CHAPTER - I

MAGNETIC MATERIALS - THE FERRITES

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1.1 Introduction :

Lode stone was the first magnetic material known to man. The chemical formula for lode stone is $FeOFe_2O_3$ (Ferrous ferrite) and is nothing but naturally occuring ferrite. The ferrites are magnetic materials, essentially mixed crystals of various magnetic oxides. They may be considered to consist of oxygen ions in a closed-packed structure with cations fitted in to interstices.

Hilpart (1909) was working with synthetic ferrites to reduce eddy current losses in inductors and transformers. However, Hilpart's attempt was inadequate to achieve the goal. After some years ferrites were studied in theory by Kato and Takai(1), Foreotier(2), Barth and Posjnak(3) from various points of view.

During the Second-World-War, Snoek(4) and his colleagues carried out extensive experimental work on ferrites with particular interest of preparation of ferrite and their magnetic properties. In the same period, Neel's(5) theory of ferrimagnetism added impetus to the research activity in this class of magnetic material. Successes were achieved due to the fact that, ferrites have importance as magnetic materials possessing a wide range of magnetization, property of electrical insulation(4) low attenuation which leads to the propogation of high field electromagnetic wares.

At present in the field of electronic industry, communication (at high frequency and microwave frequency) and computers (memory storage and memory switching circuits), researchers are working in manufacturing and towards improvement of ferrites.

1.2 Classification of Magnetic Materials :

The magnetic moments are associated with atoms of any substance due to orbital angular momentum about the nucleus, spin with which electrons endowed and orbital momentum induced by an applied magnetic field. The magnetic properties of material in bulk depend on the magnetic moments of free atoms or molecules, thermal energy and interatomic forces in the crystals.

Magnetic materials are broadly classified into diamagnetic, paramagnetic and ferromagnetic based on experimental fact, first observed by Faraday. If magnetization (M) produced in the magnetic material, due to applied magnetic field (H), is in the same direction as that of H, sample will be attracted towards the region of stronger field in the field gradient, while sample will be repelled when M is produced in the reverse direction.

Diamagnetic Materials : The material in which every electron in the bulk produces negative component of intensity of magnetization M with reference to applied field H, irrespective of original and unchanging angle between applied field and precessing axes are known as diamagnetic materials. This class of materials have small and negative susceptibility χ ($\chi = \frac{M}{H}$). Net diamagnetic behaviour is observed in a number of salts and metals and in the rare gases, in which there is zero moment.

Paramagnetic Materials : The material in which each atom or molecule produces component of intensity of magnetization (M) in the field direction (H) as described by the classical Langevin function are known as paramagnetic materials. This class of materials have small and positive susceptibility (χ), which is a function of absolute temperature. These substances contain atoms or ions with at least one incomplete electron shell, rendering them a non-zero atomic or ionic magnetic moment.

Ferro-magnetic Materials : The materials in which "spontaneous magnetization" exists due to strongly coupled atomic dipole moments tend to be aligned parallel, even in the absence of external magnetic field are known as, ferromagnetic materials. Above a critical temperature, T_C, called the ferromagnetic Curie temperature, the spontaneous magnetization vanishes.

In case of ferromagnetic materials, χ is small and positive above Curie temperature while large for smaller fields.

In this class of materials, magnetic moment is mostly due to spin. Orbital moments are quenched by the electric fields of the neighbouring atoms/ions in the crystal lattice.

For small M, the Langevin function gives,

$M = \frac{CH}{T}$, where C is a constant. Weiss pointed out that if, the field H were intensified by an additional field, NM, proportional to magnetization, the temperature dependence becomes

$$M = \frac{CH}{T-T_c} \quad , \quad \text{where } T_c = NC.$$

This is the Curie - Weiss law approximately obeyed by ferromagnetic materials above Curie point.

The Weiss molecular field is the result of quantum mechanical exchange interactions.

Only a few materials exhibit ferromagnetism. The great majority of ferromagnetic materials are metals (Viz. Fe, Co, Ni, Gd and Dy) and their alloys. Some ionic compounds also exhibit the same.

Antiferromagnetic Materials : These are materials in which an antiparallel arrangement of the strongly coupled atomic dipoles is favoured. Exchange forces align magnetic moments antiparallel in antiferromagnetic materials; so that there is no external permanent moment. The sign of exchange force depends on atomic spacing and other things. The exchange interactions in some antiferromagnetic materials take place through an intervening atoms such as oxygen. This type of interaction is called "super exchange" interaction. Antiferromagnetic materials have small positive χ for zero external moment, which is maximum at Neel temperature (T_N).

Ferrimagnetic Materials : Ferri-magnetic materials may be regarded as a special case of antiferromagnetic materials, in which more than one type of magnetic ion is present. In this class of material, "Spontaneous magnetization" is exhibited below certain temperature which arises from non-parallel arrangement of the strongly coupled atomic dipoles.. Ferrites, also called "ferrimagnetics", are important examples of this class.

1.3 Crystal Structure of Ferrite :

Ferrites are the magnetic oxides restricted(6) to exhibit spinel structure having the general chemical formula MFe_2O_4, where M represents a divalent metal ion (M^{2+}) and iron is trivalent ion (Fe^{3+}). The compounds of these type have generally a cubic, face centered crystal structure. The oxygen ions form essentially a face centered cubic lattice. The smallest cubic unit cell consists of eight molecules of $M\,Fe_2O_4$ having the range of lattice parameter 'a' from 8.3°A upto 8.5°A(7). Therefore, 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 — Type one is known as, "tetrahadral" or "A-site", in which magnetic ion is surrounded by four oxygen ions, located at the corners of a tetrahedron as shown in Fig. 1.1(a). And the type two is known as, "octahedral" or "B-site", in which magnetic ion is surrounded by six oxygen ions placed at the vertices of an octahedron, as shown in Fig.1.1(b). There are in all 96 interstitial sites per unit cell out of which 64 being tetrahedral and 32 octahedral. Not all, but 8 tetrahedral and 16 octahedral sites are occupied by cations per unit cell. The tetrahedral and octahedral sites are represented in the Fig. 1.2(a) of a unit cell of the spinel lattice. Fig.1.2(b) represents atomic arrangement in (001) plane of the spinal lattice. In this diagram cations in B-sites lie in linear chain. The small unshaded spheres represent A-sites, that are situated either slightly above (M) or below (N), the plane of the diagram. The dotted lines indicate a face of the unit cell. The fcc stacking of the oxygen ions are indicated by large spheres.

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 ferrites are classified on the basis of cation distribution as follows.

1.3 : (a) Normal Spinel Ferrites : In the normal spinel ferrites all the M^{2+} ions occupy the tetrahedral A-sites, while

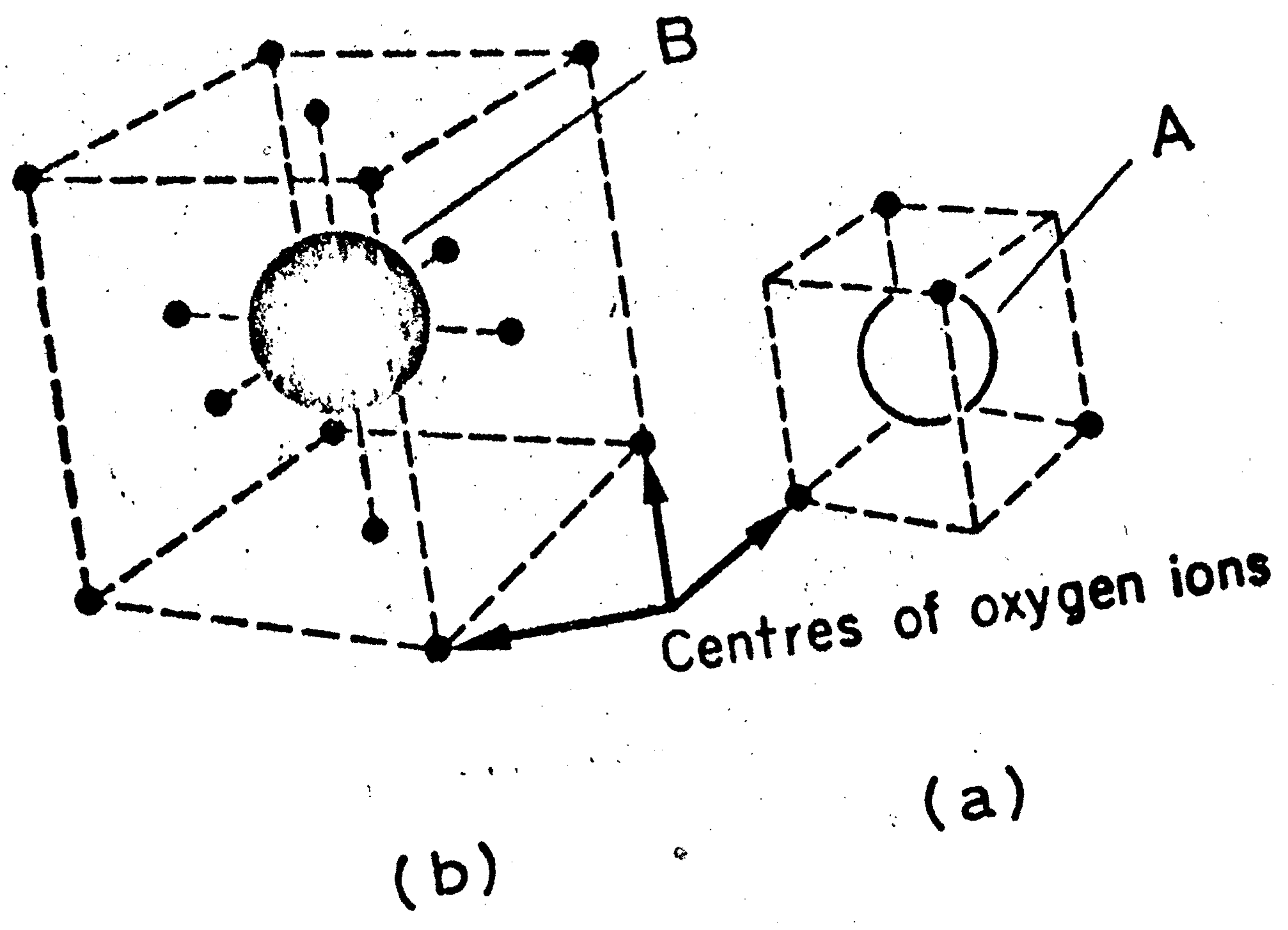


Fig. 1.1

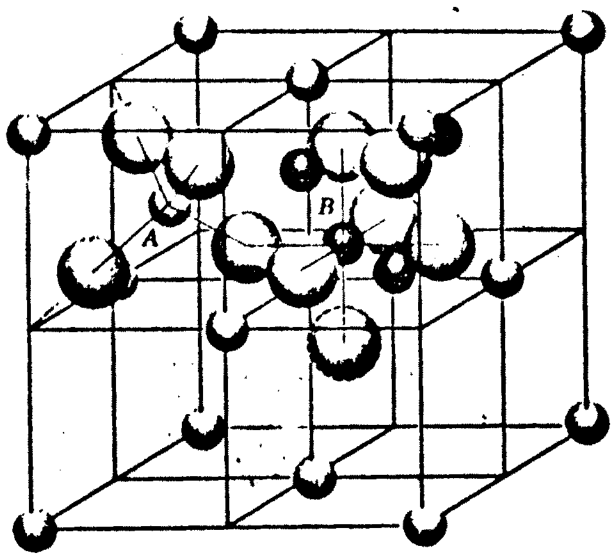


Fig. 1.2(a)

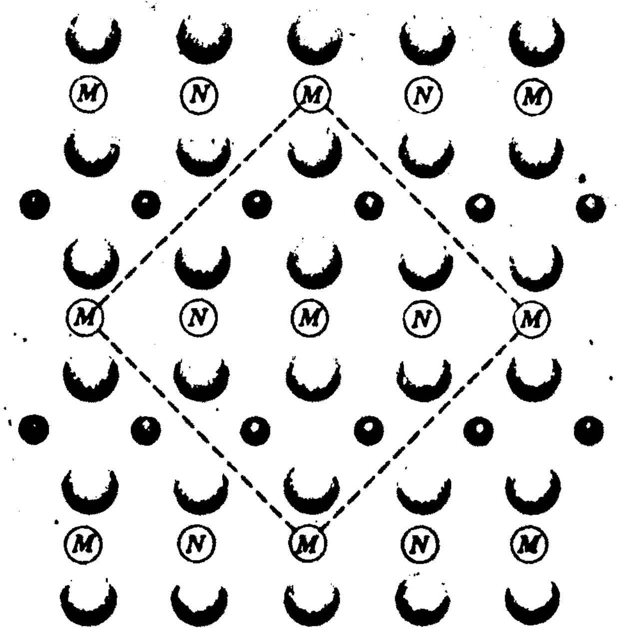


Fig. 1.2(b)

Fe^{3+} ions are in the octahedral B-sites.

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

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

The normal - spinel ferrites do not show ferrimagnetic behaviour.

1.3 : (b) Inverse Spinel Ferrites : In the inverse spinel ferrites, M^{2+} cation and one Fe^{3+} ion occupy B-site while, the second Fe^{3+} ion occupy A-site (i.e. Fe^{3+} ions lie in equal proportion on A and B site). In general the cation distribution may be represented by

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

The inverse spinel ferrites show ferrimagnetic behaviour.

1.3 : (c) 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 preparation. The general formula for the partially inverted ferrites is usually written as

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

An example of the partially inverse spinel structure is manganese ferrite(8) given by

$$[Mn_{0.8}\,Fe_{0.2}]^{A}\;(Mn_{0.2}\,Fe_{1.8})^{B}\,O_4$$

Every oxygen ion the ferrite is surrounded by three B-cation and one A-cation. The angles(9) between A-O-A, B-O-B and A-O-B are given below :

$$A - O - B \simeq 80^\circ$$
$$B - O - B \simeq 90^\circ$$
$$\text{and } A - O - B \simeq 125^\circ$$

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 weaker of the three. In case of ferro-spinels interactions are all negative.

1.4 Substitutional Ferrites :

A few or all divalent metal ions or the iron ions in a ferrite can be substituted by an alternative cation of magnetic or non-magnetic nature(10). The resulting ferrites are called substitutional ferrites. The substitution can be done by two ways :

i) Replacing divalent M' ion by other divalent M'' ion.

ii) Replacing the trivalent iron ions by other trivalent M''' ions.

$$M'Fe_2O_4 \xrightarrow[XM''']{yM''} M'_{1-y}\, M''_y\, Fe_{2-x}\, M'''_2\, O_4.$$

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

($Ni_{1-x}\,Co_xFe_2O_4$ ---> Nickel - Cobalt ferrite)

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

($Ni\,Fe_{2-x}Al_xO_4$ --> Nickel Aluminium ferrite)

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

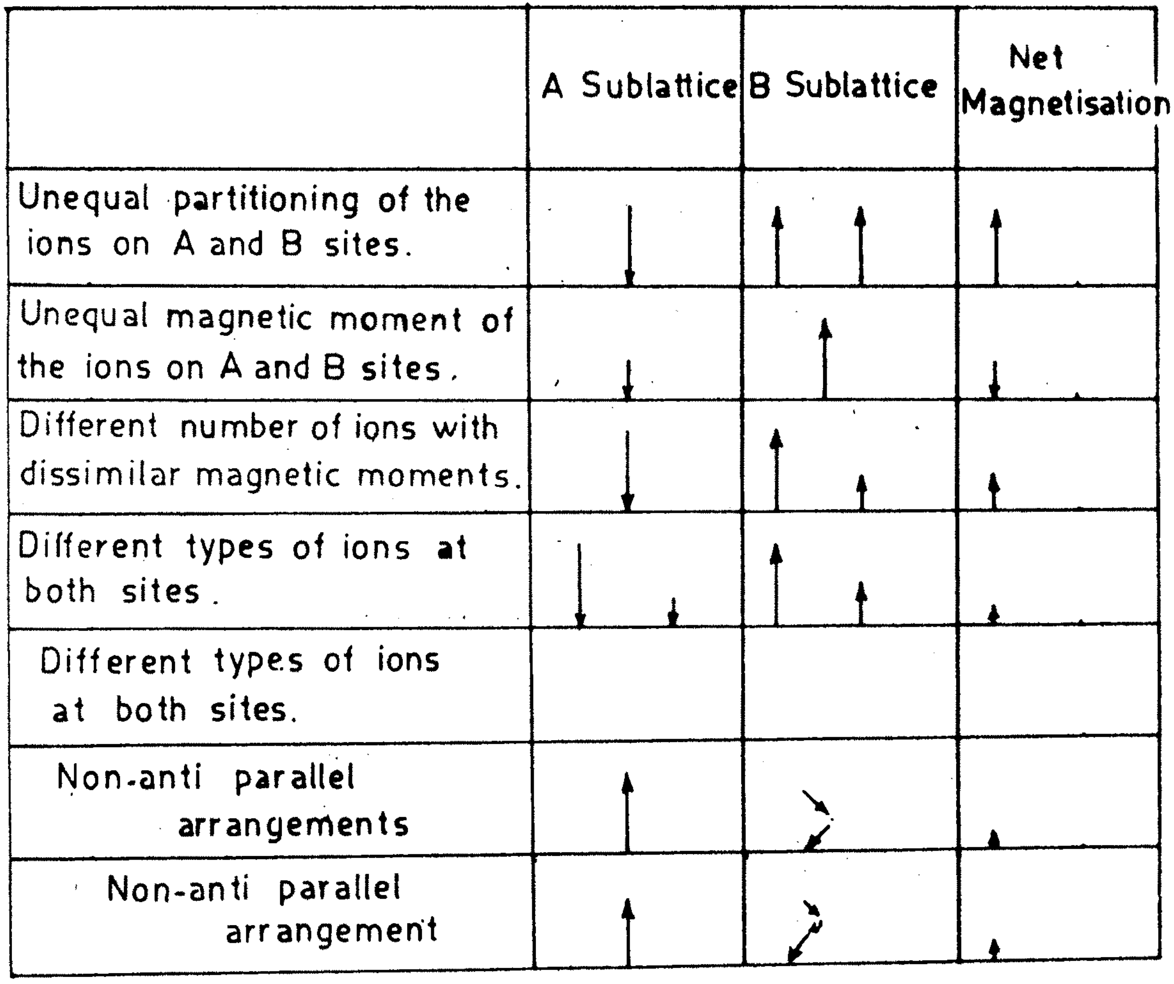
1.5 Magnetic Properties of Ferrites :

1.5 : a) Magnetization In Ferrites : The magnetization exhibited by ferrites was first explained on the basis of Weiss's field theory. However, Weiss field theory neglect(11) two physical phenomenon, one, at very low temperatures single spin interacts with a field that is parallel to the magnetization of its neighbouring rather than with a uniform field parallel to the net magnetization. This attribute small deviation of atomic moment from alignment with its neighbour. Second at and just above Curie point, the Weiss theory predicts that for T > Tc in the absence of external field, the spin order vanishes completely. However, materials show considerable short range magnetic order which has been verified by neutron diffraction.(12,13)

With the help of two-sublattice model, denoted by A and B, ferrimagnetism was explained in detail by Neel(5). The magnetic ions, N per unit volume may be situated on A and B sites. The material possesses net magnetic moment for $\lambda \neq \mu$, where λ, function of magnetization on A-site and $\mu = (1 - \lambda)$ fraction of magnetic ion on B-site. The unequal distribution of magnetic ions occur either due to unequal number of sites on the two sub-lattice or due to ions prefer site on one sub-lattice over those on the other. The site preference depends on, (i) ion size, resite size, (ii) electron configuration of the ion and (iii) symmetry and strength of the crystalline field at a site. For $\lambda = \mu$, material may exhibit ferrimagnetism if magnetic moments of ion on the A and B sites are unequal. The inequality arises due to (i) elements in different ionic states Fe^{2+}, Fe^{3+}, (ii) different elements in the same or different ionic states e.g. Fe^{3+} and Co^{2+} and (iii) different crystalline fields acting at the two sites. Also non-antiparallel arrangements may be possible which attributed to net magnetic moment. The different possible ferrimagnetic arrangements are shown in the Fig. 1.3.

1.5 : b) <u>Structural Explanation of Magnetization In Ferrite</u> :

The ferrites with normal spinel structure do not exhibit ferrimagnetism, e.g. $ZnFe_2O_4$ and $CdFe_2O_4$. In these ferrites,



	A Sublattice	B Sublattice	Net Magnetisation
Unequal partitioning of the ions on A and B sites.	↓	↑ ↑	↑
Unequal magnetic moment of the ions on A and B sites.	↓	↑	↓
Different number of ions with dissimilar magnetic moments.	↓	↑ ↑	↑
Different types of ions at both sites.	↓ ↓	↑ ↑	↑
Different types of ions at both sites.			
Non-anti parallel arrangements	↑	↘ ↙	↑
Non-anti parallel arrangement	↑	↘ ↙	↑

Fig. 1.3

the A-B interaction does not exist due to absence of unpaired electrons in the divalent metal ion (like Zn or Cd); B-B interaction is between similar ions which magnetizes the alternate planes of B-site in opposite direction which results in net zero magnetization.

The intrinsic magnetization exhibited in the ferrite can be explained on the basis of "inverse spinel structure" and the antiparallel arrangement of spins on A and B-sites. The inverse spinel structure have cation distribution

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

The unit cell of a ferrite contains eight molecules. If M_A, the magnetic moment of $8Fe^{3+}$ cations on the A-site and M_B, the net magnetic moment of $8(M^{2+} + Fe^{3+})$ cations on the B-site, the magnetization is given by

$$M = M_B \sim M_A$$

$$\therefore\ M = 8(m_M + m_{Fe}) \sim 8\ m_{Fe}$$

$$\therefore\ M = 8\ mM\ ,$$

where M_A and M_B denote the magnetic moments of the A and B sublattice respectively, m_M and m_{Fe} are the spin magnetic moments of individual ions. Due to super exchange(14) interaction between two cations via an intermediate oxygen ion, provided that, if the three ions are collinear and their separations are not too great, sublattice magnetization are antiparallel.(15)

The ions arranged in the spinels are shown(16) in Fig.1.4. In Fig.1.4 (a) both angle and distance between the ions are favourable for super exchange interaction while for other figures either the angle (1.4 c), distance (1.4 b-d) or both (1.4 e) are unfavourable. This arrangements of ions in the spinel lead us to conclude that interaction between sublattices, A-B, is stronger than those within sublattice A-A or B-B.

The net magnetic moment associated with one formula unit of an inverse spinel ferrites can not exceed 5 Bohr magnetono. 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. Added Zn^{2+} ions have tendency to occupy A-site and therefore it force the same number of Fe^{3+} ions from A-site to B-site(17). The cation distribution of ferrite ($M^{2+}\ Fe_2^{3+}O_4$) can be written as -

$$\overrightarrow{\left[Fe^{3+}\right]^{A}O} \qquad \overleftarrow{(Fe^{3+}M^{2+})^{B}\ O_3}$$

where arrow represents the direction of magnetic moment. On addition of X ($ZnOFe_2O_3$) and (1-X) $\left[FeO(FeM)O_3\right]$, the cation distribution become

$$\left[\overrightarrow{Fe^{3+}_{1-x}}\ Zn^{2+}_{x}\right]^{A}O \qquad (\overleftarrow{Fe^{3+}_{1+x}} + \overleftarrow{M^{2+}_{1-x}})^{B}O_3$$

Therefore, the resultant magnetic moment becomes,

$$n = \left[5(1-x) + m\ (1-x) - 5(1-x)\right] \text{ Bohr magneton}$$
$$= \left[m + (10-m)x\right] \text{ Bohr magneton.}$$

where, m is the magnetic moment of M^{2+} ion in Bohr magnetons.

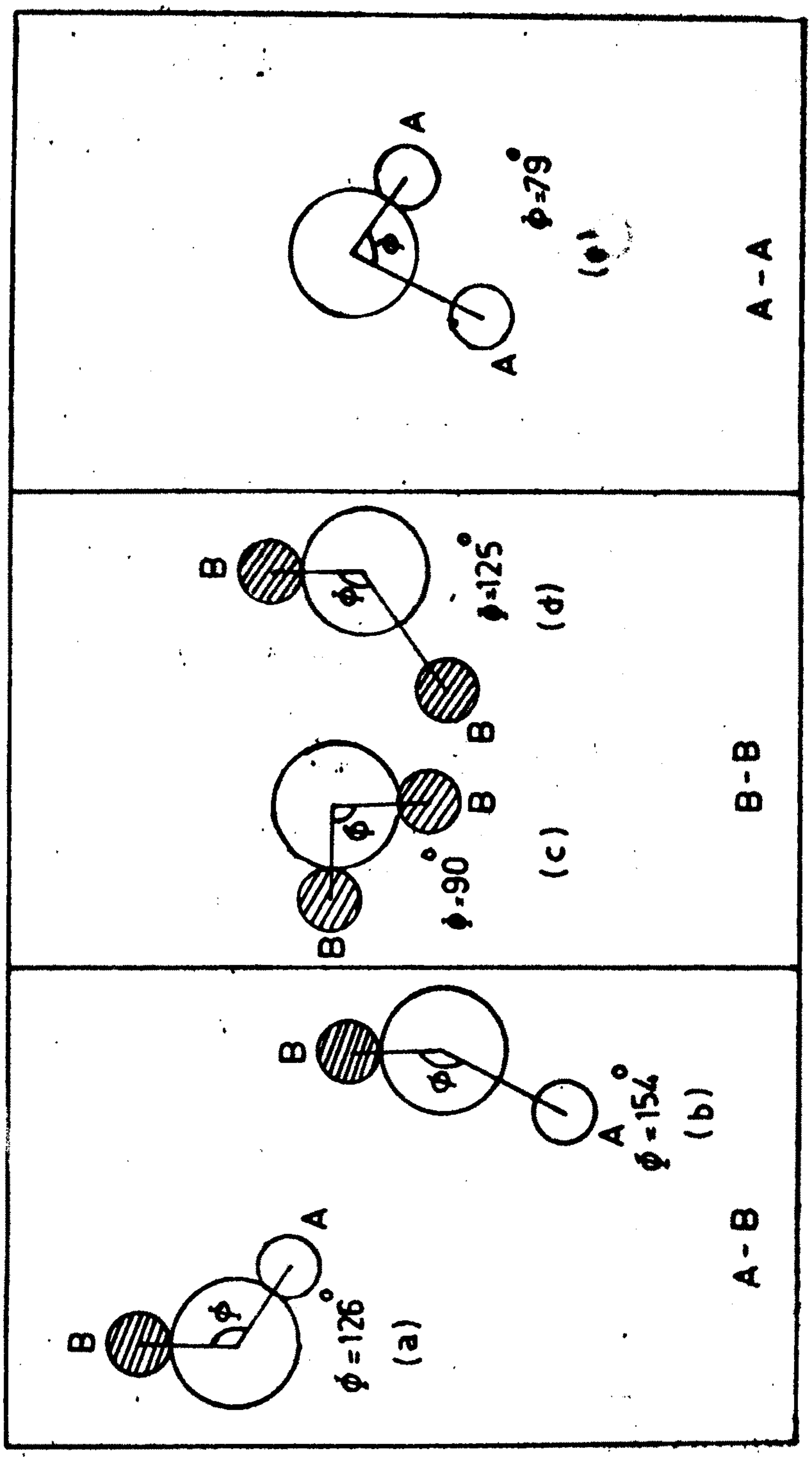


Fig. 1.4

Thus, on addition of Zn^{2+} ($m = o$), the magnetic moment tend to 10 per formula unit. Gortex has verified experimentally the increase of magnetization for small concentration of the added ferrite, but with the increase in the concentration of Zn^{2+} deviation increases.

1.5 : (c) : Néel's Theory of Ferrimagnetism (18) : N'eel proposed theory of ferrimagnetism by assuming two sub-lattices formed due to location of magnetic ions at crystallographically different sites. The computation of magnetization and susceptibility in terms of molecular field coefficient can be done with the help of N'eel's theory. Further, theory characterizes the A-A, B-B and A-B interactions.

If λ is the fraction of ion on A-site and μ is the fraction of ion on B-site, provided $\lambda + \mu = 1$. The distribution of cations under the above mentioned condition is,

$$\left[Fe^{3+}_{2\lambda} \, M_{1-2\lambda}\right]^A \quad (Fe^{3+}_{(2-2\lambda)} \, M^{2+}_{2\lambda})^B \, O_4$$

$$\text{or} \quad \left[Fe^{3+}_{2\lambda} \, M^{2+}_{1-2\lambda}\right]^A \quad (Fe^{3+} \, M^{2+}_{2\lambda})^B \, O_4$$

Similar to ferromagnetic molecular field concept, the effective magnetic fields acting on ions are,

$$\left.\begin{aligned} H_A &= H_{AA} + H_{AB} \\ H_B &= H_{BB} + H_{BA} \end{aligned}\right\} \text{---------} \quad (1.11)$$

where, H_A, the molecular field acting on ion of A-site is the sum of molecular fields, H_{AA} from neighbouring A-atom and H_{AB} from B-atom. Similarly H_B is the sum of molecular fields, H_{BB} from neighbouring B-atom and H_{BA} from A-atom.

If γ_{AA}; γ_{BB} and γ_{AB} are the molecular field coefficients, molecular field components may be written as,

$$\left.\begin{aligned} H_{AA} &= \gamma_{AA} M_A \\ H_{AB} &= \gamma_{AB} M_B \end{aligned}\right\} \text{------------} \quad (1.12)$$

$$\left.\begin{aligned} H_{BB} &= \gamma_{BB} M_B \\ H_{BA} &= \gamma_{BA} M_A \end{aligned}\right\} \text{------------} \quad (1.13)$$

M_A and M_B are magnetic moments of A and B sublattices.

At equilibrium(19) $\gamma_{AB} = \gamma_{BA}$. However, now $\gamma_{AA} \neq \gamma_{BB}$ because of crystallographically inequivalent sublattices.

N'eel showed that, $\gamma_{AB} < 0$, causes antiparallel arrangements of M_A and M_B and hence give rise to ferrimagnetism.

With the help of equation (1.11), in the presence of applied field Ho, magnetic field acting on each sub-lattice may be written as,

$$\left.\begin{aligned} H_a &= H_o + \gamma_{AA} M_A + \gamma_{AB} M_B \\ \text{AND} \quad H_b &= H_o + \gamma_{BB} M_B + \gamma_{BA} M_A \end{aligned}\right\} \text{------------} \quad (1.14)$$

Paramagnetic Region : Volume susceptibility χ , for an assembly of N paramagnetic ions per unit volume, each with angular momentum quantum number J and total magnetization M is,

$$\chi = \frac{M}{H} \text{ -------------------- } (1.15)$$

In the above equation H can be replaced by (H + Hm), where Hm = M, Weiss molecular field.

$$\text{Therefore, } \frac{M}{H+H_m} = \frac{M}{H+\gamma_M} \text{ -------- } (1.16)$$

and this lead to Curie-Weiss law,

$$\chi = \frac{C}{T - T_c} \text{ ------------- } (1.17)$$

where $T_c = \gamma C$, which gives experimental determination for molecular field coefficient. N'eel applied this theory to ferrite with $\lambda + \mu = 1$, fraction of the same magnetic ion distributed in two sublattice. With the help of equation (1.17), magnetization of each sub-lattice A and B can be written as,

$$\left.\begin{aligned} M_A &= \left(\frac{\lambda C}{T} \right) H_a \\ \text{and } M_B &= \left(\frac{\mu C}{T} \right) H_b \end{aligned}\right\} \text{ ---------- } (1.18)$$

where λC and μC are volume occupied by magnetic ion in each sublattice.

Since $\chi = \frac{M}{H}$ and $M = M_A + M_B$,
the equation for paramagnetic susceptibility become,

$$\frac{1}{\chi} = \frac{T^2 - C\gamma_{AB}(\lambda\alpha + \mu\beta)T + C^2\lambda\mu\gamma_{AB}^{\;2}(\alpha\beta - 1)}{C\left[+T - \lambda\mu C\gamma_{AB}(2+\alpha+\beta)\right]} \quad \ldots\ldots (1.19)$$

Where, $\alpha = \frac{\gamma_{AA}}{\gamma_{AB}}$

and $\beta = \frac{\gamma_{BB}}{\gamma_{AB}}$

following N'eel for clear explanation we rewrite equation (1.19) as ,

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} + \frac{\xi}{T-0} \quad \text{-----------------} \quad (1.2)$$

Where,

$$\frac{1}{\chi_0} = \gamma_{AB}(2\lambda\mu - \mu^2\alpha - \mu^2\beta)$$

$$\theta = {}_{AB}\,\lambda\,\mu C\,(2+ \quad +\beta)$$

$$\xi = {}^{2}_{AB}\,\lambda\,\mu C\left[\lambda(1+\alpha) - \mu(1+\beta)\right]^2$$

In the equation (1.2) the first two terms of R.H.S. gives Curie-Weiss law in ferromagnetism, where as, last term has no contribution in ferromagnetic case. Further, equation (1.2) represents an hyperbola with asymptote $\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0}$ as shown in the Fig.1.5. The negative intercept on T-axis is at T_A, known as "asymptotic Curie point" and is given by,

$$T_A = \frac{-C}{\chi_0}$$

T_P is the paramagnetic curie point, may be obtained by equating $\frac{1}{\chi}$ to zero as,

$$T_P = \frac{\gamma_{AB}C}{2}\left[\lambda\alpha + \mu\beta + \left\{(\lambda\alpha - \mu\beta)^2 + 4\lambda\mu\right\}^{\frac{1}{2}}\right] \quad \text{---} \quad (1.21)$$

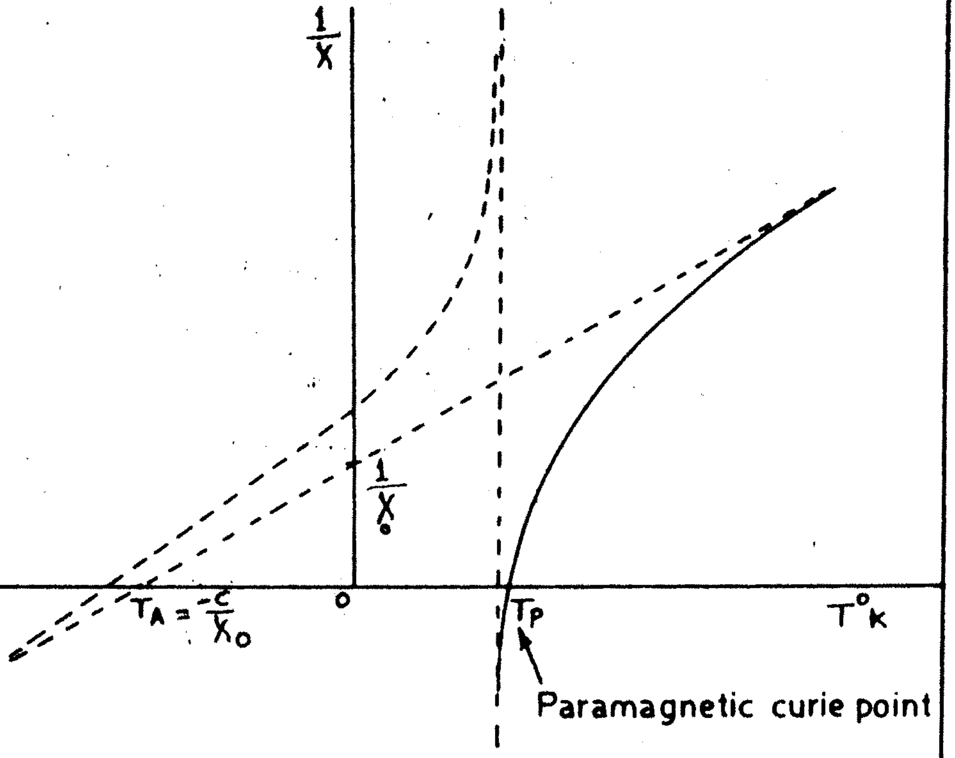

$\frac{1}{\chi}$
$\frac{1}{\chi_0}$
$T_A = -\frac{C}{\chi_0}$
0
T_P
$T\,{}^\circ K$
Paramagnetic curie point

Fig. 1.5

The ferrimagnetic material is paramagnetic at temperatures above T_P and is spontaneously magnetized in the region $0 \leq T \leq T_P$.

The rapid change of $\frac{1}{\chi}$ close to T_P is in contrast with ferro and antiferromagnetic case. This fact is due to relative magnetization of the sublattice magnetizations and an antiparallel effect.

Ferrimagnetic Region (Spontaneous Magnetization) :

Equation (1.21) can be written as,

$$T_P = \frac{1}{2} \gamma_{AB}\, C \left\{ \lambda\alpha + \mu^{\beta} + \left[(\lambda - \mu B)^2 + 4\lambda\mu\right]^{\frac{1}{2}} \right\} \text{------} \qquad (1.22)$$

$$T_P' = \frac{1}{2} {}_{AB}\, C \left\{ \lambda\alpha + \mu^{\beta} - \left[(\lambda\alpha - \mu^{\beta})^2 + 4\lambda\mu\right]^{\frac{1}{2}} \right\} \text{------} \qquad (1.23)$$

assuming positive square root is taken at each time. T_P is the Curie temperature for M_A and M_B antiparallel and T_P' Curie temperature when M_A and M_B parallel.

If $T_P' > T_P$, the antiparallel arrangement of magnetization will occur and be stable at all temperatures, below T_P. This is in agreement with negative interactions of A and B sublattices.

The individual magnetization M_A and M_B can not be observed independently, therefore, net magnetization M, can be written as,

$$M = M_A + M_B$$

But due to antiparallel arrangement of magnetization, net magnetization is, $|M| = |M_A| - |M_B|$ or $|M| = |M_B| - |M_A|$.

Like ferromagnetic material the spontaneous magnetization in case of ferrimagnetic material, for both A and B ions can be written as,

$$M_{ASP} = \lambda N g J \mu_B \, B_J \, (\mu_0 \, g J \mu_B \, H_A/KT) \quad \text{-----------} \quad (1.24)$$

and $M_{BSP} = \lambda \, N g J \mu_B \, B_J \, (\mu_0 g J \, \mu_B \, H_B/KT)$ ----------- (1.25)

from above equations (1.24) and (1.25), we may directly write,

$$\left.\begin{aligned} \frac{M_{ASP}}{M_{A\,Sat.}} &= B_J \, (\mu_0 \, g \, \mu_B J \, H_A/KT) \\ \text{and} \quad \frac{M_{BSP}}{M_{B\,Sat.}} &= B_J \, (\mu_0 \, g \, \mu_B J \, H_B/KT) \end{aligned}\right\} \quad \text{---------} \quad (1.26)$$

where $M_{A\ Sat.}$ and $M_{B\ Sat.}$ are saturation magnetization of sub lattice A and B respectively.

B_J ---> Brillouin function

g ---> Landaufactor

and other notations have their usual meanings.

Since $J \simeq S$, the spin quantum number, the observed spontaneous magnetization may be written as,

$$M_{SP} = M_{BSP} - M_{ASP} \quad \text{---------------------} \quad (1.27)$$

The analytical solutions of equation (1.27) is not possible, therefore, graphical methods(20) are used to solve it. This graphical solution lead us to curve (σ, T) as shown in Fig.1.6, where,

$$\sigma = \frac{M_{SP}}{M_{Sat.}} \quad \text{---------------------} \quad (1.28)$$

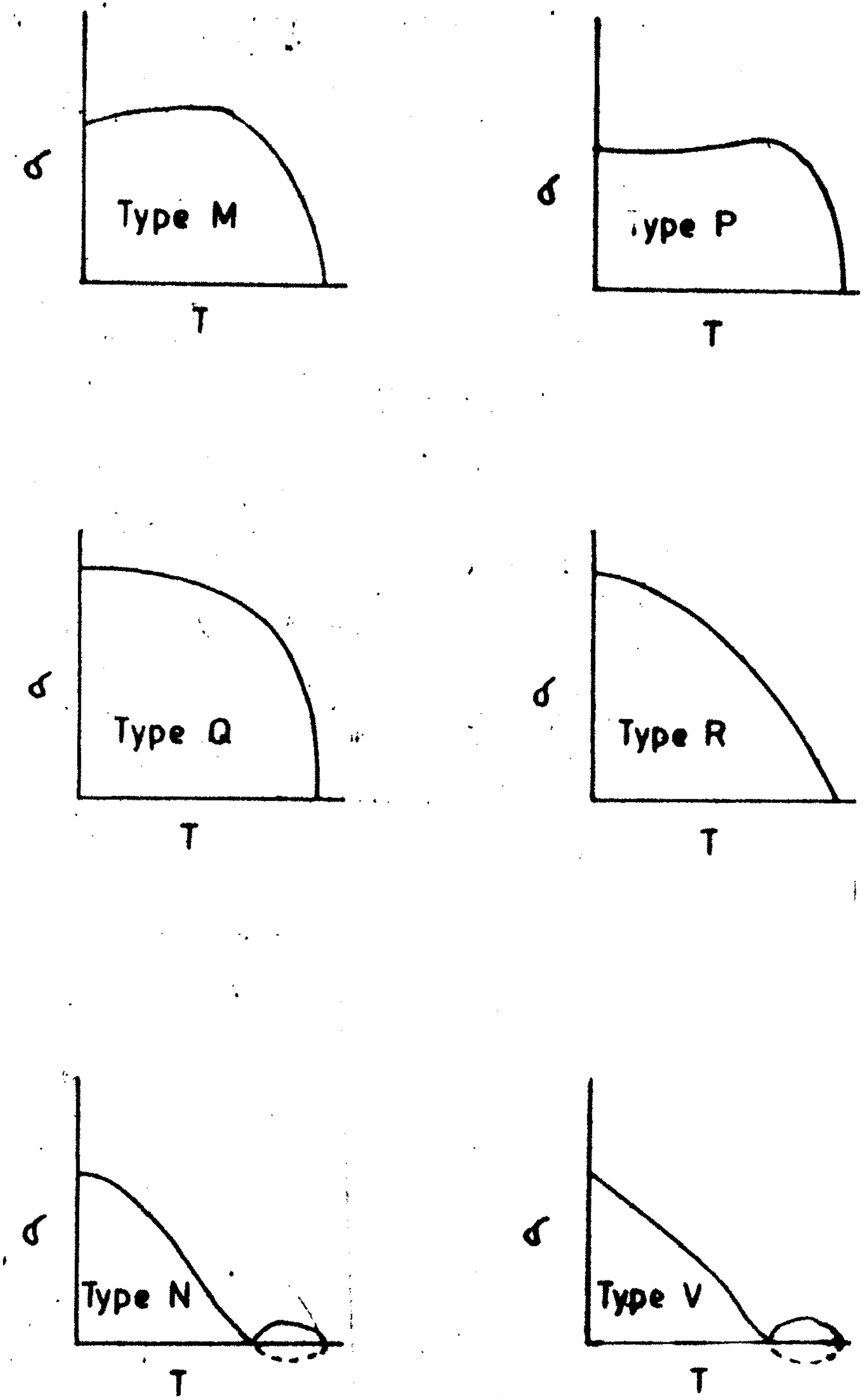


Fig. 1.6

and $\tau = \frac{T}{T_P}$ -------------------- (1.29)

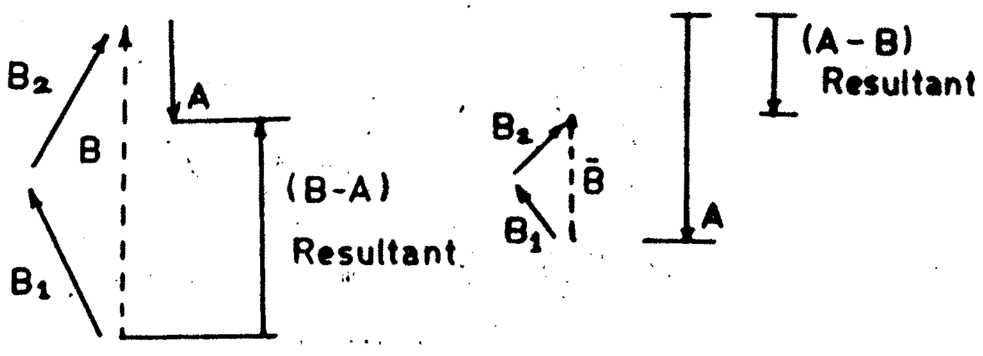
(δ, T) curves provide useful information regarding spontaneous magnetization, exchange interaction and temperature of ferrite.

1.5 (d) : <u>Yafet-Kittel Theory</u> : In the some class of ferrites, namely, ferrites containing major constituent other than Fe, observed magnetization(21) is less than calculated by N'eel model. Further calculation leads us, that net magnetization increases or decreases as absolute zero is approached; i.e. $\frac{dM}{dT} \neq 0$ at T = 0°K. In fact it is prohibited by the third law of thermodynamics.

To overcome this difficulty, Yafet and Kittel (1952) extended N'eel's theory of magnetic sub lattice. Yafet and Kittel(26) postulated trangular type of spin arrangement. They showed that, for strong negative interaction exists within sub-lattice B, the two equivalent structures B_1 and B_2 magnetizes spontaneously. Further, their magnetizations are not exactly antiparallel but they are aligned at some angle other than 180°. The resultant magnetization of B-lattice (i.e. B_1 and B_2) sets antiparallel with magnetization of A sub-lattice as shown in the Fig.1.7.

1.6 Electrical D.C. conductivity :

Ferrites exhibit semiconducting properties having resistivity range, 10^3 to 10^{11} Ohm-cm. at room temperature(22). The physical and chemical properties of ferrites are dependent on charge transport mechanism. The mechanism can be studied from the



(a) (b)

Fig.1.7

measurement of electrical conductivity, thermoelectric power, magneto-resistance and Hall coefficient.

The electrical conductivity of ferrite is influenced by heat treatment, rate of cooling, impurity and porosity etc. According to Verwey and de Boer(23) electronic conduction in ferrites is due to the presence of ions of a given element in more than one valance state. Therefore, ions having two valance states get distributed randomly over the crystallographically equivalent sites.

Verwey, Haayman and Romeijn(24) have shown that the conductivity of high resistivity oxide can be increased by addition of small elements of foreign oxides to the structure whose metal ions have valancies different from that of host cation. In general, the substitution of a cation of low valance state gives rise to P-type of conduction while the substitution of a cation of high valance states gives rise to n-type conduction.

1.7 : Applications of Ferrites :

The ferrites are widely used in the electronic industry due to high permeability over the frequency range from 50 KH_z upto 150 KH_z, which is suitable for filter inductors for band pass filters in carrier telephone circuits. The high permeability also makes the ferrites useful for IF transformers in radio circuits. Due to the high resistivity of the ferrites, they can be used as a pole piece for concentrating flux in h-f induction heaters.(25)

Ferrites with square magnetic loops find applications in digital computer as switching and the memory circuits. Ferrites are useful to manufacture components like, inductors and transformer due to low power considerations. The temperature rise in the transistor circuits is usually low so that use of high permeability materials having low Curie temperature is allowed at this low power.

1.8 : Orientation of Present Work :

The ferrimagnetic oxides generally known as ferrites owing to their important electrical and magnetic properties have immense industrial applications and, therefore, have aroused considerable interest during last two decades. It was observed that when a divalent ion in the general formula $M^{2+} Fe_2^{3+}O_4^{2-}$, where M is a magnetic ion, has been replaced by a non-magnetic ion like Zn^{2+} surprisingly the net magnetic moment gets enhanced. This was later explained on the two sublattice model by N'eel. It was, therefore, proposed to prepare the mixed soft ferrite system $Cu_xNi_{1-x}Fe_2O_4$ by substitution of Ni^{2+} by Cu^{2+} partially, to maintain the stoichiometry of the ferrites.

The standard ceramic method is to be employed, giving the details of the stages involved, in the preparation of the samples. The X-ray crystal structure characterisation would be carried out to decide upon the structure of the each composition ($0 < x < 1$) while confirming the single phase formation of the ferrite samples. After doing the X-ray diffraction work, the samples of each composition would be hydraulically pressed to pellet form of 1 cm. diameter and nearly having the same thickness. Once again sintering the pellets, the physical density and x-ray density would be compared, to estimate the porosity in the sample as the preparation would be influenced by this parameter to a large extent.

After getting thus prepared series of $Cu_xNi_{1-x}Fe_2O_4$, the ferrite samples would be subjected to the systematic study in the following ways.

i) Determination of Curie Temperatures : The ferrimagnetic oxides exhibit a magnetic transformation when heated above room temperature. At room temperature $NiFe_2O_4$ and $CuFe_2O_4$ are ferrimagnetic in nature and at certain temperature they change over to paramagnetic. Therefore, by fabricating a set up to measure this magnetic change over the transition temperatures (Tc) would be measured.

ii) Saturation Magnetization (Ms) : By studying the hysteresis losses in these samples on a standardised instrumentation set up, known as HIGH FIELD LOOP TRACER HS 869, available at IIT, Powai, the saturation magnetization in these samples could be studied. The interest in the saturation magnetization would be because if the study is carried out at cryogenic temperatures, and if the graph is extrapolated to 0°k, helpsto determine the cation distribution in the ferrites, which decides their final properties.

iii) Electrical conductivity : For the measurement of conductivity a simple cell can be developed and used to note down current through the sample at a fixed voltage with increasing temperature. As discussed in (i) above, a magnetic transformation with temperature is expected. This becomes obvious if graph of log of resistivity (ρ) versus inverse temperature ($^1/_T$) is plotted. The graph shows a change in slope distinguishing ferrimagnetic and paramagnetic regions clearly. These transition temperatures would be compared with measured Curie temperatures. A discussion regarding possible conduction mechanism in the mixed ferrites $Cu_xNi_{1-x}Fe_2O_4$ can also be done depending upon the behaviour of these ferrites; ~~in~~ taking into consideration the recent work on the similar system.(27,28,29)

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