INDUCED MAGNETIC ANISOTROPY IN A SINGLE CRYSTAL OF THE HEXAGONAL FERRITE $BaCo_{1.5}Fe_{16.5}O_{27}$

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The influence of thermomagnetic treatment on the magnetic anisotropy energy of a single crystal of the hexagonal ferrite of composition $BaCo_{1.5}Fe_{16.5}O_{27}$ was investigated experimentally. The anisotropy induced in a hexagonal crystal is described by a phenomenological formula (3) with four constants whose values are: $U_1 = -1.5 \times 10^5$, $U_2 = -3.0 \times 10^5$, $U_3 = 1.3 \times 10^5$, and $U_4 = 2.0 \times 10^5$ erg/cm^3. The kinetics and the activation energy of the process of magnetic annealing were also investigated. Some features of the appearance of the magnetic anisotropy, due to the influence of thermomagnetic treatment, are explained.

INTRODUCTION

THE phenomenon of induced anisotropy, appearing in the cooling of a ferromagnet in a magnetic field (known as thermomagnetic treatment or magnetic annealing), has been investigated quite thoroughly both for alloys and for ferrites (cf., for example,[1,2]). Among ferrites, those investigated most are the cubic cobalt ferrites with the spinel structure.

The main features of the thermomagnetic treatment of cubic ferrites are as follows:

A. A slow cooling of a cubic crystal from temperatures of the order of 300°C in a magnetic field leads to the appearance, at room temperature, of a stable uniaxial anisotropy with the energy W_U, superimposed on the "normal" cubic anisotropy energy W_A. A preferred direction of easy magnetization appears in such a crystal (without the thermomagnetic treatment there are several equivalent easy magnetization axes in a cubic crystal). The direction of the preferred axis may or may not coincide with the direction of the magnetic field during annealing, depending on the orientation of the field with respect to the symmetry elements of the crystal. In general, the induced anisotropy of cubic crystals is described by the following formula:

$$W_U = -F(\alpha_1^2\beta_1^2 + \alpha_2^2\beta_2^2 + \alpha_3^2\beta_3^2) - G(\alpha_1\alpha_2\beta_1\beta_2 + \alpha_2\alpha_3\beta_2\beta_3 + \alpha_3\alpha_1\beta_3\beta_1), \quad (1)$$

where α and β are the direction cosines of the magnetization vector in the measurement of the energy and in the magnetic annealing, respectively; F and G are constants which depend on the crystal structure of the substance.

B. The process of the appearance of the induced anisotropy is of the diffusion type and obeys the laws of chemical reactions of the first kind with a simple exponential growth, which is characterized by a relaxation time

$$\tau = \tau_0 e^{E/kT}, \quad (2)$$

where E is the activation energy, which is close to 1 eV. The higher the annealing temperature, the faster the maximum possible induced anisotropy is reached at a given temperature. On the other hand, the value of this anisotropy decreases as the temperature increases.

C. Thermomagnetic treatment affects particularly strongly those ferrites which contain cobalt ions. In cobalt ferrites, the induced anisotropy is greater than in ferrites free of cobalt.

D. It has been noticed that the kinetics and the magnitude of the induced anisotropy are affected by the presence of cation vacancies, as indicated by tests on samples oxidized to various extents.[3]

The most probable mechanism, which explains the appearance of the induced anisotropy, is based on the so-called theory of directional ordering and its modifications.[4] Applied to cobalt ferrites, this mechanism predicts the migration, at high temperatures, of cobalt ions located at octahedral lattice sites, in order to reduce the energy. The fact that the induced anisotropy is stronger in cobalt ferrites is explained by the fact that the energy of the Co^{2+} ion depends strongly on the angle between its spin moment and the symmetry of the neighborhood of an octahedral lattice site. The application of a field, which alters the direction of the spontaneous magnetization, causes the migration of the Co^{2+} ions, which is aided by high

temperatures and the presence of cation vacancies in the lattice. The cooling of the crystal reduces the rate of diffusion and "freezes" the directional ordering of the cobalt ions. The nature of the spontaneous deformation in the crystal changes and this is accompanied by a change in the symmetry.

The principal relationships governing thermomagnetic treatment, as listed above, and their theoretical explanation may be applied in toto to hexagonal barium ferrites, as indicated by the results obtained by Bickford.[5] This is because the structure of a unit cell in hexagonal ferrites includes "blocks" of the cubic packing of oxygen ions, similar to the structure of spinel ferrites. The ions of a divalent metal Me, in our case the Co^{2+} ions in the ferrite $BaMe_2Fe_{16}O_{27}$, occupy, as in spinel ferrites, octahedral sites in these blocks. This feature of the structure makes it possible to understand many properties of hexagonal ferrites, for example the influence of the cobalt ions on the magnetocrystalline anisotropy energy.[6,7] The explanation of the properties of the magnetic anisotropy energy is based completely on the analogy with spinel ferrites. The main difference between hexagonal and spinel ferrites lies not so much in the nature of a given property as in the symmetry, since, in spite of the presence of spinel structure blocks, the crystal as a whole has a hexagonal structure.

In the case of hexagonal ferromagnets, formula (1) is inapplicable since it has been obtained on the assumption that initially the crystal has cubic symmetry. The corresponding formula for hexagonal crystals has not yet been given in the published literature. It may be obtained from the most general symmetry considerations, irrespective of the model on which the explanation of thermomagnetic treatment defects is based. Formula (1) is similar to the expression for the magnetomechanical energy of a cubic crystal, i.e., the change in the magnetic anisotropy energy under the action of an external stress on the crystal. In spite of the difference in the nature of the external agency, the change in the crystal symmetry is the same in both cases. Using these considerations, the formula for the induced anisotropy of a hexagonal crystal may be written in the following form:

$$W_U = U_1\alpha_3^2\beta_3^2 + U_2(\alpha_1\beta_1 + \alpha_2\beta_2)^2 + U_3(\alpha_2\beta_1 - \alpha_1\beta_2)^2 + 2U_4\alpha_3\beta_3(\alpha_2\beta_2 + \alpha_1\beta_1). \quad (3)$$

The direction cosines and the constants in Eq. (3) have the same meaning as in Eq. (1). The coordinate axes are selected to make the hexagonal c-axis coincide with the X_3 axis, and the axes X_1 and X_2 lie in the basal plane.

The purpose of the present work was to investigate experimentally the anisotropy produced by the thermomagnetic treatment of a hexagonal crystal containing cobalt, $BaCo_{1.5}Fe_{16.5}O_{27}$; to obtain a quantitative estimate of the induced anisotropy effect and to check the validity of formula (3); to study the magnetic annealing kinetics and determine the activation energy E in the formula (2); and also to explain certain features detected in the study of the magnetic anisotropy energy.

SAMPLES AND INVESTIGATION METHOD

Single-crystal hexagonal barium ferrite of the composition $BaCo^{2+}_{1.5}Fe^{2+}_{0.5}Fe^{3+}_{16}O_{27}$ (the so-called W structure) was used in the investigation. The single crystals were grown by the Verneuil method. The selection of this composition was determined by the fact that the magnetic anisotropy energy of this crystal had a cone of easy magnetization at room temperature,[7] which leads to interesting and as yet unobserved features in the appearance of the induced anisotropy.

The magnetic anisotropy energy was investigated on a spherical sample, 4 mm in diameter, using the torque method. The sample was heated in a cylindrical resistance furnace with bifilar winding, which was placed between the polepieces of an electromagnet. The temperature was measured with a copper-constantan thermocouple. The thermomagnetic treatment consisted of heating the sample to 250°C, keeping it at this temperature for 15 min in a magnetic field of 15,000 Oe, and subsequently cooling it slowly in this field to room temperature at the rate of 3 deg/min. The magnetic anisotropy was, as a rule, measured in a field of 24,500 Oe, except in those cases when the dependence of the torque on the field was specifically investigated. Where necessary the torque curves were corrected for the angle of lag of the magnetization vector behing the external field direction.

EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic anisotropy energy in our case may be written as follows:

$$W = W_A + W_U,$$

where W_A is the usual magnetic anisotropy energy of a hexagonal crystal (before magnetic annealing), and W_U is the energy induced by thermomagnetic treatment, and given by Eq. (3). For such a crystal, the energy W_A is given by the formula

$$W_A = K_1 \sin^2\theta + K_2 \sin^4\theta, \quad (4)$$

in which, as usual, the direction cosines are replaced by the polar angle θ between the X_3 axis (c-axis) and the magnetization vector direction. The anisotropy in the basal plane of the crystal $BaCo_{1.5}Fe_{16.5}O_{27}$ at room temperature is practically absent and, therefore, Eq. (4) does not include terms depending on the orientation of the magnetization vector in the basal plane.

The absence of anisotropy in the measurement of the torque in the X_1X_2 plane (sample rotated about the c-axis) makes this orientation of the sample very convenient for the study of the magnetic annealing kinetics, since in this case the induced anisotropy appears in its "pure form." It follows from Eq. (3) that the induced anisotropy in the basal plane is determined by the terms associated with U_2 and U_3 since $\alpha_3 = \cos\theta = 0$. The torque curve for this orientation is given by

$$L = -\partial W_U / \partial\varphi = (U_2 - U_3)\sin 2(\varphi - \psi), \quad (5)$$

where φ and ψ are the angles between the X_1 axis (or the X_2 axis) and the magnetization vector direction in the measurement of the torque and during magnetic annealing, respectively. Equation (5) shows that if the direction of the magnetic field during thermomagnetic treatment lies in the basal plane, then it becomes an easy magnetization direction.

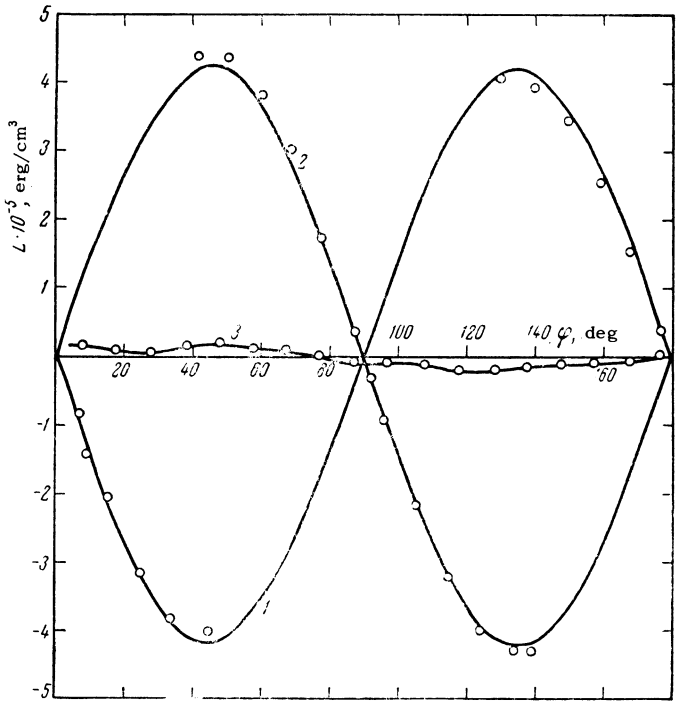

FIG. 1. Dependence of the torque L on the orientation of magnetization in the basal plane. Curves 1 and 2 were obtained after thermomagnetic treatment along the directions $\varphi = 0$ and $\varphi = 90°$; curve 3 represents the state before thermomagnetic treatment and after the removal of its effects. The measurements were carried out in a field of 24,500 Oe.

The points in Fig. 1 give the values of the torques in the basal plane at room temperature after two successive treatments, during which the field direction coincided with $\varphi = 0$ (curve 1) and $\varphi = 90$ (curve 2). The two continuous curves in Fig. 1 are plotted from formula (5) for the cases $\psi = 0$ and $\psi = 90°$, respectively, with $U_2 - U_3 = -4.3 \times 10^5$ erg/cm^3. Curve 3 illustrates the dependence of the torque L on the orientation of the magnetization in the basal plane of the sample before thermomagnetic treatment and after the destruction of the induced anisotropy by simple annealing of the sample at 250°C followed by slow cooling in the absence of a magnetic field. The small values of L may be associated with the inaccurate orientation of the crystal and the nonspherical shape of the sample.

Figure 2a illustrates the relaxation of the induced anisotropy in the basal plane at various temperatures. The induced anisotropy was in each case produced by heating the sample to 250°C and slowly cooling it in a magnetic field at $\psi = 0$ to the test temperature. After keeping the sample at this temperature, the initial value of the maximum torque was measured at $\varphi = 45°$ (cf. curve 1 in Fig. 1). Then the sample was rapidly rotated by 90° with respect to the initial magnetic annealing direction and the drop in the amplitude of $U_2 - U_3$ at $\varphi = 45°$ was measured at fixed time intervals. The arrows indicate the half-life of the process. From the curves, it is evident that although at 100°C one hour is insufficient to destroy the induced anisotropy, the latter is removed completely after one minute at 170°C; after approximately 30 min, maximum anisotropy of the opposite sign is induced (in other words, a curve of type 1 transforms into a curve of type 2 in Fig. 1). If the sample is then again moved by 90° and the time is plotted from right to left, the process will follow the curve which is shown dashed. Thus one can observe a remarkable time "hysteresis loop" of this process.

Figure 2b shows the dependence of the logarithm of the total decay lifetime τ and the half-life $\tau_{1/2}$ on the reciprocal of temperature. In accordance with formula (2), this dependence can be used to determine the activation energy of the process. The value of the activation energy, found to be 0.93 ± 0.03 eV, coincides with the well-known activation energy for the cobalt ferrite with the spinel structure,[8] which confirms the suggestion that the nature of the thermomagnetic treatment is the same in spinel and hexagonal ferrites.

Figure 3 shows the results of measurements of the torque in the X_1X_3 plane, containing the c-axis,

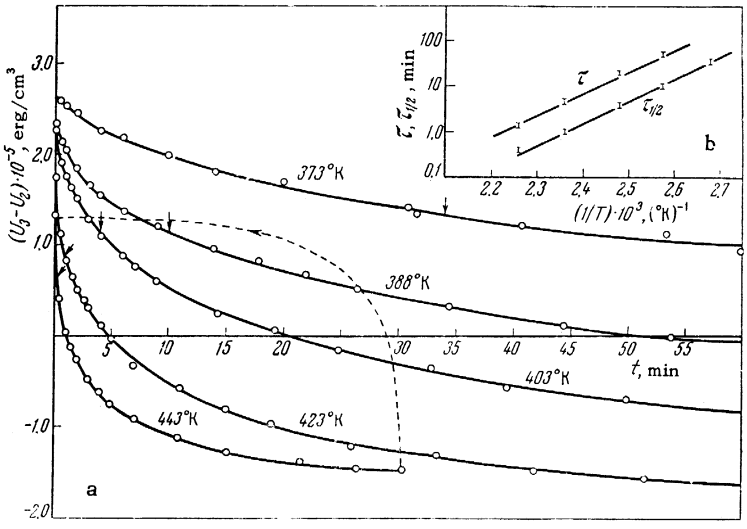

FIG. 2. a) Relaxation curves of the induced anisotropy at various temperatures. The arrows denote the half-life $\tau_{1/2}$; b) dependence of the time for the total decay τ and of the half-life $\tau_{1/2}$ on the reciprocal of temperature. The slope of the two lines corresponds to an activation energy E = 0.93 ± 0.03 eV.

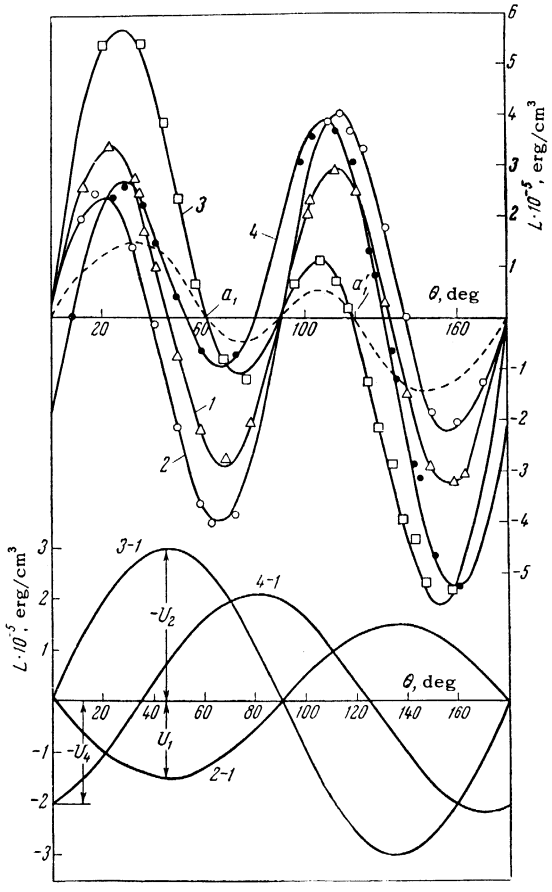

FIG. 3. Dependence of the torque on the orientation of the magnetization in the X_1X_3 plane after various thermomagnetic treatments: 1) initial curve; 2) after annealing in H ∥ X_3; 3) after annealing in H ∥ X_1; 4) after annealing at an angle of 45° with the X_3 and X_1 axes. Curves 1 – 4 were recorded in a field of 24,500 Oe; the dashed curve was recorded in a field of 2300 Oe after treatment in H ∥ X_1. The curves in the lower part of the figure, representing the differences between curves 2, 3, 4 and 1, give the resultant anisotropy.

obtained by rotating the sample about the X_2 axis. Curve 1 represents the initial state of the magnetic anisotropy at room temperature. The torques are given by

$$L = -\partial W_A / \partial\theta = -(K_1 + K_2)\sin 2\theta + {}^1/_2 K_2 \sin 4\theta \quad (6)$$

with the following values of the constants: $K_1 = -6.6 \times 10^5$ erg/cm³, $K_2 = 6.3 \times 10^5$ erg/cm³. The initial magnetic anisotropy of the crystal $Co_{1.5}W$ has a circular cone of easy magnetization with the angle $\theta_0 = 46°$ between the generators of the cone and the c-axis, determined from the relationship $\sin^2\theta_0 = -K_1/2K_2$.

Curve 2 in Fig. 3 was obtained after thermomagnetic treatment of the same sample along the X_3 axis (along the c-axis). In this case the torque curve for the induced anisotropy is given by

$$L = -\partial W_U / \partial\theta = U_1 \sin 2\theta. \quad (7)$$

Curve 2—1 in the lower part of Fig. 3 represents the difference between the curves 2 and 1. It is in agreement with Eq. (7) for $U_1 = -1.5 \times 10^5$ erg/cm³.

Curve 3 was obtained in the same plane after thermomagnetic treatment along the X_1-direction (magnetic annealing in the basal plane). Here, the torques for the induced anisotropy are given by

$$L = -U_2 \sin 2\theta. \quad (8)$$

Curve 3—1 in the lower part of the figure represents the difference between curves 3 and 1, plotted using Eq. (8) with $U_2 = -3.0 \times 10^3$ erg/cm³.

Thermomagnetic treatment along a direction making 45° with the c-axis makes it possible to determine the constant U_3 in Eq. (3). Curve 4 in Fig. 3 illustrates the dependence of the torque on the direction of magnetization in the X_1X_3 plane after the treatment described above. In this case, Eq. (3)

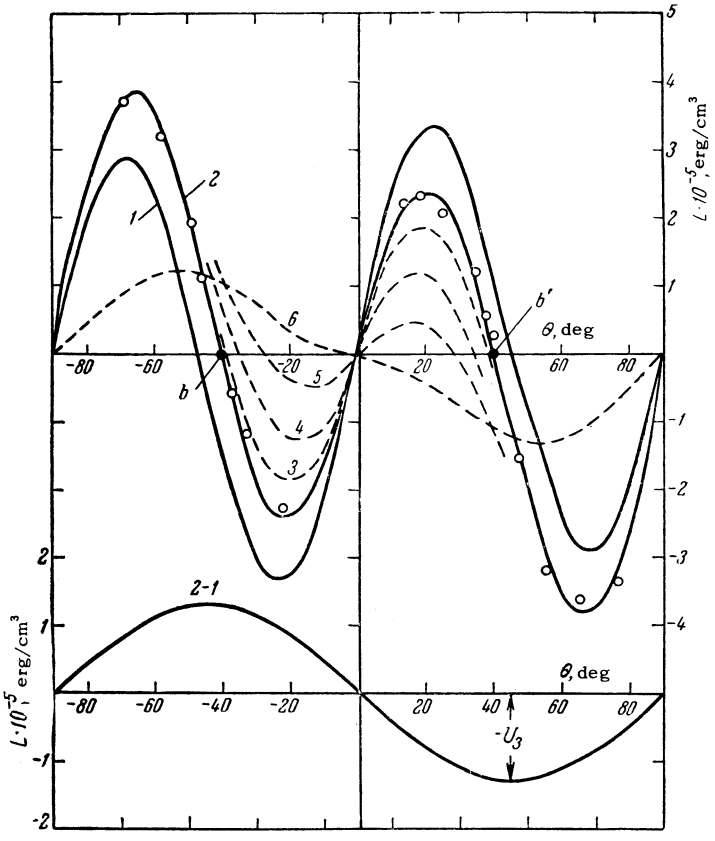

FIG. 4. Dependence of the torques measured in various fields on the orientation of magnetization in the X_2X_3 plane after thermomagnetic treatment in $\mathbf{H} \parallel X_1$: 2) 24,500 Oe; 3) 14,700 Oe; 4) 10,000 Oe, 5) 5000 Oe; 6) 2300 Oe. Curve 1 represents the initial state of the sample in a field of 24,500 Oe. The lower part of the figure gives the difference between curves 2 and 1.

yields the following expression for the induced anisotropy torque:

$$L = -\partial W_U / \partial\theta = {}^1/_2(U_1 - U_2)\sin 2\theta - U_4 \cos 2\theta. \quad (9)$$

Curve 4—1 represents the difference between curves 4 and 1; it agrees with experiment for the following values of the constants in Eq. (9):

$$U_1 = -1.5\cdot 10^5 \text{ erg/cm}^3, \quad U_2 = -3.0\cdot 10^5 \text{ erg/cm}^3,$$
$$U_4 = 2.0\cdot 10^5 \text{ erg/cm}^3.$$

Using these values of $U_2 - U_3$, U_1, U_2, and U_4, we can determine all four constants in Eq. (3); the constant U_3 is found to be 1.3×10^5 erg/cm^3. The latter may be determined also by the thermomagnetic treatment along a direction lying in the basal plane, for example, along X_1, and subsequent measurement of the torque in the perpendicular plane X_2X_3 on rotation of the crystal about the X_1 axis (curve 2 in Fig. 4). The induced anisotropy torques are in this case given by the formula

$$L = -\partial W_U / \partial\theta = -U_3 \sin 2\theta. \quad (10)$$

Curve 2—1 in Fig. 4, obtained by subtracting the initial curve 1 from curve 2, satisfies Eq. (10) with $U_3 = 1.3 \times 10^5$ erg/cm^3, which is identical with the value of U_3 determined earlier by tests along a different direction in the crystal.

Thus the validity of Eq. (3) for the induced anisotropy in a hexagonal ferromagnet is well confirmed by the experimental data.

We shall note some characteristic features of the appearance of the induced anisotropy in a crystal having a cone of easy magnetization.

The thermomagnetic treatment along the hexagonal axis direction is not accompanied by any change in the crystal symmetry. The easy magnetization directions form, as before, a circular cone of revolution, but the angle θ_0 is now smaller and given by the relationship $\sin^2\theta_0 = -(K_1 - U_1)/2K_2$ (the cone appears to "shrink" toward the c-axis). It is evident from curve 2 in Fig. 3 that, as a result of the thermomagnetic treatment along the c-axis, the angle θ_0 decreases from 46 to 39°. The dashed circle 1 in Fig. 5 represents the stereographic projection of the easy magnetization directions of the crystal in its initial state (the plane of the figure coincides with the basal plane) while circle 2 illustrates the change in the vertex angle of the cone due to the thermomagnetic treatment along the X_3 axis.

After thermomagnetic treatment along any direction other than the c-axis, the easy magnetization cone becomes distorted due to the appearance of the uniaxial induced anisotropy. For example, after annealing in a magnetic field directed along

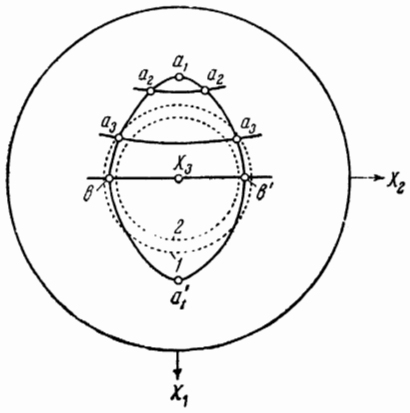

FIG. 5. Stereographic projection of the easy magnetization directions (the c-axis is perpendicular to the plane of the figure): 1) the initial state; 2) after thermomagnetic treatment along the c-axis.

the X_1 axis, two directions, whose projections are indicated by the points a_1 and a_1' in Fig. 5, become preferred compared with other directions of the distorted cone. The two directions correspond to the stable positions of the magnetization vector, denoted by a_1 and a_1' in Fig. 3, in the measurement of the torque in the X_1X_3 plane. These stable positions remain unaltered when there is a reduction in the intensity of the field in which the torque is measured, right down to relatively very weak fields (the dashed curve in Fig. 3 was recorded in a field of 2300 Oe).

However, a strong dependence of the stable position of the magnetization vector on the magnetic field intensity is observed in measuring the torque in the perpendicular plane X_2X_3, which is shown by the dashed curves in Fig. 4. In a field of 2300 Oe, the magnetization vector remains practically fixed in the positions a_1 and a_1' (Fig. 5), which do not lie in the measurement plane X_2X_3. In this plane, the crystal behaves as uniaxial (which is evident from curve 6 in Fig. 3), since the projections of the directions a_1 and a_1' on the X_2X_3 plane coincide with the X_3 axis. When the magnetic field intensity increases, the magnetization vector begins to depart from the direction a_1 toward the plane X_2X_3. When there is rotation of the field in this plane, the stable positions, as shown schematically in Fig. 5, correspond to the points a_2—a_2, a_3—a_3, etc., representing energy minima in given fields. The torque curves then change, as shown by the dashed curves 5, 4, and 3 in Fig. 4. In sufficiently strong fields (curve 2 in Fig. 4), in which the magnetization vector may be regarded as coinciding with the field direction, the stable position corresponds to the directions b and b′ in Figs. 4 and 5.

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