CRYSTAL DISLOCATIONS AND COERCIVITY IN FINE GRAINED MAGNETITE

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Summary

Interaction of the stress field of a favourably oriented edge dislocation with the magnetostriction in a ferromagnetic domain wall in magnetite causes the dislocation to act as a potential well for the domain wall. The coercivity of 20 μm grains, in which the domain structure is considered to be particularly simple, can be explained on this basis if the dislocations are arranged so that the effects of several of them are additive. The required density of edge dislocations is 10^9 cm^{-2}, which is entirely reasonable; screw dislocations are not effective in magnetite. To explain the variation of coercivity with grain size it appears necessary to assume that the arrangement of dislocations is neither regular nor random but is partially ordered.

I. Introduction

The coercivity H_c of dispersed powders of ferromagnetic materials, in which each grain is a single crystal, shows a regular increase with decreasing grain diameter d, being well represented by

$$H_c \propto d^{-n}. \tag{1}$$

The origin of coercivity of fine grains is of particular interest in rock magnetism, and in this connection a number of measurements have been made on magnetite, notably by Gottschalk (1935) and Parry (1965). Gottschalk's data gave $n \simeq 0{\cdot}8$ and this was shown by Stacey (1959, 1963) to be explicable in terms of a simple model in which domain wall movements are impeded by potential barriers arising from randomly distributed crystal defects. However, Parry (1965) found that the value of n was reduced by annealing the grains; for magnetite that was carefully annealed and dispersed in a magnetically inert matrix, so that the grains were magnetically independent, he obtained $n \simeq 0{\cdot}4$. No reasonable juggling with the parameters of Stacey's theory makes it compatible with this result, and we have therefore undertaken a re-appraisal of the fundamental mechanism of coercivity in magnetite, following a suggestion that crystal dislocations may be responsible.

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We may approach the problem in a general way by supposing that the domain structure is a function of grain diameter d, such that the average area A of the domain walls within a grain is given by

$$A \propto d^l, \tag{2}$$

and that the energy barriers impeding domain wall translation are given by

$$E \propto A^m. \tag{3}$$

Then for barriers of a particular type

$$H_c \propto E/A \propto d^{l(m-1)}, \tag{4}$$

so that from the observations we have

$$l(1-m) = 0{\cdot}4. \tag{5}$$

We have no reason to suppose that l can be less than unity for any domain model. Stacey (1959) obtained from domain theory $l = 1{\cdot}5$, and for very small grains (< 20 μm) $l = 2$ appears appropriate. Thus for $1 < l \leqslant 2$ we have $0{\cdot}6 < m \leqslant 0{\cdot}8$, the important point being that the value $m = 0{\cdot}5$ must be ruled out. The value $0{\cdot}5$ was deduced by assuming that the energy barriers are due to large numbers of crystal defects randomly dispersed within the grains and that the number of defects N within a domain wall fluctuates statistically by $\pm N^{\frac{1}{2}}$ as the wall moves. Therefore we conclude either that the crystal defects responsible for coercivity are non-random or else that they are so few in number that the statistical theory is inapplicable. In the following section we calculate the magnitude of an energy barrier arising from a single dislocation and find it to be too small, by a factor of about 10, to explain the coercivity of small grains, so that a superposition of effects of several dislocations is required.

II. Interacting Stress Fields of a Domain Wall and an Edge Dislocation

The normal components of the stress field of an edge dislocation oriented along the z axis and with its Burgers (displacement) vector **b** in the x direction are (Cottrell 1953)

$$\left.\begin{aligned} \sigma_{xd} &= -\frac{\mu b}{2\pi(1-\nu)}\frac{y(3x^2+y^2)}{(x^2+y^2)^2}, \\ \sigma_{yd} &= \frac{\mu b}{2\pi(1-\nu)}\frac{y(x^2-y^2)}{(x^2+y^2)^2}, \\ \sigma_{zd} &= \nu(\sigma_{xd}+\sigma_{yd}). \end{aligned}\right\} \tag{6}$$

There are also shear stresses that do not enter the present calculation. Here μ is the rigidity, ν is Poisson's ratio, and the subscript d refers to dislocation stresses, to

distinguish them from magnetostrictive stresses for which the subscript λ is used. The corresponding lattice strains are

$$\left.\begin{aligned} \epsilon_{xd} &= \{(1+\nu)/q\}\,(\sigma_{xd}-\sigma_{zd}), \\ \epsilon_{yd} &= \{(1+\nu)/q\}\,(\sigma_{yd}-\sigma_{zd}), \\ \epsilon_{zd} &= 0, \end{aligned}\right\} \tag{7}$$

where q is Young's modulus.

The interaction of these stresses with the magnetostriction of a domain wall is only significant if the dislocation lies in the plane of the wall, which in magnetite is a (110) plane. For consideration of its mechanical properties we may regard magnetite as a face-centred cubic lattice of oxygen ions with interstitial Fe^{3+} and Fe^{2+} ions, and the Burgers vector for a unit dislocation is therefore a [110] axis, the crystal axis of closest packing. This reduces the possible geometrical situations to two, in which the Burgers vector is in the plane of the wall, as in Figure 1, or normal to it. The interaction energy is zero in the second case so that only the first is of interest.

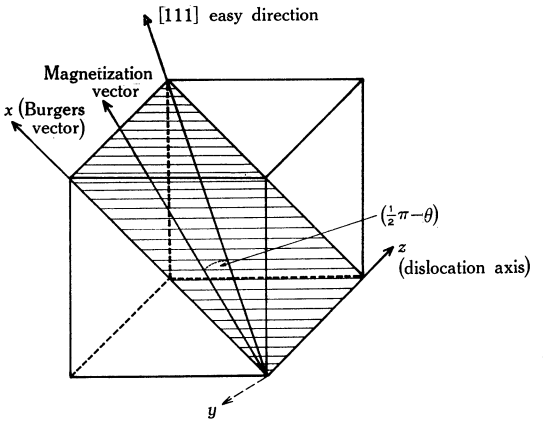

Fig. 1.—Geometry for the interaction of an edge dislocation with a domain wall in magnetite. The cube edges are [100] axes and the plane of the wall is shaded.

We consider the magnetite crystal to be large and the domain wall extensive relative to the thickness of the wall. Then within the x–z plane of the wall the lattice dimensions are constrained to conform to the bulk of the crystal, i.e. there is a magnetostrictive stress but no strain. Normal to the wall, magnetostrictive strains are freely accommodated and no stress appears. Then if the components of magnetostriction at any point in the wall would be λ_x, λ_y, λ_z if unconstrained, the actual magnetostrictive strains and stresses are

$$\left.\begin{aligned} \epsilon_{x\lambda} &= \epsilon_{z\lambda} = 0, \\ \epsilon_{y\lambda} &= \lambda_y+\{\nu/(1-\nu)\}\,(\lambda_x+\lambda_z), \\ \sigma_{x\lambda} &= -\{q/(1-\nu^2)\}\,(\lambda_x+\nu\lambda_z), \\ \sigma_{y\lambda} &= 0, \\ \sigma_{z\lambda} &= -\{q/(1-\nu^2)\}\,(\lambda_z+\nu\lambda_x). \end{aligned}\right\} \tag{8}$$

The values of λ_x, λ_y, λ_z are determined by the orientation of the magnetic vector at each point in the wall. The rotation of the vector through the wall is confined to the plane of the wall, and we represent the orientation within the wall by an angle θ, such that $\theta = 0$ at the centre ($y = y'$), and use a simple result, obtained by Landau and Lifshitz (1935), which is sufficiently precise for our purpose, namely,

$$\sin\theta = \tanh\{(y-y')/y_0\} \qquad \text{or} \qquad \cos\theta = \operatorname{sech}\{(y-y')/y_0\}, \tag{9}$$

where y_0 is a parameter that we may term the half-thickness of the wall. The values of λ_x, λ_y, and λ_z are obtained in terms of θ from the general equation for crystal magnetostriction

$$\lambda = \tfrac{1}{2}\lambda_{100} + \tfrac{3}{2}\lambda_{100}(\alpha_1^2\beta_1^2 + \alpha_2^2\beta_2^2 + \alpha_3^2\beta_3^2) + 3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2 + \alpha_2\alpha_3\beta_2\beta_3 + \alpha_3\alpha_1\beta_3\beta_1), \tag{10}$$

where the α's and β's are direction cosines relative to [100] axes of the direction of magnetization and the direction in which the magnetostriction has the value λ. For magnetite $\lambda_{100} = -20\times10^{-6}$ and $\lambda_{111} = 78\times10^{-6}$. From (10), with the geometry of Figure 1,

$$\left.\begin{aligned} \lambda_x &= \tfrac{1}{2}\lambda_{111} + (\lambda_{100}+\lambda_{111})\{(1/\sqrt{2})\sin\theta\cos\theta - \tfrac{1}{4}\cos^2\theta\}, \\ \lambda_y &= -\tfrac{1}{2}\lambda_{111} + (\lambda_{100}-\lambda_{111})\{(1/\sqrt{2})\sin\theta\cos\theta - \tfrac{1}{4}\cos^2\theta\}, \\ \lambda_z &= \lambda_{100}\{\tfrac{1}{2}\cos^2\theta - (\sqrt{2})\sin\theta\cos\theta\}. \end{aligned}\right\} \tag{11}$$

III. Interaction Energy

We write the energy density of the interaction of the stress and strain fields of the domain wall and dislocation as a sum of six products

$$E_\delta = \sigma_{x\mathrm{d}}\,\epsilon_{x\lambda} + \sigma_{x\lambda}\,\epsilon_{x\mathrm{d}} + \sigma_{y\mathrm{d}}\,\epsilon_{y\lambda} + \sigma_{y\lambda}\,\epsilon_{y\mathrm{d}} + \sigma_{z\mathrm{d}}\,\epsilon_{z\lambda} + \sigma_{z\lambda}\,\epsilon_{z\mathrm{d}}. \tag{12}$$

This expression is simplified using relations (6), (7), and (8) and noting that

$$\lambda_x + \lambda_y + \lambda_z = 0,$$

whence

$$E_\delta = -\sigma_x\lambda_x + \{(1-3\nu)/(1-\nu)\}\sigma_y\lambda_y - \sigma_z\lambda_z, \tag{13}$$

the subscript d being now dropped from the notation for stresses as no confusion arises. The explicit form obtained by substituting from (6) and (11) and re-arranging terms is then

$$E_\delta = \frac{Cy}{(x^2+y^2)^2}\Big(\lambda_{111}\{x^2 + (1-2\nu)y^2\} + (Ax^2 + By^2)(2\sqrt{2}\sin\theta\cos\theta - \cos^2\theta)\Big), \tag{14}$$

where

$$\begin{aligned} A &= \lambda_{111} + \lambda_{100}(2-5\nu+2\nu^2) = 60\times10^{-6}, \\ B &= (1-2\nu)(\lambda_{111}-\nu\lambda_{100}) = 41\times10^{-6}, \\ C &= (\mu b/4\pi)(1-\nu)^{-2} = 6{\cdot}7\times10^3 \text{ dyn/cm},* \end{aligned}$$

* Assuming that $\mu = 8\times10^{11}$ dyn/cm^2, $\nu = 0{\cdot}25$, and $b = c/\sqrt{2}$, where $c = 8{\cdot}4$ Å is the unit cell size.

and $\sin\theta$ and $\cos\theta$ are given in terms of y by (9). The total energy of the wall for a length z_0 of dislocation is therefore

$$E = \int_{-\frac{1}{2}z_0}^{\frac{1}{2}z_0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_\delta \, dx \, dy \, dz . \tag{15}$$

The term in (14) that is independent of θ vanishes in this integration, being an odd function of y. The z integration is trivial and we can therefore write

$$E = Cz_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \operatorname{sech}^2\left(\frac{y-y'}{y_0}\right)\left\{2\sqrt{2}\sinh\left(\frac{y-y'}{y_0}\right)-1\right\} \frac{y(Ax^2+By^2)}{(x^2+y^2)^2} \, dx \, dy . \tag{16}$$

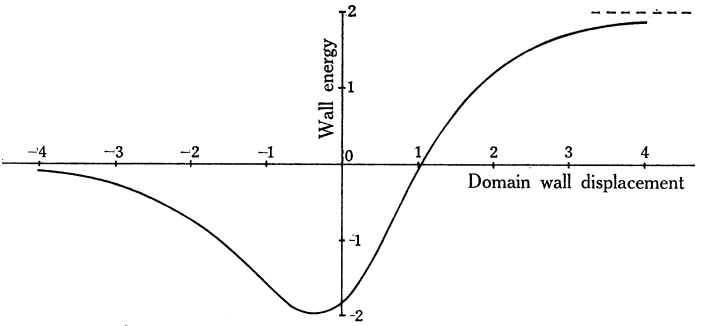

Fig. 2.—Energy of a domain wall as a function of its displacement from a dislocation, by equation (17). The unit of distance is the wall thickness y_0 and the unit of energy is $\pi C(A+B)z_0 y_0$.

The integration with respect to x involves only the last term in the integrand, which integrates to the form

$$\tfrac{1}{2}(A+B)[\tan^{-1}(x/y)]_{x=-\infty}^{\infty} .$$

This has the value $\pm\frac{1}{2}\pi(A+B)$ according to the sign of y. The integral thus has a discontinuity at $y = 0$ and we must write it in the form

$$E = \pi C(A+B)z_0 \operatorname*{Lim}_{\substack{\alpha\to\infty \\ \beta\to 0}} \int_{-\alpha}^{-\beta} \operatorname{sech}^2\left(\frac{y-y'}{y_0}\right)\left\{2\sqrt{2}\sinh\left(\frac{y-y'}{y_0}\right)-1\right\} dy ,$$

whence

$$E = \pi C(A+B)z_0 y_0\{1+\tanh(y'/y_0)-2\sqrt{2}\operatorname{sech}(y'/y_0)\} . \tag{17}$$

This is the energy of the domain wall with its centre at a distance y' from the dislocation. The principal effect is that the dislocation acts as a potential well for the wall, as shown in Figure 2.

In similar calculations on screw dislocations and differently oriented edge dislocations the energy integrals vanish. The energy barriers to domain wall movements arise only from favourably oriented edge dislocations.

IV. Coercive Force of a Small Grain with a Single Dislocation

A domain wall of area a separating domains of spontaneous magnetization I_s, which are exposed to a field H parallel to one of the domains, has a gradient of magnetic energy E_m given by

$$dE_m/dy' = 2a I_s H . \tag{18}$$

When this is equal to the maximum gradient of the barrier energy in equation (17), H is equal to the coercive force H_c, because it is then just sufficient to impel a domain wall past a potential barrier. Taking an average of the maximum gradients in opposite directions, i.e. neglecting the second term in (17), which imparts an asymmetry to the potential well,

$$\begin{aligned} |\,dE/dy'\,|_{max} &= 2\sqrt{2}\,\pi C(A+B)z_0\,|\tanh(y'/y_0)\,\mathrm{sech}(y'/y_0)\,|_{max} \\ &= \sqrt{2}\,\pi C(A+B)z_0 , \end{aligned} \tag{19}$$

from which the coercive force is

$$H_c = \pi C(A+B)z_0/\sqrt{2}\,aI_s = 3\cdot 15\times 10^{-3}(z_0/a)\ \text{oersted} , \tag{20}$$

for $I_s = 480$ e.m.u./cm^3 and z_0/a in units of cm^{-1}.

We consider the particular case of a grain of diameter $d = 20\ \mu$m, in which the domain structure is simple, the four-domain structure being favoured (Stacey 1963). Then $z_0 = 20\ \mu\text{m} = 2\times 10^{-3}$ cm and $a = \frac{1}{2}(\frac{1}{4}\pi)(2\times 10^{-3})^2$ cm^2, so that

$$H_c \simeq 4\ \text{Oe} .$$

This compares with the observed coercivity of about 40 Oe for 20 μm grains.

V. Conclusions

The energy barrier presented to a domain wall by the stress field of a single dislocation is deficient by a factor of about 10 to explain the coercivity of fine grained magnetite. It seems unlikely that the energy barrier has been underestimated by this factor, so that if dislocations are responsible for the observed coercivity several must act together. To determine whether this is possible we can estimate the required density of dislocations. The cross sectional area a' of a wall of thickness $2y_0$ that extends half way across a grain of diameter d is $y_0 d$, and taking $2y_0 = 3\times 10^{-5}$ cm and $d = 20\ \mu\text{m} = 2\times 10^{-3}$ cm we have $a' = 3\times 10^{-8}$ cm^2. This area must be crossed by a number of dislocations N whose value depends upon the way the dislocation effects are superimposed, being 10 if they are regularly arranged and act together but 100 if they are random, so that $N^{\frac{1}{2}}$ dislocations are effective on average, as in the statistical model. As has already been pointed out, the index n in equation (1) is too small to be compatible with the statistical model; it is also too large for dislocations to be arranged regularly because that would lead to $n = 0$. It therefore appears that the dislocations must be partially ordered, so that $N \simeq 30$ and the required dislocation density is therefore $N/a' \simeq 10^9$ cm^{-2}. This value is well within the observed range of

dislocation densities (Friedel 1964), so that dislocations are probably responsible for the observed coercivity of magnetite. This is, of course, not the only possible mechanism, but at least it provides an entirely satisfactory explanation.

The dislocation theory of coercivity is also compatible with the details of Parry's (1965) measurements. Work-hardening of magnetite grains by crushing them increases the dislocation density and increases coercivity, but, what is more interesting, it has the effect of increasing the index n in equation (1). Thus our model is compatible with the hypothesis that dislocations introduced by work-hardening are more nearly random in arrangement than the smaller number of dislocations that remain in the annealed state. The dislocations that remain during annealing tend to spread out by mutual repulsion of their stress fields so that they are semi-regular in arrangement.

VI. References

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