MAGNETOELASTIC INTERACTION IN HEMATITE

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An experimental study was made of the influence of uniaxial pressure p_{33} along the threefold axis C_3 on the critical field H_c at which the magnetic sublattices of antiferromagnetic α-Fe_2O_3 overturn. The measurements were performed on samples of synthetic hematite at T = 20.4°K in a pulsed magnetic field directed along C_3. It was observed that the critical field decreased under pressure. The calculated derivatives of the magnetodipole component of the anisotropy energy of the crystal with respect to the deformations have a sign opposite to that obtained in the experiment. It is proposed that the predominant contribution to the magnetoelastic properties of hematite is made by the anisotropy-energy component connected with the spin-orbit interaction. In this connection, the results of measurements of the influence of the pressure and of the particle dimensions on the Morin temperature are discussed; these results could not be attributed to the properties of the magnetodipole component of the anisotropy energy.

THE antiferromagnetic α-Fe_2O_3 has been under intensive study during the last few years. It has been established that at low temperatures the direction of the spin ordering coincides with the threefold symmetry axis, and the magnetic anisotropy energy is $+2\times10^{+5}$ erg/cm^3 [1]. One of the main sources of this energy is the magnetic dipole interaction $K_{md} = -92\times10^5$ erg/cm^3 [2]. It is partly offset by the anisotropy energy connected with the presence of spin-orbit interaction; the latter is just as large in absolute magnitude, but has an opposite sign. The dependence of the indicated components on the interatomic distances indeed determines the magnetoelastic properties of α-Fe_2O_3. The question of the predominance of any particular contribution to the magnetoelastic properties has not yet been finally answered. The magnetostriction of single-crystal hematite in strong magnetic fields was investigated in detail by Levitin and co-workers[3].

Direct information on the dependence of the anisotropy energy on the interatomic distances can be obtained by investigating the pressure dependence of the critical overturning field of the magnetic sublattices H_c. Such measurements were performed by us by a method described earlier[4] in a pulsed magnetic field parallel to the C_3 axis, on samples of synthetic hematite grown in the Crystallography Institute of the USSR Academy of Sciences[5]. Application of a pressure p_{33} along the C_3 axis shifts the maximum of the differential magnetic susceptibility $\chi_d = dM/dH$ corresponding to the critical field H_c towards weaker fields (see the figure). The dependence of the critical field on the pressure is characterized by the derivative

$$\frac{1}{H_c}\frac{dH_c}{dp_{33}} = -6{,}9\cdot10^{-12}\ \text{cm}^2/\text{dyn}$$

and makes it possible to calculate the pressure dependence of the anisotropy energy K:

$$H_c = \left(\frac{2K}{\Delta\chi}\right)^{1/2},\quad \frac{dK}{dp_{33}} = \frac{2K}{H_c}\frac{dH_c}{dp_{33}} = -2{,}7\cdot10^{-6}. \qquad (1)$$

Here $\Delta\chi$ is the difference of the magnetic susceptibilities of a uniaxial antiferromagnet above and below H_c.

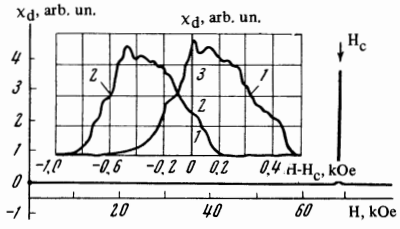
The derivative of the anisotropy energy with respect to the pressure can be compared with data obtained by measurement of the magnetostriction[3]. We use to this end a relation analogous to the Clapeyron-Clausius equation for first-order phase transitions in a magnetic field[6]:

$$dH_\kappa/dp_{33} = -\Delta u/\Delta\sigma,\qquad dH_c/dp = -\Delta v/\Delta\sigma, \qquad (2)$$

where $\Delta v = \Delta V/V$ and $\Delta u = \Delta c/c$ are the relative jumps of the volume and length of the crystal along the C_3 axis, and $\Delta\sigma$ is the change of the magnetization in the phase transition. We note that such a comparison is not always obvious. If the investigated crystal has foreign inclusions or a block structure, then the jumps of the magnetostriction turn out to be too low, whereas the dependence of the critical field on the pressure makes it possible to calculate correctly the derivative of the anisotropy energy with respect to the pressure. On the other hand, Eqs. (2) no longer hold if the magnetization is carried out along a thermodynamically nonequilibrium curve and metastable states are realized near the transition field. In this case we find from the values of the jumps of the crystal dimensions[3]

$$dK/dp_{33} = -2.5\cdot10^{-6},\quad dK/dp = +8.7\cdot10^{-6}, \qquad (3)$$

where the first figure is in good agreement with the results of our experiment.



Differential magnetic susceptibility $\chi_d = dM/dH$ of an α-Fe_2O_3 sample vs. the magnetic field intensity. $\mathbf{H} \parallel C_3$, T = 20.4°K. The region of the curve near the critical field H_c is shown on an enlarged scale (stretched out by a factor of 25). Curve 1 was obtained with a free sample and curve 2 under a pressure p_{33} = 1.04 katm.

The contribution of the magnetodipole interaction to the experimentally observed values can be estimated numerically. The dependence of K_{md} on the interatomic distances in hematite was calculated by Artman and coworkers[2] with a computer. Their results take into account the fields of the magnetic ions located at a distance $R \lesssim 30$ Å from the point under consideration, and are characterized by the following derivatives:

$$\partial K_{md}/\partial u = -23\cdot 10^6 \text{ erg/cm}^3, \quad \partial K_{md}/\partial v = +17\cdot 10^6 \text{ erg/cm}^3. \quad (4)$$

To calculate the dependence of the energy of the magnetodipole interaction on the pressure, it is necessary to have data on the pressure dependence of the parameter ω of the special position of the magnetic ions[7]. There are no such data at present, and it is usually assumed in the calculations[8,9] that ω is independent of the pressure. This assumption lowers the accuracy of the calculation. In addition, Voigt's earlier measurements of the elastic constants[10] were made on rather imperfect samples of natural hematite. Apparently, owing to the presence of internal voids, the compressibility κ obtained in[10] turned out to be several times larger than the later results of Lewis et al.[8], where the following constants were obtained in the low-pressure region:

$$S_{33} + 2S_{13} = 0.068\cdot 10^{-12} \text{ cm}^2/\text{dyn} \quad \kappa = 0.22\cdot 10^{-12} \text{ cm}^2/\text{dyn}$$

Assuming correctness of the ratio of the elastic constants in the central-force model[11], then $S_{33} = 0.11 \times 10^{-12}$ cm^2/dyn. Then the sought derivatives can be calculated from the following expressions:

$$\frac{dK_{md}}{dp_{33}} = -\left[\frac{\partial K_{md}}{\partial u}S_{33} + \frac{\partial K_{md}}{\partial v}(S_{33}+2S_{13})\right] = +1.4\cdot 10^{-6},$$

$$\frac{dK_{md}}{dp} = -\left[\frac{\partial K_{md}}{\partial v}\kappa + \frac{\partial K_{md}}{\partial u}(S_{33}+2S_{13})\right] = -2.2\cdot 10^{-6} \quad (5)$$

We note that independently of the choice of the elastic constants

$$\kappa = S_{33} + 2(S_{11}+S_{12}) + 4S_{13} > S_{33} > S_{33} + 2S_{13}$$

and the pressure dependence of the magnetodipole component of the anisotropy energy has a sign opposite to that obtained in experiment.

In this connection, in order to verify the signs obtained for (4) from the plots of[2], we have calculated approximately the magneto-dipole interaction and its derivatives with respect to the lattice parameters in α-Fe_2O_3, by summing the co tributions of the nearest neighbors of the point under nsideration. The interaction energy of two parallel ($P_i = +1$) or antiparallel ($P_i = -1$) magnetic dipoles oriented at an angle θ to the line joining them can be represented in the form

$$E(1,2) = P_i\frac{\mu_1\mu_2}{R^3}(1-3\cos^2\theta),$$

and the anisotropy energy and its derivatives are given by

$$K_{md} = K_0\sum_i P_i\frac{2z_i^2 - r_i^2}{(z_i^2+r_i^2)^{5/2}},$$

$$\frac{\partial K_{md}}{\partial u_z} = 3K_0\sum_i P_i z_i^2\frac{3r_i^2 - 2z_i^2}{(z_i^2+r_i^2)^{7/2}}, \quad (6)$$

$$\frac{\partial K_{md}}{\partial u_r} = 3K_0\sum_i P_i r_i^2\frac{r_i^2 - 4z_i^2}{(z_i^2+r_i^2)^{7/2}}.$$

Here the positions of the magnetic ions are indicated in cylindrical coordinates r_i and z_i, $K_0 = (3/4)Nn^2\mu_B^2$, $N = 3.98\times 10^{22}$ cm^{-3} is the number of ions per unit volume, and n is the number of Bohr magnetons μ_B per magnetic dipole. The summation (6) of the contributions of the nearest 50 neighbors gives for the anisotropy energy and its derivatives values that coincide in sign with those given in (4), and are close to them in magnitude. A gradual increase of the number of magnetic ions involved in the calculation to 115, bounded by a sphere of radius 10 Å, causes the results to oscillate about the values presented above by not more than 10% in the case of K_{md} and $\partial K_{md}/\partial u_r$ and 30% for $\partial K_{md}/\partial u_z$. This confirms the values used in the calculations.

Let us estimate the pressure and strain dependences of the anisotropy-energy component connected with the spin-orbit interaction, using (1), (2), and (5):

$$\frac{dK_{so}}{dp_{33}} = -4.1\cdot 10^{-6}, \quad \frac{dK_{so}}{dp} = +10.9\cdot 10^{-6},$$

$$\frac{\partial K_{so}}{\partial u} = +84\cdot 10^6 \text{ erg/cm}^3,$$

$$\frac{\partial K_{so}}{\partial v} = -75\cdot 10^6 \text{ erg/cm}^3.$$

Thus, the spin-orbit component makes the predominant contribution and determines the sign of the magnetoelastic properties of hematite.

When this circumstance is taken into account, the results of an investigation of the influence of hydrostatic compression on the Morin temperature T_M[9] become understandable. It was shown earlier that an examination of the properties of only the magnetodipole component in K does not explain these results by Wayne and Anderson. For our estimates, we use the pressure dependence of the total anisotropy constant (1), (2). From the condition that the anisotropy and its infinitesimally small increments vanish along the phase-equilibrium curve in the P—T plane, we can write

$$\frac{dT_M}{dp_{33}} = -\frac{\partial K}{\partial p_{33}}\Big/\frac{\partial K}{\partial T}, \quad \frac{dT_M}{dp} = -\frac{\partial K}{\partial p}\Big/\frac{\partial K}{\partial T},$$

where $\partial K/\partial T|_{T=T_M} = -2.6\cdot 10^3$ erg-cm^{-3}deg^{-1}[12]. Assuming that $\partial K/\partial p|_{T=T_M} \approx \partial K/\partial p|_{T=0}$, we get

$$dT_M/dp_{33} = -1{,}0 \text{ deg/katm}, \quad dT_M/dp = +3{,}4 \text{ deg/katm},$$

where the second figure agrees with experiment, ($dT_M/dp = 3.6 \pm 0.3$ deg/katm[9]).

We can explain analogously the sign of the effect of decreasing the Morin temperature in small hematite particles. This effect was interpreted earlier as a consequence of the increase of the lattice constants in these particles[13]. However, when only the magnetodipole interaction is taken into account, as was done by Yamanoto[13], the sign of the effect is reversed.

Thus, the main contribution to the magnetoelastic properties of hematite is made by the spin-orbit interaction, which is the reason for the appearance of both single-ion anisotropy and exchange-interaction anisotropy. In spite of the fact that the ground state of the free Fe^{3+} ion is $^6S_{5/2}$, the influence of the spin-orbit interaction can be appreciable because of the admixture of closely lying excited states.

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[1] S. Foner, Proc. Intern. Conf. on Magnetism, Nottingham, 1964, p. 438.
[2] J. O. Artman, J. C. Murphy and S. Foner, Phys. Rev. 138, A912, 1965.
[3] R. Z. Levitin, A. S. Pakhomov and V. A. Shchurov, Zh. Eksp. Teor. Fiz. 56, 1242 (1969) [Sov. Phys.-JETP 29, 669 (1969)].
[4] K. L. Dudko, V. V. Eremenko, and V. M. Fridman, Fiz. Tverd. Tela 12, 83 (1970) [Sov. Phys.-Solid State 12, 65 (1970)].
[5] R. A. Voskanyan and N. S. Zheludev, Kristallografiya, 12, 539 (1967) [Sov. Phys.-Crystallography 12, 478 (1967)].
[6] A. I. Mitsek, FMM 16, 168 (1963).
[7] R. E. Newnham and Y. M. deHaan, Zs. Krist., 117, 235, 1962.
[8] G. K. Lewis, Jr. and H. G. Drickamer, J. Chem. Phys. 45, 224, 1966.
[9] R. C. Wayne and D. H. Anderson, Phys. Rev. 155, 496, 1967.
[10] W. Voigt, Ann. der Phys. 22, 129, 1907.
[11] G. Leibfried, Encyclopedia of Physics, 7, Part 2, Springer–Verlag, 104, 1955, p. 104.
[12] D. J. Simkin and R. A. Berkeim, Phys. Rev. 153, 621, 1967.
[13] N. Yamanoto, J. Phys. Soc. Japan, 24, 23, 1968.

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