Magnetic properties of the ferrimagnetic iron oxide γ-Fe_2O_3

E. V. Babkin, K. P. Koval', and V. G. Pyn'ko

L. V. Kirenskiĭ Institute of Physics, Siberian Branch, USSR Academy of Sciences
(Submitted 4 January 1990)
Zh. Eksp. Teor. Fiz. **100**, 582–589 (August 1991)

The results of a study of the magnetic properties of the iron oxide γ-Fe_2O_3 are presented. Epitaxial crystallization on a magnesium oxide substrate insured the stability of this compound over a wide temperature range. The temperature dependence of the magnetization and of the magnetic anisotropy constants was measured. The magnetizations of the sublattices and the single-ion anisotropy constants of the Fe^{3+} ion were determined. The effect of the onset of magnetic anisotropy induced by the film growth was observed; the character of the anisotropy depends on the crystallographic orientation of the substrate. It is shown that the onset of anisotropy is due to the ordering of the cation vacancies during the film growth.

1. INTRODUCTION

Iron oxide γ-Fe_2O_3 has the crystal structure of spinel $Fe^{3+}[Fe^{3+}_{5/3}\square_{1/3}]O_4$, where $\square$ is a cation vacancy. The presence of a fractional number of vacancies causes the γ-Fe_2O_3 unit cell to have tetragonal symmetry ($c/a = 3$), and the arrangement of the cation vacancies forms a fourfold screw axis.[1] Depending on the degree of long-range order in the arrangement of the cation vacancies, the macroscopic symmetry of the crystal can change from cubic to tetragonal. The compound γ-Fe_2O_3 is unstable, and when heated above 600 K, changes irreversibly into the rhombohedral modification α-Fe_2O_3. This fact substantially complicates the study of its properties. For example, it is impossible to grow massive single crystals, since all the known growing methods are high-temperature ones. This creates difficulties in the study of magnetic anisotropy, magnetostriction and other properties characteristic of single crystals. For γ-Fe_2O_3, the Curie temperature is unknown, since it is beyond the stability limits of this phase. Thus far, there has only been a study[2] in which epitaxial films of γ-Fe_2O_3 were obtained by decomposition of halides. The object of the present work was to develop a gas-transport technology for preparing single-crystal films of γ-Fe_2O_3 and to study their magnetic properties.

2. PHASE STABILIZATION MECHANISM; FILM DEPOSITION TECHNOLOGY; CERTIFICATION OF SAMPLES

The phase stabilization of γ-Fe_2O_3 is based on the concept of the size effect, which is connected with the influence of surface energy on the thermodynamic properties of films and particles.[3] The surface energy of a film may be determined by the surface tension of the given material, and also by the film-substrate interaction. By selecting the substrate, one can obtain a change in the phase transition temperature and broaden the temperature range where a given phase is stable.

In the case of the phase transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$, the analysis of the choice of the substrate is fairly simple, since these phases have different crystal lattice symmetries. To stabilize the γ-Fe_2O_3 phase, it is obviously necessary to have a substrate for a cubic crystal that has a similar lattice constant or multiple thereof and pronounced epitaxial-properties. This requirement is met by the crystal of magnesium oxide MgO, which is widely used in the technology of epitaxial films.

Monocrystalline films of γ-Fe_2O_3 were prepared by the method of chemical transport reactions in a hydrogen chloride atmosphere on different faces of magnesium oxide crystal. A thermodynamic analysis of the transport conditions made it possible to determine the optimum deposition conditions.

X-ray diffraction and electron microscope analyses established that the films obtained were monocrystalline, with lattice constant $a = 8.36$ Å. The growth of the films took place in accordance with the direct epitaxial scheme.

The single-phase character of the films was preserved up to thicknesses of 3 μm, and their magnetic properties at room temperature were identical to the properties of finely divided γ-Fe_2O_3.

3. MAGNETIC PROPERTIES OF γ-Fe_2O_3 FILMS

Saturation magnetization

The temperature dependence of the saturation magnetization $M(T)$ of γ-Fe_2O_3 films was measured in the range 77–750 K by the torque method with a torque magnetometer in accordance with the technique described in Ref. 4. Figure 1 shows the results of the measurements. Approximation of the $M(T)$ curve in the low-temperature range gives the value 1.14 μ_B per molecule for the magnetic moment, which is in satisfactory agreement with the value 1.18 μ_B for γ-Fe_2O_3 particles.[5] The Curie temperature is 700 ± 5 K, which differs somewhat from the corresponding value of 743 K

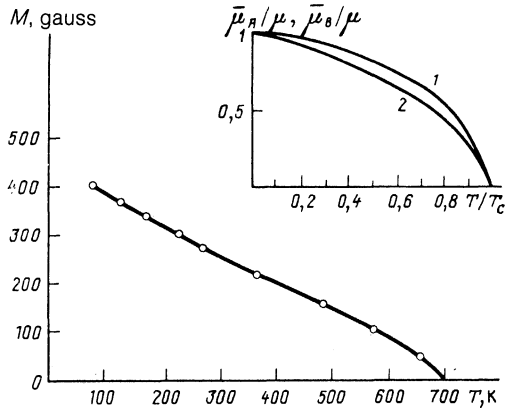

FIG. 1. Temperature dependences of saturation magnetization M and of relative magnetizations of the sublattices $\bar{\mu}_A/\mu$ (curve 1) and $\bar{\mu}_B/\mu$ (curve 2) of γ-Fe_2O_3.

 0038-5646/91/080321-05$03.00

obtained for films,[2] but is considerably below the value determined for particles by the indirect method of Ref. 6.

The temperature dependence of the magnetization of the sublattices was calculated from the experimental $M(T)$ curve in accordance with Néel's theory for a two-sublattice ferrimagnetic substance with inclusion of the intersublattice A-B-exchange interaction.

The equations for the magnetizations of the sublattices are

$$\frac{\bar{\mu}_A}{\mu} = B_{5/2}\left(-\frac{10\mu\bar{\mu}_B K}{kT}\right), \tag{1}$$

$$\frac{\bar{\mu}_B}{\mu} = B_{5/2}\left(-\frac{6\mu\bar{\mu}_A K}{kT}\right), \tag{2}$$

where μ is the magnetic moment of the Fe^{3+} ion, $\bar{\mu}_A$ and $\bar{\mu}_B$ are the magnetizations of the sublattices, $B_{5/2}$ is the Brillouin function for spin $S=\frac{5}{2}$, k is Boltzmann's constant, $K = I_{AB}{}^2(\frac{5}{2})/\mu^2$, and I_{AB} is the exchange integral. Hence

$$\frac{6\bar{\mu}_A}{\mu} F\left(\frac{\bar{\mu}_A}{\mu}\right) = \frac{10\bar{\mu}_B}{\mu} F\left(\frac{\bar{\mu}_B}{\mu}\right), \tag{3}$$

where F is a function which is the inverse of the Brillouin function. Equation (3) and the equation for the magnetization of ferrite

$$\frac{M(T)}{M(0)} = \frac{1}{n_B - n_A}\left(n_B\frac{\bar{\mu}_B}{\mu} - n_A\frac{\bar{\mu}_A}{\mu}\right), \tag{4}$$

where n_A and n_B are the number of ions in sublattices A and B per unit volume, form a system of equations for the unknown $\bar{\mu}_A$ and $\bar{\mu}_B$. The system was solved numerically. The obtained temperature dependence of the magnetizations of the sublattices is shown in Fig. 1.

Magnetic anisotropy induced by film growth

An unexpected finding was a strong uniaxial anisotropy in films grown on the (001) face of the magnesium oxide crystal. The anisotropy constant, $\sim 10^5$ erg/cm^3, does not permit the explanation of the initiation of anisotropy by the magnetoelastic effect caused by stresses in the film on the substrate side. The anisotropy is strongly dependent on the film-deposition conditions.

In order to explain the character and nature of the induced anisotropy, the latter was studied on films grown under different growth faces. Since the selected direction during growth of the film is the normal to its surface (direction of the crystallization front), in general the energy of the growth-induced anisotropy is[7]

$$E = F\sum_i \alpha_i{}^2\beta_i{}^2 + G\sum_{i\neq j}\alpha_i\alpha_j\beta_i\beta_j, \tag{5}$$

where α_i are the direction cosines of the magnetization vector, β_1 are the direction cosines of the selected direction, and F and G are phenomenological constants.

Inclusion of the shape anisotropy of the sample and of magnetic crystallographic anisotropy makes it possible to obtain an analytic expression for the torque of the film during when the external magnetic field is rotated in a specified crystallographic plane. In particular, in the case of the (110) growth face ($\beta = (2^{-1/2}, 2^{-1/2}, 0)$) and rotation of the magnetic field in the (001), (1$\bar{1}$0), and (110) planes, the corresponding expressions for the torque are

$$L_{(001)} = (2\pi M^2 + G/2)\,V\sin 2\Psi - {}^1/_2 k_1 V\sin 4\Psi, \tag{6}$$

$$L_{(1\bar{1}0)} = (2\pi M^2 + F/2 + G/2)\,V\sin 2\Psi + k_1 V\sin^3\Psi\cos\Psi + {}^1/_2 k_1 V\sin 4\Psi + k_2 V\sin^3\Psi\cos^3\Psi - {}^1/_2 k_2 V\sin^5\Psi\cos\Psi, \tag{7}$$

$$L_{(110)} = (F/2 + G/4)\,V\sin 2\Psi + k_1 V\sin^3\Psi\cos\Psi + {}^1/_2 k_1 V\sin 4\Psi + k_2 V\sin^3\Psi - k_2 V\sin 5\Psi\cos\Psi, \tag{8}$$

where V is the volume of the film, and ψ is the angle between the specified crystallographic axis and the direction of the magnetic field (see Fig. 5 below); in the first two expressions, ψ is reckoned from the plane of the film, and in the third expression, from the [1$\bar{1}$0] direction; k_1 and k_2 are the constants of magnetic crystallographic anisotropy.

Comparison of the experimental results obtained by the torque method with the results calculated for γ-Fe_2O_3 films under the (110) growth face, made it possible to determine the constants of induced anisotropy:

$$F = -3\cdot 10^5\ \text{erg/cm}^3, \quad G = -2\cdot 10^4\ \text{erg/cm}^3.$$

In general, the quantitative relation between the constants is determined by the symmetry of the local field acting on the d ion:[8]

$$F = c\sum_i (\gamma_{i1}{}^2\gamma_{i2}{}^2 - \gamma_{i1}{}^4), \tag{9}$$

$$G = c\sum \gamma_{i1}{}^2\gamma_{i2}{}^2, \tag{10}$$

where c is a constant, and γ_i are the direction cosines of the local field relative to the principal crystallographic axes.

Analysis shows that in this case we have $\gamma \| [100]$. This may indicate the presence of a tetragonal modification of γ-Fe_2O_3, which arises from the ordering of the cation vacancies.[1] Thus one of the possible causes of induced anisotropy is the ordering of the cation vacancies, which is characteristic of the tetragonal phase of γ-Fe_2O_3.

Magnetic crystallographic anisotropy

On the assumption that the onset of induced anisotropy is caused by the ordering of the cation vacancies, then depending on the degree of ordering a correlation between the first constant of magnetic crystallographic anisotropy (MCA) and the induced anisotropy constant should be observed. The first constant of MCA in the single-ion model is determined by the sum of the terms[7]

$$k_1(T) = n_A\left[a_A r(m_A) + \frac{\gamma_A D_A{}^2 t(m_A)}{kT}\right] + n_B\left[a_B r(m_B) + \frac{\gamma_B D_B{}^2 t(m_B)}{kT}\right], \tag{11}$$

where a_i and D_i are the crystal field parameters, r and t are known functions of the magnetizations of the sublattices, and m_i, γ_i are coefficients characterizing the direction of the local field acting on the d ion. The even terms in Eq. (11) determine the contribution of the uniaxial local field to the first constant of MCA in the case of a statistically uniform distribution of the tetragonal axes over the principal crystallographic directions. When the cation vacancies are ordered in one of the directions (single-domain crystal), the contri-

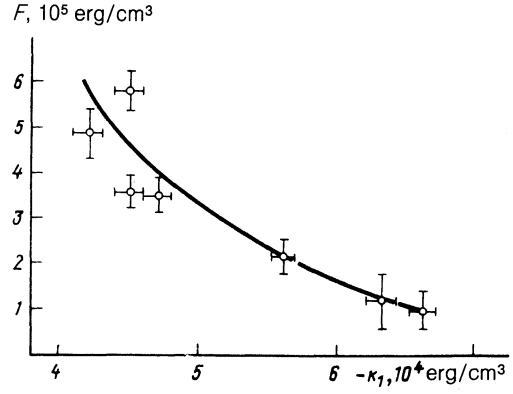

FIG. 2. Correlation between the constants of induced magnetic anisotropy F and magnetic crystallographic anisotropy k_1 of single-crystal γ-Fe_2O_3 films.

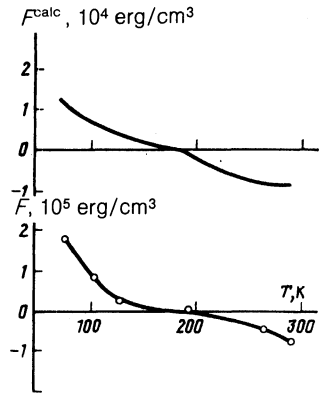

FIG. 4. Temperature dependences of induced magnetic anisotropy constant F and of the calculated dependence $F^{\text{calc}} = \Sigma_{i=A,B}(\gamma_i D_i^2/kT)$.

bution of these terms to k_1 is absent, but it gives rise to uniaxial anisotropy in a given selected direction. This conclusion is in qualitative agreement with the results presented in Fig. 2, which shows a correlation between k_1 and F for a series of films. The magnitude of the constant F in the experiment was specified by the technological conditions of film growth, i.e., the deposition rate and the degree of hardening at the end of the synthesis. It follows from Fig. 2 that the local uniaxial field makes a negative contribution to k_1.

The same conclusion is reached on the basis of the results of the study of the temperature dependence of the first constant of MCA. In Fig. 3, the solid line represents the calculated dependence $k_1(T)$ with the parameters $a_A = 0.005$ cm^{-1}; $a_B = 0.019$ cm^{-1}; $|D_A| = 1.0$ cm^{-1} ($\gamma_A = -\frac{2}{3}$); $|D_B| = 1.1$ cm^{-1} ($\gamma_B = \frac{4}{9}$).

The values of the parameters a_A and a_B are in good agreement with the corresponding values for the Fe^{3+} ion in other ferrites. The nonzero values of D_A and D_B indicate a contribution of uniaxial fields to the constant k_1. This is reflected in Fig. 4, which shows the experimentally measured temperature dependence of the uniaxial anisotropy constant F (a point) and the calculated dependence

$$F^{\text{calc}} = \sum_{i=A,B} \frac{\gamma_i D_i^2}{kT}.$$

The correlation in the change of these quantities confirms the assumption that the anisotropy is noncubic. This is also consistent with the general theoretical statements in Ref. 9 concerning the induction of uniaxial anisotropy with the constant $F \approx 10^5$ erg/cm^3 and $D \approx 1$ cm^{-1} in a single-domain tetragonal crystal.

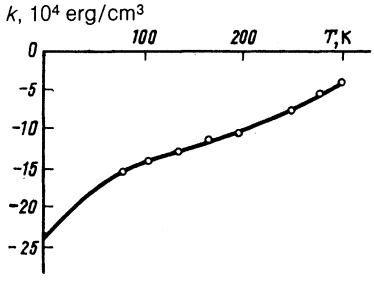

FIG. 3. Temperature dependence of the magnetic crystallographic anisotropy constant k_1 of monocrystalline γ-Fe_2O_3 films.

Second constant of magnetic crytallographic anisotropy

This section will discuss the method and results of measurements of the second constant of MCA for single-crystal films of γ-Fe_2O_3, on which no data are available. The method is based on the measurement of the torque of the film, whose plane makes an arbitrary angle with the axis of the suspension.

The free energy density of the film may be represented by the sum of several terms:

$$E = E_{\text{MCA}} + E_{\text{MSA}} + E_{\text{IMA}} + E_H, \tag{12}$$

where E_{MCA} is the energy density of MCA; E_{MSA} is the density of magnetostatic anisotropy; E_{IMA} is the energy density of induced magnetic anisotropy (IMA); E_H is the energy density of interaction of the magnetic moment of the film with the external magnetic field.

In a spherical coordinate system, for films of (001)-type crystallographic orientation, these terms can be reduced to the form

$$E_{\text{MCA}} = {}^1/_4 k_1(\sin^4\Phi \sin^2 2\varphi + \sin^2 2\Phi) + {}^1/_2 k_2 \sin^2 2\varphi(\sin^4\Phi - \sin^6\Phi), \tag{13}$$

$$E_{\text{MSA}} = 2\pi M^2 \cos^2\Phi, \tag{14}$$

$$E_{\text{IMA}} = F\cos^2\Phi, \tag{15}$$

$$E_H = -MH[\sin\Phi \sin\Psi(\cos\varphi\cos\psi + \sin\varphi\sin\psi) + \cos\Phi\cos\Psi]. \tag{16}$$

The angles Φ, φ, and Ψ, ψ characterize the directions of the vectors M and H relative to the principal crystallographic directions (Fig. 5).

The equilibrium conditions of the system are found from the equations

$$\frac{dE}{d\Phi} = 0, \quad \frac{dE}{d\varphi} = 0. \tag{17}$$

To apply the indicated method of measurements, it is necessary to determine the torque component relative to the axis of suspension of the film, whose plane is oriented at some angle Ψ^* to the axis (Fig. 5). The torque may be generally represented as

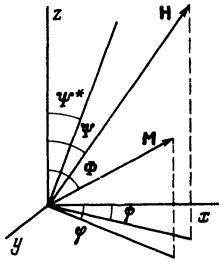

FIG. 5. Orientation of the crystallographic axes and directions of vectors M and H relative to the axis of the suspension in the spherical coordinate system.

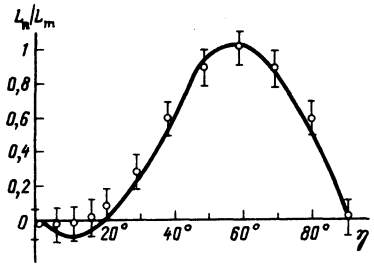

FIG. 6. Angular dependence of the torque of a single-crystal γ-Fe_2O_3 film oriented at an angle $\Psi^* = 60°$ with respect to the axis of the suspension (L_m being the maximum value of the torque).

$$\mathbf{L}=V[\mathbf{MH}]. \tag{18}$$

The change to a new coordinate system where the axes are the axis of the suspension **n** and one of the [010] crystallographic directions is made by means of the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \sin\Psi^* & \cos\Psi^* \\ 0 & -\cos\Psi^* & \sin\Psi^* \end{pmatrix}. \tag{19}$$

In this coordinate system, there are two torque components: the one being sought, relative to the axis of the suspension,

$$L_n=MVH[\sin\Psi'\sin\Phi\sin\Psi(\sin\psi\cos\varphi-\sin\varphi\cos\psi) -\cos\Psi'(\sin\Psi\cos\Phi\cos\psi-\sin\Phi\cos\Psi\cos\varphi)], \tag{20}$$

and the parasitic component relative to the [010] crystallographic direction,

$$L_{[010]}=MVH[\sin\Psi'(\cos\Phi\sin\Psi\cos\psi-\sin\Phi\cos\Psi\cos\varphi) +\cos\Psi'\sin\Phi\sin\Psi(\sin\psi\cos\varphi-\sin\varphi\cos\psi)]. \tag{21}$$

It is convenient to consider the case of a fairly high magnetic field

$$\Phi\approx\Psi, \quad \varphi\approx\psi.$$

Considering Eqs. (20) and (21), we obtain

$$L_n=V\sin\Psi'[{}^1/_2k_1\sin^4\Psi\sin4\psi+{}^1/_2k_2\sin4\psi \times(\sin^4\Psi-\sin^6\Psi)]-V\cos\Psi' \times\cos\psi[{}^1/_2k_1(2\sin^3\Psi\cos\Psi\sin^2 2\varphi +\sin4\Psi)+{}^1/_2k_2\sin^2 2\psi\cos\Psi(2\sin^3\Psi-3\sin^5\Psi) -(2\pi M^2+F)\sin2\Psi]. \tag{22}$$

The polar angle Ψ and azimuthal angle ψ are related to the angle η being measured from the [010] direction by the equations

$$\cos\Psi=\sin\eta\cos\Psi', \tag{23}$$

$$\cos\psi=\cos\eta(1-\sin^2\eta\cos^2\Psi')^{-1/2}. \tag{24}$$

Using Eqs. (22) and (23), for known values of $(2\pi M^2+F)V$ and k_1V, measured by independent methods, one can determine k_2V by optimizing the agreement between the calculated and experimentally measured dependences $L_n(\eta)$.

The expression (22) in cases of vertically and horizontally oriented films changes into the previously obtained expressions[10]

$$1.\ \Psi'=0,\quad \psi=0,\quad \Psi=\eta:$$
$$L_n=(2\pi M^2+F)V\sin2\eta+{}^1/_2k_1V\sin4\eta,\quad L_{[010]}=0. \tag{25}$$

$$2.\ \Psi'=\pi/2,\quad \Psi=\pi/2,\quad \psi=\eta:$$
$$L_n={}^1/_2k_1V\sin4\eta,\quad L_{[010]}=0. \tag{26}$$

This method imposes constraints on the selection of the films being measured. This is because the expression (22), in addition to the constants k_1 and k_2, additively includes a term, proportional to $2\pi M^2+F$, that usually surpasses them considerably in magnitude. This may lead to a large error in the determination of k_2. The situation is favorable to the samples being studied. The low saturation magnetization and presence of induced magnetic anisotropy insure the equality of at least two constants: $2\pi M^2+F$ and k_1.

Monocrystalline films of γ-Fe_2O_3 of (001) orientation were used in the studies. The measurements were taken with a torque magnetometer at room temperature. It was established experimentally that the presence of the $L_{[010]}$ component does not introduce an error into the measurement of L_n: the minimum deflection of the suspension from the vertical is balanced by the weight moment of the sample. Measurements of the torque in different fields showed that, starting with the magnetic field strength $H = 12$ kOe, no change in $L_n(\eta)$ takes place. This supports the validity of the approximations for the given field range. Figure 6 shows the angular dependence of the torque of a γ-Fe_2O_3 film 1.3 μm thick with constants $k_1 = -0.7\times10^5$ erg/cm^3 and $F = -1.7\times10^5$ erg/cm^3. The measurements were taken in an external magnetic field with $H = 16$ kOe, $\Psi^* = 60°$. In the same figure, the solid line represents the corresponding calculated $L_n(\eta)$ curve with $k_2 = (1.9\pm0.4)\times10^5$ erg/cm^3.

5. CONCLUSION

We have synthesized single-crystal films of γ-Fe_2O_3, stable over a wide temperature range. This made it possible to measure the temperature dependences of the magnetization and of the first constant of MCA, and to establish the Curie temperature of iron γ oxide. We observed the effect of formation of induced magnetic anisotropy, whose character depends on the crystallographic orientation of the substrate. It was shown that the onset of induced anisotropy is caused by the ordering of the cation vacancies, which transforms the crystal symmetry from cubic to tetragonal.

The authors are deeply grateful to G. V. Bondarenko, A. S. Dolgarev, A. S. Komalov, and I. S. Édel'man for the detailed certification of the samples studied.

[1] G. W. Oösterhout and C. J. M. Roimans, Nature **181** B, 44 (1958).
[2] H. Takei and S. Chiba, J. Phys. Soc. Jpn. **21**, 1255 (1966).

[3] A. I. Bublik and B. Ya. Pines, Dokl. Akad. Nauk SSSR **87**, 215 (1952).
[4] S. Chikazumi, J. Appl. Phys. **32**, 81S (1961).
[5] W. F. Henry and M. J. Boehm, Phys. Rev. **101**, 1253 (1956).
[6] W. F. Brown and C. E. Jonson, J. Appl. Phys. **33**, 2752 (1962).
[7] S. Krupicka, *Physics of Ferrites and Related Magnetic Oxides* Mir, Moscow, 1976), Vol. 2.
[8] E. M. Gyorgy and F. J. Schnettler, J. Appl. Phys. **35**, 1648 (1964).
[9] P. Novak, Czech J. Phys. B **16**, 723 (1966).
[10] R. F. Soohoo, *Magnetic Thin Films* (Harper and Row, London, 1965; Mir, Moscow, 1967).

Translated by Adam Peiperl