CHAPTER - III

ELECTRICAL PROPERTIES

CHAPT ER - III

Electrical Properties

3.1 Introduction

Magnesium ferrite has high resistivity, low magnetic and dielectric loss and with its derivatives, has wide applications in microwave technology. Among the binary ferrites that include Mg ferrites as one of the components, Mg-Cd ferrite has been thoroughly examined. The selection of suitable additives and use of appropriate firing procedure make Mg-ferrite useful in widespread applications at microwave frequencies.

In this chapter conduction in oxides and ferrites is briefly discussed. The explanation of the results on the temperature dependent measurement of resistivity of the Mg-Cd ferrites doped with the rare earth element samarium is presented.

3.2 The Conduction Mechanism

The metal oxides have a predominant ionic bonding character. The electrical conductivity is mainly ascribed to the electrons with 3d like wave functions, the outer electronic configuration of oxygen being stable. As far as the electrical properties of oxides are concerned, the models are successful only

in providing the semiqualitative explanations of experimentally established results.

Energy level schemes in solids can be derived on the basis of the following postulates –

i) Nearly free electron approximation and

ii) Tight bonding approximation

In the free electron model, the electrons are assured to move throughout the solid with small perturbation.It is assumed that the solid consists of an array of atoms and interaction may be treated as a small perturbations of the properties of the free atoms.

The 3d levels in the first transition elements are systematically filled from Sc to Ni. In the crystalline field of solid, the levels are splits into a triplet and doublet. The triplet state lie below doublet states in oxides with the rocksalt structure. These oxides are then expected to be metallic conductors at least above the antiferromagnetic disorder temperature.[1] Below the Neel temperature, exchange process could give rise to further splitting of 3d band. The oxides behave as semiconductors at all temperature and have intrinsic activation energies. It is evident from this that descriptions in terms of conventional band theory fail to account for the electrical

transport properties. The failure has its origin in the low mobility of electrons in 3d band.

3.3 Conduction in Oxides

The majority of transition metal oxides are semiconductors and the temperature variation of their conductivity can be expressed by an equation

$$\sigma = A / T^{\beta-1} \exp(-B/kT) \quad \ldots (3.1)$$

where A and B are constants. β is 1 to 2. The activation energy can have values upto 1.5 eV though much smaller values are encountered at lower temperature for an oxide of composition MeO. The activation energy of a conduction electron may be represented by

$$O^{2-} Me^{2+} O^{2-} Me^{2+} O^{2-} - O^{2-} Me^{1+} O^{2-} Me^{3+} O^{2-} \quad \ldots (3.2)$$

The energy needed for the creation of an ion pair Me^{3+}, Me^{1+} corresdponds to a gap in the density of states. The following terms are considered to be contributing to the activation energy which arises from an electron correlation effect –

1) The difference between the ionization energy and the electron affinity of the free Me^{2+} ion.
2) The difference in Madelung energy of the two configurations represented by equation 3.2

3) The difference in crystal field stabilization of the above configuration.

4) Energies of polarization of the surrounding crystal lattice.

The terms 1 to 4 are of important significance depending upon the conditions that prevail during conduction.

3.4 Conduction in Ferrites

Ferrites are semiconducting in nature having resistivity in the range of 10^{-3} to 10^{11} Ohm 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. The low resistivities of ferrites are caused by the simultaneous presence of ferrous and ferric ions on equivalent lattice sites viz. octahedral sites.[2,3]

The high resistivities in ferrites are 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 electons. The two mechanisms of conductivity can be represented as

$$Fe^{2+} + Fe^{3+} == Fe^{3+} + Fe^{2+} + \Delta E \qquad \ldots \quad (3.3)$$

$$Me^{2+} + Fe^{3+} == Me^{3+} + Fe^{2+} + \Delta E$$

Where Me denotes divalent metal ions like Co, Ni etc. and ΔE is the activation energy i.e. the energy required to transfer the electron from Me^{2+} to Fe^{3+} and vice versa. As an example, the presence of nickel on octahedral site of the spinel favours a conduction mechanism as,

$$Ni^{2+} + Fe^{3+} \longrightarrow Ni^{3+} + Fe^{2+} \quad \ldots \quad (3.4)$$

which can explain the predominant conduction mechanism in the nickel-zinc ferrite.[4]

A mechanism of conduction can be proposed as long as ions of the same parent atom having different valance states are found in crystallographically equivalent positions in the lattice. Thus the extra electron on a ferrous ion requires little energy to move to a similarly situated adjacent ferrit ion. The valence states of the two ions are interchanged, under the influence of an electric field, extra electrons can be considered to constitute the conduction current, jumping from one ion to the next. Since the materials are semiconductors, one may expect their resistivity to decrease with increase in temperature.

3.5 Activation Energy

Band gap is defined as the difference in energy between the lowest point of conduction band and highest point in valence

band. Besides, there may be some impurities present giving rise to trap levels and localised states.[5-9] The presence of pores provides insulating path to the conduction electrons. Magnetization states also affect the conduction mechanism. There is an additional splitting of 3d band and the Bloch type wave function are not appropriate for the description of electrons which are fully localised on specific cations. Thus the conventional band theory does not give a satisfactory account of the conduction properties of ferrites. The idea of band gap which is used for semiconductors need to be augmented by the concept of energy of activation in case of oxide semiconductors. It is necessary to imagine some discrete conducting states rather than conduction band and valence bond. Some minimum energy is needed for an election to jump from one state to the other as there exists certain potential well within the two. The conduction can not occur unless the carriers are able to cross the potential well and for this purpose they need to be activated by some external agency such as thermal energy. According to kinetic theory of heat, the energy is imparted to the particles and if this is just sufficient, the conduction can take place. This is called as thermal activation and the minimum energy needed for the current carriers to go to conducting state may be defined as energy of activation. Activation can also be achieved by using other forms of energies such as optical or by the application of

magnetic field.

3.6 Effect of other factors

As in the case of many other semiconductors the resistivity of ferrites is very susceptible to temperature changes. The charge transport takes place by thermally activated hopping involving interactions with phonons. From this consideration, the temperature variation of resistivity can be represented by an exponential relation

$$\rho = C \exp (\Delta E / kT) \quad \ldots (3.5)$$

where C is constant. In ferrites, C can be identified to a different constant ρ_o which is not dependent on temperature. Thus, the above equation takes the form

$$\rho = \rho_o \exp (\Delta E / kT) \quad \ldots (3.6)$$

Komar and Klivshin[5] showed that the graph of logarithm of resistivity versus reciprocal temperature is linear and the break in linearity appears at Curie temperature. The slope of the straight line gives $\Delta E/K$ from which energy of activation can be calculated.

The conductivity can be suppressed by the use of impurities when the corresponding partially filled levels are situated above half way over the band gap. The ΔE value for Mn

ferrite is smaller than that for Ni and Co-ferrites. This is in agreement with the decrease in conductivity that was obtained by Van Uitert[3] by substitution of a few mole % of Mn for the divalent ions in Ni and Co ferrite. The variation in dc resistivity for various dopant concentration of indium in a manganese zinc ferrite has been reported.[4] The indium ions are observed to occupy both tetrahedral and octahedral sites. In the same ferrite, Rao and his co-workers have observed the effect of chromium impurity on the dc resistivity[10-12].

The presence of ferrous (Fe^{2+}) ions reduces magnetostriction but it is highly undesirable in microwave ferrite applications[13-17]Snoek[18] pointed out that the presence of ferrous ions can be reduced strogly by taking iron less than the stoichiometric ratio in the composition. Van Ultert[3] showed that an excess of iron above stoichiometry and high firing temperature both cause remarkable reduction in resistivity.

3.7 Hopping of Polarons Model

In the lattice of spinel ferrites there exists the electrostatic crystal field due to the presence of ions. There is coulomb interaction between the charge carriers and the crystal field. As the charge carriers move during the conduction process the ions get partially dragged along with it. Such a displacement of ions leads to the polarization of the surrounding region. Thus

the carriers get situated at the center of the polarization potential well. If the well is sufficiently deep the carrier is trapped at the lattice site and conduction is achieved by thermal activation. The combination of potential strain and the electron is described as a "polaron". It has been concluded that for ferrites the conduction is determined by thermally activated hopping of polarons[19,20]. The charge transport by polarons from site to site is more commonly known as "polaron hopping".

3.8 Experimental

The dc conductivity in the present case was measured by two probe method (Fig.3.1) on compressed and sintered pellets of about 1 cm diameter and ~ 0.2 cm in thickness. The measurements were carried out with the help of a conductivity cell. The cell consists of two brass rods fitted in two porcelein discs. The fitting screws are provided to keep the assembly of discs and rods firmly held together. The screws provided on the rod are also used for external contacts. To have a good ohmic contact, the pellets were polished and silver pasted on both the faces. The conductivity cell was placed inside the furnace whose temperature was controlled. The calibrated chromel-alumel thermocouple was used to measure the temperature of pellet. The dc voltage of 5 volts was applied across the pellet through TPSU. The thermo e.m.f. was measured with the help of a digital

voltmeter and the current with adigital multimeter.

The temperature of furnace was gradually increased from room temperature to 750°C and corresponding current was measured at an interval of 1 mV in thermo e.m.f. for each sample. The resistance of the pellet was calculated by Ohm's law.

$$R = V/I$$

where V - voltage across the pellets in volts

I - current through the pellet in ampere

The resistivity of the pellet was calculated by the formula

$$\rho = R \frac{A}{t} \qquad \ldots (3.7)$$

where A - area of cross-section of a pellet

t - thickness of a pellet

3.9 Results and Discussion

Figures 3.2 to 3.5 show the variation of log ρ versus $10^3/T$ for $Mg_2Cd_{1-x}Sm_yFe_{2-y}O_4$ samples with x=0.5 and y=0, 0.1, 0.2, 0.3, 0.4 and 0.5 respectively. The slope of the each straight line changes at a particular value of temperature. The change in the slope has been attributed to the effect of magnetic ordering and conduction mechanism of ferrites. The value of temperature at which the slope changes has been identified as the Curie temperature. Table 3.1 gives values of Curie temperatures

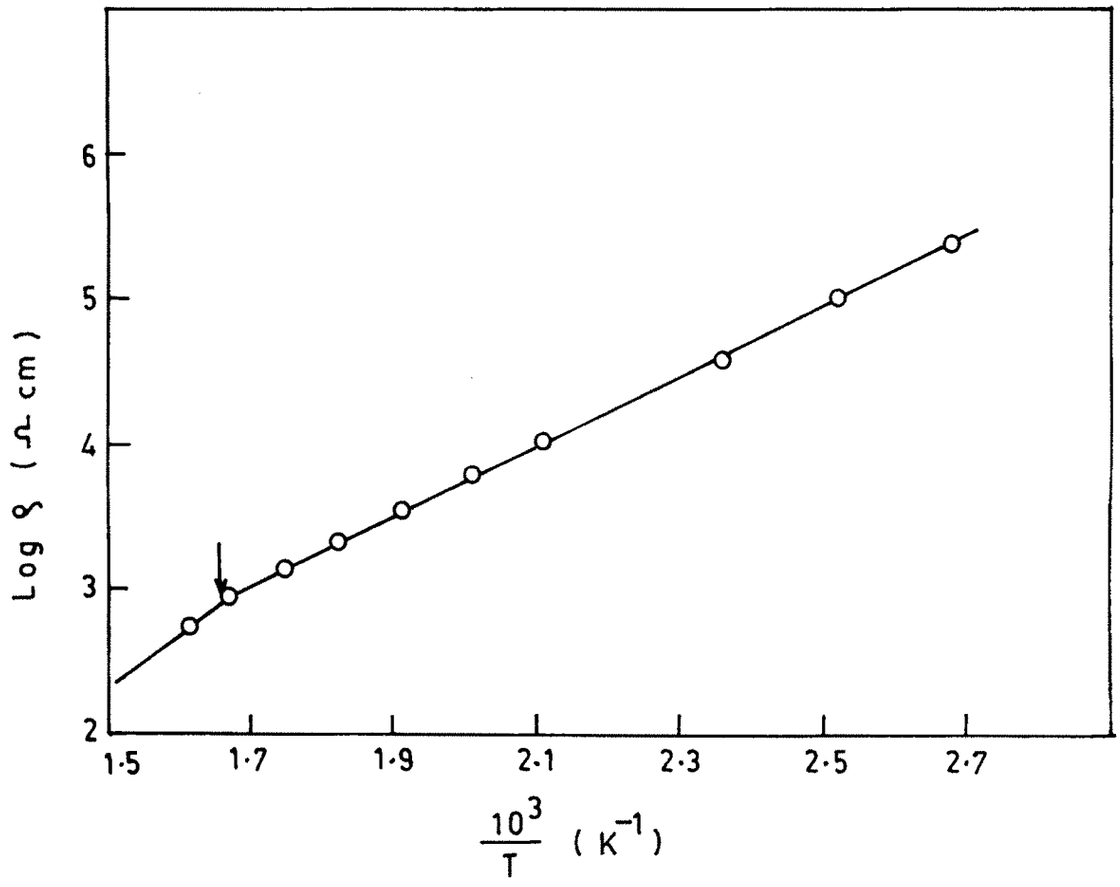

FIG. 3·2 – VARIATION OF Log ρ WITH $\frac{10^3}{T}$ FOR SYSTEM $Mg_{0.5}\ Cd_{0.5}\ Sm_{0.1}\ Fe_{1.9}\ O_4$.

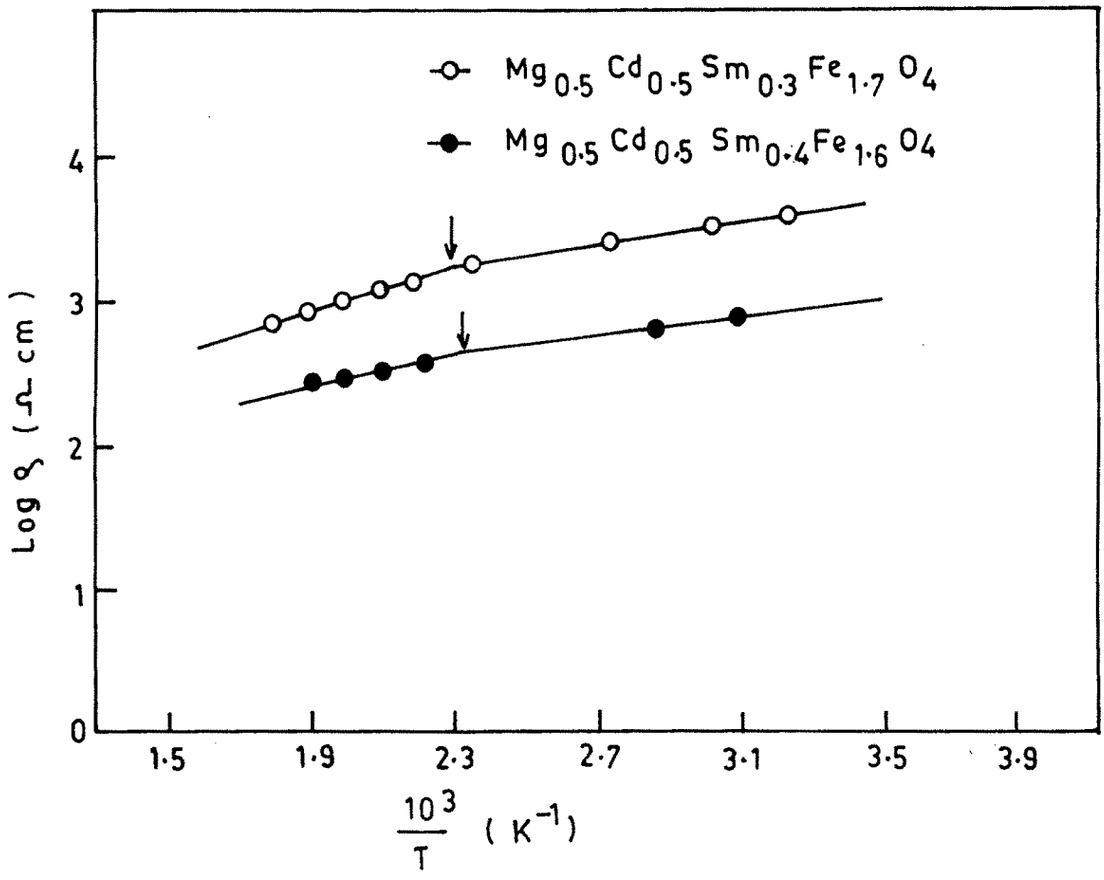

FIG. 3·3 — VARIATION OF Log ρ WITH $\frac{10^3}{T}$ FOR $Mg_{0.5}Cd_{0.5}Sm_{0.3}Fe_{1.7}O_4$ FERRITE AND $Mg_{0.5}Cd_{0.5}Sm_{0.4}Fe_{1.6}O_4$ FERRITE.

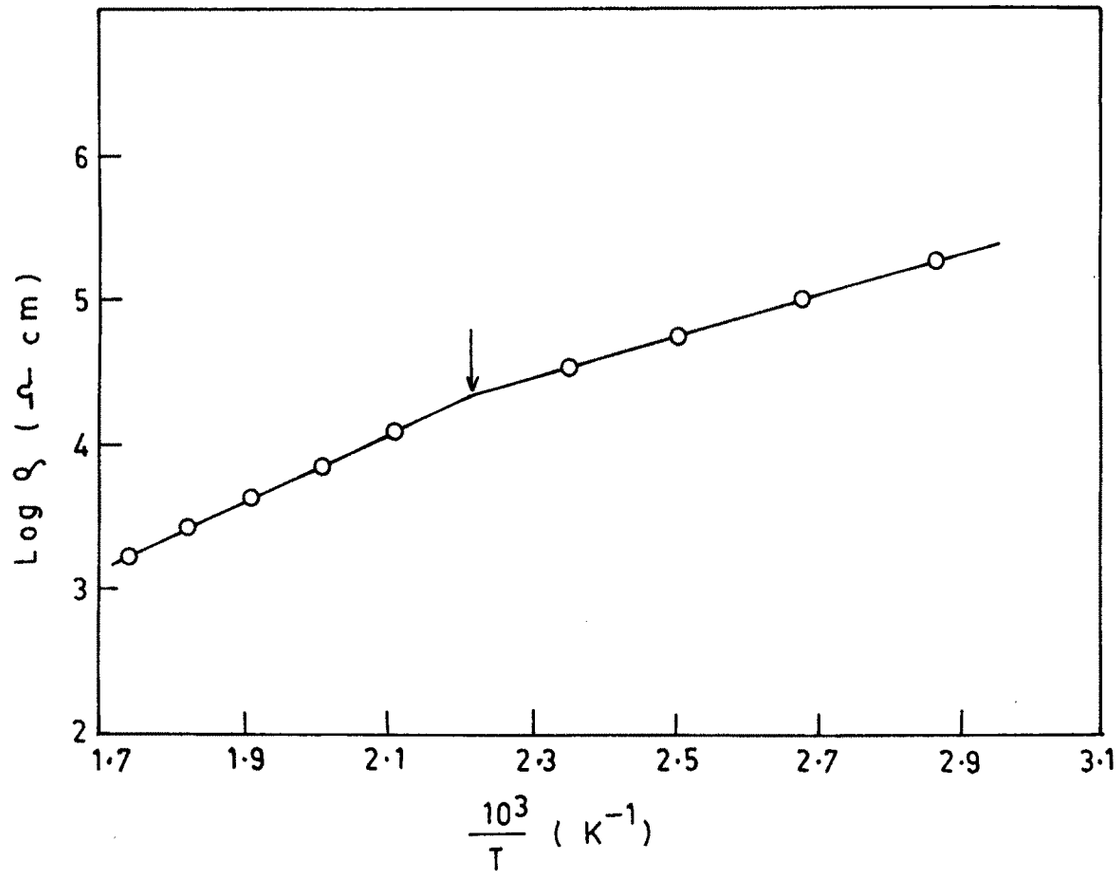

FIG. 3·4 — VARIATION OF Log ρ WITH $\frac{10^3}{T}$ FOR $Mg_{0.5}Cd_{0.5}Sm_{0.2}Fe_{1.8}O_4$ FERRITE .

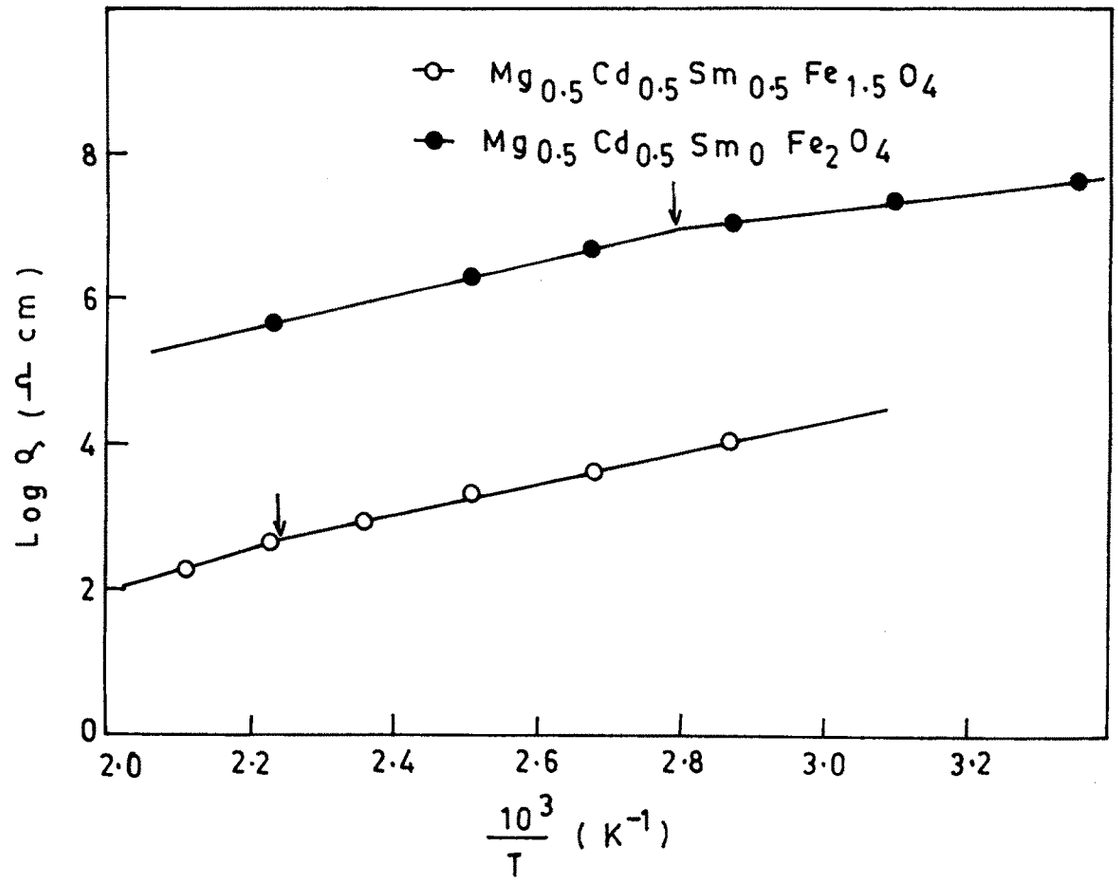

FIG. 3·5 — VARIATION OF Log ρ WITH $\frac{10^3}{T}$ FOR $Mg_{0.5}Cd_{0.5}Sm_{0.5}Fe_{1.5}O_4$ AND $Mg_{0.5}Cd_{0.5}Fe_2O_4$ FERRITES.

at different samarium concentration. It is seen that there is derease in the values of Tc with the addition of samarium in Mg-Cd ferrite. According to the Neels model the magnetic interaction between the ions via oxygen governs the Curie temperature. Also the angles Fe^{3+}_{A} - O - Fe^{3+}_{B} and distances Fe_{A} - O, Fe_{B} - O determine Curie temperature.

The activation energy for conduction has been calculated by using the relation

$$\rho = \rho_{o} \exp (\Delta E/kT) \qquad \ldots (3.8)$$

Distinct break is observed in the temperature variation of the resistivity. The breaks and discontinuities can be attributed to several sources. Komar and Klivshin[21] have observed the changes in slopes of conductivity plots near Curie temperature. They have attributed this to the magnetic transition i.e. from para-magnetism to ferrimagnetism. Verwey et al[22-26] have also observed such breaks in Mn-Zn ferrite. Irkhin and Turov[27] have proposed a theoretical explanation for existance of kink at the Curie temperature. They have concluded that the activation energy and effective mass of current carrying excitations in the intrinsic semiconductor depend on the spontaneous magnetization. This leads to an additional temperature dependance of electrical resistance which is sharp near the Curie temperature. The kink is most marked for those case in which there is strong exchange

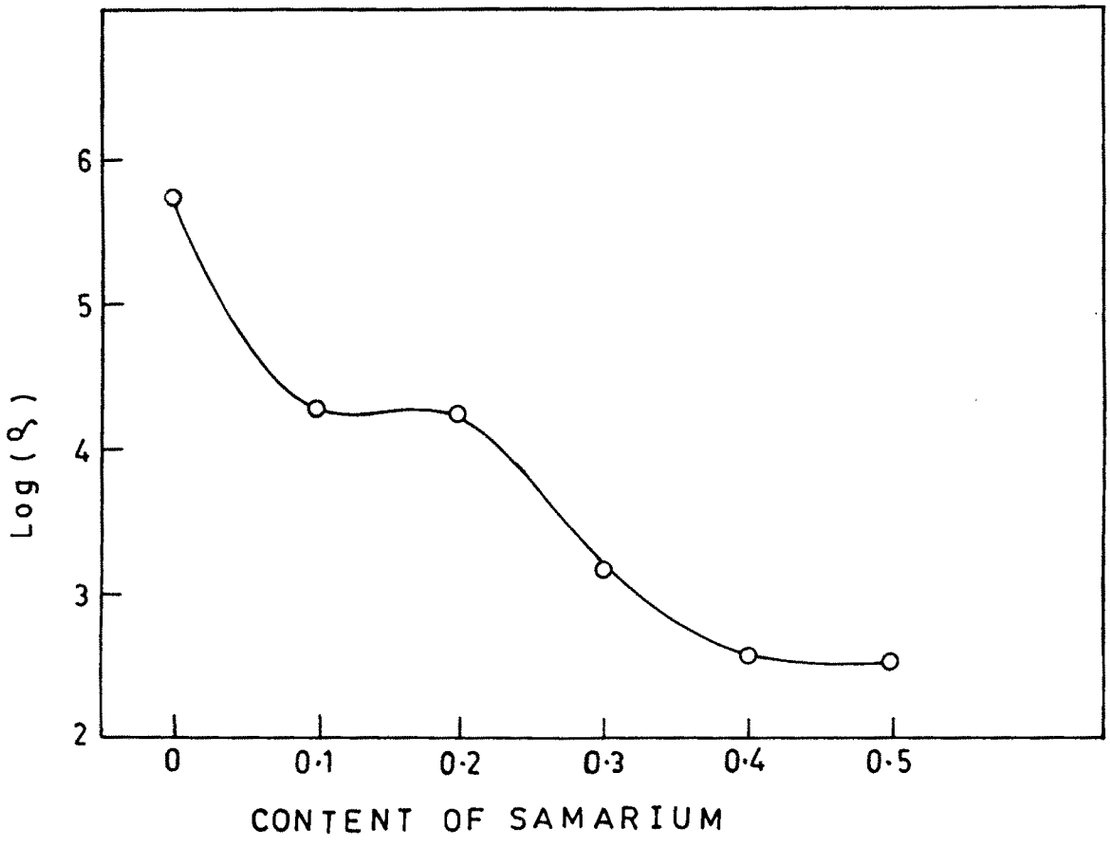

FIG. 3·6 —VARIATION OF D.C. RESISTIVITY WITH SAMARIUM CONTENT AT 175°C,

interaction between the outer and inner electrons. The activation energy in paramagnetic region is higher than that in ferrimagnetic region. This is also in good agreement with the theory developed by Irkhin and Turov. The fall of resistivity of the samples with more and more addition of Sm has been explained by assuming that Sm tends to impede the hopping of polarons. The lowering of Curie temperature values also suggests the fact that some magnesium ions are transferred to the A-site.

The observed variation in the d.c. resistivity with increasing samarium concentration can be explained as follows. The increased concentration of Sm is associated with the replacement of Fe^{3+} ions by Mg^{2+} and Sm^{3+} ions at the B site. Therefore, the general cation distribution of this series can be written as

$$(Cd_xFe_{1-x})^A\ [\ Mg_{1-x}Sm_yFe_{1+x-y}]^B\ O_4^{2-}$$

The magnesium ferrite is partially inverse and sensitive to heat treatment. The B-site preference energy of Mg is 13 K cal whereas Fe^{3+} ion has no site preference energy Since the Sm ions occupy B-sites, addition of Sm ions reduce the total number of Fe^{3+} ions in the system. This accounts for the observed increase of ρ.

Table 3.1

Activation Energy and Curie temperature data for

$Mg_xCd_{1-x}Sm_yFe_{2-y}O_4$ ferrites with x = 0.5

Y	Composition	Activation Energy in		Curie Temp. ^oC
		para region	ferri region	
0 0	$Mg_{0.5}Cd_{0.5}Fe_2O_4$	0.5385	0.1679	85
0.1	$Mg_{0.5}Cd_{0.5}Sm_{.1}Fe_{1.9}O_4$	0.7653	0.4578	332
0.2	$Mg_{0.5}Cd_{0.5}Sm_{.2}Fe_{1.8}O_4$	0.5412	0.2888	167
0.3	$Mg_{0.5}Cd_{0.5}Sm_{.3}Fe_{1.7}O_4$	0.2409	0.1543	162
0.4	$Mg_{0.5}Cd_{0.5}Sm_{.4}Fe_{1.6}O_4$	0.3968	0.1984	157
0.5	$Mg_{0.5}Cd_{0.5}Sm_{.5}Fe_{1.5}O_4$	0.4762	0.3602	172

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