnetization  $(0.83-0.87)4\pi I_s$  in comparison with  $0.5(4\pi I_s)$  for polycrystalline magnetically uniaxial magnets. In order to obtain  $4\pi I_r = (0.83-0.87) \cdot 4\pi I_s$  in the latter case, it is necessary to use special methods of producing magnetic texture (compression in a magnetic field, plastic deformation, etc.).

It seems that a procedure for obtaining high  $H_c$  via the fine-crystal or amorphous state may prove very promising for obtaining high-energy-capacity permanent magnets from other RT compounds with high  $(BH)_{mt}$  (~60 MG Oe) and a not too high value of  $H_a$  (~20 kOe), such as, for example, quasibinary compounds of the type  $(R_1, R_2)_2T_{17}$  or  $R_2(T_1, T_2)_{17}$ . The first experiments<sup>[119]</sup> in this direction, on  $\text{Sm}_2(\text{Co}_{0.7}\text{Fe}_{0.3})_{17}$ , made it possible to obtain  $(BH)_m = 12$  MG Oe in the isotropic state, a value that could not be reached by other methods (see Fig. 1). The improvement of this method, for the purpose of obtaining textured high-coercivity polycrystals, is of great interest for realization of the enormous potential possibilities, with respect to  $(BH)_m$ , of this type of rare-earth intermetallic compound.

## 8. COMPOUNDS OF REM WITH 3d METALS WITH ULTRAHIGH MAGNETIC ENERGY AT LOW TEMPERATURES

### A. Narrow domain boundaries and low-temperature permanent magnets

In treatment of domain-boundary energy in ferromagnets, it is usually assumed that the crystal is an uninterrupted continuum of spins, with constant density along an arbitrary direction, but with varying orientation. If the angle between neighboring spins is small, then there is satisfactory agreement between the theoretical and experimental values of the DB energy ( $\gamma = 4\sqrt{AK}$ ). This treatment actually assumes that the thickness of the DB is very great, theoretically infinite. But the deviation of the spins from an AEM of the crys-

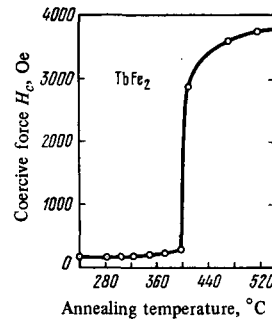


FIG. 30. Effect of annealing temperature on coercive force of amorphous TbFe<sub>2</sub>. Annealing time 2 hours for all specimens except the two annealed (for 17 hours) at the highest temperatures.<sup>[23]</sup>

tal and their misorientation angles at distances larger than  $\delta/2 \approx \sqrt{A/K}$  are very small, and these sections make no important contribution to the DB energy. This approximation is quite valid if the width of a DB is much larger than the interatomic distance ( $a$ ). If this condition is not satisfied, for example in magnetic materials with a value of  $K$  comparable with or exceeding the value of the exchange-energy density, then the treatment the DB as continuous is not justified. In this case it is necessary to take into account the discreteness in orientation of the magnetic moments.<sup>[17,204-208]</sup> In narrow DB, the angle of misorientation between spins may be large. In equilibrium, the center of the DB is between two spins, and the DB has energy  $\gamma_1$ . During a transition, the central spin is perpendicular to the AEM, and the energy of the DB is  $\gamma_2$ . Consequently, during displacement of a wall in a perfect crystal there occurs a change of its energy equal to  $\Delta\gamma = \gamma_2 - \gamma_1$ , and the intrinsic coercive force will be<sup>[17]</sup>

$$H_w = -\frac{1}{2I_s} \left( \frac{d\gamma}{dn} \right)_{\max} = -\frac{\pi}{2aI_s} \Delta\gamma, \quad \text{or} \quad h_w = \frac{H_w}{H_a} = \frac{\pi}{4aK} \Delta\gamma. \quad (5)$$

Since the angle between neighboring spins is larger, the narrower the wall, and since  $\delta \sim \sqrt{A/K}$ , the value of  $H_w$  will depend on the ratio  $K/A$ . When this is relatively large,  $H_w \approx H_a$ . Thus there is a possibility in perfect crystals of obtaining by hindrance of DB displacement very high values of coercive force, i. e., of obtaining high-coercivity permanent magnets. Up to the present there are a number of compounds in which the effect described apparently occurs:  $\text{Dy}_3\text{Al}_2$ ,<sup>[207]</sup>  $\text{TbNi}_{1-x}\text{Cu}_x$  ( $x < 0.4$ ),<sup>[209]</sup>  $\text{Sm}(\text{Co}_{1-x}\text{Ni}_x)_5$ ,<sup>[109]</sup>  $\text{R}_3\text{Co}$ ,<sup>[213,214]</sup> and others. By way of example, Fig. 31 shows hysteresis loops of the compounds  $\text{Dy}_3\text{Al}_2$ <sup>[207]</sup> and  $(\text{Tb}_{0.8}\text{Gd}_{0.2})_3\text{Co}^4$  at  $T = 4.2^\circ\text{K}$ . The value  $(BH)_m \approx 100$  MG Oe is a record value at the present time.

During magnetization reversal of crystals with narrow DB, as a rule a large after-effect occurs,<sup>[211]</sup> and the values of  $H_c$ , for example, in pulsed and in static magnetic fields may differ appreciably.<sup>[214]</sup> Is it possible by means of this mechanism to obtain permanent magnets operating at room temperature? Estimates show that for a magnet with  $T_c \approx 1000^\circ\text{K}$  it is necessary that  $K(300^\circ\text{K}) \approx 10^9$  erg/cm<sup>3</sup>. To obtain such materials is of course a quite complicated problem, but in principle it is possible.

<sup>4)</sup>The investigations of the magnetic properties of monocrystals of the system (Tb, Gd)<sub>3</sub>Co were carried out by the author together with N. V. Baranov and A. N. Maslov.

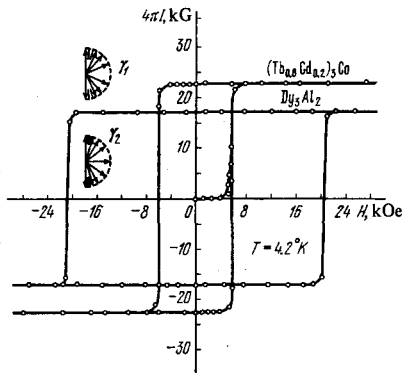


FIG. 31. Hysteresis loops of monocrystals of  $\text{Dy}_3\text{Al}_2$ <sup>[207]</sup> and  $(\text{Tb}_{0.8}\text{Gd}_{0.2})_3\text{Co}$ , with  $(BH)_m = 73$  and  $102$  Mg Oe, respectively.

At the same time, it must be mentioned that up to the present there are still many unsolved problems in this area. In particular, it would be desirable to have more definitive experiments demonstrating the very fact that narrow DB exist and have a high intrinsic coercivity. It would be interesting to study the influence of defects of the crystal lattice on  $H_w$ , because such defects as dislocations, antiphase boundaries, and packing defects on the one hand can lower the field for generation of narrow domain boundaries (NDB) and the value of  $H_w$  as compared with the theoretical values, since they produce irregularities in the magnetic structure, and on the other hand can be very effective obstacles to the displacement of NDB in consequence of the fact that their magnetically active size  $d' \approx \delta$ . It is also not excluded that at least some RT compounds with NDB may in essence be regarded, during the magnetization-reversal process, as magnetically heterogeneous systems, which in consequence of different values of the exchange integrals between different neighborhoods consists of small magnetically ordered regions (clusters) that behave, during magnetization reversal, like single-domain (or rather quasisuperparamagnetic) particles<sup>5)</sup>; this is suggested, for example, by the large after-effect and by the exponential character of the temperature dependence of  $H_c$ . In this case, although a DB may still exist in the magnets, nevertheless during magnetization and magnetization reversal the NDB will not be displaced in the usual sense of this word.

### B. Rare-earth metamagnets and magnetic hysteresis

Metamagnets are antiferromagnets in which the magnetic anisotropy field ( $H_a$ ) is equal to or larger than the effective field of exchange interaction between sublattices ( $H_{ex}$ ).<sup>[4]</sup> According to this condition, in metamagnets under the influence of a magnetic field the phenomenon of flipping of the magnetic sublattices is not observed. As was shown theoretically in<sup>[227]</sup>, a transition from the antiferro- to the ferromagnetic state may occur either by uniform rotation of the magnetization of one of the sublattices at field  $H_t = \sqrt{(H_a + H_{ex})H_a}$  or by the

<sup>5)</sup> Similar ideas were used earlier by K. P. Belov and others to explain the maximum of  $H_c$  in Dy and Tb near the magnetic phase-transition temperature.<sup>33, 234</sup>

appearance and growth of an antiferromagnetic phase at  $H'_t \lesssim H_t$ . The reverse transition may also occur either by rotation of  $I_s$  at  $H_{0t} = H_a - H_{ex}$  or by appearance and growth of nuclei of an antiferromagnetic phase at  $H'_{0t} < H_{0t}$ . Thus according to the calculation, the metamagnetic transition should be accompanied by magnetic hysteresis. It has been observed experimentally in the layered metamagnet  $\text{FeCl}_2$ ; the width of the hysteresis loop depended on the rate of change of the magnetic field and decreased from 4 kOe at  $7.5 \cdot 10^7$  Oe/sec to zero for measurement in static fields.<sup>[235]</sup>

Among RT compounds, the metamagnets include some  $\text{R}_3\text{Co}$  and  $\text{R}_3\text{Ni}$ ,<sup>[214-217]</sup>  $\text{RAl}$ ,<sup>[218-223]</sup>  $\text{RGe}$ ,<sup>[224]</sup>  $\text{R}_5\text{Ge}_3$  ( $\text{R} = \text{Tb, Dy, Ho, Er}$ ),<sup>[225]</sup>  $\text{RCu}_2$ ,<sup>[226]</sup> and others. Because of the high concentration of rare-earth element, they have high values of  $4\pi I_s$  in the ferromagnetic state ( $\sim 20$  kG), of the anisotropy constant ( $\sim 10^8$  erg/cm<sup>3</sup>), and of the critical field  $H_t$  (up to 70 kOe). Because the magnetic ordering temperature in them is below room temperature, these compounds are of interest for high-energy-capacity permanent magnets only at low temperatures. Unfortunately, in the majority of them there is practically no metamagnetic hysteresis, perhaps because the ratio  $H_a/H_{ex}$  is insufficiently large or because demagnetization of them occurs relatively easily by DB displacement. And in those cases in which the hysteresis is appreciable, it is not clear (in the absence of neutron-diffraction investigations of the magnetic structure) whether we have to do with a metamagnet or with a ferromagnet with a high ratio  $K/A$ , and consequently with narrow domain boundaries.

It should be mentioned that there are very few experimental papers devoted to elucidation of the physical conditions for the formation of metamagnetic hysteresis. Meanwhile such problems as explaining the effect on its magnitude of the degree of collinearity of the magnetic structure, the relation between  $H_a$  and  $H_{ex}$ , defects of the crystal lattice, and the size of the metamagnet are probably important, because, for example, with a high ratio  $H_a/H_{ex}$  the DB in a metamagnet should be very narrow, and their appearance and displacement in the metamagnetic transition process is impeded. It is to be expected that at small dimensions of the metamagnet, the appearance of transitional metamagnetic DB will prove energetically disadvantageous because of the large increase of the contribution to the energy of the metamagnet from the DB energy. In this case the metamagnetic transition in such "single-domain" particles will occur by rotation of the magnetization of one of the sublattices, and this leads, as has already been mentioned, to a large value of the metamagnetic hysteresis. Solution of these problems will probably facilitate realization of the high potential possibilities of rare-earth metamagnetic materials as materials for low-temperature permanent magnets.

### 9. CONCLUSION

On analyzing the development of investigations in the area of materials for permanent magnets in recent years, one can note that the most rapid progress in this

area has resulted from the discovery and intensive investigation of the magnetic properties of a new class of high-anisotropy magnetic materials—intermetallic compounds of REM with 3d transition metals, and primarily with cobalt. The great variety of compounds and the interchangeability of the REM in them, which makes it possible to obtain multicomponent alloys with various combinations of the fundamental magnetic constants (saturation magnetization, Curie temperature, and magnetocrystalline anisotropy constant), have permitted the development of permanent magnets with high magnetic energy and temperature stability, capable of operating under conditions of quite strong demagnetizing fields over a broad temperature range. Already at the present time, on the basis of them, a number of important technical problems have been solved, which it was previously hopeless to pose, and radical improvements have been made in the operating parameters of magnetic systems and devices, with appreciable decreases of their weights and sizes.

At the same time, in the field of rare-earth magnetically hard materials there are still many fundamental and applicational problems, on the solution of which their further development and wider application depend. Foremost is explanation of the nature of the exchange interactions and of the magnetic anisotropy of *fd* compounds; this will make it possible to approach more knowingly the problem of synthesis of new high-anisotropy materials with high Curie temperature. One of the important problems is the establishment of a more exact relation between the magnetic hardness and the structure-phase state in rare-earth permanent magnets, and also of the causes that lower the value of the coercive force as compared with the maximum theoretical limit. This would facilitate raising the level of the magnetic characteristics and broadening the temperature interval for use of the magnets. Great interest attaches to investigations of the possibility of practical use of rare-earth monocrystalline magnets with value of the energy product 30–40 MG Oe. Here the fundamental problem is the development of an effective procedure for obtaining perfect monocrystals of *fd* compounds of sufficiently large size, the attainment in them of higher values of the coercive force, and increase of the stability of the single-domain state to various kinds of physical actions (thermal, chemical, mechanical, etc.) that occur during operation of permanent magnets. Exceptionally important, both from the academic and from the practical point of view, are investigations of the magnetic properties of magnets in the amorphous state; these may point the way to attainment of a high coercive force in materials in which this cannot be done by traditional methods. It seems promising to study the magnetic properties of and search for new magnetic materials in which the energy density of magnetocrystalline anisotropy is comparable with or exceeds the density of exchange energy, since from such materials, in certain cases, it is possible by simple technical means to obtain high-coercivity permanent magnets with ultrahigh magnetic energy at low temperatures. In this respect rare-earth metamagnets are also of interest. Thus it can be assumed that solution of the above-indicated

problems will facilitate further improvement of the magnetic properties of rare-earth magnetically hard materials and their broader application in various branches of technology.

In closing, it would be desirable to mention that the author has deliberately refrained from discussing in this review certain questions of methodological or technological character, which, although important, are somewhat removed from the theme chosen for the review. Therefore the bibliography given must not be considered complete; it nevertheless reflects to a sufficient degree the papers that reveal the physical essence of the questions considered.

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