CHAPTER-I

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1.1 INTRODUCTION :

Ferrite is an artificial magnetic material of immense importance in our modern age of science. Mixed metal oxides with iron (Fe^{3+}) oxide as their main componant are known as ferrites. Ferrites continue to evoke interest because they are most important electronic and magnetic ceramics. The simultaneous twin requirements of optimal electrical and magnetic properties in the advanced electronics, microwave and computer technologies have focused the attention of research workers on ferrites. Ferrites can be easily prepared by standard ceramic method and moulded in any desired shape according to variety of requirements.

1.2 HISTORICAL DEVELOPMENT OF FERRITE MATERIALS :

Load stone (Fe_3O_4) was the first natural magnetic material known to man since prehistoric times. There arose a need for the magnetic materials to reduce eddy current losses, which was met by preparing synthetic ferrites.

The credit of synthesis of magnetic materials goes to Hilpert (1909) [1] , who, in Bell laboratory prepared magnetite with a view to reduce eddy current losses. His very purpose was not then served but the foundation stone for the preparation of ceramic magnets was laid. This is a remarkable achivement in the history of magnetic materials. A large number of ferrites were prepared by Hilpert, who also identified the basic formula for the ferrites as $MOFe_2O_3$, where

M is a divalent metal ion. In thirties Kato and Takei [2] and Forestier [3] studied ferrites from electromagnetic, chemical and crystallographic point of view. The structure of ferrites was established to be that of spinel type. Barth and Posnjak (1932)[4] carried out X-ray analysis of ferrites. They found that it is necessary to assume that the divalent and trivalent metal ions inter change positions in the crystal. Thus, they discovered inverted spinel structure, which is required for the existance of the ferromagnetic properties of ferrites.

Snoek [5] carried out extensive systematic studies of preparation of ferrites and their magnetic properties. This led to various applications of ferrites. Verwey et al [6] reported that the electrical conductivity of ferrites is mainly due to hopping (the exchange of electrons between Fe^{2+} and Fe^{3+} ions) of electrons through the crystal lattice. His study on crystal structure of various ferrites showed ferrites with inverted spinel structure to be ferrimagnetic, whereas those with normal structure to be non magnetic.

Saturation magnetisation of magnetite was first measured by De Bois (1890) [7]. Pierre Weiss (1907) [8] studied other magnetic properties of the same and found the saturation magnetisation and Curie temperature to be similar to those for Nickel.

Neel [9] put forth the basic theory of spin-spin interaction in ferrites. He introduced the concept of magnetic sublattices. The two sublattices were designated as A-sublattice and B-sublattice. A more detailed explanation of basic interaction was given by Anderson [10] and Van-Vieck [11] who developed the theory of super exchange. Yafet and Kittle [12] extended the theory of magnetic sublattices by postulating a " triangular" arrangement of three sublattices, when the antiferromagnetic exchange interaction between sublattices is comparable to that among the spin moments within the sublattices formed by Fe^{3+} ions on tetrahedral and octahedral sites.

Currently, the work on ferrites is progressive in many directions including preparation and application. The present trend of research is to develope ferrites essential in electronic industry for various electronic equipments. The international conferences on ferrites (ICF 1 to ICF 6) have thrown light on the domain of applications of ferrites.

1.3 CRYSTAL STRUCTURE OF SPINEL FERRITE:

In general ferrite shows the following four different types of crystal structure

1) Spinel structure
2) Hexagonal structure
3) Garnet structure
4) Perovskite structure

As the present work is concerned with the characterisation of spinel structure, its details are given below.

The general chemical formula for ferrospinel is MFe_2O_4, where M is a divalent metal ion and Fe is trivalent. All such compounds have a cubic, face centered crystal structure (Fig.1.1) with space group O_h^7-F_3 dm. The conventional unit cell contains 8 formula units of MFe_2O_4. In this structure two types of interstitial positions occur with respect to oxygen lattice and these

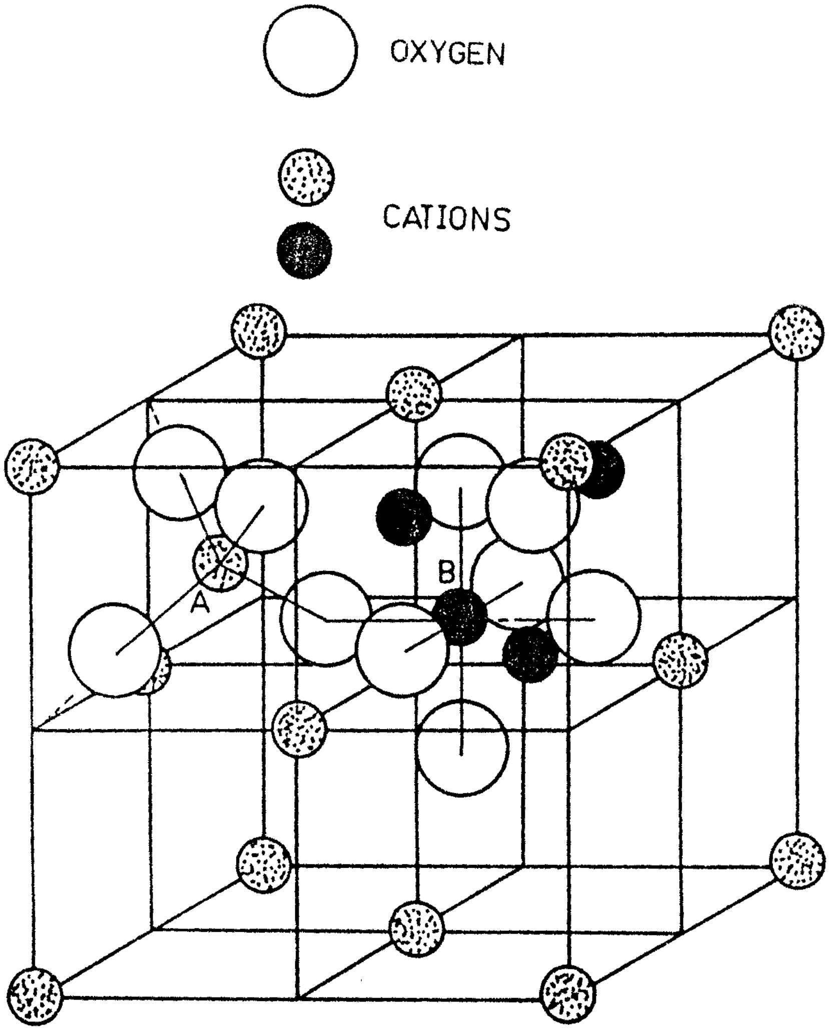

Fig.1·1 THE SPINEL STRUCTURE.

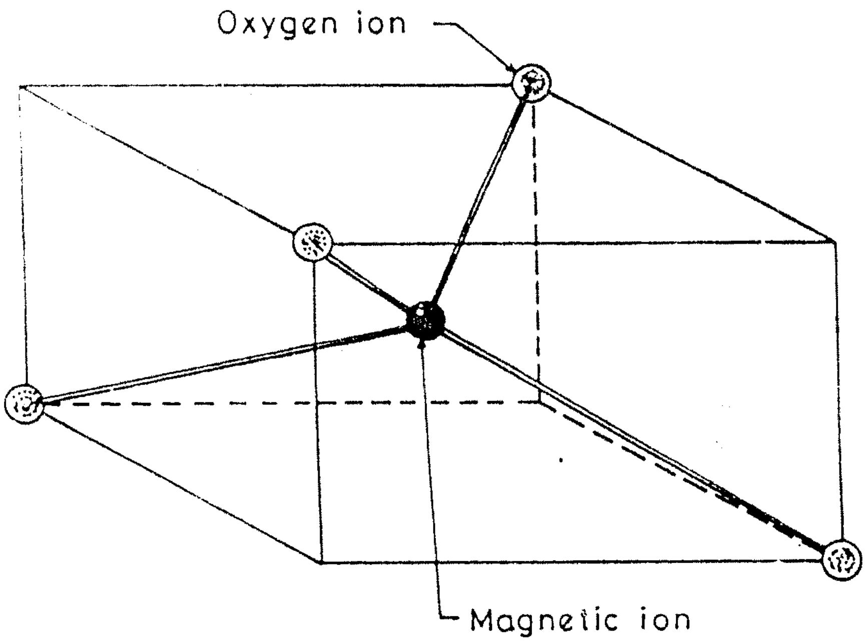

Fig. 1·2 (a): THE MAGNETIC ION OCCUPIES A "TETRAHEDRAL LATTICE SITE" WHERE IT IS SURROUNDED BY FOUR NEAR-NEIGHBOUR OXYGEN IONS.

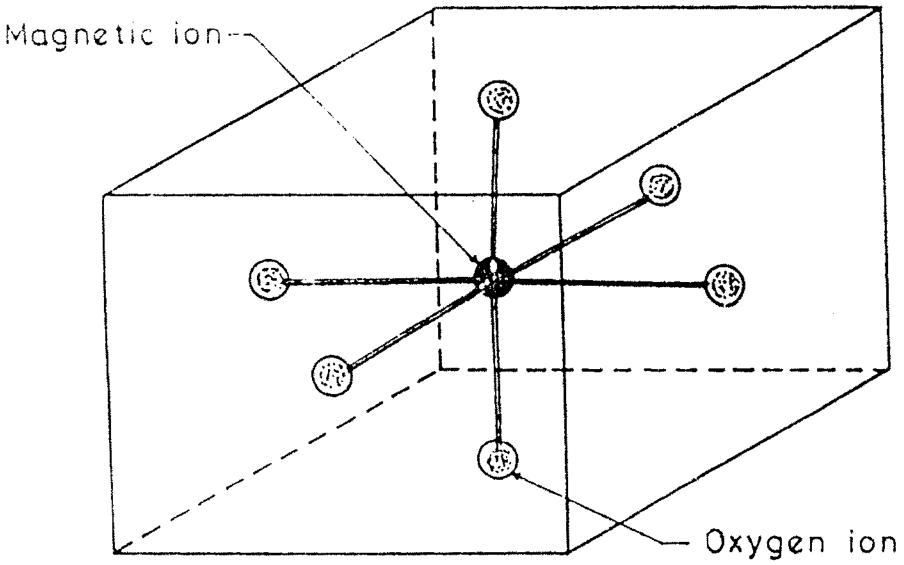

Fig. 1·2 (b): THE MAGNETIC ION IS SAID TO OCCUPY AN "OCTAHEDRAL LATTICE SITE" WHERE IT IS SURROUNDED BY SIX NEAR NEIGHBOUR OXYGEN IONS.

positions are occupied by metal ions. There are in all, 96 interstitial sites per unit cell . 64 being tetrahedral sites usually called as A-sites and 32 octahedral usually called as B-sites. Out of these 8 tetrahedral and 16 octahedral sites are occupied by the cations. In the A-site, metal ion is surrounded by four oxygen ions located at the corners of a tetrahedron as shown in Fig. 1.2a. In the B-site. metal ion is surrounded by six oxygen ions placed at the vertices of an octahedron as shown in Fig. 1.2b .

The spinel ferrites are classified on the basis of cation distribution as follows :

1.3(a) THE NORMAL SPINEL FERRITE :

In the normal spinel ferrite all the M^{2+} ions occupy the A-sites, while Fe^{3+} ions occupy the B-sites. The cation distribution in normal spinel ferrites as follows

$$(M^{2+})^A\ (Fe^{3+}Fe^{3+})^3\ O_4^{2-}$$

Ferrites like $CdFe_2O_4$ and $ZnFe_2O_4$ have this type of structure and they are non magnetic.

1.3(b) THE INVERSE SPINEL FERRITE :

In the inverse spinel ferrite, all divalent metal ions occupy B-sites and trivalent Fe^{3+} ions are equally divided between A and B sites. They may be represented as,

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

Ferrites like $CoFe_2O_4$ and $NiFe_2O_4$ have this type of structure and they are all ferrimagnetic.

1.3(c) THE RANDOM SPINEL FERRITE :

X-ray and neutron diffraction studies have shown that the structure of some ferrites is neither a perfect normal nor a perfect inverse and so it is known as random spinel structure. In this type of ferrite a fraction of divalent and trivalent ions get distributed randomly over A and B sites depending on the physicochemical conditions of preparation and compositional variation. The general cation distribution can be indicated as,

$$(M_{\delta}^{2+}\ Fe_{1-\delta}^{3+})^{A}\ (M_{1-\delta}^{2+}\ Fe_{1+\delta}^{3+})^{B}\ O_4^{2-}$$

where δ -coefficient of normacy and (1- δ)-coefficient of inversion.

Ferrites like $CuFe_2O_4$ and $MgFe_2O_4$ have this type of structure and they are ferrimagnetic.

1.4 MAGNETISATION IN FERRITES :

The magnetisation of solid material as a whole is the vector sum of magnetisation of each of the domains, the contribution of each being weighed by its fractional volume. Thus, the net magnetisation of a solid ranges from zero, if the weighed vector sum is zero, to a maximum value if the solid is a single domain with all atomic moments aligned .

The two sublattice model applied to spinel structure to explain the magnetisation of the ferrites is successful to a large extent. The inverse spinel magnetisation can be deduced as follows.

The inverse spinel structure is given by

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

The Fe^{3+} ions on A-site are coupled with their spins antiparallel to those of Fe^{3+} ions on B-site. Therefore the net moment is only due to M^{2+} divalent metal ions. In case of Fe_3O_4 , M^{2+} is Fe^{2+}. Hence the net moment is 4 Bhor magnetons. as 4 electon spins are unpaired.

For M as a transition element with n electrons in d shell, the magnetic moment per formula unit is n Bhor magnetons or (10-n) Bohr magnetons depending on whether the d-shell is less or more than half filled respectively. The net magnetic moment is the difference between the moments on A and B sites.

1.5 NEEL'S THEORY OF FERRIMAGNETISM :

Neel developed the theory of ferrimagnetism. He introduced the concept of magnetic sublattices. According to this the ferrimagnetic crystal lattice can be divided into two sublattices formed by A-site (tetrahedral) and B-site (octahedral) in spinel structure. He defined the magnetic interaction within the material considering the Weiss molecular field. The magnetic field acting upon an atom or ion is given as,

$$H = H_o + H_m \qquad ....(1.1)$$

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

$$H_A = H_{AA} + H_{AB}$$

$$H_B = H_{BB} + H_{BA} \qquad ....(1.2)$$

The molecular field components may be written as,

$$H_{AA} = \gamma_{AA} M_A \, , \; H_{AB} = \gamma_{AB} M_B$$

$$H_{BB} = \gamma_{BB} M_B \, , \; H_{BA} = \gamma_{BA} M_A \qquad \ldots\ldots(1.3)$$

where, γ's are appropriate molecular field coefficients and M_A and M_B are magnetic moments of A and B sublattices.

1.5(a) PARAMAGNETIC SUSCEPTIBILITY :

In paramagnetic region magnetisation is given by,

$$M = NgJ \, \mu_B \, B_j(x) \qquad \ldots\ldots(1.4)$$

where, N is the number of free paramagnetic ions per unit volume and J is the angular magnetic momentum quantum number.

The Brillouin function $B_j(x)$ is given by,

$$B_j(x) = \frac{2J+1}{2J} \operatorname{Coth} \left[\frac{2J+1)\,x}{2J} \right] - \frac{1}{2J} \operatorname{Coth} \left(\frac{x}{2J} \right) \qquad \ldots\ldots(1.5)$$

where

$$x = \mu_o \, Jg \, \frac{\mu_B H}{kT} \qquad \ldots\ldots(1.6)$$

k = Boltzmann's constant and

T = absolute temperature

Writing $\chi = M/H_o$ and $M = M_A - M_B$ and after necessary simplification, Neel rewrite the equation of susceptibility such as,

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_o} - \frac{\xi}{T - \theta} \qquad \ldots\ldots(1.7)$$

Where,

$$1/\chi_o = \gamma_{AB} (2\lambda\mu - \lambda^2\alpha - \mu^2 B)$$

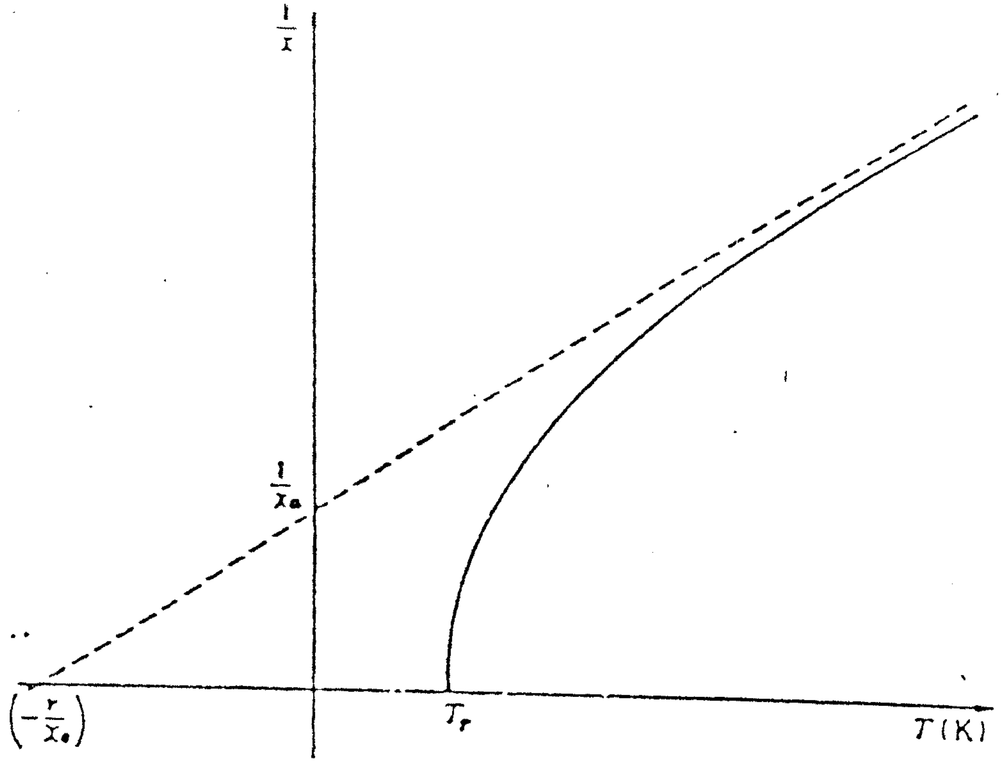

Fig. 1·3 : Predicted susceptibility curve of a ferrimagneto material above the curie point.

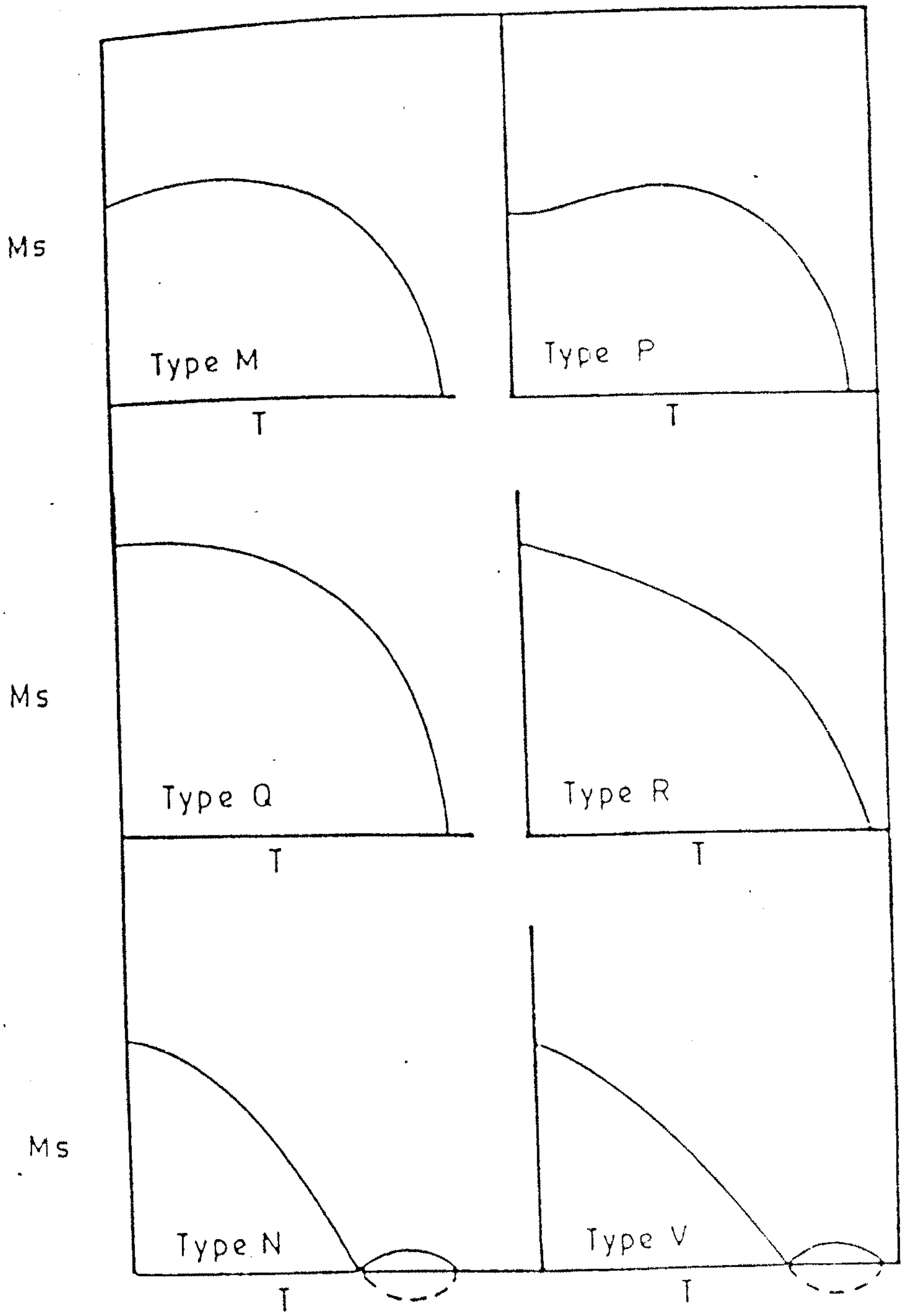

Fig. 1·4 - Ms vs T Curves for ferrimagnetic substances predicted by Neel's Theory.

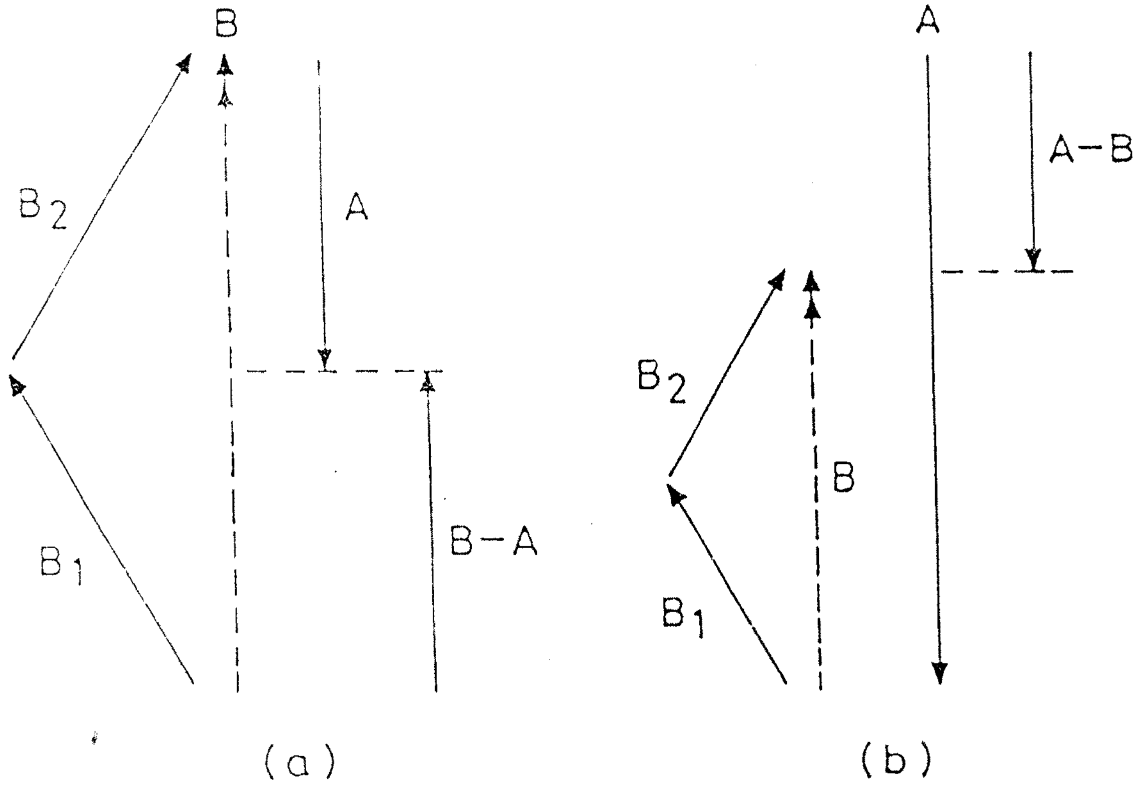

Fig. 1.5 - Triangular spin configuration.

$$\theta = \gamma_{AB} \; \lambda \mu C \, (2 + \alpha + \beta)$$

$$\xi = \gamma^2_{AB} \; \lambda \mu C \; \{ \lambda \, (1 + \alpha) - \mu (1 + \beta) \}^2$$

where $\alpha = \gamma_{AA} / \gamma_{AB}$ and $\beta = \gamma_{BB} / \gamma_{AB}$ and C is Curie constant λ and μ are the fractions of same magnetic ions appearing on A site and B site respectively, such that

$$\lambda + \mu = 1$$

Equation (1.7) represents an hyperbola Fig.1.3a. Asymptote to hyperbola is given by.

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_o} \qquad \text{.......(1.8)}$$

It cuts the temperature axis at $T_A = - C/\chi_o$ and is called as the asymptotic Curie point.

The paramagnetic Curie point T_p is found by equating $1/\chi$ to zero which yields,

$$T_p = \frac{\gamma_{AB}}{2} \, C \, [\lambda\alpha + \mu\beta + \{ (\lambda\alpha - \mu\beta)^2 + 4\lambda\mu \}^{1/2}] \qquad \text{.........(1.9)}$$

where T_p is Curie temperature when M_A and M_B are antiparallel.

1.5(b) SPONTANEOUS MAGNETISATION:

The equation (1.9) may be written as,

$$T_p' = \frac{\gamma_{AB} \, C}{2} \, [\lambda\alpha + \mu\beta - \{ (\lambda\alpha - \mu\beta)^2 + 4 \lambda\mu \}^{1/2}] \qquad \text{.........(1.10)}$$

where T_p' is the Curie temperature when M_A and M_B are parallel.

In ferromagnetic material the spontaneous magnetisation Msp may depend on temperature and is given by,

$$M_{sp} = NgJ \ \mu_B B_j(x) \qquad ......(1.11)$$

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

$$x = \frac{\mu_o gJ \quad \mu_B \gamma \ M_{sp}}{kT} \qquad ....(1.12)$$

As magnetisation M_A and M_B cannot be observed independently, so net magnetisation M can be written as,

$$M = M_A - M_B \qquad ......(1.13)$$

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

$$\frac{M_{Asp}}{M_{Asat}} = BJ \left(\mu_o g \quad \mu_B J \quad \frac{H_A}{kT}\right) \qquad .....(1.14)$$

$$\frac{M_{Bsp}}{M_{Bsat}} = BJ \left(\mu_o g \ \mu_B J \quad \frac{H_B}{kT}\right) \qquad .....(1.15)$$

The observed total spontaneous magnetisation is given by,

$$M_{sp} = M_{Bsp} - M_{Asp} \qquad ......(1.16)$$

Since , the analytical solution of the above equation is not possible, the graphical method is always used. The graphs are known as (σ , τ)curves Fig.1.4 , where,

$$\sigma = \frac{M_{sp}}{M_{sat}} \quad \text{and} \quad \tau = \frac{T}{T_p} \qquad \ldots\ldots(1.17)$$

The (σ , τ)curves are of different types which depend on relative values of interactions and relative magnitudes of sublattice magnetisations

1.6 YAFET-KITTLE THEORY OF FERRIMAGNETISM

In case of spinels containing chief metal ions other than Fe, the observed magnetisation is smaller than the Neel's model values. To remove the thermodynamic difficulties near 0 k of third law, in 1952 Yafet and Kittle [12] proposed triangular arrangement of moments due to the subdivision of sublattice as shown in the Fig.1.5. The B_1 and B_2 are spontaneous magnetion vectors with angle other than 180° and their resultant B is antiparallel to A. This arrangement results in reduced magnetisation of the order of Neel and free from thermodynamic difficulties. They also proved that the Neel's structure is stable if the total number of sublattices is restricted to six with a condition on ratio of exchange energies.

1.7 ELECTRICAL PROPERTIES OF FERRITES :

The conduction mechanism can be studied from the measurement of electrical conductivity, thermoelectric power, magnetoresistance and Hall coefficient. The physical and chemical properties of ferrites depend on the mechanism of charge transport. The charge transport can vary with the composition and the method of preparation of ferrites.

1.7(a) D.C. ELECTRICAL CONDUCTIVITY:

During the course of ferrite preparation, oxygen dissociation set up above 1200°C [13], giving rise to Fe^{2+} ions. The Fe^{2+} ions are responsible for the electrical conduction. As the amount of Fe^{2+} ions in ferrite is sensitively dependent on heat treatment, the electrical conductivity of a ferrite is influenced by heat treatment and also by the accompanying factors like impurities. porosity, rate of cooling. Thus the electrical conduction in ferrites is to be associated, as reported by Varwey and De Bore [14], with the presence of ions of a given element in more than one valance state, in general [15]. These ions get distributed randomly over the crystallographically equivalent sites. Thus, the high conductivity of Fe_3O_4 has been attributed to the presence of both Fe^{2+} and Fe^{3+} ions on the octahedral sites [13]. The electrons move from divalent iron ion to the trivalent iron ion in between the octahedral positions and the transitions do not cause a change in the energy state of the crystal.

The presence of Fe^{2+} is desirable in certain cases [16] as it reduces magnetostriction and resistivity. Formation of Fe^{2+} shows disaccomodation property. It reduces magnetostriction and increases permeability.

1.7(b) THERMOELECTRIC POWER :

Hall effect and thermoelectric properties are widely used in the interpretation of the conduction mechanism in semiconductors. The interpretation of Hall effect is more straight forward. However, in case of low mobility materials such as ferrites, thermoelectric power measurement is the only alternative. The sign of thermo e.m.f. gives information about p or n type conduction. Another important significance of thermo e.m.f. is that it enables one to calculate the fermi energy and carrier concentration [17].

1.8 ORENTATION OF THE PROBLEM :

Ferrites are technologically imporant materials. They are widely used in electronic and microwave devices. The physical properties of ferrites can be modified by changing the composition and preparative parameters.

Amongst the simple ferrite copper ferrites seems to be interesting because its structural change can be brought about by variation in composition or in heat treatment . This ferrite shows switching behaviour. The elements like Cr and Co are Jahn Teller ions and they cause perturbed magnetic behaviour in ferrites when dopped . Therefore $Cu_{0.5}$ $Co_{0.5}$ $Fe_{2-x}Cr_xO_4$ with x=0 to 1 system has been selected for the present work.

The following studies will be carried out .

1) Preparation of $Cu_{0.5}$ $Co_{0.5}$ $Fe_{2-x}Cr_xO_4$ with x=0 to 1 by ceramic method.
2) X-ray studies for the confirmation of single phase formation and to calculate lattice constant and bond lengths .
3) To understand the magnetic behaviour and spin glass state of the matrial with the help of measurement of magnetisation hysteresis and a-c susceptibility.
4) To understand conduction phenomenon of these ferrites the study of electrical resistivity and thermo emf measurement will be done.

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