CHAPTER — I

FERRITES : AN INTRODUCTION

C H A P T E R - I

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INTRODUCTION

After 1930, the rapid development and increasing complexity of radiofrequency equipment emphasized the need for a ferromagnetic material in which, the eddy current losses are less. For this reason an intensive search was made for a homogeneous material of low eddy current losses at high frequencies. This resulted in the formation of ferrimagnetic oxides or ferrites. These newly formed magnetic materials are technologically very important, as they exhibit interesting physical properties. The ferrites possess wide range of magnetization and the property of electrical insulation. It allows the propagation of high field electromagnetic waves through them with low attenuation.

The properties of ferrites are consequences of their internal structure. The tailor-making of ferrites to suit any particular application depends on factors such as chemical structure, thermochemical history of the substance etc. The comprehensive understanding of the inter-relationship of properties with crystal structure, magnetic interaction, cation distribution and processing conditions is therefore necessary.

In this chapter important aspects such as historical developments, crystal structure, properties of ferrites etc., are included. The orientation of the problem is added at the end.

1.1 HISTORICAL DEVELOPMENTS

The first magnetic material, magnetite or ferrous ferrite $[FeO. Fe_2O_3]$ was used by Thale's of Miletus. After the discovery of theory of magnetism, interesting magnetic phenomena fascinated the minds of ancient scientists, to prepare the artificial magnets. Their efforts in the formation of synthetic magnets, resulted in the formation of ferrimagnetic oxides or ferrites.

In 1909, Hilpert [1] produced magnetic oxides of very low conductivity so that, reduction of eddy current losses in the components such as inductors and transformers can be achieved. The materials which he produced had very low permeability, were lossy hence, were not so technologically attractive. Wedekind [2], Forestier and Chaudron [3] investigated magnetic properties of compounds in relation to stoichiometric composition, magnetic transformation etc. Later on Kato and Takei [4] investigated magnetic materials for permanent magnets. Takei, Yasuda and Ishihara [5] studied high temperature effects on magnetization of cobalt ferrites.

Snoek in 1946, carried out a systematic study on the preparation of ferrites and successfully obtained a wide range of ferrites of greater technical importance [6]. Some studies on electrical conduction in ferrites were carried out by Verwey [7]. He reported that electrical conductivity in ferrites is due to the exchange of electrons between divalent Fe^{2+} and trivalent Fe^{3+} ions of iron in ferrites. It is recognized as hopping mechanism for conduction in ferrites. Further, Verwey [8] carried out crystal

structure analysis of ferrites and concluded that ferrites with inverse spinel structures are ferrimagnetic whereas those with normal spinel structure are non-magnetic.

The publication of Neel's [9] theory on ferrimagnetism, intensified the magnetic research by several orders of magnitude. Neel introduced the concept of two sublattice model, and designated them as A-sublattice and B-sublattice. According to him coupling occurs between atoms in A-sites as well as B-sites. Since A-B interaction is strong and predominent, the resultant spin may be parallel or antiparallel. When spins in both the sites are parallel (equal or unequal magnitude) substance is ferromagnetic. If spins in both the sites are antiparallel and equal in magnitude the resultant becomes zero and substance is antiferromagnetic. If spins are antiparallel but unequal in magnitude resultant becomes non-zero and spontaneous magnetization occurs in case of ferrimagnetic substance. In 1952, Yafet and Kittle [10] considered triangular antiparallel spin in the magnetic two sub-lattice model. In 1951, Shull [9] et al proved the correctness of Neel's model of ferrimagnetism by Neutron diffraction experiments.

In 1954, Gorter [11] showed that theory of anti ferromagnetism can be applicable to mixed ferrites. Also, he measured the magnetization of Mg, Co, Fe, Ni, Mn and Cu ferrites with Zn ferrite as a function of Zn composition. Gilleo [12] developed a formula to co-relate observed Curie temperature, magnetization and cation distribution. Guillaud, Roux and Creveaux [13, 14] gave discription of variation of magnetization as a function of temperature. Pauthenet [15] in 1958 introduced three sublattice model for ferrites.

1.2 COMPOSITION AND STRUCTURE OF FERRITES

### 1.2.1 Chemical structure of Ferrites

The ferrites are ferrimagnetic substances which have the general formula $M^{2+} Fe_2^{3+} O_4^{2-}$, where M is divalent metallic ion such as Fe, Mn, Co, Ni, Cu, Zn, Cd etc.,. Chemically MFe_2O_4 is the combination of the solid ionic solution of the two oxides, MO and Fe_2O_3. The lattice structure of the ferrite is of spinel type, like mineral spinel $MgAl_2O_4$.

1.2.2 Lattice Structure of Ferrites

The spinel ferrites are derived from naturally occuring mineral spinel $MgAl_2O_4$. The spinel ferrites crystallize into cubic system. The unit cell consists of 8 molecules, hence unit cell formula is,

$$M_8^{2+} \quad Fe_{16}^{3+} \quad O_{32}^{2-}$$
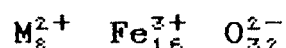
The 32 oxygen anions form the lattice of face centred cubic structure. In a unit cell, there are 96 interstitial sites available between 32 oxygen ions. These are divided into 64 tetrahedrally co-ordinated A sites and 32 octahedrally coordinated B sites. The metal ions occupy suitably 24 intersitices [16]. The oxygen ion close packed face centered cubic structure is as shown in fig.1.1. The position of metal
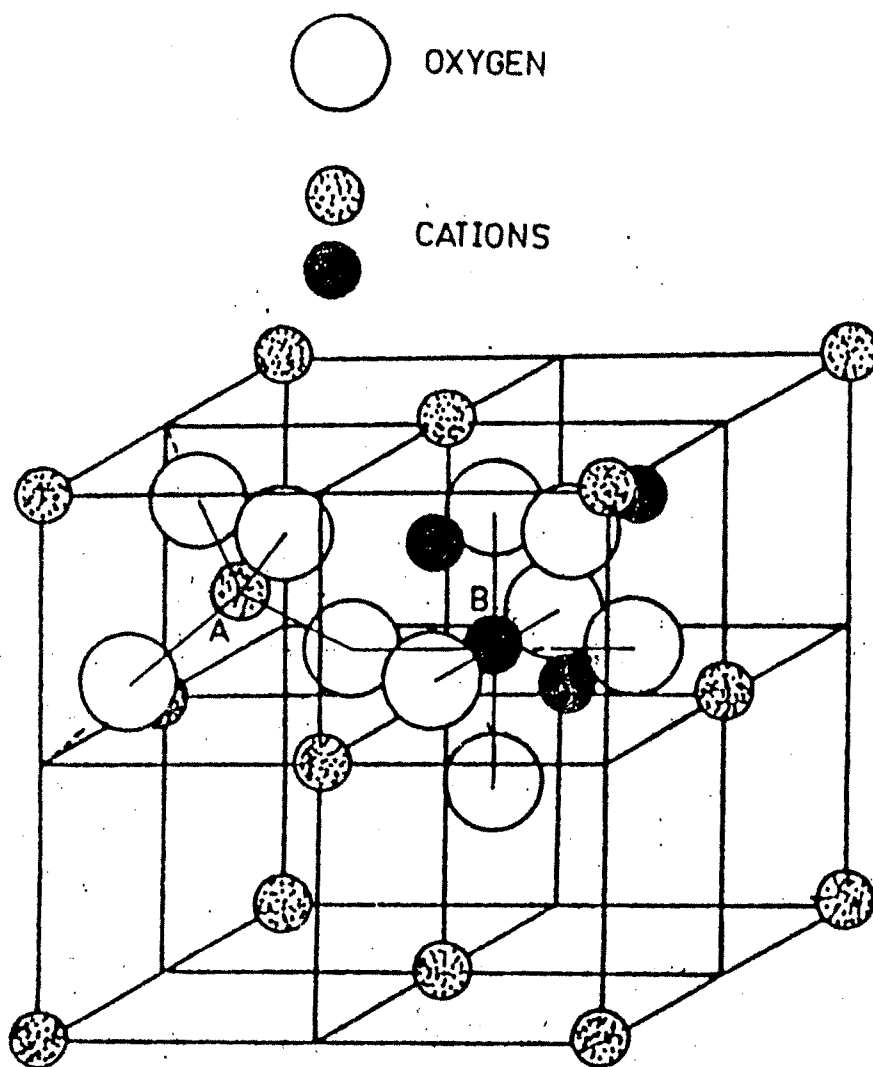
THE SPINEL STRUCTURE (SCHEMATIC)

Fig. 1·1

ion in a void surrounded by four nearest neighbour oxygen ions which are situated at the corners of tetrahedron is called as tetrahedral or A site. The position of metal ion in a void surrounded by six oxygen ions which are situated at the corners of an octahedron is called as octahedral or B site.

It is quite interesting to study which ions out of 24 metal ions occupy A and B sites. The distribution of 24 metal ions among A site and B site is determined by "cation distribution". The site preference energies of the cations, determine the cation distribution on A and B sites. Also, the distribution of cations on A and B sites depends on ionic radius, electronic configuration, electrostatic energies and polarization effect.

Mc-Clure[17] and Dunitz and Orgel [18] studied electronic structure of $CoFe_2O_4$. Taking review of site preference of cations in spinel lattice, they stated that, thermodynamic stabilization energy values are available for both octahedral and tetrahedral sites in the spinel AB_2O_4. The difference between these values is the site preference energy. When there is no appreciable site preference energy, the ionic radius decides cation distribution [19]. Larger cations prefer octahedral sites and smaller cations prefer tetrahedral sites.

1.2.3 Crystallography of spinels

In   1951,   Wyckoff [20]   gave the   spinel space group as O_h^7 (Fd3m).   The ionic positions are :

anion
32 b
$$u, u, u; \quad u, \bar{u}, \bar{u}; \quad \bar{u}, u, \bar{u}, \quad \frac{1}{4} - u, \quad \frac{1}{4} - u, \quad \frac{1}{4} - u;$$
$$\frac{1}{4} - u, \quad u + \frac{1}{4}, \quad u + \frac{1}{4}; \quad u + \frac{1}{4}, \quad \frac{1}{4} - u, \quad u + \frac{1}{4}; \quad u + \frac{1}{4}, \quad u + \frac{1}{4}, \quad \frac{1}{4} - u.$$

Cation 16 c
$$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}; \frac{5}{8}, \frac{7}{8}, \frac{7}{8}; \frac{7}{8}, \frac{5}{8}, \frac{7}{8}; \frac{7}{8}, \frac{7}{8}, \frac{5}{8}.$$

Cation 8F
$$0, 0, 0, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$$

With   the   translation   for a   face   centered   lattice

$$0, 0, 0; \quad 0, \frac{1}{2}, \frac{1}{2}; \quad \frac{1}{2}, 0, \frac{1}{2}; \quad \frac{1}{2}, \frac{1}{2}, 0.$$

Packing   of   the ions within the lattice is   perfect when the oxygen parameter $u = \frac{3}{4}$.

The   values   of   oxygen   parameter   for   Mg—ferrite   and Coferrite   are found   to be same, i.e. u = 0.381 [21]. Wyckoff (1951)   found the lattice parameter for magnesium ferrite and cobalt   ferrite to be   8.37 A^o and   8.35 A^o respectively [21]. Smith   and   Wijn   (1959)   calculated   A   and   B   site radii for $MgFe_2O_4$ and $CoFe_2O_4$ using the formulae [22],

$$r_A = \left[u - \frac{1}{4} \right] a \sqrt{3} - r(o^{2-})$$

$$r_B = \left[\frac{5}{8} - u \right] a - r(o^{2-})$$
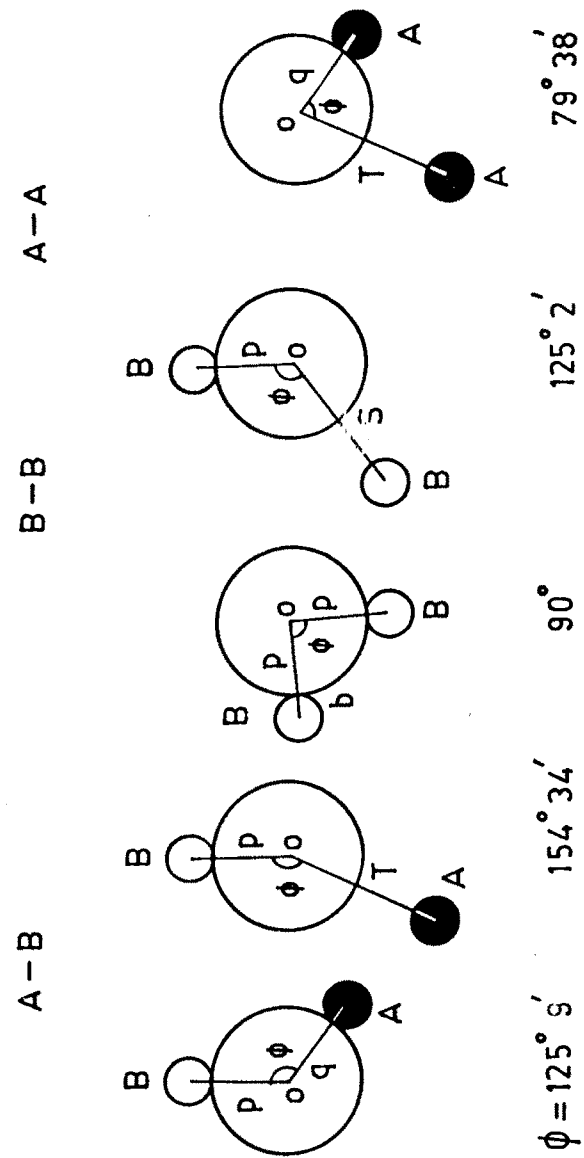
The calculated values of site radii are as follows.

Sample	Tetrahedral Site		Octahedral Site	
	rA $\overset{o}{A}$	Occupant	rB $\overset{o}{A}$	Occupant
$MgFe_2O_4$	0.54	Mg^{2+} Fe^{3+}	0.69	Mg^{2+} Fe^{3+}
$CoFe_2O_4$	0.54	Co^{2+}	0.69	Co^{2+} Fe^{3+}

In spinel ferrites every oxygen ion is surrounded by three B-cations and one A-cation [fig. 1.2]. The angles are given as [23].

$$A - O - B = 125^{o}\ 9^{'}\ ;\ 154^{o}\ 34^{'}$$

$$A - O - A = 79^{o}\ 38^{'}$$

$$B - O - B = 90^{o}$$

A—B   B—B   A—A

$\phi = 125° 5'$ 154° 34'   90°   125° 2'   79° 38'

Fig. 1·2

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

If metal oxygen distances are small and $M - O - M$ angle is close to 180°, the maximum direct coupling exists between metallic ions A and B. Hence A-B interaction is stronger. If the angle is close to 90° the interaction is weaker e.g. B-B and A-B interaction.

1.2.4 General Ferrite Structures

In addition to spinel structure, ferrites have other important chemical structures such as -

      i) Garnet structure

      ii) Hexagonal structure

and   iii) Pervoskite structure·

Garnet structure materials were first identified by Bertaut et al. Jonker et al first studied extensively hexagonal ferrites. Pervoskite materials have been studied by Geller and his co-workers (1956-58).

On the basis of cation distribution the spinel ferrites are classified into three groups.

1.3 DISTRIBUTION OF CATIONS IN SPINELS

Regarding the distribution of the divalent and trivalent cations on A and B sites, it might be thought at first that the eight divalent cations are situated on eight occupied A sites and the 16 trivalent iron ions on 16 occupied B sites. But this does not hold in all cases. Experiments shows that whole range of distributions is possible [24]. Distribution of cations in spinel can be represented in general terms by,

$$Me_\delta^{2+} \quad Fe_{1-\delta}^{3+} \; [\; Me_{1-\delta}^{2+} \quad Fe_{1+\delta}^{3+} \;] \; O_4 \qquad \cdot 1.1$$
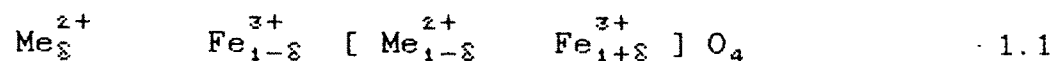
where the brackets indicate octahedral sites.

The term 'ε' is called as coefficient of normalcy and (1-ε) is coefficient of inversion.

The limiting case $\varepsilon = 1$ is called "normal spinel".

Well known examples of normal spinel are $ZnFe_2O_4$ and $CdFe_2O_4$. These spinels are generally non-magnetic and stable.

The limiting case $\varepsilon = 0$ is called "inverse spinel". The case $\varepsilon = 0$ appear more likely because $r_B > r_A$ and $rme^{2+} > rme^{3+}$.

Ferrites such as Mg, Co, Ni, Cu, occurs in completely inverse form. The extent of inversion depends on the heat treatment [25].

For a random (statistical) distribution $\varepsilon = 1/3$. In random spinel structure, the metal ions Me^{II} and iron ions Fe^{III} get distributed randomly over tetrahedral and octahedral. The distribution depends or physico- chemical conditions of preparation of variation in composition. Generally such ferrites are partially inverse. The distribution of ions on terahedral and octahedral sites can be investigated by means of X-ray diffraction, neutron diffraction and magnetic measurements. For $MgFe_2O_4$ and $CuFe_2O_4$ the temperature dependence of the distribution is shown to correspond to a Boltzmann distribution,

$$\frac{\varepsilon(1+\varepsilon)}{(1-\varepsilon)^2} = e^{-E/KT} \qquad 1.2$$

It is possible to replace some or all the metal ions with other cations of magnetic or non-magnetic nature in spinel ferrite.

The two important catagories of substitution may be possible as follows.

a) Replacement of divalent metal ion by other magnetic or non-magnetic divalent metal ion. Replacement may be partial. e.g. In magnesium ferrites part or all of the magnesium cations may be replaced by cobalt as

$$Mg_{1-x} Co_x Fe_2O_4 \quad for \quad 0 \leq x \leq 1$$
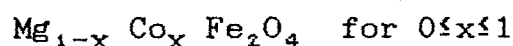
This is magnesium cobalt or cobalt substituted magnesium ferrite.

b) Replacement of trivalent iron ion by other trivalent ion . Part of trivalent iron may be replaced by trivalent nonmagnetic element such as aluminium chromium eg.

$$Mg \ Fe_{2-y} \ Al_y \ O_4$$
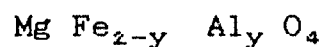
This is magnesium ferrite aluminate.

1.4 PROPERTIES OF FERRITES

Ferrites are ionic compounds. At room temperature they possess semiconducting properties. Their resistivity varies from 5×10^3 Ωcm in case of Fe_3O_4 to 10^{11} Ωcm in magnesium ferrites. Polycrystalline ferrites show variation in electrical properties with respect to heat treatment process markedly, because of dissociation of oxygen at high temperature above 1400°C [26].

The general electrical properties exhibited by ferrites such as a.c. and d.c conductivity, dielectric constant etc., depend upon parameters like purity of compounds, physico-chemical history, stoichiometry, porosity, density, chemical inhomogeneity, grain size, sintering temperature etc. The

dependence of electrical resistivity on temperature is having greater importance in ferrites. The dependence is according to relation,

$$\rho = \rho_0 \ e^{\Delta E/KT}$$

where,

$\Delta E =$ Activation energy i.e. energy required to cause electron jump.

$K =$ Boltzmann constant.

$T =$ Absolute temperature.

When the ferrite samples are quenched they exhibit switching phenomenona. Hisatake et al studied switching phenomenon in lithium ferrite. This property is assumed to be due to the distortion of crystal lattice structure called John-Tellor distortion [27]. Ferrites exhibit Hall effect and Seebeck effect. In case of ferrites hysteresis lag occurs when it is subjected to the cyclic magnetization just like ferromagnets. They exhibit magnetostriction as well as magnetocrystalline anisotropy. Magnesium ferrite has negative crystalline anisotropy where as cobalt ferrite has positive crystalline anisotropy. The electrical and magnetic properties of ferrites are explained in more details in Chapter III and Chapter IV respectively.

1.5 APPLICATIONS OF FERRITES

Ferrites are some of the most important electronic ceramics. Magnetically soft ferrites having permeability and saturation magnetization lower than magnetic metals are widely used in places where possibility of using metallic cores is ruled out due to eddy current losses. In ferrites high

frequency losses are very small. The major application of ferrites are high frequency transformer cores, antenna rods, induction tuners, deflection yokes in T.V. sets, chokes, recording heads etc.

Property of ferrites of offering rectangular hysteresis loop is required in computer memory devices and flip-flops. The degree of regularity, uniformity and stability of characteristics have a direct suitability in a memory and hence upon the strong capacity of memory. The values of coercive force determine how rapidly the formation can be handled. Cores of Mg-Mn ferrites have been produced with a good degree of rectangularity and expected uniformity is achieved through control of composition and processing.

The alternate selection and control of variables used in manufacturing of ferrites leads to somewhat lowering of permeability but to enhanced magnetostriction. This is an important consideration while using ferrites in accelarometers mechanical filters and ultrasonic generators.

Ferrites are finding numerous applications in microwave fields due to their unique gyromagnetic resonance properties. The applications in this area include phase shifters, circulators and modulators. The HQ product of ferrites is high over the frequency range 50 KHz to 150 KHz, which renders them suitable for filter inductors, band pass filters in carriers and telephone circuits. The precise control over inductance and good stability are necessary for the function of the separating channels. This requirements are met by the conventional coil, normally of the pot type construction. The high HQ products also makes the ferrite useful for both

transformers in radio circuits and slug tuned inductors.

Ferrities also occupy an important place in a manufacture of miniature components like inductors and transformers. Magnetically hard ferrites having uniaxial anisotropy have equally important areas of applications such as loud speaker, television, telephone, generators etc.

Recently, scientists have developed ferrites for fascinating applications. Saburo Motozaw of Japan used sintered nickel ferrite as granulated materials for electrolyzing water [28]. Averbukh [29] proposed a ferrite accelarating resonator for developing accelarating machine for ion synchroton.

1.6 ORIENTATION OF THE PROBLEM

Technologically, ferrimagnetic oxides or ferrites are important magnetic materials. With the advent of developments in microscopical devices, such as, scanning electron microscope, transmission electron microscope, AAS etc., it is possible to relate the microstructural dependence with characteristics properties of materials. The research forwarded in ferrite technology thus has became ever interesting during last few decades.

The initial permeability and hysteresis loop properties of ferrites are strongly influenced by microstructure of the material and hence the method of preparation [30]. The microstructural changes which occur during heat treatment are also contributed to a variation of cation distribution [31]. Methods of fabraction sensitively determines the microwave properties, particularly, dielectric and magnetic losses [32]. It has been found that the presence of porosity in samples influences markedly the electrical and magnetic properties.

Hence for the formation of 100% dense homogeneous ferrites, more advanced hot pressing technique can be used [33]. Improvements has been made in reducing porosity, particularly eliminating pores within the grains and also in controlling the grain size [34]. The decreased porosity in sample reduces eddy current losses [35]. This would form the better meterial for electrical devices operating at high frequencies.

Thus it is clear that ferrite microstructure highly controls the properties of ferrites. The modern research workers in ferrite technology are interested in controlling the properties through the microstructure control. In the present work, studies on magnesium, magnesium-cobalt and cobalt ferrites with respect to electrical and magnetic properties are carried out. Also, the role of microstructure in affecting these properties is included. These ferrites possess wide range of applications. In 1983, Johnson and Robbis et al [36] have reported that, magnesium based ferrites can be used as negative temperature coefficient thermistors. The important application of this mixed Mg-Co ferrite is associated with the switching behaviour, as it has square hysteresis loop [25]. The addition of 40% cobalt in magnesium ferrite increases the resistivity of the sample, hence the magnetic and dielectric losses are less. Hence it is widely used in microwave technology. The substitution of cobalt in magnesium ferrites also varies the microstructure and hence the relevant properties. In order to establish co-relationship between structure and properties, the following experimental studies have been undertaken.

1) Preparation of magnesium-cobalt ferrites with the general formula,

$$Mg_{(1-x)} \, Co_x \, Fe_2O_4 \; (\; x = 0.0, \; 0.4, \; 1.0)$$

2) Characterization of the ferrites by X-ray diffraction.

3) Resistivity studies of samples.

4) Measurment of magnetization.

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