

CHAPTER - III

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D. C. ELECTRICAL RESISTIVITY

INTRODUCTION

The mechanism of charge transport can be understood from the measurement of electrical conductivity, thermoelectric power, Hall coefficient and magnetoresistance (1). The electrical conductivity of ferrites at room temperature can vary from 10^3 to 10^{-11} ohm⁻¹ cm⁻¹ depending on the chemical composition and nature of the constituent ions. The low electrical conductivity in comparison with that of magnetic metals has been the main aspect of ferrites. The low conductivity of ferrites compared to metals greatly influences its various applications at microwave frequencies. Resistivity as low as 10^{-2} ohm-cm is found in iron-rich ferrites. The frequency dependent dielectric behaviour creates considerable interest in understanding many physical and chemical properties. This high and low resistivities of ferrites are mainly explained on the basis of actual location of cations in the spinel structure and hopping mechanism (2,3).

The electrical conductivity of ferrites mainly depends upon the chemical composition, temperature, porosity, density and

method of preparation. The room temperature resistivity of pure NiOFe_2O_3 and some ferrites and garnets exceeds $10^{10} \Omega \text{ cm}$ so that they can be regarded practically as insulators. The increasing demand for low loss ferrites prompted the scientists to undertake detailed investigation of various aspects of conductivity and the influence of various substitutions on the electrical properties of ferrites.

The conductivity is found to influence the dielectric and magnetic behaviour of ferrites. Van Uitert has described how the incorporation of small amount of manganese or cobalt alters the resistance of ferrites (4).

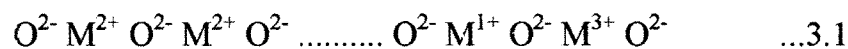
The electrical properties of ferrites are affected by the distribution of cations in the lattice site by non magnetic and magnetic substitutions, amount of Fe^{2+} present, sintering conditions, grain size and grain growth etc. The conduction in ferrites is attributed to a hopping process and activation energy can be interpreted as the energy required for causing an electron jump from one ion to another.

The spin alignment and electrical conduction relationship can be inferred from comparison of conductivity versus temperature studies observed below Curie or Neel temperature with high

temperature studies for many oxides, the spontaneous magnetization does not affect the electrical transport properties. Ferrites exhibit a marked change in the slope of $\log \rho$ versus $1/T \times 10^3$ relationships. The electrical properties of nickel ferrites have been studied by several investigators. Van Uitert (1) investigated the effect of iron stoichiometry and sintering temperature on the resistivity of Nickel ferrites. Murthy and Sobanadri (5) have investigated the d.c. conductivity of some Ni-Zn ferrites as a function of temperature from room temperature to 300°C . The ferrites that contain iron in excess show n-type conduction and those with iron deficiency show p-type conduction.

3.1. CONDUCTION IN OXIDES

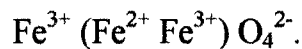
The lattice structure of oxides consists of a large number of oxygen ions and metal ions are substituted at different sites depending upon the structure of the lattice. For an oxide of chemical composition MeO where Me is the metal ion, the activation of electrons can be represented as ,



The resistivity of such oxides is generally high due to higher activation energy. On the other hand, the oxides which contain a substantial amount of metal ions in two different valence states

on crystallographically equivalent sites are characterized by relatively small activation energies which results in high conductivity.

Magnetite (Fe_3O_4) is an excellent semiconductor having a specific resistance of about 10^{-2} ohm-cm compared to the values of the order of 10^{10} ohm-cm for many stoichiometric transition metal oxides. Fe_3O_4 has spinel type crystal structure. The structure of magnetite can be described as,

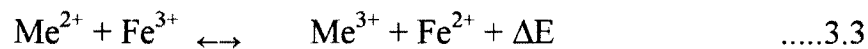
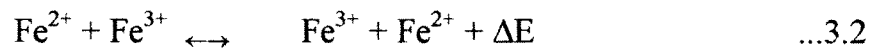


The good electrical conductivity of magnetite is related to the random location of Fe^{2+} and Fe^{3+} ions on octahedral sites, so that the electron transfer from cation to cation can take place.

3.2 CONDUCTION IN FERRITES

Ferrites have very wide range of resistivities from 10^{-3} to 10^{11} Ω cm, at room temperature. This can be explained on the basis of actual location of cations in the spinel structure and hopping mechanism (6). 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 an arrangement requires higher activation energy for hopping of electrons. The two mechanisms of conductivity can be represented as,



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

As ferrites are semiconducting oxide magnetic materials, it is reasonable to think of the conduction mechanism in terms of electrons and holes. Therefore, conduction can be written as,

$$\sigma = e (n_e \mu_e + n_h \mu_h) \quad \dots 3.4$$

where e = electronic charge

n_e = concentration of electrons

n_h = concentrations of holes

μ_h = mobility of holes

μ_e = mobility of electrons

In ferrites mobility is found to be much smaller than that of semiconductors. This made Heikes and Johnson (7) to propose the hopping of polaron model for conduction mechanism in ferrites. The electron interacts with ions of the lattice creating a local

deformation of the lattice. The combination of electron and strain field is called 'polaron'. The displacement of lattice causes the polarization of surrounding region and electron gets trapped at the center of potential well. When the well is deep enough, the electron may be trapped at the lattice site and its transition to neighbouring sites may be governed by thermal activation. Due to thermal activation lattice is set into periodic vibrations which are quantized into phonons.

The strength of the lattice interaction is measured by electron phonon coupling constant defined as,

$$\frac{\alpha}{2} = \text{deformation energy}/\hbar\omega \quad \dots 3.5$$

where ω = longitudinal phonon frequency.

The coupling constant determines the nature of polarons. The polaron is said to be large for higher values of coupling constant. Such polarons are found in ionic crystals. At higher temperatures, conduction is due to hopping of electrons from one site to the next. This hopping mechanism contributes to conductivity at high temperatures. At lower temperatures, electrons, tunnel slowly through the crystal giving rise to the observed conductivity. Parkar (8) has given a strong experimental evidence for small

polarons. The diffusion of charge carriers from one state to other is possible only when their energy exceeds a certain minimum energy called as activation energy.

The thermal vibrations consistently give rise to phonons and electrons hop between the pairs of states either by absorption or by emission of phonons. The transport of charge carriers is achieved by hopping process through interaction with phonons. On the basis of this the temperature dependence of resistivity of ferrites, is given by the relation.

$$\rho = \rho_0 \exp(-\Delta E/kT) \quad \dots 3.6$$

where ρ_0 = Temperature dependent constant

ΔE = activation energy

k = Boltzmann constant

T = absolute temperature.

The plot of $\log \rho$ vs $1/T$ shows a break at Curie temperature due to the transition from ferrimagnetic region to paramagnetic region. This indicates two parallel conductivity mechanism with different activation energies. It is observed that activation energy in ferrimagnetic region is less than the activation energy in paramagnetic region.

3.3 EXPERIMENTAL TECHNIQUES

The d.c. resistivity measurements were made using two probe method on pellets from room temperature to 600⁰ C. Silver paste was applied on both sides of the pellets for good ohmic contact. The pellet was mounted in a sample holder consisting of two steel rods, in which sample can be held tightly with the help of screws.

3.4 RESULTS AND DISCUSSION

The variation of electrical resistivity vs temperature for the samples in the series $\text{Ni}_{(0.5-x)} \text{Mg}_{(x-0.01)} \text{Zn}_{0.5} \text{Co}_{0.01} \text{Fe}_2\text{O}_4$ where $x = 0.1, 0.2, 0.3, 0.4, 0.5$ is shown in Figs. 3.1 to 3.5. It is observed that slope of the plot of $\log \rho$ versus $1/T$ changes at a particular temperature which has been identified as the Curie temperature of the sample. The resistivity decreases with temperature. It can be seen that variation is linear upto the temperature at which it shows a transition where the ferrimagnetic state of the material changes to a paramagnetic state. Similar results have been reported by Komar and Klivshin (9) in the case of several other ferrites and they have stated that change in the activation energy of conduction at a particular temperature has some relation with the ferrimagnetic Curie temperature of ferrites.

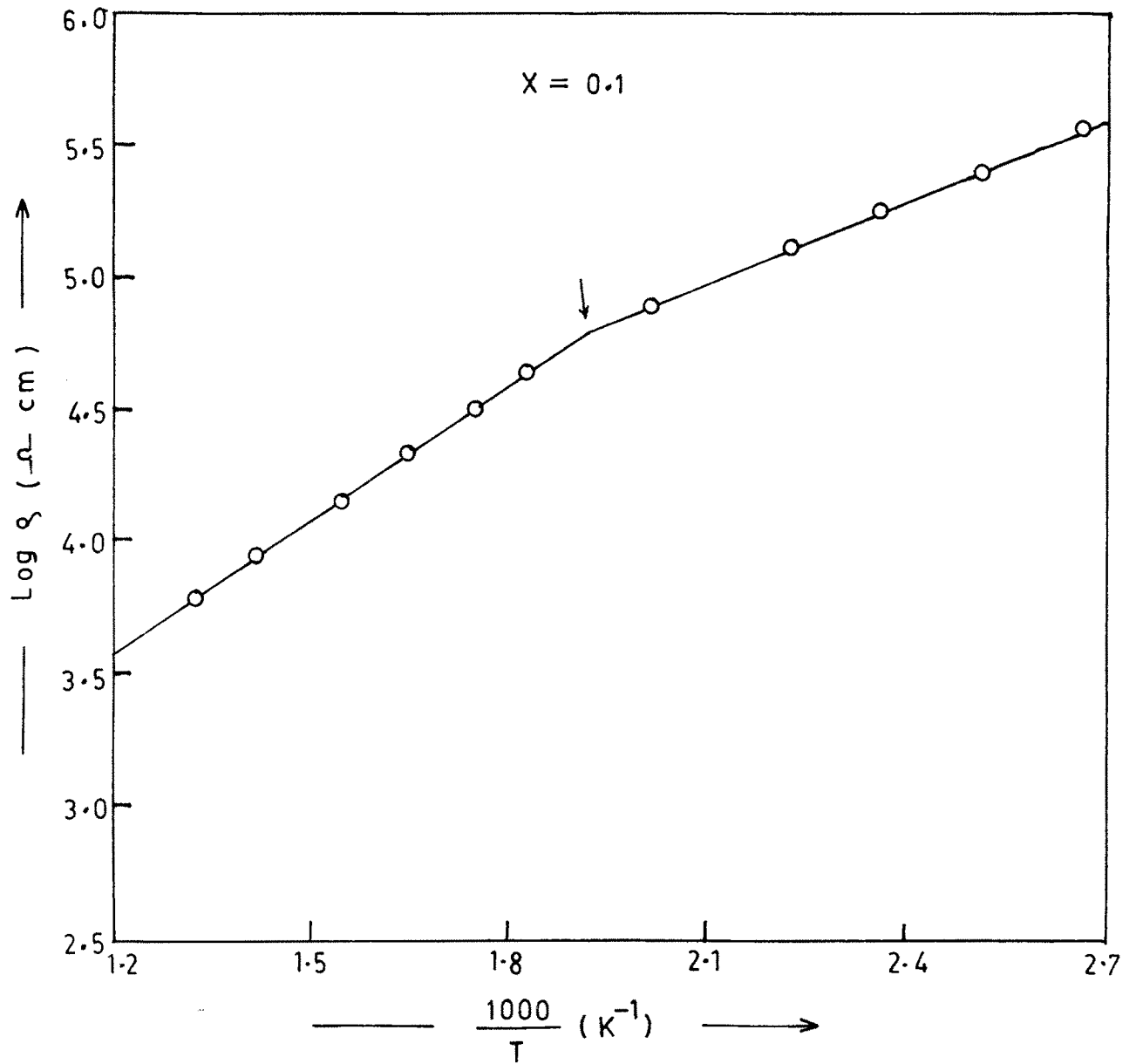
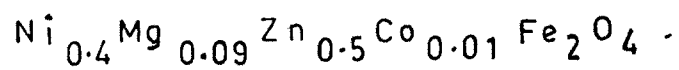


FIG.3-1-VARIATION OF RESISTIVITY WITH TEMPERATURE FOR



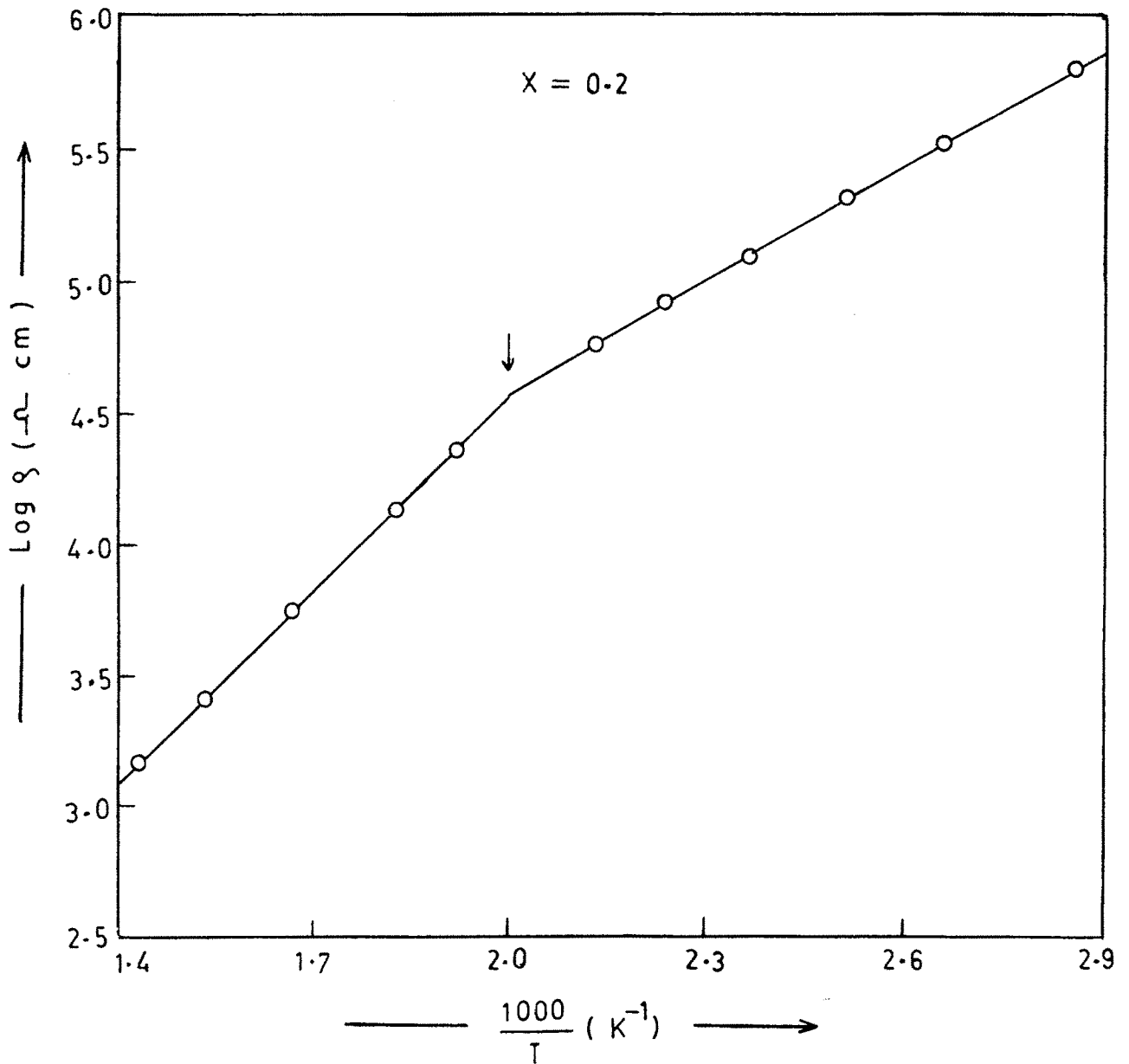
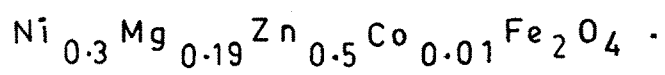


FIG.3-2-VARIATION OF RESISTIVITY WITH TEMPERATURE FOR



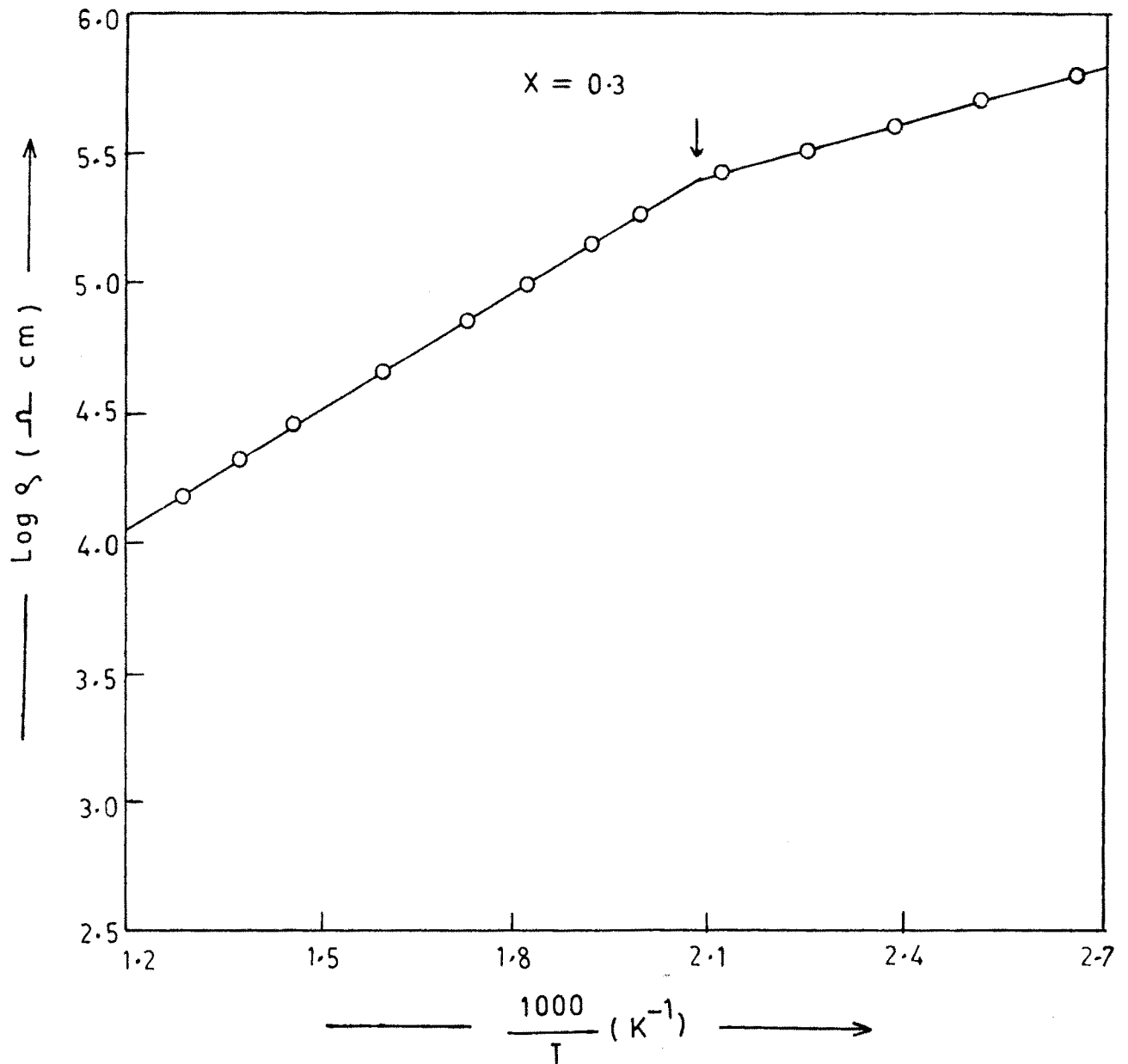
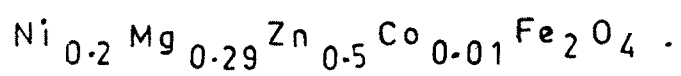


FIG. 3.3-VARIATION OF RESISTIVITY WITH TEMPERATURE FOR



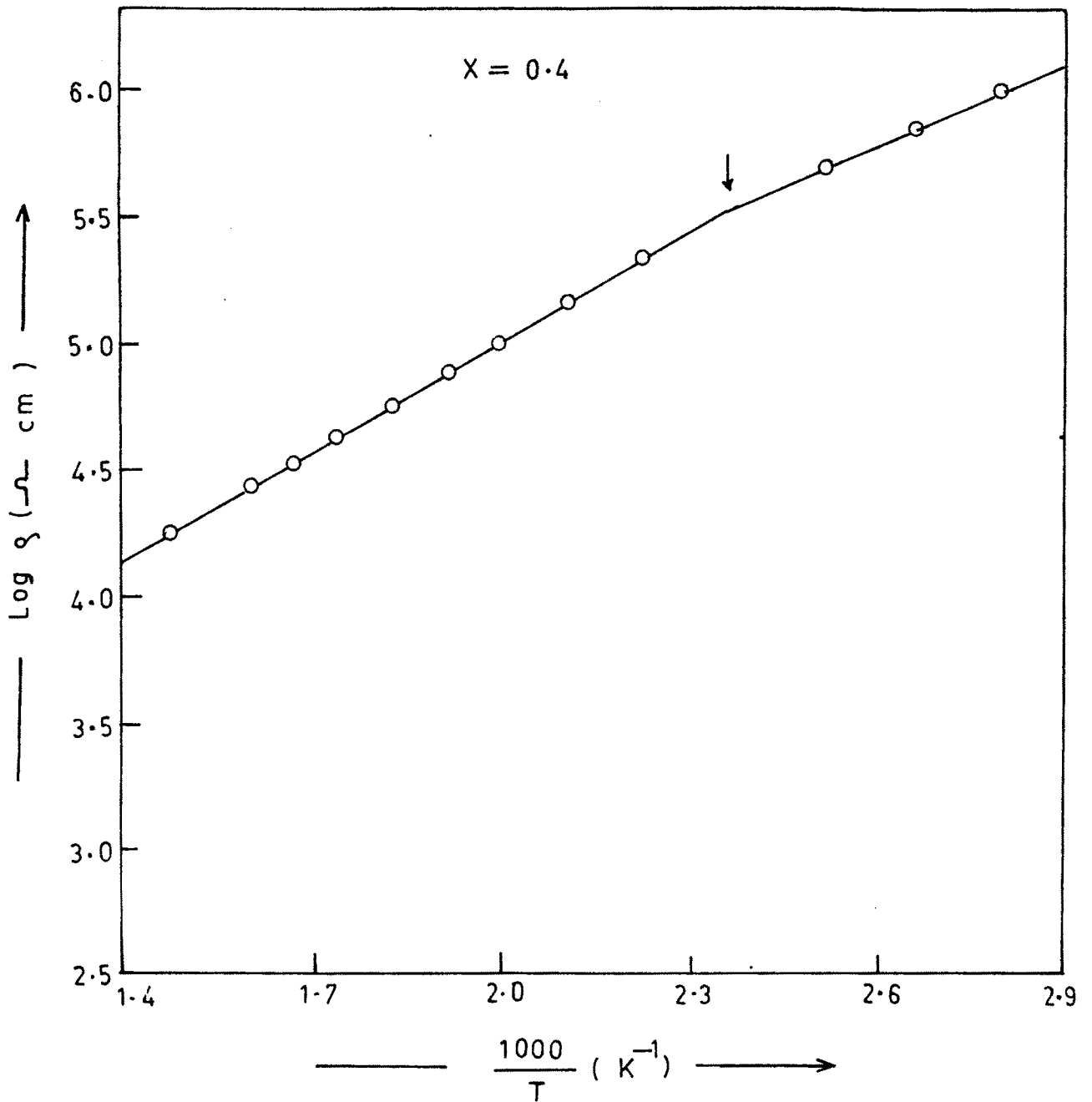


FIG.3.4-VARIATION OF RESISTIVITY WITH TEMPERATURE FOR
 $\text{Ni}_{0.1}\text{Mg}_{0.39}\text{Zn}_{0.5}\text{Co}_{0.01}\text{Fe}_2\text{O}_4$.

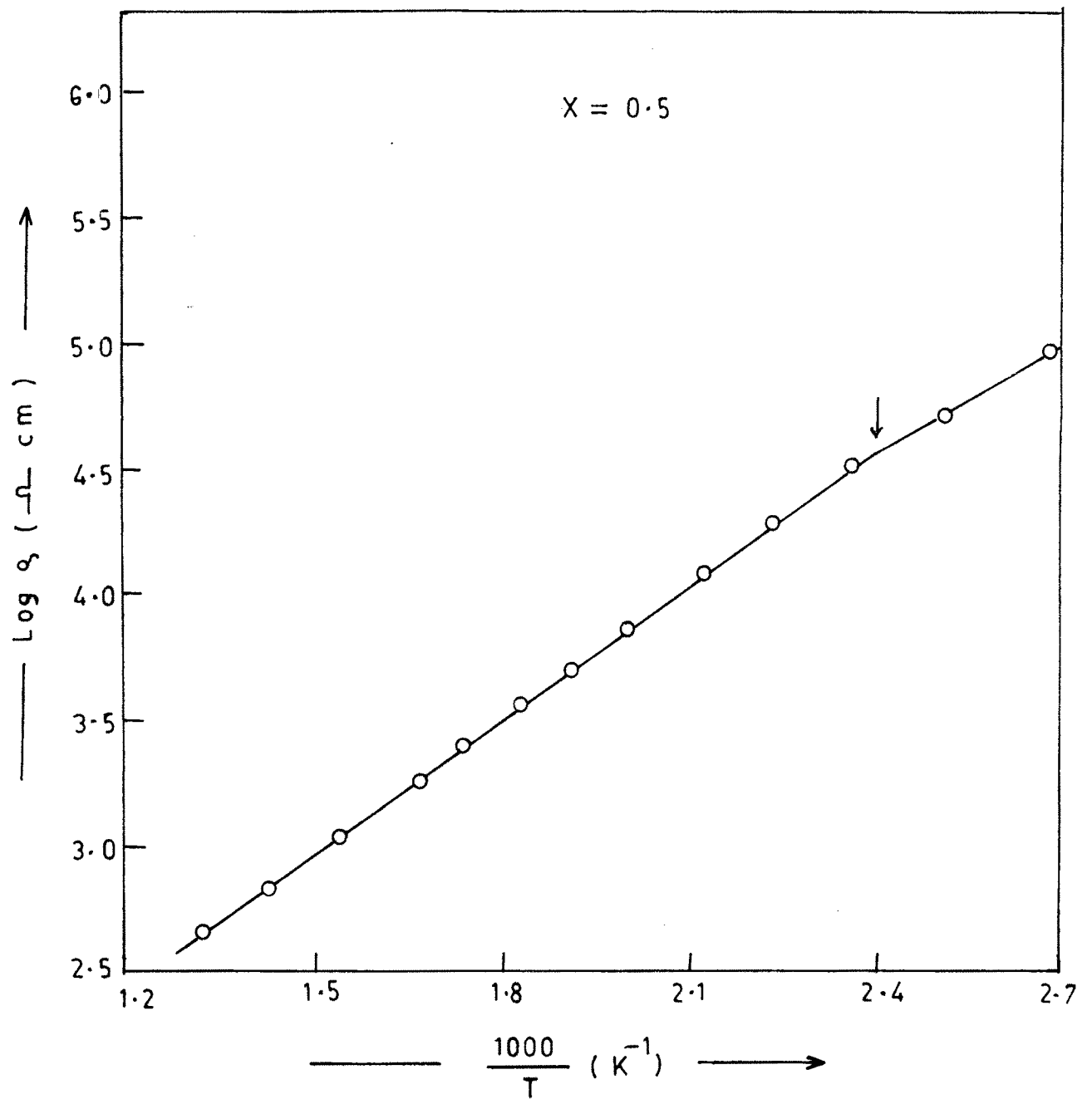
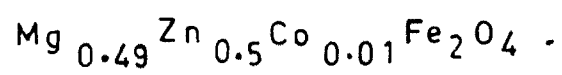


FIG. 3.5 - VARIATION OF RESISTIVITY WITH TEMPERATURE FOR



The magnetic order in spinel ferrites is mainly due to superexchange interaction occurring between metal ions in A and B sublattices (10). There are three types of interactions in ferrites viz. A-A, A-B and B-B interactions. During sintering some Fe^{3+} ions change to Fe^{2+} so the electronic conductivity occurs due to exchange of electrons between trivalent iron ions and divalent iron ion on octahedral site. The existence of B-B exchange interaction between ions on the B-site of such a ferrite will affect the activation energy required for transfer of electrons between Fe^{2+} and Fe^{3+} .

The activation energies corresponding to para and ferrimagnetic region were calculated using the relation 3.6.

They are given in Table 3.1 alongwith the values of dc resistivity of the samples at room temperature. It is clear from the table that the activation energy in the paramagnetic region is greater than that in ferrimagnetic region. The lower activation energy in ferrimagnetic region is attributed to the magnetic ordering. The lower activation energy also suggests the hopping electron mechanism of conduction in these ferrites.

The variation of d.c. resistivity with x is shown in Fig. 3.6. It increases upto $x = 0.2$ and then it decreases The sample

Table 3.1

Data on dc resistivity, activation energy, porosity and Curie temperatures of the samples

x	Dc resistivity $\rho_{dc} \times 10^5$ ohm-cm	Activation energy Ferri region (eV)	Activation energy Para region (eV)	Po, %	Curie temperature ($^{\circ}$ K)
0.1	12.56	0.20	0.35	18	518
0.2	20.00	0.27	0.47	16	500
0.3	16.96	0.26	0.32	18	476
0.4	13.66	0.21	0.31	20	423
0.5	4.97	0.27	0.36	13	416

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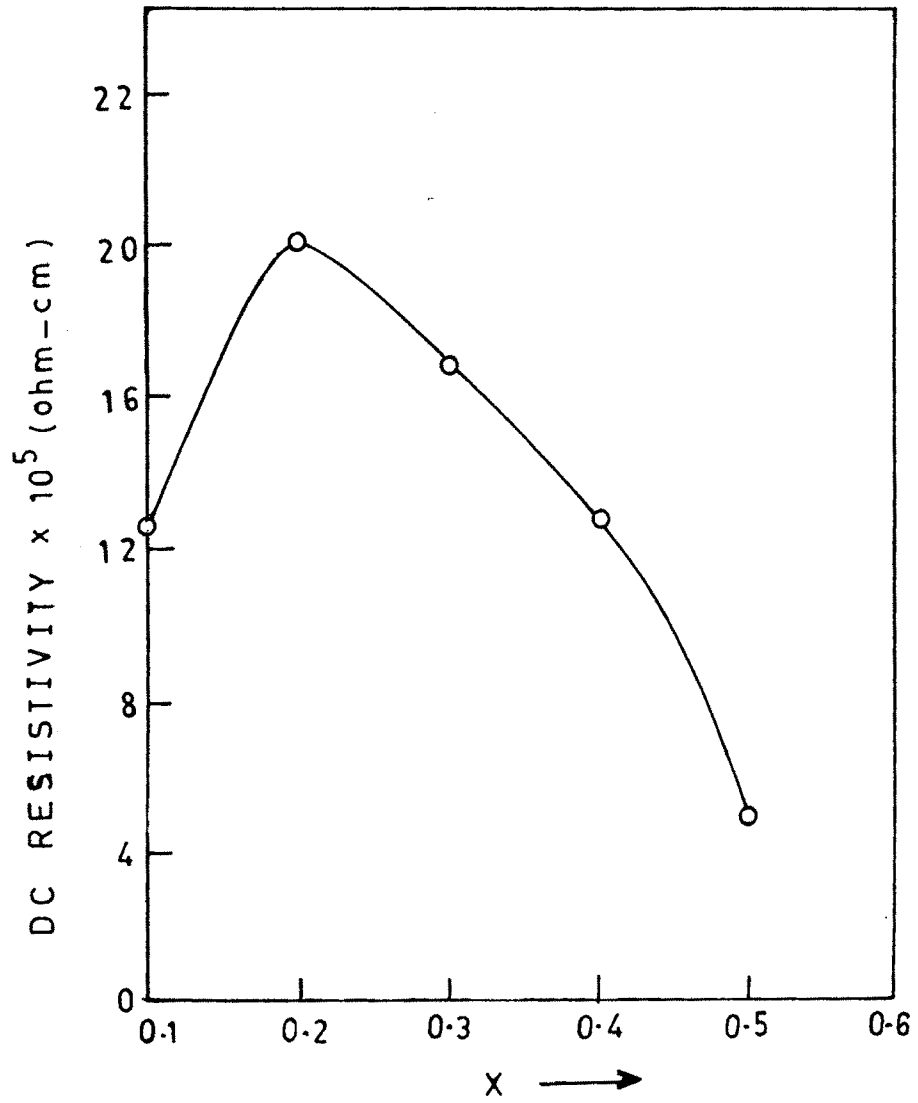


FIG.3.6- VARIATION OF DC RESISTIVITY WITH X .

with $x = 0.2$ has the maximum resistivity of 20×10^5 ohm-cm, while the sample with $x = 0.1$ and $x = 0.5$ have resistivities of 12.56×10^5 ohm-cm and 4.97×10^5 ohm-cm respectively.

The Curie temperatures obtained from $\log \rho$ vs. $1/T$ plots are given in Table 3.1. From this table it can be seen that transition temperature T_c decreases with x . Such a variation can be explained on the basis of the strength of exchange interaction between the magnetic ions, which in turn depends upon their density and magnetic nature. As the number of Mg ions increases in the samples, the number of Ni^{2+} ions go on decreasing. The non-magnetic Zn^{2+} ions occupy the A site. The substitution of Mg which has a partially inverse nature, has the effect of transferring some Fe^{3+} ions from B to A site. These together decrease the strength of the A-B interaction and hence T_c decreases.

According to Josyulu et. al. (11) in case of Co-Zn and Ni-Zn ferrites the conduction at lower temperature is due to $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ while at higher temperature it is due to $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$ and $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$. The oxides which contain a substantial amount of metal ions in two different valence states on crystallographically equivalent sites require relatively small activation energies (12) and this is reflected in low resistivities in the present case also.



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