Chapter-I

Ferrites - An Inbroduction.

CHAPTER- I

FERRITES - AN INTRODUCTION

1.1 INTRODUCTION :

First natural magnetic material known to man was load stone. The chemical formula for the load stone is $FeOFe_2O_3$ (ferrous ferrite). Ferrites are important class of ferrimagnetic materials. Now a days ferrites are artifically prepared by mixing metal oxides and iron oxides. Ferrites possess wide range of magnetisation and shows hightened electrical resistivity which can be used to propagate high field electromagnetic waves with low attenuation.

The technological importance of ferrites can be gauged from the spectrum of applications. Magnetically soft ferrites finds wide application in high frequency and pulse transformers, inductors. reflection coils. antennas, modulators and number of other applications depending on the requirements of high permeabilities and low losses at high frequencies. Ferrites with square loop characteristics of B-H curve, find extensive use in computers, memory devices and flip-flops. Ferrites of lower permeability and larger magnetostriction are useful in acclerometers, mechanical filters and ultrasonic generators. Microwave applications depends on the nature of gyromagnetic resonance of ferrites which are exemplified in faraday rotation, phase shifters, circulators and modulators.

1.2 HISTORICAL :

The first known magnetic material was made available by

nature itself is magnetite $(FeOFe_2O_3)$. Hilpert¹ was working with synthetic ferrites to reduce eddy curret losses in inductors and transformers. But ferrite prepared by him did not meet some of the above said properties and exhibited heavy losses and low permeability. After some years Kato and Takai², Forestier³, Barth and Posnjack⁴ have undertaken studies of these materials from the point of view to understand the theories of ferromagnetism.

Latter on Snoek^{5,6} carried out extensive and systematic studies of preparation of ferrites and their magnetic properties. This leads to various applications of ferrites. Verwey⁷ showed that the crystal structure of various ferrites with inverted spinel structure to be ferrimagnetic, whereas those with normal structure to be nonmagnetic.

The basic theory of spin-spin interaction in ferrites was announced by Neel⁸ and introduced the idea of magnetic sublattices by applying the same molecular field theory of exchange interaction in ferromagntic materials except the possibilities of spin alignment in the antiparallel sense. A more detailed examination of basic interaction was made by Anderson⁹ and Van-Vleck¹⁰ who developed the theory of superexchange.

.

Kittel¹¹ extended and Yafet the theory of magnetic by postulating a 'triangular' arrangement of sublattices three sublattices. When antiferromagnetic exchange interactions between sub-lattices is comparable to that among spin moments within

sublattices formed by Fe^{3+} ions on tetrahedral and octahedral sites. Gorter¹² and Gulliaud¹³ gave the direct experimental proof of Neel's theory. Gorter measured the magnetisation of Mn, Fe, Co, Ni, Cu and Mg ferrites mixed with Zn ferrite as a function of Zn composition.

Gulliaud et al explained the variation of magnetisation as a function of temperatue for mixed ferrites. Neel modified the earlier theoretical treatment which could not account for the temperature dependence of Weiss molecular interaction constant as per experiments. The modified theory was confirmed positively by results. The direct proof of Neel's model experimental of ferrimagnetism came up only with neutron diffraction studies on Smart¹⁴ Gorter¹⁵ magnetite and zinc ferrites. and co-related independently the cation distribution found out by microwave resonance and magnetisation.

During last thirty years, a substantial effort has been put in various laboratories to prepare ferrite materials to cater the quantitative and qualitative demands of the industry. The present hightened interest in the ferrites is brought about by the recent growth in the use of high frequency power supplies primarily for computers and digital devices.

The table 1.1 shows the wide spectrum of applications of ferrites.¹⁶

TABLE 1.1

Crystal structure		Magnetic property		Composition	Applications
A)	Spinel +	a)	Soft ferrite	M ²⁺ F ³⁺ ₂ O	Transformer core,
	(cubic)			where,	recording head,
				M = Mg,Mn,	antenna rod, loading
				Fe, Co, Ni,	coil, memory
				Zn, Cu, Cd	microwave devices.
		b)	Square loop	Mg-Mn-Zn-Fe	Computer memory
			ferrite	Li-Ni-Fe	logic devices.
B)	Hexagonal ferrite		Hard ferrite	м ²⁺ ғе ₁₂ 0 ₁₉	Permanent magnet relays, loud speakers
					small motors,generators
C)	Garnet		Microwave	R ₃ Fe ₅ O ₁₂	Phase shifter, swithes
	(cubic)		ferrite	R =yttrium	isolators, bubble
				or rare	memory, and tunable
				earth element	devices
D)	Ortho		Microwave	RFe ³⁺ 0₄	Bubble memory.
	ferrites		ferrite	R≌ yttrium or rare earth	
				element.	

WIDE SPECTRUM OF APPLICATIONS OF FERRITRES.

1.3 CRYSTAL STRUCTURE :

Magnetic oxides shows different types of crystal structure.

~

a) Spinel structure (b) Hexagonal structure

c) Garnet structure (d) Perovksite struture

The salient features of the spinel structure are given below.

1.3 (a) SPINEL STRUCTURE :

Ferrites, generally have the chemical formula $M^{2+}Fe_2^{3+}O_4^{-}$ or $MOFe_2O_3$, where M is divalent metal ion and Fe is trivalent ion. All the compounds of this type have a cubic face centred crystal structure (Fig. 1.1) of the space group Q_h^7 (Fd₃m) with a unit cell containing 8 formula units. Wyckoff (1951) gives the spinel space group as Q_h^7 (Fd₃m) and the ionic positions as :

Cation (5/8, 5/8, 5/8, 5/8, 7/8, 7/8, 7/8, 5/8, 7/8, 7/8, 5/8) 16C

Cation : (0,0, 0; 1/4, 1/4, 1/4)8_F

with the translations, for a face-centred lattice, (0,0,0), (0, 1/2, 1/2) (1/2, 0, 1/2) (1/2, 1/2, 0)

There are two distinctly different types of interstitial positions, one as 'tetrahederal' or 'A-site', in which magnetic ion





Fig. 1.1

is surrounded by four oxygen ions located at the corners of a tetrahedron and the second as 'octahedral' or 'B-site', in which magnetic ion is surrounded by six oxygen ions. There are in all 96 interstitial sites per unit cell, out of which 64 being tetrahedral and 32 being octahedral. Not all, but 8 tetrahedral and 16 octahedral sites are occupied by cations per unit cell.

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

1.3.(a-1) NORMAL SPINEL FERRITE :

It has been stated that there are 16 B-sites and 8 A-site occupied in unit cell and there are 16 trivalent and 8-divalent cations. How the ions the ions are distributed over the sites ? ^{One} abvious guess would put the trivalent ions on B-sites and divalent ions on A-site and is known as normal spinel ferrite. The cation distribution of normal spinel ferrite as,

$$(M^{2+})^{A}$$
 $(Fe^{3+}Fe^{3+})^{B}O_{4}^{2-}$ (1.1)

This does not show ferrimagnetic in behaviour. The examples of normal spinel ferrites are $CdFe_2O_4$ and $ZnFe_2O_4$.

1.3.(a-2) INVERSE SPINEL FERRITE :

In this case 8-divalent ions are on B-sites and 16-trivalent

ions occurs, 8-on B-sites and 8-on A-site. Then the structure is called as inverse or inverted spinel. The general cation distribution may be represented as,

$$(Fe_1^{3+})^A(M_1^{2+}Fe_1^{3+})^B O_4^{2-} \dots \dots (1.2)$$

The inverse spinel ferrites shows ferrimagnetic behaviour. The examples are Fe_3O_4 , $NiFe_2O_4$.

1.3.(a-3) RANDOM SPINEL FERRITES :

ions and Fe³⁺ м²⁺ this type ions are randomly In Α В sites depending distributed over the and on the physico-chemical condition of preparation. The general formula for the partially inverse ferrites is represented by,

$$(M_x^{2+} Fe_{1-x}^{3+})^A (M_{1-x}^{2+} Fe_{1-x}^{3+})^B O_4^{2-} \dots \dots (1.3)$$

where X = is coefficient of normacy and 1 - X = is coefficient of inversion.

The examples are $MgFe_2O_4$ and $CuFe_2O_4$.

1.4 MAGNETIC PROPERTIES OF FERRITES :

In ferrites the oxygen ion give rise two sub-lattice which are characterised by different oxygen environments for the metal atoms. Magnetic interactions within the sub-lattice gives rise to a sub-lattice magnetisation. Magnetisation of the two sub-lattices are not equal at a temperature, and are opposite, so the net magnetisation results as the case of ferromagnetic materials. Therefore the ferrites exhibit all the properties similar to those of ferromagnetic materials.

The properties of ferrites can be classified into two categories such as intrinsic and structure sensitive, saturation magnetisation, anisotropy, magneto-striction and Curie temperature are the intrinsic properties, while permeability, hysteresis, resistivity and dielectric constant are very much structure sensitive. The structural aspects such as grain size, porosity, impurities and inclusions of non magnetic ions, which are very much sensitive to above said properties.

1.4.(a) MAGNETISATION IN FERRITES :

The two sub-lattice model is used to explain the magnetisation process in spinel ferrites. The normal spinel ferrites are non-magnetic. On the other hand inverse spinel ferrites are magnetic. However, for the mixed ferrite system the observed magnetisation could not be explained.

For the inverse spinel ferrite, the formula is,

$$(Fe^{3+})^{A}(M^{2+}Fe^{3+})^{B}O_{4}^{2-}$$
(1.4)

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

$$(Fe_A^{\dagger 5} \mu_B) (Fe_B^{\dagger 5} \mu_B^{\dagger 5} M_B^{\dagger}) \qquad \dots \dots (1.5)$$

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

 $((1 - x) M_A^{\dagger} XFe_A) ((1 - x) Fe_B^{\dagger} X M_B^{\dagger} \dots (1.6))$

The net moment $\mu_{_{\mathbf{B}}}$ is written as,

$$\mu_{B} = M((1-X) -X) -5(1 + (1-X) -X)$$

= M(1-2X) - 10(1-X)(1.7)

But for normal spinels, X = 0and for Inverse spinels, X = 1.

The indirect exchange coupling between metallic ions acting through the oxygen ions is maximum. For those ions A and B, for which the angle AOB is close to 180° . For the perfect spinel lattice the major angles between the ions are A - O -B = 125° g and $154^{\circ}34^{\circ}$, B - O - B = 90° and $125^{\circ}9^{\circ}$ and A - O -A = $79^{\circ}34^{\circ}$ (Fig.1.2). The nearest to perfect alignment are those Fe_A and Fe_B ions making $154^{\circ}34^{\circ}$ which gives the strong antiferromagnetic coupling.

1.4 (b) ANISOTROPY :

The term anisotropy describe the directionality of magnetisation along certain crystallographic direction, known as easy



direction. The energy which can be applied to change the direction of magnetisation from easy direction to hard direction is known as anisotropy energy. It plays an important role in determining the properties like permeability, hysteresis and magnetostriction.¹⁷

In cubic material, the energy is described as,

$$E = K_0 + K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + K_2(\alpha_1^2 \alpha_2^2 \alpha_3^2) \qquad \dots \dots (1.8)$$

where K_0 , K_1 and K_2 are anisotropy constants and $\alpha_1, \alpha_2, \alpha_3$ be the direction cosines.

When mangetisation vector deviates from preferred direction, the anisotropy energy increases. This increase in energy is due to the effective field (Ha) acting on the spins. The anisotropy constant varies with crystal structure and kind of magnetic ions. electronic structure of magnetic ions The also contributes to anisotropy constant¹⁸ Magnetic anisotropy may also arises due to stress anisotropy and shape anisotropy. Stress anisotropy may be reduced by slow cooling of specimen. Shape anistropy may be reduced by preparing ferrites in such a way as voids are spherical and few in number with the help of prolonged sintering.¹⁹

1.5 NEEL'S THEORY FOR FERRIMAGNETISM :

Neel assumed that the ferrimagnetic crystal lattice could be divided into two sublattices formed by A-site (tetrahedral) and B-site (octahedral) in a spinel structure. He defined the interaction within the material from the Weiss molecular field. The magnetic field acting upon an atom or ion is written as,

$$H = H_0 + Hm$$
(1.9)

where H_0 is external applied field and Hm is internal or molecular field. When the concept of molecular field is applied to ferrimagnetic material, we have,

$$H_A = H_{AA} + H_{AB}$$
 and $H_B = H_{BB} + H_{BA} \dots (1.10)$

The molecular field components may be written as,

$$H_{AA} = \gamma_{AA}M_{A}, \quad H_{AB} = \gamma_{AB}M_{B}$$
$$H_{BB} = \gamma_{BB}M_{B}, \quad H_{BA} = \gamma\gamma_{BA}M_{A} \qquad \dots \dots (1.11)$$

where γ 's are appropriate molecular field coefficient and M_A and M_B are magnetic moment of A and B sublattices.

1.5 (a) PARAMAGNETIC REGION :

In this region, the magnetisation is given by,

$$M = NgJ \mu_B BJ(X)$$
(1.12)

where N is free paramagnetic ions per unit volume.

J is angular momentum quantum number.

The Brilliouin function BJ(X) is given by,

$$BJ(X) = \frac{2J + 1}{2J} \operatorname{coth} \left(\frac{2J + 1}{2J} - \frac{1}{2J} \operatorname{coth} \left(\frac{X}{2J}\right) \right)$$
....(1.13)

and
$$X = \mu_0 g_J - \frac{\mu_{B}}{kT} \dots \dots (1.14)$$

where, K is Boltzman's constant

and T is absolute temperature.

writting $\chi = M/H_0$ and $M = M_A + M_B$ and after necessary algebric manipulation, Neel rewrite the equation of susceptibility as,

$$1/\chi = T/c + 1/\chi_{0}^{0} - \xi/T - \theta \qquad(1.15)$$

where $1/\chi_{0} = \gamma_{AB}(2\lambda\mu - \lambda^{2}\alpha - \mu^{2}\beta)$

$$\theta = \gamma_{AB} \lambda \mu c (2 + \alpha + \beta)$$
and
$$\xi = \gamma_{AB} \lambda \mu c (\lambda (1 + \alpha) - \mu (1 + \beta))^{2}$$

The λ and μ are the fractions appeared on A-site and on B-site respectively such that $\lambda + \mu = 1$.

The paramagnetic Curie point $T_{\rm p}$ is found by equating $1/\chi$ to zero and yields

$$T_{p} = \frac{\gamma_{AB}C}{2} \left(\lambda \alpha + \mu \beta + \left(\left\{ \lambda \alpha - \mu \beta \right\}^{2} + 4\lambda \mu \right)^{\frac{1}{2}} \right) \dots (1.16)$$

1.5 (b) SPONTANEOUS MAGNETISATION :

The equation (1.16) may be written as,

$$T'_{P} = \gamma_{AB} C/2 (\lambda \alpha + \mu \beta - ((\lambda \alpha - \mu \beta)^{2} + 4\lambda \mu)^{1/2})$$
..... (1.17)

 T_P is Curie temperature when M_A and M_B are antiparallel and T_P^i is Curie temperature when M_A and M_B are parallel.

In ferromagnetic material, the spontaneous magnetisation M_{SP} may depends on the temperature and is given by,

$$M_{SP} = NgJ\mu_B BJ (X) \dots (1.18)$$

In the absence of an applied field, the Brillouin function parameter becomes,

$$X = \mu_0 Jg \quad \mu_B \gamma M_{SP} / kT \qquad \dots (1.19)$$

The magnetisation M_A and M_B cannot be observed independently, so the net magnetisation 'M' can be written as,

$$M = M_A + M_B$$
(1.20)

Spontaneous magnetisation can be written by assuming the similar behaviour below and above Cuire point. Thus

$$MA_{SP}/MA_{Sat} = BJ (\mu_0 g \mu_B J H_A/kT) \dots (1.21)$$

and $MB_{SP}/MB_{sat} = BJ$ ($\mu_0 g \ \mu_B JH_B/kT$)(1.22) The observed total spontaneous magnetisation is given by,

- -

$$M_{SP} = MB_{SP} - MA_{SP} \qquad \dots \dots (1.23)$$

The solution of M_{SP} with variation of temperatures cannot be found analytically. For solving these, graphical method²⁰ are used and known as (σ ,T) curves (Fig. 1.3) where

$$\sigma = M_{SP} / M_{sat}$$
 and $\tau = T / T_P$ (1.24)



Fig 1.3

i

.

(σ , T) curves must depend on relative values of interactions and relative magnitudes of sub-lattice magnetisations. In simple Neel's model, where only on type of magnetic ion is present and σ must depend on α , β and λ (hence $\mu = 1 - \lambda$).

1.6 YAFET- KITTLE THEORY :

Neel's model was inadequate for the spinel containing chief constituents other than Fe, where the observed magnetisation is much smaller than calculated by Neel's model for spin arrangement. There is difficulty regarding M, R and V types of curves arises from an oversimplication. This was first suggested by Yafet and Kittel ²¹ by considering triangular spin arrangement.

They considered the possibility of subdivision of each sublattice in order to take into account ordering within a sublattice of a type other than parallel arrangement of all spins. They found that when strong interaction exist with sublattice B, the two equivalent substructure B_1 and B_2 are both spontaneously magnetised, but their magnetisation are not exactly antiparallel. Instead of this, they are aligned at some angle other than 180° . Thus there is resultant magnetisation of the B lattice which gets antiparallel with the magnetisation of A-sublattice.

These so called triangular arrangement within the lattice results in the values of reduced magnetisation of the same order as that prdicted by Neel's model, but they have lower free energy

and are free from thermodynamic difficulties near $O^{O}K$, which Neel's calculation encounter.

1.7 PERMEABILITY :

In ferrites, it was found that the permeability strongly depends on chemical composition and temperature. When magnetic material is subjected to an a-c field, certain amount of energy is absorbed by the material as dissipated as heat. The permeability is given by,

$$\mu = B/H$$
(1.25)

The complex permeability is denoted by,

$$\bar{\mu} = \mu' - J\mu''$$
(1.26)

where μ' is the component of the magnetisation which is in phase with the driving magnetic field and μ'' is the component which is delayed in phase by 90⁰ from the field. The energy loss associated with the delay angle ' δ ' of magnetisation is usually expressed by loss factor as,

$$\mu'' \mu' = \tan \delta$$
(1.27)

The important mechanism of losses are hysteresis, eddy current, spin resonance and wall resonance. The relaxation losses in ferrites are due to exchange of electrons between Fe^{2+} and Fe^{3+} ions. Because of loss mechanism cause a phase difference between B and H. If μ_1 and μ_2 are the permeabilities at the temperature θ_1 and θ_2 then, the temperature factor ${}^{\prime}\alpha_{\rm F}{}^{\prime}$ is given by,

$$\alpha_{\rm F} = \mu_2 - \mu_1 / \mu_1 \mu_2 (\theta_2 - \theta_1) \qquad \dots (1.28)$$

The permeability is normally taken to be the real part of initial permeability.

1.8 ELECTRICAL PROPERTIES OF FERRITES :

Ferrites are semiconductors and their resistance can vary from $10^{-3} \Omega$ cm to $10^{11} \Omega$ cm at room temperature.²² The mechanism of charge transport controls the physical and chemical properties of ferrites, which can be studied from the measurement of electrical conductivity, thermo-electric power and Hall-coefficient. The charge transport can vary with the composition of ferrites and methods of preparation.

1.8(a) CONDUCTIVITY :

Being a semiconductor, resistivity of ferrite obeys the relation as,

$$\rho = \rho_{exp}$$
 (Eg/kT)(1.29)

where Eg is energy required to cause an electron jump. Plot of \log_{ρ} versus 1/T shows a linear behaviour and break occurs near the temperature which corresponds closely with Curie temperature.²⁸ The range of values of 'Eg' varies between 0.1 eV to 0.5 eV approximately. In general the substitution of a cation that tends

to stay in lower valance state leds to P-type conduction and substitution of cation that tends to stay in higher valance state leads to n-type. conduction.

Electronic conduction of ferrites can be associated with the presence of ions of given element in more than one valance states distributed randomly over crystallographically equivalent lattice points. In ferrite conductivity is attributed to the occurance of both Fe^{2+} and Fe^{3+} ions on identical lattice sites in spinel structure. Under this situation the electron can move from trivalent iron ion to divalent iron ion within octahedral positions without causing the change in the energy state of a crystal as a result of transitions. The example is $Fe^{2+}Fe^{3+}_2O^{4-}$, one of the non metallic conductors.²³ The presence of Fe^{2+} ion will be considered to assure reduced resistivity in ferrite system. The resistivity will also be caused by following factors apart from the inherent properties of the material.

1.8 (b) DIELECTRIC PROPERTIES :

Ferrite is an insulator, but eventhough in a ferrite eddy current may flow due to dielectric displacement. In ferrites three principle mechanism of polarisation can be distinguished within a frequency range from zero to ultra-voilet frequency region. At high optical frequency and ultra-violet frequency, the abosrption due to actual electron transition become important. The absorption caused by conduction electrons migrating between iron ions on the octahedral

sites by transition from 3d to 45 states and by transition involving the oxygen anions and various cations. At frequency below infrared, the mechanism is atomic or ionic polarisation which arises by the movement of cations and anions. Below the microwaye frequency polarisation arises from the macrostructure of region the polycrystalline material and from the migration of free charge carrier. These charge carriers are trapped at the grain boundaries. Field distribution results due to space charge and shows an increase in permittivity. The ferrites have permittivity is in between 10 to 20.

Koop's²⁴ described good phenomenological theory of dielectric dispersion in ferrites at low frequencies. This theory is based on the assumption of parallel resistance and capacitance of material results from an equivalent circuit and which is equivalent to solid state model consisting of compact of relatively good conducting grains seperated by poor conducting layers or grains. The theoretical and observed frequency variation of dielectric constant and resistivity are in good agreement for same samples.

Kamiyoshi²⁵ and Fairweather²⁶ obtained the activation energy from temperature variation with relaxation time. This energy agrees well with those obtained from temperature variation with resistivity. The high dielectric constant may arises at low frequency due to oxygen ion which have three B-site and one A-site neighbours. This is justified in the view of the fact that the oxygen possesses the maximum polarizability.

1.9 ORIENTATION OF THE PROBLEM :

Ferrites are magnetic oxides containing iron as a major metallic component. Magnetic performance of ferrites leads to their classification as soft, hard, square loop and microwave ferrites. The application of ferrites in telecommunication and other microwave devices are widely known and a number of review articles, technical reports and proceeding of international conference are available.¹⁶ The properties of ferrites for technical application depend on the combination of intrinsic properties, such as saturation magnetisation, Curie temperature etc. and the microstructure of ferrites commercially important ferrites required high purity, chemical homogeneity and grain size and high density. High density with minimum uniform grain size is desired for low loss ferrites.

During the early days of soft ferrites, applications were primarly in the telecommunication. When television arrived, they were used as flyback transformers or deflection yokes. Prof. Takai.²⁷ pointed out the need of new power ferrite material in the international conference on ferrites (1980). The characteristics of power ferrites are, (i) They have to possess high saturation, (ii) They require relatively low core losses at high flux densities (near the position of maximum permeability) and at fairly high frequencies. To achieve these properties new compositions have to be formulated to obtain high saturation. Secondly, for the losses conditions of operations, the microstructure also have to be optimised.

Most widely used ferrites are Ni-Zn, Mg-Zn, and Mn-Zn and the amount of these materials used are much larger than the other ferrites. The studies of Ni-Cd ferrites by other workers indicate that their magnetic properties are comparable to those of Ni-Zn ferrites, where as these have low resistivity resulting in the higher losses. Recent work have been concerned with the effect of additives, such as V_2O_5 , C_0O and Al_2O_3 which act as a flux on sintering and magnetic properties of Mn-Zn, Ni-Zn ferrites.²⁸ It was earlier shown that the incorporation of tetravalent dimagnetic ions like Ti, Sn, Si in Ni-Zn can significantly improve their electrical properties.²⁹ ferrites Recently, the electrical and magnetic properties of Sn substituted Ni-Cd ferrite were studied by Puri³⁰ et al. They have observed that the resistivity increases increasing Sn content, with where as saturation magnetisation decreasess.

In view of these facts it was thought worth while to undertake the following studies of Ni-Cd system substituted with tetravalent Mn. i) Preparation of the series with the formula $Cd_{0.3}^{Ni}_{0.7+t}Mn_t^{Fe}_{2-2t}_4$ where t = 0 to 0.4 by ceramic method.

ii) X-ray diffraction studies : Confirmation of single phase formation and spinel structure. Calculation of lattice constant and bond length.

Microstructure : Study of microstructure by using S.E.M.
 technique to observe the developed microstructure, grain size, grain
 growth etc.

1

iv) Magnetisation and permeability : To understand the magnetic behaviour of the substituted element and cation distribution and Curie temperature.

v) D.C. and A.C. conductivity : To understand the conduction phenomenon.

REFERENCES

- Hilpert, Ber Deut Chem. Ges. 42, 2248 (1909). 1. Kato Y. Takai, Trans Am. Electrochem. Soc. 57, 297 (1930). 2. 3. Forestier H., Vetter M., Compt. rend 209, 164 (1939). Barth T.F.W., Posnjack E., Z. Krist 82,325 (1932). 4. 5. Snoek J.L., Physica 3, 463 (1936). Snoek J.L., "New Developments in Ferromagnetic material" 6. 2nd Ed. Elsevier Press Inc. New York (1949). Verwey E.J.W., F.C. Romeijn and E.L. Heilman, J.Chem. Phys. 7. 15 174, 181 (1947). Neel L., Proc. Phys. Soc. (London) A 65, 869 (1952). 8. 9. Anderson P.W., Phys. Rev. 79, 350 (1950). Theory 10. Van-Vleck J.H., of electric and magnetic susceptibilities. Clarendon Press, Oxford (1932). J.Phys. Radium, Paris 12, 262 (1951). 11. Yafet Y and Kittel C., Phys. Rev. 87, 290. (1952). 12. Gorter E.W., Phillips Res. Report 9, 295 (1954). 13. Gulliaud C.J., Phys. Radium 12, 239 (1951).
- 14. Smart J.S., Phys. Rev. <u>94</u>, 847 (1954).
- 15. Gorter E.W., Nature <u>173</u>, 123 (1954).
- K.C.Patil, S.Sundar Manoharam and D. Gajapathy, 'Hand book of ceramics and composites Vol <u>1</u>. Ed. Nicholos P.Cheremisionoff M. Dekker. Inc. N.Y. (1990).
- 17. Broese van Groenov, Bongers P.F., Stuyts A.L., Mater. Sci. Eng. 3, 317 (1968/1969).

- J.Kanamori, in 'Magnetism' G.T. Rado and Shull C.G., edi.
 Academic Press N.Y. P-127 (1963).
- 19. Gray T.J., "Oxide Spinels" In high temperature oxides part IV Edited by A.M. Alper, Academic Press, New York P-77 (1971).
- 20. Standley K.J., 'Oxide magnetic material' 2nd Edition Clarendon Press Oxford P.139 (1972).
- 21. Yafet Y., Kittel C., Phys. Rev. 87, 290 (1952).
- 22. Van Uitert L.G., Proc. I.R.E. 44, 1294 (1956).
- Komar A.P., Kliushin V.V., Bull. Acad. Sci. USSR <u>18</u>, 403 (1954).
- 24. Koops C.G., Phys. Rev. <u>83</u>, 121 (1951).
- 25. Kamiyoshi K., Sci. Rep. Res. Insts. Thooku Univ. <u>A-3</u>, 716 (1957).
- 26. Fairweather A., Frost E.I., Proc. Inst. elect. Engine <u>100</u>, 15, (1953).
- 27. C.M. Srivastava, M.J. Patni, Edi. Proc. ICF-5 Oxford and IBH publishing Co. Pvt. Ltd., New Delhi, 1989.
- 28. SU-IL PYUN and JONG-TAE BAEK, Am. Ceram. Soc. Bull 64(4) 602-05 (1985).
- 29. B.K. Das, Preparation and characterisation of materials, Edi by J.M. Honig, C.N.R. Rao, Academic Press N.Y.(1981).
- 30. R.K.Puri and Vijayalakshmi Satyen, Proc. ICF. 5. 1989 India. 245.