2.1 CRYSTAL STRUCTURE OF FERRITE

The first natural magnetic material known to man from ancient time was magnetite (Fe₃O₄), which is now called as ferrous ferrite. The story of ferrites begins with the search for ferromagnetic material of usual high resistivity of the order of 10⁷-10⁹ to obtain reasonable low eddy current and dielectric losses.

Ferrites with the general formula MO-Fe₂O₃ have the cubic spinel structure, named after the mineral spinel MgAl₂O₄. This crystal structure was first determined by Braggs[1]. The structure may be considered as a cubic close-packed arrangement of the large oxygen ions (a unit spinel cell contains 32 of them), in the interstices of which the much smaller metal ions are situated. A closer inspection shows that not all interstices are the same, but
that two types can be distinguished, viz. tetrahedral (A) and octahedral (B) interstices, surrounded by four and six oxygen ions respectively. Of the sixty-four tetrahedral interstices in a unit cell, only eight are occupied, and of the thirty-two octahedral interstices, sixteen are occupied by metal ions (Fig. 2.1).

Thus, for any “molecule” MFe$_2$O$_4$, one A and two B sites are available. If the divalent metal ion M occupies the tetrahedral A site, then the structure is normal and if it occupies one of the octahedral B sites, then the structure is inverse. If the scattering power of the M ion and that of the ferric ion are not much different, then X-rays cannot distinguish between the two structures.

Fig.2.1: Unit cell of spinel ferrite

Wyckoff [2] gives the spinel space group as $O_h^{7}(Fd3m)$:

\begin{equation}
\text{anion: } \begin{cases} u, u, u; u, u, u, u, u, u; u, u; \frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u \\ 32b; \frac{1}{4}-u, \frac{1}{4}-u, u+\frac{1}{4}, u+\frac{1}{4}; u+\frac{1}{4}-u, u+\frac{1}{4}-u, u+\frac{1}{4}-u, u+\frac{1}{4}-u, u+\frac{1}{4}-u \end{cases}
\end{equation}
cation 16c \( \frac{5}{8}, \frac{5}{8}, \frac{5}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8} \)

cation 8f \( 0, 0, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \)

with the translations, for a face-centered lattice,

\[ +0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}, 0 \]

Packing of the ions within the lattice is perfect when the oxygen parameter \( u = \frac{3}{8} \)

(I) Tetrahedral Sites:

In tetrahedral (A) site, the interstitial is in the centre of a tetrahedron formed by four lattice atoms. Three anions, touching each other, are in plane; the fourth anion sits in the symmetrical position on the top at the center of the three anions. The cation is at the center of the void created by these four anions. In the tetrahedral configuration, four anions are occupied at the four corners of a cube and the cation occupying the body center of the cube. Here the anions at A, B, C are in a plane, and the anion D is above the center of the triangle formed by the three anions. The cation occupies the void created at the center of the cube. For charge neutrality of the system only 8 tetrahedral (A) sites are occupied by cations out of 64 sites per unit cell in FCC crystal structure. Normally, the cations with smaller ionic radii can occupy tetrahedral (A) site.

Fig.2.2 shows the tetrahedral position in the FCC lattice.
(II) Octahedral Sites:

In an octahedral [B] site, the interstitial is at the center of an octahedron formed by 6 lattice anions. Four anions touching each other are in plane, the other two anions sites in the symmetrical position above and below the center of the plane formed by four anions. Cation occupies the void created by six anions forming an octahedral structure. The configuration shows that six anions occupy the face centers of a cube and cation occupies the body center of the cube. For charge neutrality, 16 octahedral [B] sites are occupied by cations out of 32 sites in a spinel structure. In FCC there are 4 octahedral sites per unit cell. Fig.2.3 shows octahedral site in an FCC lattice.
2.2 TYPES OF SPINEL FERRITES

The spinel ferrites have been classified into three categories on the basis of distribution of cations on tetrahedral (A) and octahedral [B] sites [3].

(1) Normal spinel ferrite
(2) Inverse spinel ferrite
(3) Intermediate spinel ferrite

(1) **Normal Spinel Ferrite:**
If there is only one kind of cations that is divalent metal ion on tetrahedral (A) site, the spinel is recognized as normal spinel. In these ferrites the divalent cations occupy tetrahedral (A) sites while the trivalent cations are on octahedral [B] sites. Square brackets are used to indicate the ionic distribution of the octahedral [B] sites. Normal spinel have been represented by the formula \( (M^{2+})_A[Me^{3+}]_B\text{O}_4 \), where \( M \) represent divalent ions and \( Me \) for trivalent ions. A typical example of normal spinel ferrite is bulk ZnFe\(_2\)O\(_4\) (Zinc ferrite) and CdFe\(_2\)O\(_4\) (Cadmium ferrite). The distribution of ZnFe\(_2\)O\(_4\) (Zinc ferrite) and CdFe\(_2\)O\(_4\) (Cadmium ferrite) can be written as:

\[
(\text{Zn})^A[\text{Fe}]^B\text{O}_4 \text{ and } (\text{Cd})^A[\text{Fe}]^B\text{O}_4.
\]

The spin arrangement in normal ferrite is shown in following Fig.2.5:

![Figure 2.5: Normal Ferrites](image)

**Figure 2.5: Normal Ferrites**

(2) Inverse Spinel Ferrites:

In this structure, half of the trivalent ions occupy tetrahedral (A) sites and half octahedral [B] sites, the remaining cations being randomly distributed among the octahedral [B] sites. These ferrites are represented by the formula \( (\text{Me}^{3+})_A[M^{2+}\text{Me}^{3+}]_B\text{O}_4 \). A typical example of inverse spinel ferrite is Fe\(_3\)O\(_4\) in which divalent cations of Fe occupy the octahedral [B] sites [4].

![Diagram](image)
Figure 2.6: Normal Ferrites

(3) Intermediate spinel ferrites:

Spinel with ionic distribution, random between normal and inverse are known as intermediate spinel ferrites or mixed spinel e.g. \((M^{2+}\delta Me^{3+1-\delta})_A[M^{2+1-\delta}Me^{3+1+\delta}]_BO_4\) where \(\delta\) is called inversion parameter. Quantity \(\delta\) depends on the method of preparation and nature of the constituents of the ferrites. For complete normal spinel ferrites \(\delta = 1\), for complete inverse spinel ferrites \(\delta = 0\), for mixed spinel ferrite, \(\delta\) ranges between these two extreme values. For completely mixed ferrites \(\delta = 1/3\). If there is unequal number of each kind of cations on octahedral sites, the spinel is called mixed. Typical example of mixed spinel ferrites are \(MgFe_2O_4\) and \(MnFe_2O_4\) [5].

![Diagram](image)

Figure 2.7: Intermediate Ferrites

Néel suggested that magnetic moments in ferrites are sum of magnetic moments of individual sub-lattices. In spinel structure, exchange interaction between electrons of ions in A and B-sites have different values. Usually interaction between magnetic ions of A and B-sites (A-B sites interaction) is the strongest. The interaction between A-A sites is almost ten times weaker than that of A-B site interaction whereas the B-B sites interaction is the weakest. The dominant A-B sites interaction results into complete or partial (non-compensated) antiferromagnetism known as ferrimagnetism [6]. The dominant A-B sites interaction having greatest exchange energy, produces antiparallel arrangement of cations between the magnetic moments in the two types of sub-lattices.
and also parallel arrangement of the cations within each sub-lattice, despite of A-A sites or B-B sites antiferromagnetic interaction [7].

If the scattering power of the M ion and that of the ferric ion are not much different, then X-rays cannot distinguish between the two structures. Verwey and Heilmanns concluded from a discussion of the lattice constants that Mn, Fe, Co, and Ni ferrites are inverted, whereas Zn and Cd ferrites are normal. This is confirmed by neutron diffraction which is a powerful tool for such problems[8].

2.3 U PARAMETER

While considering the crystal structure of spinel ferrite it is mentioned that the oxygen ions from an FCC structure is true is not absolute. In reality there slight deviations may exist owing to a deformation caused by the metal ions. The tetrahedral sites, which are smaller than the octahedral ones, are too small to contain metal ions, if we regard the metal ions as well as the oxygen ions as solid spheres. A consequence is that all tetrahedral sites are expanded by equal displacement of the four oxygen ions outwards along the body diagonals of the cube. These four oxygen ions thus still occupy the corners of an enlarged tetrahedron, so that the surrounding of each A ion remains cubic symmetry. However, the four oxygen ions of the octahedral octants are shifted in such a way that this oxygen tetrahedron shrinks by the same amount as the first expands. The oxygen surrounding of each B ion no longer has cubic symmetry, but symmetry similar to that of the neighboring B ions. The oxygen ions are displaced along the body diagonal. The quantitative measure of this displacement is could as the oxygen parameter u and is the distance between an oxygen ion and a face of the cubic the displacement of the
oxygen ions make the tetrahedral sites larger, the octahedral sites are reduced in size so that size of the two interstitial sites become more equal.

The interstices available in an ideal close packed structure of rigid oxygen anions can incorporate in the tetrahedral sites, only metal ion with a radius $r_{\text{tetra}} \leq 0.30$ Å and in octahedral sites only ions with a radius $r_{\text{oct}} \leq 0.55$ Å. In order to accommodate cations like Co, Cu, Mg, Mn, Ni and Zn the lattice has to be expanded. The difference in the expansion of octahedral and tetrahedral sites is characterized by a parameter called oxygen parameter ($u$). In an ideal spinel, the tetrahedral and octahedral sites are enlarged in the same ratio and accordingly the distance between the tetrahedral site (0,0,0) and the oxygen site is 3/8 and hence

$$u_{\text{ideal}} = \frac{3}{8}$$

However, the incorporation of divalent metal ions in tetrahedral sites induces a larger expansion of the tetrahedral sites, leading to a large value for $u$ than the ideal value. The tetrahedral sites are expanded by an equal displacement of the four oxygen ions onwards, along the body diagonals of the cube, still occupying the corners of an expanded regular tetrahedron. The four oxygen ions of the octahedral sites are shifted in such a way that this oxygen tetrahedron shrinks by the same amount as the first expands. The oxygen ions move along the arrow as shown in Fig.2.8.
2.4 MAGNETIC INTERACTIONS

The magnetic properties of spinel ferrites have the general formula $\text{AB}_2\text{O}_4$ are governed by intricate interplay between the intra-site $\text{A-O-A}$ and $\text{B-O-B}$ ($J_{\text{AA}}$ and $J_{\text{BB}}$ respectively) and inter-site $\text{A-O-B}$ ($J_{\text{AB}}$) super-exchange 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 $\text{O}^{2-}$ ions, by super-exchange mechanism,


2] B-O-B interaction.

In general, the magnitude of the interaction energy between the magnetic ion, \( \text{Me}^I \) and \( \text{Me}^{II} \) depends upon (i) the distances of the ions from oxygen ions and (ii) the angle \( \text{Me}^I\text{-O-Me}^{II} \) represented by the term \( \Phi \) as shown in Fig. 2.9.

![Fig. 2.9: Me\(^I\) – O - Me\(^{II}\) angle in ferrites.](image)

An angle of 180° 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 are given in Fig. 2.10. 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.

![Fig. 2.10 Configuration of ions pairs in spinel ferrites with favorable distance and angles for effective magnetic interaction.](image)
The A and B ions shown in Fig. 2.8 refer to ions occupying tetrahedral and octahedral sites respectively. The different exchange interaction follows that the A-B interaction is greatest. For the 1\textsuperscript{st} 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 1\textsuperscript{st} B-B configuration drawn in Fig. 2.8. 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 MAGNETIC PROPERTIES OF FERRITES

The magnetic properties of solids are important and attempts to understand them have lead to a deep insight into the fundamental structure of many solids, both, metallic and non-metallic. However, in many cases the understanding is still far from complete. In addition to the fundamental interest in the magnetic properties of solids there is great interest in the application of magnetic materials.

Magnetic properties play an important role in the applications of soft magnetic materials. It depends upon composition, temperature, size, shape orientation of grains, the concentrate and distribution of various crystal imperfections and the state of the lattice.

Magnetic properties are divided into two groups viz. intrinsic or structure insensitive and extrinsic or structure sensitive. Structure insensitive properties include saturation magnetization and the Curie temperature. Eddy current loss, resonance spins and domain walls, induction, permeability, hysteresis loop, coercive force and remanence are structure sensitive properties.
2.5.1 Magnetization:

Magnetic hysteresis is a key factor determining the possible applications of the magnetic materials. Generally it is related to domain wall [9]. Hysteresis studies provide useful information relating to saturation magnetization, squareness ratio, coercive force etc. These parameters are technologically important as the usefulness of a particular composition for particular applications is dictated mainly by these parameters. For example – large magnetic induction with high resistivity is the requirement of a ferrite core transformer. Large squareness ratio is the requirement of memory cores. For making a permanent magnet large coercive force is required. In addition, the shape of hysteresis loop and thermal variation of retentivity and coercivity furnish information about the type of magnetic grains. i.e. Multi Domain (MD), Single Domain(SD), Super-paramagnetism (SP) present within the material.

2.5.2 Saturation magnetization:

The saturation magnetization of ferromagnetic material is defined as the maximum attainable intensity of magnetization per unit volume. This is denoted by $M_s(T)$, signifying that it varies as a function of temperature. As $T \rightarrow 0K$, $M_s(T) \rightarrow M_0$, which is called absolute saturation magnetization for each material, $M_0$ is the largest value of $M_s$. The saturation magnetization $M_s$, is determined by conducting a saturation measurement under a strong field. Absolute saturation magnetization is determined by conducting a series of saturation measurements at 4.2 K (the boiling point of liquid helium at 1 atmospheric pressure) and extrapolating the $M_s$ value to 0 K. The
experimental method for the determination of saturation magnetization is reviewed by McGuire and Flanders [10].

The absolute saturation magnetization is given by

\[ M_o = N I g \mu_B \] ....(2.1)

where \( N \) is number of atoms per unit volume

\( I \) is total angular momentum and quantum number of the atom

\( g \) is the Lande factor and

\( \mu_B \) is Bohr magneton.

Name of the parameters \( N, I \) and \( g \) is this expression \( N, I \) and \( g \) are the structure sensitive parameter.

2.5.3 Magneto- Crystalline Anisotropy:

The magnitude of Magneto-Crystalline anisotropy constant \( K_1 \) represents the extents to which the magnetization of an individual grain favors particular crystallographic directions. In other words, it is a measure of the energy required to rotate the magnetization from an easy to a hard direction. Magneto- Crystalline anisotropy energy will depend upon the angles between the magnetization vector and crystal axes as well as strength with which the magnetization is bound to the easy axes.

A cubic crystal possesses crystal anisotropy energy \( E_A \)

\[ E_A = K_0 + K_1 (l^2 m^2 + m^2 n^2 + n^2 l^2) + K_2 (lmn)^2 \] ...(2.2)
In which $K_0 =$ value of minimum energy position

$K_1 =$ anisotropy constants of [110] direction

$K_2 =$ anisotropy constants of [111] direction

$l =$ Projection of unit magnetization vector upon X axis

$m =$ Projection of unit magnetization vector upon Y axis

$n =$ Projection of unit magnetization vector upon Z axis

When the easy direction of magnetization is parallel to a cube edge [100]

then $E_A = E_0 = 0$.

When the easy direction is along face diagonal

$E_A = K_1 / 4$.

When the magnetization lies along a cube diagonal

$E_A = K_1 / 3 + K_2 / 27$.

The anisotropy field is given by

$H_A = 2K_1 / Ms. \quad \ldots (2.3)$

Magneto-crystalline anisotropy is solely function of the crystal structure and chemical composition and is independent of microstructure. Important properties such as permeability, coercive force and resonance frequency depends upon anisotropy, but
other factors such as grain size may cause the properties to be microstructure sensitive even though anisotropy is not.

Anisotropy is temperature dependent because thermal energy disorders spins and loosens the lattice binding. This action reduces spin orbit coupling so that anisotropy energy decreases sharply generally in a logarithmic manner [11]. Since magnetization also decreases with temperature, the anisotropy field decays rapidly.

The values of $K_1$ for the various ferrites vary roughly between $10^3$ and $10^5$ erg/cm$^3$ and so it is much smaller than the maximum shape anisotropy. A peculiar property of crystalline anisotropy is that in most cases, it falls very rapidly with increasing temperature i.e. much faster than $M_s^2$ [12].

Because $K_1$ is responsible for most of the technical properties of ferromagnetic materials, it is important to understand its dependence on temperature. This influence of temperature is in fact in two ways –

1) temperature dependence of the basic mechanism of $K_1$ and
2) the change in anisotropy due to temperature variation of the saturation magnetization $M_s$.

2.5.4 A.C. Susceptibility:

The low field A. C. susceptibility plays a very important role in describing the behaviour of substance and is defined as the ratio of the magnetization $M$ produced in a substance to the magnetic field strength ($H$) to which it is subjected

$$\chi = \frac{M}{H} \quad \text{emu/cm}^2\text{Oe} \quad \text{...(2.4)}$$
High temperature a.c. susceptibility measurement were first carried out on iron by Hopkinson[13] and showed that, it reaches a peak value just before Curie temperature $T_c$ and becomes zero rapidly. The hysteresis and susceptibility studies at various temperature can provide an idea of whether a magnetic sample contains single domain (SD), multi-domain (MD) or super magnetic particles (SP).

**2.5.5 Magnetic Hysteresis:**

A typical magnetic induction ($B$) versus magnetizing field ($H$) graph for a magnetic material (Hysteresis loop) is shown in Fig.3.3 Starting from demagnetized sample if $H$ is increased, $B$ increases and reaches to saturation value ($B_s$). If $H$ is now decreased and brought to zero saturation decreases to $B_r$ (remanence). If the decrease in $H$ is continued by making it negative, the induction decreased further till it reaches zero at the field $H_c$. $H_c$ is known as coercivity of the material. The field required to bring ‘$B$’ to zero is known as $BH_c$, while that required to bring ‘$I$’ to zero is known as $IH_c$.

The permeability depends on the state of magnetization of the sample. For small signals the permeability given by the slope of the $B$ versus $H$ curves near its origin is known as initial permeability $\mu_0$. The maximum value of the permeability is designed as $\mu_m$. The differential permeability is defined as $dB/dH$, the slope of magnetization curve at the point of interest.

Materials with low coercivity $H_c$ are known as soft magnetic materials, while those with high coercivity $H_c$ are known as hard magnetic materials. The hysteresis properties are highly sensitive to crystal structure, heat treatment, chemical constitution, porosity and grain size.

**2.5.6 Coercive Force:**
The influence of the non magnetic inclusion upon the coercive force of ferromagnetic materials was first studied by Kersten [14] and by Neel [15]. It follows from both the theories that in a ferromagnetic material the domain wall extend preferably from pore to pore. According to Kersten this is due to the reduction in area of the wall. Neel points to the fact that the internal stray fields which are produced by the inclusions in the ferromagnetic materials will be smaller if the Bloch walls cross them. If the wall thickness is comparable to the diameter of the pore or inclusion, a very large field will be needed to detach the walls from it, this field being essentially the coercive force[16].

2.5.7 Remanence Ratio:

The remanent magnetization is determined to a large extent by the nucleation of reverse or 90° spike domains about a pore or grain boundary. As a consequence, the size of any spike domains will directly contribute to the reduction in R. Remanence ratio depends on microstructure, magneto-crystalline anisotropy and stress sensitivity. The relation between R and K₁ is less clear because of possible competing effects. Saturated toroids in which the magnetization vector is forced to lie in the direction of an applied field, reducing the field to zero will cause a relaxation of magnetic vectors to the closed preferred direction in each crystallite. For example in the spinel crystals which give spontaneously square loops, the sign of K₁ is negative. There are in case eight preferred directions of magnetization the cube diagonals [111]. Under these circumstances it has been calculated that Mr / Ms = 0.87 [17].

There are two conditions for this high ratio to be obtained. First shape anisotropy must be low in magnitude. In a closed magnetic circuit (a crack free toroids) shape
anisotropy can still occur if pores or other non-magnetic inclusions are present. Free poles are formed at those boundaries of pores which intersect the internal field directions. To minimize the associated energy, the domains of reverse magnetization (Neel’s spike domain) are formed. The value of these domains presents at remanence, of course, subtracted from the total magnetization. Second, stress anisotropy must be minimized. If the internal stress energy is predominant over magneto-crystalline energy, there are two preferred magnetization directions, which for negative magnetostriction correspond to direction of greatest compressive strain. In this case Mr / Ms = 0.5. If the internal stress energy is small compared to magneto-crystalline energy, it still can have an effect on magnetization vectors. The saturation magnetization vector returns to an easy direction closed to the field only if the energy in that direction is less than that of crystallographically equivalent direction.

For several SLF’s, the ratio of Mr / Ms has been found to be in the range of 0.7 to 0.8 at room temperature[18]. Reasons from the deviation from the predicted value of 0.87 are perhaps the porosity effects, residual internal stress effect, or the failure to take into account the presence of reverse domains at grain boundaries in arriving at the predicted Mr / Ms.

2.5.8 Permeability (µ):

The absolute permeability (µ) is defined as the ratio of the magnetic induction (B) to the applied magnetic field (H), this definition refers to the normal permeability when the material is cyclic magnetic state. A ferromagnetic is said to be in such a state if responds equally to field applied to either of the two opposite directions. To attain a
cyclic state, the specimen must be demagnetized completely by either of the following two methods.

1. Heating to a temperature above the Curie point, followed by slow cooling in zero field.
2. Magnetizing under an alternating field, first to a value close to saturation induction by gradually decreasing the amplitude of the field.

2.5.9 Curie temperature:
All ferromagnetic materials exhibit a characteristic temperature known as the Curie temperature ($T_c$). This is the critical temperature at which thermal energy is just enough to destroy the spontaneous magnetization. Thus, the Curie temperature marks the transition point at which a ferrimagnet is converted into paramagnet upon heating. Neel [19] and Gorter [20] reported the dependence of Curie temperature on the distribution of metallic ions on tetrahedral (A) and octahedral (B) sites. Forestier [21] studied with zinc content. Sager [22] have reported studies on tetravalent Ge$^{4+}$, Ti$^{4+}$ and Sn$^{4+}$ ions substituted magnesium ferrites. The influence of preparation techniques and cation distribution on various properties of copper and magnesium mixed ferrites has been reported in the literature. They observed that migration of cations on tetrahedral sites shifts the Curie temperature to lower temperature.

The expression for the Curie temperature $\theta_c$ is given by

$$\theta_c = \frac{z J_{ex}}{J(J + 1) / 3 k}$$

...(2.5)

where, $z$ is the coordination number

$J_{ex}$ is the exchange integral
J is the total angular momentum quantum number and 
k is the Boltzmann constant.

2.6 MAGNETISM

The magnetism $M$, when relatively small, is then often found to increase
proportionally with a magnetic field $H$ according to,

$$M = \chi H \quad \text{...(2.6)}$$

where, $\chi$ is the (constant) susceptibility per unit volume.

For isotropic materials, $M$ and $H$ are in the same direction, i.e., $\chi$ is scalar. For
anisotropic materials, $M$ and $H$ are not necessarily in the same direction, and $\chi$ is a
tensor. Depending upon size and the magnitude of $\chi$, magnetism may be classified as
diamagnetism, Paramagnetism, ferromagnetism, antiferromagnetism and
ferrimagnetisms.

2.6.1 Diamagnetism:

For this phenomenon to occur there need to be no permanent dipole presents, the
magnetic field induces a magnetic moment i.e. oppose to $H$. This is really the most
natural form of magnetism and occurs in principle in all substances. The value of $\chi$ is
usually of the order of $10^{-5}$, it is very small compared to other materials. Thus, for a
diamagnetic material susceptibility is negative and has a very low value. The
diamagnetism occurs through deformation of the electric charge distribution when a
field is applied and it disappears when the field is removed.

2.6.2 Paramagnetism:

When susceptibility is positive but small, magnetic moments are already present but
which have a random orientation, are to a slight extent aligned in the field, this
alignment being opposed by thermal agitation. In this property spin and orbitally derived magnetic moments co-exists. The materials are also called magnetically dilute systems. There is no interaction between the individual atoms. The substance obeys Curie law.

2.6.3 Ferromagnetism:
In the ferromagnetic materials, magnetic moments are present as in case of paramagnetism, the difference is the spins of neighboring ions are already more or less parallel. This does not mean that the whole specimen is necessarily uniformly magnetized (i.e. any arbitrary piece of soft iron is not magnet), for if it were, the finite dimensions would give rise to large demagnetizing forces.

In ferromagnetic materials, such as metallic iron, cobalt and nickel the electron spins of each of the atom couple together to form resultant unit cell magnetic moment. The individual magnetic moments are considered together. The building block being the unit cell of the crystalline solid.

2.6.4 Antiferromagnetism:
In antiferromagnetic materials, the transition metal ions are separated usually by small legends such as oxides and halides. In such compounds adjacent metal ions couple with their spins antiparallel. There are always equal numbers of two alignments so that in the absence of magnetic field there is no resultant magnetization. In other words, magnetic moments are antiparallel to each other and the net moment is zero.

2.6.5 Ferrimagnetism:
Ferrimagnetism is a modification of antiferromagnetism, which results when the antiparallel moments are unequal, so that there is a net overall magnetization. A
ferrimagnetic material is one in which the magnetic moments of the atoms on different sub-lattices oppose as an antiferromagnetism, but opposing moments are unequal and a spontaneous magnetization remains. This behavior was first recognized in the technologically important group of materials called ferrites. Most of the materials, whose magnetic properties are of commercially important are either ferromagnetic or ferrimagnetic.

2.7 ELECTRICAL PROPERTIES

2.7.1 D. C. Resistivity:

At high frequencies, eddy current losses may be high resulting in a significant loss of energy, so the d.c. bulk resistivity is an important property since eddy current losses in the ferromagnetic materials are inversely proportional to the resistivity, they can be minimized by the use of magnetic materials of high resistivity.

Electrical properties of ferrites have been the subject of many researchers since the artificial production of spinels by Snoek [23]. The amount of charge transported through a unit block material on the application of a unit electric field per unit volume is known as the electrical conductivity of the solids. Magnetic oxides, which are commonly known as ferrites, attracted the attention of physicist and technologists because they are magnetic semiconductors as well as electric insulator. Hence ferrites, which are ferrimagnetic semiconductor, opened a new area in the physics of material and the need for high resistivity ferrite led to the synthesis of the various ferrites. The increasing demand for low loss ferrites resulted in detailed investigations on the various aspects of the conductivity and on the influence of the various substitutions on the electrical conductivity, thermo-electric power, hall mobility etc.
It is an experimental fact that, electrical conductivity of ferrite depends much upon the amount of iron present in the lattice in the ferrous state. A high concentration of ferrous ions leads to high electrical conductivity. In ferrites the electron concentration is of the order of $10^{22}$ per cm$^3$. The low mobility of electrons ($10^{-4}$ cm$^2$/vs.) and holes ($10^{-8}$ cm$^2$/vs.) limits their conductivity. Suitable preparation technique and chemical composition control the conductivity in the ferrites [24]. The order of magnitude of conductivity influences the dielectric and magnetic properties [25,26]. It has been observed that electrical conductivity markedly changed by controlling the sintering temperature, sintering atmosphere, by substituting with appropriate type and amount of substituent. Many workers has studied the electrical properties of ferrites[27-29].

Ferrites behave like a semiconductor, the values of resistivity varies from about $10^{-4}$ to $10^{-9}$ ohm-m at room temperature. In ferrite, the law of conductivity is associated with the simultaneous presence of ferrous and ferric ions on the equivalent lattice sites (usually on octahedral site). The conduction mechanism in ferrite is quite different from that in semiconductor. The mechanism of conduction in ferrite is known[30].The extra electrons on ferrous ions require small energy to move to similarly situated adjacent ferric ions. The valency states of two ions are interchanged (Fe$^{2+}$ and Fe$^{3+}$). Under the influence of an electric field, these extra electrons can be considered to constitute the conduction current, jumping or hopping from one iron ion to the next. Assuming all the Fe$^{2+}$ ions at the B-site to participate in hopping transport, the number of charge carries (n) works out to be of the order of $10^{22}$ per cm$^3$ since the mobility is very low, the conductivity is low, even through n is large. The electrical resistivity of soft ferrites is high compared to those of the magnetic materials at room
temperature in the range about $10^{-4}\Omega\cdot m$ to $10^9\Omega\cdot m$. This factor is responsible for the wide use of ferrites in microwave frequencies. The resistivity of soft ferrites is of the order of $10^6\Omega m$ like semiconductor. The conductivity is due to the presence of Fe$^{3+}$ and Me$^{2+}$ (Me = Ni, Co etc.) ions. The presence of Fe$^{3+}$ results in n type behaviour and of Me$^{2+}$ in P type behaviour. The conductivity arises due to the mobility of the extra electron from (Fe$^{3+}$) or the positive hole (Me$^{2+}$) 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 [36] and Elwell et al. [37] 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,

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

Therefore unbounded electron transfer process can take place.

According to Verwey [38], 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 [39]. The presence of Fe$^{2+}$ ions is sometimes desirable [40] 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 [41-45]. 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 polaron and since it is confined to a small region it is termed as small polaron. Since these materials behave like semiconductors, their resistivity should decrease with increase in temperature according to the relation of the form,

\[ \rho = \rho_0 \exp \left[ \frac{E_g}{kT} \right] \]  \hspace{1cm} \text{(2.7)} \]

Where \( E_g \) - the activation energy

\( k \)- Boltzmann constant and

\( T \)- The absolute temperature

\( E_g \) is the energy required for the hopping of the electrons. The plot between \( \log \rho \) and \( 1/T \) breaks at temperature; which corresponds, closely with the observed ferrimagnetic Curie temperature. The value of \( E_g \) which varies between 0.1 eV to 0.5 eV, The high activation energy is associated with the high resistivity at room temperature [46].
The activation energy increases on changing from ferrimagnetic to paramagnetic region, this anomaly strongly support the influence of magnetic ordering pen conductivity process in ferrites. Many reports are available where in the slope of the plot log $\rho$ versus $1/T$ varies at Curie temperature [47-49]. The value of resistivity of various ferrites at room temperature varies on a wide range. For example; the resistivity at room temperature of cobalt ferrite is 106 ohm-cm [50]. It has been reported that electrical resistivity depends on stoichiometric [51] the presence of excess iron (x>2) leads to the formation of Fe$^{2+}$ and reduced resistivity. A very small amount of impurity in an otherwise stoichiometric material can also lower the resistivity ferrites, it is necessary to avoid excess iron in the lattice and it is not unusual to add small quantity of manganese or cobalt. [52]

In general, substitution of cation that tends to reaming in a lower valance state leads to p-type conduction and substation of cation that tends to remain in higher valance state leads to n–type conduction. A part from the inherent properties of the material, there are various contributions to the measured low frequency resistivity.
1. Polycrystalline samples are sintered and contain pores. The pores, probably air filled will be of resistivity different from that of ferrites.

2. The grain size of the individual crystallites in polycrystalline sample can affect among the other things, the number of grain to grain contact and thus influences the conduction path and hence the resistivity.

3. The chemical and/or heat treatment may result in chemical in homogeneity, which affect the resistivity.

### 2.8 DIELECTRIC PROPERTIES

Ferrites have vast applications from microwave to radio frequencies. The low conductivity of ferrite causes them for its use in microwave applications. They exhibit high resistivity and dielectric properties.

The dielectric properties used for preparation, chemical composition and grain structure or size. When a ferrite is sintered under slightly reducing condition, the ferrites are dependent upon several factors including the method of valence state changes, the individual cation found in the sample leads to high conductivity and when such a material is cooled in a 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 \((10^2 \text{ Hz} - 10^5 \text{ Hz})\) dielectric behaviour of ferrite. Among the many workers involved in this
type of studies, the prominent ones are Wahab [53] Moltgen [54], Kamiyoshi [55], Iwauchi et. al. [56], Rezlescu [57,58] and Josyolu [59].

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 [60], the process of dielectric polarization in ferrite takes place through a mechanism similar to conduction process.

Fig.2.12: Experimental setup for dielectric measurement

2.8.1 Dielectric measurement

The measurements of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan\delta$) were carried out as a function of temperature and frequency both on a LCR-Q meter (HP make, 4192). The measurements were performed on circular pellet of 10 mm diameter and 2 mm thickness using two-probe method. The measurements
of frequency dependence were carried out from 100 Hz to 1 MHz at room temperature.

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