Chapter III
Electrical Properties

3.1 INTRODUCTION

Ferrites are widely used in high frequency devices. An important property of these materials that makes them suitable for these applications is their high electrical resistivity (10^{-3} to 10^{11} Ω cm at room temperature). The low electrical conductivity in comparison with that of magnetic metals has been the main aspect of ferrites. For applications at microwave frequencies conductivity lower than 10^{-8} Ω^{-1} cm^{-1} are required since the dielectric loss tangent depends on conductivity [1]. The electrical properties of ferrites are influenced by the distribution of cations, magnetic and nonmagnetic substitutions, the amount of Fe^{2+} present, sintering condition, grain size and grain growth effects etc. The early investigators have tried to increase the resistivity of ferrites for their use in transmission lines, wave guides and microwave cavities. The transport mechanism of the ferrite system can be deduced from the studies on its electrical conductivity, Hall coefficient, magneto-resistance etc.

In ferrites the electron concentration can reach the value of 10^{22}/cm^3. Since the mobility of electrons (10^{-4}cm^2/v sec.) and holes (10^{-8}cm^2/v sec) is considerably less, it limits their conductivity.

Conduction in ferrites is mainly due to the exchange of 3d electrons, localized at the metal ions i.e. from Fe^{3+} to Fe^{2+} and vice versa [2]. Jonker [3] derived an expression for mobility from hopping conduction model, based on the localized levels for electrons. Band polaron model based on electron transition between localized cells was suggested by Dogowe et al [4], Haubenteisser [5], Lorentz and Ihle [6] introduced small polaron model and explained the electrical properties on the basis of thermally activated motion of electrons.

The conduction in ferrites is attributed to hopping process and can be interpreted as the energy required to cause the electron jump from one ion to another. Ghani et al [7] have observed three regions in resistivity plots of Cu-Ni ferrites. They have attributed the conduction mechanism in the first region to the presence of impurities, second region to phase transition and third region to the magnetic disorder. Suitable preparation techniques and chemical composition control the conductivity in ferrites [8].

3.2 CONDUCTION MECHANISM IN OXIDES

Unlike the conduction in intrinsic and extrinsic semiconductors, the conduction in compound semiconductors does not require doping for introducing the localized donor or accepter levels. In transition metal oxides, the narrow half filled band could provide the current carriers by excitation, therefore many of these metal oxides are semiconductors. Nonstoichiometry provides the source of current carriers, many a times the ion themselves. In metal oxides containing an ion with variable valency a smaller activation energy as compared to the band gap could be visualized as −

$$M^{2+}O^{2-}-M^{2+}O^{2-} \longleftrightarrow O^{2-}-M^{1+}O^{2-}-M^{3+}O^{2-} \quad \text{... 3.1}$$
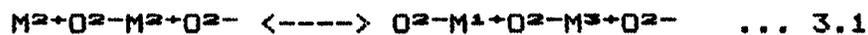
where M is the divalent transition metal ion.

The energy needed for the formation of ion pairs $(M^{2+}M^{2+})$ and $(M^{3+}M^{1+})$ corresponds to the gap in density of state. The resistivity of such oxides is generally high due to higher activation energy. On the other hand, the oxides which contain substantial amount of metal ions in two different valance states on crystallographically equivalent sites, are characterized by relatively small activation energies which results in high conductivity.

The magnetite, Fe_3O_4, has a spinel type structure with specific resistance of about 10^{-2} ohm cm. In this structure the oxygen ions are nearly on a closed packed cubic lattice, cations are partly in tetrahedral sites and partly in octahedral sites. The structure of Fe_3O_4 can be described as

$$Fe^{3+}(Fe^{2+}Fe^{3+})O_4{}^{2-}$$
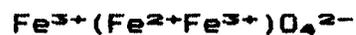
This denotes that one third of iron ions (all having plus three valances) are on tetrahedral sites and remaining two third (both divalent and trivalent ions) are on octahedral positions. The good electrical conductivity of magnetite is related to the random location of Fe^{2+} and Fe^{3+} ions on the octahedral sites so that the electron transfer from cation to cation can take place. This has been illustrated by the order disorder transformation occurring at about 120 °K [9]. Above this temperature the Fe^{2+} and Fe^{3+} positions are randomly distributed [10] and below this temperature the Fe^{2+} and Fe^{3+} ions are distributed in an ordered pattern on the octahedral sites.

3.3   CONDUCTION IN FERRITES

As specified earlier, ferrites have very wide range of resistivities from 10^{-3} to 10^{11} Ω cm, at room

temperature. This low and high resistivities of ferrites are mainly explained on the basis of actual location of cations in the spinel structure and the hopping mechanism. Their high conductivity is due to simultaneous presence of ferrous and ferric ions in the crystallographically equivalent sites. The high resistivity in ferrites is associated with the occupation of B sites by divalent metal ions and trivalent iron ions. Such as arrangement requires higher activation energy for hopping of electrons. The two mechanisms of conductivity can be represented as

$$Fe^{2+} + Fe^{3+} <--> Fe^{3+} + Fe^{2+} + \Delta E$$

$$Me^{2+} + Fe^{3+} <--> Me^{3+} + Fe^{2+} + \Delta E \quad ... 3.2$$

where ΔE is the activation energy, the energy required to transfer an electron from Me^{2+} to Fe^{3+} and vice versa. Me denotes divalent metal ions like Cu, Co, Mg, Mn, Ni and Cd etc.

The conductivity of ferrites can be explained in terms of electronic charge carriers like electrons and holes by the relation.

$$\sigma = e (ne\ \mu e + nh\ \mu h) \quad .... 3.3$$

where $\dot{n}$ and μ stand for concentration and mobilities of electrons (e) and holes (h) respectively. As electrons move in one direction, the holes moves in

opposite direction. Though the velocities of electrons and holes are the same but mobility of electron is much higher than the mobility of hole.

The hopping mechanism of conductivity in ferrites is associated with activation energy, which can be calculated from $\log \varsigma$ vs $1/T$ plots. As temperature increases, the ferrite changes its magnetic state from a ordered ferrimagnetic state to a disordered paramagnetic state. When such a change occurs there is an abrupt change in activation energy. It is observed that the activation energy in ferrimagnetic region is less than the activation energy in paramagnetic region.

Two types of scatterings exist in ferrites.

1. The lattice scattering arising out of thermal vibration of lattice and

2. the impurity scattering.

The lattice scattering increases with increasing amplitude of vibration at higher temperatures. The mobility is proportional to the mean free path between scattering events. Hence conductivity becomes temperature dependent and it is written as

$$\sigma = \sigma_0 \exp (-\Delta E / kT) \qquad \ldots \quad 3.4$$

where σ_0 = temperature dependent constant

k = Boltzmann constant.

In ferrite lattice there is an interaction between orbitals of neighbouring ions and electrons resulting in to the polarization of the lattice. This effect is more pronounced due to strong Coulomb interaction in ionic crystals such as ferrites. The combination of an electron and its polarization field is called as polaron.

When such an association is weak it constitutes large polarons. Such polarons are found in ionic crystals and conductivity of ionic crystal is similar to the one explained above. But when the electron plus lattice deformation has a linear dimension smaller than lattice constant, it constitutes small polarons. They are usually found in covalent crystals. Due to such deformation the effective mass of electron increases as it partially drags the ion along with it. Therefore mobility of electron decreases and becomes highly temperature dependent. With the help of binding energy E_p of electron and polarized lattice, the mobility of electron be written as

$$\mu \text{ polaron } \alpha \exp (- E_p / kT) \qquad \ldots \quad 3.5$$

$$\text{where } Ep = e^2 / Keff \sqrt{p} \qquad \ldots \quad 3.6$$

$$\sqrt{p} = \text{dimension of lattice deformation.}$$

1/keff = difference of reciprocal of optical and static dielectric constant.

The mobility is always less than 1 cm^2/v sec and is very low. With the help of small polarons the conductivity is related to Eg, Ep and T by the relation.

$$\sigma \propto n\mu \propto \exp [(-Eg / kT) - (Ep / kT)] \quad ... \ 3.7$$

Due to the polarization, the electrons are trapped at the potential well. When such a potential well is deep enough, the electrons may be trapped at lattice site. Therefore its transition to neighbouring site may be governed by thermal activation. Hence due to thermal activation lattice is set into periodic vibrations which are quantized into phonons.

The hopping mechanism contributes to conductivity at high temperature. At low temperatures electrons tunnel slowly through the crystal resulting into small conductivity and at high temperatures electrons jump from one site to another by thermal activation.

The temperature dependence of mobility (1) is given by

$$\mu = (e^2 a^2 w^2 / kT) \exp (\triangle E / kT) \quad .... \ 3.8$$

where w = polaron frequency

a = distance between the neighbouring site

i.e. jump length.

Verway et al [11], Van Uitert [12,13], Jonker [14] and Klinger [15] etc. have studied the d.c. electrical properties of ferrites. The salient features of study the d.c. was to increase the electrical resistivity, minimize the eddy current losses and explain the conduction behaviour. Van Uitert [16] studied the conductivity of nickel ferrite with small additions of manganese and cobalt. Rosenberg [17] studied the variation of resistivity and thermoelectric power with temperature. Many other workers [18-22] explained the small polaron model for conductivity mechanism.

3.4 EXPERIMENTAL TECHNIQUES

The experimental set-up used for the measurement of d.c. resistivity of the samples consisted of an electrically heated furnace, a digital d.c. microvoltmeter and a transistorized power supply unit (TPSU) to provide the d.c. voltage. The silver paste was applied on both sides of the pellet for good ohmic contacts. The pellet was mounted in a sample holder consisting of two brass rods in which the sample can be sandwiched tightly with the help of screws provided to the apparatus. A calibrated cromel-alumel thermocouple

was used to measure the temperature of the furnace. Resistivity measurement were carried out by measuring the current at a constant voltage of 5 volts, from room temperature to 500 °C. The measurements were carried out while heating and cooling and sufficient time was allowed for the sample to attain an equilibrium temperature. The resistivity (ς) was determined by the relation

$$\varsigma = \pi\ r^2\ /\ t \times v/i \qquad \ldots\ 3.9$$

where t = thickness of pellet

r = radius of pellet

i = current through the sample

3.5   RESULTS AND DISCUSSION

The Figures 3.1 and 3.2 shows the variation of logς against $10^3/T$. The following salient features of the results are worth noting.

1. The resistivity behaves according to the Arrhenius relation

$$\varsigma = \varsigma_0\ e^{\Delta E / KT} \qquad \qquad \ldots\ 3.10$$

where ΔE is the activation energy,

k is the Boltzmann constant and
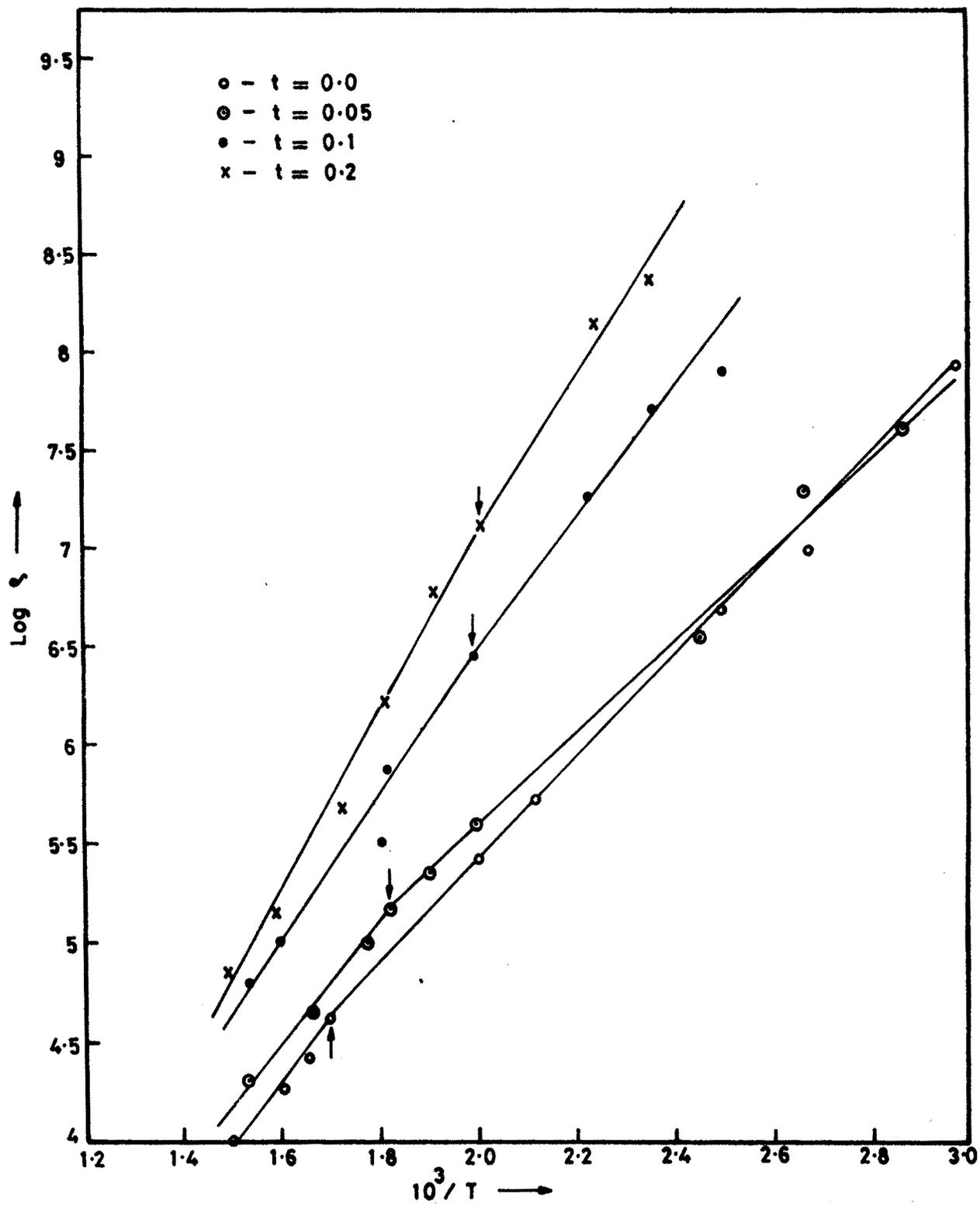
T is the absolute temperature.

FIG. 3.1 – VARIATION OF LOG ς VERSUS 1/T FOR $Zn_xMg_{1-x+t}Ti_tFe_{2-2t}O_4$
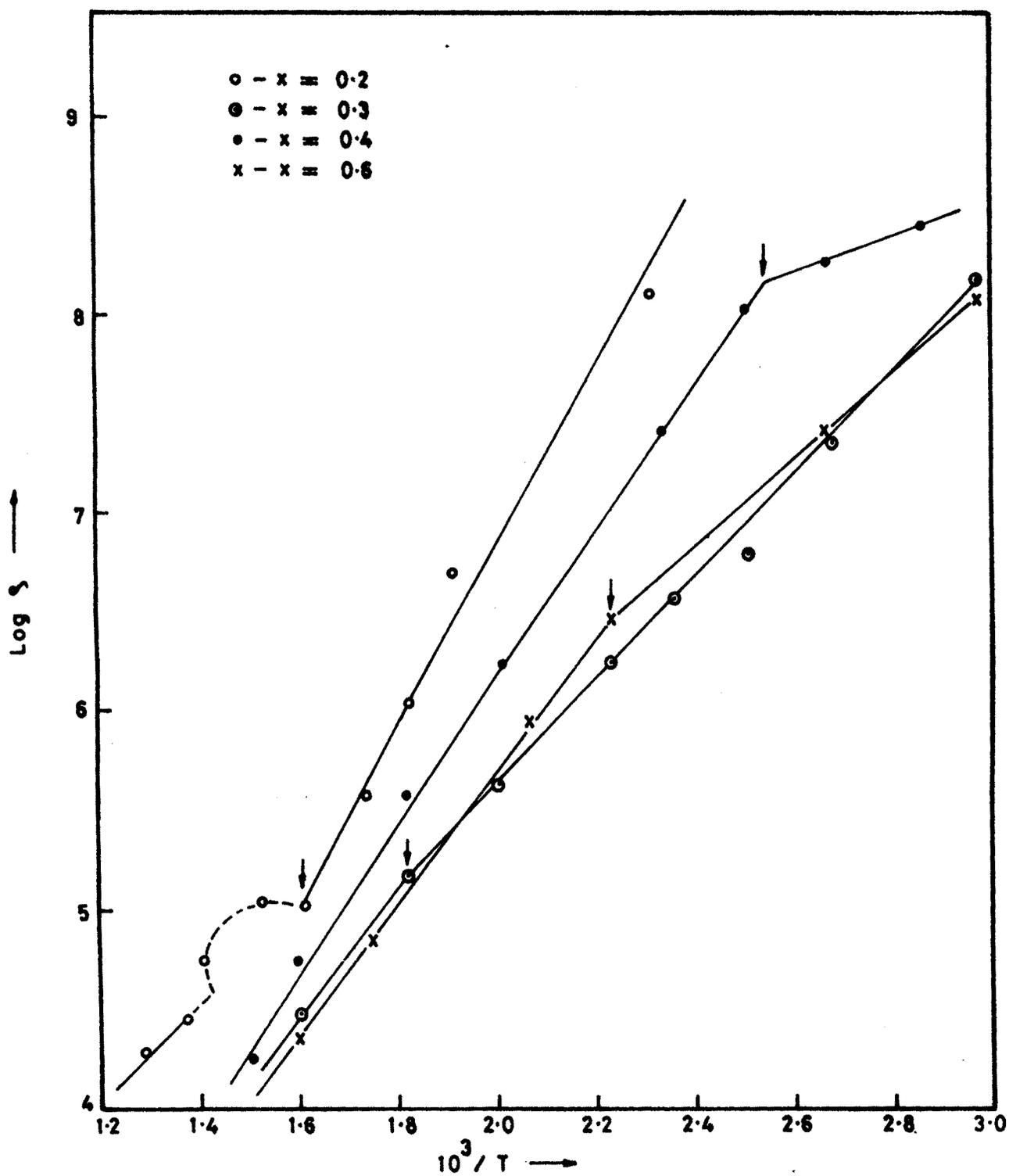(where x = 0.3)

FIG. 3.2 – VARIATION OF LOG ξ VERSUS 1/T FOR $Zn_x Mg_{1-x+t} Ti_t Fe_{2-2t} O_4$
(where t = 0.05)

2. Distinct break is observed for each measured
sample which takes place at a temperature which, when
compared with the reported data is identified as the
Curie temperature.

3. Activation energies in the ferrimagnetic and
paramagnetic region were calculated from the plot of
$\log \varsigma$ against $10^3/T$ and it was found that the
observed values of the activation energies in the
paramagnetic region are higher than those found in the
ferrimagnetic region.(Table 3.1 & 3.2)

4. The resistivity at a given temperature
increases with increase of the titanium concentration. ✳

The observed variation in the d.c. resistivity
with increasing Ti^{4+} concentration can be explained as
follows. The increased concentration (t) of Ti^{4+} ions
is associated with the replacement of 2t Fe^{3+} ions by
tMg^{2+} and tTi^{4+} ions. The cation distribution of the
series can be written as

$Zn_{0.3}Fe_{0.7-y}Ti_y[Mg_{0.7+t}Fe_{1.3-2t+y}Ti_{t-y}]O_4$
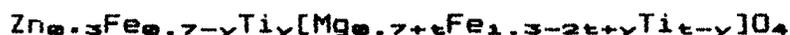
The tTi^{4+} ions are distributed over the A and B
sites. The tetravalent ion is able to form stable
electrical bonds with Fe^{2+} ions [23-25]. Since titanium
is tetravalent, it localizes Fe^{2+} ions which may be
formed during sintering.

Table 3.1

Activation energy and Curie temperature data for
$Zn_{0.3}Mg_{0.7+t}Ti_tFe_{2-2t}O_4$ ferrites

t	Activation Energy, ev		Curie temp.,°C	
	Ferri Regn.	Para Regn.	DC Res.	Susc.
0	0.44	0.62	263	—
0.05	0.55	0.63	250	253
0.1	0.66	0.70	200	177
0.2	0.77	0.92	171	139

Table 3.2

Activation energy and Curie temperature data for
$Zn_xMg_{1.05-x}Ti_{0.05}Fe_{1.9}O_4$ ferrites

x	Activation Energy, ev		Curie temp.,°C	
	Ferri Regn.	Para Regn.	DC Res.	Susc.
0.2	1.09	0.45	300	267
0.3	0.55	0.63	250	239
0.4	0.45	0.70	150	147
0.6	0.20	0.77	116	77

$$2Fe^{3+} \ \text{-----}> Fe^{2+} + Ti^{4+} \qquad \ldots 3.11$$

The phenomenon hinders the Verway – de Boer mechanism between statistically distributed Fe^{2+} and Fe^{3+} ions at the equivalent lattice sites, resulting in an increase in bulk resistivity.

The breaks and discontinuities can be attributed to several sources. Komar and Klivshin [26] observed change in activation energies for conduction at high temperature are correlated with the high ferrimagnetic Curie temperature of the ferrites. This offers high evidence for the influence of magnetic ordering upon conductivity in ferrites [9]. The breaks may also be due to the change in conduction mechanism. Recently, Ghani et al [27] and Sankpal et al [28] have shown more than one breaks in the temperature variation of resistivity in the case of Cu-Ni ferrites.

The Table 3.1 and 3.2 show the data on activation energy and Curie temperatures. It is observed that the activation energy in the paramagnetic region is found to be more than for the ferrimagnetic region. This can be attributed to the effect of magnetic ordering in the conduction process [29]. According to the theoretical consideration the anomalous changes in the activation energy occur at the disordered temperature. The

activation energy ΔE is in the range of (0.44 ev to 0.77 ev) it is seen that the conduction is clearly to be intrinsic type. The decrease of Tc is due to the weakening of A-B interactions. The Curie temperature Tc obtained from conductivity studies and from susceptibility agree satisfactorily.

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