

Chapter - 1

Ferrites An Introduction

1.1 INTRODUCTION

Lode stone was first magnetic material known to man. The chemical formula for Lode stone is FeOFe_2O_3 (Ferrous Ferrite) and is nothing but naturally occurring ferrite. The ferrites are magnetic materials, essentially mixed crystals of various magnetic oxides.

Ferrite continue to evoke interest because they are the most important electronic and magnetic ceramics. The simultaneous twin requirements of optimal electronic and magnetic properties in the advanced electronics , microwave and computer technologies have focused the attention of research workers on ferrites.

The technological importance of the ferrites can be gauged from the spectrum of application in high frequency and pulse transformer, inductances, deflection coils, antennas and modulators and numerous other applications depending on the requirements of high permeability and low loss at high frequencies.

Ferrites with squareloop characteristics of B-H curve, find extensive use in computer memory as core devices. Alternate selection and control of variables in preparation of ferrites has been used to give ferrites of lower permeability and larger magnetostriction. Microwave applications depend on

the nature of gyromagnetic resonance of ferrites which are exemplified in Faraday rotation, phase shifters, modulators.

1.2 (a) HISTORICAL :

The first known magnetic material was made available by nature itself in magnetite which is nothing but ferrous ferrite. There arose a need for the magnetic materials to reduce eddy current losses, which was met by preparing synthetic ferrites.

Hilpert⁽¹⁾ (1909) was working with synthetic ferrites to reduce eddy current losses in inductor and transformer. After some years when the utility of ferrites was proven beyond doubt, the studies of ferrites from the point of view of electrical and magnetic properties and chemical and crystallographic characteristics gathered impetus. In thirties Kato⁽²⁾ and Takai, Forestier,⁽³⁾ Barth and Posjnak have studied ferrites from various points of view. The structure of the ferrite was established to be of spinel type.

A decade later Snoek^(5,6) carried out extensive systematic studies of preparation of ferrites and their magnetic properties. This led to various applications of ferrites. Verwey⁽⁷⁾ established that the electronic conductivity of ferrites is mainly due to the exchange of electron between divalent and trivalent ions of iron in the ferrites.

His study on crystal structure of various ferrites showed ferrites with inverted spinel structure to be ferrimagnetic, whereas those with normal structure to be non magnetic.

The basic theory of Spin-spin interaction in ferrites was announced by Neel⁽⁸⁾. He introduced the concept of magnetic sub-lattices, applying the same molecular field theory of exchange interaction in ferromagnetic materials except the possibility of spin alignment in the antiparallel sense. A more detailed examination of basic interaction was made by Anderson⁽⁹⁾ and VanVleck who developed theory of super exchange. Yafet and Kittle⁽¹⁰⁾ extended the theory of magnetic sublattices by postulating a "triangular" arrangement of three sublattices when the antiferromagnetic exchange interaction between sublattices is comparable to that among spin moments within sublattices formed by Fe^{+3} ions on tetrahedral and octahedral sites.

Gorter⁽¹¹⁾ and Gulliaud⁽¹²⁾ gave the direct experimental proof of Neel's theory. Gorter measured the magnetization of Mn, Fe, Co, Ni, Cu and Mg ferrites mixed with Zn ferrites as a function of Zn composition.

Gulliaud ~~and~~ et al explained the variation of magnetization as a function of temperature for mixed ferrites with varying composition and temperature in ferrimagnetic region. Neel modified the earlier theoretical treatment which

could not account for the temperature dependence of Weiss molecular interaction constant as per the experiments. The modified theory was confirmed positively by experimental results. The direct proof of Neel's model of ferrimagnetism came up only with neutron diffraction studies on magnetic and zinc ferrite.

Other research workers especially Smart⁽¹³⁾ and Gorter⁽¹⁴⁾ also correlated independently the cation distribution found out by microwave resonance and magnetization.

Recently the work on ferrites has assumed large proportions during the last two decades and it has proceeded on all the fronts starting from better control of structural parameters as in single crystals and epitaxial films to the use of information on ferrites towards understanding of ferrites.⁽²⁹⁾

1.3 CRYSTAL STRUCTURE :

The magnetic oxides exhibit the following structures in general.

- | | |
|----------------------|--------------------------|
| (1) Spinel Structure | (3) Hexagonal Structure |
| (2) Garnet Structure | (4) Perovskite Structure |

1.3 (a) SPINEL STRUCTURE :

The general chemical formula for ferros spinel is MFe_2O_4 Where M is divalent metal ion and Fe is a trivalent ion.

All the compounds of this type have a cubic, face centred crystal structure (Fig.1.1) of the space group $O_h^7 - F_{23}d$ with a unit cell containing 8 formula units.

The cations occupy interstitial positions of which there are two distinctly different types - Type one known as "tetrahedral" or "A-site", in which magnetic ion is surrounded by four oxygen ions located at the corners of a tetrahedron as shown in Fig.(1.2a). And the type two is known as "Octahedral" or B-site, in which magnetic ion is surrounded by six oxygen ions placed at the vertices of an octahedron as shown in fig.(1.2 b). There are in all 96 interstitial sites are occupied by cations per unit cell.

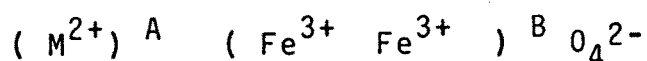
The distribution of cations on the A and B site is obtained by relative site preference energies of the respective metal ions present in the ferrite.

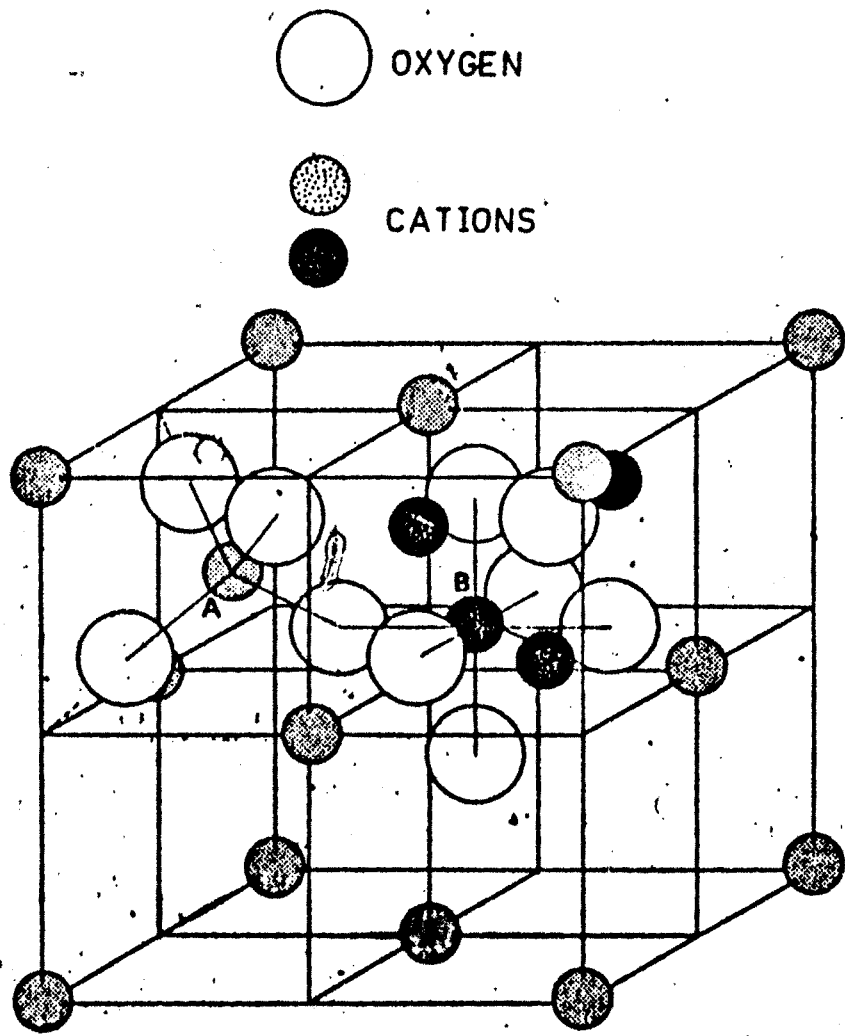
The spinel ferrites are classified on the basis of cation distribution as follows :

i) NORMAL SPINEL FERRITES :

In the normal spinel ferrites all the M^{+2} ions occupy the tetrahedral A-sites, while Fe^{+3} ions are in the octahedral B-sites.

The cation distribution of Normal-Spinel ferrites as follows:





The spinel structure.

Fig. 1-1

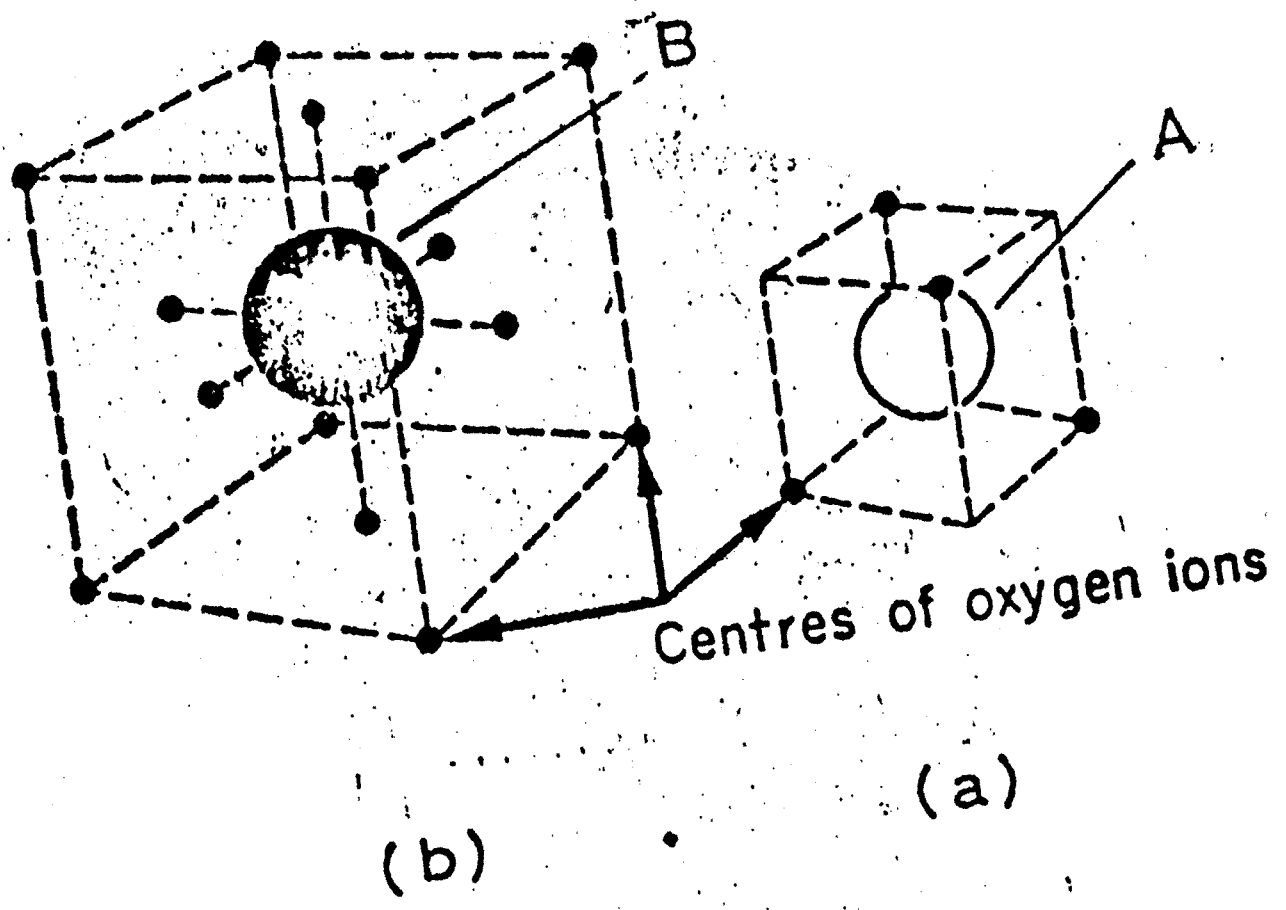


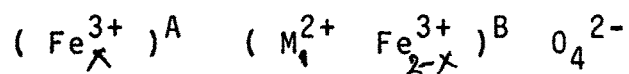
Fig. 1.2

91.2

ii) INVERSE SPINEL FERRITES :

If the tetrahedral sites are occupied by 8 trivalent ions instead of by divalent ions, occupy the octahedral sites along with the remaining 8 trivalent ions then the structure is called as "inverse " Spinel.

The general the cation distribution may be represented by :

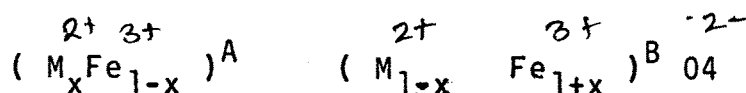


The inverse spinel ferrites shows ferrimagnetic behaviour.

iii) RANDOM SPINEL FERRITES :

In the random spinel ferrites M^{+2} and Fe^{+3} are randomly distributed over the A and B sites depending on the physicochemical conditions of preparation.

The general formula for the partially inverted ferrites is usually written as



where x - coeff. of normalcy
 $1-x$ - coeff. of inversion.

1.3 (b) GARNET STRUCTURE :

The natural garnet is grossularite $Ca_3 Al_2 (SiO_4)_3$
 The most widely studied garnet is YIG-Yittrium Iron Garnet and chemical formula is $5Fe^{2+} \cdot 3Y^{3+} \cdot 23O_3$ Garnet structure was fully explained by Bertaut⁽¹⁵⁾ and Farrat and by Geller and Giello⁽¹⁶⁾.

The garnet structure is cubic and space group is O_h^{10} Ia₃d. The garnet structure has three types of cation site designated as a, c, d.

The metal ion position 16a have octahedral 24C have dodecahedral and 24d have tetrahedral oxygen surroundings.

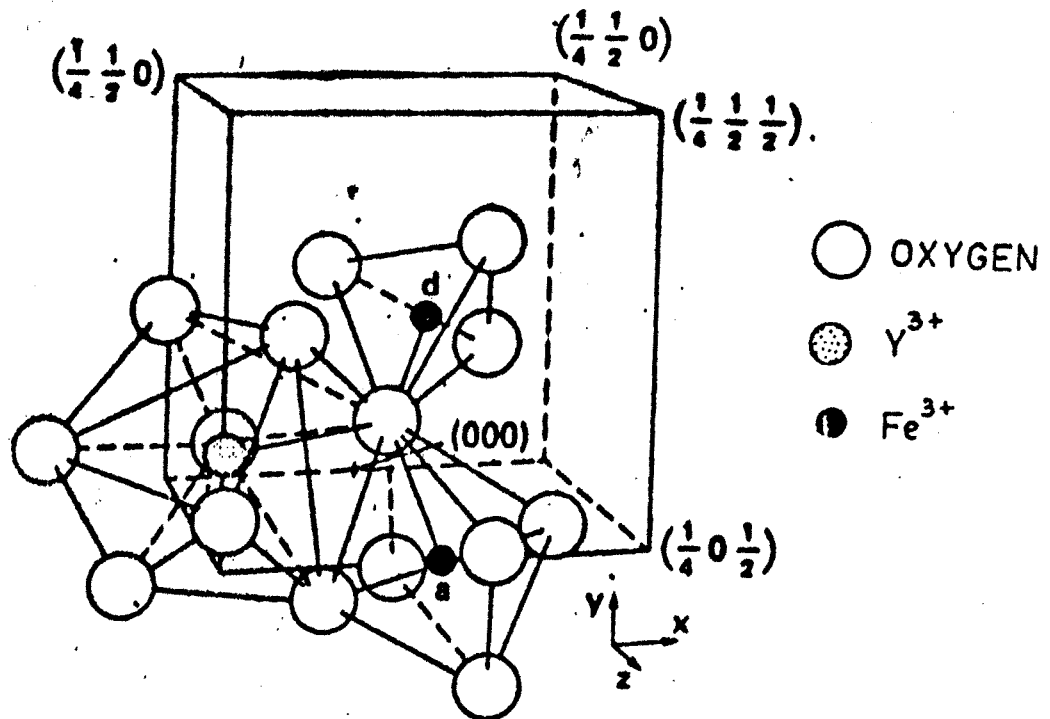
The large Y ions are located in dodecahedral sites and small Fe ions are located in tetrahedral and octahedral sites. Each oxygen ions has two Y^{+3} ions, one Fe^{+3} ions from 'a' site and one Fe^{+3} ions from 'd' site as nearest neighbours.

In Fig.1.3 the garnet structure is shown with respect of the feature in connection with the interpretation of the saturation magnetization data.

The Y ions in YIG formula can be replaced wholly or in part by trivalent rare earth ions substitutionally. This changes the magnetic properties. The Fe ion may be replaced by other trivalent ions which may prefer one of the two a, d, sublattices depending on size and other unknown considerations.

1.3 (C) HEXAGONAL STRUCTURE :

The Hexagonal structure has chemical formula $M Fe_{12} O_{19}$ Where M can be Ba, Sr, Ca and Fe may be substituted by Al or Ga.



The garnet structure.

Fig. 1-3

The garnet structure.

The magnetoplumbite compounds also have the Hexagonal structure and their chemical formula is $X BaO \cdot Y Fe_2O_3 \cdot Z M^{+2}O$ Where M is the transition metal . They are generally known as permanent magnetic materials .

The crystal structure fig 1.4 consists of closely packed oxygen ions, built up of layers of cubic and hexagonal stacking alternately.

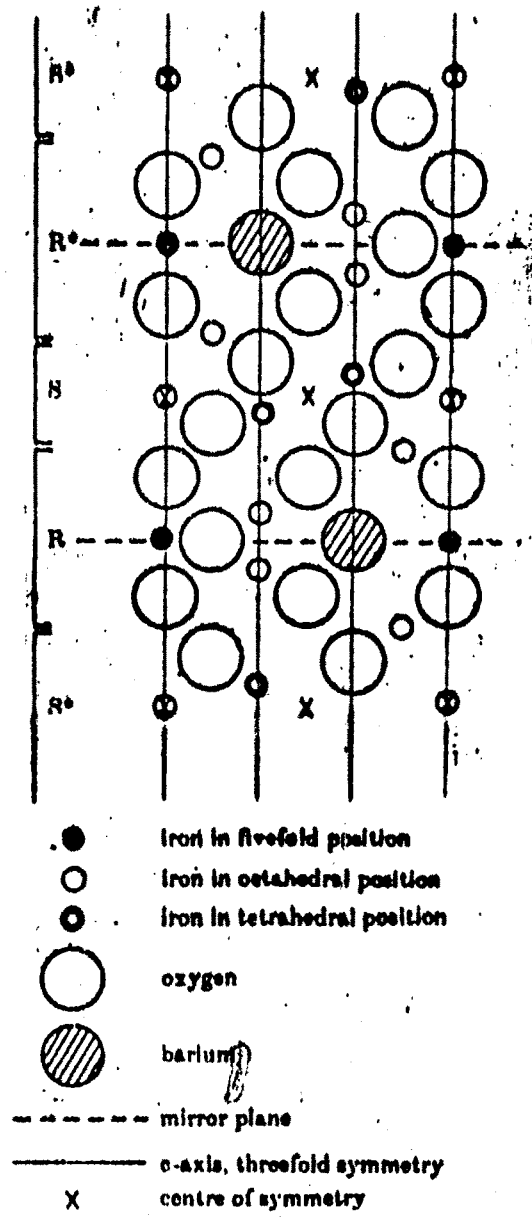
The structure consists of cubic blocks which have their triad axis (iii) parallel to the C-axis coupled by hexagonal blocks containing oxygen - barium layers and iron with unique five fold coordination. The Fe ion may be located in three different interstices octahedral and tetrahedral and sites surrounded by five oxygen atoms forming a single bipyramidal site with triangular base in barium-oxygen layers.

In this hexagonal structure only one metallic ion is available for two adjacent tetrahedral sites which occupied an intermediate position along C-axis.

1.4 MAGNETIC PROPERTIES OF FERRITES

The properties of ferrite can be clasified in two catagories, intrinsic and structure sensitive.

Saturation magnetisation, anisotropy, magnetostriction and curie temperature are basically the intrinsic properties, while permeability hysteresis and other



∴ Hexagonal structure.

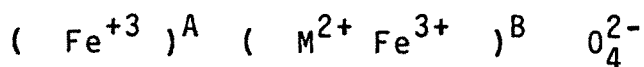
Fig. 1.4

losses, resistivity and dielectric constant etc. very much structure sensitive.

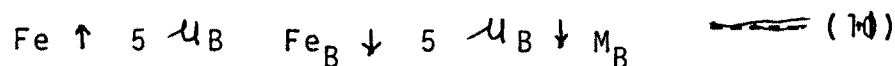
1.4 (a) MAGNETIZATION IN FERRITES

The magnetization exhibited by ferrites was explained on the basis of Weiss's ^{molecular} field theory. Weiss field theory neglects two physical phenomena one, at very low temperature single spin interacts with a field that is parallel to the magnetization of its neighbouring ^{atom} rather than with a uniform field ^{not} parallel to the magnetization. This attribute small deviation of atomic moment from alignment with its neighbour. Second at and just above curie point, the Weiss theory predicts that for $T > T_c$ in the absence of external ^{magnetic} field the spin order vanishes completely.

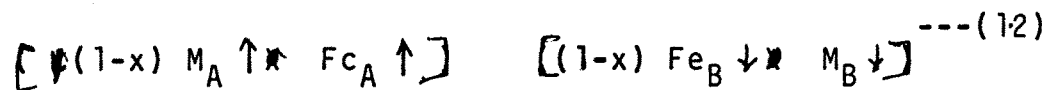
The normal spinels ferrites are non magnetic e.g. $ZnFe_2O_4$ and $CdFe_2O_4$ while inverse spinels are ferrimagnetic. However, for a mixed ferrite system on a simplistic approach, the observed magnetization could not be explained.



The Fe^{+3} ions on A site are coupled with their spins antiparallel to those of Fe^{+3} ions on B site. So that the net moment is only due to divalent M^{+2} metallic ions.



Suppose that M is a transition element with n electrons in d shell, the magnetic moment μ_B per unit formula is $n\mu_B$ or $(10-n)\mu_B$ depending on d shell which is filled less than half or more than half respectively. The degree of inversion is a fraction X of the divalent metal ions that are on B site. The arrangement of moments could be written as



The net moment μ_B is written as

$$\begin{aligned} \mu_B &= M ((1-x) - X) - 5 (1 + (1-x) - X) \\ &= M (1-2x) - 10 (1-x) \quad \text{----- (13)} \end{aligned}$$

For normal spinels $X=0$

inverse spinels $X=1$

The indirect exchange coupling between metallic ions acting through the oxygen ions is maximum for those ions X and Y for which the angle XOY is closet to 180° , for the perfect spinels lattice the major angles between the ions are AOB $125^\circ 9'$ and $154^\circ 34'$ BOB 90° and $125^\circ 9'$ and AOA $79^\circ 34'$ (fig.1.5)⁽³⁴⁾

1.4 (b) ANISOTROPY :

Anisotropy term is used to describe directionality of magnetisation along certain crystallographic direction which is called as a easy direction. It is also known as anisotropy energy which can be applied to change the direction of magnetization from easy direction to hard direction. It plays

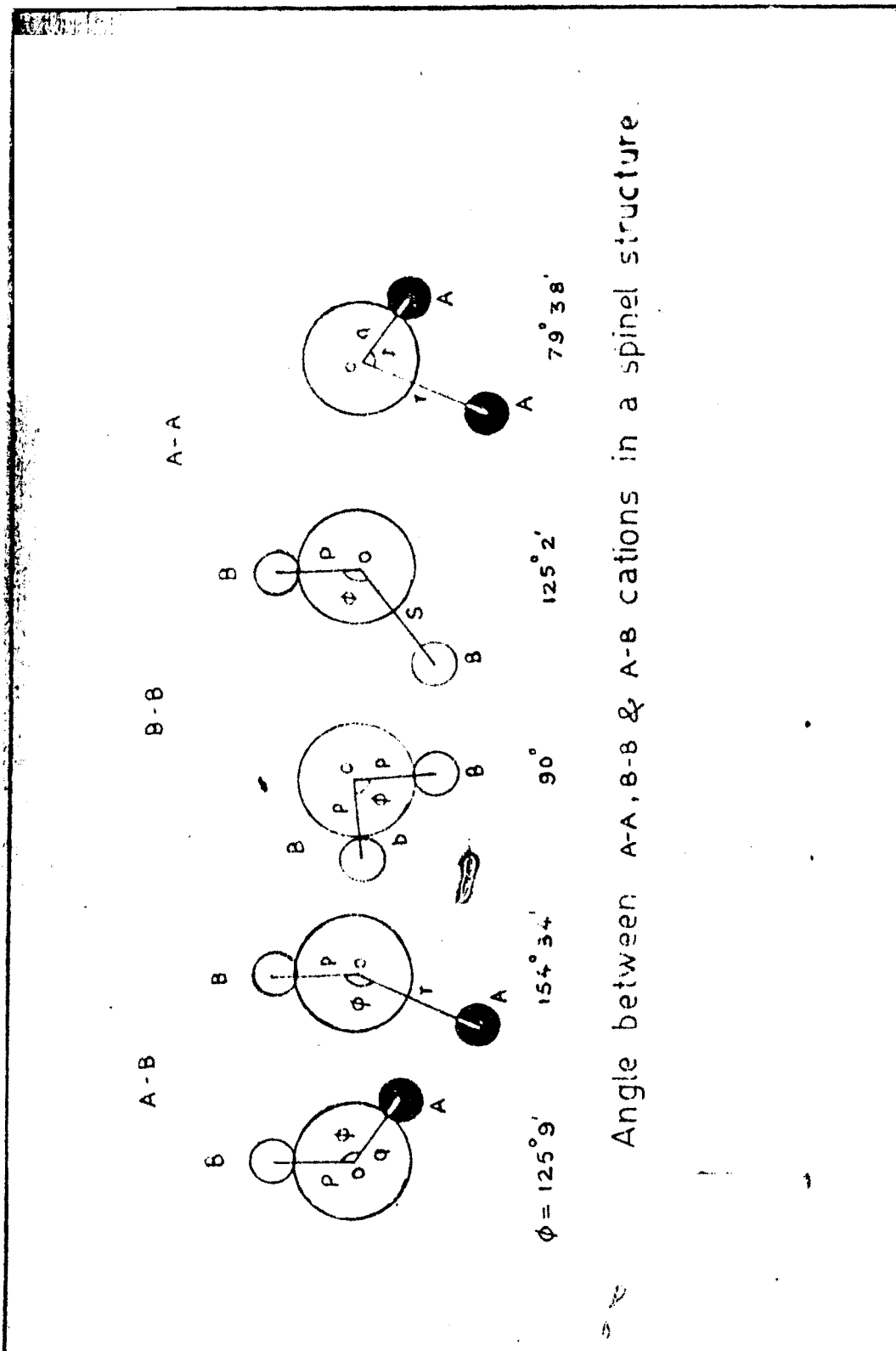


Fig. 1.5

an important role in determining the properties like permeability, hysteresis and magnetostriction.

This energy arises from spin orbit interaction and dependent upon the orientation of magnetisation with respect to crystallographic axis.

In cubic material the energy is described as ...

$$E = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) + \dots$$

Where K_0 , K_1 and K_2 are called as anisotropy constant and $\alpha_1, \alpha_2, \alpha_3$ be the direction cosines.

When magnetization vector deviates from preferred direction the anisotropy energy increases. This increase in energy is due to the effective field (H_a) acting on spins.

The anisotropy constant varies with crystal structure and kind of magnetic ion involved.

The electronic structure of magnetic ion also contributes to anisotropy constant.⁽¹⁷⁾ Magnetic anisotropy may also arise due to stress anisotropy and shape anisotropy. Stress anisotropy may be reduced by slow cooling of specimen. This can be effectively reduced by incorporation of Fe^{+2} in small amount in the crystal such as it reduces the magnetostriction to

zero. Shape anisotropy may be reduced by preparing ferrites in such a way as voids are spherical and few in number with the help of prolonged sintering.⁽¹⁸⁾

1.5 NEEL'S THEORY FOR FERRIMAGNETISM

Neel has considered the two sublattice model for ferrites to describe the ferromagnetic properties. Then the molecular fields for ferrite magnetic material is given by

$$\begin{aligned} H_A &= H_{AA} + H_{AB} \\ H_B &= H_{BB} + H_{BA} \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \\) \end{array} \right\} (14)$$

H_A is molecular field acting on ion of A site is sum of molecular fields H_{AA} from neighbouring A atoms and H_{AB} from B atoms.

Molecular field components may be written

$$\begin{aligned} H_{AA} &= \gamma_{AA} M_A, & H_{AB} &= \gamma_{AB} M_B \\ H_{BB} &= \gamma_{BB} M_B, & H_{BA} &= \gamma_{BA} M_A \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \\) \end{array} \right\} \text{--- (15)}$$

γ s are the appropriate molecular field coefficient and M_A and M_B are magnetic moments of A and B Sublattices.

Then $\gamma_{AB} = \gamma_{BA}$ where $\gamma_{AA} \neq \gamma_{BB}$ unless two sublattice are identical (and exchange integral -ve for

parallel alignment) $\gamma_{AB} < 0$ favouring antiparalel alignments of M_A and M_B gives rise to ferrimagnetism. In the presence of applied field H_0 the total magnetic field acting on each sublattice may be written by using above equations.

$$\begin{aligned}
 H_a &= H_0 + H_A \\
 &= H_0 + \gamma_{AA} M_A + \gamma_{AB} M_B \\
 H_b &= H_0 + H_B \\
 &= H_0 + \gamma_{BB} M_B + \gamma_{BA} M_A
 \end{aligned}
 \left. \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} \begin{array}{l} 0 \\ 0 \\ \\ \\ \\ \\ \\ \\ \end{array} \quad (1.6)$$

a) PARAMAGNETIC REGION :

In an assembly of N paramagnetic ions per unit volume each with angular momentum quantum number J and total magnetisation M then volume susceptibility can be defined as

$$X = \frac{M}{H} \dots\dots\dots (1.7)$$

If the magnetic field H from equation (1.7) taken to be (H+Hm), then we have...

$$\frac{M}{H + H_m} = \frac{M}{H + \gamma_m} \dots\dots\dots (1.8)$$

and this leads curie weiss low.

$$X = \frac{C}{T - T_c} \dots\dots\dots (1.9)$$

Where $T_c = \vartheta_c$ this gives experimental determination for molecular field coefficient Neel applied this to Ferrites and λ and μ are defined as fraction of same magnetic ion distributed in two sublattice where

$$\lambda + \mu = 1 \quad \dots\dots\dots (1.10)$$

Then we can write using equation (1.9).

$$M_A = \left(\frac{\lambda c}{T} \right) H_a \quad \text{and} \quad M_B = \left(\frac{\mu c}{T} \right) H_b \quad \dots\dots (1.11)$$

Where λc and μc are volume occupied by magnetic ions in each sublattice writing $X = \frac{M}{H}$ and $M = M_A + M_B$ the equation for paramagnetic susceptibility becomes...

$$\frac{1}{X} = \frac{T^2 - C \vartheta_{AB} (\lambda + \mu) T + C^2 \lambda \mu \vartheta_{AB}^2 (\alpha \beta - 1)}{C (T - \lambda \mu c \vartheta_{AB} (2 + \alpha + \beta))} \quad \dots\dots (1.12)$$

$$\text{Where } \alpha = \frac{\vartheta_{AA}}{\vartheta_{AB}} \quad \text{and} \quad \beta = \frac{\vartheta_{BB}}{\vartheta_{AB}}$$

following Neel for clear explanation we rewrite (1.12) as

$$\frac{1}{X} = \frac{T}{C} + \frac{1}{X_0} + \frac{\Theta}{T - \Theta} \quad \dots\dots\dots (1.13)$$

$$\text{Where } \frac{1}{X_0} = \vartheta_{AB} (2 \lambda \mu - \lambda^2 \alpha - \mu^2 \beta)$$

$$\Theta = \vartheta_{AB} \lambda \mu c (2 + \alpha + \beta)$$

$$\Theta_2 = \vartheta_{AB}^2 \lambda \mu c (\lambda (1 + \alpha) - \mu (1 + \beta))^2$$

The first two terms of equation (1.13) gives the temperature

dependence of susceptibility of Curie-Weiss law and third term has no contribution in ferromagnetic case. Equation (1.13) represents a hyperbola which cuts the axis.

$$T_A = - \frac{C}{\chi_0} \quad \text{where } T_A \text{ is asymptotic Curie point}$$

This is considered above Curie temperature. Above Curie point ferrimagnetic interactions play a little part.

T_p the paramagnetic Curie point is found by equating $\frac{1}{\chi}$ to zero and gives T_p as

$$T_p = \frac{\vartheta_{AB}^C}{2} \left(\lambda\alpha + \mu_B + \sqrt{(\lambda\alpha - \mu_B)^2 + 4\lambda\mu} \right) \quad \dots (1.14)$$

If $T_p < 0$ i.e. negative the material remains with paramagnetic values of susceptibility down to absolute zero of temperature. If $T_p > 0$, χ becomes theoretically infinite at this temperature below which a spontaneous magnetisation of the material appears and remains finite as the applied magnetic field is reduced to zero.

b) SPONTANEOUS MAGNETISATION :

Equation (1.14) can be written as

$$T_p = \frac{1}{2} \vartheta_{AB}^C \left[\lambda\alpha + \mu_B + \left[(\lambda\alpha - \mu_B)^2 + 4\lambda\mu \right]^{1/2} \right] \dots (1.15)$$

$$T_p' = \frac{1}{2} \vartheta_{AB}^C \left[\lambda\alpha + \mu_B - \left[(\lambda\alpha - \mu_B)^2 + 4\lambda\mu \right]^{1/2} \right] \dots (1.16)$$

assuming positive square root is taken at each time. T_p is

curie temperature where MA and MB antiparallel and T_p' curie temperature when MA and MB parallel.

If $T_p' > T_p$ the antiparallel arrangement of magnetisation will occur and be stable at all temperatures below T_p . This is in agreement with negative interaction of A and B sublattices.

The individual magnetisations MA and MB cannot be observed independently but net magnetization M can be written as $M = M_A + M_B$.

As the two magnetisations are oppositely directed then $M = M_A - M_B$ or $M_B - M_A$ spontaneous magnetisation can be written assuming the similar behaviour below and above curie point.

$$M_{ASP} = \lambda N g_J \mu_B B_J \left(\frac{0.9 J M_B H_A}{KT} \right) \dots (1.17)$$

OR

$$\frac{M_{ASP}}{M_{ASat}} = B_J \left(\frac{\mu_0 g J \mu_B H_A}{KT} \right) \dots (1.18)$$

the terms have their usual meaning.

In general $J \approx S$ spin quantum number since orbital contribution is small.

Total observed spontaneous magnetisation is given by....

$$M_{SP} = M_{BSP} - M_{ASP} \dots\dots (1.19)$$

The solutions of M_{SP} with variation of temperatures can not be found analytically, for solving these graphical methods are used and known as (σ, T) curves where

$$\sigma = \frac{M_{SP}}{M_{Sat}} \quad \text{and} \quad T = \frac{T}{T_p} \dots\dots(1.20)$$

and shown in fig (1.6).

(σ, T) curves must depend on relative values of interaction and relative magnitudes of sublattice magnetisations must depend on λ, μ and β in simple Neel Model where only one type of magnetic ion is present.

1.6 YAFET - KITTLE THEORY :

Neels model was inadequate for the spinels containing chief constituents other than Fe, where the observed magnetisation is much smaller than calculated by Neel's model for spin arrangement. The type M₂R and V also conflict the third law of thermodynamics. Therefore Yafet and Kittle⁽¹⁹⁾ have proposed a triangular type of spin arrangement.

The interaction energy E between two atoms having spins S_i and S_j given by Heisenburg as

$$E = 2J_e S_i S_j \dots\dots (1.21)$$

Where J_e is exchange integral measure of extent to which electronic charge of the two atoms concerned overlap



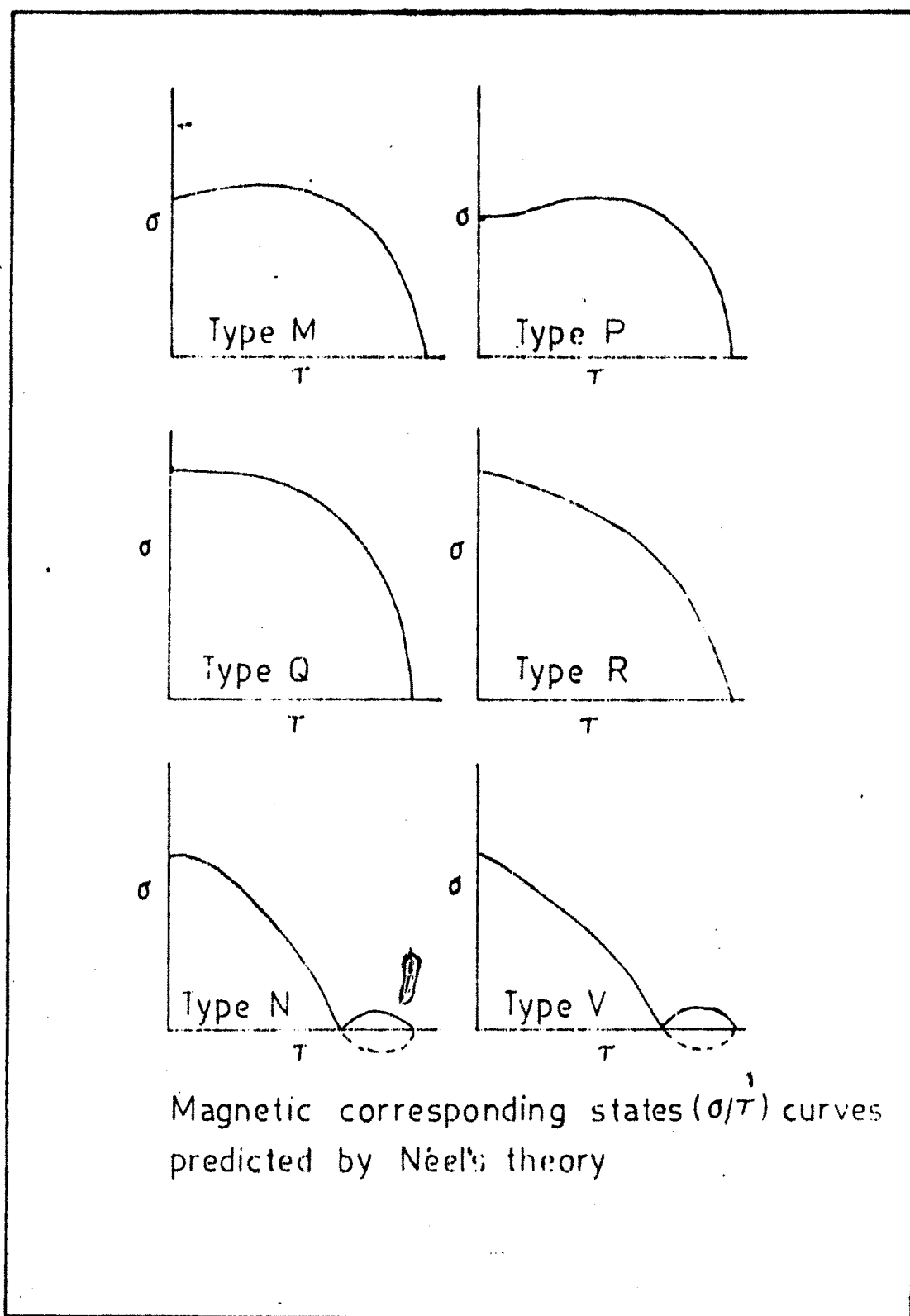


Fig. 1-6

another.

They showed that for certain ratios of exchange interaction in spinels there can exist three sublattices with triangular spin configuration and has lower energy than two sublattice structure. In such a case there exists a possibility of negative interaction within the sublattice itself giving rise to B_1 , B_2 sublattices which are neither exactly antiparallel to each other nor to A sublattice individual. However, their resultant magnetization of B_1 and B_2 remain antiparallel with that of A sublattice, holding in store all the possibilities of ferrimagnetism and antiferrimagnetism.

The interaction energy E for this case has been given as

$$E = 8N (6 J_{ab} S_a S_b \cos \theta - J_{bb} S_b^2 (2 \cos \theta - 1)) \dots (1.21)$$

θ is angle between magnetisation of two sublattices. E is minimum for J_{ab} negative and J_{bb} positive if $\theta = 0$ is Neel's state. If J_{bb} is also negative and ratio of exchange energies is given by γ_{ex} as

$$\gamma_{ex} = J_{bb} S_b / J_{ab} S_a > 3/4 \dots (1.22)$$

Then Neel's state will not become minimum and magnetisation vector of sublattice will bend from colinear position by an angle θ

Where $\cos \theta = 3 J_{ab} S_a / 4 J_{bb} S_b \dots (1.23)$

They proved that Neel's structure is stable for $\gamma_{ex} < 3/4$ if the total number of sublattices are restricted to six (i.e. number of different magnetic ion).

1.7 SPIRAL ~~STRUCTURE~~ ^{Structure} :

Kapalan⁽²⁰⁾ studied and showed that γ -K model does not minimise the exchange energy if $J_{ab} > 0$ and he proposed spiral type of spin configuration by neutron diffraction in some compounds. He found that they have lower energy for all values of $\gamma_{ex} > 2/3$. The theory of spiral configuration was further developed by Lotgering.⁽²¹⁾ This theory he applied to his own experimental results on oxides and sulphides.

1.8 ELECTRICAL PROPERTIES OF FERRITES :

Ferrites are semiconductor by nature. Their resistance can vary from $10^{-3} \Omega\text{-cm}$ to $10^{11} \Omega\text{-cm}$ at room temperature.⁽²²⁾ The physical and chemical properties of ferrites are dependant on the mechanism of charge transport. The mechanism of charge transport can be studied or derived from the measurement of electrical conductivity, thermoelectric power, magneto resistance and Hall Coefficient. The charge transport can vary with the composition of ferrites and method of preparation of ferrites and also greatly affected by the presence of impurities.

1.8 (a) CONDUCTIVITY :

Ferrites are semiconductors and their resistivity should decrease with increase in temperature according to relation.

$$\rho = \rho_0 \exp (E_g/KT) \dots (1.24)$$

E_g is the energy required to cause an electron jump, Linear relationship of $\log \rho$ vs $1/T$ resulting a straight line and break occurs at a temperature which corresponds closely with the observed ferrimagnetic curie temperature.⁽²³⁾ The value of E_g results between 0.1 eV to 0.5 eV. The high E_g is associated with high resistivity at room temperature.⁽²⁴⁾ In general the substitution of a cation that tends to stay in lower valence state leads to P-type conduction and substitution of cation that tends to stay in higher valence state leads to n-type conduction. Electronic conduction of ferrites can be associated with the presence of ions of given element in more than the valence states distributed randomly over crystallographically equivalent lattice points. In ferrite the conductivity is attributed to the occurrence of both Fe^{+2} Fe^{+3} ions upon identical lattice sites in spinel structure. If this is the situation the electron can move from trivalent iron to divalent iron ion within octahedral positions without causing the change in the energy state of a crystal as a result of transition. The classic example is $Fe^{+2} Fe_2^{+3} O_4$ one of the non metallic conductors.⁽²⁵⁾ The presence of Fe^{+2} ion will be considered to assure reduced resistivity in ferrite system. To

achieve high resistivity it is common practice to avoid an excess of Fe_2O_3 and oxidising atmosphere during sintering.

The resistivity will also be caused by following factors apart from the inherent properties of the material 1) porosity and porosity is filled by air (2) The grain size of individual crystallite influence the conduction path due to number of grain to grain contact. ⁽²⁶⁾ (3) chemical in homogeneity caused during preparation or heat-treatment.

General methods for determination of resistivity is two probe contact method or four probe contact method. The four probe contact method is always free from contact resistance difficulties, and is always used to measure low resistivity materials.

1.8 (b) DIELECTRIC PROPERTIES :

Ferrite is also an insulator, ~~but~~ even though in a ferrite eddy current may flow due to dielectric displacement. In ferrites three principle mechanism of polarisation can be distinguished with in a frequency range extending from zero frequency to U.V. frequency region. At optical frequencies the polarisation mechanism is electronic. Total electronic polarisation is sum of polarisation of individual electrons plus effect of interactions. At higher optical frequency and at U.V. frequency, absorption due to actual electron transitions become important. The absorption caused by conduction electrons migrating between iron ions on the octahedral sites by transition from 3d to 4S States, and by

transitions involving the oxygen anions and various cations. At frequencies below infrared the mechanism is atomic or ionic polarisation, and arises from the movement of cations, anions with in the crystal lattice. The part of the permitivity at microwave frequency is due to this mechanism. Below the microwave frequency region the polarisation arises from the macrostructure of polycrystalline material and from the migration of free charge carriers. These charge carriers are trapped at the grain boundries. Field distortion results due to build up of space charge and shows an increase in permitivity. This phenomenon is known as interfacial polarisation. The ferrites have permitivity between 10 to 20. Abnormally high dielectric constant have been reported by several authors as result of low frequency measurement on ferrites.⁽²⁷⁾

Koops⁽²⁸⁾ described the good phenomenological theory of dielectric dispersion in ferrites at low frequencies. The dielectric dispersion theory is based on the assumption of parallel resistance and capacitance of material results from an equivalent to solid state model consisting of compact of relatively good conducting grains separated by poor conducting layers. The theoretical and observed frequency variation dielectric constant and resistivity are in good agreement for some samples.

1.9 ORIENTATION OF PROBLEM :

After 1950 ferrites are used considerable interest because of their electrical electronic microwave and computer applications. Being technologically important materials they have been extensively studied from the point of view of determination of their electric and magnetic properties to check the suitability of certain applications. They were also subjected to rigorous investigations using the techniques like X-rays diffraction, neutron diffraction Mössbauer techniques, etc, in order to understand the Physico-chemical State and structure, property relationship. The results obtained are most controversial in quite few cases.

The controversies may be due to structural aspects ^{dependent} on preparation conditions or partly due to lack of understanding. However this circumstance although trouble some in itself endows with the possibilities of tailor making of ferrites with desirable properties to understand the role of various parameters of conditions of preparation in determining and affecting the structural aspects including cation distribution. Copper ferrite appeared to be interesting from the above point of view because it shows electrical switching lattice distortion, structural changes with composition and temperature of preparation including quenching. Recently most of studies on Cu mixed ferrites have under taken.

The compositional variation of Ni, Zn, Mn, Cd with Cu ferrite have been carried out. By many workers, ^(30 to 33) ~~(20 to 33)~~ They tried to

establish the conduction mechanism and structural relationship with composition.

In order to unravel the role of composition in affecting the crystal structure, cation distribution and conduction mechanism and also the behaviour of quenching temperature on the magnetisation and electrical resistivity of the ferrites, we have undertaken the following studies on $Cu_x \cdot Co_{1-x} Fe_2O_4$ system.

1) Preparation of $Cu_x Co_{1-x} Fe_2O_4$ where ($x=0.2, 0.4, 0.6, 0.8$) by ceramic method at an appropriate temperature due care being taken for non reduction of copper ions.

X-ray diffraction studies ^{on} ferrite samples for finding the Bravais lattice and lattice parameter with view to find out variation of C/a ratio with composition.

2) Electrical resistivity and Curie temperature measurement studies for finding out the conduction mechanism involved in ferrites and behaviour of resistivity with composition of Co.

3) Magnetisation studies on these ferrites for finding out the cation distribution and magnetic moment behavior with the composition. With view to find out the role of Co ion in changing the magnetisation with composition and quenching temperature.

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