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Magnetocrystalline Anisotropy of Magnetite at Low Temperature

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The magnetocrystalline anisotropy of magnetite has been measured by the torque method between 4.2 and 110°K. The anisotropy energy of the orthorhombic phase which exists below 114.5°K is represented by the formula $E_a=K_a\alpha_a^2+K_b\alpha_b^2+K_{aa}\alpha_a^4+K_{ab}\alpha_a^2\alpha_b^2+K_{bb}\alpha_b^4$, where α_a and α_b are the direction cosines of the magnetization with respect to the hard and intermediate axes, respectively. The five anisotropy coefficients were determined from torque values measured in the cubic (001) and (011) planes in fields as large as 25 000 G. The values of K_a and K_b confirm the conclusion of Slonczewski that the anisotropy of the orthorhombic phase cannot be accounted for simply by a consideration of magnetic dipole, spin-orbit, and intra-atomic spin-spin interactions. With the exception of K_b, the anisotropy coefficients show little temperature dependence. An increase of K_b by more than 40% between 4.2 and 110°K is attributed to local disorder which is generated with an activation energy of 0.016 eV.

I. INTRODUCTION

MORE than thirty years ago it was found that the magnetic and electrical properties of magnetite undergo abrupt changes when the crystal is cooled below about 115°K. Weiss and Forrer[1] observed that the material became more difficult to magnetize to saturation, and Okamura[2] found an almost 100-fold decrease in electrical conductivity. A peak in the specific heat curve at the transition temperature was reported by Millar.[3] Li[4] observed that the magnetic symmetry reduced from cubic to uniaxial and that the orientation of the axis of symmetry could be influenced by the presence of a magnetic field.

The above effects clearly indicated a low-temperature phase transformation, and determining the nature of this transformation has been the object of a number of subsequent investigations. Verwey *et al.* concluded from the electrical properties[5] and from the value of the oxygen parameter[6] that Fe_3O_4 is an inverse spinel and proposed that upon cooling through the transition temperature the distribution of Fe^{2+} and Fe^{3+} ions on *B* sites changes from one of dynamic disorder to one of long range order. The most probable ordered structure consists of {100} planes containing rows of Fe^{3+} ions aligned along a ⟨110⟩ direction alternating with planes containing rows of Fe^{2+} ions aligned along the orthogonal ⟨110⟩ direction, as shown in Fig. 1. Such ordering would produce an orthorhombic lattice whose *c* axis coincides with a cubic ⟨100⟩ axis and whose *a* and *b* axes lie along the orthogonal ⟨110⟩ axes. A small orthorhombic distortion with these axis orientations has been detected by x-ray[7,8] and strain-gauge[9] measurements, and more direct verification of the above ordering scheme has been provided by neutron diffraction.[10]

The purpose of this investigation has been to study the magnetic anisotropy of magnetite at low temperature. The symmetry of the magnetocrystalline energy of the ordered phase is, like that of the unit cell, orthorhombic. Ignoring isotropic terms, this energy may be written to terms in the fourth degree in the following form[11]:

$$E_a=K_a\alpha_a^2+K_b\alpha_b^2+K_{aa}\alpha_a^4+K_{ab}\alpha_a^2\alpha_b^2+K_{bb}\alpha_b^4, \quad (1)$$

where α_a, α_b and α_c are the direction cosines of the magnetization with respect to the *a*, *b*, and *c* axes, respectively, and the identity $\alpha_a^2+\alpha_b^2+\alpha_c^2=1$ has been used to eliminate terms in α_c. In the work reported here the five coefficients in Eq. (1) have been determined by the torque method between 4.2°K and temperatures as near the transition temperature as the measuring technique would permit.

II. EXPERIMENTAL PROCEDURE

The magnetite sample was an 8.57-mg single-crystal sphere. The crystal from which the sample was cut was

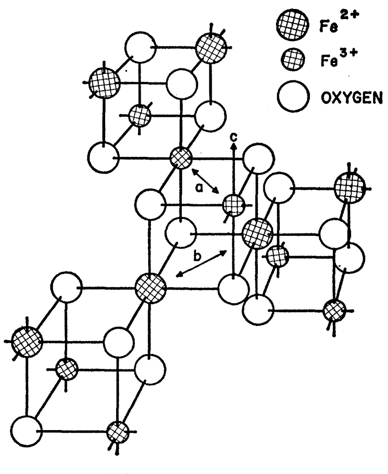

FIG. 1. The *B* sublattice and neighboring oxygen ions in ordered magnetite.

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[1] P. Weiss and R. Forrer, Ann. Phys. (Paris) **12**, 279 (1929).

[2] F. Okamura, Sci. Rept. Tohoku Univ. First Ser. **21**, 231 (1932).

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

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

[5] E. J. W. Verwey and J. H. de Boer, Rec. Trav. Chim. **55**, 531 (1936).

[6] E. J. Verwey, P. W. Haayman, and F. C. Romeijn, J. Chem. Phys. **15**, 181 (1947).

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

[8] S. C. Abrahams and B. A. Calhoun, Acta Cryst. **8**, 257 (1955).

[9] L. R. Bickford, Jr., Rev. Mod. Phys. **25**, 75 (1953).

[10] W. C. Hamilton, Phys. Rev. **110**, 1050 (1958).

[11] B. A. Calhoun, Phys. Rev. **94**, 1577 (1954).

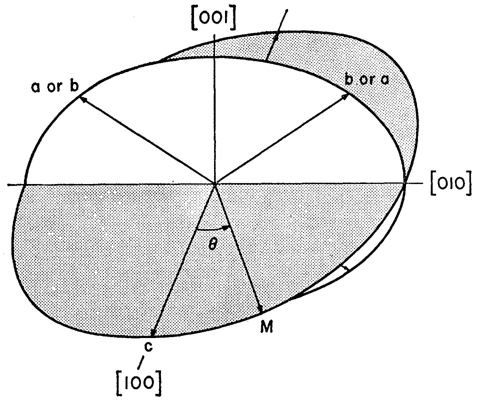

FIG. 2. Orientation of the orthorhombic axes with respect to a cubic (001) plane containing the easy axis.

grown from the melt in an atmosphere of pure CO_2 and cooled in an atmosphere of CO_2 and H_2 so as to yield as nearly as possible a stoichiometric ferrite.[12] The sample was oriented by x rays to an accuracy of better than 1° and mounted on a small brass block.

Torque measurements were made with a self-balancing torque magnetometer which was enclosed in a vacuum to allow measurements to be made at liquid helium temperature. Temperatures above 4.2°K were maintained with a resistance heater attached to the sample holder and were measured with a 2 at. % cobalt gold-copper thermocouple whose cold junction was soldered to the brass sample mount. Magnetic fields as large as 25 000 G were provided by an ADL iron-core electromagnet which could be rotated about the sample.

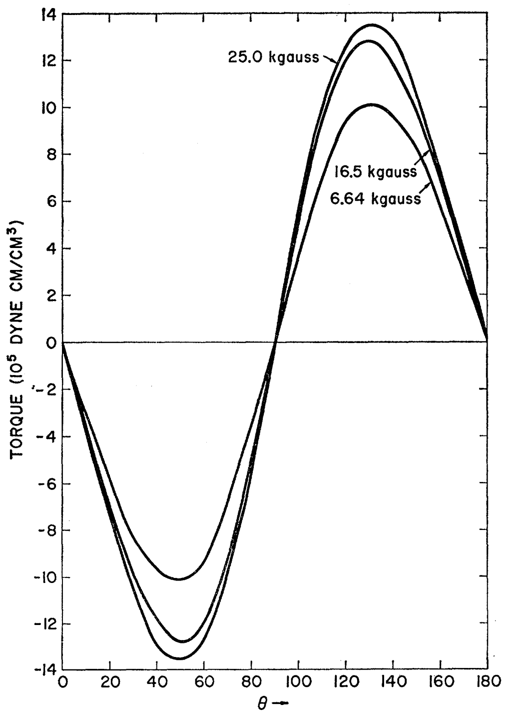

FIG. 3. Torque curve at 4.2°K in the cubic (001) plane containing the easy axis.

III. DETERMINATION OF ANISOTROPY COEFFICIENTS

The magnetocrystalline energy of magnetite in the ordered phase will depend upon the orientation of the orthorhombic axes throughout the crystal. In the absence of any external orienting influence, the crystal will hybridize upon cooling through the transition, distributing its *c* axes equally among the three equivalent ⟨100⟩ axes and its *a* and *b* axes equally among the six equivalent ⟨110⟩ axes. However, the inequivalence of the three orthorhombic axes, both in regard to magnetic hardness and lattice parameter, makes the application of external magnetic fields or stresses during the cooling process effective in producing a desired axis configuration.

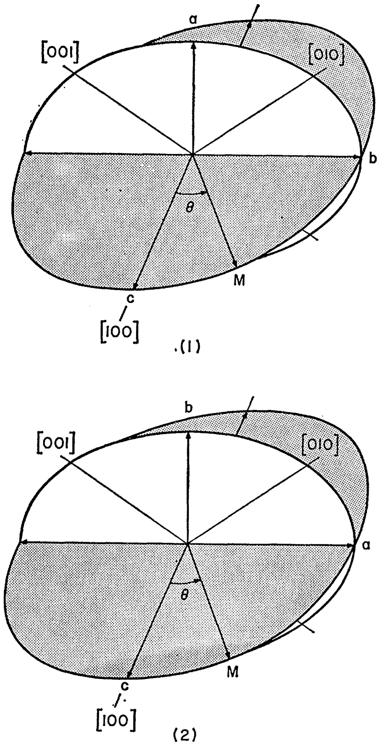

FIG. 4. Orientation of the orthorhombic axes with respect to a cubic (011) plane containing (1) the easy and intermediate axes, and (2) the easy and hard axes.

Determination of the five anisotropy coefficients in Eq. (1) requires torque measurements in the cubic (001) and the cubic (011) planes. The measurements in these two planes are interpreted as follows.

Cubic (001) Plane

The *c* axis has been shown to be magnetically easy.[13] If the crystal is cooled through the transition in a mag-

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[12] L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. **68**, 798 (1946).

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

netic field applied near the [100] axis, the energy will be a minimum if this axis is adopted as the c axis throughout the crystal. Since the measuring plane very nearly coincides with the orthorhombic (110) plane, the energy is practically independent of the orientation of the a and b axes. Twinning of an orthorhombic crystal with respect to the orientation of the a and b axes introduces a strain component ϵ_{xy}. This component, however, does not contribute an angularly dependent magnetoelastic energy in the cubic (001) plane.[14] The anisotropy energy for this configuration (shown in Fig. 2) can thus be written, as for an unstrained crystal,

$$E_a=\tfrac{1}{2}(K_a+K_b)\sin^2\theta+\tfrac{1}{4}(K_{aa}+K_{ab}+K_{bb})\sin^4\theta,$$

where θ is the angle between the magnetization and the [100] axis. The torque is given by

$$L=-\frac{\partial E_a}{\partial\theta}=-\tfrac{1}{4}(2K_a+2K_b+K_{aa}+K_{ab}+K_{bb})\sin2\theta+\tfrac{1}{8}(K_{aa}+K_{ab}+K_{bb})\sin4\theta. \quad (2)$$

Torque curves[15] obtained in the cubic (001) plane at 4.2°K are shown in Fig. 3. Since the anisotropy energy does not have reflectional symmetry with respect to the orthorhombic (110) plane, the equilibrium direction of the magnetization in a finite applied field does not generally lie in the measuring plane, but approaches it asymptotically as the field becomes infinite. The torque curves are consequently field-dependent. Values of the sums K_a+K_b and $K_{aa}+K_{ab}+K_{bb}$ can be obtained from amplitudes of the $\sin2\theta$ and $\sin4\theta$ components extrapolated as a function of $1/H$ to infinite fields. The amplitudes at 82°K in a field of 12 000 G[16] are in good agreement with those obtained at this temperature and field by Pearson and Cooper.[17]

Cubic (011) Plane

If the crystal is cooled through the transition with a field applied so as to align the c axis with the [100] axis, two axial configurations can exist depending upon the orientation of the a and b axes, as shown in Fig. 4. The anisotropy energy of the twinned crystal in the (011) plane, neglecting the effect of strain, is

$$E_a=f_a[K_a\sin^2\theta+K_{aa}\sin^4\theta]+f_b[K_b\sin^2\theta+K_{bb}\sin^4\theta],$$

where f_a and f_b are fractions of the crystal volume for which the a axis and b axis, respectively, lie in the measuring plane, and $f_a+f_b=1$. The torque is given by

$$L_{(011)}=-f_a[(K_a+K_{aa})\sin2\theta-\tfrac{1}{2}K_{aa}\sin4\theta]-f_b[(K_b+K_{bb})\sin2\theta-\tfrac{1}{2}K_{bb}\sin4\theta]. \quad (3)$$

The b axis is defined as the energetically intermediate axis, and one finds that by applying a field at a lower temperature (between 50°K and the transition temperature) at a large angle (>55°), one can produce the minimum energy state for which $f_b=1$. K_b and K_{bb} can then be determined from the torque curve for this state. A large value of f_a can be obtained by cooling the crystal with a field applied as near $\theta=0$ as possible. In such circumstances a slight misalignment of the cubic (011) plane with respect to the measuring plane will serve to align the b axis of much of the crystal perpendicular to the measuring plane.

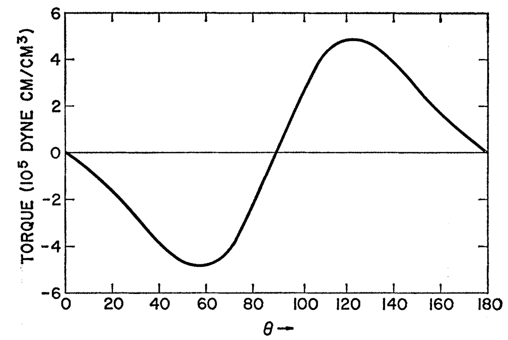

FIG. 5. Torque curves at 4.2°K in a cubic (011) plane containing the easy and intermediate orthorhombic axes.

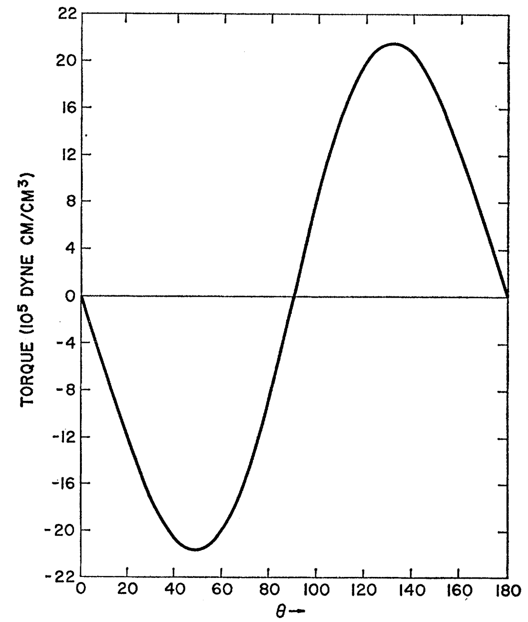

FIG. 6. Torque curves at 4.2°K in a cubic (011) plane containing, for 91.1% of the crystal volume, the easy and hard orthorhombic axes.

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[14] J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959), p. 57.

[15] The angle δ between the directions of the applied field and the magnetization is determined from the relation $L=MH\sin\delta$.

[16] Complete torque curves could be determined in this plane only up to about 50°K, since above this temperature the easy axis switches from [100] to [010] if $45°<\theta<135°$. However, torque values outside this region are sufficient for determining amplitudes of the $\sin2\theta$ and $\sin4\theta$ components.

[17] R. F. Pearson and R. Cooper, Proc. Phys. Soc. (London) **78**, 17 (1961).

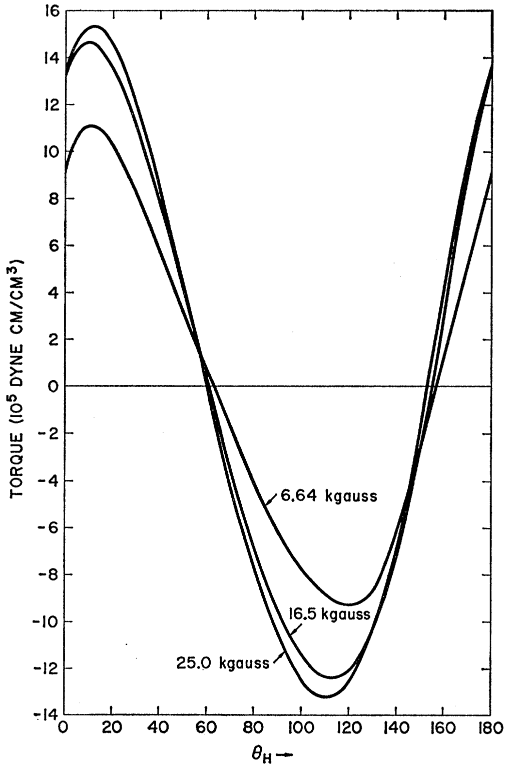

FIG. 7. Torque at 4.2°K in a cubic (011) plane containing none of the orthorhombic axes as a function of the angle θ_H between the field direction and the cubic [100] axis.

Once K_a+K_b has been determined from measurements in the cubic (001) plane, and K_b and K_{bb} have been determined from measurements in the (011) plane, then values of f_a and K_{aa} for any twinned crystal can be found from Eq. (3), if the amplitudes of the $\sin2\theta$ and $\sin4\theta$ components of the torque are known.[18] K_{ab} can be found by subtracting K_{aa} and K_{bb} from the value of $K_{aa}+K_{ab}+K_{bb}$ determined from the torque in the cubic (001) plane.

Torque curves in the cubic (011) plane at 4.2°K are reproduced in Figs. 5 and 6. Figure 5 shows the torque curve for which the amplitude of the $\sin2\theta$ component was a minimum and for which it is presumed that $f_b=1$. Figure 6 shows the curve for which this amplitude was the largest that could be obtained. It corresponds to a value of $f_a=0.911$. Since the anisotropy energy has reflectional symmetry with respect to orthorhombic {100} planes, the magnetization for these two cases lies in the measuring plane for applied fields greater than $2[K_a-K_b+2K_{aa}-K_{ab}]/M$, and for such fields the torque curves are field-independent.

Additional configurations in the cubic (011) plane can be prepared by cooling the crystal through the transition with a magnetic field applied at a large angle ($55°<\theta_c<125°$) and thereby distributing the c axes between the cubic [010] and [001] axes. The torque is given by

$$L=(f_<-f_>)\left\{\left(\frac{4K_a-4K_b+3K_{aa}-3K_{bb}}{4\sqrt{2}}\right)\cos2\theta+\left(\frac{K_{aa}-K_{bb}}{4\sqrt{2}}\right)\cos4\theta\right\}+\left\{\left(\frac{4K_a+4K_b+3K_{aa}+3K_{ab}+3K_{bb}}{16}\right)\sin2\theta-\left(\frac{7K_{aa}+7K_{bb}-9K_{ab}}{32}\right)\sin4\theta\right\},\quad(4)$$

where $f_>$ and $f_<$ are the fractions of the crystal for which, at $\theta<90°$, the direction of magnetization makes a smaller or larger angle, respectively, with the intermediate axis than with the hard axis. Either $f_>$ and $f_<$ can be set equal to unity by making θ_c either less than or greater than 90°. In Fig. 7 torque values as a function of the angle of the applied field θ_H are shown for a crystal in which $f_<=1$. A field dependence of the torque is again evident, since the anisotropy energy for this configuration lacks reflectional symmetry with respect to the measuring plane.

The temperature dependence of the anisotropy coefficients was determined by measuring the temperature

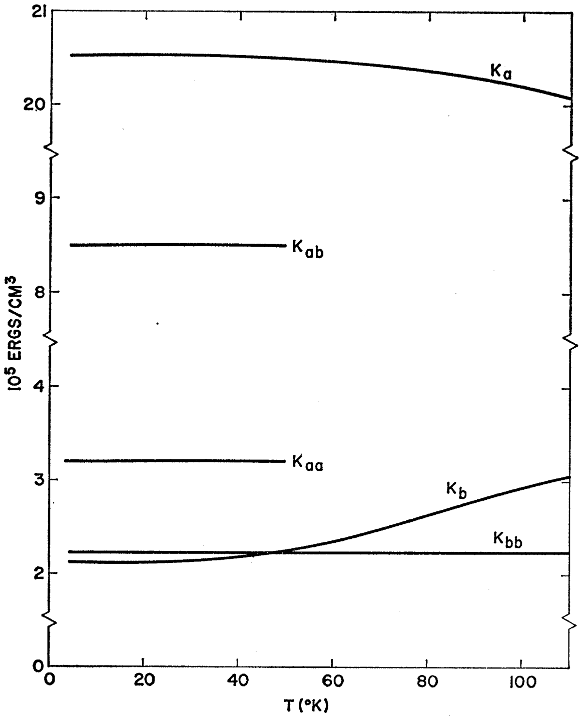

FIG. 8. Anisotropy coefficients as a function of temperature.

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[18] Complete torque curves could be determined for a twinned crystal in this plane only below 50°K, because at higher temperatures f_a reduces to zero in the presence of a magnetic field.

dependence of the torque at a number of field directions. High sensitivity was achieved by canceling with a dc voltage the output of the torque magnetometer corresponding to the torque at 4.2°K and adjusting the sensitivity of the output recorder to a level appropriate to the magnitude of the temperature dependence of the torque. Values of the anisotropy coefficients over the temperature range for which they could be determined are shown in Fig. 8. Since the value of each coefficient is calculated from a number of temperature-dependent curves, individual data points are not shown. The values of the coefficients are not in good agreement with those obtained by Williams *et al.*[19] by the torque method at 77°K and by Calhoun[11] from magnetization curves at 85°K, and the discrepancy probably arises from a failure in the earlier work to take account of the field dependence of the direction of magnetization. The agreement is somewhat better with the values obtained at 4.2°K from microwave resonance by Bonstrom *et al.*[20] but the temperature dependence reported by these workers was not observed in this study.

IV. DISCUSSION

Anisotropy at 0°K

Slonczewski[21] has calculated the anisotropy of magnetite in the ordered phase by adding estimates of the anisotropy contributions from interatomic magnetic dipole interactions,[22] spin-orbit coupling, and intra-atomic spin-spin interactions. The calculated anisotropies are $K_a=-12\times10^6$ ergs/cm^3 and $K_b=12\times10^6$ ergs/cm^3. As Slonczewski noted with regard to earlier results, these values disagree with the present experimental values both in regard to order of magnitude and to the direction of the easy axis.

It is doubtful that incomplete long-range order can account for the above discrepancy, or for other reported discrepancies between calculated and observed values of the orthorhombic unit cell dimensions[21] and the neutron diffraction intensity of the (002) reflection.[10] The almost constant value of K_a indicates that no significant change in the apparent degree of long-range order occurs at temperatures more than 3°K below the transition temperature[23] (114.5°K). If electron-exchange processes do not become prohibitively difficult in the course of ordering, and the persistence of electrical conductivity below the transition indicates that this is the case, then it is likely that the ionic configuration achieved in this small temperature range is the stable configuration of complete long-range order.

Temperature Dependence of Anisotropy

Several investigators[24–26] have shown that decreases of magnetization and anisotropy which result from thermal dispersion of the orientations of individual spin vectors should observe a simple relationship which depends upon the symmetry of the magnetocrystalline energy. Specifically, the reduced coefficients of components of the magnetocrystalline energy with the symmetry of $Y_l^m(\theta,\phi)$ should vary as the power $l(l+1)/2$ of the reduced magnetization. In magnetite this relation requires K_a and K_b to vary as the third power of the reduced magnetization, and K_{aa}, K_{ab}, and K_{bb} to vary as the tenth power.

The small temperature dependence of K_a is consistent with the above theory. Using the value of J_{AB} determined by Brockhouse[27] from neutron scattering measurements, one obtains[28] a decrease in the magnetization at 100°K by a factor of 0.0015 from the value at 0°K. The decrease in the B sublattice magnetization is probably comparable, since at the lowest temperatures, the A site and B site spins precess in phase and at equal angles to the magnetization axis.[28]

A different process is probably responsible for the unusual temperature dependence of K_b, which increases by more than 40% between 4.2 and 110°K. The coefficient K_b in this range is accurately represented by the function

$$K_b=K_{b0}+Ae^{-Q/kT} \qquad (5)$$

for constants with the values $K_{b0}=2.12\times10^5$ ergs/cm^3, $A=5.2\times10^5$ ergs/cm^3, and $Q=0.016$ eV. A thermally activated process is thus indicated, and the most likely one is local disorder, since the activation energy Q is comparable to kT at the transition temperature.

Anderson[29] has pointed out that long-range order in magnetite is brought about principally by the electrostatic interaction of next-nearest cation neighbors, since the effect of nearest neighbor interactions in the B sublattice is merely to produce a structure of short-range order in which each tetrahedron is occupied by two divalent and two trivalent cations. The low-transition temperature in magnetite is thus a measure of the interactions between next nearest and more remote neighbors, rather than the far stronger nearest neighbor interactions. Local disorder below the transition temperature will consequently involve configurations which least disturb the arrangement of nearest neighbors.

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[19] H. J. Williams, R. M. Bozorth, and M. Goertz, Phys. Rev. **91**, 1107 (1953).

[20] D. B. Bonstrom, A. H. Morrish, and L. A. K. Watt, J. Appl. Phys. **32**, 272S (1961); D. B. Bonstrom, thesis, University of Minnesota, 1959 (unpublished).

[21] J. C. Slonczewski, J. Appl. Phys. **32**, 253S (1961).

[22] R. A. Johnson and D. W. Healy, Jr., J. Chem. Phys., **26**, 1031 (1957).

[23] This transition temperature is somewhat lower than the highest temperatures (ca. 119°K) which have been reported. Verwey and Haayman [Physica **8**, 979 (1941)] have shown that the transition temperature is very sensitive to the iron-oxygen ratio. An iron deficiency of 0.3% is sufficient to produce the observed lowering of the transition temperature.

[24] C. Zener, Phys. Rev. **96**, 1335 (1954).

[25] F. Keffer, Phys. Rev. **100**, 1692 (1955).

[26] E. R. Callen, J. Appl. Phys. **33**, 832 (1962).

[27] B. N. Brockhouse, Phys. Rev. **106**, 859 (1957).

[28] H. Kaplan, Phys. Rev. **86**, 121 (1952).

[29] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).

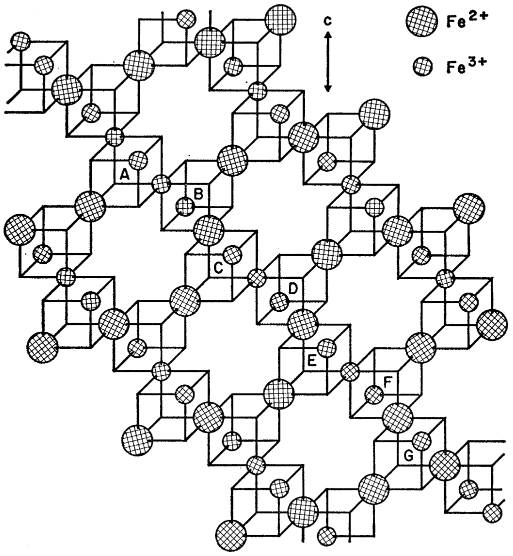

FIG. 9. Local disorder of the B sublattice in the form of a chain of switched tetrahedra. Oxygen ions are not shown.

Such a configuration is the short chain of "switched" tetrahedra $ABCDEFG$ shown in Fig. 9. Only in the terminal tetrahedra A and G is there an imbalance in the number of divalent and trivalent cations. For long chains, the greater energy of these terminal tetrahedra can be neglected and the activation energy Q for local disorder will be the energy required to make one electron exchange and lengthen the chain of switched tetrahedra by two units. Since the complement of next-nearest neighbors is less disturbed by an extension of the chain in its established direction than in a new one, the chains will tend to grow in straight lines.

The contribution of switched tetrahedra to the torque in the (110) plane is probably of the order of $(K_a+K_b)/2$ per cc of switched tetrahedra. This quantity exceeds K_b, and disorder should thus increase the apparent value of K_b, as observed. Disorder should decrease the apparent value of K_a, and part of the observed change is no doubt from this source. Disorder has little effect on K_{bb}, probably because K_{aa} and K_{bb} are of similar magnitude.

V. SUMMARY AND CONCLUSIONS

The octahedral sublattice in magnetite undergoes a transition from disorder to sensibly complete long-range order upon cooling from 114.5 to 112°K. The anisotropy coefficients of the ordered phase at 4.2°K confirm the conclusion of Slonczewski that the anisotropy cannot be accounted for simply by a consideration of magnetic dipole, spin-orbit, and intra-atomic spin-spin interactions. The temperature dependence of the anisotropy coefficients between 4.2 and 110°K is due primarily to the increasing abundance of local disorder in the form of chains of switched tetrahedra which lengthen with a characteristic activation energy of 0.016 eV.

ACKNOWLEDGMENTS

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