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Inhibition of domain wall formation and its effects on the bulk magnetic properties of certain spinels

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Abstract. It is shown that hysteresis and susceptibility studies at various temperatures could provide an idea whether a magnetic sample contains multidomain, single-domain or superparamagnetic particles. Our results on titanomagnetites with those of others on cobalt substituted magnesium ferrites suggest that domain wall formation is inhibited in some of them whereby only single-domain or superparamagnetic particles occur irrespective of the physical grain size of such materials. At high concentration of titanium in titanomagnetites, the magnetic behaviour is similar to a spin glass, which we interpret as a transition of optimum single-domains going over to superparamagnetic state.

Keywords. Multidomain; single-domain; superparamagnetism; domain walls; titanomagnetite; spin glass.

1. Introduction

The demagnetised state of a ferro- or ferrimagnetic body is normally presumed to be due to the subdivision into Weiss domains with Bloch walls between them. Grains which have domain walls in them are known as multidomains (MD). Theoretical estimates yield typical wall thickness in the range of few hundred to few thousand Angstroms for different materials. Magnetic grains which are a few hundred Angstroms across, or even larger if the particles are acicular, cannot contain domain walls due to energy considerations and these are termed the single domains (SD) for which the magnetisation direction is fixed in space. However, if the temperature of an SD is increased it may so happen that the thermal energy may become comparable to the effective magnetic anisotropy energy when the magnetisation direction fluctuates between the easy axes of the grain. In such a state the grain is said to be exhibiting superparamagnetism (SP) and for the volume v of the grain, the temperature is referred to as the blocking temperature T_b which will be less than the Curie point T_c of the concerned material. These parameters are related (Neel 1955) as:

$$vJ_sH_c = 2kT_b,$$

where J_s is the saturation intensity, H_c is the coercive field and k is the Boltzmann constant. Hence, the magnetic states of SD and SP are interchangeable by temperature. Although an individual SD would be in magnetised condition below T_c, a sample containing a large number of them could have a net zero magnetisation due to a random orientation of their moments.

Thus, a polycrystaline magnetic material may consist of the three types of states (MD, SD, and SP), though any one of them may be made to predominate by an appropriate method of sample preparation. However, magnetic alloys are usually made by an initial melting of the mixture of the constituent metals in the required proportion, while ferrites are normally prepared by the ceramic method involving the firing of the oxide mixture to facilitate a solid state reaction. Other annealing and/or sintering processes are also used to get the required properties for the final product.

While the presence of domain walls in certain materials has been established using some techniques, for many other materials it remains as a matter of belief or speculation. Moreover, domain wall observations in the case of materials which have low T_c would be difficult. Hence, the possibility does exist that domain walls may not form at all, even in some bulk magnetic materials, due to different reasons and this point has not been considered adequately so far in the literature.

We shall describe some magnetic measurements by which a reasonable idea could be obtained about the domain state of the grains in a sample and also discuss the results of studies on two spinel systems which suggest an inherent tendency for inhibiting the domain wall formation in some members of these systems.

2. Hysteresis

Although hysteresis phenomenon is shown by any magnetic sample, the maximum values for saturation remanence J_r and coercive force H_c are obtained when the sample contains only optimum SD grains of the material. Stoner and Wohlfarth (1948) showed that if a sample contains randomly distributed SD particles having uniaxial anisotropy, J_r would be one half of J_s. It is normal to assume theoretically (Bean 1955) that samples containing MD or SP particles of any material, do not show any hysteresis: however, practically some little hysteresis may arise due to defects and stresses in MD samples and interaction effects in SP samples. By measuring the hysteresis parameters of a sample at low-temperatures, it is possible to deduce if it contains SP or MD for in the case of SP sample the H_c and J_r tend to reach the values pertinent to an SD case as the temperature is lowered (Berkowitz and Schuele 1959), while for the MD case there would be only some marginal increase in the values of these parameters.

In figures 1a and 1b the hysteresis loops of a piece of natural magnetite ore and of a

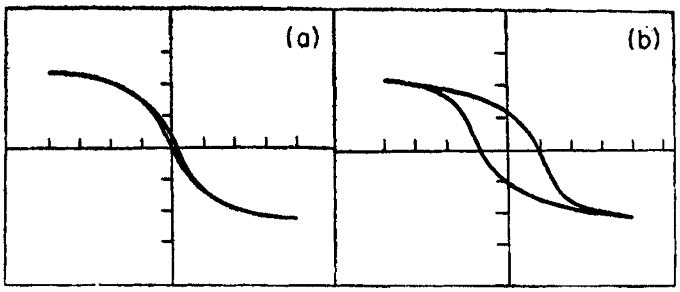

Figure 1. Hysteresis loops obtained in a peak field of 1500 Oe for **a.** a piece of natural magnetite ore and **b.** a small quantity of commercial magnetite powder having acicular SD particles.

sample of commercial magnetite powder which is known to be consisting of acicular SD particles, obtained with an improved version of the apparatus described earlier (Likhite *et al* 1965), are given. The hysteresis loop of the magnetite ore (figure 1a) is indicative of MD grains while that of the powder shows the expected SD behaviour. It should be mentioned here that even for a large natural crystal of magnetite, the hysteresis loop is similar to the one shown in figure 1a if obtained in some arbitrary direction of the crystal. Needless to emphasise that a sample containing a mixture of domain states would show a loop whose shape would be an average of the two extreme types given in figure 1.

While the above features are common for most of the magnetic materials, in alloys like Cu-Co-Fe-Sm the large H_c and J_r obtainable have been attributed to domain wall pinning (Livingston and Martin 1977).

3. Thermal variation of initial susceptibility

Magnetisation measurements in low-fields ($\ll 1$ Oe) and at high temperatures first carried out on iron by Hopkinson (1889) showed that it reaches a peak value just before T_c and becomes zero rapidly. For this type of measurement, the sample is taken in the form of a ring or long rod to avoid demagnetisation effects. However, many modern magnetic materials are made and used in the form of small lumps, pellets or micropowders. If such samples are used in low-field magnetisation work, the sharp fall before T_c could still be observed in the case of MD samples, though the peak may be reduced considerably due to demagnetisation effects. The measured signals would be proportional to the apparent susceptibility χ, which is related to the real susceptibility χ', by the relation (Neel 1955)

$$\chi = \chi'/(1+N\chi'), \tag{2}$$

where N is the demagnetisation factor.

Figure 2 shows the normalised χ-T curves obtained for the same magnetite samples

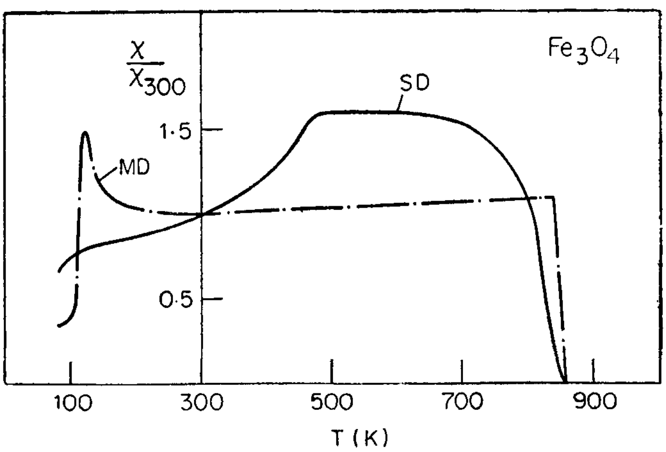

Figure 2. Susceptibility-temperature curves for the magnetite samples of figure 1.

of figure 1 in a field of 0·5 Oe by a double coil method (Radhakrishnamurty and Likhite 1970). It may be noted that for the magnetite ore sample (MD in figure 2) the relative increase in χ over the room temperature value is small and it sharply falls at the T_c. On the low temperature side, a peak is obtained at the isotropic point, about 130K (Bickford 1950), of magnetite. In contrast, the shape of the χ-T curve of the SD sample is quite different. Since, the H_c of the SD sample at room temperature is large its χ, which is inversely proportional to H_c, is low and reaches a broad maximum as the particles become superparamagnetic at temperatures approaching T_b. Also, for the acicular SD magnetite particles, the shape anisotropy dominates even at the isotropic point and hence the χ-peak at that temperature is suppressed to a large extent; this fact seems to be not emphasised sufficiently for such cases. Thus, for a material the behaviour at the isotropic point is an extra criterion for distinguishing between SD and MD grains. However, it should be emphasised that the high temperature part of the χ-T curves, by virtue of their distinct shapes, could provide sufficient clues for distinguishing between SD and MD behaviour of a sample as exemplified by the known magnetite samples.

By a judicial extrapolation of the criteria discussed above, it can be expected that a sample containing a narrow range of SD particles could show a peak in χ at their T_b and it could be sharp.

Thus, there would be three types of susceptibility peaks in the χ-T curves. (i) Hopkinson peak is the one occurring just before the T_c of any magnetic material in MD state, (ii) SD peak which could be obtained only if the sample under investigation has a substantial proportion of SD particles in it and occurs at the T_b of the particles and (iii) isotropic peak which could be seen clearly for a magnetic material in MD form and only if the material has a temperature at which the magnetocrystalline anisotropy is zero.

In contrast to the low-field measurements, the use of high magnetic fields obliterates the differences in the magnetisation versus temperature (J_s-T) curves of SD and MD samples of any material; for pure ferromagnets the Brillouin curve is obtained whereas ferrimagnets could show a resultant of two or more Brillouin curves (Smit and Wijn 1959). It has been reported (Sato *et al* 1970) that the apparent magnetisation at 300K in a field of 9·2 kOe was zero for particles of size 100 A for $Mn_{0 \cdot 6}Co_{0 \cdot 4}Fe_2O_4$ and of 150 A for $MnFe_2O_4$. Using this experimental fact and the equation (1), it can be calculated that manganese ferrite particles of 190 A would show a zero apparent magnetisation in similar fields at 600K which is far from its T_c of 665K. From these considerations it could be expected that magnetic samples containing a distribution of fine particles would show ' tails ' in J_s-T curves causing ambiguities in the determination of T_c. A theoretical treatment of this aspect was given by Evdokimov (1964).

4. Magnetite-ulvospinel solid solution series

It has been well established that magnetite (Fe_3O_4) and ulvospinel (Fe_2TiO_4) form a continuous solid solution known as titanomagnetites and a review of their properties was given by Akimoto (1962). However, the magnetic domain state of several members of this series has not been investigated adequately so far.

Samples of $(1-x)$ $Fe_3O_4 \cdot xFe_2TiO_4$, with $x=0$ to 1, designated hereafter as TM0 to

TM100, the number after TM indicating the percentage of ulvospinel, were prepared by a dry method using pure Fe_2O_3, TiO_2 and electrolytic iron powder. Mixtures with proper ratios of the ingredients were enclosed in evacuated quartz capsules, kept at 1300 K for 12 hr and then quenched. X-ray analysis of all the samples thus prepared showed that each one contained a single spinel phase and the lattice parameters agreed well with those reported by earlier workers. χ-T curves were obtained for all the samples. However, for the present purpose the results of three crucial samples are described and a full account of all the samples will be reported later on.

The χ-T curves for TM0, TM56 and TM96 are shown in figure 3. One extra curve (dashed line) for TM56 is also given and it is the one expected for an MD sample and constructed using the value of T_c as 500K and isotropic point as 233K. The isotropic point for this composition was estimated from the magnetocrystalline anisotropy study made on a single crystal by Syono and Ishikawa (1964).

The magnetite curve (TM0 in figure 3) shows a peak, though small, at about 130K which indicates that some MD grains have formed in it. The full curve (not shown in figure 3 due to enlarged temperature scale) can be understood in terms of the sample containing a mixture of SP, SD and MD grains, which is quite likely because the sample was prepared by quenching. The experimental curve of TM56 does not show any peak at the isotropic point of 233K, though there is some change of slope, implying the total absence of MD grains in the sample. The shape of the curve suggests that the sample may contain only SP and SD states of the grains.

More interesting is the χ-T curve for TM96, drawn taking the peak value as unity. The sharp cusp resembles that of a spin glass (Mydosh 1977; Wohlfarth 1977). However, it is just what can be expected of a sample containing a narrow range of particles being optimum SD at 77K and becoming mostly superparamagnetic at 135K.

5. Solid solution of spinels $MgFe_2O_4$ and Co_3O_4

Several samples of the solid solution $(1-m)$ $MgFe_2O_4 \cdot m\, Co_3O_4$ where $m<1$, were prepared by the ceramic method and their properties were studied and

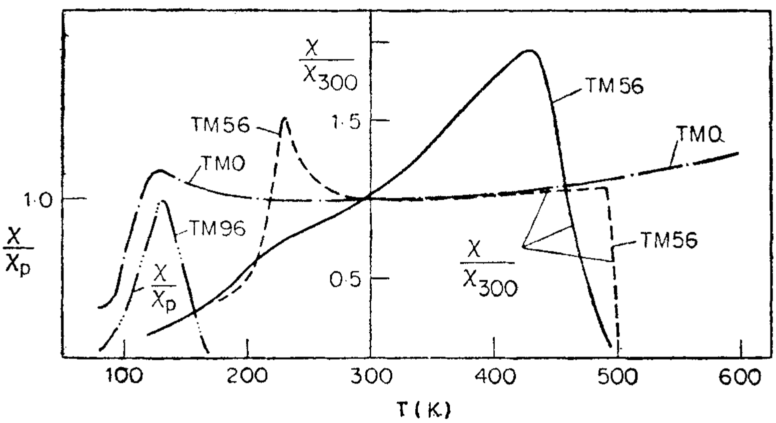

Figure 3. Susceptibility-temperature curves for the synthetic samples. TM0-Fe_3O_4; TM56-$0.44Fe_3O_4 \cdot 0.56Fe_2TiO_4$; TM96-$0.04Fe_3O_4 \cdot 0.96Fe_2TiO_4$.

Table 1. Magnetic and other properties of the solid solution (1-*m*)$MgFe_2O_4 \cdot mCo_3O_4$ for m=0·01 to 0·06 (after Venkatesh Rao 1975)

Sample No.	*m* value	Lattice parameter (A)	Saturation Intensity (emu/g)	Curie point (K)	Remanence ratio at		Coercive force (Oe) at	
					300K	80K	300K	80K
1	0·01	8·36	30·03	708	—	0·20	—	140
2	0·02	8·36	30·3	703	0·2	0·70	215	430
3	0·04	8·33 (?)	30·8	698	0·2	0·64	341	425
4	0·06	8·37	34·61	703	0·2	0·63	377	430]

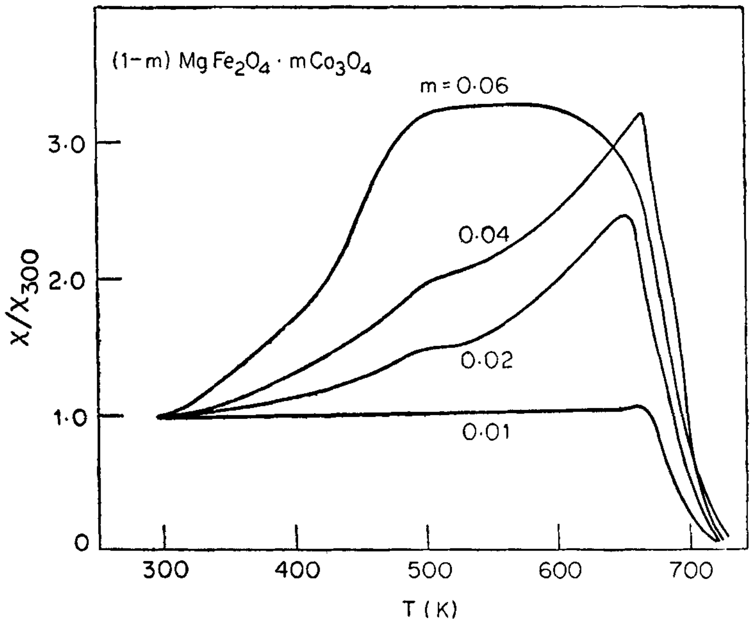

Figure 4. Susceptibility-temperature curves for the samples of the series (1-*m*) $MgFe_2O_4 \cdot mCo_3O_4$ for m=0·01, 0·02, 0·04 and 0·06.

reported by Venkatesh Rao (1975). The magnetic parameters for the samples with m=0·01 to 0·06, are given in table 1 and their corresponding *X-T* curves are shown in figure 4. It is interesting to note the changes taking place in the shape of the *X-T* curves as the proportion of Co_3O_4 is increased in the solid solution; while for m=0·01 (curve 1 of figure 4) the shape is akin to that of an MD sample, for m=0·06 (curve 4) it is similar to that of an SD sample (see figure 2). From the overall magnetic studies, Venkatesh Rao (1975) concluded that the samples contained mixed domain states. The point of relevance to the present discussion is the tendency in the increase of SD content in the solid solution as indicated by the gradual change in the shape of the *X-T* curves (figure 4) and H_c (see table 1) by an increase in the Co_3O_4 content in the samples.

6. Domain wall thickness

A simple formula for estimating domain wall thickness t_w in a bulk material is given (Brailsford 1966) as:

$$t_w = a \sqrt{J_s} \, [3 \, kT_c/2 \, n_B \, \mu_B \, K_1)]^{1/2}$$

where a is the distance between nearest dipoles, J_s is the saturation intensity, k is the Boltzmann constant, T_c is the Curie point, n_B is the magneton number per formula unit, μ_B is the Bohr magneton and K_1 is anisotropy constant for the material. This formula has been derived for a ferromagnet and is presumed to hold good even for ferrimagnets. As per the formula, t_w mainly increases with increasing exchange interaction and reducing anisotropy.

The estimated values of t_w along with other relevant parameters for iron, magnetite and titanomagnetites are given in table 2. It can be seen that t_w of titanomagnetites reduces with increasing proportion of ulvospinel in the solid solution. These estimated values are believed to correspond to those in bulk material or single crystal samples. In special cases like small grains containing only a single wall, it was shown (Amar 1958) that the wall thickness could be very much reduced; thus, in the case of a two-domain iron particle t_w could be as low as 145 A compared to the value of 1510 A in bulk iron. Also, in highly anisotropic materials like $SmCo_5$ for which K_1 is of the order of 10^8 ergs/cc, t_w may be about 26 A (Kronmuller 1978). Such considerations seem to suggest that domain walls should form in almost all magnetic materials with large enough grains in them.

7. Discussion

The essential parameters required for characterising a magnetic material adequately are J_s, T_c and K_1 besides the other physical constants. While J_s and T_c could be measured for a polycrystalline sample, the determination of K_1 needs a single crystal of the material. Since the preparation of a single crystal, particularly of complex materials, is often difficult, K_1 values are not available for many materials.

Table 2. Domain wall thickness and other parameters for iron, magnetite and two titanomagnetites.

Sample	Lattice parameter (A)	K_1 at 300K (ergs/cc) $\times 10^5$	Saturation intensity at 300K (emu/g)	T_c (K)	Domain wall thickness t_w (A)
Fe	2·861	4·4	222·10	1043	1510
Fe_3O_4	8·390	1·1	98·86	858	1877
TM56	8·478	1·0	26·90	480	1526
TM96	8·528	5·8*	5·00*	142	338*

*values at 77K; TM56 = $0.56Fe_2TiO_4 \cdot 0.44Fe_3O_4$; TM96 = $0.96Fe_2TiO_4 \cdot 0.04Fe_3O_4$

From the discussion on the thermomagnetic measurements (§ 3), it seems that ambiguities could arise even in the determination of T_c if a material does not readily form multidomains. Thus the questions, if a particular sample contains MD and if some materials form MD at all, attain great significance.

Considering the specific case of TM96, the X-T curve shows a sharp cusp at 132K (figure 3). A single crystal of almost the same composition (TM95) was prepared and its magnetic properties were reported by Ishikawa (1967). Although, he mentioned that its T_c as 142K, the J_s-T curve obtained by him in a field of 30 kOe shows that 20% of the magnetic intensity still persists even beyond 200K. The remanent magnetisation of the sample was shown to be zero at 142K by J_r-T measurements. A reasonable explanation for these observations seems to be that the single crystal has clusters with a maximum T_b of 142K at which the remanence becomes zero and at higher temperatures the clusters exhibit superparamagnetism. The hysteresis loops given by him at 78K and 20K and other measurements (Ishikawa and Syono 1971) clearly show that the magnetocrystalline anisotropy constant for TM95 increases rapidly at low temperatures. All these observations become consistent if it is assumed that around the composition of TM95, titanomagnetites could have only spin clusters irrespective of the sample being in single crystal or polycrystalline form. In other words, such a material has no tendency whatsoever to form domain walls and hence multidomains.

Even TM56 seem to be capable of forming SD only, as per the experimental observations given in § 4. However, the cluster size in this case must be larger as indicated by the maximum T_b at 430K (figure 3).

Thus, the results of the magnetic studies on TM0, TM56 and TM96 clearly indicate that substitution of Ti in magnetite would inhibit the formation of domain walls in the titanomagnetites even though they may be chemically and crystallographically homogeneous.

A similar case where Ti seems to play a role in the formation of small clusters was recently reported (Kneller *et al* 1978). From combined Mössbauer and magnetic measurements, it was shown that the R-type hexaferrite $BaFe_4Ti_2O_{11}$ orders ferrimagnetically in small clusters below its T_c. This crystallographically and chemically homogeneous material is considered to be magnetically inhomogeneous due to statistical fluctuations in composition. It may be mentioned in this context that the formation of domain walls in normal barium hexaferrite ($BaFe_{12}O_{19}$) has been well established (Smit and Wijn 1959) though sintering seems to increase the volume fraction of superparamagnetic particles as was deduced by magnetic studies by Dietrich (1970).

Inomato *et al* (1978) showed that substitution of Ti enhances the H_c of Sm-Cu-Co-Fe magnets; however, it was mentioned by them that the mechanism of H_c enhancement by Ti is not clear.

The few results presented in § 6 suggest that addition of cobalt oxide to magnesium ferrite aids the formation of SD fraction in the mixed ferrites. For the mixed ferrites of iron and cobalt, the process of elementary magnetisation was attributed to rotations rather than domain wall displacements by Guillard (1953). Such an explanation needed the hypothesis that the microcrystalline structure of the iron-cobalt ferrites prevents wall displacements, which implies the presumption of the presence of domain walls.

All the cases described above indicate that addition of Ti or Co to a magnetic material can increase H_c which can be treated as the result of single domain formation in the materials. Since the physical grain size in these materials normally be much larger than the critical SD size, it will have to be presumed that each grain contains several clusters in it. However, the exact mechanism as to how these clusters form, particularly with the addition of Ti or Co, is difficult to comprehend and any details which may be attempted may at best be speculative for the time being.

One likely mechanism is to assume a statistical fluctuation in composition as was done in the case of $BaFe_4Ti_2O_{11}$, with Ti atoms helping such a process. A second one seems to be to think of the formation of compensation planes in which the sublattice magnetisations cancel each other and these planes breaking the magnetic homogeneity in the material. However, even this mechanism, first proposed by Krumme and Hansen (1973) and later elaborated by Krumme (1974), requires compositional gradients and is restricted to ferrimagnets only. Thus, it appears that magnetic inhomogeneity and spin clustering could be present, inhibiting domain wall formation, even though a material is homogeneous from the point of chemical and crystallographic aspects. Ions like Ti and Co aids the creation of magnetic inhomogeneity.

The problem of domains and domain walls in three dimensions comes under micromagnetics and a review of the developments in this area was given by Brown (1978). According to him it appears that to solve the domain structure problem for a specimen of 1 cm diameter using currently available concepts and a modern computer may require 10^{24} to 10^{27} years!

8. Conclusions

(i) Three types of susceptibility cusps could be encountered in the thermomagnetic studies on magnetic materials. The Hopkinson type and the single-domain type could be obtainable for any magnetic materials but the former will be well defined in the case of the sample having large grains with multidomain structure whereas the latter can be resolved with narrow range of fine particles. The isotropic peak can be seen only if the magnetocrystalline anisotropy constant of the material has the zero value at some temperature and it is clearer in multidomain state of the material than in single-domain state.

(ii) Substitution of titanium and cobalt in some magnetic materials may enhance the formation of single domains and inhibit domain wall formation.

(iii) It has been shown that certain titanomagnetites can contain only single domains or spin clusters and it may be considered as an inherent property of these compositions.

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References

Amar H 1958 *J. Appl. Phys.* **29** 542
Akimoto S 1962 *J. Phys. Soc. Jpn. Suppl.* B-1 **17** 706
Bean C P 1955 *J. Appl. Phys.* **26** 1381
Berkowitz A E and Schuele W J 1959 *J. Appl. Phys.* **30** 134S
Bickford Jr L R 1950 *Phys. Rev.* **78** 449
Brailsford F 1966 *Physical principle of magnetism* (London: Van Nostrand) p 166
Brown Jr W F 1978 *J. Appl. Phys.* **48** 1937
Dietrich H 1970 Ferrites, *Proc. Int. Conf.* (Japan: University Park Press) p. 283
Evdokimov V B 1964 *Russ. J. Phys. Chem.* **38** 1080
Guillaud C 1953 *Rev. Mod. Phys.* **25** 64
Hopkinson J 1889 *Phil. Trans. R. Soc. (London)* **A180** 443
Inomata M, Oshima T, Ido T, Yamada M and Yamamiya H 1978 *Jpn. J. Appl. Phys.* **17** 1993
Ishikawa Y 1967 *Phys. Lett.* **A24** 725
Ishikawa Y and Syono Y 1971 *J. Phys. Soc. Jpn.* **31** 461
Kneller E, Velicescu M and Habery F 1978 *J. Magn. Magnetic Mater.* **7** 49
Kronmuller H 1978 *J. Magn. Magn. Mater.* **7** 341
Krumme J P 1974 *Phys. Status Solidi* **23** 33
Krumme J P and Hansen 1973 *Appl. Phys. Lett.* **22** 312
Likhite S D, Radhakrishnamurty C and Sahasrabudhe P W 1965 *Rev. Sci. Instrum.* **36** 1558
Livingston J D and Martin D L 1977 *J. Appl. Phys.* **48** 1350
Mydosh J A 1978 *J. Magn. Magn. Mater.* **7** 237
Neel L 1955 *Adv. Phys.* **4** 191
Radhakrishnamurty C and Likhite S D 1970 *Earth Planet. Sci. Lett.* **7** 389
Sato T, Kuroda C and Saito M 1970 *Proc. Int. Conf.* (Japan: University Park Press) p. 72
Smit J and Wijn H P J 1959 Ferrites Philips' Technical Library p 30
Stoner E C and Wohlfarth E P 1948 *Philos. Trans. R. Soc. (London)* **240** 599
Syono Y and Ishikawa Y 1964 *J. Phys. Soc. Jpn.* **19** 1752
Venkatesh Rao 1975 Ph.D. Thesis Indian Institute of Technology Bombay (unpublished)
Wohlfarth E P 1977 *Physica* **B86-88** 852