CHAPTER - I

INTRODUCTION TO FERRITES

1.1 INTRODUCTION

Ferrites form a class of important magnetic materials. One way of writing their formula is : $Me^{++}Fe_2^{+++}O_4$, where Me^{++} stands for a divalent metal ion like Co, Mn, Ni, Fe, Zn, Cd, Mg and Fe^{+++} is the trivalent iron ion. If for example, Ni is inserted for Methen the compound would be called nickel ferrite. The Me ion could be the ferrous ion Fe^{++} and in this special case the compound is ferrous ferrite written $Fe^{++}\ Fe_2^{+++}\ O_4$ or in more familiar symbols, Fe_3O_4. The natural mineral ferrous ferrite is magnetite and is the original lodestone. The synthetic ferrites were developed in the early days by Hilpert.[1]

Ferrites have very high potential applications in the field of electronics and computers. Studies on properties like saturation magnetization, Curie temperature, coercivity, magneto-crystalline anisotrophy play an important role in the development of the devices. In addition to these, microstructure, chemical homogeneity, porosity and stiochemistry are also equally responsible. Ferrites are mainly employed for high frequency operation where it is impossible to use ferromagnetic metals and alloys due to high energy losses.

There are many other parameters which also play an important role in determining the applications of the ferrite materials in technology. One can have a control over preparation technique, sintering condition etc. The intrinsic properties, however, depend upon the nature of divalent metal ions and their distribution on various lattice sites.

1.2 HISTORICAL DEVELOPMENTS

The first known and naturally occuring magnetic material to man is mineral magnetite Fe_2O_4 i.e. $FeO.Fe_2O_3$. The origin of magnetite is magnetic but its property of attracting small pieces of iron was known before Christ. The formation of magnetic oxides consisting of MeO where (Me = Mg, Mn, Zn, Ni, Cu) and Fe_2O_3 which exhibited magnetic properties and were able to attract magnet was noted by List.

The credit of preparation of synthetic magnets by the use of high temperature solid state reaction goes to Hilpert who successfully developed them in the year 1902 and was the first to realize that such materials might be useful magnetic core materials because of their higher resistivities.

Forestier[2] prepared several ferrites by precipitation with alkali hydroxides from chloride solutions and further heating the precipitate upto 900°C. He then prepared the materials with the compositions M Fe_2O_4 in which M = Cu, Ni, Mg, Si, Ba, Pb, Ca, Cd and determined the magnetization and Curie temperatures.

Kato, Takai,[3] Barth and Posjank[4] studied ferrites from the point of view of their electric and magnetic properties and chemical and crystallographic characteristics. They established structure of ferrite to be of spinel type (1933 to 1939). Van Arkel, Verwey and Van Bruggen in 1936 determined the phase relations in several systems $MO.Fe_2O_3$ (M = Mn, Cu, Ni, Mg) systems. Snoek confirmed and supplimented their results by the measurement of coercive force together with saturation magnetization in these systems.

Snoek[5] in 1941 carried out systematic investigations on artificial ferrite materials in order to study the effect of preparation technique and composition on eddy current losses and magnetic properties.

Verwey[6] established that the electronic conductivity of ferrites is mainly due to the exchange of electrons between divalent Fe^{2+} and trivalent Fe^{3+} ions in ferrites. He revealed that ferrites with inverse spinel structure are ferri-magnetic and those with normal structure are non-magnetic. They were shown, later, to possess magnetic transformation below room temperature.

Neel[7] introduced the fundamental theory of spin-spin interaction in ferrites. The concept of two sublattice model for the ferrite designated as A-sublattice and B-sublattice was introduced by him. Anderson[8] and Van Vleck[9] proposed a theory of super-exchange forces. Soon after Yafet and Kittel[10] extended the theory by introducing the idea of triangular arrangement of spins for the magnetic two sublattice model. Neel's theory was confirmed by neutron diffraction of magnetite[11] and zinc ferrite.[12] Gorter and Guilliad measured the variation of magnetization as a function of temperature for mixed ferrites with varying composition and temperature in ferrimagnetic region. They measured magnetization of Mn, Fe, Co, Ni, Cu, Mg ferrites as a function of Zn composi- tion. Smart and Gorter working independently correlated the cation distribution found out by microwave resonance with magnetization.

The formula related to the Curie temperature, magnetization and cation distribution was developed by Gilleo for the ferrites containing non-magnetic divalant cations. Advances in the use at high frequencies, especially in the commercial television made the development of ferrites essential. Further, as they exhibit switching and memory phenomena, ferrites have applications in computer industry. Today magnetic ferrites are considered as a very important ceramic material in electronic technology.

1.3 CRYSTAL STRUCTURE OF SPINEL FERRITES

The ferrites exhibit the following chemical structural groups -

a) Spinel structure
b) Garnet structure
c) Hexogonal structure
d) Perovskite structure

1.3.1 SPINEL STRUCTURE, ANGULAL RELATIONSHIPS AND INTERACTIONS

The salient features of spinel structure are as follows

The general chemical formula for the ferrospinel is $MeFe_2O_4$ where Me is a divalent metal ion and Fe is a trivalent iron ion, the ferrite exhibits spinel structure similar to crystal structure of mineral spinel $MgAl_2O_4$. All the compounds of this type have a cubic face centered crystal structure belonging to a space group of Oh^7 - Fd 3m. The length of each edge of the cell is 8 A^o. 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) and octahedral (or B site) (fig. 1.1). When magnetic ion is surrounded by four oxygen ions located at the corners of a tetrahedran as shown in fig. 1.1, it is called as tetrahedral or A site whereas whena magnetic ion is surrounded

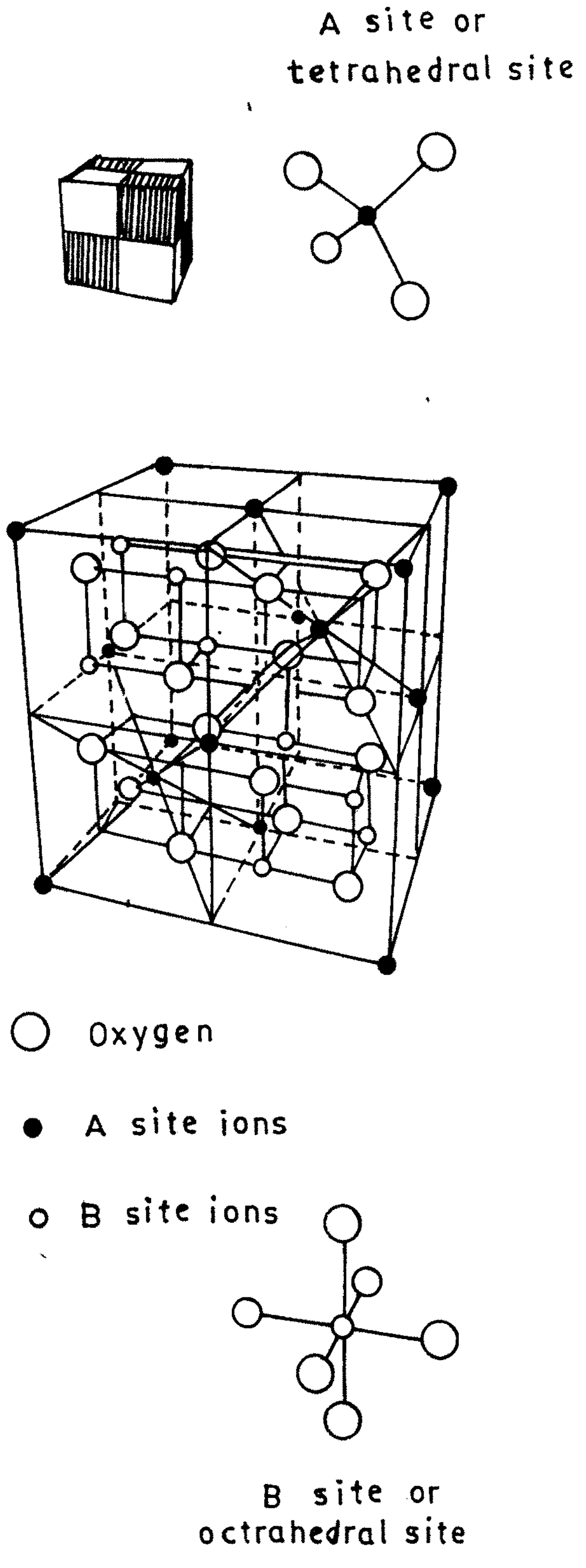
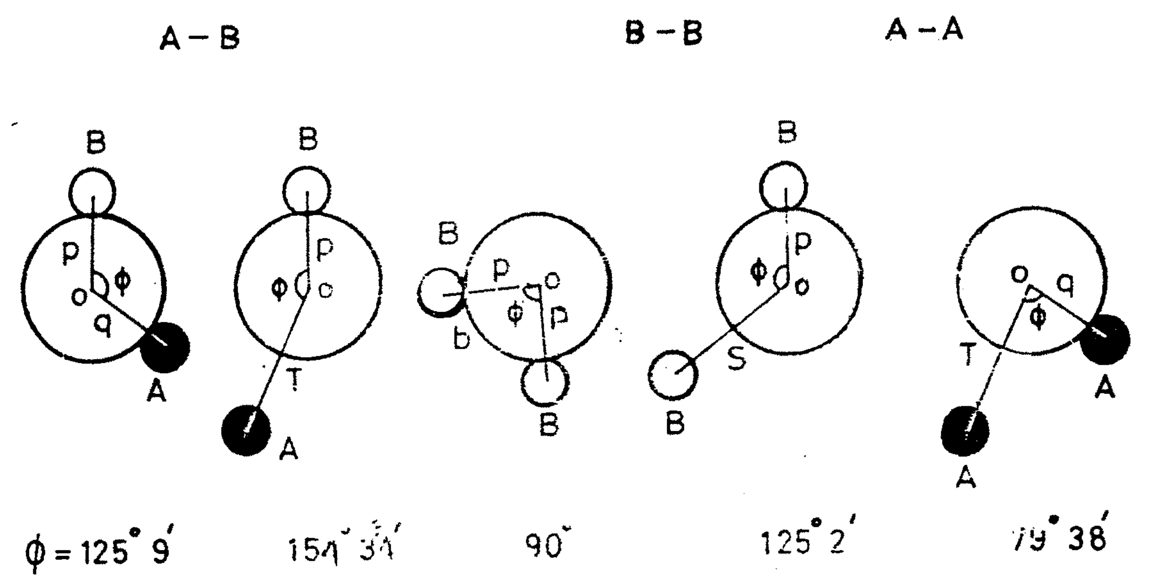


FIG. 1·1 — UNIT CELL OF THE SPINEL LATTICE.



Angle between A–A, B–B & A–B cations in a spinel structure.

Fig. 1·2

by six oxygen ions places at vertices of octahedral 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.

In ferrites, each B ion has 6 nearest A ions and each A ion has 12 nearest B ions. The angles between the ions are as shown in Fig. 1.2 and are as follows –

$$A - O - B = 125^\circ,9'$$

$$A - O - A = 79^\circ,58'$$

$$B - O - B = 90^\circ$$

In general, if the metal ion-oxygen distances are small and M-O-M angles are 180°, the interactions are strong. Thus, A-B interaction is the strongest, B-B interaction is the weak and A-A interaction is the weakest.

1.4 TYPES AND CLASSIFICATION OF SPINEL FERRITE

1.4.1 SIMPLE FERRITES

When divalent ferrous ion Fe^{2+} is replaced by another divalent metal ions such as Mn, Co, Ni, Cu, Mg, Zn and Cd, the ferrites so formed (such as $MnFeO_4$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ etc.) are called simple ferrites.

1.4.2 MIXED OR SUBSTITUTIONAL FERRITES

When divalent metal ions and trivalent metal ions are replaced by other magnetic or non-magnetic 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 other divalent Me ion e.g. $Co_{1-x}Zn_xFe_2O_4$ $(o < x < 1)$ is zinc substituted cobalt ferrite.

ii) Replacing the trivalent iron ion by another trivalent Me ion e.g. $Co_xZn_{1-x}Al_tFe_2O_4$ is called as Aluminium substituted cobalt zinc ferrite.

1.4.3 NORMAL SPINEL FERRITES

In the normal spinel ferrites all the Me^{2+} ions occupy tetrahedral or A-site and all the Fe^{3+} ions are in the octahedral or B-site. The structural formula for such a ferrite is given by-

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

Both $CdFe_2O_4$ and $ZnFe_2O_4$ have this type of structure and they are non-magnetic. The cation distribution of $CdFe_2O_4$ is therefore given as

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

and the cation distribution of $ZnFe_2O_4$ is given as

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

1.4.4 INVERSE SPINEL FERRITES

In the inverse spinel ferrites all the Me^{2+} ions occupy B-sites and the trivalent Fe^{3+} ions are equally divided between A and B sites. The arrangement may be represented as

$$\left[Fe^{3+} \right]^{A} \left[Fe^{3+}\ Me^{2+} \right]^{B} O_4^{2-}$$

ferrites like $MnFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$ etc. have this type of structure and they are all ferrimagnetic. The cation distribution in the case of inverse spinel is

$$\left[Fe_x^{3+} \right]^{A} \left[Me^{2+}Fe_{2-x}^{3+} \right]^{B} O_4^{2-} .$$

1.4.5 RANDOM SPINEL FERRITES

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 depeond upon physico-chemical conditions of preparation. The general formula for partially inverted ferrite is usually written as

$$\left[Me_{x}^{2+} Fe_{1-x}^{3+} \right]^{A} \left[Me_{1-x}^{2+} Fe_{1+x}^{3+} \right]^{B} O_{4}^{2-}$$

for example $CuFe_2O_4$.

1.5 ELECTRICAL PROPERTIES OF FERRITES

I) CONDUCTIVITY :

Ferrites are semiconducting in nature with low mobility for the charge carriers. The resistivity of ferrites lies in the range 10^{-3} to 10^{11} Ω cm at room temperature[13]. The conductivity of ferrites depends upon intrinsic properties such as purity of the compound, stoichiometry, surface conditions, sintering temperature and time, sintering atmosphere, physico-chemical history, density, porosity, grain size and chemical inhomogeneity[14]. To explain the electrical properties of ferrites the energy band model and Bloch type wave functions are not suitable since the electrons are situated on specific cations. Heikes and Johnson[15] have derived a relation for mobility of charge carriers as

$$\mu = [e^2 a^2 \omega^2 / kT] \exp (-\Delta E/kT) \qquad \ldots \quad (1.1)$$

where a is the distance between the nearest neighbour cations, ω – is the frequency of vibration of the crystal lattice and

ΔE is the activation energy. It is the energy required to cause the electron jump from one iron ion to another. The conductivity in ferrites is mainly attributed to hopping process which is governed by the law

$$\rho = \rho_o \exp (\Delta E / kT) \qquad \ldots \quad (1.2)$$

The low conductivity of ferrites is associated with the simultaneous presence of Fe^{2+} and Fe^{3+} ions on octahedral sites.

The electrical properties of ferrites have been extensively studied by Verwey[16]. In his mechanism, the electrons move from Fe^{2+} ion to Fe^{3+} ions within the octahedral positions, without causing a change in the energy state of the crystal as a result of transition. Van Ultert, Economus[17], Rezlescu and Cuciureanu[18] etc. have made important contributions towards the understanding of electrical properties of ferrites. Recently, Klinger[19] has explained the conduction process in ferrites with the help of hopping of polarons.

In the ferrites different oxides of different expansion coefficient are used and hence boundary stresses are set up between the two phases when they are cooled to room temperature. Hence all ceramics shows some porosity. The porosity affects the electrical properties of ferrites[20,21]. The air filled pores increase the resistivity of the samples. The grain size in the polycrystalline ferrites affects the number of grain to grain contacts and thus increase the resdistivity of the samples.

ii) THERMODELECTRIC POWER

If in an electric circuit two dissimilar semiconductors or a metal and semi-conductor are connected in series and the junctions between the materials are held at different temperatures an e.m.f. is produced. This is called Seebeck effect.[22] When one end of the semiconductor is more hot than the other, the free carriers at the hot end will have higher energies and speeds than those at the colder end. As a consequence, the flow of free carriers diffusing from the hot region into the cold region will be stronger than the counter flow of free carriers. If densities or mobilities of electrons and holes are different in magnitude, the semiconductor ends accumulate charges opposite in sign. An equilibrium sets when counter flow due to temperature gradient equals the flow due to electric field. The thermo e.m.f. in equilibrium is called space thermo e.m.f. The thermoelectric power with respect to unit temperature difference is called differential thermo e.m.f. and leads to evaluation of Seebeck coefficient.

$$\alpha = \frac{dv}{dt}$$

The value of α is given by the relation

$$\alpha = \frac{(\alpha n \sigma n + \alpha p \sigma p)}{\sigma n + \sigma p} \qquad \ldots (1.3)$$

$$\left.\begin{array}{lll} \sigma n & = & n\ e\ \mu n\ , \qquad \sigma_p = pe\ \mu p \\ \alpha n & = & -\frac{k}{e}\ [\ A_n - E_f / \ kT\ ] \\ \alpha p & = & \frac{k}{e}\ [\ Ap + \frac{Eg + Ef}{kT}\ ] \end{array}\right\} \qquad \ldots (1.4)$$

where n and p are electron and hole densities, μn and μp are the electron and hole mobilities, Ef is the fermi energy and Eg is the band gap.

If the bands are partially filled, the Seebeck coefficient (α) changes linearly with the change of temperature

$$\alpha_n = -\left(\frac{\pi^2 k^2}{3e}\right) T \left[\frac{d}{dE}\, l_n\ \sigma(E)\right]_{E=E_f} \qquad \ldots (1.5)$$

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

The temperature dependent thermoelectric power in case of a ferrite material having one kind of carriers is expressed as

$$\alpha = \frac{k}{e}\left[\, l_n\ (\frac{No}{n} - 1) + \frac{a}{kT}\right] \qquad \ldots (1.6)$$

where k and e are the Boltzmann constant and the electronic charge respectively, No is the concentration of trivalent ion on B-site, n is the concentration of Fe^{2+} ions. The term 'a' is the part of activation energy transported by the electrons and T is the absolute temperature.

iii) CURIE TEMPERATURE

The dependance of Curie temperatures on the distribution of metallic ions on tetrahedral and octahedral sites in the ferrites was suggested a long time ago by Gorter[23] and Neel.[24] Rezlescu et al investigated the influence of preparation techniques and cation distribution of various properties of copper and manganese mixed ferrites. They observed that the migration of cations to tetrahedral site shifts the Curie temperature to lower temperatures. In zinc mixed ferrites, the A-B interaction reduces with zinc ions and Curie point drops with the result of substitution of zinc.

Forestier studied the variation of Curie temperature for $Me_xZn_{1-x}Fe_2O_4$ (Me = Nl) with zinc content.

Recently, Sagar et al have reported their results on tetravalent Ge^{4+}, Ti^{4+} and Sn^{4+} ions substituted magnesium ferrites. They have found that Curie temperature decreases with addition of tetravalent ions in magnesium ferrites.

1.6 MAGNETIC PROPERTIES OF FERRITES

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 magnetization results. The term ferrimagnetism was coined by Neel in connection with properties of ferrites. Weiss[25] first attempted to give explanation of ferrites on the basis of his molecular field theory. Ferrimagnetic substances exhibit sponteneous magnetization which arises due to the alignment of magnetic moments under the exchange forces. The coupling between atomic magnets in a substance causes either parallel or antiparallel alignment of spines. When the spin alignment is antiparallel and magnetic moments are equal, antiferromagnetism results; when spin alignments are antiparallel and magnetic moments are unequal, ferrimagnetism resdults. The exchange interaction between neighbouring atom is indirect and take place via intermediate non magnetic ion such as oxygen.

The magnetic properties of ferrites are classified into two groups -

i) Intrinsic propeties - such as permeability, saturation magnetization, Curie temperature, magnetization etc. and

ii) Structure sensitive properties - such as hysteresis, resistivity, dielectric constant etc.

The grain size, impurity, inclusion, porosity affect structure sensitive properties.

As discussed earlier, ferrites which possess inverse spinel structure have the cation distribution -

$$Fe^{3+} [Me^{2+} Fe^{3+}] O_4^{2-}$$

where the cations shown in the bracket are on the B-site and those in the outer are on the A-sites. The unit cell of ferrite contain eight molecules. Hence magnetic moment of A-sublattice is due to 8 Fe^{3+} cations and on B-sublattice the magnetic moments is due to 8 (Fe^{3+} + Me^{2+}) cations present.

The resultant magnetization is given by

$$M = M_B - M_A$$
$$M = 8 [m_M - m_{Fe}] - 8 m_{Fe}$$
$$M = 8 m_M$$

where M_A - magnetic moment of A-sublattice
M_B - magnetic moment of B-sublattice
m_M - spin magnetic moment of metal ion
m_{Fe} - spin magnetic moment of Fe ion.

The parallel alignment of moments on each sublattice is characteristic of ferrimagnetic substances. Ferrite with normal spinel structure are non-magnetic. In these ferrites 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 magnetized in opposite direction with resulting ferrite to be non-magnetic (The angles between A-A, B-B and A-B cations are as shown in Fig. 1.2).

1.6.1 MAGNETISATION IN FERRITES

The exchange interaction between the magnetic moments of neighbouring atoms is responsible for the magnetisation in ferrites. The interaction is said to be positive when moments are parallel and negative when the moments are antiparallel. For incomplete shells the exchange interaction may be either +ve or -ve. Thus, intrinsic magnetization in ferrites can be attributed to the antiparallel arrangement of spins of sublattices assuming inverse spinel type ion distribution. Generally, ferrites have mixed inverse structure with fraction of trivalent ions on A sites and reminder on B sites. The parallel arrangement results either in antiferromagnetism or ferrimagnetism depending on whether the moments cancel completely or partially.

The spinning electrons are exchanged between neighbouring atoms, giving rise to exchange force and exchange energy. The exchange energy forms an important part of the total energy in spinel ferrites. The interaction energy of atom i and j with spins S_i and S_j is represented by equation

$$\begin{aligned} E_{ex} &= - 2 S_i S_j J_{ex} \\ &= - S_i S_j J_{ex} \cos \phi \qquad \ldots \quad (1.7) \end{aligned}$$

where J_{ex} = exchange integral

ϕ = angle between spin vectors S_i and S_j

The total exchange energy is obtained by taking summation over equation

$$W_{ex} = -2\, S^2 J \sum_{i=j} \cos \phi\, ij \qquad \ldots \quad (1.8)$$

where S = Total spin momentum

J = total exchange integral.

When the exchange integral is positive, parallel alignment of spins is favoured resulting in ferromagnets. In general exchange integral is negative resulting in antiparallel spin arrangements giving rise to antiferromagnetism. Such an ordered arrangement of spins results in the resultant spontenous magnetization in ferrites, in absence of any external magnetic field.

The temperature at which the long range order sets in (Neel temperature) is determined largely by the strength of interaction between neighbouring ions. In case of both ferromagnetics and antiferromagnetics the interaction arises from an indirect exchange mechanism in which magnetic ions are coupled through electron transfer with intermediate anions. This concept of indirect exchange was put forward by Kramers and then developed by Anderson in the form of super exchange. The idea of super exchange is used to explain magnetization in normal and inverse spinels.

1.6.2 NEEL'S THEORY OF FERRIMAGNETISM

Neel's theory has been successfully used to explain the magnetic properties of several spinel ferrites. He generalised the concept of the Weiss molecular field theory to explain the phenomenon of ferrimagnetism. His original theory holds for spinel compounds containing only one type of magnetic ions.

The molecular field H_{AB} at the A site due to the presence of magnetic ions on the B-site is given by

$$H_{AB} = \frac{2\ Z_{AB}\ J_{AB}}{N_A g_A g_B \mu_B{}^2}\ M_B = \gamma_{AB}\ M_B \qquad \ldots \quad (1.9)$$

where Z_{AB} – the exchange integral

J_{AB} – number of B-site neighbours of a given A-site ion

g_A and g_B – the Lande 'g' factors for A and B-site ions, and N_B – the total number of B atoms in the lattice with M_B – the magnetic moment of the B-sublattice. He thus considered that the mechanism of exchange occurs by super exchange process in spinels and the magnetic properties can be explained on the assumption that the interactions between tetrahedral and octahedral metal ions (A-B interaction) are strong and negative and the interaction between ions of the same sublattice (AA and BB interactions) are relatively weak. Similarly,

$$H_{AA} = Y_{AA}M_A$$

$$H_{AB} = Y_{AB}M_B$$

$$H_{BA} = Y_{BA}M_A \text{ , } H_{BB} = Y_{BB}M_B \qquad \dots (1.10)$$

$$Y_{AB} = Y_{BA} \text{ ; but } Y_{AA} = Y_{BB}$$

Neel further showed that the susceptibility in the paramagnetic range very hyperbolically

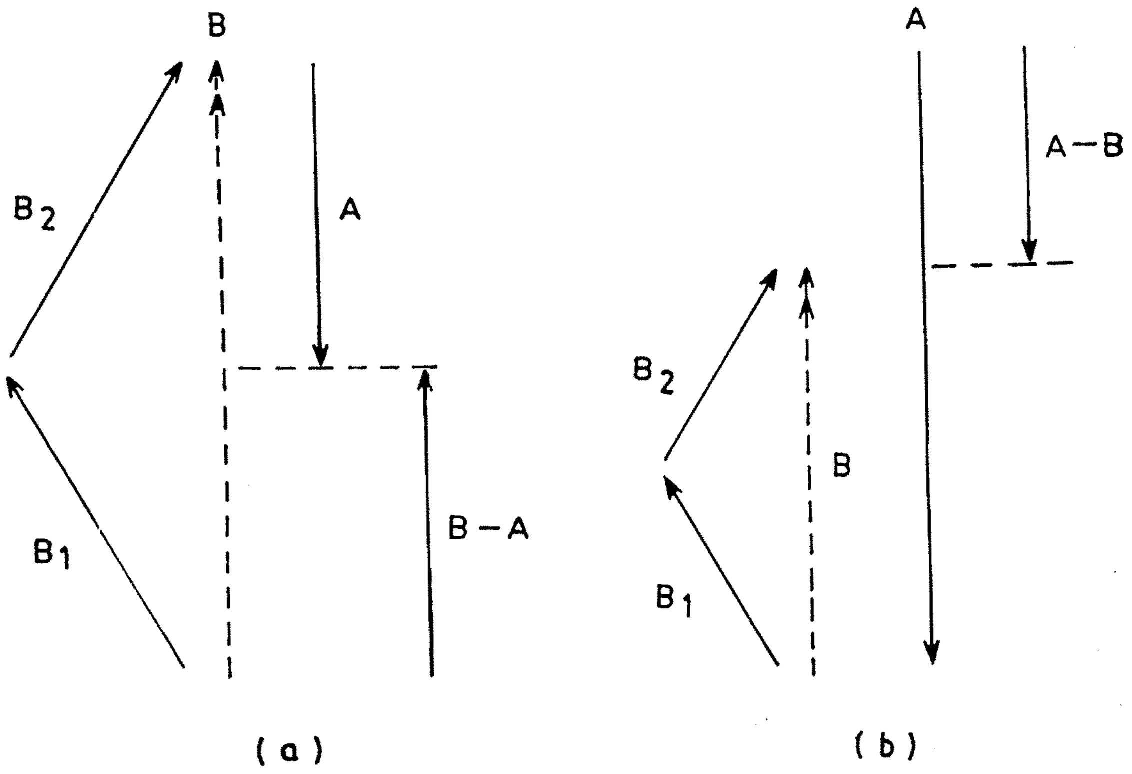
$$\frac{1}{\varphi} = \frac{T}{C} + \frac{1}{\varphi_0} - \frac{\sigma}{(T-\theta')} \qquad \dots (1.11)$$

C – is Curie constant and is equal to $(C_A + C_B)$

C_A and C_B are Curie constants of A and B sub-lattices respectively. Similarly φ_0, σ, θ' are constants. At high temperature the equation represents a straight line with intercept $\theta' = -c/\varphi_0$ on the T-axis, where θ' is called as asymptotic Curie point. The critical temperature above which the spontenous magnetization of a ferrimagnetic vanishes, is called the Curie or Neel temperature. The ferrimagnetic Neel temperature (T_{FN}) when positive the ordering temperature is observable. The ferrimagnetic material is sponteneously magnetised in the region $0 \le T \le T_{FN}$.

1.6.3 YAFET-KITTEL THEORY

Neel's theory is applicable to pure ferrites, but it is inadequate for spinels which contain ions other than Fe ions where the observed magnetization is much smaller than calculated



(a) (b)

FIG. 1·3 — TRIANGULAR SPIN CONFIGURATION.

by Neel's model for spin arrangement. Yafet and Kittel[26] therefore proposed triangular type of spin arrangement (Fig.1.3) They showed that for certain ratios of exchange interaction in spinels there can exists three sublattices with tiangular spin arrangement and has lower energy than the two sub-lattice model. In such a case there exists a possibility of negative interaction within sub-lattice itself giving rise to B_1, B_2 sublattices which are neither exactly antiparallel to each other nor to sublattice A. Instead, they align at some angle other than 180°. Thus there is a resultant magnetization of B lattice setting itself antiparallel to the magnetization of A lattice as shown in Fig.1.3. This rectangular arrangement within the lattice results in values of reduced magnetization of the same order and magnitude as those predicted by Neel model.

Neel theory predicted (M_s, T) curves of different types. But these curves cannot occur in practice because they require $\frac{\partial M_s}{\partial T}$ to be finite as $T = 0°K$ in contradiction to the third law of thermodyamics, this diffuculty was removed by Yafet-Kittel model.

The interaction energy E in this case is given by

$$E = 8 N [\sigma J_{ab} S_a S_b \cos \phi - J_{bb} S_b^2 (2 \cos \phi - 1)] .. \quad (1.12)$$

where ϕ - angle between A and subdivisions of B

$J's$ - exchange integrals

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

$$r_{ex} = \frac{J_{bb}\, S_b}{J_{ab}\, S_a} > 3/4 \qquad \ldots \quad (1.13)$$

Under this condition Neel's state will not be minimum and magnetization of sublattices B_1 and B_2 will be inclined to sublattice A at an angle given by

$$\cos \phi = \frac{3}{4} \; \frac{J_{ab}\, S_a}{J_{bb}\, S_b} \qquad \ldots \quad (1.14)$$

Yafet and Kittel pointed out that Neel's structure is stable for $r_{ex} < 3/4$ if the total number of sublattices is restricted to six. The existance of trangular arrangement has been reported by Lotergring[27] in some particular cases.

1.6.4 SPIRAL SPINS

Kaplan[28] 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[29] 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 $V_{ex} > 2/3$. Croll and Hasting[30] observed existance of such configuration in manganese chromite. Spiral spin configuration was also developed by Lotgering. Lotgering applied the theory of his own toresults on oxides and sulphides. Spiral spin configuration has been reported by Enz[31] in case of hexagonal ferrites.

1.6.5 HYSTERESIS BEHAVIOUR, MAGNETIZATION AND DOMAINS

The variation of magnetisation with magnetic field usually depends on the nature of the material but the curve have a general shape shown in Fig.1.4. In the beginning, the material is in the demagnetized state indicated by the point O'. On the application of a magnetic field, the magnetization increases until the saturation value is reached, the behaviour shown by the curve OABC. This part of the curve is called the magnetization curve. By carrying out the operation of reducing the magnetic field to zero, increasing it in the reverse direction, decreasing it to zero and then increasing it to the original value, the curve CDEFGC results. This curve is known as hysteresis curve or hysteresis loop and is symmetric about the origin.

The process of magnetization of the specimen to saturation involves its conversion to a single domain state so that the magnetisation vector lies parallel to the applied field. According to the domain theory, this can happen in two ways

1) Domains that are oriented favourably with respect to the applied magnetic field may grow at the expense of the other domains that are unfavourably oriented. On reversing the field, however, the domain boundaries return to their original position This process of magnetisation is called reversible boundary displacement and requires only a small magnetising force.

2) The magnetisation vector within each domain may rotate in the direction of the field when the applied field is large. This process is known as magnetisation by domain rotation. Here the spins have to be returned from an easy direction to a hard one and work must be done against the anisotropy forces. Therefore magnetisation by domain rotation requires large energies.

In between boundary movement and domain rotation, there is another process - sudden reversal of domains, by which the magnetisation change can occur. The domains gain energy from the applied field and reverse the direction instantaneously such that it lies along an axis. Such domain reversals involve no increase in the anisotropy energy and are called 'Barkhausen jumps'.

For bulk crystals, with more complicated domain structure, there are no theoretical calculations regarding the magnetisation process. Shur et al.[32] assumed that in bulk uniaxial crystals, near saturation, curling mechanism might be possible at the surface of the crystal. Mitzek[83] has shown that such a mechanism is possible only if in the superficial region the anisotropy constant is negative and has an order of magnitude equal to the geometric average of the exchange and anisotropy constant inside the crystal, but this condition seems to be unlikely. More recent experiments[34] have showed that even in bulk crystals the last stage of magnetization does not occur by curling but by disappearance of cylindrical reverse domains of finite radius. Stability conditions for single cylindrical (bubble) domains were analysed by Bobeck[35] and Thiele[36] in connection with their application for magnetic storage and logic devices.

A ferro- or ferrimagnetic substance becomes magnetized due to domain boundary displacements and domain rotation. Both these processes can take place irreversibly resulting in 'hysteresis loop'. Domain reotations are mostly associated with the intrinsic properties viz. the chemical composition of the material. Domain boundary displacements, on the other hand, depend not only on the intrinsic properties but also on factors concerned with the sintering process such as porosity, size and shape of the pores, size and shape of the crystals etc.

In the initial part of the hysteresis curve reversible wall displacement takes place. Barkhausen jumps and irreservible wall displacements predominant in the central part of the curve. In the upper part of the curve domain rotation occurs. On reducing the field, the domains 'relax' to the nearest easy directions of magnetisation because of the anisotropy forces. On reversing the field, some boundry movements followed by Barkhausen jumps take place. Towards the bottom of the curve, rotations predominate again and the saturation in the reverse direction is reached.

1.6.6 INITIAL PERMEABILITY

Initial permeability is defined as the ratio of the variation of flux density ΔB to that of the field strength ΔH, measured with a magnetically closed core without air gap. It is assumed that magnetisation only takes place at very weak a.c. field

$$\mu_i = \frac{1}{\mu_o} \lim_{H \to o} > \frac{B}{H}$$

μ_i – is the initial permeability

μ_o – is the absolute permeability of vacuum

H – is the amplitude of the alternating field strength in A/m

B – is the flux density in wb/m^2 .

The measurement of permeability can be done with

i) The Maxwell Bridge

ii) Resonance method

iii) The standing wave method etc.

From audio to microwave frequencies the behaviour of μ versus frequency is called permeability spectrum.

A demagnetised magnetic material is divided in a number of Weiss domains. All magnetic moments are oriented in parallel and the magnetization has its saturation value M_s. In the walls the magnetization direction changes gradually from the direction of magnetisation in one domain to that in the next. The walls are bound to equilibrium position. These positions result from the integrations with the magnetization in neighbouring domains and from the influence of pores, crystal boundaries and chemical inhomogeneities which tend to favour certain wall positions.

μ_i depends on the method of preparation and its value changes markedly, with the firing temperature. μ_i can be resolved into two types of mechanism[97]. They are –

i) contribution from spin reaction and

ii) contribution from domain walls. But contribution from spin rotation is smaller than that of domain wall motion. The permeability due to domain walls motion is given by the equation[98]

$$(\mu_o - 1)_w = 3 \pi M_s^2 D / 4 \gamma \qquad \ldots \quad (1.15)$$

M_s is the saturation magnetization

D is the mean grain size and

γ is the magnetic domain wall energy which is propertional to Global anisotrophy constant[39].

i) TEMPERATURE DEPENDANCE

In most magnetic materials μ_i increases with temperature upto Curie temperature. This is because the anisotrophy field usually decreases with temperature much faster than Ms. The initial peremability Vs crystal anisotropy curve passes through zero at the temperature T_k and the permeability then rises to a high peak at this point. Some times μ_i - T curve exhibits double peak feature. It is caused by the presence of excessive ferrous ions within the material.

1.7 APPLICATIONS OF FERRITES - THE FERRITE SPECTRUM

Ferrites find wide applications in electronic technology,as aerial rods[40], in accelerators for elementary particles[41]and digital computers.[42] In synchroton a ferrite accelerating resonator is being proposed by Aver bukh[43]. Ferrites are widely used for antenna cores in broadcast radio receivers. They are also used as flyback transformers in television picture tubes. Magnetically soft ferrites having lower permeability and saturation magnetization find better replacement for metallic cores, which were discarded for high eddy current losses. Soft ferrites find their major use in high frequency transformer, deflection yokes in T.V. sets, recording leads etc. Power ferrites find high frequency applications. In these applications gyrometric dielectric losses which arises 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 50 KHz to 150 KHz in telephone circuits (ii) as IFT in radio receivers (iii) as an inductor in T.V. receiver (iii) 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.[44]

Spinel structure has physical flexibility which leads to a broad spectrum of its practical applications.[45] 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[46] and Attura[47] used Mn-Zn ferrites for this purpose. Piezomagnetic ferrites are used in ultrasonic transducers. Piezomagnetic ferrites were developed by Van der Burgt and Stuijts[48]. Recently piezomagnetic nickel magnesium cobalt ferrites[46] have been developed for their wide applications in ultrasonic and r.f. applications.

Hexagonal ferrites (e.a. $BaFe_{12}O_{19}$)[49-58] 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

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1. <u>For Radio</u> :
    1) IF band pass filters
    2) Antennas
    3) Elements for permeability tunning
    4) Transformers
2. <u>For Television</u> :
    1) Line output transformer
    2) Deflection coils
    3) Linearity and width control of image
    4) Noise suppresdsion plates
3. <u>For Telecommunications</u>
    1) Filters for carrier telephony
    2) hf chokes
    3) Equalizing cores
    4) Delay lines
    5) Broad band audio transformers
    6) Pulse transformers
4. <u>Miscellaneous</u>
    1) Ultrasonic vibrator
    2) Mechanical filters
    3) Recording tapes in tape recorder
    4) Frequency modulation
    5) h.f. coupling
    6) Ignition coils
    7) low power transmission
    8) Magnetic amplifiers
    9) Saturation reactors
    10) Various parts in proton accelerators
    11) Modulation of uhf in waveguides, gyrators.

1.8 ORIENTATION

The magnesium ferrite is one of the most widely used component of microwave ferrite family.[59] The Mg-ferrite has low magnetic losses and find use in low power devices. Hysteresis loop characteristics make Mg-ferrites are particularly useful in latching type phase shifter elements. The Mg-ferrite is also an important material in the radio engineering and refractory industries[60]. Also it is a typical spinel in which the cation distribution in the crystal lattice sites is very much sensitive to heat treatment[64]. Further Mg-ferrite has a negative crystalline anisotropy. It is ferrimagnetic and its magnetic behaviour can be well explained on the basis of the Neel's two sub-lattice model. The super-exchange interaction responsible for its magnetic behaviour such as magnetic moment, Curie temperature is mainly through the A-B interaction. The Mg-ferrite has saturation magnetization (M_s = 27 emu/gm at 20°C and its Curie temperature (Tc) = 440°C.[62]

The spinel ferrites with varying amount of non-magnetic ions like zinc and cadmium have been the subject matter of many researchers today.[63-73] The interest arises mainly because of their applications at microwave frequencies and their interesting properties. The effect of Zn^{2+} ions on the magnetic properties of Mg-Zn ferrite has been recently investigated by

Kulkarni et al[72]. The infrared absorption studies on some magnesium zinc ferrites have been carried out by Shobanadri et al[74]. In order to see the effect of the rare earth impurity doping on the electrical conductivity and magnetization we have undertaken the following studies on some samarium doped magnesium-cadmium ferrites.

1) Preparation of samarium doped Mg-Cd ferrites with the general formula $Mg_xCd_{1-x}Sm_yFe_{2-y}O_4$ with $x = 0.5$ and $y = 0$, 0.1, 0.2, 0.3, 0.4, 0.5 by the standard ceramic technique.
2) XRD studies to confirm the single phase formation and to calculate the lattice parameters.
3) Infrared absorption studies to obtain knowledge about the internal vibrations, find out positions of absorption bands and to study the variation of force constant with band lengths.
4) Measurement of electrical conductivity as a function of temperature to propose the conduction mechanism.
5) Magnetization studies to see the effect of samarium content.
6) To establish the correlation between the electrical and magnetic properties and the chemical structure of the samples.

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