# Surface anisotropy and helicoidal magnetic structure on the basal faces of hematite

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A uniaxial magnetic surface anisotropy is observed, by the magneto-optical method, on the basal faces of hematite; it leads to the formation of a helicoidal magnetic structure with an angle, controllable by an external field, between the spin directions on the surface and in the volume of the crystal. Magnetization of the surface layer to saturation along the hard axis occurs at field $H_{cr} \sim 1$ kOe. The surface density of anisotropy energy on a (111) face is $\sim 0.035$ erg/cm$^2$. The existence of surface anisotropy is due to the presence, on the basal faces of hematite, of microscopic growth steps.

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## 1. INTRODUCTION

On nonbasal faces of hematite, of the (100) type, surface magnetism, caused by the presence of surface anisotropy on these faces, has been observed and investigated.[1] The appearance of magnetic surface anisotropy on nonbasal faces of $\alpha-Fe_2O_3$ is caused by the change of the symmetry of the environment of the magnetic $Fe^{3+}$ ions on the surface as compared with the volume. The field at which magnetization of the surface to saturation occurs is ~20 kOe. In the present work, uniaxial magnetic surface anisotropy is also observed, by the magneto-optic method, on the basal faces (111) of hematite. The anisotropy energy density on the basal faces is an order of magnitude smaller than on hematite faces of the (100) type, and the field at which magnetization of the surface to saturation occurs is one to two orders smaller than the corresponding field for faces of the (100) type.

## 2. MEASUREMENT METHOD AND SPECIMENS

The magneto-optical investigation of the basal faces of hematite was made by measurement of the equatorial and meridional Kerr effects and of the meridional intensity of the magneto-optical effect.[2] Since the light penetrates into the specimen to a depth of less than 0.1 $\mu m$, and since the linear magneto-optical effects are proportional to the magnetization, in a magneto-optical experiment it is in principle possible to obtain magnetization curves of a thin surface layer of the specimen.

In the research we used a dynamic magneto-optical setup with automatic recording of the signal. The setup was augmented, as compared with that described previously,[3] by a unit for sweeping the magnetic field and by an $xy$ recorder.

Measurements of the volume magnetic properties of single crystals of hematite were made on a null apparatus, which consisted of a solenoid and two measurement coils of 2000 turns each. The measurement coils were connected in opposition and were placed in a solenoid through which flowed an alternating current of audio frequency (~130 Hz). The signal that occurred when the specimen was placed in one of the coils, and which was proportional to the magnetization of the specimen, was followed with a U2-6 measuring resonance amplifier.

The magneto-optical measurements were made on natural basal faces of synthesized single crystals of hematite, of area 20–30 mm$^2$. The specimens were obtained by the method of growing single crystals from solution in the melt.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION OF THEM

Figure 1 shows the angular variation of the equatorial Kerr effect on a hematite face of the (111) type, at field $H = 10$ Oe (all magneto-optical measurements were made at $\lambda = 0.55$ $\mu m$ and angle of incidence of the light $\varphi = 45°$), when the specimen was rotated in the basal plane. The curve given in the figure demonstrates the presence on the basal face of uniaxial magnetic anisotropy. Figure 2 shows the variation with field of the equatorial Kerr effect in the direction of the hard (HA) and easy (EA) magnetization axes. Figure 2a shows the initial section of the magnetization curves. Shown dotted are the volume magnetization curves, measured on the null apparatus for the same magnetic-field directions as the magneto-optic curves. It is evident from Fig. 2a that the magnetization curves on the specimen surface, determined by the variation of the Kerr effect with the field, and the volume magnetization curves are qualitatively different. While anisotropy is practically absent within the volume, on the surface of the specimen the magnetization curves have a clearly expressed anisotropic character. Since the spins of the ions are coupled to each other by strong exchange interaction, the change of direction of the magnetic moments of the $Fe^{3+}$ ions in a magnetic field, upon passage from the surface to the volume, must occur in a continuous man-

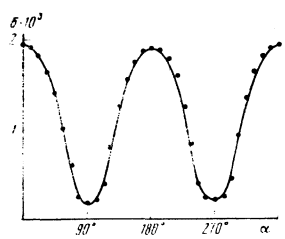


FIG. 1. Angular dependence of the value of the magneto-optical Kerr effect on a basal face of hematite ($\alpha = 0$ corresponds to the EA direction); $H = 10$ Oe.

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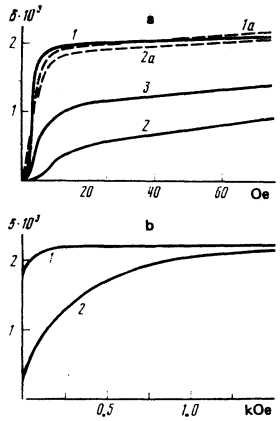


FIG. 2. Field dependence of the equatorial Kerr effect on a (111) face of hematite along the EA (Curve 1) and along the HA (Curve 2), and for magnetization at angle 60° to the EA (Curve 3). Shown dotted in Fig. 2a are magnetization curves within the volume, in relative units (Curves 1 and 1a, 2 and 2a correspond to the same directions of the magnetizing field).

ner; that is, on the surface there is formed a magnetic transition layer of the domain-boundary type, similar to the transition layer on nonbasal faces of hematite.[1] On increase of the intensity of the magnetic field along the HA, the spins at the surface of the crystal gradually rotate, approaching the field direction.

In weak fields, when $H \perp$ EA, the angle between the directions of the spins on the surface and within the volume of hematite must be close to 90°. In fact, it is evident from Fig. 2a that at field $H \sim 10$ Oe, the volume of the specimen is already magnetized to saturation, whereas the surface spins deviate from the EA by an angle ~10°. But measurements of the meridional effect from the component of magnetization parallel to the EA, when $H \perp$ EA, showed that the resultant magnetization on the EA was zero. This is explained by the fact that in the transition from the surface to the volume, when $H \perp$ EA, spin rotations with different directions of rotation in oppositely magnetized domains are energetically equivalent. But if we magnetize the specimen in a direction close to the HA, then in consequence of the presence of surface anisotropy there must exist a component

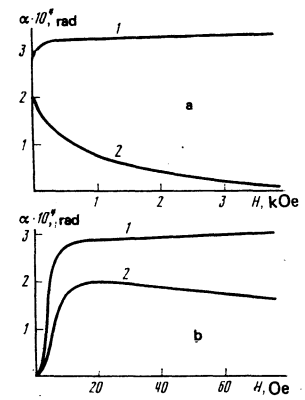


FIG. 3. Meridional Kerr effect due to the component of magnetization parallel to the field when $H \parallel$ EA (Curve 1), and perpendicular to the field in the case when $H$ makes an angle $\alpha = 60°$ with the EA (Curve 2).

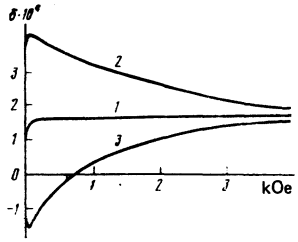


FIG. 4. Sum of the equatorial and of the meridional-intensity effects for three cases: the specimen is magnetized along the EA ($\alpha = 0$), the angle $\theta$ between the plane of polarization of the light incident on the specimen and the plane of incidence of the light is 65° (Curve 1); $\alpha = 60°$, $\theta = 65°$ (Curve 2); $\alpha = 60°$, $\theta = -65°$ (Curve 3).

of magnetization perpendicular to the field. Curve 1 in Fig. 3 shows the field dependence of the ordinary meridional Kerr effect when $H \parallel$ EA. Curve 2 is the meridional Kerr effect in the equatorial geometry, from the component of magnetization perpendicular to the field, when the specimen is magnetized at angle 60° to the EA. As was to be expected, the component of magnetization perpendicular to the field initially rises abruptly with increase of $H$ and reaches a maximum at the same field values ($H \sim 20$ Oe; the projection on the EA ~ 10 Oe) at which the meridional effect for $H \parallel$ EA (curve 1) approaches saturation ($H \sim 10$ Oe); it then falls, tending to zero. The maximum value on Curve 2 is 0.73 of the value on Curve 1 at the same field. If we take it into account that the angle between the EA and the direction along which the projection of the magnetization is measured by the meridional Kerr effect is 30°, and also the fact that the spins in the surface layer are rotated through an angle ~6° from the EA toward the field direction when $H \sim 20$ Oe (the value 54° for the angle between the spins at the surface and the external field is obtained by comparison of Curves 1 and 3 in Fig. 2a), then we get an estimate of the ratio mentioned above: $\sin 54° \approx 0.81$, in sufficiently good agreement with the experimental value (0.73). Thus it follows from Fig. 3 that in a magnetic field 20 Oe directed at angle 60° to the EA, in the surface region of hematite there occurs a rotation of the magnetization from the surface to the volume through an angle ~54°; that is, in the surface layer of hematite there is a helicoidal transition structure with spin-rotation angle 50–60°.

Figure 4 gives curves of the variation with field of the sum of the equatorial and meridional intensity effects, in a measurement in the geometry of the equatorial Kerr effect,[2] for three cases: Curve 1, $\alpha = 0$ ($\alpha$ is the angle between the EA and $H$), $\theta = \pm 65°$ ($\theta$ is the angle at which the plane of polarization of the light is inclined to the $p$ component); Curves 2 and 3, $\alpha = 60°$, $\theta = \pm 65°$ (when the polarizer is inclined at angle $\theta$ to the $p$ component, the meridional-intensity effect changes sign without change of magnitude, while the equatorial effect remains unchanged[2]). The angle $\theta = 65°$ was chosen so that the equatorial and meridional intensity effects would be approximately equal in magnitude. Curve 1 in Fig. 4, taken for magnetization of the specimen along the EA, is the pure equatorial effect, since the meridional-intensity effect in this case is zero because of the absence of a projection of the magnetization

on the plane of incidence of the light. Curve 1 shows approximately what fraction the equatorial Kerr effect is of the algebraic sum of the equatorial and of the meridional-intensity effects, shown in Curves 2 and 3. Curves 2 and 3 in Fig. 4 illustrate in principle the same fact as in Fig. 3, namely that with increase of field the projection of the magnetization perpendicular to $H$ at first abruptly increases to a maximum and then tends monotonically to zero. The meridional-intensity effect, which is proportional to this component of the magnetization, varies according to the same law; but the equatorial Kerr effect, which is proportional to the projection of the magnetization on $H$, increases at first abruptly, and then monotonically with the field.

It follows from the results described that when hematite is magnetized in a direction close to the EA, there is formed in the surface region of the specimen a magnetic structure with a smooth rotation of the spins during passage from the surface of a basal face to the volume. Since at room temperature the spins and the resulting weak ferromagnetic moment in hematite lie in the basal plane,[4] the rotation of the spins within the transition layer occurs about the $C_3$ axis, perpendicular to the (111) plane of hematite. Thus the surface transition layer has a helicoidal structure, with an angle between the directions of the spins at the surface and in the volume of the crystal that can be controlled by the external magnetic field.

Reference 1 considered theoretically the problem of the structure of the magnetic transition layer in hematite, in the case of pinning of the spins at the surface of the crystal, and of the behavior of this layer in a magnetic field. We shall apply the calculation made to the case under consideration. For a basal face, the surface-anisotropy energy can be written as follows:

$$\sigma_a = -a \sin^2 \varphi_0,$$

where $a > 0$ and where $\varphi_0$ is the angle between the EA and the antiferromagnetism vector $L$ at the surface. The expression (18) of Ref. 1 for $\partial\gamma_\varphi/\partial\varphi_0$ (where $\gamma_\varphi$ is the energy of the transition layer in the magnetic field), in the case of basal faces, can be simplified by using the fact that erasure of the surface magnetism on these faces occurs at a field $H_{cr} \sim 1$ kOe (Fig. 2b), therefore $H_{cr}/H_D \ll 1$ (where $H_D \sim 20$ kOe is the Dzyaloshinskiĭ field[4]). Namely, for $H \perp$ EA

$$\frac{\partial \gamma_\varphi}{\partial \varphi_0} = -\gamma_w \cos\frac{\varphi_0}{2} = -0{,}51 \cdot 10^{-2} H^{1/2} \cos\frac{\varphi_0}{2} \left[\frac{\text{erg}}{\text{cm}^2}\right].$$

The equilibrium value of $\varphi_0$ is determined by the minimization condition for the sum of the energies $\gamma_\varphi$ and $\sigma_a$:

$$\frac{\partial}{\partial \varphi_0}(\gamma_\varphi + \sigma_a) = -\gamma_w \cos\frac{\varphi_0}{2} - a \sin 2\varphi_0 = -0{,}51 \cdot 10^{-2} H^{1/2} \cos\frac{\varphi_0}{2} - a \sin 2\varphi_0 = 0. \quad (1)$$

For known anisotropy constant $a$, equation (1) determines the $\varphi_0(H)$ relation. For some critical field $H_{cr}$, magnetization of the surface layer to saturation occurs. Then $\varphi_0(H_{cr}) = \pi$. Solution of the converse problem is also possible: determination of the anisotropy constant $a$ according to a known experimental magnetization curve; that is, for known $H_{cr}$. For $H_{cr} = 800$ Oe, the calculated magnetization curve of the surface layer [the curve $m = m_s \cos\varphi_0(H)$[1]] agrees well with the experimental curve 2 in Fig. 2b in the initial and middle parts. For different specimens, the value of $H_{cr}$ varies over the range 800–1000 Oe. Divergence of the curves in the region $H \sim H_{cr}$ is apparently attributable to a change of the shape of the magneto-optical signal from sinusoidal to rectangular with increase of the field when $H > H_{cr}$. If $\varphi_0 \to \pi$ in (1), we get the following formula relating $a$ and $H_{cr}$:

$$a = \gamma_w/4 = 1{,}25 \cdot 10^{-3} H_{cr}^{1/2} \ [\text{erg/cm}^2]. \quad (2)$$

For $H_{cr} = 800$ Oe, we get $a \approx 0.035$ erg/cm$^2$. For comparison we mention that the value of the uniaxial anisotropy constant on a nonbasal face of hematite, of the (100) type, is 0.2–0.3 erg/cm$^2$.[1]

If the condition $H_{cr} \ll H_D$ is satisfied, then the expression for the effective width $\delta_\varphi$ of the surface transition layer simplifies considerably as compared with the general case.[1] Namely, $\delta_\varphi \approx 1.2 \cdot 10^{-3} H^{1/2}$ [cm]. In particular, when $H = 100$ Oe, $\delta_\varphi \approx 1\ \mu m$. It is interesting to note that when $H \to 0$, the effective width of the transition layer increases without limit. The larger $\delta_\varphi$ is, the stronger is the coupling of the transition layer with the magnetic field. Because of this fact, the emergence from the origin of coordinates of the magnetization curve of the surface layer along the HA is very steep (Fig. 2b, Curve 2). As is well known, in the case of uniaxial volume anisotropy the magnetization curve along the HA has a constant angle of inclination to the axis of abscissas all the way to saturation.

We remark that the controlled helicoidal surface transition layer investigated in this paper is a convenient means of investigating the interaction of light with an inhomogeneous magnetic structure with characteristic dimensions of the order of $\lambda$.

The occurrence of uniaxial magnetic anisotropy on basal faces of hematite was unexpected, since the magnetic symmetry of a surface layer of basal faces does not permit the existence of uniaxial anisotropy of the Néel type because of the presence among the symmetry elements of a third-order axis, perpendicular to the (111) face.

The existence of uniaxial surface anisotropy on (111) faces can be explained by the fact that at the time of growth of the crystal, steps form on its surface. On the lateral surface of such steps there must occur a discompensation of large single-ion and magnetic-dipole energies, which are approximately equal within the volume of the crystal.[5] It is discompensation of these energies that was used in Ref. 1 to explain the occurrence of uniaxial surface anisotropy on (100) faces of hematite, with axis of easy magnetization parallel to the line of intersection of (100) and (111) planes. If we suppose for simplicity that the lateral surface of a step is a plane of the (100) type, then, as follows from the estimates given above for the surface anisotropy constant for faces of (100) and (111) types, the ratio of the total area of the lateral surfaces of the steps to the area of the basal face should be ~0.1.

From the character of the magnetization curves of the

surface layer on a (111) face in the EA and HA directions, shown in Fig. 2a, it may be concluded that the sources of the uniaxial anisotropy (whatever their origin) are distributed over the face surface in a continuous manner; that is, the distance between individual growth bands, $d$, must be much smaller than the effective width $\delta_\varphi$ of the transition layer ($d \ll \delta_\varphi \sim 1\ \mu m$). This conclusion follows from the fact that Curve 2 in Fig. 2a lies below Curve 1 at the smallest fields. If the condition $d \ll \delta_\varphi$ were violated, there would be sections of the crystal surface on which uniaxial anisotropy was absent; and then, because of these sections, Curve 2 would coincide with Curve 1 at small fields.

An indication of the possibility of the existence of microscopic growth bands is the presence on most basal faces of visible macroscopic growth bands. On many basal faces, the easy axis of anisotropy was parallel to the growth bands.


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