

electronic Gd^{+++} ion in gadolinium iron garnet.⁶ The anisotropy field seems to decrease to a very low value by about 40°K.

In the temperature interval from 160 to 300°K $g=2.00\pm 0.01$. We believe the displacement from 2.00 below that has to do with magnetostatic modes or with a size effect.

⁶ G. P. Rodrigue, H. Meyer, and R. V. Jones, *J. Appl. Phys.* **31**, 3765 (1960).

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Expansions for Magnetization Characterization for Polycrystalline Orthorhombic and Cubic Magnetite at Low Temperatures

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Taylor series expansions are obtained for the reduced magnetization and crystalline anisotropy energy which do not require that the magnetization vector lie in a plane formed by the easy axis and the applied field. The free energy which is assumed to be composed of magnetostatic and crystalline anisotropy energy is minimized with respect to the spherical coordinates of the magnetization vector. The expansions for the magnetization in terms of the crystalline anisotropy constants are used to find the mean magnetization at different magnetic field intensities for polycrystalline magnetite, which undergoes an order-disorder transition at -155°C . Experimental results for the magnetization of polycrystalline magnetite are compared with those predicted by the expansions and good agreement is observed.

INTRODUCTION

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 change in magnetization as a result of the transition for natural and synthetic magnetite with varying degrees of doping and oxidation and found rather surprising results which will be reported 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 weighting 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.

Three assumptions are usually made^{3,4}: that the free energy is predominantly magnetostatic and magnetoelastic; that it can be expanded as a series in the direction cosines and strains, consistent with the symmetry of the system; and that the magnetization vector remains in the plane of the applied field and of a direction of easy magnetization.

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 assumptions 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 direction cosines. The minimization of the total energy will also be carried out in spherical coordinates. A Taylor series with two variables is obtained both for the magnetization and the crystalline anisotropy energy. The mks system of units will be used.

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).

² D. C. Ray, doctoral dissertation, The University of Michigan, 1962 (unpublished).

³ R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951).

⁴ E. W. Lee, *Proc. Phys. Soc. (London)* **72**, 249 (1958).

⁵ H. J. Williams, R. M. Bozorth, and M. Goertz, *Phys. Rev.* **91**, 1107 (1953).

DEVELOPMENT

The first two assumptions will be used in the analysis for both the orthorhombic and cubic phase for magnetite.

It will also be assumed that the magnetization and crystalline anisotropy energies are expressible in Taylor series with the independent variables, the spherical coordinates of J or H .

The results for the cubic configuration can be found elsewhere in the literature⁶ and are included in the Appendix.

The first assumption says that the free energy can be expressed by the following equation:

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

where E_0 = isotropic energy term; E_k = energy needed to turn the magnetization from an easy direction to a direction dictated by H ; $\mu_0 \mathbf{H} \cdot \mathbf{J}$ = 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 sr and are noted in Eq. (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 Eq. (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

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

where $F(\omega')$, the weighting 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.

⁶ R. Gans, Ann. Physik 15, 28 (1932).

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.

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. Since the direction sines are not independent, neither are the K 's. For the orthorhombic phase in magnetite, the c axis is the easy axis while a and b are axes of increasing difficulty for magnetization.

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

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

To simplify the notation somewhat, let

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

The integration for the case of the orthorhombic phase is carried out over one octant so that the ω appearing in the above equation is $\pi/2$. To integrate f it is best to change the direction sines into sines of the spherical coordinate angles. Upon doing this, f can be written as

$$\begin{aligned} f &= \left(\frac{K_b}{K_c} + \frac{K_a}{K_c} + \frac{K_b'}{K_c} + \frac{K_a'}{K_c} \right) + \sin^2\theta + \frac{K_c'}{K_c} \sin^4\theta \\ &+ \frac{K_a'}{K_c} (\sin^4\theta \cos^4\phi) - \left(\frac{K_a}{K_c} + \frac{2K_a'}{K_c} \right) \sin^2\theta \cos^2\phi \\ &+ \frac{K_b'}{K_c} (\sin^4\theta \sin^4\phi) - \left(\frac{K_b}{K_c} + \frac{2K_b'}{K_c} \right) \sin^2\theta \sin^2\phi. \end{aligned} \quad (9)$$

It should be evident from Eqs. (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 require that

$$\int f d\omega' - \frac{\mu_0 H J_s}{K_c} \int \Omega d\omega' = \text{minimum}. \quad (10)$$

Akulov's⁷ assumption that the minimal conditions on the integrands will suffice, will be used. With this approach, one obtains

$$f_{\theta} - \zeta \Omega_{\theta} = 0, \quad (11)$$

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

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

$$\zeta = \mu_0 J_s H / K_c. \quad (13)$$

f and Ω are expanded in two Taylor series 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 about θ_1, ϕ_1 . θ_1, ϕ_1 is a point on the unit sphere about which we want the expansion to hold. For weak 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 , f and Ω can be represented as

$$f = f_0 + \alpha f_1 + \beta f_2 + \frac{1}{2}(\alpha^2 f_{11} + 2\alpha\beta f_{12} + \beta^2 f_{22}) + \frac{1}{6}(\alpha^3 f_{111} + 3\alpha^2\beta f_{112} + 3\alpha\beta^2 f_{122} + \beta^3 f_{222}), \quad (14)$$

$$\Omega = \Omega_0 + \alpha\Omega_1 + \beta\Omega_2 + \frac{1}{2}(\alpha^2\Omega_{11} + 2\alpha\beta\Omega_{12} + \beta^2\Omega_{22}) + \frac{1}{6}(\alpha^3\Omega_{111} + 3\alpha^2\beta\Omega_{112} + 3\alpha\beta^2\Omega_{122} + \beta^3\Omega_{222}), \quad (15)$$

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 Eqs. (11) and (12) yields Eqs. (16) and (17), respectively.

$$f_1 + \alpha f_{11} + \beta f_{12} + \frac{1}{2}(\alpha^2 f_{111} + 2\alpha\beta f_{112} + \beta^2 f_{122}) = \zeta [\Omega_1 + \alpha\Omega_{11} + \beta\Omega_{12} + \frac{1}{2}(\alpha^2\Omega_{111} + 2\alpha\beta\Omega_{112} + \beta^2\Omega_{122})], \quad (16)$$

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

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

$$\begin{aligned} \Omega_0 &= -\Omega_{11} = \cos^2\theta', \\ \Omega_1 &= -\Omega_{111} = -\Omega_{221} = \sin^2\theta', \\ \Omega_2 &= \Omega_{22} = \Omega_{12} = \Omega_{222} = \Omega_{112} = 0, \end{aligned} \quad (19)$$

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. A direct application of Eqs. (11) and (12) with the small-angle approximation coupled with Eqs. (21) and (22) yield for the first two constants in each expansion

$$C_1 = \frac{1}{2}(\sin\theta') [1 - \sin^2\phi' ((K_b/K_c) + (2K_b'/K_c)) - \cos^2\phi' ((K_a/K_c) + (2K_a'/K_c))]^{-1}, \quad (23)$$

$$C_2 = -\frac{1}{4}(\cos\theta' \sin\theta') [1 - \sin^2\phi' ((K_b/K_c) + (2K_b'/K_c)) - \cos^2\phi' ((K_a/K_c) + (2K_a'/K_c))]^{-2},$$

$$D_1 = \frac{\sin 2\phi' ((K_b/K_c) + (2K_b'/K_c)) - \sin 2\phi' ((K_a/K_c) + (2K_a'/K_c))}{2[1 - \sin^2\phi' ((K_b/K_c) + (2K_b'/K_c)) - \cos^2\phi' ((K_a/K_c) + (2K_a'/K_c))]}, \quad (24)$$

$$D_2 = -(C_1^3/\sin\theta') [(K_a/K_c) \cos^2\phi' \sin 2\phi' + (K_b/K_c) \sin^2\phi' \sin 2\phi'],$$

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

⁷ N. Akulov, Z. Physik **69**, 882 (1931).

terms of D_1 and D_2 . It does not enter the expansion for Ω in weak fields because the first nonzero term in the expansion which it multiplies is Ω_{221} .

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

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

This proceeds in a straightforward fashion to yield

$$\bar{\Omega} = 0.5 + \{3[(K_c - K_b - 2K_b')(K_c - K_a - 2K_a')]^{1/2}\}^{-1} \mu_0 J_s H \frac{3(K_a + 2K_a' - K_b - 2K_b')}{32\sqrt{2}[(K_c - K_b - 2K_b')(K_c - K_a - 2K_a')]^{3/2}} \mu_0^2 J_s^2 H^2. \tag{26}$$

The evaluation of \bar{E}_k can be obtained by the appropriate integration of f with the values for the expansion given by Eqs. (20)–(24).

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

$$\begin{aligned} \alpha &= \theta - \theta_1 = \theta - \theta', \\ \beta &= \phi - \phi_1 = \phi - \phi'. \end{aligned} \tag{27}$$

It is then found that

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

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 (11) and (12) then yield the following two equations, respectively:

$$f_1 + \alpha f_{11} + \beta f_{12} = -\zeta[\alpha + (\beta^2/2) \cos\theta' \sin\theta'] \tag{29}$$

and

$$f_2 + \alpha f_{12} + \beta f_{22} = -\zeta(\beta \sin^2\theta' + \alpha \beta \cos\theta' \sin\theta'). \tag{30}$$

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.

$$\alpha = (A_1/\zeta) + (A_2/\zeta) + \dots, \tag{31}$$

$$\beta = (B_1/\zeta) + (B_2/\zeta) + \dots. \tag{32}$$

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

$$\begin{aligned} A_1 &= f_1/\Omega_{11}, \\ A_2 &= \frac{1}{\Omega_{11}} \left(\frac{f_{11}f_1}{\Omega_{11}} + \frac{f_{12}f_2}{\Omega_{22}} - \frac{1}{2}\Omega_{122} \frac{f_2^2}{\Omega_{22}^2} \right), \end{aligned} \tag{33}$$

$$\begin{aligned} B_1 &= f_2/\Omega_{22}, \\ B_2 &= \frac{1}{\Omega_{22}} \left(\frac{f_{21}f_1}{\Omega_{11}} + \frac{f_{22}f_2}{\Omega_{22}} - \Omega_{122} \frac{f_1f_2}{\Omega_{11}\Omega_{22}} \right). \end{aligned} \tag{34}$$

These constants then give

$$\begin{aligned} \bar{\Omega} &= \frac{1}{\omega} \int d\omega' \left\{ 1 + \frac{1}{2} \frac{1}{\Omega_{11}} \left[f_1 \right. \right. \\ &\quad \left. \left. + \frac{1}{\zeta} \left(\frac{f_{11}f_1}{\Omega_{11}} + \frac{f_{12}f_1}{\Omega_{22}} - \frac{\Omega_{122}}{2} \frac{f_2^2}{\Omega_{22}^2} \right) \right]^2 \frac{1}{\zeta^2} \right. \\ &\quad \left. + \frac{1}{2\Omega_{22}} \left[f_2 + \frac{1}{\zeta} \left(\frac{f_{21}f_1}{\Omega_{11}} + \frac{f_{22}f_2}{\Omega_{22}} - \Omega_{122} \frac{f_1f_2}{\Omega_{11}\Omega_{22}} \right) \right]^2 \frac{1}{\zeta^2} \right. \\ &\quad \left. + \frac{\Omega_{221}}{2} \left(\frac{A_1}{\zeta} + \frac{A_2}{\zeta^2} \right) \left(\frac{B_1}{\zeta} + \frac{B_2}{\zeta^2} \right)^2 \right\}. \end{aligned} \tag{35}$$

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

$$\begin{aligned} \bar{\Omega} &= \frac{1}{\omega} \int d\omega' \left[1 - \frac{1}{2\zeta^2} \left(f_1^2 + \frac{f_2^2}{\sin^2\theta'} \right) \right. \\ &\quad \left. + \frac{1}{\zeta^3} \left(f_{11}f_1^2 + \frac{2}{\sin^2\theta'} f_{12}f_1f_2 \right) \right. \\ &\quad \left. + \frac{1}{\sin^4\theta'} f_{22}f_2^2 - \frac{\cos\theta'}{\sin^3\theta'} f_1f_2^2 \right]. \end{aligned} \tag{36}$$

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

yields

$$\bar{\Omega} = 1 - \frac{1}{630} \frac{1}{K_c^2 \zeta^2} \{ K_c 168 [(K_c - K_a - K_b) + 384(K_c' - \frac{1}{2}(K_a' + K_b'))] \\ + 256K_c' [K_c' - \frac{3}{4}(K_b' + K_a')] + K_a [168(K_a - K_c - K_b) + 384(K_a' - \frac{1}{2}(K_c' + K_b'))] \\ + 256K_a' [K_a' - \frac{3}{4}(K_c' + K_b')] + K_b [168(K_b - K_c - K_a) + 384(K_b' - \frac{1}{2}(K_c' + K_a'))] \\ + 256K_b' [K_b' - \frac{3}{4}(K_c' + K_a')] \} + (1/105 K_c^3 \zeta^3) [-16(K_c^3 + K_b^3 + K_a^3) \\ + 24(K_a K_b^2 + K_a^2 K_b + K_a K_c^2 + K_a^2 K_c + K_b K_c^2 + K_b^2 K_c) - 96 K_c K_a K_b]. \quad (37)$$

Recall that

$$\zeta = \mu_0 J_s H / K_c. \quad (13)$$

NUMERICAL EVALUATION

The amount of data available on the orthorhombic phase of magnetite is rather limited. Williams⁵ 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 Eqs. (38) and (39).

$$K_c = 370 \times 10^2 \text{ J/m}^3 \quad K_c' = 620 \times 10^2 \text{ J/m}^3 \\ K_a = 890 \times 10^2 \text{ J/m}^3 \quad K_a' = -400 \times 10^2 \text{ J/m}^3 \\ K_b = -620 \times 10^2 \text{ J/m}^3 \quad K_b' = 120 \times 10^2 \text{ J/m}^3 \\ J_s = 502 \times 10^3 \text{ A/m}.$$

Weak field:

$$\bar{\Omega} = \bar{J} / J_s = (0.5 + 4.58 \times 10^{-6} H \\ - 1.28 \times 10^{-11} H^2 + \dots). \quad (38)$$

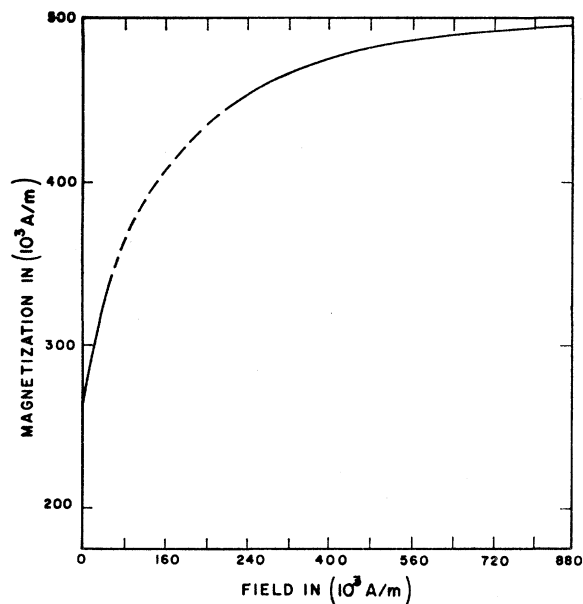


FIG. 1. Polycrystal magnetization curve for magnetite at -196°C based on the data of Williams for single crystal.

Strong field:

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = \left(1 - 1.33 \times 10^{10} \frac{1}{H^2} + 7.26 \times 10^{14} \frac{1}{H^4} + \dots \right). \quad (39)$$

Equations (38) and (39) are plotted in Fig. 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 Eqs. (A1) and (A2).

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 phase but will saturate the cubic phase.¹ A magnetic field intensity of $160 \times 10^3 \text{ A/m}$ 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 Fig. 3. The Weiss and Forrer⁸ 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 uppermost 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.

⁸ P. Weiss and R. Forrer, *Ann. Phys. (Paris)* **12**, 279 (1929).

⁹ Supplied by E. F. Westrum, Jr., Department of Chemistry, The University of Michigan.

DISCUSSION OF ERRORS AND REFINEMENTS

The preceding analysis gives approximate equations for the behavior of the polycrystalline magnetic material. A comparison of the curves obtained by using this analysis and the experimentally obtained curves revealed no major differences. This may not always be the case for at least two reasons. The analysis assumes uniform magnetic fields throughout and neglects the internal magnetic field due to the magnetization of neighboring crystallites. A correction for this effect has been obtained for the cubic¹⁰ system which indicates that the H^{-2} term in the strong field analysis should be reduced by 0.707 for $H \ll 4\pi J_s$. A correction for the H^{-3} term was not considered and no work has been reported on the orthorhombic system. A reduction in the second term might be expected for this system too. A weighting factor which would account for field interaction and history effects could also be introduced. A more elegant analysis of the approach to saturation is given by Brown¹¹ which accounts for nonuniformities inherent in polycrystalline materials. This analysis might be applied if better agreement is demanded. An extension of computer searching¹² for energy minima to orthorhombic monocrystalline magnetite was considered to fill in more of the curve. The extension of this approach to the polycrystal analysis was not deemed warranted because of the uncertainties men-

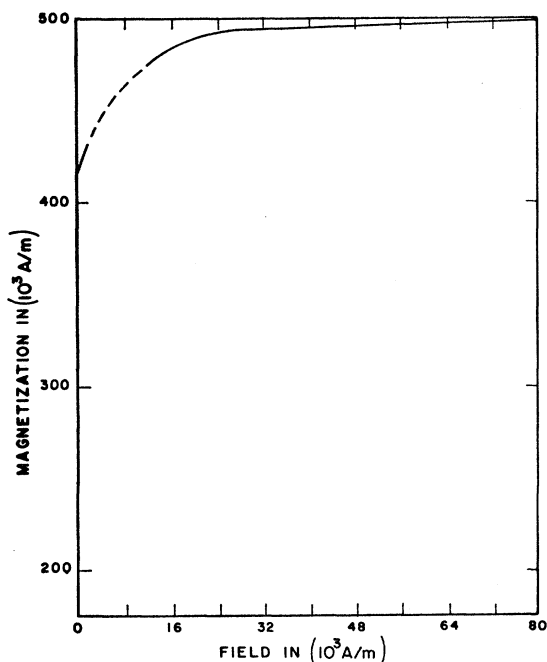


Fig. 2. Polycrystal magnetization curve for magnetite at -153°C based on data of Bickford for single crystal.

¹⁰ T. Hostein and H. Primakoff, *Phys. Rev.* **59**, 388 (1941).

¹¹ W. F. Brown, Jr., *Phys. Rev.* **58**, 736 (1940).

¹² C. E. Johnson, Jr., and W. F. Brown, Jr., *J. Appl. Phys.* **32**, 243S (1961).

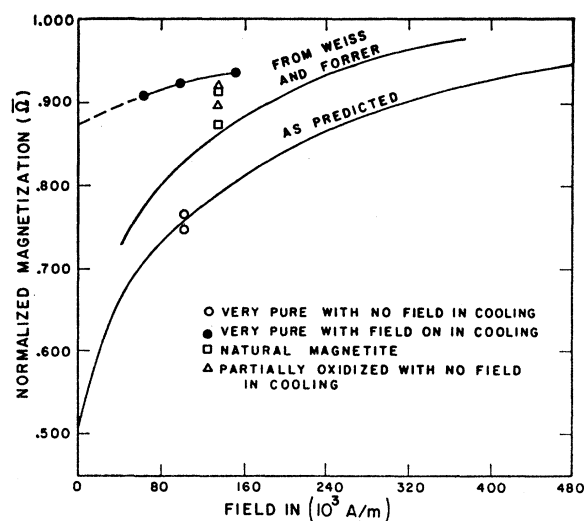


Fig. 3. Normalized magnetization for polycrystalline magnetite at -196°C versus magnetic field intensity with an indication of results from experiment. The experimental results give the Ω 's just below the transition temperature.

tioned above and the relative ease¹³ with which the approximate equations are obtained.

SUMMARY

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

(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 and -153°C . These equations are plotted in Figs. 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 Fig. 3.

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¹³ An inclusion of cross product terms in Eq. (6) and the use of better anisotropy constants with known temperature characteristics would make computer searching much more attractive. The needed anisotropy constants for the low-temperature range can be found in W. Palmer, *Phys. Rev.* **131**, 1057 (1963).

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APPENDIX

The development for the cubic system can be found in Gan's⁶ paper. The limitations to strong and weak fields are carried over.

Because the behavior of magnetite in the order-disorder temperature range was of prime interest, it was desired to evaluate both of Gan's Eqs. (35) and (37) just above the ordering temperature. The best available values for anisotropy constants in this region are those of Bickford.¹⁴ The equations and values are listed below and give the magnetization equations for polycrystalline magnetite in either weak or strong fields

¹⁴L. R. Bickford, Jr., J. M. Brownlow, and R. F. Penoyer, Proc. Inst. Elec. Engrs. (London) **104**, 238 (1956).

at -153°C .

$$\begin{aligned} K_1 &= 42 \times 10^2 \text{ J/m}^3, \\ K_2 &= 20 \times 10^2 \text{ J/m}^3, \\ J_s &= 498 \times 10^3 \text{ A/m}. \end{aligned}$$

Weak fields:

$$\bar{\Omega} = 0.8312 + 0.1496\zeta - 0.08705\zeta^2 + \dots, \quad [\text{Gan's (35)}]$$

where

$$\begin{aligned} \zeta &= \mu_0 J_s H / K_1, \\ \bar{\Omega} &= \bar{J} / J_s = (0.8312 + 22.3 \times 10^{-6} H \\ &\quad - 5.70 \times 10^{-10} H^2 + \dots). \end{aligned} \quad (\text{A1})$$

Strong fields:

$$\begin{aligned} \bar{\Omega} &= 1 - \left[\frac{8}{105} + \frac{16}{1155} \frac{K_2}{K_1} + \frac{8}{5005} \left(\frac{K_2}{K_1} \right)^2 \right] \frac{1}{\zeta^2} \\ &\quad - 0.05201 \frac{1}{\zeta^3} + \dots, \quad [\text{Gan's (37)}] \end{aligned}$$

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = \left(1 - \frac{6.42 \times 10^6}{H^2} - \frac{1.57 \times 10^7}{H^3} + \dots \right). \quad (\text{A2})$$

Heat Capacity of Palladium and Dilute Palladium: Iron Alloys from 1.4 to 100°K

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Heat-capacity measurements have been made on pure palladium and a series of dilute palladium-iron alloys over the temperature range 1.4 to 100°K. All alloys exhibit a ferromagnetic specific heat anomaly, the entropy of which is proportional to iron concentration. This entropy corresponds to a mean spin of 1.1 ± 0.3 per iron atom. The disagreement between the latter figure and the value obtained from the saturation moment of more concentrated alloys is discussed. For the most concentrated alloy a $T^{3/2}$ spin-wave term is observed, the magnitude of which is in approximate agreement with theory. The Debye θ for pure palladium appears to have an anomalous temperature dependence.

I. INTRODUCTION

THE saturation moment of dilute palladium-iron alloys was first measured by Crangle,¹ who found ferromagnetic behavior in all cases, with an abnormally large mean moment per iron atom. This result was interpreted as being due to the polarization of those palladium atoms adjacent to each solute atom. If it is assumed that the exchange interaction polarizes each of these palladium atoms to the extent of 0.6 holes, the number presumed to exist in the $4d$ band of pure palladium, it may be shown that approximate agree-

ment with experiment is obtained. As shown by Clogston *et al.*,² however, such an assumption cannot easily be reconciled with the observed moments on Pd-Rh dilute iron alloys. Instead, they propose a model, based on the work of Anderson³ and Wolf,⁴ which gives a total spin depending on the *density of states* at the Fermi level, rather than the number of unfilled states in the d band. Such a model satisfactorily explains the observed correlation of local moment with susceptibility.

The existence of an abnormal spin moment, associated with these alloys on either model, should be readily observable in terms of the spin-dependent entropy of

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¹J. Crangle, Phil. Mag. **5**, 335 (1960).

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³P. W. Anderson, Phys. Rev. **124**, 41 (1961).

⁴P. A. Wolff, Phys. Rev. **124**, 1030 (1961).