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Theoretical analysis of thermomagnetic properties, low-temperature hysteresis and domain structure of titanomagnetites

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Magnetic hysteresis of coarse-grained titanomagnetites at room temperature is characterised by low coercive force, low relative remanence, and a high ratio of coercivity of remanence to coercive force. These properties are generally interpreted in terms of multidomain structure. At low temperatures, however, ulvöspinel-rich compositions exhibit hysteresis properties similar to those of single-domain assemblages, and on this basis Radhakrishnamurty and Deutsch have proposed an alternative interpretation of the domain structure of titanomagnetites having $x \geqslant 0.3$ in terms of a mixture of single-domain and superparamagnetic particles. Low apparent Curie temperatures are attributed to the effects of thermal agitation above the blocking temperature.

We have examined theoretically the effects of thermal agitation on the low- and high-field thermomagnetic curves and find that observed Curie temperatures in general represent an intrinsic property of the magnetic mineral present, rather than reflecting thermal agitation. The high coercive force and relative remanence at low temperatures for titanomagnetites having $x > 0.5$ can be explained on the basis of the interaction of domain walls with crystal defects when the large increases in magnetocrystalline anisotropy and magnetostriction with decreasing temperature are taken into account. We discuss the evidence for the existence of domain walls in coarse-grained ulvöspinel-rich titanomagnetites and conclude that multidomain structure is well established.

It is also shown that fine titanomagnetite grains may have more than one blocking temperature. In any temperature interval for which superparamagnetic grains are present they will disproportionately influence susceptibility and low-field hysteresis.

1. Introduction

Magnetic hysteresis is frequently used to characterise the domain state of titanomagnetite (TM) grains in rocks and synthetic samples (e.g., Parry, 1965; Dunlop, 1969, 1972; Day et al., 1976, 1977; Rahman and Parry, 1970; Radhakrishnamurty et al., 1971, 1977, 1978, 1981). Theory predicts the occurrence of TM grains ($Fe_{3-x}Ti_xO_4$, hereafter denoted TM($100x$)) in three magnetic states: very fine superparamagnetic (SPM) particles; small, stable single-domain (SD) particles; and, above a threshold grain size, multidomain (MD) grains. Butler and Banerjee (1975) have calculated theoretical grain-size thresholds for the SPM–SD and SD–MD transitions as a function of composition and grain shape. It follows from the theory that TM grains of diameter greater than a few microns (μm), such as are commonly found in basalts and other igneous rocks, should form domain walls and therefore should possess nonuniform magnetisation.

Hysteresis studies at room temperature of samples containing predominantly coarse TM grains,

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which are characterised by low coercive force H_c and a low saturation remanence to saturation magnetisation ratio J_{rs}/J_s, are generally interpreted adequately on the basis of the MD model, irrespective of the composition of the grains. This interpretation is based on the hysteresis properties of SD particles, for which H_c is greater than several hundred oe, $J_{rs}/J_s \geq 0.5$, and the coercivity of remanence $H_{cr} < 2H_c$, whereas larger TM grains typically have $H_c < 100$ oe, $J_{rs}/J_s < 0.1$, and $H_{cr} \simeq 5H_c$ (Parry, 1965; Day et al., 1976, 1977). Stacey and Banerjee (1974, Table 4.1) have shown that these latter relationships accord well with MD theory.

It is important to establish criteria for determining the domain state of TM grains in rocks because this has major implications for palaeomagnetic and palaeointensity studies, for the interpretation of seafloor spreading magnetic anomalies, and for geophysical prospecting. Therefore alternative interpretations of the domain structure in TM's are of considerable interest.

Recently Radhakrishnamurty, Deutsch and coworkers (Radhakrishnamurty and Deutsch, 1974; Murthy et al., 1976; Radhakrishnamurty et al., 1977, 1978, 1979, 1981; Deutsch and Pätzold, 1976, 1980; Deutsch et al., 1981) have questioned the applicability of the MD model to TM's having $x \geq 0.3$, and have proposed an alternative explanation of the hysteresis properties for these compositions in terms of mixtures of SD and SPM particles. Their interpretation is based on three main lines of experimental evidence.

(1) *Low-temperature hysteresis properties.* Titaniferous compositions ($x > 0.5$) exhibit high coercive force (e.g., ~700 oe for TM56, ~1800 oe for TM68), $J_{rs}/J_s \geq 0.5$, and $H_{cr}/H_c \ll 5$, at ~80 K (Radhakrishnamurty et al., 1981), suggesting that they consist essentially of SD grains at low temperatures.

(2) Low-field thermomagnetic (k−T) curves. TM's having $x \geq 0.3$ have low susceptibility at ~80 K, which rises steadily with increasing temperature up to a Hopkinson-type peak (Radhakrishnamurty and Likhite, 1970) before dropping to an apparent Curie point. It is suggested that this behaviour represents progressive unblocking of fine particles which are stable SD at low temperatures, but SPM above their blocking temperature. Because the blocking temperature is well below the Curie temperature, the drop in susceptibility above the Hopkinson-peak region is attributed to thermal agitation and does not represent a true Curie point, which is an intrinsic property of the material. It is presumed that the fine particles which are responsible for this behaviour in fact have a composition close to either stoichiometric or cation-deficient magnetite (TM0), with a true Curie temperature $T_c \geq 580°C$. These k–T curves are classed as SP- and SD-type, according to the temperature at which the susceptibility peak occurs.

(3) Hysteresis in low fields (Rayleigh loops in ~10 oe). Synthetic TM's having $x \geq 0.1$ exhibit some hysteresis in low fields, the Rayleigh loops becoming more prominent with increasing titanium content (Radhakrishnamurty et al., 1981). This behaviour is not attributable to MD grains (Deutsch and Pätzold, 1976) and therefore indicates the presence of SPM particles. Analogous behaviour is frequently observed for basalts containing coarse titaniferous TM grains, which also exhibit the high-field hysteresis and k–T behaviour typical of synthetic TM's having $x \geq 0.5$ (Murthy et al., 1976; Deutsch and Pätzold, 1976, 1980; Radhakrishnamurty et al., 1979, 1981).

The fundamental explanation of this curious apparent tendency of TM's to form only SPM and SD particles, irrespective of the size of the grains, is unclear; however, it has been suggested that the titanium physically subdivides the grains on a very small scale, below optical resolution (Radhakrishnamurty and Deutsch, 1974; Deutsch and Pätzold, 1976, 1980), or that titanium inhibits the formation of domain walls in TM's, and statistical fluctuations of composition produce monodomain regions or spin clusters (Radhakrishnamurty and Nanadikar, 1979; Radhakrishnamurty et al., 1980).

Senanayake and McElhinny (1981) have questioned this interpretation and proposed a reassessment of the k–T curve classification schemes of Radhakrishnamurty and Deutsch (1974) and Radhakrishnamurty et al. (1977, 1978). Consensus now appears to have been reached on the titaniferous nature of coarse TM grains associated with low susceptibility and high coercive force at ~77 K, but these grains are regarded by Senanayake

and McElhinny (1981) as homogeneous ulvöspinel–magnetite solid-solution members having MD structure, their susceptibility–temperature variation being explained on the basis of the strong temperature dependence of magnetocrystalline anisotropy found by Syono (1965) for samples having $x > 0.5$.

To aid assessment of the arguments for and against the MD structure of coarse-grained TM's, we have examined theoretically the thermomagnetic properties of SD and MD TM's. The aim of this analysis is to establish probable limits to underestimation of the Curie temperatures due to thermal agitation above the blocking temperature, and to model the experimentally observed variation of susceptibility and high-field magnetisation with temperature. We also examine the problem of the low-temperature hysteresis properties of TM's and seek an explanation in terms of MD structure.

2. Theoretical low-field thermomagnetic curves

2.1. Single-domain grains

We consider an assemblage of aligned, identical, noninteracting SD grains in a small applied field. Below the blocking temperature the component of magnetisation M in the direction of the field is initially

$$M(\theta) = k_{SD}(\theta) H \qquad (1)$$

where θ is the angle between the applied field H and the easy axis of the grains, and k_{SD} the susceptibility of stable SD grains. For cubic anisotropy k_{SD} is independent of θ, and for uniaxial shape anisotropy it has been tabulated as a function of θ by Stoner and Wohlfarth (1948).

Given sufficient time, the magnetisation of the assemblage will relax exponentially towards its equilibrium value $J_s \tanh(\upsilon J_s H \cos\theta / kT)$ with a time constant τ (Stacey and Banerjee, 1974, p. 106). Here υ is the volume of the grains, J_s the spontaneous magnetisation, k is Boltzmann's constant (not to be confused with susceptibility), and T is the absolute temperature.

Therefore at time t,

$$M(\theta) = k_{SD}(\theta) H \exp(-t/\tau) + J_s \cos\theta \tanh(\upsilon J_s H \cos\theta / kT)[1 - \exp(-t/\tau)] \qquad (2)$$

The magnetisation of a randomly oriented assemblage may be obtained by integrating over all orientations. Assuming τ to be independent of θ, this yields

$$M = \bar{k}_{SD} H \exp(-t/\tau) + J_s F'(\upsilon J_s H / kT)[1 - \exp(-t/\tau)] \qquad (3)$$

The function $F'(a)$ has been tabulated by Stacey and Banerjee (1974, Appendix I). For small values of the argument, which is the case of interest (as we are considering initial susceptibility), $F'(a) \simeq a/3$.

In the derivation of eq. (2) it is assumed that the magnetic moments of the grains are essentially constrained to lie along the easy directions. This is very closely true, except immediately below the Curie temperature (Stacey and Banerjee, 1974, p. 107). In any case, the initial susceptibility of a randomly oriented assemblage of SPM particles is independent of this condition (Bean and Livingston, 1959), and therefore eq. (3) will be valid irrespective of departures of grain moments from easy directions due to thermal agitation. The assumption used to derive eq. (3) from (2), namely that τ is independent of θ, is a good approximation in the case of interest, where the applied field is small compared with the intrinsic coercive force of the grains. For this case (Dunlop and West, 1969),

$$\tau \simeq (1/2f_0)\exp(E/kT) \qquad (4)$$

where f_0 is a frequency factor of the order of 10^{10} Hz and E is the energy barrier between easy directions. Eq. (4) is dominated by the exponential factor. The frequency factor is a weakly varying function of volume, temperature and coercive force, which will be hereafter taken as constant.

From eq. (3) the effective susceptibility k_0 in a DC field is given by

$$k_0 = M/H \simeq \bar{k}_{SD}\exp(-t/\tau) + (\upsilon J_S^2/3kT)[1 - \exp(-t/\tau)] \qquad (5)$$

where t is a typical laboratory measurement time.

The blocking temperature T_b is the temperature at which $\tau = t$. Well below the blocking tempera-

ture, τ is very large and the measured susceptibility is simply $\bar{k}_{SD}$. Above T_b the SD contribution disappears and the susceptibility is given by the SPM contribution, which is much greater than the stable SD susceptibility, except very near the Curie point.

For SD grains in the form of prolate spheroids with demagnetising factors N_a and N_b along the major and minor axes (of length $2a$ and $2b$, respectively), the energy barrier due to shape anisotropy is given by

$$E = (N_b - N_a) J_s^2 v/2 \tag{6}$$

Osborn (1945) has given expressions for the demagnetising factors of prolate spheroids:

$$N_a = \left[4\pi/(m^2-1)\right]\left\{\left[m/2(m^2-1)^{1/2}\right] \times \ln\frac{\left[\left(m+(m^2-1)^{1/2}\right)\right]}{\left(m-(m^2-1)^{1/2}\right)} - 1\right\} \tag{7}$$

$$N_b = 2\pi - N_a/2$$

where $m = a/b$. The corresponding susceptibility is

$$\bar{k}_{SD} = (2/3)/(N_b - N_a) \tag{8}$$

The energy barrier due to magnetocrystalline anisotropy is

$$E = \begin{cases} (-K_1/12 - K_2/27)v & (K_1 < 0) \\ K_1 v/4 & (K_1 > 0) \end{cases} \tag{9}$$

where K_1 and K_2 are the conventional cubic anisotropy constants. The susceptibility in this case is given by

$$\bar{k}_{SD} = \begin{cases} J_s^2/2(-K_1 - K_2/3) & (K_1 < 0) \\ J_s^2/3K_1 & (K_1 > 0) \end{cases} \tag{10}$$

In general, the anisotropy energy will involve terms of the form of both eqs. (6) and (9). For example, the energy barrier for a prolate grain, whose easy direction of magnetisation is nevertheless constrained by dominant magnetocrystalline anisotropy to be [111], takes the form

$$E = (-K_1/12 - K_2/27)v \pm (N_b - N_a) J_s^2 v/2 \tag{11}$$

The plus sign applies when the shape anisotropy augments the magnetocrystalline anisotropy, and the minus sign when shape anisotropy detracts from the magnetocrystalline anisotropy.

The susceptibility in this case is

$$\bar{k}_{SD} = J_s^2/\left[2(-K_1 - K_2/3) \pm \tfrac{3}{2}(N_b - N_a) J_s^2\right] \tag{12}$$

Analogous expressions can be derived simply for the cases when the cube axes are easy directions, or when shape anisotropy predominates and the polar axis of the grain is the easy axis.

In order to use eqs. (4)–(12) for the calculation of theoretical k–T curves, knowledge of the temperature variation of spontaneous magnetisation and the magnetocrystalline anisotropy constants is necessary. Syono (1965) has determined the low-temperature variations of K_1 and K_2 for the compositions TM0, TM10, TM18, TM31, TM56 and TM68, and Pauthenet and Bochirol (1951) have measured $J_s(T)$ for magnetite. We assume the same functional dependence of $J_s(T/T_c)$ for compositions with $x > 0$. The high-temperature variation of K_1 for magnetite has been determined by Fletcher and Banerjee (1969). They found $K_1 \propto J_s^{8.5}$ and we assume the same form for compositions with $x > 0$ above room temperature.

For this analysis to be valid the assumed grain size must be less than the critical SD size across the temperature range considered. Butler and Banerjee (1975) have calculated room-temperature threshold grain sizes for the SD–two-domain (TD) transition for titanomagnetites of the above compositions, as well as room-temperature SPM thresholds. For cubic magnetite grains they obtained a particle length of 0.076 μm for the SD–TD transition, which is not much larger than the SPM threshold size. From this value we have calculated the SD–TD threshold diameter d_0 at 290 and 80 K for each of these compositions, using the approximation (Stacey and Banerjee, 1974, p. 59)

$$d_0 \propto \sigma/J_s^2 \propto (AK_1)^{1/2}/J_s^2 \tag{13}$$

where σ is the domain wall energy per unit area and A is the exchange constant, for which, following Butler and Banerjee (1975), we assumed

$$A(x,T) = A(0,\mathrm{RT})\left[T_c(x)/T_c(0)\right] \times \left[J_s(x,T)/J_s(x,\mathrm{RT})\right] \tag{14}$$

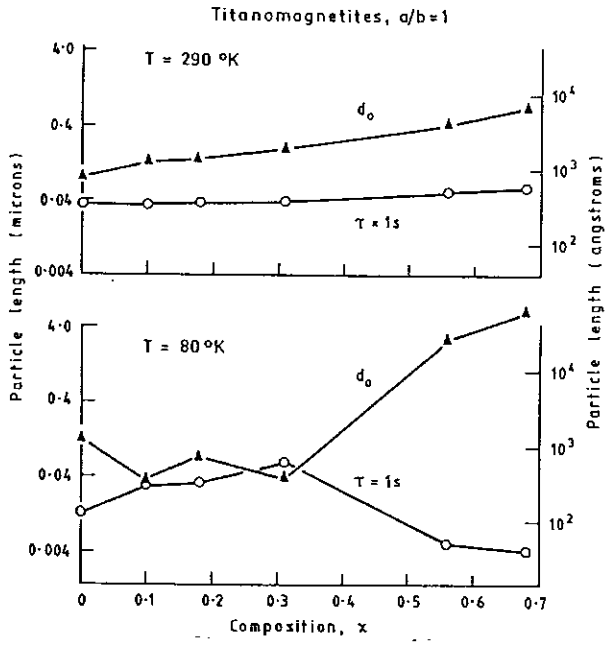

Fig. 1. Stable SD size ranges at 290 and 80 K for cubic TM grains as a function of composition. The SD–TD threshold size d_0 is indicated by the solid triangles; the SPM–SD threshold, calculated using $\tau = 1$ s in eq. (4), is indicated by the circles.

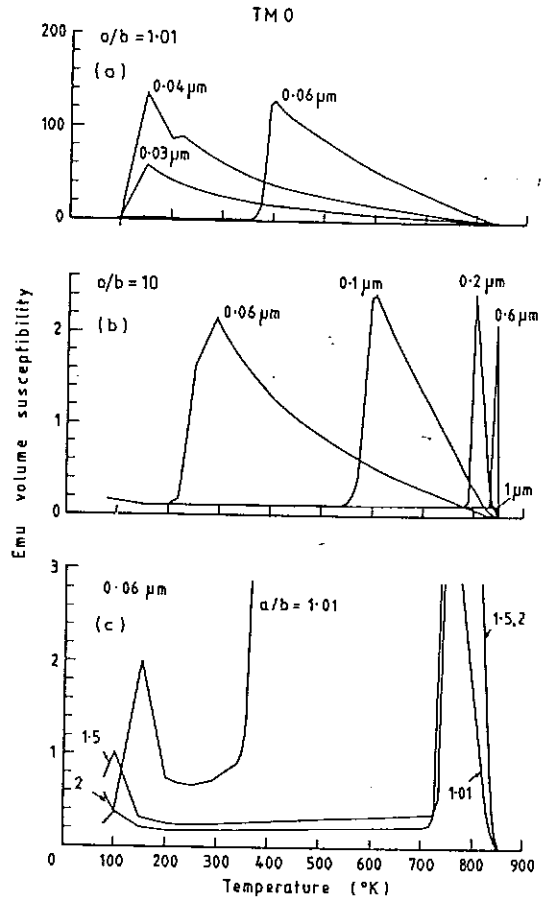

Fig. 2. Theoretical k–T curves for SD magnetite: (a) as a function of grain size for nearly spherical ($a/b = 1.01$) grains; (b) as a function of grain size for acicular ($a/b = 10$) grains; (c) as a function of axial ratio for grains of length 0.06 μm.

(where RT = room temperature). The grain-size limits to stable SD behaviour at 290 and 80 K are shown in Fig. 1. The data points for the SD–TD transition at 290 K essentially duplicate those plotted in Fig. 8 of Butler and Banerjee (1975) based on their more rigorous calculations which took into account the variation of domain wall width and energy with grain size. In either case the estimation of exchange energy from the Curie temperature is not strictly valid for a diluted ferrimagnetic in which the interactions are antiferromagnetic, as pointed out by Stacey and Banerjee (1974, p. 59), and this will lead to some uncertainty in the calculated maximum SD size.

The most remarkable feature of Fig. 1 is that the stable SD size range at 80 K is wider for some compositions (TM0, TM56 and TM68) but significantly narrower for the compositions TM10, TM18 and TM31. This reflects the decrease in K_1 at low temperatures for these latter compositions. There is in fact no stable SD size for TM31 at 80 K, whereas there is a significant SD size range at room temperature. Similar remarks pertain to other compositions at temperatures in the vicinity of their isotropic points (e.g., TM0 and TM56, for which K_1 changes sign between room temperature and liquid-nitrogen temperature). Thus rocks may in some cases contain TM grains which are superparamagnetic both at low and high temperatures, but which are stable over an intermediate temperature range. This interesting behaviour has been predicted previously for small spherical magnetite particles by Tropin (1967).

Calculated k–T curves for various grain sizes and axial ratios are shown in Figs. 2 and 3 for the compositions TM0 and TM68, respectively. The

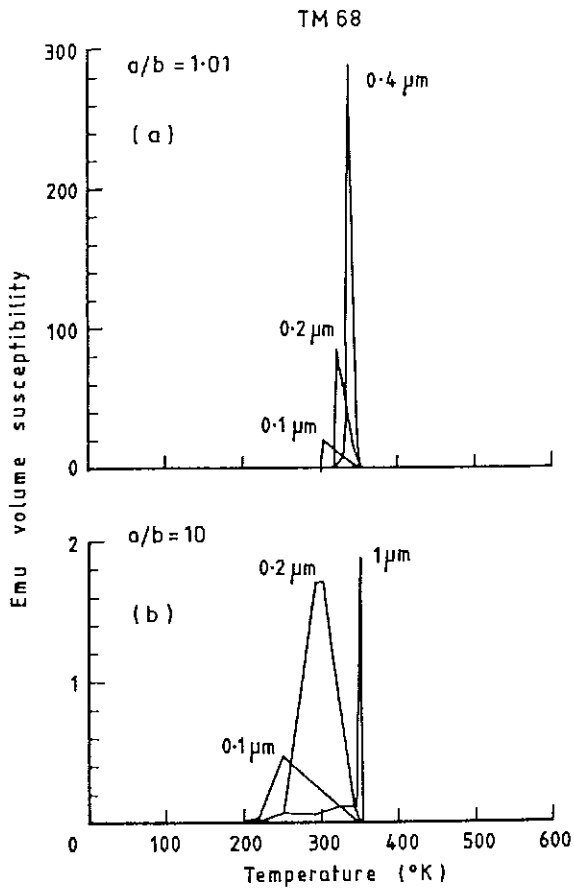

Fig. 3. Theoretical $k-T$ curves for SD TM68: (a) as a function of grain size for nearly spherical ($a/b = 1.01$) grains; (b) as a function of grain size for acicular ($a/b = 10$) grains.

curves for TM10, TM18 and TM31 resemble qualitatively those for TM0, and TM56 behaves similarly to TM68. It can be seen that spherical grains exhibit very large thermal enhancement of susceptibility (Dunlop, 1974) at the blocking temperature. The approximate thermal enhancement can be calculated using eqs. (4)–(10). Putting $\tau =$ 1 s in eq. (4), the unblocking criterion is $E/kT =$ 23.7. If the susceptibility is controlled by magnetocrystalline anisotropy, the critical SPM volume v_{SPM} is given by

$$v_{SPM} = \begin{cases} 23.7 \times 12kT_b/|K_1| & (K_1 < 0) \\ 23.7 \times 4kT_b/K_1 & (K_1 > 0) \end{cases} \quad (15)$$

Then the ratio of susceptibility immediately above the blocking temperature to the SD susceptibility immediately below T_b is

$$k_{SPM}/k_{SD} \simeq \begin{cases} \left(\frac{v_{SPM} J_s^2}{3kT_b}\right) \Big/ \left(\frac{J_s^2}{-2K_1}\right) = 190 \\ (K_1 < 0) \\ \left(\frac{v_{SPM} J_s^2}{3kT_b}\right) \Big/ \left(\frac{J_s^2}{3K_1}\right) = 95 \\ (K_1 > 0) \end{cases} \quad (16)$$

For susceptibility controlled by shape anisotropy, eqs. (6) and (8) give

$$k_{SPM}/k_{SD} \simeq 24 \quad (17)$$

Eqs. (16) and (17) represent the theoretical maximum values of thermal enhancement of susceptibility. In practice a range of blocking temperatures will always be represented, which will broaden the Hopkinson peak and lower the relative peak amplitude. Interactions between particles will also reduce the thermal enhancement, as will phase-lag effects when the susceptibility is measured in an alternating field.

A small fraction of SPM particles can contribute significantly to the room-temperature susceptibility of a rock. If the volume fraction of spherical SPM grains having T_b just below room temperature is f, the contribution to the susceptibility, from eqs. (10) and (16), is

$$k_{SPM} = \begin{cases} 95fJ_s^2/|K_1| & (K_1 < 0) \\ 32fJ_s^2/K_1 & (K_1 > 0) \end{cases} \quad (18)$$

For example, as little as 0.001% of these optimal grains could contribute 1600×10^{-6} G oe^{-1} in the case of TM0 ($J_s = 480$ G, $K_1 = -1.35 \times 10^5$ erg cm^{-3}) or 108×10^{-6} G oe^{-1} in the case of TM68 ($J_s = 78$ G, $K_1 = 0.18 \times 10^5$ erg cm^{-3}). This is important, because very fine grains may contribute significantly to the low-field properties of a rock (initial susceptibility and Rayleigh loops), yet have negligible effects on remanence and high-field properties.

From Fig. 2 it is apparent that the $k-T$ curves for magnetite grains which are SPM at room temperature decrease rather gradually to zero at the Curie temperature, and therefore that estimates of

T_C from k–T curves for samples in which SPM grains dominate the volume proportion of magnetic carriers will not be very accurate. T_C could possibly be underestimated by up to 100°C, but it is highly improbable that fine-grained magnetite could produce apparent Curie temperatures of less than 300°C, which would then be attributed incorrectly to ulvöspinel-rich titanomagnetites. Taking for example the case of grain length 0.06 μm, $a/b = 10$, for which $T_b \simeq 300$ K, the susceptibility does not decrease below the low-temperature ($T < T_b$) value until ~ 70°C below T_C. We therefore believe that reversible k–T curves with apparent Curie temperatures well below 578°C represent titaniferous magnetites, rather than the effect of thermal agitation on fine-grained magnetite particles as proposed by Radhakrishnamurty and Deutsch (1974) and Radhakrishnamurty et al. (1979). In any case, high-field thermomagnetic measurements can distinguish between these two possible explanations, as will be shown later.

In Figs. 2 and 3 magnetocrystalline anisotropy is assumed to augment the shape anisotropy of the elongated grains at room temperature. In the case of TM0 the effect of this is to shift the low-temperature peak associated with the isotropic point to lower temperatures (Fig. 2(c)). The presence of significant shape anisotropy also tends to suppress the peak. If the easy axis of an elongated grain is a crystallographic hard axis of magnetisation the peak will be shifted to a higher temperature. Thus if the shape and crystallographic axes are uncorrelated, the low-temperature susceptibility peak will be broadened and therefore less prominent. For this reason SD magnetite particles should in general exhibit less-prominent peaks at the isotropic point than MD grains and, if they are acicular, should have effectively no low-temperature peak, as observed by Senanayake and McElhinny (1981) and Radhakrishnamurty et al. (1981).

In Fig. 2(b) the Hopkinson-peak region becomes rapidly narrower as T_b approaches T_C with increasing grain size. The apparent drop in the amplitude of the Hopkinson peak for the larger grains is an artefact of insufficiently fine digitisation of the temperature scale. By eqs. (16) and (17) the relative height of the Hopkinson peak of a dilute assemblage of identical acicular SD grains should be independent of grain size.

The second hump in the k–T curve above 300 K for 1-μm grains of TM68 (which also occurs for TM56), which is shown in Fig. 3(b), is due to the assumed rapid variation of K_1 (as $J_s^{8.5}$) above room temperature, whereas there is little change in K_1 between 250 and 300 K (K_1 varies more slowly than J_s^2). If a weaker variation of K_1 above 300 K is assumed, until T_C is approached more closely, or a slower variation of J_s below 300 K, this peak will disappear and a more familiar single-peaked curve will result.

We now consider briefly the effect of grain interactions on the conclusions reached above concerning the proximity of true and apparent Curie points. Evdokimov (1963) has shown that clusters of strongly interacting SPM particles can behave as SD grains below a certain transition temperature where thermal agitation is insufficient to overcome the alignment of particle magnetic moments due to magnetostatic interaction. Although termed a "Curie temperature", this transition represents in fact a blocking temperature below which the assemblage exhibits SD "ferromagnetism" and above which the assemblage is superparamagnetic, with a higher susceptibility (given by $fvJ_s^2/3kT$).

Above the magnetostatic blocking temperature the effect of interactions is negligible, and our analysis of Curie-point underestimation for k–T curves is therefore unaffected by interactions. The magnetostatic interaction field is, at most, ~ 1000 oe, and therefore high-field thermomagnetic curves measured in a field of several koe will not be influenced by interactions at any temperature.

Although the theoretical k–T curves do not correspond to the behaviour of SD assemblages in rocks, which have a range of blocking temperatures, we believe them to be useful as an aid to the visualisation of curves representing experimentally observed k–T variations. Realistic k–T behaviour can be modelled by superposition of curves corresponding to a range of grain sizes and shapes. The theoretical curves can also reveal unexpected behaviour, such as the possibility of two blocking temperatures, and allow an approximate quantitative evaluation of maximum errors in Curie-point estimation that are due to thermal agitation.

2.2. *Multidomain grains*

In MD grains, domain wall displacement as well as domain rotation contributes to the intrinsic low-field susceptibility. In addition, the observed susceptibility is controlled by self-demagnetisation of the grains. Our treatment of this problem is based on the development given by Stacey and Banerjee (1974).

The intrinsic susceptibility perpendicular to the domain spontaneous magnetisation, as for the SD case, is given by

$$\chi_\perp = \begin{cases} J_s^2/\frac{4}{3}(-K_1 - K_2/3) & (K_1 < 0) \\ J_s^2/2K_1 & (K_1 > 0) \end{cases} \tag{19}$$

The intrinsic susceptibility due to domain wall displacement is structure-dependent and is inversely correlated with coercive force. The relationship may be expressed as

$$\chi_\parallel H_c \propto J_s \delta/d \propto J_s^{9/4}/K_1^{3/4} \tag{20}$$

as δ, the domain wall thickness, is proportional to $(A/K_1)^{1/2}$, and d, the thickness of lamellar domains, is proportional to $d_0^{1/2}$ (Soffel, 1971).

At room temperature the coercive force for coarse-grained TM's is practically independent of x (Day et al., 1977). For 10-μm grains, $H_c \simeq 90$ oe, and for grains larger than 100 μm, $H_c \simeq 32$ oe. Using the relationship $\chi_\parallel H_c \simeq 45$ e.m.u., applicable to magnetite, the result is obtained that, at 290 K,

$$\chi_\parallel(0) = \begin{cases} 45/90 = 0.5 & (10\text{-}\mu\text{m grain}) \\ 45/32 = 1.41 & (100\text{-}\mu\text{m grain}) \end{cases} \tag{21}$$

$$\chi_\parallel(x) = \chi_\parallel(0)\left[J_s(x)/J_s(0)\right]^{9/4}\left[K_1(0)/K_1(x)\right]^{3/4} \tag{22}$$

Then for each composition, the temperature dependence of $\chi_\parallel$ for a lamellar domain structure may be calculated from the relation

$$\chi_\parallel(T) \propto J_s^2\delta^2/dE_0 \propto J_s^{15/4}/K_1^{5/4}E_0 \tag{23}$$

where E_0 is the energy barrier between stable wall positions.

Energy barriers arise owing to the interactions of domain walls with crystal defects such as dislocations and inclusions. The temperature dependence of E_0 will depend on the details of the model adopted to account for the coercive force for MD titanomagnetites. The average number of such defects within a wall of area a is proportional to δa. If the interaction energy of a domain wall with a single defect is ϵ, then E_0, which is equal to the fluctuations in the potential energy of the wall, satisfies

$$E_0 \propto \epsilon(\delta a)^m \quad (0.5 \leqslant m \leqslant 1) \tag{24}$$

where $m = 0.5$ for randomly distributed defects, $m = 1$ for ordered defects, and takes intermediate values for partial order.

The value of m may be estimated from the grain-size dependence of H_c in the small MD region where domain structure is determined mainly by grain size. Over the size range 2–20 μm, the data of Day et al. (1977) are consistent with a relationship $H_c \propto (\text{diameter})^{-n}$ with $n \simeq 0.75$. Domain theory predicts the average wall area in a grain to be proportional to $(\text{diameter})^{1.5}$ (Stacey, 1963). The parameters m and n then satisfy $1.5(1-m) = n$ (Stacey and Wise, 1967), which gives $m \simeq 0.5$, implying nearly complete disordering of defects in the unannealed samples examined by Day et al. (1977). On the other hand, a lamellar domain structure, which the calculations of Butler and Banerjee (1975) suggest is applicable in this size range, gives wall area proportional to $(\text{diameter})^2$, and thus $m \simeq 0.63$. For larger grains (> 50 μm) the power-law index changes ($n \simeq 0.23$), presumably reflecting weaker dependence of domain size on grain size.

The temperature dependence of E_0 may therefore be expressed as

$$E_0(T) \propto \epsilon(T)\left[\delta(T)\right]^m \tag{25}$$

Soffel (1970), Day et al. (1976) and Tucker and O'Reilly (1980) have discussed MD coercive-force models in relation to properties of TM's at room temperature. The energy well due to a single defect, ϵ, and the coercive force h_c due to it can be related by eq. (4.27) of Stacey and Banerjee (1974, p. 73), which is equivalent to

$$\epsilon(T) \propto J_s(T)\delta(T)h_c(T) \tag{26}$$

For instance, strain models, including dislocation models, give h_c approximately proportional to λ/J_s, where λ is the isotropic magnetostriction.

Therefore

$$\epsilon(T) \propto \lambda(T)\delta(T)$$
$$E_0(T) \propto \lambda(T)[\delta(T)]^{1+m}(\text{strain}) \quad (27)$$

The temperature dependence of λ has been determined from 80 to 290 K for TM0, TM10, TM18, TM30 and TM51 by Syono (1965), and above 290 K for TM0 by Klapel and Shive (1974). We assume a linear decrease of λ above room temperature to zero at T_C, consistent with the variation found for magnetite.

The temperature dependence of the energy terms due to different types of defects and different interaction mechanisms of defects and stresses with domain walls varies greatly and, as will be shown in the next section, $E_0(T)$ may be dominated by different mechanisms at different temperatures. At each temperature $E_0(T)$ should be calculated for the various models to ascertain the dominant mechanism impeding wall motion. The value of $E_0(T)$ appropriate to this mechanism can then be used to calculate $\chi_{\parallel}$.

The observed susceptibility k_{MD} can then be calculated using the relations

$$\chi_i = \chi_{\parallel}/3 + 2\chi_{\perp}/3 \quad (28)$$
$$k_{MD} = \chi_i/(1 + N\chi_i) \quad (N \simeq 4\pi/3) \quad (29)$$

At room temperature, where the anisotropy constants are relatively small, it can be seen that the intrinsic susceptibility of the TM's considered is high, and that the observed susceptibility is controlled by self-demagnetisation ($k_{MD} \simeq 1/N$). At low temperatures, however, the very large increases in K_1 and λ for TM56 and TM68 lead to a great reduction in intrinsic susceptibility and a consequent drop in the measured susceptibility ($k_{MD} \simeq \chi_i \ll 1$).

At high temperatures the magnetisation of MD grains in an applied field will be affected by thermal fluctuations and will relax towards equilibrium with a time constant τ given by

$$\tau = (1/2f_0')\exp(E_0/kT) \quad (30)$$

The preferred value for f_0' is 10^8 Hz, which is approximately the frequency of a spin-wave of half-wavelength equal to a domain wall thickness in magnetite (Stacey and Banerjee, 1974, p. 96).

As pointed out by Dunlop (1976), E_0 can be expressed as

$$E_0 = v_{act} J_s H_c/2 \quad (31)$$

where v_{act} is the volume affected by a single thermal-activation event. In spite of the relatively low coercive force of MD grains, the activation volume is generally much larger than the grain volume of SD particles, and thus E_0, and hence T_b, is higher than for the SD case.

The observed susceptibility due to MD grains of volume v can then be expressed as

$$k_0 = k_{MD}\exp(-t/\tau) + (vJ_s^2/3kT) \times [1 - \exp(-t/\tau)] \quad (32)$$

H_c and E_0 are related (Stacey and Banerjee, 1974, p. 73) by

$$H_c = \pi E_0/(3a\delta J_s) \quad (33)$$

Therefore, from eq. (29),

$$v_{act} \simeq 2a\delta \ (T < T_b) \quad (34)$$

For an 8-μm cubic magnetite grain which contains 21 domains (Moskowitz and Banerjee, 1979), v_{act} is therefore $\sim 2 \times 10^{-5} \times (8 \times 10^{-4})^2 \simeq 1.3 \times 10^{-11}$ cm^3, which is considerably greater than the volume of a large SD grain ($\sim 4 \times 10^{-16}$ cm^3).

Calculated k–T curves for 10-μm TM grains having $x = 0.0$, 0.1, 0.18, 0.31, 0.56 and 0.68 are shown in Fig. 4. In practice, a particular coercive-force model was assumed to apply over the whole temperature range, E_0 at 290 K was calculated using eq. (33), and the k–T curve calculated for the appropriate $E_0(T)$ variation. This was done for various models and the resulting curves compared. The final curves consist of segments corresponding to the particular energy-barrier model expected to dominate in a particular temperature range, assuming realistic inclusion densities, etc. Below room temperature it was found that the choice of model made little quantitative and no qualitative difference, even when extremes in behaviour of E_0 as a function of temperature were considered. This is largely because of the behaviour of $\chi_{\perp}$, which is model-independent. Above room temperature all models give essentially the same k–T dependence except that a marked unblocking peak occurs 20–40°C below T_C for inclusion models. The presence of dislocations or stresses within a grain suppresses these peaks, since near T_C magnetostriction

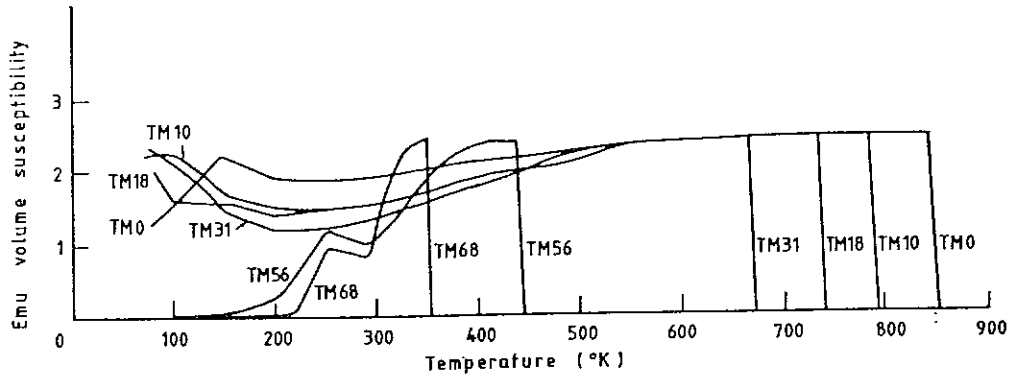

Fig. 4. Theoretical k–T curves for 10-μm MD titanomagnetite grains.

tends to zero much more slowly than K_1.

The theoretical curves in Fig. 4 correspond well with curves observed experimentally, with the exception of that for TM31 which is expected to show an increase in k at low temperatures, but which actually has lower susceptibility at 80 K (Senanayake and McElhinny, 1981; Radhakrishnamurty et al., 1981). This suggests that stress anisotropy must be important for this composition at least, and possibly for others. Rahman and Parry (1978) concluded that stress anisotropy controls the hysteresis properties of TM30, on the basis of hysteresis measurements at room temperature as a function of oxidation parameter.

TM0 exhibits the familiar susceptibility peak at the isotropic point (~ 130 K), whereas TM10 and TM20 show a gradual rise in susceptibility with decreasing temperature. TM56 and TM68, on the other hand, show a marked decrease in susceptibility at low temperatures.

Radhakrishnamurty et al. (1979) have presented an inferred k–T curve for MD TM56 which resembles a compressed version of the TM0 curve, and remarked that the inferred behaviour is never found in Nature. It can be seen from Fig. 4 that their curve, which is based on qualitative analogy, is unrealistic, because the temperature dependence of K_1 is quite different for TM0 and TM56. Because the observed susceptibility is limited by self-demagnetisation in MD grains, wherever $|K_1| \ll J_s^2$ over a temperature interval, the interval may be regarded as essentially isotropic and the "isotropic point" loses its special significance.

The fact that a double susceptibility peak is not observed experimentally suggests that K_1 varies much more slowly than $J_s^{8.5}$ for TM56 and TM68 in the vicinity of room temperature, or that around room temperature J_s varies more slowly as a function of reduced temperature T/T_c for TM56 and TM68 than for TM0. Alternatively, stress anisotropy K_s may be important for these compositions. If K_s dominates K_1 above ~ 250 K, $\chi_\perp$ will be controlled by stress anisotropy in this region and the k–T curve will be smoothed into a single-peaked form.

3. The effect of thermal agitation on high-field thermomagnetic curves

Radhakrishnamurty et al. (1979) opined that both low- and high-field thermomagnetic determinations of Curie points can be invalidated by the effects of thermal agitation on fine grains above the blocking temperature. We have seen in Section 2 that k–T curves for fine-grained titanomagnetites display a rather gradual decrease of susceptibility between T_b and T_C, which could produce uncertainty in the estimated Curie temperature, although gross underestimation is unlikely. If a significant proportion of hyperfine grains is present, high-field thermomagnetic measurements are preferable for determination of the Curie temperature, as saturation magnetisation is an intrinsic property of the magnetic mineral, whereas susceptibility is much more dependent on

grain size and structure. It remains to be shown that $M(T)$ curves for TM's in fields of several koe in fact reliably reflect $J_s(T)$.

Provided that the applied field H is much greater than the intrinsic coercive force of the grains, the fractional magnetisation of an assemblage of SD particles subject to thermal agitation is given by the Langevin function (Bean and Livingston, 1959). Therefore

$$M(T) = J_s L(vJ_s H/kT)$$
$$= J_s[\coth(vJ_s H/kT) - kT/vJ_s H] \qquad (35)$$

If $vJ_s H/kT \geq 100$, then $M(T) \geq 0.99\ J_s(T)$ and the experimental curve will correspond to $J_s(T)$ to within 1%. Substituting numerical values for magnetite, it can be seen that the effect of thermal agitation on the 5 koe $M(T)$ curve for particles with a zero-field blocking temperature of 300 K is negligible until a few degrees from the Curie temperature. In Fig. 5, $J_s(T)/J_s(0)$ and $M(T)/J_s(0)$ in 1 koe and 5 koe are plotted for hyperfine magnetite ($v = 10^{-18}$ cm^3, $T_b \ll 80$ K), and it can be seen that negligible error in T_C estimation is to be expected. Bean and Jacobs (1956) have shown experimentally that saturation magnetisation data for iron are unaffected by particle size down to less than 30 a.u.

The experimental data of Dunlop (1973, Fig. 2) illustrate this point for magnetite. The general forms of the M–T curves and the indicated Curie points are not perceptibly different for four different-sized magnetite samples ranging from ~0.23 to 0.04 μm with very different blocking-temperature spectra.

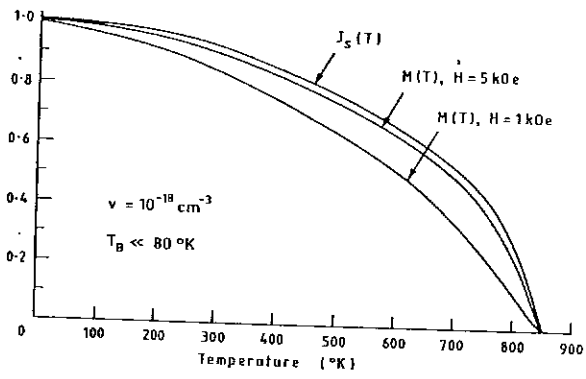

Fig. 5. Comparison of $J_s(T)/J_s(0)$ and $M(T)/J_s(0)$ for applied fields of 1 and 5 koe. The volume of the hyperfine magnetite particles is assumed to be 10^{-18} cm^3.

Most of the reported difficulties in Curie-point determination for rocks in high-field experiments, which have been discussed by Radhakrishnamurty et al. (1979), must therefore reflect chemical alteration during heating rather than grain-size effects. In some cases unambiguous measurement of Curie temperatures is rendered impossible by instability of the magnetic grains to heating, but suitable experimental techniques can often reduce these problems. It is particularly important to test thermomagnetic curves for reversibility by recooling a sample during and immediately after descent of the curve to an apparent Curie point before proceeding to higher temperatures. Moskowitz (1981) has given a technique for extrapolation of $J_s(T)$ data from below the Curie temperature to determine T_C in cases where chemical change in the vicinity of T_C precludes direct measurement.

We conclude from the above discussion that the many instances of low apparent Curie temperatures determined from $M(T)$ measurements for basalts are true Curie points reflecting high titanium content, and are not explicable in terms of SPM particles of pure or cation-deficient magnetite.

4. Low-temperature hysteresis properties of titanomagnetites

In MD grains coercive force and initial susceptibility are structure-sensitive properties. The temperature variation of these properties therefore depends on the nature of the energy barriers to domain wall motion and on how these barriers change with temperature. Theories of coercive force in bulk materials fall into two categories: strain models and inclusion models. In strain models E_0 and H_c are correlated with magnetostriction λ, and $\chi_\parallel$ is inversely correlated with λ. In inclusion models E_0 and H_c are controlled dominantly by magnetocrystalline anisotropy, and $\chi_\parallel$ is accordingly inversely correlated with K_1. The large increases in H_c observed for TM56 and TM68 at low temperatures (Radhakrishnamurty et al., 1981)

may therefore reflect the marked increases in λ and K_1 found by Syono (1965). As discussed in Section 2, the large drop in susceptibility at low temperatures found for ulvöspinel-rich titanomagnetites is associated essentially with an increase of K_1, and is not very sensitive to the temperature dependence of E_0.

Soffel (1970), Day et al. (1976) and Tucker and O'Reilly (1980) have discussed various models of coercive force in MD titanomagnetites. Dislocations appear readily able to account for the observed values of H_c for coarse-grained TM's at room temperature. The most detailed treatment of the effect of dislocations has been given by Stacey and Wise (1967). For magnetite, they found for a single edge-dislocation of length Z_0 that

$$H_c = 1.5 \times 10^4 \, (1.5 \, \lambda_{111} + 0.75 \, \lambda_{100}) Z_0 / a J_s \quad (36)$$

The numerical factors involve the rigidity and Poisson's ratio, and we here assume the same values of these parameters for all compositions.

A model which is capable of accounting for typical room-temperature values of H_c, and also for very large increases in H_c as K_1 increases, is the Kersten inclusion model (see Day et al., 1976), for which

$$H_c \simeq 5 K_1 f^{2/3} / 2 J_s \quad (37)$$

where f is the volume fraction of nonmagnetic inclusions, assumed to be arranged on a regular cubic lattice. We consider only the case for which the inclusion diameter equals the domain wall thickness, as these inclusions contribute most to H_c.

Considering eq. (37) in the case of TM68, a volume fraction of 0.06 can account for a coercive force of 90 oe at 290 K ($K_1 = 0.18 \times 10^5$ erg cm^{-3}). At 80 K ($K_1 = 120 \times 10^5$ erg cm^{-3}) the corresponding H_c would be 3×10^4 oe, assuming the same volume fraction of inclusions of the appropriate diameter. This is far larger than the observed value, suggesting that the Kersten inclusion model is not realistic at room temperature.

Néel (1946, 1949) criticised the Kersten inclusion model as physically unrealistic, providing an alternative in his dispersed-field models, which consider the effect of magnetostatic energy due to fluctuations in the direction and magnitude of J_s associated with randomly distributed stresses and inclusions. The expressions obtained are

$$H_c \simeq 0.19 \, \lambda^2 s^2 f' \left[1.39 + \log\left(1 + 2\pi J_s^2 / |K_1|\right)^{1/2} \right] / |K_1| J_s \quad (3\lambda s/2 \ll |K_1|) \quad \text{(strain)} \quad (38)$$

$$H_c \simeq 1.04 \, \lambda s f' \left[1.39 + \log\left(1 + 4.5 J_s^2 / \lambda s\right)^{1/2} \right] / J_s \quad (3\lambda s/2 \gg |K_1|) \quad \text{(strain)} \quad (39)$$

$$H_c \simeq 2 |K_1| f \left[0.39 + \log\left(1 + 2\pi J_s^2 / |K_1|\right)^{1/2} \right] / \pi J_s \quad \text{(inclusions)} \quad (40)$$

where f' is the volume fraction affected by stress variations of magnitude s, and f is the volume fraction of inclusions.

The logarithmic terms in eqs. (38)–(40) differ slightly from the final equations derived by Néel (1946) in that, for the cases considered by him, the arguments of the logarithms are much greater than unity and the additive term of unity could be neglected. We require the more general form.

The order of magnitude of the numerical terms in these equations is not significantly affected by the different approximations applicable to iron and nickel, on the one hand, and TM's on the other.

Theoretical values of H_c at 290 and 80 K are given in Table I for the dislocation model, and the strain and inclusion models of Néel. It is assumed that five (ordered) dislocations act simultaneously on a domain wall of area $(10 \, \mu\text{m})^2$, $f' = 0.1$, $f = 0.02$, and $s = 10^9$ dyn cm^{-2}. The dislocation density assumed is that observed by Soffel (1970) for naturally occurring TM65. Dislocations can account for the observed H_c of ~TM60 at room temperature, but a systematic variation of dislocation density with composition is required to explain the composition independence of H_c. If the dislocations are disordered the dislocation densities required to account for a coercive force of 90 oe are $\sim 8 \times 10^8$ cm^{-2} for TM0 and $\sim 10^7$ cm^{-2} for TM56, which are entirely feasible.

It can be seen from Table I that the mechanism dominating the room-temperature coercive force is

TABLE I

Coercive force (oe) of 10-μm MD grains ($T=80$ and 290 K)

x	Dislocations (density $=5\times10^6$ cm^{-2})	Dispersed-field models	
		Strain ($s=10^9$ dyn cm^{-2}; $f'=0.1$)	Inclusions ($f=0.02$)
290 K			
0.0	16	1	6
0.1	26	1	9
0.18	39	4	14
0.31	50	6	8
0.56	132	160	6
0.68	–	–	3
80 K			
0.0	8	0.1	11
0.1	5	1	2
0.18	43	72	4
0.31	85	128	1
0.56	458	9	189
0.68	–	–	428

not necessarily dominant at low temperatures. For instance, internal stresses may make a negligible contribution to H_c for TM31 at 290 K, but may contribute significantly at 80 K.

In the case of TM56, inclusions as well as dislocations may account for the large coercive force at 80 K. For TM68, magnetostriction is expected to be very large at low temperatures and therefore dislocations will probably be important, but inclusions will probably make a major contribution to H_c. As an illustration, we consider the case of TM56 in detail. If the contribution to room-temperature H_c from dislocations is 78 oe and from inclusions 12 oe, at 80 K the respective contributions will be 271 oe and 378 oe, or a total of 649 oe. Tucker (1981) calculated H_c for MD TM56 using a slightly different model, and obtained similar values. It should be noted that the calculated contributions from dislocations and inclusions to H_c of TM56 and TM68 at 80 K are minimum estimates, as the values of K_1 and λ determined by Syono (1965) are undersaturated. Any tendency for inclusions to be ordered will also significantly increase the contribution to H_c.

We therefore conclude that the very high coercive forces at low temperatures exhibited by TM's having $x>0.5$ are not diagnostic of the SD state and are readily explicable on the basis of MD structure, taking into account the large increases in K_1 and λ at low temperatures shown by these compositions. This is in agreement with the conclusions of Tucker (1981).

For these compositions small MD grains will also become SD at low temperatures owing to the increase in d_0. For instance, 4-μm cubic grains of $\sim$TM60 will be pseudo-single-domain (PSD) at 290 K, but true SD at 80 K, and consequently will be magnetically harder.

The fundamental explanation for the remarkable temperature dependence of the magnetocrystalline anisotropy of TM's is not yet fully apparent, but a plausible mechanism based on the unusual cation distribution in TM's has been suggested (Banerjee and O'Reilly, 1966; Banerjee et al., 1967; Fletcher and O'Reilly, 1974). With increasing titanium substitution, additional ferrous ions occupy tetrahedral sites, imposing an additional trigonal distortion on the geometry of the octahedral ferrous ions, which results in unquenched orbital angular momentum and a large, highly temperature-sensitive, anisotropy.

The high coercive force of MD grains will pro-

duce wide hysteresis loops with necessarily high relative remanence. It follows from the self-demagnetisation of MD grains that $J_{rs} \simeq H_c/N$ (Néel, 1955). In the limit of very high H_c, J_{rs} approaches the appropriate value for SD grains. It also follows from the relationship between external applied field and internal field for MD grains that $H_{cr} \simeq H_c (1 + N\chi_i)$ (Stacey and Banerjee, 1974, p. 82). Therefore at low temperatures, where χ_i is very small for TM56 and TM68, these compositions will have H_{cr}/H_c ratios close to unity. Thus the empirical relationships between hysteresis parameters which are diagnostic of domain state at room temperature should not be extrapolated to low temperatures. Hysteresis loops of ulvöspinel-rich TM's at low temperatures exhibit high H_c, high J_{rs}/J_s and low H_{cr}/H_c (Banerjee and O'Reilly, 1966; Radhakrishnamurty et al., 1981), but these features are compatible with MD grain structure when the effect of high magnetocrystalline anisotropy on H_c and χ_i is taken into account.

5. Domain structure in titanomagnetites

Radhakrishnamurty and co-workers have expressed the view that the coarse-grained optically homogeneous ~TM60 grains typically found in basalts do not exhibit MD behaviour and that synthetic TM's having $x \geq 0.3$ cannot form MD structures (Radhakrishnamurty et al., 1979, 1981). Further, they reject the applicability of the generally accepted titanomagnetite solid-solution series to the magnetic properties of basalts, suggesting that ulvöspinel-rich TM's break down over a geologically short time to produce very fine magnetite particles within the large TM grains, accounting for the SD and SPM behaviour which they interpret from their thermomagnetic and hysteresis measurements for a large number of basalt samples.

Wohlfarth (1977) has pointed out the similarity between the k–T curves associated with basalts containing ulvöspinel-rich TM's and those of spin glasses. Radhakrishnamurty and Nanadikar (1979) and Radhakrishnamurty et al. (1980) have suggested that the presence of titanium inhibits the formation of domain walls in TM's and that statistical fluctuations in composition produce monodomain regions or spin clusters irrespective of the grain size.

We have seen in the previous Sections, however, that the thermomagnetic and hysteresis properties of basalts containing large TM grains can be explained on the basis of the MD model and that alternative explanations involving exotic physical behaviour are probably unnecessary. It remains to assess the positive evidence in favour of the existence of domain walls in TM's.

The most direct evidence for MD structure in titaniferous compositions is provided by the observations of Soffel (1971). Using the Bitter-pattern technique on TM55 grains in two basalts he observed domain structures, domain wall movement in an applied field, and a systematic variation of domain number with grain size, allowing an empirical estimate of the critical SD diameter which was in reasonable agreement with theory.

Indirect evidence of MD structure is afforded by the dependence of coercive force on grain size in the sized synthetic TM samples ($x = 0.0$, 0.2, 0.4, 0.6) examined by Day et al. (1977). If TM60 grains consist of SD and SPM spin clusters the coercive force should be essentially independent of grain size, whereas the observed inverse correlation of coercive force and grain diameter follows explicitly from the MD model. Furthermore the room-temperature hysteresis parameters for small TM grains (< 1 μm) produced by wet-grinding clearly demonstrate that no significant SPM component can be present, particularly for $x \geq 0.3$. For these compositions $H_c \geq 700$ oe, $J_{rs}/J_s \geq 0.5$, and $H_{cr}/H_c \leq 1.3$. Therefore no SPM component could be expected in even larger grains, and the low coercive force and relative remanence must be attributed to nonuniform magnetisation of grains due to the formation of domain walls. The relationships between the hysteresis parameters ($J_{rs}/J_s = H_c/NJ_s$, and $H_{cr} = H_c(1 + N\chi_i)$) predicted by MD theory are in very good agreement with the experimental data at room temperature and, as has been seen in the previous Section, are also compatible with the low-temperature data of Banerjee and O'Reilly (1966) and Radhakrishnamurty et al. (1981).

On the basis of the model of Néel (1955),

Deutsch and Pätzold (1976) have shown that MD grains cannot explain the prominent Rayleigh loops they observed on many basalt samples in 10 oe. They found BH_c/A ratios of typically 1.25 (A and B are the reversible and irreversible susceptibilities, respectively), whereas a maximum value of this ratio for MD grains should be ~ 0.06. However, as was shown in Section 2, a very small fraction of SPM particles may contribute significantly to the low-field susceptibility but have negligible effects on the high-field properties and thermoremanence, as all the magnetic grains contribute to these latter properties, with stable grains dominating. Rayleigh loops in low fields are diagnostic of the presence of a small fraction of SPM particles, which is of intrinsic interest, but do not reflect properties representative of the bulk of the magnetic grains in a rock.

Overall the MD model seems well established, requiring the k–T curve classification scheme of Radhakrishnamurty and Deutsch (1974) and Radhakrishnamurty et al. (1977, 1978) to be re-assessed. The large experimental data set on which these classification schemes are based is a very useful contribution to our knowledge of the magnetic properties of basalts and other rock types, but only if the data can be interpreted correctly. We propose, in agreement with Senanayake and McElhinny (1981), that the k–T curves classified as SP-type and SD-type in these schemes in fact represent titaniferous magnetites having Curie temperatures ≤ 400°C. Senanayake and McElhinny (1981) have demonstrated that CD-type curves are often associated with large titanomagnetite grains containing many exsolved ilmenite lamellae, and have given a theoretical explanation of the low-temperature k–T behaviour on this basis. It appears well established, on the other hand, that the MD-type curves do represent MD nontitaniferous magnetite. As can be seen from the data of Radhakrishnamurty et al. (1981), the compositions TM10 and TM20 also show an increase of susceptibility at low temperatures, and may in some cases be responsible for CD-type curves. However, $k(80)/k(290)$ ratios greater than ~ 1.6 require alternative explanations. Radhakrishnamurty et al. (1978) have found cases of basalts having $k(80)/k(290)$ much greater than 1.6, up to 4 or 5, and suggest that they are due to hyperfine particles denoted SP*, which are SPM at liquid-nitrogen temperature. The results of Section 2 suggest that SP* grains may also be small SD grains which are stable in a temperature region above 80 K, but have isotropic points, close to which they unblock, in the vicinity of 80 K. A small fraction of such grains could account for SP*-type behaviour. This possibility is supported by our observations of Rayleigh loops for rocks which have well-defined susceptibility peaks at ~ 130 K (MD-type curves of Radhakrishnamurty and Deutsch (1974); group 3 curves of Senanayake and McElhinny (1981)). At the isotropic point an opening-out of the Rayleigh loop is frequently observed, in many cases where no loop is perceptible either below 130 K or at room temperature. The most likely explanation for this behaviour is the unblocking of a small fraction of equant SD or small MD grains in the region where K_1 is very small and the SPM threshold size becomes large.

Finally, we consider the stability of ulvöspinel-rich TM's over geological time. Radhakrishnamurty et al. (1979) reported a single instance of SD titanomagnetite in a very young (< 30000 years) pillow basalt. The characteristic properties of this sample are SD hysteresis characteristics and no low-field hysteresis at 290 K; low susceptibility at 80 K rising to a peak just above room temperature; and $T_C \simeq 200$°C. The Woy Woy basalt (40 My) from New South Wales and the Bunbury basalt (minimum age 100 My) from Western Australia exhibit very similar behaviour, suggesting that compositions approximating TM60 are stable for geologically long times.

6. Conclusions

(a) The thermomagnetic and hysteresis properties of coarse-grained titanomagnetites of all compositions are consistent with multidomain structure. The high coercive force and relative remanence of titanomagnetites having $x > 0.5$ at low temperatures can be explained on the basis of the interaction of domain walls with crystal defects when the large increases in magnetocrystalline anisotropy and magnetostriction with decreasing tem-

perature for these compositions are taken into consideration. The empirical relationships which characterise multidomain titanomagnetites at room temperature ($H_c < 100$ oe, $J_{rs}/J_s \leq 0.1$, $H_{cr}/H_c \simeq 5$) are not applicable at low temperatures.

(b) Curie temperatures deduced from both low- and high-field thermomagnetic measurements on titanomagnetite-bearing rocks in general reflect an intrinsic property of the magnetic minerals, rather than the effect of thermal agitation on fine particles having low blocking temperatures.

(c) Single-domain grains of composition approximating TM60 are not confined to very young rocks. Ulvöspinel-rich titanomagnetites are certainly stable for at least 100 million years.

(d) Fine titanomagnetite grains may have more than one blocking temperature. In any temperature interval in which superparamagnetic grains are present they will disproportionately influence susceptibility and low-field hysteresis.

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