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PIEZOMAGNETIC EFFECT IN α-Fe_2O_3

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Magnetization curves of natural crystals of hematite (α-Fe_2O_3) have been investigated under elastic stresses in various crystallographic directions. It was found that a piezomagnetic effect is present in the low-temperature modification of hematite, in agreement with predictions based on the theory of magnetic symmetry. The components of the piezomagnetic tensor were determined. In the high-temperature modification, a piezomagnetic effect could be observed only for one orientation of the crystal.

1. INTRODUCTION

THE possibility of the existence of a piezomagnetic effect in a number of antiferromagnetic crystals was predicted by Dzyaloshinskii.[1] Of the antiferromagnetics considered in this work, piezomagnetism has been observed experimentally in MnF_2 and CoF_2 [2] and in $FeCO_3$.[3] It was especially interesting to investigate this effect in hematite (α-Fe_2O_3), which can exist in two states with different magnetic structures. Hematite has a rhombohedral structure (space group D_{3d}^6). Below $T_N = 950\,°K$ it goes over into an antiferromagnetic state with weak ferromagnetism.[4] The antiferromagnetic vector **l** then lies in the basal plane.[5] At $T = 250\,°K$ the magnetic structure of hematite changes. Below this temperature the vector **l** is directed along the principal axis,[5] and weak ferromagnetism is absent. Piezomagnetism is theoretically possible both in the lower and in the higher modification.[1, 6]

According to [1], a piezomagnetic moment in α-Fe_2O_3 in the low-temperature modification should be observable only along the x and y axes:

$$m_x = \Lambda_1(\sigma_{xx} - \sigma_{yy}) - 2\Lambda_2\sigma_{yz},$$
$$m_y = -2\Lambda_1\sigma_{xy} + 2\Lambda_2\sigma_{xz}. \tag{1}$$

Here and hereafter we use a rectangular coordinate system in which the z axis is directed along the trigonal axis, the x axis is along one of the binary axes, and the y axis lies in the plane of symmetry; σ_{ik} are the components of the stress tensor. Thus for the low-temperature modification of α-Fe_2O_3, the tensor of piezomagnetic moduli Λ_{ijk} has eight nonvanishing components, which can be expressed in terms of two independent constants Λ_1 and Λ_2.

For the high-temperature modification, the expressions for the piezomagnetic moment have the form (see, for example, [6])

$$m_x = 2\Lambda_1'\sigma_{xz} + 2\Lambda_2'\sigma_{yz}, \qquad m_y = 2\Lambda_3'\sigma_{yz} + 2\Lambda_4'\sigma_{xz},$$
$$m_z = \Lambda_5'\sigma_{xx} + \Lambda_6'\sigma_{yy} + \Lambda_7'\sigma_{zz} + 2\Lambda_8'\sigma_{xy}. \tag{2}$$

In this case the piezomagnetic tensor is described by eight independent constants. Birss and Anderson[7] detected in the low-temperature modification of α-Fe_2O_3 the effect thermodynamically inverse to piezomagnetism, linear magnetostriction. The present paper is devoted to an experimental study of piezomagnetism in hematite.

2. APPARATUS AND SPECIMENS

The magnetic measurements were made on a magnetic torsion balance with press, developed in [2]. The construction of this apparatus permitted compression of the specimen with a force as great as about 7 kg. It was possible to measure the magnetic moment in a direction perpendicular to the direction of compression of the specimen. To decrease the corrections for magnetism of the case in which the specimen under study was placed, it was made of fused quartz. The room-temperature measurements were made in an electromagnet of large size, with which fields up to 6 kOe could be obtained.

In our research we used natural crystals of hematite from the Kamenka river deposit in the Urals, obtained from the Mineralogical Museum of the U.S.S.R. Academy of Sciences.[1)] Crystals with

1)The authors sincerely thank Professors G. P. Barsanov and N. A. Kruglov for making the crystals available and for help in selecting them.

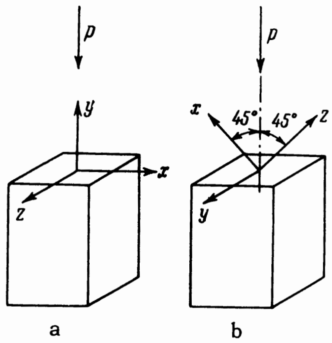

FIG. 1. Orientation of two hematite specimens investigated: a, specimen I; b, specimen II.

linear dimensions of about 0.5 cm had very good faceting, which made it easy to orient them on the goniometer. By means of a special mounting on the polishing wheels, two specimens, in the form of parallelepipeds of height about 2 mm and base about 0.5 mm^2, were sawed out from the best crystals. The orientation of the crystallographic axes in these specimens is shown in Fig. 1. After preparation of the specimens, Laue photographs of them were taken; these showed that the inaccuracy of orientation of the specimens did not exceed 5°.

3. RESULTS OF THE MEASUREMENTS

For each of the two specimens, the dependence of the magnetic moment m on the applied field H along the principal crystallographic directions was studied at room temperature (T_1 = 295° K) and at liquid-nitrogen temperature (T_2 = 77° K). In each case curves were taken in the absence of pressure (p = 0) and under application of the maximum pressure ($p = p_{max}$). The amount of the

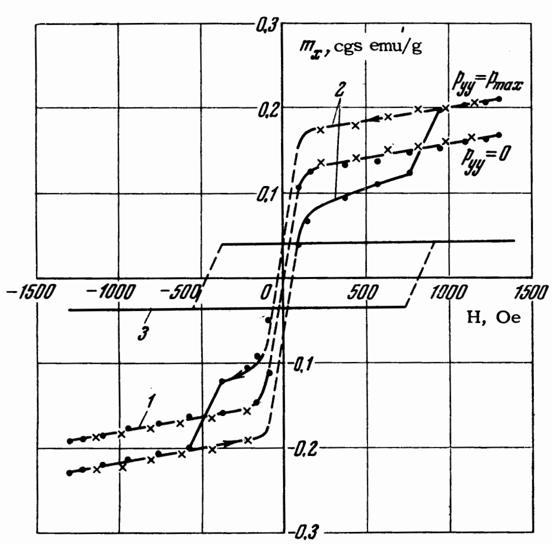

FIG. 2. Field-dependence of the specific magnetic moment of hematite along the x axis (at T = 77°K): curve 1, in the absence of pressure; curve 2, under a pressure that produces stress σ_{yy} = 980 kg/cm²; curve 3, difference curve.

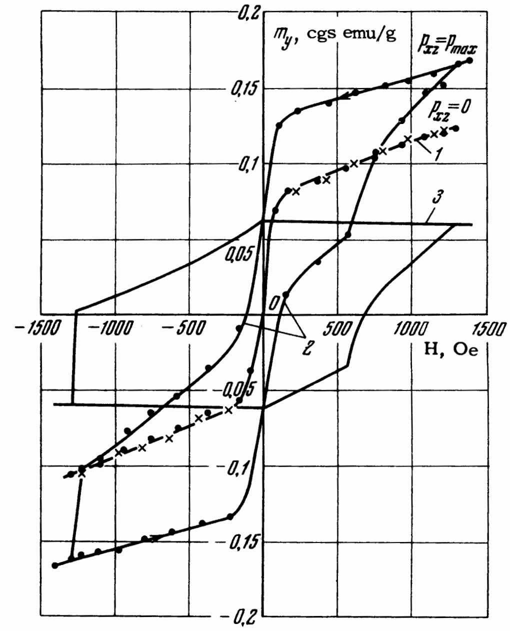

FIG. 3. Field-dependence of the specific magnetic moment of hematite along the y axis (at T = 77°K): curve 1, in the absence of pressure; curve 2, under a pressure that produces stress σ_{xz} = 480 kg/cm²; curve 3, difference curve.

maximum pressure depended on the cross section of the specimen for the given direction. Thus for specimen I, the magnetization was measured in the directions of the x, y, and z axes. For each direction, the $m_i(H_i)$ curves were studied for the two directions of applied pressure perpendicular to it. For specimen II, the $m_y(H_y)$ dependence was plotted. In it, the pressure was applied along the bisector of the angle between the x and z axes. Under these conditions there developed in the specimen uniform stresses $\sigma_{xz} = p/2$ and $\sigma_{xx} = \sigma_{zz} = p/2$.

For the low-temperature modification (at T_1 = 77° K), in the absence of pressure, the following results were obtained. For the x and y directions (the basal plane), the magnetization curve rises rapidly in weak fields, whereas at fields above about 200 Oe (see curves 1 in Figs. 2 and 3) there is observed a linear dependence of the form

$$m_i = m_{i0}' + \chi_i H_i. \qquad (3)$$

On change of the sign of the field, the curves do not remain completely symmetrical. The value of χ_i remains unchanged, but the size of the spontaneous moment changes somewhat, so that

$$m_{i0}' = \pm m_{i0} + \Delta m_{i0}. \qquad (3a)$$

The sign of Δm_{i0} depends on the direction of the field in which the specimen was cooled from room temperature to 77° K. Experimental values of the constants in formulas (3) and (3a) are given

Table I

Direction of axis	Specimen	$\chi_i \cdot 10^6$, cgs emu/g	$m_{i0} \cdot 10^3$, cgs emu/g	$\Delta m_{i0} \cdot 10^3$, cgs emu/g
x	I	28	139	11
y	I	28	132	10
	II	32	65	12
z	I	<18	~100	0

in Table I. Along the z axis we did not reach complete saturation, and the magnetization curve had large hysteresis. Nevertheless, a backward traversal of the hysteresis loop was described sufficiently well by a straight line of the type (3), the parameters of which are also given in Table I.

On application of pressure (T = 77° K), changes in the magnetization curves were observed in only two cases out of the seven orientations investigated. First, in specimen I, when the pressure was applied along the y axis, $p_{yy} = \sigma_{yy} = 980$ kg/cm^2, and the moment was measured along the x axis (see curve 2 in Fig. 2); second, in specimen II, with pressure $p = 960$ kg/cm^2 applied along a direction that divides the angle between the x and z axes in two. In this case $\sigma_{xz} = 480$ kg/cm^2. The magnetic moment was measured along the y axis. As a result, curve 2 in Fig. 3 was obtained. In both cases similar changes of the magnetization curves are observed on application of pressure. Large hysteresis occurs. In sufficiently strong fields, the points fall on a straight line of the type (3), but with larger values of m_{i0}^p. The corresponding values of the constants are given in Table II. On backward traversal, this straight line continues to very small fields. The hysteresis loop for crystal II is appreciably asymmetric.

In all the remaining five positions of specimen I, the value of the magnetization never changed on application of pressure by more than the limits of statistical scatter (about 5%.

In the investigation of our specimens at room temperature, it was found that in measurements along the x and y directions, which lie in the basal plane, we were unable to reach complete saturation and exceed the limits of the technical magnetization curve of a weakly ferromagnetic moment. Therefore the observed changes of the magnetization curves with pressure are difficult to interpret unambiguously. In the direction of the z axis, however, saturation was attained in fields

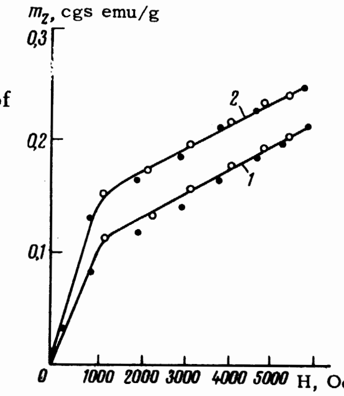

FIG. 4. Field-dependence of the specific magnetic moment of hematite along the z axis (T = 292°K): curve 1, in the absence of pressure; curve 2, under a pressure that produces stress $\sigma_{yy} = 980$ kg/cm^2.

of about 1 kOe (specimen I). Above this field the magnetization follows the linear law (3) with the constants

$$m_{z0} = 85 \cdot 10^{-3} \text{ cgs emu/g}, \quad \chi = 21 \cdot 10^{-6} \text{ cgs emu/g}.$$

No hysteresis was observed (see curve 1 in Fig. 4). On application of pressure $p_y = \sigma_{yy} = 980$ kg/cm^2, the straight line moved upward (see curve 2 in Fig. 4), so that

$$m_{z0}^p = 130 \cdot 10^{-3} \text{ cgs emu/g}.$$

The slope of the line did not change ($\chi_z^p = \chi_z$). In measurement of the magnetization along the z axis, application of pressure $p_x = \sigma_{xx}$ did not change the value of the magnetization. This pressure, however, was three times smaller than p_y.

4. DISCUSSION OF RESULTS

A. From a comparison of our data on the magnitude of the parasitic ferromagnetic moment in the low-temperature modification of hematite, presented in Table I, with the data of other authors, it must be concluded that the crystals used by us were not very pure. The value of the parasitic moment in the basal plane in our experiments (about 0.1 cgs emu/g) was somewhat smaller than in the work of Néel and Pauthenet[4] (about .2 cgs emu/g), but larger than in the work of Lin[8] (about 0.02 cgs emu/g). Of our two specimens, specimen II gave smaller parasitic moments.

Parasitic ferromagnetism in antiferromagnetic hematite can be of twofold origin. First, it can be due to comparatively large regions of ferromag-

Table II

Direction of axis	Specimen	σ, kg/cm^2	$\chi_i^p \cdot 10^6$, cgs emu/g	$m_{i0}^p \cdot 10^3$, cgs emu/g	$\Delta m_{i0}^p \cdot 10^3$, cgs emu/g
x	I	$\sigma_{yy} = 980$	30	175	9
y	II	$\sigma_{xz} = 480$, $\sigma_{xx} = \sigma_{zz} = 480$	28	128	0

netic inclusions, weakly coupled to the antiferromagnetic structure of the basic crystal. Magnetization reversal of such regions does not require reversal of direction of the antiferromagnetic sublattices. There can exist also another type of parasitic ferromagnetism, which is connected with the antiferromagnetic structure. Such ferromagnetism can be produced by incomplete compensation of the antiferromagnetic sublattices, because of the presence of impurities. It should then be observed along the axis of antiferromagnetism—the z axis, in the low-temperature modification. In addition, internal magnetization in a crystal can be produced by a ferromagnetic moment of piezomagnetic origin. Still another supposition may be advanced, that in certain regions of the crystal there is retained a magnetic structure with weak ferromagnetism; this can give a parasitic moment also in the basal plane.

Our experimental data are insufficient for an unambiguous explanation of the nature of the parasitic ferromagnetic moment. Nevertheless it is possible, in the light of what was said above, to suggest that in the low-temperature modification, the basic parasitic moment is due to ferromagnetic inclusions, for which the basal plane is a plane of easy magnetization. The additional moment Δm_0, which causes the asymmetry of the magnetization curves, may be due to stresses in the crystal.

B. It can be asserted quite definitely that the change of the magnetization curves on application of pressure (Figs. 2 and 3), observed in the low-temperature modification for two orientations of the crystal, is due to the piezomagnetic effect. The following considerations speak in favor of this. Increase of the spontaneous moment of the specimens is observed only for those mutual orientations of the magnetization and of the stress for which, from symmetry considerations, the existence of a piezomagnetic moment is allowed. Especially graphic in this respect are the results with specimen I. Here the pressure was applied along all three axes, and the moments were measured also along three axes. A resulting change of moment, however, is observed only along the x axis, in accordance with formula (1). Furthermore the magnetization that arises under pressure possesses appreciably larger hysteresis. Such hysteresis is also peculiar to the piezomagnetic effect, since magnetization reversal of the piezomagnetic moment requires reversal of the antiferromagnetic sublattices.[2] Finally, the magnitude of the additional moment that arises under pressure is equal to the parasitic moment along the y axis and amounts to 40% for measurement along the x axis (see Tables I and II). Such large changes of ferromagnetic moments under pressure are not observed.

Curves 3 in Figs. 2 and 3 were obtained by subtracting the curves taken without pressure from the magnetization curves taken under pressure. They show the process of magnetization reversal of the piezomagnetic moment. We are unable to explain the reason for the pronounced asymmetry of the hysteresis cycle in Fig. 3. It should also be mentioned that we observed no time effects, such as occurred in the case of CoF_2.[2]

The values obtained for the piezomagnetic moduli for the low-temperature modification of $\alpha\text{-}Fe_2O_3$ are as follows:

$$\Lambda_1 = 3.6\cdot 10^{-5} \quad \frac{\text{cgs emu/g}}{\text{kg/cm}^2}$$

$$\Lambda_2 = 6.4\cdot 10^{-5} \quad \frac{\text{cgs emu/g}}{\text{kg/cm}^2}$$

These values are about an order of magnitude smaller than the piezomagnetic moduli of CoF_2.[2] The results of Birss and Anderson[7] on the linear magnetostriction give appreciably smaller values of the moduli ($\Lambda_1 \sim \Lambda_2 \sim 10^{-6}$). Such a large discrepancy can be explained by the presence of antiferromagnetic domains in the specimen studied in [7].

C. In the high-temperature modification, we succeeded in obtaining trustworthy results only for one orientation: magnetization along the z axis, stress σ_{yy}. The increase of magnetization obtained amounts to about 50% and can also be explained by the piezomagnetic effect. The absence of hysteresis in this case is due to the fact that magnetization reversal of the antiferromagnetic sublattices takes place by rotation in the basal plane. Such rotation takes place practically without hysteresis, as is confirmed by the form of the magnetization curves of the weakly ferromagnetic moment. Our data permit estimation of the value of the piezomagnetic modulus Λ_6' (see formula (2)):

$$\Lambda_6' = 5\cdot 10^{-5} \quad \frac{\text{cgs emu/g}}{\text{kg/cm}^2}$$

It should be mentioned that the absence of the effect on application of stress σ_{xx} indicates that

$$\Lambda_5' \leqslant 10^{-5} \quad \frac{\text{cgs emu/g}}{\text{kg/cm}^2}$$

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