Geophys. J. R. astr. Soc. (1975) **41**, 1–10.

Stability of Anhysteretic Remanent Magnetization in Fine and Coarse Magnetite and Maghemite Particles*

H. P. Johnson, W. Lowrie and D. V. Kent

(Received 1974 December 9)†

Summary

Further experiments have been performed to investigate the biasing-field dependency of alternating field demagnetization curves of anhysteretic remanent magnetization as a simple test for the domain state of magnetite and maghemite particles. The biasing-field dependency in fine-grained particles was opposite to that in coarse-grained particles. The experiments were conducted on well sized synthetic specimens in the single domain, pseudo-single domain and multi-domain grain size ranges. A single domain-like biasing-field dependency was observed in equidimensional particles up to $0 \cdot 2\mu$ in mean grain size and up to $0 \cdot 4\mu$ in elongated grains. Either the single domain/pseudo-single domain boundary lies above at least $0 \cdot 2\mu$ grain size or this field dependency test does not distinguish between single domain and pseudo-single domain states. A multidomain-like trend was observed in very coarse magnetite. The test may possibly distinguish the change from pseudo-single domain to multi-domain states. If both fine and coarse fractions are present a confusing overlap of the demagnetization curves occurs.

Introduction

In order to understand the nature of the remanent magnetism which records the palaeomagnetic history of a rock, it is necessary to identify both the size and the magnetic state of the particles carrying the magnetic remanence. Many tests have been devised to determine if the stable remanent magnetization is held in small, uniformly magnetized, single domain (SD) particles or in large, multi-domain (MD) particles with well-developed domain wall structures. Recently, attention has focused on particles of intermediate particle size that are too large to be uniformly magnetized, but are either too small to have well-developed domain walls or to allow wall movements other than in discrete jumps. These pseudo-single domain (PSD) particles (Stacey 1963) have magnetic properties more similar to SD than to MD particles (Parry 1965; Dunlop 1973a, b; Dunlop, Stacey & Gillingham 1974).

Lowrie & Fuller (1971) suggested a test to determine whether the thermoremanent magnetization (TRM) of a magnetic sample was carried by single domain or multidomain particles. Their test relied on the observation that for single domain particles

---

* Contribution No. 108, Institut für Geophysik, ETH–Zürich

† Received in original form 1974 August 23

the stability of TRM against alternating field (AF) demagnetization *decreases* with increasing strength of the biasing field, while for multidomain particles the stability of TRM *increases* with increasing biasing field strength. They proposed a simple test which compared AF demagnetization characteristics of weak field TRM with strong field isothermal remanence (IRM). This should give rapid identification of either single domain or multidomain behaviour. If the normalized stability of the IRM was less than that of the weak field IRM, the sample was considered single domain-like in behaviour. If the converse was true, it was considered multidomain-like in behaviour. Lowrie & Fuller (1971) also suggested that weak field anhysteretic remanent magnetization (ARM) might be used to avoid the irreversible effects that often result from heating some magnetic minerals.

Dunlop & West (1969) found that for elongated (7 : 1) submicron magnetite particles the AF demagnetization curves of weak field TRM and ARM were similar. Also, they observed that with increasing biasing-field strength both ARM and TRM became progressively softer. This trend would correspond to what Lowrie & Fuller (1971) called a characteristic of single-domain particles. Their results also indicated the potential usefulness of ARM for this test. However, the grain size descriptions of their samples were made prior to annealing at 600 °C and 900 °C for from 4 to 24 hr. As Dunlop & West (1969) mentioned, and as will be described further below, heating at these high temperatures, even for short periods, causes sintering and subsequent changes in both grain size and magnetic properties.

In more recent work, Dunlop, Hanes & Buchan (1973) applied the Lowrie–Fuller test to both natural and artificial samples. They found that some rocks containing titanomagnetite with particle sizes of 200–600μ and 80–100μ showed multidomain-like field dependency, although this was thought likely to be a rare occurrence in nature. They also found that heated magnetite particles that had a mean particle size of 0·1μ prior to heating had, after heating, a biasing field dependency of ARM that was the same as for TRM and which showed single domain-like behaviour in the application of the Lowrie–Fuller test. In subsequent work, Dunlop (1973a) applied this stability test, using TRM, to heated particles that were 0·1μ and 0·037μ in size prior to heating. These particles also showed single domain-like field dependency, although 0·1μ is somewhat larger that the critical range of grain sizes predicted for true single domain behaviour in magnetite (Morrish & Yu 1955; Stacey 1963).

Dunlop *et al.* (1973) established the interchangeability of ARM and TRM in applying the Lowrie–Fuller test to single domain synthetic samples. Less satisfactory was their multidomain ARM study which was carried out on a coarse-grained rock whose exact grain size distribution was less well defined. We do not dispute their multidomain or single domain findings but prefer to establish the ARM biasing-field dependencies in more closely controlled synthetic specimens.

Experimental results

Studies were undertaken to supplement Dunlop's observations by describing the stability trends of ARM in both single domain and multidomain particles. Synthetic samples of carefully sized, unheated grains were used to avoid complications which might arise from heating fine particles or from the complexity of grain size and mineralogy in a natural rock. At the same time it was possible to study the behaviour of the Lowrie–Fuller test as a function of grain size.

The descriptions and bulk magnetic properties of the specimens used are shown in Tables 1 and 2, respectively. The coarsest specimen was a cylinder 5 mm in diameter and 8 mm long drilled in a (111) direction from a highly pure natural crystal of magnetite. The next coarsest sample consisted of a 210–250μ sized fraction of magnetite grains, ground from this same single crystal, and dispersed in a plaster matrix. These two samples were certainly multidomain. The two next largest particle sizes

Table 1

Compositional and size descriptions of the specimens.

	Mean particle size (Å)			% Magnetite in β–γ solid solution	
Identification	X-ray line broadening	Transmission electron microscopy	Range min/max (Å)	from cell parameter	from X-ray (111)/(311) ratio
Z	160	140	50/300	48	—
LTM	270	260	100/400	69	50
LR	1000	1100	400/2400	89	90
CC	>2000	2100	800/3400	82	79
TODA magnetite rods	—	350×4000	—	65	62
NAFTONE maghemite rods	—	800×4000	—	0	—
L44	—	2μ	$<44\mu$	100	—
G44	—	—	—	100	—
Magnetite dispersion	—	—	210μ–250μ	100	100
Magnetite single crystal	—	—	5 mm×8 mm	100	100

Table 2

Bulk magnetic properties of the specimens at room temperature and at liquid nitrogen temperature (77 °K). J_s, J_{rs} and H_c refer to the saturation magnetization, saturation remanent magnetization and coercive force, respectively.

	Room temperature			77 °K		
Particle identification	J_s (emu g^{-1})	H_c (Oe)	J_{rs}/J_s (%)	J_s (emu g^{-1})	H_c (Oe)	J_{rs}/J_s (%)
Z	50	16	2·5	56	140	14·3
LTM	70	53	7·9	76	230	24·3
LR	70	130	13·3	74	210	20·0
CC	83	175	17·7	86	420	23·7
TODA magnetite rods	84	420	43·0	—	—	—
NAFTONE maghemite rods	73	330	40·0	—	—	—
L44	92	78	8·6	92	110	14·0

were also from a ground single crystal of magnetite. The ground particles were sieved using a 44-μ mesh; the fraction which was less than 44μ was labelled L44 and the fraction which did not pass through the sieve was labelled G44. The mean particle size of the L44 fraction was determined by scanning electron microscopy to be two microns, but numerous larger particles were present. The mean size of the G44 fraction was not determined. As will be shown later, the representative grain size state of the L44 and G44 samples was more complex than that of 210–250μ dispersion or the single crystal.

At the single domain end of the scale, two types of long, thin, sub-micron rods were used, one of maghemite (Naftone) and one of magnetite (Toda). These submicron particles were single domain by virtue of their strong shape anisotropy.

Between the extremes of large multidomain particles and long, thin, single domain rods, were four sets of equi-dimensional magnetite particles. One problem associated with using very small magnetite particles is that they always tend to be partially oxidized (Colombo *et al.* 1965; Gallagher, Feitknecht & Mannweiler 1968). These submicron magnetite particles, formed by the precipitation of chloride salts in water, were no exception. The four sets of particles were converted into stoichiometric magnetite by heating at 600 °C for 2 hr in a reducing environment (10^{-3} Torr, with N_2 as the residual gas, and carbon present as a getter). This treatment caused all four groups of particles to sinter and grow in mean particle size to above $0 \cdot 2\mu$. The particle sizes, after heating, were determined by quantitative X-ray line broadening and transmission electron microscopy. The growth in particle size made it impossible to compare directly the properties of ARM in unheated particles with those of TRM in heated particles. Since the heated particles were all roughly the same size, ARM and TRM properties could not be determined as a function of particle size. The present study, therefore, concentrated on the properties of ARM in the unheated, but in some cases non-stoichiometric, particles.

Sample preparation for all but the largest two samples was identical. The particles were dispersed as well as possible by mixing at 2 per cent concentration with NaCl powder. As magnetite particles always tend to clump together, it is probable that the particles are only partially dispersed. The NaCl-magnetic particle mixture was then compressed into a standard 1-in. cylinder mould at 0·5 kbar pressure. The amount of oxidation (Table 1) was obtained by determining the lattice parameter and assuming a linear dependency of lattice parameter upon oxidation between magnetite (8·40 Å) and maghemite (8·33 Å). The spinel phase was the only one present in the X-ray patterns. A second technique used for determining the amount of oxidation was that of Readman & O'Reilly (1970). This consisted of taking the ratio of the (111) and (311) X-ray diffraction intensities and assuming that the ratio varies linearly with oxidation between magnetite and maghemite. The agreement in some cases was rough, and the cell parameter data are probably more reliable.

The bulk magnetic properties of the smaller particles (Table 2) were measured in a vibrating sample magnetometer, both at room temperature and at liquid nitrogen temperature. The single domain rods have a very high coercive force; the magnetite cubes have a coercive force that decreases with decreasing particle size. This may be deceptive as part of the particle size distribution of the smaller cubes was in the super-paramagnetic size range (Johnson 1972). Since coercive force is measured in a magnetic field, the presence of superparamagnetic material will give an induced magnetization contribution that results in an artificially low value of coercive force.

The ratio of saturation remanence to saturation magnetization (J_{rs}/J_s), which from magnetization theory for a random distribution of uniaxial single domain particles should be 50 per cent (Stoner & Wohlfarth 1948), are shown in the third and sixth columns of Table 2. Again, the presence of superparamagnetic material gives artificially low values. However, the long thin single domain rods give values of 40 and 43 per cent even at room temperature. From these bulk properties it may be concluded that the J_{rs}/J_s test may be a reasonable positive test for single-domain particles, but cannot be used as a negative test.

The single-domain rods and the four sets of smallest magnetite cubes were given ARM in an alternating field of 2000 Oe and in biasing fields of 0·25, 0·50 and 11 Oe. In all cases, the sample was fixed in orientation and the alternating and biasing fields were parallel. Strong field IRMs were given to the samples in a 2000 Oe field. Fig. 1 shows a comparison of the 0·50 Oe, 2000 Oe ARM with the 2000 Oe IRM in the single domain rods of magnetite and maghemite. The stability of the remanence of

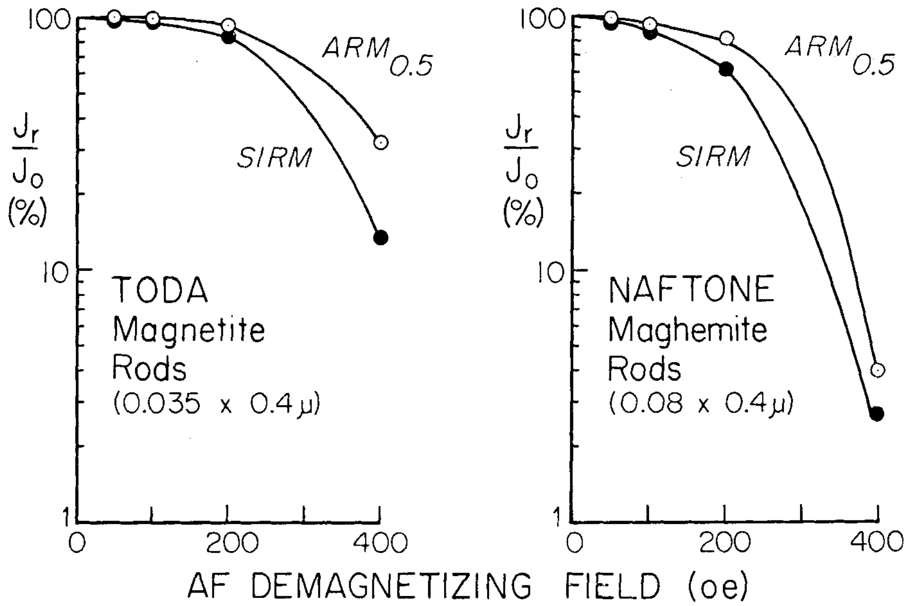

FIG. 1. Alternating field (AF) demagnetization of saturation isothermal remanent magnetization (SIRM) and anhysteretic remanent magnetization produced in an alternating field of 2000 Oe and a biasing field of 0·5 Oe ($ARM_{0.5}$) in single-domain magnetite and maghemite.

both sets of single domain rods decreases with increasing biasing field. Table 3(a) shows that the dependency of stability on ARM biasing field is not strong. However, the ARM coercivities can be clearly distinguished from the IRM coercivities. This type of field dependency, and the comparison of weak field ARM and strong field IRM shown in Fig. 1 were observed in what are surely single-domain rods. This illustrates that one half of the Lowrie–Fuller test, delineating fine particle behaviour, is valid using ARM instead of TRM.

Fig. 2 shows the ARM field dependency test for a 1 Oe biasing field applied to the large single crystal and the 200μ magnetite particles. Table 3(b) shows that, similar to the smaller particles, the differences in stability for different ARM biasing fields is very small (within experimental error in some cases), but can be clearly distinguished from IRM stabilities. Both of these coarse-grained samples give test results typical of multidomain behaviour, indicating that for truly multidomain particles, the Lowrie–Fuller test is valid using ARM instead of TRM. It would appear from Figs 1 and 2 that the end members of our particle size series behave as predicted; that is, SD rods show a SD-like field dependency and very large MD grains give a MD-like dependency.

Fig. 3 shows the Lowrie–Fuller test, using ARM, applied to the four sets of very fine magnetite cubes. Field dependency for all four sets of cubes is the same as that shown in Fig. 3(d) for the largest particle size. As observed in the single-domain rods, the stability of the remanence decreases with increasing biasing field strength. It can be seen from Table 3(a) that the ARM stabilities are again not strongly dependent on biasing field, but are higher than the equivalent IRM stabilities. According to the Lowrie–Fuller criterion, this would be termed single domain-like behaviour. One other interesting point which can be made from Fig. 3 is that the AF coercivity (here defined as the median destructive alternating demagnetizing field) of the 0·5 Oe ARM in the magnetite cubes decreases as the particles get smaller. This is the same trend as observed in the hysteresis loop coercive force data and is consistent with Néel's (1949) theory for single-domain particles. However, this type of behaviour is occurring in

Table 3

Median demagnetizing fields for samples given SIRM in 2000 *Oe and ARM in various biasing fields. Units of MDF are Oersteds.*

Table 3(a)

Fine particles

Particle identification	Median destructive field (Oe) $ARM^{0.25}_{2000}$	$ARM^{0.50}_{2000}$	$ARM^{11.0}_{2000}$	IRM_{2000}
Z	~150	~150	~150	128
LTM	~150	~150	~150	95
LR	165	159	152	117
CC	245	225	209	126
TODA magnetite rods	326	315	285	254
NAFTONE maghemite rods	230	230	230	210

Table 3(b)

Coarse particles

Particle identification	Median destructive field (Oe) $ARM^{0.50}_{2000}$	$ARM^{1.0}_{2000}$	$ARM^{2.0}_{2000}$	$ARM^{11.0}_{2000}$	IRM_{2000}
210–250μ dispersion	30	30	30	—	38
5 mm × 8 mm single crystal	32	35	35	35	40

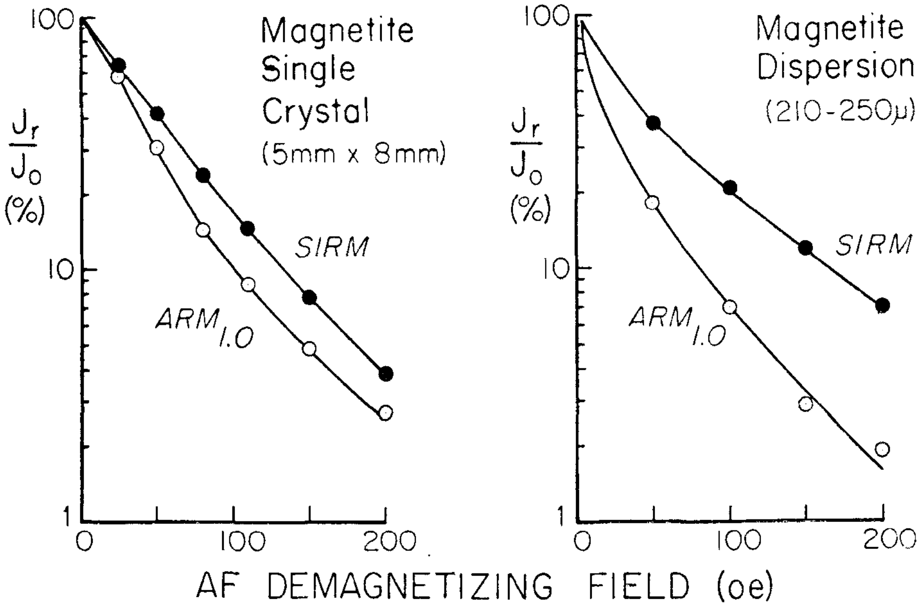

FIG. 2. AF demagnetization of SIRM and ARM with a 1 Oe biasing field in a multidomain magnetite dispersion and a large magnetite single crystal.

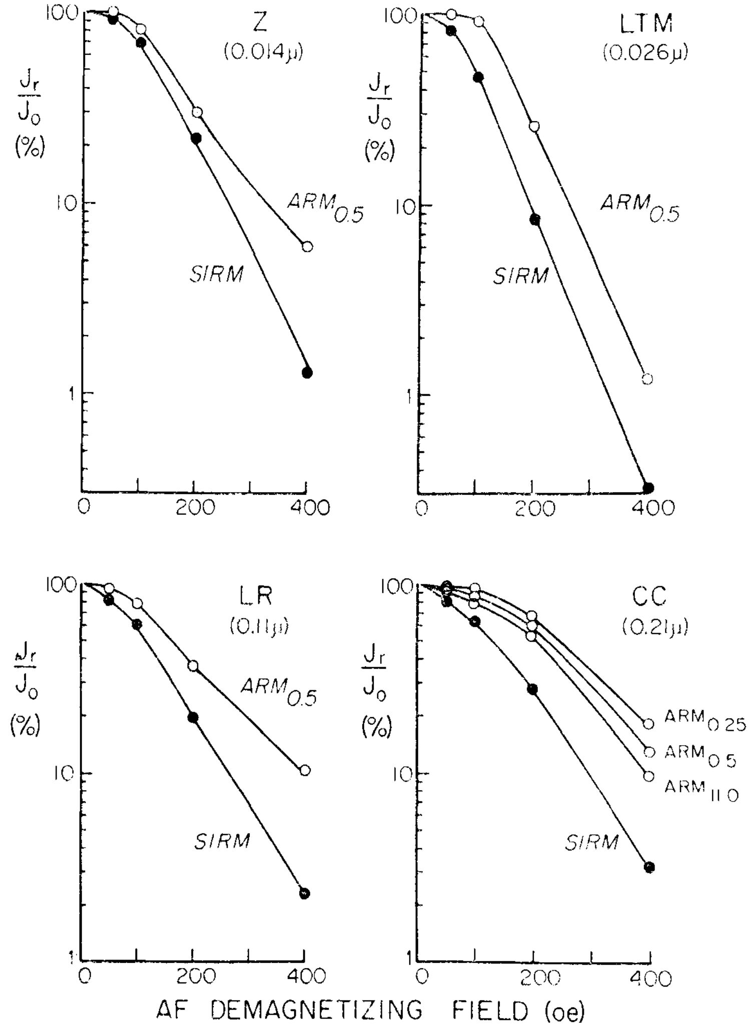

FIG. 3. AF demagnetization of SIRM and ARM in very fine equidimensional magnetite particles. All showed the same dependency on biasing field as the CC particles.

the 0·11-μ and 0·21-μ particles that are much larger than previously have been considered single domain (e.g. Dunlop 1973b). This is also a different trend from that obtained by Dunlop (1973a) for particles that, prior to heating, had a particle size that spanned the same size range.

A possible explanation is that the equidimensional submicron particles have a trend in oxidation state as well as in particle size (i.e. the smallest are more oxidized than the largest). Previous work (Johnson & Merrill 1972) on some of these same particles has shown that the microscopic coercivity is not strongly altered by large changes in the oxidation state. It is probable that the trends seen in the magnetic properties more closely reflect variations of particle size than of oxidation state in the non-stoichiometric samples.

Fig. 4 shows the behaviour of the two sieved magnetite fractions, L44 and G44. The less than 44-μ fraction (L44) showed single domain-like field dependency (Fig. 4(a)). These particles were two orders of magnitude larger than normally con-

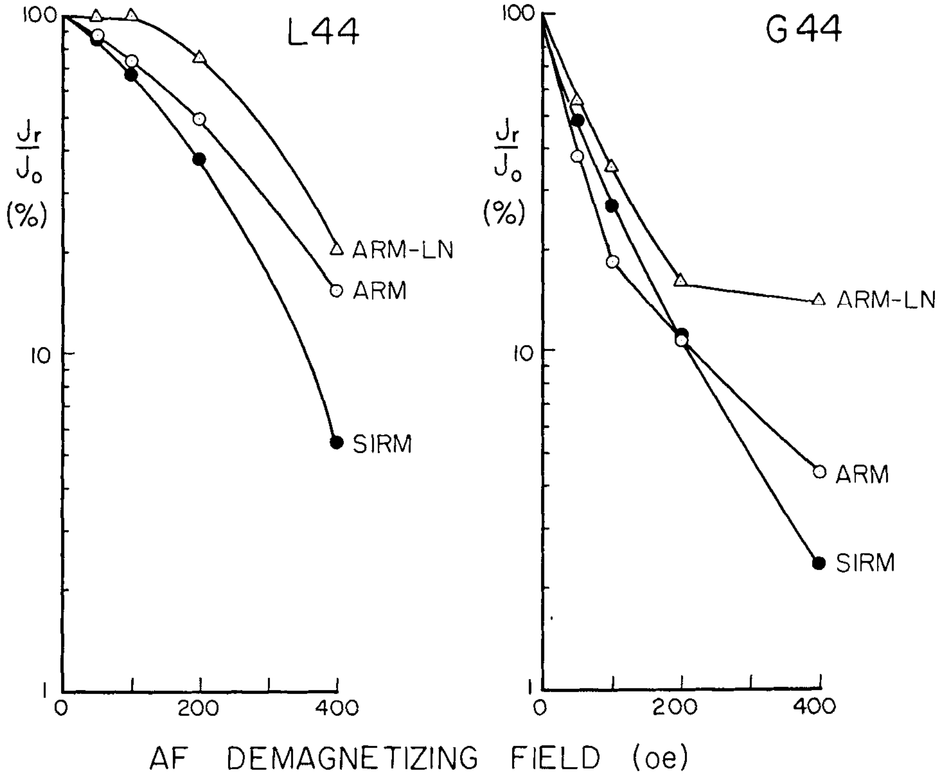

FIG. 4. Comparison of ARM and SIRM demagnetizations in two sieved magnetite fractions, L44 and G44 (see text). ARM–LN corresponds to ARM that was cooled to liquid nitrogen temperature (77 °K) and then warmed to room temperature prior to AF demagnetization.

sidered single domain. However, if single domain-like field dependency is exhibited by pseudo-single domain particles, this result is then consistent with the work of Parry (1965) who found pseudo-single domain behaviour in magnetite grains as large as 17*μ*.

The coarser than 44-*μ* fraction (G44) shown in Fig. 4(b) probably consisted of large multidomain grains and also of smaller pseudo-single domain or single-domain grains clumped together sufficiently to prevent their passing through the 44-*μ* sieve. This sample showed a mixed behaviour involving the crossing of the demagnetization curves of ARM and IRM. Since cycling of the sample in zero magnetic field to below the isotropic temperature of magnetite (130 °K) preferentially reduces the remanence held in multidomain grains of magnetite (Nagata, Kobayashi & Fuller 1964; Ozima, Ozima & Akimoto 1964; Merrill 1970), we gave the G44 sample a 0·5 Oe ARM and then cooled it to 77 °K in a field-free space. After allowing it to warm up to room temperature the AF demagnetization of the low temperature cycled sample showed a single domain-like field dependency (Fig. 4(b)) supporting the idea that this fraction also contains a very fine-grained component.

Discussion and conclusions

These results establish satisfactorily that ARM and TRM show the same stability trends against AF demagnetization in single-domain materials and that this is opposite to their common stability trend in multidomain materials. This result is analogous to that of Dunlop, Hanes & Buchan (1973), but in the present study it was obtained in synthetic samples of well-controlled grain sizes. It, therefore, appears that ARM is a reasonable substitute for TRM in applying the Lowrie–Fuller test. However, the results also indicate limits that must be invoked when interpreting the test.

The finest equidimensional magnetite grains were surely single domain, and gave a single domain-like stability trend. So, also, did the coarser equidimensional grains, whose size was around $0 \cdot 2\mu$. If these coarser grains are single domain, the upper limiting grain size for single domain must be raised above $0 \cdot 2\mu$. Alternatively, if they are pseudo-single domain, the pseudo-single domain grains must exhibit the same stability trend against AF demagnetization as single domain grains, and the field dependency test does not distinguish between these two magnetic states. It is possible that the test may distinguish pseudo-single domain from multidomain grains, although that cannot be established here. This transition, involving as it does a progressive increase in mobility of domain walls, is not likely to be abrupt and the application of the test to grains in the intermediate condition may result in a confusing overlap of the ARM and IRM demagnetization curves.

A similar confusion was displayed by the mixture of single domain, pseudo-single domain and multidomain grains in our sample G44 (Fig. 4(a)), and may be common in rocks with a wide range of grain sizes. It may be concluded, therefore, that the Lowrie–Fuller test, using ARM, may serve only to distinguish whether the dominant remanence carriers in a rock are very fine- or coarse-grained magnetic particles.

Acknowledgments

The authors are grateful for useful discussions of this work with R. T. Merrill and Shaul Levi. Aviva Brecher and Michael Fuller provided helpful reviews. Shaul Levi supplied the single domain magnetite and maghemite rods. This work was supported by NSF grants GA-3525, GA-26190 and GA-30569.

D. V. Kent:
Lamont-Doherty Geological Observatory,
Palisades, New York 10964.

H. P. Johnson:
CIRES,
University of Colorado,
Boulder, Colorado 80302.

W. Lowrie:
Institut für Geophysik,
ETH-Honggerberg,
Postfach 266,
CH 8049, *Zürich,*
Switzerland.

References

Colombo, U., Gazzarini, F., Lanzavecchia, G. & Sironi, G., 1965. Magnetite oxidation: A proposed mechanism, *Science*, **147**, 1033.

Dunlop, D. J., 1973a. Thermoremanent magnetization in submicroscopic magnetite, *J. geophys. Res.*, **78**, 7602–7613.

Dunlop, D. J., 1973b. Superparamagnetic and single domain threshold sizes in magnetite, *J. geophys. Res.*, **78**, 1780–1793.

Dunlop, D. J. & West, G. F., 1969. An experimental evaluation of single domain theories, *Rev. Geophys. Space Phys.*, **7**, 709–757.

Dunlop, D. J., Hanes, J. A. & Buchan, K. L., 1973. Indices of multidomain magnetic behavior in basic igneous rocks: Alternating field demagnetization, hysteresis, and oxide petrology, *J. geophys. Res.*, **78**, 1387–1394.

Dunlop, D. J., Stacey, F. D. & Gillingham, D. E. W., 1974. The origin of thermoremanent magnetization: contribution of pseudo-single domain magnetic moments, *Earth Planet. Sci. Lett.*, **21,** 288–294.

Evans, M. E. & McElhinny, M. W., 1969. An investigation of the origin of stable remanence in magnetite-bearing igenous rocks, *J. Geomag. Geoelect.*, **21,** 757–773.

Gallagher, K. J., Feitknecht, W. & Mannweiler, U., 1968. Mechanism of oxidation of magnetite to δ-Fe_2O_3, *Nature*, **217,** 1118–1121.

Johnson, H. P., 1972. An irreversible low temperature transition in magnetite, *E.O.S. Trans. A.G.U.*, **53,** 973.

Johnson, H. P. & Merrill, R. T., 1972. Magnetic and mineralogical changes associated with low-temperature oxidation of magnetite, *J. geophys. Res.*, **77,** 334–341.

Lowrie, W. & Fuller, M., 1971. On the alternating field demagnetization characteristics of multidomain thermoremanent magnetization in magnetite, *J. geophys. Res.*, **76,** 6339–6349.

Merrill, R. T., 1970. Low-temperature treatments of magnetite and magnetite-bearing rocks, *J. geophys. Res.*, **75,** 3343–3349.

Morrish, A. H. & Yu, S. P., 1955. Dependence of coercive force on density of some iron oxide powders, *J. appl. Phys.*, **26,** 1049–1055.

Nagata, T., Kobayashi, K. & Fuller, M., 1964. Identification of magnetite and hematite in rocks by magnetic observation at low temperature, *J. geophys. Res.*, **69,** 2111–2120.

Neél, L., 1949. Théorie du trainage magnetique des ferromagnetiques en grains fins avec applications aux terres suites, *Ann. Geophys.*, **5,** 99–136.

Ozima, M., Ozima, M. & Akimoto, S., 1964. Low temperature characteristics of remanent magnetization of magnetite, *J. Geomag. Geoelect.*, **16,** 165–177.

Parry, L. G., 1965. Magnetic properties of dispersed magnetite powders, *Phil. Mag.*, **11,** 303–312.

Readman, P. W. & O'Reilly, W., 1970. The synthesis and inversion of non-stoichiometric titanomagnetites, *Phys. Earth planet. Int.*, **4,** 121–128.

Stacey, F. D., 1963. The physical theory of rock-magnetism, *Adv. Phys.*, **12,** 45–133.

Stoner, E. C. & Wohlfarth, E. P., 1948. A mechanism of magnetic hysteresis in heterogeneous alloys, *Phil. Trans. Roy. Soc.*, **A240,** 599–642.