
CHAPTER - I

INTRODUCTION

1.1 Introduction

Ferrites are magnetic materials having general formula $M Fe_2O_4$. The synthetic ferrites were developed by Hilpert in 1909 to reduce eddy current losses in inductors and transformers but without success. Later, ferrites were developed by Kato and Takai¹, Foresteier², Barth and Posjnak³ from various points of view. Snoek⁴ and his colleagues carried out intensive experimental work on ferrites with particular interest of preparation and their magnetic properties. Neel⁵ proposed theory of ferrimagnetism. The experimental confirmation was provided by neutron diffraction studies on magnetite⁶ and zinc ferrite⁷. The substitutional ferrites were successfully developed to suit the requirements of permeability values for the high frequency applications in the field of communication. The pace of the work was further accelerated due to the fact that the ferrites exhibit a wide range of magnetisation, property of electrical insulation⁴, low attenuation that lead to the propagation of high field electromagnetic waves through them.

The present aim of developing ferrites is for their applications in communication, high and microwave frequencies, computers for memory cores and switching circuits.

1.2 Crystal Structure of Ferrites

The mineral $MgAl_2O_4$ and the naturally occurring magnetite Fe_3O_4 are said to have spinel structure. Ferrites are the magnetic oxides exhibiting the spinel structure and having the general chemical formula MFe_2O_4 where M represents a divalent metal ion (M^{2+}) and iron is a trivalent ion (Fe^{3+}). The compounds of this type have generally a cubic, face centered crystal structure. The oxygen ions form essentially a face centered cubic lattice. The smallest unit cell consists of eight molecules of MFe_2O_4 . Hence the unit cell formula becomes $M_8^{2+}Fe_{16}^{3+}O_{32}^{2-}$. The cations occupy interstitial positions of which there are two distinctly different types, "tetrahedral" or "A site" and "Octahedral" or "B site". When the magnetic ion is surrounded by four oxygen ions, located at the corners of a tetrahedron as shown in fig. 1.1, it is called tetrahedral or A site and when the magnetic ion is surrounded by six oxygen ions placed at the vertices of an octahedron as shown in fig. 1.1 it is known as 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.

The distributions of cations on the A and B sites is dominated by relative site preference energies of the respective metal ions present in the ferrites. The ferrites are classified on the basis of cation distribution as follows.

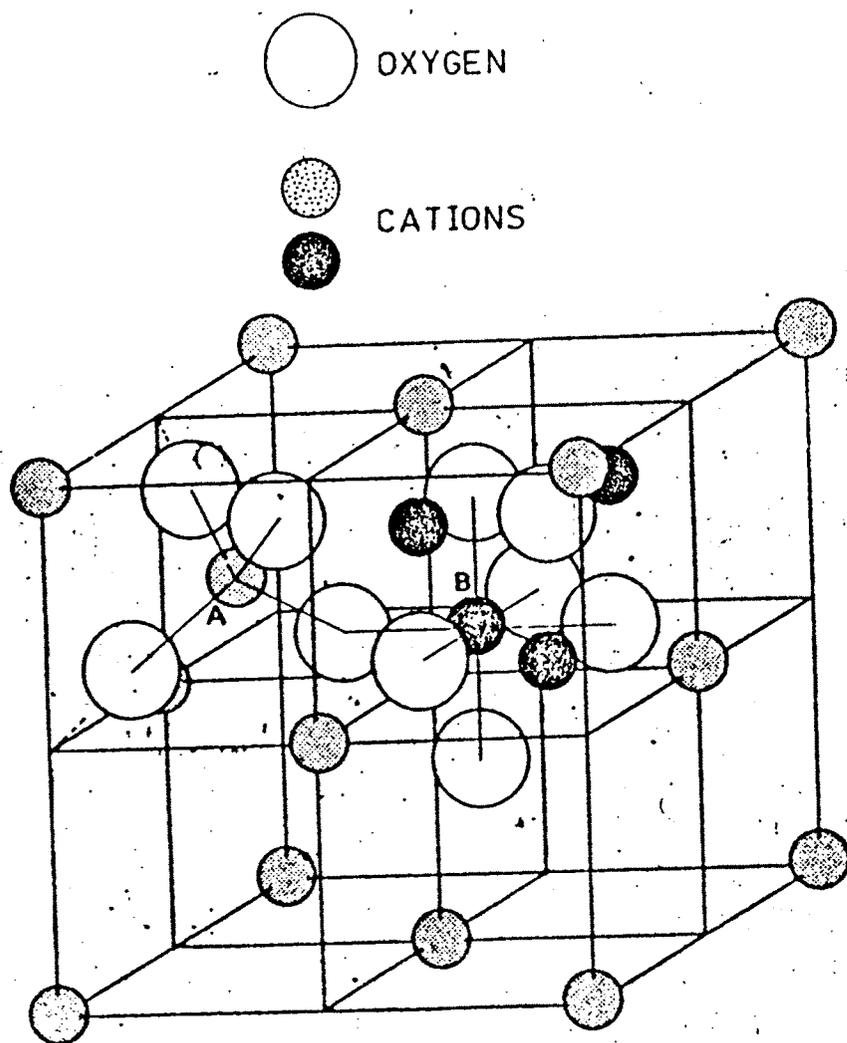
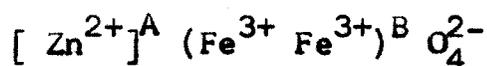


Fig. 1.1 The spinel structure.

1.2.1 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.

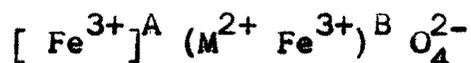
$ZnFe_2O_4$ and $CdFe_2O_4$ are the ferrites with normal spinel structure. The cation distribution of $ZnFe_2O_4$ is as shown below :



The normal spinel ferrites do not show ferrimagnetic behaviour.

1.2.2 Inverse Spinel Ferrites

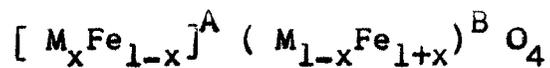
In the inverse spinel ferrites, the eight divalent metal ions lie on B sites. The trivalent iron ions (Fe^{3+}) lie in equal numbers on A and B site. The cation distribution here is represented by



The inverse spinel ferrites show ferri magnetic behaviour. $MgFe_2O_4$ and $CuFe_2O_4$ show inverse spinel structure.

1.2.3 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 physico-chemical conditions of preparations. Intermediate degrees of freedom are also exhibited by ferrite systems. The general formula for partially inverted ferrites is usually written as



$MnFe_2O_4$ and $CuFe_2O_4$ are examples of partially inverted ferrites.

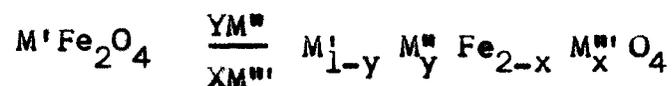
In ferrites every oxygen ion is surrounded by three B-cations and one A-cation. The angles⁸ are given as A-O-B = $125^{\circ}9'$, A-O-A = $79^{\circ}58'$, B-O-B = 90° .

The interaction is expected to be strong for smaller metal-oxygen distances and for M-O-M angle, are nearly 180° ⁹ which leads us to conclude that, A-B interaction is strongest, while B-B interaction is weak and A-A interaction is weakest of the three. In case of ferro-spinels interactions are all negative.

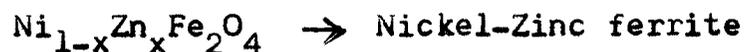
1.3 Substitutional Ferrites

All the divalent metal ions or few of them can be substituted by an alternative cation of magnetic or non-magnetic nature⁹. The resulting ferrites are called substitutional ferrites. The substitution can be done by two ways :

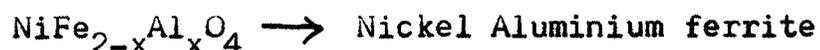
- 1) Replacing divalent M' ion by other divalent M'' ion.
- 2) Replacing the trivalent iron ions by other trivalent M''' ions



For example in nickel ferrite, $NiFe_2O_4$, nickel may be substituted partly or completely by zinc



or a part of iron may be substituted by one of trivalent non-magnetic, Al, Cr or Ga elements



The resulting substitutional ferrites are equivalent to a solid solution of the two pure and end member ferrites.

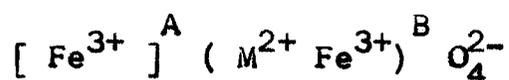
1.4 Magnetic Properties of Ferrites

1.4.1 Magnetization in Ferrites

The ferrites are ferrimagnetic oxides. The magnetization in ferrites results from the distribution and alignment of magnetic ions on the octahedral and the 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 magnetization 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 given by



where the cations shown in the square bracket are on the A site

and in the other bracket are on the B site⁹. The unit cell of ferrite contains eight molecules. Accordingly, on the A sub-lattice the moments of 8 Fe³⁺ cations are located while on the B sub-lattice the magnetic moments of 8 (Fe³⁺ + M²⁺) cations are present per unit cell. The resultant magnetization is given by

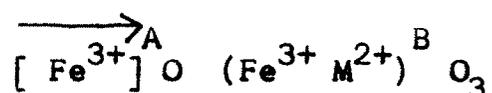
$$\begin{aligned} M &= M_B - M_A \\ &= 8 (m_M + m_{Fe}) - 8 m_{Fe} \\ &= 8 m_M \end{aligned}$$

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 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 requires 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, e.g. ZnFe₂O₄ and CdFe₂O₄. In these ferrites the A-B interaction 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 opposite direction so that alternate planes of B sub-lattice are magnetised in opposite directions rendering these ferrites non-ferromagnetic.

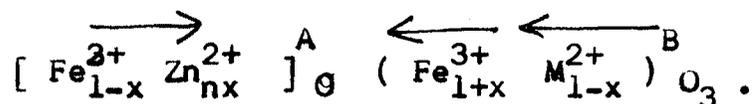
Due to super exchange¹⁰ interaction between two cations via an intermediate oxygen ion, if the three ions are collinear and their separations are not too large, the sublattice magnetisations are antiparallel¹¹.

The ions arranged in the spinels are shown¹² 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 of 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 increases. The Zn^{2+} ions, on addition, occupy A sites and an equal number of Fe^{3+} ions are transferred to B sites⁸. For the ferrite $M^{2+} Fe_2^{3+} O_4$ can be written as



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



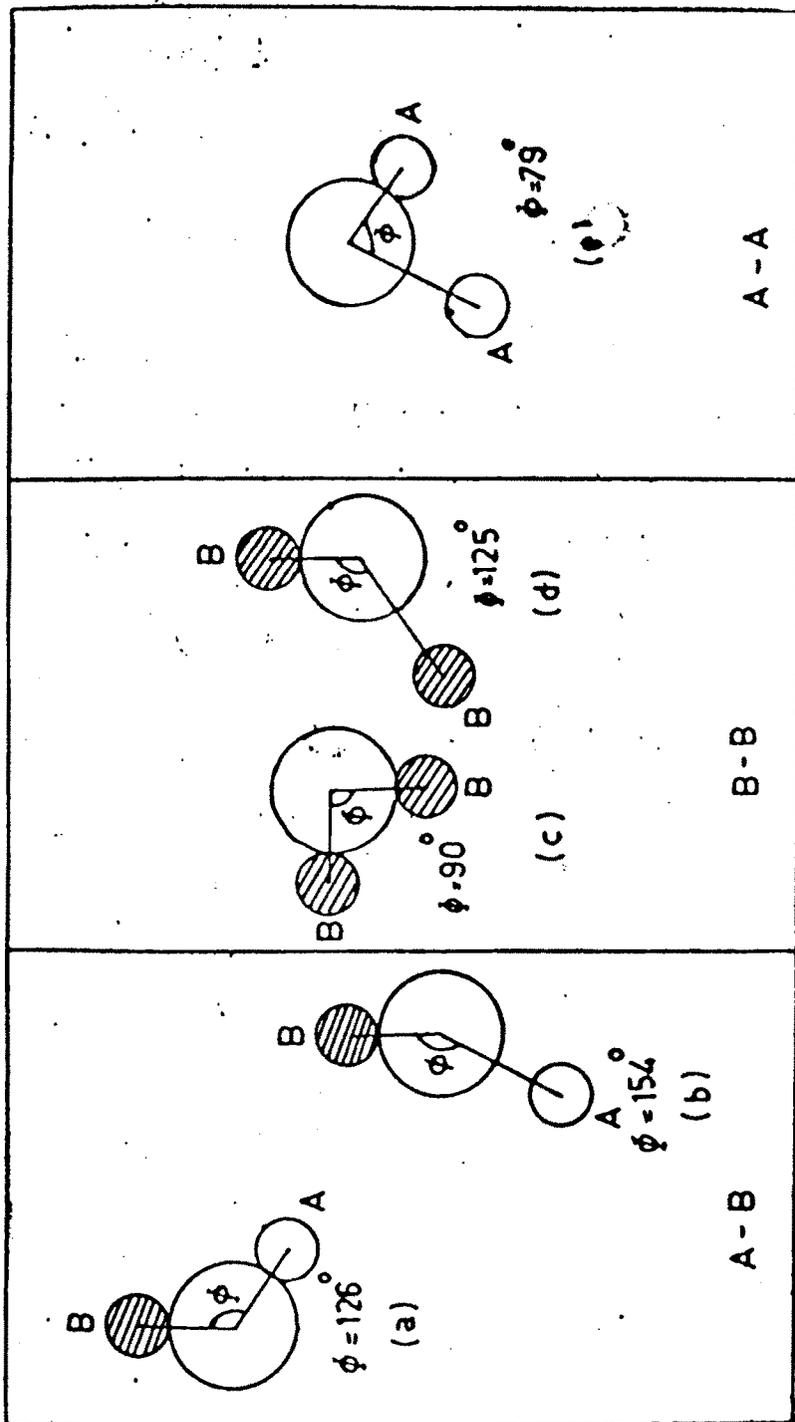


Fig. 1.2

Hence, the resultant magnetic moment becomes

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

where m is the moment of M^{2+} ion in Bohr magnetons. Thus, on addition of Zn^{2+} ($m=0$), the moment should tend to 10.

Gorter has 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

Neel formulated the theory of antiferromagnetism using the same approach as that used for Weiss molecular field theory of ferromagnetism. In a non-atomic solid the simple exchange interaction as that of ferromagnetism is not possible because of the 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 sub-lattices the exchange interaction, direct or indirect, is said to be responsible for antiferromagnetic coupling¹³. 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 magnetizations leading to non-compensation, the material is

called ferrimagnetic. Ferrites are typical of ferrimagnetics. In a simple ferrimagnetic substances 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's¹⁴ theory of ferromagnetism, the magnetisation and the susceptibility can be expressed in terms of the molecular field coefficients that characterise the AA, 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 in the absence of an external magnetic field as

$$\begin{aligned} H_a &= \lambda_{aa} M_a + \lambda_{ab} M_b \\ H_b &= \lambda_{ab} M_a + \lambda_{bb} M_b \end{aligned} \quad \dots \quad (1.1)$$

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

$$M_a = \frac{C_a}{T} (H_0 + H_a), \quad M_b = \frac{C_b}{T} (H_0 + H_b) \quad \dots \quad (1.2)$$

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

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

$$M_b = \frac{C_b(T - \lambda_{aa}C_a) + C_aC_b\lambda_{ab}}{(T - C_a\lambda_{aa})(T - C_b\lambda_{bb}) - C_aC_b\lambda_{ab}^2} \cdot H_o$$

The increase susceptibility in the paramagnetic region is given by

$$\frac{1}{\chi} = \frac{H_o}{M_a + M_b} = \frac{T}{C} + \frac{1}{\chi_o} - \frac{K}{T-\theta} \quad \dots \quad (1.4)$$

where $C = C_a + C_b$ and

$$\frac{1}{\chi_o} = -\frac{1}{C^2} (\lambda_{aa}C_a^2 + \lambda_{bb}C_b^2 + 2\lambda_{ab}C_aC_b) \quad \dots \quad (1.5)$$

$$K = \frac{-C_aC_b}{C^2} [C_a^2 (2\lambda_{ab}\lambda_{aa} - \lambda_{ab}^2 - \lambda_{aa}^2) + C_b^2 (2\lambda_{ab}\lambda_{bb} - \lambda_{ab}^2 - \lambda_{bb}^2) + 2C_aC_b(\lambda_{ab}^2 - \lambda_{ab}\lambda_{aa} - \lambda_{ab}\lambda_{bb} + \lambda_{aa}\lambda_{bb})] \quad \dots (1.6)$$

$$\theta = \frac{-C_aC_b}{C} (2\lambda_{ab} - \lambda_{aa} - \lambda_{bb}) \quad \dots \quad (1.7)$$

The equation (1.4) represents a hyperbola with the asymptote

$$\left(\frac{1}{\chi_A} \right) = \frac{T}{C} + \frac{1}{\chi_o} \quad \dots \quad (1.8)$$

The y-intercept of the line is $\frac{1}{\chi_o}$, given by equation (1.5) and the line extrapolates to the point

$$\Theta_A = -C/\chi_0 \quad \dots \quad (1.9)$$

which is called asymptotic Curie point. The hyperbola of equation (1.4) is shown in Fig.(1.3).

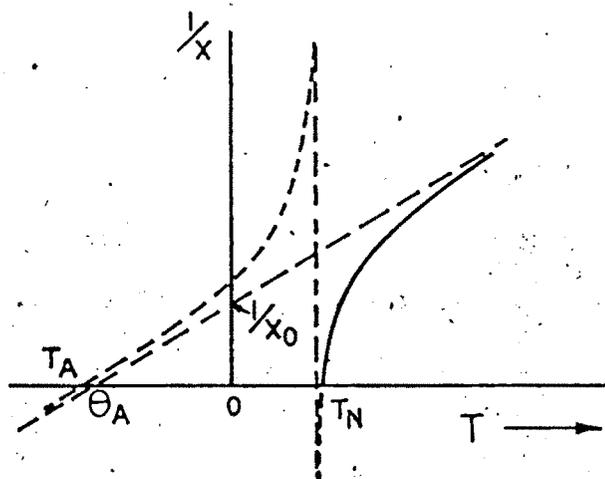
The ferrimagnetic material is paramagnetic at temperature above T_N and is spontaneously magnetised in the region $0 \leq T < T_N$. The Neel temperature may be expressed as

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

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

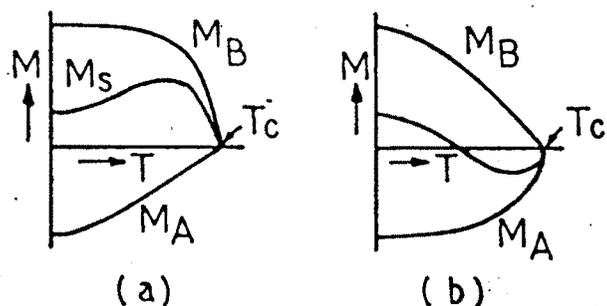
Experimental results of the susceptibility data in the paramagnetic region have been successfully used to find out the interaction parameters which, in turn were applied to compute the magnetisation curve below the Neel temperature. The agreement with the experimental results demonstrated the applicability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



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

Fig. 1.3a



— The anomalous shapes of the spontaneous magnetisation vs. temperature curves for ferrimagnetic substances according Neel's theory.

Fig. 1.3b

$$\frac{M_A}{M_{SA}} = B_S \left(\frac{g_S \mu_B H_A}{KT} \right); \quad \frac{M_B}{M_{SB}} = B_S \left(\frac{g_S \mu_B H_B}{KT} \right) \quad \dots \quad (1.11)$$

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 sublattices (Fig.1.4). The net magnetisation curves provide useful data about the ferrites from the point of view of their applications. However, in substitutional ferrites¹⁵, or due to temperature effect, the relative magnitudes of A-B and B-B interactions become comparable leading to Lotgering¹⁶ triangular arrangements. Further, structural complications lead to helical and canted spin configurations determined by the minimisation of energy considerations¹⁷.

1.4.4 Yafet-Kittel Theory

When the major constituent in a ferrite is other than Fe, observed magnetisation¹⁸ 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 sub-lattice was therefore extended by Yafet and Kittel¹⁵ in 1952. They showed that for certain ratios of exchange interactions in spinels there can exist three sublattices with triangular spin configuration instead of two sublattices. In such a case there exist a possibility of negative interaction within sub-lattice B, giving rise to sub-lattices B_1 and B_2 with their magnetisations neither exactly antiparallel to each other nor to A sub-lattice. However, the resultant

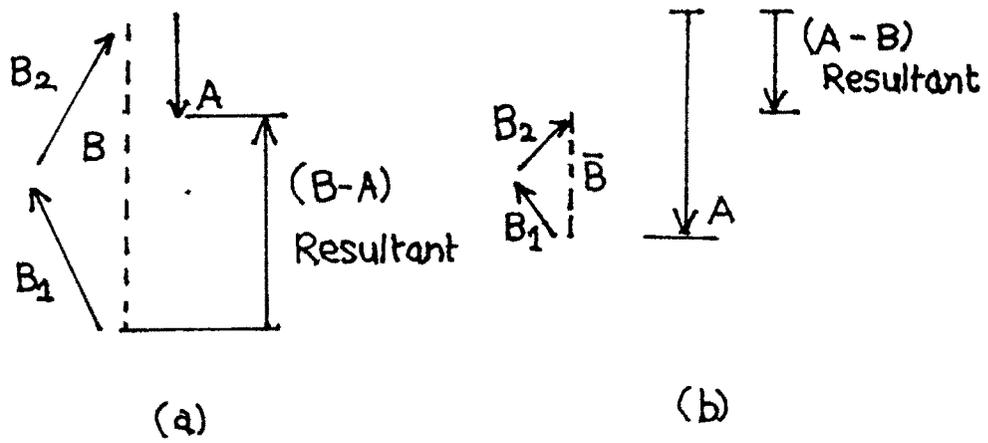


Fig. 1.4

magnetisation of B_1 and B_2 remain 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 $\frac{C}{\lambda}$ meter at room temperature. For magnetite Fe^{2+} $Fe_2^{3+}O_4^{2-}$ 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 (octahedral) 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 the 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) Porosity and pores filled by air (2) Grain size (3) Chemical inhomogeneity caused during preparation, heat treatment, rate of cooling.

The temperature dependance of resistivity ρ can be expressed by

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

The different values of ΔE (the activation energy) determined from the slope of $\log \rho$ versus $1/T$ plot represent different conduction mechanisms. Komar and Klivshin¹⁹ observed breaks in the vicinity of the ferromagnetic Curie temperature of several ferrites. Ghani et al.²⁰ have observed more than two breaks in the $\log \rho$ versus $1/T$ 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 50 kHz to 150 kHz in telephone circuits, in IF Transformers and in slug tuned inductors. Because of their high resistivity they can be used as pole pieces for concentrating flux in h.f. induction heaters²¹. Ferrite cores are now widely used in the field of memory and switching circuits in digital computers.

1.7 Orientation of the Present Work

The numerous applications of the ferrites in various fields make them technologically important and hence they are extensively studied with a view to determining their magnetic and electrical properties, to check the suitability for certain applications, and also to understand the structure property relationship. Eventhough, it is not very difficult to prepare a ferrite with some optimum property various parameters of

conditions of preparation which naturally affect the properties are to be carefully considered.

The mixed Ni-Zn ferrites system has been studied by many workers. It was therefore, considered to study the effect of addition of copper in small percentages in the Ni-Zn ferrites. Not much work on this system seems to have been reported in the literature.

Thus the two systems $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.8-x}\text{Zn}_x\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ were chosen for study with a view to understanding the role of addition of copper in affecting the structural, electrical and magnetic properties. The following studies were undertaken

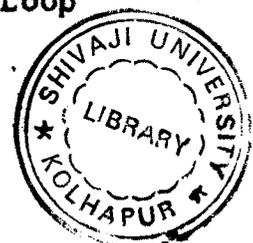
(1) By using the standard ceramic technique the following ferrites were prepared.

Series A $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with
 $x = 0, 0.2, 0.4, 0.6, 0.8, 1$

and

Series B $\text{Ni}_{0.8-x}\text{Zn}_x\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ with
 $x = 0, 0.2, 0.4, 0.6, 0.8$

- (2) X ray diffraction study for the determination of crystal structure.
- (3) Determination of Curie temperatures.
- (4) Electrical conductivity from room temperature upto 1000°K and the plots of ρ versus $1/T$
- (5) Saturation magnetisation (M_s). High Field Loop Tracer at TIFR was used for this purpose.



References

1. Kato, Y., Takai, T., Trans. Am. Electrochem. Soc., 57 (1930) 297.
2. Foresteier, H., Vetter, M., Compt. rend., 209 (1939) 164.
3. Barth, T.F.W., Posnjak, E., Z. Krist. 82 (1932) 325.
4. Snoek, J.L., "New Developments in Ferrimagnetic materials" Elsevier Amsterdam (1949).
5. Neel, L., Ann. Physique, 3 (1948) 137.
6. Shull, C.G., and Strauser, W.A., Phys. Rev. 81 (1951) 483.
7. Hastings, J.M., Carliss L.M., Rev. Mod. Phys. 25 (1953) p 114.
8. John, E. Thompson, "The Magnetic Properties of Ferrites", the Himalayan Publishing Group Ltd., Middlesex (1968).
9. Hudson, A.S., Iceram, M.A., "Review of Microwave Ferrites and Garnets". The Marconi Review, (1st Sept. 1970) 1-55.
10. Brailsford, F., "Physical Principles of Magnetism", D. Van Nostrand Co., Ltd., (1966) 202.
11. Allen, H. Morrish, "The Physical Principles of Magnetism" John Wiley and Sons, Inc.
12. Gorter E.W., Phillips Res. Rept., 9 (1954) 295.
13. Lax B. and Button K.J., "Microwave Ferrites and Ferrimagnetism", Mc-Graw-Hill Book Co. Inc. N.Y.
14. Neel, L., "Propriétés de magnétiques des ferrites, ferromagnétisme et antiferromagnétisme.

15. Yafet, Y. and Kittel, C., "Antiferromagnetic arrangements in Ferrites", Phys.Rev. 87 (1952) 290.
16. Lotgering, F.K., "On the ferrimagnetism of some sulphides and oxides", Phillips Res.Repts. Vol.11 (1956) 190.
17. Kaplan T.A. et al., "Classical Theory of the ground state spin spinel", J.Appl.Phys. vol.32 (1961) p.135.
18. Allen H.Morrish, "The Physical Principles of Magnetism" John Wiley and Sons.Inc. p.499.
19. Komar, A.P., Klivshin, V.V., Bull.Acad.Sci. USSR Phys. 18 (1954) p.96 (Columbia Uni.Tech.Translation).
20. Ghani, A.A., Etach, A.I., Mohamed, A.A., Phase transition and Conductivity in Cu.Ni ferrites. Proceedings of I.C.F.3, Japan (1980), Dordrenchity Netherlands. Reidel (1982), p.216-20.
21. Proceedings of the IRE, vol.44, No.10 (1956).