A Three-Dimensional Micromagnetic Investigation of the Magnetic Properties and Structures of Magnetite

by

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DECLARATION

This thesis has been composed solely by myself. The work presented is my own unless otherwise acknowledged.

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ABSTRACT

This work is a three-dimensional micromagnetic study of the magnetic properties and structures of magnetite. Large cubic magnetite crystals in the size range 10 - 50 μm were modelled using a relatively low resolution model. A vortex configuration, where the magnetization forms a loop to prevent flux leakage, was found to be stable for this size range. A flower type structure with magnetization deflection at the cube corners was also obtained with large, uniformly magnetized domains lying approximately in magnetocrystalline easy directions.

A global optimisation algorithm called simulated annealing (SA) was used to minimize the total free magnetic energy and hence find stable structures for crystals in the sub-micron size range. The resolution of the model was limited by computer constraints when using SA for optimisation. The structures obtained were interpolated to a higher resolution and input as the initial configuration for a fast local optimisation technique called the conjugate-gradient method. This combination of techniques allowed high resolution models in the ground state configuration to be obtained. Below ~ 0.06μm, nearly uniform structures magnetized in the magnetocrystalline easy directions were obtained. Between 0.06 μm and 1.0 μm, only the vortex configuration was obtained. These are the lowest energy states found by any method to date.

A modified SA algorithm was used to introduce thermal fluctuations into a micromagnetic model, and hence to determine blocking temperatures of grains up to 0.08 μm in size. The model gave results consistent with Néel's single domain thermoremanent magnetization theory for grains up to 0.065 μm. Between this size and 0.07 μm a reduction in blocking temperature was observed to take place for cubic grains. This is due to the magnetization reversal taking place via vortex propagation, which requires less thermal energy than reversal via uniform rotation to overcome the potential barrier separating local minima. When shape anisotropy is present in crystals, the size range over which the reduced blocking temperatures are observed is dramatically increased.

The magnetic structures and properties of octahedral magnetite crystals in the sub-micron size range were studied by using a model which approximated a regular octahedron. As in cubic models, the predominant configurations found were the flower state and the vortex state. The hysteresis properties of the octahedral model were found to agree well with experimental values.
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CHAPTER 1

Introduction

1.1 A Brief History of Magnetism

Magnetism is possibly the first phenomenon to arouse what could be called scientific curiosity. The Chinese may have used lodestone (which contains magnetite) as a compass as early as 2600 B.C. The first observations on magnets which could be referred to as scientific were supposed to have been made by the Greek philosopher Thales in the 6th century B.C. Petrus Peregrinus, an Italian scientist, discovered the dipolar nature of the magnet and the repulsion/attraction law of like/opposite poles and documented these observations in what is probably the first scientific treatise ever written, in a paper entitled 'Epistola de Magnete', published in 1269. In the 16th century, William Gilbert, who studied terrestrial magnetism and magnetic induction amongst other things, found that a magnet lost its magnetization when heated to a certain temperature. The Coulomb law of magnetic interaction between two magnetic poles was discovered at the end of the 18th century. At the beginning of the 19th century, magnetism due to electric currents was being investigated by Oersted, Ampere, Biot and Savart. It was during this productive period that discoveries were made of diamagnetism (by Faraday), magnetostriction (by Joule), the Curie law (by Pierre Curie) and hysteresis (by Ewing). Ewing tried to explain hysteresis in terms of magnetic interaction between molecular magnets. His work was further developed by Pierre Weiss (who postulated the 'molecular field' to explain ferromagnetism in 1907) and Langevin, who explained para- and ferromagnetism at the atomic level.

The discovery that rocks could acquire a magnetization in the direction of the ambient magnetic field in which they formed was made independently by Delesse [1849], and shortly afterward by Melloni [1853]. However, it was already known that some rocks possessed a strong remanent magnetization due to their effect on a compass needle, and this was attributed to lightning strikes by Alexander von Humboldt [1797], a German scientist and explorer. David [1904] and Brunhes [1906] studied material which had been baked by lava flows and found evidence that the geomagnetic field had undergone reversal throughout geological time. This led to an enormous interest in palaeomagnetism culminating in one of the major scientific discoveries of the 20th century, namely that of continental drift, which was hypothesised in 1924 by Wegener, although the theory was not readily
accepted within the scientific community until around the mid 1960's.

1.2 Overview of Palaeomagnetism

Palaeomagnetism is the study of the ancient magnetization in rocks and other magnetic artifacts. The primary source of data for its analysis is magnetite-bearing rocks which are able to record the direction (and, under favourable conditions, the intensity) of the ambient magnetic field at the time of the rock's formation. From measurements of the magnetization of such rocks we can study changes in the geomagnetic field through geological time. We can therefore investigate phenomena such as geomagnetic field reversals, variations in the intensity of the dipole moment and secular variation. The movement of the lithospheric plates through geological time can also be determined from palaeomagnetic measurements, and it was from such investigations that the theory of plate tectonics was confirmed.

Unfortunately, these phenomena cannot be studied simply by measuring the natural remanent magnetization (NRM) of a sample and assuming this accurately represents the magnetic field at the time the rock formed. The magnetization of the sample can change to some degree during the time which lapses between it's being sampled and being measured (due to magnetic viscosity), which could be of the order of only a few days, so it is hardly surprising that the magnetization of a rock can change significantly over a period of many millions of years. As the geomagnetic field changes, so it affects the magnetization of the rock sample (which we are going to study a few million years hence), and this secondary (viscous) magnetization must be removed in order to isolate the primary magnetization (i.e. the magnetization acquired at the time of the rock's formation). Techniques are available to remove these secondary overprints, such as alternating field or thermal demagnetization - so called cleaning techniques.

As in all scientific disciplines, workers require to know how accurate their measurements are, and how reliable and accurate their instruments are. If a rock is being used to determine information about the ancient geomagnetic field, then it is being used as a magnetic recording media and it is necessary to know how accurate this recording is. This led to the development of rock magnetic research as a discipline in its own right. The aim of the rock magnetist is to develop a theory to explain such things as how a rock can acquire a remanent magnetization; how stable it is; how it behaves when subjected to outside interference such as changing magnetic fields and temperatures; how rocks which are good recorders
differ from those which are not. These uncertainties depend on the properties of the magnetic constituents of the rock under investigation. It is the theoretical understanding of such properties with which this study is concerned.

1.3 The Need for a Micromagnetic Approach

Ferromagnetic domain theory (e.g. Kittel, 1949a) predicts a discontinuity in the magnetic properties of single domain (SD) and multi-domain (MD) grains. This discontinuity has never been observed experimentally, either in saturation remanence and coercive force (Kneller and Luborsky, 1963) or in TRM (Parry, 1965). Instead, a gradual decrease in coercivity in remanence is observed, with increasing grain size. In magnetite, the size range over which this pseudo-single domain (PSD) (Stacey, 1962, 1963) behaviour is observed is \( \sim 0.05 \mu m - 15 \mu m \). It is crystals within this size range which are thought to be largely responsible for the stable magnetic remanence of many rocks. At the present time, it is extremely difficult to examine directly the domain structure of crystals \( \sim 1.0 \mu m \) in size (Smith, 1980) and so we must resort to theory in an attempt to describe this PSD behaviour. This thesis will describe in detail the numerical modelling of magnetite crystals in the PSD size range.

1.4 Statement of Goals

There were several problems to be addressed during the course of this work, all independent to a degree, but all inter-related by a micromagnetic approach to contemporary problems in rock magnetism. The results are presented in chapters 6 - 8.

The first problem was to attempt to model large magnetite grains (\( \geq 10\mu m \)) in an attempt to obtain lamellar domains as are observed experimentally.

The second objective was to incorporate a simulated annealing algorithm into the modelling program in order to obtain very low energy states not easily attainable using other optimisation techniques. A further objective at this stage was to use the simulated annealing algorithm to introduce thermal fluctuations into the model in order to simulate a thermoremanent magnetization (TRM) and hence to determine blocking temperatures.

The third objective was to model octahedral magnetite grains, since this is the most common morphology, and, until now, only cubic and parallelepiped structures have been modelled. The aim was to use both simulated annealing and conjugate gradient methods of optimisation to determine stable micromagnetic
structures. A further objective in this section was to investigate the hysteresis properties of these octahedral models and compare the results with experimental measurements.
CHAPTER 2

The physics of ferromagnetic domains

2.1 Early observations and theories

The main characteristics of a ferromagnetic material are embodied in the following experimental observation [Kittel, 1949a]:

It is possible to change the over-all magnetization of a suitably prepared ferromagnetic specimen (e.g. iron) from an initial value of zero (in the absence of an applied magnetic field) to a saturation value of the order of 1000 gauss (10⁶ A.m⁻¹), by the application of a field whose strength may be of the order of 0.01 oersted (10⁻⁶ Tesla).

Thus, a ferromagnetic sample may reach saturation magnetization by the application of a very small external field, and the same sample may possess zero net magnetic moment in a zero field environment.

When these observations were first made, at the turn of the 20th century, it was known that the application of a field of the order of 10⁻⁶ Tesla to a paramagnetic substance had virtually no effect on the net magnetization due to thermal agitation. Therefore, unlike a paramagnetic material, a ferromagnet could not be composed of independent, non-interacting elementary moments.

Weiss (1907) showed that the problem of thermal agitation could be overcome if the elementary spin moments were not independent of each other, but were subjected to some force which tended to align them. He termed this force the 'molecular field', but did not propose a physical mechanism for its origin. A significant problem for Weiss' theory arose from the required magnitude of the molecular field. An order of magnitude calculation is easily carried out since, at the Curie temperature $T_c$, the thermal energy $k_B T_c$, where $k_B$ is Boltzmann’s constant, of an electron spin moment, must be of the same order of magnitude as the interaction energy between the elementary spin moment $\mu_B$ (1 Bohr magneton) and the molecular field $H_{m,I}$ if the molecular field is to overcome thermal agitation. We can therefore calculate $H_{m,I}$ from:

$$k_B T_c \approx \mu_B H_{m,I}$$

(2.1)
Thus, below $T_c$, this force dominates over thermal disturbances and aligns the magnetic moments. However, this field intensity is between one and two orders of magnitude larger than any field which can be produced in the laboratory, even as a pulse. It is not surprising, therefore, that the ordinary dipole-dipole interaction between spins is much too small (by a factor of around $10^{-4}$, Kittel [1949a]) to provide a mechanism for the molecular field. The correct explanation was given by Heisenberg [1928].

After explaining how saturation magnetization could be attained by a small applied field, Weiss had to explain how, if his molecular field theory was correct, it was possible for a ferromagnetic specimen to have zero net magnetic moment in zero field. He did this by assuming that the specimen could have discrete volume elements of uniform magnetization whose directions could vary with respect to one another so that, as a whole, the moments could cancel, leaving a zero net moment. In other words, he postulated the existence of ferromagnetic domains.

Weiss had now given an explanation for ferromagnetic behaviour. The increase in magnetization by a small applied field could be accounted for by the growth of domains whose direction was in the direction of the external field, and also by the rotation of domains whose magnetization was not in the direction of the external field. And the same specimen could have zero net moment due to random orientation of domain magnetization directions. Weiss did not give an explanation of why domain formation should take place. This will be dealt with in the following section.

### 2.2 The origin of ferromagnetic domains

The formation of ferromagnetic domains is a consequence of the ferromagnet attaining a minimum energy state and of the competition between the various energy contributions to the total magnetic energy. It is necessary, therefore, to examine each component of the total magnetic energy individually. Section 2.3 will deal with domain formation in greater detail.
2.2.1 Exchange Energy

The exchange energy of two electron spins is given by (Heisenberg [1928]):

\[ E_{\text{ex}} = -2J_\text{E}S_1 \cdot S_2 \]  

(2.3)

where \( J_\text{E} \) is a quantity known as the exchange integral and \( S_1 \) and \( S_2 \) are the electron spin vectors (\( | S | \) is the total spin angular momentum quantum number). Magnetite is a ferrimagnetic mineral. This means there are two sublattices, usually denoted A and B, which have opposite and unequal moments. This leads to the mineral having a net spontaneous magnetization. This is a result of a super-exchange mechanism, whereby the electron spins are coupled anti-parallel to each other via intermediary coupling to the oxygen atom. Thus the effect of the oxygen atom is to change the sign of the exchange interaction, but since we can treat magnetite as if it had the properties of a ferromagnetic material, \( J_\text{E} \) is assigned a positive value. From this point, magnetite will be treated as if it were ferromagnetic, its net spontaneous magnetization being treated in the same manner as we would treat the spontaneous magnetization of a ferromagnet. We can then see from the above equation that the minimum energy state is attained when the electron spins are parallel. The exchange integral is assumed to account for all quantum mechanical effects. An important feature of the exchange force is that it is a short range force between nearest neighbours.

2.2.2 Magnetocrystalline Anisotropy Energy

Many ferro- and ferrimagnetic materials have an intrinsic anisotropy due to magnetic coupling of the spin magnetic moment and the orbital magnetic moment. The orbital moment is coupled directly to the crystal lattice which in turn produces a directionally dependent spin energy called the magnetocrystalline anisotropy energy. It is a purely local force (the spin-orbit coupling has a relativistic explanation, see e.g. Smit and Wijn [1959], pg. 369).

Ferro- and ferrimagnetic materials thus have preferred directions of magnetization called easy directions. It is possible to rotate a spin out of its easy direction, e.g. by application of an external field. The energy required to do this is termed the magnetocrystalline anisotropy energy.

The anisotropy energy of cubic materials such as magnetite at room temperature and above may be described by two empirical constants, \( K_1 \) and \( K_2 \), and the anisotropy energy may be written in terms of the direction cosines of the
magnetization vector with respect to the [100] axes of the crystal:

\[ E_K = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) \quad (2.4) \]

\( K_1 \) and \( K_2 \) are highly temperature dependent, decreasing as the temperature increases, and it is often possible, especially at elevated temperatures, to neglect the second term with no significant error.

It is possible to calculate the energy in any direction from the above equation. The most important directions are parallel to a cube edge [100], diagonally along a cube face [110] and diagonally along the body of the cube [111] yielding the energies;

\[ E_{100} = 0 \quad (2.5) \]

\[ E_{110} = \frac{K_1}{4} \quad (2.6) \]

\[ E_{111} = \frac{K_1}{3} + \frac{K_2}{27} \quad (2.7) \]

If \( K_1 \) and \( K_2 \) are negative, as in magnetite, then, from equation 2.7, the easy directions are the [111] directions i.e. the cube diagonals along which the crystalline anisotropy energy is a minimum, and, from equation 2.5, the [100] directions are the hard directions, along which the crystalline anisotropy energy is a maximum.

2.2.3. Magnetostatic energy

There are two distinct contributions to the magnetostatic energy; one is the mutual potential energy of the elementary molecular moments of the ferromagnetic specimen and the other is due to the interaction of these moments with an external field. To avoid confusion, in the remainder of this work, magnetostatic energy will refer to the mutual potential energy of the elementary moments of the crystal and the symbol \( E_D \) will be used. The energy due to interaction with an external field will henceforth be referred to as external field energy and will be denoted by \( E_H \) and it will be described in section 2.2.4. The magnetostatic energy results from the dipole-dipole type interaction between elementary molecular magnetic moments. It is a long range force and decays as \( \approx \frac{1}{r^3} \). Due to the repulsion of like poles, its effect is to align the spin moment parallel to the
ambient field. The magnetostatic energy may be written as:

\[ E_D = -\frac{1}{2} \mu_0 \int \mathbf{M} \cdot \mathbf{H}_D dV \]  

(2.8)

where \( \mathbf{H}_D \) is the local demagnetizing field at the coordinates of \( \mathbf{M} \) due to all dipoles in the crystal and \( \mathbf{M} \) is the dipole moment per unit volume. Analytical expressions for the magnetostatic energy of crystals magnetized to saturation are obtainable only for ellipsoids of revolution, cubes and parallelepipeds. For an ellipsoid of revolution of volume \( V \), magnetized to saturation:

\[ \mathbf{H}_D = -NM_s \]  

(2.9)

where \( N \) is a geometrical parameter called the demagnetizing factor and \( M_s \) is the saturation magnetization. \( \mathbf{H}_D \) depends upon which axis the ellipsoidal specimen is magnetized along. With respect to the three principal axes of the ellipsoid \( a, b \) and \( c \), the demagnetizing factors are related by

\[ N_a + N_b + N_c = 1 \]  

(2.10)

The magnetostatic energy of a uniformly magnetized ellipsoid of revolution can then be calculated analytically as:

\[ \frac{1}{2} \mu_0 NM_s^2 V \]  

(2.11)

The factor of \( \frac{1}{2} \) is common to all self-energy expressions and ensures that each interaction is counted only once, otherwise each dipole of each interacting pair would be counted once as a field source and once as a dipole interacting with the field of the other, i.e. each would be counted twice. It is not generally possible to use a single demagnetizing factor to calculate the magnetostatic energy of non-uniform magnetization configurations, although this has been attempted by Dunlop [1983, 1987] and used in the development of analytical multi-domain theory, where tensor representation of the demagnetization factor is required (see Newell et al., 1993).

2.2.4 External Field Energy

The external field energy, as mentioned in the previous section, is the energy due to each atomic dipole moment interacting with an external field. It is given
by:

\[ E_H = -\mu_0 \int M \cdot \mathbf{H}_{\text{ext}} \, dV \]  

(2.12)

where \( \mathbf{H}_{\text{ext}} \) is the external field.

### 2.2.5 Magnetoelastic Energy

It is observed experimentally that when a ferromagnetic sample is magnetized, there is a change in the dimensions of the sample. This phenomenon is called magnetostriction. Magnetostriction is due to the interaction of the magnetization of the crystal and the mechanical strain of the lattice and this results in a magnetoelastic energy term. This also implies there will be a complementary effect, namely a change in magnetization of the crystal under the influence of an applied stress. This effect is also observed and is called the Villari effect (Morris [1965], pg. 321). There exists a close physical relationship between the crystalline anisotropy energy and the magnetoelastic energy. A crystal lattice will deform spontaneously if this will lead to a reduction in the anisotropy energy. To treat the magnetoelastic energy properly, tensor representation is required and the reader is again referred to Kittel [1949a]. For the simplest case of isotropic magnetostriction, the magnetoelastic energy is given by [Morrish [1965], pg. 325]:

\[ E = \frac{1}{2} \lambda_s \sigma^2 \cos^2 \theta \]  

(2.13)

where \( \lambda_s \) is the magnetostriction constant, \( \sigma \) is the magnetoelastic stress and \( \theta \) is the angle between the stress and the magnetization direction. For a non-isotropic cubic crystal, the strain tensor is required and the magnetoelastic energy is given by [Chikazumi, 1986]:

\[ E_\sigma = \frac{1}{2} c_{11} (e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \frac{1}{2} c_{44} (e_{xy}^2 + e_{yx}^2 + e_{zz}^2) + c_{12} (e_{yx} e_{xx} + e_{yy} e_{xx} + e_{zz} e_{xx}) \]  

(2.14)

where \( e_{ij} \) are the strain tensor components and \( c_{11}, c_{44} \) and \( c_{12} \) are the elastic moduli.

### 2.3 Domain Formation

In this section it will be shown how the individual energy components described in the preceding sections, which together make up the total magnetic energy of the system, lead to the formation of domains.
In order for a physical system to be stable, it must attain a minimum energy state (or be in a local energy minimum - this point will be considered later) i.e. any infinitesimal perturbation of the system from a minimum energy state will result in an increase in the free energy of the system. In order to determine stable magnetic configurations, it is necessary to minimize the total magnetic energy of the system, which comprises the energy terms described in the previous five sections, and is given by:

$$E_T = E_{ex} + E_K + E_D + E_H + E_a$$  \hspace{1cm} (2.15)

This minimization is easily shown to be a plausible mechanism for domain formation by considering the component energies of a particle whose size is allowed to increase. Explicit particle sizes will not be given for the purposes of this example. In magnetite, $E_a$ is at least two orders of magnitude smaller than the next smallest energy contribution (the magnetocrystalline anisotropy energy), and for this reason it will be neglected in the remainder of this work. Consider a cubic particle with uniaxial anisotropy in zero applied field. Let its size be sufficiently small that the exchange interaction dominates (the exchange interaction between two spins is $\approx 10^3$ times stronger than their magnetostatic interaction, Stacey and Banerjee [1974], p.10). The electron spins will be aligned parallel to one another. Now consider the anisotropy energy. The system will have minimum anisotropy energy when all spins are aligned along an easy axis. In this state, the system will have minimum exchange and anisotropy energy. The magnetostatic energy will be high but any attempt to reduce it will lead to a net increase in the total magnetic energy due to an increase in the exchange and anisotropy energy contributions. The stable state is illustrated in Fig. 2.1 (a). The demagnetizing energy increases with crystal volume, as does the magnetocrystalline anisotropy energy, while the exchange energy increases linearly with the length of a cube edge. Thus if the particle size is allowed to increase, the magnetostatic energy will increase more rapidly than the exchange energy and it will reach a critical size where the magnetostatic energy is too large for the uniform structure to be stable. The magnetostatic energy will be reduced if the cube is split into two blocks, i.e. magnetic domains, of oppositely directed magnetization as in figure 2.1(b). This reduction in magnetostatic energy will be accompanied by an increase in exchange energy, but not anisotropy energy, since all elementary moments are still parallel to the easy direction. The transition region (the domain wall) in reality is not sharp as is depicted here and will be dealt with in
section 2.2.7. The net effect of the formation of the two domains is to reduce the total magnetic energy of the system. This is the essence of why ferromagnetic domains exist - they serve to minimize the magnetic energy of the crystal and consequently produce stable magnetic configurations. The two domain state is a very simple model and much more complex domain structures are found in real crystals. As the crystal size increases still further, more domains will be formed and the magnetocrystalline anisotropy energy will play a more prominent role, by constraining the magnetization direction of the domains to lie in a direction of easy magnetization.

![Diagram](a) Diagramatic representation of a single domain, magnetized along an easy direction and (b) two domains, magnetized in opposite directions, along an easy direction.

2.4 Domain walls

2.4.1 The Bloch wall

The transition region between the simple two domain structure illustrated in figure 2.1(b) was of zero width i.e the angle between spins at the transition region is 180°. This is a high energy configuration and a lower energy state is achieved by a transition region of finite width. The reason why this is so will be explained in this section. This transition layer is called a Bloch wall after F. Bloch [1932] who was the first to study such transitions. The physical principles which determine the width and energy of the Bloch wall are outlined in this section. For a comprehensive review, the reader is referred to Kittel [1949a] and Stacey and Banerjee [1974] (pp. 53 - 58).
Equation (2.3) gives the exchange energy between nearest neighbour spin moments as a continuous function of the angle between their spins. If a system consisted of only two isolated spins, quantization of angular momentum would constrain the moments to lie either parallel or anti-parallel to one another. In an ensemble of spin moments, it is the total angular momentum of the system which is quantized, and provided the net magnetic moment of the system in a given direction has one of the values permitted by quantum mechanics [Rae, 1986], the angle between any two spins in the system may have an arbitrarily small value. If the angle between spins is small, equation (2.3) may be approximated by:

\[ E_{\text{ex}} = -2J_E S^2 + J_E S^2 \theta^2 \]  

(2.16)

\[ \Rightarrow E_{\text{ex}} = E_{e_0} + J_E S^2 \theta^2 \]  

(2.17)

where \( E_{e_0} \) represents the minimum energy state when neighbouring spins are exactly parallel. The second term represents the increase in energy due to spin misalignment. In micromagnetics, it is this increase which is referred to as the exchange energy. An important feature of equation (2.17) is the dependence of the exchange energy on the square of the spin angle. This means that the exchange energy decreases as the width of the transition layer increases. To see why this is so, consider a line of \( n + 1 \) spins with an angular difference of 180° between the spins at either end of the line. Let us first calculate the exchange energy associated with a zero width transition layer as illustrated in figure 2.2(a). From equation (2.17) the exchange energy is:

\[ E_{\text{ex}} = E_{e_0} + J_E S^2 \theta^2 \]  

(2.18)

Now allow the spins to make the 180° transition gradually by a gradual rotation of spins as illustrated in figure 2.2(b). In a Bloch wall, the spins rotate in a plane parallel to the plane of the wall. Assuming that the spin angle changes by \( \frac{\pi}{n} \) for each spin pair, the exchange energy is given by equation (2.17):

\[ E_{\text{ex}} = E_{e_0} + \frac{J_E S^2 \pi^2}{n} \]  

(2.19)

As \( n \) increases, the exchange energy decreases. Thus the exchange energy decreases with increasing wall thickness, when there is a gradual rotation of spins.

The wall energy also includes crystalline anisotropy energy. The anisotropy
Figure 2.2 Two possible transition regions for a 180° wall. (a) shows a high energy transition region where there is a 180° transition and (b) an energetically favourable transition region where the spins rotate gradually through 180°.
energy will increase as the wall thickness increases since more spins will be rotated out of the easy direction, and a critical wall thickness exists beyond which the corresponding increase in anisotropy energy will make the wall unstable. A system with uniaxial anisotropy will be used to illustrate this point. The anisotropy energy of a uniaxial system is given by:

$$ E_K = K \sin^2 \phi $$

(2.20)

where $\phi$ is the angle between the spin and the easy direction, and $K$ is the uniaxial magnetocrystalline anisotropy constant. For a line of $n + 1$ spins, $\phi$ small, this leads to:

$$ E_K = nK\phi^2 \quad (n >> 1) $$

(2.21)

The wall energy is the sum of the exchange and anisotropy energies. The exchange energy is proportional to $\frac{1}{n}$; the anisotropy energy is proportional to $n$. A function $f(n)$ comprising the sum of two terms, one of which is inversely proportional to $n$, and the other linear in $n$, has a minimum value when the two terms are equal. Thus a domain wall is stable when the width is such that the exchange and anisotropy energy contributions are equal (neglecting magnetoelastic energy). This was the approach used by Landau and Lifschitz [1935] to determine the wall thickness, $t_w$, and the wall energy, $E_w$. From Stacey and Banerjee [1974] (pp 54 - 55), $t_w$ and $E_w$ for magnetite (with cubic magnetocrystalline anisotropy) are:

$$ t_w = \pi S \left( \frac{J_E}{a} \right)^\frac{1}{2} (-0.115K_1 - 0.021K_2)^{-\frac{1}{2}} $$

(2.22)

which gives a wall thickness $\approx 0.1\mu$m for magnetite, and the wall energy:

$$ E_w = \pi S \left( \frac{J_E}{a} \right)^\frac{1}{2} (-0.115K_1 - 0.021K_2)^{\frac{1}{2}} $$

(2.23)

which gives a wall energy density $\approx 10^{-3}J/m^2$ for magnetite.

2.4.2 The Néel Wall

Néel [1955] was the first to investigate the nature of domain walls in thin films. He showed that the magnetostatic energy, due to free poles where the domain wall intersects the surface of the thin film, increases as the thickness of the thin film decreases. He therefore predicted a rotation of the magnetic moments from being parallel to the plane of the wall to being normal to the plane of the wall,
since this is an energetically more favourable state, as is illustrated in figure 2.3.

Figure 2.3 A two domain structure with a Néel wall on the top surface (a Néel cap), allowing spins to remain parallel to the surface. It is energetically preferable for the spins in the body of the crystal to rotate as in figure 2.2 (b) i.e. a Bloch wall.

Thus in this type of transition, the spins rotate normal to the plane of the wall, and the wall will have free poles on its surface. Due to these free poles on the wall surface, it is expected that Néel walls will be attracted to each other to form double walls and these have been observed by Williams and Sherwood [1957].

The magnetostatic energy associated with each type of wall will determine which type of transition will be favoured in a particular situation. For example, in a cubic grain, it may be reasonable to expect the Bloch wall transition to occur within the body of the grain since a Néel type transition would lead to a high magnetostatic energy by virtue of the free poles which would be generated on the wall surface. On the surface of the grain, however, the Néel type transition may be favoured since it avoids the formation of free surface poles. In reality it is likely, therefore, that domain walls will be hybrids of both Bloch and Néel type walls.
CHAPTER 3
Experimental Evidence for Ferromagnetic Domains

The existence of ferromagnetic domains was predicted from theory by Weiss in 1907. The first experimental evidence for their existence came from a very indirect source from an experiment by a German engineer called Barkhausen [1919]. He found that the magnetization curve of a ferromagnet is not as smooth as it appears on first inspection, but is made up of discrete jumps. In order to observe these irregular jumps, Barkhausen wound a coil of wire round an iron rod and connected this coil to a pair of earphones through an amplifier. When the field due to the coil was increased he heard a rustling noise, but when the field was increased very slowly, he observed that this noise was made up of discrete clicks. These clicks were produced by a momentary electromotive force being generated in the coil, which in turn was being caused by a change in the magnetic flux within it. Barkhausen suggested that this change in magnetic flux was due to changes within the magnetic structure of the iron rod, i.e. changes in the domain structure. His hypothesis of how the magnetic structure was changing, by rotating, is now known to be incorrect, but the experiment provided the first experimental insight into what is happening when a ferromagnetic substance is being magnetized.

The most direct and convincing experimental proof came thirteen years later from Bitter [1932]. He developed a technique which made it possible to view domains directly. In this section, a brief review will be given of the experimental evidence for the existence of domains and of the techniques used to observe them.

3.1 Bitter Patterns

3.1.1 Introduction

The Bitter pattern technique gave the first direct evidence of domain existence. The name ‘Bitter pattern’ is nowadays taken to cover all techniques using the principle that small ferro- or ferrimagnetic particles will collect along lines of flux leakage on a suitably prepared surface of a ferromagnetic specimen, allowing direct observation of the surface domain structure. This method is based upon the attraction of fine magnetic particles to areas of stray field on the surface of the material being studied. These areas occur when a domain wall intersects the surface of the specimen, and hence the small magnetic particles will outline the domain walls at the surface. The first observations were made by Bitter [1931], who sprinkled a powder of fine magnetic particles onto a ferromagnetic material. These experiments provided convincing proof of ferromagnetic domains but
it was not possible to determine the structure of the underlying domains from the patterns which were obtained in this fashion. Bitter [1932] then improved the technique by using a suspension of \( \gamma \)-ferric oxide in alcohol instead of just a powder. This was more successful since it allowed the magnetic particles to settle more slowly as the alcohol evaporated, but it was still not possible to obtain representative domain patterns. There are two reasons for Bitter's failure to obtain good quality domain patterns. One was that he did not use sufficiently small magnetic particles. They were probably multi-domain particles with insufficient net moment to respond to the stray magnetic field (see section 3.1.2). The other reason was that the surface of the specimen was not prepared to the standard now known to be essential to produce clear domain patterns.

3.1.2. Conditions for pattern formation

As was mentioned in section 3.1.1, Bitter was unsuccessful with his first attempts to observe representative domain structures because the iron particles he sprinkled on the surface were too large and the surface of the specimen was not properly prepared. McKeehan and Elmore [1934] prepared the first true colloidal particles of magnetite in the approximate size range 0.001-0.1 \( \mu \)m and a soap solution was used as a dispersant. The suspensions used today to obtain Bitter patterns are called ferrofluids. Modern ferrofluids still use fine magnetite particles, and soap to prevent them from aggregating. Different viscosities of ferrofluids are available for observations at different temperatures. The magnetic particles in the colloid are attracted to areas of high field intensity. Kittel [1949b] determined the conditions required for the formation of a Bitter pattern. He assumed single-domain, non-interacting particles in thermal equilibrium and subject to Brownian motion. The density distribution of particles in the liquid is then given by the Boltzmann distribution function. From this, Kittel gives the particle density \( \rho(H, \theta) \) at a point, where \( H \) is the field intensity and \( \theta \) is the angle the magnetic moment of the particle makes with \( H \), as it relates to the density \( \rho(0) \) where \( H \) is zero:

\[
\rho(H, \theta) = \rho(0) \exp \left( \frac{\mu_m H \cos \theta}{k_B T} \right)
\]

(3.1)

where \( m \) is the magnetic moment of the particle, \( k_B \) is Boltzmann's constant and \( T \) is absolute temperature. Kittel then averaged \( \rho(H, \theta) \) over all angles:
\[ \rho(H) = \frac{1}{4\pi} \int_0^\pi \exp \left( \frac{\mu_m H \cos \theta}{k_B T'} \right) 2\pi \sin \theta d\theta \]

\[ \implies \rho(H) = \frac{\sinh x}{x} \]  

where \( x = \frac{\mu_m H}{k_B T'} \).

A plot of this function is shown in figure 3.1. From this graph, the particle density rises sharply when

\[ x > 3k_B T \]  

Equation (3.3) gives the conditions to be satisfied by \( m \) and \( H \) for pattern formation to occur. It essentially states that the tendency for particle agglomeration must be greater than the dispersive influence of thermal agitation. As stated
earlier, this equation assumes single domain particles, and requires modification if the particles are large enough to be multidomain, Kittel [1949b]. Equation (3.3) shows that if a particle has a sufficiently reduced net moment, such as in a multidomain particle used by Bitter in his early experiments, the conditions for pattern formation may not be fulfilled.

3.1.3. Refinements of the Colloid Technique

The colloid technique has changed little since the 1940's when it was refined to a high level of sophistication by Williams and co-workers, as was demonstrated in the definitive paper by Williams et al. [1949]. The importance of properly preparing the crystal surface was appreciated at this time, and was achieved by electrolytic polishing (see e.g. Collinson [1983], pg. 163). Williams et al. [1949] developed several useful techniques, to be used in conjunction with the colloid method, which made it possible to determine the orientation of magnetization within the domains, namely the scratch technique, use of the colloid striations, the probe technique and also the effects due to stress. The materials studied in their 1949 paper were single crystals of iron containing 3.8 % silicon by weight. They found many different domain patterns depending on the orientation of the surface being examined with respect to the crystallographic axes; they found good agreement between theory and experiment for the more complex tree patterns (see figure 3.2) using theoretical values for the wall energy. Perhaps the most striking result from this paper is the determination of spin orientation within a Bloch wall by determining the polarity of the surface charges by vertical field experiments. By applying a small vertical field which does not appreciably deform the domain structure, the underlying field is slightly reinforced or slightly weakened depending on its direction. This leads to an asymmetrical colloid distribution allowing the polarity of the surface poles to be determined and hence allows the spin orientation through a Bloch wall to be inferred. Since the width of a Bloch wall is of the order of 0.1 \( \mu m \), this was a remarkable achievement by such a simple technique (although the width of the colloid may be a factor of 10 greater than this).

To sum up, the colloid technique is still the most widespread technique used today. It is the simplest and probably the most useful and widely applicable technique overall.
3.2 Magneto-Optical Techniques

When plane polarized light is reflected from a metal surface, the reflected light is elliptically polarized, (see e.g. Carey and Isaac [1966]). However, if the plane of polarization is parallel or perpendicular to the plane of incidence, the reflected light is also plane polarized. If the surface is magnetized, the reflected light will always be elliptically polarized, even if the plane of polarization is parallel or perpendicular to the plane of incidence. This can be regarded as a rotation of the plane of polarization of the incident light and is known as the Kerr effect after the scientist who discovered it, Kerr [1876].

A similar phenomenon occurs when plane polarized light passes through a sufficiently thin magnetized material, when a rotation of the plane of polarization of the transmitted light is produced by the component of the specimen magnetization which lies along the direction of propagation. This is known as the Faraday effect.

Both the Kerr effect and the Faraday effect are used to observe ferromagnetic domains. For a comprehensive review, the reader is referred to Carey and Isaac [1966], and to Rave et al. [1987]. Figure 3.3 shows domains as seen using the
magneto-optical Kerr effect.

Hoffmann et al. [1990] have shown that it is possible to determine the magnetization direction at every point on the surface of a titanomagnetite crystal using the polar, longitudinal and transverse Kerr effects. This will be of great importance in comparing micromagnetic simulations of domain structures with the domain structures of real crystals.

Figure 3.3 Domains in a bloomed film of nickel-iron using the longitudinal Kerr effect (from Prutton, 1960).

3.3 Electron Beam Techniques

When a negatively charged electron with charge $e$ moves in a magnetic field $B$, with velocity $v$, it is subject to the Lorentz force given by:

$$ F = ev \times B $$

Thus the deflection of an electron beam can be used to detect variations of a magnetic field, such as are present due to ferromagnetic domains. Since an electron microscope uses an electron beam to scan the surface of a specimen,
it can be used to examine domain structure due to the direct interaction of the electron beam and a suitably prepared magnetic surface. This technique is known as Lorentz microscopy. McVitie [1990] used a variation of this technique to make domain wall width measurements on thin films of Permalloy (Ni$_{82.5}$Fe$_{17.5}$).

3.4 Probe Techniques

Probe techniques make use of the variation of the local magnetic field directly above a specimen, due to changes in the domain structure. There are two main problems to be overcome in order that satisfactory results may be obtained. Since the width of a domain wall is of the order of 0.1 $\mu$m, the probe must be very small in order to be able to resolve the variation in magnetization as it traverses the specimen surface. The second problem is due to the fact that the strength of the magnetic field decays rapidly with increasing distance from the surface. It is therefore necessary for the specimen surface to be highly polished in order to be as flat as possible so that the variation in the measurements is primarily due to changes in the surface magnetization and not irregularities in the surface topography. For a review of such techniques, the reader is referred to Carey and Isaac [1966]. A recent development of a probe technique is the Magnetic Force Microscope (MFM). The MFM scans the surface of a highly polished magnetic material with a very fine magnetic needle (tip diameter $\approx 50$ nm) on the end of a cantilever, at an average height of $\approx 80 - 150$ nm. The probe experiences a force due to the specimen's magnetic field and this vertical force can be measured via a change in the electrostatic coupling between the cantilever and a reference charged plate above it. See e.g. Williams et al. [1992].

3.5 Synthetically grown crystals

Theorists deal with models which are, by necessity, much simpler than the complex systems found in nature. The micromagnetic models with which this thesis is concerned will deal with crystals which have no inclusions, vacancies, dislocations etc., i.e. perfect crystals. Crystal imperfections lead to a more complex magnetic structure, and in order to make meaningful comparisons of theoretical models with real crystals, it is necessary to obtain real crystals which are as defect free as possible. Heider [1988] grew magnetite crystals using a hydrothermal technique and made observations of their magnetic structure using the colloid technique. In many of these synthetically grown crystals, simple lamellar type domain structures with closure domains were observed. Figure 3.4 illustrates some of the domain patterns obtained by Heider [1988]. These are mainly
Figure 3.4 (a) a 30 \( \mu m \) grain at 20°C in two different remanence states. The structure is lamellar with spike domains at the surface. (b) shows possible remanence states for a 12 \( \mu m \) grain. (From Heider [1988])
lamellar in nature. The upper left figure shows lamellar domains with spike domains at the surface. These spike domains serve to reduce the magnetostatic energy by having opposite magnetization to the lamellar domain into which they are intruding. A particularly interesting domain structure from Heider [1988] is sketched in figure 3.5 and a possible representation of the magnetization directions is also illustrated. This type of structure minimizes the magnetostatic energy by

Figure 3.5 (a) a sketch of a domain structure of a 10 μm hydrothermally grown magnetite grain observed by Heider [1988] and (b) a possible representation of the magnetization direction within the domains.

forming a complete flux circuit, i.e. it minimizes flux leakage from the surface of the crystal. I will refer to this type of pattern again in chapter 6. These relatively simple structures tend to indicate that these crystals are relatively free from imperfections, which would lead to more complex structures. Thus
meaningful comparisons of the magnetic properties of these crystals can be made with theoretical calculations, and in chapter 8 the theoretical hysteresis properties of the model used in this study will be compared with the experimental results from Heider's work.

An important experimental observation is that fewer domains are observed experimentally than are expected theoretically. This may be due to poor imaging of some domain walls by the Bitter pattern method or in some cases the Bitter pattern may not be truly representative of the underlying domain structure. I will return to this point in chapter 6. Lamellar type domain structures have been observed on other magnetic minerals such as pyrrhotite (Halgedahl and Fuller [1983]) and also by using other techniques (Hoffmann et al. [1990]). However, most domain patterns observed experimentally are complex and careful sample preparation is necessary to obtain structures such as those illustrated in figures 3.3 - 3.5.
CHAPTER 4

The History of Micromagnetics

Some of the earliest micromagnetic calculations were made by Bloch [1932]. Bloch was the first to attempt a theoretical analysis of the transition layer between domains which came to be known as the Bloch wall. In his original analysis, Bloch assumed that the spontaneous magnetization \( M_s \) reduced to zero at the middle of the wall. Modern micromagnetic calculations assume a constant value of the spontaneous magnetization and allow its direction to vary spatially. This approach was pioneered by Landau and Lifshitz in their now famous 1935 paper. In determining the structure of a domain wall, Landau and Lifshitz considered only the exchange energy (although they did not refer to it as such) and the magnetocrystalline anisotropy energy. They assumed an infinitely large system which would have no surface poles, and therefore no magnetostatic energy. This system would actually have no domains as postulated by Landau and Lifshitz since there would be no internal demagnetizing field, and this is stated in their paper. In order to perform the wall calculations, they postulate the existence of domains, and in order to calculate the domain properties, they postulate walls. Wall calculations are still essentially based on this model; the magnetization \( M_s \) remains constant throughout the wall but its direction changes as a function of position along a path e.g. in the \( z \) direction, which lies normal to the plane of the wall. The magnetization is constrained to lie in a particular direction at \( z = \pm \infty \). Using this model, Landau and Lifshitz calculated the width of a domain wall, its surface energy density and the direction of magnetization through the wall as a function of position. The main difference between their 1935 calculations, and wall calculations being carried out today, is that magnetostatic effects are now considered. Around 1935, calculations were also analytic and constrained, whereas, with fast computers, we are now able to solve highly non-linear equations numerically and obtain unconstrained solutions.

To determine magnetic structures, all the energy components discussed in chapter 2, which make up the total magnetic energy, should be taken into consideration. If we regard the magnetization structure as a continuum, this leads to the total free energy of the system being expressed as a volume integral. This was the method developed by Brown [1963]. The integrand is a function of the direction angles of the magnetization vectors and also (for the exchange energy) of their spatial derivatives. This in turn leads to two non-linear partial differential
equations in the unknown angles, which must be solved to obtain a free energy minimum. In general, it is not possible to solve these equations analytically. One exception is in the case of a one dimensional wall calculation such as was solved for by Landau and Lifshitz. Another analytic calculation was done by Bitter [1937], pg. 185. He considered only magnetocrystalline energy and external field energy and assumed a variation in only one direction.

In three dimensions it is quite impossible to solve the equations analytically. The equations are usually called Brown's equations. For an in depth review, see Brown [1963], pages 46 - 48. For the sake of completeness, a brief derivation is given below:

Brown formulates the total free energy, $G$, as a volume integral plus a surface integral:

$$G = \int \frac{1}{2} C[(\nabla \alpha)^2 + (\nabla \beta)^2 + (\nabla \gamma)^2] + w_a - \frac{1}{2} \mathbf{M} \cdot \mathbf{H}' - \mathbf{M} \cdot \mathbf{H}_0 \, d\tau + \int \frac{1}{2} K_s (\mathbf{n} \cdot \mathbf{v})^2 \, dS$$

(4.1)

where $C = 2A$ and $A$ is the exchange constant, $\alpha$, $\beta$ and $\gamma$ are the direction cosines of the magnetization $\mathbf{M}_s$ with respect to the [100] crystal basis vectors, $w_a$ is the magnetocrystalline anisotropy energy density, $\mathbf{H}'$ is the self-demagnetizing field, $\mathbf{H}_0$ is the external field, $\tau$ denotes the volume of the body and $S$ its surface, $K_s$ is the surface anisotropy constant, $\mathbf{n}$ is the unit outward normal from the surface and $\mathbf{v}$ is the unit vector in the direction of the spontaneous magnetization $\mathbf{M}_s$.

He used the calculus of variations to minimize this definite integral. To derive the equilibrium condition it is necessary to retain only terms of first degree in the small variation $\delta \mathbf{M} = M_s \delta \mathbf{v} = M_s (\alpha \mathbf{i} + \beta \mathbf{j} + \gamma \mathbf{k})$. The resulting variation of $G$ is:

$$\delta G = \int C[(\nabla \alpha) \cdot \delta (\nabla \alpha) + (\nabla \beta) \cdot \delta (\nabla \beta) + (\nabla \gamma) \cdot \delta (\nabla \gamma)] + \frac{\partial w_a}{\partial \mathbf{v}} \cdot \delta \mathbf{v} - \frac{1}{2} (\mathbf{M} \cdot \delta \mathbf{H}' + \delta \mathbf{H}' \cdot \mathbf{M}) - \mathbf{H}_0 \cdot \delta \mathbf{M} \, d\tau$$

$$+ \int K_s (\mathbf{n} \cdot \mathbf{v}) \mathbf{n} \cdot \delta \mathbf{v} \, dS$$

(4.2)
Using
\[ C \int (\nabla \alpha) \cdot \nabla \delta \alpha \, d\tau = C \int \frac{\partial \alpha}{\partial n} \delta \alpha \, dS - C \int (\nabla^2 \alpha) \delta \alpha \, d\tau \] (4.3)
and
\[ -\frac{1}{2} \int (H' \cdot \delta M + M \cdot \delta H') \, d\tau = - \int H' \cdot \delta M \, d\tau \] (4.4)

Equation 4.2 becomes:

\[ \delta G = \int [-C \nabla^2 v + \frac{\partial w_a}{\partial v} - M_s H] \cdot \delta v \, d\tau + \int [C \frac{\partial v}{\partial n} + K_s n \cdot vn] \cdot \delta v \, dS \] (4.5)

where \( H = H_0 + H' \). Equation 4.5 is of the form:

\[ \delta G = - \int P \cdot \delta v \, d\tau - \int P_s \cdot \delta v \, dS \] (4.6)

Setting \( \delta v = \delta \theta \times v \), where \( \delta \theta \) is a small vector rotation, equation 4.6 becomes:

\[ \delta G = - \int v \times P \cdot \delta \theta \, d\tau - \int v \times P_s \cdot \delta \theta \, dS \] (4.7)

For equilibrium, \( \delta G = 0 \) for arbitrary \( \delta \theta \), i.e. \( v \times P = 0 \) at each point of \( \tau \) and \( v \times P_s = 0 \) at each point on the surface \( S \). The resulting equations are commonly referred to as Brown’s equations. The full equations are:

\[ v \times [C \nabla^2 v - \frac{\partial w_a}{\partial v} + M_s H] = 0 \text{ in } \tau \] (4.8)

\[ v \times [-C \frac{\partial v}{\partial n} - K_s n \cdot vn] = 0 \text{ on } S \] (4.9)

When the surface anisotropy is neglected (the surface anisotropy is due to stress effects, and the surfaces of the models in this study are stress free) equation 4.9 becomes:

\[ v \times \frac{\partial v}{\partial n} = 0 \text{ on } S \] (4.10)

Differentiating the constraint \( v^2 = 1 \) gives:
\[ \mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial n} = 0 \]  
(4.11)

Equations 4.10 and 4.11 can both be true only if

\[ \frac{\partial \mathbf{v}}{\partial n} = 0 \text{ on } S \]  
(4.12)

and this is often given as the surface boundary condition.

Three dimensional problems were considered from a qualitative viewpoint by Elmore [1938] who summarized the free energy formulae, but did not attempt to minimize the total free energy of the system. This was done by Brown [1940] for the linear approximation to the resulting equations, which is valid when the external field is large. The main problem in solving these equations is due to the magnetostatic energy which makes the equations highly non-linear.

In most of the domain theory developed in the 1930's, domains were simply postulated. The aim of micromagnetics is to examine the physics which cause the formation of domains and hence to determine a material's magnetic properties. It was illustrated in chapter 2 that domains form in order to reduce the free magnetic energy of a ferro- or ferrimagnet. It is a central aim of micromagnetics to solve this problem quantitatively. This has been delayed due to the highly non-linear nature of the equations involved. With the more widespread availability of supercomputers and advances in numerical algorithms, it is becoming possible to overcome these problems. We are now well into the third era of micromagnetics. The first era consisted of the calculations of Landau and Lifshitz [1935], among others, who postulated the existence of domains in order to perform their wall calculations. The work of Kittel [1946] and Stoner and Wohlfarth [1948] ushered in the second era. In their calculations, the magnetostatic energy was taken into account in the determination of domain structures. The methods used consisted essentially of calculating the free energy of several hypothesised domain structures in order to ascertain which one would be most likely to occur. There was, therefore, no guarantee that a more favourable state did not exist. For a review of this theory, the reader is referred to Wohlfarth [1959].

We are now in a position where it is unnecessary to postulate domains and domain walls. It has become possible, through the advent of supercomputers, for theoreticians to show that domains and domain walls are a natural consequence of a ferromagnetic material attaining a minimum energy state. By designing programs which incorporate the energy equations discussed in chapter 2, and
by using numerical methods to minimize the total free magnetic energy of the system, it has become possible to model the magnetic structure of magnetic materials and also to model their behaviour in the presence of external factors such as applied fields and changing temperatures. The first calculations of this type were done by Brown and LaBonte [1965]. Using an early digital computer, they replaced the continuous magnetization of a $180^\circ$ one dimensional domain wall in a thin film with a discrete distribution in which the magnetization was constant and had a value equal to $M_s$, and the direction of which could assume an arbitrary value, as in figure 4.1. They considered the exchange, anisotropy

![Figure 4.1 Geometry of the one-dimensional domain wall problem in ferromagnetic thin films with discrete variation of the magnetization. The $z$ axis is the direction of easy magnetization and the $y$ axis is normal to the plane of the film. The magnetization is constrained to be $-M_s k$ for $x < 0$ and $+M_s k$ for $x > a$. Each prism $I$ in the range $0 \leq x \leq a$ is assumed to have uniform magnetization of magnitude $M_s$ and arbitrary direction. (After Brown and LaBonte [1965])](image)

and magnetostatic contributions to the total magnetic energy and minimized this using the method of Lagrange multipliers. They found that only Bloch and Néel type walls occurred. They calculated the energy and width of the Bloch wall and found the wall energy density to be approximately a linear function of the film thickness.

LaBonte [1969] extended this work to a two dimensional model of a Bloch-type wall in a thin ferromagnetic film. The structures he obtained were very different from the one-dimensional results. The two dimensional results were characterised by extensive flux closure in the internal structure of the wall and very low free pole densities on the surface of the film. He also found a significantly lower
wall energy than that predicted by the most accurate one dimensional models. Two-dimensional models were also developed by Aharoni and Jakubovics [1986], Fredkin and Koehler [1987] and Zhu and Bertram [1988].

Enkin and Dunlop [1987] investigated the magnetic properties of magnetite using a one dimensional model and a second-order modified Newton method to minimize the free energy. Their formulation was more complex than that of Brown and LaBonte [1965], and took into account crystal elongation and external fields. They were able to model more complex structures due to faster computers and more efficient numerical optimisation techniques. They studied the properties of single domain (SD), two and three domain structures at room temperature and in zero applied field. They calculated the critical SD size $d_0$, at which the SD state becomes unstable and is replaced by a two domain state, and found it to be $0.084 \pm 0.012 \mu m$. They also developed a technique for studying the transition mechanism between stable states, which was found to be by coherent rotation just above the critical superparamagnetic size, and by domain wall nucleation, propagation and denucleation for larger crystal sizes.

During the late 1980's, the widespread availability of supercomputers was making its mark on many fields of theoretical physics, and micromagnetics was no exception. The computing resources were now available to allow modelling of micromagnetic structures in three dimensions. The first numerical three dimensional micromagnetic calculations were done independently by Schabes and Bertram [1988], and Williams and Dunlop [1989], using a discretized cubic grid as illustrated in figure 4.2 (a). The dimensions of the grid are specified by the number of sub-cubes in the $x$, $y$ and $z$ directions, respectively $N$, $M$ and $L$. Each sub-cube contains a magnetization vector, located at the centre of the sub-cube which represents the average moment of all the atomic moments contained within that volume. Figure 4.2 (b) shows how the orientation of the magnetization vector is described in this study, using spherical polar coordinates. Schabes and Bertram studied particle sizes in the range $0.01 \mu m - 0.052 \mu m$ using a relatively low resolution grid consisting of $5 \times 5 \times 5$ sub-cubes. They considered only exchange, uniaxial anisotropy and magnetostatic energy contributions to the total magnetic energy. They did not refer to a specific material, but gave values for the material parameters (uniaxial anisotropy constant $= 18,500 \text{ erg/cm}^3$ $(1.85 \times 10^8 \text{ J/m}^3)$, spontaneous magnetization $= 370 \text{ emu/cm}^3$ $(3.7 \times 10^5 \text{ A.m}^{-1})$ and exchange constant $= 10^{-6} \text{ erg/cm (10}^{-11} \text{ J/m})$ ). In order to obtain stable configurations, they used a quantity called the effective field, $\mathcal{H}$ (see Brown [1963]), defined to
Figure 4.2 (a) The discretized cubic model used in this study. \( \mathbf{m} \) is the magnetization vector. Its magnitude is constant, but its direction is arbitrary and is described by \( \theta \) and \( \phi \) as in (b).
be the negative gradient of the total magnetic energy with respect to the vector magnetization:

$$\mathcal{H} = -\frac{\partial E}{\partial M}$$  \hspace{1cm} (4.13)

This effective field, being the gradient of the energy, defines a force acting on each magnetic dipole. The condition required for an equilibrium structure is that the magnetization at any lattice point must be parallel to the effective field at that point so that there is zero torque exerted by the effective field. The torque is given by:

$$L = M \times \mathcal{H}$$  \hspace{1cm} (4.14)

The zero torque condition was satisfied using a modified Gauss-Siedel iterative algorithm. Schabes and Bertram found two distinct structures using this model. Using specified values for the magnetic parameters (exchange constant, anisotropy constant and spontaneous magnetization), they obtained a 'flower' state below 0.052 μm, which is essentially a single-domain state with deflection of the magnetization taking place at the corners. Above 0.052 μm the flower state was found to be unstable and was replaced by a vortex configuration. These configurations are shown in figure 4.3. They also calculated remanent magnetization and switching fields (the switching field is the value of the applied field which is necessary to induce an irreversible jump to the reversed state, Schabes and Bertram [1988]) as a function of particle size and found the switching field to be greater than the corresponding Stoner-Wohlfarth [1948] value, for the flower state. This was attributed to a form of anisotropy which they termed configurational anisotropy. Configurational anisotropy is an intrinsic property of the non-uniform magnetization of a body. It is attributable to neither the magnetocrystalline anisotropy nor to shape anisotropy, which refers to the uniformly magnetized state and does not exist in a cube. Schabes and Bertram obtained a flower state at a particle size of 0.045 μm. By solving the infinitely damped Landau-Lifshitz [1935] equation, which describes the dynamic evolution of a magnetic system:

$$\frac{d\alpha_{ijk}}{dt} = -\alpha_{ijk} \times (\alpha_{ijk} \times \mathcal{H}_{\text{eff},ijk})$$  \hspace{1cm} (4.15)

where $\alpha_{ijk}$ are the direction cosines of the magnetization vector with respect to the [100] axes, t is time and $\mathcal{H}_{\text{eff}}$ is the effective field, they showed that particles
Figure 4.3 Equilibrium states in zero applied field: (a) The flower state; $D = 400 \text{ Å}$. (b) Projection of the moments of the bottom plane of the flower state of (a) onto the $xy$ plane. (c) The vortex configuration; $D = 550 \text{ Å}$. (d) Projection of the moments of the bottom plane of the vortex configuration of (c) onto the $xy$ plane. Figures (a) and (c) have been stretched slightly along the $z$ direction for clear separation of the planes. (After Schabes and Bertram [1988]).
≤ 0.045 \, \mu m switched by approximately uniform rotation. In order to achieve this switching mode, the flower state must first close up. An applied reverse field, below the switching field, actually causes the reverse to happen, and the ‘flower’ opens up slightly. This causes an increase in exchange and magnetocrystalline anisotropy energy, and a reduction in magnetostatic and external field energy. The total energy, of course, is reduced. As the external field is increased, the degree of flowering increases until the switching field is reached. At this point, the increase in exchange and magnetocrystalline anisotropy energies can no longer be compensated for by a corresponding reduction in the other energy terms. The flower then closes up and the magnetization undergoes approximately uniform rotation. As the particle size increases, the exchange interaction becomes less dominant, and a greater degree of flowering results in response to the applied field, which increases the value of the switching field. This deviation from the uniform state is the source of configurational anisotropy. This type of anisotropy is present to some degree in all non-uniform magnetic configurations, not just the flower state.

Williams and Dunlop [1989] developed a three-dimensional micromagnetic model using the magnetic parameters of magnetite and the same energy contributions as Schabes and Bertram, but using cubic anisotropy instead of uniaxial anisotropy. A much higher resolution was obtained by using a Cray supercomputer and a very fast numerical optimisation algorithm called the conjugate-gradient method, which will be discussed in section 5.5.1. They found the critical size to be 0.05 \, \mu m for magnetite which is in exact agreement with a theoretical estimate by Kittel [1949a]. The value predicted by one-dimensional modelling [Enkin and Dunlop, 1987] of 0.084±0.012 \, \mu m, is probably inaccurate due to their model being overly constrained. In addition to the flower state found by Schabes and Bertram, Williams and Dunlop found more complex two and five domain structures which have much lower energies than the conventional lamellar type domain structures. They extended their work [Williams and Dunlop, 1990] to investigate the influence of grain shape, temperature and external fields upon the magnetic structure of magnetite. For a comprehensive review of modern micromagnetic theory the reader is referred to Schabes’ 1991 paper, although this is mainly in the context of magnetic recording media.
CHAPTER 5

Methodology

5.1 The Micromagnetic Approach

Micromagnetics, as its name suggests, is the study of magnetism on a microscopic scale, and the science of micromagnetics strives to determine the magnetic structure of ferromagnetic materials. The most rigorous way of determining the micromagnetic structure of a ferromagnetic body would be to design a model which had a molecular magnetic moment for each unit cell of the crystal, and to formulate an expression which gives the total free magnetic energy of the model as a function of the orientation of all the elementary moments. This expression would have to contain all of the physics which determine the magnetic behaviour of a real crystal. It would then be necessary to find stable magnetic states by locating energy minima on a hypothetical energy surface which would have the same number of dimensions as there were independent variables in the expression for the free energy. The only way to locate all minima would be to search the entire configuration space by perturbing the elementary moments until all possible states had been found (there would be quite a lot!). The free energy of each state would be determined from the aforementioned expression and local minima would be taken to be points on the energy surface when

\[ \frac{\partial E_{tot}}{\partial p_i} = 0, \text{for all } i \]  \hspace{1cm} (5.1)

and

\[ \frac{\partial^2 E_{tot}}{\partial p_i^2} > 0, \text{for all } i \]  \hspace{1cm} (5.2)

where \( E_{tot} \) is the total free magnetic energy, each \( i \) represents a lattice site and \( p_i \) represents a spatial coordinate, such as \( \theta \) or \( \phi \) in figure 4.2, which describes the orientation of the elementary moment at lattice site \( i \). Equation 5.1 is the condition to be satisfied when a local optimum has been located on the energy surface, i.e. when the partial derivatives of the total energy with respect to an infinitesimal perturbation of each elementary moment are equal to zero. Equation 5.2 ensures that this is a minimum and not a maximum. The most stable configuration would be the one which occupied the potential well on the energy surface with the steepest sides. During the search of the entire configuration...
space, all metastable states would be found, and this point will be discussed further in sections 5.5 and 7.1. It is unlikely that mathematics will ever develop to the point where we are able to solve such problems analytically.

Unfortunately, with our present knowledge and technology, none of the above applies. We are restricted by the present state of computer technology, and our model requires to be correspondingly simplified. We also cannot be sure that our physical understanding of ferromagnetism is complete (it almost certainly isn’t), and hence we can only include those terms of which we are aware. Indeed, in order to simplify our model further, and to reduce computation time, we even neglect certain terms, which we know should be included, if it is thought they can be excluded without making a significant difference to our results.

To sum up, micromagnetics is concerned with determining the magnetic structure and behaviour of a ferromagnetic material on a microscopic scale. This is achieved by designing a model which comprises a representation of the elementary magnetic moments, and finding the configuration which corresponds to the minimum free magnetic energy of the model. This is the essence of the micromagnetic approach.

5.2 The Model

The model used for the work in this thesis is based upon that developed by Williams and Dunlop [1989]. Considerable insight has already been gained from one and two-dimensional models but, in order for the model to mimic nature as closely as possible, it must be three-dimensional, and the magnetization vectors must be free to assume arbitrary directions, i.e. the model must be unconstrained.

Although magnetite is ferrimagnetic, it can be modelled as if it were ferromagnetic. Magnetite has two sub-lattices, usually denoted A and B. The formula for magnetite, Fe₃O₄, can be written $\text{Fe}^{2+}\text{O}^2^- . \text{Fe}^{3+}\text{O}^2^-$. There are two types of spaces left between the oxygen atoms, as illustrated in figure 5.1, namely tetrahedrally coordinated A sites where each oxygen atom has four nearest neighbours, and octahedrally coordinated B sites where each oxygen atom has six nearest neighbours. There are two B sites per formula unit, one containing the ferrous ion and one containing the ferric ion, and one A site which contains the other ferric ion. The exchange forces cause the spins of the A sites to be antiparallel to the spins of the B sites. There are nine Bohr magnetons in the two B sites, and five in the A site of each formula unit, giving a net moment of four Bohr magnetons for each formula unit. This gives a spontaneous magnetization of
Figure 5.1 Part of a crystallographic structure representative of the A and B sub-lattices of magnetite. Large open circles represent the oxygen atoms, small open circles the octahedrally coordinated B sites, and the small hatched circle a tetrahedrally coordinated A site. (From O'Reilly, 1984).
475 \times 10^3 \text{ A.m}^{-1}. \text{ We can therefore model magnetite as if it were a ferromagnet with the same value of spontaneous magnetization, and this treatment will now be developed.}

In order to describe the magnetic structure, a three-dimensional discretized grid is used as illustrated in figure 4.2(a). This is, in the general case, a parallelepiped composed of $N \times M \times L$ sub-cubes, where $N$, $M$ and $L$ are the number of sub-cubes in the $x$, $y$ and $z$ directions, respectively. Each sub-cube contains a magnetization vector, $m_i$, located at its centre, which represents the net moment of all the atomic spin moments contained within that volume element. All such dipoles in the model have a constant magnitude, $m_i$, but their directions can assume any arbitrary value, described by polar coordinates $\theta$ and $\phi$ as in figure 4.2(b).

5.3 Formulation of Energy Terms for the Model

The contributions to the total magnetic energy, as described in chapter 2, are the exchange, magnetocrystalline anisotropy, magnetostatic and external field energies. The magnetostrictive strain energy is omitted on the basis that, in magnetite, it is at least two orders of magnitude smaller than the next smallest energy term, namely the magnetocrystalline anisotropy energy. These terms are formulated in the manner described by Brown [1963].

5.3.1 The Exchange Energy

The exchange energy, $E_{\text{ex}}$, is due to coupling of spins $S_i$ and $S_j$ of nearest neighbour atoms:

$$E_{\text{ex}} = -2 \sum_x \sum_y \sum_z J_i S_i \cdot S_j$$

where the summations over $x$, $y$ and $z$ denote interactions between nearest neighbour spins in those directions. We can write equation (2.3) for the exchange energy between two spins as :

$$E_{\text{ex}} = -2J_i S^2 \cos \gamma$$

where $\gamma$ is the angle between two spins. This can be rewritten as :

$$E_{\text{ex}} = -C_E a \cos \gamma$$

where $C_E = 2J_i S^2 / a$ is the exchange constant and $a$ is the lattice spacing. The
exchange constant is sometimes given as \( A = \frac{C_E}{2} = \frac{J_E S^2}{a} \). The exchange interaction is very strong and forces neighbouring spins to be almost parallel. Accordingly, \( \gamma \) must be small. We can then write equation 5.5 as:

\[
E_{ex} = -C_E a \left( 1 - \frac{\gamma^2}{2} \right)
\]  

(5.6)

Williams and Dunlop [1989] assume a linear variation between spin angles. Assuming we can represent the super-exchange interaction, which aligns the A and B sub-lattices anti-parallel, by an equivalent exchange interaction between the net moments of each unit cell of magnetite, we can integrate equation 5.6 over all spins between two representative magnetization vectors in the model to obtain:

\[
E_{ex} = -C_E \Delta \left( 1 - \frac{\Gamma^2}{2} \right)
\]  

(5.7)

where \( \Delta \) is the spacing between the magnetization vectors in the model and \( \Gamma \) is the angle between them. In the formulation used by Williams and Dunlop [1989], equation 5.7 was approximated by:

\[
E_{ex} = -C_E \Delta \cos \Gamma
\]  

(5.8)

Thus they are equating \( 1 - \frac{\Gamma^2}{2} \) and \( \cos \Gamma \):

\[
1 - \frac{\Gamma^2}{2} \approx \cos \Gamma
\]

\[
\rightarrow \frac{\Gamma^2}{2} \approx 1 - \cos \Gamma
\]  

(5.9)

Figure 5.2 shows plots of \( \Gamma^2 \) and \( 2(1 - \cos \Gamma) \) versus angle \( \Gamma \). The value of the ordinate axis is proportional to the exchange energy. The approximation is good for \( \Gamma \leq 60^\circ \), but for \( \Gamma > 60^\circ \), the approximation using \( \cos \Gamma \) results in a very small increase in the exchange energy as \( \Gamma \) increases. Following a suggestion by Enkin and Williams [1993], it was decided it would be better to keep the form of equation 5.7 for the formulation of the exchange energy. This results in a greater exchange energy for larger angles between the magnetization vectors, making it more difficult, for example, to form \( 180^\circ \) domain walls across neighbouring magnetic vectors, where the approximation of equation 5.9 clearly breaks down. It should be noted, however, that this modification made very little difference to the magnetic structures obtained, since the angle between magnetization vectors
Figure 5.2 Plots representing the difference in exchange energy when expressed as a function of $1 - \Gamma^2$ and $\cos \Gamma$. 
is usually < 60° anyway. \( \Gamma \) was calculated by using a standard trigonometric identity for the cosine of an angle between two vectors described by spherical polar coordinates. The formulation of the exchange energy is then (neglecting constant terms):

\[
E_{ex} = \sum_{i=1}^{N-1} A\Delta (\cos^{-1}[\sin \phi_i \sin \phi_{i+1} \cos(\theta_i - \theta_{i+1}) + \cos \phi_i \cos \phi_{i+1}])^2 \\
+ \sum_{j=1}^{M-1} A\Delta (\cos^{-1}[\sin \phi_j \sin \phi_{j+1} \cos(\theta_j - \theta_{j+1}) + \cos \phi_j \cos \phi_{j+1}])^2 \\
+ \sum_{k=1}^{L-1} A\Delta (\cos^{-1}[\sin \phi_k \sin \phi_{k+1} \cos(\theta_k - \theta_{k+1}) + \cos \phi_k \cos \phi_{k+1}])^2
\]  

(5.10)

The value of the exchange energy was, as in the formulation of Williams and Dunlop [1989], defined to be zero for parallel spins, and therefore the constant part of equation 5.7 was omitted.

5.3.2 Magnetocrystalline Anisotropy Energy

The magnetocrystalline anisotropy energy is a purely local energy term depending only on the orientation of each magnetization vector. Both uniaxial and cubic anisotropy were used for different modelling purposes and the formulation of each will be described here. The uniaxial anisotropy energy is given by:

\[
E_{Au} = K_A \Delta^3 \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{L} \sin^2 \phi_{ijk}
\]  

(5.11)

where \( K_A \) is the uniaxial anisotropy constant, \( \Delta \) is the edge length of a sub-cube and \( \phi \) is the angle between the magnetization vector and the easy axis.

The cubic anisotropy energy is given by:

\[
K_1 \Delta^3 \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{L} (\alpha_{1ijk}^2 \alpha_{2ijk}^2 + \alpha_{2ijk}^2 \alpha_{3ijk}^2 + \alpha_{3ijk}^2 \alpha_{1ijk}^2)
\]  

(5.12)

where \( \alpha_{1ijk}, \alpha_{2ijk}, \) and \( \alpha_{3ijk} \) are the direction cosines of the magnetization vector with respect to the [100] axes. The 2\textsuperscript{nd} term in equation 2.4 was neglected on the grounds that it is small in comparison with the first term (at room temperature, \( K_1 \) is greater than \( K_2 \) by a factor of just over 3).
5.3.3 Magnetostatic Energy

This is by far the most complex energy term to formulate, and the most expensive to calculate in terms of computer time, since it is a non-linear, long-range interaction. In chapter 6, models of resolution $21 \times 21 \times 21$ will be used to model cubic grains of magnetite. The number of interaction calculations per iteration for the magnetostatic energy is of the order of $\frac{1}{2} N^2$ where $N$ is the total number of sub-cubes in the model. Therefore, for $21^3$ sub-cubes, $\sim 43$ million interaction calculations are required to evaluate the demagnetizing energy of each configuration. The demagnetizing energy is treated in the form described by Rhodes and Rowlands [1954]. This method calculates the magnetostatic energy by resolving each magnetization vector into its equivalent surface charges on the faces of each sub-cube. The mutual potential energy of every surface with every other surface is calculated by the product of an invariant demagnetizing coefficient, all of which are calculated only once at the beginning of the program, and the equivalent surface charges of the sub-cubes whose magnetostatic interaction is currently being evaluated. Thus the mutual potential energy of two parallel sheets with constant surface charge density and a distance $c$ apart is given by (Rhodes and Rowlands, [1954]):

$$E_D = \sigma_2 \int \int V(x_2, y_2, c) dx_2 dy_2$$  \hspace{1cm} (5.13)

where

$$V(x_2, y_2, c) = \sigma_1 \int \int [(x_2 - x_1)^2 + (y_2 - y_1)^2 + c^2]^{-\frac{1}{2}} dx_1 dy_1$$  \hspace{1cm} (5.14)

The integrations in the expression for $V$ extend over the region in which the surface charge density is $\sigma_1$ and those in the expression for $E_D$ extend over the region in which the surface charge density is $\sigma_2$. The $x_i, y_i$ coordinates extend over the surfaces of the planes under consideration. Equation 5.13 can also be used to calculate the self-energy of a plane. $x_1, y_1$ and $x_2, y_2$ then both cover the same range of values, and a factor of 1/2 must be inserted in the expression for $E_D$. Evaluation of these integrals leads to the aforementioned invariant demagnetizing coefficients for different values of $c$. Of course, a three-dimensional model will also require the calculation of interactions between orthogonal sheets of charge, and an expression similar to equation 5.13 can be obtained, along with the corresponding orthogonal demagnetizing coefficients. The evaluated integrals and the
corresponding demagnetizing coefficients are given in appendix I. Fast Fourier transform techniques, which dramatically reduce the number of interaction calculations necessary to calculate the magnetostatic energy, are now available. A brief outline of this method, which was not used in this study, is given in appendix II.

5.3.4 External Field Energy

The external field energy is due to the interaction of each dipole moment \( m_i \) of the model with an external field \( H_{\text{ext}} \), and is formulated as:

\[
E_H = -\mu_0 \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{L} m_{ijk} \cdot H_{\text{ext}}
\]  

(5.15)

The total magnetic energy of the model is therefore given by:

\[
E_T = E_{\text{ex}} + E_A + E_D + E_H
\]  

(5.16)

In order to obtain stable magnetic structures, it is necessary to minimize the total free magnetic energy \( E_T \) and find its corresponding structure. How this is done will be dealt with in section 5.5. The material constants for magnetite used in the above expressions are given in appendix III.

5.4 Resolution of the model

In order to give sensible results, the model requires a resolution (i.e. number of sub-cubes, or cells) which is sufficiently high to describe the features of the micromagnetic structure. Thus the grid cell size must be small compared to the 'wavelength' of the micromagnetic features. Schabes and Bertram [1988] identified two intrinsic length scales:

\[
l_w = \sqrt{\frac{A}{2K}}
\]  

(5.17)

and

\[
l_{\text{ex}} = \sqrt{\frac{A}{M_s^2}}
\]  

(5.18)

\( l_w \) is proportional to the wall thickness, and \( l_{\text{ex}} \) is referred to as the exchange length. The relative sizes of \( l_w \), \( l_{\text{ex}} \) and particle size \( D \) is significant for the properties of the energy function, e.g., for \( D \ll l_w \) and \( l_{\text{ex}} > l_w \), the exchange interaction will dominate, resulting in a uniform magnetic structure.
The smallest structure which we are likely to encounter is a domain wall. For magnetite at room temperature, equation 5.17 (also in Landau and Lifschitz [1935]) gives $l_w \approx 0.1\mu m$. If we assume this to be approximately the width of a domain wall, it is reasonable to put an upper limit on the grid cell size of $\approx 0.03\mu m$, and to expect that the model would then be capable of resolving domain wall structure.

5.5 Optimization

Optimization is the art / science of finding the maximum or minimum value of a given function. In this work we are concerned with the minimization of an energy function, and any further reference to optimization will refer to this operation.

It is appropriate to point out at this point that, in general, a function will have more than one optimum value - it will possess both local and global optima and these will be discussed more fully in section 7.1. Two types of optimization techniques were used in the course of this work, namely local optimisation techniques which terminate at the first minimum they encounter, and global optimisation techniques which, theoretically, find the global minimum (in practice it is only possible to say that it is likely the global optimum has been found; there is always a non-zero probability that a more optimal state exists).

Williams and Dunlop [1989] used the conjugate-gradient method (a local optimisation algorithm) in the original formulation of the model and this was used extensively in the course of this work. It will be described briefly in this section. A second technique, known as simulated annealing (a global optimisation algorithm), was incorporated into the program and will be described in detail in chapter 7.

5.5.1 The Conjugate-Gradient Method of Optimization

The conjugate-gradient method is a numerical optimization algorithm for solving large-scale (i.e. many variable) optimization problems. It is a first-order method in that it requires calculation of the first partial derivatives of the function with respect to each of the free parameters. Second-order methods, which require the second partial derivatives to be calculated, converge faster, but were not used since computer memory constraints did not allow storage of the Hessian matrix, which contains the second partial derivatives. In addition, the time taken to calculate the Hessian leads to an overall increase in the time taken to
optimize the function. The conjugate-gradient method uses the gradient information in a very efficient manner. An initial line search for the minimum is made in the direction of steepest descent. When it reaches a minimum on this line, subsequent directions are chosen such that they are all mutually conjugate with respect to the Hessian of the energy function, even though the Hessian has not been calculated. The algorithm will stop searching when the gradients become sufficiently small. This is fine if they have become small because the system is in a local (or global) minimum, but they may also become small if the energy surface is gently sloping in parts. It then becomes necessary to renormalize the gradients and restart the algorithm. Ideally, the algorithm should be restarted until it terminates twice with the same magnetic configuration. We can then be reasonably sure of being in a true minimum energy state. Figure 5.3 illustrates how the conjugate gradient method finds a local energy minimum. The general trend of the plot is a reduction in the total magnetic energy, by a factor of about 5, but there are many peaks which represent an increase in the energy of the system. These states are not accepted, and it may be necessary to choose several new search directions before a reduction in the magnetic energy is obtained. For example, at iteration numbers 20 - 22 the algorithm returns two states which result in an increase in the total energy. These states are rejected, until a small reduction in the total energy leads to a new configuration being accepted as the lowest energy state obtained thus far at iteration 23. For a discussion of the conjugate-gradient method, the reader is referred to Press et al. [1986]. The minimization subroutine used in the formulation of Williams and Dunlop [1989] was an IMSL routine. The gradients are calculated analytically for each energy term.

5.6 Tests of the Model

A few special cases were used to test the exchange and anisotropy energy terms. If all the moments in the model are aligned parallel, the exchange energy should be zero. With uniaxial anisotropy, the anisotropy energy should be zero when all the moments point in an easy direction. For cubic anisotropy, if $K_1$ is negative, as in magnetite, the easy axes of magnetization are the [111] axes (cube body diagonals), and the hard directions are the [100] axes (cube edges). From equation 2.7, when using cubic anisotropy the anisotropy energy should be $K_1/3$ when the structure is uniformly magnetized along a cube body diagonal, $K_1/4$ along a face diagonal and 0 along a [100] direction. All these predictions were confirmed. The demagnetizing energy was checked against analytical calculations.
for uniformly magnetized structures. For a cube, this is given by $1/6\mu_0 M_s^2 V$ regardless of the direction of magnetization. The energy gradients were checked numerically. The exchange, anisotropy, demagnetizing and external field energy gradients were all checked separately and found to be correct. The solutions obtained are also consistent with those of other workers, e.g. flower and vortex structures as found by Schabes and Bertram [1988].

Figure 5.3 Plot showing how the conjugate gradient technique behaves when optimizing a function. There are no restarts in this example.
CHAPTER 6

The Magnetic Domain Structure of Large Magnetite Crystals

6.1 Introduction

In this chapter I attempted to gain some insight into the magnetic domain structures of large magnetite crystals, and how their magnetic configuration would change as the crystal size of the model was increased. Cubic crystals in the size range 10 μm - 50 μm were investigated. Previous numerical modelling of domain structures (e.g. Schabes and Bertram, 1988; Williams and Dunlop, 1989) have been concerned only with sub-micron sized grains. Obviously, this means that the sub-cube size will be far in excess of the recommended 0.03 μm, but it was hoped that some useful information could be obtained provided the magnetization direction was slowly varying. In particular it was hoped that lamellar domains would be observed in the models, but this was not the case. All structures are at room temperature and in zero field. A resolution of 21 × 21 × 21 is used throughout. A DEC alpha T1.5 supercomputer was used to obtain this resolution. The algorithm was restarted until no further reduction in energy was obtained.

6.2 Micromagnetic structures

Figures 6.1 - 6.3 illustrate the magnetic structure of a 10 μm crystal obtained using the conjugate gradient method with an initial configuration uniformly magnetized parallel to a cube edge. The model used for the work in this chapter has cubic magnetocrystalline anisotropy, where the easy axes of magnetization lie along the cube body diagonals. The material parameters for magnetite are given in appendix III. Figure 6.1 (a) shows the surface magnetization and the orientation with respect to a cartesian coordinate system. Figures 6.1 (b) - (g) show the internal magnetic structure of the crystal at regular intervals from the surface to the middle plane, as viewed along the x axis. Figures 6.2 (a) - (f) show the internal magnetic structure along the y axis, and figures 6.3 (a) - (f) along the z axis. The basic structure is essentially the same as that described by Schabes and Bertram [1988] as the 'flower' structure, and a simplified diagram showing the main features is shown in figure 6.4. Almost identical structures were obtained for 20 μm and 30 μm crystals. The normalized net moments for the 'flower' type
Figure 6.1 (a) An overall view of the surface magnetization of a 10 μm crystal. Figures 6.1 (b)-(g) show the internal magnetic structure on the planes indicated along the x axis as the view progresses through the crystal until the centre plane is reached. There are 21 planes. Plane 1 is at $x = 1$, plane 11 is at $x = 11$, etc.

(continued overleaf)
Figure 6.2 (a)-(f) show the internal magnetic structure on the planes indicated along the y axis for a 10 μm crystal.
Figure 6.3 (a)-(f) show the internal magnetic structure on the planes indicated along the $z$ axis for a 10 $\mu$m crystal.

(continued overleaf)
Figure 6.3

(e) Plane 9

(f) Plane 11
Figure 6.4  The basic flower structure of the 10 micron grain.

The top of the cube is positively charged and the bottom is negatively charged.
structures for the 10, 20 and 30 \( \mu \text{m} \) crystals are 0.60, 0.57 and 0.57, respectively. Figure 6.5 illustrates the structure obtained for a 40 \( \mu \text{m} \) crystal. An almost identical configuration was obtained for a 50 \( \mu \text{m} \) crystal. The normalized net moment for the 40 and 50 \( \mu \text{m} \) crystals is 0.53 in both cases. These values are much higher than are observed experimentally, although similar structures to these models may exist in nature, but will be relatively rare. This would be due to their high energy, and in order to model the configurations which will occur most frequently in nature, a much higher resolution model will be required. This will allow a more gradual variation in spin direction, thereby allowing lower energy states to be attained. Few generalizations which pertain to real crystals can be made from such models which attempt to determine the magnetic structure of relatively large grains using a relatively low resolution. The most significant and obvious feature of the configurations in figures 6.1 - 6.5 is that the spins are arranged in large domains which are oriented along the easy directions. However, the resolution is inadequate to resolve, with any accuracy, the magnetic structure of any domain walls. Indeed, large angle transitions between spins are observed (e.g. figure 6.5 (d)), which are known to be extremely unfavourable from energy considerations as described in section 2.4. Thus it appears that the limited resolution of the model is leading to an inaccurate representation of the true magnetic structure. Due to the large magnetocrystalline anisotropy energy contribution in relation to the other energy terms at these large grain sizes, it is likely that more local energy minimum states will exist in larger grains than in smaller ones, since in large crystals, uniformly magnetized domains are observed to lie in easy directions, and their orientation could change to other easy directions, corresponding to other local minima.

A vortex structure was obtained by using an initial two domain configuration as in figure 6.6. The vortex configuration is illustrated in figure 6.7 for the 10 \( \mu \text{m} \) grain, the vortex structure for the 20 - 50 \( \mu \text{m} \) crystals being almost identical. The vortex is essentially four domains magnetized at right angles to each other. Note that the domains are magnetized in the hard directions. This will increase the anisotropy energy, but since the main reason for the existence of vortices is to form a complete flux circuit, the reduction in magnetostatic energy compensates for this (recent work by Wright and Williams [pers. comm.], has demonstrated that a higher resolution model results in the four domains aligning themselves along the easy directions). The reverse is true for the flower structure; it has a
Figure 6.5 (a) An overall view of the surface magnetization of a 40 μm crystal. Figures 6.5 (b)-(g) show the internal magnetic structure on the planes indicated along the z axis as the view progresses through the crystal until the centre plane is reached. (Continued overleaf)
Figure 6.6 The initial two domain configuration used as the initial state to obtain the vortex configuration for crystal sizes 10 μm - 50 μm.
Figure 6.7. (a) An overall view of the surface magnetization of the vortex state obtained for a 10 μm crystal. (b)-(e) show the magnetization along the $x$ direction at the planes indicated.
Figure 6.8 (a)-(c) show the vortex structure along the $y$ direction at the planes indicated.
high magnetostatic energy which is compensated for by the reduction in magnetocrystalline anisotropy energy. The vortex structure may also be considered a two domain grain with closure domains. An interesting feature of the vortices obtained for these grain sizes is the orientation of the core of the vortex. This is most easily seen by looking at the structure at discrete points along the y axis. From figure 6.8 (b) of the middle plane along the y axis, the vortex core appears to have enlarged and elongated. This results in a more gradual variation of the spins and will lead to a reduction in the exchange energy. By comparing figures 6.8 (a), (b) and (c) it is also apparent that the points at which the vortex core intersect the surface of the cube, are slightly off centre. The enlarged part of the core in the middle plane (figure 6.8 (b)), has also dipped below the level of the surface intersections of the core, i.e. is not symmetric. This core line distortion is more apparent in higher resolution models (32 x 32 x 32, Wright and Williams, pers. comm.) and it serves to reduce the magnetocrystalline anisotropy energy, by allowing some of the spins to align more closely to an easy axis. Figure 6.9 shows the internal magnetic structure of the vortex configuration viewed along the z direction. Figure 3.5 from Heider [1988] shows a domain pattern for a 10 μm grain which may be interpreted as a type of vortex configuration. It is possible that domain configurations exist in nature in this size range which are very similar to the vortex state illustrated in figure 6.7.

For all grain sizes from 10 μm - 50 μm, the reduced energies (the energy of the system divided by the energy of a cube uniformly magnetized along a [100] axis) of the flower and vortex states are very nearly equal at ≈ -0.5 (the reduced energy in this case is negative due to the large magnetocrystalline anisotropy energy contribution, which is negative because the first magnetocrystalline anisotropy constant for magnetite is negative). It is not possible to state a likely value of the critical size above which the vortex structure becomes unstable, using this model, although, due to the close proximity of the reduced energy values for the two states it is reasonable to say that in a real crystal this size may be in the size range ≈ 10 μm - 100 μm. In this size range, the anisotropy energy makes a significant contribution to the total energy. It is essential to bear in mind that due to the low resolution of these models, it is not possible to guarantee that lower energy states will not be achieved when the resolution is increased. Some evidence that this does in fact occur has been shown by Wright and Williams (personal communication). If a significantly higher resolution was possible, the flower structure in this larger size range may transform to a lamellar domain.
Figure 6.9 (a)-(c) show the vortex structure along the $z$ direction at the planes indicated.
structure since the flower structure has a high magnetostatic energy term and this would be greatly reduced by the formation of lamellar domains. This reduction would be offset by an increase in exchange energy, but a high resolution would help to keep this increase to a minimum in the model. However, it is also possible that these observations are not indicative of a uniformly magnetized structure, since it is not possible to state conclusively that a specimen is uniformly magnetized from surface observations alone. The vortex structure has a very small remanence whereas the flower structure has a relatively large net moment. As stated earlier, the normalized net moment for the flower state is 0.6 - 0.57 for crystals in the size range 10 μm - 30 μm, whereas the normalized net moment for the vortex state in the size range 10 μm - 50 μm is almost constant at ≈0.27. If the grain cooled through its Curie point in an applied field, it is likely that the flower structure would be the favoured configuration, and would therefore be responsible for a significant part of the remanence in a multi-grain specimen. The flower structure in larger grains would exhibit pseudo-single domain behaviour. A significant feature of the flower structures obtained for the 10, 20 and 30 μm crystals is the straight line of free poles observed on the surfaces of the planes perpendicular to the z axis, as in figure 6.3(a). When there is uniform magnetization parallel to a surface, no free poles result, and thus no Bitter pattern would be observed. However, a line of free poles as in figure 6.1(a) will lead to a bitter pattern consisting of a single straight line in the centre of the grain (in general, it is necessary to calculate the square of the surface field due to the magnetization in the entire crystal, in order to determine what the Bitter pattern would look like). This would be interpreted as a two domain grain, although the actual micromagnetic structure of the crystal is much more complex. It is entirely possible that the type of structures depicted in figures 6.1 - 6.5 will occur in real magnetite (as well as other ferro- and ferrimagnetic materials) and these structures may be observed and interpreted as two domain particles using the Bitter pattern technique. It is possible that many lamellar domains, as observed in Bitter patterns, are attributable to the type of structures described above and are not truly lamellar as they are normally thought to be.
Chapter 7

Simulated annealing of three-dimensional micromagnetic structures and simulated thermoremanent magnetization

7.1 Introduction

Igneous rocks are magnetized as they cool in the presence of a magnetic field. The physics of this thermal remanent magnetization (TRM) was first explained by Néel [1949]. At high temperatures (above the Curie temperature) there is sufficient thermal energy to randomize the directions of the electron spins within fine magnetic grains in the rock matrix. This results in a zero net magnetic moment in zero field. An external field will induce a net moment in the grains, in the direction of the field. Néel defined the relaxation time to be the time for a magnetic system to reach equilibrium, and the blocking temperature to be the temperature at which the relaxation time becomes longer than the duration of the experiment being performed to measure it. He considered an assembly of uniaxial, non-interacting, single domain grains with their easy axes aligned at an angle $\theta$ to a small applied field $H$. In such a model there will be only two stable states corresponding to alignment along the easy axis. Thermal agitation may cause the magnetization of each grain to change from one easy direction to the other if the temperature is sufficiently large. Grains which have a component of magnetization in the direction of $H$ have the lower energy of the two available states. Using Boltzmann statistics he derived the following expression for the net magnetization in the direction of the applied field:

$$M = M_s \tanh \left( \frac{m H \cos \theta}{k_B T_B} \right)$$

(7.1)

where $M_s$ is the saturation magnetization, $m$ is the magnetic moment of a single grain, $\theta$ is the angle between the easy axis and the applied field, $k_B$ is Boltzmann's constant and $T_B$ is the blocking temperature. As the temperature is reduced, the thermal energy available for crossing potential barriers, i.e. for the magnetization to flip from one easy direction to the other, is reduced, and, simultaneously, the height of these barriers increase. This results in a sharply defined blocking temperature, when the relaxation time increases rapidly from a few seconds to greater than the age of the Earth.

Simulated annealing (SA), introduced by Kirkpatrick et al. [1983], is a computer technique for finding the global minimum of complicated functions of many
independent variables. It is based on an analogy with the annealing of a solid to a highly ordered crystalline state. However, it is essential to bear in mind that there is no rigorous method of proving that the global minimum has in fact been found. The parameters used to specify the function are randomly perturbed many times. Each time, if the function decreases, the new parameters are accepted. But if the function increases then the perturbation may be accepted according to a Boltzmann probability function using a hypothetical temperature. This temperature is slowly decreased from a high value, where nearly all perturbations are accepted, to a value sufficiently low that the function is locked into a local, or possibly global, minimum.

In this chapter, it is demonstrated that SA is a feasible and useful optimisation technique to determine three-dimensional micromagnetic structures. I then applied the SA algorithm to the TRM process to study and test Néel's TRM theory.

7.2 Micromagnetism and Simulated Annealing

Optimisation techniques can be put into two broad classes; local optimisation techniques, which only accept transitions which correspond to a decrease in the cost function, and global optimisation techniques, which attempt to locate the global minimum. To date, almost all published micromagnetic studies have employed gradient or 'effective field' methods, which are local optimisation techniques, to minimize the energy function. In gradient methods, a set of parameters is iteratively perturbed such that only decreases in the energy function are accepted, until a local energy minimum (LEM) is located. The located minimum depends upon the initial configuration input into the calculation and lower energy minima may be available to the system. One approach to overcome this difficulty is to execute the algorithm a large number of times with different initial configurations and accept the best solution (lowest energy) obtained.

There is no universal global minimization technique short of a complete search of the parameter space (which is not practical from a computational viewpoint). But nature does a very good job of finding minimum energy configurations using random processes during annealing, and simulated annealing attempts to mimic this process. For a comprehensive discussion of the SA algorithm, the reader is referred to the review by van Laarhoven and Aarts [1987] (a useful introductory review is also given by Pannetier [1990]).

In the micromagnetic formulation, the system is perturbed by randomly choosing a sub-cube and changing its magnetic vector direction by a randomly chosen
amount in a randomly chosen direction. The minimum step length was arbitrarily set to 5° (any smaller would make only negligible modifications to the structure). If the step length is allowed to be too big, the exchange energy increases by too much and the step is certainly rejected, so I limited the step length to 30°.

After each perturbation, the free energy of the magnetic structure must be calculated. The most time consuming term is the demagnetizing energy, or self-magnetic interaction, where it is necessary to calculate the interaction of every sub-cube with all other sub-cubes. Since only one magnetic vector is perturbed before each new calculation of the total energy, it is only necessary to calculate the new interactions, i.e., the interactions of the perturbed sub-cube with all other sub-cubes, representing $N^3$ rather than the total $\frac{1}{2}N^6$ calculations ($N$ being the number of sub-cubes on a side). This represents a considerable saving of calculation time. It is necessary to store all the interactions involved in the calculation of the demagnetizing energy and this leads to a constraint on the resolution of the model dependent upon computer memory available. Thus, computer time for each perturbation varies as $N^3$ and memory requirement varies as $N^6$.

In the annealing process, thermal fluctuations produce random perturbations which may cause the free energy of the system to decrease or increase. A new state is accepted if the energy is reduced, but if the energy increases then the new state is randomly accepted, subject to the probability:

$$\Pr(\text{accept}) = \exp\left(-\frac{\Delta E}{k_B T}\right), \quad \Delta E > 0$$

(7.2)

where $\Delta E$ is the energy difference due to the perturbation, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The greater the increase in energy ($\Delta E$) the less likely is the acceptance of such a transition. Following this criterion, after a sufficiently large number of perturbations, the probability distribution of states approaches thermal equilibrium, characterised by the Boltzmann distribution. When using SA to find micromagnetic structures, the temperature is just an artificial control parameter, and $k_B$ is omitted. This artificial control parameter will be denoted by the symbol $c$ and substituted for $k_B T$ in equation 7.2. Equation 7.2 is then known as the Metropolis criterion. The magnetic parameters for the material are held constant at values appropriate for the (real) temperature at which the structure is being modelled.

The probability of acceptance in equation 7.2 can be made arbitrarily close to 1 by setting $c$ sufficiently high. This probability is reduced as the algorithm...
proceeds by reducing $c$, in order to 'freeze' the system into a local, or global, energy minimum. The initial value of the temperature (control parameter) must be set high enough that virtually all transitions are accepted (analogous to heating a solid until it melts). After a sufficient number of iterations the temperature is then reduced. This cycle is repeated until the algorithm is terminated at some low temperature at which virtually no transitions corresponding to an increase in the cost function are accepted. Note that if the temperature is set to zero, the algorithm becomes a local optimisation algorithm, where only steps that reduce the energy of the system are accepted, analogous to quenching a heated solid.

The performance of the SA algorithm depends critically on four parameters: (1) the initial temperature; (2) the number of perturbations attempted at each temperature step; (3) the cooling rate; and (4) the final temperature. The determination of these parameters for each individual problem requires experiment and there is as yet no satisfactory theoretical framework for their choice.

The initial temperature, $T_0$, is chosen such that $\approx 80$ percent of all perturbations are accepted. This is estimated by doing a series of perturbations, accepting them all, and calculating [van Laarhoven and Aarts, 1987]:

$$T_0 = \frac{\langle \Delta E^+ \rangle}{\ln(A^{-1})}$$  \hfill (7.3)

where $\langle \Delta E^+ \rangle$ is the average of the $\Delta E$ values for which $\Delta E > 0$ and $A$ is the proportion of perturbations that we wish to accept initially.

The number of perturbations attempted at each step and the cooling rate are interdependent. If a small number of iterations are attempted at each temperature it is necessary to cool the system slowly. If a larger number of iterations are used, the system can be cooled more quickly. I found that $10^4$ iterations worked well for all resolutions up to $9 \times 9 \times 9$ in conjunction with a cooling schedule (that is, the temperature at the $i$th step, $T_i$, as a function of the previous temperature, $T_{i-1}$) given by van Laarhoven and Aarts [1987]:

$$T_i = T_{i-1} \left[ 1 + \frac{\ln(1 + \delta T_{i-1})}{3\sigma(T_{i-1})} \right]$$  \hfill (7.4)

where $\delta$ is a small positive number determined by trial and error and $\sigma$ is the standard deviation of the energy steps. If the standard deviation is large, indicating that the system is jumping between LEM wells, only a small decrease in temperature results. Conversely, once the system settles into a minimum, the standard deviation will be smaller and larger decreases in temperature can take
place. This cooling schedule makes the algorithm largely insensitive to the number of iterations per temperature. The SA algorithm is terminated when the acceptance rate falls below \( \approx 25 \) percent, since the structure is well optimized by that point. Figure 7.1 illustrates how the algorithm behaves when attempting to find the global minimum of a function of many variables, by plotting the normalized free magnetic energy against iteration number. Initially, when the value of the control parameter is high, transitions which correspond to large increases in the free magnetic energy of the system are accepted, and this is indicated by the high peaks in the early stages of the optimisation. This prevents the system from becoming trapped in a local energy minimum during this initial period. As the algorithm progresses, the control parameter is reduced, and this in turn reduces the probability of acceptance (from the Metropolis criterion, equation 7.2) of a transition for a given \( +\Delta E \). In its final stages, only very small peaks are observed on the plot, corresponding to accepted perturbations which resulted in

![Figure 7.1](attachment:image.png)

Figure 7.1. Plot of total energy v. iteration number, illustrating how the total magnetic energy is optimized by the simulated annealing technique. As the minimization proceeds, progressively smaller increases in energy are accepted.
only a very small increase in the free magnetic energy of the system. At this stage, the system is essentially trapped in an energy minimum, hopefully the global minimum.

I did most of the SA calculations on cubical grains with $5 \times 5 \times 5$ resolution. As expected, in the finest grains relatively uniform magnetization in an easy direction was found. In the large sub-micron range, a vortex structure was invariably determined. There are, however, several vortex LEMs which are very difficult to separate using gradient minimization methods. For example, in a sufficiently large grain, a uniform structure will convert to a vortex structure with the axis running right up the centre of the grain using the conjugate gradient method, whereas the SA method finds a lower energy structure where the magnetic moments lie roughly parallel to the surface, but the centre of vorticity lies such that the anisotropy energy is minimized by allowing most of the dipoles to lie roughly in an easy direction. The vortex state is the lowest energy state found so far, by any optimization method, for grains in the size range $0.1 - 1 \mu m$ and so it would appear that the SA algorithm is successful at finding the global energy minimum.

Since it was only feasible to use rather coarse resolution using the SA method, I interpolated the $5 \times 5 \times 5$ SA solution up to $15 \times 15 \times 15$ and then determined the closest LEM structure using conjugate gradient methods. In other words, the optimal method of determining the global minimum is to use SA to locate the minimum, and conjugate gradient methods to refine the structure to its optimal configuration at a higher resolution. A vortex state for a $0.2 \mu m$ crystal is illustrated in figure 7.2. The easy axis is along the $z$ direction (as previously stated, the core of the vortex lies perpendicular to the easy axis to allow most of the spins to lie along an easy direction). This was obtained by using the SA algorithm to determine a $9 \times 9 \times 9$ resolution, then interpolating this solution to $15 \times 15 \times 15$ and using this as the initial guess for the conjugate-gradient technique.
Figure 7.2. A vortex state for a 0.2 µm grain obtained by optimizing a low resolution model and interpolating the solution for final minimization by the conjugate gradient technique.

7.3 Simulated Thermoremanent Magnetization

In order to gain insight into the important rock magnetic mechanism of thermoremanent magnetization, I applied simulated annealing methods to the physics of magnetic particles. The SA algorithm is similar to the TRM process except that the energy function as well as the thermal energy varies with temperature. We shall not be concerned so much with the final structures obtained at the end of cooling, but rather the temperature at which these structures block.

Néel [1949] hypothesised that in an assemblage of identical SD grains the total moment relaxes exponentially towards some equilibrium value. The relaxation time $\tau$ is given by
The relaxation time becomes

\[
\frac{1}{\tau(T)} = f_0 \exp \left( - \frac{\mu_0 H_K(T) M_s(T) V}{2 k_B T} \right)
\]

where \( f_0 \approx 10^{10} \text{s}^{-1} \) is a frequency factor or crudely the number of reversal attempts per second, and \( E_B \) is the height of the energy barrier separating LEM states. In grains of volume \( V \), saturation magnetization \( M_s \) and microscopic coercivity \( H_K = 2K/(\mu_0 M_s) \), where \( K \) is a uniaxial anisotropy constant equal to the first cubic magnetocrystalline anisotropy constant for the purposes of this study, and assuming coherent rotation and small external fields, the relaxation time becomes

Over a very small temperature range, the relaxation time jumps from well under a second to more than the age of the earth as energy barriers grow and the energy available to jump over the barriers decreases. To find the temperature, \( T_B \), at which grains of volume \( V \) block, \( \tau \) is set to some value, say 1 s, and \( T \) in equation 7.6 is determined numerically or graphically. The dependence of \( T_B \) with \( V \) is shown in Figure 7.3.

Simulated thermoremanent magnetization (STRM) is performed by doing a large number of structure perturbations at a sequence of temperatures from the Curie temperature down, accepting perturbations according to the probability defined in equation 7.2, and determining at what temperature the structure is blocked into a single LEM. Many trials to find \( T_B \) must be done, each one simulating one grain in an assemblage of non-interacting grains.

There are three aspects of the model that must be scaled to reality to give interpretable results; the perturbation mechanism, the frequency factor and the Boltzmann constant. In reality the perturbation mechanism by which magnetic structures change involves phonon-magnon coupling which is very complicated. In this model it is assumed that atomic scale fluctuations are incorporated into the temperature variation of the material constants (magnetization, exchange and anisotropy constants), while the larger scale fluctuations are modelled as coherent rotation of large portions of the grains (i.e. sub-cubes). In the case of single-cell models, the magnetization in the whole grain rotates coherently. The number of perturbations in a laboratory experiment probably far exceeds \( 10^{10} \) but we do not have computing power sufficient to simulate anything near that number.
Figure 7.3. Blocking Temperatures v. Grain Size for uniaxial grains whose magnetization is constrained to rotate coherently. The solid line is the theoretically determined blocking temperature from equation 7.6, assuming reversal by coherent rotation. The histograms show the frequency of occurrence of the simulated blocking temperatures. Note that the distribution of simulated blocking temperatures are centered on the predicted values. $k_s = 2.01 \ k_B$ for all points on the curve.
The probability of the system overcoming a potential barrier depends principally on two factors, namely the thermal energy available to the system and the number of attempts it has at crossing the barrier. Since the model is rather limited in the number of perturbations (attempts), it seems reasonable to compensate for this by making more thermal energy available to the system. This was accomplished by scaling up the Boltzmann constant which effectively gives the system more thermal energy ($k_B T$ is of the order of the energy of one molecule in a macroscopic body at absolute temperature $T$). To find the simulated Boltzmann constant, $k_S$, for a system which is constrained to rotate coherently (modelled by a single magnetic vector), a grain volume was arbitrarily chosen and the material constants were set to the values corresponding to the Néel blocking temperature. The Néel blocking temperature was determined numerically from equation 7.6 for that particular volume and for a relaxation time of $\tau = 1s$. Equation 7.2 was then used to determine $k_S$. The energy barrier for a uniaxial grain constrained to rotate coherently is $K(T)V$, where $K$ is the uniaxial anisotropy constant, which, for the purposes of determining $k_S$, is constant and equals $K(T_B)V$. $T$ in equation 7.2 is set to the aforementioned blocking temperature. The SA algorithm is then executed as normal, randomly perturbing the single magnetic vector, and using equation 7.2, except that $k_B$ is replaced by an initially high value of $k_S$ (as opposed to an initially high value of the control parameter $c$). This value of $k_S$ is then slowly reduced, which in turn reduces the acceptance probability, until the system becomes blocked, i.e. when the direction of magnetization is unable to reverse. The value of $k_S$ at which blocking occurs is the required substitute value of Boltzmann’s constant. The direction of magnetization was monitored by plotting the component of magnetization in the easy direction, $M_{\text{easy}}$, as a function of perturbation number (see Figure 7.4). Once $k_S$ is determined it can be substituted in equation 7.2 and the temperature $T$ can be reduced from the Curie temperature to room temperature to determine the blocking temperature. This is a circular argument, of course, but the reason for doing it is to verify that $k_S$, determined in this fashion, will be constant regardless of the volume chosen to determine it. This was found to be the case, and therefore this approach is a viable method of simulating a TRM acquisition. It is important to verify the validity of the method before attempting to model non-uniform reversal processes which is the main goal of this section.

It was found that for single-cell simulations, $k_S$ was largely insensitive to the maximum step length up to $50^\circ$, above which the moment could jump right over
the energy barrier, and in effect did not feel the 'height' of the energy barrier. As the number of perturbations at each step is increased, the value of $k_S$ drops towards $k_B$, as expected. Usually 10,000 perturbations were performed for each temperature, where the value for $k_S$ was taken to be $2.01k_B$. (Figure 7.4 shows $k_S = 2.57k_B$ for this particular determination. An average of 30 results was taken to obtain the final value of $k_S$ and the standard deviation of these results was found to be $0.30k_B$)

![Graph showing perturbation number vs $k_S/k_B$]

Figure 7.4. $k_S/k_B$ v. Perturbation number. The thin line represents the normalized magnetization varying between $\pm 1$ and the thick line follows the reduction in $k_S/k_B$. The value of $k_S$ used in the simulation is that which no longer allows the magnetization to change direction. In this case blocking occurred at $k_S = 2.57k_B$. After obtaining 30 values in this way, the average was found to be $2.01k_B$. This average was used to simulate a TRM.

To confirm that the SA approach can be applied to study TRM, uniaxial magnetocrystalline anisotropy was imposed on the model and the magnetic structures were initially constrained to be perfectly uniform, and to rotate coherently, by modelling grains using a single cell. This is, in effect, what Néel imposed on SD grains. Always using the same value of $k_S$ ($2.01k_B$ for the single cell model),
each run starts with the temperature set to the Curie temperature for magnetite, 580°C, and every 10,000 perturbations the temperature is reduced by 10°C (there is no cooling rate dependence of blocking temperature in this model). The resulting curve of $M_{\text{easy}}$ (the component of magnetization along the easy axis) as a function of step number is very similar to that seen in figure 7.4. At high temperatures, the energy barrier is negligible compared to the thermal energy, so practically every perturbation is accepted and the magnetization direction is random. Towards the blocking temperature, the magnetization reverses less often, until it becomes blocked in one polarity. There was no externally applied field in the model during TRM simulations, since the low field approximation is being used. A field of $\sim 1\mu T$ makes no discernible difference to the results obtained.

For each volume, I determined the blocking temperature 30 times, and these are plotted as histograms on Figure 7.3. Clearly the results follow Néel's curve. I went further, by determining the dependence of the blocking temperature on the strength of external fields of 1 - 5 mT using Néel's [1949] equation which takes external fields into consideration, i.e. when the low field approximation is not valid. At each temperature, I applied the field in both directions along the easy axis to determine at which temperature the magnetization could no longer flip. Again, the blocking temperatures followed the Néel theory.

It may at first be somewhat surprising that the blocking temperatures found by the addition of many random perturbations give the same result as that of Néel's theory, which considers reversals due to a single energy jump. However it is easily demonstrated that the probability (Pr) of successive energy jumps of values $E_1 - E_0$, $E_2 - E_1...E_n - E_{n-1}$ being accepted in the case of STRM is equivalent to the probability of a single jump of $E_n - E_0$ being accepted since

$$Pr(E_1 - E_0) \times Pr(E_2 - E_1) \times ... \times Pr(E_n - E_{n-1})$$

$$= \exp(-\frac{E_1 - E_0}{kT}) \times \exp(-\frac{E_2 - E_1}{kT}) \times ... \times \exp(-\frac{E_n - E_{n-1}}{kT})$$

$$= \exp(-\frac{E_n - E_0}{kT})$$

Equation (7.7)

and thus the STRM formulation is a valid way of modelling single domain TRM.

More important results are obtained by relaxing the constraint of uniform magnetization. I would have liked to try the STRM method with high resolution models of grains, but due to computing restraints, I could not get usable results
for cubes divided into more than eight cells (2 x 2 x 2).

The low resolution is not a serious problem because all LEM structures which have so far been found for fine particles (< 0.1 μm), using micromagnetic modelling, can be modelled with a 2 x 2 x 2 subdivision. Figure 7.5 shows the energy of the LEM states available to the 2 x 2 x 2 and 7 x 7 x 7 models. In single domain structures the magnetization is mostly uniform except for a degree of 'flowering' at the corners, and in vortex structures the magnetization curls around the central axis of the grain. The line marked SD is for structures with magnetization along the easy axis, and the line marked y-SD is for the hard axis. Enkin and Williams [in press] show that such diagrams contain a great deal of information about the energy surface (free energy as a function of sub-cube magnetization directions). Broadly speaking, the least energy transition mechanism between different orientations of the SD state pass by the next LEM up in the energy vs size diagram, i.e. the configuration with the next highest energy state. For very small grains (< 0.05 μm), reversal is accomplished by coherent rotation of the structure, while in large SD grains a mechanism of vortex propagation is energetically favoured.

A $k_S$ value was determined for the eight-cell model in exactly the same manner as described previously for the single-cell model. The $k_S$ value (determined on a grain size sufficiently small that we expect coherent rotation to be the only reversal mode) for eight-cell STRM is lower than for single-cell STRM because the system is now divided into eight elementary volumes and perturbing one of these sub-cubes results in a smaller energy increase than does perturbing the magnetization through the whole grain in the single cell model. This is because the change in energy due to the exchange and anisotropy contributions for a volume element of the eight cell model are less than the anisotropy energy contribution (the energy barrier for coherent reversal is $KV$) for a perturbation of a single cell model representing the same volume. There is therefore less chance of a particular step being rejected by the Metropolis criterion and $k_S$ is accordingly smaller ($k_S = 1.7k_B$ for the eight-cell model).

For any particular grain size a blocking temperature range rather than a single temperature will be found. This is because of the probabilistic nature of the method in which a minimum energy domain state is found. This dispersion of blocking temperatures around those predicted by Néel theory will increase when the grains are modelled by more than one cell even though domain reversal occurs by coherent rotation in each case. For the case of the small single-domain grain ($\ll d_o$) modelled by a single cell and having 'thermal' energy $25k_S T$ where $T$ is
Figure 7.5. Plots of Normalized Energy v. Grain Size for $7 \times 7 \times 7$ resolution and $2 \times 2 \times 2$ resolution for single domain structures in the easy and y-directions and for the vortex configuration. The energy surfaces of these systems are very similar.
near the expected blocking temperature, the grain will sometimes block slightly above or below this temperature because of the chance acceptance of an uphill climb greater than $25k_bT$ or the chance failure to overcome a barrier of even $25k_bT$ (Figure 7.3). For eight-cell STRM (Figure 7.6), the blocking temperatures for grain sizes up to $\approx 0.07\mu$m agree with Néel theory, but the spread of results is wider than for single-cell STRM because the rotation is no longer strictly coherent. In a multi-cell system, the increased number of degrees of freedom allow the system to find both energetically less favourable and energetically more favourable paths than those afforded to the system when it is constrained to rotate absolutely coherently.

The inset in Figure 7.6 shows the energy of the LEMs available at 300°C. The energy curves are illustrated at this temperature since it is representative of the temperatures at which blocking occurs in this size range. We can understand the favoured reversal paths from this inset. Up to size $d_1$, the favoured path is by coherent rotation. In the size range between $d_1$ and $d_0$, the energy of the vortex state is lower than that of the y-SD state. This allows the system to rotate via a lower energy path than that allowed by coherent rotation. This vortex propagation mechanism was verified by printing out intermediate structures obtained during a reversal of the magnetization direction. Above $d_0$, the vortex state is the global minimum and sometimes no blocking is observed to occur. The blocking temperatures obtained for grain sizes $> d_0$ are attributed to grains which are in a metastable SD state. No blocking was observed to take place in this study above the grain sizes plotted in figure 7.6. (Note: The criterion for blocking in this study is when the grain moment remains fixed in one polarity, and the vortex state has zero net moment in the eight-cell model. The perturbations therefore cause a small fluctuating moment about zero and the system is not observed to block.)

For grain sizes between $d_1$ and $d_0$, where coherent rotation is not the minimum energy reversal mechanism, the blocking temperature dispersion is even larger. This is an important observation and can be understood in terms of the form of the minimum energy path between antiparallel states. In the case of coherent rotation the path is relatively broad in terms of parameter space. That is to say, for a small grain near the blocking temperature there are a number of closely related routes which have energies not much greater than the absolute minimum energy path. For similar deviations from the minimum energy path the increase in energy is roughly proportional to the grain volume. Thus in larger grains,
Figure 7.6. Blocking Temperatures v. Grain Size for grains which are permitted to rotate non-coherently, by using an eight-cell model. The solid line is the theoretically determined blocking temperature for coherent rotation from equation 7.6. The histograms show the frequency of the simulated blocking temperatures at different grain volumes. For grains up to $3 \times 10^{-22} \text{ m}^3$ the simulated results are in agreement with Néel SD theory. For grains larger than $3 \times 10^{-22} \text{ m}^3$ a reduction in the simulated blocking temperatures is observed. This is due to non-coherent rotation via a vortex propagation mechanism. It is this energetically more favourable path at this size range which results in a lower blocking temperature. The inset diagram illustrates the energy curves for the available configurations in this size region at 300°C.
where vortex propagation occurs, the minimum energy path is much more con-
strained, and deviation from the absolute minimum energy path is difficult be-
cause it requires a much larger increase in energy than a similar deviation in
the case of coherent rotation in smaller grains. Therefore, random perturbations
of the magnetization directions will have a much smaller chance of finding the
minimum energy reversal path, and the grain will thus have a smaller probability
of blocking at the corresponding low temperature. In a real thermodynamic sys-
tem, the lowest energy path is likely to be found. It is due to the nature of the
perturbation mechanism and the relatively small number of iterations possible in
this model that this is not always the case here. Hence, a wide range of blocking
temperatures is obtained, the lowest one corresponding to the minimum energy
path.

What this result demonstrates is that large SD grains, which carry the largest
remanence (α volume), do not follow Néel theory. They have lower relaxation
times and blocking temperatures. The anomalous size range is quite small for
this simple model. Were we to take shape anisotropy into account, for example,
the energy barrier to coherent rotation would not become so small at high tem-
peratures, so the vortex propagation mode would be the favoured reversal mode
over a larger size range. To demonstrate what happens when shape anisotropy is
present, I modelled elongated grains. This was accomplished by using the eight
cell cubic model as before, but increasing the value of the uniaxial anisotropy
constant, such that instead of magnetocrystalline anisotropy, I use an energy
barrier which is equivalent to that due to shape anisotropy for a particular aspect
(elongation) ratio. The value of the uniaxial anisotropy constant was determined
by equating the barrier energy due to magnetocrystalline anisotropy energy to
the barrier energy due to shape anisotropy:

\[ K_A(T)V = \frac{1}{2} \mu_0 (N_\perp - N_\parallel) M_s^2(T)V \]  \hspace{1cm} (7.8)

where \( K_A \) is the anisotropy constant (due to shape anisotropy), \( V \) is the grain
volume, \( \mu_0 \) is the permeability of free space, \( M_s \) is the spontaneous magnetization
and \( N_\perp \) and \( N_\parallel \) are the demagnetizing factors for a uniformly magnetized ellip-
soid of revolution when the grain is magnetized in the hard and easy directions,
respectively. From equation 7.8:

\[ K_{A_0} = \frac{1}{2} \mu_0 (N_\perp - N_\parallel) M_{so}^2 \]  \hspace{1cm} (7.9)
where $K_{Ao}$ and $M_{so}$ are the (shape) anisotropy constant and spontaneous magnetization, respectively, at room temperature. Thus $K_A(T)V$ is now the energy barrier due to shape anisotropy at temperature $T$. Combining equations 7.8 and 7.9 gives:

$$K_A(T) = K_{Ao} \left( \frac{M_s(T)}{M_{so}} \right)^2$$  \hspace{1cm} (7.10)

Values for $N_\perp$ and $N_{||}$ were obtained from Osborn [1945] for the calculation of $K_{Ao}$ for different aspect ratios. These are given in table 7.1. Thus from equation 7.10, a value for $K_A$ can be obtained for any temperature and the computer program was modified accordingly for the calculation of blocking temperatures of elongated grains. Most importantly, the values of the simulated Boltzmann constant remain as before, since, as in the case of the real Boltzmann constant, it should be a universal constant for a fixed number of perturbations.

Figure 7.7 illustrates two examples, for aspect ratios of two and five. Figure 7.7 (a) illustrates the case for an aspect ratio of two. When the system is constrained to rotate coherently, the simulated results agree well with Néel SD TRM theory. When this constraint is removed, a significant reduction in the simulated blocking temperature is observed, and over a much greater size range than for non-elongated crystals. This is due to the vortex propagation mechanism being the favoured mode of reversal due to the much increased energy expenditure required for the crystal to reverse its magnetization coherently. At a grain size of 0.01 μm, both the theoretical and simulated blocking temperatures are below room temperature. At a grain size of 0.02 μm the simulated blocking temperature is 180°C - 200°C and so the grain becomes superparamagnetic somewhere between 0.01 μm - 0.02 μm. This size was found to be 0.014 μm which is also the point at which the Néel curve and the simulation curve cross for an aspect ratio of 2, i.e. for 0.015 μm and greater, the model always returned a lower blocking temperature than the Néel curve. Dunlop [1990] gives the superparamagnetic size for equidimensional magnetite grains to be $\approx 0.03\mu m$. This is consistent with the above result, since an elongated grain will have a slightly lower critical superparamagnetic size due to its shape anisotropy. The dispersion of blocking temperatures is much less than for non-elongated grains. This is not significant and is caused by a more rapid decrease in the acceptance probability due to a higher value, on average, of $|\Delta E|$. In other words, for a given decrement of $T$ (10°C in this model) along with a higher $|\Delta E|$, the probability of acceptance is
Table 7.1 Table of demagnetizing factors for various aspect ratios.

<table>
<thead>
<tr>
<th>aspect ratio = y/x</th>
<th>N_x (= N_\perp)</th>
<th>N_y (= N_\parallel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.04</td>
<td>0.92</td>
</tr>
<tr>
<td>0.1</td>
<td>0.07</td>
<td>0.86</td>
</tr>
<tr>
<td>0.5</td>
<td>0.235</td>
<td>0.53</td>
</tr>
<tr>
<td>1.0</td>
<td>0.333</td>
<td>0.333</td>
</tr>
<tr>
<td>2.0</td>
<td>0.415</td>
<td>0.17</td>
</tr>
<tr>
<td>3.0</td>
<td>0.445</td>
<td>0.11</td>
</tr>
<tr>
<td>4.0</td>
<td>0.46</td>
<td>0.08</td>
</tr>
<tr>
<td>5.0</td>
<td>0.47</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure 7.7 (a) Plot of blocking temperatures v. grain size showing the Néel theoretical curve (solid line) and simulated blocking temperatures for coherent and non-coherent rotation for an aspect ratio of 2 and (b) for an aspect ratio of 5. The vertical lines represent the spread of simulated blocking temperatures determined from the model. The short vertical lines following the theoretical curve are for coherent rotation of the model. The lower vertical lines (not much lower for an aspect ratio of 5) represent the non-coherent reversal mode.
reduced in larger steps, since

\[ | \Delta P_2 | > | \Delta P_1 | \]  \hspace{1cm} (7.11)

where

\[ \Delta P_2 = \exp \left( \frac{-\Delta E_2}{k_B T'} \right) - \exp \left( \frac{-\Delta E_2}{k_B T} \right) \]  \hspace{1cm} (7.12)

and

\[ \Delta P_1 = \exp \left( \frac{-\Delta E_1}{k_B T'} \right) - \exp \left( \frac{-\Delta E_1}{k_B T} \right) \]  \hspace{1cm} (7.13)

and \( \Delta E_2 > \Delta E_1; T' > T \).

Therefore, there is a more sharply defined blocking temperature. This is illustrated graphically by the curves sketched in figure 7.8.

Figure 7.7 (b) illustrates the results obtained for an aspect ratio of five. Again, for coherent rotation, simulated blocking temperatures agree well with Néel SD TRM theory, but a smaller decrease in the blocking temperature is observed in this case. The superparamagnetic size was found to be 0.0117 \( \mu \text{m} \) and again this was the size at which the theoretical and simulated curves met. Caution must be exercised when interpreting this result for an aspect ratio of five. The resolution of the model is not adequate to resolve a realistic transition mechanism for such an elongated grain. Although a lower energy transition path is found, it is not significantly lower than that provided by coherent rotation. We would intuitively expect the blocking temperature to increase as the aspect ratio increases, but the blocking temperature in a real crystal may well show a larger difference than is illustrated in figure 7.7(b), since the real system will have a much larger number of degrees of freedom, and this will enable it to find a more energetically favourable transition path than that permitted in this simple model. Experimentally observed blocking temperatures are much higher than predicted by Néel SD TRM theory for grains without elongation. This is probably due to the grains in a real sample having some degree of elongation. Even a small degree of elongation (\( \sim 10\% \)) will cause a significant increase in the blocking temperature. Dunlop and Bina (1977) observed a blocking temperature for magnetite of 555 °C for a bulk sample with a mean grain size of 0.076 \( \mu \text{m} \). They give a room temperature value for \( H_K \) (the microscopic coercive force) of 210 Oe (\( \sim 1.67 \times 10^4 \text{ A.m}^{-1} \)). If the corresponding \( K_{Ao} \) value (\( H_K = 2K_A/(\mu_0 M_s) \)) is inserted into equation 7.10,
Figure 7.8 Plot showing how the probability of acceptance decreases more rapidly for a higher average value of $+\Delta E$. 

Probability curve decreases more rapidly for higher average $+\Delta E$. 

Aspect ratio = 2

Aspect ratio = 5
to determine $K_A(T)$, the corresponding Néel blocking temperature, as determined from equation 7.6, is ≈510°C. The aim of this work is not (at present) to predict accurate blocking temperatures for magnetite, but rather to predict trends and find basic rules for reversal mechanisms such as vortex propagation. Thus although the 0.076 μm sample from Dunlop and Bina (1977) appears to be undergoing coherent reversal in accord with Néel’s SD theory, it is reasonable to expect that above a critical size, a reduction in the blocking temperature will be observed. Thus in PSD grains, blocking temperatures should be lower than those predicted by Néel SD theory, due to non-coherent reversal.
CHAPTER 8

Micromagnetic Modelling of Octahedral Magnetite Grains

8.1 Introduction to the Model

Almost all theoretical work to date has dealt with cubic grains of magnetite or elongated grains represented by parallelepipeds. Magnetite also occurs as octahedral crystals but there is very little literature on theoretical work on this morphology. This chapter will describe the micromagnetic modelling of octahedral magnetite grains in the size range 0.05 μm - 1.0 μm. The structures obtained will be described, and the hysteresis properties of the model will be determined and compared with experimental data where possible. The changes in the magnetic structure of the crystal during hysteresis will also be described in detail.

The model is again based on that developed by Williams and Dunlop [1989] and the energy terms are formulated as described in section 5.2. Thus the only difference is in the shape of the model. The implementation was not trivial since the interactions for the exchange and magnetostatic energy terms in the computer program required extensive modification. The model configuration is illustrated in figure 8.1. Two important points must be mentioned here. Magnetite, in its octahedral form, grows as a regular octahedron due to its crystallographic structure (see e.g. Frye, 1981, p.662). The model used here is not a regular octahedron, whose relation to a cube is illustrated in figure 8.2 (a). The model is merely an eight sided polyhedron, formed by taking the cubic model and removing certain portions of it to leave the polyhedron as illustrated in figure 8.2 (b). It is not possible to model (exactly) a regular octahedron using a sub-cube approach. In view of this, and since the shape of the model is not significantly different from a regular octahedron, I decided to investigate the properties of octahedral magnetite using the model illustrated in figure 8.1. The possible differences in the results, had the model been a regular octahedron, will be discussed at appropriate points in this chapter. Nevertheless, the model will be referred to as the octahedral model. The second point to note is that the faces are not flat, as they were in the models for cubic grains, but now have a step nature as shown in figure 8.3 (a). Provided the resolution is reasonably high, this approximation should not significantly affect the results. If the approximation is a good one, moments should tend to lie parallel to the ‘flat’ octahedral surface, and the free poles should tend to cancel out on the sub-cube faces as illustrated in figure 8.3 (a), giving a good approximation to the moments lying parallel to a flat surface with zero free
Figure 8.1  The model configuration for an octahedral magnetite grain, showing the sub-cube composition.
Figure 8.2 (a) The relation of a regular octahedron to a cube and (b) the relation of the model used in this study to a cube.
Figure 8.3 (a) Illustrating the step nature of the octahedral model, and the tendency of the free poles to cancel when the magnetization vectors lie parallel to the surface.

Figure 8.3 (b)

Showing the relationship of the magnetocrystalline easy axes to the model faces
pole density. In the micromagnetic solutions which follow, it is indeed observed that the surface moments appear, in general, to lie parallel to the imaginary 'flat' octahedral face. In a real octahedral magnetite crystal, the magnetocrystalline easy axes [111] are perpendicular to the faces of the octahedron (Frye, 1981, p.109, p.228). It is not possible to have the easy axes exactly perpendicular to the faces of the model used here due to its geometry. The angles of intersection between the faces and the easy axes in the model are illustrated in figure 8.3 (b). In other words, I have rotated the cubic easy (body diagonals) axes by 45° in the $xy$ plane (see figure 8.1 for $xy$ plane) from their position in the cubic model so that they make the oblique angles with the octahedral model faces as depicted in figure 8.3 (b). This discrepancy is unavoidable in the present model but it does not noticeably affect the resulting structures since the magnetocrystalline anisotropy is the weakest interaction. To test this claim I attempted several minimisations of different sized crystal models using very different positions of the easy axes and found no significant differences in the resulting structures. However, there was a difference in the orientation of some structures. Thus it is reasonable to conclude that only a small difference in orientation of the structure will result from the approximate directions of the magnetocrystalline easy directions. I also plotted the total magnetic energy for a uniformly magnetized octahedral grain as a function of the angle of the magnetization from the $+z$ axis, in a plane containing two magnetocrystalline easy axes. This plot is shown in figure 8.4. Both curves are monotonically decreasing with increasing angle from the vertical. Thus there is no metastable state at $\approx 45^\circ$ from the vertical, which might have been expected when the magnetization lies close to the magnetocrystalline easy directions. The difference between the total magnetic energy and the magnetostatic energy is due to the magnetocrystalline anisotropy energy. As expected, this difference is greatest when the magnetization is oriented at $\approx 45^\circ$ to the vertical, i.e. along an easy direction. The resolution of the octahedral model is defined as the number of sub-cubes along an edge of the centre $xy$ plane as in figure 8.1 (to be referred to from now on as the main plane of the octahedron). Horizontal is defined as meaning parallel to this plane and vertical is defined as meaning perpendicular to this plane. The crystal size also refers to the width of this plane, e.g. a 0.5 $\mu$m grain measures 0.5 $\mu$m along an edge of the main plane.
Figure 8.4 This is a plot of the normalized energy of a uniformly magnetized octahedral crystal (normalized with respect to a crystal magnetized uniformly in the vertical orientation) against the angle of the magnetization from the vertical. The solid line represents the total magnetic energy and the dashed line represents the magnetostatic energy only. The difference is due solely to the magnetocrystalline anisotropy energy.
8.2 Micromagnetic Structures of Octahedral Magnetite Grains

The micromagnetic structure of crystals between 0.05 μm and 1.0 μm were investigated. A resolution of 31 was made possible by using a DEC alpha T1.5 supercomputer. This resolution gives a sub-cube size of ≈ 0.032 μm for the 1.0 μm model and, as discussed in section 5.2, this should be adequate to describe most of the significant micromagnetic features. For smaller grains a lower resolution may be used provided the sub-cube size is not greater than ≈ 0.03 μm. The simulated annealing algorithm and the conjugate-gradient method were used both independently and together to minimize the free energy of the system. When using the conjugate-gradient method, the solutions obtained were input again as the initial configuration of a new conjugate-gradient minimization until two identical solutions were returned.

Figure 8.5 shows a 31 resolution model of a 0.05 μm crystal. Even this simple system contains interesting information. This was obtained using the simulated annealing technique initially for a model of resolution 9 and interpolating the resolution to 31, and optimizing it further using the conjugate-gradient method. As we would expect, it is uniformly magnetized due to the dominant effect of the exchange interaction. There is a small degree of flowering (this term was coined by Schabes and Bertram [1988] to describe the deflection of the magnetization from a perfectly uniform state, especially at the vertices of a crystal). It is magnetized parallel to the main plane in order to reduce the magnetostatic energy. If it was magnetized perpendicular to the main plane, the free pole density would be twice that when the system is magnetized parallel to the main plane. If R is the resolution of the model, the number of free poles (of one sign) is $R^2$ when the model is magnetized perpendicular to the main plane. When the system is magnetized parallel to the main plane the number of free poles is $\frac{1}{2}(R^2 + 1)$ (proof by simple arithmetic sum). Thus:

$$\lim_{R \to \infty} \frac{N_H}{N_V} = \frac{1}{2}$$ (8.1)

where $N_H$ and $N_V$ denote the number of free poles when the system is magnetized horizontally and vertically, respectively. When $R = 31$, $\frac{N_H}{N_V} = 0.5005$. Thus the free pole density is reduced by half if the magnetization lies parallel to the main plane of the octahedron. In a regular octahedron (as in a real magnetite crystal), the magnetostatic energy will still be reduced if the magnetization lies parallel to the main plane but will only be reduced by a factor of $\frac{1}{2} \approx 0.7$, due
Figure 8.5 31 resolution model of a 0.05 µm crystal.
to the different geometry of the regular octahedron. This can be shown by a straightforward calculation of the pole densities for each orientation. This is still a significant reduction in pole density, however, and will lead to the system becoming preferentially magnetized parallel to the main plane. If only the exchange and magnetostatic energy terms were involved in this simple system, then it would be equally energetically favourable for the magnetization to assume any azimuthal direction in the main plane. The magnetocrystalline anisotropy, however, leads to energy minima when the magnetization also lies in a plane which contains two of the easy axes. The shape anisotropy is much stronger than the magnetocrystalline anisotropy (by almost one order of magnitude in this model, and by a factor of $\approx 6$ in a regular octahedron) and the latter is unable to cause any noticeable vertical deflection of the magnetization from its horizontal configuration as illustrated in figure 8.5.

I found the octahedral critical single domain (SD) grain size to be $\approx 0.11\mu$m. A modelled octahedral grain of width 0.1 $\mu$m has the same volume as a cubic grain of 0.05 $\mu$m width, which Williams and Dunlop [1993, in press] found to be the critical SD size for a cubic grain of magnetite, so the critical volume is found to be almost the same as for cubic grains. This is surprising since it might have been expected that the shape anisotropy of the octahedral system would have increased the critical volume. Experimentally, the critical SD size is found to be $\sim 0.05\mu$m - 0.1$\mu$m, Dunlop [1990]. From the above result, this variation may be due to different grain shapes.

Figure 8.6 illustrates the procedure used to find the critical SD size. A resolution of 11 was used to obtain these plots. This gives a sub-cube size of 0.018 $\mu$m for a 0.2 $\mu$m crystal, which was the largest crystal size used in the determination of the critical SD size, thus a resolution of 11 should be sufficient. Curve A was obtained by starting with a crystal size of 0.05 $\mu$m and using the conjugate-gradient method to find a stable configuration, using a uniform magnetization in the $+z$ direction as the initial configuration. This resulted in the flower state, as illustrated in figure 8.7 (a), which was used as the initial configuration for a 0.06 $\mu$m crystal and so on up to a size of 0.2 $\mu$m in steps of 0.01 $\mu$m, the stable configuration found for each crystal size being used as the initial configuration for the next size up. Curve B was obtained by starting with a 0.2 $\mu$m crystal, finding its optimum structure, a vortex state as in figure 8.7 (b), and using this as the initial configuration for the next size down, decreasing in steps of 0.01 $\mu$m, until a crystal size of 0.05 $\mu$m is reached. Inspecting curve A from left to right,
Figure 8.6 Energy curves to find the critical SD size of an octahedral crystal. Curve A was obtained by starting with a grain size of 0.05 μm and finding the minimum energy state (the 'flower' state). This state was input as the initial configuration (using the conjugate-gradient algorithm) for a grain size of 0.06 μm and so on up to a grain size of 0.2 μm. Curve B was obtained in a similar manner, but starting with an initial size of 0.2 μm and reducing the size in steps to 0.05 μm.
Figure 8.7 (a) Flower structure at 0.11 μm and (b) vortex structure at 0.2 μm.
there is a small reduction in energy from 0.05 μm to 0.18 μm. During this increase
in size, the magnetic structure remains in the flower state as in figure 8.7 (a), the
magnetization deflection becoming more pronounced as the crystal size increases,
to reduce the demagnetizing energy. Above 0.18 μm, the flower state becomes
unstable and the structure changes abruptly to a vortex configuration as in figure
8.7 (b). Inspecting curve B from right to left, the system is in the vortex state at
0.2 μm (figure 8.7 (b)) and, as the grain size is reduced, the energy of this state
increases until a grain size of 0.07 μm is reached when the vortex is no longer
stable and the system changes abruptly to the flower state. Between 0.08 μm and
0.18 μm, both states are stable, the lower energy state probably being the more
stable. The point at which the curves cross, i.e. when the two available states
have equal energy, is taken to be the critical SD size, namely 0.11 μm. Figure 8.7
(a) shows the stable flower state at this size and figure 8.8 shows the vortex state
at the critical SD size. However, the vortex state at the critical size is different
from that in figure 8.7 (b). The essential difference in the two vortices is in the
orientation of the core, around which the magnetization curls. At 0.2 μm, the
core lies perpendicular to a face (figure 8.7 (b)), and at 0.11 μm it is oriented
vertically (figure 8.8). The reason for this changing orientation of the vortex is
due to a compromise between the exchange and anisotropy energy contributions.
At \( \approx 0.2\mu m \) the core of the vortex occupies a substantial proportion of the whole
volume, and the energy is minimized by aligning the spins of the vortex core
with a magnetocrystalline easy direction. As the crystal size decreases, the total
energy can be reduced by orienting the vortex such that the bulk of the spins curve
around the \( z \) axis, allowing a reduction in the exchange energy to take place. The
longest path around the octahedron is around this axis and thus allows the most
gradual variation of the spin direction. In order to find out if using an increased
resolution model would affect the critical size, I interpolated the flower and vortex
structures from resolution 11 up to resolution 31 and minimized them for a 0.11
μm crystal size. The reduced energies were decreased by a factor of slightly
greater than 2 for both morphologies. This is because the higher resolution
model can reduce its exchange energy by allowing a more gradual variation of
spin direction. To verify this, I plotted the exchange, anisotropy, magnetostatic
and total magnetic energies as the interpolated structures were being optimized,
for both the flower and vortex states. These plots are shown in figure 8.9, and it
is clear that the form of the plots for the total energy is very similar to the form
of the plots for the exchange energy, supporting the idea that the reduction in
Figure 8.8 Vortex structure at critical size of 0.11 μm.
Figure 8.9 (a) Plot of energy components vs. iteration number during optimisation via the conjugate-gradient method for the vortex configuration. The plots for the total and exchange energies overlap. (b) shows the plots for the flower state. The total and exchange energy plots have the same form but the exchange energy is less.
total energy is brought about almost entirely by a reduction in the exchange energy. This is true for both the vortex and flower states. In figure 8.9(a), the plots for the total and exchange energies overlap, and in figure 8.9(b), these plots have the same form, but the exchange energy is lower. Due to the enormous amount of CPU time required to repeat the whole procedure as outlined above for a 31 resolution model, I minimized the flower and vortex structures for 0.1 \( \mu m \) and 0.12 \( \mu m \) crystals and found that, as expected, the flower structure had the lowest energy for the 0.1 \( \mu m \) crystal size, and the vortex state had the lowest energy at 0.12 \( \mu m \). The energies were approximately equal for the 0.11 \( \mu m \) crystal, as before, and thus the critical size, as determined from the model, was unchanged by the increased resolution. It is reasonable to suppose, therefore, that all configurations in this size range can be reasonably well represented by a resolution 11 model. This is an important result, and will be used in section 8.3 on the hysteresis properties of octahedral magnetite.

The vortex configuration in figure 8.10 was found to have the lowest energy throughout the size range 0.2 \( \mu m \) - 1.0 \( \mu m \) at a resolution of 31. As the grain size increases, the core of the vortex becomes narrower, and reorientates itself from being aligned along a magnetocrystalline easy direction to being parallel to the main plane and perpendicular to an edge of the main plane. This is to allow the majority of the spins to align along a magnetocrystalline easy direction, since, as the core becomes narrower, it is the directions of the spins outwith the vortex core, relative to an easy axis, which are important in reducing the magnetocrystalline anisotropy energy, whereas, when the core is relatively thick, it is necessary for the core spins to align along an easy axis. For grain sizes \( \leq 0.5 \mu m \) the vortex state was found most easily by using the simulated annealing algorithm at a low model resolution and interpolating this structure to a resolution of 31 and using it as the initial configuration in the conjugate-gradient algorithm. Above 0.5 \( \mu m \), the conjugate-gradient method will find the vortex state as the first minimum which it encounters. However, another metastable state was found for crystal sizes 0.2 \( \mu m \) - 0.4 \( \mu m \). Figure 8.11 shows this metastable state for a 0.3 \( \mu m \) crystal. The reduced energy of this configuration is \(-1.74 \times 10^{-2}\), and the reduced energy for a 0.3 \( \mu m \) crystal in the vortex configuration is \(-0.24\), which is much lower. This metastable configuration is not noticeably different for crystal sizes 0.2 \( \mu m \) and 0.4 \( \mu m \). Figure 8.11 (a) shows an overall view of the surface magnetic structure. It is very likely that this is the next lowest energy state, after the flower configuration becomes unstable, and it appears to consist of two oppositely
Figure 8.10 (a) Overall surface view of a 31 resolution 0.1 µm crystal in the vortex state. Reduced energy = 0.26. (b) A view along the x axis. (c) and (d) (overleaf) show the internal magnetic structure along the x and y axes, respectively.
Figure 8.11  (a) An overall view of the surface magnetization of a 0.3 μm crystal using a 31 resolution model. (b) and (c) (overleaf) show surface views along the x and y axes, respectively. (d) and (e) (overleaf) show the internal magnetic structure along the x and y axes, respectively.
Figure 8.11 (continued)
Figure 8.11 (continued)
directed vortices. As the grain size increases, the magnetostatic energy of the system will cause the spins, or, more precisely, groups of spins, to align themselves anti-parallel to one another, at the expense of exchange energy. This is only possible near the main plane where the long range dipole-dipole interaction has sufficient distance over which to exert an influence. This effect is illustrated most clearly in figure 8.11 (d) which shows the central plane which is perpendicular to the $x$ axis. The spins near the left and right edges of the main plane are approximately anti-parallel to the spins of the central vertical column, thereby reducing the magnetostatic energy. At the top and bottom portions of the crystal, the exchange interaction prevents any noticeable misalignment of the spins, and these regions remain uniformly magnetized.

Figure 8.12 shows a 31 resolution model of a crystal in its vortex state. A 0.8 $\mu$m crystal is illustrated as a representative example. As stated previously, this is the lowest energy state found for crystals in the size range 0.2 $\mu$m - 1.0 $\mu$m. It is easy to see why; the vortex configuration forms a complete magnetic circuit preventing field lines from existing outside the crystal, thereby greatly reducing the magnetostatic energy. Since the direction of magnetization varies gradually, the angle between nearest-neighbour dipoles is small, reducing the exchange energy, and the majority of the moments are also able to align themselves approximately in an easy direction, keeping the magnetocrystalline anisotropy energy to a minimum. For this size of crystal, it is energetically favourable for the narrow core to orient itself in the main plane of the crystal, and perpendicular to an edge, as opposed to being perpendicular to a crystal face for the reasons mentioned above.

8.3 Hysteresis Properties of Octahedral Magnetite Crystals

8.3.1 Introduction

The model was used to obtain hysteresis plots for octahedral magnetite crystals. A relatively low resolution of 11 was used due to the large amount of CPU time required for the calculations. This is not a serious impediment in modelling the micromagnetic structures obtained during hysteresis, because all configurations found during the course of this study for crystal sizes up to 1.0 $\mu$m, can be well represented by an 11 resolution model. From these plots I obtained values for the saturation remanence and coercivity. The hysteresis loops were obtained by modelling the crystal in an applied field, increasing it from zero to +150 mT, then decreasing it to -150 mT, then increasing it again to +150 mT to form a closed hysteresis loop. This value of peak field was used by Dunlop [1986] due to
Figure 8.12 A 31 resolution model of a 0.8 μm crystal. The conjugate-gradient method found only the vortex state after \( \approx 15 \) restarts. (a) shows an overall surface view, (b) and (c) (overleaf) show the surface magnetization along the \( x \) and \( y \) axes, respectively. (d) and (e) (overleaf) show the internal magnetic structure along the \( z \) and \( y \) axes, respectively.
experimental constraints. 150 mT is not sufficient to saturate the grain, but, as is explained in section 8.3.3, this does not affect the results. At each stage of the optimisation, the stability of each state found was checked by restarting the conjugate-gradient algorithm until two identical solutions were returned, thus ensuring that the system was in a local (or perhaps global) energy minimum. Coercivities and saturation remanences were obtained for applied fields oriented perpendicular and parallel to the main plane of the octahedron. The reason for doing this is that in a randomly oriented assembly of octahedral grains, the net remanence and coercivity of the sample will be the result of the individual coercivities and remanences of crystals oriented at a range of angles with respect to the applied field. By taking the field orientations which may reasonably be expected to give the extremes of remanence and coercivity (i.e. with the field oriented parallel and perpendicular to the main plane), it is likely that the values obtained from a random assembly will lie somewhere between these extremities. I compared the results of this simulation with experimental results obtained by several workers. The evolution of the magnetic structure undergoing hysteresis will be described in detail.

8.3.2 Coercivity and Saturation Remanence of Octahedral Magnetite Crystals

The results of the simulated hysteresis of octahedral magnetite grains are plotted in figures 8.13 (a) and (b). Figure 8.13 (a) shows the values of the coercive force compared with experimental results by several researchers, and figure 8.13 (b) shows the saturation remanence. The experimental results most relevant to this study are those obtained by Heider [1988] who manufactured equidimensional magnetite grains using the hydrothermal recrystallisation technique, and those of Levi and Merrill [1978].

The significant results from this study are for magnetite crystals in the size range 0.1 μm - 1.0 μm. The result for a 0.1 μm crystal has two extreme values; this is due to the shape anisotropy of the crystal, and is understood in terms of Stoner-Wohlfarth theory [1948], who considered single-domain particles whose magnetization follows the applied field via coherent rotation. They showed that, for uniaxial grains, with the applied field directed along an easy axis, the coercivity is given by:

$$H_K = \frac{2K}{\mu_0 M_s}$$ (8.2)
Figure 8.13 (a) Plot of coercive force $v.$ grain size. Data sets from various workers are plotted. The results from this study are represented by the vertical lines.

Coercive Force (mT) vs. Grain Size (microns)

- □ - □ Dunlop [1986]
- ◇ - ◇ Heider [1988]
- △ - △ Levi and Merrill [1978]
- □ - □ This study
Figure 8.13 (b) Plot of reduced saturation remanence $r$ vs. grain size. Data sets from various workers are plotted. The results from this study are represented by vertical lines.
where $K$ is the uniaxial anisotropy constant, $\mu_0$ is the permeability of free space and $M_s$ is the spontaneous magnetization of the grain. In the case of an octahedral crystal, the anisotropy is due to the geometry of the crystal, and is not magnetocrystalline, but the principle is the same. When the easy axis is aligned perpendicular to the applied field direction, the remanence and coercivity are zero for a single-domain grain. Figures 8.14 (a) and (b) show the hysteresis loops obtained by applying the field perpendicular and parallel, respectively, to the main plane. Although the vortex state is stable at 0.1 $\mu$m, the applied field forces the crystal to remain in an SD state, by 'guiding' the system into the local energy minimum which corresponds to the SD state. Thus when the field is reduced to zero, the system remains in the SD state.

There is good agreement between the coercivities obtained from the model and experimental results in the range 0.2 $\mu$m - 1.0 $\mu$m, as is evident from figures 8.13 (a) and (b). The higher value of coercivity is obtained when the field is applied parallel to the main plane and the lower bound is obtained when the applied field is perpendicular to this plane. In other words, the coercivity is higher when the applied field is directed along an easy direction of magnetization. The only exception to this is for the 0.2 $\mu$m crystal, when the opposite was found to be true. This is because the crystal finds a stable configuration with the vortex core oriented vertically as in figure 8.8. This state will be shown in section 8.3.3 on transition mechanisms. This state also leads to a higher remanence for the vertical field for these two grain sizes. For grain sizes $\geq 0.4\mu$m, the remanence is higher for a horizontally applied field. Heider's result for a sample of grain size 0.76±0.31$\mu$m for the coercive force is $\approx 6$ mT. The upper and lower values from this study lie above and below this value ($\pm \approx 2$ mT) around this size, as illustrated in figure 8.13 (a). Thus in an assemblage, where the grains are randomly oriented, it is probable that the value of the coercive force lies somewhere between these limits, giving a good correlation with Heider's and also Levi and Merrill's [1978] results. I also applied a field at an angle of 45° to the main plane to check that the value obtained was within the limits described above (since I am assuming these give the upper and lower limits). This was the case in six out of nine instances.

The results for 0.2 $\mu$m - 0.7 $\mu$m from the model show a decreasing trend, as is observed experimentally, but when all the results are viewed as a whole, it is not possible to say conclusively that there is a downward trend of the modelled results. Above 1.0 $\mu$m, the results show a large deviation from Heider's and this is most likely to be due to insufficient resolution of the model. In addition to
Figure 8.14 (a) Hysteresis loop for a 0.1 μm crystal with a vertically applied external field.

Figure 8.14 (b) Hysteresis loop for a 0.1 μm crystal with a horizontally applied external field.
this, the model only gives flower and vortex states, whereas, between 5 and 10 μm, lamellar domains occur and domain wall motion occurs. The energy barrier of the model will be resolution dependent, and a low resolution may only allow reversal via a relatively high energy transition mechanism, thus artificially increasing the coercivity. As described in section 8.2, a higher resolution allows a reduction in energy of a particular morphology, e.g. 'flower' or vortex, by reducing the exchange energy. The exchange energy should approach an asymptotic value as the resolution is increased. It is reasonable to expect, therefore, that increasing the resolution for these larger grain sizes would allow a lower energy transition path to be found, by permitting greater deformation of the magnetic structure to take place. Less deformation can occur at lower resolutions due to the corresponding greater increase in exchange energy. Thus a higher resolution model may produce lower coercivities in accord with experiment for these larger grains.

The values for the saturation remanence are shown in figure 8.13 (b). Good agreement is again obtained with Heider's [1988] results in the size range 0.2 μm - 1.0 μm. The simulated saturation remanence of a 0.2 μm crystal agrees well with an experimental value from Levi and Merrill [1978]. A downward trend is more obvious for the saturation remanence than for the coercivity, but, as for the coercivity, the model does not give good results above 1.0 μm, again most likely due to the lack of resolution in the model.

The hysteresis loops obtained by the model for crystals in the size range 0.2 μm - 1.0 μm are illustrated in appendix IV.

8.3.3. Transition mechanisms

This section will describe and discuss changes in the micromagnetic structure of the magnetite crystal as it undergoes hysteresis. Only two grain sizes will be used to illustrate these changes, since they are representative of the other crystal sizes examined in this study. The 0.1 μm crystal will be used to describe the transition mechanism for crystals in the size range 0.05 μm - 0.1 μm (uniform rotation) and a 0.2 μm crystal will be used because its transition mechanism (vortex propagation) is essentially the same for all crystals up to 1.0 μm in size. Only the field values, at which the various transitions occur, differ.

Figure 8.15 shows the 0.1 μm crystal, originally magnetized in the 'flower' state, parallel to the main plane, in an applied field which is oriented along the z axis. I will use the convention that the field has a positive value when it is directed along the +z direction and a negative value when it is directed along the
**Figure 8.15** Overall view of the surface magnetization of a 0.1 μm crystal in a vertically oriented external field.
—z direction. Figures 8.15 (a) - (f) show the changing magnetic structure as the applied field is increased to +150 mT then back to zero field and decreased to -150 mT. This field is not quite sufficient to saturate the grain. Using a stronger field to saturate the grain will make no difference to the results obtained. This was checked by minimizing from a perfectly uniform initial state, which is equivalent to saturating the crystal with a very strong applied field. In zero field, the crystal returns to its 'flower' configuration, oriented along the z axis. Hence there is zero remanence (magnetization in the direction of the applied field). The spins at the apexes and the interior of the octahedron respond more readily to the applied field. At an apex there is a relatively small increase in free pole density when the spins are rotated vertically, making it relatively easy for the dipoles to align with the external field to reduce the external field energy. At and near the surface of the main body of the crystal (just above and below the main plane), rotation of the spins from a horizontal to a vertical orientation would lead to a very large increase in free pole density, which would not be offset by a corresponding reduction in external field energy. The external field energy can, however, be reduced, without significantly increasing the free pole density, by rotation of the interior magnetization, in the direction of the applied field. The increase in exchange energy is compensated for by this reduction. To illustrate the increase in free pole density due to surface spin rotation, consider the main plane, of resolution R. When the magnetization is parallel to the plane, the number of free poles (of one sign) is R. If the magnetization is perpendicular to this plane, the number of free poles increases to 4(R-1). Thus,

$$\lim_{R \to \infty} \frac{M_v}{M_h} = 4$$  \hspace{1cm} (8.3)$$

Thus the spins in the main plane are the most difficult to rotate. For all other planes in the model, except the top and bottom, which contain only one spin, this ratio = 2, but the main plane affects all other planes via exchange coupling. Rotation from a horizontal to a vertical orientation of the two dipoles at the apexes results in a reduction of one free pole in the model, and the effect is small but noticeable, due to the relatively large volume represented by one sub-cube. In a real system, this effect will not occur, due to exchange coupling between the large number of spins in a real system. Figure 8.16 (a) shows the internal demagnetizing field of a crystal which is uniformly magnetized in the +z direction. The size of the arrows is proportional to the strength of the internal
Figure 8.16 (a) The internal demagnetizing field for a crystal which is uniformly magnetized in the $+z$ direction and (b) in the $+x$ direction.
Figure 8.16 (c) Plots of saturation field v. grain size for magnetic saturation in the x and z directions.
field. It is clear from this figure that the demagnetizing field is strongest at the edges of the main plane. At the apexes, the internal field is in the direction of the magnetization. This is surprising at first sight, but it is due to the sub-cube nature of the model. The free poles on the planes below the apex result in the net internal field being in the same direction as the magnetization. In a real crystal, the internal field will be similar; it will reduce in magnitude towards the apexes, though not as dramatically as in the model and it will not be in the same direction as the magnetization at the apex itself. Hence in a real crystal, the magnetization at the apexes is also likely to respond first to an applied field. For the sake of completeness, figure 16 (b) shows the internal field for an octahedral crystal which is uniformly magnetized in the +z direction. Figure 16 (c) shows a plot of the field necessary to achieve saturation as a function of crystal size. I assumed saturation to have occurred when the normalized magnetization in the direction of the applied field was > 0.99. As expected for the reasons given previously, a higher field is necessary to saturate the crystal in the z direction.

Figures 8.17 (a) - (h) show the same model of a 0.1 μm crystal responding to a horizontally applied field, i.e. in the plane of easy magnetization, due to the shape anisotropy. Figures 8.17 (a) and (b) show the configuration in zero field and in +150 mT, along the x axis, respectively. The only discernible difference is a very small amount of closure of the flower state, i.e. the flower structure becomes more uniformly magnetized. Figures 8.17 (c) - (h) show the magnetization rotating almost uniformly as the field strength is gradually increased in the −x direction. The magnetization at the apexes shows the greatest response to the external field, for the same reasons as explained above, until, at ≈ -80 mT, the magnetization direction switches abruptly. This is the reason for the discontinuity in the hysteresis loop at the corresponding point in figure 8.14. Figures 8.17 (e) and (f) show the middle plane viewed along the y axis as the field is increased in the −x direction.

Figures 8.18 - 8.23 show the other transition mechanism found, namely that of vortex propagation (cf chapter 7). This mechanism is more favourable when the crystal size is greater than the critical size, because uniform rotation then incurs a penalty in the form of a high magnetostatic energy contribution. There are several analogies between this section and section 7.4 on TRM simulation and blocking temperatures. In both cases, the system is attempting to find the lowest energy path available to accommodate magnetization reversal, the energy in the case of TRM simulation being provided by thermal fluctuations, and by an
Figure 8.17 Surface magnetization of a 0.1 μm crystal with a horizontally oriented external field, parallel to the z axis. (e) and (f) show the internal magnetic structure as viewed along the y axis.
Figure 8.18 Overall view of the surface magnetization of a 0.2 μm crystal in a vertically oriented external field.
Figure 8.19 Internal magnetic structure of a 0.2 μm crystal as viewed along the x axis in a vertically oriented external field.
Figure 8.20 Internal magnetic structure of a 0.2 μm crystal as viewed along the y axis in a vertically oriented external field.
Figure 8.21 Overall view of the surface magnetization of a 0.2 μm crystal in a horizontally oriented external field. (parallel to the x axis)
Figure 8.22 Internal magnetic structure of a 0.2 μm crystal as viewed along the x axis in a horizontally oriented external field. (parallel to the x axis)
Figure 8.23 Internal magnetic structure of a 0.2 μm crystal as viewed along the y axis in a horizontally oriented external field. (parallel to the z axis)
Figure 8.24 (a) The vortex state of a 0.2 μm crystal and (b) a surface view of its internal demagnetizing field. (c) and (d) show the internal field in the middle of the crystal as viewed along the $x$ and $y$ planes, respectively.
external field in the case of hysteresis. Figure 8.18 shows an overall view of the crystal as it is subjected to an applied field oriented along the z axis. Figures 8.19 and 8.20 show the internal structure of the central planes as viewed along the x and y axes, respectively. As for the 0.1 μm crystal, 150 mT is not a sufficiently strong field to saturate the magnetization in this direction, due to the high self-demagnetizing field. Figure 8.18 (c) shows the equilibrium structure obtained at 150 mT. It is that of a vortex with its core oriented vertically. Figure 8.18 (d) shows that this state persists when the field is reduced to zero. Thus there are two local minima corresponding to the vortex state, one in which the core lies perpendicular to a crystal face as in figure 8.19 (a) (as the grain size increases in the sub-micron size range, the core comes to lie in the main plane, parallel to an edge) and one in which it lies vertically. At crystal sizes of \( \geq 0.4 \) μm, the vortex configuration with its core in the z direction is not stable and when the field is reduced to zero, the core orientates itself perpendicular to a crystal face or in the main plane, perpendicular to an edge depending on the crystal size, for the reasons explained earlier in this chapter. Apart from this, the transition mechanism is essentially the same. As the field strength is increased in the \(-z\) direction, the vertical core of the vortex rotates abruptly at -25 mT so that it is perpendicular to a crystal face. This is best shown in figure 8.19 (e) and (f).

As the field is increased still further to 150 mT in the \(-z\) direction, the core spins rotate towards the external field direction until the state in figure 8.18 (h) is attained.

Figures 8.21 - 8.23 show the response of the crystal to a horizontally applied field. Figures 8.21 (a) - (j) show an overall surface view and figures 8.22 and 8.23 show the internal magnetic structure as viewed along the y and x axes, respectively. Figures 8.21 (a) - (e) illustrate the crystal becoming magnetically saturated as the field is increased in the +x direction to +150 mT. Figures 8.22 (a) - (e) show the response of the core of the vortex to the increasing field. As the field is increased in the \(-x\) direction, the vortex structure flips abruptly such that the vortex becomes a mirror image of the vortex obtained upon removal of the field used to attain saturation in the +x direction. Figure 8.24 shows the internal field for a 0.2 μm grain in the vortex state. The internal field is strongest at the apexes and at the surface where it is intersected by the vortex core. This explains why the apexes and core respond most readily to the applied field.

Some researchers have doubts as to whether the vortex state will exist in real crystals. The conclusion from my investigation is that they are very likely
to exist in nature. This is supported by two facts. A domain wall consists of gradually rotating spins over a distance of \( \approx 0.1 \, \mu m \), in magnetite (equation 5.17). A grain whose dimensions are of the order of 0.1 \( \mu m \) cannot therefore possess a uniform magnetization structure. From the dimensions of a domain wall, it is reasonable to suppose that the magnetic structure of such a grain is composed of gradually rotating vectors, in order to keep the exchange energy to a minimum, while allowing a reduction in the magnetostatic energy to occur. A vortex type structure satisfies these requirements. Further evidence for the validity of the vortex structure comes from the fact that they give good agreement with experimental measurements of coercivity and remanence for both octahedral and cubic morphologies (Williams, Pers. Comm.).
CHAPTER 9

Summary

In this chapter I will summarize the work which constituted the main core of this thesis. This work is described in detail in chapters six, seven and eight.

Chapter six dealt with magnetic domain structure in relatively large magnetite crystals in the size range 10 μm - 50 μm. Previous investigations have dealt with sub-micron sized crystals, due to inadequacy of the model resolution. A 21 × 21 × 21 resolution grid was used for this part of the study, which for a 40 μm grain, for example, results in a sub-cube size of almost 2 μm. This is, of course, completely inadequate to show any domain wall structure, but it was thought that some interesting results may nevertheless be obtained. Only two distinct domain configurations were found for crystals in the size range 10 μm - 50 μm, namely a structure similar to the flower state described by Schabes and Bertram [1988], and a vortex structure. Both states had an almost identical value of reduced energy. Some nearest-neighbour spins were observed to make 180° angles with one another, indicating that the low resolution of the model was resulting in an inaccurate representation of the domain structure. In the flower type structure, uniform domains magnetized in the easy directions were observed, indicating that although the magnetocrystalline anisotropy is the smallest energy contribution, it becomes important at large crystal sizes. This section also described how Bitter patterns may not be representative of the true magnetic structure, although, strictly speaking, the square of the field at the surface should be calculated in order to determine the form of the resulting Bitter pattern.

Chapter seven dealt with the application of a global numerical optimisation algorithm called simulated annealing (SA), to micromagnetic models. SA is based on an analogy with the annealing of a solid. It searches the configuration space of the function to be optimised (although not exhaustively) and does not become trapped in local energy minima as do local optimisation algorithms. This allows very low energy configurations to be found, which are not easily located by other optimisation techniques. For the size range investigated (< 1.0μm), only flower type structures along the easy axes for grains ≤ 0.06μm, and vortex structures for grains 0.06 – 1.0μm, were found. No new structures were found which had not been previously obtained using other optimisation techniques. The SA algorithm was also employed to incorporate thermal fluctuations into a micromagnetic model in order to simulate the acquisition of a thermoremanent magnetisation
(TRM), and hence to determine blocking temperatures. Only a $2 \times 2 \times 2$ resolution model was possible, since computer constraints led to poor quality results when a higher resolution was used. The Boltzmann constant was scaled to compensate for the perturbation mechanism used during simulated annealing, and also for the relatively low number of perturbations used in the model. By substituting this constant in the Metropolis criterion, the system effectively has more thermal energy available to overcome energy barriers between local energy minima. The results were compared with Néel's single domain TRM theory when the magnetization of the system was constrained to rotate coherently. The close agreement of the modelled blocking temperatures and those from Néel's equation indicated that the model was a valid representation of single domain TRM acquisition. When the constraint for coherent rotation was removed, a reduction in the blocking temperatures was observed within a small size range of $0.065 - 0.07 \, \mu m$ for grains with no shape anisotropy. This was found to be due to a lower energy transition mechanism being afforded to the system than when the magnetization was constrained to rotate uniformly. The favoured reversal mechanism for grains in this small size range was found to be via vortex propagation. Elongated grains were also modelled and were found to rotate non-coherently, and thus have lower blocking temperatures than predicted by Néel single domain TRM theory, over a much greater size range, dependent upon the aspect ratio.

Chapter eight described the magnetic structures and hysteresis properties of the octahedral morphology of magnetite for crystals in the size range $0.05 \, \mu m - 1.0 \, \mu m$. The model used was not a regular octahedron but an eight sided polyhedron which was a reasonable approximation. In the uniform single domain state, the magnetocrystalline anisotropy energy is insignificant compared to the intrinsic shape anisotropy of the octahedral crystal, and this results in the magnetization lying in the main plane of the octahedron. The critical SD size of the octahedral crystal was found to be $\approx 0.11 \mu m$. As in cubic models, the predominant configurations were found to be flower and vortex type structures. The vortex state was observed to have several stable orientations due to the magnetocrystalline anisotropy and also due to the balance between the exchange and magnetocrystalline anisotropy energies. I investigated the hysteresis properties of octahedral magnetite and compared the coercivities and remanences with experimental results and found good agreement. The switching mechanisms were examined, and these were found to be similar to the reversal mechanisms observed to occur during simulated TRM as detailed in chapter seven.
CHAPTER 10

Conclusions and suggestions for further work

10.1 Conclusions

In chapter six, I attempted to model cubic magnetite crystals in the size range 10 \( \mu \)m - 50 \( \mu \)m. The resolution of the model was inadequate for this task but several interesting points can be made from the results obtained. Two configurations were obtained; a flower type state and a vortex state. In the flower state, large domains magnetized in the magnetocrystalline easy directions were observed. Thus the magnetocrystalline anisotropy becomes important in large crystals. The vortex state may be stable even at large grain sizes. It is possible that, even though the resolution is restricting the available states, these two types of structure will be stable in a real system in this size range. A higher resolution may merely increase the number of metastable states available to the system (including, perhaps, lamellar domain structures). The flower type configuration obtained in this size range resulted in a sharply defined line of free poles on one face of the cube. This would result in a Bitter pattern image which superficially resembles the pattern obtained for a classic two domain grain. In general, the square of the field at the surface should be calculated to determine the Bitter pattern. This problem of ambiguous colloid patterns has been remarked upon by previous workers (e.g. Williams and Dunlop, [1989]). It is possible that some Bitter patterns, which are interpreted as being indicative of lamellar domain structures, are of a more complex nature than has previously been considered.

In chapter seven, the optimisation technique known as simulated annealing (SA) was used to optimize micromagnetic structures, and also to incorporate thermal fluctuations into the model. The technique was found to be very CPU time intensive, and was also constrained by computer memory limits. The algorithm was found to be successful in finding the global minimum of the micromagnetic energy function. It was found that the most efficient method to obtain a reasonably high resolution representation of a global minimum energy configuration, was to first of all bring the system into a global minimum using the SA algorithm at a low resolution. This solution was then interpolated up to a higher resolution, and the resulting configuration was then further optimized by a fast local optimisation algorithm called the conjugate-gradient method by inserting it as the initial configuration. No previously unknown configurations were obtained using this technique.
A very successful application of SA was in the introduction of thermal fluctuations into a micromagnetic model. This allowed the construction of a dynamic model of Néel's single domain thermoremanent magnetization (SD TRM) theory. The model was not able to simulate anything like the number of thermal fluctuations which occur in nature, but it was found to be possible to compensate for this by appropriate scaling of Boltzmann's constant. Close agreement was obtained with Néel's theory when the magnetization of the model was constrained to rotate coherently, but when this constraint was removed, as in nature, a decrease in the blocking temperatures was observed for cubic grains in the size range \( \approx 0.065 \mu m - 0.07 \mu m \). This was found to be due to a lower energy reversal path being available to the system when it was allowed to rotate non-coherently, namely that of vortex propagation. This reduction in blocking temperatures takes place over a larger range of grain sizes when there is shape anisotropy present, i.e. when the grains are elongated. Since most grains will have a degree of elongation present in a real sample, it is likely that many grains will reverse via non-uniform rotation, resulting in a lower blocking temperature than if they were constrained to reverse coherently. In larger grains still, no grains were ever blocked in the single domain state, but rather in a vortex mode with lower remanence and it is likely that, in size-sorted powders of sub-micron grain size, the single domain fraction, which will invariably exist in such a sample, will contribute significantly to the pseudo-single domain behaviour of these powders, by reversing non-coherently.

In chapter eight, the magnetic structures and properties of octahedral magnetite crystals were examined. Two approximations to the regular octahedral morphology of magnetite were made and found to be reasonable. The first was that an eight sided polyhedron made up of isosceles triangles was used for the morphology of the model, as opposed to the regular octahedron made up of equilateral triangles for a real crystal. The second approximation is that the model is composed of sub-cubes and this leads to the faces of the model having a step nature instead of being flat. The magnetization was found to lie approximately parallel to a crystal face, resulting in a mutual cancellation of free poles, and thus approximating the situation at a real flat surface. Octahedral crystals of magnetite were found to have an intrinsic shape anisotropy which leads to the uniformly magnetized state becoming preferentially magnetized in the main plane of the octahedron. The shape anisotropy dominates the magnetocrystalline anisotropy by a factor of \( \approx 6 \) in a regular octahedral crystal at room temperature. The critical SD size was found to be \( 0.11 \mu m \). This means that the critical volume of the
The octahedral model is almost exactly the same as that found by previous research for the cubic model. Above the critical SD size, three stable states were found to exist; a flower type state, an exaggerated type of flower structure which can be regarded as a double vortex structure, and a (single) vortex state. The vortex state had the lowest free energy above the critical single domain size. The vortex state is unlikely to be an artifact caused by inadequate model resolution, at sub-micron crystal sizes, since even at relatively high resolutions of 31 (along an edge of the main plane) it showed no signs of transforming into some other configuration. It seems reasonable to conclude that the vortex state will occur in nature, or some configuration which closely resembles a vortex. It seems unlikely, from the results of this study, that the SD state will transform directly into a classic two domain state as the grain size increases, but may instead favour a vortex configuration for an appreciable size range above the critical size. The vortex state may also have implications for Dunlop's [1977] PSARK theory, which attempts to explain the source of PSD remanence, and puts forward the hypothesis that the intrinsic domain wall moment may be a likely candidate. The vortex state can be thought of as a wall which entirely fills the volume of a grain. Thus a vortex type moment may be a source of PSD remanence. Further evidence for the existence of the vortex state in real crystals comes from the good agreement with experimental results for the hysteresis properties obtained from the model in this study. By modelling hysteresis loops for two different orientations of the model with respect to the applied field, it was found that the values obtained bracketed the experimentally obtained values of coercivity and remanence. The hysteresis properties of the octahedral model are in agreement with the hysteresis properties of the cubic model (Williams, Pers. comm.), although the saturation remanence as predicted by the cubic model is slightly lower than is observed experimentally. The switching mechanisms for magnetization reversal during hysteresis were found to be essentially the same as those for reversal during TRM acquisition.

10.2 Suggestions for further work

The most computer-time intensive part of micromagnetic calculations is the calculation of the long-range magnetostatic interaction, where it is necessary to calculate the interaction of every cell of the model with every other cell. Fast fourier transform (FFT) techniques are already being employed to greatly speed up this part of the calculation. Only when significantly greater resolutions can be obtained will it become possible to accurately model crystals of the order of
10µm and greater. The FFT technique should also be applied to the octahe-
dradal morphology to determine metastable structures perhaps not seen at lower
resolutions, and also to model hysteresis properties for larger grain sizes for the
octahedral morphology. It is possible to approximate a regular octahedron by
using a sub-cube model [Fabian, pers. comm.], and it would be of interest to see
how the structures and properties of such a model compare with the model used
in this study (the model used in this study was not a regular octahedron).

There are many avenues of research still to be explored using simulated an-
nealing. Further work needs to be done on blocking and unblocking temperatures,
using higher resolution models if possible. It is straightforward to examine how
domain structures change with temperature using this technique, which is not
possible using local optimisation algorithms. It would be helpful if the execu-
tion time of the algorithm could be reduced to allow higher resolution models.
It should be possible to model partial thermoremanent magnetization using SA,
but since the model can only emulate the behaviour of a single grain, this proce-
dure would have to be performed many times, for different sized grains, then the
results analyzed as if they formed an assembly of non-interacting particles. No
work has been done so far on the micromagnetic structures of octahedral grains at
high temperatures, nor on high temperature hysteresis properties. The computer
programs developed during the course of this work are able to do this without
any modification. A parallel implementation of the SA algorithm (Boissin and
Lutton, 1993) would allow higher resolution models to be obtained, both for
optimization purposes and STRM.
Appendix 1

(From W. Williams, personal communication)

The demagnetizing energy

The demagnetizing energy arises from the Coulomb dipole-dipole interactions between the elemental sub-cubes of the model. The magnetostatic energy between two dipoles is:

\[ U = -\frac{3M_s^2}{4\pi\mu_0 r^3} (\cos^2 \theta - \frac{1}{3}) \] (1)

where \( r \) is the distance between the dipole centres, \( \theta \) is their angular separation and \( M_s \) is the dipole magnetic strength.

Because this force is long ranged and non-linear every dipole in the model will interact with every other dipole. Thus for a cubic model with a resolution of \( N^3 \) elements, \( \frac{1}{2}N^6 \) interactions need to be calculated to evaluate the energy function for each iteration of the minimization.

Much computer time can be saved by resolving each dipole into its equivalent magnetostatic surface charges, and evaluating the interaction between these 'charged' sheets (in the manner of Rhodes and Rowlands, 1954). In this way the angular and spatial components of the interactions can be separated and the invariant spatial components evaluated once and stored in a look-up table. The angular component simply represents the varying magnetostatic charges on the surface as the dipole direction changes.

If we represent the magnetostatic charges on a pair of interacting sheets in the x-y plane as \( \sigma_1 \) and \( \sigma_2 \), then the interaction energy \( E_m \) is given by

\[ E_m = \sigma_2 \int_{\alpha}^{\beta} \int_{\gamma}^{\delta} V(x_2, y_2, z_2) dx_2 dy_2 \] (2)
where $V(x_2, y_2, z_2)$ is the magnetic potential at the point $(x_2, y_2, z_2)$ on the second sheet, due to the magnetic charge of the first. Thus

$$V(x_2, y_2, z_2) = \sigma_1 \int_0^a dx_1 \int_0^b ((x_2 - x_1)^2 + (y_2 - y_1)^2 + z_2^2)^{-1/2} dy_1 \quad (3)$$

where $a$ and $b$ are the dimensions of the sheets in the $x$ and $y$ directions respectively.

For one dimensional models, only interactions between parallel sheets need be evaluated. However for three dimensional models both parallel and orthogonal interactions must be calculated. Care must be taken when evaluating the integral to ensure that the limits are of the same sign. The case of interacting parallel sheets has been described by Rhodes and Rowlands (1954), and can be described in terms of a function $F(x, y, z)$.

$$2F(x, y, z) = x^2 \sinh^{-1}\left(\frac{x}{y^2 + z^2}\right) + x^2 \sinh^{-1}\left(\frac{x}{x^2 + y^2}\right) + y^2 z \sinh(z/y)$$

$$+ y^2 \sinh^{-1}(x/y) + xyz \tan^{-1}\left(\frac{(x^2 + y^2 + z^2)^{1/2}}{xz}\right)$$

$$+ \frac{2}{3} y^2 (x^2 + y^2 + z^2)^{-1/2} + \frac{1}{3} x^2 (x^2 + y^2)^{-1/2} + \frac{1}{3} x^2 (y^2 + z^2)^{-1/2}$$

$$+ \frac{2}{3} y^3 - y^2 x \sinh^{-1}\left(\frac{x}{y^2 + z^2}\right) - y^2 z \sinh^{-1}\left(\frac{x}{x^2 + y^2}\right) - \pi xyz$$

$$- \frac{1}{3} (x^2 + z^2)(x^2 + y^2 + z^2)^{-1/2} - \frac{2}{3} y^2 (x^2 + y^2)^{1/2}$$

$$- \frac{2}{3} y^2 (y^2 + z^2)^{1/2}$$

for interaction between pairs of $x$-$z$ planes. Similar functions can be generated for the other parallel planes by symmetry.

For interacting orthogonal planes a similar function can be obtained. The integral to be evaluated is similar to equation 2 except that for an $x$-$y$ plane interacting with an $x$-$z$ plane the integration is now over $x$ and $z$.

As in Rhodes and Rowlands the integral can be reduced to a number of standard integrals. The result can be represented in terms of a function $G(z, y, z)$:
\[ G(x, y, z) = xyz + \ln(p + x) + \frac{1}{2} x^2 y \ln(p + z) + \frac{1}{2} x^2 z \ln(p + y) \\
+ \frac{1}{12} y^3 \ln(x^2 + y^2) + \frac{1}{12} x^3 \ln(x^2 + z^2) \\
+ \frac{1}{6} z^3 \ln(\sqrt{x^2 + y^2} + y) + \frac{1}{6} y^3 \ln(\sqrt{x^2 + y^2} + z) \\
+ \frac{1}{6} x^3 \tan^{-1} \left( \frac{px}{yz} \right) + \frac{1}{2} y^2 x \tan^{-1} \left( \frac{py}{xz} \right) \\
+ \frac{1}{2} x^2 x \tan^{-1} \left( \frac{pz}{xy} \right) + \frac{1}{3} z(y^2 + z^2)^{1/2} \\
- \frac{1}{2} xyz \ln(y^2 + z^2) - \frac{1}{6} y^3 \ln(p + z) \\
- \frac{1}{6} z^3 \ln(p + y) - \frac{1}{4} x^2 y \ln(x^2 + y^2) - \frac{1}{4} x^2 z \ln(x^2 + z^2) \\
- \frac{1}{6} y^3 \ln(y) - \frac{1}{6} z^3 \ln(z) - \frac{1}{1} \pi x(x^2 + 3y^2 + 3z^2) \\
- \frac{1}{3} pzy \]

where \( p = \sqrt{x^2 + y^2 + z^2} \).

The functions needed for interactions between other pairs of orthogonal sheets can be obtained by symmetry.

The functions \( F \) and \( G \) are equivalent to integration limits of \( \alpha = \gamma = 0 \) in equation 2, and interaction coefficients can be completely specified in terms of the above two functions (and their associated functions generated by interchanging \( x, y \) and \( z \)), by combining them in the order necessary to avoid changes of sign in the integral limits.

Using these functions the necessary interaction coefficients can be calculated. There are three types of interaction coefficients, type A between orthogonal sheets, type B for a sheets self interaction, and type C for parallel sheets. The interaction between an \( xy \) plane and an \( xz \) would then be denoted as \( A_{xy}^{zz} \).

The demagnetizing energy, \( E_D^{ijk} \) between two volume elements at coordinates \( ijk \) and \( i'j'k' \), each containing a magnetic dipole whose directions are specified by \( (\theta, \phi) \) and \( (\theta', \phi') \) is:
\[ E_{D}^{ijk}_{ij'k'} = \sin \phi \sin \phi' A_{y'z}^{zz}(\sin \theta \cos \theta' + \cos \theta \sin \theta') \]
\[ + \sin \phi \cos \phi'(A_{x'y'}^{zz} \sin \theta + A_{y'y'}^{zz} \cos \theta) \]
\[ + \cos \phi \sin \phi'(A_{x'y'}^{zz} \sin \theta' + A_{y'y'}^{zz} \cos \theta') \]
\[ + \sin \phi \sin \phi'(C_{zzz} \sin \theta \sin \theta' + C_{yyz} \cos \theta \cos \theta') \]
\[ + \cos \phi \cos \phi'C_{zy} \]

for \( i, j, k \neq i', j', k' \).

When \( i, j, k = i', j', k' \) it corresponds to calculation of the self demagnetizing energy of the volume element, and this is given by:

\[ E_{D}^{ijh}_{self} = 2 \sin^2 \phi (B_{zz} \sin^2 \theta + B_{zy} \cos^2 \theta) \]
\[ + 2 \cos^2 \phi B_{zy} \]
\[ - \sin^2 \phi (C_{zzz} \sin^2 \theta + C_{zyz} \cos^2 \theta) \]
\[ - \cos^2 \phi C_{zy} \]

Because the limits of integration of equations (2) and (3) have to be split differently depending on the relative positions of the interacting sheets the following conditions have to be taken into consideration:

1. When \( i \neq i', j \neq j', k \neq k' \)
\[ A_{zz}^{zz} \neq 0, A_{yz}^{zz} \neq 0, A_{zy}^{zz} \neq 0 \] and \( C_{zy} = C_{yz}, C_{zz} = C_{zz}, C_{yyz} = C_{yyz} \)

2. When \( i \neq i', j \neq j', k = k' \)
\[ A_{zz}^{zz} = 0, A_{yz}^{zz} = 0, A_{zy}^{zz} = A_{yy}^{zz}, \text{ and } C_{zy} = C_{zy}, C_{zz} = C_{zz}, C_{yyz} = C_{zy} \]

3. When \( i = i', j \neq j', k \neq k' \)
\[ A_{zz}^{zz} = A_{zy}^{yz}, A_{zy}^{zz} = 0, A_{yz}^{zz} = 0 \] and \( C_{zz} = C_{yyz}, C_{zz} = C_{yyz}, C_{yyz} = C_{yyz} \)
(4) When \( i \neq i', j = j', k \neq k' \)
\[
A^{xx}_{xy} = 0, \quad A^{yz}_{xy} = A^{py}_{xy}, \quad A^{zz}_{xy} = 0,
\]
and \( C_{xy} = C_{5cxy}, C_{zz} = C_{8zz}, C_{yz} = C_{6cys} \)

(5) When \( i \neq i', j = j', k = k' \)
\[
A^{xx}_{xy} = 0, \quad A^{yz}_{xy} = 0, \quad A^{zz}_{xy} = 0,
\]
and \( C_{xy} = C_{2a2y}, C_{zz} = C_{2azz}, C_{yz} = C_{1yz} \)

(6) When \( i = i', j = j', k \neq k' \)
\[
A^{xx}_{xy} = 0, \quad A^{yz}_{xy} = 0, \quad A^{zz}_{xy} = 0,
\]
and \( C_{xy} = C_{2cxy}, C_{zz} = C_{2bzz}, C_{yz} = C_{2byz} \)

(7) When \( i = i', j \neq j', k = k' \)
\[
A^{xx}_{xy} = 0, \quad A^{yz}_{xy} = 0, \quad A^{zz}_{xy} = 0,
\]
and \( C_{xy} = C_{5cxy}, C_{zz} = C_{1zz}, C_{yz} = C_{3cys} \)

(8) When \( i = i', j = j', k = k' \)
\[
This gives rise to the self energy of the volume element \( E\) \( D\) self.

The interaction coefficients in terms of the functions \( F \) and \( G \) are:

\[
A^{xx}_{xy} = 2G(\Delta + a, b, 2\Delta + c) - 4G(\Delta + a, b, 2\Delta + c) + 2G(\Delta + a, b, c)
\]

\[
- G(a, b, 2\Delta + c) + 2G(a, b, \Delta + c) - G(a, b, c)
\]

\[
- G(2\Delta + a, b, 2\Delta + c) + 2G(2\Delta + a, b, \Delta + c) - G(2\Delta + a, b, c)
\]

\[
- 4G(\Delta + a, \Delta + b, 2\Delta + c) + 8G(\Delta + a, \Delta + b, \Delta + c) - 4G(\Delta + a, \Delta + b, c)
\]

\[
+ 2G(a, \Delta + b, 2\Delta + c) - 4G(a, \Delta + b, \Delta + c) + 2G(a, \Delta + b, c)
\]

\[
+ 2G(2\Delta + a, \Delta + b, 2\Delta + c) - 4G(2\Delta + a, \Delta + b, \Delta + c) + 2G(2\Delta + a, \Delta + b, c)
\]

\[
+ 2G(\Delta + a, 2\Delta + b, 2\Delta + c) - 4G(\Delta + a, 2\Delta + b, \Delta + c) + 2G(\Delta + a, 2\Delta + b, c)
\]

\[
- G(a, 2\Delta + b, 2\Delta + c) + 2G(a, 2\Delta + b, \Delta + c) - G(a, 2\Delta + b, c)
\]

\[
- G(2\Delta + a, 2\Delta + b, 2\Delta + c) + 2G(2\Delta + a, 2\Delta + b, \Delta + c) - G(2\Delta + a, 2\Delta + b, c)
\]

And from symmetry

\[
A^{yz}_{xy}(\alpha, \beta, \gamma) = A^{zx}_{xy}(\beta, \alpha, \gamma)
\]
The coefficient $A_p$ is given by

$$A_p^{xx}(\alpha, \beta, \gamma) = A_p^{yx}(\gamma, \beta, \alpha)$$

And from symmetry

$$A_p^{yx}(\alpha, \beta, \gamma) = A_p^{yx}(\beta, \gamma, \alpha)$$

The coefficient $C_{1zz}$ is given by:

$$C_{1zz} = 4(2F(\Delta, \Delta + b, \Delta) - F(\Delta, b, \Delta) - F(\Delta, 2\Delta + b, \Delta))$$

And from symmetry

$$C_{1zy}(\alpha, \beta, \gamma) = C_{1zz}(\alpha, \beta, \gamma)$$

$$C_{1yz}(\alpha, \beta, \gamma) = C_{1zz}(\beta, \alpha, \gamma)$$

The coefficient $C_{2azz}$ is given by:

$$C_{2azz} = 4(F(2\Delta + a, 0, \Delta) - 2F(\Delta + a, 0, \Delta) + F(a, 0, \Delta) - F(2\Delta + a, \Delta, \Delta) + 2F(\Delta + a, \Delta, \Delta) - F(a, \Delta, \Delta))$$

And from symmetry

$$C_{2bzz}(\alpha, \beta, \gamma) = C_{2azz}(\gamma, \beta, \alpha)$$
\( C_{2xyz}(\alpha, \beta, \gamma) = C_{2azz}(\beta, \alpha, \gamma) \)

\( C_{2az} = C_{2azz} \quad C_{2by} = C_{2bzz} \quad C_{2cz} = C_{2czz} \)

The coefficient \( C_{3zz} \) is given by:

\[
C_{3zz} = 2(F(2\Delta + a, 0, 2\Delta + c) - 2F(2\Delta + a, 0, \Delta + c) + 2F(\Delta + a, 0, c) \\
- 2F(\Delta + a, 0, 2\Delta + c) + 4F(\Delta + a, 0, \Delta + c) - 2F(\Delta + a, 0, c) \\
+ F(a, 0, 2\Delta + c) - 2F(a, 0, \Delta + c) + F(a, 0, c)) \\
- 2(F(2\Delta + a, \Delta, 2\Delta + c) - 2F(2\Delta + a, \Delta, \Delta + c) + F(2\Delta + a, \Delta, c) \\
- 2F(\Delta + a, \Delta, 2\Delta + c) + 4F(\Delta + a, \Delta, \Delta + c) - 2F(\Delta + a, \Delta, c) \\
+ F(a, \Delta, 2\Delta + c) - 2F(a, \Delta, \Delta + c) + F(a, \Delta, c))
\]

And from symmetry

\( C_{3zy}(\alpha, \beta, \gamma) = C_{3zz}(\alpha, \gamma, \beta) \)

\( C_{3yz}(\alpha, \beta, \gamma) = C_{3zz}(\beta, \alpha, \gamma) \)

The coefficient \( C_{4zz} \) is given by:

\[
C_{4zz} = 2(F(2\Delta + a, \Delta + b, 2\Delta + c) - 2F(2\Delta + a, \Delta + b, \Delta + c) + F(2\Delta + a, \Delta + b, c) \\
- 2F(\Delta + a, \Delta + b, 2\Delta + c) + 4F(\Delta + a, \Delta + b, \Delta + c) - 2F(\Delta + a, \Delta + b, c) \\
+ F(a, \Delta + b, 2\Delta + c) - 2F(a, \Delta + b, \Delta + c) + F(a, \Delta + b, c) \\
- F(2\Delta + a, b, 2\Delta + c) + 2F(2\Delta + a, b, \Delta + c) - 2G(2\Delta + a, b, c) \\
+ 2F(\Delta + a, b, 2\Delta + c) - 4F(\Delta + a, b, \Delta + c) + 2F((\Delta + a, b, c) \\
- F(a, b, 2\Delta + c) + 2F(a, b, \Delta + c) - F(a, b, c) \\
- F(2\Delta + a, 2\Delta + b, 2\Delta + c) + 2F(2\Delta + a, 2\Delta + b, \Delta + c) - F(2\Delta + a, 2\Delta + b, c) \\
+ 2F((\Delta + a, 2\Delta + b, 2\Delta + c) - 4F((\Delta + a, 2\Delta + b, \Delta + c) + 2F((\Delta + a, 2\Delta + b, c) \\
- F(a, 2\Delta + b, 2\Delta + c) + 2F(a, 2\Delta + b, \Delta + c) - F(a, 2\Delta + b, c)
\]
And from symmetry

\[ C_{4zz}(\alpha, \beta, \gamma) = C_{4zz}(\alpha, \gamma, \beta) \]
\[ C_{4yz}(\alpha, \beta, \gamma) = C_{4zz}(\gamma, \alpha, \beta) \]

The coefficient \( C_{5azz} \) is given by:

\[ C_{5azz} = 2 (\mathcal{F}(2\Delta + a, \Delta + b, \Delta) - 4 \mathcal{F}(\Delta + a, \Delta + b, \Delta) + 2 \mathcal{F}(a, \Delta + b, \Delta) \]
\[ - \mathcal{F}(2\Delta + a, \Delta) + 2 \mathcal{F}(\Delta + a, b, \Delta) - \mathcal{F}(a, b, c) \]
\[ - \mathcal{F}(2\Delta + a, 2\Delta + b, \Delta) + 2 \mathcal{F}(\Delta + a, 2\Delta + b, \Delta) - \mathcal{F}(a, 2\Delta + b, c) \]

And from symmetry

\[ C_{5aaz}(\alpha, \beta, \gamma) = C_{5azz}(\beta, \alpha, \gamma) \]
\[ C_{5baa}(\alpha, \beta, \gamma) = C_{5azz}(\gamma, \beta, \alpha) \]
\[ C_{5bab}(\alpha, \beta, \gamma) = C_{5azz}(\beta, \gamma, \alpha) \]
\[ C_{5cay}(\alpha, \beta, \gamma) = C_{5azz}(\alpha, \gamma, \beta) \]
\[ C_{5acay}(\alpha, \beta, \gamma) = C_{5azz}(\gamma, \alpha, \beta) \]

The coefficient \( C_{Lzz} \) is given by:

\[ C_{Lzz} = 4 \mathcal{F}(\Delta, \Delta, \Delta) \]

And from symmetry

\[ C_{Lyz} = C_{Lzz} = C_{Lzz} \]
APPENDIX II

The Fast Fourier Transform (FFT)

Fast Fourier transform techniques which speed up the calculation of the magnetostatic interaction are now available. They reduce the number of interaction calculations from $O(N^2)$ to $O(N \log_2 N)$ (Yuan and Bertram [1992]).

Given the magnetization state of the system $\mathbf{M}(r)$, the magnetostatic interaction field, $\mathbf{H}(r)$, can be evaluated, as in this study, via the demagnetization matrix $N$:

$$\mathbf{H}(r) = \sum_{r'} N(r - r') \mathbf{M}(r') \quad (B1)$$

This convolution can be changed into a scalar product in frequency space using the FFT. The Dirichlet conditions are satisfied using standard zero padding techniques to take care of the finite size effect of the system. The discrete Fourier transform $\mathcal{F}$, in two dimensions, of the field $H$ is:

$$\mathcal{F}(k_1, k_2) = \sum_{n_1=0}^{n_x-1} \sum_{n_2=0}^{n_y-1} H(n_1, n_2) \cdot \exp \left( 2 \pi i \left( \frac{k_1 n_1}{n_x} + \frac{k_2 n_2}{n_y} \right) \right) \quad (B2)$$

and similarly for $\mathcal{N}$ and $\mathcal{M}$. Expansion to three dimensions is straightforward. Equation (B1) can then be written as:

$$\mathcal{H}(k_1, k_2) = \mathcal{N}(k_1, k_2) \cdot \mathcal{M}(k_1, k_2) \quad (B3)$$

where $\mathcal{H}, \mathcal{N}$ and $\mathcal{M}$ are the Fourier transforms of $\mathbf{H}, \mathbf{N}$ and $\mathbf{M}$, respectively. This results in the aforementioned reduction of the number of interaction calculations.
Appendix III

This appendix gives the values of the material parameters for magnetite used in this study. The values for the anisotropy constants $K_A$ and the spontaneous magnetization were taken from Enkin [1986]. The exchange constant was obtained from the polynomial given below.

<table>
<thead>
<tr>
<th>$T (^\circ C)$</th>
<th>$K_A$ (J/m$^3$)</th>
<th>$M_0$ (A.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$1.25 \times 10^4$</td>
<td>$4.8 \times 10^5$</td>
</tr>
<tr>
<td>50</td>
<td>$1.10 \times 10^4$</td>
<td>$4.73 \times 10^5$</td>
</tr>
<tr>
<td>100</td>
<td>$8.27 \times 10^3$</td>
<td>$4.58 \times 10^5$</td>
</tr>
<tr>
<td>150</td>
<td>$6.02 \times 10^3$</td>
<td>$4.42 \times 10^5$</td>
</tr>
<tr>
<td>200</td>
<td>$3.91 \times 10^3$</td>
<td>$4.20 \times 10^5$</td>
</tr>
<tr>
<td>250</td>
<td>$2.34 \times 10^3$</td>
<td>$3.96 \times 10^5$</td>
</tr>
<tr>
<td>300</td>
<td>$1.29 \times 10^3$</td>
<td>$3.70 \times 10^5$</td>
</tr>
<tr>
<td>350</td>
<td>$6.61 \times 10^2$</td>
<td>$3.43 \times 10^5$</td>
</tr>
<tr>
<td>400</td>
<td>$2.75 \times 10^2$</td>
<td>$3.10 \times 10^5$</td>
</tr>
<tr>
<td>450</td>
<td>$8.67 \times 10^1$</td>
<td>$2.72 \times 10^5$</td>
</tr>
<tr>
<td>500</td>
<td>$1.26 \times 10^1$</td>
<td>$2.18 \times 10^5$</td>
</tr>
<tr>
<td>550</td>
<td>$8.47 \times 10^{-2}$</td>
<td>$1.23 \times 10^5$</td>
</tr>
<tr>
<td>570</td>
<td>$3.10 \times 10^{-5}$</td>
<td>$5.0 \times 10^4$</td>
</tr>
<tr>
<td>578</td>
<td>$2.34 \times 10^{-11}$</td>
<td>$1.0 \times 10^4$</td>
</tr>
<tr>
<td>579</td>
<td>$1.00 \times 10^{-15}$</td>
<td>$3.0 \times 10^4$</td>
</tr>
<tr>
<td>580</td>
<td>$4.06 \times 10^{-20}$</td>
<td>$1.0 \times 10^4$</td>
</tr>
</tbody>
</table>

The exchange constant (units are J.m$^{-1}$) was determined as a function of the absolute temperature $T$ (Heider and Williams, 1988):

$$A(T) = (a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4) \times 10^{-11} \text{ J/m}$$

where $a_0 = -1.344$, $a_1 = 2.339 \times 10^{-2}$, $a_2 = -0.706 \times 10^{-4}$, $a_3 = 8.578 \times 10^{-8}$ and $a_4 = -3.868 \times 10^{-11}$.
Appendix IV

This appendix contains plots of the hysteresis loops obtained from the octahedral model described in chapter 8. It is of interest to note that the hysteresis loops generally become narrower as the grain size increases, denoting a reduction in coercivity as is observed experimentally.
0.2 micron grain

Vertically applied field

\[ \frac{\text{Mrs}}{\text{Ms}} = 0.15 \]

Hc = 15 – 20 mT
0.2 micron grain
horizontally applied field
Mrs/Ms = 0.085
Hc = 10 mT
0.3 micron grain

Vertically applied field

Mrs/Ms = 0.07

Hc = 10 mT

Field (T)
0.3 micron grain
Horizontally applied field
Mrs/Ms = 0.055
$H_c = 5 \text{ mT}$
0.4 micron grain
Vertically applied field
Mrs/Ms = 0.03 - 0.04
Hc = 5 mT
0.4 micron grain
Horizontally applied field

$\frac{M_r}{M_s} = 0.22$

$H_c = 10 \text{ mT}$
0.5 micron grain

Vertically applied field

\[ \frac{M_r}{M_s} = 0.03 \]

\[ H_c = 4 \text{mT} \]
0.5 micron grain

Horizontally applied field

Mrs/Ms = 0.06

Hc = 8 mT
0.6 micron grain

Vertically applied field

Mrs/Ms = 0.02

Hc = 4 mT
0.6 micron grain
Horizontally applied field
Mrs/Ms = 0.06
Hc = 8 mT
0.7 micron grain
Vertically applied field
Mrs/Ms = 0.035
Hc = 4 mT
0.7 micron grain

Horizontally applied field

Mrs/Ms = 0.033

Hc = 6 mT
0.8 micron grain

Vertically applied field

\( \frac{M_r}{M_s} = 0.02 \)

\( H_c = 5 \text{ mT} \)
0.8 micron grain
Horizontally applied field
Mrs/Ms = 0.07
Hc = 9 mT
0.9 micron grain

Vertically applied field

Mrs/Ms = 0.04

Hc = 7 mT
0.9 micron grain

Horizontally applied field

Mrs/Ms = 0.07

Hc = 9 mT
1.0 micron grain

Vertically applied field

\( \frac{M_{rs}}{M_s} = 0.016 - 0.038 \)

\( H_c = 5 \, \text{mT} - 10 \, \text{mT} \)
1.0 micron grain

Horizontally applied field

Mrs/Ms = 0.10 - 0.11

Hc = 10 mT
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