

THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

EXPANSIONS FOR MAGNETIZATION CHARACTERIZATION
FOR ORTHORHOMBIC AND CUBIC MAGNETITE AT LOW-TEMPERATURES

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INTRODUCTION

The study of the temperature dependent order-disorder effect in magnetite as manifested by the change in magnetic characteristics can be quite revealing if one is fortunate enough to have available monocrystals of the material. One can study directional properties which will reveal the crystalline transition from cubic to orthorhombic symmetry. Not only can one study directional properties of these materials with ease experimentally, one can also invoke symmetry relationships that make the mathematical description much more tractable. Practically all the research reporting the order-disorder transition observed in magnetite at -155°C is concerned with monocrystalline properties⁽¹⁾. This does not mean that polycrystals of the same material do not exhibit a like effect⁽²⁾. This researcher studied the transition of natural and synthetic magnetite with varying degrees of doping and oxidation and found rather surprising results which will be reported on at a later time.

Because the material that was being studied was polycrystalline a direct comparison with other results was not possible. To obtain the polycrystalline magnetic behavior one must be able to average the magnetization or the crystalline anisotropy energy over all possible directions with an appropriate weighing function. Even before one reaches the averaging process, one must be able to represent the total energy of the system in a form which will make the magnetization process progress in a fashion which will make the total energy a minimum. There are three assumptions which are made by most people studying the magnetization process^(3,4).

The first usually assumes that the total energy is predominantly magneto-static and magnetoelastic energy. The second assumption states that the crystalline anisotropy or mechanical energy can be expanded in a series of direction cosines with appropriate anisotropy constants or strain components which is consistent with the symmetry of the system. The third assumption requires that in the magnetization process the magnetization vector approach the direction of the applied field by moving from an easy direction to the applied field direction as the field is increased in a plane formed by the easy direction and the applied field. All of these assumptions are applicable in the studies on magnetite as verified by the comparison of experimental results with predicted results based on the above assumptions⁽⁵⁾. The first two assumption will be used in the analysis to follow and the third one will be shown to be a good first order approximation. In order to facilitate the averaging process the energies to be considered will be expressed in spherical coordinates rather than in polar angles. The minimization of the total energy will also be carried out in spherical coordinates. A Taylor series expansion of a function of two variables is used both for the magnetization and the crystalline anisotropy energy. The mks system of units will be used.

DEVELOPMENT

The assumption that will be used in the analysis for both the orthorhombic and cubic phase for magnetite are as follows:

- (1) The free energy of interest for the system is the sum of the magnetostatic and crystalline anisotropy energy.

- (2) The magnetization process proceeds entirely by domain rotation.
- (3) The crystalline anisotropy energy can be expressed by a series expansion in direction cosines of the magnetization vector which are consistent with the symmetry of the system.
- (4) The magnetization and crystalline anisotropy energies are mathematically well behaved above and below the low-temperature ordering transition. This last assumption is required if the Taylor series expansion is to be used with any degree of confidence.

The results for the cubic configuration can be found elsewhere in the literature⁽⁶⁾ and are included in the Appendix.

It is assumed (1) that the free energy can be expressed by the following equation:

$$E = E_0 + E_k - \mu_0 H \cdot J \quad (1)$$

where

E_0 = isotropic energy term

E_k = energy needed to turn the magnetization from an easy direction to some other direction

$\mu_0 H \cdot J$ = magnetostatic energy

For the polycrystalline samples under study use must be made of the average crystalline anisotropy and magnetostatic energy. These averages are with respect to the possible spread in domain orientations over the total solid

angle of 4π steradians and are noted in Equation (2) by the bars.

$$\bar{E} = E_0 + \bar{E}_k - \mu_0 H J_S \bar{\Omega} \quad (2)$$

One seeks a distribution over the allowed angular displacements for the magnetization vector that will make the free energy a minimum. To facilitate the averaging over all possible orientations the cosine of the angle between H and J which can be written in the direction cosines of H and J as follows

$$\Omega = \alpha_1 \alpha'_1 + \alpha_2 \alpha'_2 + \alpha_3 \alpha'_3 \quad (3)$$

and the direction cosines which appear in the expression for E_k are expressed in the spherical coordinates for the unit sphere as follows:

$$\begin{aligned} \alpha_1 &= \sin \theta \cos \phi \\ \alpha_2 &= \sin \theta \sin \phi \\ \alpha_3 &= \cos \theta \end{aligned} \quad (4)$$

The primes in Equation (3) and the equations to follow denote the direction cosines for the effective field and the subscripts denote the x, y, z axes or $\langle 100 \rangle$, $\langle 010 \rangle$, $\langle 001 \rangle$ directions, respectively. Also, the following reduced or normalized magnetization is defined as

$$\bar{\Omega} \triangleq \frac{J}{J_S} = \frac{1}{4\pi} \int_{\text{unit sphere}} F(\omega') \Omega d\omega' \quad (5)$$

where $F(\omega')$, the weighing function, is assumed to be unity for the system if it has no magnetic history. $d\omega'$ is an incremental area on the unit sphere or incremental solid angle.

Because H is assumed fixed at all fields (neglecting demagnetizing effects) and J_s turns under the application of the field, it is assumed that the spherical coordinates of H are known and those of J_s are the variables. Invoking the symmetry requirements allows or requires that the integration be carried out over only a fraction of the total solid angle. The characteristics relative to this fraction of the total solid angle are then representative for the symmetry class under study.

The crystalline anisotropy energy for the orthorhombic structure is given by

$$E_k = K_a \sin^2 \theta_a + K_b \sin^2 \theta_b + K_c \sin^2 \theta_c + K'_a \sin^4 \theta_a + K'_b \sin^4 \theta_b + K'_c \sin^4 \theta_c \quad (6)$$

where the angles θ_a , θ_b and θ_c are measured from the a , b , c axes, respectively, of the orthorhombic structure. For the orthorhombic phase in magnetite, the c axis is the easy axis which is in the $\langle 001 \rangle$ direction.

The average crystalline anisotropy energy for the polycrystal with no magnetic history is given by

$$\begin{aligned} \bar{E}_k &= \frac{K_c}{\omega} \int (\sin^2 \theta_c + \frac{K_b}{K_c} \sin^2 \theta_b + \frac{K_a}{K_c} \sin^2 \theta_a) d\omega' \\ &+ \frac{K_c}{\omega} \int (\frac{K'_c}{K_c} \sin^4 \theta_c + \frac{K'_b}{K_c} \sin^4 \theta_b + \frac{K'_a}{K_c} \sin^4 \theta_a) d\omega' \end{aligned} \quad (7)$$

To simplify the notation somewhat, let

$$\bar{E}_k = \frac{K_c}{\omega} \int f d\omega' \quad (8)$$

The integrations for the case of the orthorhombic phase are carried out over one octant so that the ω appearing in the above equations is $\frac{\pi}{2}$.

To integrate f it is best to change the direction sines into sines of the spherical coordinate angles. This is accomplished by noting that

$$\begin{aligned}\sin^2\theta_a &= 1 - \sin^2\theta \cos^2\phi \\ \sin^2\theta_b &= 1 - \sin^2\theta \sin^2\phi \\ \sin^2\theta_c &= \sin^2\theta\end{aligned}\tag{9}$$

Using this substitution, f can be written as

$$\begin{aligned}f &= \left(\frac{K_b}{K_c} + \frac{K_a}{K_c} + \frac{K'_b}{K_c} + \frac{K'_a}{K_c} \right) + \sin^2\theta + \frac{K'_c}{K_c} \sin^4\theta \\ &+ \frac{K'_a}{K_c} (\sin^4\theta \cos^4\phi) - \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \sin^2\theta \cos^2\phi \\ &+ \frac{K'_b}{K_c} (\sin^4\theta \sin^4\phi) - \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) \sin^2\theta \sin^2\phi\end{aligned}\tag{10}$$

It should be evident from Equations (5) and (8) that \bar{E}_k and $\bar{\Omega}$ cannot be found unless the equilibrium conditions are known for θ and ϕ in terms of θ' and ϕ' for the particular crystal system of interest. The equilibrium conditions are such that

$$\bar{E}_k - \mu_0 H J_S \bar{\Omega} = \text{minimum}\tag{11}$$

or in terms of Equations (5) and (8)

$$\int f d\omega' - \frac{\mu_0 H J_S}{K_c} \int \Omega d\omega' = \text{minimum}\tag{11a}$$

Gans⁽⁶⁾ suggests that a partial integration of Equation (11a) with respect to θ and ϕ will yield the necessary conditions for equilibrium. Instead of this, use will be made of Akulov's⁽⁷⁾ assumption that

the minimal conditions on the integrands will suffice. Either technique will work as is evidenced by the fact that the results obtained for the cubic system using the second approach give the same results as Gans reported. With this approach, one obtains:

$$f_{\theta} - \zeta \Omega_{\theta} = 0 \quad (12)$$

$$f_{\phi} - \zeta \Omega_{\phi} = 0 \quad (12a)$$

where the subscripts denote a partial differentiation with respect to θ and ϕ , respectively, and

$$\zeta = \frac{HJ_s}{\mu_0 K_c} \quad (13)$$

It will be assumed that f and Ω can be expanded in a Taylor series in two variables where the variables will be selected in accordance with a weak or strong field analysis. A weak field will be defined as one which moves the magnetization vector only slightly out of line with the easy direction. A strong field will be defined as one which is only separated by a small angle from the magnetization vector. With appropriate consideration of the conditions under study, f and Ω will be expanded only to the fourth term. For instance,

$$\begin{aligned} f(\theta, \phi) = & f(\theta_1, \phi_1) + \frac{\partial f}{\partial \theta} \bigg|_{\theta_1, \phi_1} (\theta - \theta_1) + \frac{\partial f}{\partial \phi} \bigg|_{\theta_1, \phi_1} (\phi - \phi_1) + \frac{1}{2!} \left[\frac{\partial^2 f}{\partial \theta^2} \bigg|_{\theta_1, \phi_1} (\theta - \theta_1)^2 \right. \\ & + \frac{\partial^2 f}{\partial \phi^2} \bigg|_{\theta_1, \phi_1} (\phi - \phi_1)^2 + 2 \frac{\partial^2 f}{\partial \theta \partial \phi} \bigg|_{\theta_1, \phi_1} (\theta - \theta_1)(\phi - \phi_1) \left. \right] + \frac{1}{3!} \left[\frac{\partial^3 f}{\partial \theta^3} \bigg|_{\theta_1, \phi_1} (\theta - \theta_1)^3 \right. \\ & + \frac{\partial^3 f}{\partial \phi^3} \bigg|_{\theta_1, \phi_1} (\phi - \phi_1)^3 + 3 \frac{\partial^3 f}{\partial \theta^2 \partial \phi} \bigg|_{\theta_1, \phi_1} (\theta - \theta_1)^2 (\phi - \phi_1) \\ & \left. + 3 \frac{\partial^3 f}{\partial \phi^2 \partial \theta} \bigg|_{\theta_1, \phi_1} (\phi - \phi_1)^2 (\theta - \theta_1) \right] \end{aligned} \quad (14)$$

where $\theta_1 \phi_1$ is a point on the unit sphere about which we would want the expansion to hold. For weak fields this would be the coordinate for the easy axis and for strong fields this would be the coordinate for the effective magnetic field. Now if we replace $(\theta - \theta_1)$ by α and $(\phi - \phi_1)$ by β , it is found that f and Ω can be represented as

$$f = f_0 + \alpha f_1 + \beta f_2 + \frac{1}{2} (\alpha^2 f_{11} + 2\alpha\beta f_{12} + \beta^2 f_{22}) + \frac{1}{6} (\alpha^3 f_{111} + 3\alpha^2\beta f_{112} + 3\alpha\beta^2 f_{122} + \beta^3 f_{222}) \quad (15)$$

$$\Omega = \Omega_0 + \alpha \Omega_1 + \beta \Omega_2 + \frac{1}{2} (\alpha^2 \Omega_{11} + 2\alpha\beta \Omega_{12} + \beta^2 \Omega_{22}) + \frac{1}{6} (\alpha^3 \Omega_{111} + 3\alpha^2\beta \Omega_{112} + 3\alpha\beta^2 \Omega_{122} + \beta^3 \Omega_{222}) \quad (16)$$

where the subscripts on f and Ω indicate the order of the partial derivative by the number of subscripts and subscript one means with respect to θ and subscript two with respect to ϕ .

The evaluation of Equation (12) and (12a) yields Equations (17) and (17a), respectively.

$$f_1 + \alpha f_{11} + \beta f_{12} + \frac{1}{2} (\alpha^3 f_{111} + 2\alpha\beta f_{112} + \beta^2 f_{122}) = \zeta [\Omega_1 + \alpha \Omega_{11} + \beta \Omega_{12} + \frac{1}{2} (\alpha^2 \Omega_{111} + 2\alpha\beta \Omega_{112} + \beta^2 \Omega_{122})] \quad (17)$$

$$f_2 + \alpha f_{12} + \beta f_{22} + \frac{1}{2} (\alpha^2 f_{112} + 2\alpha\beta f_{122} + \beta^2 f_{222}) = \zeta [\Omega_2 + \alpha \Omega_{12} + \beta \Omega_{22} + \frac{1}{2} (\alpha^2 \Omega_{112} + 2\alpha\beta \Omega_{122} + \beta^2 \Omega_{222})] \quad (17a)$$

In weak fields it should not be necessary to utilize the triple subscript terms in Ω because of the magnitude of ζ . Also notice that

in the strong field case the triple subscript terms in f will be extremely small compared to the other terms. The f 's will be dependent on the particular form of the crystalline anisotropy energy used while the Ω 's will be the same in all cases.

Weak Fields

In weak fields the following substitutions are used:

$$\alpha = \theta \quad \text{and} \quad \beta = \phi - \phi' \quad (18)$$

and with these it is found that

$$\begin{aligned} \Omega_0 &= -\Omega_{11} = \cos \theta' \\ \Omega_1 &= -\Omega_{111} = -\Omega_{221} = \sin \theta' \\ \Omega_2 &= \Omega_{22} = \Omega_{12} = \Omega_{222} = \Omega_{112} = 0 \end{aligned} \quad (19)$$

and the f 's are

$$\begin{aligned} f_0 &= \left(\frac{K_b}{K_c} + \frac{K_a}{K_c} \right) + \left(\frac{K'_b}{K_c} + \frac{K'_a}{K_c} \right) \\ f_{11} &= 2 \left[1 - \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) \sin^2 \phi' - \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \cos^2 \phi' \right] \\ f_{112} &= -2 \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) \sin 2\phi' + 2 \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \sin 2\phi' \end{aligned} \quad (20)$$

$$f_1 = f_2 = f_{22} = f_{12} = f_{111} = f_{222} = f_{221} = 0$$

Let us assume that α and β can be represented by the following polynomials

$$\alpha = c_1 \zeta + c_2 \zeta^2 + c_3 \zeta^3 + \dots \quad (21)$$

$$\beta = D_1 \zeta + D_2 \zeta^2 + D_3 \zeta^3 + \dots \quad (22)$$

which go to zero as ζ goes to zero. Evaluation of cubic and higher order coefficients is not warranted at this time. A direct application of Equations (12) and (12a) with the small angle approximation coupled with Equations (21) and (22) yield for the first two constants in each expansion

$$C_1 = \frac{\sin \theta'}{2} \frac{1}{\left[1 - \sin^2 \phi' \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) - \cos^2 \phi' \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \right]} \quad (23)$$

$$C_2 = - \frac{\cos \theta' \sin \theta'}{4} \frac{1}{\left[1 - \sin^2 \phi' \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) - \cos^2 \phi' \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \right]^2}$$

$$D_1 = \frac{\sin 2\phi' \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) - \sin 2\phi' \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right)}{2 \left[1 - \sin^2 \phi' \left(\frac{K_b}{K_c} + \frac{2K'_b}{K_c} \right) - \cos^2 \phi' \left(\frac{K_a}{K_c} + \frac{2K'_a}{K_c} \right) \right]} \quad (24)$$

$$D_2 = - \frac{C_1^3}{\sin \theta'} \left[\frac{K_a}{K_c} \cos^2 \phi' \sin 2\phi' + \frac{K_b}{K_c} \sin^2 \phi' \sin 2\phi' \right]$$

As long as only the single and double subscript terms are used in Ω , there is no need to know the value for β in terms of D_1 and D_2 . It does not enter the expansion for Ω in weak fields because the first non-zero term in the expansion which it multiplies is Ω_{221} .

To obtain the reduced magnetization, it is then necessary to evaluate

$$\bar{\Omega} = \frac{1}{\omega} \int d\omega' (\Omega_0 + \alpha\Omega_1 + \frac{\alpha^2}{2} \Omega_{11}) \quad (25)$$

This proceeds in a straightforward fashion to yield

$$\begin{aligned} \bar{\Omega} = & 0.5 + \frac{1}{3[(K_c - K_b - 2K'_b)(K_c - K_a - 2K'_a)]^{1/2}} \cdot \mu_0 J_S H \\ & - \frac{3(K_a + 2K'_a - K_b - 2K'_b)}{32 \sqrt{2} [(K_c - K_b - 2K'_b)(K_c - K_a - 2K'_a)]^{3/2}} \cdot \mu_0^2 J_S^2 H^2 \end{aligned} \quad (26)$$

The evaluation of \bar{E}_k can be obtained by the appropriate integration of f with the values for the expansion given by Equations (20) - (24). This will not be done at this time.

Strong Fields

For strong fields higher-order terms in Ω must be used because of the relative size of ζ , but the number of terms needed in the expansion for f can be reduced. The selection of θ_1 and ϕ_1 is such that they can be replaced by θ' and ϕ' . This means that

$$\begin{aligned} \alpha &= \theta - \theta_1 = \theta - \theta' \\ \beta &= \phi - \phi_1 = \phi - \phi' \end{aligned} \quad (27)$$

It is then found that

$$\begin{aligned} \Omega_0 &= -\Omega_{11} = 1 \\ \Omega_{22} &= -\sin^2 \theta' \\ \Omega_{221} &= -\cos \theta' \sin \theta' \\ \Omega_1 &= \Omega_2 = \Omega_{12} = \Omega_{111} = \Omega_{222} = \Omega_{112} = 0 \end{aligned} \quad (28)$$

The f 's do not simplify as they did for the weak field case and it is to be understood that the constant terms in the Taylor series for f are evaluated at the θ' and ϕ' point on the unit sphere. Equations (12) and (12a) then yield the following two equations, respectively.

$$f_1 + \alpha f_{11} + \beta f_{12} = -\zeta \left(\alpha + \frac{\beta^2}{2} \cos \theta' \sin \theta' \right) \quad (29)$$

and

$$f_2 + \alpha f_{12} + \beta f_{22} = -\zeta \left(\beta \sin^2 \theta' + \alpha \beta \cos \theta' \sin \theta' \right) \quad (29a)$$

Again α and β can be expanded as before keeping in mind the fact that α and β must go to zero with ζ going to infinity.

$$\alpha = \frac{A_1}{\zeta} + \frac{A_2}{\zeta} + \dots \quad (30)$$

$$\beta = \frac{B_1}{\zeta} + \frac{B_2}{\zeta} + \dots \quad (31)$$

Using the first two terms in the expansion for α and β , it is found that

$$A_1 = \frac{f_1}{\Omega_{11}} \quad (32)$$

$$A_2 = \frac{1}{\Omega_{11}} \left(\frac{f_{11}f_1}{\Omega_{11}} + \frac{f_{12}f_2}{\Omega_{22}} - \frac{1}{2} \Omega_{122} \frac{f_2^2}{\Omega_{22}^2} \right)$$

$$B_1 = \frac{f_2}{\Omega_{22}} \quad (33)$$

$$B_2 = \frac{1}{\Omega_{22}} \left(\frac{f_{21}f_1}{\Omega_{11}} + \frac{f_{22}f_2}{\Omega_{22}} - \Omega_{122} \frac{f_1f_2}{\Omega_{11}\Omega_{22}} \right)$$

These constants then give:

$$\begin{aligned}
 \bar{\Omega} = & \frac{1}{\omega} \int d\omega' \left\{ 1 + \frac{1}{2} \frac{1}{\Omega_{11}} \left[f_1 + \frac{1}{\zeta} \left(\frac{f_{11}f_1}{\Omega_{11}} + \frac{f_{12}f_1}{\Omega_{22}} - \frac{\Omega_{122}}{2} \frac{f_2^2}{\Omega_{22}^2} \right) \right]^2 \frac{1}{\zeta^2} \right. \\
 & + \frac{1}{2\Omega_{22}} \left[f_2 + \frac{1}{\zeta} \left(\frac{f_{21}f_1}{\Omega_{11}} + \frac{f_{22}f_2}{\Omega_{22}} - \Omega_{122} \frac{f_1f_2}{\Omega_{11}\Omega_{22}} \right) \right]^2 \frac{1}{\zeta^2} \\
 & \left. + \frac{\Omega_{221}}{2} \left(\frac{A_1}{\zeta} + \frac{A_2}{\zeta^2} \right) \left(\frac{B_1}{\zeta} + \frac{B_2}{\zeta^2} \right)^2 \right\} \quad (34)
 \end{aligned}$$

If we restrict the number of terms to those in $\frac{1}{\zeta^2}$ and $\frac{1}{\zeta^3}$, it is found that $\bar{\Omega}$ can be represented simply as

$$\begin{aligned}
 \bar{\Omega} = & \frac{1}{\omega} \int d\omega' \left[1 - \frac{1}{2\zeta^2} \left(f_1^2 + \frac{f_2^2}{\sin^2\theta'} \right) + \frac{1}{\zeta^3} \left(f_{11}f_1^2 + \frac{2}{\sin^2\theta'} f_{12}f_1f_2 \right. \right. \\
 & \left. \left. + \frac{1}{\sin^4\theta'} f_{22}f_2^2 - \frac{\cos\theta'}{\sin^3\theta'} f_1f_2^2 \right) \right] \quad (35)
 \end{aligned}$$

The region of integration is such that ω is $\frac{\pi}{2}$ and θ' and ϕ' both range from 0 to $\frac{\pi}{2}$. The integration yields

$$\begin{aligned}
 \bar{\Omega} = & 1 - \frac{1}{630} \frac{1}{K_3^2} \frac{1}{\zeta^2} \left\{ K_c \cdot 168 \left[(K_c - K_a - K_b) + 384 \left(K_c' - \frac{1}{2} (K_a' + K_b') \right) \right] \right. \\
 & + 256 K_c' \left[K_c' - \frac{3}{4} (K_b' + K_a') \right] + K_a \left[168 (K_a - K_c - K_b) + 384 \left(K_a' - \frac{1}{2} (K_c' + K_b') \right) \right] \\
 & + 256 K_a' \left[K_a' - \frac{3}{4} (K_c' + K_b') \right] + K_b \left[168 (K_b - K_c - K_a) + 384 \left(K_b' - \frac{1}{2} (K_c' + K_a') \right) \right] \\
 & \left. + 256 K_b' \left[K_b' - \frac{3}{4} (K_c' + K_a') \right] \right\} + \frac{1}{105K_c^3\zeta^3} \left[-16 (K_c^3 + K_b^3 + K_a^3) \right. \\
 & \left. + 24 (K_a K_b^2 + K_a^2 K_b + K_a K_c^2 + K_a^2 K_c + K_b K_c^2 + K_b^2 K_c) - 96 K_c K_a K_b \right] \quad (36)
 \end{aligned}$$

Recall that

$$\zeta = \frac{\mu_0 J_S H}{K_S} \quad (13)$$

NUMERICAL EVALUATION

The amount of data available on the orthorhombic phase of magnetite is rather limited. Williams⁽⁵⁾ does have anisotropy constants for this phase at a temperature of -196°C. Using his data, which is tabulated below, it is found that weak and strong field magnetizations for polycrystalline magnetite are given by Equations (37) and (38).

$$\begin{aligned}
 K_c &= 370 \times 10^2 \text{ joules/m}^3 & K'_c &= 620 \times 10^2 \text{ joules/m}^3 \\
 K_a &= 890 \times 10^2 \text{ joules/m}^3 & K'_a &= -400 \times 10^2 \text{ joules/m}^3 \\
 K_b &= -620 \times 10^2 \text{ joules/m}^3 & K'_b &= 120 \times 10^2 \text{ joules/m}^3 \\
 J_s &= 502 \times 10^3 \text{ amp/m}^3
 \end{aligned}$$

Weak field:

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = (0.5 + 4.58 \times 10^{-6} H - 1.28 \times 10^{-11} H^2 + \dots) \quad (37)$$

Strong field:

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = (1 - 1.33 \times 10^{-10} \frac{1}{H^2} + 7.26 \times 10^{14} \frac{1}{H^3} + \dots) \quad (38)$$

Equations (37) and (38) are plotted in Figure 1 with the dashed portion indicating the region not covered satisfactorily by the equations. Figure 2 is the corresponding plot for cubic magnetite based on Equations (A-14) and (A-15).

COMPARISON WITH EXPERIMENT

At this time there are no magnetization curves available for either orthorhombic or cubic, polycrystalline magnetite in the low-temperature range of interest. Normally the ordering transition is

observed by cooling the sample through the transition without a magnetic field applied and then the magnetization is measured as the temperature rises at a field which will not saturate the orthorhombic sample but will saturate the cubic sample⁽¹⁾. A magnetic field intensity of 160×10^3 amperes per meter would be such a field. It is also observed that the saturation magnetization just above and below the ordering temperature is the same. The ordering transition does not change the saturation magnetization. In fields large enough to saturate both phases, it is observed that the magnetization shows no transition. Using this fact, comparison can be made between the predicted magnetization curve at -196°C and the change in magnetization through the transition. This is shown in Figure 3. The Weiss and Forrer⁽⁸⁾ curve and the other points above it (data obtained by this researcher on synthetic magnetite and natural magnetite) are affected by lack of purity. The two points on either side of the predicted curve were obtained from measurements on a very pure sample of magnetite⁽⁹⁾. The upper most curve demonstrates what happens when the sample is cooled through a magnetic field and allowed to warm up in the same field. This curve was also run on the very pure sample mentioned above. A subsequent paper will report the findings on the lithium doped, oxidized, and natural magnetite. An apparent double transition with these samples cannot be explained within the scope of this paper.

SUMMARY

A characterization of the magnetization process for orthorhombic and cubic magnetic materials is developed that assumes:

- (1) That the free energy for the system is composed primarily of magnetostatic and crystalline anisotropy energy.
- (2) That the magnetization process proceeds entirely by domain rotation.
- (3) That the crystalline anisotropy energy can be expressed by a series expansion in the direction cosines of the magnetization vector.
- (4) That the magnetization and crystalline anisotropy energy are mathematically well behaved above and below the low-temperature ordering transition.

Applying these assumptions and expressing the reduced magnetization (Ω) and normalized crystalline anisotropy energy (f) in Taylor series of functions of two variables (α and β), the following are obtained:

- (1) A minimization of the total free energy without restricting the magnetization vector to lie in a plane formed by an easy direction and the applied magnetic field.
- (2) Magnetization equations in terms of anisotropy constants and applied magnetic field (weak and strong fields) for mono- and polycrystalline, orthorhombic and cubic material when the easy axis is in the $\langle 001 \rangle$ or c direction.
- (3) An evaluation of the magnetization equation for polycrystalline magnetite at -196°C and -153°C . At these temperatures the easy axis for magnetite is in the proper direction to make the analysis applicable, and the

necessary anisotropy constants are available. These equations are plotted in Figures 1 and 2.

- (4) A comparison of $\bar{\Omega}$ in fields which will saturate cubic magnetite but not orthorhombic magnetite is made between the predicted values and experimental values and good correspondence is observed. This is shown in Figure 3.

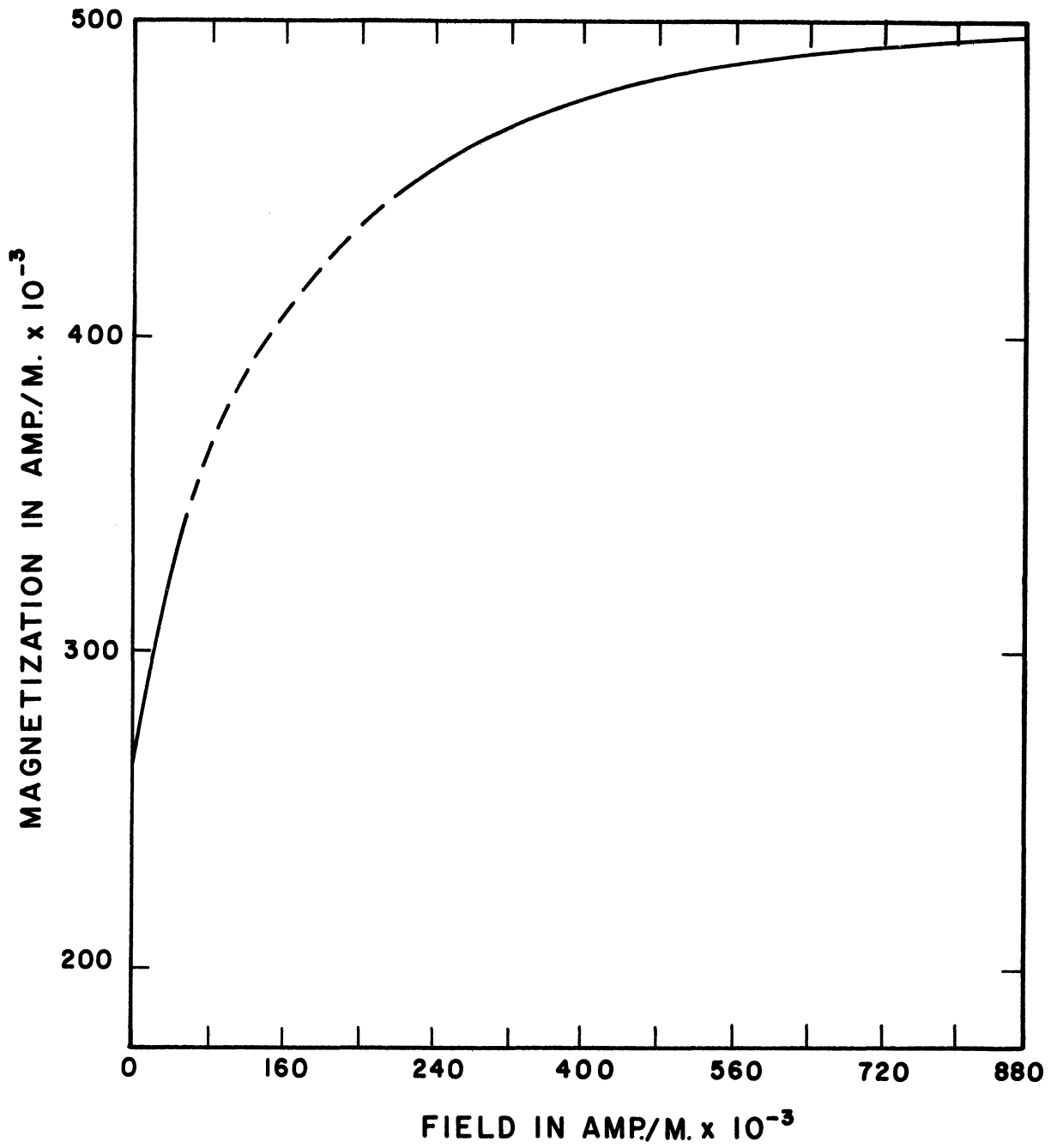


Fig.1. Polycrystal magnetization curve for magnetite at -196°C based on the data of Williams for single crystal.

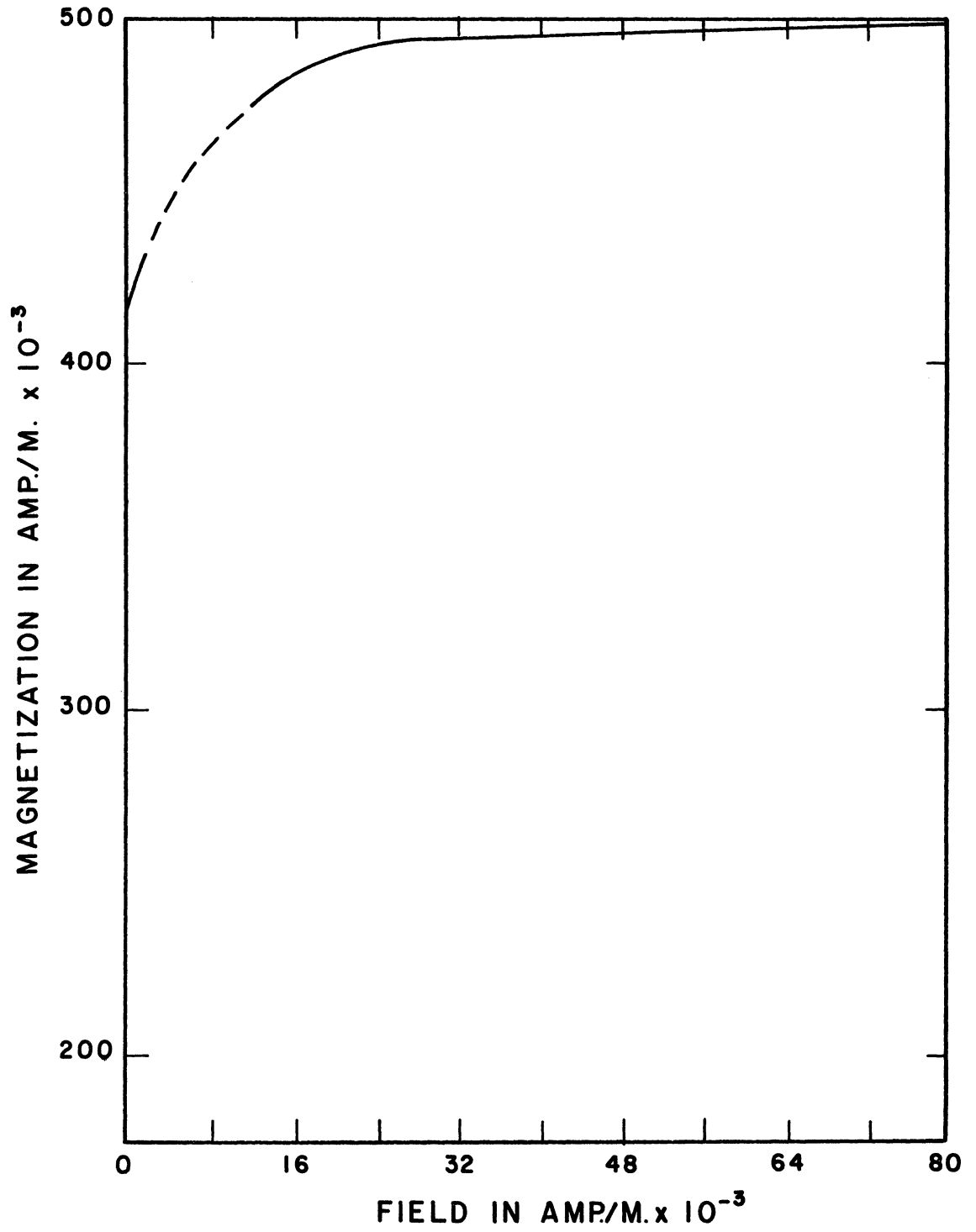


Fig.2. Polycrystal magnetization curve for magnetite at -153°C based on data of Bickford for single crystal.

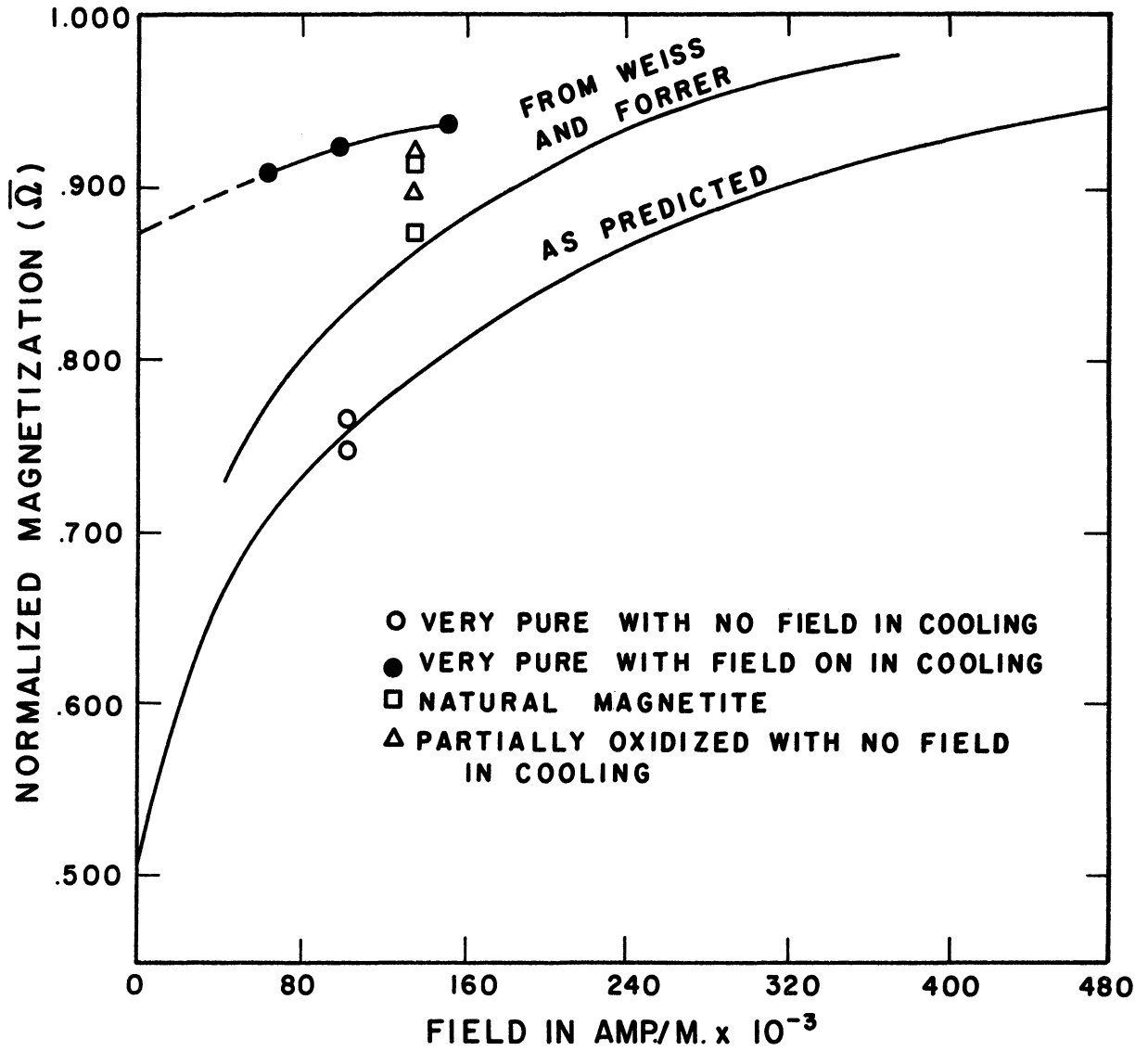


Fig.3. Normalized magnetization for polycrystalline magnetite at -196°C versus magnetic field intensity with an indication of results from experiment. The experimental results give the $\bar{\Omega}$'s just below the transition temperature.

APPENDIX

For the cubic structure with the easy directions the cube edges, one can limit the averaging process to the portion of the unit sphere defined by the surface area in one-sixth the octant formed by the arcs extending between $\langle 001 \rangle$ to $\langle 101 \rangle$ and $\langle 111 \rangle$ and the arc from $\langle 101 \rangle$ to $\langle 111 \rangle$. In this case the easy direction is $\langle 001 \rangle$.

The crystalline anisotropy energy can be written in terms of the direction cosines of J as follows:

$$E_k = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) \quad (\text{A-1})$$

In terms of the spherical coordinates this reduces to

$$\begin{aligned} E_k &= K_1 (\sin^4 \theta \sin^2 \phi \cos^2 \phi + \sin^2 \theta \cos^2 \theta) \\ &+ K_2 (\sin^4 \theta \sin^2 \phi \cos^2 \phi \cos^2 \theta) \end{aligned} \quad (\text{A-2})$$

This then gives

$$\begin{aligned} \bar{E}_k &= \frac{K_1}{\omega} \int (\sin^4 \theta \sin^2 \phi \cos^2 \phi + \sin^2 \theta \cos^2 \theta) d\omega' \\ &+ \frac{K_2}{\omega} \int (\sin^4 \theta \sin^2 \phi \cos^2 \phi \cos^2 \theta) d\omega' \end{aligned} \quad (\text{A-3})$$

where ω corresponds to the solid angle defined by the arcs indicated above. To simplify the notation somewhat, let

$$\bar{E}_k = \frac{K_1}{\omega} \int f d\omega' \quad (\text{A-4})$$

where f is the normalized crystalline anisotropy energy.

The normalized or reduced magnetization is, as given earlier,

$$\bar{\Omega} = \frac{1}{\omega} \int \Omega \, d\omega' \quad (5)$$

In spherical coordinates this becomes

$$\bar{\Omega} = \frac{1}{\omega} \int \left[\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi') \right] d\omega' \quad (A-5)$$

The equilibrium conditions require that

$$\bar{E}_k - \mu_0 H J_S \bar{\Omega} = \text{minimum} \quad (11)$$

or in terms of Equations (A-4) and (A-5)

$$\int f d\omega' - \frac{\mu_0 H J_S}{K_1} \int \Omega \, d\omega' = \text{minimum} \quad (A-6)$$

The determination of the dependence of θ and ϕ on θ' and ϕ' proceeds as with the orthorhombic case. The analysis will be with respect to weak and strong field conditions where "weak" and "strong" are as defined earlier.

Weak Field

Equations (18) and (19) again apply but the values for f are much more simplified.

$$\begin{aligned} f_{11} &= 2 \\ f_0 = f_1 = f_2 = f_{22} = f_{12} = f_{111} = f_{222} = f_{112} = f_{221} &= 0 \end{aligned} \quad (A-7)$$

It is again assumed that α and β can be represented by the polynomials given in Equations (21) and (22). The first two constants in

these expansions are evaluated and are found to be

$$\begin{aligned} C_1 &= \frac{\sin\theta'}{2} \\ C_2 &= - \frac{\sin\theta' \cos\theta'}{4} \end{aligned} \tag{A-8}$$

and

$$\begin{aligned} D_1 &= 0 \\ D_2 &= - \frac{\sin^2\theta' \sin 4\phi'}{16} \end{aligned} \tag{A-9}$$

Thus for weak fields

$$\Omega = \cos\theta' + \frac{\sin^2\theta'}{2} \zeta - \frac{3}{8} \sin^2\theta' \cos\theta' \zeta^2 \tag{A-10}$$

Notice that the terms in β do not enter into the calculation if terms in ζ^3 and above are neglected.

To obtain the average reduced magnetization for the polycrystal without any magnetic history, we again assume a statistical weighing factor of unity and note that ϕ' varies from 0 to 45° and θ' from 0 to $\cos^{-1} \frac{1}{\sqrt{3}}$ and

$$\omega = \frac{\pi}{12}$$

Gans⁽⁶⁾ performs the integration using an iterated integral of the following form:

$$\bar{\Omega} = \frac{12}{\pi} \int_0^{45^\circ} d\phi' \int_0^{\cos\theta_0} \Omega \sin\theta' d\theta' \tag{A-11}$$

where

$$\cos\theta_0 = \frac{\cos\phi'}{(1 + \cos^2\phi')^{1/2}}$$

The integration then yields the average magnetization normalized to the saturation magnetization given by Equation (A-12).

$$\bar{\Omega} = 0.8312 + 0.1496 \zeta - 0.08705 \zeta^2 + \dots \quad (\text{A-12})$$

where

$$\zeta = \frac{\mu_0 J_s H}{K_1}$$

Strong Field

For strong fields Equations (27) through (35) are used and Gans⁽⁶⁾ shows that the normalized average magnetization equation can be integrated as above to give

$$\bar{\Omega} = 1 - \left[\frac{8}{105} + \frac{16}{1155} \frac{K_2}{K_1} + \frac{8}{5005} \left(\frac{K_2}{K_1} \right)^2 \right] \frac{1}{\zeta^2} - 0.05201 \frac{1}{\zeta^3} + \dots \quad (\text{A-13})$$

Numerical Evaluation

Because the behavior of magnetite in the order-disorder temperature range was of prime interest, it was desired to evaluate both Equations (A-12) and (A-13) just above the ordering temperature. The best available values for anisotropy constants in this region are those of Bickford⁽¹⁰⁾. They are listed below and give the magnetization equations for polycrystalline magnetite in either weak or strong fields at -153°C.

$$K_1 = 42 \times 10^2 \text{ joules/m}^3$$

$$K_2 \approx 20 \times 10^2 \text{ joules/m}^3$$

$$J_s = 498 \times 10^3 \text{ amp/m}^3$$

Weak field:

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = (0.8312 + 22.3 \times 10^{-6} H - 5.70 \times 10^{-10} H^2 + \dots) \quad (\text{A-14})$$

Strong field:

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = \left(1 - \frac{6.42 \times 10^6}{H^2} - \frac{1.57 \times 10^7}{10^3} + \dots\right) \quad (\text{A-15})$$

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Footnotes

1. There have been numerous investigations into the order-disorder transition for magnetite and references are too numerous to detail. For an excellent listing of references and experimental results see, C. A. Domenicali, Phys. Rev., 78, 458 (1950).
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