Chapter 2

CRYSTAL STRUCTURE AND MAGNETISM IN FERRITE

2.1 INTRODUCTION

The mixed metal oxides with iron (III) oxides as their main constituents are known as ferrites and are the most important magnetic ceramics. The structure of a ferrite can be regarded as an interlocking network of positively charged metal ions and negatively charged divalent oxygen ions. The different arrangement of ions gives rise to various close packed structures and accordingly depends upon the crystal structure.

The structural, magnetic and electrical properties of hexagonal ferrite are strongly depend upon the synthesis condition and the site occupation of the substituted cations among five different Fe$^{3+}$ sublattices, namely octahedral (12k, 2a and 4f$_2$), tetrahedral (4f$_1$) and trigonal bipyramidal (2b) of hexagonal structure [1].
2.2 CRYSTAL STRUCTURE OF M-TYPE HEXAGONAL FERRITE

M-type ferrites crystallize in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites (P6$_3$/mmc space group). There are 10 layers of oxygen atoms along the c-axis. The structure is built up from smaller units: a cubic block S, having the spinel type structure and a hexagonal block R, containing the Sr$^{2+}$ ions. The iron atoms are positioned at five crystallographically different sites of 2a, 2b, 4f1, 4f2 and 12k respectively [2-4].

A schematic M-type structural representation and the surroundings of five Fe$^{3+}$ sites are shown in Fig.2.1 [5].

---

**Fig. 2.1 Unit cell of the M-type SrFe$_{12}$O$_{19}$**

(* indicates a rotation of a block over 180° around the vertical c-axis)
The structure is symbolically described as RSR*S*, where R is the three layer block, two O₄ containing one SrO₃ with composition (Sr²⁺ Fe₆³⁺O₁₁²⁻) and S is a two O⁺ layer block with composition (Fe₆³⁺ O₈²⁻)²⁺, where the asterisk means that the corresponding block has been turned 180° around the hexagonal c-axis. The smaller Fe³⁺ ions are arranged in five distinct sites: three octahedral sites (12k, 2a and 4f₂), one tetrahedral site (4f₁) and one bipyramidal site (2b)¹⁶⁻¹⁷.

The unit cell contains two formula units, and can be divided into four blocks, designated as SRS*R*. The S blocks have the spinel structure, but are oriented, so that the [111] direction is parallel to the c-axis. Since the R-blocks have a rhombohedral structure, the overall symmetry of the unit cell is rhombohedral (since this has a lower symmetry), with a = 0.588 nm and c = 2.32 nm.

This rhombohedral unit cell has one third of the volume of the hexagonal unit cell and has the same symmetry. The relationship between the two unit cells is shown in Fig. 2.2.

Fig. 2.2 Relationship between rhombohedral (R) and hexagonal (H) unit cells in SrFe₁₂O₁₉ and BaFe₁₂O₁₉.
For crystallographic studies it is usually more convenient to use the smaller rhombohedral cell, though BaFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$ and similar material are often referred to as the hexagonal ferrites.

The ferrimagnetism is produced entirely by the 24 Fe$^{3+}$ ions, each of which has a magnetic moment of 5 $\mu$B. These ions occupy three kinds of crystallographic sites: tetrahedral, octahedral and fivefold coordination sites. One of the most important properties of SrFe$_{12}$O$_{19}$ is very high uniaxial magneto-crystalline anisotropy. The easy directions of magnetization are of course parallel and antiparallel to the hexagonal $c$-axis, so that a single crystal can be easily saturated along this axis.

**Table 2.1**

Crystallographic and magnetic properties for the various cation sublattices of M-type hexagonal ferrite

<table>
<thead>
<tr>
<th>Sublattices</th>
<th>Coordination</th>
<th>Block</th>
<th>Ions per f. u.</th>
<th>Spin direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>12k</td>
<td>Octahedral</td>
<td>R-S</td>
<td>6</td>
<td>Up</td>
</tr>
<tr>
<td>4f$_i$</td>
<td>Tetrahedral</td>
<td>S</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4f</td>
<td>Octahedral</td>
<td>R</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>2a</td>
<td>Octahedral</td>
<td>S</td>
<td>1</td>
<td>Up</td>
</tr>
<tr>
<td>2b</td>
<td>Fivefold</td>
<td>R</td>
<td>1</td>
<td>Up</td>
</tr>
</tbody>
</table>
2.3 MAGNETISM IN FERRITE

The origin of magnetism lies in the orbital and spin motion of electrons and how the electrons interact with each other. Atoms have magnetic moments ($\mu$) which are produced for electron spin and also for the rotation of electrons around the nucleus. The nucleus has a small magnetic moment which nevertheless is negligible as compared to the one of the electron. Electron can be imagined as a tiny circuit that is carrying a tiny magnetic moment. They respond to external magnetic field and give rise to magnetization (M) that is defined as the net magnetic dipole moment per unit volume ($v$) in the material [8-10].

$$M = \frac{\mu_{\text{total}}}{v}$$ \hspace{1cm} (2.1)

The total magnetic field inside the material (magnetic induction ‘B’) is a function of the applied external field and the magnetization.

$$B = B_{\text{ext}} + \mu_0 M$$ \hspace{1cm} (2.2)

where, $B_{\text{ext}}$ is the strength of external magnetic field and $\mu_0$ is the permeability of free space.

The magnetic field strength ‘H’ depends only on the strength of external magnetic field:

$$H = \frac{B_{\text{ext}}}{\mu_0}$$ \hspace{1cm} (2.3)

Putting the value of ‘$B_{\text{ext}}$’ in equation (2.2)

$$B = \mu_0 (H + M)$$ \hspace{1cm} (2.4)

The relationship between magnetization ‘$M$’ and the applied field ‘$H$’ is defined as

$$\chi = \frac{M}{H}$$ \hspace{1cm} (2.5)
where, ‘χ’ is the magnetic susceptibility of the material which is a measure of the increase in magnetic moment caused by external field.

### 2.4 MAGNETIC MATERIALS

Magnetic materials can be divided into two groups soft and hard magnetic materials. The soft magnetic materials are those materials which are magnetized and demagnetized easily while the hard magnetic materials are those which are difficult to magnetize and demagnetize.

The hard magnetic materials have high coercivity, because the high coercivity resists the magnetization action. The basic difference of two types of permanent magnets was described on the basis of hysteresis loop. The soft magnetic materials exhibit a narrow hysteresis loop, whereas; the hard magnetic materials show a broad hysteresis loop. In the narrow hysteresis loop magnetization follows the variation of the applied field without significant loss. The broad hysteresis loop shows the magnetic energy that can be stored in the materials [11].

#### 2.4.1 Soft magnetic materials

Soft magnetic materials can be easily magnetized and demagnetized. They retain their magnetization only in presence of a magnetic field. They show a narrow hysteresis loop, so that the magnetization follows the variation of applied field nearly without hysteresis loss [12]. They are used to enhance the flux, produced by an electric current in them. The quality factor of a soft magnetic material is to measure of its permeability with respect to the applied magnetic field. The other main parameter is the coercivity, saturation magnetization and the electrical conductivity. An ideal soft magnetic material would have low coercivity (Hc), a very large saturation
magnetization (Ms), zero remanence (Mr), zero hysteresis loss and very large permeability [13, 14]. Few important soft magnetic materials are Fe, Fe-Si alloys, soft ferrites (MnZnFe₂O₄), silicon iron etc.

2.4.2 Hard magnetic materials

Hard Magnetic materials also called as permanent magnets are used to produce strong field without applying a current to coil. Permanent magnets require high coercivity, so they should exhibit a strong net magnetization and is stable in the presence of external fields, which requires high coercivity. In hard magnetic materials uniaxial magnetic anisotropy is necessary and the following magnetic properties are required [15]. Important properties of hard magnetic materials are as below:

I) **High coercivity**: The coercivity, also called the coercive field of a ferromagnetic material is the intensity of the applied magnetic field required to reduce the magnetization of that material to zero after the magnetization of the sample has been driven to saturation. Coercivity is usually measured in oersted or ampere/meter units and is denoted Hc. Materials with high coercivity are called hard ferromagnetic materials, and are used to make permanent magnets [16].

II) **Large magnetization**: The process of making a substance temporarily or permanently magnetic, as by insertion of the material in a magnetic field.

III) **Rectangular hysteresis loop**: A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). Hard magnetic materials have rectangular hysteresis loop [17]. Hard magnetic material has the wide hysteresis loop due to strong magnetization as shown in the Fig. 2.3.
Fig. 2.3 Hysteresis loop for hard magnetic materials

2.5 CLASSIFICATION OF MAGNETIC MATERIALS

All substances display certain magnetic property at all temperatures regardless of their composition and strength. Different kinds of magnetism are present in the solids. According to their magnetic properties magnetic materials are classified into five groups.

1) Diamagnetic (e.g. MgO)
2) Paramagnetic (e.g. Gd₂O₃)
3) Ferromagnetic (e.g. EuO)
4) Anti-ferromagnetic (e.g. Cr₂O₃)
5) Ferrimagnetic (e.g. Fe₃O₄)
2.5.1 Diamagnetic materials

In a simple term, a solid is said to be diamagnetic if it is repelled by a permanent magnet. Diamagnetism is a property of closed electron shells and is a non-co-operative magnetism characterized by a weak negative, temperature independent magnetic susceptibility.

These substances do not contain any unpaired electron. The diamagnetic material is distinguished from all other by the fact that its susceptibility is negative. The diamagnetism offers through deformation of the electric charge distribution when field is applied and it disappears when the field is removed. Diamagnetic substances consist of atoms or molecules with no net angular momentum. When an external magnetic field is applied, there creates a circulating atomic current that produces a very small bulk magnetization opposing the applied field [18].

![Diagram](image)

**Fig.2.4 Diamagnetic material:**

(a) When $H=0$: $M=0$, because the atoms do not possess magnetic moment. (b) When $H = H_0$: $M = -M_0$. When a magnetic field $H_0$ is applied, the atoms acquire induced magnetic moment in a direction opposite to the applied field that results a negative susceptibility.
The diamagnetic effect in a material can be observed only if the paramagnetic effect or the ferromagnetic effect does not hide the weak diamagnetic effect. It can be understood through Fig.2.4 (a) and (b).

When a material is placed in a magnetic field, electrons in the atomic orbital’s tend to oppose the external magnetic field by moving the induced magnetic moment in a direction opposite to the external magnetic field. Due to this fact, the material is very weakly repelled in the magnetic field. This is known as diamagnetism. The induced dipole moments disappear when the external field is removed. Diamagnetism is exhibited by all common materials but so feeble that it is covered if material also exhibits paramagnetism or ferromagnetism [19].

Examples of some diamagnetic materials are gold, silver, mercury, copper and zinc [20]. Diamagnetic materials have very small negative susceptibility. Due to this fact, a diamagnetic material is weakly repelled in the magnetic field. When the field is removed, its magnetization becomes zero. In the absence of the external magnetic field, the atoms have zero magnetic moment as shown in Fig. 2.4 (a). But when an external magnetic field Ho is applied in the direction as shown in Fig.2.4 (b), the atoms acquire an induced magnetic moment in the direction opposite to that of the field.

2.5.2 Paramagnetic material

A solid is said to be a paramagnetic, if it is attracted by a permanent magnet. Ideal paramagnetism is a non co-operative magnetism that arises from atomic moments that are identical and located in isotopic surroundings, sufficiently separated from one another.
The temperature dependent susceptibility follows the Curie law

$$\chi = \frac{C}{T}$$

Here $\chi$ is the paramagnetic susceptibility, $T$ is the absolute temperature and $C$ is called the Curie constant.

Ideal paramagnetism is exception rather than the rule because the susceptibility of real systems follows the Curie-Weiss law. Curie-Weiss law behaviour employs a co-operative magnetism that can manifest itself if the thermal energy of the moments in the paramagnet is reduced sufficiently at temperatures $T<T_0$ and ordered magnetic state exists.

Examples of paramagnetic elements are aluminum, calcium, magnesium and sodium [201]. Paramagnetism is found in atoms, molecules and lattice defects possessing an odd number of electrons as the total spin of the system cannot be zero. Metals, free atoms and ions with partly filled inner shell, transition elements and few compounds with an even number of electrons including oxygen also show paramagnetism [21].

Paramagnetism occurs in materials with permanent magnetic dipole moment, such as atomic or molecular with an odd number of electrons, atoms or ions in unfilled orbital’s. Paramagnetic materials are attracted when subjected to an applied magnetic field. Paramagnetic materials also exhibit diamagnetism, but the latter effect is typically very small. These materials show weak magnetism in the presence of an external magnetic field but when the field is removed, thermal motion will quickly disrupt the magnetic alignment. These materials have very weak and positive magnetic susceptibility to an external magnetic field.
In certain materials, each atom or molecule possess permanent magnetic moment individually due to its orbital and spin magnetic moment. In the absence of an external magnetic field, the individual atomic magnetic moments are randomly oriented. The net magnetic moment and the magnetization of the material becomes zero.

When an external magnetic field is applied, the individual atomic magnetic moments tend to align themselves in the direction of externally applied magnetic field and results in to a non-zero weak magnetization as shown in Fig. 2.5 (a) and (b). Such materials are paramagnetic materials and phenomenon is called paramagnetism [20].

![Diagram showing paramagnetic material]

Fig. 2.5 Paramagnetic material

(a) Each atom possesses a permanent magnetic moment. When H=0, all magnetic moments are randomly oriented: so M=0. 
(b) When a magnetic field Ho is applied, the atomic magnetic moments tend to orient themselves in the direction of the field that results a net magnetization M=Mo and positive susceptibility.
2.5.3 Ferromagnetic material

In ferromagnetic materials, such as metallic iron, cobalt and nickel, the individual moments of the atoms or ions are strongly coupled and are more or less parallel, one to another even in the absence of magnetic field their results have a very large magnetic moments.

Ferromagnetism is a co-operative phenomenon in which there is a long-range co-linear order of all the moments in the solids. A ferromagnetic solid is spontaneously magnetized even in the absence of field. To maximize its magneto-static energy a crystalline ferromagnet divides into domains, which are spontaneously magnetized nearly to saturation but the moment of each domain is oriented so as to produce a zero net moment. An external field changes the size of the domains, enlarging those of favorable orientation at the expense of others. Thus in ferromagnetism, external field is just an agent to make evident on a macroscopic scale the ordering that exists microscopically. The spontaneous magnetization decreases with temperature and disappear at the Curie temperature $T_c$. Above $T_c$ an ideal ferromagnet becomes a paramagnet obeying the Curie-Weiss law. Both amorphous and crystalline ferromagnets are known.

Ferromagnetism appears only below a certain temperature, known as Curie temperature. Above Curie temperature, the moments are randomly oriented resulting the zero net magnetization $^{[22]}$. Examples of ferromagnetic materials are transition metals Fe, Co and Ni, but other elements and alloys involving transition or rare-earth elements are also ferromagnetic due to their unfilled 3d and 4f shells. A ferromagnetic material has spontaneous magnetization due to the alignment of its atomic magnetic moments even in the absence of external magnetic field $^{[20]}$. 


These materials have a large and positive magnetic susceptibility to an external magnetic field. They exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties after the external field is removed.

Ferromagnetism is a phenomenon of spontaneous magnetization. It has the alignment of an appreciable fraction of molecular magnetic moments in some favorable direction in the crystal. Ferromagnetism is only possible when atoms are arranged in a lattice and the atomic magnetic moment can interact to align parallel to each other as shown in Fig. 2.6.

![Parallel alignment](image)

**Fig. 2.6 Ferromagnetism**

### 2.5.4 Antiferromagnetic materials

In antiferromagnetic materials (the transition ions) adjacent metal ions are coupled with their spin anti parallel. There is always equal number of two alignments so that in the absence of magnetic field there is no resultant magnetization.

Antiferromagnetism, like ferromagnetism is characterized by long-range ordering of identical moments. But since exchange parameter ‘\( j \)’ is negative, the moments of neighbouring atoms are exactly opposite; there is
no overall spontaneous magnetization. Antiferromagnet below the Neel (ordering) temperature ‘\( T_N \)’ consists of two identical inter-penetrating sub–lattices in which the spins of one sub-lattice are oppose to those of the other. Simple anti-ferromagnetism can exist only in crystalline solids, since it is not possible to divide an amorphous system into two identical sub-lattices. Most anti-ferromagnet are insulating solids e.g. MnO, NiO, MnS etc. But antiferromagnetism is known among metal and alloys as well (Cr, \( \alpha \)-Mn etc.).

The theory of antiferromagnetism was developed chiefly by Neel in 1932. Chromium is the only element exhibiting antiferromagnetism at room temperature \(^{[22]}\). There are also materials with more than two sublattices with triangular, canted or spiral spin arrangements. Due to these facts, antiferromagnetic materials have small non-zero magnetic moment \(^{[23]}\).

They have a weak positive magnetic susceptibility of the order of paramagnetic material at all temperatures, but their susceptibilities changes in a particular manner with temperature. Antiferromagnetic materials are those in which the dipoles have equal moments, but adjacent dipoles point in opposite directions \(^{[24]}\).

Like ferromagnetic materials, these materials become paramagnetic above transition temperature, known as the Néel temperature, \( T_N \) (Cr: \( T_N \sim 37^\circ C \)). The antiparallel arrangement of magnetic dipoles in antiferromagnetic materials is the reason for small magnetic susceptibility of antiferromagnetic materials.

Antiferromagnetic materials are very similar to ferromagnetic materials but the exchange interaction between neighboring atoms leads to the anti-parallel alignment of the atomic magnetic moments as shown in Fig. 2.7.
Therefore the magnetic field cancels out and the material appears to behave in the same way as the paramagnetic material.

**Antiparallel alignment**

![Antiparallel alignment diagram]

**Fig. 2.7 Antiferromagnetism**

### 2.5.5 Ferrimagnetic materials

Several oxide magnetic materials have been found to be ferrimagnetic. These oxides possess a net resultant magnetism due to the unequal antiparallel spin moments. The ions have opposed the spin arrangement. But unlike anti-ferromagnetic materials they do not cancel each other. Therefore there is a resultant permanent magnetic moment. The best-known example is iron oxide (Fe₃O₄), which is also called magnetic iron oxide or ferrous ferrite.

Ferrimagnetism requires two or more magnetic species that are chemically different. They occupy two kinds of lattice sites in ferrimagnets producing two sub-lattices A and B as in spinels. The moments of ions in each sub-lattice are ferromagnetically coupled, but the coupling between the moments of A and B is antiferromagnetic. Since the net magnetic moments of A and B are different, there is a resultant spontaneous magnetization. The temperature dependence of ferrimagnetism is similar to that of the
spontaneous magnetization and decreases more rapidly with increasing temperature. In paramagnetic state, there is deviation from Curie-Weiss law particularly close to Curie temperature (Tc).

The magnitude of magnetic susceptibility for ferromagnetic and ferrimagnetic materials is similar, however the alignment of magnetic dipole moments is drastically different. Ferrimagnetism is only observed in compounds, which have more complex crystal structures than pure elements. These materials, like ferromagnetic materials, have a spontaneous magnetization below a critical temperature called the Curie temperature (Tc).

Ferrimagnetic materials have spin structure of both spin-up and spin-down components but have a net non-zero magnetic moment in one of these directions [23]. This magnetic moment may also be due to more than two sublattices and triangular or spiral arrangements of sublattices [23]. The magnetic moments of the atoms on different adjacent sublattices are opposite to each other as in antiferromagnetism, however, in ferrimagnetic materials the opposing moments are unequal as shown in Fig. 2.8.

---

**Antiparallel alignment**

![Antiparallel alignment](image)

*Fig 2.8 Ferrimagnetism*
The magnetic properties of most of the elements in the periodic table at room temperature are shown in Table 2.2.

Table 2.2

A periodic table showing the magnetic behaviour of each element at room temperature.
REFERENCES


[8] P. Atkin, J. D. Paula
Physical Chemistry, ed. 7th, Oxford University Press, UK, 2002; 802.


[10] L. E. Smart, E. A. Moore,
Solid State Chemistry An Introduction, 3rd ed. Taylor and Francis, New
York, USA, 2005; pp. 313.


[12] C. W. Chen,
Magnetism and Metallurgy of Magnetic materials, North Holland

[13] W. H. Yeadon, A. W. Yeadon,
Handbook of small Electric Motors, Mcgraw Hill Comp. Inc. USA, 2001.

[16] J. D. Livingston 
[18] J. D. Jackson 
[21] C. Kittel 
[22] B. D. Cullity 
[23] A. H. Morish 
[24] A. G. Guy, 