SOVIET PHYSICS JETP VOLUME 19, NUMBER 6 DECEMBER, 1964

MAGNETOCRYSTALLINE ANISOTROPY OF HEXAGONAL FERRITE SINGLE CRYSTALS OF THE $BaCo_xFe_{2-x}W$ *SYSTEM*

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Submitted to JETP editor January 4, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 1985-1989 (June, 1964)

A study was made of the influence of Co ions on the magnetocrystalline anisotropy of ferrite single crystals of the $BaCo_xFe_{18-x}O_{27}$ system ($0 < x < 1.5$) at room temperature and at 77°K. The easy magnetization direction changes from the c-axis to directions forming a cone whose vertex angle increases on increase of the Co content and on cooling. The strong anisotropy, detected in the basal plane at 77°K, indicates that the energy along the cone generators is not constant but has a minimum, with a period of 60°, in its dependence on the angle φ in the basal plane.

It is known that Co strongly affects the magnetic anisotropy energy of ferrites. In the case of cubic ferrites with the spinel structure, this influence manifests itself as a change in the direction of easy magnetization from axes of the [111] type to the [100] directions, which corresponds to a change of the sign of the first magnetic anisotropy constant of a cubic crystal, K_1^{cub}, from negative to positive. The influence of Co in the case of hexagonal magnetically uniaxial ferrites manifests itself as a shift of the stable position of the magnetization vector by an agle θ_0 from the hexagonal axis c, accompanied by the appearance of an easy magnetization cone ($\theta_0 < 90°$) or an easy magnetization plane ($\theta_0 = 90°$). Such a change in the magnetic anisotropy represents a positive contribution of the constant K_2^{hex} to the anisotropy energy of a hexagonal crystal.

Only one worker[1] has studied the influence of Co on the magnetic anisotropy of ferrites of the $BaCo_xFe_{18-x}O_{27}$ system using textured polycrystals and one single crystal. The present paper deals with the system $BaCo_xFe^{2+}_{2-x}Fe^{3+}_{16}O_{27}$ (or, briefly, $BaCo_xFe_{2-x}W$): only single crystals were investigated. The single crystals were prepared by the Verneuil method and had the following composition: x = 0, 0.3, 0.5, 1.0, and 1.5; the lattice parameter c was 32 Å, which corresponds to the structure of W; the crystal dimensions were sufficient to prepare spherical samples of 3–5 mm diameter.

The magnetic anisotropy energy was measured by the method of rotating moments at room temperature and at the temperature of liquid nitrogen in a field of 19,000 Oe. To describe the magnetic anisotropy energy of a hexagonal crystal, the usual formula was employed:

$$F_K = F_0 + K_1 \sin^2\theta + K_2 \sin^4\theta + K_3 \sin^6\theta \cos 6\varphi, \quad (1)$$

where the angle θ gives the orientation of the magnetization vector with respect to the c axis, and the angle φ is taken from the twofold axis in the basal plane. In a $(10\bar{1}0)$ plane, the equation for the rotating moment curve has the following form:

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

If $K_1 + K_2 > 0$ and $K_1 > 0$, then the c-axis is the direction of easy magnetization. If

$$0 < -K_1 < 2K_2, \qquad K_3 = 0 \quad (3)$$

the directions of easy magnetization form a cone with an angle θ_0 between the cone generators and the c-axis, where

$$\sin^2\theta_0 = -K_1 / 2K_2. \quad (4)$$

The condition $K_1 = -K_2$ corresponds to a cone with an angle $\theta_0 = 45°$; in this case, Eq. (2) becomes

$$L(\theta) = {}^1/_2 K_2 \sin 4\theta. \quad (5)$$

If $K_1 = -2K_2$, the angle $\theta_0 = 90°$ and the directions of easy magnetization lie in the basal plane.

If $K_3 = 0$, there should be no anisotropy in the basal plane; if $K_3 \neq 0$, the rotating moment curve in a (0001) plane obeys the equation

$$L(\varphi) = -6K_3 \sin 6\varphi. \quad (6)$$

To calculate the constants in Eq. (1), the experimental rotating moment curves $L(\psi)$ and $L(\varphi')$ (ψ is the angle between the magnetic field direction and the c-axis, φ' is the angle between the field and one of the twofold axes in the basal plane) were corrected (cf. Figs. 1 and 2) to allow for the angles $\psi - \theta$ and $\varphi' - \varphi$, by which the magnetization I_S "lags" behind the field H when a crystal is rotated in the $(10\bar{1}0)$ and (0001) planes, respectively; the corrections are carried out in accordance with the relationships

$$\sin(\psi - \theta) = L_{(10\bar{1}0)}/HI_s \quad \text{or} \quad \sin(\varphi' - \varphi) = L_{(0001)}/HI_s. \qquad (7)$$

In analyzing the experimental curves $L(\theta)$, it was always sufficient to include only the terms proportional to $\sin 2\theta$ and $\sin 4\theta$.

The experimental values of the constants K_1, K_2, and K_3 are listed in the table as functions of temperature and of the composition of $BaCo_xFe_{2-x}W$ ferrites. The magnetic anisotropic energy of crystals free of Co (x = 0) is represented by a single positive anisotropy constant K_1 both at 290°K and at 77°K. The influence of Co ions represents a positive contribution of the constant K_2 at the expense of a reduction of the constant K_1 and the change of its sign to negative, which gives rise to an easy magnetization cone if the conditions of Eq. (3) are satisfied. At 77°K, this cone appears at lower Co concentrations than at room temperature.

Figure 1 shows, by way of example, the rotating moment curves $L(\psi)$ and $L(\theta)$ for a $BaCo_{1.0}Fe_{1.0}W$ crystal. At room temperature (curve 1), the crystal has an easy magnetization axis, but the curve does not exhibit the simple $\sin 2\theta$ dependence because of a considerable contribution of the term proportional to $\sin 4\theta$. At 77°K (curve 2), the easy magnetization direction lies on the surface of a cone of angle $\theta_0 = 45°$; the $L(\theta)$ curve obeys Eq. (5), which is quite remarkable because it is similar to the curves obtained for a cubic crystal in the (100) plane. The continuous curves drawn through the corrected values of L (triangles) are plotted using Eq. (2) and the values of K_1 and K_2 listed for the $BaCo_{1.0}Fe_{1.0}W$ composition in the table.

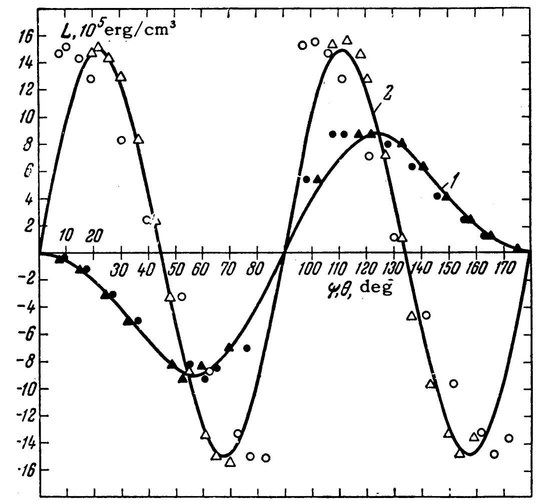

FIG. 1. Rotating moment curves for a single crystal of $BaCo_{1.0}Fe_{1.0}W$ in the $(10\bar{1}0)$ plane at 290°K (black dots) and at 77°K (open circles); the dots and the circles represent the values of $L(\psi)$, the triangles $L(\theta)$. The curves are plotted using Eq. (2) and the values of K_1 and K_2 listed in the table for this composition (curve 1 for 290°K, curve 2 for 77°K).

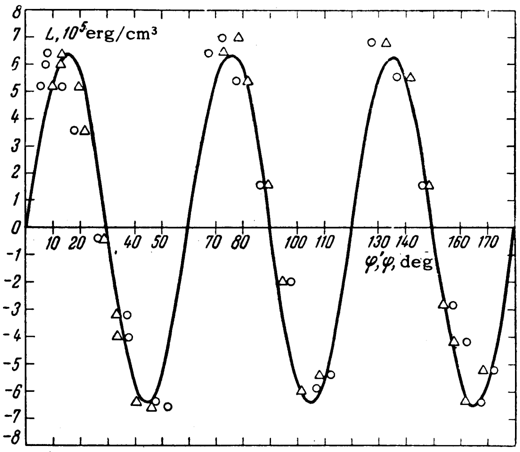

FIG. 2. Rotating moment curves for a single crystal of $BaCo_{1.0}Fe_{1.0}W$ in the basal plane at 77°K. The circles denote the values of $L(\varphi')$, and the triangles $L(\varphi)$; the curve is plotted using Eq. (6) and $K_3 = 1.07 \times 10^5$ erg/cm³.

Figure 2 shows a rotating moment curve at 77°K when the same crystal is rotated in the basal plane. It shows clearly that the dependence $L(\varphi)$ is, in agreement with the crystal symmetry, periodic with a period of 60°. The continuous curve drawn

Ferrite composition	290° K				77° K			
	Values of constants, erg/cm³			θ_0, deg	Values of contants, erg/cm³			θ_0, deg
	K_1	K_2	K_3		K_1	K_2	K_3	
Fe_2W	$34 \cdot 10^5$	0	$\leqslant 10^3$	0	$43 \cdot 10^5$	0	$\leqslant 10^3$	0
$Co_{0.3}Fe_{1,7}W$	$28 \cdot 10^5$	0	$\leqslant 10^3$	0	$25.4 \cdot 10^5$	$4.8 \cdot 10^5$	$0.6 \cdot 10^5$	6
$Co_{0.5}Fe_{1.5}W$	$23.8 \cdot 10^5$	$1 \cdot 10^5$	$\leqslant 10^3$	0	$-0.4 \cdot 10^5$	$21.4 \cdot 10^5$	$0.8 \cdot 10^5$	10
$Co_{1.0}Fe_{1.0}W$	$2.1 \cdot 10^5$	$5.6 \cdot 10^5$	$\leqslant 10^3$	0	$-30 \cdot 10^5$	$30 \cdot 10^5$	$1.07 \cdot 10^5$	45
$Co_{1.5}Fe_{0.5}W$	$-6.6 \cdot 10^5$	$6.3 \cdot 10^5$	$\leqslant 10^3$	46	$-49.8 \cdot 10^5$	$36 \cdot 10^5$	$0.8 \cdot 10^5$	56

through the corrected values (triangles) is plotted using Eq. (6) and $K_3 = 1.07 \times 10^5$ erg/cm^3.1) Such a strong basal-plane anisotropy has not yet been observed for barium ferrites.

In view of the strong basal-plane anisotropy detected at 77°K, the concept of the easy magnetization cone needs refining. At low values of K_3, all the magnetization directions coinciding with the cone generators may be regarded as energetically equivalent. However, if the constant K_3 is sufficiently large, as in the crystals considered here, then six lowest energy directions may be distinguished on the cone surface. We shall demonstrate this for $BaCo_{1.0}Fe_{1.0}W$ crystals. At 77°K, an easy magnetization cone with $\theta_0 = 45°$ is observed for these crystals; $K_1 = -K_2 = -30 \times 10^5$ erg/cm^3, $K_3 = 1.07 \times 10^5$ erg/cm^3. The magnetic anisotropy energy along the cone generators is then

$$F_K = F_0 + {}^1/_4 K_1 + {}^1/_8 K_3 \cos 6\varphi = F_0 - (7.5 - 0.134 \cos 6\varphi) \cdot 10^5 \text{ erg/cm}^3.$$

It is evident that the difference between the energy for $\varphi = 0°, 60°, \ldots$ and $\varphi = 30°, 90°, \ldots$ reaches quite a high value (27×10^3 erg/cm^3).

It should be mentioned that according to our data each Co ion makes a contribution to the magnetic anisotropy energy which is approximately half that reported by Bickford.[1] This conclusion is arrived at by comparing our dependence of the "harmonic" anisotropy constant S_4 (Bickford's notation) on the composition parameter x based on our data with the dependence reported by Bickford.[1] We did not observe the appearance of an easy magnetization plane and a thermal transition of the kind axis—cone—plane—cone. This may be because the results being compared were obtained for samples of an essentially different type (textured polycrystals and single crystals prepared by fusion in a gas flame).

Our results agree with the hypothesis that the change in the magnetic anisotropy of ferrites of the $BaCo_xFe_{2-x}W$ system is due to spinel blocks in which Co ions are localized. In fact, the addition of Co gives rise to a positive contribution of the constant K_2^{hex} of a hexagonal crystal to the magnetic anisotropy energy, which is analogous to the influence of the constant K_1^{cub} in the case of cobalt-substituted magnetite. We can understand the reason for the appearance of the strong basal-plane anisotropy, i.e., a high value of the constant K_3^{hex} at 77°K. The latter constant, responsible for the basal-plane anisotropy, corresponds to the constant K_2^{cub}, which governs the anisotropy in the (111) plane of spinels. The rotating moments in this plane are given by the equation

$$L_{(111)}^{\rm cub} = -\frac{1}{18} K_2^{\rm cub} \sin 6\varphi. \qquad (8)$$

But comparing Eqs. (8) and (6), we obtain the following relationship between the constants K_2^{cub} and K_3^{hex}: $K_2^{cub} = 108 K_3^{hex}$. According to Bickford et al.[2] and Slonczewski's calculations,[3] the constant K_2^{cub} for cobalt-substituted magnetite $Co_yFe_{3-y}O_4$ increases strongly on cooling, reaching values of the order of 10^7 erg/cm^3 at 77°K, even if the Co concentration is very low (y = 0.01—0.04). It is easily seen that the experimental values of K_3^{hex} at 77°K are of the same order of magnitude as the listed values of K_2^{cub} for cobalt-substituted magnetite.

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1) The sign of K_3 depends on the direction from which we read the angle φ in the basal plane. Such a direction may be one of the three twofold axes of the $[\bar{1}010]$ type or one of the three axes of the $[1\bar{1}20]$ type. Which of these directions corresponds to the stable position of I_s, we have not been able to determine as yet, and therefore we have assumed arbitrarily that K_3 is positive.

[1] L. R. Bickford, Jr., J. Phys. Soc. Japan, Suppl. B-1 **17**, 272 (1962).

[2] Bickford, Jr., Brownlow, and Penoyer, Proc. Inst. Elec. Engrs., Suppl. No. 5 **104B**, 238 (1957).

[3] J. C. Slonczewski, Phys. Rev. **110**, 1341 (1958).

Translated by A. Tybulewicz
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