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Magnetic and Electric Properties of Magnetite at Low Temperatures*

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The low-temperature transition in magnetite, according to Verwey, is due to the ordering of the ferrous and ferric ions in the octahedral interstices of the spinel lattice. This arrangement would require a symmetry change from cubic to orthorhombic. X-ray diffraction indicates and electric conductivity and magnetization measurements confirm that the transition leads to an orthorhombic structure. An external magnetic field applied while cooling through the transition establishes a preferred orientation for the *c* axis throughout the whole crystal. Below the transition this *c* axis can be switched to a new direction by a strong magnetic field, a process involving a co-operative rearrangement of the ferrous ions in new sites and relatively large changes in dimensions. In stoichiometric, synthetic, single crystals the transition occurs at 119.4°K and is marked by an abrupt decrease in the conductivity by a factor of 90 in a temperature interval of 1°. No thermal hysteresis is observed. The conductivity of a crystal cooled in a strong magnetic field is anisotropic below the transition as given by the relation $\sigma=A+B(1+\cos^2\theta)$, where θ is the angle between the *c* axis and the direction of measurement. The ratio $B/(A+B)$ increases rapidly as the crystal is cooled to 90°K, indicating a progressive increase in the long-range order. The *c* axis is the direction of easy magnetization below the transition, and the anisotropy energy is very much larger below than above; the anisotropy constants have been determined at 85°K.

MAGNETITE is being studied intensively in this laboratory both as a prototype of the ferrites and because of its unusual behavior at low temperatures (from −140° to −190°C).[1,2] The initial permeability passes through a maximum at *ca* −140°C and then decreases rapidly to a very small value below −155°C. Bickford[1] has shown that this maximum is due to the vanishing of the crystalline anisotropy energy. At *ca* −155°C a transition is observed. The specific heat traverses a maximum;[3] the electrical conductivity decreases by a factor of *ca* 100;[4] and the material is much harder to magnetize to saturation below the transition.[5] The direction of easy magnetization below the transition is influenced by a magnetic field applied as the sample is cooled through the transition.[6]

Verwey[4] proposed that above the transition magnetite has the inverse spinel structure, and that the transition itself is due to an ordering of the random distribution of ferrous and ferric ions in the octahedral lattice sites. The ordered arrangement of Fig. 1 appeared as the most likely one,[7] and Verwey suggested that the *c* axis of this ordered structure would lie along the cube edge closest to the direction of the external field applied during cooling.

The object of the present research was to study this unusual type of transition by electric and magnetic means as well as by x-ray analysis on single crystals of magnetite grown in this laboratory.[8]

CRYSTAL STRUCTURE

The ferrites have the same crystal structure as spinel ($MgOAl_2O_3$), space group $Fd3m\text{-}O_h{}^7$. The unit cell contains 32 oxygen ions in an almost cubic close-packed arrangement; the cations occupy 8 tetrahedral and 16 octahedral interstices in this oxygen lattice. Simple ferrites show two variations: a normal spinel structure, where each type of ion occupies only one type of site and the inverse spinel structure, where both kinds of cations occur in the octahedral

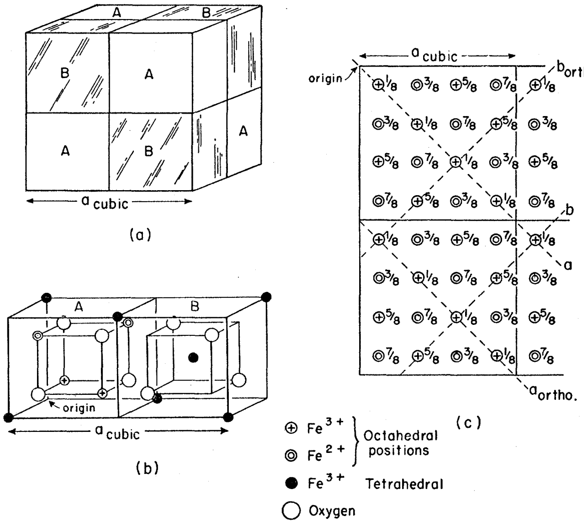

FIG. 1. Verwey's ordered structure: (a) the cubic unit cell; (b) subcells *A* and *B*; (c) projection of ions in octahedral sites on the *a-b* plane.

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* Sponsored by the U. S. Office of Naval Research, the Army Signal Corps, and the Air Force.

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[1] L. R. Bickford, Jr., Phys. Rev. 78, 449 (1950).

[2] C. A. Domenicali, Phys. Rev. 78, 458 (1950).

[3] R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929).

[4] E. J. W. Verwey, Nature 144, 327 (1939); E. J. W. Verwey and P. W. Haayman, Physica 8, 979 (1941).

[5] P. Weiss and R. Forrer, Ann. Physik. [10] 12, 279 (1929).

[6] C. H. Li, Phys. Rev. 40, 1002 (1932).

[7] Verwey, Haayman, and Romeijn, J. Chem. Phys. 15, 181 (1947).

[8] J. Smiltens, J. Chem. Phys. 20, 990 (1952).

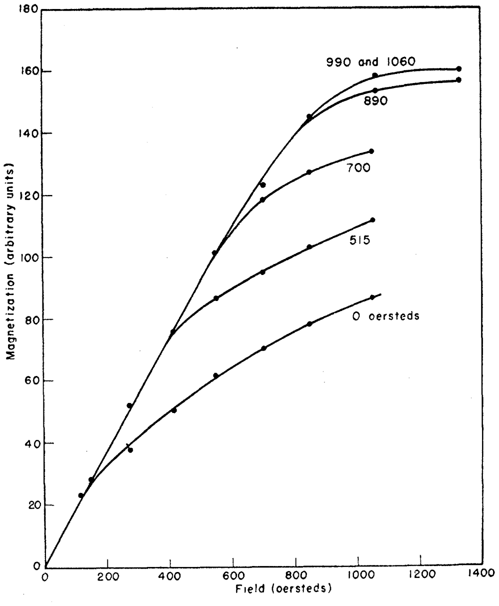

FIG. 2. Magnetization curves in the cubic [001] direction at 78°K after cooling in magnetic fields parallel to [001]; field strength as indicated.

sites. Neutron diffraction measurements[9] have confirmed the inverse structure for magnetite.

An x-ray study, undertaken in connection with the present investigation,[10] indicates the symmetry of magnetite below the transition as orthorhombic (unit cell dimensions: $a=5.912$, $b=5.945$, $c=8.388$A at 78°K), with the c axis orientated along one of the original cube edges, and the a and b axes along the cubic face diagonals normal to the c axis. These results are in agreement with Bickford's[11] measurements of the deformation of single crystals on cooling through the transition. This unit cell would also be expected on the basis of the ordered arrangement of Fig. 1.

ESTABLISHMENT OF THE MAGNETIC AXIS

The orthorhombic axis may develop in any of the six possible cube-edge orientations. Without external enforcement the axes should assume the various positions with equal probability. The effect of a magnetic field in making one or more of these orientations preferred was studied with the null-coil pendulum magnetometer developed in this laboratory.[12] Some modifications were made to permit its use down to liquid helium temperatures. The case of the instrument was evacuated and helium gas, admitted through a needle valve, regulated the rate of warming by controlling the heat loss from the sample. The sample was mounted in an aluminum boat in good thermal contact with the null coil, which also served as a heat source. The measurements were made on a circular disk cut from a (100)-plane slice of a single crystal of magnetite and ground to an oblate spheroid with axes of 4.55 and 0.89 mm.

The smallest magnetic field that establishes a magnetic axis was determined by cooling this (100) sample through the transition with magnetic fields of various strengths applied parallel to the [001] direction. The sample was then demagnetized and the magnetization curve in the [001] direction measured at −195°C (Fig. 2). The minimum field for completely establishing the magnetic axis is *ca* 1000 oersteds; approximately the same field is needed to produce technical saturation. The external field aligns the individual domains throughout the sample along the previous cube-edge direction establishing this as a unique magnetic axis, the c axis of the orthorhombic structure.

When such a sample is demagnetized, the c axis remains the direction of easy magnetization and the domain pattern consists of antiparallel domains aligned along this axis. This was verified by measuring the longitudinal magnetostriction in a [100] bar after cooling through the transition in a field parallel to its length and then demagnetizing the bar. The longitudinal magnetostriction in fields up to *ca* 10 000 oersteds was extremely small ($\delta l/l<10^{-6}$), indicating that the magnetization in this direction was almost entirely due to the motion of 180° walls.

In additional experiments the (100) sample was cooled through the transition in a field of 4700 oersteds, directed in the (100) plane at angles of 0°, 40°, 45°, 55°, and 90° to the [001] direction. The warming curves (magnetic moment as a function of temperature at constant applied field) are shown in Figs. 3 and 4. When the field is within 40° of the [001] direction, this [001] becomes the c axis. When the field is within 40° of the [010] direction, i.e., more than 50° from [001], [010] becomes the c axis and the [001] direction is magnetically hard. When the cooling field is applied at 45° to [001], warming curves show that in approximately one half the sample [001] is the c axis and in the remainder [010] is the c axis.

The effect of applying a magnetic field at various angles in the cubic (110) plane was investigated with a quasi-static B-H loop tracer for an oblate spheroidal sample prepared from a (110) slice of a magnetite

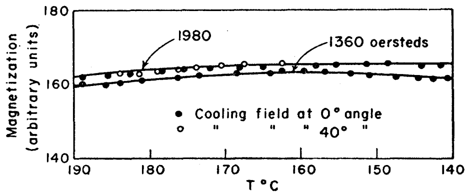

FIG. 3. Warming curves in [001] direction after cooling in field of 4700 oersteds orientated 0° and 40° to [001].

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[9] Shull, Wollan, and Koehler, Phys. Rev. **84**, 912 (1951).

[10] S. C. Abrahams and B. A. Calhoun, Acta Cryst. **6**, 105 (1953).

[11] L. R. Bickford, Jr., Revs. Modern Phys. **25**, 75 (1953).

[12] C. A. Domenicali, Rev. Sci. Instr. **21**, 327 (1950).

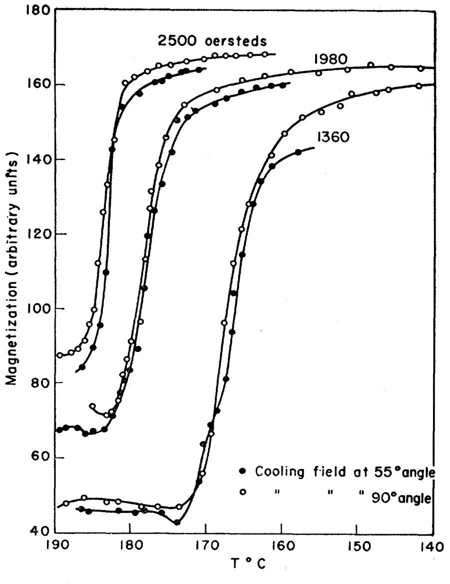

FIG. 4. Warming curves in [001] direction after cooling in field of 4700 oersteds orientated 55° and 90° to [001].

crystal. Magnetization curves were measured in the [001] direction of this sample, after cooling in a field of 10 000 oersteds directed in the (110) plane at angles of 0°, 25°, and 40° to [001]. The indentity of the curves shows that, in each case, the *c* axis is established along the [001] direction. All results are consistent with the picture that the *c* axis is established along the cube edge nearest the direction of the magnetization in each domain. Similar results have been obtained with natural crystals of magnetite by Williams and Bozorth.[13]

SWITCHING OF THE MAGNETIC AXIS

The phenomenon of axis-switching, i.e., the change of the *c* axis from one cube edge to another below the transition, was first observed by Bickford[1] in microwave resonance experiments at liquid nitrogen temperature. The effect is apparent in the warming curves of Fig. 4. The magnetic axis was established along the [010] direction so that [001] was magnetically hard, as shown by its small magnetic moment. At some temperature below the transition, there is an abrupt increase in the magnetic moment indicating that the [001] direction has suddenly become an easy direction. The external field necessary to cause axis-switching at various temperatures was determined by cooling the (100) spheroid through the transition with a field of 4700 oersteds along the [010] direction and then measuring the warming curves with fields from 1000 to 5000 oersteds applied in the [001] direction (see Fig. 4).

Axis-switching was also observed in the (110)-plane sample. An unexpected result was that axis-switching occurred only with the field applied in the $[1\bar{1}0]$ direction and in a direction at 15° to it in the (110) plane. From measurements of the change in length of a [100] bar accompanying the axis-switching, it was evident that relatively large changes in dimensions ($\delta l/l \simeq 10^{-4}$) and correspondingly, in elastic energy, are involved in this situation. This elastic energy apparently suffices, in the case just mentioned, to prevent the axis-switching from occuring at the field indicated by Eq. (2) (see below), although it may still occur in a sufficiently high field.

Transfer of the *c* axis from one cube edge to another requires an electron exchange from ferrous to neighboring ferric ions in the tetrahedra formed by the iron ions in the octahedral interstices (Fig. 5). A crystal in which the *c* axis has been established along the [010] direction, placed in a magnetic field directed along the [001] direction, can reduce its energy considerably if [001] becomes the easy direction. The dependence of this energy difference on the magnetic induction is complicated since it is determined by the anisotropy energy. Let us consider an electron and its two possible positions, an "a" site corresponding to the *c* axis in the [010] direction and a "b" site corresponding to the *c* axis in the [001] direction. Initially, there is a high probability that an electron will be at an "a" site, since the process of cooling the crystal in a field directed along [010] has lowered the energy of the "a" site relative to that of the "b" site. The application of a magnetic field in the [001] direction lowers the energy of site "b". If the change in the energy of the "b" sites is proportional to the internal magnetic induction, the net probability that an electron will jump from an "a" to a "b" site is given as

$$\exp(-U/kT)(1-\exp[-\mu B_i/kT]) \simeq (\mu B_i/kT)\exp(-U/kT), \quad (1)$$

where U is the activation energy for the electron exchange between "a" and "b" sites without field, and μB_i (μ= Bohr magneton) is the energy difference between sites "a" and "b" due to the magnetic field. We have neglected the effects of the local disordering which accompanies a jump from an "a" to a "b" site. This disordering would raise the energy of an electron in the "b" site; hence, we may expect an electron would return to an "a" site unless some of its neighbors also jumped to "b" sites before it has time to return. Crudely, the net probability [Eq. (1)] must reach

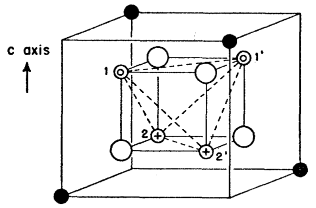

FIG. 5. Tetrahedron 1, 1′, 2, 2′ establishing *c* axis vertical; exchange of 1 and 2′ or 1′ and 2′ turns *c* axis 90°.

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[13] H. J. Williams and R. M. Bozorth, Revs. Modern Phys. **25**, 79 (1953).

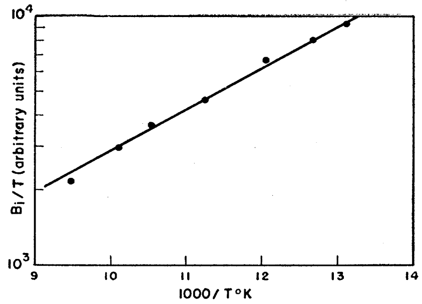

FIG. 6. Induction required to switch the *c* axis.

some critical value before the "b" sites become stable and the axis switches; that is,

$$B_i = CT(\exp U/kT), \qquad (2)$$

where B_i is the internal induction prior to the axis-switching and T the temperature at the midpoint of the switching. Figure 6 shows that the experimental data calculated from curves similar to Fig. 4 fit this equation with $U = 0.033$ ev.

CONDUCTIVITY OF MAGNETITE AND ITS RELATION TO THE TRANSITION

If the conductivity of magnetite is due to the exchange of electrons between the ferrous and ferric ions in the octahedral lattice sites, the random distribution above the transition should lead to an isotropic conductivity, but belo the transition the conductivity should be anisotropic. This anisotropy and its dependence on crystallographic orientation and magnetic field direction during cooling have been studied in detail.

The four-terminal sample holder (Fig. 7) was designed to maintain sample and contacts in as nearly an isothermal region as possible in order to minimize spurious thermal emf. Helium gas, admitted through a needle valve, allowed the pressure to be adjusted from 10^{-2} to 10^{-5} mm. Thus, the warming and cooling rates could be controlled from 3° to 50°C per hour. The temperature was measured potentiometrically by a copper-constantan thermocouple.[14] The samples were cut from two synthetic crystals in the form of rectangular bars about 1 cm in length and with a cross-sectional area of about 3 sq mm. The length direction of the bars was oriented parallel to the cubic [100], [110], and [111] directions, respectively.

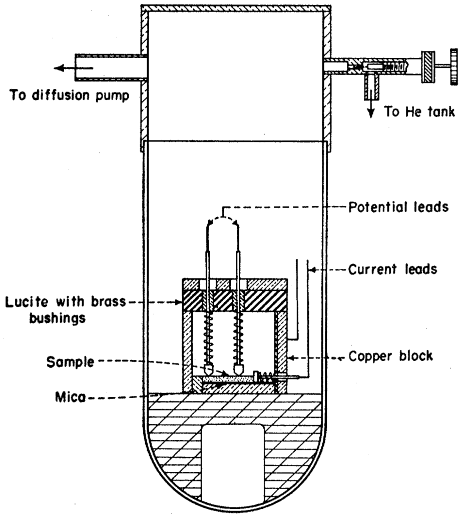

FIG. 7. Sample holder for conductivity measurements.

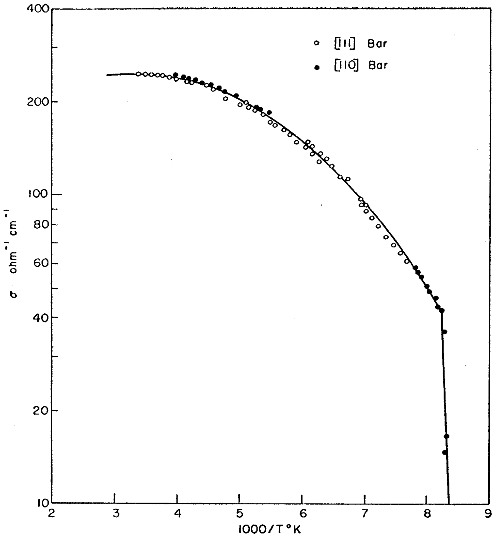

FIG. 8. Conductivity between room temperature and the transition.

The conductivity of two of the specimens from room temperature through the transition is shown in Fig. 8. Warming and cooling data coincide; no thermal hysteresis marks the transition. The conductivity is 250 $\text{ohm}^{-1}\ \text{cm}^{-1}$ at room temperature and has a broad maximum at *ca* 15°C; previous investigators[2,4] have reported this maximum for natural crystals to be at a higher temperature (*ca* 80°C). At the transition the

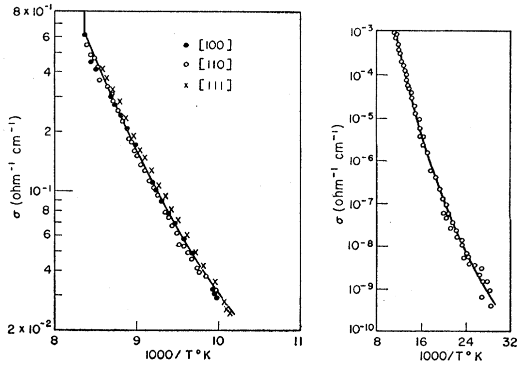

FIG. 9. Conductivity of the [111] bar below the transition after cooling in zero magnetic field.

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[14] See R. P. Teele and S. Schuhmann, J. Research Natl. Bur. Standards **22**, 431 (1939).

resistivity increases by a factor of 90 in a temperature interval of *ca* 1°. The midpoint of this interval occurred at a temperature of 119.4±0.3°K (−153.8°C).

Below the transition the conductivity for samples cooled in zero magnetic field remains isotropic (Fig. 9) but does not follow a simple exponential law,

$$\sigma = A \exp(-U/kT).$$

If fitted to this type of law over certain ranges of temperature, one obtains the values of the constants A and U as shown in Table I.

TABLE I. Conductivity of magnetite below the transition.

Temperature	A (ohm^{-1} cm^{-1})	U(ev)
78 to 90°K	8200	0.11
56 to 77°	1400	0.09
40 to 52°	1.5	0.06

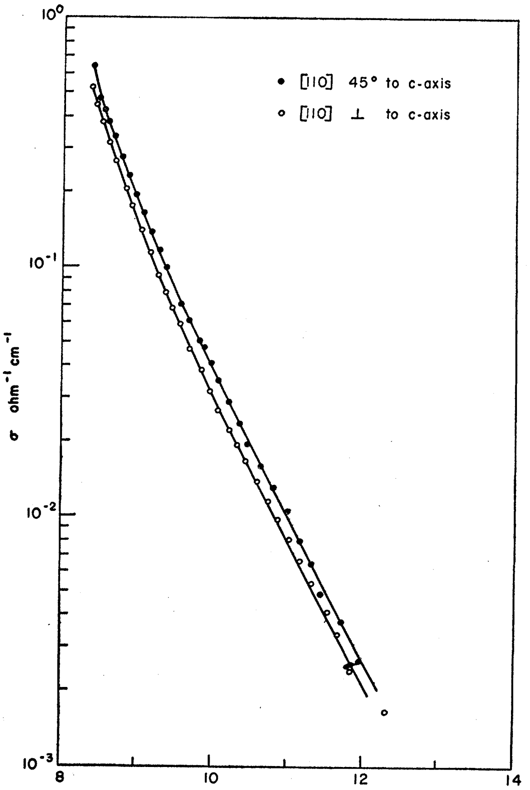

FIG. 10. Conductivity of [110] sample after cooling in two differently orientated magnetic fields.

When the samples are cooled through the transition in a magnetic field (*ca* 9000 oersteds) the conductivity is anisotropic and depends on the orientation of both the sample and the magnetic field (Fig. 10). The anisotropy increases as the sample is cooled from the transition to *ca* 95°K, and then remains practically constant at lower temperatures. Table II gives the ratios of the conductivities for a number of combinations of electrode orientation and c axis direction.

The observed anisotropy in the conductivity agrees well with that which can be predicted from Verwey's model of the low-temperature structure of magnetite. Although the exchange of electrons between ferrous and ferric ions has become much more difficult below the transition, it is still the dominant mechanism of conduction. In the ordered structure this will lead to an anisotropy since ferrous and ferric ions occupy adjacent sites in only four of the cubic [110] directions. Although the ordered structure has orthorhombic symmetry, its conductivity anisotropy corresponds to tetragonal symmetry (neglecting the small departure of the b/a axial ratio from unity). The conductivity of a tetragonal crystal in an arbitrary direction is given by

$$\sigma = \sigma_{11} \sin^2\theta + \sigma_{33} \cos^2\theta, \tag{3}$$

where θ is the angle between the direction and the c axis, σ_{33} the conductivity along the c axis, and σ_{11} the conductivity normal to the c axis. It can be seen easily from the ordered structure that the ratio $\sigma_{33}/\sigma_{11} = 2$. Thus we can write the conductivity below the transition as

$$\sigma = B(1+\cos^2\theta). \tag{4}$$

In case the order is not perfect, we would expect the conductivity to contain in addition, an isotropic term

$$\sigma = A + B(1+\cos^2\theta). \tag{5}$$

The quantity $B/(A+B)$ should be a measure of the amount of order. The values of A, B, and $B/(A+B)$ derived from our conductivity data for a number of temperatures are given in Table III. This table shows that with decreasing temperature the order increases, as one would expect, since the ordering process involves an activation energy.

MAGNETIC ANISOTROPY

The magnetic anisotropy energy is the difference between the energy required to magnetize a sample in an arbitrary direction and in the direction of easy magnetization. The angular dependence of this anisotropy energy is determined by the symmetry of the crystal. In the ordered structure of magnetite a determination of the angular dependence of the anisotropy

TABLE II. Ratio of conductivities of magnetite in different directions below the transition.

T	$\dfrac{\sigma[100]\parallel H}{\sigma[100]\perp H}$	$\dfrac{\sigma[100]\parallel H}{\sigma[110]\perp H}$	$\dfrac{\sigma[100]\parallel H}{\sigma[110]45°H}$	$\dfrac{\sigma[110]45°H}{\sigma[110]\perp H}$	$\dfrac{\sigma[100]\parallel H}{\sigma[111]}$
117.6°K	1.44	1.40	1.25	1.12	...
111.1	1.63	1.51	1.21	1.25	...
105.3	1.79	1.59	1.27	1.25	...
100.0	1.87	1.59	1.24	1.28	...
95.2	1.88	1.61	1.25	1.28	1.56
90.9	...	1.61	1.27	1.27	...
87.0	...	1.60	1.26	1.27	...
83.3	...	1.60	1.26	1.26	...

TABLE III. Anisotropy of conductivity below the transition.

T,°K	A	B	$B/(A+B)$
117.6	0.2660	0.1270	0.324
111.1	0.0718	0.0741	0.508
105.3	0.0202	0.0396	0.662
100.0	0.0079	0.0194	0.711
95.2	0.0026	0.01155	0.816

energy is particularly important since the actual deformation of the crystal structure at the transition is very small and therefore difficult to determine directly, while the anisotropy energy below the transition is very large. Consequently, the determination of the anisotropy energy provides a sensitive method for checking the crystal symmetry.

The method of calculating the dependence of the anisotropy energy on orientation for any type of crystal symmetry is well known. The anisotropy energy is expanded as a power series in the direction cosines relative to the crystallographic axes, only those terms consistent with the symmetry being retained. The existence of a plane of symmetry normal to a crystallographic axis requires the direction cosine relative to that axis to appear only in even powers. Since the ordered structure of magnetite seems to belong to the orthorhombic holohedral crystal class, it has three such symmetry planes (one normal to each axis). The remaining symmetry elements of this crystal class, i.e., the three twofold axes and the center of symmetry, can be compounded from appropriate sequences of reflections in the three symmetry planes and therefore do not impose any additional restrictions on the form of the anisotropy energy. Thus we have

$$E_a=K_1\alpha_1^2+K_2\alpha_2^2+K_{11}\alpha_1^4+K_{12}\alpha_1^2\alpha_2^2+K_{22}\alpha_2^4, \quad (6)$$

where the K's are the anisotropy constants, and the α's the direction cosines relative to the crystallographic axes. The identity $\alpha_1^2+\alpha_2^2+\alpha_3^2=1$ has been used to eliminate all the terms containing α_3. For magnetite below the transition, the c axis is the easy direction and magnetization along one of the a and b axes appears to be much more difficult than along the other. Since this difficult axis could not be experimentally identified uniquely with the a or b direction because of twinning, the b axis was arbitrary chosen as the difficult one. If this choice should prove to be incorrect, only the subscripts 1 and 2 of the anisotropy constants would have to be interchanged.

TABLE IV. Anisotropy constants of magnetite at low temperature.

Constants ergs/cc	Method Magnetization curves	Torque curves
K_1	4.0×10^5	2.8×10^5
K_2	9.0×10^5	7.5×10^5
K_{11}	2.2×10^5	2.2×10^5
K_{12}	13.0×10^5	12.4×10^5
K_{22}	10.2×10^5	7.4×10^5

The anisotropy constants were computed from the areas between the magnetization curves taken in different crystallographic directions. Fields as high as 15 000 oersteds are required to saturate magnetite below the transition. Because the pendulum magnetometer, at present, is limited to fields of less than 5000 oersteds, the quasistatic B-H loop tracer constructed in this laboratory[15] was modified to trace the magnetization curves of samples mounted in the gap of our large electromagnet. The sample was mounted at the center of a fixed coil. The contribution of the field itself to the flux linking this coil was eliminated by mounting a second coil in the gap, some distance from the sample. The two coils were connected in opposition and adjusted as nearly as possible to zero output with no sample in position. The voltage of these two coils was integrated and applied to one axis of a recorder. The second axis was driven by the output of a rotating coil gaussmeter, also mounted in the magnet gap. The curves obtained on the recorder are only proportional (not equal) to the magnetization, because of flux leakage through the small air gap between sample and coil. The saturation magnetization of magnetite at room temperature served for scale calibration since it has been measured by a number of investigators (477 cgs units/cc).[2,5] The sample was an oblate spheroid cut from a (110)-plane slice of a synthetic magnetite crystal. Its axes were 3.84 and 0.97 mm, respectively; the demagnetizing factor calculated from these dimensions is 1.82±0.08, as compared to 1.75 computed from the [111] magnetization curve at room temperature.

Room temperature magnetization curves refer to cubic holohedral symmetry, where the anisotropy energy can be written as

$$E_a=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2. \quad (7)$$

The value of K_1 at room temperature was $-1.12\pm0.05\times10^5$ ergs/cc, as determined from the areas between the [100] and [110], as well as between the [100] and [111] curves. This is in good agreement with the value of -1.12 for K_1 from microwave resonance measurements[1] and -1.22 from torque magnetometer measurements.[13] K_2 is zero, within the limits of experimental error.

The low-temperature curves were obtained by immersing the sample and the surrounding coil in liquid air. The sample reached equilibrium very quickly at a temperature of *ca* −188°C. The saturation magnetization of magnetite at this temperature was 508 cgs units/cc, in excellent agreement with the value of 510 at −195°C obtained by Domenicali.[2] Magnetization curves were obtained in the cubic [100],

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[15] Developed by D. J. Epstein and B. Frackiewicz after P. P. Cioffi, Rev. Sci. Instr. **21**, 624 (1950).

[110], and [111] directions, and also 15°, 30°, 45° and 75° to [100] after cooling in a parallel or a perpendicular magnetic field of *ca* 10 000 oersteds. Curves were also obtained in the cubic [100] and [110] directions after cooling in zero field.

The twinning that occurs in magnetite when it is cooled through the transition introduces a number of complications. A magnetic field applied to the sample as it is cooled will align the c axis along the cube edge nearest the applied field. Since the anisotropy energy is considerably lower along the a axis than along b, the a axis will tend to lie closer to the external field.[16] These two conditions are sufficient to remove the twinning only in certain orientations. In some cases, particularly when the applied field makes nearly equal angles with two or three cube edges, there is uncertainty about the relative volumes of the sample assuming each possible orientation. Because interactions occur between the different regions of the sample, a twinned sample cannot be treated by a simple superposition of the various orientations which it contains (see below).

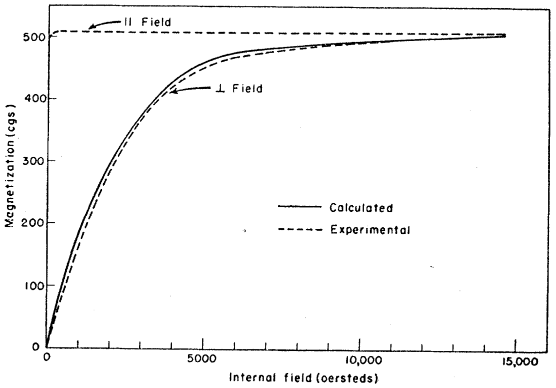

FIG. 11. Magnetization curves at 85°K in the [100] direction after cooling in a field of 10 000 oersteds at 0° and 90° to [100].

The anisotropy constants were calculated by trial and error from the areas between the magnetization curves. Due to the uncertainties introduced by twinning, a simple fitting of the measured areas between the various magnetization curves was not considered a sufficient check on the actual values of these constants. The anisotropy constants obtained from the areas were therefore used to compute the magnetization curves for the cubic [100] and [111] directions after cooling in a perpendicular field and adjusted to improve the fit between the calculated and the experimental curves. The values of the constants finally obtained by this two-step approximation are given in Table IV under "Magnetization curves." The calculated and experimental curves for the cubic [100] and [111] directions are shown in Figs. 11 and 12. The anisotropy energy, as a function of crystallographic orientation, is shown in Fig. 13. The complicated path followed by the magnetization vector and its experimental confirmation by magnetization curves lend strong support to the assumption of an orthorhombic structure for magnetite below the transition.

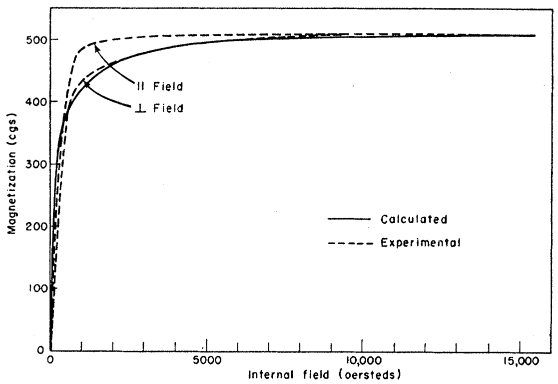

FIG. 12. Magnetization curves at 85°K in the [111] direction after cooling in a field of 10 000 oersteds at 0° and 90° to [111].

Williams and Bozorth[13,16] have measured torque curves on samples of natural magnetite at liquid nitrogen temperature, i.e., at about −195°C. When their results are expressed in terms of our constants (Table IV) the agreement between the two sets is relatively good, considering the differences in temperature and crystals used. The natural crystals are not exactly stoichiometric and consequently would not have as perfect an ordered structure as the synthetic crystals. The amount of order increases rapidly as a crystal is cooled below the transition (Table III). Thus the 7° difference in temperature between the two sets of measurements partially compensates for the inherent difference in the crystals. The differences in all constants are in the same direction; their effect

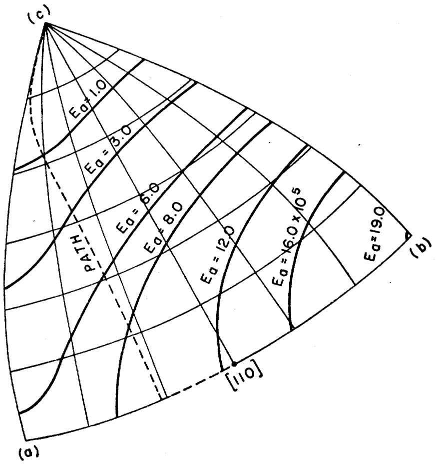

FIG. 13. Anisotropy energy of magnetite, showing the path followed by the magnetization when a field is applied in the orthorhombic [110] direction. The projections of the orthorhombic a, b, and c axis are at the corners (a), (b), and (c) (E_a = anisotropy energy [ergs/cc]).

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[16] Williams, Bozorth, and Goertz, Phys. Rev. **91**, 1107 (1953).

on the magnetization and torque curves is therefore cumulative.

INTERACTIONS BETWEEN THE REGIONS OF A TWINNED CRYSTAL

When a sample of magnetite is cooled through the transition in such a way that twinning occurs, i.e., the orthorhombic axes do not have the same orientation throughout the sample, we have a very complicated problem to deal with. The behavior of the whole sample does not represent a simple superposition of the action of the individual regions. Interactions arise between the different regions because the magnetization in neighboring regions exerts mutual torque; each region is strained owing to the distortions experienced by its neighbors, and free poles on the boundaries between the regions cause discontinuities in the internal field. The effects due to the last two causes could be very complex; lacking the information needed to even estimate them, we can only assume here that they do not greatly alter the magnetization curves.

The effect of torques exerted by the magnetization in one region on that in neighboring regions is particularly large in two of the experimental magnetization curves: the cubic [100] direction cooled in zero field, and the cubic [111] direction cooled in a parallel field. When a sample is cooled through the transition in a demagnetized state, the cubic [100] direction will become the orthorhombic [001] in $\frac{1}{3}$ of the sample, the orthorhombic [110] in $\frac{1}{3}$, and the orthorhombic $[1\bar{1}0]$ in $\frac{1}{3}$, since the orthorhombic *a* and *b* axes develop along face diagonals of the cubic unit cell. The magnetization curves in the orthorhombic [110] and $[1\bar{1}0]$ directions will be identical. The orthorhombic [110] curve can be obtained by cooling with a field normal to the cubic [100] direction, and the [001] curve with a parallel field. Since the *c* axis [001] is the easy direction, the magnetization curve for the cubic [100] direction after cooling in zero field, if there were no interaction, should be given by

$$H_0=H_\perp;\quad I_0=\tfrac{1}{3}I_{\parallel}+\tfrac{2}{3}I_\perp. \tag{8}$$

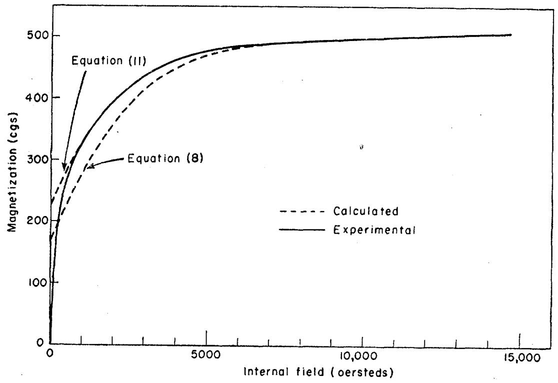

FIG. 14. Magnetization curve at 85°K in the [100] direction after cooling in zero field.

The curve calculated from Eq. (8) on the basis of the measurements in Fig. 11 is compared in Fig. 14 with the measured characteristic. Let us analyze the discrepancy on the basis that torque interaction between the different regions affects the magnetization. In part of the sample the magnetization I_s is orientated parallel to the field, in the remainder at an angle θ to the field. The torque energy will be of the form $I_s^2\cos\theta$. Thus, the energy of a region with the *c* axis perpendicular to the applied field will be

$$E_T=E_a-HI_s\cos\theta-CI_s^2\cos\theta, \tag{9}$$

where E_a is the anisotropy energy, H the internal field, I_s the saturation magnetization, and C an empirical constant. To find the equilibrium position of the magnetization, we set $dE_T/d\theta=0$ and obtain

$$H-CI_s=-(dE_a/d\theta)/(I_s\sin\theta). \tag{10}$$

The corresponding equation for a sample containing only regions with their *c* axes normal to the applied field is the same except that the term $-CI_s$ is not present. Therefore, the magnetization curve for the cubic [100] direction cooled in zero field will be given by the equation

$$H_0=H_\perp-CI_s;\quad I_0=\tfrac{1}{3}I_{\parallel}+\tfrac{2}{3}I_\perp. \tag{11}$$

The fit between this equation with $C=1$, and the experimental curve, is quite satisfactory (Fig. 14). The discrepancy in fields below 800 oersteds may be caused by strains induced in the sample as it cooled through the transition, and to the effects of the magnetostriction.

The interactions between different domain regions probably account for the fact that the anisotropy constants obtained by static methods do not explain quantitatively the microwave resonances observed by Bickford.[1] The twinning at the transition accounts qualitatively for the multiple resonances observed [in the case of the cubic (100) plane discrepancies may be due to lack of magnetic saturation in the sample]. If one calculates from the anisotropy constants the positions of the resonance peaks, the values do not agree with those observed. Interactions of the type described above produce torques which would affect the precession of the magnetization and hence the position of the resonance. The resonance experiments must be repeated under conditions excluding twinning to determine whether the static anisotropy constants will account for the observed resonance frequencies.

SUMMARY AND CONCLUSIONS

A large amount of experimental evidence indicates that the structure of magnetite below the transition is orthorhombic. Direct determination of the unit cell size, both x-rays[10] and strain-gauge measurements,[11] show that the *c* axis lies along one of the original cube edges, and the *a* and *b* axes along the perpendicular cubic face-diagonal directions. The magnetic anisotropy energy gives convincing evidence for orthorhombic symmetry. The anisotropy of the conductivity agrees well with that to be expected from Verwey's ordered structure. The increase in conductivity anisotropy with decreasing temperature (Table III) appears to be directly related to the increase in long-range order.

In addition to accounting for the anisotropic properties below the transition, Verwey's model explains the influence of a magnetic field applied during cooling on the properties of the crystal below the transition. The axis-switching effect, not previously predicted, can be readily explained. Twinning at the transition greatly complicates the magnetic behavior at lower temperatures because the different regions of a twinned crystal interact in a complex way. These interactions are quite large in special cases and probably account for the failure of the static anisotropy constants to predict quantitatively the microwave resonance frequencies.

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Absorption Spectrum of Beryllium in the Neighborhood of the *K* Edge*

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The absorption spectrum of metallic Be has been investigated in the soft x-ray region extending from 60A to 250A. The *K* discontinuity appears at 111A and coincides with the *K* edge observed in the emission spectrum. Over the spectral range studied, the values of the linear absorption coefficient range from 0.25×10^6 to 2.8×10^5 cm^{-1}. Characteristic secondary structure is also noticeable on the short wavelength side of the edge. The positions of secondary absorption maxima are compared with those previously found in the *K* absorption spectrum of Al and with theoretical calculations based on the Hayasi model. The absorption spectrum has also been studied by irradiating Be absorbers with the continuous far ultraviolet radiation emitted by relativistic electrons accelerated in the Cornell synchrotron. Partial reduction of the data indicates good agreement with determinations based on the use of line spectra as the incident radiation.

INTRODUCTION

THE electronic structure of Be ($1s^22s^2$) indicates that the initial state in an absorption transition must either be a *K* level or a level belonging to the filled portion of the conduction band. A study of the *K* emission band of Be shows that the photon energy required for the ejection of a *K* electron should be nearly 112 ev. In the absence of previous information on the absorption spectrum of this metal, an investigation was undertaken to measure the absorption in the spectral region extending from 60A to 250A. The energy of photons in this wavelength region ranges from 50 to 200 ev. Thus, a sample of Be irradiated by photons possessing the above energy spread, should reveal the behavior of the spectrum in the region of the *K* discontinuity. The present paper offers an extension of the preliminary measurements reported on previously.[1]

EXPERIMENTAL

A large portion of the experimental work was carried out by following the general method described in an earlier paper.[2] The dispersing instrument was a grazing incidence spectrograph, equipped with a lightly ruled glass grating having 30 000 lines per inch and a radius of 1.5 m. The grazing angle of incidence was set at 4.5°. The instrument was adjusted carefully in order to insure satisfactory definition in the short wavelength region approaching the cut-off wavelength whose calculated value was 30A. Lines of reasonable intensity were observed down to about 60A.

Absorbers were prepared either by depositing Be directly on a thin substrate of Zapon or by evaporating the metal on a glass surface treated with "Victawet."

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[1] D. H. Tomboulian and R. W. Johnston, Phys. Rev. **83**, 220 (1951).

[2] D. H. Tomboulian and E. M. Pell, Phys. Rev. **83**, 1196 (1951).