

# [2]

# Magnetic properties of solids

Couples and electrons have their moments.

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## 2.1 Introduction

To the man-in-the-street, matter is often thought to be either magnetic or non-magnetic. An ordinary magnet attracts magnetic material, e.g. iron filings, pins, lodestone, whereas non-magnetic material, e.g. wood, chalk, is not attracted to the magnet. In fact, all materials show some reaction to a magnetic field though in the case of conventionally 'non-magnetic' materials the reaction will be very weak. A powerful electromagnet and sensitive measuring instrument are needed to demonstrate these weak reactions.

Later chapters of this book will be mainly concerned with the more strongly magnetic materials that can, under a range of conditions, retain some of their magnetism after removal from a field. These materials are broadly referred to as **ferromagnetic** or **ferri-magnetic**. Other materials, which do not retain their magnetism are called either **paramagnetic** or **diamagnetic** according to whether they are respectively pulled into or pushed out of regions of strong magnetic field. Occasionally these relatively weak magnetic properties can dominate the magnetic behaviour of natural samples.

At the atomic scale magnetic fields arise from the motion of electrons. Two possible electron motions may be imagined within an atom; the orbital rotation of an electron about an atom's nucleus, and the spin

motion of an electron about its own axis. Both these whirling motions or currents in an atom produce a magnetic field, but in the natural iron oxide minerals, with which later chapters will be largely concerned, the spin moments are completely dominant.

## 2.2 Basic magnetic properties

### 2.2.1 *Diamagnetism*

Diamagnetism is a fundamental magnetic property. It is extremely weak compared with other magnetic effects and so it tends to be swamped by all other types of magnetic behaviour. Diamagnetism arises from the interaction of an applied magnetic field with the orbital motion of electrons and it results in a very weak negative **magnetisation**. The magnetisation is lost as soon as the magnetic field is removed. Strong magnetic fields tend to repel diamagnetic materials. The spin magnetic moments of electrons do not contribute to the magnetisation of diamagnets as all the electron spin motions are paired and cancel each other out.

Diamagnetism is for all practical purposes independent of temperature. Many common natural minerals, such as quartz, feldspar, calcite and water, exhibit diamagnetic behaviour.

### 2.2.2 Paramagnetism

Paramagnetic behaviour can occur when individual atoms, ions or molecules possess a permanent elementary magnetic dipole moment. Such magnetic dipoles tend to align themselves parallel with the direction of any applied field and to cause a weak positive magnetisation. However, the magnetisation of a paramagnet is lost once the field is removed because of thermal effects. In an applied field, paramagnetic materials behave in the opposite way to diamagnetic materials and tend to be attracted to regions of strong field. Many natural minerals, e.g. olivine, pyroxene, garnet, biotite, and carbonates of iron and manganese, are paramagnetic. The incompletely filled inner electron shells of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  ions are generally responsible for the paramagnetic behaviour of natural materials as they have unpaired electrons with free spin magnetic moments.

When a field is applied to a paramagnetic substance the spin magnetic moments tend to order and to orientate parallel to the applied field direction. However, the magnetic energies involved are small and thermal agitation constantly attempts to break down the magnetic ordering. A balance is reached between these two competing processes of thermal randomising and magnetic ordering. The magnetic moment which depends on this balance is thus a function of both the applied field and the absolute temperature. The magnetisation of a paramagnetic substance is very weak compared with that of a ferromagnet, but paramagnetic effects are in turn dominant over diamagnetic effects.

### 2.2.3 Ferromagnetism

Ferromagnetic materials such as iron are characterised by the way in which their magnetic properties change dramatically at a particular critical temperature, called the **Curie temperature**. Below the Curie temperature a ferromagnetic material can carry a strong remanent magnetisation, but above the Curie temperature, its ferromagnetic ordering is broken down by thermal energy and it behaves as a paramagnet.

The **remanent magnetisation** of ferromagnetic materials results from the phenomenon of spontaneous magnetisation – that is a magnetisation which exists even in the absence of a magnetic field. Spontaneous magnetisations arise from the group-magnetic phenomenon of exchange interactions. In

these interactions all elementary magnetic moments of neighbouring electrons are aligned parallel with one another by quantum mechanical effects.

Another important property of ferromagnetic materials is that their net magnetic moment is much greater than that of paramagnetic and diamagnetic materials. This strong magnetic moment of ferromagnets arises because the magnetic exchange interactions between neighbouring atoms are so powerful that they are able to align the ferromagnetic atomic moments despite the continual disturbance of thermal agitation.

### 2.2.4 Ferrimagnetism and antiferromagnetism

The main natural magnetic minerals we shall be dealing with are special variants of ferromagnets known as ferrimagnets and imperfect antiferromagnets. Ferrimagnetic and antiferromagnetic behaviour in natural materials arises from ordering of the spin magnetic moments of electrons in the incompletely filled 3d shells of first transition series elements, particularly iron and manganese, by exchange forces.

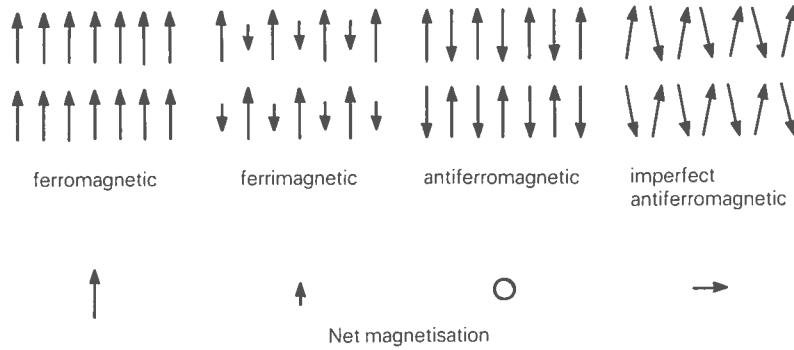
#### FERRIMAGNETISM

Ferrimagnetism is outwardly very similar to ferromagnetism; indeed it is very difficult to distinguish between the two properties even using magnetic measuring techniques. Ferrimagnetic materials carry a remanent magnetisation below a critical temperature, termed the **Curie or Néel temperature**, and like ferromagnets they are paramagnetic above this temperature.

The magnetic behaviour of ferrites (ferrimagnets) depends on their particular crystal structure. Ferrites are commonly iron oxides with a **spinel** (close-packed face-centred cubic) structure containing two types of magnetic sites which have antiparallel **magnetic moments** of different magnitudes. Therefore the elementary magnetic moments of a ferrite are regularly ordered in an antiparallel sense, but the sum of the moments pointing in one direction exceeds that in the opposite direction (Fig. 2.1) leading to a net magnetisation. The imbalance in lattice moments in ferrites may be due to different ionic populations on the two types of sites or to crystallographic dissimilarities between the two types of magnetic sites.

Ferrites have low electrical conductivities and have many industrial applications. For example, Mn and

## HYSTERESIS



**Figure 2.1** Arrangement of magnetic moments in ferromagnetic, ferrimagnetic, antiferromagnetic and imperfect antiferromagnetic materials.

Zn ferrites are used in radiofrequency cores, while Mn mixture ferrites are used in computer memories. Magnetite is an example of a natural ferrite.

### ANTIFERROMAGNETISM

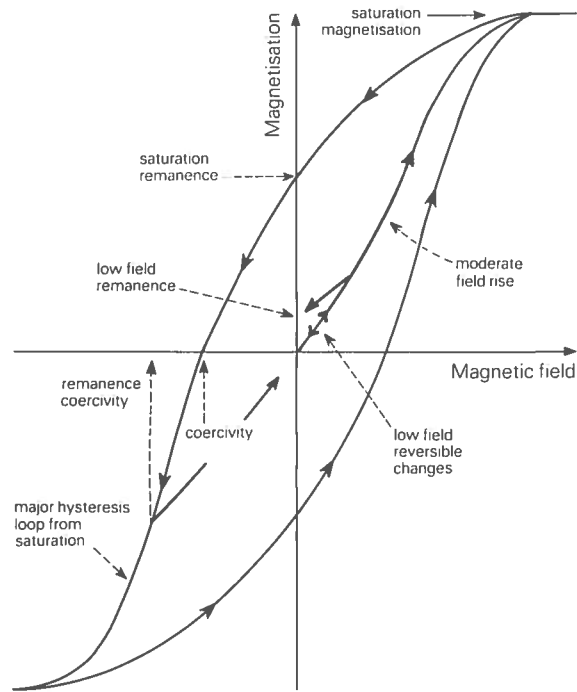
In antiferromagnetic materials there are again two magnetic sublattices which are antiparallel, but their magnetic moments are identical, and so the material exhibits zero bulk spontaneous magnetisation (Fig. 2.1). Antiferromagnetic ordering is also destroyed by thermal agitation at the Néel temperature.

Modification of the basic antiferromagnetic arrangement can, however, lead to a net spontaneous magnetisation. Two such imperfect antiferromagnetic forms are parasitic ferromagnetism which may result from heterogeneities due to impurities or lattice defects, and by spin canting, which arises from a slight modification of the true antiferromagnetic antiparallelism. Spin canting is illustrated in Figure 2.1. The mineral haematite is an example of a natural crystal with an imperfect antiferromagnetic structure caused by spin canting.

### 2.3 Hysteresis

The magnetic state of an iron bar depends on both the magnetic field to which it is subjected and the history of the bar. The field dependence of magnetisation can be described with the aid of Figure 2.2 which plots magnetisation on the vertical axis against magnetic field on the horizontal axis. Starting with an unmagnetised piece of iron it is found that its magnetisation increases slowly as a small field is applied and that if this field is removed the magnetisation returns to zero. However, on applying a stonger field, beyond a certain critical field, it is found that an

important change in magnetic behaviour takes place. The magnetisation is now no longer reversible in the straightforward way of the very low fields; instead, on removal of the field, a phenomenon referred to as **hysteresis** develops. In short, changes in magnetisation associated with the removal of the field now differ from those that occurred during the preceding increase of the field, in such a way that the magnetisa-



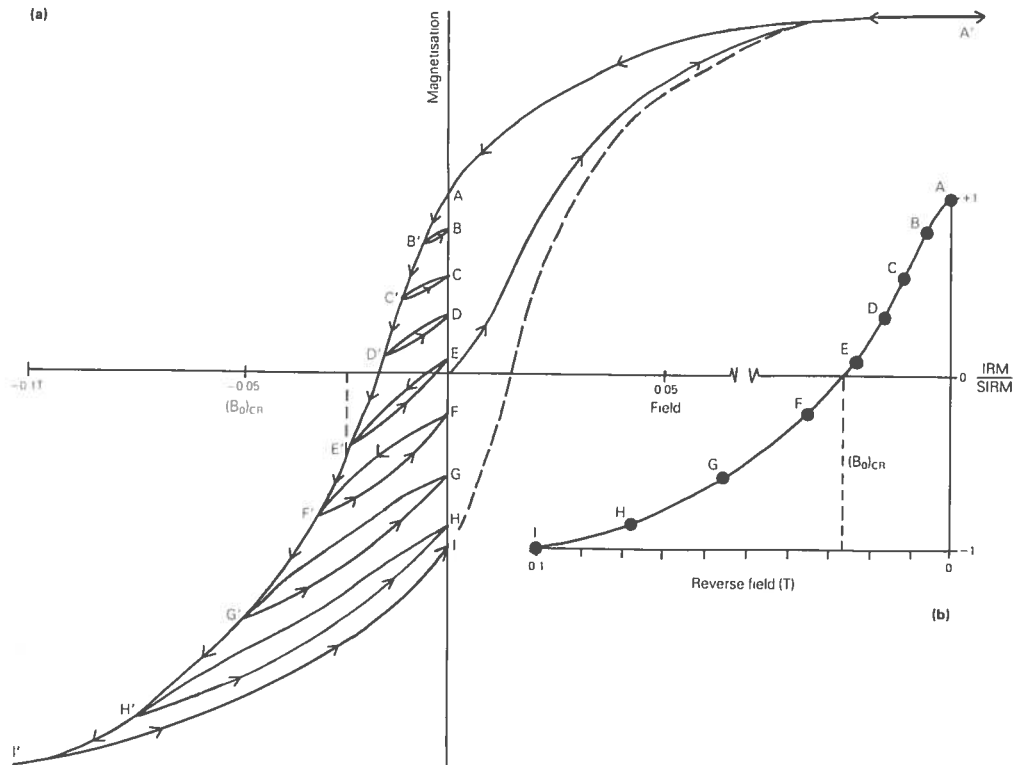
**Figure 2.2** Magnetic hysteresis loop and initial magnetisation curve showing saturation magnetisation, saturation remanence, coercivity, remanence coercivity and low field magnetisation changes.

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tion changes lag behind the field. Furthermore, it is found that on complete removal of the field, i.e. in zero field, the iron is no longer unmagnetised but has a remanent magnetisation. At moderate fields (Fig. 2.2) magnetisation rises sharply with increasing field and at still higher fields saturation of the magnetisation sets in and the magnetisation curve flattens out (Fig. 2.2). A complete hysteresis loop is obtained by cycling the magnetic field from an extreme applied field in one direction to an extreme in the opposite direction and back again.

Many of the simple magnetic properties used in later chapters to characterise materials can be classed as hysteresis parameters and the interrelationships between these properties can be best understood in terms of hysteresis loops (Fig. 2.2). Consider five of the most important hysteresis parameters. Satura-

tion magnetisation,  $M_S$ , is the magnetisation induced in the presence of a large ( $> 1$  T) magnetic field. Upon removal of this field the magnetisation does not decrease completely to zero. The remaining magnetisation is called the **saturation remanent magnetisation**,  $M_{RS}$ . By the application of a field, in the opposite direction to that first used, the induced magnetisation can be reduced to zero. The reverse field which actually makes the magnetisation zero, when measurement is made in the presence of the field, is called the **saturation coercivity** ( $B_0)_C$ . An even larger reverse field is needed to leave no remanent magnetisation after its subsequent withdrawal. This reverse field is called the **coercivity of remanence**,  $(B_0)_{CR}$ . The gradient of the magnetisation curve at the origin of Figure 2.2 is the **initial susceptibility**,  $\kappa$ .



**Figure 2.3** (a) Magnetic hysteresis changes performed by a specimen subjected to a forward saturating field ( $A'$ ) followed by a series of increasing back fields ( $B'$  to  $I'$ ). The changes take the form of a set of minor hysteresis loops ( $B'B, C'C \dots H'H$ ). The outer envelope (dashed) marks the major hysteresis loop of the material. (b) Measurements of the remanent magnetisations ( $A$  to  $I$ ) left after each magnetisation step plotted against field as a 'coercivity' curve (or remanent hysteresis curve). The reverse field at which the 'coercivity' curve crosses the zero horizontal axis is the coercivity of remanence,  $(B_0)_{CR}$ . The remanent magnetisation ( $A$ ) is the saturation remanence,  $M_{RS}$ .

## HYSTERESIS OF REMANENCE MEASUREMENTS

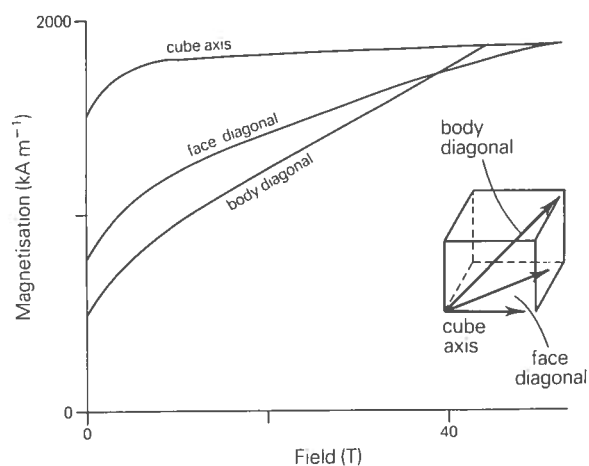
Remanent magnetisations produced by exposure to fields of various strengths are widely used in the studies described in the latter half of this book as measures of magnetic mineral concentration and of magnetic stability. A typical sequence of magnetising fields and remanence measurements is illustrated in Figure 2.3 by way of a series of minor hysteresis loops (B'B) to (H'H). In our experiments reported in Chapters 8–12 and 16 an initially unmagnetised specimen is firstly subjected to a powerful forward field which magnetises it to saturation (A' in Fig. 2.3a). On removal of the specimen from the 'saturating' field its magnetisation decreases to point A in Figure 2.3a, i.e. to its saturation remanence value. This remanence can be easily measured (6.2). Figure 2.3a plots the further effects of placing the specimen in reverse fields of increasing field strengths (B' to H'). Each time the specimen is withdrawn from the field its new remanence (B to H) is measured. The normalised remanence measurements (B/A, C/A, ... H/A) are plotted against reverse field in order to construct a 'coercivity' curve changing from +1 to -1 (Fig. 2.3b). The reverse field,  $(B_0)_{CR}$ , required to reduce the saturation to zero remanence can be found from inspection of the 'coercivity' curve. This whole process of assessing hysteresis properties through remanence measurements can be performed quite quickly as each magnetisation step takes only a fraction of a second and each remanence measurement occupies less than a minute.

## 2.4 Effects of crystal size, shape and structure

### 2.4.1 Anisotropy

The magnetic properties of crystals are modified and controlled by magnetic anisotropy. In general, any specimen will be magnetically anisotropic, that is to say its magnetic properties will vary with direction. In fact many crystal properties such as elasticity and refractive index are anisotropic, varying with direction.

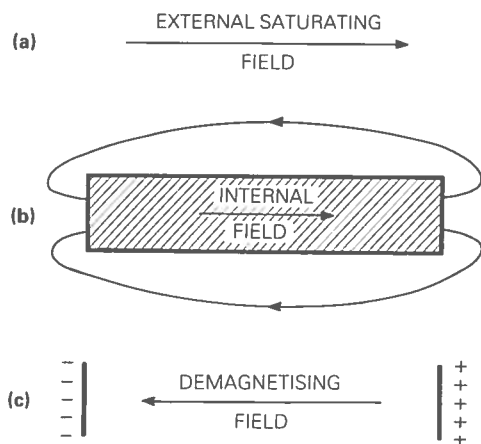
There are three forms of magnetic anisotropy. One form arises from the internal geometry of crystals, i.e. their lattice properties, and is referred to as magnetocrystalline anisotropy. The various axes of a crystal have different magnetic properties. For example in a single crystal of iron it is harder to magnetise the



**Figure 2.4** Magnetisation curves of a single iron crystal along its three principal crystallographic directions. Inset illustrates the geometry of the crystallographic axes.

crystal along certain axes (Fig. 2.4), although the saturation magnetisation is the same for all axes. Magnetocrystalline anisotropy is of considerable importance in one group of natural minerals, namely the imperfect antiferromagnets with their low spontaneous magnetisations. In these minerals, such as haematite and goethite, magnetocrystalline anisotropy leads to very high coercive forces. It also leads to characteristic low temperature magnetic behaviour as a result of extreme sensitivity of magnetocrystalline anisotropy to temperature. Magnetocrystalline anisotropy, along with spontaneous magnetisation and Curie temperature, is an important intrinsic magnetic property depending only on crystal structure and composition.

A second form of anisotropy is connected with the shape of magnetic bodies. A familiar example of this shape anisotropy is provided by the long, needle-like form of an ordinary magnetic compass. A compass needle is invariably magnetised parallel with its long axis as this is the easy direction of magnetisation. On magnetising a body (Fig. 2.5), magnetostatic forces produce magnetic charges on the end faces. (These concentrations of charge are what we usually regard as the poles of the magnet.) The field which would be produced by this apparent surface pole distribution acting in isolation is called the demagnetising field (Fig. 2.5c). This demagnetising field opposes the magnetisation and causes bodies to be magnetised most easily parallel to their long axes. An example of a natural mineral in which shape anisotropy is of great importance is the strongly magnetic ferrite, magnetite.



**Figure 2.5** Schematic diagram illustrating the origin of the demagnetising field in a magnetised body. An external field (a) magnetises the body (b). The field acting inside the body (b), is modified by the demagnetising field (c), i.e. by the field which would be produced by the apparent surface pole distribution, caused by the magnetisation. The internal demagnetising field may be viewed as the internal field which would result from replacing the magnetised specimen by a surface distribution, or array of north and south monopoles which would produce an identical field pattern to that of the magnetised specimen.

A third form of magnetic anisotropy is referred to as strain anisotropy. It may be induced by mechanical stress through the phenomenon of magnetostriction. Magnetostriction results in an alteration of the size of a magnetic specimen when it is subjected to a magnetic field. Conversely, an inverse magnetostrictive effect (the magnetic equivalent of the piezo-electric effect) occurs when stress is applied to a magnetic specimen and its magnetic properties are altered. It arises from the distortion of the crystal lattice and may be viewed as a modification of crystal-line anisotropy, although it is usually treated as a separate effect.

#### 2.4.2 Domains and domain walls

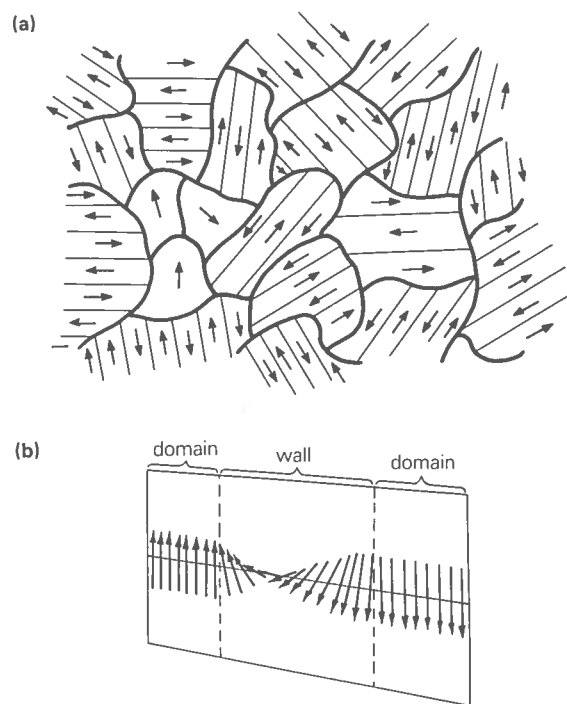
The hysteresis properties of ferromagnets are largely related to the arrangements of magnetic domains. Consequently, magnetic domains play an important role, along with anisotropy, in controlling the magnetic properties of natural magnetic materials (Dunlop, 1981).

The concept of magnetic domains was proposed by Weiss (1907) in order to explain how a material with spontaneous magnetisation can exist in a demagnet-

ised state. He suggested that the material could be split up into many domains, or regions, each spontaneously magnetised in one direction, and that the domains might be magnetised in different directions (as illustrated in Fig. 2.6a) so that the sum of the domain magnetisation could be zero. Bloch (1930) later suggested that the magnetic domains were separated by zones of finite thickness. These finite boundary regions, illustrated schematically in Figure 2.6b, have become known as domain or Bloch walls.

The reason why magnetic domains form is that they produce a state of lower total energy. They achieve this state by establishing a balance between various competing energies. The most advantageous balance is achieved by domains of about one micrometre in size.

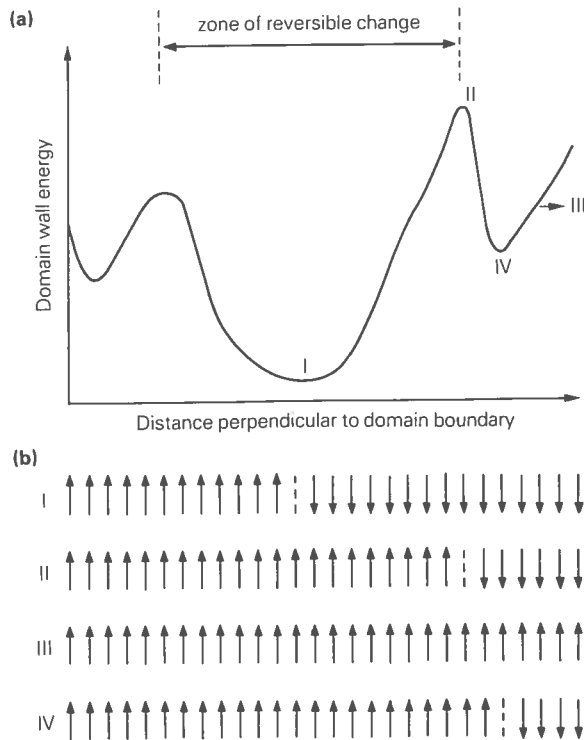
The thickness of domain walls is also a compromise between opposing influences. In this case the balance of energies leads to a zone of about 100 atoms, some  $10^{-8}$  to  $10^{-7}$  m thick, within which the direction of the magnetic spins changes continuously from that of one domain to that of the adjacent domain (Fig. 2.6b).



**Figure 2.6** (a) Domain arrangement in a polycrystalline specimen. (b) Progressive rotation of spins through a  $180^\circ$  domain wall.

### 2.4.3 Multidomain behaviour

The magnetisation curves and hysteresis properties of large **multidomain** grains can be satisfactorily explained in terms of the movements of domain walls (Fig. 2.7). On the application of an external field to a large multidomain grain, domain wall translations will take place by favouring the growth of domains with a magnetisation component in the direction of the applied field. The induced magnetisation will change as the field is slowly increased and the boundary walls move from their minimum energy positions, e.g. position I in Figure 2.7. The initial magnetisation changes will be a reversible function of field. Eventually however, the boundary translations will reach positions such as (II) in Figure 2.7 where their equilibrium is unstable and the boundaries will move spontaneously, with discontinuous and irreversible changes in magnetisation to new equilibrium positions such as (IV). Further reversible and irreversible changes will continue with any further



**Figure 2.7** Domain wall energy as a function of position. (a) Domain wall energy depends on the interaction of the wall with local crystal defects and imperfections. (b) Schematic diagram of spin arrangements for four positions of the wall.

field increases (Fig. 2.7). On removal of the external field the boundary walls may be trapped as they return towards their initial locations in local energy minima such as (IV).

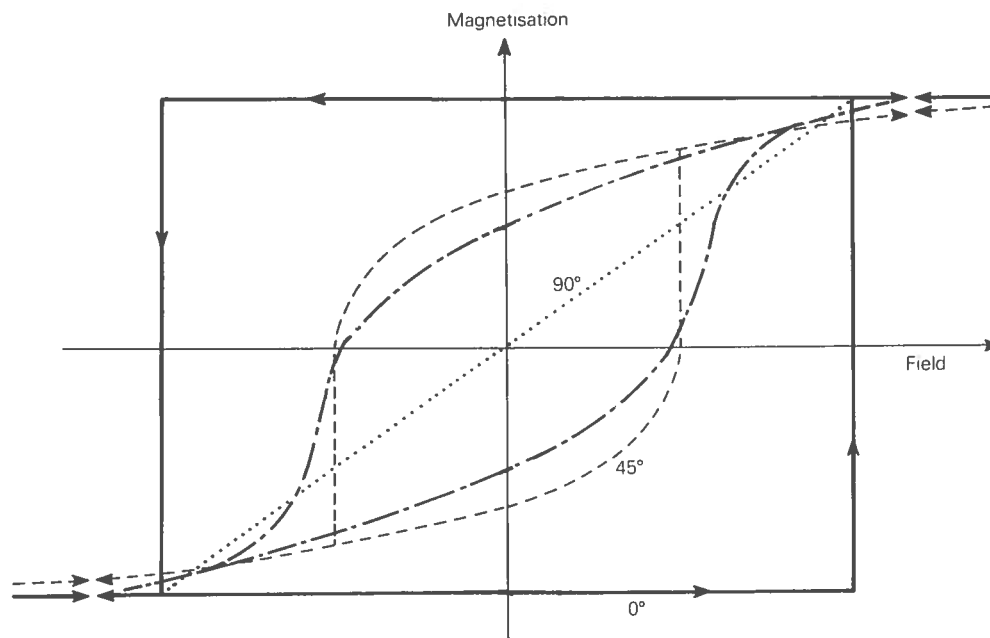
It is in this way, by the trapping of domain walls, that a remanent magnetisation can arise from the application of a magnetic field to a multidomain grain. Jumps out of the local traps cannot occur until sufficiently strong fields are applied. Irreversible domain wall movements are known as Barkhausen jumps. In specimens containing many domains the boundary movements merge and the discontinuous nature of the magnetisation changes is blurred to produce smooth hysteresis curves. By applying sufficiently strong magnetic fields, magnetisation changes are also brought about by the twisting of domain magnetisations into the applied field direction. Such twisting corresponds to the approach to saturation in the hysteresis loop of Figure 2.2. A multidomain grain is finally saturated when all the domain magnetisations are aligned in the applied field direction.

### 2.4.4 Single-domain behaviour

The magnetic properties of single-domain grains are quite different from those of multidomain grains since domain wall motions do not play a rôle in their magnetisation cycle. The magnetic remanence of single-domain grain assemblages is much higher and more stable than that of multidomain grain assemblages and there are also clear differences in their hysteresis properties.

The absence of domain walls leads to characteristic, single-domain hysteresis loops. The shape of the loop of an individual single-domain grain depends on the orientation of the grain with respect to the applied field. For example, the hysteresis loop of a single-domain grain with its easy magnetisation direction (long axis) parallel to the applied field will have the rectangular shape of the heavy line in Figure 2.8. The magnetisation simply flips through  $180^\circ$  when a field exceeding a critical field, called the coercive force, is applied in the direction opposite to that of the magnetisation. In the case of a single-domain grain with its easy magnetisation direction perpendicular to the applied field the hysteresis loop has the completely reversible form of the dotted line in Figure 2.8. On application of a field the magnetisation turns towards the field direction, but it returns to its original 'easy' axis direction perpendicular to the field direction on

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**Figure 2.8** Calculated magnetisation curves for single-domain grains. The solid, dashed and dotted curves plot magnetisation changes for grains with their long axes orientated at  $0^\circ$ ,  $45^\circ$  and  $90^\circ$  to that of the applied field. The dashed and dotted curve shows the calculated hysteresis loop of a collection of grains orientated at random (after Stoner & Wohlfarth 1948).

removal of the field. On application of a field in excess of the coercive force the magnetisation swings completely into the field direction. The dashed line of Figure 2.8 depicts the hysteresis changes of a grain with its easy axis directed at  $45^\circ$  to the field direction. In most natural samples containing single-domain grains we are dealing with assemblages with random orientations of their easy axes. The net hysteresis loop for such random assemblages takes on the modified form of the dashed and dotted curve in Figure 2.8.

### 2.4.5 Superparamagnetism

When ferro- or ferrimagnetic grains are extremely small, about  $0.001\text{--}0.01\ \mu\text{m}$  in diameter, they have thermal vibrations at room temperature which have energies of the same order of magnitude as their magnetic energy. As a consequence of this equivalence of energies these ultrafine-grained magnetic materials do not have a stable remanent magnetisation and do not exhibit hysteresis as their magnetisation is continually undergoing thermal reorientation. In the presence of an applied field they do, however, have an

overall magnetic alignment, i.e. an apparent magnetisation.

The type of behaviour these ultrafine grains exhibit is termed **superparamagnetic** (Néel 1955, Creer 1959, Vlasov *et al.* 1967). It is similar to, but much stronger than, paramagnetic behaviour. It is interesting that the susceptibility of superparamagnetic grains turns out to be much greater than that of an equivalent amount of mineralogically comparable stable single-domain or multidomain grains (Bean & Livingston 1959). This means that the presence of a small proportion of superparamagnetic grains in a natural sample can have an important effect on its susceptibility.

Superparamagnetic behaviour strongly depends on temperature. Indeed, if grains that behave superparamagnetically at room temperature are cooled sufficiently they will exhibit the usual ferro- or ferrimagnetic properties of **stable single-domain grains**.

### 2.4.6 Critical grain sizes

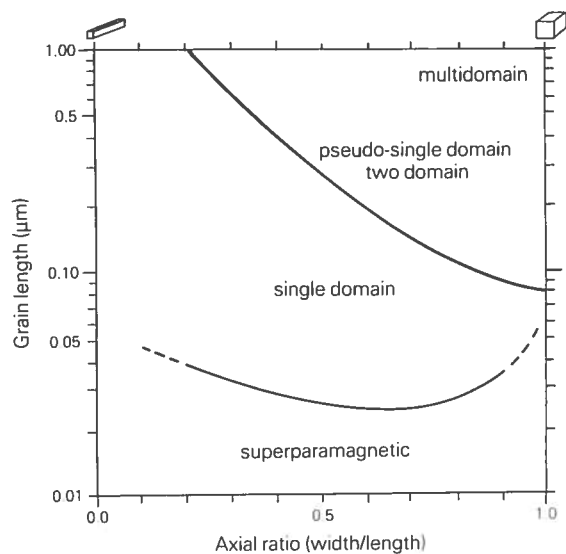
There are two important magnetic grain-size boundaries. These are (a) the division between ultra-



fine superparamagnetic grains and small stable single-domain grains and (b) the division between multidomain and stable single-domain grains.

Figure 2.9 illustrates the dependence of these critical grain sizes for magnetite on grain shape. The superparamagnetic/stable single-domain boundary occurs, at normal temperatures, in magnetite grains of around  $0.03 \mu\text{m}$  diameter (Dunlop 1973a). The precise limit between multidomain and single-domain behaviour is complicated to estimate. A likely boundary and its variation with grain shape is drawn in Figure 2.9. Theoretical calculations show that magnetite grains with diameters in excess of  $1 \mu\text{m}$  will certainly be multidomain (Kittel 1949). Spherical grains become multidomain at somewhat smaller sizes than elongated grains.

Haematite is found to have a much larger multi-domain/single-domain transition size than magnetite, mainly because of its lower saturation magnetisation (Chevallier & Mathieu 1943). This large critical grain size of over  $0.1 \mu\text{m}$  ensures that the great majority of haematite grains found in nature are single-domain.



**Figure 2.9** Multidomain, stable single-domain and superparamagnetic regions of magnetite grains as a function of grain length and axial ratio. A small change in grain length produces a large change in relaxation time at the superparamagnetic/single-domain boundary (data after Butler & Banerjee 1975).

## 2.5 Time dependence of magnetisation

The effects of time on magnetic phenomena are of great importance, especially when geological time-scales are involved. Changes in magnetisation with time are known as viscous changes. They can arise through a variety of effects. The most important viscosity phenomenon from our point of view is that of thermal activation (Dunlop 1973b, Mullins & Tite 1973).

In large multidomain grains thermal activation causes magnetic viscosity by exciting domain wall movements and allowing the walls to cross otherwise impenetrable barriers. Thermal agitation can also cause the magnetic moments of single-domain grains to rotate from one minimum energy position to another across potential energy barriers which otherwise would be too high to allow any change in moment.

Magnetic viscosity can lead to either the growth or the loss of magnetisation. A viscous sample stored in a magnetic field will increase its magnetisation and may even acquire a **viscous remanent magnetisation**. Loss of viscous remanence can be brought about by leaving a viscous sample in a zero field environment. In many cases viscous magnetisation changes are found to be proportional to the logarithm of time.

## 2.6 Grain interactions

If magnetic grains lie close to each other then magnetostatic interaction can arise between them and modify their overall magnetic behaviour. Such magnetostatic grain interactions tend to lower bulk coercivity (Davis & Evans 1976). Indeed coercivity is found to decrease regularly with increased packing, where packing is defined as the fraction of the total volume occupied by magnetic particles. The magnetisation and demagnetisation curves of magnetic assemblages are also altered by interactions. Magnetism tends to be made more difficult by grain interactions whereas demagnetisation tends to become more easy. Another example of the effect of grain interactions is that the critical grain size of the multi-/single-domain boundary is increased by interactions because of the change in magnetostatic energy. Finally, the susceptibility of a magnetic assemblage may be lowered by magnetic interactions, particularly with interactions which involve superparamagnetic grains.

## 2.7 Summary

All magnetic effects can be explained by the flow of current. On the atomic scale small circulating currents are referred to as spin, electron spin being the most important cause of magnetic phenomena in 'natural materials. Atoms in which more electrons spin one way than the opposite way behave like small magnets. The electron spins of most materials are paired or continually disordered by thermal agitation so that they only give rise to the relatively weak magnetic effects of diamagnetism and paramagnetism. Atomic magnetic moments can, however, be aligned in some crystals by quantum mechanical exchange energy forces giving rise to strong spontaneous magnetisations. Such ferromagnetic or ferrimagnetic materials can carry a remanence, i.e. retain a magnetisation even in the absence of an applied field, and they can exhibit magnetic hysteresis properties.

Large crystals of these ferro- and ferrimagnetic materials usually split up into domains in such a way as to reduce their overall magnetisation. The crystals can easily be magnetised but they lose their induced magnetisation on removal of the magnetising field.

Small grains of the same materials, too small to allow the formation of domain walls, always have strong magnetisations and make excellent permanent magnets. Even finer grains, however, are poor magnets as thermal agitations continually switch their magnetisations around.

## Further reading

### *General books*

- Lorrain and Corson 1978. *Electromagnetism: principles and applications*.  
 Chikazumi 1964. *Physics of magnetism*.  
 Craik 1971. *Structure and properties of magnetic materials*.

### *Advanced books*

- Crangle 1977. *The magnetic properties of solids*.  
 Nagata 1953. *Rock magnetism*.  
 Bates 1961. *Modern magnetism*.

# [3]

# Natural magnetic minerals

Iron is the most abundant metal in the Universe.

Lepp 1975  
*Geochemistry of Iron*

### 3.1 Iron and its abundance

Iron, the pre-eminent seat of magnetism in natural minerals (Section 2.2.4), is the fourth most abundant element in the Earth's crust. Consequently it is an important constituent of the majority of rocks found at the Earth's surface. Along with the commonest crustal metal, aluminium, it combines with the two most plentiful crustal elements, oxygen and silicon, to build up many of the common rock-forming minerals (Table 3.1).

The carriers of the magnetic properties of rocks are the more or less pure oxides of iron such as magnetite, titanomagnetite, haematite and maghaemite.. These iron oxides make up only a few percent of the volume of rocks and in most rocks they are well dispersed

amongst felsic minerals. Rock magnetic properties largely depend on these strongly magnetic iron oxides. However, if they happen to be unusually scarce then the iron sulphides or manganese oxides may become important. The weak paramagnetism of silicate or hydroxide minerals containing  $Fe^{2+}$ ,  $Fe^{3+}$  or  $Mn^{2+}$  ions is generally swamped by the stronger magnetism of the less abundant iron oxides, but it can become noticeable in special situations.

### 3.2 Iron oxides

The iron oxides can be treated as ionic crystals that consist of an oxygen framework with cations in the

**Table 3.1** Major minerals of the Earth's continental crust.

	Mineral	Igneous continental crust %	Chemical formulae
normally Fe-free	plagioclase	42	$NaAlSi_3O_8 - CaAl_2Si_2O_8$
	K-feldspar	22	$KAlSi_3O_8$
	quartz	18	$SiO_2$
Fe-bearing	amphibole	5	$NaCa_2(Mg, Fe, Al)_5Si_8O_{22}(OH)_2$
	pyroxene	4	$Ca(Mg, Fe, Al)(Al, Si)_2O_6$
	biotite (chlorite)	4	$K(Mg, Fe)_3AlSi_3O_{10}(OH)_2$
	magnetite, ilmenite	2	$Fe_3O_4, FeTiO_3$
	olivine	1	$(Mg, Fe)_2SiO_4$

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interstices. In studies of natural magnetic minerals two main groups are of interest. One group consists of minerals such as magnetite which crystallise with a spinel structure, while the other group is made up of minerals such as haematite which crystallise with a corundum structure.

3.2.1 The spinel group

A large number of oxide minerals crystallise with the spinel structure as it is an extraordinarily flexible structure in terms of the cations it can accept. The spinel unit cell is a face-centred cube. The oxide spinels contain 32 oxygen ions in the unit cell which form a nearly cubic close-packed framework, the cations occupying 16 octahedral sites and 8 tetrahedral sites within the oxygen framework. In spinels the cation sites are fixed whereas the positions of the 32 oxygen sites can vary. The entire oxygen framework can expand or contract in size in order to accommodate cations of various radii. This great flexibility of the oxygen framework allows a large number of elements to occur as important cations in natural oxide spinels or for vacancies to occur in the spinel lattice.

MAGNETITE (Fe<sub>3</sub>O<sub>4</sub>)

Magnetite is a very common magnetic mineral. It is found in the vast majority of igneous rocks and many metamorphic and sedimentary rocks and is one of the most abundant and ubiquitous of oxide minerals. It has the cubic inverse spinel structure (Table 3.2) and is ferrimagnetic (Néel 1948). The unit cell has eight tetrahedral sites filled with Fe<sup>3+</sup> cations and sixteen octahedral sites, half of which are filled with Fe<sup>3+</sup> cations and half with Fe<sup>2+</sup> cations. The magnetite Curie temperature of 580 °C corresponds to a transition from ferrimagnetic ordering to disorder. The transition is accompanied by other physical changes such as a maximum in the coefficient of thermal expansion and the specific heat. At low temperatures, near -150 °C, magnetite undergoes another magnetic transition (Verwey & Haayman 1941) involving a decrease in crystallographic symmetry and an associated change in electrical conductivity.

ULVOSPINEL (Fe<sub>2</sub>TiO<sub>4</sub>) AND THE TITANOMAGNETITES

Ulvospinel has the same inverse spinel structure as magnetite but a different composition (Table 3.2). Ti<sup>4+</sup>

Table 3.2 Spinel group iron oxides.

		a (Å)	
magnetite	Fe <sup>3+</sup> [Fe <sup>2+</sup> Fe <sup>3+</sup> ] O <sub>4</sub>	8.396	I
magnesioferrite	Fe <sup>3+</sup> [Mg <sup>2+</sup> Fe <sup>3+</sup> ] O <sub>4</sub>	8.383	I
jacobsite	Fe <sup>3+</sup> [Mn <sup>2+</sup> Fe <sup>3+</sup> ] O <sub>4</sub>	8.51	I
chromite	Fe <sup>2+</sup> [Cr <sub>2</sub> <sup>3+</sup> ] O <sub>4</sub>	8.378	N
hercynite	Fe <sup>2+</sup> [Al <sub>2</sub> <sup>3+</sup> ] O <sub>4</sub>	8.135	N
ulvospinel	Fe <sup>2+</sup> [Fe <sup>2+</sup> Ti <sup>4+</sup> ] O <sub>4</sub>	8.536	I

a = Cell edge.  
 N = Normal cation distribution X[Y<sub>2</sub>] O<sub>4</sub> where [ ] indicates octahedral cations.  
 I = Inverse cation distribution Y[XY] O<sub>4</sub>.

occupies half of the octahedral sites, which are filled by Fe<sup>3+</sup> in magnetite. Charge balance is maintained in ulvospinel by Fe<sup>2+</sup> filling all the remaining cation sites. This arrangement means that ulvospinel has the chemical formula Fe<sub>2</sub> TiO<sub>4</sub> and is antiferromagnetic, having eight Fe<sup>2+</sup> cations on the octahedral sites, eight Fe<sup>2+</sup> cations on the tetrahedral sites and a resulting net moment of zero. Solid solutions between magnetite and ulvospinel are commonly called titanomagnetites (Fig. 3.1). Variations in the unit cell size parameters 'a' and the Curie temperature along the titanomagnetite series are shown in Figure 3.2. Notice how the Curie temperature falls with increasing titanium content. The saturation magnetization similarly falls with increasing titanium content owing to the reduced exchange interactions, as does the susceptibility of single-domain titanomagnetite grains (Fig. 3.3). However, for multidomain titanomag-

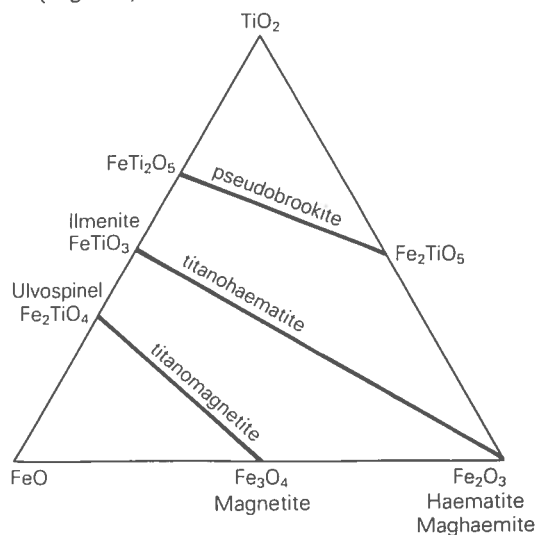
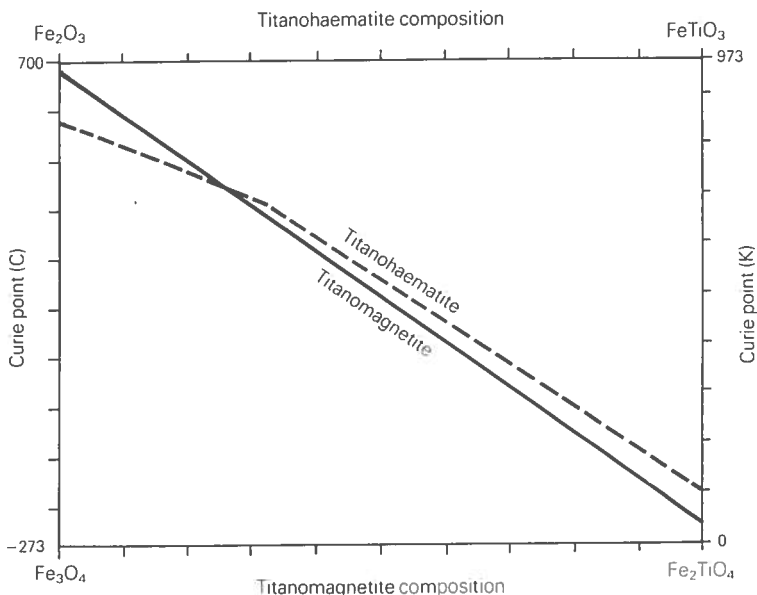


Figure 3.1 Ternary phase diagram of iron and titanium oxides showing the solid solution series.



**Figure 3.2** Variation in Curie temperature with composition in the titanomagnetite (solid line) and titanohaematite (dashed line) solid solution series.

magnetites, which are more common in nature, the susceptibility changes little with composition (Fig. 3.3). The Curie temperature also falls with inclusion of Mg, Ca, Al, Cu, V and Si impurities in the spinel structure. Inclusion of 10% aluminium, for example, reduces the Curie temperature to 535 °C (Pouillard 1950).

**MAGHAEMITE ( $\text{Fe}_2\text{O}_3$ )**

Maghaemite is an extreme example of a cation-deficient spinel. It has the same chemical composition as haematite (see below) but the spinel structure of magnetite. Maghaemite's stability and structure are not well determined. A possible structural formula is  $\text{Fe}^{3+}[\text{Fe}^{3+}_{1/3}\square_{2/3}]_2\text{O}_4$ . Maghaemite can also contain some structural hydroxide; indeed it forms most readily in the presence of water. A characteristic property is that it inverts on heating above about 300 °C to haematite. On account of this instability its Curie temperature cannot be measured exactly. Impurities such as Na and Al stabilise the maghaemite structure and decrease its Curie temperature. In addition to being an important natural magnetic mineral maghaemite is widely used in the magnetic tape industry.

**TITANOMAGHAEMITES**

Titanomaghaemites have spinel structures occupying the region between the magnetite-ulvospinel and haematite-ilmenite join in the ternary diagram of

Figure 3.1. Their chemical composition and hence their location on the ternary diagram can be conveniently expressed in terms of two parameters. One parameter, called *x*, expresses the Fe : Ti ratio; the other parameter called *z*, indicates the degree of oxidation. Natural titanomaghaemites can form above 1000 °C by solid solution and below 600 °C by metastable oxidation.

**3.2.2 The corundum group**

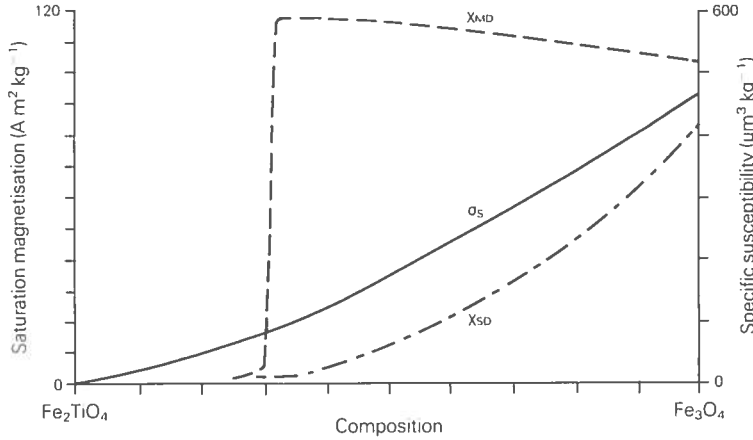
The corundum group unit cell is rhombohedral. Haematite and ilmenite form a solid solution series of rhombohedral minerals. In haematite all the cation layers are made up of  $\text{Fe}^{3+}$  ions whereas in ilmenite  $\text{Fe}^{2+}$  layers alternate with  $\text{Ti}^{4+}$  layers.

**HAEMATITE ( $\alpha\text{Fe}_2\text{O}_3$ )**

Haematite is a significant magnetic mineral in oxidised igneous rocks and sediments formed in oxidising conditions. When present as fine grains haematite has a distinctive blood-red colour.

The haematite ( $\text{Fe}_2\text{O}_3$ ) structure can be thought of as being made up of tetrahedral  $\text{Fe}-\text{O}_3-\text{Fe}$  packages. This description of the haematite structure is most helpful for describing its magnetic structure. The pair of iron ions of each such unit are coupled with anti-parallel spin moments, as a result of exchange (Section 2.2.3) interactions through the oxygen iron triplets. This spin arrangement gives haematite its

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**Figure 3.3** Dependence of saturation magnetisation ( $\sigma_s$ ) and susceptibility of multidomain ( $\chi_{MD}$ ) and single-domain ( $\chi_{SD}$ ) grains on titanomagnetite composition. Substitution of titanium in the magnetite lattice reduces the saturation magnetisation but increases the hardness of the magnetisation of single-domain grains.

basic antiferromagnetic (Section 2.2.4) magnetic structure.

Adjacent iron layers in the haematite structure are coupled antiferromagnetically. The spins within each layer are parallel to each other, but the spins of adjacent planes are not exactly antiparallel and so a weak net magnetic moment results. Deviations of just  $10^{-4}$  rad in the alignment of the spins (spin canting) can satisfactorily account for the net haematite magnetic moment (Dzyaloshinsky 1958). Although this imperfect antiferromagnetic structure results in a weak magnetisation the corundum structure ensures an extremely high stability. The intrinsic magnetic stability of haematite is of paramount importance in palaeomagnetic studies.

The Curie transition temperature of haematite is around 675 °C. Below room temperature another magnetic transition (Honda & Sone 1914) occurs when the spins move out of the plane of the iron atom layers. The transition occurs at -10 °C in pure synthetic crystals, but at lower temperatures in impure or imperfect crystals.

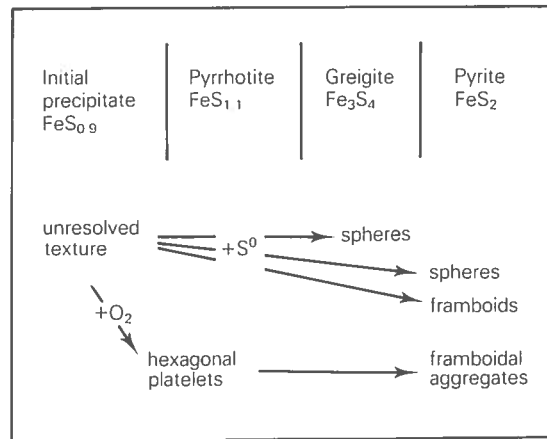
TITANOHAEMATITES

Minerals intermediate in composition between haematite ( $Fe_2O_3$ ) and ilmenite ( $FeTiO_3$ ) are commonly found in nature and are referred to as titanohaematites. In the ilmenite end-member, layers of  $Fe^{2+}$  alternate with layers of  $Ti^{4+}$  about the oxygen layers. Adjacent iron atom layers are magnetised antiparallel with each other. This alternation produces a structure which is essentially superparamagnetic (Section 2.4.5) at room temperature. Ilmenite has a Néel temperature of -218°C. In the titanohaematite

series the Curie temperature decreases fairly uniformly with increasing titanium content (Fig. 3.2). Intermediate composition titanohaematites are metastable and iron-enriched phases may form in them. These phases can lead to self-reversal properties.

3.3 Pyrrhotite (FeS) and the iron sulphides

The next most important magnetic minerals after the iron oxides are the iron sulphides. The most magnetic of these sulphides is pyrrhotite. It is ferrimagnetic with a monoclinic structure and an approximate composition of  $FeS$ . It always contains slightly less



**Figure 3.4** Forms of iron sulphides formed in sediments. Schematic sequence suggests textures developed during sulphurisation reactions (after Jones & Bowser 1978).

iron than suggested by this chemical formula, a common natural composition being  $\text{Fe}_7\text{S}_8$ . The majority of natural pyrrhotites have compositions within the range  $\text{Fe}_7\text{S}_8$  to  $\text{Fe}_9\text{S}_{10}$ . The ordered vacancies in these pyrrhotite structures lead to inequalities in the magnetic ions on the antiferromagnetically coupled sublattices and hence to net resultant ferrimagnetic moments.  $\text{Fe}_7\text{S}_8$  has a Curie temperature of 320 °C while  $\text{Fe}_9\text{S}_{10}$  has a slightly lower Curie temperature of 290 °C. Addition of impurities, such as nickel, into the pyrrhotite lattice causes the Curie temperature to be further lowered. Pyrrhotite has rarely been found to carry a useful palaeomagnetic record of the ancient geomagnetic field, but it has a high susceptibility (Clark, 1984). Its susceptibility can cause large local anomalies of the geomagnetic field which can be most helpful in mineral prospection.

Figure 3.4 illustrates the relationships between the iron sulphides and suggests a possible iron sulphide formation sequence to be found in sediments owing to sulphurisation. The formation of such authigenic iron sulphides is more common in saline than freshwater environments (Jones & Bowser 1978), although iron sulphides may be produced in sediments of productive freshwaters when oxygen deficiencies occur. Pyrite ( $\text{FeS}_2$ ) is a common mineral and is paramagnetic (Table 3.4). Greigite ( $\text{Fe}_3\text{S}_4$ ), intermediate in composition between pyrrhotite and pyrite, has rarely been found in natural samples, occurring only as an authigenic mineral in some freshwater carbonate sediments (Dell 1972).

### 3.4 Iron hydroxides and oxyhydroxides

#### GOETHITE ( $\alpha\text{FeOOH}$ )

Goethite is yellowish brown to red in colour and has an orthorhombic structure. It is a very common mineral, typically formed as a weathering product, and is the stable iron oxide in soils of humid climates. Most goethite is antiferromagnetic, but owing to uncompensated spins produced by oxygen ion vacancies some goethite is weakly magnetic, with a Néel temperature of 120 °C. On cooling through its Néel temperature goethite can acquire a weak but stable **thermoremanent magnetisation**. On heating to higher temperatures of around 300 to 400 °C goethite dehydrates to haematite.

#### LEPIDOCROCITE ( $\gamma\text{FeOOH}$ )

Lepidocrocite is brownish in colour and orthorhombic

**Table 3.3** Magnetic properties of remanence-carrying natural minerals.

Mineral	Composition	Curie temperature (°C)	Room temperature (20°C) saturation magnetisation $M_s$ ( $\text{A m}^2 \text{kg}^{-1}$ )
magnetite	$\text{Fe}_3\text{O}_4$	585	93
ulvospinel	$\text{Fe}_2\text{TiO}_4$	-153	—
haematite	$\alpha\text{Fe}_2\text{O}_3$	675	0.5
ilmenite	$\text{FeTiO}_3$	-218	—
maghaemite	$\gamma\text{Fe}_2\text{O}_3$	~740	85
pyrrhotite	~ $\text{Fe}_7\text{S}_8$	~300	~20
iron	$\alpha\text{Fe}$	780	200
goethite	$\alpha\text{FeO.OH}$	120	~1
lepidocrocite	$\gamma\text{FeO.OH}$	-196	—
magnesioferrite	$\text{MgFe}_2\text{O}_4$	440	21
jacobsite	$\text{MnFe}_2\text{O}_4$	310	77

in structure. It is less common than goethite. It has a Néel temperature of -196 °C and so cannot carry a magnetic remanence at normal temperatures. On heating it breaks down to form maghaemite at temperatures between 250 and 350 °C.

#### LIMONITE

Limonite is a geological field term for hydrated iron oxides of poorly crystalline, amorphous character. It consists mainly of cryptocrystalline goethite or lepidocrocite. Soil scientists prefer the term ferrihydrite.

### 3.5 Other magnetic minerals

A few other naturally occurring minerals are capable of carrying a magnetic remanence.

#### IRON

Iron, the archetypal ferromagnet, is found occasionally in natural samples, although it tends to be restricted to extraterrestrial samples such as meteorites and lunar samples returned by the Apollo and Luna missions (Fuller 1974). Iron being ferromagnetic has a high saturation magnetisation and a high Curie temperature (Table 3.3). It can carry a strong remanent magnetisation. The easy magnetisation axes of iron are the  $\langle 100 \rangle$  cube axes (Fig. 2.4).

#### FERROMANGANESE MINERALS

Some ferromanganese oxides and hydroxides can carry a remanent magnetisation. The jacobsite solid solution series with end members hausmannite ( $\text{Mn}_3\text{O}_4$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) is known to be ferri-

## NATURAL MAGNETIC MINERALS

magnetic (Table 3.3). The Curie temperature decreases continuously with increasing manganese content while the saturation magnetisation rises to a maximum value at the intermediate composition of  $MnFe_2O_4$ . Jacobsite is a relatively rare mineral.

Manganese oxyhydroxides such as todorokite and birnessite may be capable of carrying a remanence when formed with well developed crystal habits (Henshaw & Merrill 1980). However, little experimental or theoretical work has been carried out on their magnetic properties and we have not found these oxyhydroxides to be remanence carriers. Authigenic ferromanganese oxides and hydroxides form as crusts or nodules in freshwater or marine environments (Murray 1876). Manganese-rich oxyhydroxides with crystalline habits tend to be more abundant in deep-sea environments. Much of the material in lacustrine deposits is poorly crystalline or amorphous and is paramagnetic not ferrimagnetic.

### PARAMAGNETIC MINERALS

Iron- and manganese-bearing minerals not mentioned above tend to be incapable of carrying a magnetic remanence, at least at normal temperatures, and to be paramagnetic. Their failure to exhibit spontaneous magnetisation arises because their crystal structures are not conducive to positive exchange interactions, holding the iron or manganese ions apart at inappropriate distances or crystal geometries. Table 3.4 lists the paramagnetic susceptibilities of a number of common iron minerals. The susceptibility of these paramagnetic minerals simply depends on the number of free electrons, that is, it depends directly on the number of iron or manganese ions per gram of material.

## 3.6 Formation of natural magnetic minerals

### 3.6.1 Igneous rocks

The cooling and crystallisation of hot molten rock, called **magma**, leads to the formation of bodies of igneous rock. Magma that emerges at the Earth's surface gives rise to lava flows or, when violently ejected, to lava fountains and ash clouds. The rapid cooling of lava and ash produces fine grained volcanic rock. Magma that remains within the Earth cools slowly to form coarse grained plutonic rocks. Nearly all igneous rocks are made up of various combinations of the seven common silicate minerals of Table 3.1, with iron oxides as a small but ubiquitous accessory component. Rocks such as granites with a lot of silica are termed acidic. They consist mostly of quartz and feldspar. Basic rocks, poor in silica, are largely made up of feldspar, pyroxene and olivine crystals. Basic rocks tend to be darker in colour than acidic rocks and to contain higher concentrations of the iron oxides.

In many igneous rocks magnetite has the perfect shape and regular outline of early formed crystals. In others it is found embedded in the ground mass, having been one of the last minerals to crystallise out of the parent magma. Magnetite crystallising directly from cooling magma is generally titanium-rich. It can be produced by alteration of iron-bearing silicates and is then found as exsolved rods and as reaction rims. It often occurs with ilmenite as exsolution lamellae formed by subsolidus oxidation of titanomagnetite. Haematite is less common than magnetite and titanomagnetite in igneous rocks. When present it normally occurs as finely disseminated pigment giving the rock

**Table 3.4** Specific susceptibilities of various minerals.

Remanence-carrying minerals ( $10^{-8} \text{ m}^3 \text{ kg}^{-1}$ )		Other iron-bearing minerals ( $10^{-8} \text{ m}^3 \text{ kg}^{-1}$ )		Other minerals and materials ( $10^{-8} \text{ m}^3 \text{ kg}^{-1}$ )	
iron ( $\infty \text{Fe}$ )	$2 \times 10^7$	olivines ( $\text{Mg, Fe}_2\text{SiO}_4$ )	1→130	water ( $\text{H}_2\text{O}$ )	-0.9
magnetite ( $\text{Fe}_3\text{O}_4$ )	$5 \times 10^4$	amphiboles ( $\text{Mg, Fe, Al}$ silicates)	16→100	halite ( $\text{NaCl}$ )	-0.9
maghaemite ( $\text{Fe}_2\text{O}_3$ )	$4 \times 10^4$	siderite ( $\text{FeCO}_3$ )	~100	quartz ( $\text{SiO}_2$ )	-0.6
pyrrhotite ( $\text{Fe}_7\text{S}_8$ )	$\sim 5 \times 10^3$	pyroxenes ( $\text{Mg, Fe}_2\text{Si}_2\text{O}_6$ )	5→100	calcite ( $\text{CaCO}_3$ )	-0.5
ilmenite ( $\text{FeTiO}_3$ )*	~200	biotites ( $\text{Mg, Fe, Al}$ silicates)	5→ 95	feldspar ( $\text{Ca, Na, K, Al}$ silicate)	-0.5
lepidocrocite ( $\text{FeOOH}$ )*	70	nontronite (Fe-rich clay)	~ 90	kaolinite (clay mineral)	-2
goethite ( $\infty \text{FeOOH}$ )	70	chamosite (Oxidised chlorite)	~ 90	montmorillonite (clay)	~5
haematite ( $\text{Fe}_2\text{O}_3$ )	60	epidote ( $\text{Ca, Fe, Al}$ silicate)	~ 30	illite (clay mineral)	~15
		pyrite ( $\text{FeS}_2$ )	~ 30	plastic (e.g. perspex, PVC)	~-0.5
		chalcocopyrite ( $\text{CuFeS}_2$ )	~ 3		

\* Only remanence carrying at temperatures well below room temperature.



a characteristic red colour. Pyrrhotite is uncommon in igneous rocks. Limonite and goethite occur as secondary minerals, produced by weathering of iron silicates and oxides.

#### BASALTS

The high magnetic concentrations and small grain sizes of these basic volcanic rocks make them ideal for palaeomagnetic remanence studies of the history of the geomagnetic field (Ch. 13). Consequently their magnetic mineralogy as well as their remanent magnetisation have been studied in great detail. Basalts typically contain between 2 and 6% iron oxide grains. Sea floor basalts have been rapidly quenched and so they generally contain homogeneous titanium-rich titanomagnetites. They are also often found to contain titanomaghaemites, formed by low temperature oxidation in the presence of water. Many continental basalts are found to have been subjected to high temperature oxidation, which can have completely altered the original mineral magnetic content they acquired during crystallisation. High temperature oxidation ( $> 600\text{ }^{\circ}\text{C}$ ) progressively alters the primary titanomagnetites first to form magnetite and ilmenite, then titanohaematite and rutile and finally pseudobrookite. Oxidation at somewhat lower temperatures ( $400\text{--}600\text{ }^{\circ}\text{C}$ ) tends to produce titanomaghaemite. High temperature oxidation is related to volatile accumulation and is often pronounced in the interior of subaerially extruded basalt flows. On account of their palaeomagnetic importance such changes in magnetic mineralogy caused by high temperature oxidation have been investigated in great detail.

#### GABBROS

Some iron ore is present in all normal gabbros, generally in the form of ilmenite, titanomagnetite or magnetite. These coarse-grained basic rocks have undergone prolonged cooling so their iron oxide grains are generally very large. Such large iron oxide grains often exhibit distinctive granular or sandwich exsolution structures (Haggerty 1976). Gabbros make up a substantial proportion of the oceanic crust and their remanence may contribute to the magnetic anomalies found over the oceans. Titanohaematites may contribute to the magnetic anomalies found over the oceans. Titanohaematites are common in altered or weathered gabbros.

#### GRANITE

Slow cooling of granite plutons leads to the growth of large grains and the exsolution of ilmenite and titanohaematite. On the whole, granites are rather poor remanence carriers. Titanohaematite is generally the most important magnetic component of those granites which do carry a record of the ancient magnetic field. There is a tendency for the iron oxides in the more siliceous igneous rocks to be less titaniferous than those in basic or intermediate rocks.

#### 3.6.2 *Metamorphic rocks*

In the low grade metamorphism of the green-schist facies, growth of chlorite and epidote consumes the primary iron oxides. Any natural remanence or magnetic susceptibility of the original rocks will, in general, be reduced by over an order of magnitude by the chemical changes associated with green-schist metamorphism. Iron sulphides have been found to be the major magnetic minerals in some slates. At higher grades of metamorphism magnetite may form as an equilibrium product. It can only accommodate an appreciable amount of titanium in its structure at the highest grades of metamorphism, i.e. in the granulite facies. So metamorphic magnetite is generally pure, free of inclusions and found as large crystals (Rumble 1976a). The lamellar intergrowths of titanomagnetite and ilmenite, characteristic of igneous rocks, are rarely found in metamorphic rocks. Magnetite and ilmenite assemblages have been intensively studied in many metamorphic rocks as they played an important early rôle in geothermometric studies. The grain size is always coarse so the minerals tend to be multi-domain and any palaeomagnetic remanence tends to be unstable. A further palaeomagnetic difficulty in metamorphic rocks is that their fabric can distort the direction of any magnetic remanence, although pronounced direction signals such as those associated with field reversals can still be recognised. Haematite-ilmenite solid solution series members and rutile can be found in all metamorphic grades while pseudobrookite is found in rocks formed by high temperature contact metamorphism.

#### 3.6.3 *Sediments*

Red beds derive their distinctive colouring from haematite staining on their clastic particles and matrix. In addition to this red haematite pigment,

large black iron oxide grains may be found. The black grains are usually haematite, often having formed by *in situ* oxidation of detrital magnetites. The haematite pigment is clearly diagenetic in origin. Possible sources of iron for the haematite pigment of red beds include release of ferric hydroxides from clay minerals, dehydration of goethite and lepidocrocite, and diagenetic breakdown of clastic ferromagnesian particles. Black and green shales contain iron sulphides rather than iron oxides. Many red, haematite-bearing sediments have turned out to be excellent recorders of the ancient field.

Limestones, although having very low concentrations of magnetic minerals, can carry a highly stable remanent magnetisation. Detrital magnetite is often the main carrier of this remanence but both goethite and haematite can also contribute to the magnetic properties of limestones.

Ocean sediments generally contain a complex magnetic mineralogy of both titanomagnetites and titanohaematites with a wide range of oxidation states and titanium contents. The magnetic grains of most ocean sediments are considered to be detrital and to have been derived from long distance atmospheric or ocean current transport. Post-depositional low temperature oxidation can lead to the formation of authigenic titanomaghaemites which carry unstable secondary remanences, particularly in slowly deposited ( $< 3 \mu\text{m a}^{-1}$ ) sediments).

An excellent summary of the varied iron oxide and iron sulphide mineralogy to be found in lake sediment environments is given by Jones and Bowser (1978).

The oxygen content of a sediment at the time of its deposition is a very important factor in determining iron oxide mineralogy. For example sediments formed in oxygen-rich waters with little organic matter and with  $\text{Fe}^{3+} : \text{Fe}^{2+}$  ratios greater than one are generally oxidised to form red bed sediments. In contrast the iron minerals of sediments formed in water with free oxygen but under reducing conditions are protected against the influence of the oxygen and they faithfully reflect their source materials. This situation is found in many lake sediments and in some marine turbidites on account of the rapid deposition of organic remains. A further example of the strong influence of redox conditions on iron mineralogy is provided by the dissolution of iron oxide and the formation of iron sulphides in reducing conditions. Such conditions arise for instance in suboxic hemipelagic muds and sapropel sediments which accumulate in regions of reducing environment caused by high primary

production of organic matter coupled with slow bottom water circulation rates.

### 3.7 Summary

The commonest minerals of the Earth's crust, such as quartz and feldspar, are diamagnetic. The most widespread strongly magnetic minerals are the oxides of iron. Magnetite (and its close relations the titanomagnetites), maghaemites and titanomaghaemites are strong ferrimagnets and are found in a great variety of rock types. Haematite and its close relations the titanohaematites can hold very stable imperfect anti-ferromagnetic magnetisations and these iron oxide minerals are also to be found in many rocks and sediments. The next most important group of natural magnetic minerals is the iron sulphides. In particular pyrrhotite can be a strong ferrimagnet. The iron hydroxide goethite is also capable of carrying a remanence through an imperfect antiferromagnetism. Ferromanganese oxides and hydroxides can also be magnetic and can dominate the magnetic properties of natural materials from certain environments. Other iron- and manganese-bearing minerals tend to be paramagnetic and while they are unable to carry a magnetic remanence they can contribute significantly to magnetisation properties such as susceptibility.

### Further reading

#### *General journal paper*

Clark 1983. Comments on magnetic petrophysics.

#### *Advanced journal papers*

O'Reilly 1976. Magnetic minerals in the crust of the Earth.

#### *Advanced article*

Jones and Bowser 1978. The mineralogy and related chemistry of lake sediments.

#### *Advanced books*

Nagata 1953. *Rock magnetism*.

Rumble 1976. *Course notes on oxide minerals*.