5.1 INTRODUCTION :

The technical importance of ferrites lies primarily in their high resistivity together with useful magnetic properties. The wide range of permeability values of ferrites make them suitable for various frequency range applications. The silicon-iron ferrite maintains its place as the heavy duty low frequency material while mangenise-zinc ferrite possess high permeability at intermediate frequencies. At high frequencies, as in communications field, the advantages of the ferrites become more pronounced and at the microwave level the choice ceases to exist.

The range of coercieve force (H_c) varies from 0.1 Oe to 3 KOe. Generally ferrites with low 'H_c' are called as soft ferrites and are used in the manufacture of high frequency inductance, core of transformers, motors and generators. The overall requirements of these applications are high permeability, low coersive force and small hysteresis losses. Ferrites with high 'H_c' are called as hard ferrites and generally used in electric motors, loud speakers, telephones and as a permanent magnets.

5.2 THEORETICAL ASPECTS :

The structure and behaviour of magnetic materials may be most simply described in terms of assemblies of dipoles interacting with external and internal magnetic fields. If a substance acquires a magnetization 'M' in the presence of an applied field H the relationship between 'M' and 'H' characterises a unique property of the material, the magnetic susceptibility (X),

$$M = XH$$

Materials for which $X < 0$ are diamagnets, and paramagnets for $X > 0$. At low temperatures, the paramagnetic materials are subdivided as ferromagnets, anti-ferromagnets or ferrimagnets. The distinction is made by magnetic order with spontanious magnetization. The possible spin-arrangements are shown in fig. 5.1. All the arrangements, except the simple anti-ferromagnet exhibit a spontaneous magnetic moment called the saturation moment. The magnetic ordering introduces a magnetic unit cell (magnetic domain) that may be equal to or a small multiple of the crystallographic unit cell.

The spontaneous magnetization was first explained by Weiss[1] postulating the existance of molecular field. The attempt was made to overcome limitations of Weiss molecular field theory by Heisenberg.[2] He gave quantum mechanical treatment to explain alignment of moments in terms of exchange interaction between the un-compensated spins of electrons in the partially filled 3-d shell. He showed that under certain conditions the exchange energy produces effects similar to those of Weiss molecular field. In this case electrons with parallel spins have lower energy than those with antiparallel alignment. Spontaneous magnetization can also arise as a result of negative exchange interactions under favourable conditions of intervening ions Neel[3] showed that in this case, the neighbouring magnetic moments are antiparallel. This is the origin of spontaneous magnetization in ferrites, where there are magnetic moments arranged in anti-

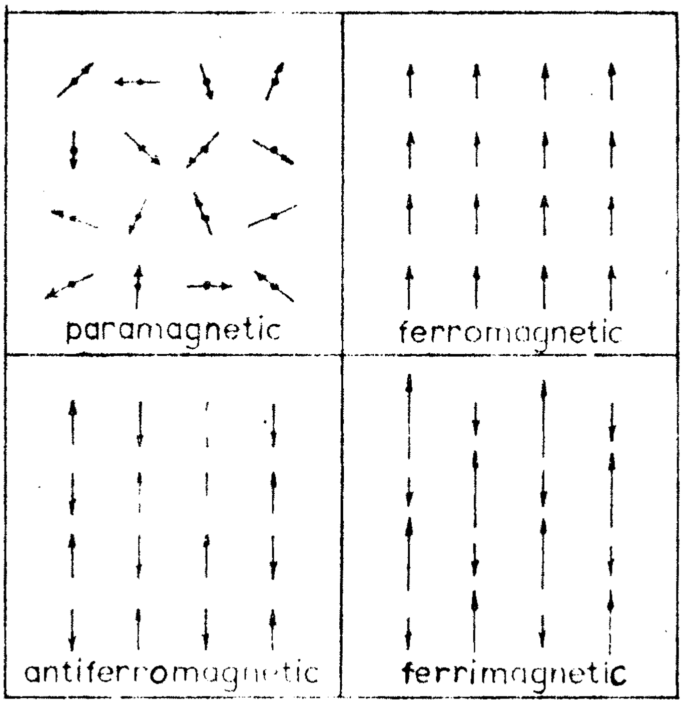

Fig. 5.1 Models of assemblies of magnetic atoms.

parallel or some other complex fashion compensating partially. The magnetic-moments contributing to the magnetization are mainly spin magnetic moments due to the quenching of orbital angular momentum. The non-integral values of magneton numbers in case of Fe, Co, Ni at 0°K could not be explained by the Heisenberg's model but has been explained on the basis of band theory of solids.[4] The exchange energy is given by,

$$W_{ex} = 2\,JeS^2 \sum_{i \neq j} \cos\theta_{ij}$$

where S = total spin momentum per atom

θ_{ij} = the angle between spin momentum vectors of atom i and j

Here anisotropy is neglected and only nearest neighbour exchange interactions are considered.

Neels theory of ferrimagnetism expresses the magnetization and susceptibility in terms of the molecular field co-efficient. Experimental evidence for Neels theory was given by Gorter[5] and also by Guillaud. Neels theory had been extended by Yafet and Kittle[6] by assuming triangular arrangement of spin in which A-A and B-B interactions are comparable in magnetidue to the A-B interaction.

5.3 HYSTERESIS AND DOMAINS :

Applications of ferrites depends on their magnetic properties such as, permeability, saturation, magnetization and coercive force. Hysteresis study on ferrites gives a valuable data of magnetic behaviour. The coercive force and permeability shows a wide spectrum of values. So the ferrites can be used in different frequency applications. The coercive force is related with crystal anisotropy, saturation magnetization, internal stresses and porosity.

Hysteresis properties are mainly dependent on chemical composition, crystal structure, cation distribution, heat treatment, atmos phere of sintering and final fabrication. Experimental technique for measurement of magnetic properties are described by Maxwell[7]. Hysteresis loop can be traced with the help of hysteresis loop tracer.

A demagnetised ferromagnetic material exhibits a state of zero magnetization. This phenomenon was first explained by Weiss.[8] He postulated that the magnetic material comprises large number of regions or domains, in which spins are aligned. These domains are arranged in such a way that the net magnetization is zero. The existance of domain is a consequence of the process which minimise the free energy of the system.

The alignment of spins in the neighbouring domains are antiparallel to each other. The change in the direction of the spins between two domain takes place via a domain wall which has thickness of few hundreds of inter-atomic distances. The spins in the domain wall gradually change from one direction to the other direction where the directions of spins are not parallel to the direction of magnetization. There are two types of domain walls; 180° and 90° walls. The spins rotate by 180° from one domain to the other in the former case and 90° in latter case.

In case of ferromagnetic material magnetization increases slowly by reversible wall motion and at very high fields and above critical field by irreversible wall motion and at very high field by irreversible rotation. The rotation of domains have been observed by Barkhahusen.[9] He has shown that discontinuous variation of magnetization at low fields take place where the field is continuously increasing. These are known as Barkhausen jumps. The wall energy is maximum at very high fields. This leads to irreversible increase in magneto-elastic and magnetostatic energies of the material under the action of external magnetic field. When magnetic field is reduced to zero the residual magnetization remains and which will not come to zero. The opposite field is applied for the reversal of domains to come to its original state of zero magnetization. This gives rise to the hysteresis of the magnetization cycle signifying the energy loss during the cycle.

5.4 MAGNETOCRYSTALLINE ANISOTROPY :

The term 'anisotropy' is generally referred to describe directional dependance of some physical properties like elasticity and strength which are markedly dependent on crystallographic direction. The magnetocrystalline energy is the difference between the energy required to magnetize crystalline sample along hard direction and that required along easy direction. This energy depends on the orientation of spin (S) with respect to the crystallographic axes.

The magnetocrystalline anisotropy is important in explaining the technical properties of magnetic materials, such as permeability and co-ercive force.

For the bulk magnetization the anisotropy energy is given by,

$$E_k = K_1 \sin^2\theta$$

where K_1 is anisotropy constant and

θ angle between L and S.

For cubic crystalline materials the anisotropy energy is given by,

$$E_k = K_1 (\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2)$$

where $\alpha_1, \alpha_2, \alpha_3$ are direction cosines.

The term of higher order in the α_i also may exist.

The influence on the temperature variation of 'Ms' on that of 'K' was first predicted by Zener.[10] He shows that the anisotropy constant 'K' decreases much faster with increasing 'T' than does saturation magnetization (Ms).

When crystal is strained there is change in anisotropy energy which is called the magneto-elastic energy. It is due to the change of interatomic spacing. One more contribution to the energy is that of magnetostatic energy which is the work required to assemble all the dipoles constituting the body. The magnetostatic energy needs to be reduced which occures as a result of division of crystal into domains This sub-division halts at a point where the energy required for the formation of an additional domain wall becomes greater than the decrease in the magnetostatic energy.

5.5 MAGNETOSTRICTION :

When the magnetization vector is rotated by a magnetic field, there will be a change in the dimensions of the sample. This phenomenon is called as magnetostriction. The major effect is a change in shape with the volume remaining approximately constant. The phenomenon provides a coupling of the magnetization vector with the lattice and can therefore, transfer magnetic energy to the heat bath. In polycrystalline or sintered materials stresses will be set up during cooling after fabrication. This is especially true when the thermal expansion is anisotropic.

The incremental change at saturation may be positive or negative for different materials. Most of the ferrites exhibit negative incremental change except for few cases like $FeFe_2O_4$.

5.6 EXPERIMENTAL :

Measurements of magnetization is carried out using high field loop tacer. It consists of an alternating current electromagnet, working on 50 Hz, which produces a sinusoidal field of 3.5 KOe in about 9 mm air gap. A special balancing coil is used to detect the magnetization of the sample placed in the air gap. The sample holder used avoides contact with poles of the electromagnet.

The signal from the balancing coil is proportional to the magnetic moment of the specimen and it fed to the vertical plates of an oscilloscope [Tektronix, model-5110] after suitable amplification. A signal proportional to the magnetic field is fed to the horizontal plates of the oscilloscope. Thus, oscilloscope displays magnetic moment versus field, that is, the hysteresis loop.

Measurements at room temperature and at liquid nitrogen temperature were repeated for each sample. The measurements were carried out at 'TIFR', Bombay.

Saturation magnetization at room temperature and at liquid nitrogen temperature was measured directly on C.R.O. screen which was properly illuminated and calibrated. Before introducing the sample in the balancing coil stray signals and phase mismatch were carefully got rid of with the aid of controls provided. Even after introducing the sample, the set up was once again tested for the above mentioned interferences when the current in the electromagnet was zero. The current was gradually increased upto 0.2 A which provides a magnetic field of 2 KOe. The reading of hysteresis loop on C.R.O. screen was noted down. Then without disturbing the alignment the experiment was repeated for same sample at liquid nitrogen temperature.

The divisions of the C.R.O. on Y-axis (magnetization axis) were calibrated using the standard 'Ni' ball.

5.7 CURIE TEMPERATURE DETERMINATION :

Experimental arrangement and schematic diagram for determination of Curie temperature is shown in fig.5.2. For the determination of Curie temperature samples were used in pellet form. An electromagnet was kept above the vertical furnace. A sample holder was attached to the electromagnet which was kept inside the furnace. Then by attaching sample to the sample holder temperature of furnace was slowly increased. Temperature at which sample falls down was noted accurately by using calibrated thermocouple. Experiment was repeated twice and accurate Curie temperature was determined for each sample.

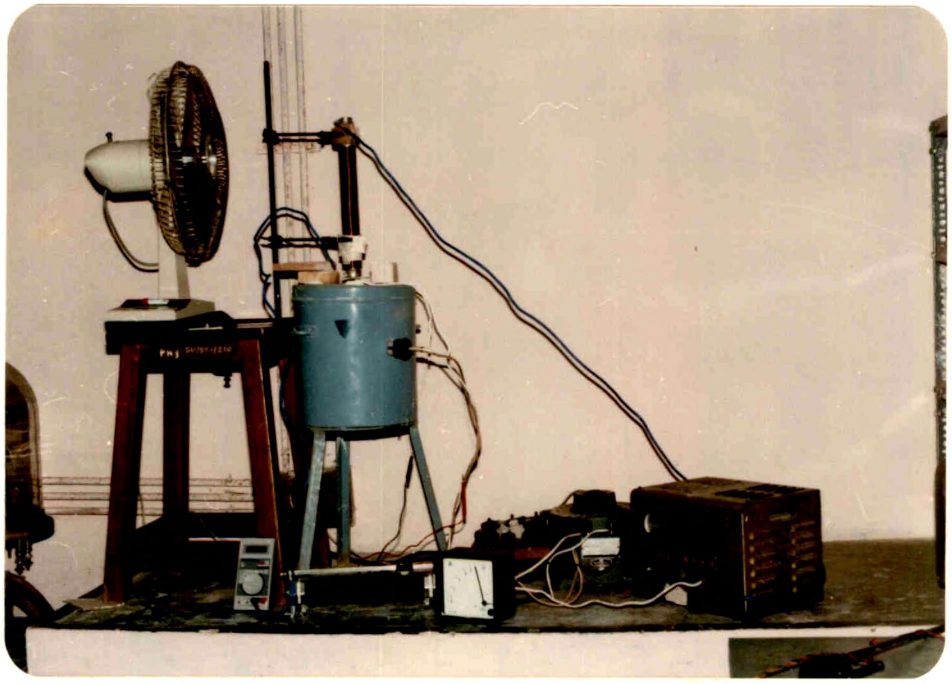

fig. 5·2

5.8 RESULTS AND DISCUSSION :

In fig. 5.3 variation of n_B (Bohr magneton) with the content of Ti^{4+} is given for the system $Mg_{1+t}Ti_tFe_{2-2t}O_4$ (t = 0, 0.1, 0.2, 0.3, 0.4, 0.5) the values of n_B have been calculated by using the formula

$$n_B = \frac{\text{(molecular weight) X Ms}}{5585 \text{ x } d_s}$$

where d_s = density of the sample

M_s = saturation magnetization.

If M_s is the saturation magnetization in e.m.u. per gm, then M_s was calculated as,

$$M_s = (1-P)\sigma_s \, d_s$$

where P is the porosity.

From fig. 5.3 it is seen that (except for t = 0.4) the values of n_B decreases almost linearly on addition of Ti^{4+} in the system. In the sample corresponding to t = 0.4 there is a sudden increase in the value of n_B. The nature of variation at 300°K and 77°K is similar Khan D.C. et.al. have carried out structure and magnetization studies on Ti substituted $Ni_{0.3}Zn_{0.7}Fe_2O_4$. They have applied Y-K theory to explain the compositional variation of magnetization. Their analysis suggests that all Ti^{4+} ions are going to A-site accompanied by half its number of vacancies for $\frac{1}{2}$ and 1 per cent, and, starts entering B-sites beyond that. The Fe^{3+} transfer is always from A to B-sites. The transfer increases from $\frac{1}{2}$ through 2 per cent samples and then decreases and reaches approximately a steady state at 5 and 10 per

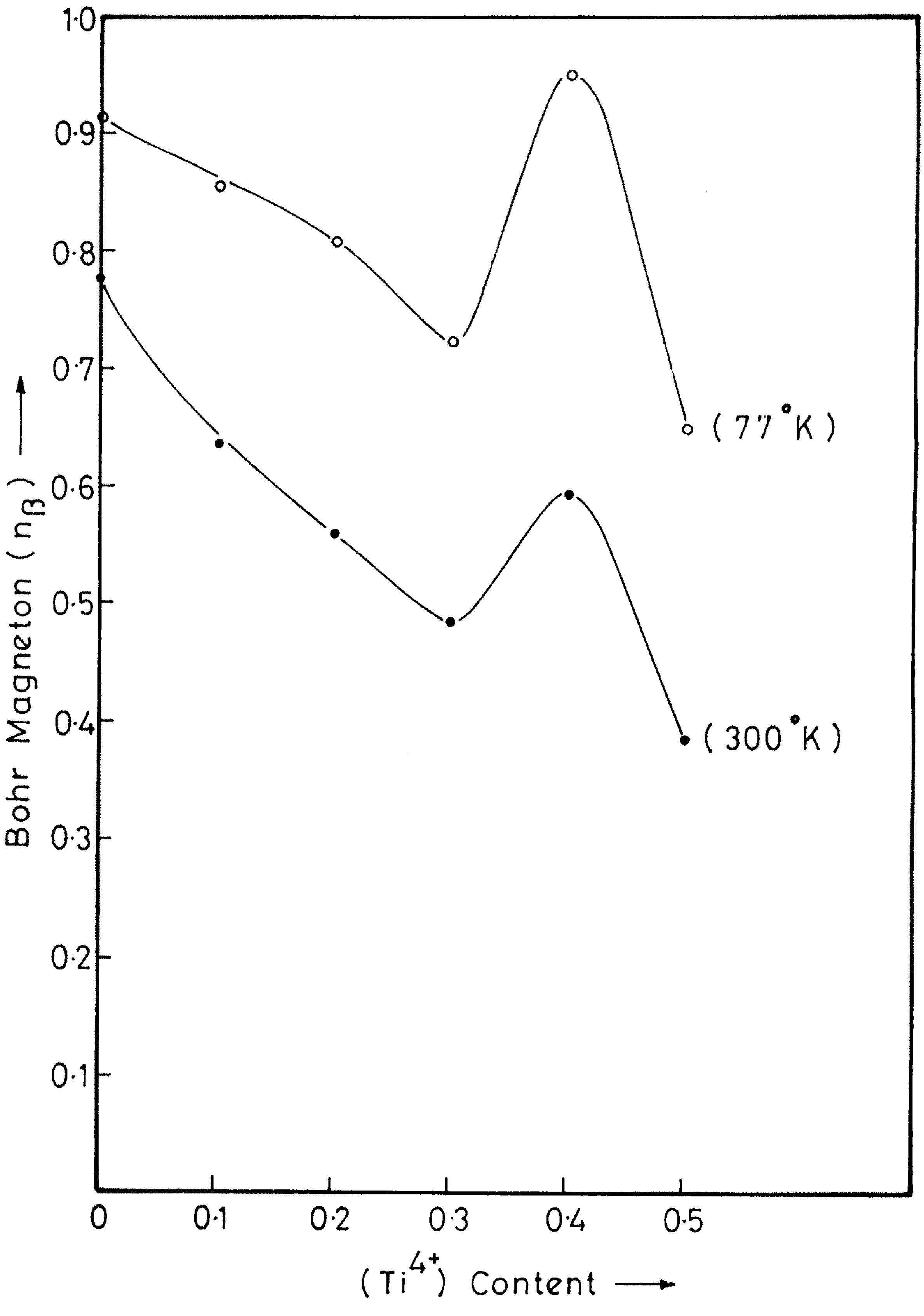
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0·1
0·2
0·3
0·4
0·5
Bohr Magneton (n_{β}) →
(Ti^{4+}) Content →
(77 °K)
(300 °K)

Fig. 5·3

cent systems.[11] Lattice parameter variation and magnetization studies on titanium, zirconium and tin substituted nickel-zinc ferrites are carried out by Das A.R. et.al.[12] They have reported that on the basis of existing predictions[13,14,15] the preferred sites for Ti, Sn, Nb and Ni are B and that for Zn is A. Theoretical estimates of σ_s variation with ions going to these preferred sites would predict monotonic behaviour particularly for low concentrations and such a variations have been reported for substitution by non-magnetic ions.[13,16]

Number of workers have postulated movement of ions to the non-preferred sites i.e. Zn^{2+} to B,[17] Sn^{4+} to A [14] and Ti^{4+} to A [13] in order to explain observed variation in properties and X-ray intensity study[17] confirmed the assumption. F.K.Lotgering has carried out studies on semiconduction and cation valancies in magnenise ferrites. It is seen that Ti^{4+} substitution has practically no influence on the resistivity, nor therefore on Fe^{2+} content. This implies that the equillibrium,

$$Mn^{2+} + Fe^{3+} \rightleftarrows Mn^{3+} + Fe^{2+} \qquad \ldots (5.3)$$

lies to the left, because in that case Ti^{4+} substitution is represented by replacing,

$$Fe^{3+} + Mn^{3+} \text{ by } Ti^{4+} + Mn^{2+} \qquad \ldots (5.4)$$

a replacement, however of,

$$2Fe^{3+} \text{ by } Ti^{4+} + Fe^{2+} \qquad \ldots (5.5)$$

represent the substitution if the equillibrium (5.5) were to the right case (5.5) is in contradiction, which would produce a ferrous content with a concentration $[Fe^{2+}] \approx 0.1$ is expected to decrease the resistivity by power of 10. The fact that the addition of Ti^{4+} in our system increases (5.5) suggest that there is no formation of Fe^{2+} ions which would have reduced the resistivity. The addition of Ti^{4+} by amount 't' reduces the Fe^{3+} ion concentration by an amount (2-2t) while increases Mg^{2+} ion concentration by an amount (1+t). Hence the reduction of the magnetic moment can be directly associated to Fe^{3+} ions. However, to understand the role of Mg^{2+} ions the distribution of cations must be known precisely. In the systems containing Cu and Mg this task is not easy as these ferrites are sensitive to heat treatment.

The distribution of cations over tetrahedral and octahedral sites is determined by a delicate balance of a number of large contribution to the energy of crystal lattice. Earlier conclusions of Verwey et.al.[18,19] based on the coloumb energy of the charged ions showed the size and valancy of cations and the crystallographic parameters of the anion to be the important factors. In order to explain the site preference of transition metal ions in oxides, two theories which differ in the chemical concept of bonding in oxides have been put forward. Dunitz and Orgel[20] and also McClure[21] have used the crystal field theory which is based on purely ionic type of bonding. Blasse[22] has used a simplified molecular orbital approach. The problem is first to calculate the energy levels of 3d orbitals in an octahedral or tetrahedral co-ordination of oxygen and then fill the energy levels with a number of electrons on the ions and calculate the energy of cation on a given lattice site. Both the treatments confirmed many simplications and the agreement differed in many cases.

For our system it is reasonable to consider the cation distribution to be of the form

$$(Fe^{3+}_{1-x}Mg_x) [Fe^{3+}_{1+x-2t}Mg_{1+t-x}Ti^{4+}_t]O_4$$

Thus whatever amount of Ti^{4+} or Mg^{2+} ions is added to the system there is reduction of Fe^{3+} ions. Also occupation of B-site by Ti^{4+} ions has an effect of forcing Fe^{3+} ions from B-site to A-site. Thus, addition of Ti^{4+} reduces A-B interaction and hence n_B.

The fact that Curie temperature decreases linearly on addition of Ti^{4+} suggests that the A-B interaction reduces in the system. The antiferromagnetic ordering in the Ti substituted ferrite has observed by many workers and also the crystal distortion. The detail understanding of this can be have from neutron diffraction studies. However, in our system triangular spin arrangement may not be favourable.

In fig. 5.4 variation of Curie temperature with the content of Ti^{4+} in the system $Mg_{1-t}Ti_tFe_{2-2t}O_4$ is shown. It is seen that the Curie temperature decreases on addition of Ti^{4+}. There is a close agreement between the experimentally measured Curie temperatures and those obtained from thermal variation of resistivity. The Curie temperature T_c is roughly proportional to the product of the concentrations of the Fe^{3+} ions on A-site and B-site. Accordingly the Curie temperature T_c varies with t and x as,

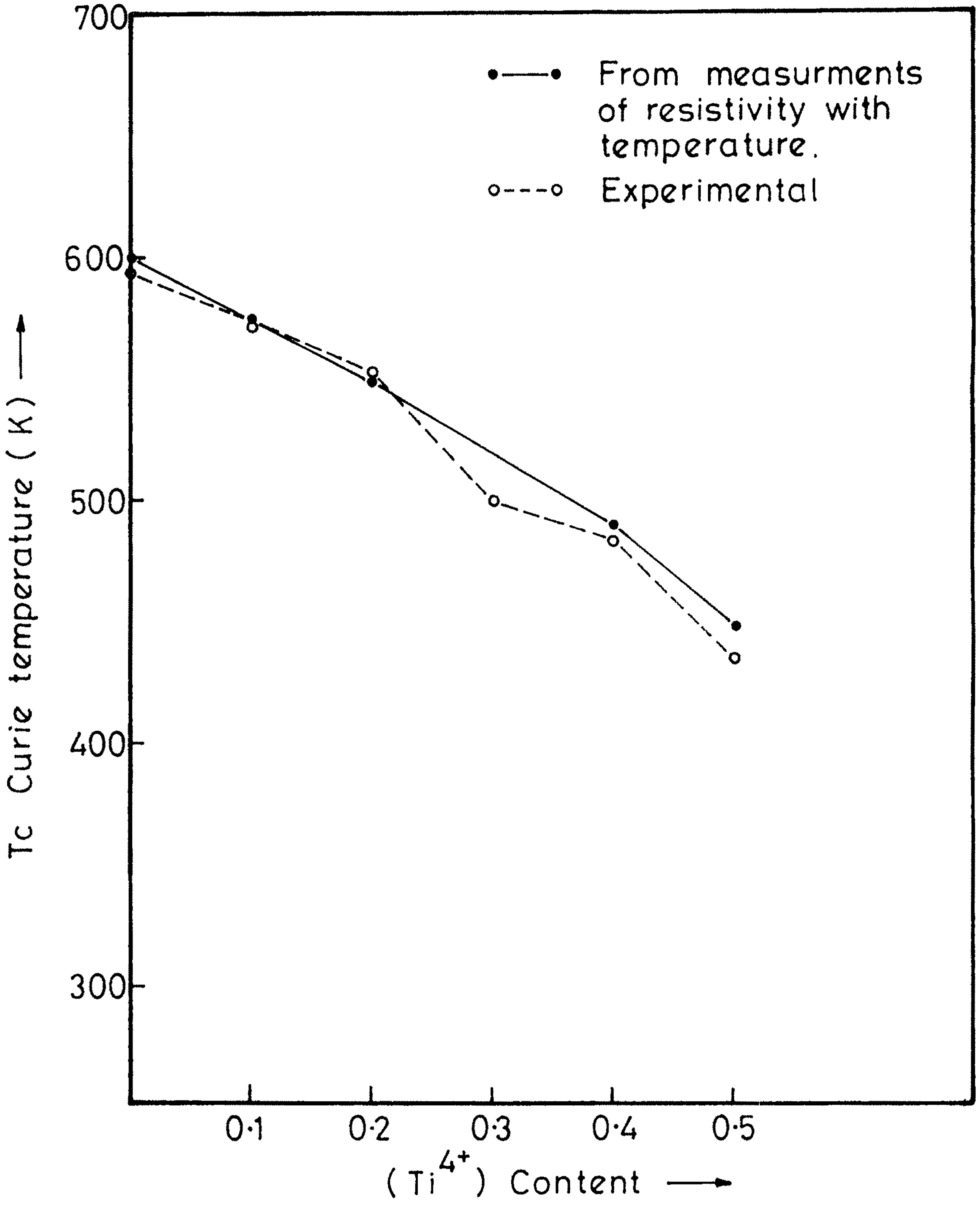
700
600
500
400
300
Tc Curie temperature (K) →
0·1
0·2
0·3
0·4
0·5
(Ti^{4+}) Content →
●—● From measurments of resistivity with temperature.
○---○ Experimental

Fig. 5·4

$$(1-x)(1+x-2t) = (1-x^2) - 2t\ (1-x)$$

The temperatures at which a break in log ρ against 1/T curve is observed satisfying the above mentioned relation. In addition, they agree with the reported values of T_c[22,23,24] Therefore, we identify these temperatures as Curie temperatures.

From the cation distribution suggested for the system,

$$(Fe^{3+}_{1-x}Mg^{2+}_{x})\ [Fe^{3+}_{1+x-2t}Mg^{2+}_{1+t-x}Ti^{4+}_{t}\ ]\ O_4$$

it is reasonable to state that reduction in T_c on addition of Ti^{4+} reduces the A-B interactions. This fact is supported by the observed reduction of n_B with addition of Ti^{4+} in the system. Also $MgFe_2O_4$ and $CuFe_2O_4$ are partially inverted ferrites and hence the values of T_c for these ferrites or ferrites containing these ions will depend on firing temperature and heating and cooling rates.

The values of T_c and energy Δ E are given in table 5.1.

Table : 5.1

Constant t of Ti t	Curie temp. T_c(K)	E"($T>T_c$) eV	E'($T<T_c$) eV	Δ E eV
0.0	698.0	0.852	0.575	0.277
0.1	578.0	0.817	0.405	0.412
0.2	548.0	0.900	0.759	0.141
0.3	508.0	0.920	0.350	0.570
0.4	487.8	0.940	0.506	0.434
0.5	448.0	0.990	0.550	0.440

The relation, $E = qKT_c$

Where, $\Delta E = E'' - E'$ is associated with the ordering temperature T_c. E' and E" are activation energies below and above T_c. The value of proportionality constant q is found to be in the range 4 to 6. The dependance of Curie temperature on distribution of the metallic ions on tetrahedral and octahedral sites in the ferrites was suggested by Gorter[25] and Neel[26]. Pautheuet[27,28] studied the temperature depend, of saturation magnetization for several ferrites. He observed that electrical and magnetic properties of copper ferrite and magnesium ferrite are highly dependent on method of preparation. If $\alpha = \beta = 0$, then Weiss field at T = 0(K) in the A-sublattice is appro ximately twice as large as that in B-sub lattice. As a result the saturatioin magnetization (M_s) vs temperature curves of A sublattice will be more convex in shape than those for B sublattice. The total magnetization is equal to the difference of B and A sublattice magnetization. A finite positive value of β makes the Weiss field in B sub lattice smaller and intensify the effect, while a finite value of makes the Weiss field in A sublattice smaller and will counteract the effect.

Rezlescu et.al.[29] investigated the influence of preparation techniques and cation distribution on properties of copper and manganise mixed ferrites. They verified the oxidation of $Cu^{1+} \longrightarrow Cu^{2+}$ and their passage from octahedral to tetrahedral site shifts Curie temperature to lower value. In zinc mixed ferrites, the A-B interaction reduces with zinc ions and curie temperature drops with the result of substitution of zinc. It is very difficult to predict the nature of magnetization at the intermediate temperature eventhough the Curie points and saturation moments are known exactly.

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