Geophys. J. R. astr. Soc. (1985) **83**, 731–751

Step-wise and continuous thermal demagnetization and theories of thermoremanence

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Accepted 1985 April 19. Received 1985 March 25; in original form 1984 November 12

Summary. The difference between step-wise and continuous thermal demagnetization of rock specimens is examined with particular reference to the presence of multi-component magnetizations. The effect of the thermal dependence of the intensity of spontaneous magnetization is clearly evident in recordings of continuous demagnetization when a least-squares analysis of a two component system is performed. The differences between spontaneous magnetization, saturation magnetization and high-field magnetization are discussed and it is shown that the normalized thermal dependence of spontaneous magnetization can be determined with negligible error by measuring magnetization as a function of temperature in sufficiently high fields (> 0.1 T for magnetite, > 1 T for pyrrhotite). Using experimentally determined thermal dependence of high-field magnetization to correct the continuously observed intensities leads to analyses comparable to those of step-wise demagnetization data. Experiments designed to compare the temperature dependence of an apparent spontaneous magnetization, derived from the observed thermal decay of saturation remanence carried by a multi-domain (MD) magnetite bearing sample, with the true spontaneous magnetization of magnetite reveal a systematic difference, with the apparent spontaneous magnetization decreasing more rapidly than the true spontaneous magnetization. This difference is minor, however, compared to the thermal decay of spontaneous magnetization and to a first-order approximation the use of the thermal decay of saturation magnetization to correct intensities should usually be adequate. Similar conclusions are supported by experiments with MD pyrrhotite bearing samples. These experiments serve to constrain models of MD remanence.

The approximate proportionality of blocked remanence (TRM and saturation remanence) to spontaneous magnetization which is observed for these samples, which contain predominantly MD grains, resembles the behaviour expected for non-interacting single domain (SD) grains. Conventional MD theories assume that domain structure remains stable below the blocking temperature and attribute remanence carried by MD grains to Barkhausen discreteness of domain wall positions. However, if the domain multiplicity does not change with temperature, remanence due to Bark-

hausen moments should exhibit very strong temperature dependence below the blocking temperature, with significant departures from proportionality to spontaneous magnetization, when the reversible movement of domain walls in response to the self-demagnetizing field is taken into account. Published experimental results show that partial TRM of assemblages of large magnetite grains exhibit anomalous behaviour, reflecting domain structure readjustment, during initial cooling. Furthermore, isothermal application of a moderate field preferentially activates true MD Barkhausen moments and the resulting remanence is found not to vary proportionally to spontaneous magnetization. This evidence suggests that Barkhausen moments, which show anomalous temperature dependence, make a negligible contribution to the TRM and saturation remanence of our samples.

We propose that TRM and saturation remanence of assemblages containing MD grains is predominantly carried by a fraction of metastable nucleation-controlled SD grains and by MD grains of anomalously low domain multiplicity with undemagnetizable moments. According to this hypothesis the PSD moments are independent of MD processes because they are associated with distinct grains. The spontaneous moments of the MD grains reflect equilibrium domain wall positions, in the absence of pinning, for grains with an odd number of domains and for irregular grains with an even, but asymmetrically disposed, number of domains. Provided the domain walls are compressed relative to their equilibrium width in bulk material, a condition which is favoured if the grain occupies a local energy minimum state with fewer than the equilibrium number of domains, such domain structures are very stable to temperature change. Below the unblocking temperature remanence carried by such grains is proportional to the spontaneous magnetization. Unblocking of remanence carried by these grains occurs upon nucleation of a new domain wall.

Key words: multidomains, pseudo-single domains, spontaneous magnetization, thermal demagnetization, TRM.

1 Introduction

In palaeomagnetic and rock magnetic studies two thermal demagnetization techniques are in common usage: the progressive or step-wise method (Irving *et al.* 1961; Stephenson 1967) and the continuous or dynamic method (Creer 1967). The basic difference between the two methods is the temperature at which the measurement of magnetization is made. With the former the measurements are made at room temperature, the furnace and magnetometer being separate pieces of equipment, while with the latter the measurements are made while the rock specimen is actually heating and the furnace and magnetometer are integrated.

The advantage that step-wise heating has over continuous heating is the ability to heat many specimens simultaneously which accounts for its greater general popularity. When greater detail of magnetic components is required it is desirable to perform measurements at many temperatures, favouring continuous heating as the most effective method, particularly since the advent of three-axis cryogenic magnetometers enhances the potential for routine application of continuous demagnetization. With continuous heating there is the additional bonus of reducing the possibility of spurious magnetizations that may affect the measurements, thus this method may also be the most appropriate when dealing with magnetically viscous materials. Other advantages of the continuous thermal demagnetization method

include the capability of observing self-reversed remanence components and studying screening effects produced by a high permeability matrix of relatively low Curie temperature surrounding an inclusion with a high Curie temperature (Rahman & Parry 1975; Stephenson 1975; Veitch 1980; Hartstra 1982). The purpose of the present work is to compare the two heating methods discussed above, particularly when multiple components of remanence are present.

For simplicity we consider only the case when the remanence components are carried by a single magnetic mineral. The intensity of magnetic remanence is a function of temperature. Below the unblocking temperature, T_B, the remanent intensity varies essentially reversibly with the spontaneous magnetization, J_{sp}. Above T_B the remanence is irreversibly destroyed, so that during thermal demagnetization to temperature T of a rock specimen containing grains with a range of unblocking temperatures the remanence of all grains with $T_B < T$ is eliminated. If continuous demagnetization is being carried out the residual remanence $J_r(T)$ due to grains with $T_B > T$ is measured. In stepwise demagnetization the residual remanence changes along with the spontaneous magnetization as the specimen is cooled to room temperature T_o (normally the intensity increases with decreasing temperature, but this is not true of all magnetic substances). Provided the remanence remains proportional to spontaneous magnetization, as is assumed in most theories of thermoremanent magnetization (TRM), the measured remanence is then $J_r(T)[J_{sp}(T_o)/J_{sp}(T)]$.

When the form of $J_{sp}(T)$ is known for the magnetic mineral concerned it is therefore possible to convert the remanence measured during continuous demagnetization to that which would have been obtained by step-wise demagnetization and vice versa. To determine the feasibility of this approach, demagnetization experiments using both the step-wise and the continuous thermal methods have been carried out with well-characterized rock specimens.

2 Determination of spontaneous magnetization

The quantum-corrected molecular field theory of spontaneous magnetization in a ferromagnetic substance with independent electron spins, as discussed by Stacey & Banerjee (1974, chapter 1), is adequate for the present purpose. Below the Curie temperature, T_C, there is an ordered arrangement of electron spins which produces a spontaneous magnetization, even in the absence of an applied field. In this case the alignment of spins is attributed to the molecular or exchange field $H_{ex} = \lambda J_{sp}$, where λ is the molecular field coefficient and J_{sp} is the magnetization within each uniformly magnetized magnetic domain. The intrinsic magnetization, J, within a domain is a function of the applied field H as well as the absolute temperature T, so that $J = J(H, T)$. By definition, $J_{sp}(T) = J(0, T)$.

$J(H, T)$ satisfies the equation (Stacey & Banerjee 1974, p. 6).

$$J(H, T)/J(H, 0) = \tanh\{\mu[H + \lambda J(H, T)]/kT\} \quad (1)$$

where $J(H, 0) = J(0, 0)$ is the spontaneous magnetization at absolute zero, μ is the electron spin moment and k is Boltzmann's constant. The tanh function in (1) is the Brillouin function for spin 1/2. For the case where the atomic magnetic moments correspond to several coupled electron spin moments, together with orbital contributions, μ represents the effective atomic moment and the tanh function must be replaced by the Brillouin function corresponding to the appropriate total angular momentum quantum number.

An expression for the spontaneous magnetization is obtained by setting $H = 0$ in (1) and rearranging

$$J_{sp}(T)/J_{sp}(0) = \tanh[T_C J_{sp}(T)/TJ_{sp}(0)] \quad (2)$$

where T_C is given by

$$T_C = \mu\lambda J_{sp}(0)/k. \tag{3}$$

Except for notation, equation (2) is equation (1.23) of Stacey & Banerjee (1974).

If the Curie temperature of a ferromagnetic substance is known, the temperature dependence of spontaneous magnetization can be obtained by solving (2) numerically or graphically for $J_{sp}(T)/J_{sp}(0)$. $J_{sp}(T)$ decreases smoothly with increasing temperature due to thermal agitation, which increasingly disrupts the spin alignment, until the spontaneous magnetization disappears at T_C.

In ferrimagnetic substances, such as titanomagnetites and monoclinic pyrrhotite, the spontaneous magnetization of each spin sublattice decreases with increasing temperature analogously to the ferromagnetic case. However the thermal decay of J_{sp} may occur at different rates for each sublattice, leading to a complicated behaviour of the net spontaneous magnetization. As an extreme case the spontaneous magnetization of an N-type ferrite passes through zero and reverses its direction at a compensation point below T_C (Néel 1955).

Rather than calculating spontaneous magnetization curves the usual procedure is to determine $J_{sp}(T)$ experimentally by measuring the high-field magnetization as a function of temperature. Fig. 1 shows such a high-field thermomagnetic curve for magnetite (Pauthenet & Bochirol 1951). The field must be sufficiently large to remove the domain structure and to rotate the grain magnetic moments into the applied field direction. Fields of 0.1–1 T are generally used.

In this context the terms 'saturation magnetization' and 'spontaneous magnetization' are often used interchangeably and are assumed to correspond to the measured high-field magnetization $M(H, T)$. This is not strictly valid, firstly because of the field dependence of the intrinsic magnetization $J(H, T)$ which is evident from (1) and secondly because of incomplete saturation. The true saturation magnetization $J_{sat}(T)$ must be obtained by extrapolation of $M(H, T)$ to $H = \infty$, provided correction for the increase of $J(H, T)$ over the spontaneous value is made.

Well below T_C the exchange field is of the order of 10^3 T. In this case an applied field of ~1 T represents a very small perturbation of the exchange field, so that the true saturation magnetization very closely approximates the spontaneous ($H = 0$) magnetization. According to Morrish (1965, p. 266) the difference between saturation and spontaneous magnetization

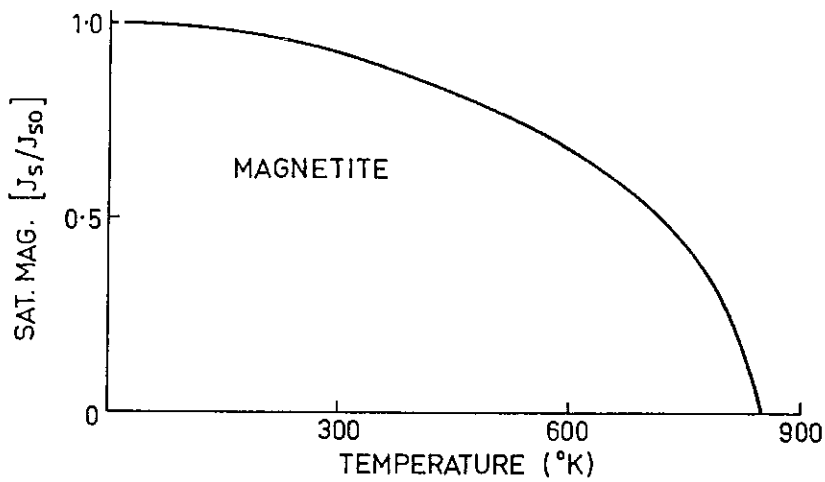

Figure 1. The thermal dependence of saturation magnetization (from Pauthenet & Bochirol 1951).

is negligible for $T < 0.8\ T_C$. As the Curie temperature is approached H_{ex} decreases rapidly until it is comparable with H. The spontaneous magnetization is then significantly perturbed by the applied field and in these circumstances there is a clear distinction between saturation and spontaneous magnetization, although the difference is only of the order of 1 per cent until a few degrees below T_C (Morrish 1965).

Above the Curie temperature the material becomes paramagnetic, the spontaneous magnetization is zero, whereas the high-field magnetization is non-zero (due to the positive susceptibility) but shows little tendency to saturate as H is increased. Thus for $T > T_C$ the differences between J_{sp}, J_{sat} and M are marked.

It is found empirically that for $T < T_C$ the high-field magnetization is given by

$$M(H, T) = J_{sat}\,(1 - a/H - b/H^2) + cH \tag{4}$$

where a/H is a small term which is generally attributed to crystal defects and is hereafter neglected. The presence of some superparamagnetic particles could also produce a term of this form. The b/H^2 term represents the approach to saturation due to rotation of grain moments against anisotopy and cH represents the pertubation of the spontaneous magnetization by the applied field (Chikazumi & Charap 1978, chapter 13).

For a mineral with cubic anisotopy, b in (4) is given by

$$b \cong 0.0762\ K_1^2 / J_{sp}^2 \tag{5}$$

where K_1 is the first magnetocrystalline anisotropy constant. Substituting the values for K_1 and J_{sp} from table 3.1 of Stacey & Banerjee (1974) into (5) gives $b = 6.1 \times 10^{-5}\ T^2$ for magnetite at room temperature. Thus for an applied field of 0.1 T we can expect an undersaturation of only 0.6 per cent at room temperature, and even less at higher temperatures because K_1 decreases more rapidly than J_{sp} as $T \to T_C$.

Clark (1983) obtained an empirical value for b of $6 \times 10^{-2}\ T^2$ for monoclinic pyrrhotite, implying undersaturation of 6 per cent for an applied field of 1 T.

We conclude that thermomagnetic curves in fields of 0.1–1 T for magnetite-bearing rocks represent the temperature variation of spontaneous magnetization with neglible error, except possibly within a few degrees of T_C. Stronger fields are required to saturate pyrrhotite-bearing rocks, but the relative temperature variation $(M(T)/M(T_o))$ is less seriously affected by undersaturation than the absolute variation, except close to the Curie point.

3 Equipment

For step-wise thermal demagnetization a Schonstedt TSD-1 low-field furnace was used for heating and cooling specimens, while a DIGICO flux-gate spinner magnetometer was used for remanence measurements. This latter instrument is fitted with a high temperature attachment which is used for the continuous thermal demagnetization experiments. Users familiar with this apparatus will also recognize the difficulties inherent in measuring full vector magnetizations at high temperatures with what is basically a single component sensor. While two orthogonal components are recovered by spinning the rock specimen about an axis perpendicular (vertical) to the flux-gate, the third component is only sensed by rotating the rock specimen about another axis, in the plane perpendicular to the spinning axis. At ambient temperatures this latter requirement presents no difficulty, but at elevated temperatures the specimen can not be handled and as it is not desirable to interrupt the heating process the continuous method requires a remotely controlled action. The DIGICO capstan arrangement designed to perform this task works well until moderately high temperatures ($> 450^\circ C$), at which point increases in friction (due to oxidation of the

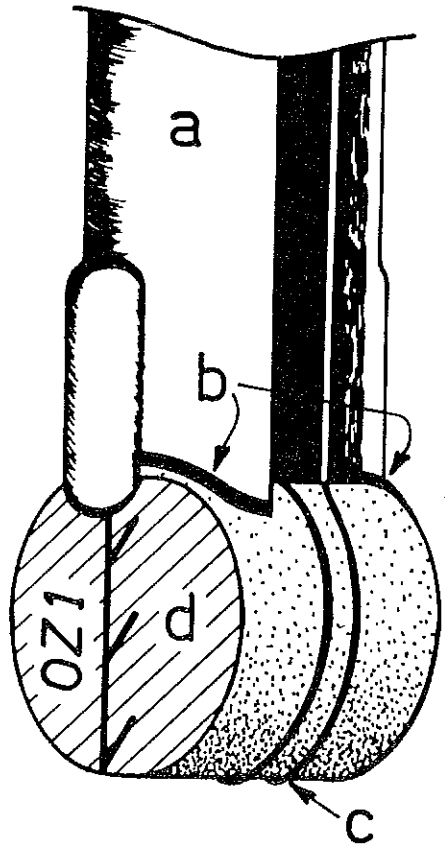

Figure 2. Schematic diagram depicting the rotation mechanism of the DIGICO high-temperature rig, with modified bearing surfaces: (a) main shaft, (b) molybdenite bearings, (c) capstan string and (d) rock specimen.

graphite used as a lubricant) renders rotations inaccurate and unrepeatable, and the silica string used often breaks. Some workers (Heiniger & Heller 1976) have greatly improved this system but not without expending considerable effort. A simpler implementation providing ease of rotation at high temperatures (> 600°C) is to substitute molybdenite for graphite, which oxidizes more slowly. It was found that if thin slivers of molybdenite were fixed to the bearing surface (Fig. 2 using a high temperature cement such as AUTOSTIC – Carlton Brown and Partners, Tamworth, Staffordshire, UK) in excess of 20 high temperature runs were possible before replenishment of the bearing surfaces was necessary.

4 Spontaneous magnetism decay and multi-component remanences

When a single component of remanence is present in a rock sample (probably reflecting a single event in the history of the rock such as its original formation or a complete remagnetization episode at some later time) the direction of the remanence vector remains constant and only the magnitude changes during the demagnetization process. The magnitude of the magnetization will decrease faster with increasing temperature on continuous demagnetization than it will on step-wise demagnetization. This would normally be of no consequence since most palaeomagnetic investigations are only concerned with determining the direction of the remanence vector. However, if two (or more) remanence components are present (possibly some portion of an initial component plus a partial overprint) such that the angle between them is large, as is often the case, then the thermal decay of spontaneous magnetization (e.g. Fig. 1) must be considered when estimating the direction

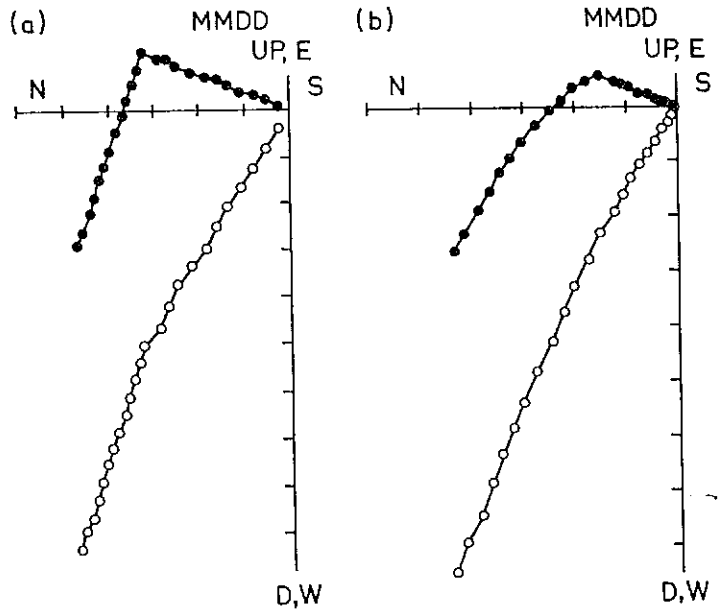

Figure 3. Hypothetical orthogonal demagnetization plots for: (a) a rock specimen possessing two components of magnetization and (b) the expected appearance of the data displayed in (a) with intensity decay of spontaneous magnetization resulting from observation at elevated temperature. Axes are arbitrary although by convention closed symbols refer to the horizontal plane while open, vice versa.

of magnetization of the overprint component. Fig. 3(a) represents an orthogonal plot (Zijderveld 1967) of the magnetization vector during the step-wise thermal demagnetization of a hypothetical two component system with adjacent, non-overlapping, uniform unblocking temperature spectra. The directions of the components were chosen to emphasize the above point, i.e. the angle between the components is fairly large (55°). Fig. 3(b) is a transformation of the plot shown in Fig. 3(a) using the spontaneous decay curve shown in Fig. 1, thus simulating continuous thermal demagnetization. The two plots are clearly different. Ordinarily there would not appear to be too much of a problem fitting a least-squares line (Kirschvink 1980) to the overprint component in Fig. 3(b), not withstanding the slight curvature as the break-point is approached. The direction of this component is dec = 307°, inc = 54°, using a maximum angular deviation of 2° (Kirschvink 1980). However, a least-squares line similarly fitted to the overprint component depicted in Fig. 3(a) yields a significantly different (by 14°) direction of dec = 290°, inc = 45° (which is the true direction). Thus from a theoretical stand-point the effect of the decay of spontaneous magnetization is of considerable importance in continuous thermal demagnetization studies of multi-component remanence.

To determine the effect of the decay of spontaneous magnetization upon the continuous thermal demagnetization of rock specimens the above simulated experiments have been performed on three specimens of the Milton Monzonite, which has been shown to possess practically pure magnetite with MD structure (Schmidt & Embleton 1981) and is therefore representative of many rock types. The Milton Monzonite has a broad range of unblocking temperatures, from < 200 to 580°C, and bears a natural remanent magnetization consisting of a primary TRM overprinted by an ancient viscous PTRM. Thermomagnetic curves of Milton Monzonite samples heated in air are completely reversible, indicating that chemical alteration of the magnetic carriers in this rock is minimal during laboratory heating to > 600°C. Remanent magnetizations were impressed on specimens which had been through several heating cycles, thereby ensuring they were stabilized against thermally-induced

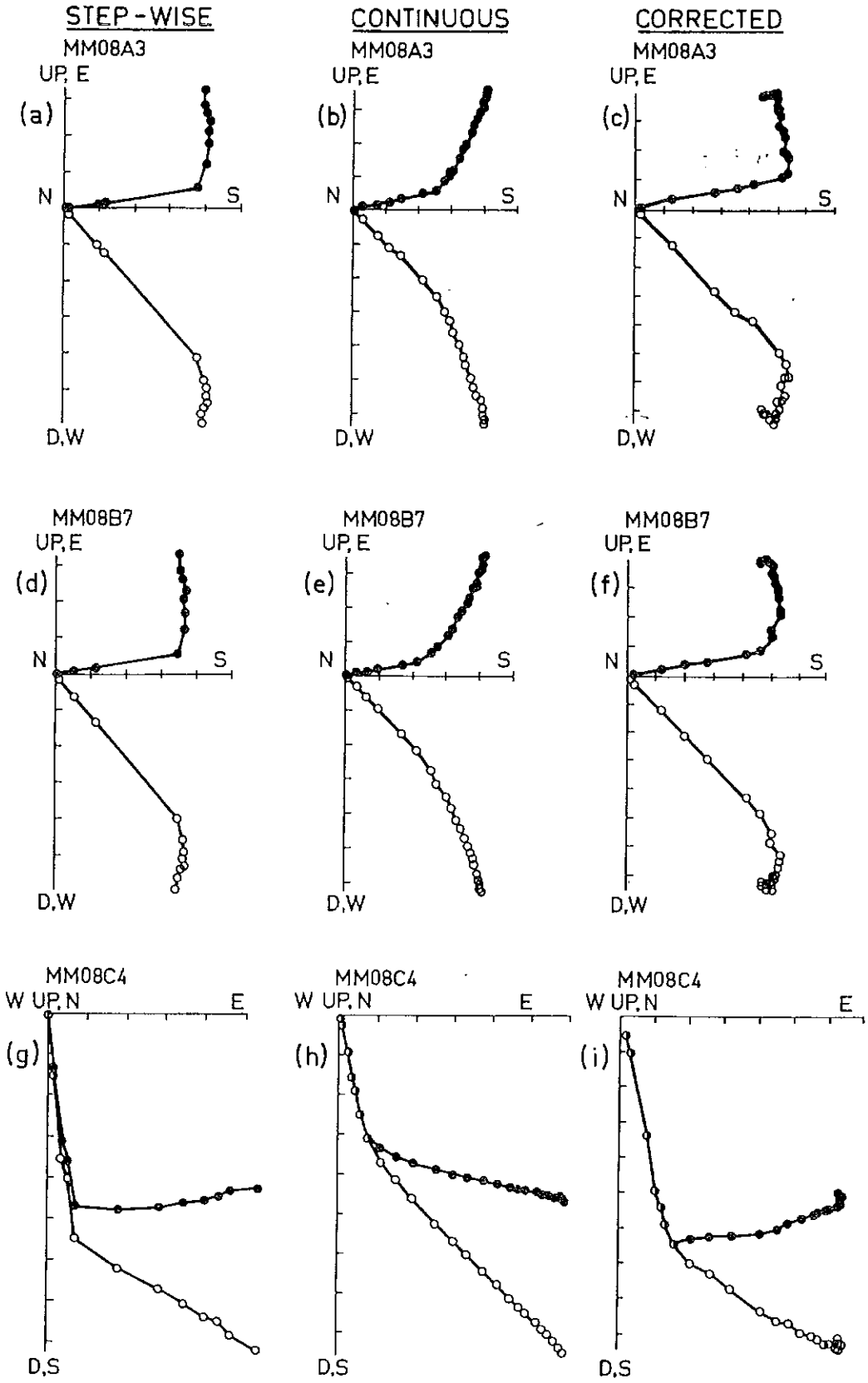

Figure 4. Orthogonal demagnetization plots for three specimens of Milton Monzonite containing practically pure magnetite carrying two artificial PTRMs. The figures are arranged such that each row pertains to the same specimen while each column pertains to the same treatment. The specimen mnemonics are labelled while the treatments are, column 1 – stepwise thermal demagnetization (steps of 50C° from 150 to 450°C then 25 to 550 and 560°C), column 2 – continuous thermal demagnetization (steps of approximately 20 to 500°C then of 10 to 550°C), column 3 – column 2 corrected according to Fig. 1 for intensity decay due to observation at elevated temperature, cf. column 1.

chemical changes. The specimens were first given a total thermal remanent magnetization (TRM) followed by a partial TRM in the vertical component of the ambient geomagnetic field. The difference in the direction of the total and partial TRMs was controlled by altering the orientation of the specimens. Each specimen was step-wise demagnetized using temperature increments of 50°C from 150 to 450°C, then 25 to 550°C and 10 to 580°C. The specimens were then remagnetized using the same conditions as those described above and continuously demagnetized using temperature increments of between 10 and 25°C depending upon the rate of change of magnetization, the smaller increments applying as the temperature increased towards the Curie temperature. Each continuous thermal demagnetization run took about 60 min at a heating rate of about 10°C min^{-1}. The resulting components plotted in Fig. 4 have been rotated for convenience of display.

The general appearance of the orthogonal plots representing step-wise and continuous demagnetization data derived from the same specimen in Fig. 4, is evidently similar to their equivalents depicted in Fig. 3. Fig. 4(a, d, g) represents step-wise demagnetization while Fig. 4(b, e, h) represents continuous demagnetization. The premature intensity decay during continuous demagnetization and curvature of overprints, as compared to step-wise demagnetization, is confirmed by experiment. Also shown in Fig. 4(c, f, i) are orthogonal plots of the continuous demagnetization data corrected using the relationship shown in Fig. 1. The resemblance of these plots with those representing the stepwise data (Fig. 4a, d, g) is also evident, confirming the fundamental validity of correcting for the decay of the variation of spontaneous magnetization with temperature. It is of interest, however, to note some artefacts of this procedure. During the initial heating period of continuous demagnetization (to about 120°C) an appreciable temperature gradient through the rock specimen is apparent. When correcting for magnetization according to theory, this produces a spurious

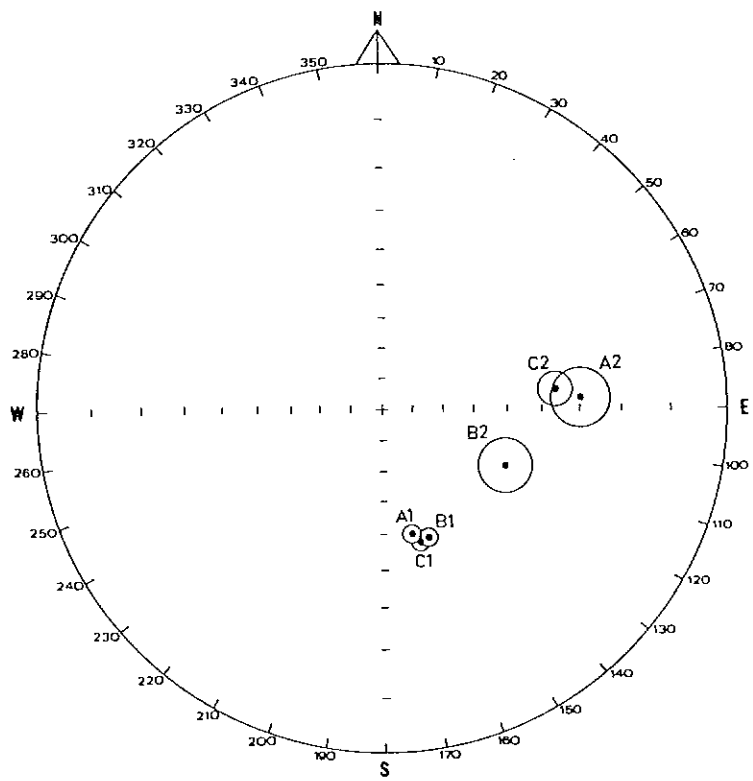

Figure 5. Equal-angle projection of mean directions and their cones of confidence derived from data plotted in Fig. 4 by fitting least-squares lines. A, B and C refer to step-wise, continuous and corrected data while 1 and 2 refer to high and low temperatures respectively.

increase in intensity at the low temperature end of the orthogonal plots Fig. 4(c, f, i). This could obviously be overcome by slowing the initial heating rate. Nevertheless the overall aim to determine the validity of applying a correction for temperature dependence of spontaneous magnetization has been achieved. Fig. 5 shows the agreement between the step-wise and the corrected demagnetization overprint (A2 and C2 in Fig. 5) directions, as opposed to the continuous demagnetization overprint direction (B2), and the general accord of all three directions of the initial magnetization (A1, B1 and C1). The minor residual variations between the directions derived from the different data sets can be attributed to the errors associated with the physical alignment of specimens during inducing the laboratory TRMs.

5 Thermal decay of remanence and spontaneous magnetization

In Section 4 the correction of continuous thermal demagnetization data to derive results equivalent to those obtained from step-wise demagnetization rested on the assumption that blocked remanence of a grain is proportional to the spontaneous magnetization. The successful recovery of the true remanence components from continuous demagnetization data establishes the validity of this assumption, to a first approximation, under the given experimental conditions and demonstrates its adequacy for palaeomagnetic purposes. We now consider departures from precise proportionality of remanence and spontaneous magnetization, and discuss the implications for theories of remanence carried by MD and PSD grains.

It was established in Section 2 that the spontaneous magnetization can be well estimated (except for $T \simeq T_C$) by measuring the magnetization in a field which is sufficiently high to achieve near-perfect alignment of grain magnetizations with the applied field, but which is still negligibly small compared to the exchange field. Provided these conditions are met, we can equate the measured high-field magnetization to true spontaneous magnetization, for all practical purposes.

On the other hand, an apparent normalized spontaneous magnetization $J'_{sp}(T)/J'_{sp}(T_o)$ can be determined from the temperature dependence of residual remanence below T_B. Comparison of the temperature variation of the apparent and true spontaneous magnetizations enables various theories of remanence to be tested. Results of experimental comparisons of $J'_{sp}(T)$ and $J_{sp}(T)$ for magnetite and pyrrhotite will now be presented.

Using the continuous heating magnetometer a series of heatings and coolings was performed on a specimen of Milton Monzonite carrying a saturation remanence. Magnetization measurements were made after the temperature stabilized (> 60 min after each temperature change) and after recooling to room temperature. The temperature was increased for successive heatings, increasingly partially demagnetizing the specimen. The magnetization at a given steady temperature was compared to that measured after the specimen cooled, their ratio thereby reflecting the reversible decrease due to thermal agitation and small displacements of domain walls. This procedure is therefore equivalent to conducting continuous and step-wise demagnetization runs in tandem. The plotted data points represent $J'_{sp}(T)/J'_{sp}(T_o)$ and are compared to the measured saturation magnetization curve of the Milton Monzonite (Fig. 6). Determination of the apparent spontaneous magnetization was possible almost up to the Curie temperature because the maximum unblocking temperature in this specimen is just below T_C. Over most of the temperature range, the apparent spontaneous magnetization curve approximates the curve defined from the measured saturation magnetization very well, although there is a small but significant departure between 200 and 500°C where the apparent spontaneous magnetization decreases more rapidly than does the saturation

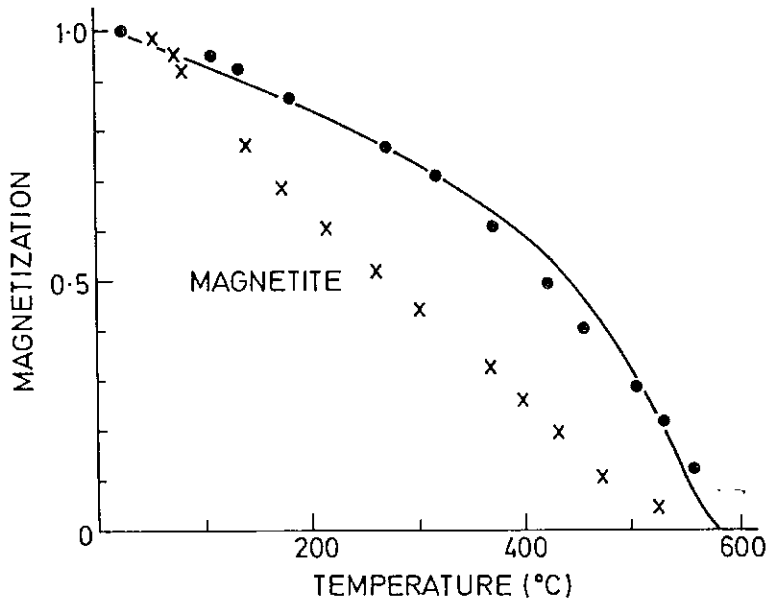

Figure 6. Comparison of measured thermal dependence of saturation magnetization for the Milton Monzonite (curve) with the experimentally derived thermal dependence of apparent spontaneous magnetization (dots) for magnetite. The temperature dependence of remanence (crosses) is also shown for comparison.

magnetization. There is little doubt that this effect is real since the most likely sources of error, i.e. non-equilibration of temperature, would cause the opposite effect. For the purposes of this study thermal equilibrium would appear to have been reached judging from the convergence of both curves at the Curie point, where in fact they should meet. It must be stressed that the apparent spontaneous magnetization, as plotted in Fig. 6, is corrected for unblocking effects. This contrasts with conventional $J_r(T)$ curves (e.g. Dunlop 1973) which follow $J_{sp}(T)$ only up to the minimum unblocking temperature for the specimen. Between the minimum and maximum unblocking temperatures the $J_r(T)$ curve falls below the $J_{sp}(T)$ plot due to unblocking of grains with $(T_B)_{min} < T_B < T$. To emphasize this point the measured $J_r(T)$ curve for the Milton Monzonite is also plotted in Fig. 6. It falls well below the $J_{sp}(T)$ curve because of the broad spectrum of unblocking temperatures in this rock. The decay of high temperature partial TRM with increasing temperature has been shown by Sugiura (1981) to be almost entirely due to the change of saturation magnetization, presumably because unblocking is negligible until just below T_C for the large PSD to large MD grain size fractions studied.

Fig. 6 confirms that the use of the saturation magnetization curve for the correction of palaeomagnetic data from continuous thermal demagnetization of MD magnetite-bearing rocks is quite adequate.

Comparison of $J'_{sp}(T)$ and $J_{sat}(T)$ for pyrrhotite was carried out in the same way as for magnetite. The high-field (1.2 T) thermomagnetic curve for monoclinic 4C pyrrhotite is from Clark (1983, p. 61) and indicates a Curie temperature of about 320°C. A specimen containing MD grains of the same composition (Fe_7S_8) was used for the continuous demagnetization of remanence experiment. The results (Fig. 7) show close agreement between $J'_{sp}(T)$ and the high-field magnetization, indicating the acceptability of the approximation $J'_{sp}(T) = J_{sp}(T)$ for MD pyrrhotite.

The experiments reported in this paper confirm that blocked remanence varies proportionally to spontaneous magnetization during heating from room temperature and

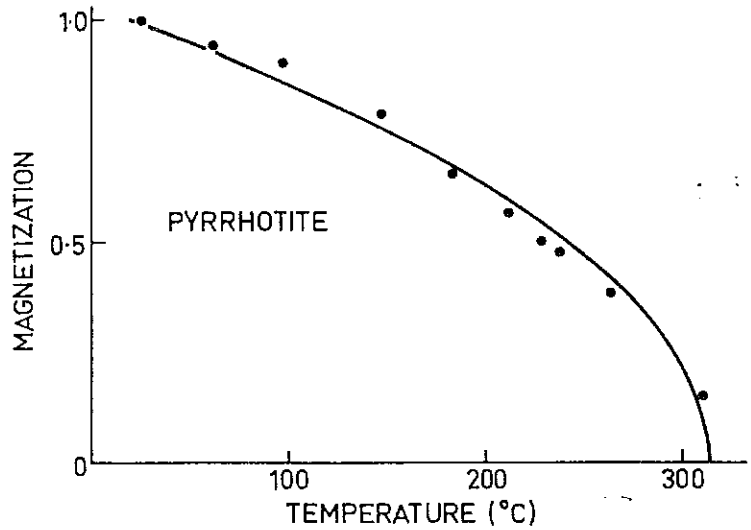

Figure 7. Comparison of measured (Clark 1983) thermal dependence of saturation magnetization (curve) with the experimentally derived thermal dependence of apparent spontaneous magnetization (dots) for pyrrhotite.

during subsequent cooling for weak-field (P)TRM and for SIRM of the MD magnetite-bearing Milton Magnetite sample, and for SIRM of the MD pyrrhotite-bearing sample. Similar behaviour during heating from room temperature may be deduced for weak-field TRM carried by small PSD magnetite grains, based on the results of Dunlop (1973), and for a high temperature PTRM (acquired between 585 and 530°C in a 1 mT field) carried by magnetite over a wide range of grain sizes (Sugiura 1981). We conclude that the proposed simple correction of continuous thermal demagnetization data, to obtain results equivalent to those which would be obtained by step-wise demagnetization, is satisfactory for palaeomagnetic purposes and should enhance the utility of the continuous demagnetization procedure.

6 Implications for theories of MD and PSD remanence

Closer examination of MD and PSD theories of remanence, however, reveals a conflict between the experimental results and most of the theories, once they are correctly formulated. In fact, the observed behaviour conforms much better to SD theory. This disagreement is borne out by some published data and by our own observations of thermal hysteresis at high temperatures of residual (~ 0.5 per cent of the total TRM) TRM carried by the Milton Monzonite. It therefore appears that departures from the standard procedure can result in anomalous behaviour, which presumably reflects thermally induced perturbation of domain structure. The simple behaviour observed in the experiments described herein reflects the type of remanence and the experimental procedure. In terms of a comprehensive MD theory of remanence, this simple behaviour is somewhat fortuitous. The anomalous behaviour will now be described in some detail.

Parry (1979) shows that PTRMs acquired by 200 μm grains behave irreversibly below the blocking temperature and exhibit gross departures from proportionality to $J_{sp}(T)$. The magnetization blocked below 500°C decreases with cooling once the inducing field is removed, outweighing any increase due to the augmentation of spontaneous magnetization. On reheating from room temperature the resulting, anomalously low, PTRM appears to decrease more or less normally with increasing temperature.

Sugiura (1981) reports analogous results for PTRMs acquired by sized magnetite fractions between 585 and 530°C. From 530°C to room temperature the PTRM carried by 100–150 μm grains is virtually constant, in spite of the large increase in spontaneous magnetization. For 30–40 μm grains the PTRM does exhibit some increase during cooling, but $J_r(T)$ varies much more slowly than $J_{sp}(T)$. Furthermore, the behaviour is irreversible, because on reheating $J_r(T)$ is approximately proportional to $J_{sp}(T)$ for both these size fractions. As a result of this irreversibility the remanence remaining at 530°C after a cooling and heating cycle is only about 40 and 60 per cent of the original PTRM at 530°C for the larger and smaller grains respectively. For grains in the 10–15 μm size range, on the other hand, $J_r(T)$ varies almost reversibly below T_B and is closely proportional to $J_{sp}(T)$, for both increasing and decreasing temperature.

The evidence demonstrates, therefore, that blocked thermoremanence carried by assemblages of what are conventionally termed 'true' MD grains (those larger than ~20 μm) behaves anomalously during inital cooling, but suggests that TRM is thereafter well behaved during heating and cooling cycles. This accounts for the successful correction of the continuous demagnetization data from the Milton Monzonite but implies that estimates of TRM intensity carried by MD grains, obtained using theories which assume $J_r(T) \propto J_{sp}(T)$, will be significantly in error.

Sugiura (1981) also demonstrates that the temperature dependence of isothermal remanence acquired in moderate fields (usually 3 mT) at elevated temperatures is highly anomalous for all three grain-size fractions mentioned above. The IRM is found to decrease sharply when the temperature is either decreased or increased from the acquisition temperature. The behaviour also reflects the previous thermal history, depending, for instance, on whether the sample has been cooled from T_C or heated from T_o before application of the field. Sugiura invokes a model of interacting domain walls to explain the experimental results.

We now consider various theories of TRM in the light of the experimental results and discuss the utility of comparisons between continuous and step-wise thermal demagnetization for testing theories of remanence carried by PSD and MD grains.

Because SD grains are uniformly magnetized, the magnetic moment of each SD grain is simply the product of the spontaneous magnetization and the grain volume. Thus, once the grain moments are 'frozen' into position below T_B, the remanence of an assemblage of non-interacting SD grains is strictly proportional to the spontaneous magnetization. Magnetostatic interactions between grains may significantly affect the equilibrium magnetization of an assemblage of SD grains above the blocking temperature, thereby influencing the intensity and field dependence of TRM (Dunlop 1969), but are relatively insignificant below T_B.

According to conventional MD theory, on the other hand, in MD grains each domain wall is trapped in a potential energy trough below the unblocking temperature, but the walls remain capable of small reversible displacements within their respective energy wells. According to this picture MD remanence is due to Barkhausen discreteness of wall positions. In this case the magnetic moment associated with each domain is not precisely proportional to the spontaneous magnetization because the effective volume of the domain may also vary with temperature as the equilibrium position of the bounding walls shifts in response to the self-demagnetizing field of the grain. The net remanence carried by the MD grains is therefore not strictly proportional to $J_{sp}(T)$.

Using the approximation, which is reasonable in particular for large MD grains containing many domains, that the effective demagnetizing field acting on the domain walls is equal to the mean demagnetizing field $-NJ$ it is straightforward to show that, providing the domain

structure does not change during cooling, the thermoremanence at $T < T_B$ is given by

$$J_{TRM}(T) = J_{TRM}(T_B)\, J_{sp}(T)/(J_{sp}(T_B)\,[1 + N\chi_i(T)]) \quad (6)$$

where χ_i is the intrinsic susceptibility due to domain wall displacement. For the case of saturation remanence χ_i in (6) should be replaced by S, the slope of the intrinsic hysteresis (J–H) loop in the vicinity of the saturation remanence point. The form of $J_{TRM}(T_B)$ depends on the particular model of the blocking process. For instance, the MD theory presented by Stacey & Banerjee (1974, p. 108) is equivalent to (6) with $J_{TRM}(T_B) = H/N$, where H is the inducing field at T_B.

Other MD theories, which are based on more realistic blocking conditions than the Stacey–Banerjee model, come under the umbrella of the generalized Néel theory (Dunlop & Waddington 1975; Day 1977). In their usual formulation these models, which consider the blocking of a single domain wall in a grain with a rectangular intrinsic hysteresis loop, neglect the effects of self-demagnetization below the blocking temperature and therefore omit the shielding factor $(1 + N\chi_i)^{-1}$ from the expressions for $J_{TRM}(T_o)$. This omission may have resulted from a perceived analogy between the hypothesized rectangular intrinsic hysteresis loop of a two-domain grain and the rectangular external hysteresis loop parallel to the unique axis of uniaxial SD grains, along which the low-field susceptibility is zero. O'Reilly (1984, pp. 104–107) discusses this model and points out that 'The removal of the field and the magnetostatic term at T_o allows a final motion of the domain wall. . .This final adjustment in position of the wall can be described in terms of the reversible parallel susceptibility at T_o.'

Dunlop (1977) has rectified the omission of the shielding factor from earlier versions of the expression for $J_{TRM}(T_o)$, giving formulae consistent with our equation (6). At a fixed temperature omission of the shielding factor merely causes an overestimation of the intensity of TRM. This is likely to be overlooked because of adjustable parameters in the thoery, but does not affect the relationships which have been the focus of attention for MD theories, viz. the dependence of TRM on inducing field and coercive force. We can estimate the error in TRM intensity of two-domain grains due to neglect of self-demagnetization by using the data of Dunlop (1984) for 0.22 μm magnetite grains. Taking $N = 0.15$ (SI), $\chi_i = 6.2$ (SI) gives $1 + N\chi_i = 1.9$, so omission of the shielding factor causes the TRM intensity to be overestimated by a factor of $\sim$2.

From (6) it follows that when self-demagnetization of the MD grains is taken into account the ratio of apparent to true spontaneous magnetization, $J'_{sp}(T)/J_{sp}(T)$, is predicted to be proportional to the shielding factor $[1+N\chi_i(T)]^{-1}$. The intrinsic susceptibility is a strong function of temperature, increasing rapidly at high temperatures. Stacey & Banerjee (1974, p. 74) suggest that the appropriate expression for χ_i is an average over all orientations of the intrinsic perpendicular and parallel susceptibilities, denoted $\chi_\perp$ and $\chi_\parallel$ respectively, i.e.

$$\chi_i = 2\chi_\perp/3 + \chi_\parallel/3. \quad (7)$$

For magnetite $\chi_\perp$ is given by (Stacey & Banerjee 1974, p. 72).

$$\chi_\perp \simeq 3\mu_o J_{sp}^2/4|K_1| \quad (8)$$

where K_1 varies approximately as $[J_{sp}(T)]^{8.5}$ (Fletcher & Banerjee 1969), therefore

$$\chi_\perp(T) \propto [J_{sp}(T)]^{-6.5}. \quad (9)$$

For magnetite $\chi_\perp(T_o) \simeq 16$ (in SI).

The parallel intrinsic susceptibility measures the ease of domain wall displacement in the internal field and is dependent on microstructure. The temperature dependence of $\chi_{\parallel}$ is therefore less certain. We give a simplified calculation based on theory given by Clark & Schmidt (1982), which in turn relies on a model due to Stacey & Banerjee (1974). The parallel susceptibility is related to other temperature dependent parameters by

$$\chi_{\parallel} H_c \propto J_{sp} \delta / d \tag{10}$$

where H_c is the coercive force, δ is the domain wall thickness and d is the thickness of lamellar domains.

According to elementary domain theory (see, e.g. O'Reilly 1984, chapter 4),

$$\delta \propto (A/K_1)^{1/2} \tag{11}$$

$$d \propto \sigma^{1/2}/J_{sp} \propto (AK_1)^{1/4}/J_{sp} \tag{12}$$

where A is the exchange constant, which is proportional to $[J_{sp}(T)]^2$ (Chikazumi & Charap 1978, p. 273), and σ is the specific domain wall energy. Expressing the temperature dependence of these parameters in terms of $J_{sp}(T)$ we get

$$\delta \propto [J_{sp}(T)]^{-13/4}, \quad d \propto [J_{sp}(T)]^{13/8} \tag{13}$$
$$\sigma \propto [J_{sp}(T)]^{21/4}, \quad \chi_{\parallel} H_c \propto [J_{sp}(T)]^{-31/8}.$$

It is found experimentally that $H_c(T) \propto [J_s(T)]^n$ where n commonly lies in the range 1–2 (Day 1977). Taking $n \simeq 1.6$ we obtain

$$\chi_{\parallel}(T) \propto [J_{sp}(T)]^{-5.5}. \tag{14}$$

A completely independent theory (due originally to Kersten), which models interactions between flexible domain walls and a regular array of non-magnetic inclusions, is discussed by Chikazumi & Charap (1978, pp. 271–274). This theory predicts a somewhat slower increase of $\chi_{\parallel}$ with T: $\chi_{\parallel}^{i} \propto J_{sp}/(K_1)^{1/2} \propto J_{sp}^{-3.25}$, and is found to explain very well the observed temperature dependence of the initial permeability of iron, nickel and cobalt.

At room temperature the inferred value of $\chi_{\parallel}$ for 50 μm magnetite grains is ~ 20 (Stacey & Banerjee 1974, p. 74), which is similar to the value of $\chi_{\perp}$. Equation (7) then implies that $\chi_i \simeq 17$ at room temperature for these grains. At ~ 470°C, where $J_{sp}(T)/J_{sp}(T_0) = 0.5$, equations (7), (9) and (14) predict χ_i (470°C) ≈ 1270, representing an increase over the room temperature value by a factor of ~ 90. Applying the more conservative Kersten theory the corresponding factor is ~ 60. Taking the SI demagnetizing factor as $3.9/4\pi = 0.31$ the corresponding shielding factor changes by a factor of ~ 60 (or ~ 50 for the Kersten model) over this temperature range.

The strong temperature dependence of χ_i corresponds to a relatively slight increase in observed susceptibility $\chi = \chi_i/(1 + N\chi_i)$, which for large χ_i is approximately equal to $1/N$, independent of $\chi_i(T)$. The predicted value of χ varies from 2.7 to 3.2, an increase of only 19 per cent, between T_0 and 470°C. This is consistent with the observed χ–T curve for the Milton Monzonite (Schmidt & Embleton 1981).

Levi & Merrill (1978) pointed out that as the domain wall thickness increases, its magnetostatic energy will increase relative to σ, exerting a braking effect on the thermal dependence predicted by (13). A cross-over temperature will eventually be reached above

which δ remains roughly constant. In this case the wall energy is given by (Amar 1958).

$$\sigma = (\sigma_0/2)\,(\delta/\delta_0 + \delta_0/\delta) \simeq \sigma_0\delta_0/2\delta \qquad (15)$$

where σ_0 and δ_0 are the equilibrium wall energy and thickness in an extended medium, with temperature dependences given by (13), so that $\delta_0 \gg \delta$ above the cross-over temperature. It follows from (12) and (15) that δ = constant implies d is constant, in which case $\chi_\parallel H_c \propto J_{sp}$, by (10). Thus the temperature dependence of $\chi_\parallel$ varies from rapidly increasing at low temperatures to relatively slowly increasing ($\chi_\parallel \propto J_{sp}^{1-n}$) above the cross-over temperature. The cross-over temperature is difficult to estimate without a detailed calculation of magnetostatic energy as a function of δ, but the median destructive field versus temperature data of Levi & Merrill (1978) suggest that it lies well above 400°C for large magnetite crystals.

Whatever the detailed behaviour of $\chi_\parallel(T)$ it is apparent that, according to (6), MD TRM should behave reversibly below T_B but that the temperature dependence of J_{TRM} should be highly anomalous. Furthermore, equation (6) predicts that J_{TRM} will increase much faster than $J_{sp}(T)$ during cooling, whereas measured thermoremanence carried by MD grains exhibits an anomalously slow increase, or even a decrease, during initial cooling (Parry 1980; Suguira 1981). Thus standard MD theory, which leads to (6), is violently contradicted by experimental measurements of the variation of remanence with temperature.

Moreover, the validity of (6) is contingent upon maintenance of the domain structure throughout the initial cooling. This is an implicit assumption of all MD theories of TRM, but there is reason to believe that the domain structure of large grains undergoes major readjustment during cooling from high temperatures. According to (13), elementary domain theory predicts that the domain spacing decreases markedly at high temperatures, corresponding to large increases in domain multiplicity. Direct observations of the domain structure of strontium hexaferrite support the theory (Rosenberg, Tanasoiu & Florescu 1970). Therefore, as a large grain carrying a TRM cools from high temperatures it seeks to reduce the number of domains. The self-demagnetizing field of the grain favours elimination of domains magnetized parallel to the blocked remanence, thereby limiting or overwhelming the augmentation of remanence associated with the increase in spontaneous magnetization within each domain and with the reversible motion of remaining domain walls within energy wells. This probably explains the anomalous behaviour of coarse grains during initial cooling to which we have already alluded.

Domain structure observations of magnetite, titanomagnetite and pyrrhotite at room temperature (Soffel 1971, 1977; Halgedahl & Fuller 1980, 1981, 1983) reveal little evidence of grains with anomalously high domain multiplicity (in fact anomalously few domains are often observed) indicating that denucleation of walls during cooling is a relatively easy process. Denucleation mechanisms for merging domain walls have been discussed by Dunlop (1977).

During reheating of MD grains from room temperature maintenance of the equilibrium domain structure requires nucleation of domain walls. Nucleation requires rotation of spin moments against magnetocrystalline anisotropy, which cannot occur within the bulk of a perfect unstressed crystal unless the resultant internal back-field exceeds the anisotropy field, which is proportional to K_1/J_{sp} and is of the order of 30–100 mT for titanomagnetites. Surface defects reduce the effective barrier to domain wall nucleation, but significant impediments to nucleation remain. Halgedahl & Fuller (1981, 1983) have shown that barriers to domain wall nucleation are a major influence on the domain structures and hysteresis properties of titanomagnetites and pyrrhotite at room temperature.

It might be expected therefore, that domain structure is more stable to heating than cooling, at least initally, so that the room temperature TRM associated with pinned domain

walls should exhibit temperature dependence described by (6). In this case, J_{TRM} should decrease much more rapidly than $J_{sp}(T)$ because of the shielding factor. At high temperatures the barriers to wall nucleation become negligible and the domain multiplicity increases. The self-demagnetizing field favours nucleation of reversed domains, further decreasing the remanence. The overall effect of a cooling and heating cycle on remanence due to domain wall pinning should be effectively to demagnetize MD grains in analogous fashion to low temperature demagnetization of MD magnetite grains which involves disruption of the room temperature domain structure by cooling below the isotropic point.

In summary, there is a striking disagreement between the predictions of domain theory concerning the remanence associated with the classical MD process of domain wall displacement between pinning sites and the experimentally observed temperature dependence of TRM and saturation remanence carried by assemblages of ostensibly MD grains. This is evidence that remanence associated with domain wall pinning makes only a minor contribution to weak-field thermoremanence and saturation remanence in such grain assemblages.

We now examine various models of PSD behaviour in the light of the experimental evidence. Undemagnetizable sub-domain moments due to Barkhausen discreteness of domain wall positions can be immediately ruled out as important contributors to the remanence of our samples because they are subject to self-shielding (Dunlop 1977) and should therefore conform to (6).

A prime candidate for PSD moment in fine (<1 μm) grains is the 'psark' or domain wall moment (Dunlop 1977). The mean magnetization of a 180° domain wall, approximated as a rigid array of atomic moments with orientation varying linearly through the wall, is $2J_{sp}/\pi$. Neglecting self-demagnetization of the wall, the total moment of a wall of thickness δ and area a is $2J_{sp}\delta a/\pi$. Remanence carried by psarks should therefore vary with temperature as $J_{sp}(T)\,\delta(T)$.

According to (13), which is based on equilibrium domain theory, the temperature dependence of psark remanence should depart strongly from proportionality to $J_{sp}(T)$. Shielding of the wall moment by magnetizations induced within the wall and the neighbouring domains by the demagnetizing field of the psark provides an additional complication, but may be neglected if the wall is sufficiently thin. Equilibrium domain theory predicts, however, that domain wall thickness should be comparable to domain thickness (Moon & Merrill 1984), which is contrary to domain structure observations. The observed thinness of domain walls suggests that most grains are not in their ground state, occupying instead local energy minima with lower domain multiplicity. The calculations of Moon & Merrill suggest that for this case the (compressed) wall width δ is almost independent of the equilibrium domain multiplicity, and thus should vary little with temperature. This is reinforced by a feedback mechanism operating to maintain the domain structure over a wide range of temperatures, as noted by Shcherbakov (1978). This follows from the condition $\delta \simeq$ constant $\ll \delta_0$, in which case (13) and (15) imply that the domain wall energy $\sigma \propto (AK_1)^{1/2}\ (A/K_1)^{1/2} = A \propto J_{sp}^2$, which is the same temperature dependence as the magnetostatic energy of the domains and walls. This feedback ensures that the psark moments vary approximately as $J_{sp}(T)$ by maintaining the wall thickness almost constant. There appears to be no experimental evidence bearing on the temperature dependence of remanence carried by sub-micron grains, but it would be straightforward to apply the procedure of Section 5 to test models of remanence in assemblages of such grains.

Fine grains containing an odd number of domains are expected to have irremovable moments, even in the absence of crystal defects (Shcherbakov 1978; Dunlop 1983). The calculated remanence of such grains is consistent with experimentally determined values. In

such grains, with an even number of domain walls, the psark moments should cancel. Irregular grains with an even number of domains may also possess irremovable moments due to asymmetry of the equilibrium wall positions. Domain structure observations suggest that these grains have compressed domain walls and, by the above argument, should have a domain structure which is relatively stable to temperature change. In these circumstances the remanence should vary as $J_{sp}(T)$ until the domain structure readjusts. Application of moderate fields causes only reversible changes in the magnetization of such grains. The unblocking temperature in such grains should correspond to the temperature at which the domain structure changes with the nucleation of an additional domain wall.

Halgedahl & Fuller (1983) suggest that much of the remanence associated with assemblages of ostensibly MD grains may be carried by grains which, although they are much larger than the critical SD size, have failed to nucleate a domain wall and therefore behave effectively as single domains. Such grains, which may be called quasi-SD or metastable SD, need only constitute a small fraction of the total assemblage to account for the PSD moments which are inferred from remanence measurements. Because the probability of wall nucleation failure decreases with increasing grain size this model appears to be consistent with the observed grain-size dependence of hysteresis properties.

In the present context the model of nucleation-controlled quasi-SD grains has two advantages. First, the remanence carried by such grains varies as $J_{sp}(T)$ until an effective unblocking temperature is reached where a wall can nucleate, thereby destroying the remanence. Secondly, the problem of decoupling the PSD moments from adjustments of the main domain structure within the MD grains is avoided because the PSD moments are associated with distinct grains. The same argument may be extended to metastable two domain, three domain, etc. grains with spontaneous moments, which may also contribute significantly to the PSD remanence.

The experimentally observed approximate proportionality of $J_r(T)$ and $J_{sp}(T)$ is therefore consistent with a model in which TRM and saturation remanence are dominated by PSD moments associated with grains which have unpinned spontaneous moments, particularly grains with anomalously low domain multiplicity, including metastable SD grains. Barkhausen moments associated with pinning must make only a minor contribution to these types of remanence. However, Barkhausen moments should be emphasized for isothermal remanence acquired in moderate fields. Moderate field IRMs are expected to show anomalous temperature dependence, in accord with Sugiura's (1981) observations. Because the well-behaved PSD moments become less important with increasing grain size, the relative contribution of MD Barkhausen moments should increase for assemblages of large grains, increasingly producing departures from the relationship $J_r(T) \propto J_{sp}(T)$. Again this predicted trend is confirmed by the data of Sugiura (1981) and also by our own measurements of $J_r(T)$ for synthetic sized magnetite dispersions, which will be described elsewhere. The results suggest, however, that Barkhausen moments make a relatively minor contribution to TRM carried by grain assemblages with mean size even as large as 220 μm.

We propose that unpinned PSD moments dominate TRM over a wide range of mean grain sizes. This may explain the consistent power law characterizing the grain-size dependence of TRM over five decades of diameter, or 15 decades of grain volume (Dunlop 1981). A common mechanism for TRM acquisition for small and large MD grains could also explain the remarkably similar field dependence of TRM for samples with very different grain-size distributions (Dunlop & Waddington 1975). Unblocking of remanence carried by these PSD moments is associated with domain wall nucleation rather than thermally activated Barkhausen jumps of domain walls between pinning sites. Levi & Merrill (1978) and Halgedahl & Fuller (1983) have already hypothesized metastable SD grains, unblocking by

wall nucleation, as important carriers of TRM. It remains to develop quantitative theories of TRM carried by such PSD moments. Several problems must be overcome to achieve a satisfactory theory – in particular a mechanism for generating a proportion of grains with anomalously few domains during cooling is required.

7 Conclusions

It has been shown that a simple correction of continuous thermal demagnetization measurements on samples containing MD grains, assuming that blocked remanence is proportional to the spontaneous magnetization, enables satisfactory simulation of stepwise demagnetization. The correction is necessary for correct estimation of palaeofield directions associated with remanence components other than the most stable component. High field thermomagnetic curves allow estimation of the temperature dependence of spontaneous magnetization with negligible error.

The experimentally determined temperature dependence of the blocked remanence of the samples [$J_r(T) \propto J_{sp}(T)$, $T < T_B$] is consistent with the behaviour expected for remanence carried by SD grains. Examination of conventional MD theories, however, reveals a conflict with the experimental results. Self-shielding of MD remanence associated with Barkhausen discreteness should produce a highly anomalous temperature dependence, provided all the domain walls remain within their respective energy wells (which is a fundamental assumption of conventional MD theories). In fact blocked TRM carried by large MD grains is observed to remain roughly constant, or even decrease, during initial cooling. This is attributed to readjustment of the domain structure with denucleation of domain walls in order to maintain the equilibrium domain multiplicity. On reheating the residual TRM varies approximately as $J_{sp}(T)$ below the unblocking temperature, indicating the self-shielding and domain structure readjustment, both of which would produce a much more rapid decrease, are inoperative. This shows that Barkhausen moments make only a minor contribution to the room temperature TRM. During initial cooling assemblages of large grains may acquire a substantial TRM associated with wall pinning but it appears that this is largely demagnetized by denucleation of domain walls on further cooling.

Halgedahl & Fuller (1983) have proposed that PSD remanence in fine particle assemblages is associated with nucleation-controlled metastable SD grains. We extend the list of plausible candidates for carriers of PSD remanence to grains with metastable domain structures, containing an odd number of domains or an even number of asymmetrically disposed domains, separated by unpinned compressed domain walls. Somewhat surprisingly, such domain structures should be stable over a wide range of temperatures. Remanence carried by such grains varies as $J_{sp}(T)$ until an effective unblocking temperature is reached, at which point an additional domain wall nucleates, thereby destroying the spontaneous moment. We also hypothesize that weak-field TRM and saturation remanence of assemblages of large grains ($> 100\,\mu m$) are dominated by PSD moments of the same type.

Isothermal application of a moderate field to coarse-grained assemblages preferentially activates the Barkhausen moments, which can be regarded as true MD moments. Such remanence is found to exhibit highly anomalous temperature dependence, apparently controlled by domain structure readjustments rather than by self-demagnetization.

The proposed carriers of SD-like remanence have several advantages, in addition to explaining the behaviour of $J_r(T)$. The grain-size dependence of hysteresis properties and TRM can be explained, at least qualitatively. The PSD moments are decoupled from wall displacements within the grains exhibiting true MD behaviour. The striking similarity of TRM behaviour for all grain sizes receives a natural explanation, if there is a single

underlying mechanism. It remains to develop a quantitative theory of TRM based on the properties of metastable SD particles and grains with unpinned spontaneous moments.

MD descriptions of TRM in terms of Barkhausen moments are shown by the experimental results to be unsatisfactory. Study of the temperature dependence of remanence may have many other applications. For instance the nature of the PSD moments in sub-micron grains could be probed using the experimental method described herein.

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