

# CHAPTER-I

## INTRODUCTION

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#### 1.1 INTRODUCTION :

The term "Ferrites" is used in connection with the class of magnetic materials which are artificial versions of the first magnetic material viz. the loadstone or magnetite. Loadstone has a chemical formula  $\text{Fe}_3\text{O}_4$  ( i.e.  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ), it is simply a ferrous ferrite. Ferrites are ferrimagnetic substances and essentially are mixed crystals of various magnetic oxides. They are superior to the other magnetic materials due to their wide range of magnetisation, high electrical resistivity and their use in the propagation of electromagnetic waves at high field with low attenuation. They exhibit magnetic properties which are sensitively dependent on chemical as well as thermo-physical history, method of preparation. etc. This allows their suitability over wider range of applications.

The comprehensive understanding of ferrites need the interrelationship of their properties with crystal structure, cation distribution, magnetic interactions, preparation conditions, preparation methods etc. The technological importance of ferrites can be gauged from spectrum of applications in high frequency pulse transformer, inductances, deflection coils, antennas, modulators and number of other application in which high permeability and low loss at high frequency is desired. Ferrites with square loop of B-H curve find use as

core devices in computer memory. The microwave applications of ferrite depend on nature of gyromagnetic resonance of ferrites which are exemplified in Farady rotation, phase shifters, modulators.

## 1.2 HISTORICAL

The first known and naturally occurring magnetic material, to man was mineral magnetite<sup>1</sup>  $\text{Fe}_3\text{O}_4$ . ie.  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . The origin of magnetite is magmatic, but its property of attracting small pieces of iron was known before Christ.

List<sup>2</sup> noted the formation of magnetic oxides consisting of  $\text{MeO}$  (where  $\text{Me} = \text{Mg}, \text{Mn}, \text{Zn}, \text{Ni}, \text{Cu}$ ) and  $\text{Fe}_2\text{O}_3$  which exhibited magnetic properties and these were able to attract magnet.

Hilpert<sup>3</sup> realised that such a magnetic material would be a better replacement of  $\text{Fe}_3\text{O}_4$  in magnetic cores. He identified the basic formula of ferrites as  $\text{MeO} \cdot \text{Fe}_2\text{O}_3$  where  $\text{Me}$  is divalent metal ion. He developed synthetic ferrites with an objective of reducing eddy current losses in transformers and inductors.

Kato and Takai<sup>4</sup>, Foresteir, Barth and Posjnak<sup>5</sup> studied ferrites from the point of view of electric and magnetic properties and chemical and crystallographic characteristics. They established structure of ferrites to be of spinel type.

Snoek<sup>6,7</sup> carried out systematic investigations on artificial ferrite materials in order to study the effect of preparation technique

and composition on eddy current loss and magnetic properties.

Verwey<sup>8</sup> and De Boer investigated ordering of divalent and trivalent ion in magnetite and showed that electronic conductivity of ferrite is mainly due to exchange of electrons between adjacent  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. Their study on crystal structure showed ferrite with inverted spinel structure to be ferrimagnetic, whereas those with normal spinel structure to be nonmagnetic.

Neel<sup>9</sup> announced basic theory of spin-spin interaction in ferrites. He introduced the concept of two magnetic sublattices to explain ferrimagnetism. Neel applied molecular field theory of exchange interactions in ferromagnetic materials except the possibility of spin alignment in antiparallel sense.

Anderson<sup>10</sup> and Van Vleck<sup>11</sup> developed the theory of superexchange interaction.

Yafet and Kittel<sup>12</sup> extended Neel's theory of magnetic sublattices in ferrites by postulating a triangular or "canted" spin arrangement in the three sublattices, when antiferromagnetic exchange interaction between sublattice is comparable to that among spin moments within sublattice by  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral sites. Neel's theory was confirmed by neutron diffraction of magnetite and zinc ferrite.

Gorter<sup>13</sup> and Guillad<sup>14</sup> measured the variation of magnetisation as a function of temperature for mixed ferrite with varying

composition and temperature in ferrimagnetic region. They measured magnetisation of Mn, Fe, Co, Ni, Cu, Mg ferrites as a function of Zn composition.

Smart<sup>15</sup> and Gorter<sup>16</sup> working independently correlated the cation distribution; found out by microwave resonance with magnetisation.

Gilleo<sup>17</sup> established correlation between observed Curie temperature and magnetisation. Koops<sup>18</sup> studied the relation between conductivity and dielectric constant and obtained the formula for a.c. conductivity.

### 1.3 CRYSTAL STRUCTURE :

The magnetic oxides exhibit following structures in general

1. Spinel structure,
2. Hexagonal structure,
3. Garnet structure,
4. Perovskite structure.

The salient features of spinel structure are described below

#### 1.3.1 SPINEL STRUCTURE :

The general chemical formula of ferros spinel is  $\text{MeFe}_2\text{O}_4$  where Me is a divalent metal ion and Fe is a trivalent metal ion. The ferrite exhibits spinel structure, similar to crystal structure of mineral spinel  $\text{MgAl}_2\text{O}_4$ . The compounds of this type have generally cubic, face centered cubic structure of space group  $O_h^7$  (Fd3m).

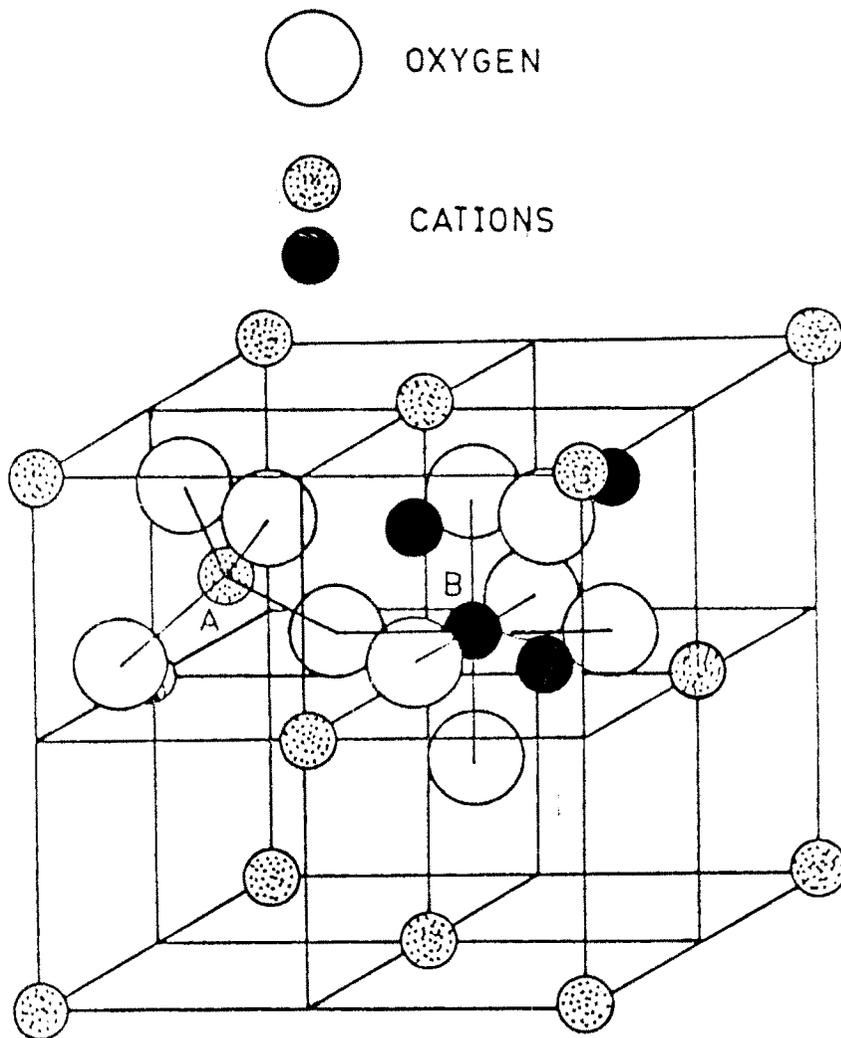


FIG.1.1 : THE SPINEL STRUCTURE .

The length of each edge of cell is  $8a_0$ . The spinel structure is shown in Fig.1.1. The unit cell contains eight formula units of  $MeFe_2O_4$ . Hence the unit cell formula becomes  $Me_8^{2+}Fe_{16}^{3+}O_{32}^{2-}$ . The cations occupy interstitial positions of which there are two distinctly different types tetrahedral (or A site) Fig.1.2 and octahedral (or B site) Fig.1.3 when magnetic ion is surrounded by four oxygen ions located at the corners of a tetrahedron as shown in Fig.1.1, it is called as tetrahedral (or A site). Whereas when a magnetic ion is surrounded by six oxygen ions placed at vertices of octahedron as shown in Fig.1.1, it is known as an octahedral (or B site). There are in all 96 interstitial sites per unit cell out of which 64 are tetrahedral and 32 octahedral. Out of these 8 tetrahedral and 16 octahedral sites are occupied by cations per unit cell.

### 1.3.2 CLASSIFICATION OF SPINEL FERRITES :

Ferrites can be classified on the basis of cation distribution into

- a) Normal spinel,
- b) Inverted spinel,
- c) Random spinel.

#### 1.3.2(a) NORMAL SPINEL

The spinel ferrite in which all (i.e. 8)  $Me^{2+}$  ions occupy tetrahedral or A site and all (i.e. 16)  $Fe^{3+}$  ion occupy octahedral or B site, is referred to as ferrite with normal spinel structure,

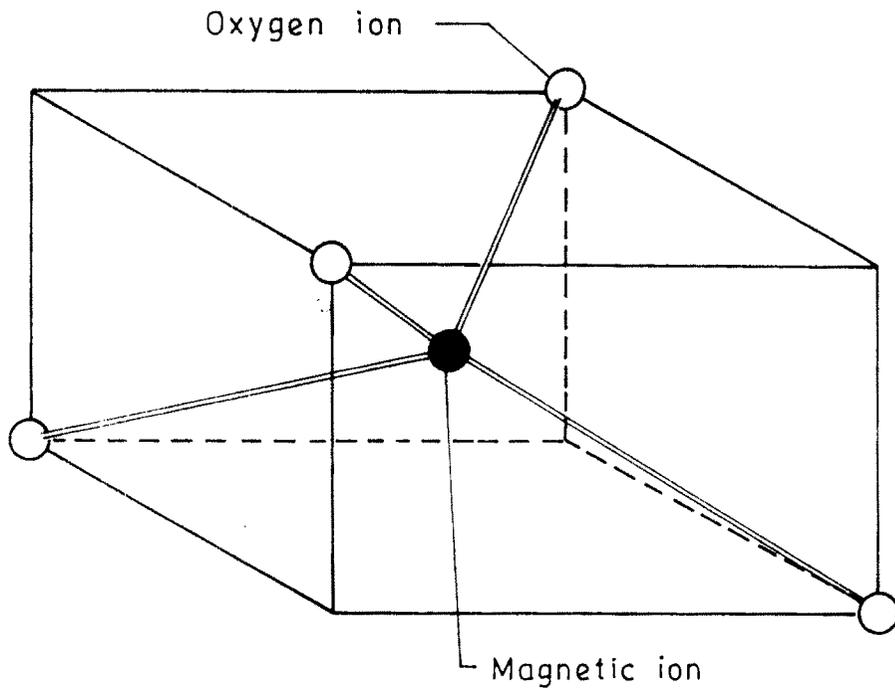


Fig. 1-2 : The magnetic ion occupies a "Tetrahedral lattice site" where it is surrounded by four near-neighbour Oxygen ions.

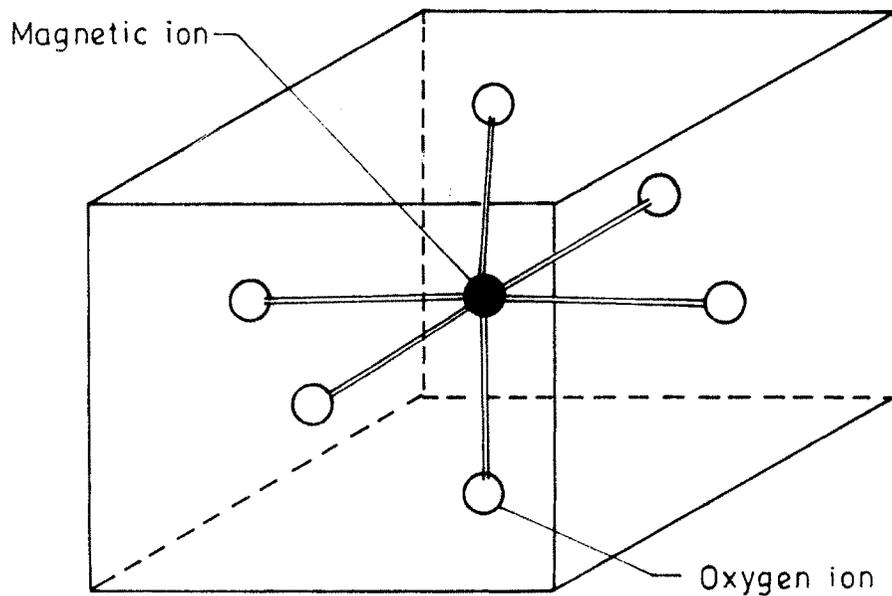
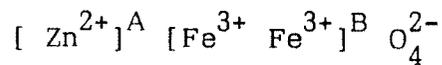


Fig. 1-3 The magnetic ion is said to occupy an "Octahedral lattice site" where it is surrounded by six near-neighbour Oxygen ions.

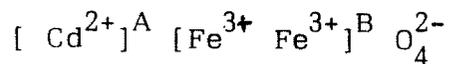
e.g.

$\text{ZnFe}_2\text{O}_4$  with cation distribution



and

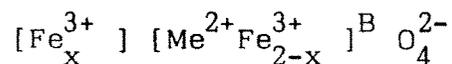
$\text{CdFe}_2\text{O}_4$  with cation distribution



Normal spinels do not exhibit ferrimagnetic behaviour.

### 1.3.2(b) INVERSE SPINEL

The spinel ferrite in which eight tetrahedral sites are occupied by trivalent ions instead of the divalent ions and the divalent metal ions occupy the octahedral sites along with remaining eight trivalent ions, then the structure is called as Inverse spinel. The cation distribution in case of inverse spinel is



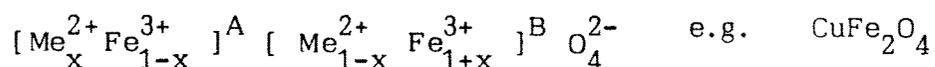
e.g.  $\text{MnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  etc.

Inverse spinel ferrite show ferrimagnetic behaviour.

### 1.3.2(c) RANDOM SPINEL

A spinel ferrite in which divalent metal ions and trivalent iron ions are randomly distributed over A and B sites is referred to as a random spinel ferrite. The distribution of divalent metal ion and trivalent ions over A and B sites depend on physico chemical

conditions of preparation. The general formula for partially inverted ferrite is usually written as,



#### 1.4 TYPES OF FERRITES :

##### 1.4.(a) SIMPLE FERRITES :

When divalent ferrous ion  $Fe^{2+}$  is replaced by another divalent metal ions such as Mn, Co, Ni, Cu, Mg, Zn or Cd, the ferrites so formed (such as  $MnFe_2O_4$ ,  $CoFe_2O_4$ ,  $NiFe_2O_4$ ,  $ZnFe_2O_4$  etc.) are called simple ferrites.

##### 1.4.(b) MIXED OR SUBSTITUTIONAL FERRITES :

When divalent metal ions and trivalent metal ions are replaced by other magnetic or nonmagnetic ions in the spinel structure, the resulting ferrites are called as substitutional ferrites. The substitution can be done in two ways.

i) Replacing divalent Me ion by another divalent Me ion e.g.  $Co_{1-x}Zn_x Fe_2O_4$  ( $0 < x < 1$ ) is zinc substituted cobalt ferrite.

ii) Replacing the trivalent iron ion by another trivalent  $Me^{3+}$  ions.

e.g.  $Co_x Zn_{1-x+t} Al_t Fe_2 O_4$  is called as Aluminium substituted Cobalt-zinc ferrite.

#### 1.5 ELECTRICAL PROPERTIES OF FERRITES :

Ferrites are semiconducting by nature. Their resistivity varies in the range of  $10^{-3} \Omega - \text{cm}$  to  $10^{+11} \Omega - \text{cm}$  at room

temperature<sup>19</sup>. The electrical properties of polycrystalline ferrites above 1200°C show marked variation with respect to heat treatment and preparation condition.<sup>20</sup> The resistivity of ferrite decreases with increase in temperature in accordance with relation,

$$\rho = \rho_0 \exp (\Delta E/kT)$$

where E -activation energy,

k- Boltzmann's Constant

T- Absolute temperature

If a graph of  $\log \rho$  versus  $1/T$  is plotted in accordance with above relation, it should be a straight line. But breaks occur in curves, <sup>slope of</sup> closely to ferrimagnetic Curie temperature.<sup>21</sup> The activation energy varies from 0.1 eV to 0.5 eV. The high activation energy is associated with high resistivity at room temperature.<sup>22</sup> In general, the substitution of cations that tends to stay in lower valence state leads to p-type conduction and the substitution of cation that tends to stay in higher valence state leads to n-type conduction. In ferrites, the conductivity is attributed to the occurrence of both  $Fe^{2+}$  and  $Fe^{3+}$  ions in the identical sites; in spinel structure. In this situation extra electron on ferrous ion requires little energy to move to similarly situated ferric ion. (hopping) Thus the valency states of two ions are interchanged. These extra electrons constitute conduction current by hopping from one ion to next.

The conductivity in ferrites depends on porosity, grainsize<sup>23</sup> and chemical inhomogeneity caused by heat treatment.

## 1.6 MAGNETIC PROPERTIES OF FERRITE :

Ferrimagnetism is a special case of antiferromagnetism. In ferrimagnetism, atomic magnetic moments of neighbouring atomic magnets are antiparallel, but of different magnitudes, hence the net magnetisation results. The term ferrimagnetism was coined by Neel in connection with properties of ferrites.

Weiss first attempted to give explanation of ferrites on the basis of his molecular field theory. Ferrimagnetic substance exhibit spontaneous magnetisation which arises due to the alignment of magnetic moment under the exchange forces. The coupling between atomic magnets in a substance causes either parallel or antiparallel alignment of spins. When the spin alignment is antiparallel and magnetic moments are equal, antiferromagnetism results. When spin alignments are antiparallel and magnetic moments are unequal, ferrimagnetism results. The exchange interaction between neighbouring atom may be indirect and take place via intermediate nonmagnetic ion such as oxygen or sulphur.<sup>24</sup>

### 1.6(a) CLASSIFICATION OF MAGNETIC PROPERTIES :

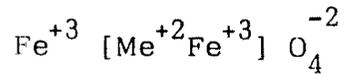
The magnetic properties are classified into two groups.

- i) Intrinsic properties- Such as permeability, saturation magnetisation, Curie temperature, magnetostriction etc.
- ii) Structure sensitive properties -Such as hysteresis, resistivity, dielectric constant etc.

The grain size impurity inclusion porosity affect structure sensitive properties.<sup>25</sup>

### 1.6(b) STRUCTURAL EXPLANATION OF FERRIMAGNETISM :

The cation distribution in inverse spinel structure is given by,



where bracketed cations are on B sites and those outside bracket are on A site.<sup>26</sup> The unit cell of ferrite contain eight molecules. Hence magnetic moment of A sublattice is due to  $8\text{Fe}^{+3}$  cations, and on B sublattice, the magnetic moments is due to  $8(\text{Fe}^{+3} + \text{Me}^{-2})$  cations present. The resultant magnetisation is given by,

$$M = M_B - M_A$$

$$M = 8(m_M + m_{\text{Fe}}) - 8m_{\text{Fe}}$$

$$M = 8m_M$$

where  $M_A$  - magnetic moment of A sublattice

$M_B$  - magnetic moment of B sublattice

$m_M$  - spin magnetic moment of metal ion

$m_{\text{Fe}}$  - spin magnetic moment of Fe ion.

The parallel alignment of moment on each sublattice is characteristic of ferrimagnetic substances. Ferrite with normal spinel structure are non magnetic. In these ferrite A-B interaction does not exist, because there is no magnetic ion on A site and the B-B interaction lines up half the magnetic ions in one direction so that alternate planes of B-sublattice are magnetised in opposite direction with resulting ferrite to be nonmagnetic. The angles between A-A, B-B and A-B cations are as shown in Fig.1.4.

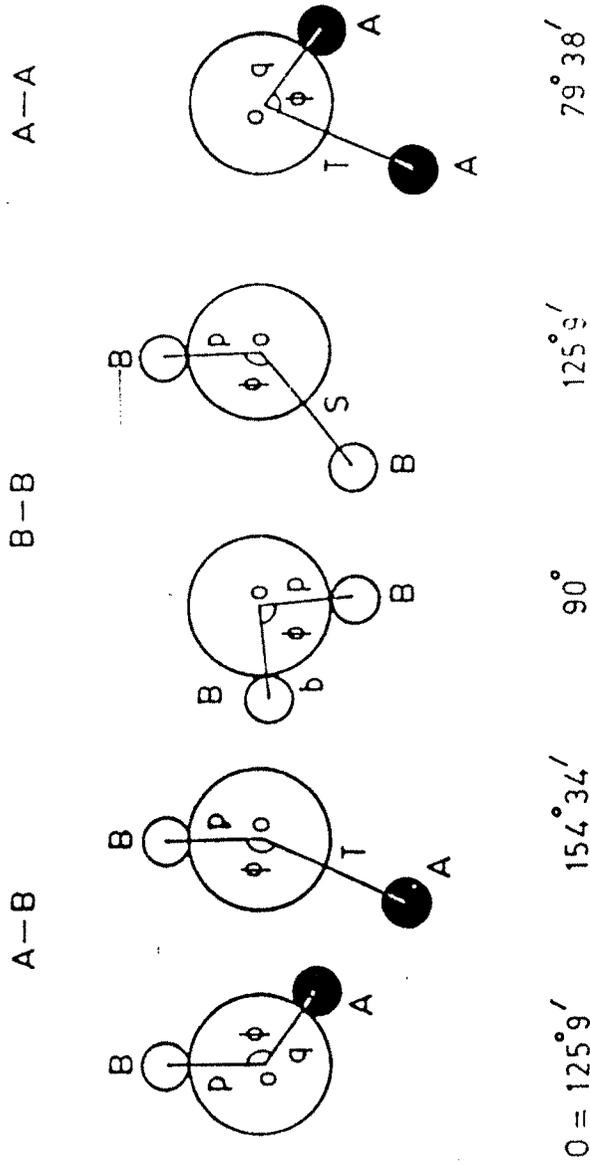


Fig.1.4: ANGLE BETWEEN A-A, B-B & A-B CATIONS IN A SPINEL STRUCTURE .

### 1.7 NEEL'S THEORY OF FERRIMAGNETISM :

Neel's explanation of ferrimagnetism is based on two ideas

- 1) Weiss molecular field theory
- 2) Two sublattice model

Ferrimagnetic crystal lattice could be divided into two sublattices such as tetrahedral (or A site) and octahedral (or B site) and ferrimagnetic crystal lattice consist of identical type of magnetic ions.

Consider a ferrimagnetic substance and an ion or atom in it. Let  $H_0$  be the externally applied field on the substance. Then the total magnetic field acting upon the atom or ion under consideration will be  $H = H_0 + H_m$  .....(1.3)

where  $H_m$  is the internal field due to interaction with other atoms according to Weiss molecular field idea.

Now consider A and B sites of an atom. Applying Weiss molecular field concept we can write,

$$H_A = H_{AA} + H_{AB} \quad \text{.....(1.4)}$$

$$H_B = H_{BB} + H_{BA}$$

According to Weiss concept ,

$$H_{AA} = \gamma_{AA} M_A \quad H_{AB} = \gamma_{AB} M_B \quad \text{.....(1.5)}$$

and,

$$H_{BB} = \gamma_{BB} M_B \quad H_{BA} = \gamma_{BA} M_A \quad \dots\dots(1.6)$$

where  $\gamma$ 's are Weiss molecular field coefficients and  $M_A$  and  $M_B$  are the magnetic moments of neighbouring A and B sublattices.

Neel has shown.

$$\gamma_{AB} = \gamma_{BA} \quad \text{and} \quad \gamma_{AA} \neq \gamma_{BB} \quad \dots\dots(1.7)$$

unless the two sublattices are identical. Further Neel has shown that  $\gamma_{AB} < 0$  favouring antiparallel arrangements of  $M_A$  and  $M_B$  and which gives rise to ferrimagnetism.

Thus when external field  $H_0$  is applied the total magnetic field on an ion in A and B sublattice will be

$$\begin{aligned} H_a &= H_0 + H_{AA} + H_{AB} \\ &= H_0 + \gamma_{AA} M_A + \gamma_{AB} M_B \end{aligned} \quad \dots\dots(1.8)$$

and

$$\begin{aligned} H_b &= H_0 + H_{BB} + H_{BA} \\ &= H_0 + \gamma_{BB} M_B + \gamma_{BA} M_A \end{aligned} \quad \dots\dots(1.9)$$

I) Paramagnetic region :

Ferrimagnetic substances at high temperatures behave like paramagnetic substances.

Consider an assembly of  $N$  free paramagnetic ions per unit volume each with total angular momentum quantum number  $J$ , then

$$\text{Magnetisation, } M = NgJ \mu_B B_J(x) \quad \dots(1.10)$$

where N = Number of free ions

g = Lande's splitting factor

J = Total angular momentum quantum number

$B_J(x)$  = Brillouin function

$\mu_B$  = Bohr magneton

Brillouin function,

$$B_J(x) = \left( \frac{2J+1}{2J} \right) \text{Coth} \left[ \left( \frac{2J+1}{2J} \right) x \right] - \frac{1}{2J} \text{Coth} (x/2J) \quad \dots(1.11)$$

$$\text{and } x = \mu_0 g J \mu_B H / kT \quad \dots(1.12)$$

where k = Boltzmann's constant

T = absolute temperature

When  $x \ll 1$  i.e. when T is high

$$B_J(x) = \left( \frac{J+1}{3J} \right) x \quad \dots(1.13)$$

Using this value of  $B_J(x)$  and x, the magnetisation

$$M = \mu_0 N g^2 \mu_B^2 J(J+1) H / 3kT \quad \dots(1.14)$$

From this susceptibility

$$\chi = \frac{\mu_0 N g^2 \mu_B^2 J(J+1)}{3kT} = C/T \quad \text{Curie law-} \quad \dots(1.15)$$

for paramagnetism

At high temperature the magnetic field H is to be taken as  $H + H_m$

$$\chi = M/H = M/(H + H_m) = M/H + \gamma M = C/T$$

i.e.  $(M/H) / [1 + \gamma (M/H)] = C/T$

$$\text{i.e. } \chi / (1 + \gamma \chi) = C/T$$

$$\chi [ T - \gamma C ] = C$$

$$\chi = C/[T - \gamma C] = C/[T - T_C] \quad \dots\dots(1.16)$$

$$\text{where } T_C = \gamma C$$

This relation can be used to determine the value of  $\chi$  experimentally.

From the relations  $\chi = C/T$  and  $\chi = C/[T - T_C]$

it is seen that  $\chi$  is directly proportional to the applied magnetic field and inversely proportional to the temperature. Neel applied these arguments to each sub-lattice of ferrimagnetic material and wrote down the relations

$$M_A = \left( \frac{\lambda C}{T} \right) H_a \quad \text{and} \quad M_B = \left( \frac{\mu C}{T} \right) H_b \quad \dots\dots(1.17)$$

$C$  refers to unit volume and  $\lambda C$ ,  $\mu C$  refer to the volumes occupied by the magnetic ions in each sub-lattice. Total magnetisation on both sites will be

$$M = M_A + M_B \quad \dots\dots(1.18)$$

Using the values of  $M_A$  and  $M_B$  and  $H_a$  and  $H_b$  as given in the above discussion, after necessary algebraic manipulation we get,

$$\frac{1}{\chi} = \frac{T^2 - C \gamma_{AB} (\lambda \alpha + \mu \beta) T + C^2 \lambda \mu \gamma_{AB}^2 (\alpha \beta - 1)}{C [T - \lambda \mu \gamma_{AB} (2 + \alpha + \beta)]} \quad \dots\dots(1.19)$$

$$\text{where } \alpha = \gamma_{AA} / \gamma_{AB} \quad \text{and} \quad \beta = \gamma_{BB} / \gamma_{AB} \quad \dots\dots(1.20)$$

Following Neel the above relation for inverse susceptibility can be written as

$$1/\chi = T/C + 1/\chi_0 - \xi/T - \theta \quad \dots\dots(1.21)$$

where  $1/\chi_0 = \gamma_{AB} (2\lambda\mu - \lambda^2\alpha - \mu^2\beta)$

$$\theta = \gamma_{AB} \lambda\mu C (2 + \alpha + \beta)$$

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

The first two terms in the above relation give Curie-Weiss form of temperature dependence of  $1/\chi$  as observed in ferromagnetics above Curie temperature, but the term  $\xi/T - \theta$  has no counterpart in ferromagnetism. This term is special to ferrimagnetic materials.

The above Eq.(1.21) represents a hyperbola.

If we plot a graph of  $1/\chi$  versus  $T$  we get the hyperbola which cuts at a point so called paramagnetic Curie point. The asymptote cuts temperature axis at  $\theta = -C/\chi_0$  which gives asymptotic Curie point (fig.1.5). Experimental  $1/\chi$  versus  $T$  curve for Gadolinium iron garnet is shown in Fig.1.6.

## II) Spontaneous magnetisation :

For ferromagnetic substance the spontaneous magnetisation is given by,

$$M_{sp} = NgJ \mu_B B_J(\mu_0 gJ \mu_B H/kT) \quad \dots\dots(1.22)$$

To explain behaviour of ferrimagnetic material above Curie point, the equation of above form was used.

The spontaneous magnetisations for sublattice A,

$$M_{Asp} = \lambda Ng J \mu_B B_J(\mu_0 gJ \mu_B H_a/kT) \quad \dots\dots(1.23)$$

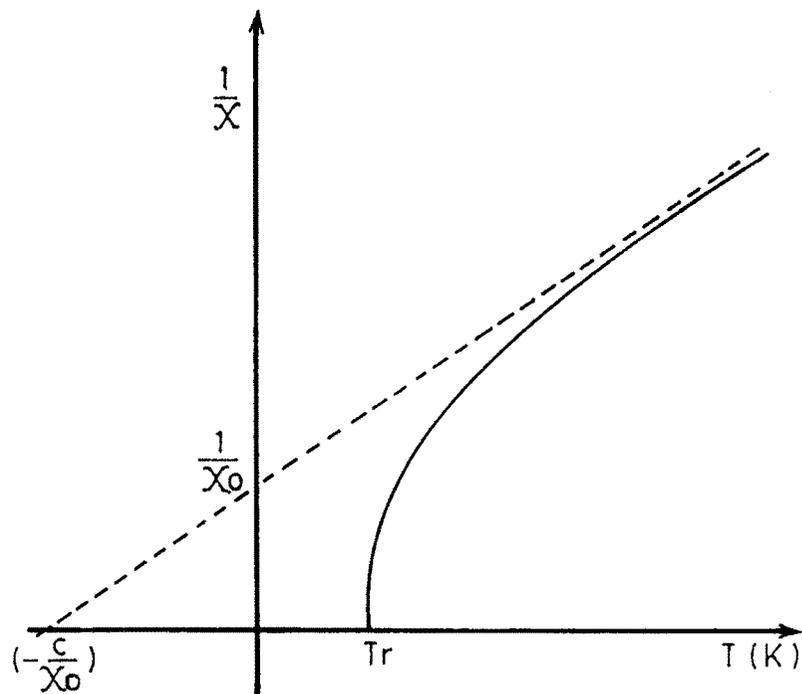


Fig. 1-5: Predicted susceptibility curve of a ferroelectric material above the curve point.

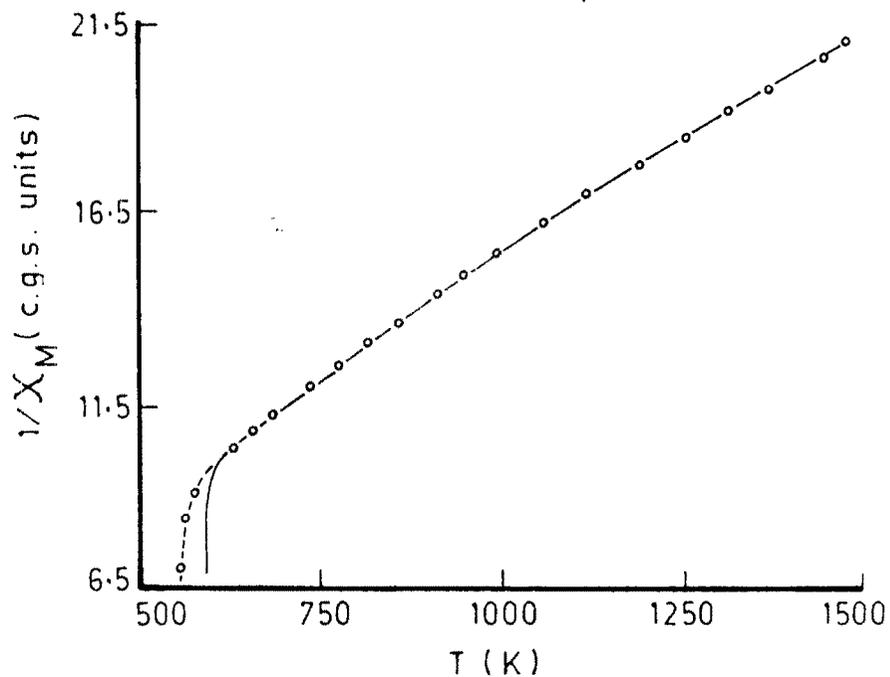


Fig. 1-6: Experimental susceptibility/ temperature curve for gadolinium-iron garnet.

The spontaneous magnetisations for sublattice B,

$$M_{Bsp} = \mu N_B g_B J_B B_J \left( \frac{\mu_B g_B J_B H_B}{kT} \right) \quad \dots\dots(1.24)$$

Where  $B_J$ 's represent Brillouin function and  $N$ 's are number of atoms per unit volume of respective lattice.

The net observable spontaneous magnetisation

$$M_{sp} = | M_{Bsp} - M_{A sp} | \quad \dots\dots(1.25) \quad \dots$$

The graphs of  $M_s$  versus  $T$  are of different types (Fig.1.7). They provide information about spontaneous magnetisation and exchange energy at different temperatures. The above theory is supported by experimental curves of Neel<sup>26</sup>, Gorter<sup>27</sup> and Smart.<sup>28</sup>

### 1.8 YAFET-KITTEL THEORY :

Neel's theory was adequate for pure ferrites. Neel's model was inadequate for spinels containing chief constituent other than Fe, where observed magnetisation is much smaller than calculated by Neel's model for spin arrangement. Therefore, Yafet and Kittel<sup>12</sup> proposed a triangular type of spin arrangement. They showed for certain ratios of exchange interaction in spinels, there can exist three sublattices with triangular spin configuration and has lower energy than two sublattice model. In such a case there exists a possibility of negative interaction within sublattices itself giving rise to sublattices  $B_1, B_2$  which are neither exactly antiparallel to each other nor to sublattice A or B. Instead they get aligned at some angle other than  $180^\circ$ . Thus there is resultant magnetisation

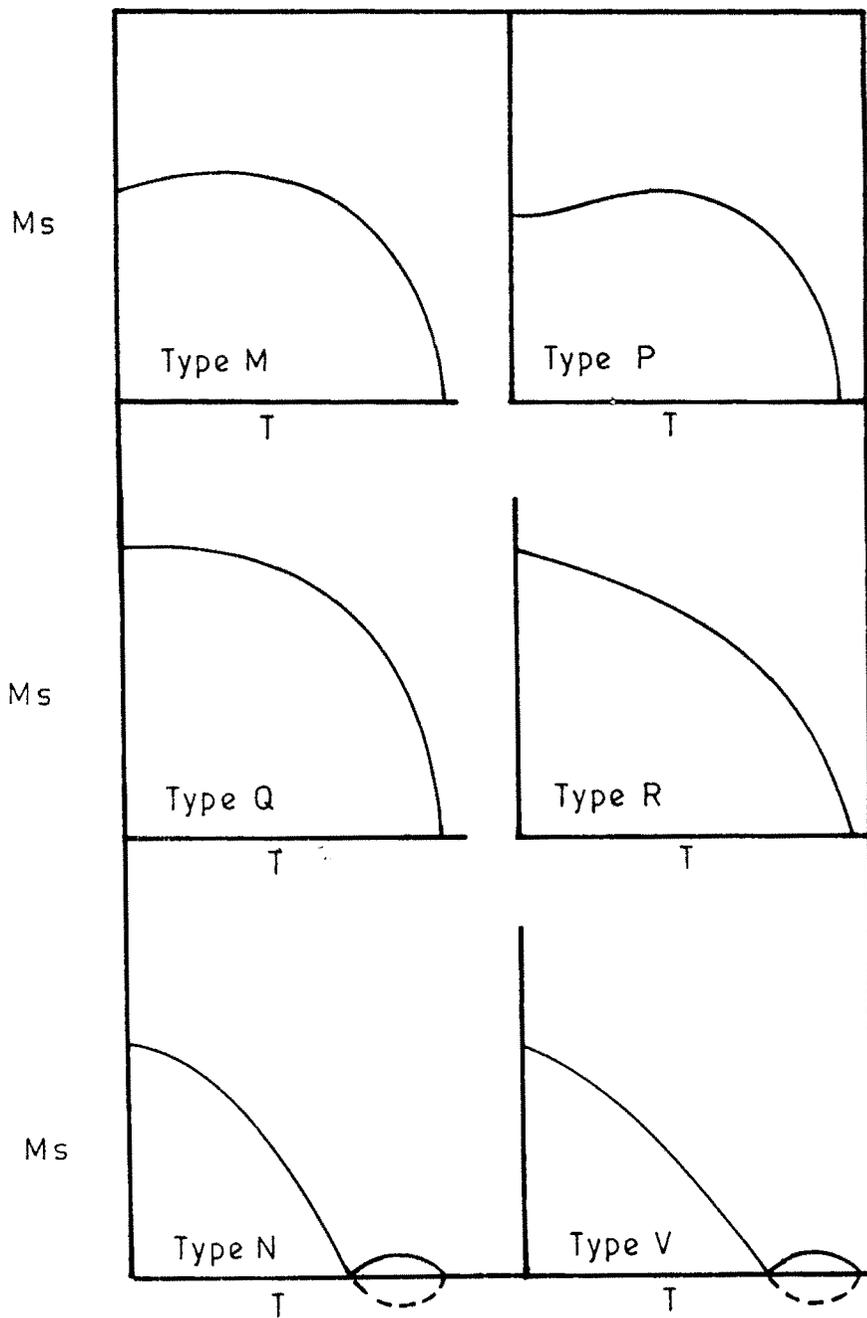


Fig.1-7  $M_s$  vs  $T$  Curves for ferrimagnetic substances predicted by Neel's Theory.

of  $B_1$  and  $B_2$  sublattices setting antiparallel with that at A lattice (Fig.1.8).

These triangular arrangement within the lattice results in reduced value of magnetisation of same order and magnitude as per prediction of Neel's model.

Neel's theory predicted  $(M_s, T)$  curves of different types. But these curves do not occur in practice, because they require  $\partial M_s / \partial T$  to be finite at  $T = 0^0K$  which is in contradiction with the third law of thermodynamics. This difficulty was removed by above suggested Yafet-Kittel model. The interaction energy in this case is given by,

$$E = 8N [ 6J_{ab} S_a S_b \cos \phi - J_{bb} S_b (2 \cos \phi - 1) ] \quad \dots\dots(1.26)$$

where  $\phi$  equal to angle between sublattices

$J$ 's are exchange integrals

$E$  is minimum for  $J_{ab}$  negative and  $J_{bb}$  positive and if  $\phi = 0$ , is Neel's state. If  $J_{bb}$  is also negative then the ratios of exchange energies is given by,

$$\gamma_{ex} = \frac{J_{bb} S_b}{J_{ab} S_a} > 3/4 \quad \dots\dots(1.27)$$

Then Neel's state will not become minimum and magnetisation vector of sublattices will be inclined from colliner position by an angle  $\phi$ . Which is given by,  $\cos \phi = (3/4)(J_{bb} S_a / J_{ab} S_b)$   $\dots\dots(1.28)$

They pointed out that Neel's structure is stable for  $\gamma_{ex} < 3/4$  if total number of sublattices is restricted to six.(i.e. no.of different

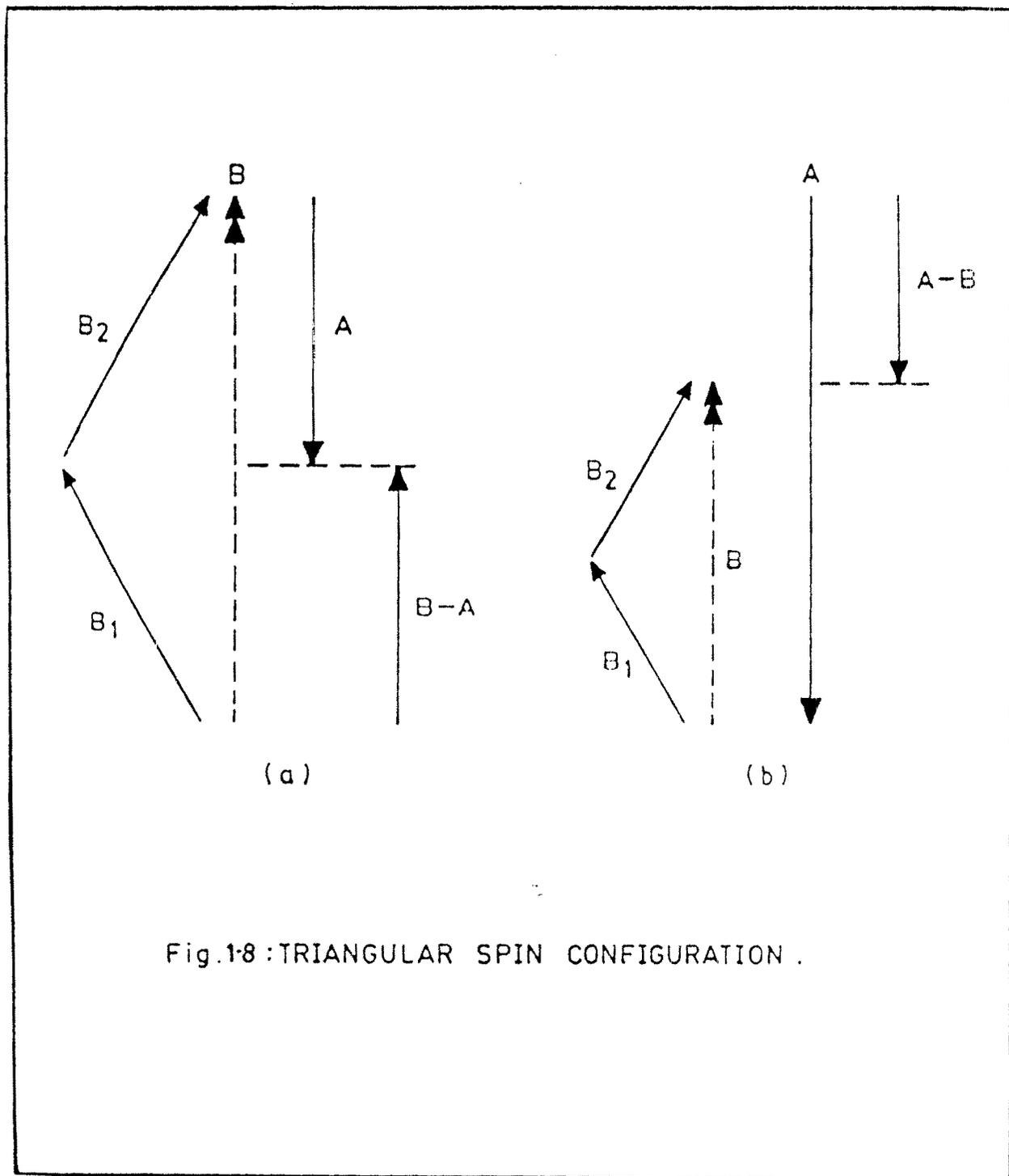


Fig.1-8 : TRIANGULAR SPIN CONFIGURATION .

magnetic ion). The existence of triangular arrangement has been reported by Lotegring<sup>29</sup> in few cases.

### 1.9 SPIRAL SPINS :

Kaplan<sup>30</sup> studied Yafet-Kittel model and showed that it does not minimise exchange energy if  $J_{ab} > 0$  and proposed spiral type of spin configuration by neutron diffraction in some compounds. Lyon and Kaplan<sup>31</sup> generalised treatment of spin configuration modifying Yafet-Kittel model. They have suggested possibility of spiral spin arrangement and showed that they have lower energy for all values of  $\gamma_{ex} > 2/3$ . Crollis and Hastings<sup>32</sup> observed existence of such configuration in manganese chromite. Spiral spin configuration was also developed by Lotegring. Lotegring<sup>29</sup> applied the theory to his own results on oxides and sulphides. Spiral spin configuration has been reported by Enz<sup>33</sup> in case of hexagonal ferrite.

### 1.10 APPLICATIONS OF FERRITES :

Ferrites are some of the most important electronic electrical and magnetic materials, hence they find wide applications in electronic and electrical industries and technology.

Ferrites find their application in aerial rods<sup>34</sup> in accelerators for elementary particles<sup>35</sup>, in digital computers<sup>36</sup> (rectangular hysteresis loop). In synchrotron a ferrite accelerating resonator is being proposed by Averbukh.<sup>37</sup> Ferrites are widely used for antenna cores in broadcast radio receivers. They are also used as flyback transformer in television picture tubes magnetically soft ferrites having lower permeability and saturation magnetisation find better replacement for metallic cores, which were discarded for high eddy current

loss. Soft ferrites find their major use in high frequency transformer, deflection yokes in T.V. sets, chokes recording head etc. Power ferrites find high frequency applications.<sup>38</sup> In these applications gyromagnetic dielectric losses which arise due to high d.c. resistivity are suppressed. As well as the low magnetic flux density is also reduced.

To overcome the limitations of iron core or air core transformers, ferrite cores are used. The high permeability of ferrites make them suitable (i) as band pass filters in the range 50KHz to 150 KHz in telephone circuits. (ii) as IFT in radio receivers (iii) as an inductor in T.V. receiver (iv) as a pulse transformer in data handling systems. Because of high resistivity, ferrites can be used as pole pieces for concentrating flux in h.f. induction heaters.<sup>39</sup>

Spinel structure has physical flexibility, which leads to a broad spectrum of its practical applications<sup>40</sup> some ferrites exhibit a typical rectangular hysteresis loop. The rectangularity of hysteresis loop and coercive force are important factors in these applications. The square loop ferrites store information by virtue of two equally stable magnetic states. Ferrites with small coercive force are used in magnetic amplifiers. Storm<sup>41</sup> and Attura<sup>42</sup> used Mn-Zn ferrites for this purposes.

piezomagnetic ferrites are used in ultrasonic transducers. Piezomagnetic ferrites were developed by Van der Burgt and Stuijts<sup>43</sup> Recently piezomagnetic nickel-magnese cobalt ferrites<sup>44</sup> have been developed for their wide applications in ultrasonic and r. f applications.

Hexagonal ferrites (e.g.  $\text{BaFe}_{12}\text{O}_{19}$ ) find their use in loudspeaker, motors, generators, because they are permanent magnetic materials. The Table 1.1 gives various applications of ferrite materials.

TABLE 1.1  
APPLICATION SPECTRUM OF FERRITES

	For radio	For Television	For Telecommunication	Miscellaneous
1	IF band -Pass filters,	1) Line output transformers	1) Filters for carrier Telephony	1) Ultrasonic vibrator
2)	Antennas	2) Deflection coils	2) hf chokes	2) Mechanical filters
3)	Elements for permeability tuning	3) Linearity and width control of image	3) Equalizing cores	3) recording heads in tape recorder
4)	Transformers	4) Noise suppression plates	4) Delay lines	4) Frequency modulation
		5) Broad band audio transformers	5) Broad band audio transformers	5) h.f. coupling
		6) Pulse transformer	6) Pulse transformer	6) Ignition coils
				7) Low power transmission
				8) Magnetic amplifiers
				9) Saturable reactors
				10) Various parts in proton accelerator
				11) Modulation of uhf in waveguides,gyrators

### 1.11 ORIENTATION OF PROBLEM :

As pointed out the ferrites-ferrimagnetic oxides are having a large number of technological and industrial applications. They form an interesting class of materials from the point of view of research and their applications in various fields such as T.V. computer, high frequency transformer etc. As such a tremendous amount of work has been carried out, both experimental and theoretical in this field. They exhibit typical magnetic and electric properties such as hysteresis loop and switching. The resistivity value of these falls in the range  $10^{-3}$  to  $10^{11}$  ohm-cm, so that by proper choice of materials power losses due to eddy current can be minimised. Hence they are found to be suitable for high frequency applications.

The electric and magnetic properties of these materials are structure sensitive and are influenced by physicochemical history, method and conditions of preparation, heat treatment etc. Their properties can also be altered by doping suitable material. As such a ferrite material with desired properties can be prepared by choosing the correct parameters to produce them.

Khan et al<sup>45</sup> have carried out work on variation of lattice parameter and magnetisation in  $Ti^{4+}$ ,  $Sn^{4+}$ ,  $Zr^{4+}$  substituted Ni-Zn ferrite. Also the effect of addition of  $V_2O_5$  in Ni-Zn mixed ferrites,  $Ti^{4+}$  in Mn-Zn mixed ferrites and  $ZrO_2$  in Mg-Zn ferrites has been reported in literature. The mixed Co-Zn ferrite system has been studied

by many workers<sup>46,47,48</sup> from the point of view of crystal structure, electric and magnetic properties. Infrared spectra<sup>49</sup> of these have also been reported. However, data on these ferrites doped with various impurities is scarce. Hence it is felt that it is worthwhile to study how doping of impurities in the mixed ferrite system affect their electrical magnetic properties and I.R. spectra.

Therefore in order to understand the influence of doping of Aluminium and  $Gd_2O_3$  in Co-Zn mixed ferrite the following studies have been carried out..

1) Preparation of  $Co_xZn_{1-x}Fe_2O_4$  ferrite system where  $x = 0, 0.3, 0.5, 0.7, 1.0$  by standard ceramic technique.

Preparation of  $Co_xZn_{1-x}Fe_2O_4$  system doped with 0.05, At.wt % Aluminium (Al)

Preparation of  $Co_xZn_{1-x}Fe_2O_4$  system doped with 0.05 mol wt.% Gadolinium Oxide ( $Gd_2O_3$ ).

2) X-ray diffraction studies for the crystal structure characterisation of ferrite samples and to investigate structural changes due to doping.

3) A.C. and D.C. conductivity measurement to understand conduction mechanism and effect of doping on electrical behaviour.

4) A.C. magnetic susceptibility measurement for determining the existence of M.D., S.D. or S.P. particles within material, for determining Curie temperature (of sample) and hence to investigate effect of doping on susceptibility.

- 5) Determination of Curie temperatures of samples and to investigate variation of Curie temperature with doping.
- 6) Hysteresis studies to determine saturation magnetisation, coercive force i.e. magnetic behaviour and to investigate effect of doping on these parameters.

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