

magnetization is

$$d\mathbf{M}/dt = \gamma[\mathbf{M} \times \mathbf{H}] - (\lambda/M^2)[\mathbf{M} \times (\mathbf{M} \times \mathbf{H})]. \quad (\text{A8})$$

From this we calculate

$$dw/dt = \mathbf{H} \cdot d\mathbf{M}/dt = (\lambda/M^2)(\mathbf{M} \times \mathbf{H})^2, \\ \left\langle \frac{dw}{dt} \right\rangle_{\text{av}} = \frac{\lambda H^2}{2M^2}(M_{x0}^2 + M_{y0}^2). \quad (\text{A9})$$

H here is the total effective magnetic field as given by Eq. (1) in the text. If we use this relation, and set $\langle dw/dt \rangle_{\text{av}} = \langle dg/dt \rangle_{\text{av}}$, we find from Eqs. (A8) and (A9),

$$\lambda = \left[\left(\frac{\partial g_{100}}{\partial \theta_x^2} \right)_{\theta_x=0} + \frac{M_{y0}^2}{M_{x0}^2} \left(\frac{\partial g_{100}}{\partial \theta_y^2} \right)_{\theta_y=0} \right] \\ \times \frac{\gamma^2 \tau}{1 + (\omega\tau)^2} \frac{1}{1 + (M_{y0}^2/M_{x0}^2)}. \quad (\text{A10})$$

In our experiments most of the torque on the magnetization is due to the steady applied field, and is therefore circularly symmetrical about the z axis. Even the torque due to crystal anisotropy is circularly symmetrical in the $[100]$ and $[111]$ directions. We therefore assume that $M_{y0}^2 \cong M_{x0}^2$, and Eq. (A10) becomes

$$\lambda = \frac{1}{2} \left[\left(\frac{\partial^2 g_{100}}{\partial \theta_x^2} \right)_{\theta_x=0} + \left(\frac{\partial^2 g_{100}}{\partial \theta_y^2} \right)_{\theta_y=0} \right] \frac{\gamma^2 \tau}{1 + (\omega\tau)^2}. \quad (\text{A11})$$

Now by Eq. (9) in the text, we see that the width of the line at half-power points is $(2\Delta H)$:

$$2\Delta H = \frac{1}{M_z} \left[\left(\frac{\partial^2 g_{100}}{\partial \theta_x^2} \right)_{\theta_x=0} + \left(\frac{\partial^2 g_{100}}{\partial \theta_y^2} \right)_{\theta_y=0} \right] \frac{\omega\tau}{1 + (\omega\tau)^2}. \quad (\text{A12})$$

Magnetostriction and Permeability of Magnetite and Cobalt-Substituted Magnetite*

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The principal magnetostriction constants of magnetite were determined over the temperature range from 120°K to 300°K by the strain gauge technique. Since λ_{111} and λ_{100} are different in sign and practically constant over this entire range ($\lambda_{111} \approx +80 \times 10^{-6}$; $\lambda_{100} \approx -20 \times 10^{-6}$) the change in direction of easy magnetization which occurs at 130°K is manifested by a change in structure of λ vs H curves in a polycrystalline sample. The substitution of small amounts of cobalt for divalent iron in polycrystalline magnetite causes a marked shift upwards in the temperature of the maximum in initial permeability, which in the case of magnetite occurs at 130°K. The temperature shift is practically linear with respect to cobalt ferrite content, the rate being *ca* 140°C/mole percent. Magnetostriction vs magnetic field curves for these specimens indicate that the shifted permeability peak is still associated with a change in direction of easy magnetization. The predicted anisotropy of cobalt ferrite, obtained by extrapolation of these results, is in reasonable agreement with the values measured directly by other investigators.

I. INTRODUCTION

THIS paper concerns the magnetostriction and magnetocrystalline anisotropy of magnetite over a temperature range in which its symmetry is cubic (above 120°K). The anisotropy is a rapidly varying function of temperature in the vicinity of 130°K, at which temperature the direction of easy magnetization changes from $[111]$ to $[100]$.¹ The temperature spectrum of initial permeability in this region, shown

in Fig. 1, can be correlated directly with the absolute magnitude of the first-order anisotropy constant K_1 by the empirical relationship

$$\mu_0 - 1 = 39.1 M_s^2 / (|K_1| + 1.21 \times 10^4), \quad (1)$$

in which μ_0 is the absolute magnitude of the initial permeability, and M_s is the saturation magnetization (obtained from Pauthenet's data²). The constant term in the denominator is presumably associated with magnetostrictive strain energy.

Evidence that the magnetostriction varies widely in magnitude and even changes sign at low temperature has been reported.^{3,4} In order to check this temperature dependence directly, we have measured the principal

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

² R. Pauthenet, Ann. Physik **7**, 710 (1952).

³ C. A. Domenicali, Phys. Rev. **78**, 458 (1950).

⁴ J. L. Stull and L. R. Bickford, Jr., Phys. Rev. **92**, 845 (1953).

TABLE I. Saturation magnetostriction of magnetite single crystals at room temperature.

| Type of crystal | Longitudinal Magnetostriction ($\times 10^6$) | | | Constants of 5-constant equation ($\times 10^6$) | | | | |
|----------------------------------|---|-----------------|-----------------|--|-------|-------|-------|-------|
| | λ_{100} | λ_{110} | λ_{111} | h_1 | h_2 | h_3 | h_4 | h_5 |
| Natural | -16.7 | 65.4 | 90.6 | -15.3 | 142.4 | -9.43 | -9.70 | -50.5 |
| Synthetic | -19.5 | 57.1 | 77.6 | -24.5 | 123.3 | -0.40 | -4.76 | -20.1 |
| Synthetic (Calhoun) ^a | -19.4 | 98.7 | 86.4 | | | | | |

^a B. A. Calhoun, Technical Report 68, Laboratory for Insulation Research, Massachusetts Institute of Technology, July, 1953 (unpublished).

magnetostrictive coefficients of magnetite single crystals from 120°K to room temperature.

During an investigation of the effect of minor additions of various foreign cations on the magnetite 120°K cubic to orthorhombic transition, we noticed that small amounts of cobalt profoundly affected the temperature of the permeability peak. We studied this effect by means of magnetostriction and permeability measurements.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Magnetite Single Crystals

The constants of the familiar five-constant magnetostriction equation⁵ between 120°K and 300°K were determined for two magnetite single crystals: a naturally occurring crystal from New York state and a synthetic crystal grown from the melt by Smiltens⁶ and kindly furnished us by Professor A. R. von Hippel of Massachusetts Institute of Technology.

The samples were (110) plane circular disks *ca* 8 mm in diameter and *ca* 1 mm thick, with their edges rounded so that they approximated oblate ellipsoids. Resistance strain gauges (Baldwin type A19) cemented to the flat face parallel to the principal crystal directions ([001], [110] and [111]) were used to detect the deformation. Magnetostriction was measured as a function of crystal orientation with respect to an applied static magnetic field of *ca* 3500 oersteds (sufficient to

achieve technical saturation) lying in the plane of the disk. The procedure outlined by Bozorth and Hamming⁷ was used to obtain the magnetostriction constants, thus obviating the necessity of making any assumptions regarding the demagnetized state of the crystal. Values of saturation magnetostriction for the principal crystal directions were calculated from these constants.

The strain-gauge manufacturer's room temperature value of gauge factor was assumed to be valid at the lower temperatures. It has been reported⁸ that the calibration factor of this type of gauge does not change by more than 5% over the temperature range covered in this investigation. The probable error from all sources combined is estimated to be $ca \pm 20\%$ at the lower temperatures, and somewhat less than this at room temperature.

Table I presents the five constants of the magnetostriction equation together with values of saturation longitudinal magnetostriction for the principal crystallographic directions of magnetite at room temperature. The temperature variation of λ_{100} , λ_{111} , and λ_{110} for the synthetic single crystal is shown in Fig. 2. Corresponding results for the natural crystal are similar.

B. Polycrystalline Magnetite

One of the interesting features of the magnetostrictive behavior of magnetite is that λ_{111} and λ_{110} are positive and larger in magnitude than λ_{100} , which is negative. As a result the net magnetostriction of polycrystalline magnetite is positive, whereas it is negative for most other ferrites. Since the relative magnitudes of λ_{111} , λ_{110} , and λ_{100} do not change appreciably between 120°K and 300°K, the structure of a curve of λ vs H in polycrystalline magnetite contains features which are characteristic of the direction of easy magnetization. Lack of knowledge concerning the exact details of the magnetization process in polycrystalline samples prevents us from making an exact analysis of a λ vs H curve. However, certain definite conclusions can be drawn from the qualitative behavior of such a curve in the vicinity of zero magnetization and in the region of large magnetic field.

A large part of the magnetostrictively active magneti-

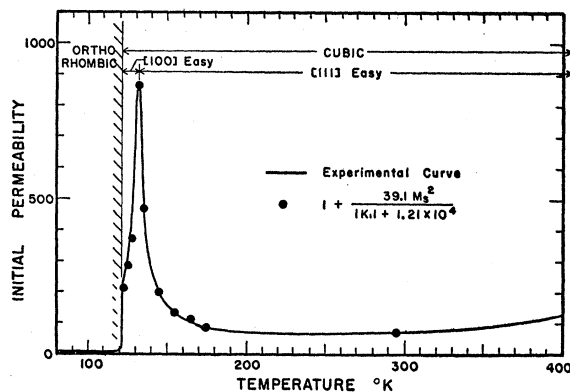


FIG. 1. Initial permeability of polycrystalline magnetite at 10 kc/sec as a function of temperature.

⁵ R. Becker and W. Döring, *Ferromagnetismus* (Verlag Julius Springer, Berlin, 1939), p. 275; see also reference 7.

⁶ J. Smiltens, *J. Chem. Phys.* **20**, 990 (1952).

⁷ R. M. Bozorth and R. W. Hamming, *Phys. Rev.* **89**, 865 (1953).

⁸ E. E. Day and A. H. Sevand, *Proc. Soc. Exptl. Stress Anal.* **8**, 133 (1950).

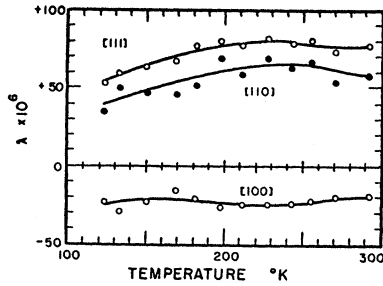


FIG. 2. λ_{100} , λ_{111} , and λ_{110} versus temperature for synthetic magnetite single crystal.

zation process at field strengths near the condition of zero net magnetization (demagnetized state) is domain wall motions (other than 180° domain walls) in those grains so oriented that one of the easy directions makes a small angle with the direction of the applied magnetic field. The magnetization process at high field strength is largely due to rotation of the magnetization in grains so oriented that one of the directions of most difficult magnetization makes a small angle with the field direction. Consequently the longitudinal magnetostriction of a polycrystalline material should have the same sign at weak fields as the longitudinal magnetostriction in the easy direction of the single crystal. In strong fields the λ vs H curve should approach its saturation value with a slope which has the same sign as the longitudinal magnetostriction in the hard direction of the single crystal. The features were observed in the λ vs H curves of polycrystalline magnetite.

The method used in preparing the specimen is described in the next section. The experimental arrangement, including sample size and shape, positioning of the strain gauge, and orientation of the magnetic field relative to the plane of the sample, was the same as for the single crystal measurements. However, for this experiment the sample remained stationary while the magnetic field intensity varied linearly and periodically so as to cause the sample to traverse a hysteresis loop. A special current source described by Levinson⁹ supplied the magnet current. The output voltage of the strain gauge bridge was recorded as a function of time.

Figure 3 is a reproduction of two strain vs time curves for polycrystalline magnetite: one obtained at room temperature, where $[111]$ is the direction of easy magnetization; and the other at 123°K , where $[100]$ is easy. Curve (a) starts off from the state of zero magnetization with a positive magnetostriction (λ_{111} is positive, $[111]$ easy, at room temperature) and approaches saturation with a negative slope (λ_{100} is negative). Curve (b), on the other hand, starts off from the demagnetized state in the negative direction (λ_{100} is negative, $[100]$ easy), then reverses direction and approaches saturation with a positive slope (λ_{111} is positive). This type of reversal, called the Villari

reversal, has been observed¹⁰ to occur in polycrystalline iron, in which λ_{111} is negative and λ_{100} is positive. For magnetite the shape of the λ vs H curve changes from type (a) to type (b) at 130°K . Therefore the onset of a reversal in the curve serves as an indicator of the change in direction of easy magnetization from $[111]$ to $[100]$.

C. Cobalt-Substituted Magnetite

The Fe_3O_4 lattice will tolerate a deficiency of Fe^{2+} ions; that is, the spinel structure survives if the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ exceeds unity ($\text{Fe}^{3+}/\text{Fe}^{2+} > 2/1$). It has been demonstrated¹¹ that the 120°K cubic-orthorhombic transition in magnetite is very sensitive to this type of deficiency. The temperature of the transition and magnitude of the discontinuity in electrical conductivity accompanying it both decrease with increasing ratio of $\text{Fe}_2\text{O}_3/\text{FeO}$.

One phase of our investigation was to study the behavior of the transition temperature in polycrystalline samples as the composition is changed by adding small amounts of foreign cations. It was necessary that the oxidation state remain stoichiometric with respect to the ratio of trivalent to divalent cations in order that the effects of the foreign cations would not be obscured.

The samples were prepared according to standard ceramic techniques, involving wet ball-milling of oxides and carbonates, dry-pressing, calcining at *ca* 1000°C , ball-milling, pressing into disks and firing at *ca* 1400°C . The calcining and firing operations were carried out in an atmosphere of CO and CO_2 , in proportions varying with temperature according to the schedule reported by Smiltens.⁶

The optimum firing schedule was worked out with polycrystalline Fe_3O_4 , using the temperature of the cubic-orthorhombic transition as quality criterion. Initial permeability measurements provided a very convenient means of monitoring the transition temperature, for this parameter drops precipitously at the transition (see Fig. 1). We were able to obtain polycrystalline Fe_3O_4 with a transition temperature only *ca* 1° lower than that of the synthetic crystal, which had been found by chemical analysis⁶ to be stoichio-

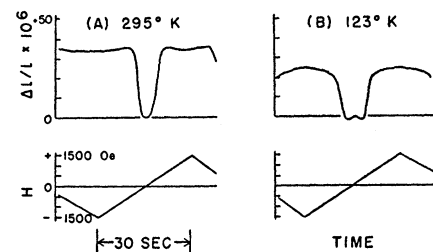


FIG. 3. Recorded magnetostriction versus time curves for polycrystalline magnetite. Corresponding magnetic fields are shown below. Curve (a) was obtained at room temperature, $[111]$ easy direction; curve (b), at 123°K , $[100]$ easy.

⁹ J. Levinson, Phys. Rev. **95**, 651 (1954); Office of Naval Research Technical Report ONR III, Alfred University, January, 1954.

¹⁰ M. Kornetzki, Z. Physik **87**, 560 (1933).

¹¹ E. J. W. Verwey and P. W. Haayman, Physica **8**, 979 (1941).

metric with respect to $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Assuming that the substitution of small amounts of foreign cations into the magnetite lattice does not appreciably affect the oxidation equilibrium conditions, we used the same firing schedule for all samples, with slight variations in peak temperature. Cations added, in amounts not exceeding 5 mole percent, included the transition elements and Mg, Al, Cu, Zn, Ga and Ba.

Toroidal shaped specimens (ca 13 mm o.d. \times 10 mm i.d. \times 1 mm) were cut from the fired disks for permeability measurements. The edges of the remaining center core were rounded to form a sample for magnetostriction measurements. The toroids were served with two concentric monolayer windings covering most of the core (leaving a small section for contact with the copper-constantan thermocouple used for temperature measurements). The voltage induced in the inner winding by a sinusoidal 10-kc signal of known amplitude applied to the outer winding was measured. A simple calculation yielded the absolute magnitude of the permeability.

All cation substitutions were found to lower the transition temperature, with no significant correlation possible between the amount of lowering and the type of lattice site thought to be occupied by the ion. The amount of lowering per mole percent ranged from less than 1° (for barium) to 13° (for manganese). According to the work of Verwey and Haayman¹¹ the rate is approximately 9° per mole percent of holes in the octahedral cation lattice sites.

The substitution of foreign cations into the Fe_3O_4 lattice also caused a shift in temperature of the permeability peak shown in Fig. 1. Some cations raised the temperature of the maximum; others lowered it. In no case was the temperature interval between peak and transition decreased. With but two exceptions, manganese and cobalt, the amount of temperature shift per mole percent of foreign ion was less than 10° . It was very difficult to obtain good reproducibility in the properties of Mn-containing magnetite fabricated at different times. In some of the manganese-substituted samples the peak temperature was raised by as much as 20° per mole percent; in others it was lowered. The

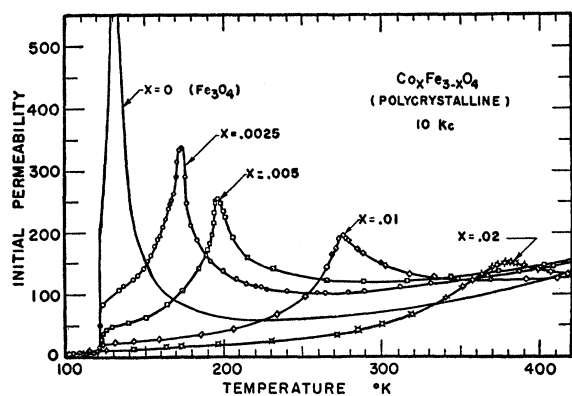


FIG. 4. Initial permeability of cobalt-substituted magnetite.

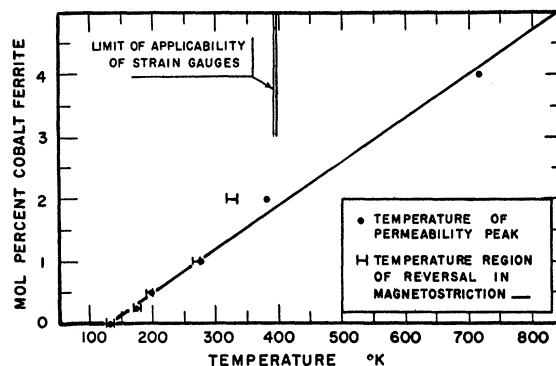


FIG. 5. Correlation between temperature of the permeability peak and temperature of first appearance of reversals (on cooling) in magnetostriction curves of cobalt-substituted magnetite.

addition of cobalt caused such a large and reproducible shift in the peak temperature that its effect can be regarded as unique among the cations studied.

Figure 4 shows permeability *vs* temperature curves for four different concentrations of cobalt, together with the curve for Fe_3O_4 . Compositions are identified by the parameter X , which is the mole fraction of cobalt ferrite. The effect of the cobalt additions is to cause a very large shift upwards in the temperature of the permeability peak; also to broaden the peaks and decrease the value of permeability at the maximum. The amount of temperature shift is approximately linear with respect to cobalt ferrite content, the rate being ca 140° per mole percent.

Since the permeability peak in magnetite is a direct manifestation of the change in direction of easy magnetization, one would intuitively expect that the shifted peak in the cobalt substitution series could be attributed to the same cause. It was not possible to confirm this correlation directly, since single crystals of these compositions are not available. However, curves of longitudinal magnetostriction *versus* magnetic field obtained from the polycrystalline samples provided convincing indirect evidence that such a correlation is valid.

In the case of magnetite, since λ_{100} is negative and the average magnetostriction is positive, a low-field reversal occurs in the λ *vs* H curve of polycrystalline Fe_3O_4 when $[100]$ is the preferred direction of the magnetization (Fig. 3). The presence of such a reversal in cobalt-substituted magnetite could be regarded as evidence that $[100]$ is the direction of easy magnetization provided it could be assumed that the cobalt substitution does not affect the magnetostrictive characteristics of magnetite appreciably. To the extent that this assumption is valid the low-field magnetostriction reversals should first occur at the temperature at which the easy direction changes from $[111]$ to $[100]$.

Figure 5 shows the temperature of the permeability peak and the temperature range in which reversals

first appeared (on cooling) in the longitudinal magnetostriction curves; both plotted as a function of cobalt concentration. The strain gauges could not be used above 390°K. Therefore, the only information obtained concerning the reversal for the sample containing 4 mole percent cobalt ferrite was that if it disappears it does so at a higher temperature.

III. DISCUSSION OF RESULTS

Our results concerning magnetostriction in magnetite single crystals at room temperature are in general agreement with the results of Calhoun (see Table I) and also with the early measurements of Heaps.¹² The only noteworthy disagreement concerns the relative magnitudes of λ_{110} and λ_{111} .

The principal magnetostriction constants of Fe_3O_4 have been found to be relatively insensitive to temperature between 120°K and 300°K. It is probably for this reason that the temperature spectrum of initial permeability can be correlated very well with magneto-crystalline anisotropy, with the stress anisotropy expressed by a constant [Eq. (1)]. The apparent changes in sign of λ_{100} previously reported^{3,4} to occur at low temperature were probably caused by spontaneous changes in the domain distribution of the demagnetized state accompanying the change in direction of easy magnetization. The previously reported¹³ spontaneous deformation accompanying the change in direction of easy magnetization in the synthetic single crystal serves as evidence of a change in initial domain distribution.

Substitution of small amounts of cobalt into the magnetite lattice has been found to cause a large shift upwards in the temperature of the permeability peak (Fig. 4). The correlation evident in Fig. 5 between the temperature of the peak and the temperature at which reversals appeared in the magnetostriction curves is regarded as sound evidence that the permeability peak in all cases is associated with a change in direction of easy magnetization. The divergence of the two sets of data at the higher cobalt concentrations may well be due to a breakdown of the assumption that cobalt does not affect the magnetostrictive

behavior of magnetite. The magnetostriction of cobalt ferrite is negative and very large.¹⁴ Therefore, the addition of more than one percent of cobalt ferrite to magnetite might be expected to upset the qualitative relationship between magnitudes of the magnetostriction in the various crystal directions. We therefore conclude that the effect of the cobalt additions is to raise the upper limit of the temperature region in which the cube edge is the preferred orientation of the spontaneous magnetization.

If the straight line of Fig. 5 is extended to 100% cobalt ferrite, it falls at a value greatly in excess of the Curie temperature of cobalt ferrite. This extrapolation infers that [100] is the easy direction for cobalt ferrite over its entire cubic range. Moreover, it is possible to estimate from our data the value of the anisotropy constant of cobalt ferrite at room temperature. The anisotropy constant for Fe_3O_4 at room temperature is -1.12×10^5 ergs/cc.¹ We can assume that the constant for 1.18% cobalt ferrite is zero, since the permeability peak falls at room temperature for this composition. Making a linear extrapolation to higher percentages of cobalt ferrite we predict a value of $+7.5 \times 10^6$ ergs/cc for 80% and $+9.4 \times 10^6$ ergs/cc for pure cobalt ferrite. Recently the anisotropy constants of single crystals (approximately 80% cobalt ferrite) have been determined independently by two different investigators. Shenker¹⁵ found that K_1 at room temperature is $+3.82 \times 10^6$ erg/cc; Bozorth¹⁶ found a value of $+3.4 \times 10^6$ ergs/cc. In view of the extensive nature of our extrapolation the agreement between predicted and observed values of anisotropy constant is regarded as satisfactory.

All the observed effects are completely understandable, phenomenologically at least, on the basis of a very strong interaction between the spins of the cobalt ions and the lattice. This spin-lattice interaction aligns the cobalt spins parallel to a cube edge of the spinel lattice. The presence of a small amount of cobalt in the magnetite lattice is sufficient to align the entire spin system in this direction. Presumably cobalt would have the same effect on other ferrites.

¹² C. W. Heaps, Phys. Rev. **24**, 60 (1924).

¹³ L. R. Bickford, Jr., Revs. Modern Phys. **25**, 75 (1953).

¹⁴ R. M. Bozorth and J. G. Walker, Phys. Rev. **88**, 1209 (1952).

¹⁵ H. Shenker, thesis, University of Maryland, 1955 (unpublished).

¹⁶ R. M. Bozorth (private communication).