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The magnetisation processes in barium ferrite micro-powders subjected to various annealing and milling treatments were investigated by the methods of magnetic analysis.

The anisotropy field distributions were found to vary with the coercive force, being dependent on the dislocation density. The samples with the lower values of the coercive force had more particles in the low-anisotropy-field region than the samples with the higher coercive forces.

Wohlfarth's remanence relationships are not obeyed, the discrepancies being attributed to the presence of domains. A particular type of domain structure, the cylindrical domain, was postulated to explain an asymmetrical magnetisation process occurring. The discrepancies from Wohlfarth's relationships and the extent of the asymmetry are related to the dislocation density in a manner similar to that used to explain the anisotropy field distribution results.

The role of dislocations in reducing the anisotropy and in acting as domain-wall nucleation centres was considered and justified by a brief theoretical account of the possible dislocations in barium ferrite.
ACKNOWLEDGEMENTS

I would like to acknowledge with gratitude the debt I owe to Profs. K. Hoselits and K. Puttick, who suggested the topic on which I worked, and provided advice and encouragement throughout.

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During the three years that this work occupied, I made many friends among my colleagues in the Department of Physics at Battersea with whom I had discussions of my work, which, although they may not have enlightened my friends very much, enabled me to straighten out my ideas. For this, and for the encouragement offered to me, I am most grateful.

My gratitude is due also to Mr. C. P. Southworth, and Mr. A. K. Jordan, of Mullard Magnetic Components, Southport, Lancs., who provided the samples I used, and with whom I had fruitful discussions.

I would like to thank too Miss M. Dew, secretary to Prof. Hoselits, who typed the difficult chapters 1 and 2, and who was of great help throughout the three years I was at Mullard Research Laboratories. Thanks are due also to Mrs. B. Jones who typed the second half of the thesis.

Finally, I would like to thank my wife, Anna, who checked my manuscript before it was typed and who, by her constant interest, encouragement and self-sacrifice over the past three years, made the completion of this thesis possible.
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The magnetisation processes in barium ferrite micro-powders were investigated by the methods described in Chapter 2. The experimental results are given in Chapter 3, and are discussed in Chapter 4.

The theory of fine-particle permanent magnets is briefly reviewed (1.1.1) and the suitability of barium ferrite as a permanent magnet material is discussed (1.1.2). The published results on barium ferrite are summarised (1.2) and the scope and object of the research, the results of which are given in this thesis, are given in (1.3).

1.1 Permanent magnet theory

1.1.1. The theory of fine particle permanent magnets has been reviewed by Wohlfarth, Feuerman, and Zijlstra. In a ferromagnet, the mechanism of magnetic reversal may be:

a) domain wall motion;
b) coherent rotation;
c) incoherent rotation;

or else d), a mixture of two or even all three processes.

The barriers to domain-wall motion are in general small, so that materials undergoing reversal by method (a) will have a low coercivity. This is not desirable for applications as a permanent magnet material. Thus the formation and movement of domains in a material must be suppressed, so that each particle is a single domain. Neal and Kittel have shown that under these circumstances, the coercive force can be high. The particle size must be less than a certain critical size, the single-domain size, so that it is energetically unfavourable for domains to be present. The critical diameter has been estimated to be 230 \( \mu \) and 520 \( \mu \) for spherical samples of iron and nickel respectively. For needle-shaped samples, the values are 1620 \( \mu \) for iron and 3700 \( \mu \) for nickel. For a sample of barium ferrite, the critical diameter is about 1 micron. No calculation has been done for NiMn but observations of domain structures suggested that the critical diameter was about 10 microns.

The usual method of calculating the single-domain size is to assume that the particle consists of two domains, i.e. one domain wall is present, and to compute the total energy which is made up of magnetostatic and wall energies. This energy is compared with the
Fig. I.I. (1) Field $H$ applied at an angle $\theta$ to the easy axis of a single-domain particle with uniaxial anisotropy.

Fig. III. (2) The magnetization curves for single-domain particles with uniaxial anisotropy. The parameter on the curves is the angle which the field makes with the easy axis. Ref. 6.
magnetostatic energy of the particle in the single-domain state, when there is no domain wall energy. The particle size at which these two configurations have the same total energy is the critical single-domain size. Particles smaller in size than this critical size will be single
domains.

The barrier to reversal of the magnetisation of a single-domain particle is provided by magnetostatic, strain, or magnetocrystalline energy, which opposes the rotation of the magnetisation.\[3,4,5\].

There will be certain directions in the particle, depending on the total magnetic energy of the configuration, along which the magnetisation will preferentially lie. Those directions, known as easy directions, will be positions of energy minima in zero field. When a magnetic field is applied opposite to the direction of the magnetisation of the particle, the field must supply the energy for the magnetisation to overcome the energy barriers to reversal. Stoner and Wohlfarth\[6\] have considered the magnetisation curves of single-domain particles with only two easy directions, i.e., with uniaxial anisotropy, which reverse their magnetisation by coherent, i.e., uniform, rotation of the magnetisation vector. The energy in an applied field \( H \) is

\[
E = K_a \sin^2 \theta - N_S H \cos(\theta - \phi)
\]

where the angles are as shown in fig. 1.1.1. \( K_a \) is the anisotropy constant, which can arise from one or more of the energies above. \( N_S \) is the saturation magnetisation. When the field is along the easy axis, the coercive force was shown to be \( H_c = 2K_a/N_S = H_a \), the anisotropy field. The magnetisation loops for individual particles are shown in fig. 1.1.1(2), where the parameter \( \phi \) is the angle between the field and the easy axis.

It is desirable to have the coercive force and the critical single-domain size as large as possible. For a prolate ellipsoid with shape anisotropy only, where the demagnetising factors along the major and minor axes are \( N_a \), \( N_b \), respectively, \( H_c = 2K_a/N_aH_a \) and \( N_a = \frac{1}{\sqrt{N_a + N_b}} \); this requires \( N_b \) and \( N_S \) large, \( N_a \) small, for

large \( H_c \) and \( H_a \) and \( N_S \) small for large \( H_c \). When the anisotropy is magnetocrystalline, \( H_c = 2K/H_a \) and \( H_a \approx H_a^2/N_a \); this requires \( K \) and \( N_S \) small for large \( H_a \), and also for large \( H_c \). For permanent magnet applications, \( N_S \) should be large. Thus a compromise between these various requirements must be made, no matter what type of anisotropy is present.
Random

Aligned

Fig. III (3) Magnetization curves for assemblies of single-domain particles with uniaxial anisotropy. Ref. 6

Curling  Twisting  Buckling  Parallel rotation  Fanning

Coherent

Fig. III (4) Coherent and incoherent modes of magnetization reversal in cylinders, chains of spheres and prolate ellipsoid. Ref. 3
Fig. 11.1(5) Size dependence of coercive force of an infinite cylinder for various modes of reversal Ref. 3

Fig. 11.1(6) Theoretical dependence of the reduced coercive force, $h_c$, on the angle $\Omega$ between the cylinder axis and the field with the reduced radius $S=R/R_0$ as a parameter Ref. 21
The coercive force of an assembly of non-interacting single-domain particles is \( H_c = H_A \) for an assembly with all their easy axes parallel, and \( H_c = 0.48 H_A \) for an assembly with spatially random distribution of their easy axes. The remanences are \( H_S \) and \( 0.5 H_S \) respectively. The magnetization curves are shown in fig. 1.1.1. (5).

Disagreement with the theoretical predictions may arise from several effects. Wohlfarth has pointed out that the usual estimate of the single-domain size is made by comparing the energy of an arbitrary multi-domain configuration with the single-domain configuration, with no external field in either case, i.e., at the remanence point. In an applied field, opposed to the particle magnetization, it may be energetically favourable for the particle to split into domains. Thus reversal could proceed by domain wall nucleation and movement, a process which could be magnetically easier, i.e., occur at lower reverse field strengths, than reversal by either coherent or incoherent rotation of the magnetization.

Wohlfarth has given an alternative definition of the critical size as that size below which reversal always takes place by coherent rotation. This size is much smaller than the usual critical size. An approach to the field dependence of the critical size has been made by Craik and McIntyre. The problem of domain nucleation in a previously saturated particle has been reviewed by Aharoni. Some progress has been made by the application of micromagnetics and the theoretical identification of some nucleated domain structures has been made by Muller.

A second effect by which the coercive force may be reduced is the reversal of the magnetization by incoherent, i.e., non-uniform, rotation. Various mechanisms have been studied. Jacobs and Bean studied the fanning mechanism in chains of spheres. Aron and the group at the Weismann Institute, Israel, i.e., Frei, Shtrikman and Aharoni, studied the mechanisms of curling, buckling and twisting. These studies were reviewed by Shtrikman and Traves. These modes of magnetization reversal are shown in fig. 1.1.1. (4). The size dependence of the coercive force of infinite cylinders, which have only shape anisotropy is shown in fig. 1.1.1. (5). The cylinder axis is the easy axis. The angular dependence of \( H_c \) is shown in fig. 1.1.1. (6), where the curve for \( S = 0 \) is the same one as for Stoner-Wohlfarth coherent rotation. \( S = R/R_c \) is the reduced diameter of the cylinder, where \( R_c = A^1/4 \beta_k \) is a critical radius and \( A \) is the exchange constant. In a ferromagnetic system, the energy is a minimum when all the spins are parallel, due to the quantum-mechanical exchange interaction. If the
Fig. III (7)
Angular variation of coercive force of an infinite chain of spheres for various modes of reversal. The parameter $S$ is a reduced radius. Ref. 22

Fig. III (8)
Angular variation of coercive force for coherent rotation S.W and domain-wall motion D-W. $h_S$ is the field at which irreversible jumps of the magnetization takes place in the S.W theory $\mathbf{N} < 45^\circ$, $h_c = h_S$
Fig. 11.1(9) Magnetization curves due to reversible rotation and irreversible wall displacement for a substance with uniaxial anisotropy (numerical values are those of $\theta_0$, $H_{0//} = 0.2K_u/I_s$ is assumed). Ref. 24

Fig. 11.1(10) Magnetization curve of the aggregate of fine uniaxial particles with a multidomain structure. Ref. 24
parallelism is destroyed, energy will be introduced into the system. If the direction cosines of the spins are \((c_1, c_2, c_3)\), it can be shown that the exchange energy is proportional to \((v_1^2 + v_2^2 + v_3^2)\). The constant of proportionality is \(A\), the exchange constant. The angular variation of \(H_0\) in an infinite chain of spheres is shown for various modes of reversal in fig. 1.1.1. (7).

If there are domains present in the particles, reversal by domain-wall motion can take place. This is known as completely incoherent reversal. Only the component of the applied field parallel to the easy axis is effective. The angular variation of coercive force is given by

\[ H_0(\theta) = H_0(0^\circ) \text{ sec } \theta \]

where \(\theta\) is the angle the field makes with the easy axis. This variation is shown in fig. 1.1.1. (8), where it was arbitrarily assumed that \(H_0(0^\circ) = H_{A,0}/10\). For large values of \(\theta\), the coercive force for coherent rotation, also shown in fig. 1.1.1. (8), may be smaller than that for domain-wall motion. The hysteresis loops of particles with the field applied at various angles \(\theta\) to the easy axis are shown in fig. 1.1.1. (9) and the hysteresis loops of assemblies of particles with both random distribution and perfect alignment of the easy axes are shown in fig. 1.1.1. (10).

In the above discussion, \(K_A\) has been called the anisotropy constant. No specific type of anisotropy has been assumed. In the case of shape anisotropy, \(K_A = 1/2 (K_p + K_m) M_S^2\), where \(K_p, K_m\) are the principal demagnetising factors for prolate spheroids, or particles equivalent to prolate spheroids by the Brown-Norrish theorem. For magnetocrystalline anisotropy, \(K_A = K\), the magnetocrystalline anisotropy constant. For strain anisotropy, \(K_A = J\sigma/2\), where \(J\) is the saturation magnetostriction coefficient and \(\sigma\) is the uniaxial stress. In many cases, two or more of these types of anisotropy may be superimposed.

For example, with uniaxial magnetocrystalline anisotropy superimposed on uniaxial shape anisotropy and with the two easy axes perpendicular to each other, \(K_A = K - 2J\sigma M_S^2\). This would be the case in a platelet with the magnetocrystalline easy axis perpendicular to the plane of the platelet.

It was also assumed that the anisotropy was uniaxial i.e. with two stable positions for the magnetisation in zero applied field. It can be seen that the fewer the number of stable positions for the magnetisation of a single-domain particle in zero field, the harder it will be to reverse the magnetisation i.e. the higher the theoretical coercive force. Ideally, one should have just a single
Fig. 11.1. (11) Theoretical dependence of $\Theta_k$, the maximum angle between the easy axis and the applied field for which a sphere remains a single domain after saturation, on $K/l_s^2$. Here $K$ is the magneto-crystalline anisotropy constant, and $l_s$ the saturation magnetization.

Ref. 36
stable position for the magnetisation i.e. unidirectional anisotropy. This may be possible in materials with exchange anisotropy (Balikajohn and Bean\textsuperscript{29}, Jacobs and Bean\textsuperscript{30}). However, these unidirectional systems are not commercially viable and uniaxial anisotropy is used as the next best system.

It is known from micromagnetic theory\textsuperscript{22,31} that particles with magneto-crystalline anisotropy $K > H_g^2$ do not reverse their magnetisation by incoherent rotation, but by coherent rotation. The critical size is infinite and except for very small particles\textsuperscript{22}, the coercive force should be independent of particle size. For a particle with the applied field along the easy axis, the nucleation field $-H_n = 2K/H_g$, which is the same field as that at which coherent rotation takes place. Since $-H_n$ is, by definition, the field at which the magnetisation just starts to reverse by domain-wall nucleation, and since $H_g$ is the field at which the magnetisation is zero, it can be seen that reversal by coherent rotation is easier than by domain-wall nucleation and movement. Thus the coercive force should be at least $H_n$. In practice\textsuperscript{6}, $H_q > H_n$, and in some cases, domain nucleation has been observed in positive fields\textsuperscript{32,33}. This discrepancy with theory is known as Brown's paradox\textsuperscript{34}.

From previous discussion and figs. 1.1, 5. to 1.1.8., it can be seen that when the applied field is along the particle easy axis, reversal by incoherent rotation takes place for all geometries and most types of anisotropy, except magneto-crystalline with $K > H_g^2$. However, even when reversal is incoherent with the field along the easy axis, it becomes coherent when the field is applied at angles near $90^\circ$ to the easy axis. Since, for particles with magneto-crystalline anisotropy $K > H_g^2$, reversal is coherent even when the field is along the easy axis, it may be assumed that reversal is coherent at all angles of the applied field with the easy axis.

A particle which remains single-domain after saturation along its easy axis may however split into domains after saturation perpendicular to its easy axis\textsuperscript{19,35,36}. The range of angles for which this may happen is given for a sphere in fig. 1.1.1. (11), as a function of the ratio of magneto-static to magneto-crystalline energies. This result is relevant when discussing the remanent torque measurements of section 2.1., as also is the result that the magnetisation rotates coherently when the field is applied perpendicular to the easy axis.

It should also be noted that when $K > H_g^2$, there should be no dependence of coercive force on packing density of the material\textsuperscript{8}. 
1.1.2. From what has been said previously it can be seen that various requirements must be met to provide a material suitable for permanent magnet applications. The anisotropy must be, preferably, magnetocrystalline, with $K > H^2$, to ensure that reversal of the magnetization is by coherent rotation and that there is no dependence of coercive force on packing density. The ratios $2K/H^2$ and $K/H^3$ should be large, i.e., $K$ large, $H^3$ small, to give a large anisotropy field, $H^2$, and hence a large $H^3$, and a large critical single-domain size. However $H^3$ is required to be large to give a material useful for permanent magnets. These last two requirements are contradictory and hence a compromise is reached.

Barium ferrite is a ferrimagnetic material with uniaxial magnetocrystalline anisotropy described by an anisotropy constant $K = 3.5 \times 10^6$ erg cm$^{-3}$. The saturation magnetization at room temperature is $H_0 = 350$ gauss, giving $2K/H^2 = 17.5$ koe. The single-domain size has been calculated by Went et al. as 1.1 microns, which is reasonably large compared with most other permanent-magnet materials. Thus barium ferrite satisfies the requirements for a suitable material for permanent magnet applications.

1.2. Review of published results on barium ferrite

Reviews of the properties of barium ferrite have been made by Smit and Wijn,37 Haspels,38 Wohlfarth,39 Eriksen,39 Von Aulock,40 and Schieker.41

The uniaxial hexagonal ferrites of lead, barium and strontium have very similar properties. The domain structures of these three materials and of MnB$_2$ are very similar, since the domain structure of a uniaxial material depends on the ratio $H^2/H^3$, which is > 1 for all four materials.

1.2.1. Development of hexagonal permanent magnets. The initial development of barium ferrite as a permanent-magnet material was done by Went et al.,35 and independently by Fahlenbrach and Heister.43 Further development, including the production of magnetically anisotropic samples, was done by Bathenau and his co-workers44-46, Fahlenbrach,47, and Breekman and his co-workers48,49. This has led to the development of modified barium ferrite and strontium ferrite magnets, with improved permanent-magnet properties, due to the inclusion of various additives, as reviewed by Cochardt.52 The magnetic properties of those samples are close to the theoretical maximum.

1.2.2. Preparation of hexagonal ferrites. Paulus and Lacour,55 have reviewed the methods of growing single crystals of the hexagonal ferrites and have described a method of growing large single crystals in the solid state. Usually,54,55 crystals are grown in a melt of
(a) M-Type Hexagonal Ferrites

Unit cell = TSTSTS = 3(Ba$_2$Me$_2$Fe$_{12}$O$_{22}$).

(b) Y-Type Hexagonal Ferrites.

Fig. 1.2.3. (1) Crystal structures. Ref. 40.
© Oxygen ions

- Barium or divalent metal ion in (a) and (b), potassium iron in (c).
- Iron ion on octahedral site.
- Iron ion on tetrahedral site.
- Iron ion on trigonal site.

Unit cell: $5R'S^*R'I^*$

$$= 2(KFe_{11}O_{17})$$

(c) $KFe_{11}O_{17}$

Fig. 1.23 (I) Crystal structures. Ref. 40.
(a) Spinel Crystal Structure with [111] Axis Vertical

- Octahedral
- Tetrahedral

(b) Structure of R-block

Fig. 1.2.3. (2)
Fe₂O₃ with either the halide or carbonate of the required divalent metal ion, where the ratio of iron to the divalent ion is 6 to 1. An oxygen atmosphere is used. Electrolytic co-precipitation has also been used⁵⁶, then grown for use as a permanent magnet material, large crystals are not required. The techniques are those usually used for ceramic materials⁵⁷,⁵⁸. The presence of impurities has been found to affect the magnetic properties, not always adversely, and certain impurities have been deliberately introduced in order to enhance the permanent magnet properties⁵⁹-⁶². If the impurities are such as to replace some of the iron ions, changes in the magnetic properties will also be made⁶⁰-⁶¹.

The method of preparation of the powders used in the present work is described in section 2.4 and is the industrial method for preparing the permanent magnet material⁶².

1.2.3. Crystal structure and intrinsic magnetic properties of barium ferrite. The chemical formula of barium ferrite is BaFe₁₂O₁₉. It has the magneto-plumbite structure (Adelheid) which is shown in fig. 1.2.3. (1) which shows the unit cell and its dimensions. The oxygen layers are close-packed, but the packing changes from cubic close-packed to hexagonal close-packed along the c-axis⁴⁰. The layer in which barium replaces one of the oxygen ions is h.c.p. with respect to the layers on either side of it, while all the other oxygen layers are c.o.p. with respect to each other. A description of the structure in terms of a layer-structure is particularly useful when discussing dislocations in the lattice.

The iron ions are in five crystallographically inequivalent cation sites, interstitial in the oxygen layers. The structure may be considered as a stacking of spinel blocks 3 and hexagonal blocks 2, fig. 1.2.3. (2), where the [111] axis of the cubic spinel block is along the c-axis. The stacking sequence is SBS⁴², where an asterisk denotes the specified block turned through 180°. The unit cell contains two formula units i.e. 2 x BaFe₁₂O₁₉.

The five inequivalent sites are octahedral 12k on the border between the 3 and 2 blocks, tetrahedral 4 f₁, and octahedral 2a in the 3-block, octahedral 4 f₂ in the 2-block, and trigonal 2b in the layer containing barium in the 1-block. These sites are identified in fig. 1.2.3. (2).

The magnetic structure has been determined by Cortez⁶⁵, All the magnetic ions are Fe³⁺, and lie on five magnetic sub-lattices. The interaction between the sub-lattices is ferrimagnetic⁶⁶,⁶⁷, the mechanism of superexchange acting to align the magnetic moments of
Fig. 123 (3) Trigonal Site.
neighbouring layers of iron ions antiparallel. Thus, along the c-axis, the direction of the spins alternates from one layer to the next, but all the moments are parallel to the c-axis due to the ion on the 2b site, which is responsible for the high uniaxial anisotropy \( K = 3.3 \times 10^6 \text{ erg cm}^{-3} \). The five magnetic sublattices may be combined to give two sub-lattices, a majority one, \( a \), formed from the ions on the \( 12k \), \( 2a \) and \( 2b \) sites and a minority one, \( b \), from the ions on the \( 4f \), and \( 4g \) sites. These two sub-lattices are antiparallel. The net magnetisation per unit cell is 16 ferric moments from \( a \) and 6 ferric moments from \( b \), giving a resultant moment of 8 ferric moments or 40 Bohr magnetons at absolute zero. This is in good agreement with experiment \( \text{eqn. 1.2.3.} \)  

The anisotropy of barium ferrite is attributed to the ferric ions on the \( 2a \) site. A calculation of the dipole-dipole interactions in the lattice gives a resultant anisotropy constant at low temperatures of \( -1.3 \times 10^6 \text{ erg cm}^{-3} \), which would require the magnetisation to lie in the basal plane \( \text{eqn. 1.2.3.} \). The experimental value of \( K \) is \( 4.4 \times 10^6 \text{ erg cm}^{-3} \) at low temperatures, which means that the magnetisation lies along the c-axis. The difference between the two values, \( 5.9 \times 10^6 \text{ erg cm}^{-3} \), must be explained by some mechanism other than the dipole-dipole interaction. By comparison with the structures of hexagonal \( \text{Ba}_2\text{Fe}_2 \text{O}_7 \), \( \text{eqn. 1.2.3.} \) and \( \text{Fe}_{11} \text{O}_{17} \), \( \text{eqn. 1.2.3.} \), in which the magnetisation lies in the basal plane, it was found that the major difference was the absence of ferric ions on the \( 2a \) sites in these two structures. The anisotropy of these materials was negative and could be accounted for by dipole-dipole interactions. The large positive anisotropy of barium ferrite is thus attributed to the ferric ions on the \( 2a \) sites, with five-fold oxygen co-ordination, \( \text{fig. 1.2.3.} \).  

The mechanism by which the anisotropy arises is thought to be spin-orbit coupling for the ion on the trigonal \( 2a \) site. The unusual five-fold symmetry in \( \text{eqn. 1.2.3.} \) of a low order develops in the ion and orbital quenching is to be expected. The spin of the ion, and hence the magnetic moment, will thus be constrained to lie along the symmetry axis of the site i.e. parallel to the c-axis. The ground state of the ferric ion is \( 6^5S \) in which the orbital angular momentum is zero. The energy of spin-orbit coupling is

\[
E_{L,s} = NL^2 \sin^2 \theta \quad \text{eqn. 1.2.3. (1)}
\]

where \( L \) is the orbital angular momentum, \( S \) is the spin angular momentum and \( \lambda \) is the spin-orbit coupling constant. If \( L \) is zero, there can be no spin-orbit energy and no quenching. This is the case for an ion in a \( 6^5S \) state. However, the theory of superexchange \( \text{eqn. 1.2.3.} \) requires the
Fig. 12.4. (1) Curves of (a) remanence $B_r$ and (b) intrinsic coercive force $M_{Hc}$, versus sintering temperature, where the sintering time was (1) 30 mins (2) 1 hour (3) 5 hours. Ref. 79
Fig. 1.2.4. (2) Hysteresis loops at room temperature of BaFe$_{12}$O$_{19}$ with random crystal orientation, sintered at (a) 1350 and (b) 1400°C, so that the average grain sizes are about (a) 10 and (b) 1 micron respectively. Dashed: demagnetization curves for pure rotation. Ref 44.
Fig. 1.2.4 (3) Coercive force $mH_c$ and remanence $B_r$ versus sintering temperature for aligned samples. The values before firing are marked on the ordinates thus ( ) — Ref. 49.
Fig. 1.2.4 (4) Hysteresis loops at room temperature measured for pseudo-unicrystalline material along the direction of preferred magnetization, to be compared with Fig. 5. (a) small crystals (b) large crystals, higher density. Dashed: curves for coherent rotation. Ref. 4.4

Fig. 1.2.4. (5) Coercive force versus remanence for aligned and random samples.
partial transfer of an electron from an oxygen anion to the ferric cation. The resultant state of the cation has a non-zero L and hence quenching may occur. Spin-orbit interaction may also occur, which, taken with the quenching and the low symmetry of the site, may give rise to magnetocrystalline anisotropy with the magnetic moments along the c-axis. A quantum-mechanical treatment of the anisotropy of magnetoplumbite-type hexagonal ferrites \(^{75}\) shows that the values of the crystal-field parameters required to explain the observed anisotropy are of a reasonable magnitude.

Mössbauer-effect measurements on barium ferrite \(^{75-77}\), while confirming the existence of five magnetic sub-lattices, seem to cast some doubt on the role of the Fe site cation in determining the anisotropy, but no alternative scheme to the one discussed above has been proposed. This scheme will be used in the discussion of the effects of dislocations on the magnetic properties of barium ferrite, section 4.1.1.

1.2.4. Effect of orientation, milling and annealing on the magnetic properties of barium ferrite. During the preparation of barium ferrite for use as a permanent-magnet material, the raw starting materials are prefired at about 1100\(^{\circ}\)C to give an inhomogeneous, polycrystalline mass of the ferrite\(^{49,57}\). This material is crushed and milled, then pressed into shape and sintered. The final sintering may be done at temperatures up to 1600\(^{\circ}\)C. Below about 1000\(^{\circ}\)C, the amount of sintering which takes place is very small and the process is known as annealing.

Sintering, or firing, at temperatures near 1100\(^{\circ}\)C gives a fine-grained material; while at temperatures near 1600\(^{\circ}\)C, a coarse-grained material results\(^{49}\). The better permanent magnetic properties are obtained\(^{76,79}\) by sintering in the temperature range 1200 - 1250\(^{\circ}\)C. Results for unoriented samples are given in fig. 1.2.4. (1), while the effect on the hysteresis loop is shown in fig. 1.2.4. (2). It is seen that the coercive force is highest at the lowest sintering temperatures, and decreases continuously with temperature. The remanence exhibits a maximum at about 1200 - 1250\(^{\circ}\)C, decreasing both at low and high temperatures.

For aligned samples i.e. ones in which all the easy axes are parallel, or nearly parallel, to each other, it is seen from fig. 1.2.4. (3) that the coercive force follows the same trend as for the randomly aligned samples. The hysteresis loops for two samples fired at different temperatures are shown in fig. 1.2.4. (4). The sintering of aligned samples is done after the orientation procedure\(^{46}\).\n
It is found that the remanence decreases with increasing coercive force for aligned samples\(^{52}\), in contrast with the behaviour of randomly orientated samples fig. 1.2.4.\((5)\). The remanence and orientation are improved by sintering\(^{46,80}\), but the coercive force decreases. The coercive force of aligned samples is less than that of unaligned ones\(^{46}\), when the degree of orientation is high.

The dependence of coercive force on sintering temperature for the unaligned samples is due to the dependence of the final grain-size produced on the temperature used\(^{46}\). The higher temperatures given the larger particles, which are multidomain and hence have the low coercive force associated with domain-wall movement\(^{6}\). The lower temperatures produce smaller particles, of single-domain size, which have the high coercive force associated with coherent rotation of the magnetisation\(^{6,8}\). Theoretically even large particles should remain single-domain after saturation\(^{2}\), but Rathenau et al.\(^{46}\) presumed that dislocations act as nucleation centres and allow the formation of domains, which lower the coercive force and remanence. The probability of domain formation increases with particle size, and hence the effect of domain nucleation is more pronounced for the larger particles produced at the higher temperatures. On this view, the remanence and coercive force should increase together, since the conditions necessary for a high value of one are conducive to a high value of the other.

For the aligned samples, the dependence of the coercive force on sintering temperature is partly due to the effect of varying grain-size, as for the randomly-aligned samples. Another effect also comes into play when all the particles have their easy axes aligned parallel\(^{37}\): this is the movement of domains forced in one particle, through another one, thus reversing the magnetisation of the second particle by domain-wall motion, rather than by coherent rotation. In addition, the movement of domains by an applied field is easier in aligned particles than in particles whose easy axes make an angle with the applied field\(^{23}\). The orientation of aligned samples is also improved by sintering\(^{80,61}\), thus increasing the remanence, but causing the formation of larger grains, and facilitating the passage of domain-walls between grains, hence lowering the coercive force. A simple theoretical analysis of domain formation by Rathenau et al.\(^{46}\) indicates that domains will form at fields below a critical field given by

\[
H_c(\theta) = \frac{4\pi M}{\cos \theta} = 4\pi M \cos \theta \quad \text{eqn. 1.2.4.(1)}
\]

where \(\theta\) is the angle the field makes with the easy axis, \(H\) is the demagnetising factor along the easy axis, \(M\) is the magnetisation and \(H_s\) the saturation magnetisation.
For a particle with the easy axis along the applied field, \( H_a(0^\circ) = 0 \) and domain nucleation takes place in negative fields. If \( 0^\circ < 0^\circ \), \( H_a(0) > 0 \) and domain nucleation takes place in positive fields. Hence departures from coherent rotation will take place in unaligned particles in positive fields, but in aligned particles in negative fields. Also, the better the degree of alignment, the higher the remanence will be, since more particles will remain saturated. These remarks are borne out by figs. 1.2.b.(2) and 1.2.a.(a) where the curves for coherent rotation are shown dashed.

An alternative explanation of the variation of coercive force with sintering temperature has been given by Ivanov et al.\textsuperscript{82} and Shol'ts.\textsuperscript{85} It is presumed that the sintering at the lower temperatures gives a non-equilibrium structure, which gives rise to the higher coercive force. The existence of a second phase is postulated, which has inferior magnetic properties compared to the barium ferrite. The mechanism by which this second phase gives a high coercive force is not stated, but it may act in a similar way to a weakly magnetic or non-magnetic matrix in certain other magnetic systems,\textsuperscript{6} where strongly magnetic particles are isolated from one another by the matrix. The amount of this second phase is presumed less after sintering at the higher temperatures and hence the coercive force is less. Further support for this theory is obtained from results on the saturation magnetization, which is lower for the higher coercive force material, as it would be if there were more of the weakly magnetic phase. This theory is also supported by the results of Brockman et al.\textsuperscript{49} who reported the presence of a second phase in high coercive force material sintered at the lower temperatures. The material with the best permanent-magnetic properties was also prepared from a non-stoichiometric ratio of starting materials, and the firing cycle was such as to produce a non-equilibrium material.

Various investigators have reported on the effect of milling on the magnetic properties of permanent-magnetic materials.\textsuperscript{49,64-91} For barium ferrite, two types of behaviour have been found. If the sintered material has a low coercive force initially, i.e. less than about 1000 Oe, milling increases the coercive force, the value of which may then tend to a limit or decrease to a low value again. If the coercive force is initially high, i.e. greater than about 2000 Oe, milling decreases the coercive force which may then tend to a limit or continuously decrease for the longest milling times used. Several theories have been used to explain these results. All theories explain the increase of coercive force of the low-coercive force materials with initial milling by the reduction of particle size from multidomain to single-domain size. The reduction of the coercive force of the
Fig. 1.2.4 (6)
Coercive force versus milling time for barium ferrite
(a) presintered at 1370°C for 4 hours.
(b) presintered at 1160°C for ½ hour.
Curves a' and b' are for the material which had been milled then annealed at 1000°C for ½ hour. Ref. 89

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Fig. 1.2.4 (7)
Ref. 89

(a) Coercive force versus milling time for barium ferrite, presintered at 1350°C. The dashed curve is for the milled sample which was annealed at 1000°C for ½ hour.

(b) Saturation magnetization per gramme and Fe²⁺ concentration as a function of milling time for the sample of (a).
Fig. 1.2.4 (8) Samples (a) and (b) are the same as in Fig. 1.2.4 (6). The figures on the right hand side are the milling time in minutes before the annealing at 1000°C. Ref. 89

Fig. 1.2.4 (9) Dependence of the coercive force of barium ferrite powders on the duration of ball milling. Parameter on curves is temperature at which $M_{Hc}$ was measured. Ref. 90

Fig. 1.2.4 (10) Effect of static pressure on the coercive force of barium ferrite powder. Ref. 90
high-coercive force material, the tending to a limit with extended milling or the reduction after an initial increase, are explained by other theories.

Hains 

has used the idea of Rathenau et al. that dislocations act as nucleation centres for domains. The dislocations reduce the anisotropy by changing the ferrimagnetic coupling scheme in the crystal. Abraham and Aharoni have shown theoretically that a region in a crystal where the anisotropy is reduced can act as a domain-wall nucleation centre. Milling the high-coercive-force sample reduces its saturation magnetisation; this result may also be explained by the changing of the ferrimagnetic coupling in the crystal. The shape of the $H_0$ versus milling time curve is explained for the low-coercive-force material, curve "a" fig. 1,2,4. (6) by the influence of two opposing factors: the reduction of particle size increases $H_0$, but the increase in the dislocation density decreases $H_0$. The former factor outweighs the latter, giving a net increase in $H_0$. If the equilibrium dislocation density is reached before the optimum particle size, the curve tends to a limit, the value of which depends on the type of mill used. If the optimum particle size is reached before the equilibrium dislocation density is established, the coercive force may decrease again. For the high-coercive-force sample, curve "b" fig. 1,2,4. (6), the particle size is assumed to be optimum before milling. Hence the introduction of dislocations lowers $H_0$, which tends to a limit, if the milling time is long enough, which depends on the equilibrium dislocation density. The type of mill used determines the value of this limit. Annealing milled samples is presumed to heal dislocations, thus increasing $H_0$, and the saturation magnetisation, fig. 1,2,4. (7). The effect of prolonged annealing is shown in fig. 1,2,4. (8) where it is seen that the value of $H_0$ tends to a constant value, dependent on the initial value and the amount of milling. The difference in this final value of $H_0$ for material "b" milled for two different times is less than the difference for material "a" milled for the same time. This result is explained by the dependence of the coercive force on the final particle size after milling and prolonged annealing. The particles of sample "a" were multidomain and hence the reduction in size to single-domain had a large effect on the coercive force. For material "b", the particles were already at or near single-domain size before milling and hence the change in particle size had only a small effect. The value of $H_0$ depends on the particle size, which is less for "b" than it is for "a".
Tenser has explained his results, fig. 1.2.4. (9), by presuming that milling introduces particles of superparamagnetic size. In these particles, the thermal energy is comparable to the anisotropy energy, so that the magnetization may be reversed by thermal agitation. The superparamagnetic size, below which the thermal effects are important, $V_a$, is given by

$$V_a = 25 \, \text{k}^2/\text{K}$$

where $k$ is Boltzmann's constant, $T$ is the absolute temperature and $K$ is the anisotropy constant. The initial increase in $H_c$ is again ascribed to the reduction in particle size from multi- to single-domain size. The decrease with prolonged milling is due to the increase of the amount of superparamagnetic material present, which has zero coercive force and resonance and hence has a detrimental effect on the magnetic properties. The effect of temperature changes on the coercive force are also explained on this basis, fig. 1.2.4. (9). For short milling times, reducing the temperature lowers $H_c$, due to the critical single-domain size decreasing i.e. particles which were below the single-domain size are now above it. For long milling times, reducing the temperature increases $H_c$ due to the reduction in the critical superparamagnetic size i.e. particles which were superparamagnetic at room temperature become single-domain at low temperatures. Thus after prolonged milling, the amount of superparamagnetic material present has a marked effect on the magnetic properties. The effect of hydrostatic pressure on the coercive force of a powder milled for a long time provides support for this explanation, fig. 1.2.4. (10). The coercive force initially increases, due to the effective particle size increasing i.e. the effective amount of superparamagnetic material decreases due to increased contact between the particles. After reaching a maximum, the coercive force decreases, due to the easier passage of domains between particles. For a sample with initially high $H_c$, static pressure causes a decrease, fig. 1.2.4. (10), presumably due to multidomain effects due to the easier passage of domain-walls between particles. Annealing milled samples increases $H_c$, due to the superparamagnetic particles being more reactive than the larger ones. Thus annealing reduces the amount of superparamagnetic material present, thereby improving the magnetic properties.

Pahnenbrach has explained his results in a similar manner, except that he presumes that dislocations lower the anisotropy constant $K$ and hence increase the critical superparamagnetic size, $V_a$. 
Powder no.

<table>
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<tr>
<th></th>
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<th>2</th>
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<tbody>
<tr>
<td></td>
<td>( H_e )</td>
<td>( C )</td>
</tr>
<tr>
<td>A</td>
<td>1270</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>1170</td>
<td>2.52</td>
</tr>
<tr>
<td>C</td>
<td>1140</td>
<td>2.98</td>
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<tr>
<td>D</td>
<td>1120</td>
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</tr>
<tr>
<td>E</td>
<td>1090</td>
<td>4.0</td>
</tr>
<tr>
<td>F</td>
<td>1125</td>
<td>4.0</td>
</tr>
<tr>
<td>G</td>
<td>1175</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Powder 1: untreated
Powder 2: annealed 30 min. at 1100°C.
A: ½ Araldite, ½ barium ferrite, unpressed
B-E: pressed to different densities
F: 10% by wt. Polyvinylalcohol
G: 20% " " "

Table 1.2.4(1)

<table>
<thead>
<tr>
<th>Barium ferrite sintered at 1400°C.</th>
<th>( H_e = 20 ) oe.</th>
</tr>
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<tr>
<td>( d ): sintered specimen 280µ</td>
<td>55µ  3.5µ  1-2µ</td>
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<tr>
<td>( \sigma_s ) e.m.u. 70</td>
<td>69   67   69</td>
</tr>
</tbody>
</table>

Barium ferrite sintered at 1200°C. \( H_e = 2000 \) oe.

| \( d \): sintered specimen 4.7µ | 1.6µ  1.5µ  1.1µ |
| \( \sigma_s \) e.m.u. 67         | 63.5 63.0 57.5 49.5 |

Table 1.2.4(2)

<table>
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<th>Diameter D</th>
<th>0.50</th>
<th>0.43</th>
<th>0.42</th>
<th>0.38</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_s )</td>
<td>150</td>
<td>134</td>
<td>105</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 1.2.4(3)

\( \sigma_s \) is the saturation magnetisation per unit mass.
\( H_s \) is the " " " " volume.
It is only possible to convert from one to the other if the density is known.

\( H_s = \theta \sigma_s \)
(a) Variation of the coercive force with particle size for barium ferrite sintered at 1400°

(b) Variation of the coercive force with particle size for barium ferrite sintered at 1200°

Fig. 1.2.4. (11) Coercive force $H_C$ as a function of particle diameter (or particle thickness), for iron, barium ferrite, and manganese bismuth. Ref. 96

Fig. 1.2.4. (12) Reversible susceptibility in three different magnetic states with $B-H=0$, plotted versus the reciprocal of intrinsic coercive force. Ref. 96.
Annealing reduces the number of superparamagnetic particles, both by causing them to react, as above, and by healing dislocations. The effect of pressure i.e., packing density, on the coercive force, table 1.2.4, (1), is due to the introduction of defects by the pressure. The effect is more marked for the samples with high \( H' \) than for those with low \( H' \) because the fractional change in dislocation density is greater for the high \( H' \) samples, which had the lower initial dislocation density. The addition of a binder, which acts as a lubricant, gives a higher \( H' \), even though the same sample density is used. Also, sintering of an aligned sample to a high density gives a higher \( H' \) value than for a pressed, unaligned sample, contrary to the usual reduction of \( H' \) in aligned samples\(^{52} \). The presence of a lubricant reduces the stress on the particles thus reducing the number of dislocations introduced, while the sintering process in assumed to introduce no dislocations.

Ivanov et al.\(^{82,83} \) have explained the reduction in \( H' \) of their high-coercive-force sample with milling, fig. 1.2.4. (11), as being due to the milling process changing the crystal structure of the barium ferrite into the second phase (with inferior magnetic properties compared with the bulk material) which caused the high-coercive-force state in the sintered material. The presence of large amounts of this second phase with lower coercive force and remanence than barium ferrite reduces the permanent-magnetic properties of the sample. The saturation magnetization of the sample is also reduced by milling, table 1.2.4. (2), and this is taken as further evidence of the presence of a second phase with inferior magnetic properties, due to a change in crystal structure. The effect of milling on \( H' \) for a sample with an initially low value is due to the reduction in particle size from multi-to single-domain. The amount of second phase also increases, but the reduction in particle size is more important for this sample. The saturation magnetization also decreases, table 1.2.4. (2) but not as much as for the high \( H' \) sample. Sintering the milled samples increases \( H' \) and the saturation magnetization by reducing the amount of second phase. It is not stated what the form of this second phase may be, but it may be the same as that found by Brodhman et al.\(^{49} \) or else it may be the defect barium ferrite structure of Heinke\(^{50} \) and Fahlenbroch\(^{51} \).

Torkar and Frederiksen\(^{57} \) have also observed a decrease of saturation magnetization with decrease of particle size, table 1.2.4. (3). They attributed this to the presence of a disturbed surface layer on the particles, introduced by milling. This layer, with inferior magnetic properties compared to the bulk material may be
Fig. 1.2.4. (14)(a) 
The saturation magnetization of dense BaO:6Fe₂O₅ as a function of temperature.
Ref. 45

Fig. 1.2.4. (14)(b) 
The intrinsic coercive force $H_c$ as measured for fine-grained BaFe₁₂O₁₉ as a function of temperature, compared with the quantity 0.96 $K_1/M_s$
Ref. 45

Fig. 1.2.4. (14)(c) 
Constant of crystal anisotropy $K$ of BaO·6Fe₂O₅ as a function of temperature. 
(From $E_c = K \sin^2 \theta + \cdots$)
Ref. 45

Fig. 1.2.4. (14)(d) 
The quantity $K^{1/2}/M_s$ as a function of temperature.
(BaO·6Fe₂O₅)
Ref. 45
The dependence of coercive force on particle size may be found in the preceding results. The results of various workers are shown in fig. 1.2.4. (12), which includes some results for other materials (13). It is seen that, in general, $H_C$ increases with decreasing particle size, although for sintered samples of barium ferrite for which the initial coercive force is high, milling reduces it i.e. $H_C$ decreases with decreasing particle size. However, annealing the milled samples which show this anomalous behaviour increases $H_C$ back to a higher value than the initial one, thus giving agreement with the general trend fig. 1.2.4. (12). The anomalous behaviour of these samples with an initially high $H_C$ is due to other effects, apart from reduction in particle size, being predominant i.e. dislocation density second phase, supersuperparamagnetic particles or disturbed surface layer.

The influence of domains on the magnetic properties of barium ferrite may also be seen in the variation of the susceptibility with coercive force. Sixtus et al. (14) have considered the value of the susceptibility $\chi$ for three different magnetic states of their samples: (a) after thermal demagnetization, (b) after A.C. demagnetization, and (c) at the $H_C$ point. They found, fig. 1.2.4. (13), that $\chi_a > \chi_b > \chi_c$ and that varied inversely with $H_C$. $\chi_c$ for all samples, and all values of $\chi$ for high-coercive-force samples, were close to the value for coherent rotation. It was supposed that the domains formed after (a) were more mobile than those present after (b). After (a) the domains would be expected to be randomly distributed in almost all particles, but after (b) some particles might remain single-domain, and the domains which were present would be expected to have stopped moving at points in the particles where there were barriers to motion. Thus $\chi_a$ should be greater than $\chi_b$. At the $H_C$ point, (c), the predominant process is coherent rotation, and any domains which were present would have been nucleated preferentially at points of low anisotropy and would tend to stick there. Thus $\chi_c$ should be the lowest of the three. The higher the value of $H_C$, the fewer domains there will be present, and all values of susceptibility would be reduced towards the coherent rotation value.

The temperature dependence of $H_C$ provides further support for the influence of domains on the magnetic properties of barium ferrite. The following properties are shown in fig. 1.2.4. (14) as a function of temperature: a) saturation magnetization; b) theoretical and experimental coercive force for randomly aligned samples; c) anisotropy constant; and d) the critical single-domain size, which...
Fig. 1.2.5 (1) Theoretical and experimental dependence of reduced magnetization $j = M(H)/M_s$ on reduced field $h = H/H_A$ for a $6Fe_2O_3 - PbO$ crystal. Ref. 97

Fig. 1.2.5 (2) Magnetization curves and hysteresis loops for different maximal fields of Sr0.4Fe2O₅·2Al₂O₃ single crystal with $S=0.21 \times 10^{-2}$ cm$^2$ and $L=1.08$ mm. Ref. 100

Fig. 1.2.5 (3) Nucleation field of a Sr0.4Fe₂O₅·2Al₂O₃ single crystal as a function of the saturating field
is proportional to $K^2/h_o$. Except for samples with very low values of $h_o$, the temperature variation of the coercive force of all samples is similar to that in fig. 1.2.4. (24) b). There is a characteristic maximum at about 500°C, and the curve falls below the theoretical one at low temperatures. This is explained by a balance between two opposing factors. The critical single-domain size, which is proportional to $K^2/h_o$, varies with temperature as in fig. 1.2.4. (24), reaching a maximum just below the Curie point, 450°C. Hence some particles which were multidomain size at room temperature became single-domain at high temperatures, thus increasing $h_o$. The mobility of the domain-walls, which varies with temperature as $K^2$, increases with temperature, and hence any domains which are present are more effective at causing reversal at the higher temperatures, thus reducing $h_o$. There are less domains at higher temperature, but they are more mobile. The balance between the two factors gives the maximum at 500°C, and not just below the Curie point. At low temperatures, the inverse applies: there are more domains, but they are less mobile. Presumably, there might be a minimum at low temperatures in the $h_o$ versus $T$ curves, but measurements have not been made at low enough temperatures. Sixnin et al. 56, taking into account the variation of $h_A$ and the critical size with temperature and assuming that a demagnetizing field $-4\pi M_s$ acted in each particle, modified the theoretical $h_o$ curve to give better agreement between theory and experiment. The samples with high $h_o$ approached very closely to the theoretical predictions.

The temperature variation of the susceptibility exhibits a minimum at about 500°C, as one would expect from its inverse dependence on $h_o$, fig. 1.2.4. (13) and the temperature variation of $h_o$, fig. 1.2.4. (14).

1.2.5. Magnetisation curves and hysteresis loops of single crystals and particle assemblies of hard ferrites. In the previous section, the dependence of coercive force on preparative treatment and particle size was discussed. This section discusses the general dependence of the shape of the magnetisation curves and hysteresis loops on particle size, without any reference to the methods of preparation.

For large multidomain particles, the magnetisation curves show very little hysteresis 57,59, as expected when the coercive force arises from barriers to domain-wall motion. The dependence of the shape of the curves on the angle, $\theta$, between the applied field and the easy axis is shown in fig. 1.2.5. (1). The initial linear portion of the curve is governed by the requirement that the internal field should remain zero: the magnetisation changes so that the demagnetising field $H_D = -4\pi M_s$ exactly cancels the applied field. This is achieved
by the relative volume of domains orientated favourably with respect to the field growing at the expense of unfavourably orientated domains. When the magnetisation equals $H_B$, only the favourably orientated domains exist, and the magnetisation changes by rotation of the magnetisation vector. In the special cases of $\beta = \frac{\pi}{2}$, saturation is reached in fields of $H_B$ and $H_D = H_A$ respectively, where $H_A$ is the anisotropy field. For other angles, saturation is only achieved in infinitely large fields.

For particles just above the single-domain size, which have only a few domains, the process of domain-wall movement is theoretically harder than in very large particles. Rosenberg et al. used a crystal of SrO, $4\text{Fe}_2\text{O}_3$, 2 $\text{Al}_2\text{O}_3$, for which the single-domain size is about $3\mu$, in which there were only a few domains, to study the magnetisation process. Starting from the thermally demagnetised state, a field $H_{B1}$ was applied, just sufficient to saturate the particle, fig. 1.2.5. (2). Reversal of the magnetisation took place by domain-wall nucleation and growth, in a field $H_{B2}$. The magnitude and sign of the nucleation field varied with the maximum applied field, fig. 1.2.5. (3). Above a maximum value of $H_{B2}$, the reversal of the magnetisation was too abrupt to be observed by the technique used, but the magnetisation loop became rectangular. For some crystals the reversal field of the rectangular loop was $H_{B2}$, while for others, the maximum value of the reversal field was much higher. In all cases, the maximum reversal field was less than the value necessary for coherent rotation. It was presumed that structural imperfections acted as domain-wall nucleation-centres, but that the behaviour of these centres depended on the magnetic history of the particle, giving rise to the variation of nucleation field with maximum applied field. Similar results have been reported for $\text{MnBi}$ and $\text{WFeO}_3$.

Baird measured the remanent magnetisation curve for a 1 micron particle of barium ferrite. He found that the remanence coercivity, $H_{\text{re}}$, of this particle was less than that of a larger particle, contrary to expectation. Annealing the particle also reduced $H_{\text{re}}$. He tentatively explained these results by the effect of strain in the particles; the large particle was assumed to be more strained than the 1 micron one, and annealing the particle reduced the strain. If $H_{\text{re}}$ depends on strain for barium ferrite, this would explain his results. He suggested that further evidence was required.

The hysteresis loops of assemblies of large and small particles were treated in the previous section, figs. 1.2.4. (2) and 1.2.4. (4). The curves for the smaller particles showed better agreement with the theoretical curves for coherent rotation, than the curves for
Experimental minor loops for anisotropic strontium ferrite. It is seen that $\mu H_C$ increases as the maximum applied field increases, but the magnetization remains almost constant.

Ref. 107

The type of loop postulated to explain the minor loops in (a) of this figure. The particle is initially multidomain and has the magnetization curve 1. When the applied field exceeds $H_S$, the particle becomes single-domain and has the curve 2.

Ref. 107
Fig. 1.2.5 (a) Magnetization curves of Sr0.4.4Fe$_2$O$_5$.1.6Cr$_2$O$_3$ at different temperatures. Field applied in the direction of axis c. Ref. 109

Fig. 1.2.5. (b) Hysteresis loops of Sr0.4.4Fe$_2$O$_5$.1.6Cr$_2$O$_3$ with the field parallel to the hexagonal axis, recorded at 333.5°C Ref. 109
the large particles showed. A mixture of coherent rotation and domain-wall motion was postulated to explain the curve. Hee and Jacobsen prepared samples by chemical co-precipitation, in which the particle size was about 1000 Å. The hysteresis loops and temperature variation of the coercive force were in very good agreement with theory, assuming that each particle had a demagnetizing field of $4\pi M$. Thus, in these very small particles, the only magnetization process acting was coherent rotation of the magnetic vector. Ohresfeld and Capitelli explained their investigations on aligned samples of barium ferrite by reference to the fanning mechanism of Jacobs and Bean, ignoring magneto-crystalline anisotropy. However, Kandaurova et al. considered the inclusion of fanning in the reversal process of aligned MnSi, and decided that for high anisotropy materials, the effect was negligible.

Heinsohn and Muller studied the initial magnetization curves and minor hysteresis loops of aligned strontium ferrite magnets. The existence of a plateau in the positions of the tips of certain minor loops, for which the coercive force increases markedly with increased maximum applied field, with very little increase in the magnetization, fig. 1.2,5. (4), was taken to be indicative of the presence of Coey-Ens type loops. The nucleation field for these loops was negative; this required the postulation of a positive interaction between the crystallites. Heinsohn measured the dimensions of the crystallites in several aligned strontium-ferrite magnets, and treated the interaction of an assembly of oblate ellipsoids having these dimensions, with the easy axis of magneto-crystalline anisotropy along the polar axis. He found that the interaction fields were positive and increased with increased width to height ratio of the ellipsoids and increased coercive force. Using this fact and assuming a model of a linear chain of particles, with a spread in anisotropy fields, he deduced that the demagnetizing curve should begin to fall at a field equal to the smallest anisotropy field, and that the steepness of the falling portion depended on the ratio of interaction field to spread in anisotropy field, increasing with this ratio, which itself increased with coercive force. Thus he confirmed the experimental result that the fall in the demagnetizing curve was steeper for the higher coercive force materials.

Elkins and Koreleva found a region of constant magnetization in the initial magnetization curve, and minor hysteresis loops shifted along the magnetization axis, in grain-oriented, chromium-substituted strontium ferrite, fig. 1.2,5. (5). Two explanations were considered: either a second phase with different magnetic properties was present, or else a spiral spin structure existed, with the spins...
(a) Magnetization curves for the direction $\phi = 0^\circ$.
(a) after demagnetization by an alternating field at a temperature of $-196^\circ$C
(b) after demagnetization by recoil from negative fields
(c) after demagnetization by recoil from positive fields
Particle size $25\mu$

(b) Magnetization curves for the direction $\phi = 0^\circ$
after demagnetization by recoil from positive fields at room temperature.
Powder particle sizes:
1 = $250\mu$
2 = $25\mu$
3 = $6\mu$
Fig. 1.2.5 (7) Minor loops for powders of MnBi of particle size 1 micron after:
(a) AC demagnetization at -196°C
(b) recoil demagnetization from negative fields at room temperature.
Ref. 113
painting along the generators of a cone with its axis along the o-axis. The first hypothesis was ruled out by X-ray evidence that only a single phase existed, and it was decided that further evidence was needed to confirm or deny the second hypothesis.

The magnetisation processes in aligned samples of MnSi have been studied by Shtel'ts et al. They investigated initial magnetisation curves and minor hysteresis loops after three methods of demagnetisation: (a) A, C, demagnetisation at -196°C, where the anisotropy constant is zero, and recoil demagnetisation from (b) negative fields and (o) positive fields, where the initial magnetisation curves were taken in positive fields. The results showed that the initial magnetisation curves were different after the three methods (a), (b), (c) and that a plateau of constant magnetisation was present in the curve after (a) fig. 1.2.3. (6). The minor hysteresis loops were shifted along the magnetisation axis, fig. 1.2.3. (7). The extent of the plateau and the amount of shifting, for a given maximum field, increased with decreasing particle size. Results on samples with random orientation of the easy axis confirmed these results and indicated that the behaviour was due to the intrinsic magnetic structure of the particles rather than to the alignment. It is known that small particles of MnSi near the single-domain size exhibit a transitional domain-structure. Depending on the magnetic history of the sample, the same particle may exhibit multi- or single-domain behaviour. After (a), the particle will be multidomain, with zero remanence, and magnetisation takes place by 180° - domain-wall motion. After the application of moderate fields, the particle consists of a basic domain magnetised in one direction, with small conical or cylindrical domains magnetised in the opposite direction. The volume of these reverse domains is small and hence the magnetisation almost equals H. After (b) or (c), the volume of the cylindrical domains equals the volume of the basic domain, since the magnetisation is zero. It is theoretically easier for the volume of the cylindrical domains to grow rather than decrease, and hence the magnetisation change when an external field is applied in the same direction as the magnetisation of the cylindrical domain will be greater than when the field is applied opposite. Thus for minor loops, when the magnetisation changes by increase or decrease of the volume of the cylindrical domains, asymmetry results. If the reversal were by plane-wall motion, symmetric loops would be obtained. The increase of the effect in smaller particles is ascribed to the increase in magnetostatic energy of the wall making wall movement more difficult. It should be pointed out that particles assemblies reversing by coherent rotation would have asymmetric loops after recoil demagnetisation but
Fig. 1.2.6. (1) Variation of the domain width $d$ in magneto-plumbite with specimen thickness $L$. Ref. 1.2.8.

Fig. 1.2.6. (2) Schematic representation of the nucleation. Ref. 124.

Fig. 1.2.6. (3) Dependence of relative magnitude $L/L_0$ of relevant honeycomb domains on field $H$, acting parallel to $c$ axis in the direction of magnetization of honeycombs (a) and "basic" domain (b). Ref. 116.
any loops not entering all four quadrants would pass through the zero magnetisation point at zero field. If the reversal process were a mixture of coherent rotation and cylindrical domain growth or reduction, minor loops might be shifted along the magnetisation axis.

1.2.6. Domain structure of uniaxial hexagonal ferrites and MnBi. The domain structure of uniaxial ferrites and of MnBi, for which $K_1/k_T^2 > 1$, are similar to each other. They have the feature that closure domains with magnetisation perpendicular to the easy axis are not found. In small crystals, less than about ten microns thick, very simple domain structures are found, all the walls being $180^\circ$ and parallel to the easy axis. The wall spacing, $d$, depends on the specimen thickness, $D$, as in fig. 1.2.6. (1). As the thickness $D$ increases, the walls begin to undulate near the surface to reduce the magnetostatic energy. When $D$ is about 100 microns, isolated star domains appear, and the pattern becomes complicated, with spike domains of reverse magnetisation. The intersection of the domain structure with the prism planes shows an arrangement of straight lines where the main domain boundaries cut the surface, and wedge shaped spike domains, where the small domains, which serve as closure domains, reducing the magnetostatic energy, cut the surface. From fig. 1.2.6. (1), a particle of about one micron extent in all directions should have a domain spacing equal to the particle size, and hence should perhaps be single domain. This is the basic idea in barium ferrite fine-particle magnets. Craik and Tobble measured the dimensions of the crystallites in grain-orientated barium ferrite, and counted the number of domains in each grain. They found that grains of about one micron in size did not contain any domains. The observation of domains in small isolated particles of barium ferrite near the single-domain size is difficult. Crystals of substituted barium ferrite, or of MnBi, for which the single domain size is large enough to be convenient, are used.

Starting from the saturated state, the process of magnetisation as the field is reduced depends on the crystal size. For large crystals, large round mobile spots appear in certain parts of the crystal and move to cover the whole surface. These spots become smaller and less mobile, until eventually, spike domains of reverse magnetisation are formed. These spikes grow and interact to form undulating domains at the remanence point, where the magnetisation is zero. In a reverse field, the process is entirely reversible, except that the field at which the spots disappear is higher than that at which they first appeared. The last spots to disappear are in the part of the crystal where they first appeared. The process of nucleation
and the magnetisation in the cylindrical domains, fig. 1,2,6. (3). If field and magnetisation were in the same direction, the domains grew after the field exceeded a certain minimum value. If field and magnetisation were opposed, the minimum field-strength required to reduce the size of the domains was higher, the domain structure remaining constant up to much higher fields than in the previous case. Thus it was found to be easier for the cylindrical domains to grow rather than to shrink, in agreement with theory. This asymmetrical magnetisation process has been used to explain asymmetrical minor loops found in NiBi. Kojima and Goto found that the conditions necessary for the production of honeycomb domains were small demagnetising fields and absence of crystal defects.

The domain structure of Al-substituted strontium ferrite and its behaviour in a magnetic field was found to be similar to that of thin crystals of the unsubstituted material, even when large crystals of the substituted material were used\(^{119}\). This is as expected from the higher anisotropy field and larger single-domain size of the substituted material. Some crystals contained only a few domains and had non-zero remanence. It was found possible to obtain a single-domain remanent state in small pieces broken off a larger crystal. One of the crystals with only a few domains was used to study the hysteresis loops\(^{100}\) (ref. section 1,2,5). The magnetisation process of these nearly-single-domain particles showed a dependence on the magnetic history of the sample. Below a certain critical field, reversal occurred by domain-wall nucleation and movement. Above this field, the loop was rectangular, and reversal was abrupt. In NiBi, which has a large single-domain size, about 30 microns, this dependence of reversal process on the maximum applied field was found\(^{122,123}\), and was attributed to a transitional domain structure, similar to the honeycomb domain structure. The behaviour of the sample after saturation in very large fields is due to the destruction of all nuclei of reverse magnetisation, so that the particle behaves as a single-domain. Reversal is presumed to be by irreversible rotation, but may be by a domain-nucleation and growth process, too fast to be detected experimentally.

### 1.2.7. Scope and objectives of the research, the results of which are included in this thesis.

The theoretical permanent-magnetic properties of barium ferrite magnets are not achieved in practice\(^{8}\). The discrepancies are presumed due to the presence of domains\(^{44,45}\), incoherent magnetisation processes\(^{105}\), interaction fields\(^{107,108}\), super-paramagnetism\(^{90,91}\), or a second magnetic phase with inferior magnetic properties\(^{82,83}\). This second magnetic phase may be a defect crystal structure introduced by dislocations\(^{89}\), a disturbed surface layer\(^{87}\),
or it may be introduced by milling. Dislocations act as domain-wall nucleation centres or else decrease the critical single-domain size by reducing the anisotropy. The saturation magnetisation is also reduced by the presence of a defect structure. In considering interaction fields, Heinecke found that the effect depended on the spread in the values of anisotropy fields present. Flanders and Satrikian found that there was a spread in anisotropy field values, centred on 12 koe, with a half-width at half-value of 3 koe. If, as was usually assumed, all particles had a demagnetising field of \( N = -3k_0 \), one would expect the effective anisotropy field to be \( N = N_A - N_D = 12 \text{koe} \), approximately, but any deviations from this would be towards higher \( N_A \), since \( N_D = -3k_0 \) is the maximum demagnetising field possible. Thus the spread in anisotropy fields is perhaps indicative of a spread in values of \( k \), the anisotropy constant. However, the anisotropy distribution was found to be independent of coercive force, which is surprising, if the value of the coercive force is influenced by the spread in anisotropy fields.

To investigate the influence of anisotropy distributions on the value of the coercive force, it was thus decided to measure the anisotropy distributions for samples, the coercive forces of which were altered by milling and annealing treatments. This would also test whether the anisotropy constant changed with these treatments. The method used also allowed one to calculate the absolute volume of material reversing by coherent rotation. Under the experimental conditions, this enabled one to estimate the amount of material reversing by domain-wall motion.

From the results of measurements of minor hysteresis loops of Néel samples, the presence of asymmetrical magnetisation processes, due to cylindrical domains, was deduced. The particles were presumed to be of single-domain size, or nearly so. From the similarity in the domain-structures of Néel and barium ferrite, the possibility arose that particles of barium ferrite just above the single-domain size, might have domain-structures similar to the transitional domain structures of Néel, which were presumed to give asymmetrical shifted hysteresis loops. It was decided to study minor hysteresis loops of the barium ferrite samples to see if shifted hysteresis loops were present. The anisotropy distributions already found could be used to predict e.g. resonance curves of the barium ferrite samples, on the coherent-rotation theory. Any discrepancies would have to be accounted for by domain-wall motion, or incoherent rotation.

A quantity independent of the anisotropy distribution is the rotational hysteresis integral. The measurement of this quantity was undertaken to give an indication of the reversal processes
occurring. The shape of the rotational hysteresis versus field curves is dependent on the anisotropy distribution, and hence the curves for coherent rotation could be predicted from the distributions previously found. The discrepancies would again, have to be explained by domain-wall motion or incoherent rotation.

Thus the objectives of the present research are several:

a) to determine if the anisotropy distribution depends on the coercive force and to study the effect of milling and annealing treatments on the distribution;
b) to determine what fraction of the volume of the samples reverses by coherent rotation;
c) to study minor hysteresis loops to see if shifted loops, as found in MnBi and substituted barium ferrite, are present;
d) to measure the amount of material which reverses by non-coherent processes, giving rise to large rotational hysteresis;
e) to study the theoretically possible dislocations in barium ferrite, which may reduce the anisotropy and saturation magnetisation, and may give rise to helical spin-structures, which can give shifted hysteresis loops.
The techniques of magnetic analysis, reviewed by Hoselitz, and Wohlfarth, have been applied to many magnetic systems. The results obtained in such systems as ferromagnetic precipitates in a non-magnetic matrix (Berkowitz and Flanders, Kneller and Wolff), ferromagnetic thin films (Doyle, Doyle et al., Cundall, Robinson), ferromagnetic powders used for coatings of magnetic recording tapes (Johnson and Brown, Flanders and Shtrikman), powders used for permanent magnets (Shtrikman and Treves, Deryugin and Segal), and polycrystalline permanent magnet material (Flanders and Shtrikman, Shtrikman and Treves), illustrate the scope of these techniques.

The three most important measurements, from the point of view of this present work, were of remanence curves, rotational hysteresis and remanent torque curves. From the theoretical dependence of remanence on the applied magnetic field (Wohlfarth, Shtrikman and Wohlfarth) and using various relationships between remanences acquired in different ways (Wohlfarth, Shtrikman and Treves) it is possible to derive a distribution of anisotropy fields. When the magnetic anisotropy is due to shape anisotropy, it is possible to convert the anisotropy field distribution to a shape distribution. If the magnetic anisotropy is mainly of magneto-crystalline origin, it may not be possible to separate out any contribution due to shape anisotropy. This is the case in powders of barium ferrite.

Similarly, the theoretical field dependence of rotational hysteresis (Jacobs and Luborsky, Shtrikman and Treves, Doyle et al., Schiller) and remanent torque curves (Flanders and Shtrikman, Berkowitz and Flanders, Robinson, Doyle) may be used to derive an anisotropy distribution. The anisotropy distribution derived by one technique may be used to predict the results of another technique (Deryugin and Segal, Wohlfarth, Gomond) as in the present work, or may be compared with the distribution derived by another technique (Johnson and Brown). The agreement or otherwise between the predicted and experimental results, or between the distributions of different origin, then shows the validity of the assumptions made about the magnetization processes occurring or may indicate the presence of magnetization processes not included in the theoretical analysis.
Fig. 2.1.2 (1) Remanence after thermal demagnetization.

Fig. 2.1.2 (2) Remanence after saturation

Fig. 2.1.2 (3) Rotation of sample through an angle $\theta_m$

Fig. 2.1.2 (4) Part of sample contributing to torque is shaded portion of Fig. 2.1.2 (3)

Fig. 2.1.2 (5) Situation for remanent torque curves

Fig. 2.1.2 (6) Remanent torque curve for uniaxial single-domain particle with the applied field at $\frac{\pi}{2}$ to the easy axis.

Fig. 2.1.2 (7) Remanence after $H_{app}$ in Fig. 2.1.2 (4) has exceeded the anisotropy field $H_A$. 

$M_s$
In the present work, anisotropy field distribution derived by the method of static, i.e. remanent, torque curves were used to predict the results of measurements of resonance curves, static hysteresis loops, both major and minor, and rotational hysteresis, including the value of the rotational hysteresis integral \(^ {19,27,23} \).

### 2.1. Remanent torque curves

#### 2.1.1. The method used is that of Flanders and Stibritsman \(^ {10,13} \) in which the specimen, in the form of a disc with random orientation of the easy axes of the particles, is suspended from an automatic torque magnetometer, between the poles of an electromagnet. The field \( H \) of the electromagnet is in the plane of the disc. A field \( H_{\text{sat}} \), sufficiently large to saturate the sample, is applied, then reduced to zero. The sample, (or, equivalently, the magnet, as in the present case) is rotated through a small angle \( \theta \). With \( \theta \) constant, the torque as a function of applied field is measured in fields up to \( H_{\text{sat}} \), where the field is cycled \( 0 \rightarrow H_1 \rightarrow 0 \). \( H_1 \) is increased in steps of \( 1 \) up to \( H_{\text{sat}} \). The fraction, \( f_i \), of particles with anisotropy fields in the range \( H_1 \) to \( H_{i+1} \) is derived from the area between the torque curves \( 0 \rightarrow H_1 \) and \( 0 \rightarrow H_{i+1} \). The anisotropy field distribution is given by a graph of \( f_i \) versus \( \frac{1}{2}(H_i + H_{i+1}) \). An accumulative frequency distribution may be plotted as the fraction of particles which have anisotropy fields less than \( H_{i+1} \), for values of \( H_{i+1} \) up to \( H_{\text{sat}} \). The difference between two successive torque curves is known as the incremental torque curve.

#### 2.1.2. Consider a sample with random orientation of the particle easy axes. In the thermally demagnetised state, the remanences are distributed as in fig. 2.1.2. (1) where the circle is a section in the plane of the disc. After application and removal of the applied field \( H_{\text{sat}} \), the remanences are as in fig. 2.1.2. (2). If a field \( H \) is applied along the original direction of \( H_{\text{sat}} \), the torque on the sample is zero, since there are as many particles with their magnetisations at remanence in the easy directions between \( 0 \) and \( \theta = \frac{\pi}{2} \) as there are with their magnetisations at remanence in the easy directions between \( 0 \) and \( \theta = -\frac{\pi}{2} \). Thus all the torques cancel. If, however, after the application and removal of \( H_{\text{sat}} \), the sample is rotated through a small angle \( \theta \), the remanence directions are distributed as in fig. 2.1.2. (3). If now a field \( H \) is applied along the original direction of \( H_{\text{sat}} \), the torque due to the particles in the range \( 0 \rightarrow \frac{\pi}{2} \) cancels the torque due to the particles in the range \( 0 \rightarrow \frac{\pi}{2} \) since the torques in these two ranges are of opposite sign. But the torque due to the particles in the range \( 0 \rightarrow \frac{\pi}{2} \) cancels the torque due to the particles in the range \( 0 \rightarrow \frac{\pi}{2} \). fig. 2.1.2. (4).
is not balanced, since there are no particles with their remanences in the range \( \theta = -\frac{H}{2} + \theta_R \) to \(-\frac{H}{2} - \theta_R\). Thus there is a nett torque on the sample.

The torque on a uniaxial single-domain particle of volume \( V \), saturation magnetization \( M_s \) and anisotropy field \( H_A \), when the applied field \( H \) is perpendicular to the easy axis, as in fig. 2.1.2. (9) is given by

\[
L = M_s V \left[ \frac{1 - \left( \frac{H}{H_A} \right)^2}{2} \right]^\frac{1}{2} \text{ eqn. 2.1.2.(1)}
\]

The dependence of \( L \) on \( H \) is shown in fig. 2.1.2. (6). This is known as a remanent torque curve. For small \( \theta_R \), the torque curve will be almost the same as eqn. 2.1.2. (1). The torque curves for a series of angles \( \theta_R \) have been calculated by Cundell. Baryugin and Legal have considered the effect on the anisotropy distributions of \( H \) not being perpendicular to all the easy axes and have shown that for fixed \( \theta_R \), the anisotropy distributions are shifted to lower fields by a constant amount.

Consider two particles with equal anisotropy fields \( H_A \), one with its remanence at an angle \( \frac{H}{2} - \theta_R \) to the applied field, and the other with its remanence at an angle \( \frac{H}{2} + \theta_R \) to the field, where \( \theta_R < \theta_R \) as shown in fig. 2.1.2. (8). When the applied field \( H \) is increased from zero, the torques on the two particles are of the same sign, and add. When the field \( H \) exceeds the anisotropy field \( H_A \), the particle which had its remanence at \( \frac{H}{2} + \theta_R \) will switch its magnetisation so that the nearest easy direction is \(-\frac{H}{2} + \theta_R\), fig. 2.1.2. (7). The torque due to this particle will now be equal and opposite to that of the particle for which the nearest easy direction is \( \frac{H}{2} - \theta_R \). The two torques cancel and these particles have zero resultant torque. Thus the field \( H \) above which the torque becomes zero is the anisotropy field \( H_A \). One may apply this procedure to particles having a range of anisotropy fields and orientations in the region \( \frac{H}{2} - \theta_R \) to \( \frac{H}{2} + \theta_R \) and, from the variation of torque with applied field, cyclic as discussed in section 2.1.1., the anisotropy field distribution may be found.

For an assembly of particles which all have the same \( H_A \) and for which the easy axes are randomly distributed in space, the area under the torque curve is

\[
A = \frac{\int_0^{H_A} M_s \left[ \frac{1 - \left( \frac{H}{H_A} \right)^2}{2} \right]^\frac{1}{2} \int_{-\theta_R}^{\theta_R} \int_0^V H_A \frac{d\rho d\theta}{2\pi}} \text{ eqn. 2.1.2.(2)}
\]
Fig 2.13.1 Schematic diagram of the automatic torque magnetometer
Fig 2.1.3.(2) Remanent torque curves. The figures on the curves denote the maximum field (koe), for that particular cycle.
Fig 2.1.3 (3) Incremental torque curves taken from fig 2.1.3 (2)
\( V \) is the volume of the particles with anisotropy field \( H_A \).

\( \beta \) is the azimuthal angle in polar co-ordinates.

The volume \( V \) is given by

\[
V = \frac{6A}{\varepsilon_H H_S H_A^2}
\]  

eqn. 2.1.2. (3)

When there is a spread in anisotropy fields, the volume of particles \( V_1 \) with anisotropy fields in the range \( H_1 \) to \( H_{2 \pm 1} \) is given by

\[
V_1 = \frac{6A_1}{\varepsilon_H H_S \left[ \frac{1}{2}(H_A + H_{2 \pm 1}) \right]^2}
\]  

eqn. 2.1.2. (4)

where an average \( H_A = \frac{1}{2}(H_1 + H_{2 \pm 1}) \) is used.

\( A_1 \) is the area between the torque curves for the cycles 0 to \( H_1 \) and 0 to \( H_{2 \pm 1} \).

The absolute volume \( V_2 \) of particles contributing to the torque is obtained from an absolute measure of the area under curves, in units of dyne-cm-orested, using the relationship

\[
V_2 = \frac{6}{\varepsilon_H H_S} \sum_{i=0}^{n} \frac{A_i}{\left[ \frac{1}{2}(H_A + H_{2 \pm 1}) \right]^2}
\]  

eqn. 2.1.2. (5)

\( n \) is the total number of field cycles.

2.1.3. The instrument used is an automatic torque magnetometer, as described by Pearson, and shown schematically in fig. 2.1.3. (1). The electromagnet, a Hulland MM 1000, gave a maximum field of 27.7 koe in a 1 in. gap. This was more than sufficient to switch all the particles and to saturate the specimen. The torque \( L \) was measured by the current necessary to balance the torque in a field \( H_0 \), and \( H \) was measured by a Reysen rotating coil fluxmeter. The curves were recorded on an X-Y recorder. The disc-shaped samples used were powders pressed at a pressure of 515 kg/cm² and coated with Durafil to provide ease of handling. The dimensions of the samples were 3.8 mm diameter and 0.5 mm in height, giving a volume of 5.7 x 10⁻³ cm³ and a density of approx. 3.8 gm/cm³. The magnetometer could detect and balance torques in the range 1-10⁻³ dyne-cm, which meant that, with the samples used, \( A_1 = 2^6 \) gave a reasonable torque curve. The areas under the torque curves were measured by both a planimeter and Simpson’s rule.

Examples of the torque curves are given in fig. 2.1.3. (2). The differences between the consecutive field cycles are shown in fig. 2.1.3. (3) which shows that these incremental torque curves have
Fig. 2.21 (1) Schematic representation of Hall-effect magnetometer.

Fig. 2.21 (2) Current supply circuit.

Fig. 2.21 (3) Arrangement of Hall probes in perspex block.

Fig. 2.21 (4) Clover leaf and cruciform shaped Hall probes.
the same shape as the theoretical curve in fig. 2.1.2. (6).

2.2. Static hysteresis loops

2.2.1. The method used is an adaptation of one used by Abaroni. Two Hall probes are placed parallel to each other in the field of an electromagnet, fig. 2.2.1. (1). The probe currents $i_H$ are provided from transistor circuits, one for each probe, which provide constant current, fig. 2.2.1. (2). The two supplies are thus independent of each other, and are relatively noise-free since they are battery-driven. A resistance $R$ in series with each probe ensures that changes in the probe resistance due to magneto-resistance are only a small fraction of the total resistance in the circuit. This, combined with the constant current supplies, ensured that the output was linear in the fields used 1.0 to 10 koe.

The Hall probes were made of epitaxial $n$-type gallium arsenide layers on semi-insulating substrates. For high-field linearity, a high level of doping was required. Typical parameters of a probe were: mobility $= 4.25 \times 10^3 \text{cm}^2/\text{volt sec.}$; resistivity $= 0.37 \text{cm ohm}$; doping $= 8.6 \times 10^{16}$. This gave an output of $0.7 \text{mV/koe}$, which was quite sufficient to operate a Hoselay 7050A X-Y chart recorder.

The samples were cylinders of length 1.3 cm and diameter 0.38 cm made by pressing powders at a pressure of 315 kg/cm$^2$. The outsides were coated with a thin layer of Durofix to provide ease in handling. Two equal cylinders were made of each sample and were placed one on either side of the Hall probe B, fig. 2.2.1. (1). The Hall probes were contained in slits in a block of Perspex. A hole, just larger in diameter than the samples, was drilled through the block perpendicular to the Hall probe B, which had its centre over the centre of the hole, fig. 2.2.1. (3). The Hall probes were of either clover leaf or cruciform shape, fig. 2.2.1. (4). The samples were placed in the cylindrical hole with their axes parallel to the applied field and perpendicular to the Hall probe B. They were retained in position by expanded polyethylene plugs, and were in contact with the Hall probe. The gap $d$ between the sample faces, fig. 2.2.1, (1) was 0.4 mm, and was made up of the thickness of the Hall probe and of the two layers of Durofix.

Abaroni has shown that a gap of 0.5 mm produced no distortion of the hysteresis loops of a thin film. It was assumed in the present case that the field measured by the Hall probe B was made up of the external field $H_{ext}$ and a contribution equal to, or a constant fraction of, the magnetisation $M_0 (1-N)$, where $N$ is the demagnetising factor of the samples. The method of calibration used, discussed in
Fig. 2.2.1. (5) Hysteresis loops of a thermally demagnetized sample
Fig. 2.2.1 (6) Calibration curve for Hall-probe magnetometer
the following paragraph provided a check on the validity of this assumption. The probe \( H \) measured the applied field \( H_{\text{ext}} \). With no samples in position, the currents were adjusted to give equal Hall voltages from both probes. The outputs of the two probes were subtracted so that the resultant was zero at all fields up to 10 kOe. With the samples in position the output of \( B \) has been assumed to be proportional to \( H_{\text{ext}} \), while the output of \( H \) was proportional to \( H_{\text{ext}}^2 \). Thus, taking into account the fact that with no samples the outputs are equal, subtracting the outputs with a sample in gives a resultant proportional to \( M \) i.e., proportional to \( 4x^2 \). The subtracted outputs were applied to one axis of an X-Y recorder and the field output \( H \) applied to the other, as in fig. 2.2.1. (1). Thus magnetization versus field curves could be drawn. Examples are shown in fig. 2.2.1. (5).

The calibration procedure was an adaptation of the method of Case and Harrington for calibrating a vibrating sample magnetometer. Two cylindrical pieces of soft ferrite, of diameter 0.36 cm and length 1.05 cm each, with saturation magnetization \( 4x^2 S = 3250 \) gauss, were placed in the sample holder. The magnetisation curve, shown in fig. 2.2.1. (6) consisted of an initial linear portion, which turned over to a constant value at high fields. On the sloping portion, if \( N \) is large, the internal field \( H_1 = H_{\text{ext}} - l MN \) is zero i.e., the slope \( 1/N \). The constant portion of zero slope is when the sample is saturated i.e., \( H = H_5 \). The magnetisation on the sloping portion is

\[
4xM = H_{\text{ext}}/N
\]

and the magnetisation on the constant portion is

\[
4xM = 4xM_5
\]

The intersection of the two linear portions of the curve occurs at a field \( H_4 \), at which

\[
4xM_5 = H_4/N
\]

This gives \( H = H_4/4xM_5 \)

The measured field \( H_4 \) was found to be 170 cgs which gave

\[
H_{\text{experimental}} = \frac{170}{3250} = 0.052. \quad \text{The theoretical demagnetisation}
\]

factor for a cylinder of diameter \( d = 0.36 \) cm and length \( l = 2.06, \) (which is the length of the two cylindrical portions together, i.e., an aspect ratio \( p = 1/d = 5.66 \)), is \( H_{\text{theoretical}} = 0.016 \) (Joseph, Neukirch et al., 27). The agreement between the two values is not very good, due perhaps to the fact that \( N \), the permeability, is not large enough to be neglected. However, it will be seen that even using the larger demagnetising factor, the demagnetising field can still be
Fig. 2.2.2 (1) Recoil demagnetization from negative field.
Definition of reduced remanences $R_{J1}^d(H) - R_{J10}^d(H)$. 

Fig. 2.2.2. (2)
neglected. The fact that the shape of the calibration curve is the same as the theoretically expected one is taken as a check on the validity of the assumption that the output of probe B is proportional to the magnetic induction in the sample. The hysteresis of the soft ferrite was not noticeable on the scale used. This provides a calibration of the magnetisation axis since the value of $4\pi M_s$ is known.

The demagnetising field at saturation for the barium ferrite was given by $H_D = -4\pi M_s = 230$ esu., and at remanence $H_D = -4\pi M R = -65$ esu., where the remanent value used was the highest measured for any of the samples i.e. $4\pi M_R = 1600$ gauss; neglecting the shearing of the loops due to the demagnetising field was estimated to give a maximum error of 2% in the remanent magnetisations which was about the same as the instrument error. The demagnetising field was neglected in all the measurements.

2.2.2. The samples were demagnetised by three methods

1) thermal demagnetisation, by heating above the Curie point
2) recoil demagnetisation from positive fields
3) recoil demagnetisation from negative fields.

Recoil demagnetisation is shown in fig. 2.2.2. (1).

Initial magnetisation curves, remanence curves and hysteresis loops, both major and minor were measured on the samples after the three demagnetisation processes. The initial susceptibility could be measured from the initial magnetisation curves. When measuring the hysteresis loops, the field was cycled 0 to $-H_m$ to 0 to $+H_m$ to 0. It was found necessary to cycle the field twice before drawing the loops in order to stabilise them i.e. the loops were drawn on the third cycle. $H_m$, the maximum field in a particular loop, was increased in steps of 1 koe from 0 to 10 koe. 10 koe was found to be sufficient to produce the major loop. No changes in the hysteresis loop were found when the maximum field was 25 koe, as compared with the maximum field used in all the hysteresis measurements, i.e. $H_m = 10$ koe. When cycling the field to draw the minor loops, the sequence was always the same, regardless of the method of demagnetisation i.e. 0, -ve, 0, +ve, 0.

The various remanences measured may be explained with reference to fig. 2.2.2. (2). $P_j(H)$ will be used to denote the reduced remanence after application of a field $H$ i.e. the ratio of the remanence acquired to the saturation magnetisation $4\pi M_s$.

The field necessary to demagnetise the sample by recoil is called the remanence coercivity and is denoted by $H_{R_c}$. It is the same magnitude for both positive and negative recoil demagnetisation.
direct resonance after a field \( +H \) has been applied to a thermally demagnetised sample.

reverse resonance after a field \( -H \) has been applied to a sample previously saturated by a field \( +H \).

resonance after a field \( +H \) has been applied to a sample recoil demagnetised from \( +H_0 \).

resonance after a field \( -H \) has been applied to a sample recoil demagnetised from \( -H_0 \).

positive resonance for loop with maximum applied field \( 2H \), after thermal demagnetisation.

negative resonance for same loop as \( R^3_3 \).

positive resonance for loop with maximum applied field \( 2H \), after recoil demagnetisation from \( +H_0 \).

negative resonance for same loop as \( R^3_7 \).

positive resonance for loop with maximum applied field \( 2H \), after recoil demagnetisation from \( -H_0 \).

negative resonance for same loop as \( R^3_9 \).

Interchanging positive and negative in the definitions \( R^3_2 = R^3_4 \) changes the sign of the resonance but not the magnitude, whereas for the definitions \( R^3_5 = R^3_{10} \) the magnitude may also change. This is because applying the field to stabilise the loops seems to bias the centres of the loops away from zero magnetisation. The amount of the biasing depends on the method of demagnetisation. This is why \( R^3_5 \neq R^3_6, R^3_7 \neq R^3_{10}, R^3_8 \neq R^3_9 \) as they should be on the coherent rotation theory of magnetisation reversal. The relationships between the various resonances are discussed in the next chapter.

**Rotational Hysteresis**

2.3.1. For a sample with spatially random distribution of easy axes, the torque curve in a field \( H \) is theoretically and experimentally a curve of constant torque (Jacob and Luborsky\(^{17}\), Schiller\(^{19}\)). The centre line of the torque curve coincides everywhere with the torque curve itself, but the centre line is displaced from the line of zero torque by a constant amount, depending on the value of the applied field \( H \). This displacement is a measure of the work done in rotating the sample in the field \( H \). The work done in rotating the sample \( 360^\circ \) is called the rotational hysteresis\(^{32}\), and is proportional to the area between the torque curve and the zero torque line. The
Fig. 2.3.2 (1) Examples of rotating torque curves.
The figures on the right hand ends of the curves denote the field at which the measurement was made (koe).
The scale for curve 6 is different from that for curves 10, 14 c.w. Clockwise rotation of field.
A.c.w Anticlockwise rotation of field.
Fig. 2.3.2 (2) Rotational hysteresis as a function of applied field.
measurement procedure consisted in saturating the sample in the maximum field available \( H_s = 27.7 \) koe, at an arbitrary zero position of the sample, which was in the form of a disc. The field \( H_s \) was reduced to the required measuring field \( H_0 \). The torque was then measured as the sample rotated 360° with respect to the field (Beecher\(^{35}\), Beevort\(^{32}\)). The field \( H_s \) was in the plane of the disc. Rotational hysteresis was measured as a function of field at 1 koe intervals in the range 0 - \( H_s \).

From graphs of rotational hysteresis versus field, the rotational hysteresis integral \( \int_0^\infty \frac{\theta}{H} d(\theta/H) \) (Shtrikman and Wohlfarth\(^{15}\)) may be calculated. The value of the R.H.I. is an indication of the magnetisation processes occurring.

2.3.2. The measurements were made on the same apparatus as used for the remanent torque curves. The samples used were of two sorts. One type was made by pressing powder into discs of diameter 0.2 cm and height 0.05 cm. The second type were of powders dispersed in paraffin wax, with diameter 0.6 cm and height 0.05 cm. This second type was used to estimate the demagnetising fields on the first type.

Examples of torque curves and of graphs of rotational hysteresis versus field are shown in figs. 2.3.2. (1) and 2.3.2. (2).

2.4. Sample preparation

2.4.1. The powders used in the present experiments were provided by Mallard Magnetic Components Ltd. They were made by the normal industrial process for ferrites, which is as follows\(^{36}\).

Iron oxide and barium carbonate, 80 to 20 ratio by weight were dry mixed and pressed into blocks. These blocks were fired at 1200°C in air for 24 hours and were then crushed. The coarse powder thus obtained was wet ball-milled, filtered and dried.

The firing at 1200°C promoted the reaction of the constituents and also sintered the product, so that the resultant was a coarse-grained polycrystalline mass. The crushing produced a coarse powder, which was ball-milled in order to reduce the average grain size to the single-domain critical size.

The effect of purity, average particle size, mixing and pre-sintering of the starting constituents has been thoroughly investigated\(^{35,36,37}\). In the present case, the addition of a small amount of SiO\(_2\) was made to hinder grain growth. The Si does not enter the ferrite structure, but is presumed to be present as a layer on the outside of the grains.

The powders as received from Mallards had in some cases been given an annealing treatment of 1 hour at 960°C. Further
### Table 2.4.1(1)

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<th>Sample</th>
<th>$H_C^H$</th>
<th>$4M_R^H$</th>
<th>$R_C^H$</th>
<th>$H_C^M / H_C^H$</th>
<th>$R_C^M (calc.)$</th>
<th>Annealing treatment</th>
<th>Milling treatment</th>
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<td>3590</td>
<td>1.14</td>
<td>6098</td>
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</tr>
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<td>3450</td>
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<td>1 hr. @ 950°C</td>
<td>48 ball mill</td>
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### Table 2.4.2(1)

**Note:** "*" indicates that the annealing was done in the factory.
annealing and milling treatments were given to the powders and are indicated in table 2.4.1. (1), which gives a list of the samples, their magnetic properties, and the milling or annealing treatments given to them.

2.4.2. All the samples, except those in paraffin wax for the rotational hysteresis experiments, were pressed in a stainless steel die at a pressure of 315 kg/cm². For the anisotropy distribution and the rotational hysteresis measurements, discs were used. For the static hysteresis loops, cylindrical samples were used. The paraffin wax samples were discs. They were prepared by dispersing the powders in liquid wax, which was allowed to set. Disc-shaped samples were cut out.

Table 2.4.2. (1) gives the dimensions for the samples used. It should be noted that the samples for the hysteresis loop measurements were two cylinders of equal length, the total length being twice the stated one. The demagnetising factors \( N \), as defined by the equation for the demagnetising field,

\[ H_D = -4\pi N_i \]

are also given. The demagnetising factors were in the plane of the disc for the disc-shaped samples and parallel to the cylinder axis for the cylindrically-shaped samples.
\[ \frac{1}{2}(H_2 + H_{4}) \text{ koe.} \]

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<th>(45)</th>
<th>(55)</th>
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\[ \text{TABLE 3.1.1(1): } \frac{1}{2} \text{ versus } \frac{1}{2}(H_2 + H_{4}), \text{ all samples} \]
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<th>( f_{i} ) versus all samples</th>
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</table>

**Table 3.1.1(2)**

N.B. The fact that \( \sum_{i=1}^{n} f_{i} \) is not exactly 100 for all samples is due to the rounding off of the individual \( f_{i} \) to the nearest integer.
Fig. 3.1.1 Accumulative anisotropy field distributions (AAFD) for three samples:

\( \mathbf{D}(\mathbf{a})_{2} \), the sample with the highest value of \( M_{H_C} \);

\( \mathbf{D}(m)_{3} \), the sample with the lowest value of \( M_{H_C} \);

\( \mathbf{D} \), a sample with an average value of \( M_{H_C} \).
Chapter 3  Experimental Results

The anisotropy field distributions found from the remanent torque curve measurements are given in section 3.1 and are used in sections 3.2 and 3.3 to predict the theoretical curves for remanence and rotational hysteresis respectively.

3.1 Results of remanent torque curve measurements.

3.1.1 The anisotropy field distributions are given in table 3.1.1(1) in the form $f_1$ versus $\frac{1}{2}(H_1 + H_{1+1})$, and in table 3.1.1(2) in the form of $\frac{1}{2}f_1$ versus $H_{1+1}$ as discussed in section 2.1.1. The $f_1$ are given in percentages. It was found that the differences between curves were more readily apparent if the accumulative distribution $f_1$ were plotted versus $H_{1+1}$ on a log-linear system of co-ordinates.

The general trend of the curves may be seen in fig. 3.1.1(1), which contains the results for the sample with the highest coercive force, $D(a)2$, the one with the lowest coercive force, $D(m)3$, and the starting powder, $D$, which was intermediate in its value of $H_c$. The samples with the lower coercive forces have more particles with low values of anisotropy field than the samples with the higher coercive forces. This trend is repeated throughout all the results, as will be seen later.

There are two corrections which should be applied before the curves are plotted. The results should be plotted as a function of internal field by subtracting the demagnetising field from the applied field. Secondly, the angular variation of the critical field should be taken into account.

The demagnetising field should be subtracted from the applied field to give the internal field, i.e. $H_1$ should be replaced by $H_1 + H_{D1}$ where $H_{D1} = -4\pi M(H_1)$. $M$ is the demagnetising factor given in table 2.4.1(2) and $M(H_1)$ is the magnetisation at the field $H_1$. $M$ varies from remanence at $H_1 = 0$ to saturation at large applied field. For a typical sample, the demagnetising field varies from about 200 oe. at remanence to about 550 oe. at saturation. The remanence of all the samples is approximately the same, so the demagnetising fields will be much the same for
Fig. 3.1.1(2) critical switching field as a function of angle $\Theta$. 
Fig. 3.1.1(3) Uncorrected AAFD versus external field, $H_{i+1}$, and corrected AAFD versus corrected internal field, $H'_{i+1}$, for the two samples, A and B.
all the samples. The effect of this correction will be twofold. Firstly, the distribution will be shifted to lower fields, but the amount of shifting will be less at the low-field end of the curve than at the high-field end, due to the variation of $H_D$ with the magnetisation. Secondly, the volume of material with anisotropy fields in a given range $H_1$ to $H_{1+1}$ will be different, since $V_1 \propto A_1/(H_1 + H_{1+1})^2$ and $H_1$ is to be replaced by $H_1 + H_{D1}$, which will increase $V_1$.

The second correction was considered by Deryugin and Sigal. For particles for which the easy axes are not exactly perpendicular to the applied field, the critical fields will be less than the anisotropy field. If the easy axis is at an angle of $\theta$ to the applied field, the relationship between the critical field and the anisotropy field is given by:

$$H_{\text{crit}}/H_A = (1 - t^2 + \cot^2 \theta)/(1 + t^2)$$

which is plotted in fig 3.1.1(2) for values of $\theta$ up to $5^\circ$, where $t$ is cotan $\theta$. If there is a spread in the values of $\theta$, there will be a spread in the $H_{\text{crit}}$ values. The relationship between the measured anisotropy field and the actual one must be found by integrating eqn. 3.1.1(1) over all values of $\theta$, from 0 to $\theta_M$. Deryugin and Sigal showed that the correction involved multiplying the experimental value by a constant factor which depends only on the angle $\theta_M$. For the present experiments, $\theta_M = 2^\circ$, and the correction factor for this angle was 1.1. The effect of this correction will be to shift the distribution curves to higher fields, but the amount of shifting will be greater at the higher fields than at the lower. A second effect due to the angular variation of $H_{\text{crit}}$ will arise because the area under the torque curve will be less if $H_{\text{crit}}$ is less. Thus a correction must be made, taking into account the variation of $H_{\text{crit}}$ with values of $\theta$ from 0 to $\theta_M$. This correction will depend only on $\theta_M$ and will change the absolute volume calculated from the experimental curves, but not the percentage volumes, since all the volumes, including the total volume, will be increased by the same factor.

The effect of these corrections on the distribution curves is seen in fig 3.1.1(3), where both corrected and uncorrected curves are shown for samples A and B. It is seen that the remarks in the preceding two paragraphs are generally borne out. The qualitative picture for the uncorrected curves is much the same as for the corrected ones, as regards the differences between the
Fig. 3.1.2(1) AAFD for annealed samples.
Fig. 3.1.2(2) AAFD for two samples, A and D, prepared independently of each other, and the distribution for these samples after annealing, B and E.
Fig. 3.1.2(3) AAFD for three independently prepared samples.
Fig. 3.1.2(4) AAFD for milled samples.
Fig. 3.1.2(5) AAFD for a sample which was annealed and then milled.
Fig. 3.1.2(6) Coercive force versus mean anisotropy field for all samples.
curves. Since there is no theory with which to compare the results, and since the labour involved in making the corrections would have been rather great, it was not felt worthwhile to correct all the results. It might be felt that the corrected curves would be necessary to predict the results in sections 3.2 and 3.3, but here again, only qualitative deductions would be possible, which would not be altered by using the uncorrected curves.

Hence it was decided that the above corrections should not be made, but it should be pointed out that for accurate quantitative results, the corrected curves should be used.

3.1.2 The effect of annealing on the distribution curves is seen in fig 3.1.2(1). The coercive force is increased by annealing, which is accompanied by a decrease in the percentage of particles with low anisotropy fields. The sample which was annealed for the longest time, D(a)3, has a coercive force lower than that of D(a)2. This is shown up on the curves by an increase in the percentage of particles with low anisotropy fields. For samples prepared at different times, i.e. A, D, F and G, the same general trend holds, that samples with the higher coercive forces have less particles with low anisotropy fields than the samples with the lower coercive forces, figs 3.1.2(2) and 3.1.2(3). This pattern is retained after annealing, curves B and E, fig 3.1.2(2).

The effect of milling is to increase the percentage of particles with low anisotropy fields, figs 3.1.2(4) and 3.1.2(5). The coercive force is reduced by milling, although the sample milled for the medium time, D(m)2, has a higher coercive force than D(m)1 which shows up as a decrease in the percentage of low anisotropy material. Sample D(m)2 has less low anisotropy material than D, but has a lower coercive force. However, in the medium field range, the curve for D(m)2 is well above that for D. The effect of milling on the distribution curve of an annealed sample is shown in fig 3.1.2(5). Annealing reduces the percentage of low-anisotropy material, and milling increases this percentage again. The coercive force is increased by annealing and reduced by milling.

Fig 3.1.2(6) shows $H_a$ versus the mean anisotropy field, $H_a$, defined by
Fig. 3.1.3(1) Fractional volume of material which reverses its magnetization by coherent rotation, versus coercive force, for all samples.
\[ H_n = \frac{\sum_{i=0}^{n} f_i \left( R_{i-1} + R_{i+1} \right)}{2} \]
eqn 3.1.2(1)

\( n \) is the total number of field cycles.

Considering the samples \( D, D(a)1-3, D(m)1-3, E, E(m)2 \) one sees that the coercive force increases with \( H_n \); all the points lying on a fairly smooth curve, which flattens off at both high and low values of \( H_n \). All these samples were derived from \( D \). Samples prepared independently, i.e. \( A, F \) and \( G \), do not lie on this curve, but presumably on curves of their own. \( B \), which is derived from \( A \), could possibly lie on such a curve with \( A \). It appears that the value of \( H_n \) depends on the method of preparation in the factory. Two of the samples, prepared independently, i.e. \( A \) and \( D \), had the same value of \( H_n \), but different coercive forces, as found by Flanders and Shtrikman. This appears to be coincidental, although further work to determine the dependence of \( H_n \) on the production parameters is necessary to confirm this.

Thus the general features of the curves are that the higher coercive force samples have a lower percentage of particles with low anisotropy fields than the lower coercive force samples, and that this percentage is increased by milling and decreased by annealing. For samples derived from a common starting powder e.g. \( E, D(a)1-3, \) and \( D(m)1-3, \) and \( E(m)2 \) derived from \( D \), the curve of \( H_n \) versus \( H_n \) appears to be fairly smooth. For other samples, prepared independently, e.g. \( A \) and \( B, F, G \), the experimental points may not lie on the same curve as do those for the samples prepared from \( D \). It is envisaged that each group of samples prepared from a given starting powder will be associated with its own curve, different from the curve for a second, independently prepared starting powder. Thus samples with different values of \( H_n \) may have the same values of \( H_n \).

3.1.3 The fractional volume of material reversing by coherent rotation, \( V_T \), was calculated for each sample, using eqn. 2.1.2(5), and is shown in fig 3.1.3(1), plotted versus \( H_n \). The surprising feature of this figure is that the samples with the highest values of \( V_T \) occur at the lowest coercive forces and vice-versa. The values for milled samples are closely clustered in the top left-hand
Fig. 3.2.1(1) Reduced remanence curves versus reduced field, assuming coherent rotation of the magnetization.
corner, while those for the annealed samples are scattered in the bottom right-hand corner. Sample D(m)1 has a $V_T$ value of 1 which is unlikely, since it indicates that all the particles in the sample reverse coherently. Even more unlikely, not to say impossible, is the value of $V_T=1.16$ for E(m)2.

These anomalous features of fig. 3.1.3(1), which are contrary to expectation, will have to be explained in the later discussion of the results.

3.2 Remanence Curves.

3.2.1 The anisotropy distributions of section 3.1 may be used to calculate the field dependence of the various remanences defined in section 2.2.2. For a sample in which all the particles have the same anisotropy field, the remanence $j_1(H)$ has been calculated by Wohlfarth, and is given in fig. 3.2.1(1). A spread in the anisotropy fields means that the remanence curve is a summation of curves similar to that in fig. 3.2.1(1) but each curve starts at a different position on the $H$-axis.

The maximum reduced remanence will be $0.5\frac{f_2}{f_1}$ for the curve with anisotropy field $\frac{1}{2}(H_1 + H_{1+1})$. The field dependence of the reduced remanence is given by

$$j_1(H_{1+1}) = \frac{\sum f_i j_i(h_i)}{\sum f_i} \quad \text{eqn. 3.2.1(1)}$$

where $j_i(h_i)$ is the reduced remanence for the fraction $f_i$ at the field $h_i = H/\frac{1}{2}(H_1 + H_{1+1})$. The other reduced remanences defined in section 2.2.2 may be derived from $j_1$ using Wohlfarth's relationships:

$$j_2(H) = j_1(H_{\text{max}}) + 2 j_1(H) \quad \text{eqn. 3.2.1(2)}$$

$$j_3(H) = 0 \quad H < H_R \quad \text{eqn. 3.2.1(3)}$$

$$= -j_2(H), \quad H > H_R$$

$$j_4(H) = -2 j_1(H) \quad H < H_R \quad \text{eqn. 3.2.1(4)}$$

$$= -j_1(H_{\text{max}}), \quad H > H_R$$

$$j_5(H) = -j_6(H) = j_7(H) \quad \text{eqn. 3.2.1(5)}$$

$$j_7(H) = -j_10(H) = j_5(H) \quad \text{eqn. 3.2.1(6)}$$

$$j_8(H) = -j_9(H) = j_4(H) \quad \text{eqn. 3.2.1(7)}$$
Fig. 3.2.1(2) Direct remanence curves for assemblies with spatially random distribution of easy axes, reversing by coherent rotation, and for 180°-domain-wall motion.
Fig. 3.2.2(5) Sample D(a)1

Fig. 3.2.2(6) Sample D(a)2
Fig. 3.2.2(12)  $\Delta \gamma_i$ and $\Delta \gamma'_i$ for the three samples D, D(a)2 and D(m)3.
Fig. 3.2.2(13) $\Delta \gamma_1$ and $\Delta \gamma'_1$ for the annealed samples.
The field $H_{\text{r}}$ is the remanence coercivity, which may be defined as that field for which either $j_{1}(H_{\text{r}}) = 0.5j_{2}(H_{\text{max}})$ or $j_{2}(H_{\text{r}}) = 0$. $H_{\text{r}}$ may be derived from the remanence curves. If magnetization reversal proceeds by coherent rotation, both definitions give the same value of $H_{\text{r}}$, but if non-coherent processes occur, the values may be different.

The remanence curve for completely incoherent rotation, i.e. 180°-domain-wall motion, is given for comparison in fig 3.2.1(2), assuming that the anisotropy is uniaxial, the easy axes are randomly distributed in space, and the critical field for domain-wall motion when the applied field is along the axis is $H_{0} = 0.1H_{A}$. A distribution in values of $H_{0}$ would mean, as before, that the resultant remanence would be a summation of a family of curves.

3.2.2 Shown in figs 3.2.2(1) to 3.2.2(11) are the following reduced remanence curves: $j_{1}$ (theoretical), calculated taking the anisotropy field distribution into account; $j_{1}$ (experimental); $j_{1}$ (experimental), defined from eqn. 3.2.1(2) as

$$j_{1}(H) = \frac{1}{2} \left[ j_{2}(H_{\text{max}}) - j_{2}(H) \right].$$

Also shown are the differences:

$$\Delta j_{1} = j_{1}(\text{theo.}) - j_{1}(\text{exp.}) \quad \text{eqn 3.2.2(2)}$$

and

$$\Delta j_{1} = j_{1}(\text{theo.}) - j_{1}(\text{exp.}) \quad \text{eqn 3.2.2(3)}$$

where $j_{1}(\text{theo.}) = j_{1}(\text{theo.})$ on the coherent rotation theory.

The magnitudes of $\Delta j_{1}$ and $\Delta j_{1}$ are indications of the amount of material reversing its magnetization by non-coherent processes.

It may be seen that the experimental remanences are greater than the theoretical ones in fields up to 5-7 koe., but that in higher fields the pattern is reversed. Also $j_{1} > j_{1}$ in fields up to 3-5 koe., but, in general, $j_{1} < j_{1}$ in higher fields. Fig 3.2.2(12) shows $\Delta j_{1}$ and $\Delta j_{1}$ for the three samples D, D(m)2 and D(m)3. $\Delta j_{1}$ is least for the unmilled sample at the lower fields, and greatest for the milled sample at the higher fields. $\Delta j_{1}$ is greatest at both the lower and higher fields.

The effect of annealing is seen in fig 3.2.2(13). At the lower fields, $\Delta j_{1}$ (annealed) $> \Delta j_{1}$ (unannealed). At the higher
Fig. 3.2.2(14) $\Delta j_i$ and $\Delta j'_i$ for the milled samples.
Fig. 3.2.2(15) $\Delta j$ and $\Delta j'$ for a sample annealed and then milled.
Fig. 3.2.2(16) $\Delta \dot{\delta}_1$ and $\Delta \dot{\delta}_1'$ for the samples A and B.
Fig. 3.2.2(17) $\dot{\gamma}_3$, $-\dot{\gamma}_4$, $-\dot{\gamma}_2$, and $2\dot{\gamma}_1$ for samples $D$, $D(a)2$ and $D(m)3$. 
Fig. 3.2±(18) $\Delta \beta_3$ for all samples.
Fig. 3.2.2(19) \( \Delta j_{14} \) for all samples.
Fig. 3.2.2(20) Major and minor hysteresis loops for sample A after thermal demagnetization.
Fig. 3.2.2(21) $\dot{\gamma}_S$ and $-\dot{\gamma}_6$ for the samples $D$, $D(a)2$ and $D(m)3$. 
Fig. 3.2.2(22) $\Delta \delta_5$ for all samples.
Fig. 3.2.2(23) \( \Delta \delta \) for all samples.
fields, the pattern is reversed. $\Delta j_1^1$ (annealed) $< \Delta j_1^1$ (unannealed), at both the lower and higher fields.

For the milled samples, fig 3.2.2(14) shows that both $\Delta j_1$ and $\Delta j_1^1$ are greater at both the lower and higher fields than for the unmilled sample, although for the sample which had been milled for the longest time the values of $\Delta j_1$ and $\Delta j_1^1$ at the lower fields are nearer to those of the unmilled sample than are the values for the other two milled samples. Annealing a sample, then milling it, fig 3.2.2(15) and annealing of sample A, fig 3.2.2(16) bear out these observations.

It is seen from figs 3.2.2(1) to 3.2.2(16) that Wohlfarth's relationship, eqn 3.2.1(2) is not valid, since $j_1^1 \neq j_4$.

Relationships 3.2.1(3) and 3.2.1(4) do not hold either, as shown in figs 3.2.2(17) to 3.2.2(19). The discrepancies are shown in figs 3.2.2(18) and 3.2.2(19) respectively, by the quantities

$$\Delta j_3 = j_3 + j_2$$ (eqn 3.2.2(4))

and

$$\Delta j_4 = j_4 + 2j_1^1.$$ (eqn 3.2.2(5))

There are no particularly marked trends in the deltas, but $\Delta j_3$ (milled) $< \Delta j_3$ (annealed), and $\Delta j_4$ $< \Delta j_4$ seem to hold.

The remanences of the minor loops also show discrepancies from Wohlfarth's relationships. An additional effect is found, in that the minor loops are shifted along the magnetisation axis. This effect manifests itself in two ways. In the thermally demagnetised samples, the loops are not symmetrically placed with respect to the axes, as seen in fig 3.2.2(20) for sample A. Fig 3.2.2(21) shows the +ve and -ve remanences after thermal demagnetisation for the three samples D, D(a)2, and D(m)3. The non-equality of $j_5$ and $j_5$ is shown in fig 3.2.2(22) by the quantity

$$\Delta j_5 = j_5 + j_6$$ (eqn 3.2.2(6))

which is not zero everywhere. It is largest for the annealed samples and smallest for the milled ones. Annealing a sample increases $\Delta j_5$, while milling reduces it. If the sample is annealed, then milled, $\Delta j_5$ increases, then decreases. Comparison with the direct remanence curve, $j_1$ also shows discrepancies, shown in fig 3.2.2(23) by the quantity

$$\Delta j_6 = \frac{1}{2}(j_5 - j_6) - j_1$$ (eqn 3.2.2(7)).
Fig. 3.2.2(24) Major and minor hysteresis loops for sample A after recoil demagnetization from +ve H.
Fig. 3.2.2(25) \( j_1 \) and \( -j_{10} \) for samples \( D, D(a)2, \) and \( D(m)3. \)
Fig. 3.2.2(26) $\Delta f_{7}$ for all samples.
Fig. 5.2.2(27) $\Delta \hat{\phi}$ for all samples.
Fig. 3.2.3(1) Initial magnetization curves for sample A after various demagnetizing processes.
Fig. 3.2.3(2) Initial magnetization curves for sample b(a)3 after various demagnetizing processes.
follows the same pattern as \( \Delta j_5 \) above.

The second way in which the shift shows up is in the minor loops after recoil demagnetisation. If recoil is carried out from \( +H_c \), \( j_7 \) should be zero for loops with maximum applied +ve field less than \( H_c \). It is seen in fig 3.2.2(24), which shows the minor loops after recoil demagnetisation from +ve \( H \) for sample A, that the minor loops are shifted downwards and \( j_7 \) is -ve, \( H < H_c \), instead of being zero. The minor loops enter only three quadrants for \( H < H_c \), but enter all four for \( H > H_c \). Fig 3.2.2(25) shows \( j_7 \) and \( j_{10} \) for the three samples \( D_a, D(a)2 \) and \( D(a)3 \). In theory \( j_7 = j_3 \), and the discrepancies from this relationship are shown in fig 3.2.2(26) by the quantity

\[
\Delta j_7 = j_7 - j_3 \quad (= 0 \text{ in theory}) \quad \text{eqn 3.2.2(8)}
\]

Since \( j_3(H < H_c) = 0 \), all samples, the fact that \( \Delta j_7 \) is -ve for low fields for all samples means that the minor loops are shifted downwards, all samples. There is no pattern in the discrepancies, except that \( \Delta j_7 \) reaches its maximum at higher fields for the annealed samples than for the milled ones. The same remarks hold for \( j_{10} \), although, as may be seen in fig 3.2.2(25), \( j_7 \neq j_{10} \). The differences are characterised by the quantity

\[
\Delta j_8 = j_7 + j_{10} \quad (= 0 \text{ in theory}) \quad \text{eqn 3.2.2(9)}
\]

shown in fig 3.2.2(27). Again, there is no pattern visible, as the effect is apparently small and is masked by experimental errors.

3.2.3 Examples of the initial magnetisation curves are shown in figs 3.2.3(1) and 3.2.3(2) for the samples A and D(a)3. There are three types of initial magnetisation curves, taken in +ve fields:

- \( N_{J1} \): after thermal demagnetisation
- \( N_{J2} \): " recoil " from -ve \( H \)
- \( N_{J3} \): " " +ve \( H \)

In the following discussion, the magnetisation curve in -ve fields after recoil demagnetisation from +ve fields is \( -N_{J2} \).

\( N_{J1} \) lies above \( N_{J2} \) up to fields comparable to \( H_c \) and \( H_c \). Then \( N_{J2} \) becomes higher than \( N_{J1} \). For coherent rotation of the magnetisation vector, \( N_{J2} \) should lie above \( N_{J1} \) and should rejoin the major loop at \( H = H_c \), which it does not. \( N_{J3} \) is almost linear and joins onto the major loop at \( H = H_c \), as expected.
Fig. 3.2.3(3) $n_{J_1}$ and $n_{J_4}$ for sample B.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_C$</th>
<th>$M_R$</th>
<th>$H'_C$</th>
<th>$H_C/M_C$</th>
<th>$H_C$ (calc.)</th>
<th>Annealing treatment</th>
<th>Milling treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2650</td>
<td>1500</td>
<td>3100</td>
<td>1.17</td>
<td>5895</td>
<td>--------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>B</td>
<td>3150</td>
<td>1600</td>
<td>3590</td>
<td>1.14</td>
<td>6098</td>
<td>1 Hr. @ 950 C</td>
<td>-----------------</td>
</tr>
<tr>
<td>D</td>
<td>2080</td>
<td>1360</td>
<td>2580</td>
<td>1.24</td>
<td>5824</td>
<td>--------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>E</td>
<td>2600</td>
<td>1360</td>
<td>3500</td>
<td>1.35</td>
<td>6060</td>
<td>1 Hr. @ 950 C</td>
<td>-----------------</td>
</tr>
<tr>
<td>D(a)1</td>
<td>2950</td>
<td>1420</td>
<td>3450</td>
<td>1.17</td>
<td>6073</td>
<td>1 Hr. @ 950 C</td>
<td>-----------------</td>
</tr>
<tr>
<td>D(a)2</td>
<td>3000</td>
<td>1390</td>
<td>3460</td>
<td>1.16</td>
<td>6240</td>
<td>2 Hr. @ 950 C</td>
<td>-----------------</td>
</tr>
<tr>
<td>D(a)3</td>
<td>2920</td>
<td>1330</td>
<td>3430</td>
<td>1.18</td>
<td>6260</td>
<td>3 Hr. @ 950 C</td>
<td>-----------------</td>
</tr>
<tr>
<td>D(m)1</td>
<td>1550</td>
<td>1340</td>
<td>2180</td>
<td>1.41</td>
<td>5470</td>
<td>--------------</td>
<td>24 hours</td>
</tr>
<tr>
<td>D(m)2</td>
<td>1560</td>
<td>1280</td>
<td>2100</td>
<td>1.35</td>
<td>5515</td>
<td>--------------</td>
<td>48 milled in</td>
</tr>
<tr>
<td>D(m)3</td>
<td>1520</td>
<td>1100</td>
<td>2050</td>
<td>1.35</td>
<td>5530</td>
<td>--------------</td>
<td>72 rotary</td>
</tr>
<tr>
<td>E(a)2</td>
<td>1870</td>
<td>1560</td>
<td>2410</td>
<td>1.29</td>
<td>5575</td>
<td>1 Hr. @ 950 C</td>
<td>48 ball mill</td>
</tr>
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</table>

**TABLE 2.4.11**

<table>
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<tr>
<th>Experiment</th>
<th>Sample height, L</th>
<th>Sample diameter, d</th>
<th>Aspect ratio, L/d</th>
<th>Demagnetizing factor theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisotropy distribution</td>
<td>0.05 cm.</td>
<td>0.38 cm.</td>
<td>0.13</td>
<td>0.128</td>
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<tr>
<td>Hysteresis loops</td>
<td>1.3 cm.</td>
<td>0.38 cm.</td>
<td>6.84</td>
<td>0.011</td>
</tr>
<tr>
<td>Rotational hysteresis</td>
<td>0.05 cm.</td>
<td>0.20 cm.</td>
<td>0.23</td>
<td>0.195</td>
</tr>
<tr>
<td>(Paraffin wax samples)</td>
<td>0.05 cm.</td>
<td>0.60 cm.</td>
<td>0.08</td>
<td>0.0369</td>
</tr>
</tbody>
</table>

**TABLE 2.4.21**

Note: * indicates that the annealing was done in the factory
The initial susceptibility after thermal demagnetisation is greater than after recoil demagnetisation. At the remanence points \( j_1(H_{\text{max}}) \), \( j_2(H_{\text{max}}) \) and \( j_2(H_{C}) \), (i.e. \( j_2 = 0 \)) the same value of susceptibility is found, less than that after thermal demagnetisation. The susceptibilities at all remanence points decrease with increasing \( H_{C} \), as found by Sixtus et al., and are not discussed further here.

The positions of the tips of the minor loops lie lower than the initial magnetisation curves, even though the minor loops are shifted. For the thermally demagnetised samples, the tips in positive fields lie on a curve with a plateau, \( H_{J_4} \), as seen for samples A and B in figs 3.2.3(1) and 3.2.3(3). The extent of the plateau depends on the coercive force, being greater for the greater coercive force. The tips in negative fields also lie below \( -H_{J_4} \).

For the samples recoil demagnetised from positive \( H \) the tips of the minor loops in positive fields lie below the initial magnetisation \( H_{J_3} \) curve up to \( H = H_{C} \) and lie on the major loop for \( H > H_{C} \). The tips in negative fields lie on the initial curve, \( -j_2 \) up to \( H = H_{C} \), but lie below the initial curve for \( H > H_{C} \). Thus the magnetisation in positive fields up to \( H = H_{C} \) is less after the cycling procedure than after the single application of a field \( H \). There is some indication of a plateau in the positions of the tips of the loops in positive fields, but since \( H_{J_3} \) is plateau-like itself, no definite conclusion could be reached.

3.2.4 The remanence coercivity may be defined in two ways: (a) it is that field \( H_{C} \) for which \( j_1(H_{C}) = 0.5 j_1(H_{\text{max}}) \); or (b) it is that field \( H_{C} \) at which \( j_2(H_{C}) = 0 \). This second definition may be changed, using eqn 3.2.1(2) into \( j_1'(H_{C}) = 0.5 j_1'(H_{\text{max}}) \). The remanence coercivities found using the latter definition from figs 3.2.2(1) to 3.2.2(11) have been given in table 2.4.1(1), which is given again here. The values derived from \( j_1 \) (theo.), denoted by \( H_{C} \) (calc.) are larger than the experimental values for all samples, indicating that non-coherent magnetisation processes are taking place. The ratio of \( H_{C} \) to \( H_{C} \), which should be 1.09 for a sample reversing by coherent rotation, are given in table 2.4.1(1). Larger values of this ratio do not necessarily indicate the presence of non-coherent processes, as a spread in
Fig. 5.5.1(1) Reduced rotational hysteresis versus reduced applied field, for coherent rotation.
Fig. 3.3.1 (2) Theoretical and experimental rotational hysteresis versus internal field curves for sample D.
Fig. 3.3.2(1) Experimental curves of rotational hysteresis versus internal field.
### Table 3.3.2(1)

Experimental values of the R.H.I. for the barium ferrite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R.H.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.28</td>
</tr>
<tr>
<td>B</td>
<td>0.27</td>
</tr>
<tr>
<td>D</td>
<td>0.28</td>
</tr>
<tr>
<td>E</td>
<td>0.27</td>
</tr>
<tr>
<td>D(a)1</td>
<td>0.28</td>
</tr>
<tr>
<td>D(a)2</td>
<td>0.26</td>
</tr>
<tr>
<td>D(a)3</td>
<td>0.28</td>
</tr>
<tr>
<td>D(m)1</td>
<td>0.29</td>
</tr>
<tr>
<td>D(m)2</td>
<td>0.30</td>
</tr>
<tr>
<td>D(m)3</td>
<td>0.35</td>
</tr>
<tr>
<td>E(m)2</td>
<td>0.27</td>
</tr>
</tbody>
</table>

### Table 3.3.2(2)

Theoretical values of the R.H.I. for various modes of reversal.

<table>
<thead>
<tr>
<th>Mode</th>
<th>R.H.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coherent rotation</td>
<td>0.38</td>
</tr>
<tr>
<td>Fanning in chain-of-spheres</td>
<td>1.02</td>
</tr>
<tr>
<td>Domain-wall motion</td>
<td>3.41</td>
</tr>
<tr>
<td>Infinite cylinders</td>
<td>Varies from 0.38 at small radii to 3.41 at large radii</td>
</tr>
</tbody>
</table>

Table 3.3.2(1)

Experimental values of the R.H.I. for the barium ferrite samples.

Table 3.3.2(2)

Theoretical values of the R.H.I. for various modes of reversal.
the values of the anisotropy fields also raises the ratio.

3.3 Rotational Hysteresis

3.3.1 Consider an assembly of particles with uniaxial anisotropy, which reverse their magnetisation by coherent rotation, and for which the distribution of the directions of the easy axes is spatially random. The theoretical dependence of the rotational hysteresis of this assembly on the reduced field is shown in fig 3.3.1(1). The anisotropy field distributions from section 3.1.2 may be used, in conjunction with fig 3.3.1(1), to derive the theoretical rotational hysteresis curve for each sample. Each group of particles with anisotropy field \( H_A = \frac{1}{2}(H_i + H_{i+1}) \) will have a curve similar to that in fig 3.3.1(1) associated with it. For a fixed external field \( H \), since the reduced field is equal to \( \frac{H}{H_A} \), the rotational hysteresis will vary from group to group, since \( H_A \) varies, and the rotational hysteresis varies as \( H_A \) varies. The resultant rotational hysteresis for all groups of particles will be the summation of the individual values for each group. This calculation has been carried out for sample D, and the curve is shown in fig 3.3.1(2), together with the experimental curve. It is seen that the experimental curve is much lower than the theoretical one. The same is true for all samples, and the theoretical curves were not calculated for any other sample, since no new information was derivable from these curves that could not be got from the remanence curves.

3.3.2 Fig 3.3.2(1) shows the rotational hysteresis, (R.H.), versus internal field curves for the samples D, D(a)2, D(m)3. It is seen that milling a sample reduces the peak value of the R.H. and shifts it to lower fields, while annealing a sample increases the peak value of the R.H. and shifts it to higher fields.

The rotational hysteresis integral, (R.H.I.), discussed in section 2.3.1, may be found from the areas under curves of R.H. versus the inverse of internal field. The values of the R.H.I. for all samples are given in table 3.3.2(1). The theoretical values for various modes of magnetization reversal, for random assemblies of particles with uniaxial anisotropy, are given in table 3.3.2(2). The surprising fact to be seen from these tables is that the R.H.I. is less than any of the theoretical values, although the value for coherent rotation is supposed to be the lower limit of all possible values.
In general, milling a sample increases the R.H.I., while annealing a sample reduces the R.H.I. There are exceptions to these remarks in table 3.3.2(1), since the value for $E(n)2$ is less than that for $E$, and the value for $D(a)3$ is almost the same as that for $D$. 
Chapter 4 Discussion of Results

The results given in chapter 3 may be explained by making the following assumptions:

a) dislocations in the crystal lattice reduce the anisotropy;
b) the reduction in the anisotropy is proportional to the dislocation density;
c) dislocations may act as domain-wall nucleation centres;
d) the presence of domains affects the remanence curves;
and e) an asymmetrical magnetisation process, due to cylindrical domains, is present.

4.1 Anisotropy Field Distributions.

4.1.1 The possible dislocations in the barium ferrite lattice are considered in the appendix. It is shown there that certain possible dislocations may break the magnetic coupling between the spinel-like blocks in the unit cell and the iron ion on the 2b site which gives rise to the large magneto-crystalline anisotropy. If this coupling is broken, it is possible for the anisotropy constant to become zero or -ve, due to the dipole-dipole interactions. The resultant anisotropy, at 300°K, of a lattice composed of faulted and unfaulted regions will vary from \(-3.3 \times 10^6\) erg cm\(^{-3}\) for a perfect, unfaulted lattice to \(+0.05 \times 10^6\) erg cm\(^{-3}\) for a totally imperfect lattice, where only the dipole-dipole contribution is of importance. The anisotropy will depend on the amount of faulted material present.

The saturation magnetisation will also be reduced if the coupling is broken, since the dipolar coupling is expected to be antiferromagnetic, as for \(\text{KFe}_{11}\text{O}_{17}\). Provided that the ratio of \(K\) to \(M\) is reduced, however, the anisotropy field will be reduced.

There will be a contribution to the total anisotropy from shape anisotropy. This contribution is -ve and will vary from zero for a particle infinitely long along the C-axis to \(-4\pi H_s^2\) for a particle infinitely long along the C-axis to \(-4\pi H_s^2\) for a plate infinite in the direction perpendicular to the C-axis. For barium ferrite the shape component is expected to approach closely to \(-4\pi H_s^2\) since the particles are plate-shaped, with the
easy axis perpendicular to the plane of the sample. However, from the results of Heincke\textsuperscript{5} on the sizes of the crystallites in strontium ferrite magnets, it is deducible that there will be many particles with values of the shape component as low as $-\frac{\pi H^2}{5}$. Thus the anisotropy fields due to shape are expected to have a spread of values from about $-4\pi H^3_5$ to $-\pi H^5_5$ for barium ferrite. It is not possible to separate out the shape component of the total anisotropy by the methods used to obtain the results embodied in this thesis.

In the following discussion of the anisotropy distribution, the percentage of particles in the low anisotropy field range will be a useful indication of the effect of annealing and milling on the magnetic properties. This is due to Gerlach's principle\textsuperscript{6}, which states that in a mixture of magnetically soft and hard components, the soft component has a much greater effect on the magnetic properties than the hard component. Soft in the present case means having a low anisotropy field. However, the whole anisotropy field distribution must be taken into account, and this is done by using the average anisotropy field $\overline{H}_A$, defined in eqn. 3.1.2(1). The coercive force depends on $\overline{H}_A$ in two ways. Firstly, if $\overline{H}_A$ changes because of a change in the anisotropy field distribution, then the coercive force $H_c$, calculated on the coherent-rotation theory, changes also. Secondly, a change in the anisotropy field distribution means a change in the dislocation density and hence a change in the density of domain-wall nucleation centres. Thus the amount of domains present changes, and, since the coercive force is affected by the presence of domains, the coercive force changes too.

The values of $\overline{H}_A$ for all samples are given in fig 3.1.2(6).

4.1.2 In a given sample, there will be a certain density of dislocations. Annealing the sample would reduce the dislocation density, and hence reduce the percentage of particles with low anisotropy fields. Milling the sample would increase the dislocation density and hence increase the percentage of particles with low anisotropy fields.
These remarks are borne out by the results of the annealing and milling experiments quoted in chapter 3.

As shown in fig 3.1.2(1), the annealed samples have less particles in the low anisotropy field range than does the unannealed sample. The fact that the sample annealed for the longest time has more particles in the low range than the other annealed samples may be due to some slight sintering taking place during the long annealing. Faulted regions might arise at the interface between two particles which are being sintered together, thus reducing the effective anisotropy.

The annealed samples have higher coercive forces than the unannealed sample, and also higher values of $H_A$. The values of $H_A$ depend on the shape anisotropy and the dislocation density, while $H_C$ takes account of the influence of domains also. It is presumed that the shape component is uninfluenced by annealing, except perhaps in the case D(a)3. The increase in $H_C$ and $H_A$ are ascribed to a decrease in dislocation density, which means there are also less domain-wall nucleation centres. Hence $H_A$ increases because there are less dislocations and $H_C$ increases because $H_A$ increases and also because there are fewer domains.

Samples prepared independently of each other, such as A and D, fig 3.1.2(2), may have the same $H_A$, but different values of $H_C$, due not only to variations in the actual distribution of anisotropy fields, but also to the presence of different amounts of domains.

The milling of a sample increases the percentage of particles with low anisotropy fields, fig 3.1.2(4). The curve for sample D(2) lies below that of D at the lowest fields, but this does not contradict the assumed dependence of anisotropy on dislocation density, as $H_A$ for the milled samples is lower than for the unmilled sample.

The milling of a sample previously annealed, and the dependence of $H_C$ on $H_A$ for these samples confirms the role of dislocations in determining the magnetic behaviour of a sample.

Gerlach's principle stresses the effects due to the particles at the low-field end of the anisotropy-field-distributions. The preceding discussion of the effects of annealing and milling has been in terms of such particles. However, the coercive force $H_A$ depends also on the total anisotropy-field-distribution, as
is seen in fig 3.1.2(6). $\overline{H}_A$ is a parameter which depends on the total distribution, not just any particular portion of it. All the points for the samples prepared from D as a starting material lie on the same curve. The position on this curve of the point for any one of this group of samples depends on the dislocation density of that particular sample. The position may be varied by suitably annealing or milling the sample. It is presumed that in the case of other samples independently prepared, such as $A$, $F$ and $G$, each has a curve of its own, different from that for the D-group, associated with it. The position of the point for the starting powder along the $\overline{H}_A$-axis depends on the shape anisotropy and the dislocation density, while the position along the $M_O$-axis also depends on these factors, but furthermore depends on the amount of domains present. Thus two independently prepared samples may have equal values of $\overline{H}_A$, due to the resultant anisotropy of shape and magnetocrystalline anisotropies, but different values of $M_O$, due to the presence of differing amounts of domains, arising from different dislocation densities. The curve for the D-group of samples seems to tend to a limit at the low-$M_O$ end, due perhaps to the establishment of an equilibrium dislocation density. There appears to be a limit at the high-$M_O$ end also, though this limit is not as pronounced. This limit is presumed to be due mainly to the shape component, though there are still dislocations present to reduce the anisotropy and act as domain-wall nucleation centres.

4.1.3 In section 3.1.3, it was seen that $V_T$, the fraction of material reversing by coherent rotation, was apparently greater for the milled samples than for the annealed ones, contrary to expectation. The reason for this anomalous behaviour of $V_T$ is not known. Incoherent rotations and non-coherent processes could perhaps give rise to it, but the analysis of the experimental conditions in section 2.1.2 seems to exclude this possibility.

The main experimental error which could cause the anomalies would be the use of too large values of $\Theta_M$ for the annealed samples and too small values for the milled samples. If values of $\Theta_M = 2.5^\circ$ and $\Theta_M = 1.8^\circ$ for the milled and annealed samples respectively were used, the discrepancies would be removed. This error is much larger than the possible error in measuring $\Theta_M$. 
and so the possibility that errors in the magnitude of $\theta_M$ are the source of the discrepancy is excluded.

The remaining possibility and probably the most likely one, is that the various corrections considered in section 5.1.1 could alter the situation sufficiently to change the anomalous values of $V_T$ to give more reasonable agreement with expectation. These corrections were not considered important for the distribution curves. Time did not permit the evaluation of the corrected values of $V_T$ and so the matter remains to be resolved by future work.

4.2 Remanence Curves

4.2.1 In the faulted region, where the anisotropy is reduced, it is easier for the spins to rotate away from the C-axis than in the unfaulted region. Thus when a sample is first saturated, and then brought to the remanence point, it is possible that domains may be nucleated, in the manner proposed by the Russian workers, at the faulted region. Thus it may be assumed that the amount of domains present will depend on the dislocation density, and that this dependence will show up in the remanence curves.

The difference between the theoretical and calculated remanence curves is ascribed to the presence of domains, in a manner similar to other workers. However, the influence of the anisotropy field distributions on the remanence curves is to smooth out the theoretical curves, giving a less steep rise than if all particles were assumed to have the same anisotropy. However, even allowing for the anisotropy field distributions, the differences between the theoretical and experimental curves are not eliminated, but only reduced.

4.2.2 $j_1^{(exp.)}$ is greater than $j_1^{(theo.)}$ in low fields due to the presence of mobile 180°-domain-walls. $j_1^{(exp.)}$ is less than $j_1^{(theo.)}$ in high fields, due to domain wall nucleation and growth. $j_1$ is greater than $j_1^r$ in low fields because the thermally demagnetized sample has a simpler, more mobile domain structure than the sample at remanence after saturation or recoil demagnetization. One might expect that $j_1$ would be greater than $j_1^r$ at high fields also, but this is not so. This is perhaps due to some nuclei of reverse magnetisation, which are not eliminated by the applied field, growing when the field is reduced and so reducing $j_1^r$. When
the sample has been saturated, there will be less of these reverse nuclei, and so some particles which had split into domains when \( j_1 \) was being measured, might remain single-domain when \( j_1 \) was being measured, and so allow \( j_1 \) to be greater than \( j_1 \) at high fields.

Rather than considering each remanence curve, it is more instructive to deal with the deltas, defined by eqns 3.2.2(2) to 3.2.2(9).

\( \Delta j_1 \) for the annealed samples is greater than \( \Delta j_1 \) for the unannealed samples in low fields, and less in high fields. It is presumed that there are approximately the same amount of domains in all samples after thermal demagnetization, but the annealed samples have less nucleation centres. Thus the magnetization change in a given field will be about the same for all samples at low fields, but the annealed samples retain more of the magnetization at remanence, since there are less dislocations to nucleate domains which reduce the remanence. In high fields, the same reasoning applies. \( \Delta j_1 \) is less than \( \Delta j_1 \) because fewer domains are nucleated. In like manner, the annealed samples lose less of their remanence by the application of low reverse fields after saturation than do the unannealed samples, because less domains are nucleated in the annealed samples. These also retain more of their remanence after the application of large reverse fields. Thus \( \Delta j_1 \) for annealed samples is greater than that for the unannealed samples at both low and high fields.

One would expect on this picture that \( \Delta j_1 \) for the milled sample would be less than \( \Delta j_1 \) for the unmilled sample, since there are more nucleation centres in the milled sample. However, the reverse is true, \( \Delta j_1 \) being smallest for the unmilled sample. The reason for this is not clear, but it may be due to the larger number of domains present in the milled sample as shown by the larger initial susceptibility. These could produce a much larger change of magnetization in low applied fields in the milled sample than in the unmilled one. Even though the milled sample might lose a greater proportion of this change when the field was reduced to zero, due to more domains being nucleated, the initial change could be large enough for \( j_1 \) of the milled sample to be higher than \( j_1 \).
for the unmilled sample. Thus $\Delta J_4$ for the milled samples in low fields could possibly be larger than $\Delta J_4$ for the unmilled sample, as found.

$\Delta J_1$, at high fields, and $\Delta J_1^1$, at both low and high fields, are both greater for the milled sample than for the unmilled sample. This may be explained by the greater number of nucleation centres in the milled sample, causing it to have lower remanence after application of both high forward and high reverse fields, and to lose its remanence more easily in low reverse fields, than the unmilled sample.

The same reasons explain why $\Delta J_3$ for the milled samples is less than $\Delta J_3$ for the annealed samples.

The fact that $\Delta J_3$ is less than $\Delta J_4$ is an indication of the presence of an asymmetrical magnetization process, which will be also used to explain later results and will be considered then. The indications from $\Delta J_3$ are not very marked.

When the minor loop remanences are considered, the following is found, $\Delta J_5$ and $\Delta J_6$ increase if a sample is annealed, and decrease if it is milled. The fact that $\Delta J_5$ is non-zero indicates the presence of an asymmetrical magnetization process, while the variation of $\Delta J_5$ with annealing and milling shows that the effect is greater for the lower dislocation density. The $-ve$, non-zero values of $\Delta J_6$ indicate that the magnetization process is made more difficult by cycling the field, compared with the application of a direct field. These effects are ascribed to an asymmetrical magnetization process, due to Kooy-Ens type loops. In a multidomain particle it is assumed that the magnetization varies linearly with applied field, $H$, but if $H$ exceeds a certain critical saturating field, $H_s$, the loop becomes open. Reversal of the particle's magnetization after the application of $H_s$ then occurs by domain-wall nucleation and growth. If the saturating field, $H_s$, is less than the field at which nucleation takes place, $H_n$, the magnetization process in low fields may be asymmetric, as follows. Starting with the multidomain state, a $-ve$ field, $-H$, is applied first, as in the loop-drawing procedure. If the applied field is greater than $H_2$ but less than $H_n$, the magnetization reaches $-H_2$. The applied field is then reduced to zero and a field $+H$ is applied, equal
in magnitude to the -ve field first applied. Since $H$ is less than $H_n$, the magnetisation remains at $-N_S$. Thus starting from the thermally demagnetized, i.e., multidomain state, and applying fields $H_{>}$ greater than $H_S$ but less than $H_n$, the particle acquires a -ve remanence and has an asymmetric loop. However, with such behaviour, if the applied fields are greater than $H_n$, the loop becomes rectangular. The asymmetry of the minor loops would only occur for applied fields between $H_S$ and $H_n$. There are indications from the fact that $\Delta J_3 < \Delta J_4$, and from the later results on recoil-demagnetized samples, that the effect occurs over much greater field ranges than one would expect, since $H_S$ and $H_n$ would probably not be very different from each other. This could arise from a spread in the values of $H_S$ and $H_n$, or from a particular type of domain structure, which will be considered when the results on the recoil-demagnetized samples are considered. Since the effect is less in the milled samples, which contain more nucleation centres, it is presumed that the difference between $H_S$ and $H_n$ is less in these samples, and that the easier nucleation of domains reduces the asymmetry due to the different type of domain structure introduced during the loop-drawing procedure, compared with that present after thermal demagnetisation.

The results on the recoil-demagnetised samples show that $\Delta J_7$ is less than zero and $\Delta J_8$ is non-zero. The -ve values of $\Delta J_8$ indicate that there is an asymmetrical magnetisation process taking place. This cannot be the Kooy-Ena type loops considered in connection with $\Delta J_5$ and $\Delta J_6$, as this type of loop should be symmetrical after the application of $H_{\text{max}}$ to the sample, no matter what sequence of fields were then applied. An asymmetrical process may be found with the cylindrical domain structure observed in barium ferrite$^{11}$, the "honeycomb" domain structure$^{12}$, and in MnBi$^{13}$. These structures have been observed after saturation and either reduction of the applied field to zero or application of a reverse field, depending on the demagnetising field of the sample. It was shown both theoretically and experimentally that the behaviour of a cylindrical domain is asymmetric. The domain prefers to grow rather than shrink. Hence, if the magnetization in such a domain is in the -ve direction, application of a -ve field would
produce a larger magnetization change than the application of an equal +ve field would do. Hence the loop would be asymmetric, with greater -ve magnetization than +ve. The application of this idea of cylindrical domains to the thermally demagnetized sample is as follows: when the first -ve field is applied, the 180°-domain-walls present are swept out of the sample which becomes saturated in the -ve direction, with perhaps a few nuclei of +ve magnetisation remaining. In the subsequent +ve field, cylindrical domains are formed, with -ve magnetisation. Thus these domains change much more when -ve fields are applied than when +ve fields are, and the loop is displaced towards -ve magnetisation. This effect does not invalidate the assumption of Kooy-Ens type loops, but the two effects could be superimposed.

However, when considering the magnetisation processes after a saturating field has been applied, when the Kooy-Ens type loops are rectangular, the cylindrical domains provide all the asymmetry. Consider a sample recoil demagnetised from +ve field. Since the last direction of saturating field applied to the sample was -ve, the magnetisation in the cylindrical domains is -ve. Thus during the loop-tracing procedure, the -ve fields applied produce a greater magnetisation change than the +ve fields and the loops are again displaced towards -ve magnetisation, making \( \Delta j_7 \) less than zero, as observed.

When the sample is recoil-demagnetised from -ve fields, the magnetisation in the cylindrical domains is +ve. The first field applied during the loop-drawing procedure is always negative and hence in this case tends to shrink the cylindrical domains. The magnetisation change produced by the subsequent application of the +ve field next in the cycling procedure would be expected to be less than that which would have been produced if the first field to be applied were +ve. Thus the shifting of the loops towards +ve magnetisation in this case would be expected to be less than the shift considered in the preceding paragraph. Thus \( \Delta j_8 \) should be non-zero and negative. However, this effect, if present, is small, since while \( \Delta j_8 \) is non-zero, in some cases it is +ve and in others -ve. Thus the results from \( \Delta j_8 \) are inconclusive and further investigation is required.
4.2.3 $H_{J1}$ is above $H_{J2}$ up to fields comparable to $H_{E}$ and $H_{C}$, since the magnetisation processes are predominantly composed of the movement of $180^\circ$-domains for $H_{J1}$, but are a mixture of cylindrical-domain growth and coherent rotation for $H_{J2}$, since on this part of the curve for $H_{J1}$ some particles have still to be reversed by coherent rotation. On this part of the curve for $H_{J2}$ the process consists in eliminating nuclei of reverse magnetisation, since any particles which required such fields to reverse coherently would have done so on the previous application of $H_{\text{max}}^+$ and would have retained $\text{ve}$ magnetisation during application of $H_{C}^-$. The particles which reversed their magnetisation in order to make $j_2(H_{C})$ zero would have done so by domain nucleation and growth.

The existence of the plateau in the positions of the tips of the minor loops confirms the existence of the asymmetrical magnetisation process. The fact that the tips of the minor loops in $\text{ve}$ fields also lie below the initial magnetisation curve in that direction, $-H_{J1}$, shows that while the magnetisation process during the loop-draw is easier in the $\text{ve}$ direction than in the $\text{ve}$ direction, it is still not so easy as during the direct application of a field, due to the different types of domain present.

The results after recoil-demagnetisation, while not definitely confirming the assumptions made, certainly do not contradict them. There appears to be a plateau in the positions of the tips in $\text{ve}$ fields, as expected.

The existence of these plateaux show that a magnetisation process exists in which the magnetisation process exists in which the magnetisation in $\text{ve}$ fields increases only slowly with field, while the magnetisation in comparable negative fields increases much more. Such a process was observed in honeycomb domains.\textsuperscript{11}

4.2.4 The values of the remanence coercivities in figs 3,2,2(1) to 3,2,2(11) are less when derived from the curves for $j_1$ than when they are derived from the curves for $j_1^+$, indicating that the magnetisation process is easier in thermally-demagnetised samples than in samples which have been saturated. This is due to the more mobile and more numerous domains in the thermally-demagnetised samples.
The ratio of $H_C$ to $H_C^*$ is, in general, smaller for the higher $H_C$ samples, indicating only that they more nearly approach the ideal of a sample with only a single value of anisotropy field, reversing only by coherent rotation.

4.3 Rotational Hysteresis

4.3.1 The fact that the experimental values of rotational hysteresis, $R.H.$, are lower by a factor of 10 than the theoretical values, indicate the presence of non-coherent reversal processes. These non-coherent processes are due mainly to domain-wall motion, since the value of the rotational hysteresis for this process is $4JH_C^M$, where $J$ is the coercive force associated with domain-wall motion. The peak value of rotational hysteresis for coherent rotation is $1.75K$, where $K$ is the anisotropy constant. Inserting the values of $H_C$ and $K$ appropriate to barium ferrite, one finds that the two values of $R.H.$ are comparable only if $JH_C^M$ is about 1 koe., which is an order of magnitude larger than one would expect. Thus the experimental values of $R.H.$ are an order of magnitude smaller than the theoretical values.

4.3.2 The values of the rotational hysteresis integral, $R.H.I.$, in table 3.3.2(2), are much smaller than one would expect if, as postulated, reversal occurs by domain-wall motion for a portion of the material. The values are also smaller than any of the theoretical values. It has been stated that the value of the $R.H.I.$ for coherent rotation is the smallest value of $R.H.I.$ possible. Any other mode of reversal, even apart from those mentioned in table 3.3.2(1), is expected to have a higher value.

There are several possible reasons for the low values of $R.H.$ The most likely one is that $R.H.$ persists down to very low fields, of the order of magnitude of $H_C^e$, the wall coercivity. The lowest measuring field used, 1 koe., is, as stated previously, much greater than $H_C^e$, even if allowance is made for the demagnetising field. The $R.H.$ at these low fields is very important in the determination of the $R.H.I.$, which is determined from a curve of $R.H.$ versus the inverse of the internal field. Since the inverse of a quantity varies most rapidly when the quantity is small, it is readily seen that the value of the $R.H.I.$ is very sensitive to changes in the value of the low-field $R.H.$ Thus failure to measure the $R.H.$ at fields below 1 koe. is taken to
be the most likely cause of the low values of the R.H.I.

It was felt undesirable to use samples with such large demagnetising factors as the ones used, since this gave rise to large corrections for the demagnetising field. These corrections were more important at low fields and could be another possible cause of the small values of the R.H.I. Attempts to overcome these drawbacks were made by using samples dispersed in paraffin wax, and by making the measurements in low fields on demagnetised samples. The wax samples could be made with smaller demagnetising factors. These attempts were not successful, as the results obtained were not very reproducible. Reproducible results were only obtained on the pressed samples. It was not possible to make thinner pressed samples, as they broke up when removed from the press. Neither was it possible to use pressed samples of greater diameter, which also would have enabled the demagnetising factor to be reduced, as the torque magnetometer became overloaded by such samples.
Chapter 5  Conclusions and Future Work

The conclusions to be drawn from the results described in chapter 3 and discussed in chapter 4 are as stated in section 5.1. The possible future work to confirm the observed results is discussed in section 5.2.

5.1 Conclusions

5.1.1 The anisotropy-field distributions of barium ferrite micropowders vary with coercive force and dislocation density, and contain a component due to shape anisotropy. The distributions must be taken into account when considering the magnetic properties of such powders. Samples with low values of $H_C^N$ contain more particles with low anisotropy fields than do the samples with high values of $H_C^N$, in agreement with Gerlach's principle. However, as seen from the dependence of $H_C^N$ on the average anisotropy field, $H_A$, the whole distribution must be taken into account, and not just the low anisotropy field component.

The anisotropy variations are caused by changes in the dislocation density. These dislocations break the magneto-crystalline coupling which causes the high anisotropy, thus lowering the anisotropy. The reduction in anisotropy is presumed to be proportional to the dislocation density.

These dislocations may also act as domain-wall nucleation centres, since it is expected that domains will nucleate preferentially at points in the crystal where the anisotropy is reduced. The presence of domains causes departures from Wohlfarth's relationships, the extent of these departures being accounted for by the same variation in dislocation density as was required to explain the anisotropy field results.

An asymmetrical magnetisation process, due to cylindrical domains, is present in the samples. The extent of this asymmetry also depends on the dislocation density, since the reversal by domain-wall nucleation and growth is easier when there are more dislocations to act as nucleation centres. The magnetisation process in low fields is easier in thermally demagnetised samples than in recoil demagnetised ones, due to the presence of simpler, more mobile domain structures in the thermally-demagnetised samples than in the other ones.
5.2 Future Work

5.2.1 It would be desirable to separate out the component of anisotropy due to shape. This could possibly be done by measuring the shape distributions from electron micrographs of the powders. Attempts to do this in the present work were frustrated due to agglomeration. Besides, there is no way of ascribing a total anisotropy to any particle when there is a distribution both in anisotropy and shape.

To overcome this, it should be possible to determine the relationship, if any, between shape and total anisotropy, by separating powder fractions with different sizes from the starting powders. This would reduce the spread in shape anisotropy, and measuring the total anisotropy would show any connection between shape and total anisotropy.

The presence of domains and the asymmetrical magnetisation process would show up better in aligned samples. Here again, the use of fractions with different average sizes of particles would show the dependence of the asymmetry on the particle size. For particles just above the single-domain size, a transitional domain-structure, such as observed in MnBi, would be expected to appear, and should give the largest asymmetry. Direct observation of the domain-structure of such particles is probably not feasible at present.

The simultaneous observation of both dislocations and domains in barium ferrite could confirm the role of dislocations as nucleation centres. Altering the dislocation density by annealing or straining a single-crystal sample, and simultaneous measurement of the change, if any, in the magnetic properties, should permit the connection between domains and dislocations to be established.

A more detailed description of the possible dislocations in barium ferrite than is given in the appendix, and the effect on the magnetic structure of such dislocations, would indicate other possible lines of investigation.
Fig. A1. Three co-planar interpenetrating trigonal lattices: the lattice points of one of them are connected to emphasise the trigonal nature.
A2

The twelve sub-lattices of
the unit cell.
<table>
<thead>
<tr>
<th>Site</th>
<th>Normal B</th>
<th>P1</th>
<th>S1</th>
<th>P2</th>
<th>S2</th>
<th>P3</th>
<th>S3</th>
<th>P4</th>
<th>Normal B</th>
</tr>
</thead>
<tbody>
<tr>
<td>O²⁻</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{3+}$O²⁻</td>
<td>12k</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$^{3+}$O²⁻</td>
<td>4.5</td>
<td>A</td>
<td>C</td>
<td>B</td>
<td>C</td>
<td>A</td>
<td>C</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>$^{3+}$O²⁻</td>
<td>2.8</td>
<td>TA4</td>
<td>TA4</td>
<td>TB4</td>
<td>TB4</td>
<td>TC4</td>
<td>TC4</td>
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<tr>
<td>$^{3+}$O²⁻</td>
<td>4.5</td>
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<td>C</td>
<td>B</td>
<td>C</td>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

The stacking below the slip plane is normal everywhere i.e. identical with the left-hand column headed normal.

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**Fig. A3** Description of normal and faulted vanadium ferrite structure in terms of layers stacked on top of one another.
(a) M-Type Hexagonal Ferrites

Unit cell = TSTSTS = 3(Ba₂Me₂Fe₁₂O₂₂).

(b) Y-Type Hexagonal Ferrites.

Fig. 1.2.3. (I) Crystal structures. Ref. 40.
Oxygen ions

Barium or divalent metal ion in (a) and (b), potassium iron in (c).

- Iron ion on octahedral site.
- Iron ion on tetrahedral site.
- Iron ion on trigonal site.

Unit cell: $SRS^*R^* = 2(KFe_{11}O_{17})$

(c) $KFe_{11}O_{17}$

Fig. 123. (l) Crystal structures. Ref. 40.
Spinel Crystal Structure with [111] Axis Vertical

(a) Spinel Crystal Structure with [111] Axis Vertical

(b) Structure of R-block

Fig. 1.2.3. (2)
Appendix  Dislocations in the Barium Ferrite Lattice

The consideration of dislocations in the barium ferrite lattice is facilitated if the structure is considered in terms of layers of ions, following the method of Iida.

Three coplanar interpenetrating lattices are used, A, B and C, as in fig A1. Each individual lattice is divided into four sublattices, e.g., for A the sublattices are TA1, TA2, TA3 and TA4, as in fig A2, following Iida's notation. The total number of sublattices is thus twelve.

The stacking of layers in close-packed structures is normally given in terms of the three lattices A, B and C. Hexagonal close-packed is ...ABABAB..., while face-centred cubic is ...ABCABC...

In considering structures in which all the sites on a given layer are not occupied, the site occupancy may be given by naming the occupied sublattices. If, for example, all the B sites are occupied in a given layer, the site occupancy is given as B. If, however, only three out of every four sites are occupied, as happens in the barium ferrite structure, e.g., if only three out of every four B sites are occupied, the TC4 sites being empty, the site occupancy will be given as the total sites minus the vacant sites, i.e., C-TC4. The sublattice TC4 has been chosen arbitrarily as the empty one, although any one of the other three could also have been chosen. The actual empty sublattice will be found by reference to the other layers of the particular structure being considered. Note that the division of each lattice such as B into four sublattices has been done because in barium ferrite, some layers have one in four sites empty. Other structures might have one in three sites empty, in which case each lattice such as B would have been divided into three sublattices.

The description of barium ferrite in these terms is given in fig A3 in the column headed "normal". The particular ion or ions in each layer, and the site designation, if any, is given in the column headed "site". The change in packing of the oxygen ions from hexagonal close-packed in the B-block to cubic close-packed in the S-block is clearly seen.
Fig. A4: Directions of slip, \((1 \bar{1} 2 0)\), on the basal plane of martensite. The unit cell is also shown.
The possible dislocations in the barium ferrite structure are expected to be similar to those in sapphire, which were considered by Kronberg [2]. Slip will occur on the basal plane, \{0001\}, because of the large $a/c$ ratio. The direction of slip will be \langle 11\overline{2}0 \rangle, which is shown in fig. A4 with respect to the unit cell. To break the magneto-crystalline coupling requires that the slip occurs on the mid-plane of the $R$-block, i.e. the layer containing the iron ion on the trigonal site. Slip in the spinel block will be similar to that considered theoretically for MgAl$_2$O$_4$ by Hornstra [3], and observed experimentally in non-stoichiometric spinels by Lewis [4]. This type of slip will also occur in barium ferrite but will not affect the anisotropy except perhaps through the dipole-dipole contribution.

The Burgers vector of the total dislocation is \langle 11\overline{2}0 \rangle. It is energetically favourable for this to disassociate into two half-partial dislocations with a stacking fault between them. The Burgers vectors of the half-partial are \( \frac{1}{3} \langle 10\overline{7}0 \rangle \). These half-partial will also be favoured to disassociate, forming four quarter-partial, with Burgers vector \( \frac{1}{3} \langle 11\overline{2}0 \rangle \). The total dislocation and the four quarter-partial are indicated in fig. A4 with respect to the unit cell. There are three stacking faults, one between each pair of quarter-partial, and these are given in fig. A5. The partial dislocations are indicated in the figure by P1, P2 and P3. The stacking faults, indicated by S1, S2 and S3, are of two types. One involves a fault in the stacking of both the oxygen and iron ions. S1 and S3 are of this type. The middle stacking fault, S2, involves only a fault in the stacking of the interstitial iron ions, and has been termed an electrostatic fault by Kronberg.

The slipping process involves the process of synchro-shear, in which, when one oxygen layer, such as B, the layer bounding the $R$-block, slips over the oxygen layer forming the mid-plane of the $R$-block, C-TCa, in a (11\overline{2}0) direction, the interstitial iron cations, Ta4, slip in a (11\overline{2}0) direction at 60° to the direction of movement of the oxygen ions. The total dislocation for the interstitial slip is the same as for the oxygen framework, and there are four quarter-partial, but these partials are not the same as for the framework. The various partial for the framework
and the interstitials are shown in fig. A5.

The electrostatic stacking fault, S2, is the one of interest with respect to the breaking of the coupling to the 2b ion. In the normal stacking, the spins of the ions at TA4 above and below the mid-plane of the R-block are coupled by superexchange to the ion on the 2b site at TB4. The spins of the ions at TA4 are antiparallel to the spins of the ions at TB4, and hence the spins of the ions above the mid-planes at TB4 are parallel to the spins of the ions below the mid-plane at TB4. The coupling of the spins to the spin of the ion on the 2b site at TA4 provides the high magnetocrystalline anisotropy.

In the electrostatic fault, the iron ions above the mid-plane is in the position TA1, which is an unfavourable one for superexchange interaction to occur between the ion on the TB4 site and that on the TA1 site. The angle between the lines joining these two ions to any oxygen ion which could take part in the superexchange such as TC3 or TC2, is about 90°, which is most unsuitable for superexchange coupling. The most likely interaction would be the occurrence of antiparallel coupling between the ions at TA1 above the mid-plane and the ions at TA4 below the mid-plane, by a superexchange interaction via the oxygen ions at TC2 and TC3. Thus the spinel block above the slip plane would be coupled antiferromagnetically to the spinel block below the slip plane, in a manner analogous to the situation in $\text{KFe}_{11}^{4+}\text{O}_{17}^{5-}$. It is possible that some interaction between the ions at TA1 and those at TB4 might occur by overlapping of directed orbitals, although this is thought unlikely.

The ions at TA4 below the mid-plane are still in a favourable position to be coupled antiferromagnetically to those at TB4, on the 2b sites. In order to break the coupling completely throughout the crystal, it would be necessary for slip to occur both immediately above and below the mid-planes of every R-block in the crystal. For the anisotropy to be reduced, dislocations in the R-block must occur, and the probability of this is obviously dependent on the dislocation density. Thus the assertion in chapters 3 and 4 that the reduction in the anisotropy is proportional to the dislocation density is justified.
Lewis noted that in non-stoichiometric spinel crystals, the disassociation of total dislocations into four quarter-partial did not occur, but instead two half-partial occurred, with an electrostatic fault between them. He concluded that the quarter-partial would only be observed in stoichiometric crystals. The width of the electrostatic fault increased with increasing deviation from stoichiometry.

Bearing this in mind and considering the fact, mentioned in section that, commercially, barium ferrite is prepared from a non-stoichiometric ratio of starting constituents, it is seen that conditions for the breaking of the anisotropy by dislocations are improved by the method of preparation.

It is of interest that stacking faults have been observed in MnAl which change the ferromagnetic coupling into antiferromagnetic coupling, similar to the assumed situation in barium ferrite.
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11. Ref. 17, chapter 2
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2. Ref. 27, chapter 1
3. Ref. 76, chapter 1
4. Ref. 72, chapter 1
5. Ref. 108, chapter 1
6. Ref. 2, chapter 2
7. Ref. 124, chapter 1
8. cf. section 1.2.4
9. Ref. 32, chapter 1
10. Ref. 107, chapter 1
11. Ref. 117, chapter 1
12. Ref. 116, chapter 1
13. Ref. 114, chapter 1
References for the Appendix

Fig. A is the directions of slip, \( \langle 11 \bar{2} 0 \rangle \), on the basal plane of barium ferrite. The unit cell is also shown.