CHAPTER II

THEORETICAL ASPECT OF SPINEL

2.1) Introduction:-

Ferrites are electrically non-conductive ferrimagnetic ceramic compound materials. They are usually composed of oxides of iron and other metals possessing combined properties of magnetic conductor (Ferro-magnet) and electrical insulator. For discussion of their structural, magnetic and transport properties, it is convenient to group the ferrites under the following classes; a) spinel, b) garnets, c) ortho-ferrites and d) hexagonal ferrites.

Ferrites have interesting electrical and magnetic properties. These properties mainly depend upon chemical composition, method of preparation, sintering time and temperature, and distribution of cations present among the tetrahedral and octahedral sites. The ferrites by virtue of their structure can accommodate a variety of cations at different sites enabling a wide variation in properties. The ferrites have been found many technological applications due to their excellent magnetic properties such as high initial permeability and high saturation magnetization, high electrical resistivity and low eddy currents and dielectric losses. Ferrites are extensively used in microwave devices, computer memory chips, magnetic recording media etc. Ferrites are widely used in radio and television as well as in sensor for temperature control.

2.2) Crystal Structure of Spinel Ferrites:-

The ferrimagnetic oxides are known as ferrites. The spinel ferrite crystallizes in the cubic structure which is possessed by mineral spinel \( \text{MgAl}_2\text{O}_4 \). The structure of spinel was first determined by Bragg
[1] and Nishikawa [2]. The spinel ferrites have general chemical formula $\text{M}^{2+}\text{Fe}^{3+}\text{O}_4^{2-}$ or $\text{M}^{2+}\text{O}_2\text{Fe}^{3+}\text{O}_3^-$ where $\text{M}^{2+}$ is a divalent metal ion such as $\text{Fe}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Mg}^{2+}$, $\text{Zn}^{2+}$, $\text{Mn}^{2+}$, $\text{Co}^{2+}$, $\text{Cd}^{2+}$ etc. and $\text{Fe}^{3+}$ is trivalent metal ion [3].

The chemical formula cannot be criteria to decide the crystal structure because there are some exceptions like olivine ($\text{Zn}_2\text{SiO}_4$), crysolobryl ($\text{BeAl}_2\text{O}_4$) which does not have spinel structure. On the other hand, cationic radii decide the crystal structure. For oxide spinels, cations having the radii 0.45Å to 0.95Å are suitable for the formation of spinel. There are few compounds with slightly different chemical formula can have spinel structure (e.g. $\gamma\text{Fe}_2\text{O}_3$ and $\gamma\text{Mn}_2\text{O}_3$). The unit cell contains eight molecules and this can be written as $\text{M}_8\text{Fe}_{16}\text{O}_{32}$. Therefore, there are 32 $\text{O}^{2-}$ anions, 16 $\text{Fe}^{3+}$ cations and 8 $\text{M}^{2+}$ cations in the unit cell. The oxygen anions are physically the greatest and they form, ideally, a face-centered cubic (FCC) lattice. Within this lattice two types of interstitial positions occur, namely tetrahedral (A) sites and octahedral (B) sites and these are occupied by metallic cations. There are 96 interstitial sites in unit cell, 64 tetrahedral (A) sites surrounded by four oxygen ions and 32 octahedral (B) sites surrounded by six oxygen ions. Out of 24 cations, eight occupy tetrahedral (A) sites and sixteen occupy octahedral (B) sites as shown in Fig. 2.1. Therefore, the crystallographic environment of the (A) and (B) sites are distinctly different. The crystal structure can be described by subdividing the unit cell into eight octants, each of edge $a/2$ (a is the edge of unit cell) as shown in Fig.2.2. This helps to describe the location of oxygen ions and metal ions in every octant. The four shaded octants and unshaded octants have identical contents. The contents of two lower left octants in Fig. 2.2 are shown in...
Fig. 2.3. One tetrahedral site occurs at the center of the right octant and other tetrahedral sites are at certain octant corners. Four octahedral sites occur in the left octant; one is delineated by dashed lines to six oxygen ions, two of which shown dotted, are in adjacent octants, behind and below. The oxygen ions are arranged in the same way (tetrahedrally) in all octants.

2.2.1) **Space group and structural co-ordinates:**

The space group of cubic spinel structure is $O_h^7(Fd3m)$ given by Wyckoff [4]. The structural coordinate of tetrahedral, octahedral and oxygen ions in terms of the lattice parameter ($a$) are given as follows, [u varies between 0.375 and 0.395]

Equivalent positions:

$(0,0,0); \left(0, \frac{1}{2}, \frac{1}{2}\right); \left( \frac{1}{2}, 0, \frac{1}{2}\right); \left( \frac{1}{2}, \frac{1}{2}, 0\right)$

Position of A-site cations (8f)

$(0,0,0); \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$

Position of B-site cations (16c)

\[
\begin{array}{llllll}
(5 & 5 & 5) & (5 & 7 & 7) & (7 & 5 & 7) & (7 & 7 & 5) \\
(8 & 8 & 8) & (8 & 8 & 8) & (8 & 8 & 8) & (8 & 8 & 8)
\end{array}
\]

Position of oxygen ions (32b)

$(u,u,u); \left(\frac{u}{4}, \frac{u}{4}, \frac{u}{4}\right); \left(\frac{u}{4}, u, \frac{u}{4}\right); \left(\frac{u}{4}, \frac{u}{4}, u\right); \left(\frac{u}{4}, u, u\right); \left(\frac{u}{4}, \frac{u}{4}, \frac{u}{4}\right); \left(\frac{u}{4}, \frac{u}{4}, \frac{u}{4}\right)$
2.2.2) Oxygen parameter (u):-

The oxygen ions form a face centered cubic structure is true in ideal case. In reality small deviations are found due to the deformations caused by the metal ions. The tetrahedral sites which are smaller than the octahedral sites are in ferrites, too small to contain a metal ion. A consequence of this is that, the tetrahedral sites are expanded by an equal displacement of four oxygen ions outwards along body diagonals. The displacement of oxygen ion along the body diagonal is known as oxygen parameter (u) as shown in Fig.2.4. These four oxygen ions occupy the corners of enlarged tetrahedron and surrounding of each (A) ion retains cubic symmetry. However, the four oxygen ions of the octahedral octants are shifted in such a way that, this oxygen tetrahedron shrinks by some amount as first expands. As a result of this oxygen surrounding of each [B] ion no longer has cubic symmetry. In ideal case u=3/8 and in actual case u is slightly greater than ideal value.

The u-parameters generally increases linearly with \( \left( \frac{r_A - r_B}{a} \right) \)

where ‘a’ is the lattice parameter and \( r_A, \) \( r_B \) are the radii of ions in the (A) and [B] sites respectively. The radii of the spheres in both types of sites are given by the expressions,

\[
r_A = \left( u - \frac{1}{4} \right) a \sqrt{3} - R_0 \tag{2.1}
\]

\[
r_B = \left( \frac{5}{8} - u \right) a - R_0 \tag{2.2}
\]

Where \( r_A \) and \( r_B \) are radii of the tetrahedral and octahedral site cation respectively, \( R_0 \) is the radius of oxygen ion \((R_0 = 1.32 \, \text{Å})\).
2.2.3) Classification of spinels:-

The behaviour of electrical and magnetic properties of spinel ferrites is governed by the distribution of iron and the divalent metal ions among tetrahedral and octahedral sites of the spinel lattice. There are sixteen B- sites and eight A- sites occupied in the unit cell. On the basis of cation distribution and valency of cations, spinels can be classified into three groups as, 1) normal spinels, 2) inverse spinels and 3) random spinels.

2.2.3. I) Normal spinel ferrites:-

When all eight divalent metal ions $M^{2+}$ occupy the tetrahedral (A) sites and remaining sixteen trivalent ions $Fe^{3+}$ occupy the octahedral [B] sites, then the spinel is called as normal spinel. The normal spinel ferrites do not exhibit ferrimagnetic behaviour. In these ferrites A-B interaction does not exit because there are no magnetic ions on the A sites, B-B interaction helps up half the magnetic ions in one direction so that alternate planes of B-sublattice are magnetized in opposite directions rendering these ferrites non-ferromagnetic. The angle between A-A, B-B and A-B cations in a spinel structure as shown in Fig.2.5.

The non- magnetic cations like $Zn^{2+}$ and $Cd^{2+}$ have a tendency to occupy tetrahedral (A) site and therefore the cation distribution for normal spinel can be represented as,

$$ (M^{2+})^A [Fe^{3+}Fe^{3+}]^B O_4^{2-} $$

eg. $(Zn^{2+})^A [Fe^{3+}Fe^{3+}]^B O_4^{2-} \rightarrow \text{Zinc ferrite}$

$$ (Cd^{2+})^A [Fe^{3+}Fe^{3+}]^B O_4^{2-} \rightarrow \text{Cadmium ferrite} $$
2.2.3. II) Inverse spinel ferrite:

Inverse spinel ferrite is the structure of the majority of ferrites. These ferrites have half the trivalent ions on (A) site and remaining half trivalent ions and all divalent metal ions on the [B] site. The cation distribution may be written as

\[
\left(\text{Fe}^{3+}\right)^A \left[M^{2+} \text{Fe}^{3+}\right]^B O_4^{2-}
\]

eg. \(\left(\text{Fe}^{3+}\right)^A \left[Mn^{2+} \text{Fe}^{3+}\right]^B O_4^{2-}\) → Manganese ferrite

\(\left(\text{Fe}^{3+}\right)^A \left[Ni^{2+} \text{Fe}^{3+}\right]^B O_4^{2-}\) → Nickel ferrite

2.2.3. III) Random spinel ferrite:

In this ferrite \(M^{2+}\) metal ions and \(\text{Fe}^{3+}\) are randomly distributed over the A site and B site depending on the physco-chemical conditions of preparation. Intermediate degrees of freedom are also exhibited by ferrite systems. The general formula for partially inverted ferrites is written as

\[
\left(M^{2+}_x \text{Fe}^{3+}_{1-x}\right)^A \left[M^{2+}_{1-x} \text{Fe}^{3+}_{1+x}\right]^B O_4^{2-}
\]

\(\text{MnFe}_2\text{O}_4\) and \(\text{CuFe}_2\text{O}_4\) are examples of partially inverted ferrites.

2.2.4) Substitutional ferrites:

A few or all divalent metal ions or iron ions in a ferrite may be substituted by alternative cation of magnetic or non-magnetic in nature [5]. The resulting ferrites are called as substitutional ferrites. The substitution can be done by two ways:

[1] Replacing divalent M ion by other divalent \(M^{2+}\) ion.

[2] Replacing the trivalent iron ions by other trivalent \(M^{3+}\) ions.

For example, in copper ferrite \(\text{CuFe}_2\text{O}_4\) copper may be substituted partly or completely zinc

\(\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4\) → Copper zinc ferrite
or part of iron may be substituted by one of trivalent non-magnetic Al, Cr or Ga elements;

\[ \text{CuFe}_{2-x}\text{Al}_x\text{O}_4 \rightarrow \text{Copper Aluminum ferrite} \]

The resulting substitutional ferrites are equivalent to a solid solution of two phase end member ferrites.

2.3) X-ray Diffraction:-

X-rays are electromagnetic radiation having exactly same nature as light but of very much shorter wavelength. The X-rays used in diffraction have wavelength in the range 0.5 to 2.5 Å. X-rays occupy the region between gamma and ultraviolet rays in the complete electromagnetic spectrum.

X-ray diffraction technique is a well established tool in scientific and industrial work for the study of crystal structure of material, identification of the initial material and final products, chemical analysis and phase equilibrium. We have to studied powder diffraction method to conform the single phase formation of spinel ferrite. X-ray diffraction is one of the most interesting and informative properties of X-rays. This phenomenon is explained as the scattering of X-ray by metal with accompanying variation in intensity in different directions due to the interference effect. When a beam of X-ray is allowed to fall on matter, it is scattered by the atoms. These scattered radiations spreads out spherically from all the atoms in the sample and interference effect of the scattered radiation from different atoms to cause intensity of scattered radiation to exhibit maxima and minima in various directions.

As the crystallites are randomly oriented a reflection at the particular position is due to a set of atomic planes satisfying Bragg’s condition. The Bragg’s law is,

\[ n\lambda = 2d\sin\theta \]  

2.3
where \( d \) is interplanar distance
\[ \lambda \] is wavelength of X-ray radiation
\( n \) is order of reflection and
\( \theta \) is Bragg’s angle

Similar to X-rays, electron and neutron diffraction technique are also used to determine crystal structure of ferrites. In neutron diffraction, it is observed that the scattering power of an atom increases with an increase in atomic number and decreases with an increase in scattering angle, irrespective of X-ray and electron diffraction. The intensity of neutron diffraction is found to be a uniform and is independent of the values of atomic number. X-ray analysis of ferrites was carried out by Barth and Posnjack [6].

2.3.1) X-ray diffractometer and its principle:-

The essential features and principle of the diffractometer are shown in Fig 2.6. An incident beam of X-ray passing through a filter is collimated by the slit ‘A’. The monochromatic radiation is incident on the specimen kept on holder ‘C’ and reflected by crystal planes satisfying Bragg’s law. As the crystallites are randomly oriented a reflection at a particular position is due to a set of atomic planes satisfying Bragg’s condition. As a result, a convergent beam diffracted by set of all parallel planes is produced which comes to a focus at slit ‘F’ and then enters the counter ‘G’. ‘B’ is a special slit which collimates the diffracted beam. The counter ‘G’ is connected to a rate meter and the output of the circuit is fed to a fast automatic recorder which registers counts per second versus \( 2\theta \). The location of the centroid of the peak recorded gives \( 2\theta_{hkl} \) for corresponding Bragg reflection.

The receiving slits and the counter are supported on the carriage E, which can be rotated about the vertical axis ‘O’ and whose angular
position $2\theta$ can be read on the graduated circular scale ‘K’. As the counter ‘G’ moves through $2\theta$ degree through mechanical coupling between ‘E’ and ‘H’, which ensures that the complementary angles of incidence and reflection from the flat specimen are always equal to each other, the counter presents itself to receive the focused beam diffracted at a glancing angle of $\theta$. The counter is powder driven at a constant angular velocity about the diffractometer axis to any desired angular position. The other advantage of the diffractometer over the Debye-Scherrer method is that, it gives a quantitative measurement of intensity.

2.4) Infrared Spectroscopy:-

Studies on the relations between structure and electromagnetic response of ferrimagnetic semiconductors are useful in understanding their properties. Since the electric and magnetic properties of these materials are dependent on the precise configuration of atoms or ions in these structures method of non-destructive analysis such as IR are especially suited to such investigations. In particular, the vibrational, electronic and magnetic dipole spectra can give information about the position and the valence of the ions in the crystal lattice.

The electromagnetic radiation in which wavelength lie in the range of 1micron to 1mm is termed as infrared radiation (IR). Infrared spectroscopy can be used in the study of crystal chemistry of spinels. IR studies on simple ferrites with general formula $MFe_2O_4$ were carried out by Waldron [7]. Preudhomme [8] have distinguished three applications namely,

[1] the determination of co-ordination of the cations in the spinel structure,

[2] the study of cation ordering and

IR spectroscopy is based upon the fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiation, the molecule of chemical substance vibrate at many rates of vibration, giving rise to a closed packed absorption bands called as IR absorption spectrum. Various bands will be present in IR spectrum, which will correspond to the characteristic functional group and bands present in chemical substance.

Band positions in an infrared spectrum may be expressed by wave number $\nu$ (cm$^{-1}$) which is reciprocal of wavelength. Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbency (A). Transmittance is the ratio of radiant power transmitted by a sample to the radiant power incident on the sample. Absorbency (A) is given by,

$$A = \log_{10}\left(\frac{1}{T}\right)$$

The infrared spectrum of ferrites in the wave number 200 to 800 cm$^{-1}$ is useful in understanding the structural properties of ferrites. The optical spectra of ferrites give information about the vibrational modes in the presence or absence of Fe$^{2+}$ ions in the ferrite. The vibrational, electronic and magnetic dipole spectra can give information about the position and valency of the ions in the crystal lattice. The IR spectra is used to detect the presence of absorption or emission bands in ferrites, to study the position of cations in the spinel structure and to calculate the force constant for A and B sites etc. In case of ferrites the frequency of vibration depends upon the cation mass, cation oxygen bonding force and unit cell parameter. Hafner [9], Tarte [10] and other have studied the IR spectra of normal as well as inverse spinel ferrites.
2.5) Electrical Properties of Ferrite:-

2.5.1) D. C. Conductivity:-

Ferrites are dense, homogeneous ceramic structures. They exhibit properties of high resistivity, high permeability, low thermal conductivity and low loss factor. The value of conductivity of ferrite is in the range $10^{+2}$ to $10^{-10}$ $\Omega^{-1}$-$\text{cm}^{-1}$. Studies on resistivity and thermoelectric powers in ferrites render comprehensive information of the d. c. conduction mechanism. It is established that, the mechanism of conduction in ferrites is modulated by firing atmosphere, impurities inherent with the ingredient oxides and picked up while annealing. The conduction mechanism has been studied by various workers. Yet satisfactory model to explain the process of conduction completely is not available. The studies on Seebeck effect gives valuable information on conduction through impurity levels, types of carriers responsible for conduction and so on.

The conductivity of ferrites can be controlled by controlling the sintering atmosphere and trying various additives. Verwey [11] has attributed the high conduction to the presence of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions on crystallographically equivalent sites.

2.5.1. a) Conduction mechanism:-

In general oxide crystal structures may be conveniently regarded in terms of oxygen ions and relatively small metal ions occupying the interstices. Although the bonding in the transition metal oxides is predominantly ionic, the electrical conductivity will be decided by the electron with d-like wave functions and most probably the impurity states.

In the element of first transition series, 3d levels are being symmetrically filled from Sc to Ni. In the crystalline field of solid the levels are split into a triplet and doublet. The triplet states lie below the
doublet states in oxides with rock salt structure. These oxides are then expected to metallic conductor at least above antiferromagnetic temperature [12]. Below the Neel temperature the exchange forces could give rise to further splitting of 3d band. The oxides however behave as semiconductor at all temperatures and have intrinsic activation energies in excess of those which would be accounted for by exchange splitting. From this, it is clear that description in terms of conventional band structure fails to account for the electrical transport properties.

The conduction mechanism has been described by applying carrier hopping model suggested by Verwey and Heilmann [11] or on basis of band picture. The resistivity of ferrites obeys the law

$$\rho = \rho_0 \exp \left( \frac{\Delta E}{KT} \right)$$

where \( \Delta E \) is activation energy

K is Boltzmann constant

Komar et al [13] have observed breaks or discontinuities in log\( \rho \) vs. 1/T plots for many ferrites. This discontinuity occurs in the near Curie temperature and breaks represent different conduction mechanism. The conduction mechanism in ferrites is due to exchange of electron from \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) in the same (octahedral) lattice. This requires small energy to move an electron. Under the influence of electric field these extra electrons can be considered to constitute the current by hopping from one site to other. Klinger [14] has reviewed the conduction mechanism in ferrites. He stated that the hopping of polarons is the main conduction mechanism in ferrites. He has suggested two phase mechanism for hopping of polarons. Many authors have reported the d. c. electrical properties of ferrites [15-16]. Ferrimagnetic to paramagnetic phase
transition near Curie temperature, hopping mechanism and polaron model also have been studied [17-19].

2.5.1. b) Conduction in Oxides:-

The oxides has composition of MO, the activation of a conduction electron may be represented by

\[ O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} \rightarrow O^{2-} M^{1+} O^{2-} M^{3+} O^{2-} \]  \hspace{1cm} 2.6

where M is divalent transition metal ions.

The energy needed for formation of ion pair \( (M^{2+}M^{2+}) \) and \( (M^{3+}M^{1+}) \) corresponds to a gap in the density of states.

The following terms are contributing to the activation energy which arises from an electron correlation effect.

[1] The difference between ionization energy and the electron affinity of the free \( M^{2+} \) ion.

[2] The difference in madelung energy of the two configuration \( (M^{2+}M^{2+}) \) and \( (M^{3+}M^{1+}) \)

[3] The difference in crystal field stabilization energy of the above configuration


2.5.1. c) Conduction in Ferrites:-

This above mechanism of electron transport does not apply to other ferrites where all iron ions are trivalent. Transport may be then represented by

\[ M^{2+} O^{2-} Fe^{3+} \leftrightarrow M^{3+} O^{2-} Fe^{2+} + E_g \]  \hspace{1cm} 2.7

Where \( E_g \) is the activation energy may reflect the difference between third ionization potential of \( Fe^{3+} \) and \( M^{3+} \) ions in the solid. Jonkar [20] has studied the ferrite \( Co_xFe_{3-x}O_4 \) and predicated quantitatively the mechanism stated above.
Ionic state of the cations in the ionic crystal gives some insight into the effect of impurities on the electrical properties. As the ionization potential of $\text{O}^{2-}$ ions is the dominant term. Substitution up to 1% or of the cations of another element of the same valency should have little effect upon the conductivity. If the dopant have higher valency it will contribute donor centers, if it has lower valency it will provide acceptor centers.

Analogous considerations may apply to cations of mixed valency in ferrites which result from a departure from the ideal metal to oxygen ratio. An oxygen vacancy will contribute two extra electrons to 3d band. If these extra charges are detached from their vacancies by thermal agitation n-type conductivity is induced in oxygen excess materials. Some oxides are very difficult to prepare homogeneously with a stoichiometric anion to cation ratio. Extrinsic semiconductor may then prevail through out the temperature region enable to electrical measurements. In such a cases, it may still be possible to infer the activation energy of intrinsic conduction sample from which extrinsic effect have been suppressed by introduction of compensations impurities. This was first demonstrated by Van Uttert [21] in $\text{NiFe}_2\text{O}_4$ by replacing 1 to 2% Fe by Mn or Co. Electrons donated by oxygen vacancies will fill the impurity levels in preference to iron conduction levels. Mixed valency state will be confined to the impurity element if its local concentration exceeds twice that of oxygen vacancies. This technique is based on the assumption that impurity band conduction is absent and allowed impurity concentrations indicate that cation wave function do not extend significantly beyond nearest neighbour distance in B-lattice. Electrons and holes pair is known to move by thermally activated hopping mechanism expect for pseudomentallic composition region close to magnetic.
2.5.1 d) Conductivity:-

Imperfection in lattice will result in a spectrum of donor and acceptor levels within the energy gap. Total number of such levels may be very small compared to total number of metal ions and have little effect on electrical conductivity in the intrinsic region, but affect the low temperature properties. At sufficiently low temperature the transport properties have a complicated dependence on ‘T’ in semiconductor which is determined by structural defects and impurities. In analogy to the thermal activation processes encountered in ionic diffusion and ionic conductivity, the expression for the mobility [22] can be written as

\[ \mu = \frac{ed^2\nu}{KT} \exp \left( -\frac{E}{KT} \right) \]  \hspace{1cm} (2.8)

where d is the jump distance between nearest neighbours

\( \nu \) is frequency of lattice vibrations and

E is activation energy for the hopping process.

It can be seen that, the mobility in transition metal oxides is strongly temperature dependent. The conductivity is linked with the concentration of carriers and their mobility as,

\[ \sigma = e\left( n_e \mu_e + n_h \mu_h \right) \]  \hspace{1cm} (2.9)

This relation has been used by many authors to discuss the conductivity behaviour in ferrites.

Activation energy does not provide much insight as to conduction mechanism because temperature dependent hopping mechanism and activation of electrons into the conduction levels are of the same from indistinguishable included in the activation energy found out experimentally.
2.5.2) Dielectric Properties:-

Polycrystalline soft ferrites are well known dielectric materials and very useful in microwave applications. Ferrites have very high resistivity which is one of the considerations for microwave applications. They exhibit relatively high resistivity at carrier frequency, sufficiently low losses for microwave applications and a wide range of other electrical and dielectric properties. The study of dielectric properties produces valuable information on the behaviour of localized electronic charge carriers leading to greater understanding of the mechanism of dielectric polarization in ferrite studies.

The polycrystalline ferrites have high dielectric constants of the order of few thousands at low frequencies, failing to a very low value of only 10-20 at microwave frequencies. The a. c. resistivity decreases with increasing temperature like d. c. resistivity where dielectric constant increases with increase in temperature. According to Rabkin and Novikova [23] the process of dielectric polarization in ferrite takes place through a mechanism similar to conduction process.

When alternating electric field \( E = E_0 e^{iwt} \) is applied to the ferrite sample, then dipole reorientation takes place. The displacement ‘D’ and electric field ‘E’ are not necessary in phase. Due to this dielectric constant \( (\varepsilon') \) may be in phase component or an out-of-phase component. Then it may be represented in complex number \( \varepsilon^* \) as

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]

where \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary part of dielectric constant respectively. The significance of imaginary part is due to time lag between response and stimulus. This time lag is also called phase angle ‘\( \delta \)’. Then loss tangent is given by
\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{2.10}
\]

Like dielectric constant, loss tangent is frequency and temperature dependent.

2.5.3) **Thermoelectric power:-**

In an electric circuit, when two dissimilar metal wires can be joined together to form two junctions and if they are maintained at different temperatures a thermo emf is developed. This effect is called Seebeck effect.

The Seebeck effect may be thought of as a diffusion process. When one junction is hot and other junction is cold, the free carriers at the hot junction will have higher energies than at the cold. As a consequence, the flow of free carriers diffusing from hot region into cold region will be stronger than the counter flow of free carriers. If densities or mobility of electrons and holes are different in magnitude, the metal ends accumulate charges opposite in sign. Equilibrium sets when counter flow due to temperature gradient equals the flow due to electric field. The thermo emf is equilibrium called as space thermo emf. The thermoelectric power with respect to unit temperature difference is called differential thermo emf and leads to evaluation of Seebeck coefficient (\(\alpha\)). The Seebeck coefficient can be determined by the relation,

\[
\alpha = \frac{dV}{dT} \quad \text{mV} \cdot \text{K}^{-1} \tag{2.11}
\]

where \(dV\) represent emf across the junction

\(dT\) represents the temperature difference

According to quantum theory, for semiconductors with both types of carriers (\(\alpha\)) is given by

\[
\alpha = \frac{(\alpha_n \sigma_n + \alpha_p \sigma_p)}{\sigma_n + \sigma_p} \tag{2.12}
\]
where $\sigma_n = n_e \mu_n$ and $\sigma_p = p_e \mu_p$

$$\alpha_n = -\frac{k}{e} \left[ A_n - \frac{E_F}{KT} \right]$$

and

$$\alpha_p = \frac{k}{e} \left[ A_p + \frac{E_g + E_F}{KT} \right]$$

2.13

Here $n$ and $p$ is electron and hole densities, $\mu_n$ and $\mu_p$ are the electron and hole mobilities, $E_F$ is Fermi energy and $E_g$ is energy band gap.

For partially filled band, the Seebeck coefficient ($\alpha$) varies linearly with the temperature.

$$\alpha_n = -\left[ \frac{\pi^2 K^2}{3e} \right] T \left[ \frac{d}{dE} \log \sigma(E) \right]_{E=E_F}$$

2.14

where $\sigma(E)$ represent the value of conductivity for a specimen in which fermi level is at $E=E_F$.

The temperature dependent thermoelectric power for ferrite material having one type of charge carriers could be expressed as [24]

$$\alpha = \frac{K}{e} \left[ \log \left( \frac{N_O}{N} - 1 \right) + \frac{a}{KT} \right]$$

2.15

where $K$ is Boltzmann constant

e is electronic charge

$N_o$ is concentration of trivalent ions on octahedral site [B].

$\alpha$ is the part of activation energy transported by the electrons.

The value of term ‘a’ is zero in case of Mn ferrite [25] and 1ev in other cases [26]. The temperature dependence of Seebeck coefficient enables to determine the sign of the charge carriers and their density variation.
2.6) Magnetic Properties of ferrites:-

2.6.1) Introduction:-

Magnetic material exhibits different kind of magnetic ordering depending upon spin orientation. The magnetic behaviour is caused by spinning of electrons of ‘d’ orbital about their own axis gives rise to spin magnetic moments. The motion of electron in the orbit around the nucleus results in orbital magnetic moments. In case of transition element, this orbital magnetic moment gets quenched by crystalline electric field. The different magnetic behaviour is observed due to different contribution of electron spin. According to magnetic properties, magnetic materials may be divided into five main groups such as, a) diamagnetic, b) paramagnetic, c) ferromagnetic, d) ferrimagnetic and e) antiferromagnetic.

a) Diamagnetism:-

The physical origin of diamagnetism can be seen from the classical picture of an atom as electronic charges circulating around the nucleus in definite orbit. The electronic configuration of diamagnetic material is a closed shell, so that there is no resultant moment arising from the electron spin or orbital motion. The diamagnetism occurs through deformation of the electronic charge distribution when field is applied and it disappears when field is removed.

b) Paramagnetism:-

In a paramagnetic material the individual ions, atoms or molecules possess magnetic moments. These arise because the spin contains an odd number of electrons or because an inner field is unfilled. The classical explanation of strong magnetic field is that, it results from the tendency of individual moments to align with the field and opposing tendency of the thermal agitation to destroy this order.
c) **Ferromagnetism:-**

In a ferromagnetic material the individual moments of the atoms or ions are strongly coupled and are more or less parallel with one to another even in absence of magnetic field. There results a very large magnetic moment. In the macroscopically demagnetized state there are very small regions called as domains within which the moments are parallel but there is a distribution of directions in which the many domain magnetizations point so that the overall moment is zero.

d) **Ferrimagnetism:-**

The ferrimagnetic material composed of two interpenetrating lattices. One may regard each sublattice as ferromagnetic, in that the individual moments within that sublattice are aligned parallel, but the strong interaction between the two sublattices result in two macroscopic moments being oppositely directed. The antiparallel moments are unequal so that there is a net overall magnetization.

e) **Antiferromagnetism:-**

In an antiferromagnetic material, the effect of exchange interaction is to produce antiparallelism of the spins and where the net moment due to the two antiparallel spin systems is balanced. Thus the net magnetic moment is zero.

**2.6.2) Magnetization in Ferrites:-**

Ferrites are ferrimagnetic oxides. The magnetization exhibited by ferrites was firstly explained by Weiss’s [27] on basis of his molecular field theory. The magnetization is powerful tool to study the domain wall motion, anisotropy, magneto-elastic coupling, magnetic hardness or softness of the material, magnetic ordering etc.

The spontaneous magnetization is a characteristic of ferrimagnetic materials, which arises due to alignments of atomic magnets under exchange forces. The coupling between the magnetic atoms in a
substance may cause parallel or antiparallel alignments of spins of the neighbouring atoms. Ferromagnetism is observed when the alignment is parallel and ferrimagnetism or antiferrimagnetism results when alignment is antiparallel. The term ferrimagnetism was introduced by Neel in 1948 in connection with the properties of ferrites.

The magnetic properties of ferrites are classified into two groups as,
I) Intrinsic properties and
II) Structure sensitive properties

Saturation magnetization, Curie temperature and permeability are some of the intrinsic properties while hysteresis, resistivity, dielectric constant etc. are structure sensitive properties of ferrites. The grain size, impurity, inclusions and porosity affect the structure sensitive properties of ferrites [28].

2.6.2. I) Magnetic Hysteresis and Domains:-

Studies on magnetization give information about the parameters like saturation magnetization, permeability and coercive force. These parameters are technologically important. For example, large magnetic induction with high resistivity is the requirement of a ferrite cored transformer. Large squareness ratio 0.9 or more is the requirement of memory cores. For making permanent magnets a large coercive force is required. The ferrites with low coercive force are called soft ferrites and they are used in manufacturer of high frequency inductance, transformer cores, motors and generators. Ferrites with large coercive force are called hard ferrites, are used in electric motors, loudspeakers, telephones and permanent magnets.

When the ferrimagnetic substance is taken through cycle of magnetization and B is plotted against H, hysteresis curve is obtained. The characterization of soft material is low coercivity and high
permeability, resulting in a hysteresis loop which is narrow at the waist. The hysteresis loss represented by the area of loop is low. Weiss, in order to explain the state of zero magnetization, normally exhibited by demagnetized ferromagnetic materials, assumed the existence of small regions called domains, within which the ferromagnetic material is magnetized to saturation i.e. spinels are aligned in one direction. The direction of magnetization however varies from domain to domain and thus net macroscopic magnetization may have variation between zero and saturation.

The change in direction of spins between the two domains takes place through the domain wall. The thickness of this domain wall is of the order of few hundreds of inter-atomic distance. The spins in the domain walls gradually change from one direction to other direction when the direction of spin is not parallel to direction of magnetization due to applied field. The irreversibility and hysteresis in ferromagnetic materials are due to the impediments to the motion of domain walls. The wall energy is large at very high field, which leads to irreversible increase in magneto-elastic and magneto-static energies of materials. Some residual magnetization remains even when the magnetic field is reduced to zero. Therefore, in order to bring the domain to their original state of zero magnetization, the reversal field is applied which gives the hysteresis of magnetization cycle. Peloschek [29] noted that if a material has nonzero values of magneto-crystalline anisotropy and magnetostriction, both internal and external stresses will affect the easy direction of magnetization in the crystallites. Hence the controlled external stresses may be used to influence the shape of the hysteresis loop. The typical hysteresis loop is as shown in Fig. 2.7.

When applied magnetic field ‘H’ is increased, then initially the magnetic induction ‘B’ increases slowly and then it increases more
rapidly. The rate of magnetization slows down again and finally attaining a saturation value $B_{\text{sat}}$. With further increase in magnetic field, there is no increase in magnetic induction. If the field is reversed the induction decreases at a slower rate and reaches a residual value $B_r$ at zero magnetic fields. $B_r$ indicates the amount of magnetization retained in the material after removal of the field. If the magnetic field is continued to apply in opposite direction, the magnetic domains try to remove their alignment. So that at the remaining magnetic induction is removed at the certain value of the reverse magnetic field $H$ called as coercive field or force $H_c$. The reversing of magnetic domains goes on to produce a net magnetization in the opposite direction. After saturation takes place in this direction, restoring the original field direction to completes the hysteresis loop.

2.6.2. II) Neel’s Theory of Ferrimagnetism:-

Neel [30] proposed the theory of ferrimagnetism by following assumptions,
1) A ferrimagnetic crystal lattice could be divided into two sublattices such as tetrahedral (A) and octahedral [B] sites in a spinel structure.
2) There exists one type of magnetic ion in the material of which a fraction $\lambda$ appears on A-sites and fractions $\mu$ appear on B-sites.
Thus $\lambda + \mu = 1$  \hspace{1cm} 2.16
3) The A-B and B-A interactions are identical and predominate over A-A and B-B interactions and therefore the net magnetic moment is the difference between the two average sublattice magnetic moments.
4) An internal Weiss molecular field acts on the ions. For a simple ferrite of the form $\text{MFe}_2\text{O}_4$, which satisfies Neel’s assumption, the magnetic ions are trivalent ferric $\text{Fe}^{3+}$, $M$ is non-magnetic ion. The cation distribution formula can be written as,
\[
\text{Fe}_{2\lambda}\text{M}_{(1-2\lambda)}\left[\text{Fe}_{2-2\lambda}\text{M}_{2\lambda}\right]\text{O}_4
\]

where the bracketed ions are those on the octahedral sites.

Neel defines the interactions within the material from the Weiss molecular field. The magnetic field acting upon ions is written as

\[
H = H_0 + H_m
\]

where \(H_0\) is external applied field and \(H_m\) is the internal or intermolecular field which arises due to interactions with ions within the material.

By applying the molecular field concept to a ferrimagnetic material we have

\[
H_A = H_{AA} + H_{AB}
\]
\[
H_B = H_{BB} + H_{BA}
\]

The molecular field components may be written as,

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

Where \(\gamma\)'s are molecular field coefficients, \(M_A\) and \(M_B\) are the magnetic moments of A and B sublattices.

It may be shown that \(\gamma_{AB} = \gamma_{BA}\) but \(\gamma_{AA} \neq \gamma_{BB}\) unless the two sublattices are identical. Neel showed that \(\gamma_{AB} < 0\) favouring antiparallel arrangements of \(M_A\) and \(M_B\) gives rise to ferrimagnetism.

In the presence of an applied field \(H_0\), the total magnetic fields acting on each sublattice may be written as,

\[
H_a = H_0 + H_A = H_0 + \gamma_{AA} M_A + \gamma_{AB} M_B
\]
\[
H_b = H_0 + H_B = H_0 + \gamma_{BB} M_B + \gamma_{AB} M_A
\]

**a) Paramagnetic Susceptibilities:**

In paramagnetic region the total magnetization is given by,

\[
M = N g \mu_B B_J (x)
\]

where \(N\) is free paramagnetic ions per unit volume,
J is angular momentum quantum number

G is Lande’s splitting factor

µB is Bohr magneton number

The Brillouin function $B_J(x)$ is given by,

$$B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right)$$

where $X = \frac{\mu_0 g J \mu_B H}{KT}$, K is Boltzmann constant and T is absolute temperature.

When $x << 1$, $B_J(x) = \frac{(J+1)x}{3J}$

∴ $M = \frac{\mu_0 N g^2 \mu_B^2 J (J+1)}{3KT}$

The volume susceptibility is

$$\chi = \frac{M}{H} = \frac{\mu_0 N g^2 \mu_B^2 J (J+1)}{3KT}$$

$$= \frac{C}{T} \quad \rightarrow \text{Curie law.}$$

If magnetic field in Curie law is taken to be $(H + H_m)$ then we have,

$$\frac{M}{H + H_m} = \frac{M}{H + \gamma M} = \frac{C}{T}$$

and leads to Curie-Weiss law, $\chi = \frac{C}{T - T_C}$

Neel applied same arguments to each sublattice of ferrimagnetic material, that is he assumed that,

$$M_A = \left( \frac{\lambda}{T} \right) H_a \quad \text{and} \quad M_B = \left( \frac{\mu}{T} \right) H_b$$

where C is Curie constant.

By substituting $\chi = \frac{M}{H_0}$ and $M = M_A + M_B$

$$\frac{1}{\chi} = \frac{T^2 - C \gamma_{AB} (\lambda \alpha + \mu \beta) T + C^2 \lambda \mu \gamma_{AB}^2 (\alpha \beta - 1)}{C \left[ T - \lambda \mu \gamma_{AB} (2 + \alpha + \beta) \right]}$$
where $\alpha = \frac{\gamma_{AA}}{\gamma_{AB}}$ and $\beta = \frac{\gamma_{BB}}{\gamma_{AB}}$.

The temperature dependence of $\chi$ by rewriting equation (2.24) as

\[
\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \theta}
\]

where

\[
\frac{1}{\chi_0} = \gamma_{AB} (2 \lambda \mu - 2 \alpha - \mu^2 \beta) \text{ and } \theta = \gamma_{AB} \lambda \mu C (2 + \alpha + \beta)
\]

and
\[
\sigma = \gamma_{AB}^2 \lambda \mu C [\lambda(1 + \alpha) - \mu(1 + \beta)]^2
\]

Equation (2.25) represents the hyperbola which cuts the temperature exist at $\theta = -\frac{C}{\chi_0}$ where $\theta$ is asymptotic Curie point.

The asymptotic to the line is given by (as $T \to \infty$)

\[
\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0}
\]

so the expression of volume susceptibility is,

\[
\chi = \frac{C}{T - \theta} \text{ where } \theta > 0
\]

The quantity $\frac{1}{\chi}$ becomes zero at $\theta$ where $\chi$ becomes theoretically infinity or $\chi$ is practically very large and substance passes from paramagnetic to ferrimagnetic with decrease in temperature. In other words the substance obeys Curie-Weiss law with asymptotic Curie point $\theta$.

b) **Spontaneous Magnetization:**

In a ferrimagnetic material, the spontaneous magnetization ($M_{\text{sp}}$) depend upon temperature that can be represented by equation

\[
M_{\text{SP}} = N J g \mu_B B_{J(x)}
\]

where in the absence of an applied field.

The Brillouin function parameter becomes,
\[ \chi = \frac{\mu_0 J g \mu_B \gamma M_{SP}}{KT} \]

This equation was used to deduce the behaviour of ferrimagnetic material above Curie point. It is reasonable to expect a similar dependence below that temperature. Thus,

\[ M_{ASP} = \lambda \, N \, g \, J \, \mu_B \, B_J \left[ \frac{\mu_0 g J \mu_B H_A}{KT} \right] \]

\[ M_{BSP} = \mu \, N \, g \, J \, \mu_B \, B_J \left[ \frac{\mu_0 g J \mu_B H_B}{KT} \right] \]

Or

\[ \frac{M_{ASP}}{M_{Asat}} = B_J \left[ \frac{\mu_0 g \mu_B J H_A}{KT} \right] \]

\[ \frac{M_{BSP}}{M_{Bsat}} = B_J \left[ \frac{\mu_0 g J \mu_B H_B}{KT} \right] \]

Therefore, the net spontaneous magnetization is

\[ M_{SP} = |M_{BSP} - M_{ASP}| \]

The graph of inverse susceptibility and spontaneous magnetization with temperature as shown in Fig. 2.8(a and b) respectively. Such curves are of different variety. They provide information of about spontaneous magnetization and exchange energy at different temperature. The above theory supported by experimental curves of Neel [30], Gorter [31] and Smart [32].

**2.6.2 III) Yafet-Kittel Theory:**

Neel’s explanation of the origin of the magnetization in a ferrimagnetic is substantially correct for pure ferrite, but it is inadequate for spinels which contain other than iron ions. Therefore, Yafet-Kittel [33] proposed triangular type of spin arrangements.

They begin by subdividing the A and B sublattices in order to take into account magnetic ordering within a sublattice of a type other than the parallel arrangement of all spins. They found that when strong negative interactions exist within sublattice B, the two equivalent sublattices B₁ and
\( B_2 \) are both spontaneously magnetized, but their magnetizations are not exactly antiparallel. Instead they are aligned at some angle other than \( 180^0 \). Thus there is a resultant magnetization of the B lattice and it is antiparallel with A-sublattice as shown in Fig.2.9. These triangular arrangements within the lattice result in values of reduced magnetization of the same order of magnitude as those predicted by Neel’s model. But in addition they have a lower free energy and exhibit the correct thermodynamic properties near absolute zero.

The interaction energy for this case is given by,

\[
E = 8N \left[ \sigma J_{ab} S_a S_b \cos \phi - J_{bb} S_b^2 (2 \cos \phi - 1) \right]  \tag{2.26}
\]

where \( \phi \) is angle between A and Subdivisions of B, J is exchange integrals.

The interaction energy is minimum for \( J_{ab} \) negative and positive \( J_{bb} \), if \( \phi = 0 \) then Neel’s state is obtained. If \( J_{bb} \) is also negative, then the ratio of exchange energies is given by,

\[
\gamma_{ex} = \frac{J_{bb} S_b}{J_{ab} S_a} > \frac{3}{4}  \tag{2.27}
\]

Under such condition, Neel’s state will not be minimum and magnetization of sublattice \( B_1 \) and \( B_2 \) will be inclined to sublattice A at an angle is given by,

\[
\cos \phi = \frac{3}{4} \times \frac{J_{ab} S_a}{J_{bb} S_b}  \tag{2.28}
\]

They proved that Neel’s structure is suitable for \( \gamma_{ex} < \frac{3}{4} \) if the total number of sub-lattices is restricted to six. The existence of triangular arrangement has been reported by Lotering [34] in some particular cases.

**2.6.2 IV) Spiral Spins:**

Lyon and Kaplan [35] have given generalized treatment of spin configuration along with Y-K model. They have suggested the possibility
of spiral or helical spin arrangements by neutron diffraction in some compounds and showed that they have lower energy for all values of $\gamma_{ex} > \frac{2}{3}$. Corliss and Hastings [36] observed the existence of such configuration in manganese chromite. Similarly spiral spin configuration has been reported by Enz [37] in hexagonal ferrites.

2.6.2. V) Random Canting Model:-

In random canting model the non-collinear or canted spin arrangement can be explained [38]. Substitution of one sublattice in ferrimagnetic leads to spin canting in the other sublattice. Roednwaig [39] assumed that the nearest neighbour of a [B] site can considered to be canted with an average angle $<\alpha_B>$ due to (A) site. Substitution which in the average nearest neighbour appropriate estimated to be,

$$\cos <\alpha_B> = \frac{M_A (J_{AB})}{M_B (J_{BB})}$$  \hspace{1cm} 2.29

The saturation magnetization per formula unit is related to canting angle $<\alpha_B>$ by

$$N_B^C = M_B \cos <\alpha_B^C> - M_A$$  \hspace{1cm} 2.30

Where $M_A$ and $M_B$ are sublattice magnetization of A and B sites to be determined from cation distribution. The $J_{AB}$, $J_{BB}$ are exchange integrals.

2.6.2 VI) Localized Canting Model:-

In this model individual moments of one sublattice are canted at different angles, depending on the specific of the local magnetic environment. Patton and Liu [40] clearly delineate the quantities, which may be replaced by average values and those must be considered on a site statistical basis in contrast with earlier attempts at mathematical formulation of canting. Using procedure of Patton and Liu, average local canting angle $\theta_L$ for the system in zero applied fields can be written as
\[
\cos (\theta_{\text{Lav}}) = \frac{N_{B1A}}{N_{B1B2}} \times \frac{|J_{AB}|}{|J_{B1B2}|}
\]

Where \(N_{B1A}\) is the number \(B_1\) nearest neighbour of \(A\), \(J_{AB}\) and \(J_{B1B2}\) are exchange integrals.

2.6.2 VII) Villain model:-

The concept of insulating glass spin was proposed by Villain [41], considering that the spinel structure offers topological frustration resulting in perturbed magnetic ordering (Spin glass, semi spin glass, localized canting etc.) depending on the magnetic dilution of \(A\) and \(B\) sublattices. The topological frustration attributed to the competitive process between inter and intra sublattice interactions. The non-magnetic substitution prevents the long ranges ordering and gives rise to high ground state degeneracy. Villain termed such system as co-operative paramagnet. The addition of non-magnetic impurities reduces the degeneracy and stabilizes the phase of spin glass.

2.6.3) A. C. Susceptibility:-

The volume susceptibility (\(\chi\)) is defined as the ratio of the magnetization (\(M\)) produced in a substance to the magnetic field strength (\(H\)).

\[
\therefore \quad \chi = \frac{M}{H} \quad \text{emu/cm}^3 \text{ Oe}
\]

The mass susceptibility (\(\chi\)) of the substance is defined as,

\[
\chi = \frac{K}{\rho} = \frac{M}{\rho H} \quad \text{emu/gm Oe}.
\]

where \(\rho\) is the density of material. High temperature a. c. susceptibility measurement were first carried out on iron by Hopkinson [42] and show that, it reaches a peak value just before Curie temperature \(T_c\) and becomes zero rapidly. The hysteresis and susceptibility studies at various temperatures can provide an idea of whether a magnetic sample contains
single domain (SD), multi domain (MD) or super-magnetic particles (SP). The dilute samples containing magnetic grains, tens of microns, known as multi domain (MD), as well as small grains up to about a hundred angstroms, termed as super paramagnetic (SP), do not show any hysteresis at all and only optimum single domains (SD) whose size may be a few hundred angstroms exhibit a characteristics loop.

In ferro and ferrimagnetic materials, the variation of normalized a. c. susceptibility $\left( \frac{\chi_T}{\chi_{RT}} \right)$ versus temperature curve exhibit three peaks.

1. Hopkinson peak which occurs just below the Curie temperature ($T_c$) of any magnetic material in the MD state.
2. Single domain peak which could be obtained, if the material has single domain particle. It occurs at blocking temperature ($T_b$) and
3. The isotopic peaks, which are, observed when magnetic material is in MD State and at this temperature magneto-crystalline anisotropy vanishes.

The low field a. c. susceptibility plays a key role in the study of spin glass behaviour. According to Bean [43], for MD particles, very small values $H_c$ and $M_r/M_s$ are observed and for SD particles, these values are longer. It is obvious that the susceptibility $\chi$ is directly proportional to coercivity ($H_c$). Also it has been shown that $\chi_{ac}$ for small multi domain (MD) sample does not change appreciably with temperature [44].

For a single domain (SD) sample, there could be a broad hump below $T_c$ or sharp cusp near $T_c$, depending on the temperature at which the single domain becomes super-magnetic (SP). Appearance of a sharp cusp in $\chi_{ac}$-T curve is also a feature of spin glass system [45]. The temperature at which cusp appears is called freezing temperature and is associated with a freezing of magnetic moments in random direction.
2.6. 4) Curie temperature:

Thermal energy tends to randomize the aligned spins so that all ferromagnetic materials become paramagnetic at a certain temperature. This transition temperature is called the Curie temperature or Curie point.

The dependence of Curie temperatures on the distribution of metallic ions on tetrahedral and octahedral sites in the ferrites was suggested by Gorter [46] and Neel [30]. Rezlescu et al [47] investigated the influence of preparation techniques and cation distribution on various properties of copper and manganese mixed ferrites.

In zinc mixed ferrites, the A-B interaction decreases with zinc ions and the Curie point drops with the result of substitution of zinc. Forestier [48] studied the variation of Curie temperature of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ with zinc content. Gorter [46] studied the curie temperature of Barium ferrite and suggested that the existence of a strong competing interaction in Barium ferrite causes the linear curve to occur for full occupation of magnetic ions of all sublattices. Sagar et al [49] have reported study on tetrahedral $\text{Ge}^{4+}, \text{Ti}^{4+}$ and $\text{Sn}^{4+}$ 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 literature [50]. They observed that the migration of cations on tetrahedral sites shifts the Curie temperature to lower temperature.

2.7) Applications of Ferrite:

Ferrites have found many applications in different branches of science and technology due to their suitable magnetic and electrical properties [51].

Ferrites may generally be grouped as magnetic soft and magnetic hard ferrites. The magnetically soft ferrites are those composed of ferric oxide and oxides of metals like zinc, nickel and manganese. They are
used for making compact aerials for radio sets, for recording tapes for transducers. Magnetically hard ferrites are composed of ferric oxide and oxides of material like magnesium, cobalt, barium etc. They are used for focusing magnets for television tubes, information storage and switching devices in computers etc.

Ferrites have high permeability which is suitable for telephone circuits for 50 kHz to 150 kHz, pass band, IFT of radio receiver, inductors for T. V. receiver, pulse transformer in data handling system etc. Ferrites are used in antenna because of high permeability, ferrite rod antenna have improved sensitivity over the conventional loop types with air core. Typical square hysteresis loops can be obtained with ferrites. These loops can be used in solving the problem of information storage, both the digital information required by computer and the more detailed information necessary in order to record speech [52].

Ferrite cores are used in all forms of transformers, power pulse, wide band and high frequency. The extent of the ferrite contribution to this technology is demonstrated by the comment [53] that a television set normally contains at least 200 gm of ferrite in various components.

The most important use of ferrites today is in flyback transformers for T. V. picture tubes. The cores of these transformers must have low loss at high flux densities and high frequencies of the order of 100 KHz, which is effective flyback frequency used in scanning a television picture tube. In last decade, piezo-magnetic nickel manganese cobalt ferrites [54] has been developed for their wide applications in ultrasonic and radio frequency electronics. The use of ferrites is growing in the following areas i) ferrite antenna, ii) chip type inductor, iii) chip type filter, iv) High frequency power ferrite, v) bubble memories and vi) SMPS.

Ferrites are used as sensor for temperature control. They can be made using ferrite with sharp and definite Curie temperature. A radar
absorbing point containing ferrite has developed to render an aircraft or submarine invisible. Ferrites are also used for pollution control. Position and rotational angle sensor have also been designed using ferrites.

Modern ferrites are materials used in new applications, especially in broadband transformers for digital networks and in power transformers for switched mode power supplies. Very high initial permeability for one type and low power losses at high frequencies for other type are their outstanding magnetic properties [55].

A major application of ferrites in the field of magnetic memories and switching devices for digital computers and data processing circuits [56]. This application is based on the use of microsecond pulses for transmitting, storing and reading information in a binary code. The binary states correspond to the two directions of magnetization of the core. Hence for these applications, ferrite materials having a rectangular B vs. H curve are desired. A systematic diagram of applications of ferrite is as shown in the Fig.2.10.
References:

[1] Bragg W. H.
    Phil Mag. 30 (1915) 305.

[2] Nishikawa S.

[3] Lax B. and Button K. J.


    Krist, 82 (1932) 325.

    Phy. Rev. 99(1955) 1727

[8] Preudhomme J.

[9] Hafner V. S.

[10] Tarte P.
    Spectra Acta.21 (1965) 313.


[12] Craik D.J. (Editor)
costerhout G.W.


[15] Uitert Van L.G.

[16] Uitert Van L.G.
Proc. IRE 1294 (1956) 1303.

[17] Appel J.
Solid state phys. 18 (1969) 49

[18] Gillot B.

[19] Holstein T.
Ann Phys. 8 (1959) 343


[21] Van Uitert G.

[22] Mott N.F., Gurney R.W.
(1948)

[23] Robkin L. I. and Novikova
Ferrites IZs Acad. Nauk Minsk (1960) 146.

[24] Rosenberg M. Nicolau P. and Bunzet I.

[25] Sisma Z.
[26] Gonker G. H. and Van Hauten S.
Halbleiter problem 6 (1961) 118
[27] Weiss P.
J. Phy. 6(1907)667
[28] Brockman F. G.
[29] Peloschek H. P.
[30] Neel L.
Annls. Phys. 3 (1948) 137.
[31] Gorter E. W. and Schulkes
[32] Smart S.
[33] Yafet Y. and Kittel C.
Phys. Rev. 87 (1952) 290.
[34] Lotering F. K.
[35] Lyon D. H. and Kaplan T. A.
Phys. Rev. 120 (1960) 1580
[36] Corliss L. and Hastings J.
[37] Enz U.
Appl. Phys. 325 (1961) 22
[38] Coey J. M. D.
[39] Roednwaig A.
[40] Patton C. E. and Liu Y. H.

[41] Villain

[42] Hopkinson J.

[43] Bean C. P.

[44] Chaugule R. S., Radhakrishnamurthy C, Sampathkumar E.
     Malik S. K. and Vijayaraghavan


[46] Gorter E. w.

[47] Rezlesc N., Istrate S., Rezlesc E. and Lucu E. J.

[48] Forestier H.
     Refer Reference C-3 pp 158.


[50] Van Uitert L. G.
     Chem. Phys. 23 (1956) 1294.

[51] Halszujn J.
     “Principle of microwave ferrite engineering”, Wiley
[52] Standly K. J.

[53] Austen I. G. and Elwell D.

[54] Raczkowski Z.

[55] Roess E.

[56] Sinha A. P. B. and Menon P. G.
    “Oxide of magnetic materials”, P.404.
Fig. 2.1 General Spinel Structure
Fig. 2.2 The eight octants in the unit cell
Fig 2.3 Details about the crystal structure of spinel
Fig. 2.4 Basic Component of a spinel lattice

- Octahedral Metal Ions
- Tetrahedral Metal Ions
- Oxygen Ions

→ ---- Indicates the direction in which the oxygen ion moves in the case $u > 3/8$
Fig. 2.5 Configuration of ion pairs in spinel ferrites with favourable distances and angles for effective magnetic interaction.
Fig 2.6 Schematic diagram of X-ray diffractometer
Fig 2.7 A typical Hysteresis loop
Fig. 2.8 a) A sketch of the inverse susceptibility of a ferrimagnetic substance as a function of absolute temperature

Fig. 2.8 b) The anomalous shapes of the spontaneous magnetization vs. temperature curves for ferrimagnetic substance according to Neel's theory

Fig. 2.8 Variation of inverse of susceptibility and Spontaneous Magnetization with temperature according to Neel's theory
Fig 2.9 Yafet and Kittel three sublattice model
Fig. 2.10 Wide range of applications of ferrites.