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EXCHANGE ANISOTROPY OF SINGLE CRYSTALS OF HEXAGONAL FERRITES WITH AN M STRUCTURE

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The magnetic anisotropy of single crystals of the hexagonal ferrites $BaCo_xTi_xFe_{12-2x}O_{19}$ and $SrCo_{1.5}Fe_9O_{19}$ is investigated. A $\sin\vartheta$ component has been found in the Fourier expansion of the torque curve for $BaCo_{1.4}Ti_{1.4}Fe_{9.2}O_{19}$ crystals at 77°K. A rotational magnetic hysteresis which does not vanish in strong magnetic fields has been detected in all crystals with a small crystalline anisotropy. The results are discussed from the point of view of the existence of exchange anisotropy in the investigated crystals.

THE term "exchange anisotropy" was initially introduced in describing the magnetic interaction in a magnet at the boundary dividing ferromagnetic and antiferromagnetic substances. This interaction was first discovered by Meiklejohn and Bean[1] for cobalt particles covered with antiferromagnetic cobaltous oxide. When such a substance is cooled in a magnetic field below the Néel point of the antiferromagnet, shifted hysteresis loops, unidirectional (as opposed to uniaxial) anisotropy, and rotational hysteresis appear in fields exceeding the saturation fields of the ferromagnet. The explanation of this phenomenon consisted in assuming direct coupling between the cobalt atoms in the ferromagnet and those in the antiferromagnet.

Such an interaction was subsequently found not only in ferro-antiferromagnetic systems but also in ferri-antiferromagnets, as well as in certain alloy systems (for instance, in the alloy Ni_3Mn[2]). The existence of exchange anisotropy does not mean that all three characteristic signs are necessarily present: a shifted hysteresis loop, unidirectional anisotropy (i.e., a $\sin\vartheta$ component in the torque curves), and rotational hysteresis. The appearance of any of these depends on the relation between the exchange interaction constant and the constants of ferromagnetic and antiferromagnetic anisotropy.

The existence of antiferromagnetic regions entering into the crystal structure and separating ferromagnetic blocks is possible in hexagonal ferrites made up of alternating cubic and hexagonal blocks. Under these conditions one can expect the appearance of exchange anisotropy in the crystals. This paper is devoted to a study of magnetic anisotropy in the system of single crystals of the hexagonal ferrites $BaCo_xTi_xFe_{12-2x}O_{19}$ and $SrCo_{1.5}Fe_9O_{19}$ (so-called ferrites with the M structure).

The single crystals were grown by spontaneous crystallization from a solution of the components of these ferrites in a $NaFeO_2$ melt. An analysis of their composition was carried out with the aid of an x-ray microanalyzer. The composition of the investigated samples is shown in the table. Magnetization curves and hysteresis loops along the hexagonal axis and in the basal plane were obtained for each crystal on cooling from 293 down to 77°K with and without a magnetic field with the aid of a vibrating magnetometer. The existence of unshifted symmetric hysteresis loops was established for crystals of all compositions and under all experimental conditions.

Composition, magnetic anisotropy constants, and magnetization of $Ba(Sr)Co_xTi_xFe_{12-2x}O_{19}$

Abbreviated crystal notation	Composition	K_1, erg/cm^3		σ, gauss-cm^3/g	
		293° K	77° K	293° K	77° K
$BaCo_{0,25}$ **M**	$BaCo_{0,25}Ti_{0,25}Fe_{11,5}O_{19}$	$26\cdot10^5$	$38\cdot10^5$	63	90
$BaCo_{0,5}$ **M**	$BaCo_{0,5}Ti_{0,5}Fe_{11}O_{19}$	$18{,}6\cdot10^5$	$31\cdot10^5$	64	88
$BaCo_{0,75}$ **M**	$BaCo_{0,75}Ti_{0,75}Fe_{10,5}O_{19}$	$13{,}3\cdot10^5$	$18\cdot10^5$	62	90
$BaCo_{1,4}$ **M**	$BaCo_{1,4}Ti_{1,4}Fe_{9,2}O_{19}$	$3.7\cdot10^5$	~0	53	64
$BaCo_{1,5}$ **M**	$BaCo_{1,5}Ti_{1,5}Fe_9O_{19}$	$-0.5\cdot10^5$	$-0.7\cdot10^5$	40	46
$BaCo_2$ **M**	$BaCo_2Ti_2Fe_8O_{19}$	$-7{,}1\cdot10^5$	$-17.5\cdot10^5$	47	58
$SrCo_{1,5}$ **M**	$SrCo_{1,5}Ti_{1,5}Fe_9O_{19}$	$-0.15\cdot10^5$	$-0.40\cdot10^5$	42	47

The magnetic anisotropy was investigated at 293 and 77°K by the torque method. Investigation of the torque curves showed that the magnetic anisotropy energy E_k of all crystals in a plane perpendicular to the basal plane is described by the usual formula:

$$E_k = K_1 \sin^2\vartheta + K_2 \sin^4\vartheta + K_3 \sin^6\vartheta + \ldots, \tag{1}$$

where K_1, K_2, and K_3 are the first, second, and third anisotropy constants, and ϑ is the angle between the magnetization vectors and the hexagonal axis of the crystal. However, experiment shows that for the investigated crystals one can restrict oneself to the first term only, since K_2 and K_3 are so small that they can be neglected. Under these conditions, when $K_1 > 0$ the crystals have an easy magnetization axis, and when $K_1 < 0$ they have an easy magnetization plane which coincides with the basal plane of the crystal. As is seen from the table, there are among the investigated crystals both samples with an easy magnetization axis (for $x \leq 1.4$) and with a plane (for $x > 1.4$).

We found signs of the existence of exchange anisotropy only in the compositions with a small anisotropy constant K_1, i.e., for crystals of three compositions: $BaCo_{1.4}M$, $BaCo_{1.5}M$, and $SrCo_{1.5}M$. We shall now consider the properties of these crystals.

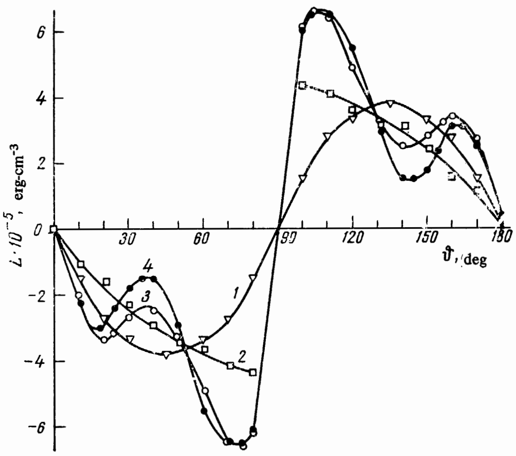

FIG. 1. Torque curve of $BaCo_{1.4}M$ crystals in the plane perpendicular to the basal plane. 1—293°K, H = 19,500 Oe; 2—77°K; H = 5000 Oe; 3—77°K, H = 15,000 Oe; 4—77°K, H = 19,500 Oe.

1. PECULIARITIES OF THE TORQUE CURVES

Figure 1 shows torque curves of the single crystal of $BaCo_{1.4}M$ at 293°K (curve 1) and at 77°K (curves 2—4) in a plane perpendicular to the basal plane. At 293°K the curve is described by Eq. (1) with $K_1 = 3.7 \times 10^5$ erg/cm^3. Cooling the crystal down to 77°K does not change the torque curve in the plane perpendicular to the basal plane in a magnetic field and without it. This curve is well described by the formula

$$L = \pm j_t \sin\vartheta - K_x \sin 6\vartheta, \tag{2}$$

where $j_t = 4.4 \times 10^5$ erg/cm^3 (K_1 at 77°K is, as is seen from the Table, close to zero). For $90° < \vartheta < 270°$ the first term is taken with the plus sign, and for $0 < \vartheta < 90°$ and $270° < \vartheta < 360°$—with the minus sign. j_t does not depend on the magnitude of the applied field, and we shall refer to it as the exchange anisotropy constant.

The torque curve (2) contains another term—$K_X \sin 6\vartheta$; K_X depends on the magnitude of the applied field. In a field of 5000 Oe, $K_X = 0$; above this field K_X increases reaching in a field of 20 kOe a value of 1×10^5 erg/cm^3. So far we cannot say anything about the physical nature of this term. We have stated above that the constants K_2 and K_3 in (1) are small. If this were not so and the term $K_X \sin 6\vartheta$ were due to the crystalline anisotropy (1) for $K_X = K_3$, then the torque curve would be described by the following formula:

$$L = -\frac{\partial E_k}{\partial\vartheta} = -\left(K_1 + K_2 + \frac{15}{16}K_3\right)\sin 2\vartheta + \left(\frac{1}{2}K_2 + \frac{3}{4}K_3\right)\sin 4\vartheta - \frac{3}{16}K_3 \sin 6\vartheta. \tag{3}$$

Comparing the experimental formula (2) with the calculated formula (3), we find

$$K_1 = {}^9/_{16}K_3, \quad K_2 = -{}^3/_2 K_3. \tag{4}$$

Under these conditions the crystalline anisotropy is indeed due to the presence of the term $K_X \sin 6\vartheta$ in curve (2). However, relation (4) between the anisotropy constants K_1, K_2, and K_3 is rather unlikely. If we consider in expression (3) the sum $-(K_1 + K_2 + 15K_3/16)$ as a new constant l_1, the sum $\frac{1}{2}K_2 + 3K_3/4$ as l_2, and $-3K_3/16$ as l_3, then the expression for the energy E_k will differ from (1):

$$E_k = l_1 \cos 2\vartheta + l_2 \cos 4\vartheta + l_3 \cos 6\vartheta. \tag{5}$$

For $BaCo_{1.4}M$ crystals $l_1 = 0$, $l_2 = 0$, and $l_3 = K_X$. Since in all other instances writing the energy in the form (5) does not introduce any appreciable changes in the discussion of the results of this paper, the expression for the anisotropy energy E_k will be expressed below with the aid of the previous Eq. (1).

It may be noted that the appearance of a sixth-order term in the torque curve in a plane perpendicular to the basal plane is not so rare in hexagonal ferrites. Thus the appearance of an easy magnetization cone in the hexagonal ferrite $BaCa_{1.65}Fe_{16.35}O_{27}$[3] at 77°K is explained by the appearance of such a term in the torque curve. Experiments which we have carried out with a single crystal of $Ba_3Co_2Fe_{24}O_{41}$ at 77°K also indicate that the appearance of an easy magnetization cone when the sample is cooled is due to the appearance of a term $K_X \sin 6\vartheta$ [and not to an increase in the second anisotropy constant K_2 in the formula for the energy of the magnetic anisotropy (1), as is usually the case].

Figure 2 shows the torque curves of $BaCo_{1.4}M$ at 77°K in the basal plane. At 293°K the anisotropy is so small that we did not observe it. At 77°K the curves have considerable anisotropy and rotational hysteresis with which we shall deal below. The average torque curve of the curves measured when the crystal was rotated clockwise and anticlockwise was plotted in order to determine the anisotropy constant in the basal plane. The curves were measured in magnetic fields of various magnitudes. An expansion of the torque

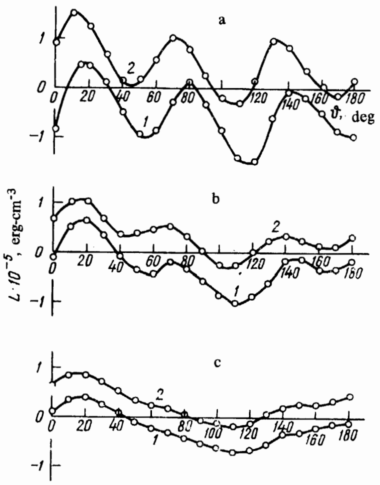

FIG. 2. Torque curves of $BaCo_{1.4}M$ crystals in the basal plane at 77°K. a—H = 4000 Oe, b—H = 8000 Oe, c—H = 19,500 Oe; 1—clockwise rotation of the crystal, 2—anticlockwise rotation of the crystal.

curves in a Fourier series shows that they contain a sixth-order component which decreases with increasing magnetic field. Such a dependence of the torque on the field in the basal plane is explained as follows.

The $BaCo_{1.4}M$ crystals have an easy magnetization axis. When they are magnetized in the basal plane (i.e., perpendicular to the hexagonal axis) the angle ϑ between the magnetization vector and the hexagonal axis changes from 0 to 90°. Saturation occurs as soon as the angle ϑ reaches 90°. Let us write the energy of magnetic anisotropy in the basal plane, E_b, in accordance with what its symmetry C6/mmc permits[4]:

$$E_6 = K_3' \sin^6 \vartheta \cos 6\varphi + K_3'' \sin^6 \vartheta \cos \vartheta \cos 6\varphi,$$

where φ is an angle in the basal plane. If K_3' is small, one can neglect the first term of this expression. The product $\sin^6\vartheta \cos\vartheta$ enters in the second term. This product decreases as ϑ approaches 90°.

No sixth-order components were observed in the torque curves of crystals of other compositions. The torque curves of the $BaCo_{1.5}M$ and $SrCo_{1.5}M$ crystals in the basal plane exhibit a small uniaxial anisotropy. The amplitude of the torque curve does not change when the crystal is cooled in a magnetic field, however, the direction of the applied field becomes the direction of easy magnetization (in the given plane).

2. ROTATIONAL HYSTERESIS

Rotational hysteresis is observed at 77°K for all crystals with a small value of the anisotropy constant K_1. (No rotational hysteresis is observed at 293°K.) The magnitude of the losses to hysteresis W is determined by the area between the torque curves obtained with the crystal rotating clockwise and anticlockwise (see Fig. 2), and does not depend on whether the sample is cooled in a magnetic field or without one. In $BaCo_{1.4}M$ crystals hysteresis is only observed in the basal plane; in $BaCo_{1.5}M$ and $SrCo_{1.5}M$ crystals—in the basal plane and in the plane perpendicular to it.

Figure 3 shows curves of the dependence of the losses to rotational hysteresis W (per half cycle) on the magnitude of the applied magnetic field in the basal plane (Fig. 3a) and in the plane perpendicular to it (Fig. 3b) for $BaCo_{1.4}M$, $BaCo_{1.5}M$, and $SrCo_{1.5}M$. Small losses were also observed in a single crystal of $BaCo_{0.75}M$. The single crystals with barium differ in the nature of this dependence from the single crystals with strontium. The losses of the single crystals $BaCo_{1.4}M$ (curve 1) and $BaCo_{1.5}M$ (curves 2) to rotational hysteresis reach saturation with increasing magnetic field, the losses of single crystals of $SrCo_{1.5}M$ (curves 3) decrease with increasing field.

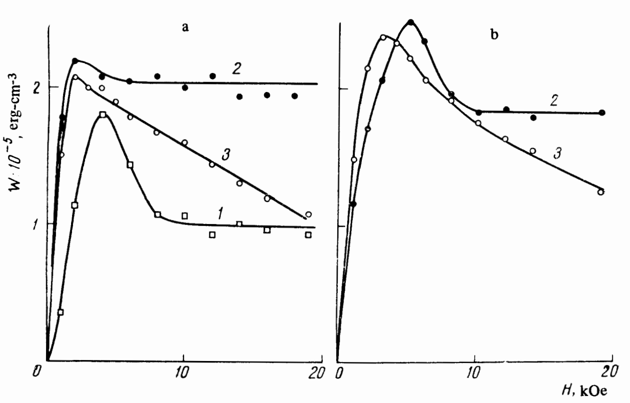

FIG. 3. Dependence of the losses to rotational hysteresis at 77°K on the magnitude of the magnetic field in $BaCo_{1.4}M$ (curve 1), $BaCo_{1.5}M$ (curve 2), and $SrCo_{1.5}M$ (curve 3) crystals: a—in the basal plane, b—in the plane perpendicular to the basal plane.

3. DISCUSSION OF THE RESULTS

It appears to us useful to discuss the results of this work from the point of view of the existence of exchange anisotropy in the investigated crystals. Meiklejohn[5] reports in his review article on exchange anisotropy the existence of a shifted hysteresis loop, a sin ϑ term in the torque curve, and losses to hysteresis in the ferrite $[xBaFe_{12}O_{19}(1 - x)KFe_{11}O_{27}]$ and explains this phenomenon by ferro-antiferromagnetic exchange interaction between the spinel and hexagonal blocks in the crystal. The crystals which we have investigated have an analogous structure.

We observe a sin ϑ term in the torque curve of $BaCo_{1.4}M$ crystals at 77°K. It cannot be explained by the lagging of the magnetization vector behind the field vector if the field is not large enough for saturation which is characteristic for crystals with a large crystalline anisotropy. The table shows that for crystals of this composition at 77°K the first anisotropy constant is close to zero, and consequently a field of about 20,000 Oe cannot be too small for achieving saturation.

The principal result of this paper is the observation of losses to rotational hysteresis which does not disappear with increasing magnetic field in crystals of three compositions. For the case when the ferromagnetic anisotropy is small we can calculate the losses to rotational hysteresis for the following simple model.[5]

Let AB be the direction of the boundary dividing the ferromagnetic and antiferromagnetic blocks (see Fig. 4). The direction of the antiferromagnetism vector AF is at an angle to that boundary, and the ferromagnetism vector **M**—at an angle β to it. The field **H** makes an angle ϑ with the dividing boundary. The energy E of the crystal will then be of the following form:

$$E = MH \cos(\vartheta - \beta) + K_{AF} \sin 2\alpha - j_t \cos(\beta - \alpha), \tag{6}$$

where K_{AF} is the antiferromagnetic anisotropy constant. Differentiation of E with respect to α and β leads to the following equilibrium conditions:

$$\begin{gathered} (j_t / K_{AF}) \sin(\beta - \alpha) = \sin 2\alpha, \\ h \sin(\vartheta - \beta) = \sin(\beta - \alpha), \end{gathered} \tag{7}$$

where $h = HM/j_t$. These equations are only solved numerically. A solution exists for $j_t/K_{AF} > 1$ and $h \geq 1$.

In Fig. 4 we present the solutions of Eqs. (7) for $j_t/K_{AF} = 1.1$ and $h = 1$. Curve 1 gives a solution for α and curve 2—for β as a function of ϑ. The curves have an S-like form. Thus, for each angle ϑ there are three values of the angles α and β. However, the central section of the curve yields unstable solutions.

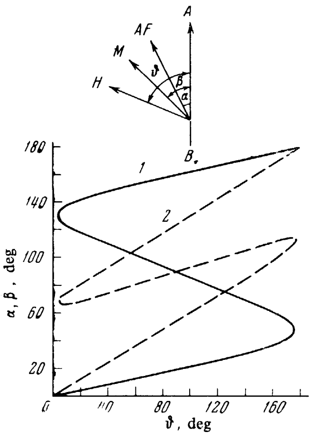

FIG. 4

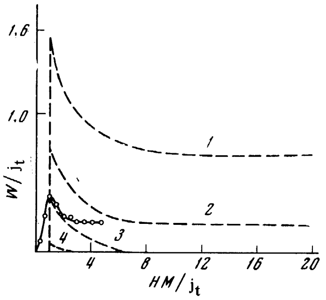

FIG. 5

FIG. 4. Dependence of the angles α(curve 1) and β (curve 2) on the angle ϑ. [Solution of Eqs. (3) for $j_t/K_{AF} = 1.1$ and h = 1].

FIG. 5. Theoretical curves of Wj_t as a function of h: 1–$j_t/K_{AF} = 1.1$; 2–$j_t/K_{AF} = 1.5$; 3–$j_t/K_{AF} = 2$; 4–$j_tK_{AF} = 3$ and the experimental curve for $BaCo_{1.4}M$ crystals at 77°K.

The rotational hysteresis is explained by a jump in α and β from the lower to the upper branch when the crystal is rotated clockwise, and, vice versa, from the upper to the lower branch, when the crystal is rotated anticlockwise. For given values of j_t/K_{AF} and h hysteresis exists in the entire range of angles ϑ, and the torque curves obtained on rotating the crystal clockwise and anticlockwise have no common sections. In other words, there is hysteresis for all values of ϑ. The curves of Fig. 2 correspond to this case. However, an increase of h (an increase of the magnetic field) narrows the region within which there is hysteresis which should be observed in a smaller range of angles ϑ. However, we have observed the existence of hysteresis in the entire range of angles ϑ, and not in a part of it.

In Fig. 5 curves of the dependence of the losses (more correctly of W/j_t) per half-cycle on the value of h calculated on the basis of Eqs. (7) are plotted as dashed lines for four values of the ratio j_t/K_{AF} : 1.1 (curve 1), 1.5 (curve 2), 2.0 (curve 3), and 3.0 (curve 4). Both nonvanishing hysteresis (curves 1 and 2) as well as hysteresis which depends on the magnitude of the magnetic field (curves 3 and 4) may exist for various ratios of j_t/K_{AF}. In our experiment we have observed both cases: for $BaCo_{1.4}M$ and $BaCo_{1.5}M$ crystals the rotational hysteresis reaches saturation ($j_t/K_{AF} \leq 1.5$), and for $SrCo_{1.5}M$ crystals losses to hysteresis decrease with increasing magnetic field ($j_t/K_{AF} > 1.5$). In the case of $BaCo_{1.4}M$ crystals one can carry out a more accurate calculation, since in this instance we were able to determine the exchange anisotropy constant $j_t = 4.4 \times 10^5$ erg/cm^3. In Fig. 5 the continuous curve indicates the dependence of W/j_t on h for this crystal. This dependence confirms our assumption concerning the existence of exchange anisotropy in the investigated crystals.

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