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WHY COBALT FOR MAGNETIC DEVELOPMENT

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WHY COBALT FOR MAGNETIC DEVELOPMENT *

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INTRODUCTION

That cobalt enjoys an outstanding position in the field of magnetism can be seen immediately by glancing at the values of magnetic constants and properties listed in Table I. At the present stage of scientific development, these data are no longer to be regarded as a collection of meaningless, though interesting values; they may have a definite bearing on technical applications, for, although it has not yet been possible to formulate a comprehensive quantitative magnetic theory in terms of the basic principles of quantum mechanics, most magnetic phenomena can now be explained qualitatively. For instance, anisotropy has been shown to affect a large number of magnetic properties, such as the initial permeability, coercivity, retentivity, response to magnetic annealing and resonance frequency; magnetostriction, which in itself finds numerous technical applications, influences the magnetic properties of polycrystalline materials through the stresses which unavoidably develop in them; a high Curie point favours the thermal stability of magnetic substances, especially at high temperatures. In conclusion, it can be safely stated, in the light of present-day knowledge, that it should generally be possible to develop a specific magnetic

material for each technical application, and that cobalt should play an important role in such developments. In a series of articles of which this is the first, an attempt will be made to expound and illustrate these ideas in some detail with reference to non-metallic magnetic compounds.

TABLE I. — MAGNETIC CONSTANTS AND PROPERTIES OF SOME MATERIALS

Material	Crystallographic system	Anisotropy constant, K_1 , 10^4 J/m^3	Magnetostriction constants at room temperature		Curie point, °C
			$10^5 \lambda_{100}$	$10^5 \lambda_s$	
Fe	Cubic	4.6	1.95	-0.35	770
Co	Hexagonal	53	—	—	1131
70 Co, 30 Fe	—	—	—	-13.0	—
Ni	Cubic	-0.51	-4.6	-3.3	358
Fe ₃ O ₄	Cubic	-1.1	-1.94	4.41	—
CoFe ₂ O ₄	Cubic	25 to 40	-51.5	-17.9	—
NiFe ₂ O ₄	Cubic	-0.6	—	—	—
Co _{0.8} Fe _{2.2} O ₄	—	—	-59.0	-16.4	—
Ni _{0.8} Fe _{2.2} O ₄	—	—	-3.6	-1.7	—

PART ONE

MAGNETIC PROPERTIES, TECHNICAL PARAMETERS AND THE INFLUENCE OF COBALT

In this first part, the phenomenological aspect of magnetism will be considered and a relationship established between the basic phenomena of magnetization and the technical parameters which describe the suitability of a given substance for a specific application. The parameters can often be expressed in terms of values related to the magnetization curve of the substance. These values in turn depend partly on the intrinsic properties of

the crystal structure (generally called structure-independent properties!) and partly on the anisotropy of the specimen as a whole and on its inhomogeneities (the properties depending on these factors are usually called structure dependent).

The types of energy and mechanisms involved in the processes of magnetization will be reviewed and the various formulae characterizing these processes will be discussed. With the help of these formulae, the influence of cobalt on the technical parameters of non-metallic compounds will then be examined.

* This research was conducted in the laboratories of the Battelle Memorial Institute, Geneva, under the auspices of the Cobalt Information Centre, Brussels.

THE STATICS OF MAGNETIZATION

THE MAGNETIZATION CURVE

In its unmagnetized state a ferromagnetic substance* is divided into Weiss domains (usually called "domains"), which are separated by Bloch walls (commonly referred to as "walls"). It is generally considered that each domain is spontaneously magnetized to saturation; recent observations, however, suggest also the possibility of the triangular arrangement proposed by Yafet and Kittel (YA52, RO58, JA59). The distribution of the direction of the magnetized domains is such that the resultant magnetization of the whole body is zero in any direction :

$$\frac{1}{V} \sum_i M_s v_i \cos \theta_i = 0, \quad V = \sum_i v_i \quad (1)$$

where v_i is the volume of the i^{th} domain, θ_i the angle between the direction of spontaneous magnetization, \vec{M}_s , of the i^{th} domain and an arbitrary but fixed direction (the magnitude of the spontaneous magnetization is assumed, as usual, to be equal in all domains), and V is the total volume of the specimen.

Upon applying an external field H (in the chosen fixed direction), a resultant magnetization δM appears in the direction of the applied field :

$$\begin{aligned} \delta M = & \frac{M_s}{V} \sum_i \delta v_i \cos \theta_i + \frac{M_s}{V} \sum_i v_i \delta (\cos \theta_i) \\ & + \frac{\delta M_s}{V} \sum_i v_i \cos \theta_i - \delta V \frac{M_s}{V} \sum_i v_i \cos \theta_i \end{aligned} \quad (2)$$

The first term represents the increase in volume of those domains in which the spontaneous magnetization, \vec{M}_s , has energetically favourable directions (with respect to that of the applied field at the expense of the volume of those domains which are less favourably oriented). The second term takes into account the rotational process of the vector, \vec{M}_s , in the domains. The third is due to a change in spontaneous magnetization, and is negligible (except in the vicinity of the Curie point). The fourth results from the change in total volume, and is also negligible. Thus, to a first approximation, two magnetization mechanisms can be distinguished : wall displacement and the rotation of magnetic moments. Both processes can be either reversible or irreversible. Irreversible rotation, however, occurs only in rotating fields.

Whether magnetization proceeds by wall displacement or by rotation in a given specimen depends on the energy required for these processes

* Unless otherwise stated, all that is said about ferromagnetics applies equally to ferrimagnetics.

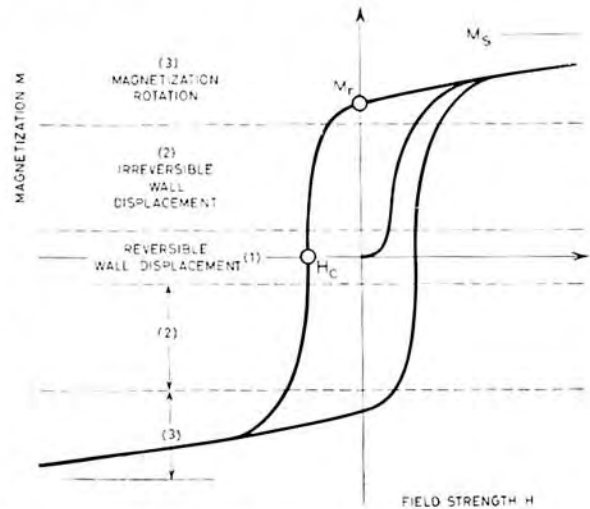


Fig. 1. — Magnetization mechanisms.

to take place. For a magnetic material in weak fields, magnetization by wall displacement is generally dominant (see Fig. 1). As the field is increased, the displacements, which were initially reversible, become irreversible. When, as the result of these displacements, the spontaneous magnetization in each domain is directed in the most favourable direction (i.e. as nearly as possible in the direction of the external field), rotation of the domains begins. In fact, displacements and rotations are often simultaneous, and it is possible to separate them only under very special experimental conditions. The theoretical study of the magnetization curve is that of the changes in domain configuration due to the application of an external field.

ENERGIES PARTAKING IN THE MAGNETIZATION PROCESSES

The domain configuration existing in a given external field is that which corresponds to the minimum energy. It is therefore useful to review here the principal kinds of energy involved in the process of magnetization. For this purpose, the usual classification of energies will be adopted : exchange energy, anisotropy energy, etc. It must be emphasized, however, that these energies are closely related to the other quantities describing ferromagnetism; the subdivisions are more or less arbitrary and too great a physical meaning should not be attached to the designations used. A few general remarks may illustrate this point.

Gyromagnetic experiments and microwave measurements show that the magnetic moment of ferromagnetics arises principally from electron spin. The orbital moments can be considered as immobilized (quenched). Their contribution to the saturation magnetization does not exceed 10 per cent. The quenched orbitals, however, play an important part in the explanation of crystal anisotropy; this anisotropy is thought to stem from the coupling of spin to (partially) quenched orbits.

Exchange energy results from a quantum effect; it is a non-classical interaction energy of carriers having magnetic moments. These carriers are usually taken to be spins, and the spin-orbit coupling is disregarded. Thus exchange energy is *a priori* isotropic, regardless of the geometric anisotropy of the crystal. The anisotropy energy is calculated in a separate step.

A final example may be quoted; the importance of the close relationship that exists between magnetostriction and crystal anisotropy is often overlooked. Magnetostriction arises from the dependence of crystal anisotropy on the state of strain of the crystal lattice.

A. EXCHANGE ENERGY

Exchange energy is responsible for the parallel (ferromagnetic) or antiparallel (antiferromagnetic) alignment of spins within a domain, which results in its spontaneous magnetization.

The first exchange interaction model was proposed by Heisenberg (HE28). In order to explain ferromagnetism in metals, this author postulated the existence of a direct interaction between metal atoms which is dependent on the extent to which the electron wave functions of adjacent metal atoms overlap. In the Heisenberg model the exchange energy (-operator) \underline{H} has the form :

$$\underline{H} = -2 \sum_{i>j} J_{ij} s_i s_j, \quad (3)$$

where s_i is the electronic spin operator (a spin vector) of the i^{th} atom, and J_{ij} is the exchange integral between the i^{th} and j^{th} atoms. The exchange integral is proportional to the overlap of the atomic wave functions. Therefore, the sum (3) is generally restricted to the z nearest neighbours

of each atom, and the exchange integral is taken to be the same, (J), for all these interactions.

When J is positive, the interaction is ferromagnetic (parallel spins); when it is negative, the interaction is antiferromagnetic (antiparallel spins). At the Curie point these interactions disappear; this provides a means of establishing an approximate relation between the exchange integral and the Curie temperature T_C :

$$J \simeq \frac{3}{2} \frac{k}{zS(S+1)} T_C, \quad (4)$$

where S is the total spin quantum number of the electrons on each lattice site; i.e. $S(S+1)$ is the eigenvalue of the operator $\underline{s} \cdot \underline{s}$.

However, what is of greater interest here is the energy associated with deviations from the homogeneity of spontaneous magnetization rather than the total exchange energy. In practice, the Bloch walls separating domains of homogeneous magnetization serve to illustrate this case. On applying hypotheses to simplify this expression, the following is obtained, for a pair of spins inclined at a small angle φ_{ij} to each other :

$$w_{ex} = JS^2 \varphi_{ij}^2 \quad (5)$$

In contrast with metals, the situation in ionic crystals (e.g., ferrites and cobaltites) is very often such that the nearest neighbours of a metallic ion are anions. For instance, planes of metallic ions are separated from one another by planes of oxygen anions, which partially obstruct the direct link between the metallic ions. Néel (NE48) has suggested that an indirect exchange mechanism occurs in which the anions act as intermediary. This mechanism had already been studied by Kramers (KR30). Variations have since been developed, including the "superexchange" (Anderson), (1AN50, 2AN50, AN53, AN59), "indirect exchange" (Slater), the "double exchange" (Zener) (ZE51), and "semicovalent exchange" (Goodenough) (1GO55, 2GO55) mechanisms.

A study of these exchange mechanisms is of fundamental importance for the understanding of magnetism in non-metallic compounds. This can only be achieved by investigating the topology and symmetry of the surrounding ions in actual crystal structures. Part 2 of the present paper will be largely devoted to such a study.

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WHY COBALT FOR MAGNETIC DEVELOPMENT

(PART ONE — Continued)

ENERGIES PARTAKING IN THE MAGNETIZATION PROCESSES

B. ANISOTROPY ENERGY

An examination of the magnetization curves of ferromagnetic single crystals reveals pronounced anisotropy of magnetic properties : there are directions of easy and directions of difficult magnetization. If the single crystal specimens contain only very small amounts of impurities, and if internal stresses are avoided, domain wall movements are completed in virtually zero fields and magnetization proceeds by rotation only. The forces opposing this rotation are those due to crystal anisotropy; it is thus easier to rotate the spins in some directions than in others.

There are few satisfactory theories of crystal anisotropy; expressions based simply on symmetry considerations, as first proposed by Akulov (AK31) are still often used.

1. Cubic symmetry

The following substances represent this type of symmetry : iron, cobalt (above $\sim 450^\circ\text{C}$), and nickel; the monoxides of iron, cobalt, and nickel; perovskites (e.g. CoBaO_3) and spinels (e.g. Co-ferrite).

The anisotropy energy density is given by :

$$f_K = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 + \dots \quad (6)$$

where α_i are the direction cosines of the saturation magnetization M_s with respect to the crystal axes. In the absence of magneto-elastic and magneto-static energy, the directions of minimum anisotropy energy are those of easy magnetization. Depending upon the signs and values of K_1 and K_2 , different cases may be distinguished (BO36) (Table II and Fig. 2).

Table II shows that the directions of easy magnetization may be the cube edges, [100], the

TABLE II. — RELATIONSHIP BETWEEN ANISOTROPY CONSTANTS AND DIRECTIONS OF EASY MAGNETIZATION FOR CUBIC SYMMETRY

Condition for K_1	Conditions for K_1 and K_2		Preferred Direction θ_0	Hard Direction θ_1
$K_1 > 0$	$9K_1 + K_2 > 0$	$9K_1 + 4K_2 > 0$	[100]	[111]
		$9K_1 + 4K_2 < 0$	[111]	[110]
$K_1 < 0$	$9K_1 + K_2 < 0$	$9K_1 + 4K_2 > 0$	[110]	[100]
		$9K_1 + 4K_2 < 0$	[111]	[110]

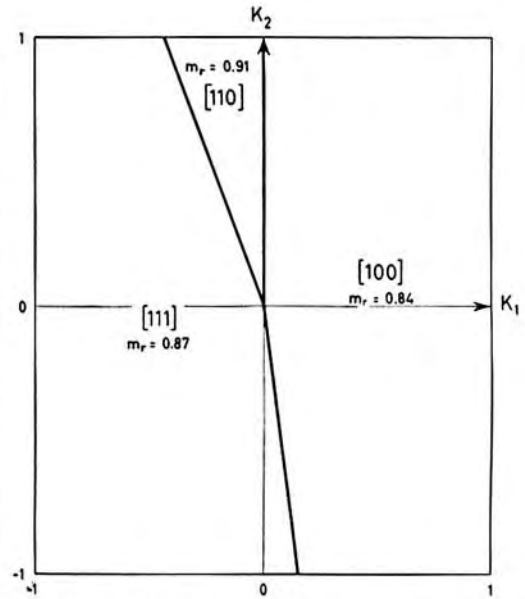


Fig. 2. — Anisotropy constants and preferred directions in the case of cubic symmetry ($m_r = M_r/M_s$).

TABLE III. — ANISOTROPY CONSTANTS FOR Fe, Co (cubic), AND Ni

Substance	T (°K)	$\frac{T}{T_c}$	K_1 (10^4 J/m ³)	K_2 (10^4 J/m ³)	Reference
Fe	575	0.55	~ 2.1	~ 1.9	BO51
Co	773	0.55	- 2.3	- 4.3	SU54
Ni	348	0.55	~ - 0.15	~ 0.4	BO51

TABLE IV. — FIRST ANISOTROPY CONSTANTS OF Fe, Co, AND Ni FERRITES

Ferrite	T (°K)	$\frac{T}{T_c}$	K_1 (10^4 J/m ³)	Reference
Fe ₃ O ₄	300	0.35	-1.1 25 to 40	BI50
CoFe ₂ O ₄	300	0.38		BO55, TA55
NiFe ₂ O ₄	300	0.35	-0.6	GA50, YA50

body diagonals of the cube, [111], or the face diagonals of the cube, [110]. In a transformation from preferred [100]-axes to preferred [111]-axes, the sign of $9K_1 + K_2$ must change. When the preferential directions turn from [111] to [110], $9K_1 + 4K_2$ changes from negative to positive. Finally, when they transform from [110] to [100], the first anisotropy constant K_1 of necessity passes through zero. Nickel illustrates the three cases: up to 80 °C, its preferred directions are the body diagonals; from 80 °C to 100 °C, they are the face diagonals; and above 100 °C, they become the cube edges.

Cobalt possesses a cubic symmetry at temperatures above ~450 °C. A comparison of iron, cubic cobalt, and nickel at the same reduced temperature, T/T_c , shows that the anisotropy constants of cubic cobalt are greater than those of the two other metals, though of the same order of magnitude (Table III).

Most ferrites have negative first anisotropy constants. Bozorth (BO55) has shown that cobalt-ferrite is different in that its first anisotropy constant is positive; furthermore, the absolute value of this constant is greater by at least a factor of 10 than that of nickel- or iron-ferrite (Table IV). As a consequence, even small additions of cobalt ferrite to other ferrites lead to a compensation of the crystal anisotropy constant K_1 . Figure 3 illustrates this effect in the case of magnetite (Fe₃O₄). Since the second order anisotropy constant K_2 is usually

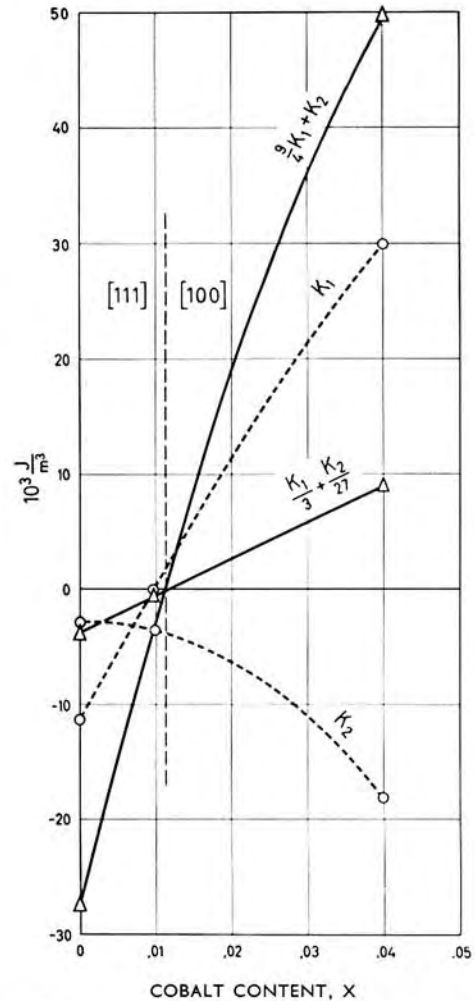


Fig. 3. — Anisotropy constants of $Co_xFe_{3-x}O_4$ at 300 °K, as a function of the cobalt content, x . (BI57).

smaller than K_1 , the compensation of K_1 is sufficient to lower to a great extent the total anisotropy energy. As will be shown later, a low crystal anisotropy is one of the prerequisites for soft magnetic materials; the latter, when based on ferrites, may thus often benefit from small additions of cobalt ferrites. On the contrary, substances with a high anisotropy energy are desirable in permanent magnet materials, which must have a large coercivity; therefore, relatively large amounts of cobalt may be used to advantage in permanent-magnet ferrites.

The effect of magnetic annealing on the anisotropy energy of materials must finally be mentioned. Magnetic annealing consists in heating the magnetic material above its Curie temperature and cooling it in a magnetic field. After cooling, the domains are found to have a preferred direction of magnetization parallel to the field. Magnetic annealing

TABLE V. — RELATIONS BETWEEN ANISOTROPY CONSTANTS AND DIRECTIONS OF EASY MAGNETIZATION FOR HEXAGONAL (CYLINDRICAL) SYMMETRY

Condition for K_1	Conditions for K_1 and K_2		Preferred Direction θ_0	Hard Direction θ_1
$K_1 > 0$	$K_1 + 2K_2 > 0$	$K_1 + K_2 > 0$	0	$\frac{\pi}{2}$
	$K_1 + 2K_2 < 0$			$\arcsin \sqrt{\frac{-K_1}{2K_2}}$
$K_1 < 0$	$K_1 + 2K_2 < 0$	$K_1 + K_2 < 0$	$\frac{\pi}{2}$	0
	$K_1 + 2K_2 > 0$			$\arcsin \sqrt{\frac{-K_1}{2K_2}}$
				$\frac{\pi}{2}$

results therefore in superimposing, on the normal anisotropy, a uniaxial anisotropy that can be expressed as follows :

$$f_u = K_u \sin^2(\theta - \theta_T) \quad (7)$$

in which θ_T is the angle between the annealing field and the nearest preferred crystal axis, θ the angle between this direction and the saturation magnetization M_s , and K_u a measure of the annealing effect. In most cases, the greater the (normal) crystal anisotropy, the greater is the effect of magnetic annealing. The addition of a small amount of cobalt ferrite to other ferrites often suffices to make them respond to magnetic annealing. In the case of the solid solutions of cobalt ferrite and magnetite already mentioned (Fig. 3), it is interesting to note that the maximum value of the anisotropy constant K_1 coincides approximately with the maximum of the effect due to annealing as measured by K_u (see Fig. 7).

2. Hexagonal symmetry

Among the substances having this symmetry are cobalt and the mixed oxides known under the commercial names of ferroxdure and ferroxplana, which have a magnetoplumbite structure.

The energy density of anisotropy of a hexagonal crystal is conveniently expressed by the formula :

$$f_K = K_1 \sin^2\theta + K_2 \sin^4\theta + K_3 \sin^6\theta (1 + K'_3 \cos 6\varphi) + \dots \quad (8)$$

where θ is the angle between the magnetization and the hexagonal axis [00.1]; the angle φ is measured in the (00.1) plane between the projection of the

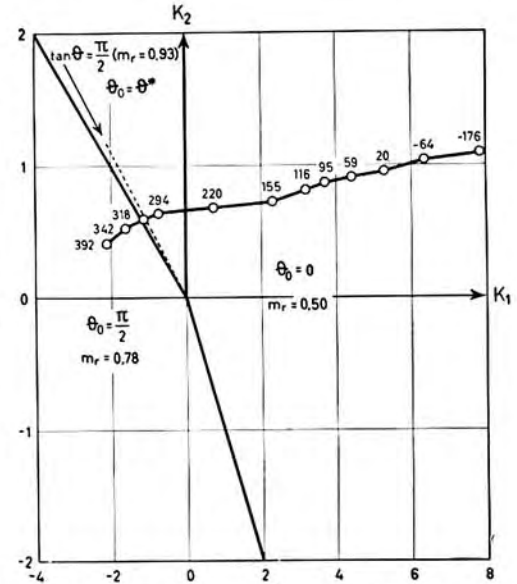


Fig. 4. — Anisotropy constants, in 10^5 J/m^3 , and preferred directions, θ_0 , in the case of hexagonal (cylindrical) symmetry.

$\theta^* = \arcsin \sqrt{-K_1/2K_2}$. The curve illustrates the thermal variation of K_1 and K_2 for cobalt (SU54). The figures on the curve indicate the temperatures in $^\circ\text{C}$. ($m_r = M_r/M_s$).

magnetization and a preferred direction in this plane. The third term thus contains the anisotropy in the basal plane. At room temperature, K_1 is usually of the order of 10^5 J/m^3 , K_2 varies from zero to 10^5 J/m^3 depending on the substance, and K_3 and K'_3 are always very small. For example, the $K_3 \cdot K'_3$ values for the compounds $\text{Co}_{1.92}\text{Fe}_{0.08}\text{Z}$ and Co_2Y (see Fig. 6) are 12.2 J/m^3 and 80.0 J/m^3 , respectively. The third term in equation (8) may therefore be neglected in most cases, but the specific hexagonal character is then ignored; the remaining terms merely express a cylindrical symmetry.

Here again, the directions of minimum anisotropy energy are, in the absence of major magneto-static and magneto-elastic contributions, directions of easy magnetization. Depending upon the signs and values of K_1 and K_2 various cases may be distinguished (SM59) (Table V and Fig. 4). The directions of easy magnetization may be either parallel or perpendicular to the hexagonal axis, or they may lie on a cone having its axis along the [00.1] direction and a semi-aperture θ^* equal to $\arcsin \sqrt{-\frac{K_1}{2K_2}}$. In a transformation from a preferential axis to a preferential plane (and vice versa), the sign of $K_1 + K_2$ must change. When

a preferential axis transforms into a preferential cone, K_1 changes from positive to negative. Finally, when a preferential cone transforms into a preferential plane, the sum, $K_1 + 2K_2$, passes through zero.

Hexagonal cobalt illustrates all three cases : up to 250 °C, it has a preferential direction; from 250 °C to 320 °C, its preferred directions lie on a cone; from 320 °C up to the temperature of transformation to cubic symmetry, it has a preferential plane. At about 300 °C, the relative retentivity, m_r , has a maximum value of 0.93 (Fig. 4). It would be of interest to examine the influence of small additions of alloying elements on the change with temperature of the anisotropy constants of hexagonal cobalt; in particular, it would be worth while trying to obtain this maximum value at room temperature (AS59).

In Table VI, the values of the first anisotropy constants of hexagonal cobalt at various temperatures are compared with those of cubic iron and nickel.

This table suggests that the anisotropy constants of hexagonal crystals are higher than those of cubic crystals. This would be expected from theory.

This impression is further reinforced by considering the first anisotropy constants of hexagonal ferrites (commercial name, ferroxdure). $BaFe_{12}O_{19}$ has an anisotropy constant $K_1 = 3.2 \times 10^5 \text{ J/m}^3$; the anisotropy constant of $BaFe_{18}O_{27}$ is $K_1 = 3.0 \times 10^5 \text{ J/m}^3$ (WE52). Comparison with the data of Table IV shows that these values are greater by one order of magnitude than those of the (cubic) ferrites of iron and nickel. The only cubic ferrite having an anisotropy of the same order is cobalt ferrite. These findings underline the distinctive character of most cobalt compounds, i.e. their great anisotropy. This peculiarity can be traced to the behaviour of Co^{2+} ions on slightly distorted octahedral sites; great anisotropy should be found in all compounds containing cobalt-ions of this kind.

As is the case for the spinels discussed above, cobalt can influence to a great extent the crystal

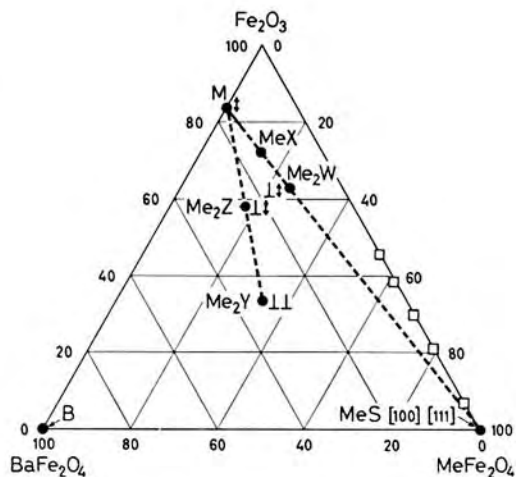
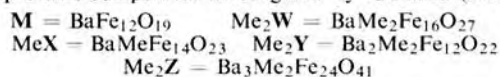


Fig. 5. — The B-S- Fe_2O_3 ternary system.

↑ and ↓ indicate, respectively, a plane and an axis of easy magnetization; the left-hand sign applies when $Me = Co^{II}$; the right-hand sign applies when $Me = Fe^{II}, Ni, Mg, Mn$ or Zn . Similarly [100] and [111] indicate the directions of easy magnetization in the case of spinels.

□ represents compounds investigated by Guillard (GU53).



anisotropy of hexagonal crystals, as well as the many properties which depend upon it. Measurements on magnetic compounds with a hexagonal structure were started later than those on spinels; though an increasing number of investigations are in progress, the results are as yet neither sufficient nor explicit enough to allow a systematic survey to be made. Some relevant information on mixed oxides of hexagonal structure is reported hereafter.

Most of the oxides with hexagonal structure that have been investigated may be located in a triangle at the vertices of which are the compounds $BaFe_2O_4$ (noted as B), $MeFe_2O_4$ (noted as MeS), and Fe_2O_3 (see Fig. 5) (JO57). The compound B is paramagnetic and has a hexagonal structure. Fe_2O_3 (or α -hematite) is an antiferromagnetic crystal showing weak, parasitic ferrimagnetism. The

TABLE VI. — ANISOTROPY CONSTANT K_1 FOR Fe, HEXAGONAL Co, AND Ni AT VARIOUS TEMPERATURES

Substance	T (°K)	$\frac{T}{T_c}$	K_1 (10^4 J/m^3)	T (°K)	$\frac{T}{T_c}$	K_1 (10^4 J/m^3)	T (°K)	$\frac{T}{T_c}$	K_1 (10^4 J/m^3)	Reference
Fe	293	0.28	4.6	217	0.21	5.0	473	0.45	2.9	BO51
Co	398	0.28	32	293	0.21	53	567	0.40	—6.8	SU54
Ni	173	0.28	—3.0	131	0.21	—4.0	293	0.46	—0.51	BO51

compounds MeS have a spinel structure; their magnetic properties depend on the divalent metal Me . In the binary system $\text{CoS-Fe}_2\text{O}_3$, a number of compounds have been investigated (GU53). They all have a spinel structure. It is interesting to observe that in the binary system $\text{B-Fe}_2\text{O}_3$, there is one ferrimagnetic compound, viz. $\text{BaFe}_{12}\text{O}_{19}$ (noted as **M**), which has a hexagonal magnetoplumbite structure. Inside the triangle two hexagonal compounds are found in the "binary" system M-MeS : $\text{BaMeFe}_{14}\text{O}_{23}$ (noted as MeX) and $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$ (noted as Me_2W). The centre of the triangle corresponds to the compound $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ (noted as Me_2Y). Finally, in the "binary" system $\text{M-Me}_2\text{Y}$, another compound can be identified, viz. $\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$ (noted as Me_2Z). These last two compounds also have a hexagonal structure.

The directions of easy magnetization shown in Figure 5 illustrate the exceptional position which cobalt compounds hold among magnetic compounds with a hexagonal structure: the compounds Me_2W and Me_2Z have a plane of easy magnetization when $\text{Me} = \text{Co}$; they have a preferential axis for the other divalent metals. It thus appears feasible, in the case of hexagonal symmetry, to control the crystal anisotropy, and the properties depending upon it, by using solid solutions of cobalt compounds with compounds of other divalent metals. As an example, the solid solutions $\text{Co}_x\text{Zn}_{2-x}\text{Z}$ (i.e. $\text{Ba}_3\text{Co}_x\text{Zn}_{2-x}\text{Fe}_{24}\text{O}_{41}$) may be mentioned. For $0 \leq x < 0.5$, there exists a preferential axis of magnetization; for $0.5 < x \leq 2.0$, there is a preferential plane. Hence, at $x = 0.5$, the sum $K_1 + K_2$, changes sign: it is positive for $x < 0.5$ and negative for $x > 0.5$. This effect of cobalt is analogous with that, already mentioned, of cobalt-ferrite additions to other ferrites.

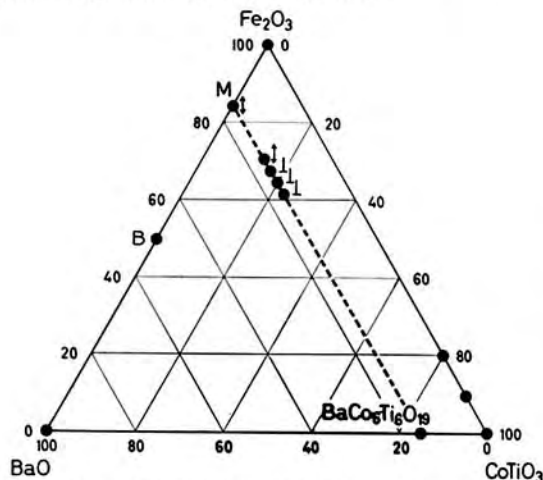


Fig. 6. — The $\text{BaO-Fe}_2\text{O}_3\text{-CoTiO}_3$ ternary system. \uparrow and \downarrow indicate, respectively, a plane and an axis of easy magnetization. **B** = BaFe_2O_4 **M** = $\text{BaFe}_{12}\text{O}_{19}$

Another interesting possibility is to replace the trivalent iron ions in the compounds **M** ($\text{BaFe}^{3+}_{12}\text{O}_{19}$) by a combination of divalent and tetravalent metals, for example $\text{Co}^{2+} + \text{Ti}^{4+}$ (GO59). This leads to the study of the ternary system $\text{BaO-Fe}_2\text{O}_3\text{-CoTiO}_3$ (Fig. 6) in which BaO is a non-magnetic compound of rock salt structure, and CoTiO_3 an antiferromagnetic with the hexagonal ilmenite structure. The binary system $\text{BaO-Fe}_2\text{O}_3$ contains the non-magnetic compound **B** and the magnetic compound **M**, both of which have already been encountered in the system depicted in Figure 5. The system BaO-CoTiO_3 does not seem to have been investigated. The system $\text{Fe}_2\text{O}_3\text{-CoTiO}_3$, however, has received some attention (NA59). Although the constituents have no resultant magnetic moment, the solid solutions rich in CoTiO_3 are ferrimagnetic, with a maximum magnetic moment at about 80 % CoTiO_3 . In the "binary" system, $\text{BaCo}_x\text{Ti}_x\text{Fe}_{12-x}\text{O}_{19}$, compounds with $0 \leq x \leq 1.9$ and $x = 6$ have been prepared. For $x = 1.0$, there is a preferential axis of magnetization at all temperatures; for $x = 1.2, 1.4, \text{ and } 1.6$, there exists a plane of easy magnetization at room temperature (GO59) (Fig. 6).

Ferromagnetic and antiferromagnetic compounds can form numerous solid solutions, few of which have been mentioned. By a suitable choice of the components, a given combination of magnetic properties (crystal anisotropy, saturation magnetization, Curie temperature, etc.) can theoretically be obtained. In order to predict with accuracy the combinations that can be achieved in practice, it is necessary to have a deeper insight into the crystal structure of the compounds entering in a solid solution and to determine the stability of a given ion in a particular type of symmetry. The crystal field theory should provide a sound basis for such a study.

Before ending this section, it may prove useful to say a few words on the technical implications of the various types of crystal anisotropy. Materials with one axis of easy magnetization are magnetically hard and suitable for permanent magnets. Materials with a plane of easy magnetization are magnetically soft and the drop in permeability occurs only at frequencies of 500 to 1000 Hz; their initial permeability, however, is not very high. Finally, in materials with a cone of easy magnetization, the relative retentivity, $m_r = M_r/M_s$, can be very high.

3. Other symmetries

Tetragonal or orthorhombic symmetry may occur in magnetic cobalt compounds as a consequence of deformations due to spontaneous inter-

actions or to magnetic annealing. The expressions of the anisotropy energy density are (MA54) :
for tetragonal symmetry :

$$f_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^4 \theta \sin^2 \varphi \cos^2 \varphi + \dots \quad (9)$$

and for orthorhombic symmetry :

$$f_K = (K_1 \cos^2 \varphi + K_2 \sin^2 \varphi) \sin^2 \theta + (K_3 \cos^4 \varphi + K_4 \sin^2 \varphi \cos^2 \varphi + K_5 \sin^4 \varphi) \sin^4 \theta + (K_6 \cos^2 \varphi + K_7 \sin^2 \varphi) \sin^2 \theta \cos^2 \theta + \dots \quad (10)$$

In both equations, φ and θ are the spherical coordinates of the direction of magnetization. These expressions are not the most general ones; it is assumed that there is an easy direction of magnetization and that it lies along the z-axis.

C. MAGNETO-ELASTIC ENERGY

The crystal-anisotropy energy discussed in the preceding section is that of a crystal which has not been permitted to deform under the influence of either magnetostriction or externally applied stresses. Such a state cannot exist during measurements, since, if no external stress is applied, the crystal is deformed by magnetostriction and, if external stresses are applied, the resulting deformation will not, as a rule, compensate exactly the magnetostrictive deformation. The anisotropy constants of single crystals are therefore always measured on unstressed, deformed substances; they are called "effective anisotropy constants" (K). The constants for undeformed crystals, often designated "intrinsic anisotropy constants" (k), must be calculated from measured values by means of formulae, an example of which is given below (BA57, LE55). In the preceding section, the notation K may remain unchanged where numerical values are concerned, but elsewhere, it should be replaced by k .

Actual polycrystalline materials are both stressed and deformed. They present a complicated problem because two closely connected effects must be taken into account; the first is that of spontaneous, magnetostrictive deformation on effective anisotropy constants, the second, that of external stresses on magnetic properties.

1. Effective anisotropy and magnetostriction

The effective anisotropy constants K depend on the intrinsic anisotropy constants k of the undeformed crystal, on the magnetostriction constants λ , and on the elastic moduli c ; in addition, a possible change of symmetry must also be taken into account. For instance, the effective anisotropy energy of an unstressed cubic crystal may be expressed (up to the fourth order of the direction cosines α_i of spontaneous magnetization) as :

$$f_K = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) \quad (11)$$

where :

$$K_1 = k_1 + \Delta K_1 \quad (12)$$

and :

$$\Delta K_1 = \frac{9}{4}(c_{11} - c_{12})\lambda_{100}^2 - 2c_{44}\lambda_{111}^2 \quad (13)$$

Here λ_{100} and λ_{111} are the saturation values of the longitudinal magnetostriction in the [100] and [111] directions respectively; c_{11} , c_{12} and c_{44} are the three elastic moduli of the cubic crystal.

It is of interest to outline briefly the derivation of the above equation, partly because some of the intermediate results will be of help in the subsequent discussion. For higher approximations, and also for other symmetries, the method will be essentially the same.

The four basic equations to start from are (eqns. 14 to 17) :

— The intrinsic anisotropy energy f_k of an undeformed cubic crystal up to the fourth power of the direction cosines α_i (see eqn. 6) :

$$f_k = k_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) \quad (14)$$

— The elastic energy f_{el} as given by the Hooke approximation :

$$f_{el} = \frac{1}{2} c_{11}(a_{11}^2 + a_{22}^2 + a_{33}^2) + c_{12}(a_{11}a_{22} + a_{22}a_{33} + a_{33}a_{11}) + 2c_{44}(a_{12}^2 + a_{23}^2 + a_{31}^2) \quad (15)$$

where the elastic moduli c_{11} , c_{12} and c_{44} are those measured in the absence of strain produced by magnetostriction or ionic ordering, or both, and a_{ij} are the components of the strain tensor.

— The energy f_m of coupling between the direction of magnetization (α_i) and the mechanical strain of the lattice (a_{ij}); the energy expresses the fact that the effective anisotropy energy depends on the strain. Consistently with the expressions used here for f_k and f_{el} , f_m should contain all terms up to the fourth power of the direction cosines α_i of spontaneous magnetization, and up to the second power of the components of the strain tensor. The terms $a_{ij} a_{kl}$ are the so-called morphic terms; they account for the fact that, as a result of spontaneous lattice distortion, the crystal loses its cubic symmetry; for pure cubic symmetry, these terms are zero. Usually, however, the following expression of more limited precision is used :

$$f_m = b_1(\alpha_1^2 a_{11} + \alpha_2^2 a_{22} + \alpha_3^2 a_{33}) + 2b_2(\alpha_1 \alpha_2 a_{12} + \alpha_2 \alpha_3 a_{23} + \alpha_3 \alpha_1 a_{31}) \quad (16)$$

where b_1 and b_2 are the magneto-elastic coupling constants. In this approximation, the symmetry of the undeformed state will of course be the same as that of the unstressed deformed state.

— The relation between the relative elongation $\delta l/l$ in a direction specified by the direction cosines β_i and the components of the strain tensor :

$$\lambda = \frac{\delta l}{l} = \sum_{i,j} \beta_i \beta_j a_{ij} \quad (17)$$

This is a purely mechanical equation, unless it is assumed that the a_{ij} depend in some way upon the direction (α_i) of spontaneous magnetization with respect to the crystal axes. Such a dependence can be established by determining the values of a_{ij} which minimize the effective anisotropy energy :

$$f_K = f_k + f_{el} + f_m \quad (18)$$

These equilibrium values of the a_{ij} are :

$$\left. \begin{aligned} a_{ii} &= b_1 \frac{c_{12} - (c_{11} + 2c_{12})\alpha_i^2}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \\ a_{ij} &= -b_2 \frac{\alpha_i \alpha_j}{2c_{44}} \quad (i \neq j) \end{aligned} \right\} \quad (19)$$

In order to relate the magneto-elastic coupling coefficients b_1 and b_2 to the magnetostriction constants λ_{100} and λ_{111} , the expressions (19) are introduced into equation (17), and the resulting equation normalized so that $\lambda = 0$ for a demagnetized crystal with a random distribution of domains; after calculating the longitudinal saturation magnetostriction λ_{100} ($\alpha_1 = \beta_1 = 1, \alpha_2 = \alpha_3 = \beta_2 = \beta_3 = 0$) and λ_{111} ($\alpha_i = \beta_i = \frac{1}{\sqrt{3}}$), the following expressions are obtained :

$$\lambda = \frac{3}{2} \lambda_{100} (\alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2 - \frac{1}{3}) + 3\lambda_{111} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1) \quad (20)$$

with :

$$\lambda_{100} = -\frac{2}{3} \frac{b_1}{c_{11} - c_{12}} \quad (21)$$

et

$$\lambda_{111} = -\frac{1}{3} \frac{b_2}{c_{44}}$$

Insertion of expressions (19) and (21) into equation (18) leads finally to the equations (11), (12) and (13).

2. Stress energy

When exterior stresses are applied to the crystal, a further term, f_s , must be added to the (density of free) energy f_K in equation (18). The stress energy density has the general form :

$$f_s = \sum_{ij} \sigma_{ij} A_{ij} \quad (22)$$

where σ_{ij} is the stress tensor. A_{ij} is the equilibrium value of the tensor of strain due to both magnetostriction (a_{ij}) and exterior stresses (e_{ij}); its general expression is thus :

$$A_{ij} = a_{ij} + e_{ij} \quad (23)$$

In the case of the cubic symmetry and uniform compression σ in a direction specified by the direction cosines γ_i , the components of the stress tensor are :

$$\sigma_{ij} = -\sigma \gamma_i \gamma_j \quad (24)$$

and the stress energy is found to be :

$$f_s = \frac{3}{2} \sigma \left[\lambda_{100} \sum_i \alpha_i^2 \gamma_i^2 + 2\lambda_{111} \sum_{i>j} \alpha_i \alpha_j \gamma_i \gamma_j \right] \quad (25)$$

It is of interest to compare equations (20) and (25). The first gives the relative elongation λ in a direction β_i , when the spontaneous magnetization has a direction α_i ; the second expresses the stress energy for an applied stress of direction γ_i and spontaneous magnetization of direction α_i . From the similarity in form of the right-hand members of both equations, it can be seen that f_s/σ is essentially the relative elongation in the direction of the applied compression σ when the direction of spontaneous magnetization is α_i :

$$f_s = \sigma \left[\lambda(\alpha) + \frac{1}{2} \lambda_{100} \right] \quad (\beta_i = \gamma_i) \quad (26)$$

The total energy of a cubic crystal under an applied uniform compression can thus be expressed by :

$$f = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + \frac{3}{2} \sigma \left[\lambda_{100} (\alpha_1^2 \gamma_1^2 + \alpha_2^2 \gamma_2^2 + \alpha_3^2 \gamma_3^2) + 2\lambda_{111} (\alpha_1 \alpha_2 \gamma_1 \gamma_2 + \alpha_2 \alpha_3 \gamma_2 \gamma_3 + \alpha_3 \alpha_1 \gamma_3 \gamma_1) \right] \quad (27)$$

In order to simplify the discussion, the magnetostriction is often assumed to be isotropic, although this supposition leads to poor quantitative agreement with experimental results.

In this case, since $\lambda_{100} = \lambda_{111} = \lambda_s$, the value of f_s is :

$$f_s = \frac{3}{2} \sigma \lambda_s \cos^2 \Psi' \quad (28)$$

where Ψ' is the angle between the direction of spontaneous magnetization and that of the applied compression :

$$\cos \Psi' = (\alpha_1 \gamma_1 + \alpha_2 \gamma_2 + \alpha_3 \gamma_3) \quad (29)$$

In evaluations based on the domain theory, even the anisotropic character of the total energy density, f , stemming from crystal anisotropy, elasticity, magnetostriction and external stresses is often neglected. The so-called anisotropy constant K' can then be expressed by :

$$K' = iK_1 + j\lambda_s \sigma \quad (30)$$

where i and j are numerical factors of the order of unity.

When discussing the directions of easy magnetization in the presence of anisotropy, magnetostriction and external stresses, it is necessary, however, to come back to equation (27). The problem becomes extremely complicated in the general case of arbitrary values for the three factors and its discussion lies outside the scope of the present article. The following qualitative conclusions can however be advanced :

— In the case of predominant crystal anisotropy ($f_K > f_s$), the directions of easy magnetization are essentially determined by crystal anisotropy; the stress merely favours one of these directions at the expense of the others.

TABLE VII. — MAGNETOSTRICTION CONSTANTS OF SOME CUBIC MATERIALS AT ROOM TEMPERATURE

Substance	$10^5 \lambda_{100}$	$10^5 \lambda_{111}$	$10^5 \bar{\lambda}_s$	$10^5 \lambda_s$	Reference
Fe ₃ O ₄	-1.94	+8.64	+4.41	+4.0	CA53
Co _{0.8} Fe _{2.2} O ₄	-59.0	+12.0	-16.4	—	BO55
CoFe ₂ O ₄	-51.5	+4.5	-17.9	-11.0	BO52
Ni _{0.8} Fe _{2.2} O ₄	-3.6	-0.4	-1.7	—	BO52
Fe	-1.95	-1.88	-0.35	—	cited after BA57
Ni	-4.6	-2.5	-3.3	—	cited after BA57
70 Co, 30 Fe	—	—	—	-13.0*	NE50

* Specimen oriented by drastic cold work.

— When the anisotropy constant K_1 is small compared to $\lambda_{100}\sigma$ and $\lambda_{111}\sigma$, the preferential directions are essentially determined by the relative values of the magnetostriction constants.

— When, the anisotropy constant still being negligible, the magnetostriction is isotropic, the directions of easy magnetization are determined by the direction of the applied stress. This case is easy to expound. In fact, the total energy is then given by expression (28) :

$$f = \frac{3}{2} \sigma \lambda_s \cos^2 \Psi' \quad (31)$$

If $\sigma \lambda_s$ is positive, as for cobalt ferrite under tension, or iron ferrite under compression, the directions of easy magnetization are situated in a plane perpendicular to the stress axis. Such materials therefore behave as crystals with preferential planes. If, on the contrary, $\sigma \lambda_s$ is negative, as for cobalt ferrite under compression, or iron ferrite under tension, the domain magnetization vectors orient themselves parallel to the stress axis. The behaviour of such substances is similar to that of a uniaxial crystal; the hysteresis loop becomes rectangular.

3. Magnetostriction constants

In concluding this section, some numerical values of magnetostriction constants will be examined. Table VII gives characteristic values for cubic materials. λ_{100} and λ_{111} are determined on single crystals, $\bar{\lambda}_s$ is the mean value calculated from the identity :

$$\bar{\lambda}_s \equiv \frac{2}{5} \lambda_{100} + \frac{3}{5} \lambda_{111} \quad (32)$$

and λ_s is obtained from measurements on polycrystalline materials.

The 70Co-30Fe alloy has, when cold-worked, an exceptionally high magnetostriction as compared with that of other alloys; however, the values of

λ_{100} for the cobalt ferrites CoFe₂O₄ and Co_{0.8}Fe_{2.2}O₄ are much higher still. This exceptionally high magnetostriction in cobalt ferrites is further enhanced by heat treatment in a strong magnetic field; values higher than 8.10^{-4} have been observed for Co_{0.8}Fe_{2.2}O₄ (BO55).

Crystal anisotropy, magnetostriction, and response to heat treatment seem to be generally related to one another. This is strikingly suggested by the curves of Figure 7, which represent, for different compositions of Co_xFe_{3-x}O₄ solid solutions, the corresponding values of the anisotropy constant K_1 , the magnetostriction constants λ_{100} and λ_{111} and

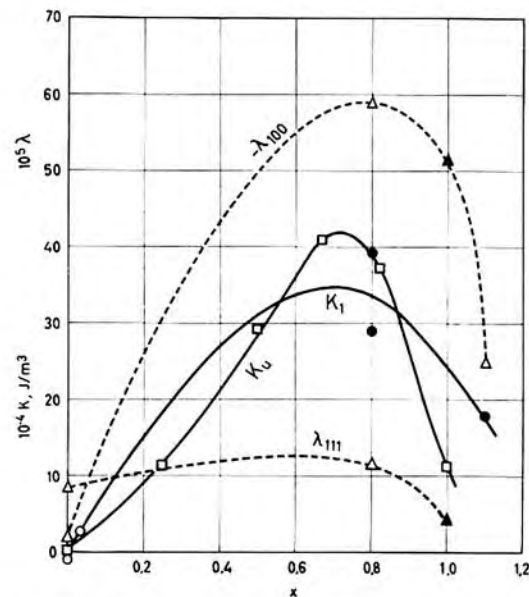


Fig. 7. — Dependence of cubic anisotropy (K_1), anneal-induced anisotropy (K_u), and magnetostriction (λ_{100} and λ_{111}) on the cobalt content in Co_xFe_{3-x}O₄ solid solutions. K_u : □ BO55. K_1 : ○ B157; ● BO55. λ : ▲ BO52; △ BO55

the response to magnetic anneal as measured by the constant of uniaxial anisotropy K_u defined in equation (7). All these constants seem to reach a maximum in the region of 75 mole % of cobalt. This result, inspiring as it may be, is however based on too few experimental data to be accepted without further experimental confirmation.

D. MAGNETOSTATIC ENERGY

The types of energy discussed so far do not exhaust the list of energies partaking in the processes of magnetization. At least two kinds of energy, both of the greatest practical importance, must still be mentioned. These are: the self-energy of a permanent magnet in its own field (demagnetizing, or shape anisotropy, energy), and the energy of interaction of such a magnet with an external field (field energy).

1. Shape anisotropy energy

The demagnetizing field of a permanent magnet stems from inhomogeneities of magnetization which may be of two kinds. Firstly, continuous variations of saturation magnetization inside a body give rise to "magnetic space charges", q :

$$q = \text{Div } \vec{M}_s \quad (33)$$

which are the sources of a so-called internal field. Secondly, the "surface pole densities", p , found at surfaces of discontinuity of saturation magnetization also act as sources:

$$p = \text{Div } \vec{M}_s - n(\vec{M}_{s2} - \vec{M}_{s1}) \quad (34)$$

\vec{n} is the vector normal to the surface of discontinuity pointing from medium 1 to medium 2, and \vec{M}_{s1} and \vec{M}_{s2} are the vectors of the saturation magnetization in these media.

Discontinuities of saturation magnetization occur not only at the external surfaces of the specimen, but also at internal surfaces constituted by grain boundaries, inclusions, and voids. When an external field is applied, the internal field opposes it, i.e. partial demagnetization occurs owing to the magnetic charges q and surface poles p . Hence

the names of "demagnetizing field" and "demagnetization energy". However, since this demagnetization energy also depends on the shape of the surfaces of discontinuity and is generally anisotropic, the name of "shape anisotropy energy" is also justified.

It is very difficult to calculate accurately the demagnetization energy, except for some very simple models. In the case of an isolated, homogeneous ellipsoid, the demagnetization energy is:

$$f_d = \frac{1}{2\mu_0} M_s^2 (N_1 \alpha_1^2 + N_2 \alpha_2^2 + N_3 \alpha_3^2) \quad (35)$$

where α_i are the direction cosines of spontaneous magnetization with respect to the axes of the ellipsoid, N_i the demagnetization factors along the three axes of the ellipsoid, and μ_0 the permeability in vacuo; the N_i factors obey the relation:

$$N_1 + N_2 + N_3 = 1 \quad (36)$$

Three limiting cases are of interest:

— the long, thin needle:

$$N_1 = N_2 = \frac{1}{2}, \quad N_3 = 0$$

— the large, thin plate:

$$N_1 = N_2 = 0, \quad N_3 = 1$$

— the sphere:

$$N_1 = N_2 = N_3 = \frac{1}{3}$$

Equation (35) implies that the shape anisotropy depends on crystal properties (through the saturation magnetization M_s) and on structure properties (through the demagnetization factors N_i).

The demagnetization energy, being reduced by the presence of domains, is responsible for their formation. Thus, if a substance is to contain large domains, its demagnetization energy should be low as compared with the other types of energies. It should be recalled here that, in most sintered ferromagnetics, the demagnetization energy is very high.

2. Field energy

The energy density of interaction of a permanent magnet of saturation magnetization M_s with an external field \vec{H} is:

$$f_e = -\vec{M}_s \cdot \vec{H} \quad (37)$$

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WHY COBALT FOR MAGNETIC DEVELOPMENT *

(PART ONE — Concluded)

WALLS

The mechanisms put forward to explain the magnetization curve will now be reviewed. In the present section, the following topics will be discussed: the energy stored in the walls, the energy necessary to move them and, finally, the conditions governing the generation of new walls.

A. WALL ENERGY

In order to diminish the demagnetization energy, it is energetically favourable for a crystal to split up into domains whose magnetization vectors point in different preferential directions. However, since energy is stored in the separating walls, there is a limit to the number of domains which can appear. This limit is reached when the sum of the two energies in question is a minimum.

The amount of energy stored in a wall can be calculated starting from the exchange energy associated with a pair of spins making a small angle φ (eqn. 5):

$$W_{ex} = JS^2\varphi^2$$

In a row of $(N + 1)$ spins, where the total change φ_0 occurs in N equal steps, the total exchange energy is:

$$W_{ex} = JS^2 \frac{\varphi_0^2}{N} \quad (38)$$

If 'a' is the lattice constant, there are $1/a^2$ such rows per unit wall area, so that, for a total change $\varphi_0 = \pi$ (180° wall), the exchange energy per unit surface will be:

$$S_{ex} = \frac{\pi^2 JS^2}{Na^2} \quad (39)$$

S_{ex} is obviously a minimum for a wall of infinite thickness. In such a wall, however, the anisotropy energy becomes infinite, since its value per unit

* This is the last instalment of the first part of this article, entitled "Magnetic Properties, Technical Parameters and the Influence of Cobalt". The first two instalments were published in *Cobalt*, No. 7, June 1960, pp. 3-5, and No. 8, September 1960, pp. 30-38.

The second part, which is devoted to the determination of relations between the crystal structure and magnetic properties of cobalt compounds, is still in preparation. It will be published as soon as it becomes available.

wall surface is approximately expressed by:

$$S_{K'} = |K'| Na \quad (40)$$

where K' is the total anisotropy constant defined by equation (30). For the sake of clarity, K' will be written instead of $|K'|$ in the following formulae. The total wall energy per unit surface:

$$S_w = S_{ex} + S_{K'} \quad (41)$$

is a minimum for

$$N = \left(\frac{\pi^2 JS^2}{K' a^3} \right)^{1/2} \quad (42)$$

The corresponding wall thickness, d , is:

$$d = Na = \pi \left(\frac{A}{K'} \right)^{1/2} \quad (43)$$

where the exchange constant, A , is given by:

$$A = \frac{JS^2}{a} \quad (44)$$

For this thickness the exchange energy, S_{ex} , and the anisotropy energy, $S_{K'}$, are equal, and the wall energy per unit surface is:

$$S_w = 2\pi(AK')^{1/2} \quad (45)$$

From this rough evaluation it may be concluded that the wall thickness, d , is proportional to $\left(\frac{A}{K'} \right)^{1/2}$, the wall energy per unit surface, S_w , is proportional to $(AK')^{1/2}$, and the energy density in the wall, $\frac{S_w}{d}$, is proportional to K' .

B. WALL DISPLACEMENTS

Walls can be displaced by application of a magnetic field. The initial susceptibility, χ_i , is a measure of the forces opposed to small wall movements around the equilibrium positions. Mathematically, χ_i is inversely proportional to the smallest curvature of the energy-position curve at its minima:

$$\chi_i \sim \frac{d}{l^2} \cdot \frac{M_s^2}{\left[\left(\frac{\partial^2 S_w}{\partial x^2} \right) \text{ at min. of } S_w \right]_{\min.}} \quad (46)$$

where d is the wall thickness and l the distance between consecutive minima of S_w .

The coercive force H_c is a measure of the magnetic field needed to displace a wall from one minimum position to another. The coercive force will thus be determined essentially by the largest obstacle encountered in this displacement. This physical description is mathematically expressed by :

$$H_c \sim \frac{l}{d} \cdot \frac{1}{M_s} \left[\left(\frac{\partial S_w}{\partial x} \right)_{\max.} \right]_{\max.} \quad (47)$$

Thus :

$$\chi_i H_c \sim \frac{M_s}{l} \cdot \frac{\left[\left(\frac{\partial S_w}{\partial x} \right)_{\max.} \right]_{\max.}}{\left[\left(\frac{\partial^2 S_w}{\partial x^2} \right)_{\text{at min. of } S_w} \right]_{\min.}} \quad (48)$$

It is clear that, in a perfectly uniform material, the initial susceptibility would be infinite and the coercive force would be zero. In actual materials, χ_i and H_c are highly structure-dependent properties, because a domain wall will have different energies according to the position it occupies. The differences may be due, for instance, to stresses varying from place to place (K' depends on position) or to inclusions and voids which have not been taken into account in the previous evaluation of wall energy. The problem is now reduced to the evaluation of $S_w(x)$. Since it is impossible to give an exact and explicit expression for it, simplified models have been proposed; the values of H_c and χ_i deduced from three of these models will be given hereafter without much comment.

1. Strain model

In this model, investigated by Becker (BE30), Kondorsky (KO37) and Kersten (KE38), the specimen is submitted to strains which change from point to point, whereas the anisotropy constant K is uniform.

The coercive force H_c is expressed by :

$$H_c \sim \frac{\lambda_s \Delta \sigma}{M_s} p \quad (49)$$

where the dispersion factor, p , is defined by :

$$p = \frac{\frac{d}{l}}{1 + \left(\frac{d}{l} \right)^2} \quad (50)$$

λ_s is the saturation magnetostriction, M_s the saturation magnetization, d the thickness of the domain wall, $\Delta \sigma$ the amplitude of the stress variation, and l the length over which this variation occurs.

For $d \ll l$, formula (49) becomes :

$$H_c \sim \frac{\lambda_s \Delta \sigma}{M_s} \frac{d}{l} \sim \frac{\lambda_s \Delta \sigma}{M_s} \frac{1}{l} \sqrt{\frac{A}{K'}} \quad (51)$$

For $d \gg l$,

$$H_c \sim \frac{\lambda_s \Delta \sigma}{M_s} \frac{l}{d} \sim \frac{\lambda_s \Delta \sigma}{M_s} l \sqrt{\frac{K'}{A}} \quad (52)$$

Since the maximum value of p ($p_{\max} = 0.5$) is found for $l = d$,

$$(H_c)_{\max} \sim \frac{\lambda_s \Delta \sigma}{M_s} \quad (53)$$

In this case the expression of the initial susceptibility becomes

$$\chi_i \sim \frac{M_s^2}{\lambda_s \Delta \sigma}, \quad (54)$$

so that

$$\chi_i H_c \sim M_s \quad (55)$$

2. Inclusion model

This model is based on the fact that, when a wall intersects a non-magnetic inclusion, its surface — and hence its energy — are diminished. In the original form proposed by Kersten (KE43) it was assumed that inclusions of identical form were distributed on a cubic lattice (with lattice constant l).

Only the case of inclusions whose diameter D is large compared to the wall d ($d \ll D$) will be treated here. The wall energy $S_w(x)$ is then given by

$$S_w(x) = S_w \frac{l^2 - \pi^2 \left(\frac{D^2}{4} - x^2 \right)}{l^2} \text{ for } |x| \leq \frac{D}{2} \quad (56)$$

and the derivatives have the following values :

$$\frac{\partial S_w(x)}{\partial x} \sim \frac{S_w}{l^2} x, \quad \frac{\partial^2 S_w(x)}{\partial x^2} \sim \frac{S_w}{l^2}$$

Hence

$$H_c \sim \frac{S_w}{M_s} \frac{1}{d} v^{1/3} \sim \frac{K'}{M_s} v^{1/3}. \quad (57)$$

In this formula, v is the fraction of volume occupied by the inclusions

$$v = \frac{\pi}{6} \frac{D^3}{l^3}. \quad (58)$$

Under the same conditions

$$\chi_i \sim \frac{M_s^2 d}{S_w} \sim \frac{M_s^2}{K'} \quad (59)$$

so that

$$\chi_i H_c \sim v^{1/3} M_s \quad (60)$$

3. Influence of the demagnetization energy

Néel (INE46, 2NE46) has pointed out that the hypothesis of the regular distribution of inclusions leads to an over-estimation of the coercivity, and that it is not correct to neglect the demagnetization

energy associated with inclusions. Other authors (e.g. Kondorski and Goodenough) have elaborated on this idea (KO49).

For non-magnetic inclusions of fractional volume v , Néel derived the relation :

$$H_c = \frac{2K'v}{\pi M_s} \left(0.386 + \frac{1}{2} \ln \frac{2\pi M_s^2}{K'} \right) \quad (61)$$

For the contribution of grain boundaries to the coercivity, Goodenough (GO54) found :

$$H_c \simeq \frac{\pi}{6} M_s \langle (\cos \theta_1 - \cos \theta_2)^2 \rangle \quad (62)$$

where θ_1 and θ_2 are the (supposedly small) angles made by the spontaneous magnetization vectors M_s of neighbouring grains and the normal to their common boundary ; $\langle \rangle$ brackets indicate that average values must be used.

C. WALL GENERATION

When a specimen of a magnetic substance is saturated, the magnetization in each domain has the direction of the applied field. In such a specimen there are no domain walls. As the field is reduced, two processes may occur :

- rotation of the atomic moments
- generation of domain walls and appearance of domains with reverse magnetization.

The generation of walls will be briefly discussed.

It is possible to show that the field strength H_n necessary for the generation of a domain wall is that for which the free energies of the states before and after the creation of the new reverse domain are equal. The sign of H_n is defined in a manner such that when H_n is positive, magnetization is reduced from saturation M_s to remanence M_r by rotation only. When, at some places in the crystal, domains of reverse magnetization are generated before remanence is reached, H_n will be negative in these places. The contribution of these reverse domains lowers M_r . A prerequisite for materials with high retentivity is therefore that H_n should be positive throughout the substance.

Domains of reverse magnetization are generated at lattice imperfections. Of these, grain boundaries and lamellar precipitates are the most important. As an illustration, the equation giving the critical field strength for reverse domain generation at a grain boundary will be stated (GO54). The following assumptions are made :

- the grain boundaries are plane;
- the reverse domains generated are prolate ellipsoids ($e = \frac{r}{l} \ll 1$) of major semi-axis l and minor semi-axis r ;
- the domains intersect the grain boundaries periodically; on the average, once in an area D^2 ; the area of intersection is r^2 ; $b = \frac{D}{r}$.

Under these conditions :

$$H_n \simeq A_1 (A_2 S_w - p^2 L) \quad (63)$$

where :

$$p = M_s (\cos \theta_1 - \cos \theta_2) \quad (64)$$

$$A_1 = \frac{b^2}{4M_s l (\cos \alpha_1 + \cos \alpha_2)}$$

and

$$A_2 = \frac{9\pi}{2b^2 e}$$

In the above four formulae, p is the surface pole density; θ_1 and θ_2 are the angles made by the spontaneous magnetization vectors M_s in the neighbouring grains and the normal to the common boundary; α_1 and α_2 are the angles between the applied field and the magnetization on either side of the grain, and S_w is the domain wall energy per unit surface.

MAGNETIZATION ROTATION

Of the two principal mechanisms of magnetization variation, only wall displacement has been examined in the preceding section; the second mechanism, i.e. magnetization rotation, will now be dealt with. The cases in which it predominates are as follows :

- when orientation of the applied field is such that no domain has an energetically more favourable situation than the others. This occurs for instance in a crystal with an axis of easy magnetization, when the field is applied at right angles to the axis.
- when there are no domain walls in the specimen. This occurs in magnetic powders of dimensions smaller than those of a domain.
- when the specimen is magnetized to saturation. In this case, too, there are virtually no domain walls.
- when domain walls are very tightly bound to their equilibrium position. This may be the case in materials containing a great number of inclusions.

In the following brief survey, only two topics will be examined, viz. retentivity and the contribution of magnetization rotation to coercivity and initial susceptibility.

A. RETENTIVITY

Throughout a specimen magnetized to saturation, the magnetization vectors of all the domains have the direction of the applied field. Now, if the field is gradually reduced to zero, the magnetization vectors turn to their nearest preferential direction, provided that no generation of reverse domains occurs (see above, 'Wall Generation'). Magnetization is thereby reduced from the saturation value M_s to the remanent value M_r .

The values of relative retentivity :

$$m_r = \frac{M_r}{M_s} \quad (65)$$

for various types of anisotropy are given below. In all cases the material is supposed to consist of randomly oriented crystallites.

1. Prevailing crystal anisotropy

Table VIII is based on the subdivisions detailed in the section, 'Anisotropy Energy' (see p. 4).

TABLE VIII. — VALUES OF m_r IN THE CASE OF PREVAILING CRYSTAL ANISOTROPY

Preferential direction	m_r
Cubic symmetry	
Directions [100]	0.84
Directions [111]	0.87
Directions [110]	0.91
Hexagonal symmetry	
Axis	0.50
Plane	0.79
Cone of aperture 2θ	$\frac{1}{2} \cos \theta + \frac{\pi}{4} \sin \theta$ *

* m_r is maximum (0.93) for $\tan \theta = \frac{\pi}{2}$

It may be emphasized that the remarkably high retentivity value of 0.93 is actually attained by cobalt at about 300 °C.

2. Prevailing stress energy

(see section, 'Stress energy', p. 10.)

Reference will only be made here to the hypothetical case of isotropic magnetostriction, in which the total energy is given by equation (31). If $\sigma\lambda_s$ is negative, $m_r = 0.50$; if, on the contrary, $\sigma\lambda_s$ is positive, then $m_r = 0.79$.

3. Prevailing demagnetization energy

(see section, 'Shape anisotropy energy', p. 12.)

Since the demagnetization energy generally results in one preferred direction at each point, it may be concluded that :

$$m_r = 0.50$$

B. CONTRIBUTION OF MAGNETIZATION ROTATION TO COERCIVITY AND INITIAL SUSCEPTIBILITY

If the angular dependence of the total energy f (sum of the effective crystal anisotropy energy f_K , the stress energy f_s and the demagnetization energy f_d) as well as the orientation of the applied field can be described by one angular variable θ , the expressions for the coercivity H_c and the initial susceptibility χ_i are the following :

$$H_c = \frac{1}{M_s} \left(\frac{\frac{\partial f}{\partial \theta}}{\sin(\Psi - \theta)} \right)_{\max} \quad (66)$$

and

$$\chi_i = M_s^2 \frac{\sin^2(\Psi - \theta_0)}{\left(\frac{\partial^2 f}{\partial \theta^2} \right)_{\theta = \theta_0}} \quad (67)$$

Here θ and Ψ are the angles between a given direction of the crystal and M_s and H , respectively. These three directions are supposed to lie in the same plane. θ_0 is the value of θ for which $f(\theta)$ is minimum. Here again, it can be concluded that $\chi_i H_c$ is proportional to M_s .

The above equations apply in each of the cases examined below.

1. Predominant crystal energy

In the case of uniaxial symmetry with the field applied along the preferred axis, it is found that :

$$H_c = \frac{2K}{M_s}, \quad \chi_i = \frac{M_s^2}{2K}, \quad \chi_i H_c = M_s \quad (68)$$

If the crystal is cubic with [100] preferential directions and if the field is applied in one [100] direction, the formulae for H_c and χ_i are the same as above (68). For randomly oriented crystallites :

$$H_c = 0.64 \frac{K}{M_s} \quad (69)$$

Crystals with a preferential plane with the applied field perpendicular to it give :

$$H_c = \frac{2|K|}{M_s}, \quad \chi_i = \frac{M_s^2}{2|K|} \quad (70)$$

Cubic crystal with [111] preferential directions and the field applied in one [100] direction lead to the same equations as above (70).

2. Predominant stress energy

In this case, H_c is given by the following equation :

$$H_c = \frac{3|\lambda_s \sigma|}{M_s}, \quad \chi_i = \frac{M_s^2}{3|\lambda_s \sigma|} \quad (71)$$

3. Predominant demagnetization energy

For particles having the shape of a revolution ellipsoid with demagnetization factors N_a in the direction of, and N_b at right angles to, the major axis, H_c and χ_i are expressed by :

$$H_c = \frac{1}{\mu_o} M_s (N_b - N_a), \quad \chi_i = \frac{1}{(N_b - N_a)} \quad (72)$$

The upper limit of $(N_b - N_a)$ for needle-like particles is $\frac{1}{2}$. Thus :

$$(H_c)_{max} = \frac{1}{2\mu_o} M_s, \quad (\chi_i)_{min} = 2 \quad (73)$$

For randomly oriented particles,

$$H_c = \frac{0.48 M_s}{\mu_o} (N_b - N_a)$$

and

$$(H_c)_{max} = \frac{0.24 M_s}{\mu_o} \quad (74)$$

CONCLUSIONS

Part I, entitled "Magnetic Properties, Technical

Parameters and the Influence of Cobalt" which is concluded here, was aimed at establishing formulae expressing more or less accurately and explicitly the most important technical magnetic parameters mainly as functions of crystal properties. Using these, the outstanding effects of crystalline anisotropy (K) and magnetostriction (λ) on the coercive force (H_c), the initial susceptibility (χ_i), the relative retentivity (m_r), and the response to magnetic annealing (K_u) were evidenced.

Simultaneously, it was shown that, among other interesting magnetic characteristics, cobalt possesses a very high magnetostriction and a very high crystalline anisotropy.

The conclusion is obvious : cobalt and many of its compounds possess exceptional magnetic properties. Moreover, by addition of cobalt to other magnetic substances, large variations of H_c , χ_i , m_r and K_u will be obtainable, thus allowing the resulting materials to meet exacting technical requirements.

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