2.1 Chemical composition of ferrite:

Ferrites are ceramic ferromagnetic materials with the general chemical composition Mo\(\text{Fe}_2\text{O}_3\). A ferrite can be considered a material containing mostly iron and metal oxides which is derived from magnetite \((\text{Fe}^{2+}\text{O}.\text{Fe}^{3+}_2\text{O}_3)\) by substituting divalent metal ions in place of \(\text{Fe}^{2+}\). Trivalent metal ions like Al, Cr, Ga etc. substituting for \(\text{Fe}^{3+}\) and other valencies (+1, +4, +5 and +6) can be incorporated into the lattice by charge compensation by the appropriate change in the \(\text{Fe}^{2+}/\text{Fe}^{3+}\) ratio. In all cases the ionic radii of the substitution ion should be between about 0.5 to 1.0 Å. The most common divalent metals are from the first transition elements: Mn, Fe, Co and Ni and metal such as Cu, Zn, Mg, Cd and Ge. Trivalent Al, Cr, Ga and Mn can replace \(\text{Fe}^{3+}\) while monovalent Li and tetravalent Ti and Sn are incorporated into the lattice by the respective decrease or increase in the \(\text{Fe}^{2+}/\text{Fe}^{3+}\) ratio.

The spinel crystal structure is determined primarily by the oxygen ions lattice. The radii of the oxygen ions are several times larger than the radii of the metallic ions in the compound. Chemistry is insufficient to define the properties of ferrites; the distribution of the cations and point defects among the crystal lattice sites is of most importance.
2.2 Crystal structure of ferrite:

Ferrites have the chemical formula $M^{2+}Fe^{3+}_2O_4^{2-}$ or MoFe$_2$O$_3$, where M is a divalent metal ion, Spinel is close packed cubic structure of oxygen atom with eight formula unit per unit cell. A unit cell of the spinel lattice is represented in Fig. 2.1.

Fig 2.1: General spinel structure

Two kinds of sites available for the cations are tetrahedral (A) sites and octahedral [B] site. Tetrahedral sites which are surrounded by four oxygen ions situated at corners of a tetrahedron (A site) and octahedral site surrounded by six oxygen ions situated at corners of an octahedron (B site). In a unit cell, there are sixty-four tetrahedral sites of which eight are filled and thirty-two octahedral sites of which sixteen are filled.

There are two types of sub-cells commonly described for the spinel structure, here shown a structure A and structure B in
Fig. 2.2-a and 2.2-b respectively. Structure A shows the filling of 2 tetrahedral sites within one-eighth of the unit cell and structure B shows a filled octahedral site. The arrangement of these two cubic sub-cells in one unit cell is shown in Fig. 2.3. There are 12 filled octahedral sites not centered in the sub-cells that are also filled to give a total of 16 filled octahedral sites.

In a normal spinel structure, all the trivalent cations are located in half the octahedral sites, while all the divalent cations occupy 1/8 of the tetrahedral sites. The inverse spinel structure will be discussed with examples below.

Fig. 2.2-a: Two kinds of occupied tetrahedral sites in spinel sub-cell a. A is in yellow and O is in red

Fig. 2.2-b: Occupied octahedral site in spinel sub-cell b. B is in gray, and O is in red.

Fig. 2.3: Arrangement of structure A and B in one unit cell. Shaded one represents structure A, while white one represents B.
2.3 U parameter:

In any octant four oxygen ions form a tetrahedron. All oxygen ions are tetrahedrally surrounded by four cations, of which three are form B-site and one form A-site. In many cases the close packing of oxygen is deformed due to the presence of the metal ions of different sizes in the interstices. Then the oxygen ion moves along the body diagonal from the ideal position. The displacement of oxygen ion along the body diagonal is known as oxygen parameter ‘u’ as shown in Fig. 2.4. In ideal case u = 3/8 and in the actual case ‘u’ is slightly greater than ideal value. The values of the parameter ‘u’ can be found with the aid of X-ray or neutron diffraction.

Fig. 2.4: Surroundings of oxygen in spinel ferrite

The u parameter generally increases linearly with \((r_A-r_B)/a\), where ‘a’ is the lattice parameter and \(r_A, r_B\) are the radii of ions in the tetrahedral (A) and octahedral [B] site respectively. The local symmetry of the cation sites is cubic in the A-position and trigonal in B. The trigonal symmetry is due to both the configuration of the neighboring
cations and the distortion of the anion octahedral, if \( u \neq 3/8 \). Each of
the four diagonal belongs to just one of the cations in the primitive
cell. Hence, these cations are non-equivalent, differing in their local
symmetry axis. Each of them may be taken as representing on face
centred cubic (fcc) sub lattice with the lattice constant ‘\( a \)’. The local
symmetry of the A-site however remains cubic even if \( u \neq 3/8 \), so that,
both sub lattices represented by A-sites in the primitive cell are
mutually equivalent.

When considering some aspect for which the local symmetry is
irrelevant, all the B-position may be treated as belonging to only one
sub-lattice (octahedral) in the same way as the A-position may be
unified to form one tetrahedral or A-sub lattice. The radii of the
spheres in both types of sites are given by the expressions.

\[
\begin{align*}
    r_A &= \left( u - \frac{1}{4} \right) a \sqrt{3} - R_0 \\
    r_B &= \left( \frac{5}{8} - u \right) a - R_0
\end{align*}
\]

...2.1
...2.2

where, ‘\( r_A \)’ and ‘\( r_B \)’ are radii of the tetrahedral (A) and octahedral
[B] site cations respectively, ‘\( a \)’ is a lattice constant and ‘\( R_0 \)’ is the
radius of oxygen ion.

2.4 Magnetic interactions:

In case of ferrites there are two sites for metal ions to reside
namely tetrahedral (A) and octahedral [B] site. According to super
exchange mechanism, the three different kinds of magnetic
interactions are possible, between the metallic ions, through the
intermediate O\(^{2-}\) ions, by super-exchange mechanism,
2] B-B interaction.

In general, the magnitude of the interaction energy between the magnetic ion, Me\textsuperscript{I} and Me\textsuperscript{II} depends upon (i) the distances of the ions from oxygen ions and (ii) the angle Me\textsuperscript{I}-O-Me\textsuperscript{II} represented by the term \(\Phi\) as shown in Fig. 2.5.

![Fig. 2.5: Me\textsuperscript{I} – O - Me\textsuperscript{II} angle in ferrites.](image)

An angle of 180\(^0\) will give rise to the greatest exchange energy and the energy decreases very rapidly with increasing distances. The various possible configurations of the ions pairs in spinel ferrites with favorable distances and angle for an effective magnetic interaction as by Gorter [1] are given in Fig. 2.6. Based on the values of the distance the angle \(\Phi\), it may be concluded that, of the three interactions, the A-B interaction is of the greatest magnitude.

<table>
<thead>
<tr>
<th>AB</th>
<th>BB</th>
<th>AA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="configuration" /></td>
<td><img src="image" alt="configuration" /></td>
<td><img src="image" alt="configuration" /></td>
</tr>
<tr>
<td>(\Phi = 125^0)9' 154034'</td>
<td>(\Phi = 90^0) 12502'</td>
<td>(\Phi = 79^038')</td>
</tr>
</tbody>
</table>

Fig. 2.6 Configuration of ions pairs in spinel ferrites with favourable distance and angles for effective magnetic interaction.
The A and B ions shown in Fig.2.6 refer to ions occupying tetrahedral and octahedral sites respectively. The different exchange interaction follows that the A-B interaction is greatest. For the 1st of two A-B configurations, the distances p and q are small and angle Φ is fairly large i.e. Φ ≠ 125° 9′. The maximum B-B exchange interaction corresponds to the 1st B-B configuration drawn in Fig. 2.6. The angle Φ = 90°. The A-A exchange interaction will be weak and the distance r is large and the angle Φ is ≅ 79° 38′.

2.5 Neel’s theory:

Neel’s theory [2] is based on the following assumptions.
1) Ferrimagnetic crystal lattice could be divided into two sub lattices namely tetrahedral (A) and octahedral [B] site in a spinel structure.
2) Amongst the three magnetic interactions (A-B, A-A and B-B) A-B interaction and B-A interaction are identical and predominant over A-A interaction and B-B interaction. Therefore the net magnetic moment is the difference between two average sub-lattice magnetic moments.
3) There exists one type of magnetic ion in the material of which a fraction λ appears on tetrahedral (A) site and remaining fraction μ appears on octahedral [B] site such that λ + μ = 1.
4) Due to magnetic interactions within the material from the Weiss molecular point of view. The magnetic field acts upon an ion is written as,

\[ H = H_0 + H_M \]

where,

\( H_0 \) is the externally applied field and
H_{\text{M}} is the internal or molecular field.

Neel’s theory of ferrimagnetism has been successfully used to explain the magnetic properties of several spinels. Assuming Neel’s model one can determine the possible cation distribution among the tetrahedral (A) site and octahedral [B] site from the knowledge of resultant saturation magnetization at 0K. The saturation magnetization M_S in spinel ferrite can be expressed as

\[ M_S = |M_B - M_A| \]

For a simple ferrite of the form MFe_2O_4, which satisfies Neel’s assumption, the magnetic ions are trivalent ferric (Fe^{3+}). M^{2+} is nonmagnetic ion. The cation distribution formula can be written as

\[(\text{Fe}_{2\lambda}\text{M}_{(1-2\lambda)})^A [(\text{Fe}_{2-2\lambda}\text{M}_{2\lambda})^B]B_4\]

or

\[(\text{Fe}_{2\lambda}\text{M}_{(1-2\lambda)})^A [(\text{Fe}_{2-2\lambda}\text{M}_{2\lambda})^B]B_4\]

Applying internal Weiss molecular field concept to a ferromagnetic material, we have

\[ H_A = H_{AA} + H_{AB} \]

\[ H_B = H_{BB} + H_{BA} \]

where,

\[ H_A \] is molecular field acting on A site ion.

\[ H_{AA} \] is field acting on A site ion due to neighboring A site ion.

\[ H_{AB} \] is field acting on A site ion due to neighboring B site ion.

Similar definitions hold for molecular field \[ H_B \], acting on a B-ion.

The molecular field components may be written as

\[ H_{AA} = \gamma_{AA}M_A, \quad H_{AB} = \gamma_{AB}M_B \]

\[ H_{BB} = \gamma_{BB}M_B, \quad H_{BA} = \gamma_{BA}M_A \]
where, $\gamma$ are appropriate molecular coefficients and $M_A$, $M_B$ are
the magnetic moments of A and B sub-lattices. It may be shown that
$\gamma_{AB} = \gamma_{BA}$ but $\gamma_{AA} \neq \gamma_{BB}$ unless the two sub-lattices are identical.

In the presence of externally applied field $H_0$, the total magnetic
field acting on each sub-lattice may be written as

$$H_a = H_0 + H_A \quad \text{or} \quad H_a = H_0 + \gamma_{AA} M_A + \gamma_{BA} M_B \quad \ldots \ 2.7$$

$$H_a = H_0 + H_B \quad \text{or} \quad H_b = H_0 + \gamma_{BB} M_B + \gamma_{BA} M_A \quad \ldots \ 2.8$$

### 2.6 Properties of ferrites:

The structural, electrical and magnetic properties of ferrite are
very much important from the point of view of their application. The
electrical and magnetic properties of ferrites can be modified by using
proper method of preparation, choosing appropriate type and amount
of dopant and sintering temperature etc.

#### 2.6.1 Magnetic properties:

The magnetic properties of ferrite mainly depend upon the
distributions of metal cations over the available sites. The magnetic
properties of ferrite are divided into two groups; intrinsic or structure-
insensitive and extrinsic or structure-sensitive. Saturation
magnetization and Curie temperature are the two prominent
structure-insensitive properties. On the other hand structure-sensitive
properties are numerous and may be classified further as static or
dynamic, according to whether or not the property displays frequency
dependence. Induction, permeability, hysteresis loop and associated
energy loss, coercive force and remanence are structure-sensitive,
static properties. Eddy current loss, resonance of spin and domain
walls are structure sensitive dynamic properties [3].
2.6.1.1 Intrinsic properties

All those properties that is characteristic of material and are unaffected by the microstructure. (e.g. grain size, crystal orientation of grains).

1) Saturation magnetization

The maximum attainable intensity of magnetization per unit volume is known as the saturation magnetization ($M_s$) of ferromagnetic material. It will depend on the strength of the dipole moment on the atom that makes the material and how densely they are packed together. The atomic dipole moment will be affected by the nature of the atom and the overall electronic structure within the compound. The packing density of the atomic moments will be determined by the crystal structure (i.e. the spacing of the moments) and the presence of any non-magnetic elements within the structure. For ferromagnetic materials, at finite temperatures, $M_s$ will also depend on how well these moments are aligned, as thermal vibration of the atoms causes misalignment of the moments and a reduction in $M_s$. For ferromagnetic materials not all of the moments align parallel, even at zero Kelvin and hence $M_s$ will depend on the relative alignment of the moments as well as the temperature.

2) Curie temperature

Ferromagnetic materials exhibit a characteristic temperature known as the Curie temperature. At temperatures below the Curie point the magnetic moments are partially aligned within magnetic domains in ferromagnetic materials. As the temperature is increased from below the Curie point, thermal fluctuations increasingly destroy this alignment, until the net magnetization becomes zero at and above
the Curie point. Above the Curie point, the material is purely paramagnetic.

At temperatures below the Curie point, an applied magnetic field has a paramagnetic effect on the magnetization, but the combination of paramagnetism with ferromagnetism leads to the magnetization following a hysteresis curve with the applied field strength. The destruction of magnetization at the Curie temperature is a second-order phase transition and a critical point where the magnetic susceptibility is theoretically infinite.

2.6.1.2 Extrinsic (structure-sensitive) properties

a) Static properties

1) Magnetic induction

If the performance of a magnetic component or device depends on the magnetization of the ferromagnetic material involved, induction, rather than magnetization is used to assess the performance. This is so because the definition of induction,

\[ B = \mu_0 (H + M) \] \hspace{1cm} (2.9)

It has made it inherently structure-sensitive static property through the \( \mu_0 \), H term and therefore induction is more useful than magnetization in practice.

2) Permeability

Magnetic permeability (\( \mu \)) is defined as ratio of magnetic induction (B) to magnetic field (H) or strength of applied field. The ratio of flux density and applied field is called as absolute permeability.

\[ \frac{B}{H} = \mu_0 \left(1 + \frac{M}{H}\right) = \mu_{\text{absolut}} \] \hspace{1cm} (2.10)
This absolute permeability is the product of the magnetic constant of free space and the relative permeability,

\[ \frac{B}{H} = \mu_0 \mu_r \] ...

There are several versions of \( \mu_r \) depending on conditions the index \( r \) is generally removed and replaced by the applicable symbol e.g. \( \mu_i, \mu_\delta, \mu_{\text{Max}} \) etc.

Following four permeability’s are particularly important.

a) Initial permeability, \( (\mu_i) \): The limiting value approached by normal permeability when \( H \) is reduced to zero.

b) Maximum permeability, \( (\mu_{\text{Max}}) \): the largest value of normal permeability obtained from a (B-H) curve.

c) Intermediate permeability, \( (\mu_\delta) \) is equal to \( B_\delta/H_\delta \), where \( H_\delta \) is an alternating field in addition to a constant biasing field and \( B_\delta \) is the alternating induction caused by \( H_\delta \).

d) Differential permeability \( (\mu_d) \) is equal to \( dB/dH \) and is simply the slope of B-H curve at each point.

3) Hysteresis loop and energy loss

In the B-H curve B lags behind H and thus the closed B-H curve is called hysteresis loop. This loop appears in the four-quadrant as shown in Fig.2.7. In the B-H plot, the area enclosed by hysteresis loop represents an energy given by

\[ W_b = \int H . dB \] ...

This magnetic energy is converted into heat, which dissipates into the lattice immediately upon generation and it is permanently lost. Thus $W_b$ is called the hysteresis loss in units of Joules per m$^3$ per cycle. With soft magnetic materials hysteresis loss is very undesirable, not only because it wastes energy, but also heat involved could create further problems in the application of the material.

4) **Coercive force and coercivity**

Hysteresis loop is shown above Fig.2.7. A characteristic field known as the coercive force $H_c$ and a characteristic induction known as remanence, $B_r$. Coercivity often is used as the most important single criterion for determining whether a ferromagnetic material is soft or hard.

The essential difference between a hard and a soft ferrite lies in their respective coercive force. $H_c$ is large (~ 100 Oe) in the former and small (<20 Oe) in the later. Keeping coercivity at a minimum is a primary goal in a preparation of soft magnetic material. Experimental data shows that coercivity is closely related to other structure sensitive magnetic properties.
5) Remanence or Retentivity

During the cycle of magnetization $B_r$ (Fig. 2.7) is the amount of induction remained ever after the field $H$ is made zero. This characteristic induction is known as remanence or retentivity.

b) Dynamic properties

1) Eddy current and associated energy losses

When an alternating field is applied to magnetize a ferromagnetic body, an electromagnetic force (e.m.f.) is setup in the body. If the material is also a good conductor, as with metal and alloys, the induced e.m.f. is produced appreciable amount of currents in different regions, these currents are known as the eddy currents and their occurrence gives rise to energy loss ($W_e$) through Joule. Thus, in a.c. application, metallic ferromagnet suffers the hysteresis as well as the eddy current losses. Also, we increase with frequency according to the second power law. Hence, the eddy current loss becomes even more burdensome than the hysteresis loss at intermediate and high frequencies.

2) Motion and resonance of domain walls

The resonance of Bloch walls is prominent phenomena detected in ferrites at high frequency. It plays an important role in the application of soft magnetic materials. It is found that, the eddy-current power loss is proportional to the square of the velocity of the domain walls. Thus to minimize the loss, we must try to keep the wall velocity at the lowest possible value. On the other hand, some applications of ferrites at microwave frequency involve the resonance of domain walls.
2.6.2 Electrical Properties:

Ferrites have vast applications from microwave to radio frequencies, because electrical conductivity of soft ferrite is low as compared to those of the magnetic materials. So this factor is responsible for the wide use of ferrites in microwave frequencies. The resistivity of soft ferrites is of the order of $10^6 \text{ } \Omega \text{m}$ like semiconductor. The conductivity is due to the presence of Fe$^{3+}$ and M$^{2+}$ (M = Ni, Co etc.) ions. The presence of Fe$^{3+}$ results in ‘n’ type behavior and of M$^{2+}$ in ‘p’ type behaviour. The conductivity arises due to the mobility of the extra electron from (Fe$^{3+}$) or the positive hole (M$^{2+}$) through the crystal lattice. The moment is described by the hopping mechanism, in which the charge carriers jump from one ionic site to the next. On this basis, the semiconducting behaviour of nickel and cobalt ferrite has been successfully treated by Jonker [4] and Elwell et. al. [5] respectively.

If the material has to be conducting, lattice must contain the same cations in at least two different valence states. In spinel, since distance between two (A) site cations is larger than the distance between adjacent [B] site cations and as tetrahedral and octahedral sites are not energetically equivalent, conductivity is mostly due to the electron exchange between [B] site cation. For example in Fe$_3$O$_4$ though the conductivity is due to hopping of electron from Fe$^{2+}$ to Fe$^{3+}$ ion at B site, in this mechanism initial and final states are equivalent,

$$\text{Fe}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$$

Therefore unbounded electron transfer process can take place. According to Verwey [6], the conductivity of high resistivity oxides can be increased by the addition of small amount of impurities to the structure. The substitution of cations of the low valence state gives
rise to ‘p’ type of conduction while the substitution of cations of high valence state to ‘n’ type of conduction [7]. The presence of Fe$^{2+}$ ions is sometimes desirable [8] as it reduces magnetostriction and resistivity. It has also been shown that conduction mechanism in spinel can be explained on the basis of small polaron hopping mechanism [9-12]. The small polaron are trapped carriers which exhibits thermally activated phonon assisted hopping from one site to other. In the case of low mobility oxides the charge carriers remains in the vicinity of the particular atomic site over an interval longer than typical vibrational period, an atoms in the vicinity of the excess charge have sufficient time to assume new equilibrium position consistent with presence of added charge. The atomic displacement generally produces a potential well for the excess carriers, if this carriers induced potential well is sufficiently deep, the carrier occupies a bound state as it is unable to move without alteration of the position of the surrounding atoms. This unit comprising of trapped carriers and its induced lattice deformation is the polarons and since it is confined to a small region it is termed as small polaron. The temperature dependence of electrical resistivity is given by the relationship,

\[ \rho = \rho_0 e^{\frac{\Delta E}{kT}} \]

... 2.13

where,

k is Boltzmann constant,

\( \Delta E \) activation energy of conduction,

\( \rho_0 \) is a constant which is the energy required for the hopping of the electron or hole.
2.6.3 **Dielectric properties :**

Dielectric properties depend upon several factors including the method of preparation, chemical composition and grain structure or size. When a ferrite is sintered under slightly reducing condition, the valence state changes, the individual cation found in the sample leads to high conductivity and when such a material is cooled in an oxygen atmosphere, it is possible to form films of high resistivity over the constituent grain. Such ferrites in which the individual grains are separated by either air gaps or low conducting layers behave as inhomogeneous dielectric material.

This aroused considerable interest in the low frequency range (10² Hz - 10⁵ Hz) dielectric behaviour of ferrite. Among the many workers involved in this type of studies, the prominent ones are Koops [13], Moltgen [14], Iwauchi et al. [15], Rezlescu [16, 17] and Josyolu [18]. The polycrystalline ferrites have high dielectric constant of the order of a few thousands at low frequencies, following to a very low value of only 10-20 at microwave frequencies. The A.C. resistivity decreases with increase in temperature like D.C. resistivity, whereas dielectric constant increases with increase in temperature. According to Rabkin and Novikova [19] the process of dielectric polarization in ferrite takes place through a mechanism similar to conduction process

2.7 **Application of ferrites :**

Polycrystalline soft ferrites materials have attached considerable attention for their potential applications in microwave devices such as isolators, circulators and phase shifters, due to their high resistivity, low dielectric losses, high Curie temperature and chemical stability. It
is interesting that the electromagnetic properties of spinel ferrites can be tailored by controlling the different type and amounts of transition metallic substitutes [20].

Ferrite cores are used in electronic inductors, transformers, and electromagnets where the high electrical resistance of the ferrite leads to very low eddy current losses. They are commonly seen as lump in a computer cable, called a ferrite bead, which helps to prevent high frequency electrical noise (radio frequency interference) from exiting or entering the equipment.

Ferrite cores are widely used in most electrical products such as computer electro-magnetic interference (EMI) field, remote control, inductors, filters, electronics watches, TV / computer games and audio systems etc.

Early computer memories stored data in the residual magnetic fields of hard ferrites cores, which were assembled into arrays of core memory. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide.

Ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft and in the absorption tiles lining the rooms used for electromagnetic compatibility measurements. Most common radio magnets, including those used in loudspeakers, are ferrite magnets.

Ferrites suppress are also used EMI (electromagnetic interference) and RFI (radio frequency interference) by using several different suppression materials that absorb conducted interference and changing it to heat. In the recently, ferrites were considered as one of the most versatile magnetic materials for multiplayer chip
inductor (MLCI) applications and surface mount devices (SMDs) due to their high electrical resistivity and permeability [21].

The rare earth ferrites have their use in the strongest and highest performance permanent magnet such as NEOMAX neodymium-iron boron magnets. These magnetic have made possible smaller and more advanced electronic device than ever before. Also, even today the stability of their magnetic properties under fluctuation temperature conditions makes them suitable for instruments and other devices that demand excellent thermal stability [22].

The ferrite material system exhibits super-paramagnetic behaviour, display little or no remanence and coercivity while keeping a very high saturation magnetization have potential applications in biomedicine [23], magnetic drug delivery and cell sorting systems [24, 25]. It is used in computer stored data in the residual magnetic fields of hard ferrite cores, which were assembled into array of core memory.
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