CHAPTER ONE: INTRODUCTION

INTRODUCTION

1.1 Historical

"Ferrites" as they are known as an artificial version of load stone (Fe_3O_4) also called Ferrous Ferrite, the first magnetic material known to man. Ferrites assume importance as magnetic materials possessing a wide range of magnetisation and due to the fact that together with their property of electrical insulation, the propagation of high field electromagnetic waves through them takes place with low attenuation.

Hilpert in 1909 tried to develop the ferrites to reduce eddy current losses in inductors and transformers but without success, as the ferrites exhibited large losses, low permeability and could not be reproduced reliably. Later Kato and Takai[1], Froesteir,[2] Barth and Posjnak[3] developed ferrites in various points of view. Snock[4] and his colleagues carried out intensive work on ferrites to study their magnetic properties. Neel[5] proposed theory of Ferrimagnetism. The experimental confirmation was offered by neutron diffraction studies on magnetic[6] and zinc ferrite.[7] Successes were achieved by the workers in processing substitutional ferrites to suit the requirements of permeability values for the high frequency applications in the field of communication.

The work was further carried out as the ferrites exhibit a wide range of magnetisation, property of electrical insulation[4] low attenuation that led to the propogation of high field electromagnetic waves through them.

At present manufacture and improvement of ferrites are possible because of their ever-growing demand in the fields of microwave components and memory switching circuits in computers.

1.2 Crystal Structure

The mineral $MgAl_2O_4$ and naturally occurring magnetic Fe_3O_4 have spinel structure. The general formula of ferrite is MFe_2O_4, where M represents a divalent metal ion (M^{2+}) and iron is a trivalent ion (Fe^{3+}). Ferrites exhibited spinel structure. Compounds of this type possess cubic or face centered structure. The oxygen ions form a face centered cubic lattice. The smallest unit cell contains eight molecules of MFe_2O_4. Hence the formula of unit cell is $M_8^{2+}Fe_{16}^{3+}O_{32}^{2-}$. The cations occupy interstitial positions of which there are two distinctly different types, "tetrahedral or A-site and octahedral or B site. In tetrahedral or A-site magnetic ion is surrounded by four oxygen ions located at the corners of a tetrahedron as shown in Fig. 1.1. When the magnetic ion is surrounded by six oxygen ions placed at the vertices of octahedron as shown in Fig. 1.1 it is called as octahedral or B site. The unit cell contains 96 interstitial sites. Sixtyfour sites are tetrahedral and 32 sites are octahedral. The cations occupy 8 tetrahedral and 16 octahedral sites.

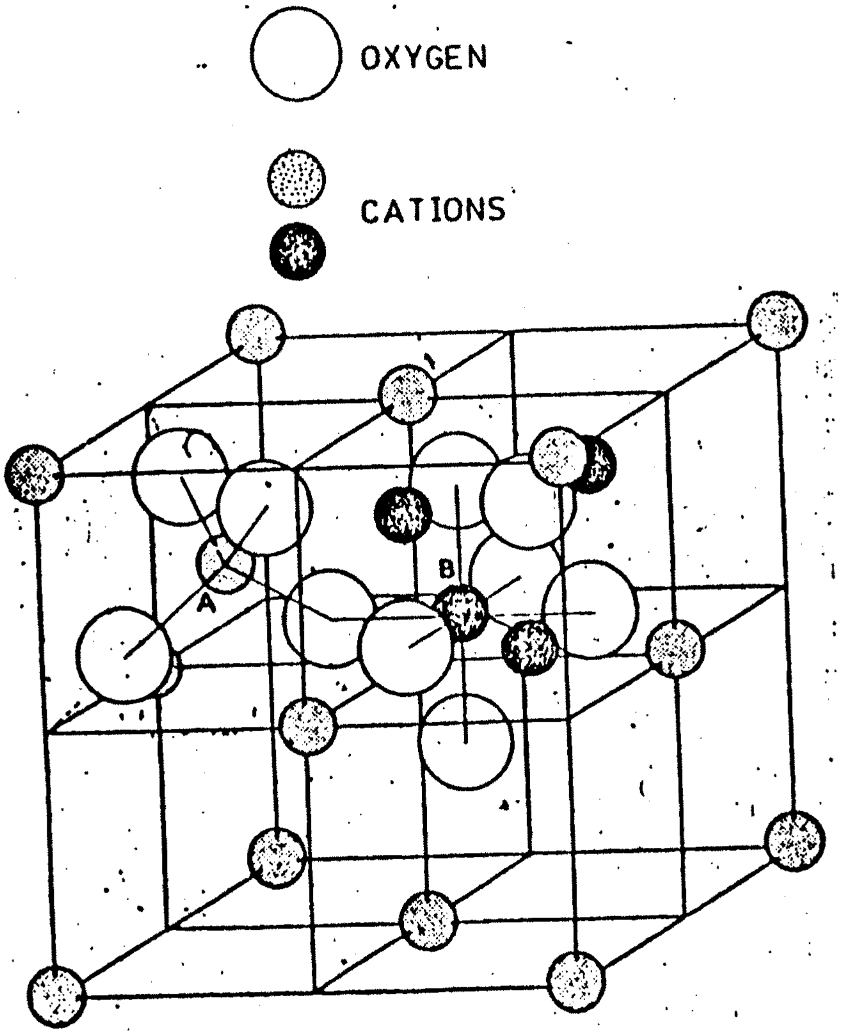


Fig. 1.1 The spinel structure.

1.2 Classification of Ferrites

1.2.1 Normal Ferrites

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

$ZnFe_2O_4$ and $CdFe_2O_4$ are the Ferrites with normal spinel structure. The cation distribution of $ZnFe_2O_4$ is

$$[\ Zn^{2+}\ ]^{A}\ [\ Fe^{+3}\ Fe^{+3}\ ]^{B}\ O_4^{-2}$$

The normal ferrites are not Ferrimagnetic.

1.2.2 Inverse Spinel Ferrites

In the inverse spinel ferrites, the eight divalent metal ions lie on B site. The trivalent iron ions (Fe^{+3}) lie in equal numbers on A and B site. The cation distribution is represented as $[\ Fe^{3+}]^{A}\ (M^{+2}\ Fe^{+3})^{B}\ O_4^{2-}$ $MgFe_2O_4$ and $CuFe_2O_4$ are inverse spinel Ferrites which are ferrimagnetic in nature.

1.2.3 Random Spinel Ferrites

Here M^{2+} and Fe^{3+} ions are randomly distributed over the A and B sites depending on the physico chemical conditions of preparations. The general formula for partially inverted ferrites is usually written as

$$[\ M_xFe_{1-x}\ ]^{A}\ (M_{1-x}\ Fe_{1+x}\ )^{B}O_4$$

$MnFe_2O_4$ and $CuFe_2O_4$ are partially inverted Ferrites.

In Ferrites every oxygen ion is surrounded by three B-cations and one A-cation. The angles[8] are given as $A\text{-}O\text{-}B = 125^\circ\ 9'$ $A\text{-}O\text{-}A = 79^\circ\ 58'$ $B\text{-}O\text{-}B = 90^\circ$. If metal oxygen distances are small and M-O-M angles are 180° the interactions are strong. So A-B interaction is the strongest. While B-B interaction is weak and A-A interaction is the weakest of the three.

1.3 Substitutional Ferrites

If the divalent metal ions are substituted by an alternative magnetic or nonmagnetic cations, the ferrites are called as substitutional ferrites. The substitution can be done in two ways:

1) Replacing divalent M ion by other divalent M ion.
2) Replacing the trivalent iron ions by other trivalent M'' ions.

In magnesium ferrite $MgFe_2O_4$ magnesium may be substituted partly or completely by zinc. $Zn_xMg_{1-x}Fe_2O_4$ some times the part of iron may be substituted by one of trivalent nonmagnetic elements Al, Cu.

$NiFe_{2-x}Al_xO_4$ - Nickel Aluminium Ferrite.

1.4 Magnetic Properties of Ferrites

1.4.1 Magnetisation in Ferrites

Ferrites are magnetic because of distribution and alignment of magnetic ions on the octahedral and tetrahedral cation sites. The cations sitting on the same sub-lattice are so oriented that their magnetic moments are in the same direction. For two sub-lattices the moment of cations on one sublattice are aligned antiparallel to the moments of cations on the other sub-lattice. The net magnetisation of the crystal is the resultant of the magnetizations on the two sub-lattices.

1.4.2 Structural Explanation of Ferrimagnetism

Magnetic ferrites possessing inverse spinel structure have cation distribution which is given by

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

where the cations shown in the square bracket are on the A site and in the other bracket are on B site.[9] The unit cell of ferrite contains eight molecules. Accordingly on the A sub-lattice the moments of 8 Fe^{3+} cations are located while on the B sub-lattice the magnetic moments of 8 $(Fe^{3+} + M^{2+})$ cations are present per unit cell. The resultant magnetization is given by

$$\begin{aligned} M &= M_B - M_A \\ &= 8\ (m_M + m_{Fe}) - 8m_{Fe} \\ &= 8m_M \end{aligned}$$

where M_A and M_B are the moments of the sub-lattices and m_M and m_{Fe} are the spin magnetic moments of the individual ions. The parallel alignment of moments on each sub-lattice is a consequence of super

[illegible]

exchange interaction between the magnetic ions on one sublattice and those on the other. The parallel alignment of moments on each sublattice which is a characteristic of ferrimagnetism required the sufficient concentration of the magnetic species on one sublattice to maintain parallel alignment on the other sublattice. Ferrites with normal spinel structure are non-ferromagnetic i.e., $ZnFe_2O_4$ and $CdFe_2O_4$. In these ferrites the interaction A-B does not exist because there are no magnetic ions on the A sites, the B-B interaction lines up half the magnetic ions in one direction and other half in the opposit direction so that alternate planes of B sublattice are magnetised in opposite directions rendering these ferrites non-ferromagnetic.

Due to super exchange[10] interaction between two cations via an intermediate oxygen ion if the three ions are colinear and their separations are not too large, the sublattice magnetions are antiparallel.[11] The ions arranged in the spinels are shown[12] in Fig. 1.2. In Fig. 1.2(a) both angle and distance between the ions are favourable for super exchange interaction while for other figures either the angle (1.2c), distance 1.2 b-d or both (1.4e) are unfavourable. This arrangement if ions in the spinel leads to the conclusion that A-B interactions are stronger than A-A or B-B.

The net magnetic moment per formula unit of an inverse ferrite structure cannot exceed 5 Bohr magnetons. However, it has been found that on addition of normal spinel ferrite like $ZnFe_2O_4$, the molecular magnetic moment of an inverse ferrite

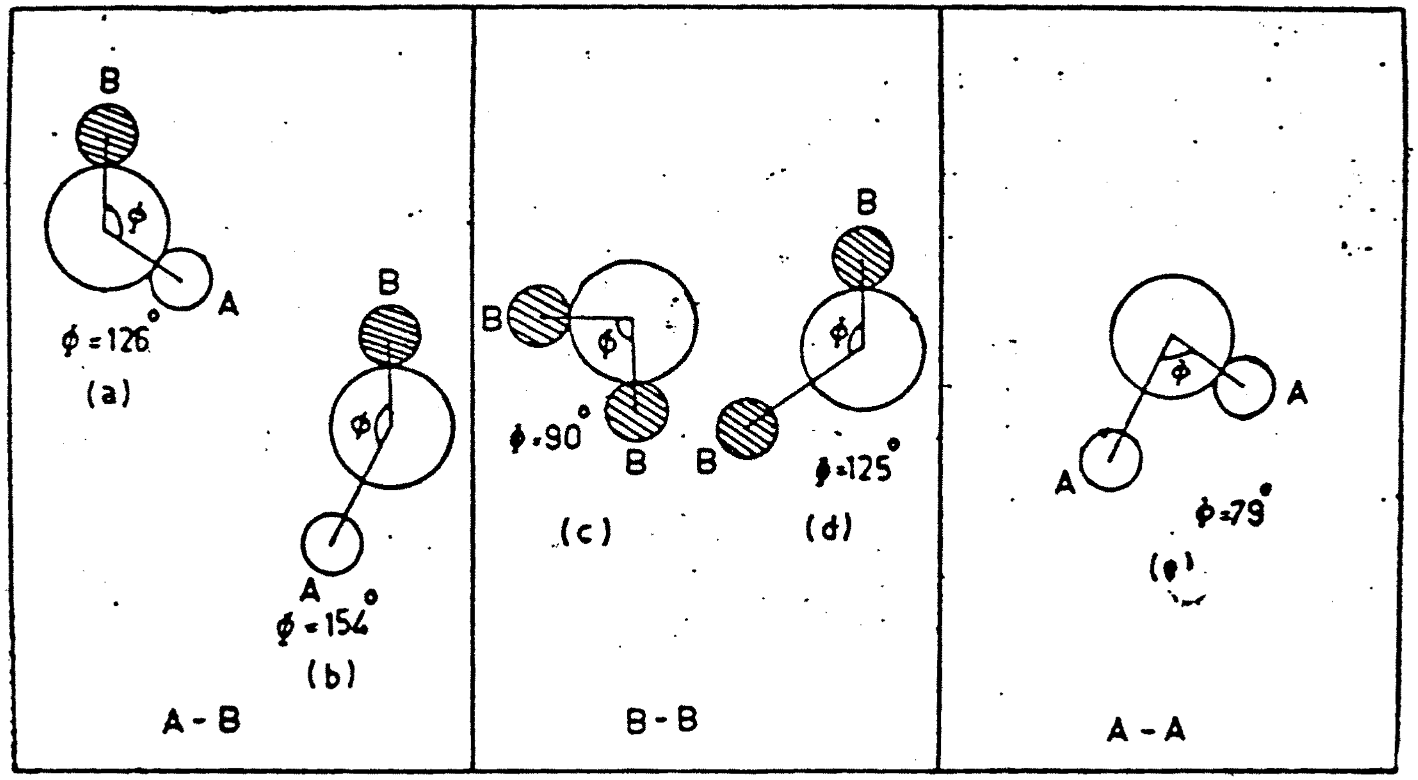


Fig. 1.2

increases. The Zn^{+2} ions, on addition, occupy A sites and an equal number of Fe^{3} ions are transferred to B sites. For the ferrites $M^{2+}Fe_2^{3+}O_4$ can be written as

$$\longrightarrow [Fe^{3+}]^{A}\, O\, (Fe^{3+}M^{2+})^{B}\, O_3$$

where arrow indicates the direction of magnetic moment. On addition of $X(ZnOFe_2O_3)$ and $(1-x)\,[FeO\,(F_eM)\,O_3]$, the cation distribution becomes

$$n = [5(1+x) + m(1-x) - 5(1-x)] \text{ Bohr magnetons}$$
$$= [m + (10-m)X]$$

where m is the moment of M^{2+} ion in Bohr magnetons. Thus, on addition of Zn^{2+} $(m=o)$, the moment should tend to 10.

Gorter[13] experimentally verified that magnetization increases for small concentrations of the added ferrite, but with the increase in the concentration of Zn^{+2} deviation increases.

1.4.3 Neel's Theory of Ferrimagnetism

Using the same approach as that used for Wiss molecular field theory of ferromagnetism Neel formulated the theory of antiferromagnetism. In a non-atomic solid the simple exchange interaction as that of ferromagnetism is not possible because of formation of sublattices due to intervening anions or other kind of atoms due to structural requirements. When in a magnetic material the magnetic ions are chemically identical but are located on two sublattices. The exchange interaction, direct or indirect, is said to be responsible for antiferromagnetic coupling.[13] Neel's theory of antiferromagnetism allows to determine the curie constant and the molecular field constants that describe the antiferromagnetism. When the two magnetic sublattices in a magnetic substance are antiparallel as in an antiferromagnetic substance, but differ in magnitude of their magnetisation leading to non-compensation, the material is called as ferrimagnetic. Ferrites are typical of ferrimagnetics. In a simple ferrimagnetic substance either there may be two sublattices occupied by the magnetic ions with different spin magnetic moments or the same magnetic ions being located on crystallographically different sites, thus forming two sublattices. In actuality both these effects may be present simultaneously as is observed for various ferrites.

According to Neel's[14] theory of Ferromagnetism the magnetisation and the susceptibility can be expressed in terms of the molecular field coefficients that characterise the A-A, BB and AB interactions, where A and B are the ions on A and B sublattices. If λ_{aa}, λ_{bb} and λ_{ab} are molecular field coefficients, the total effective field on a magnetic dipole in each sublattice and due to its neighbours can be written as in the absence of an external magnetic field as

$$H_a = \lambda_{aa} M_a + \lambda_{ab} M_b$$

$$H_b = \lambda_{ab} M_a + \lambda_{bb} M_b$$

The constants may be positive or negative. Magnetisation of each sublattice would obey the curie relation.

$$M_a = \frac{Ca}{T} (H_o + H_a), \quad M_b = \frac{Cb}{T} (H_o + H_b)$$

where C_a and C_b are curie constants. Eliminating H_a and H_b the sublattice magnetisation becomes

$$M_a = \frac{C_a (T - \lambda_{bb} C_b) + C_a C_b \lambda_{ab}}{(T - C_a \lambda_{aa}) \; (T - C_b \lambda_{bb}) - C_a C_b \lambda_{ab}^2} \cdot H_o \qquad 1.3$$

$$M = \frac{C_b \; (T - \lambda_{aa} C_a) + C_a C_b \lambda_{ab}}{(T - C_a \lambda_{aa}) \; (T - C_b \lambda_{bb}) - C_a C_b \lambda_{ab}^2} \quad H_o$$

The increase susceptibility in the paramagnetic region is given by

$$\frac{1}{X} = \frac{H_o}{M_a + M_b} = \frac{T}{C} + \frac{1}{X_o} - \frac{K}{1-0} \qquad 1.4$$

where $C_a = C_b$ and

$$\frac{1}{X_o} = \frac{1}{C^2} \; (\lambda_{aa} C_a^2 + \lambda_{bb} C_b^2 + 2 \lambda_{ab} C_{ab}) \qquad 1.5$$

$$\begin{aligned} K = \frac{-C_a C_b}{C^2} \; [& C_a^2 \; (2\lambda_{ab}\lambda_{aa} - \lambda_{ab}^2 - \lambda_{aa}^2) \\ & + C_b^2 \; (2 \lambda_{ab}\lambda_{bb} - \lambda_{ab}^2 - \lambda_{bb}^2) \\ & + 2C_a C_b (\lambda_{ab}^2 - \lambda_{ab}\lambda_{aa} - \lambda_{ab}\lambda_{bb} + \lambda_{aa}\lambda_{bb})] \end{aligned} \qquad 1.6$$

$$e = \frac{-C_a C_b}{C} \; (2 \lambda_{ab} - \lambda_{aa} - \lambda_{bb}) \qquad 1.7$$

The equation (1.4) represents a hyperbola with asymptote

$$\frac{1}{X_A} = \frac{T}{C} + \frac{1}{X_o} \qquad 1.8$$

The Y intercept of the line is $\frac{1}{X_o}$, given by the equation 1.5 and the line extrapolates to the point, which is called as asymptotic curie point. The hyperbola of equation is shown in Fig. (1.3).

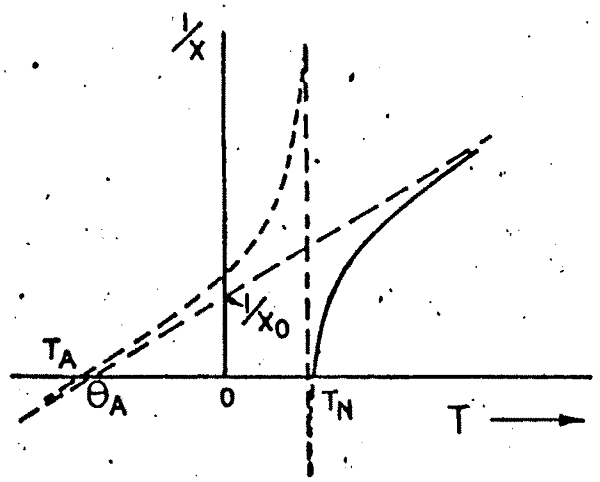
The ferrimagnetic material is paramagnetic at temperature above T_N and is spontaneously magnetised in the region $0 \angle T \angle T_N$. The Neel temperature may be expressed as

$$T_{NA} = \frac{\lambda_{aa}C_a + \lambda_{bb}C_b}{2} + [(\lambda_{aa}C_a - \lambda_{bb}C_b) + 4\lambda_{ab}^2 C_a C_b]^{1/2} \qquad 1.10$$

The susceptibility becomes infinite either at T_N (positive square root) or T_N (negative square root).

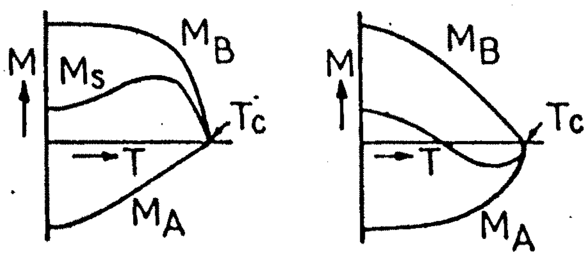
Experimental results of the susceptibility data in the paramagnetic region have been successfully used to find out the interaction parameters which, in turn were applied to compute the magnetisation curve below the Neel temperature. The agreement with the experimental results demonstrated the applicability of the molecular field treatment in explaining the ferrimagnetism.

Employing the statistical treatment developed by Neel the simultaneous equations for M_A and M_B in the form of Brillouin functions which use spin quantum number 'S' for the transition metal instead of total angular momentum quantum number 'J', can be



– A sketch of the inverse susceptibility of a ferrimagnetic substance as a function of absolute temperature.

Fig. 1.3a



(a) (b)

– The anamalous shapes of the spontaneous magnetisation vs. temperature curves for ferrimagnetic substances according neels theory.

Fig. 1.3b

solved for different temperatures.

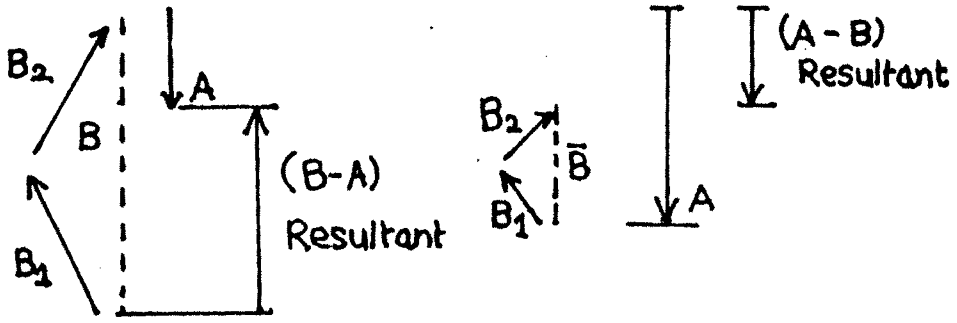
$$\frac{M_A}{M_{SA}} = B_s\left(\frac{gS\mu_B H_A}{KT}\right), \quad \frac{M_B}{M_{SB}} = B_s\left(\frac{gS\mu_B H_B}{KT}\right) \qquad 1.11$$

Thus, the theoretical analysis points out to the possibility of the different shapes for the net magnetisation curves depending on the parameters of the exchange interactions and the relative magnetisation of the individual sublattice (Fig. 1.4). The net magnetisation curves provide useful data about the ferrites from the point of view of their applications. However, in substitutional ferrites,[15] or due to temperature effect, the relative magnitudes of A-B and B-B interactions become comparable leading to Lotgering[16] triangular arrangements. Further, structural complications lead to helical and canted spin configurations determined by the minimisation of energy considerations.[17]

1.4.4 <u>Yafet Kittle Theory</u>

Whtn the major constituent in a ferrite is other than Fe, observed magnetisation[18] is less than that calculated by employing Neel's model. In addition, net magnetisation increases or decreases as absolute zero is reached and $\frac{dM}{dt} \neq 0$ at $T = 0^\circ$ K which is prohibited by the third law of thermodynamics.

Neel's theory of magnetic sublattice was therefore extended by Yafet and Kittle[15] in 1952. They showed that for certain ratio of exchange interactions in spinels there exists a possibility of



(a) (b)

Fig.1.4

negative interaction within sublattice B, giving rise to sublattices B_1 and B_2 with their magnetisation neither exactly antiparallel to each other nor to A sublattice. However, the resultant magnetisation of B_1 and B_2 remains antiparallel with that of sublattice A as shown in Fig. 1.4.

1.5 D.C. Conductivity

The resistivity of ferrites lies in the wide range 10^{-3} to 10^9 ohm-meter at room temperature. For magnetic $(Fe^{2+})^A(Fe_2^{3+})^BO_4^{2-}$ the resistivity is 5×10^{-5} ohm meter approximately. This high conductivity is associated with the simultaneous presence of Fe^{2+} and Fe^{3+} ions upon identical lattice sites in the spinel structure. The electrons move from ferrous (Fe^{2+}) to ferric (Fe^{3+}) ions through the continuous chain of the octahedral positions and those transitions of electrons do not cause any change in the energy state of crystal.

Van Uitert (1959) showed that an excess of iron above stoichiometry and high firing temperature both cause remarkable reduction in the resistivity.

The resistivity also depends upon the following factors apart from the inherent properties of the material.

1) Prosity and pores filled by air,
2) Grain size,
3) Chemical inhomogeneity caused during preparation, heat treatment rate of cooling.

The temperature dependence of resistivity ρ can be expressed by

$$\rho = \rho_0^{\frac{\Delta E}{KT}}$$

The different values of ΔE (the activation energy) determined from the slope of logs versus $\frac{1}{T}$ plot represent different conduction mechanisms. Komar and Klivshin[19] observed breaks in the vicinity of the ferromagnetic curie temperature of several ferrites. Ctaani et al.[20] have observed more than two breaks in the log ρ — 1/T plots for Cu-Ni ferrites; which are attributed to change in activation energy ΔE.

1.6 Applications of Ferrites

Ferrites find numerous applications in electrical electronic, microwave and computer fields. They are used as band pass filters from $50KH_z$ to $150KH_z$ in telephone circuits. In I^f transformers and in slug tuned inductors. Because of their high resistivity they can be used as pole pieces for concentrating flux in h.f. inductor heaters.[21] Ferrite cores are now widely used in the field of memory and switching circuits in digital computers.

1.7 Orientation of the Present Work

Ferrites assume importance since they find applications in electronic and electrical fields. Efforts are being made to prepare the Ferrites to suit their utility for core memories, core of the transformers, core of the antenna and so on. In the applications point of view, the studies on electrical and magnetic properties have been carried out by many workers. The preparation techniques have also been inovated to improve upon the factors like porosity and keep at minimum the factors that degrade these properties. Mixed MgZn Ferrite system has been studied by many workers. However, effect of quenching in modulating the electrical and magnetic properties needs to be carefully studied for the want of sufficient literature on this. We have, therefore, carried out the studies on the quenched system of MgZn mixed ferrites and compared our results with the slow cooled system. For these following studies were undertaken:

1) By using the standard ceramic technique $Zn_xMg_{a-x}Fe_2O_4$ ferrites were prepared, where $x = 0, 0.2, 0.4, 0.6, 0.8, 1$.

2) X-ray diffraction study for determination of crystal structure.

3) Electrical conductivity from room temperature upto 873°K and the plots of $\log \rho \longrightarrow \frac{1}{T}$ similarly we had the plots of $\log \rho \longrightarrow$ compositions at constant temperatures.

4) Determination of Curie temperature.

5) Saturation magnetisation.

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