

3.1 INTRODUCTION :

It is known that all ferrites have semiconductors properties.¹ The room temperature resistivity can vary from $10^{-3} \Omega \text{ cm}$ to $10^9 \Omega \text{ cm}$. Due to their high resistivity and relatively easy preparation make these materials widely usable for the cores of intermediate and high frequency electromagnetic devices^{2,3}. The conduction mechanism has been described either applying the carrier hopping model suggested by Verwey and Heilmann⁴ or on the basis of band picture. The resistivity of ferrites obeys the law,

$$\rho = \rho_0 \exp (-E/KT)$$

where E is activation energy. Komar et.al.⁵ have observed breaks or discontinuities in $\log \rho$ vs $1/T$ plots for many ferrites. This discontinuity occurs near Curie temperature and segments represent different conduction mechanisms. Anomalous results showing different values of resistivity were observed in 'Ni' ferrite.⁶

Koops⁷ has studied variation of resistivity and dielectric constant with frequency. He found that resistivity and dielectric constant fall by large amount at higher frequencies in inhomogeneous materials.

The conduction mechanism in ferrites is due to exchange of electrons from Fe^{3+} to Fe^{2+} in the same (octahedra) lattice. This requires little energy to move an electron. Under the influence of electric field these extra electrons can be considered to constitute the conduction current by hopping from one site to the other.

Recently Klinger⁸ has reviewed the conduction mechanism in ferrites. He stated that hopping of polarons is the main conduction mechanism in ferrites. He has suggested two phase mechanism for hopping of polarons.

The contributions to the resistivity of materials are from cation distribution, crystal structure, porosity, grain size impurity inclusions, chemical or oxidation states and other unknown and known scattering mechanisms.

Jefferson⁹ has studied the conductivity and Seebeck co-efficient for 'Cu' containing ferrites. Ahmad et.al.¹⁰ have observed the discrepancies in the theoretical and observed results. They measured the temperature dependance of electrical conductivity, Hall effect and thermoelectric power of 'Cu-Zn' ferrites and interpreted the results on the basis hopping of small polarons.

In this chapter, review of the conduction mechanism in oxides and ferrites and polaron theory are briefly discussed. The resistivity and thermoelectric power are also dealt with. The measurement of temperature dependent of resistivity have been carried out. The results are discussed and interpreted in terms of the present theoretical model.

3.2 CONDUCTION MECHANISM :

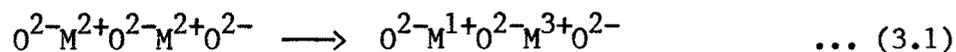
In general oxide crystal structures may be conveniently regarded in terms of oxygen ions and relatively small metal ions occupying the interstices. Although the bonding in the transition metal oxides is predominately ionic, the electrical conductivity tends to be

decided by the electron with d-like wave functions and most probably the impurity states.

In the elements of first transition series, the 3d levels are being systematically filled from Sc to Ni. In the crystalline field of a solid the levels are split into a triplet and a doublet. The triplet (t_{2g}) states lie below the doublet (e_g) states in oxides with rock salt structure. These oxides then expected to be metallic conductor at least above antiferromagnetic temperature.¹¹ Below the Neel temperature the exchange forces could give rise to further splitting of 3d band. The oxides however behave as semiconductor at all temperature and have intrinsic activation energies in excess of those which would be accounted for by exchange splitting. From this it is evident that descriptions in terms of conventional band structure fails to account for the electrical transport properties.

3.2 (a) Conduction in Oxides :

For an oxide of composition MO the activation of a conduction electron may be represented by



Where M is divalent transition metal ions.

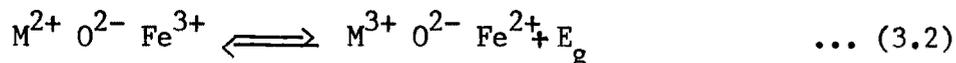
The energy needed for the formation of ion pair $(M^{2+}M^{2-})$ & $(M^{3+}M^{1+})$ corresponds to a gap in the density of states.

The following terms are contributing to the activation energy which arises from an electron correlation effect.

- 1) The difference between ionisation energy and the electron affinity of the free M^{2+} ion.
- 2) The difference in Madelung energy of the two configuration - $(M^{2+}M^{2+})$ and $(M^{3+}M^{1+})$
- 3) The difference in crystal field stabilization energy of the above configuration.
- 4) Energies of polarisation of the surrounding crystal lattice.

3.2 (b) Conduction in Ferrites :

This above mechanism of electron transport does not apply to other simple ferrites where all Fe ions are trivalent. Transport may be then represented by



where E_g the activation energy may reflect the difference between third ionisation potential of Fe^{3+} and M^{3+} ions in the solid. Jonker¹² has studied the ferrite $Co_xFe_{3-x}O_4$ and predicted qualitatively the mechanism stated above.

Ionic state of the cations in an ionic crystal gives some insight into the effect of impurities on electrical properties.

In so far as the ionisation potential of O^{2-} ion is the dominant term. Substitution upto 1% or so of the cations of another element of the same valancy should have little effect upon the conductivity. If dopant has higher valancy it will contribute donor centers, if it has lower valancy it will provide acceptor centers.

Analogous considerations may apply to cations of mixed valancy in ferrites which result from a departure from the ideal metal to oxygen ratio. An oxygen ion vacancy will contribute two extra electrons to the 3d band. If these extra charges are detached from their vacancies by thermal agitation n-type conductivity is induced in oxygen excess materials. Some oxides are very difficult to prepare homogenously with a stoichiometric anion to cation ratio. Extrinsic semiconduction may then prevail throughout the temperature region amenable to electrical measurements. In such a cases it may still be possible to infer the activation energy of intrinsic conduction samples from which extrinsic effects have been suppressed by introduction of compensations impurities. This was first demonstrated by Van Uitert¹² in NiFe_2O_4 by replacing 1 to 2% Fe by Mn or Co. Electrons donated by oxygen vacancies will fill the impurity levels in preference to iron conduction levels. Mixed valancy state will be confined to the impurity element if its local concentration exceeds twice that of oxygen vacancies. This technique is based on the assumption that impurity band conduction is absent and the allowed impurity concentrations indicate that the cation wave function do not extend significantly beyond nearest neighbour distance in the B-lattice. Electrons and holes are known to move by thermally activated hopping mechanism expect for pseudometallic composition region close to magnetite.

3.3 CONDUCTIVITY :

Imperfection in lattice will result in a spectrum of donar and acceptor levels within the energy gap. Total number of such a levels

may be very small compared to total number of metal ions and have little effect on electrical conductivity in the intrinsic region, but affect the low temperature properties. At sufficiently low temperature the transport properties have a complicated dependence on 'T' in semiconductor which is determined by structural defects and impurities. In analogy to the thermal activation processes encountered in ionic diffusion and ionic conductivity, the expression for the mobility¹³ (μ) can be written as

$$\mu = \frac{ed^2\nu}{KT} \exp\left(-\frac{E}{KT}\right) \quad \dots (3.2)$$

where,

- d = the jump distance between nearest neighbours
- ν = frequency of lattice vibrations
- E = the activation energy for the hopping process.

It can be seen that the mobility in transition metal oxides, is strongly temperature dependent. The conductivity is linked with the concentration of carriers and their mobility as,

$$\sigma = e (n_e \mu_e + n_h \mu_h) \quad \dots (3.3)$$

This relation has been used by many authors to discuss the conductivity behaviour in ferrites.

Activation energy does not provide much insight as to conduction mechanism because temperature dependent hopping mechanism and activation of electrons into the conduction levels are of the same form indistinguishable included in the activation energy found out experimentally.

3.4 THERMOELECTRIC POWER :

Two dissimilar metal wires joined together to form two junctions and if they are maintained at different temperatures an thermo e.m.f. is developed. This was first observed by Seebeck. The Seebeck coefficient (α) can be determined by

$$\alpha = \frac{dv_{12}}{dT}$$

where dv_{12} represent e.m.f. across the junction 1 and 2 and dT represents the temperature difference.

The Seebeck effect may be thought of as a diffusion process. The electrons or holes from the hot end have higher kinetic energy as compared to those from the cold end and hence the electric current is produced.

According to quantum theory, for semiconductors with both types of carriers α is given by

$$\alpha = \frac{(\alpha_n \sigma_n + \alpha_p \sigma_p)}{\sigma_n + \sigma_p}$$

where $\sigma_n = ne\mu_n$, $\sigma_p = pe\mu_p$

$$\alpha_n = -\frac{K}{e} \{ A_n - E_F / KT \} ,$$

$$\alpha_p = \frac{K}{e} \{ A_p + (E_g + E_F) / KT \}$$

Here n and p are electron and hole densities, μ_n and μ_p are the electron and hole mobilities, E_F is the Fermi energy and E_g is the band gap.

For a partially filled band, the Seebeck co-efficient (α) varies linearly with temperature,

$$\alpha_n = - \left(\frac{\pi^2 K^2}{3e} \right) T \left[\frac{d \ln \sigma (E)}{dE} \right]_{E = E_F}$$

Where $\sigma (E)$ refers to the value of the conductivity for a specimen in which the Fermi level is at E . The term $d \ln \sigma (E)/dT$ can be approximated accordingly whether the Fermi energy is temperature dependent or not.

The temperature dependance of the thermoelectric power for ferrite material having one type of charge carriers could be expressed as¹⁴

$$\alpha = \frac{K}{e} \left[\ln \left(\frac{N_o}{n} - 1 \right) + \frac{a}{KT} \right]$$

where K = Boltzman constant

e = electronic charge

N_o = concentration of trivalent ions on octahedral site

n = concentration of Fe^{2+} ions

and 'a' is the part of activation energy transported by the electrons. The value of the term 'a' is zero in case of 'Mn' ferrite¹⁵ and 1 eV in other cases.¹⁶

The temperature dependance of Seebeck coefficient enables to determine the sign of the charge carriers and their density variation.

3.5 EXPERIMENTAL TECHNIQUES :

3.5 (a) D.C. Resistivity Measurements :

The resistivity measurements were made on two probe resistivity cell specially designed. Blockdiagram of the resistivity cell is shown in fig. 3.1. It consists of two small cylindrical brass electrodes fitted in the two porcelain discs. The porcelain discs can sandwich the sample between the electrodes with the help of connecting rods provided with screws. The electrically insulated copper wire was used for external connections at the end of electrodes.

Silver paste was applied on the surfaces of the pellet and was then fixed between the electrodes. The entire assembly was kept in the temperature regulated furnace. The temperature of the sample was slowly increased. The standard Cromel-Alumel thermocouple was calibrated and the same was used for the measurement of temperature. The circuit diagram for measurement of d.c. resistivity is shown in fig. 3.2.

The d.c. electric field was provided from the regulated power supply unit [Aplab model 7111]. The current values were measured on digital multimeter. The observations were made at an interval of 25°C in the temperature range varying from room temperature to 800°K. The resistivity (ρ) was calculated using the relation

$$\rho = \frac{\pi r^2}{t} \frac{V}{I}$$

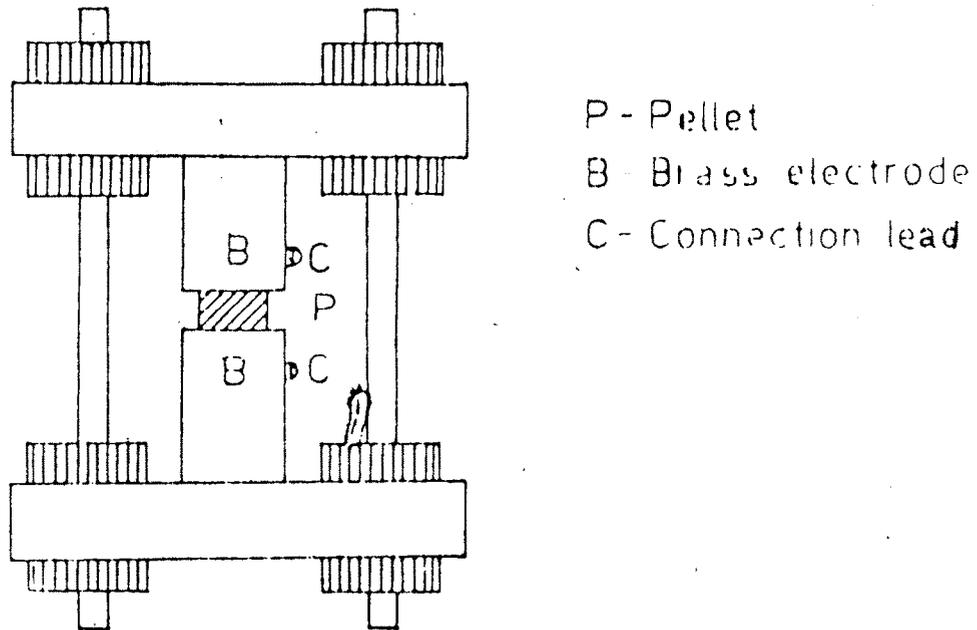
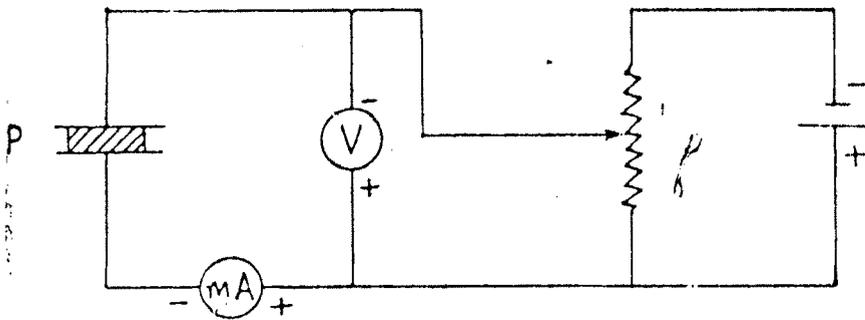
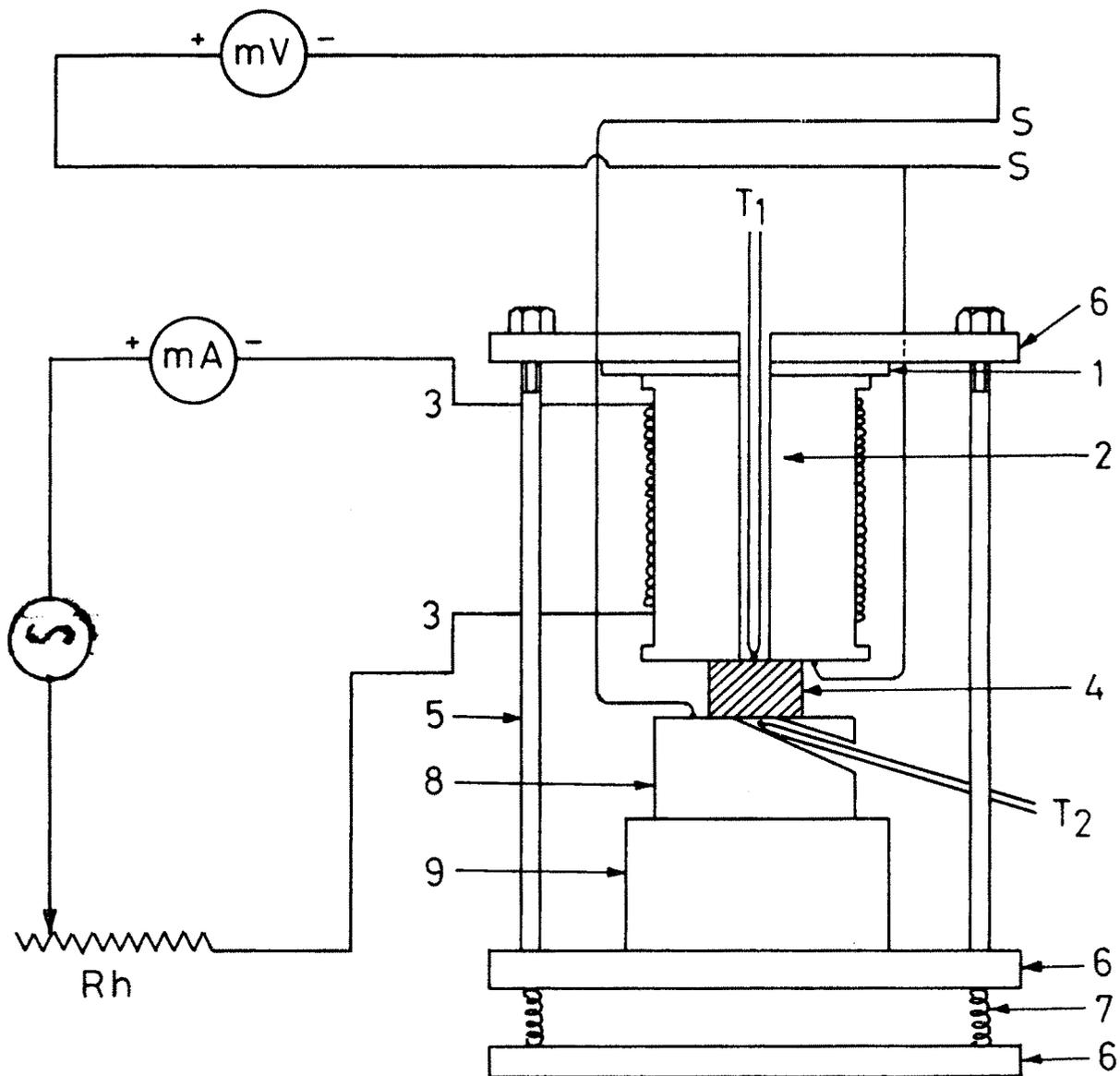


Fig 3-1



Sample holder and circuit diagram for electrical resistivity and switching.

Fig.3-2,



[1-Mion sheet; 2,8-Hard metal electrodes;3-Sub heater leads; 4-Sample pellet; 5-Metal rod; 6-Metal plates; 7-Spring;9-Metal block;T₁ T₂ - Thermocouples;S- Silver wires welded at Ag electrodes.]

• Fig. 3-3- Experimental set-up for the measurement of thermoelectric power.

The curve of $\log \rho$ vs $\frac{10^4}{T}$ for each sample was plotted and the same are presented for further discussion.

3.5 (b) Seebeck Coefficient Measurements :

Specimens in the form of pellets were used for the measurement of thermoelectric power. The sample holder used for measurement was shown in the fig. 3.3. The specimen was held in a brass block with mica sheets as insulating material. Silver foil with silver wire were used for the measurement of thermo e.m.f. The temperature difference between two ends was established by heating one end with the help of auxiliary heater. A dimmerstat was used to control the constant temperature difference.

The ambient temperature of the sample was varied by the use of temperature regulated furnace. The temperature at both ends of the specimen were measured by Chromel-Alumel thermocouples.

The thermo e.m.f. was measured on a high precision d.c. micro-voltmeter (model- Philips PP9004). A pointer of sensitive galvanometer is also provided to indicate the sign of the thermo e.m.f.

3.6 (a) RESULTS AND DISCUSSION :

In fig. 3.4 variation of $\log \rho$ vs $10^4/T$ is shown for the series of ferrites with general formula $Mg_{1+t}Ti_tFe_{2-2t}O_4$ ($t = 0.1, 0.3, 0.4$) in the temperature range from room temperature to 800°K. The nature of variation is similar in all the samples and the resistivity behaves according to Arrhenius relation

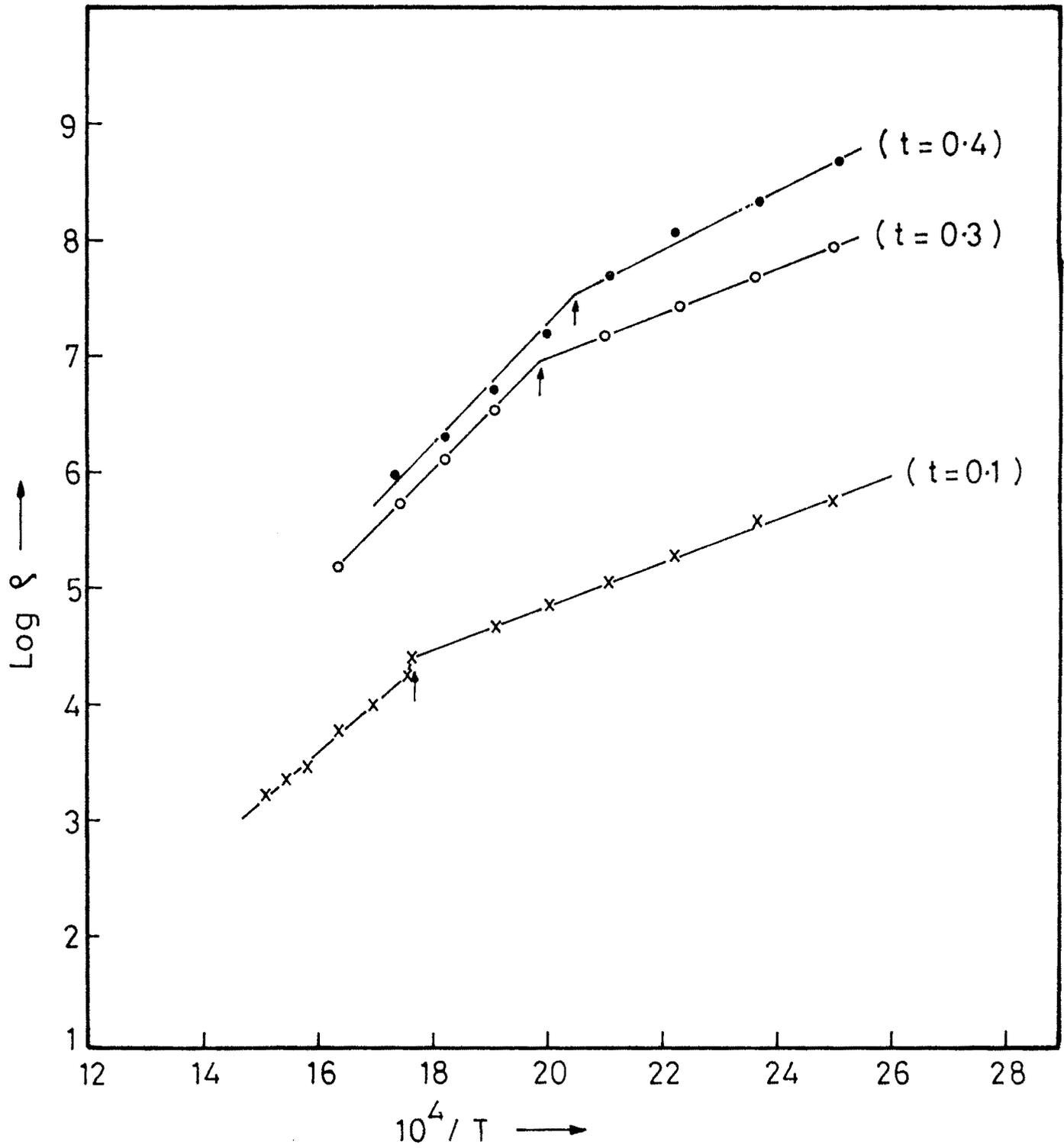


Fig. 3.4

$$\rho = \rho_0 \exp (E/kT)$$

where E is the activation energy K is Boltzman constant and T is absolute temperature.

Distinct break is observed in the temperature variation of the resistivity. The temperature at which the break occurs nearly coincides with the ferrimagnetic Curie temperature of these samples. The breaks and discontinuities can be attributed to several sources. Komar and Klivshin¹⁷ have observed changes in activation energies for conduction which occur at high temperature in several ferrites and are correlated with the ferromagnetic Curie temperature of the ferrites. This offers solid evidence for the influence of magnetic ordering upon conductivity in ferrites.¹⁸ The breaks may also be due to change in conduction mechanism. Recently Ghani et.al.¹⁹ and Sankpal et.al.²⁰ have shown more than one breaks in the temperature variation of resistivity in the case of Cu-Ni ferrites. They have attributed the conduction mechanism in the first region to the phase transition from tetragonal to cubic and in the third region to a magnetic ordering change.

From fig. 3.4 it is also seen that over the range of temperature of resistivity measurement there is increase of resistivity on addition of Ti^{4+} in the system. In our system the addition of $(1+t)$ of Mg^{2+} ions reduces the Fe^{3+} concentration by $(2-2t)$. Kainuma²¹ studied the magnetic permeability and d.c. conductivity of the $Mg_{1-x}Cu_xFe_2O_4$ ($0.1 < x < 0.6$) and observed the activation energies obtained from these two measurements to be the same. The conductivity

increased with increasing concentration of copper which indicate the formation of the ferrous ions, since the activation energies are same it is suggested that the mechanism of magnetic relaxation or the induced anisotropy might be due to the electron diffusion.

Samokhvalov and Rustamov²² have pointed out that the activation energy for an electron to jump from an excited state of Fe^{3+} to a neighbouring Fe^{2+} sites is equal to 0.1 to 0.2 eV. Thus there are lot of deviations in the activation energies for Fe^{3+} to Fe^{2+} relaxation mechanism.

Brabers²³ studied the electrical conductivity of Ti^{4+} substituted manganese-zinc ferrites, and attributed the conductivity to the hopping of electrons between the ferric to ferrous ions on the octahedral sites. He observed a change in activation energy for the substituted and unsubstituted zinc ferrites with Ti^{4+} . He further pointed out that the activation energy of the mobile charge carriers in the hopping model, which is supposed to be the conduction mechanism in these materials must increase with the increase in Ti^{4+} concentration.

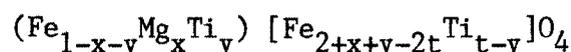
Bosman²⁴ studied the electrical conductivity and Seebeck coefficient of NiO doped with Li. He observed that mobility of charge carriers involved no activation energy and the temperature dependence of conductivity is a function of the charge carrier concentration.

Magnesium ferrite is an n-type conductor whose activation energy in the temperature range 610°C to 830°C has a value 1.16 eV. Guillaud and Bertrand²⁵ have measured the electrical conductivity

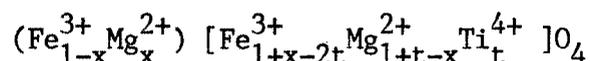
of pure magnesium ferrite and have suggested that this ferrite is suitable as a basis for the development of ferrite at the highest frequencies.

Thus, it can be seen that the conductivity depends on divalent metal ions, impurities, sintering and preparation conditions. In general the substitution of a cation of low valence state leads to p-type conduction and by a cation of higher valence state leads to n-type conduction.

For our system $Mg_{1+t}Ti_tFe_{2-2t}O_4$ the general formula of the cation distribution may be given by,



in which the cations enclosed () occupy the A-site while those enclosed [] occupy the B-site. However, there is evidence that the values of y are small²⁶ as the result of maximum charge neutralization. In other words, the tetrahedral Fe^{3+} ions are replaced by Ti^{4+} ions. Therefore, it is reasonable to consider the cation distribution to be of the form,

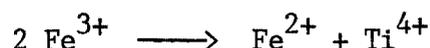


A-A hopping does not exist as there are only Fe^{3+} ions on this sub-lattice and any Fe^{2+} ions formed during processing preferentially occupy the B-site. B-B hopping is more dominant than A-B hopping, simply because the separation between an ion on A-site and an ion on a B-site. Thus the reduction of Fe^{3+} ions on addition of Ti^{4+} are responsible to increase the resistivity.

Table 3.1 : Values of T_c and the activation energies for
 $t = 0.1, 0.3, 0.4$.

Containt of Ti t	Critical temp. T_c in (K)	Activation energy $E'(T < T_c)$	Activation energy $E''(T > T_c)$	ΔE
0.1	578	.405	.817	.412
0.3	508	.35	.92	.57
0.4	487.8	.506	.94	.434

Ferric ions are also reported to be converted to ferrous ions on addition of Ti^{4+} as follows :



The resistivity is expected to increase due to localization of Fe^{2+} on B-site when Ti^{4+} is added, however, the addition of Ti^{4+} results in overall reduction of Fe^{3+} from the ferrite material and hence the reduction of conductivity or increase of resistivity.

In table 3.1 values of activation energies in the ferrimagnetic and paramagnetic regions are given. It is seen that the activation energies in the paramagnetic region are greater than those in the ferrimagnetic region. The change of ΔE is indicated by the change of slope. According to the theory of magnetic semiconductors one expects a decrease in the activation energy E due to the splitting of the conduction and valance bands below T_c . Above the Curie temperature the bands are degenerate for the two spin directions.²⁷ One therefore expects a reduction in the activation energy as the system undergoes transition from paramagnetic to ferrimagnetic states

This result is also in agreement with the theory developed by Irkin and Turov.²⁸

From the range of the values of E (0.35 eV to 0.94 eV) the conduction is clearly seen to be intrinsic type. However, the activation energy also depends upon the following factor.

1) Polycrystalline samples are sintered and contain pores. The pores probably air filled will be of a resistivity different from that of the ferrite or garnet itself.

2) The grain size of individual crystallites in a polycrystalline sample can affect, among other things, the number of grain to grain contacts and thus influence the conduction paths and hence resistivity.

3) The chemical and/or heat treatment may result in chemical inhomogeneity. Thus with a sintered rod, there may be oxidation states on the outside of the rod different from those inside, again individual grains may be inhomogeneous for a similar reason.²⁹

The electrical resistivity, the change in the activation energy at the Curie point and the relationship of the activation energy with the composition can be explained and discussed only in the light of the mechanism of the hopping polarons, which has been successfully employed to explain the conduction mechanism in ferrites.³⁰

The conductivity in ferrites has been associated in general with the presence of ions of a given element in more than one valence state.³¹ These ions get distributed over the crystallographically

equivalent sites. The high conductivity of Fe_2O_3 for example has been explained as



The values of ΔE to cause normal electron hopping are of the order of 0.2 eV and less.³² The value of ΔE given in table 3.1 suggest that the hopping process due to polaron is favoured. The theory of conductivity has been explained on the hopping of polarons due to thermal activation.³³

Therefore polaron hopping, although thermally activated in both the temperature regions appears to have a lower activation energy in the magnetic region below the Curie temperature. This is bound to be the case as the polaron in the case of ferrite does not significantly involve a strain in the ionic lattice as in the case of other ionic solids, due to the fact that the 'd' electrons contribute the polaron. The co-operative behaviour would be characteristic of such a polaron giving rise to a lower activation energy.

In solids with large coupling constant and a narrow conduction band, small polaron formation is more probable. In oxides of the iron group of metals the overlap of 3d wave functions between neighbouring metal ions is relatively small. There is strong experimental proof for the existence of small polarons and the hopping process.^{34,35} The energy levels and bands for ferrites have been calculated only after making simplifying assumptions and using suitable approximations.³⁴ Of late Klinger³⁵ has explained the conduction mechanism in magnetite like solids using a two-phase polaron model. He has concluded that

at low temperatures the conduction is via thermally activated motion of strongly correlated polarons and at high temperatures via weakly activated hopping motion or a non-activated Brownian like tunneling motion.

The activation energy in the paramagnetic region is found to be more than that ferrimagnetic region (Fig. 3.4). This can be attributed to the effect of magnetic ordering in the conduction process.³⁶ According to strict theoretical considerations the anomalous changes in the activation energy occur at the disordered temperature.

Thus both in ferrimagnetic and paramagnetic region over the range of temperature the conductivity is governed by hopping of polaron as evidenced from the value of ΔE given in table 3.1.

In fig. 3.5 relation between Seebeck coefficient and temperature is shown for the system $Mg_{1+t}Ti_tFe_{2-2t}O_4$ ($t=0,0.2,0.3,0.4,0.5$) in the temperature range from room temperature to 800°K. All the curves show almost similar thermal variation and that the Seebeck coefficient is negative. This suggested that the carriers of conduction are n-type in the entire temperature range. In all the samples as the temperature increases the Seebeck coefficient increases i.e. there is more generation of n-type carriers, however after the maximum value of Seebeck coefficient further increases in temperature tends to reduce the Seebeck coefficient. The effect appears to be more pronounced in the samples with $t = 0.3, 0.4, 0.5$. The temperatures where the maximum value of Seebeck coefficient are observed can roughly be correlated with Curie temperatures. That is

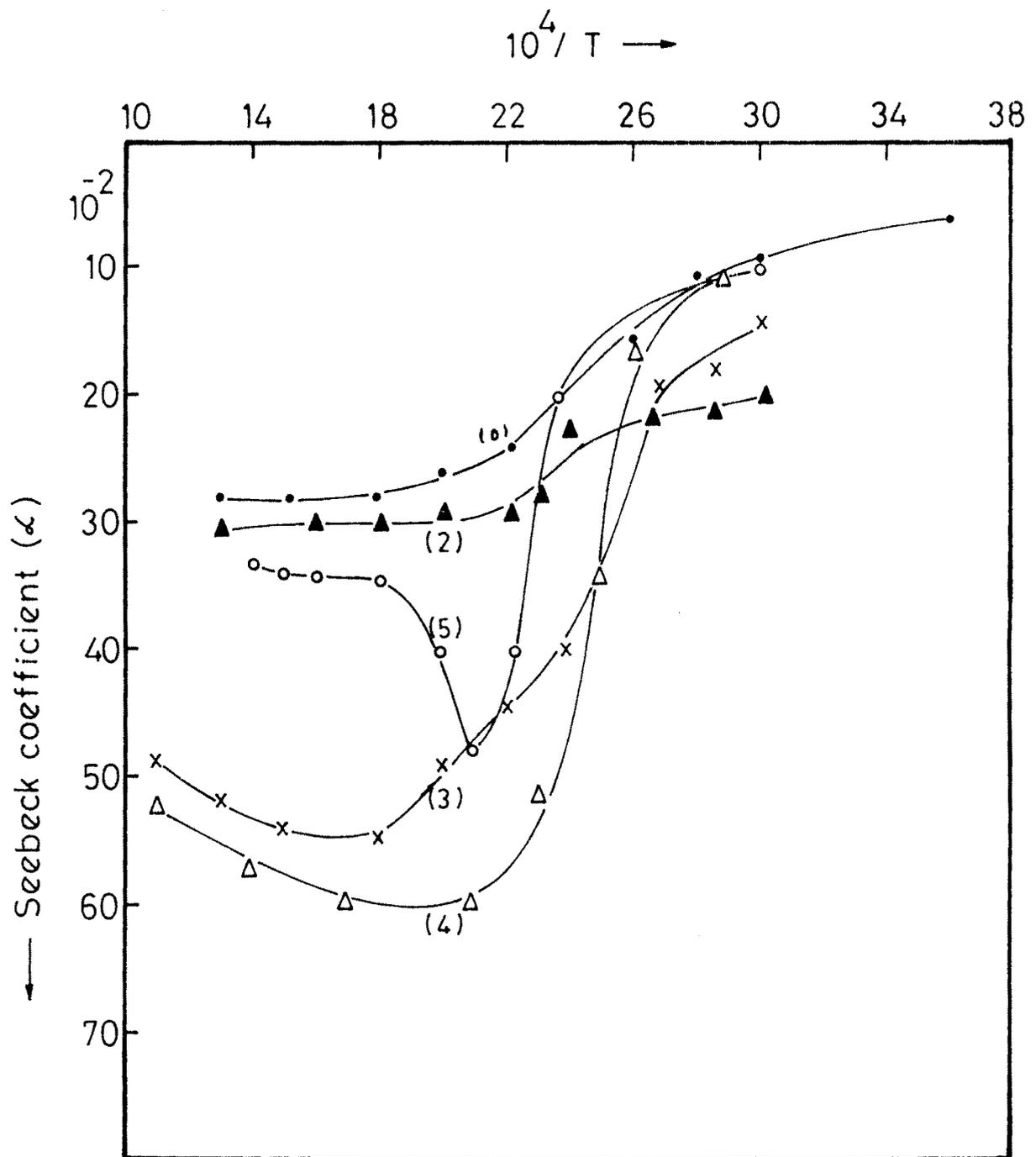


Fig. 3.5

the magnetic ordering has an influence on the Seebeck co-efficient. MgFe_2O_4 is known to be n-type. It is also seen that addition of Ti^{4+} enhances the n-type of carriers in the ferrite.

The fact that addition of Ti^{4+} increases the Seebeck co-efficient and the resistivity can be correlated according to the equation for the cubic system

$$\alpha = K_B \ln \frac{\text{total number of iron ions on B site}^{37}}{\text{total number of Fe}^{2+} \text{ ions on B site.}}$$

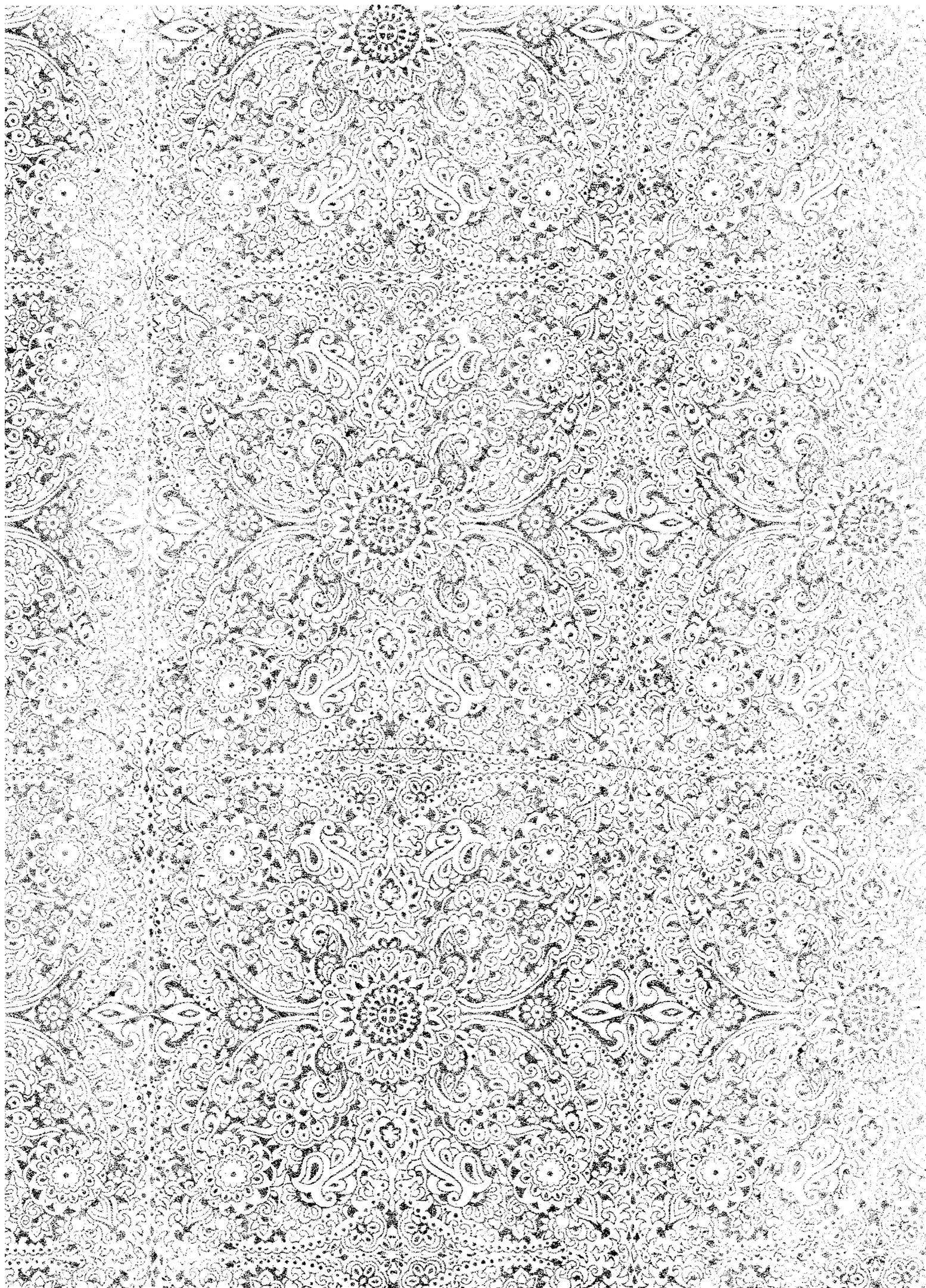
For our sample the increase in value of ' α ' on Ti^{4+} substitution suggest that addition of Ti^{4+} has an effect of reducing Fe^{2+} ion on B-site. This is responsible for increase of resistivity, however as suggested by Ghani,³⁸ electrons are generated due to the presence of Fe^{2+} ions. Thus the explanation of n-type conductivity cannot be related with the content of Fe^{2+} ions. The increase of Ti^{4+} is accompanied by increase of Mg^{2+} in the system. Thus the Mg^{2+} ions are responsible for the n-type behaviour. Copper ferrite and magnesium ferrite are sensitive to heat treatment and hence unless the cations distribution is accurately known the explanation of n-type behaviour with content of Mg^{2+} and variation of temperature will be speculative.

REFERENCES

1. Jonker G.H., J.Phys.Chem.Solids. 9 : 195 (1959).
2. Sooho R.E. "The theory and applications of ferrites"
Prentic Hall Inc. New Jersey (1960).
3. Stuyts A.L. and DeLau,K.G., Sintering 7, 147 (1975).
4. Verwey E.J.W. and El.Heilmann, J.Chem.Phys. 15, 174 (1947).
5. Komar E.J.W., Haayman P.W., Romajin F.C., Van Costerhout G.W.
Phillips Res. Rep. 5 173 (1950).
6. Morin F.J., Gaballe T.H., Phy. Rev. 99, 467 (1955).
7. Koops C.G., Phys. Rev. 83, 121 (1951).
8. Klinger M.I., Phys. Stat Solidi (B) 79, 9 (1977).
9. Jefferson C.F., J. Appl. Phys. 36 (Pt.1&2) 1165 (1965).
10. Ahmad A.G. Miryasov N.Z. Fiz. Tver Tela (CUSSR) 13, 2759
(1971) Trans-Sovt-Phys. Solid State (USA)
11. Craik D.J. (Editor) Magnetic oxide Part 1 p.421 Wiely Inter-
science publication (1975).
12. Van Uitert G., Proc. I.R.E. 44, 1294 (1956).
13. Mott N.F., Gurney R.W. "Electronic Processes in Ionic
Crystals" Oxford Uni. Press (1948).
14. Rosenberg M., P.Nicolau and I.Bunzet, Phys. Status solids
15, 521 (1966).
15. Z.Simsa, Czech. J. Phys. B 16 919 (19766).
15. Z.Simsa, Czech J. Phys. B16 919 (1966).
16. G.H.Gonker, Van Hauten S. Halbleiterprobleme 6, 118 (1961).

17. Komar A.P. and Klivshin V.V., Bull. Acad. Sci. USSR Phys. 18, 96 (1954).
18. Verwey E.J.W., Haayman P.W. and Romejn F.C., J.Chem.Phys. 15, 181 (1947).
19. Ghani A.A., Etach A.I. and Mohmed A.A. in Proceedings of International Conference on Ferrites, Kyoto Japan p.216 (1980)
20. Sankpal A.M., Sawant S.R., Vaingankar A.S., Indian J. of pure and Appl. Phys. 26, 459-61 (1988).
21. Kainuma Seiza, Japan J.Appl.Phys. 15, 1079 (1976).
22. Samokhvalov A.A. and Rustamov A.G., Sov.Phys. Solid State 7, 961 (1965).
23. Brabers V.A.M. and Willemse P.F., Phys.Let. 27A, 136 (1968).
24. Bosman A.J. and Vecoeur C.C., Phys. Review 144, 763 (1966).
25. Guillaud C. and Bertrand R. J.Rech. 11, 73 (1950).
26. Verwey E.J.W. and Heilman E.L., J.Chem.Phys., 15, 174 (1947).
27. Semary M.A., Ahmed M.A., Abbas Y., J.Mater.Sci. 18, 2890-2892 (1983).
28. Irkin Yu.P. and Turov E.A., Sov.Phys. JETP. 33, 673 (1957).
29. Standley K.J., "Oxide Magnetic Materials Clarendon Press, Oxford p. 139-40 (1972).
30. Rezlescu N. and Rezlescu E. Solid State Commun. 14, 69 (1974).
31. Verway E.J.W. and Boer J.H., Rec. Trar.Chem.Phys. Bas. 55, 531 (1936).
32. Sawant S.R., Patil R.N., Indian J. Pure and Appl. Phys., 20, 353 (1982).
33. Klinger M.I., Phys. Status Solidi (b), 79 9 (1977).

34. Mott N.F. and Gurney R.W., "Electronic Processes in ionic crystals" Oxford University Press New York (1948).
35. Klinger M.I., J. Phys. C8, 3595 (1975).
36. Relescu N. and Cuciureanu E., Phys. Status Solidi a3 873 (1970).
37. Shrinivasan G. and Srivastava C.M., Phys. Stat. Sol. (b) 108, 665[†] (1981).
38. Ghani A.A., Awad. Phys. Stat. Sol. (a) 81, K 155 (1984).



4.1 INTRODUCTION :

Ferrites show abnormally high dielectric constant and dispersion of dielectric constant and resistivity.¹ Blechstein² has observed very high dielectric constants in certain 'Mn' ferrites. Brockman, Dowling and Steneck⁹ have noted the dielectric constant of the order of 10^5 in case of Mn-Zn ferrites. They have concluded that the dimensional resonance effects in the material might be partly responsible for this value.

The dielectric dispersion of polycrystalline ferrites has been generally attributed to their heterogeneous nature discussed by Maxwell³ and Wagner.⁴ Koops has suggested a model that consists of well conducting grains, in the sample separated by lower conductivity layers. Josyulu and Sobhanadri⁵ have also reported the temperature and frequency dependence of dielectric behaviour in case of Co-Zn and Mg-Zn ferrites. They explained the dielectric dispersion on the basis of Maxwell-Wagner^{3,4} polarization. A strong correlation between the conduction phenomenon and dielectric dispersion in case of ferrites has been reported by K.Iwauchi.⁶ The decrease in dielectric constant with increasing frequency in a certain frequency range is also observed in some spinel ferrites.

In this chapter we have presented studies on the A.C. conductivity and the dielectric constant as a function of frequency in the frequency range 20 KHz to 10 MHz.

4.2 POLARISATION IN DIELECTRICS :

When an A.C. electric field applied across a ferrite material then it induce a polarisation in it. The total polarisation (P) of a multiphase material having permanent dipoles is given by,

$$P = P_e + P_i + P_o + P_s$$

where P_e = the electronic polarisation

P_i = the ionic polarisation

P_o = the orientational polarisation

P_s = the space charge or interfacial polarisation

The interfacial polarisation plays the major role in ferrites and the same is explained by Maxwell³ and Wagner.⁴

4.3 MAXWELL-WAGNER DIELECTRIC ABSORPTION :

The dissipation of energy can occur by scattering of the radiation at interfacial boundaries in a non-homogenous material. The non-homogenous dielectric may contain regions of different permittivity formed because of cracks and defects in solids and may give misleading values of permittivity. If some parts of the medium are conducting, the apparent dielectric relaxation may be expected. This is well recognised in the visible region of the transparent medium where the distribution of small particles of a second material can render it opaque. The similar feature arises in a dielectric medium, when the particles of second phase are dispersed within the principle one. The general aspects of this absorption were evaluated by Wagner⁴ and the dielectric effect is referred to as a Maxwell-Wagner absorption.

4.4 KOOPS THEORY :

In case of ferrite material the dielectric constant (relative permittivities) and resistivity are frequency dependent. It is found that dielectric constant is between about ten to twenty at high frequency but it increases abnormally high value as a result of low frequency measurement.

To explain this type of abnormal behaviour Koops⁷ gave a phenomenological theory which is based on simple model. According to Koops the measured capacitance (C_p) and parallel resistance (R_p) of the specimen results from the equivalent circuit shown in Fig.4.1 In fig. 4.1(a), C_1 , C_2 , R_1 and R_2 are all constants but the quantities C_p and R_p in fig. 4.1(b) are not, and shows a frequency dependence similar to fig. 4.2.

A sintered ferrite material is not a homogeneous. It may reasonably be supposed that the grains of ferrites are moderately good conductor and that the outer layers, the inter-grain contacts and pores are higher resistivity regions. Then the inhomogeneous structure is not unlike that discussed by Maxwell³ and Wagner.⁴ This is represented most simply as a double layer dielectric as shown in fig.4.3 where the subscript 2 refers to the ferrite grains, and 1 to the boundary layer. The resistance R_2 and possibly R_1 , may contain a contribution from the dielectric losses in addition to a purely ohmic term.

Considering the specimen as a parallel plate capacitor of plate area A

$$C_1 = \frac{\epsilon_0 \epsilon_1 A}{d} \quad , \quad C_2 = \frac{\epsilon_0 \epsilon_2 A}{d_2}$$

$$R_1 = \frac{\rho_1 d_1}{A} \quad , \quad R_2 = \frac{\rho_2 d_2}{A}$$

where $\epsilon_0 \epsilon$ is permittivity and ρ the resistivity.

It then follows by equating the impedances in the two representations of fig. 4.1(a) and 4.1(b) that,

$$\rho_p = \rho_p^\infty + \{ (\rho_p^0 - \rho_p^\infty) / (1 + \omega^2 \tau_\rho^2) \}$$

and

$$\epsilon_p = \epsilon_p^\infty + \{ (\epsilon_p^0 - \epsilon_p^\infty) / (1 + \omega^2 \tau_\epsilon^2) \}$$

Where the suffix 'P' refers to the equivalent parallel representation and the superscripts ' ∞ ' and ' 0 ' refers to very high frequency and very low frequency values respectively. The τ 's are relaxation constants and $\omega = 2\pi\nu$ where ν is the measuring frequency.

Koops made the following further assumptions,

- i) $x = \frac{d_1}{d_2} \ll 1$
- ii) $\rho_1 \gg \rho_2$
- iii) although x is small, $x\rho_1 > \rho_2$ by reasonable factor.
- iv) $\epsilon_1 = \epsilon_2$ (for most oxides this is a fair assumption)

We then found that,

$$\rho_p \approx \rho_2 + \{ x\rho_1 / (1 + b\rho_1\rho_2\omega^2/x) \}$$

and

$$\epsilon_p \approx \epsilon_2 + \{ \frac{\epsilon_2}{x} / (1 + b\rho_2^2\omega^2 / x^2) \}$$

Where b is constant.

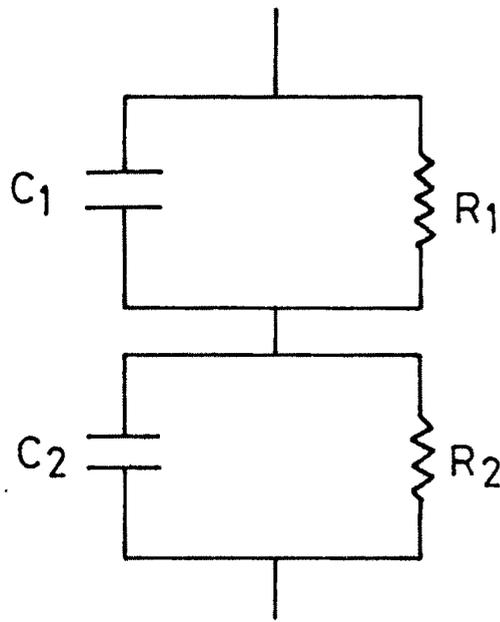


Fig. 4.1 (a)

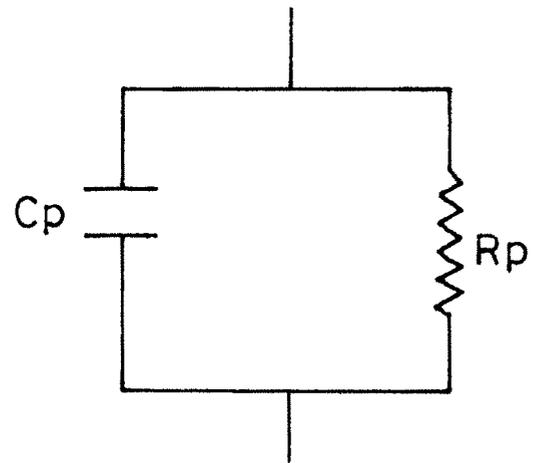


Fig. 4.1 (b)

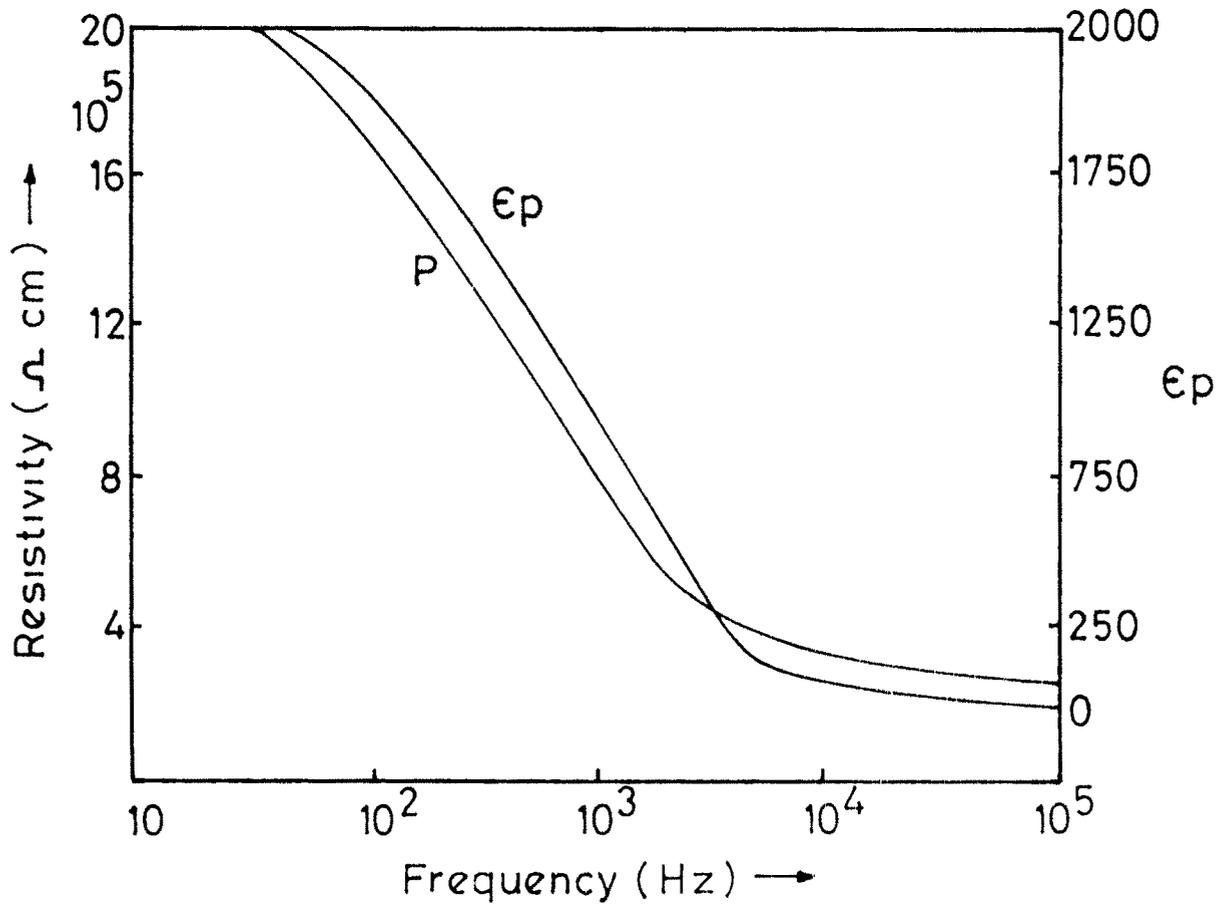


Fig. 4.2

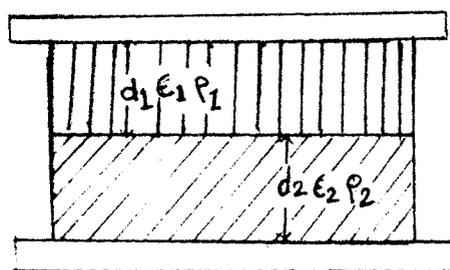


Fig. 4.3

Thus at very high frequencies

$$\rho_p^\infty = \rho_2 \quad \text{and} \quad \epsilon_p^\infty = \epsilon_2$$

and at very low frequencies,

$$\rho_p^0 = \rho_2 + x\rho_1 \quad \text{and} \quad \epsilon_p^0 = \epsilon_2 + \left(\frac{\epsilon_2}{x} \right)$$

Thus in order to obtain values of ϵ and ρ , characteristics of the ferrite itself, the measurement should be extended and extrapolated to high frequencies. Koops found value of 'x' of the order 0.01 but in those cases where low frequency dielectric constants of the order of 10^4 or 10^5 were found. The above theory would suggest an effective boundary layer of only a few \AA thick.

If the losses in the capacitor are represented by a complex dielectric constant $\epsilon = \epsilon_p - i\epsilon''$ instead of by a parallel resistance, it follows that,

$$\epsilon = 1.16 \times 10^{11} / \omega \rho_p$$

where ρ_p is in $\Omega\text{-cm}$.

The theoretically calculated frequency variation of ϵ and ρ are, in some cases, very similar to those experimentally measured. However, it is not surprising that results apparently at variance with Koops theory have been obtained.

In most modern commercial ferrites and garnets the dielectric constant is independent of measuring frequency from about 1 MHz to 10 MHz. Bady and Collins⁸ measured both the dielectric constant and loss tangent ($\tan \delta$) of a number of ferrites over the range of temperature $25^\circ\text{C} - 250^\circ\text{C}$. The dielectric constant generally increased by not more than 300 parts per million per $^\circ\text{C}$, $\tan \delta$ also generally

increases with temperature. It is not easy to be certain about changes in resistivity with frequency, since the measurement technique almost inevitably includes ohmic and dielectric losses in the one measurement. The resistivity of the oxide material itself is not expected to be frequency dependent and this is generally born out.

Further at moderately low frequencies in high apparent dielectric constant material the dimensional resonance may occur. The approximate wavelength inside the specimen is given by,

$$\lambda = \frac{C}{(\mu_i \epsilon_p)^{\frac{1}{2}}}$$

Where μ_i is initial permeability at frequency ' ν ' and 'C' is free space velocity of propogation. When this wavelength is comparable with or less than the relevant dimensions of the sample, the standing wave may be set up, with resulting high magnetic and dielectric losses. Brockman et.al.⁹ found a value of ϵ_p about 10^4 and μ_i about 10^3 in a manganese-zinc ferrite, resulting in serious losses for a specimen having dimension of 2 cm at a frequency of 2.5 MHz because of the same reason.

4.5 LOSSES :

4.5 (a) Dielectric Losses :

When a periodic electric field E of arbitrary frequency ' ω ' is applied to a dielectric material then the dipole reorientation takes place. The displacement D and electric field E are not necessarily in phase. Due to this dielectric constant (ϵ) may has an in-phase component and an out-of-phase component. It may be then represented in complex number, ϵ^*

Let the periodic field is given by,

$$E = E_1 e^{i\omega t}$$

and $D = \epsilon^* E$

where ϵ^* may be complex i.e.,

$$\epsilon^* = \epsilon_{\text{real}} - i\epsilon_{\text{img}}$$

The loss angle δ , defined as,

$$\tan \delta = \frac{\epsilon_{\text{img}}}{\epsilon_{\text{real}}}$$

and power loss 'P' is given by,

$$P = \omega E^2 \epsilon_{\text{real}} \tan \delta$$

4.5 (b) Permeability Losses :

When alternating magnetic field is applied on a magnetic material then part of magnetic energy is absorbed by the material and dissipated as heat. If alternating magnetic field is,

$$H = H_0 \exp(\omega t)$$

then magnetic induction 'B' is given by,

$$B = B_0 \exp(\omega t + \delta)$$

Hence permeability (μ) is given by,

$$\mu = \frac{B}{H} = \frac{B_0}{H_0} (\cos \delta + i \sin \delta)$$

Or $\mu = \mu' + i\mu''$

Where μ' gives that component of the flux which is in phase and μ'' the one which is 90° out of phase with the applied field. The energy loss per cycle can be shown proportional to μ'' .

The loss factor ($\tan \delta$) and the quality factor 'Q' are defined as,

$$\tan \delta = \frac{\mu''}{\mu'} \quad \text{and} \quad Q = \frac{\mu'}{\mu''} = \frac{1}{\tan \delta}$$

Further μ' describes the stored energy and μ'' describes the dissipation energy. The permeability may be measured with variation of frequencies. The behaviour of μ' and μ'' versus frequency is called a permeability spectrum.

The important mechanism of losses include, (a) hysteresis loss (b) eddy-current loss (c) residual loss.

(a) Hysteresis loss:

The energy 'dE' required to change magnetization 'M' to 'M + dM' at a field H is given by,

$$dE = HdM$$

Thus the total energy absorbed for a complete hysteresis cycle is,

$$W = \oint HdM$$

which is the hysteresis loss. The hysteresis loss is due to irreversible wall displacement.

(b) Eddy-current loss :

An electric current is induced in the magnetic core material by the alternating magnetic field. This causes heating and power loss. In technically applied cores the corresponding eddy-current losses are given approximately by,

$$\frac{(\tan \delta)_{\text{eddy}}}{\mu} \approx (2 \times 10^{-5}) f$$

where the frequency 'f' is expressed in MHz.

(c) Residual loss :

Residual loss is defined as the loss which remains after the subtraction of hysteresis loss and eddy-current loss from the total loss. The wall relaxation contribute to these losses. The wall relaxations usually have loss maxima at frequencies above 1 MHz. However, tail of these losses may extend to lower frequencies. As this tail may also vary to some extent with the frequency, it may be difficult to distinguish between eddy-current losses and residual losses.

4.6 EXPERIMENTAL :

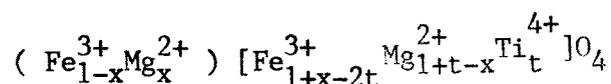
The measurements of dielectric constant, loss tangent, resistivity and quality factor with variation in frequency are carried out by using impedance analyser (Hewlett-Paackard model-4192A LF). All the measurements are done at room temperature. The samples used are in pellet form. A silver paste is applied for good ohmic contacts. Pellet is placed in the sample holder (supplied by manufacturer) firmly. The instrument is set for lower frequency to obtain steady value of R,C,Q and $\tan \delta$. Then the sample was scanned from 20 KHz to 10 MHz and readings are noted down for each step.

4.7 RESULTS AND DISCUSSION :

In fig. 4.4 variation of the dielectric constant (ϵ') as a function of frequency for the system $Mg_{1+t}Ti_tFe_{2-2t}O_4$ is shown in the frequency range 20 KHz to 10 MHz. The nature of variation exhibited by three samples ($t = 0.2, 0.3, 0.5$) is similar. The dielectric constant is high for low frequencies and as the frequency increases, the dielectric constant is found to decrease, initially at fast rate and then gradually. It is also observed that the dielectric constant ϵ' decreases on addition of Ti^{4+} in the system. A change in Ti^{4+} ion concentration by 't' reduces the iron (Fe^{3+}) concentration by $(2-2t)$ and increases Mg^{2+} ion concentration by $(1+t)$.

According to Rabkin and Novikova¹⁰ the polarization process in ferrites takes place through mechanism similar to the conduction process. By electronic exchange $Fe^{3+} \rightleftharpoons Fe^{2+}$ one obtains local displacements of the electrons in the direction of the applied electric field; these displacements determine the polarization. The decrease of polarization with increasing frequency for spinel ferrites can be explained by the fact that beyond a certain frequency of the electric field, the electronic exchange cannot follow the change in the direction of the field.

Thus the magnitude and variation of dielectric constant can be associated with the presence of Fe^{3+} and Fe^{2+} ions in the system. The cation distribution for our system is proposed as follows ;



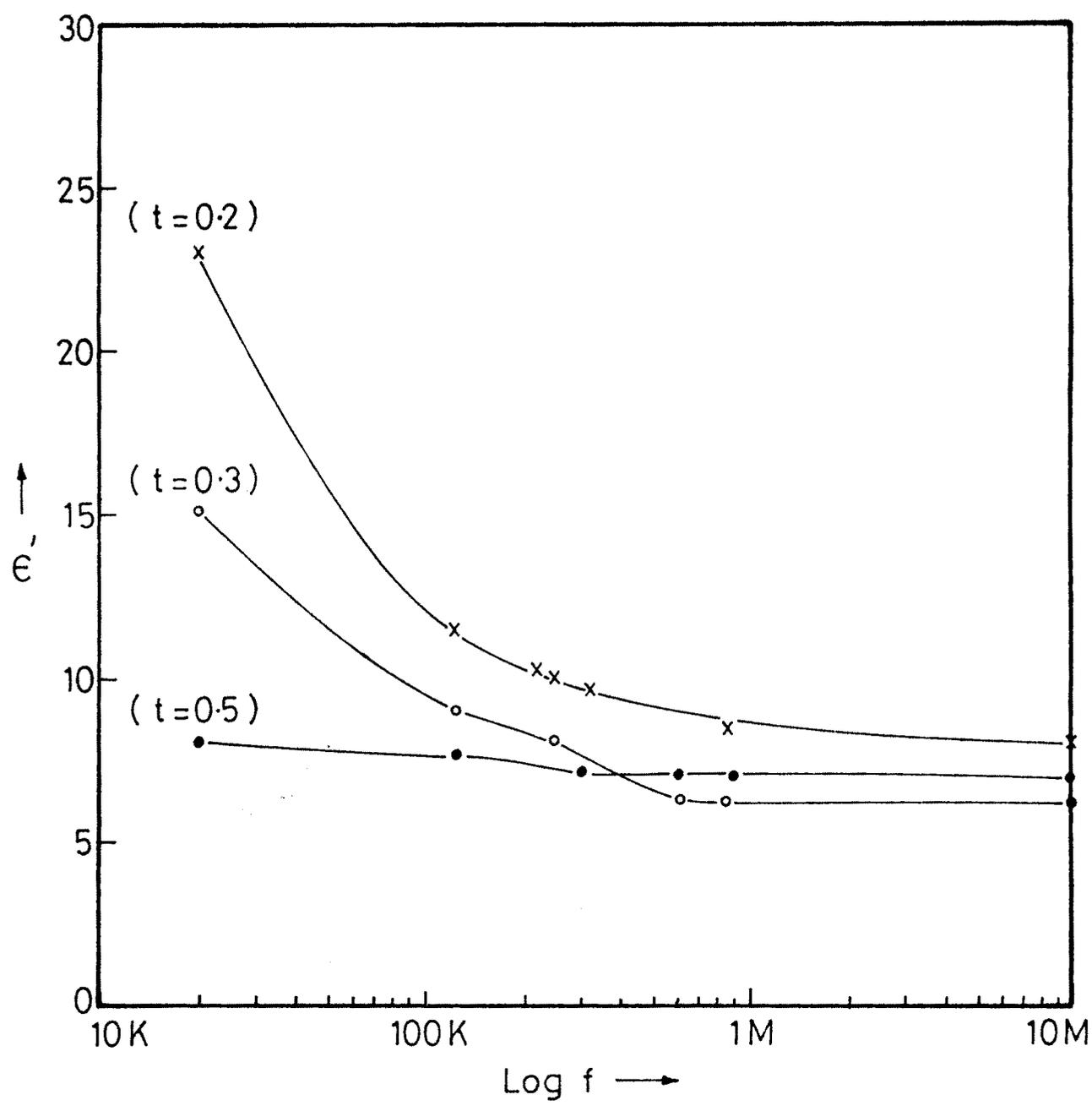


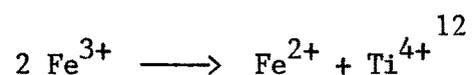
Fig. 4.4



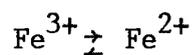
According to C.M. Shrivastav¹¹ the magnitude of Seebeck co-efficient in the cubic phase is given by,

$$\alpha = \frac{\text{total number of iron ions of B-site}}{\text{total number of Fe}^{2+} \text{ ions on B-site}} \dots (A)$$

From our studies of the Seebeck co-efficient we found that ' α ' increases with the addition of Ti^{4+} in the system. This suggests that in proportion to Fe^{3+} ions the concentration of Fe^{2+} ions in the system decreases according to equation (A). Ferric ions are also reported to be converted to ferrous ions on addition of Ti^{4+} as follow ,



Thus the decrease in the dielectric constant on addition of Ti^{4+} may be associated with the reduced number of electronic exchange of the type,



Also increase in Ti^{4+} is associated with the increase of Mg^{2+} ions. Mg-ferrite is partially inverted and depending upon the heat treatment. The distribution of Mg^{2+} ions on the A-site and B-site will differ from one ferrite to the other and hence to understand the role of Mg^{2+} ions on the dispersion of dielectric constant, will entail exact computation of the distribution of cation and valance states of various cations involved, although Mg^{2+} ions appears to abstract the electronic exchange contributing to the conductivity.

From fig. 4.4 it is also seen that the dispersion of dielectric constant in the sample $t = 0.5$ is less. This bears one to one correspondence with the content of iron ions in the system. All the samples revealed dispersion due to Maxwell³-Wagner⁴ interfacial polarization in agreement with Koops phenomenological theory.

A comparison of dispersion curve for the samples with increasing Ti^{4+} concentration shows that the change in the value of the dielectric constant at lower frequencies of the applied field is larger than that of higher frequencies. The variation of dielectric relaxation intensity i.e. the difference between low and high frequency dielectric constants with Ti^{4+} concentration is therefore primarily governed by the change in the dielectric constant at low frequencies. It decreases with increasing Ti^{4+} concentration and is in close agreement with the results obtained for magnetite by Iwauchi¹³. The observed variation in the dielectric relaxation intensity can be explained on the basis of space charge polarization due to inhomogeneous dielectric structure as discussed by Maxwell³ and Wagner⁴. The space charge polarization is governed by the number of space charge carriers and the resistivity of the sample.

The dielectric properties of ferrite materials are very sensitive to method of preparation, the sintering temperature, the sintering atmosphere and the amount and type of substitution. When the ferrite powder is sintered under slightly reducing conditions, divalent iron ion are produced in the bulk of material. These ions form high conductivity grains separated by two low conductivity layers

and as a result the ferrites behave as an inhomogeneous dielectric material.

The variations of loss tangent and resistivity as a function of frequency are shown in fig. 4.5 and 4.6 respectively. It is observed that the loss tangent goes on decreasing on increasing the frequency. The resistivity increases on increasing Ti^{4+} content and frequency. The increase in resistivity on addition of Ti^{4+} implies that the flow of space charge carriers is abstracted and thus the build up of space charge polarization is impeded. No peaks have been observed in the dispersion of loss tangent ($\tan\delta$). The conduction mechanism in the ferrites under investigation is assumed to be the hopping motion of the electron between Fe^{2+} and Fe^{3+} over the octahedral site¹⁴. A maximum in the dielectric loss is observed when the jump frequency is approximately equal to that of the external field¹⁵. Thus it is clear that the jump frequency is outside the range of the frequencies we have considered. The jump frequency may be on the low frequency side since Mg^{2+} ions are involved.

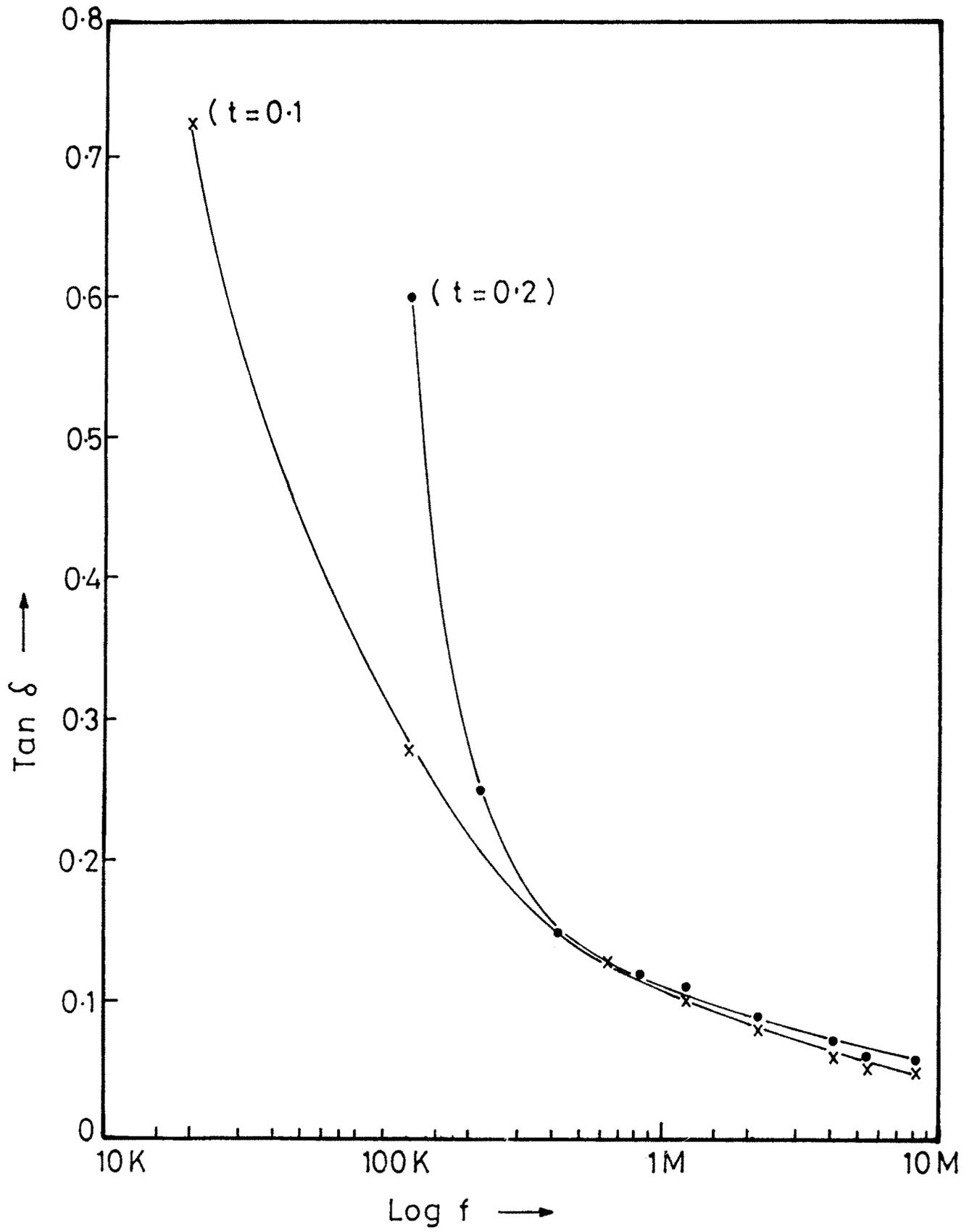


Fig. 4.5

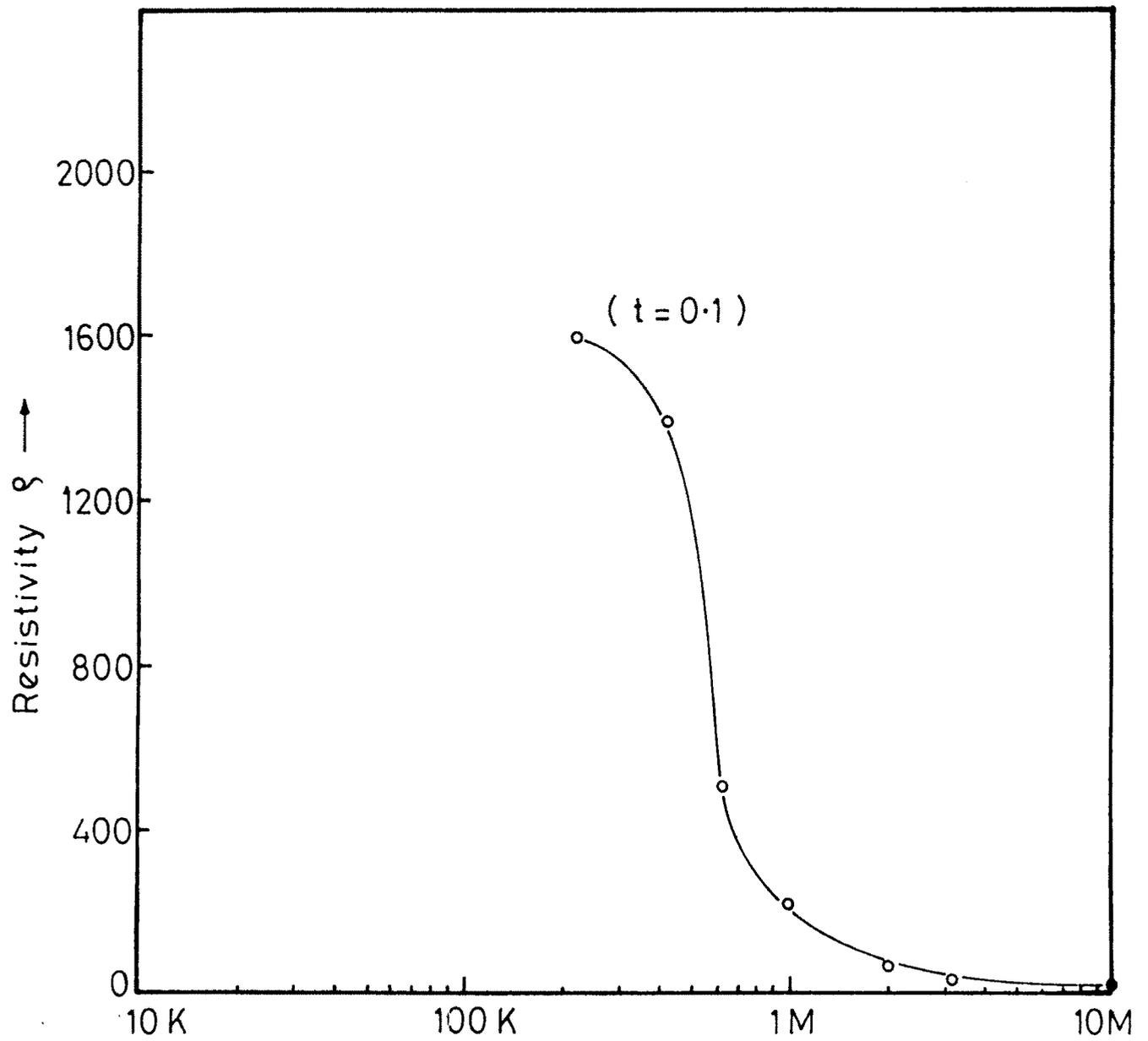


Fig. 4.6

REFERENCES

1. Kamiyoshi K., Sci. Rep. Res. Inst. Tohoku Univ. A-3, 716 (1951).
2. Blechstein, "Dielectric Properties of Mn ferrites" Physical-ische Zeitschrift Vereinght mit dem Jahrbuch dev Radio-activitat and Elektronik 39 212 (1938).
3. Maxwell J.C. "Electricity and Magnetism" Oxford Univ.Press, London Vol.I 828 (1873).
4. Wagner K.W., Ann. Physik. 40, 817 (1913).
5. Josyulu O.S. and Sobhamadri J., Phys. Stat. Sol. (a) 59, 323 (1980).
6. Iwauchi K., Japan J. Appl. Phys. 10(11), 1520 (1971).
7. Koops C.G., Phys. Rev. 83, 121 (1951).
8. Bady I and Collins T., Inst. elect. Electron Engrs. Trans. Mic. Theory, Tech. MTT 11, 222 (1963).
9. Brockman F.W., Dowling P.H. and Steneck W.G., Phys. Rev. 77, 85 (1950).
10. Rabkin L.I. and Novikova Z.I., Ferrites, p.146, Izd.Acad. Nauk BSSR Minsk (1960).
11. Shrinivasan G. and Srivastava C.M., Phys. Stat. Sol. (b) 108, 665 (1981).
12. Stijntjes T.G.W., Klerk I. and Van Groenou A.B., Philips Res. Rep. 25 No.2, 95 (1970).
13. Iwauchi K., Jpn. J. Appl. Phys. 10, 1520 (1971).
14. Prakaksh C. and Baijal J.S., Solid State Commun. 50,557(1984)
15. Murthy V.R.K. and Sobhanadri J. Phys. Status. Solidi. A-36 K-133 (1976).

