2.1: INTRODUCTION

Ever expanding electronic industry’s need of ferrites, both soft and hard ferrite, is evident from the intimated world ferrite production, due to their remarkable electrical and magnetic properties. Ferrite is a general term used for any ferrimagnetic ceramic material. On the basis of crystal structure ferrites are grouped into three classes (spinel, Garnet and hexagonal) which are equally, commercially important. Each type of ferrite has unique crystal structure and distinct set of magnetic properties.

2.2: CHEMICAL COMPOSITION

Ferrites are ceramics, mixed metal oxides with general chemical composition M$^{2+}$Fe$^{3+}_2$O$_4^{2-}$ or MO-Fe$_2$O$_3$ where M is a divalent metal ion such as manganese (Mn$^{2+}$), nickel (Ni$^{2+}$), cobalt (Co$^{2+}$), zinc (Zn$^{2+}$), copper (Cu$^{2+}$) or magnesium (Mg$^{2+}$) etc. with an ionic radius approximately between 0.6 and 1 Å [1] and the crystal structure is that possessed by the mineral Spinel MgAl$_2$O$_4$. A combination of these ions is also possible; we then speak of a solid solution of two ferrites, of mixed crystal or, in general term, of a mixed ferrite. Other combinations of equivalent valency are possible and it is also possible to replace some of all the trivalent iron ions with other trivalent metal ions. The structure of spinel ferrite was first determined by W. H. Bragg in 1915 [2] and Nishikawa [3]. These ferrites are also called as ferro-spinels because they crystallize in the same crystal structure as the mineral spinel.
2.3: STRUCTURE OF FERRITES:

The spinel lattice is composed of a close-packed oxygen ion arrangement in which 32 oxygen ions from unit cell (smallest repeating unit in the crystal structure). These anions are packed in face centered cubic (fcc) arrangement leaving two kinds of spaces (interstices) between anions. Fig. 2.1(a) where, solid lines represent the top layer of oxygen spheres and dotted line represents the bottom layer of oxygen spheres. It is found that spinel structure is only formed if the ionic radius of cation M is less than or about 1 Å. If it is greater than 1 Å then the electrostatic Coulomb force are insufficient to ensure the stability of crystal. For examples Ca$^{2+}$ (ionic radius 1.06 Å) does not form spinel crystal, where in Mn$^{2+}$ (0.91 Å) does form spinel crystal. Upon close examination, it can be seen that there are two kinds of interstices, denoted by letter (A) (tetrahedral site) and [B] (octahedral site).

![Ionic positions](image)

*Fig. 2.1: Ionic positions (a) Hexagonal Close packing (b) Tetrahedral (A) site (c) Octahedral [B] site.*
There are 96 spaces or interstices, 24 of which are filled by a cation, the remaining 72 being empty. The site occupied by the cations are of two kinds known as tetrahedral or (A) sites and octahedral or [B] sites. The (A) site of which eight are occupied, are surrounded by four oxygen ions and [B] site of which sixteen are occupied are surrounded by six oxygen ions [4] as shown in Fig. 2.1(b) and Fig. 2.1(c).

### 2.4: FERRITES AND THEIR TYPES:

The ferrite types are classified by names of common minerals which have the crystal structure of the Hexagonal, garnet and spinel. Hexagonal ferrites are important in permanent magnetic applications, magnetic garnets. Garnets have special applications in microwave devices and spinel ferrites are important in many electrical, electronic, automobile, computer etc. fields.

Classification of ferrite materials are shown in following Table. 2.1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Hexagonal</th>
<th>Garnet</th>
<th>Spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Structure</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>02</td>
<td>Molecular Formula</td>
<td>M(Fe$<em>{12}$O$</em>{19}$)</td>
<td>M$_3$(Fe$<em>5$O$</em>{12}$)</td>
<td>M(Fe$_2$O$_4$)</td>
</tr>
<tr>
<td>03</td>
<td>Space Group</td>
<td>P6$_3$/mmc, D6$_h$</td>
<td>Ia-3d</td>
<td>Fd$\overline{3}$m</td>
</tr>
<tr>
<td>04</td>
<td>Interstitial Sites</td>
<td>12k,2a,4f$_2$,4f$_1$,2b</td>
<td>a, c and d</td>
<td>(A) and [B]</td>
</tr>
<tr>
<td>05</td>
<td>Examples</td>
<td>CaFe$<em>{12}$O$</em>{19}$</td>
<td>Y$_3$Fe$<em>5$O$</em>{12}$</td>
<td>CoFe$_2$O$_4$</td>
</tr>
<tr>
<td>06</td>
<td>Lattice Constant (Å)</td>
<td>5.83</td>
<td>12.37</td>
<td>8.38</td>
</tr>
<tr>
<td>07</td>
<td>Curie Temperature (K)</td>
<td>673</td>
<td>553</td>
<td>668</td>
</tr>
<tr>
<td>08</td>
<td>Saturation Magnetization (emu/gm.)</td>
<td>66</td>
<td>26</td>
<td>63</td>
</tr>
<tr>
<td>09</td>
<td>Electrical Resistivity, (Ω-cm)</td>
<td>$1\times10^6$</td>
<td>$1\times10^{14}$</td>
<td>$1\times10^8$</td>
</tr>
</tbody>
</table>
2.4.1: Hexagonal ferrite:

The hexagonal ferrites are characterized by the chemical formula $\text{MFe}_{12}\text{O}_{19}$, where $\text{M}$ is divalent ion usually barium (Ba), strontium (Sr), or lead (Pb). The structure is related to the spinel structure in which the oxygen lattice, being f.c.c. consists of series of hexagonal layers of oxygen lying perpendicular to the (111) direction. The crystal structure is complex, but it can be described as hexagonal with a unique c axis, or vertical axis. This is the easy axis of magnetization in the basic structure. Because the direction of magnetization cannot be changed easily to another axis, hexagonal ferrites are referred to as “hard”. This lattice has three different sites occupied metal ions, tetrahedral, octahedral and trigonal bi pyramid (surrounded by 6 oxygen ions). The hexagonal ferrite accepts larger ions than garnet ferrites and is formed by replacing some of the oxygen by these large ions. Most of these large ions are divalent barium, lead, strontium and some other larger rare earth ions.

The crystal and magnetic structure of the different types of hexagonal ferrites are remarkably complex. Fig 2.2 shows the structure of Hexagonal ferrite.

![Hexagonal ferrite structure](image)
2.4.2 Garnets:

Garnets have the structure of the silicate mineral ‘garnet’ and have the chemical formula $M_3Fe_5O_{12}$ or more informatively $(3M_3O_3)(2Fe_3O_4)(3Fe_2O_3)^d$ where $M$ is yttrium or a rare-earth ion (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Lu) and the superscripts $c$, $a$, $d$, refer to dodecahedron, octahedron and tetrahedron respectively. In addition to tetrahedral and octahedral sites, such as those seen in spinels, garnets have dodecahedral (12-coordinated) sites. The net ferrimagnetism is thus a complex result of anti-parallel spin alignment among the three types of sites. Garnets are magnetically hard. The crystal structure of Garnet is as shown in fig.2.3. The structure is of a cube form with 160 atoms per unit cell and containing eight molecules of $M_3Fe_2Fe_3O_{12}$. The cell is cubic and has an edge length of approximately 12.5 Å. Within the array of 96 oxygen ions there are three interstices occupied by metal cations.

![Fig. 2.3 Garnet ferrite structure](image-url)
2.4.3: Spinel ferrite

The spinel ferrites are cubic in structure; with no preferred direction of magnetization, they are “soft” magnetically; i.e. it is relatively easy to change the direction of magnetization through the application of an external magnetic field. [5-7]. The crystal structure of spinel ferrite is best described by subdividing the unit cell into eight octants with edge $\frac{1}{2} a$ (‘a’ is the edge of unit cell). Each octant in unit cell contains four oxygen ions on the body diagonal from alternate corners of the octant. The positions of metal ions are different in the two octants sharing a face. In one of the octants an occupied tetrahedral site is located at the centre and four more sites on the corners of the octant. In the adjacent octant the central site is not occupied but owing to translation symmetry, half of the corner sites are occupied. Each tetrahedral ion is surrounded by four other tetrahedral ions, which lie in the corners of a regular tetrahedron. There are twelve nearest neighbor octahedral ions for every tetrahedral ion. Each octant contains four octahedral metal ions and these are situated at sites analogous to those of the body diagonal from the other ends of the four body diagonals of the octant. Each octahedral ion is surrounded by six nearest neighbor tetrahedral ions. Each oxygen ion is surrounded by one tetrahedral ion (A) and three octahedral ions [B]. Each (A) ion belongs to four units and each [B] ion to six. The direction of OA is that of the body diagonal of a cube and the directions OB are along the cube edges. Fig. 2.4 shows the unit cell of spinel ferrites.

The interstices available in an ideal close packed structure of rigid oxygen anions would be able to incorporate in the tetrahedral sites, only those metal ions with a maximum radius ($r_{\text{tet}} = 0.30 \text{ Å}$) and in octahedral sites, only ions with a maximum radius ($r_{\text{oct}} = 0.55 \text{ Å}$).

In order to incorporate cations like Co, Cu, Mg, Ni, Mn and Zn lattice has to expand somewhat. The difference in the expansion of the tetrahedral and octahedral interstices is characterized by an oxygen parameter ‘u’ for an ideal spinel; tetrahedral
and octahedral interstices are enlarged in the same ratio. The distance between the
tetrahedral site (0, 0, 0) and the oxygen (3/8, 3/8, 3/8) is $u_{\text{ideal}} = 3/8$.

The incorporation of divalent metal ions in tetrahedral sites induces a larger
expansion of the tetrahedral sites at the expense of the octahedral sites, leading to a
large value for $u$ from the ideal value.

2.5 CRYSTAL STRUCTURE OF SPINEL FERRITE:

The crystal structure is best described by sub dividing the unit cell into 8 octants.
The octants are of two different types. The octant shearing faces are different and
those shearing edge are same.

Each octant contains four oxygen ions on body diagonal and they lie at the
distance equal to one fourth of the body diagonal from alternate corners of the octant
as shown in Fig. 2.5. The location of the ion either in (A) or [B] sites depends
fundamentally on the ion and lattice size. Also it has been observed to depend on the
temperature and orbital preference specific co-ordinates. The spinel crystal structure
is determined primarily by the oxygen ions lattice. The radii of oxygen ions are
several times larger than the radii of metallic ions in the compound. Consequentially,
the crystal structure can be thought of as being made of the closest possible packing
of oxygen ions, with the metallic ions fit in at the interstices. In general divalent ions
are larger than trivalent ions because trivalent nuclei produce greater electronic attraction, hence their electron orbit contract. The octahedral sites are larger than tetrahedral sites, thus the divalent ions are localized in the octahedral [B] sites whereas trivalent ions are in the tetrahedral (A) sites.

In spinel structure each oxygen ion is surrounded by one tetrahedral (A) site and three octahedral [B] sites as shown in Fig. 2.6. It is found that in general normal ferrite spinels are paramagnetic while inverse spinels are ferromagnetic.

---

**Fig. 2.5 Crystal structure of spinel ferrite**

**Fig. 2.6: Locations of the oxygen and the metal ions in two adjacent octants of a single unit cell of spinel ferrites.**
To accommodate cations like Ni, Cu, and Co, the lattice has to be expanded by an equal displacement of four oxygen ions in the outward direction along the body diagonal of the cube, still occupying the corners expanded regular tetrahedron. This results in shifting of four oxygen ions of octahedral sites and hence this oxygen tetrahedron shrinks by the same amount as the first expands.

There are ninety six interstitial sites in the unit cell, sixty four tetrahedral and thirty two octahedral, out of which only eight and sixteen respectively are occupied by cations. Two kinds of oxides are available for the cation: tetrahedral sites surrounded by four oxygen ions situated at corners of tetrahedron (A) site and octahedral sites surrounded by six oxygen ions situated at corners of an octahedron [B] site.

According to Wyckoff [8] the spinel belongs to group $O_h^7$ (Fd3m) and the ionic positions are:

**Anion 32 b**: $u,u,u; \quad u,\bar{u},\bar{u}; \quad u,\bar{u},u; \quad \frac{1}{4} - u, \frac{1}{4} - u, \frac{1}{4} - u; \quad \frac{1}{4} - u, u + \frac{1}{4}, u + \frac{1}{4}; \quad u + \frac{1}{4}, \frac{1}{4} - u, u + \frac{1}{4}; \quad u + \frac{1}{4}, u + \frac{1}{4}, \frac{1}{4} - u.$

**Cation 16C**: $5/8, 5/8, 5/8; \quad 5/8, 7/8, 7/8; \quad 7/8, 5/8, 7/8; \quad 7/8, 7/8, 5/8; \quad 7/8, 7/8, 5/8.$

**Cation 8f**: $0, 0, 0; \quad \frac{1}{4}, \frac{1}{4}, \frac{1}{4}.$

with the translations, for a face centered cubic lattice as,

$+0, 0, 0; \quad 0, \frac{1}{2}, \frac{1}{2}; \quad \frac{1}{2}, 0, \frac{1}{2}; \quad \frac{1}{2}, \frac{1}{2}, 0.$

Packing of the ions within the lattice is perfect when the oxygen parameter, $u = 3/8$.

**2.6: CLASSIFICATION OF SPINEL FERRITE:**

The spinel structure contains 8 divalent and 16 trivalent ions distributed over eight tetrahedral and sixteen octahedral interstices in the unit cell. The interesting and useful electrical and magnetic properties of the spinel ferrites are governed by the distribution of the iron and the divalent metal ions among the octahedral and tetrahedral sites of the spinel lattice. Barth and Ponjak [9] observed the different arrangement of cations in spinel ferrites and classified them accordingly as normal spinel, inverse spinel and random spinel.
The spinel ferrites have the general formula \((M_d\text{Fe}_{1-d})[M_{1-d}\text{Fe}_{1+d}]\text{O}_4\). The divalent metal ion \(M\) (\(M = \text{Zn, Mg, Mn, Fe, Co, Ni or a mixture of them}\)) can occupy either tetrahedral \(\text{(A)}\) or octahedral \(\text{[B]}\) sites as depicted by round and square brackets respectively. In the above formula when \(d =1\), it is called normal spinel. \(\text{ZnFe}_2\text{O}_4\) and \(\text{CdFe}_2\text{O}_4\) are examples of normal ferrites. When \(d =0\), it is called inverse spinel and examples are \(\text{NiFe}_2\text{O}_4\), \(\text{CoFe}_2\text{O}_4\), \(\text{CuFe}_2\text{O}_4\) etc. When \(d =1/3\), it is called a random spinel.

**2.6.1: Normal spinel ferrite:**

Here all the divalent metal ions occupy \(\text{(A)}\)-sites and all the trivalent ions occupy \(\text{[B]}\)-sites. In these ferrites there is no \(\text{A-B}\) interaction, as \(\text{(A)}\)-sites do not contain any magnetic ion. The \(\text{B-B}\) interaction lines up with half the magnetic ions in one direction so that alternate planes of \(\text{B}\) sub-lattices are magnetized in opposite direction. This results in the nonmagnetic ferrite.

The cation distribution for normal spinel ferrite is given by

\[
(M^{2+})^\text{A}[\text{Fe}^{3+}]^\text{B}\text{O}_4^{2-} \quad \ldots \ldots 2.1
\]

where, \(M\) is the divalent metal ion

Examples. \(\text{ZnFe}_2\text{O}_4\), \(\text{CdFe}_2\text{O}_4\)

**2.6.2 Inverse spinel ferrite:**

Verwey and Heilmann (1947) [10] termed the later arrangement ‘inverse’ in contrast to normal arrangement. In inverse spinel ferrite, one trivalent ferric ion \(\text{Fe}^{3+}\) is at the tetrahedral \(\text{(A)}\) site while the remaining trivalent ferric ions \(\text{Fe}^{3+}\) and the divalent metallic ions \(M^{2+}\) are at the \(\text{[B]}\) site. Actually most of the simple ferrites are of the inverse spinel structure.

The cation distribution for inverse spinel ferrite is given by

\[
(\text{Fe}^{3+})^\text{A}[M^{2+}\text{Fe}^{3+}]^\text{B}\text{O}_4^{2-} \quad \ldots \ldots 2.2
\]

Examples- \(\text{MnFe}_2\text{O}_4\), \(\text{CoFe}_2\text{O}_4\) and \(\text{NiFe}_2\text{O}_4\)
2.6.3 Random spinel ferrite:

The divalent metal ions $M^{2+}$ and trivalent $Fe^{3+}$ ions are distributed at both tetrahedral (A) site and octahedral [B] site then the ferrite is termed as random spinel ferrite. The best known example of random spinel ferrite is copper ferrite. The distribution depends upon the physico-chemical conditions of preparation and sintering process. The distribution of ions between two types of sites is determined by a delicate balance of contributions, such as the magnitude of ionic radii, their electronic configuration and the electrostatic energy of the lattice.

The cation distribution of random spinel ferrite is given by

$$(M_{\delta}^{2+}Fe_{1-\delta}^{3+})^A[M_{1-\delta}^{2+}Fe_{\delta}^{3+}]^B O_4^{2-}$$

Examples- $CuFe_2O_4$, $MgFe_2O_4$

Based on the Columbic energy of charged ions and their influence in the polarization of anions [11], large divalent ions favour tetrahedral occupancy. From these considerations, it follows that 2-3 spinels favour normal configuration. However, the only consistency of experiment with predictions are most likely for $Mn^{2+}$ and $Zn^{2+}$ since these ions have solely symmetrical electron orbitals, half filled for $Mn^{2+}$ and full for $Zn^{2+}$. Applying crystal field theory and optical data relating the site preference for the d$^3$ and d$^8$ ions and the highest tetrahedral site preferences are d$^0$, d$^5$ and d$^{10}$ ions [12].

2.7 THE OXYGEN PARAMETER (U):

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.2.7. 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.
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,
\[ r_a = \left( u - \frac{1}{4} \right) a \sqrt{3} - R_0 \]  
\[
............2.4
\]
\[ r_b = \left( \frac{5}{8} - u \right) a - R_0 \]  
\[
............2.5
\]

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.

If the distance between the oxygen ion and given cube edge is \(u\)-A, \(u\)-gives a quantitative measure of displacement of an oxygen ion from its ideal position and is called oxygen ion parameter. It is 0.375 in an ideal spinel structure corresponding to perfect close packing of cations. The structural coordinates of all cation in the cubic spinel are specific and those of anions are general in terms of ‘\(u\)’.

**2.8 CATION DISTRIBUTION:**

The interesting and useful electrical and magnetic properties of the spinel ferrites are found from the distribution of the iron and the divalent metal ions among the octahedral and tetrahedral sites of the spinel lattice. The cation distribution is dependent on the method of preparation and invariable with temperature. The cation distribution can be determined by X-ray diffraction methods [13], neutron diffraction methods [14], Mossbauer spectroscopy [15] magnetic susceptibility measurements [16] and infrared absorption spectroscopy [17].

In X-ray diffraction method X-ray intensity ratio calculations were made for the planes (220), (311), (400), (440) etc. The calculated intensity ratios were then compared with observed intensity ratio. The X-ray intensity ratio calculations were made for various possible combinations of cations.

The theoretical and experimental values of X-ray intensity ratio were then compared. The combination of cations for which theoretical and experimental values agrees closely to each other is taken as correct cation distribution.
2.8.1 Factors affecting cation distribution in spinels:

In spinel ferrites the distribution of cations over the tetrahedral (A) and octahedral [B] can be obtained by X-ray diffraction, neutron diffraction, Mossbauer and magnetization measurements. The following are some of the factors, which can influence the distribution of metal ions over tetrahedral (A) and octahedral [B] sites.

a) Ionic radius:

In spinel lattice, the tetrahedral (A) site has small ionic radius as compare to the octahedral [B] site, therefore the large cations like Co, Ni generally will prefer to occupy the octahedral [B] site. In analogy, the smaller cations prefer to occupy the tetrahedral (A) site. Usually trivalent ions are smaller than the divalent ions and this tends to favour the inverse structure.

b) The electronic configuration:

It is observed that ions having filled d-shell often have tendency to form sp$^3$ hybrid orbital and occupy the tetrahedral (A) sites in spinel lattice (e.g. Zn$^{2+}$, Ge$^{4+}$) [13], whereas the ions with d$^3$ and s$^8$ electronic configuration have a tendency to form d$^3$ sp$^3$ hybrid orbital and occupy the octahedral sites in spinel (e.g. Cr$^{3+}$ and Ni$^{2+}$) [18].

c) The electrostatic energy

Depending upon the distribution of cations over the tetrahedral (A) sites and octahedral [B] sites, the spinel ferrites are classified as normal spinel and inverse spinel. The classification also depends upon the lowest lattice energy [8].

This is the electrostatic energy gained when the ions at first thought to be infinitely far apart are brought together to form the spinel lattice. In the normal arrangement the metal ions with the smallest positive charge are surrounded by four oxygen ions, and the metal ions with higher positive charge by six oxygen ions, which is electrostatically most favorable with an oxygen parameter larger than the ideal value. This state will be energetically even more favorable. According to the
calculations made by Verwey and Boer [19] it follows that, for the spinels consisting of divalent and trivalent metal ions, the inverse structure, the lowest lattice energy in the case that \( u < 0.379 \) where as the normal structure has the lowest lattice energy, when \( u > 0.379 \).

d) Method of preparation

The method of preparation can also influence the distribution of metal ions over tetrahedral (A) site and octahedral [B] site. The cation distribution is strongly dependent on the heat treatment of the material. The preparative parameters such as sintering temperature, sintering time can also affect the cation distribution. Materials of the same composition prepared by two different techniques can exhibit different magnetic, electrical properties of spinel ferrites.

2.9 MAGNETIC ORDERING IN SPINEL FERRITE:

The magnetic properties of the spinel ferrites are governed by the type of magnetic ions residing on the (A) and [B] sites and the relative strengths of the inter (\( J_{AB} \)) intra sub lattice ( \( J_{BB}, J_{AA} \) ) interactions. When the A-B inter sub-lattice interactions are much stronger than the A-A and B-B intra sub-lattice interactions, the spins have the collinear structure in which moments on (A) sites are antiparallel to the moments on [B] sites. Since, in most of the spinels all the three exchange interactions namely \( J_{AA}, J_{BB} \) and \( J_{AB} \) are negative, there exists a competition between intra and inter sub-lattice interaction which may result in frustration effect. On dilution with non magnetic atoms, frustration of certain moments should occur leading to collapse of the colinearity of the ferromagnetic phase and the effective moments are created within the ferromagnetic structure by local canting around the magnetic interactions [20]. The presence of magnetic ions such as \( \text{Co}^{2+}, \text{Mn}^{2+} \) and \( \text{Fe}^{3+} \) in the spinel ferrite system introduces the uniaxial anisotropy, which increase the possible magnetic structure and hence change the phase diagram.
A wide spectrum of magnetic structure ranging from ferrimagnetisms, antiferromagnetism, local canted spin (LCS) to semi spin glass, spin glass etc. has been observed. Recently, a tentative phase diagram of the possible magnetic structure has been proposed by Dormann et al. [21]. When one of the intra sub-lattice interactions becomes comparable with inter sub-lattice interactions, it leads to a non-collinear spin structure [22].

2.10 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$^I$ and Me$^II$ depends upon (i) the distances of the ions from oxygen ions and (ii) the angle Me$^I$-O-Me$^II$ represented by the term $\Phi$ as shown in Fig.2.8.

![Fig. 2.8 : Me$^I$ – O - Me$^II$ angle in ferrites.](image)

An angle of 180$^\circ$ 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 [23] are given in Fig.2.9.
Fig. 2.9: Configuration of ions pairs in spinel ferrites with favorable distance and angles for effective magnetic interaction.

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. The A and B ions shown in Fig. 2.9 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 $\Phi$ is fairly large i.e. $\Phi = 125^0 9'. The maximum B-B exchange interaction corresponds to the 1st B-B configuration drawn in Fig. 2.9. The angle $\Phi = 90^0$. The A-A exchange interaction will be weak and the distance r is large and the angle $\Phi$ is $\equiv 79^0 38'.

2.11 NEEL’S THEORY:

Neel’s theory [24] 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 $\lambda$ appears on tetrahedral (A) site and remaining fraction $\mu$ appears on octahedral [B] site such that $\lambda + \mu = 1$.

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

$H_M$ 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

$$(Fe^{2+}\lambda M_0 (1 - 2\lambda)^4 A [Fe^{2+}(2 - 2\lambda)M_0^{2+}\lambda]^B O_4$$

or

$$(Fe^{2+}\lambda M_0 (1 - 2\lambda)^4 A [Fe^{2+}(2 - 2\lambda)M_0^{2+}\lambda]^B O_4$$

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

$$H_A = H_{AA} + H_{AB} \quad \text{............ 2.6}$$

$$H_B = H_{BB} + H_{BA} \quad \text{............ 2.7}$$

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

$$H_{AA} = \gamma_{AA}M_A, \quad H_{AB} = \gamma_{AB}M_B \quad \text{.........2.8}$$

$$H_{BB} = \gamma_{BB}M_B, \quad H_{BA} = \gamma_{BA}M_A \quad \text{.........2.9}$$

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

$$H_a = H_0 + H_A$$

or

$$H_a = H_0 + \gamma_{AA}M_A + \gamma_{BA}M_B \quad \text{.........2.10}$$

$$H_a = H_0 + H_B$$

or

$$H_b = H_0 + \gamma_{BB}M_B + \gamma_{BA}M_A \quad \text{.........2.11}$$

### 2.12 YAFET KITTEL THEORY OF FERRIMAGNETISM:

The Neel’s theory of ferrimagnetism fails to explain the deviation observed between the variation of Neel’s magnetic moment and observed saturation magnetic moment. So the model like Yafet Kittel [22], Gilleo [25, 26] were proposed to explain this anomaly. It was shown by Yaffet and Kittel that in spinel ferrites, a noncolinear or canted spin arrangement occurs on substitution of non magnetic cation in one sub lattice. As a result, the B sub lattice splits into two, B$_1$ and B$_2$ with equal magnetic moments at angle $\theta$ so called Yaffet angle $\theta_{YK}$ with the direction of net magnetization of B sub-lattice at 0K.

The mixed ferrite system $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ or $\text{Fe}_2\text{O}_3$, $x\text{NiO}$. (1-$x$)$\text{ZnO}$ provides experimental evidence supporting the Y-K model. Pure Ni ferrite ($x = 0$) has the inverse spinel structure and the A-B interaction is dominated. Pure Zn ferrite has the normal spinel structure; $\text{Zn}^{2+}$ being non-magnetic, the (A) site carry no magnetic...
moment. The B-B interaction is expected then to give rise to antiferromagnetic ordering in the B lattice. As x is varied from 0 to 1, intermediate arrangements will arise.

The ground state and 0 K may have one of the following three configurations.

1. The spins on one side are antiparallel to those on the other (ferrimagnetism)
2. The spins on one side fall into two similar sub-lattices, each sub-lattice being ferromagnetically saturated.
3. The spin on each of the two sites have antiferromagnetism. The net magnetic moment of the system can be expressed accordingly Y-K model as

\[ \mu(x) = [2(1-x) + 5(1+x)] B \cos \theta_{YK} - [5(1-x)] B \]

The Y-K angle can be evaluated using the techniques like neutron diffraction, high field Mossbauer Spectroscopy etc.

### 2.13 MAGNETIC STRUCTURE

The magnetic behaviour of ferrites can be understood more clearly from the study of magnetic structure. The magnetic unit cell will be sufficient for the understanding of the alignment of spins and their consequent to the magnetic moment. Dimensionally magnetic structure and chemical unit cells are related to each other, they may have the same dimensions or magnetic unit cell parameter may by several times larger than chemical cell dimension. The magnetic structure can be determined using neutron diffraction [27].

The site and valence distribution in ferrites can be decided from saturation magnetization data, X-ray diffraction and neutron diffraction. The simple way of obtaining the cation distribution is the saturation magnetic moment data. In spinel ferrite MFe\(_2\)O\(_4\), the divalent M\(^{2+}\) ions have a magnetic moment appreciably different from that of Fe\(^{3+}\). Nickel ferrite has a net magnetic moment of 2.3 \(\mu_B\) per molecule. Assuming spin only magnetic moments, a normal structure of nickel ferrite gives a magnetic moment 8 \(\mu_B\) whereas inverse spinel structure of nickel ferrite gives a
magnetic moment of 2 $\mu_B$ per molecule. These results are supported by X-ray and neutron diffraction study. Thus, the saturation magnetization data is also useful for the determination of cation distribution.

The experimental value of magnetic moment may or may not match with each other. In general, the discrepancy in the experimental and calculated (theoretical) magnetic moments for several spinel ferrites is observed.

This discrepancy may be due to

i) the g factor may not be exactly 2; (e.g. Nickel ferrite has g value of 2.2-2.3).

ii) the structure may not be either completely inverse or normal.

iii) a particular ion may have different magnetic moments in A and B sites.
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