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HYSTERESIS PROPERTIES OF TITANOMAGNETITES: GRAIN-SIZE AND COMPOSITIONAL DEPENDENCE

R. DAY [1], M. FULLER [1] and V.A. SCHMIDT [2]

[1] *Department of Geological Sciences, University of California, Santa Barbara, Calif. 93106 (U.S.A.)*
[2] *Department of Earth and Planetary Sciences, University of Pittsburgh, Pittsburgh, Pa. 15213 (U.S.A.)*

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Sized fractions of $x = 0.6$, 0.4, 0.2 and 0.0 titanomagnetites were studied with a vibration magnetometer. In the coarse particles ($d > 150\ \mu m$), no compositional dependence of hysteresis parameters was found. H_C was less than 50 Oe, $H_R/H_C > 4$ and $J_R/J_S < 10^{-2}$, reflecting multi-domain behaviour. In contrast, fine particles ($d \simeq 0.1\ \mu m$) revealed systematic grain-size dependence of parameters with coercive force as high as 2,000 Oe in $x = 0.6$ titanomagnetite. Grain-size dependence studies revealed broad transition sizes for the onset of true multi-domain behaviour depending upon which factor is chosen. In magnetite it varies from 10 to 20 μm. The experimental critical size for single-domain behaviour for magnetite is about 0.1 μm and for $x = 0.6$ titanomagnetite 1–2 μm.

1. Introduction

The grain-size dependence of magnetic properties has, with the exception of the study by Parry (1965), been somewhat neglected until recently in rock magnetism. Yet, almost every aspect of the magnetic behaviour of a material shows strong dependence upon grain size. The fine-grain magnetic materials, which play an important role in paleomagnetism, often exhibit some single-domain-like characteristics, such as stable and intense thermoremanent magnetization (TRM) and multi-domain-like hysteresis characteristics. This apparent paradox draws attention to the need to establish the single-domain–multi-domain transition in these materials and to determine the behaviour in the size range of the transition. It is most curious that the acquisition of TRM obeys the same form of field dependence law above and below the transition (Day, 1973; Dunlop, 1973). Until these problems are resolved our understanding of TRM in rocks and our attempts to determine the paleointensity of the earth's magnetic field are unsatisfying. In this paper we describe experiments with varying grain-size fractions of titanomagnetites, the aim of which is to determine the single-domain–multi-domain transition in hysteresis behaviour.

2. Samples

The titanomagnetites used in this study were prepared using the ceramic method of Barth and Posnjak (1932). Weighed quantities of hematite, α-Fe_2O_3 (99.9% purity); rutile, TiO_2 (99.9%); and iron, Fe (99.999%) powder were thoroughly mixed under acetone in an agate mortar. The dried mixture was pressed into pellets, sealed in evacuated silica tubes (10^{-4}–10^{-5} torr), and fired at 1,000°C for 8 h. The tubes were then quenched from this temperature to prevent exsolution of two phases. These will be referred to as the series C titanomagnetites.

Series WG (wet-ground) titanomagnetites, prepared in the same way as series C, were ground in a water slurry for 100 h to reduce the grain size to less

TABLE I

Hysteresis properties of coarse-grain (series C) titanomagnetites

Composition, x	H_C (Oe)	H_{RC} (Oe)	$\frac{H_{RC}}{H_C}$	$\frac{J_{RS}(H=0)}{J_S(H=\infty)}$	χ_0 (G/Oe)
0.0	31	162	5.22	0.018	0.212
0.1	30	133	4.33	0.028	0.350
0.2	27	118	4.37	0.032	0.304
0.3	36	131	3.64	0.045	0.187
0.4	31	115	3.71	0.039	0.242
0.5	36	133	3.65	0.049	0.257
0.6	33	129	3.91	0.052	0.268
Mean	32	129	4.14	–	0.260

than 1 μm. Electron-microscope photographs confirmed that the grain size was less than 1 μm but the exact size spectrum could not be obtained because of magnetostatic clustering. Measurements of X-ray line broadening, when corrected for the effects of strain, gave a mean grain size of 1,100 Å (Readman, 1972). There are two disadvantages with these samples: a large quantity, up to 10% by weight, of finely-ground porcelain contaminates every sample; constant turbulence, contact with air and localized heating in the grinding process causes the samples to oxidize very slightly to cation-deficient spinels. However, all of the samples are oxidized and contaminated to about the same degree and can still be compared, within the group, for trends in the magnetic properties (A.J. Manson, private communication, 1972).

3. Measurements

The hysteresis loops were measured using a vibration magnetometer of the Foner type, but modelled more directly after the design of Flanders and Doyle (1962). Weak-field susceptibility was determined with an AC bridge of the transformer type (Fuller, 1967).

4. Coarse-grain samples (series C)

The hysteresis properties of the coarse-grain samples are given in Table I. The results show that there is essentially no compositional dependence for these coarse-grain samples. The observed values are typical for multi-domain material. The coercive force, H_C, is

TABLE II

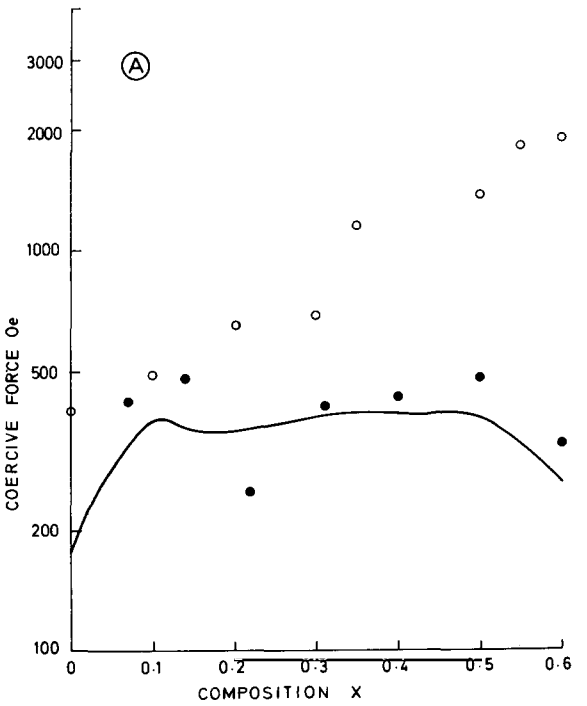
Hysteresis properties of fine wet-ground (series WG) titanomagnetites

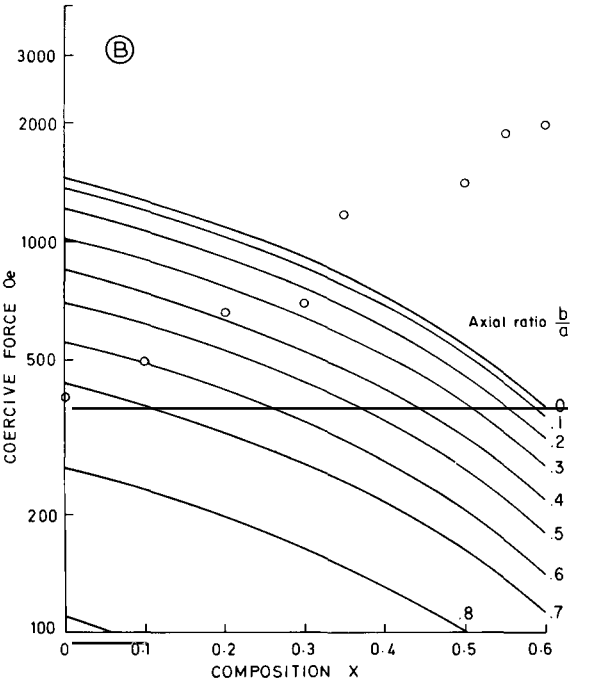
Composition, x	H_C (Oe)	H_{RC} (Oe)	$\frac{H_{RC}}{H_C}$	$\frac{J_{RS}(H=0)}{J_S(H=\infty)}$	χ_0 (G/Oe)
0	396	565	1.43	0.380	0.149
0.1	495	690	1.39	0.429	0.124
0.2	660	940	1.42	0.473	0.096
0.3	693	930	1.34	0.500	0.084
0.35	1,171	1,520	1.30	0.594	0.053
0.5	1,410	1,690	1.20	0.564	0.039
0.55	1,860	2,200	1.18	0.583	0.030
0.60	1,910	2,140	1.12	0.474	0.029

about 30 Oe. The ratio, τ, of remanent coercive force, H_{RC}, to coercive force, H_C, is greater than 4. ρ values (J_R/J_S) are less than 0.05, and the observed volume susceptibility varies from 0.2 to 0.3 G/Oe.

We compared the observed values of coercive force and initial susceptibility with the predictions of strain theories (Kersten, 1938, 1943; Néel, 1944, 1946). These theories predict a strong compositional dependence, because of the variation of the magnetostriction in the titanomagnetite series. Thus, unless the internal stress generated in the sample preparation exactly compensates the predicted compositional variation, these theories fail to account for the basic observation, namely the independence of composition. The inclusion theories (Kersten, 1938; Néel, 1944) are more promising although on either model rather high densities of inclusions appear to be required (Day, 1973). It is not clear what the nature of such inclusions may be, but they are somewhat reminiscent of those reported earlier in studies of the effect of annealing upon magnetite (Lowrie and Fuller, 1969).

The behaviour of these samples is typically that of multi-domain grains. However, the strain theories are somewhat unexpectedly unsuccessful in explaining the





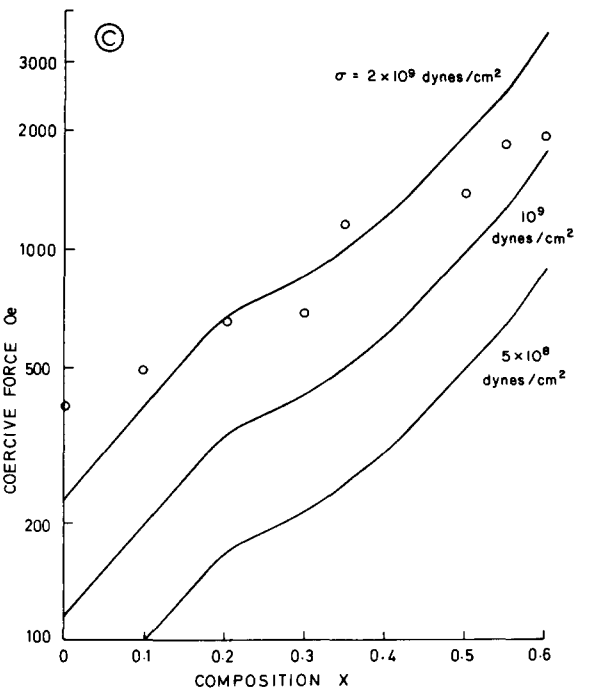


Fig. 1. Comparison of observed coercive forces of WG series with Stoner-Wohlfarth calculation.
A. Magnetocrystalline anisotropy.
B. Shape anisotropy.
C. Stress anisotropy.

observed hysteresis parameters. Inclusion theories look more promising.

5. Fine-grain samples (WG series)

The hysteretic properties of the WG series are shown in Table II. In contrast to the coarse-grain series, these samples reveal a marked dependence of properties upon the composition parameter, x. As the Ti content increases, the coercive force, H_C, the remanent coercivity, H_{RC}, and the ρ value, J_R/J_S, all increase and the initial susceptibility (χ_0) decreases, indicating that the samples are getting progressively harder. The τ values are reasonably constant and close to 1.09, which is appropriate for single-domain assemblages, so that there cannot be very much multi-domain or superparamagnetic material present. Similarly, with the exception of the low x values, the ρ values (J_R/J_S) are approximately 0.5, which is appropriate for single-domain assemblages.

The observed values of H_C are close to those expected for single-domain particles. A comparison of the measured values with those predicted by Stoner-Wohlfarth theory (Stoner and Wohlfarth, 1948; Wohlfarth, 1958) is shown in Fig. 1. It is evident that while shape and magnetocrystalline anisotropy are unable to explain the observed values, stress energy can, although the required stresses are large. In all probability each energy term is playing a role, but in the high-Ti titanomagnetites stress energy is particularly important. It should be noted that these samples are expected to have high internal stress because of the manner in which they were prepared. In natural samples the relative importance of the energy terms may be different. The observations of Robins (1972) suggest that synthetic samples produced by other methods may be more strongly controlled by magnetocrystalline energy. The susceptibility may be interpreted in a similar manner.

The behaviour of these samples is single-domain like. Their coercivity appears to be explained satisfactorily in terms of internal stress.

6. Mixtures of fine and coarse material

Rocks normally contain magnetic minerals with a relatively broad distribution of grain sizes. It is therefore important to establish the effects of such mixtures of coarse (soft) and fine (hard) material. We found that in samples containing less than 20% of the hard fraction, the coercivity is dominated by the soft fraction while the remanent coercivity and remanence increase systematically with increasing amount of the hard fraction present (Fig. 2). In samples containing 50% or more of the hard fraction the remanent coer-

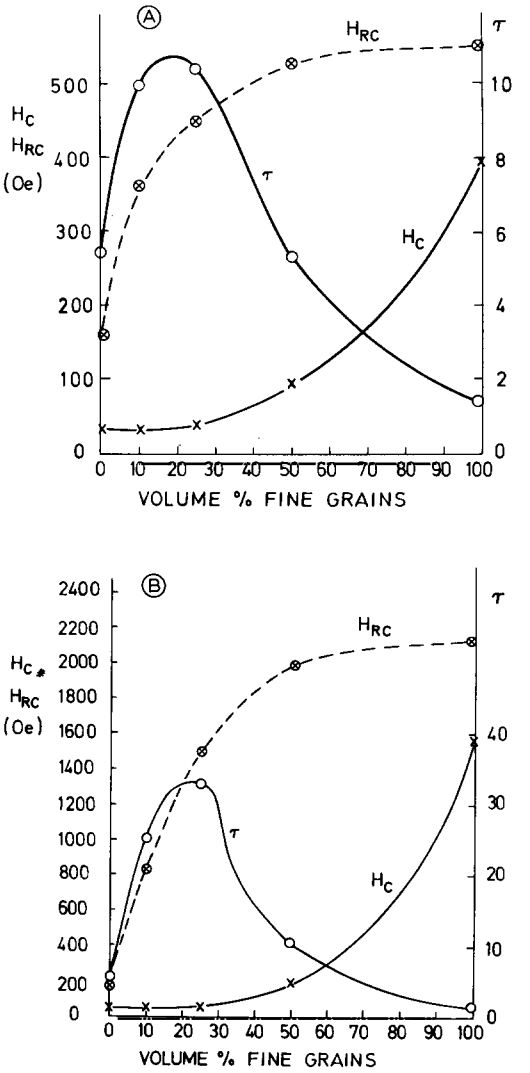


Fig. 2. Variation of H_C, H_{RC} and τ with volume fraction of hard component in mixture of hard and soft components.
A. $x = 0$.
B. $x = 0.6$.

civity is dominated by the hard fraction and constant, while the coercivity decreases systematically with the amount of soft material present. These results illustrate that one cannot ignore the effect of mixtures in studies of the grain-size dependence of hysteretic properties.

7. Interactions

In order to estimate the effect of concentration, acting through the variation of the strength of interactions, a set of samples with concentrations from 0.25 to 20% by weight were prepared. It was then found that for high Ti values no dependence upon concentration could be established. For magnetite, increasing concentration decreased H_C, H_{CR}, and J_R/J_S for concentrations greater than 5%. In the following analysis of grain-size effects the concentration used was 1% by weight.

8. Hysteretic properties of sized samples

Titanomagnetites of compositions $x = 0.0$, 0.2, 0.4 and 0.6 were ground under acetone in an agate mortar and the resulting powders were separated into size fractions using a Bahco centrifugal classifier and conventional sieves. The grain size of each fraction was checked microscopically.

Accurately weighed quantities of each size fraction were dispersed in KBr powder and the mixture was compressed in a brass die to give sample pellets containing 1% by weight of magnetic material. Optical examination of several pellet sections showed the dispersion to be reasonably uniform, but some local clumping of particles could not be avoided. The clumping could be minimized by lengthy mixing, and also, by using very dry KBr for the finer sizes and damp KBr for the larger sizes.

The hysteretic properties are shown in Table III. The grain-size dependence of coercive force and remanent coercivity (H_{RC}) are also shown in Fig. 3, which is a log-log plot. The variation can be expressed as:

$$H_C \propto d^{-n} \quad \text{and} \quad H_{RC} \propto d^{-m}$$

The power indices are not, however, constant over the whole range. Taking into account the size distribution within each fraction, the variation is best expressed by two power-law segments. The first index n_1 is always larger than the second n_2 (Table IV). The coercive-force transition is between 20–30 μm and the remanent coercivity at 20 μm.

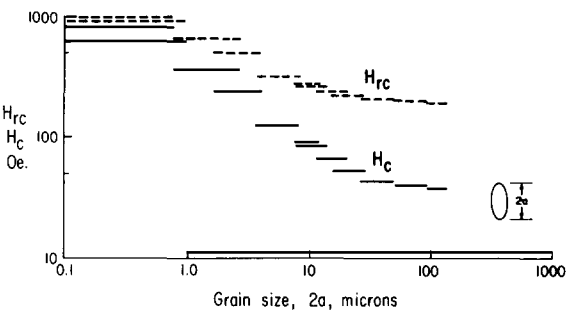


Fig. 3. Grain-size dependence of H_C and H_{RC} for $x = 0.2$.

Stacey and Wise (1967) related the power index to the domain-wall area and the ordering of dislocations. They gave n to be $l(1 - m)$, where l is related to the wall area and m depends on the degree of order of the dislocations. The value of l varies between 1 and 2, while m equals 0.5 for a random array of dislocations and 1 for an ordered array. Hence n can vary from 0 to 1. However, there are alternative explanations. Micromagnetic theory predicts that for grains larger than the critical size for coherent rotation a grain-size dependence will enter. The curling mode gives:

$$H_C \propto d^{-2}$$

while the buckling mode gives:

$$H_C \propto d^{-0.67}$$

Mixed reversal modes therefore can give intermediate values. The values of n found in the titanomagnetites are consistent with both explanations, however neither theory is sufficient to explain the second segment. The systematic variation of H_C with grain size has been reported for a number of materials and is likely to be a fundamental property (Luborsky, 1961).

The interpretation of the variation of isothermal remanence (J_R) and susceptibility (χ_0) is not so readily treated as the coercive force, as the data are not so good. However, there are again indications of a change in behaviour at about 6 μm and 20–30 μm.

TABLE III

Hysteretic properties of titanomagnetites as a function of grain size

Size (μm)	Standard deviation	H_C (Oe)	H_{RC} (Oe)	$\frac{H_{RC}}{H_C}$	J_{RS}/J_S	χ_0 (G/Oe)
(a) x = 0:						
0.8	–	295	551	1.87	0.133	0.139
0.96	–	245	501	2.04	0.117	0.144
1.9	1.1	165	432	2.62	0.103	0.159
3.8	1.5	108	359	3.32	0.082	0.118
6.4	2.4	84	300	3.57	0.056	0.224
9.3	2.9	70	280	4.00	0.047	0.224
13.4	4.2	60	250	4.16	0.043	0.192
18.2	5.2	55	209	3.80	0.025	0.218
30	9.0	42	195	4.64	0.021	0.218
57	17.0	37	181	4.89	0.020	0.216
87	13.5	35	169	4.83	0.020	0.203
131	25.1	32	160	5.00	0.019	0.212
(b) x = 0.2:						
0.8	–	811	998	1.23	0.361	0.083
1.0	–	620	940	1.52	0.327	0.098
1.8	1.0	360	660	1.83	0.261	0.138
2.9	1.2	240	500	2.08	0.188	0.197
6.1	2.5	125	325	2.60	0.096	0.242
9.8	2.6	92	278	3.02	0.068	0.263
11.1	3.3	85	269	3.16	0.055	0.262
16.5	4.6	66	245	3.71	0.040	0.274
23	7.1	53	225	4.25	0.031	0.291
40	12.0	43	210	4.88	0.021	0.306
75	21.0	40	198	4.95	0.024	0.317
118	19.0	38	195	5.13	0.024	0.301
(c) x = 0.4:						
0.8	–	1,551	1,900	1.23	0.449	0.036
0.95	–	1,076	1,600	1.49	0.427	0.054
1.64	0.9	594	1,030	1.73	0.362	0.088
3.5	1.8	275	580	2.11	0.250	0.137
6.0	2.6	152	385	2.53	0.146	0.182
8.6	2.9	112	320	2.86	0.095	0.208
13.0	3.2	82	270	3.29	0.079	0.224
17.0	5.1	66	235	3.56	0.053	0.236
32	8.7	44	210	4.77	0.034	0.265
61	18	39	185	4.74	0.030	0.279
84	16	36	176	4.89	0.027	0.294
112	21	34	186	4.94	0.033	0.271
(d) x = 0.6:						
0.8	–	1,584	2,130	1.34	0.473	0.018
0.94	–	1,115	1,815	1.63	0.511	0.030
1.7	1.0	581	1,115	1.94	0.459	0.048
3.3	1.3	280	625	2.23	0.339	0.074
6.4	2.4	132	330	2.50	0.210	0.105
9.0	3.1	92	260	2.83	0.131	0.118
12.0	3.7	82	235	2.82	0.117	0.176
16.0	5.4	73	201	2.75	0.075	0.217
25.5	7.9	61	185	3.03	0.063	0.237
41	11.2	52	175	3.37	0.058	0.258
78	19	46	160	3.48	0.051	0.266
140	24	39	148	3.79	0.043	0.268

9. Experimental estimates of the critical size for single-domain behaviour

A comparison of the observed hysteretic properties with the values predicted by the Stoner-Wohlfarth model shows that the critical size increases with increasing x. The magnetite samples show no single-domain properties, hence it has to be concluded that the single-domain size is well below 1 μm. The results from the wet-ground samples indicate that the single-domain size is closer to 0.1 μm. For $x = 0.2$, the critical size is above 0.1 μm but below 1 μm. H_C and τ variations indicate that the critical size is just below 1 μm while J_R/J_S indicates a lower value. The composition $x = 0.4$ shows single-domain behaviour in the two smallest size fractions placing the transition at about 1 μm. For $x = 0.6$, the transition occurs at about 2 μm. Soffel (1971) looked at the domain patterns on the surface of titanomagnetite grains of composition $x = 0.55$ and concluded that the single domain critical size could be as high as a few microns.

The transition from single-domain to truly multi-domain behaviour is not abrupt; there is a transition region. Multi-domain grains are characterized by:

$$\frac{J_{RS}}{J_S} \sim 0.05 \qquad \text{and} \qquad \tau \sim 5.0$$

although Parry (1965) suggests that multi-domain behaviour begins for $\tau \sim 3.0$. Using these values for truly multi-domain grains, the minimum size for multi-domain behaviour can be estimated. The results indicate that this transition size is about 10–20 μm for magnetite, depending on the property considered. This compares favourably with Stacey's (1962) value of 18 μm for magnetite. The transition size increases with increasing x to a value of about 30–40 μm for $x = 0.6$. At these sizes τ is nearer to 3.5–4 than 3 or 5.

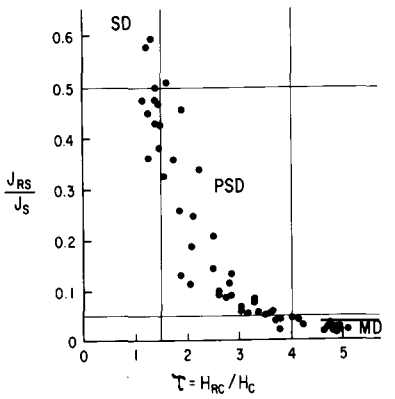


Fig. 4. J_R/J_S versus H_{RC}/H_C.

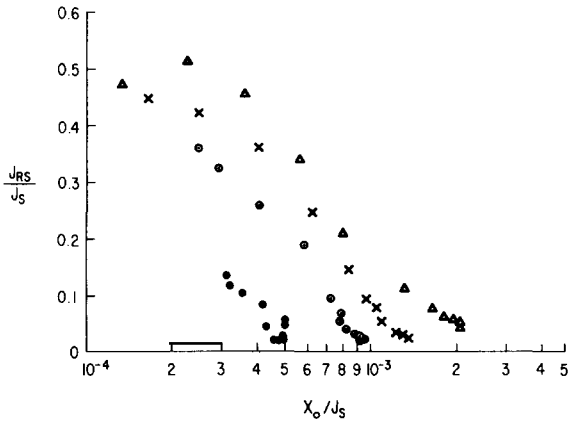


Fig. 5. J_R/J_S versus χ_0/J_S.

Another method of estimating the transition sizes is a graphical approach using two or more magnetic properties. Fig. 4 shows J_{RS}/J_S against τ where it can be seen that the samples follow a definite trend from truly multi-domain behaviour at the bottom right to single-domain behaviour at the top left. Many of the samples fall in the transition region between SD and MD behaviour.

Fuller (1974), while investigating the magnetic behaviour of lunar samples, suggested that a plot of J_{RS}/J_S against χ/J_S should show the same trends. Fig. 5 shows this graph for the titanomagnetites. The same trend is evident but note that the graph also shows a compositional dependence. This reduces its use as an indicator of the domain state if the composition is unknown, but when used in conjunction with Fig. 4, it may be possible to determine the approximate composition of the sample.

10. Discussion

The single-domain critical sizes found experimentally are generally higher than the calculated sizes. Assuming a mean elongation of 1.4, the calculated critical sizes for $x = 0$, 0.2, 0.4 and 0.6 are 0.08–0.15,

0.1–0.12, 0.12–0.18 and 0.16–0.26 μm respectively; the actual value depends upon the model used (Day, 1973). Butler and Banerjee (1975) considered the freepoles associated with the surface terminations of the domain wall and the dependence of domain-wall energy on wall width in their estimates of the critical size. The theoretical transition in spherical (cubic) grains then varies from 0.05 μm in magnetite to 0.3 μm for $x = 0.6$. As can be seen from their article in this volume, their values for elongated particles are considerably larger than those quoted above.

Experimentally the critical size varies from about 0.1 μm for magnetite to 1 or 2 μm for $x = 0.6$. The agreement is reasonable for magnetite giving the critical size as about 0.1 μm. Dunlop (1972) found a critical size for magnetite of 0.05 μm. Wall-width calculations suggest that a magnetite grain of width less than 0.1 μm cannot accept a normal wall even if it is otherwise energetically favorable. The experimental critical size for composition $x = 0.6$ is higher than the calculated values, and an order of magnitude higher than the size that can accommodate a domain wall. Soffel (1971) found that the domain walls in high-Ti titanomagnetite ($x = 0.55$) were predominantly 180°-walls, but that they were not straight. Walls were often hung up by dislocations (which appear as etch pits when they intersect the grain surface), and there was no evidence of closure domains. Curved walls, dislocation pinning and the absence of closure domains will increase the total energy of a multi-domain grain and increase the critical size. Soffel's work also suggests that the number of domains in a grain is not solely determined by the size of the grain.

It appears that theoretical and experimental estimates of the single-domain–multi-domain transition are converging. However, it is not yet clear whether all, or indeed the most important factors have been incorporated into the theoretical models. This must be established, if one is to place faith in their results to much better than an order of magnitude. Meanwhile the experimentalists still have to demonstrate the behaviour of the titanomagnetites in the critical domain-size range of 0.05–1 μm.

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