chapter IV

Electrical Properties

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ELECTRICAL PROPERTIES

D.C. ELECTRICAL CONDUCTIVITY

4-1 Introduction

Ferrites are magnetic substances which are semiconductors in nature. Their resistivity changes in very wide range from 10^{-3} Ω -cm to 10^{11} Ω -cm (1). Many physical and chemical properties of solids have some sort of relation with the mechanism of the charge transport. The d.c. conductivity provides valuable information about conduction mechanism in ferrites. The electrical properties mainly depend on the method of preparation and presence of impurities, porosity, thermal treatment during preparation. Verway et al (2) have shown that the conduction can be increased by mixing a small amount of foreign oxides as impurities in the high resistivity ferrites. Conduction in ferrites is attributed to a hopping process which obeys the law $\int = \int_0 Exp$ ($\Delta E/KT$), Where ΔE is activation energy. Komar et al (3) have observed breaks in the resistivity plots of many ferrites, near the Curie temperature.

The magnetic nature of ferrites is highly influenced by the magnitude of conductivity. This has created considerable interest in the research workers to study the electrical conductivity of ferrites (4,5). Maizen (6) has studied the conduction mechanism on the basis of band

picture and hopping model. Klinger (7) has suggested two phase mechanism for hopping of polarons. In the hopping process electrons are exchanged from Fe^{2+} to Fe^{3+} ions on octahedral sites giving rise to conduction in ferrites.

4.2 Conduction in Oxides

In case of metal oxide MO where M is divalent metal ion, the orientation of the activated electron may be represented as

$$O^{2-}\ M^{2+}\ O^{2-}\ M^{2+}\ O^{2-}\ ---\ O^{2-}\ M^{1+}\ O^{2-}\ M^{3+}\ O^{2-}$$
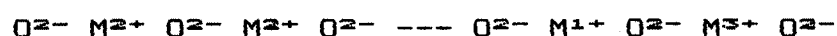
Such type of oxides exhibit high resistivity due to high activation energy. If there exists substantial quantity of metal ions in two different states on equivalent lattice sites the activation energy will be relatively small and hence high electrical conductivity. The energy needed for the formation of ion pairs $(M^{2+}\ M^{2+})$ and $(M^{3+}\ M^{1+})$ corresponds to the gap in density of states. Again, there are additional factors contributing to the activation energy which are

i) the difference between ionization energy and electron affinity of the free M^{2+} ion.

(ii) the difference in madelung energy of the configurations $(M^{2+}\ M^{2+})$ and $(M^{3+}\ M^{1+})$,

(iii) the difference in crystal field stabilization energy of the above configurations,

iv) energies of polarisations of the surrounding crystal lattice.

4.3 Conduction in Ferrites

The conductivity in ferrite is mainly explained on the basis of actual location of cations in the spinel structure and hopping mechanism. The 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

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

$$Me^{2+} + Fe^{3+} \ ------ \ Me^{3+} + Fe^{2+} + \Delta E$$
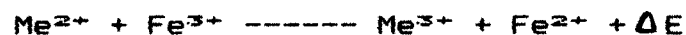
where ΔE is the activation energy, the energy required to transfer of electron from Me^{2+} to Fe^{3+} and vice versa. Me denotes divalent metal ions like Cu, Co, Mg, Mn, Ni and Cd etc. The valence states of the two ions get interchanged under the influence of an electric field, these extra electrons can be regarded to constitute the current by jumping or hopping process.

The free electron model cannot explain the electrical conductivity of ferrites because of the fact

that the electrons in ferrite are not free and energy
band model is not suitable to explain the electrical
conductivity for the lack of Bloch type wave fuctions for
electrons in ferrites. The conductivity of ferrites can
be however, explained in terms of electronic charge
carriers like electrons and holes by the relation

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

where n and μ are the concentration and mobilities
of electron and holes.

4.4 Electron hopping and Polarons

In spinel ferrite lattice due to presence of ions
there exists the electrostatic crystal field. There is
Coulomb interaction between the charge carriers and the
ions. During the conduction process the motion of the
electrons or holes drift the ions along with them. The
electrostatic interaction between electron and the
neighbouring ions results into the polarization of the
lattice. The combination of an electron with its strain
field is called Polaron. When such association is weak it
constitutes large polaron. Such polarons are found in
ionic crystals. When electron plus lattice deformation
has a linear dimension smaller than lattice constant it
constitute small polarons. Such polarons are found in
covalent crystals.

In the above electrostatic interaction, the carriers get situated at the centre of the polarisation potential well. If the potential well is deep enough the carrier may be trapped at the lattice site and conduction is achieved by thermal activation. The mechanism of charge transport by polarons from site to site is described as hopping of polarons.

The mobility of the charge carriers during hopping mechanism is given by relation

$$\mu = \frac{e^2 \, a^2 \, \nu_0}{K \, T} \, \text{Exp} \, (\Delta E/KT)$$

Where a = the distance between the nearest neighbouring cations.

ν_0 = frequency of vibration of crystal lattice and

ΔE = activation energy for hopping process.

The strength of the electron lattice interaction is measured by the coupling constant (α) defined as

$$\frac{1}{2} \, \alpha = \frac{\text{deformation energy}}{h \, W_L}$$

Where W_L is the longitudinal phonon frequency near zero wave vector. The $1/2 \, \alpha$ represents the number of phonons which surround a slow moving electron in a crystal. The polaron may be called as 'large Polaron' when coupling constant possesses the higher values and the 'Small

Polaron' when this value is lower. Frohlich (8) formulated the interaction Hamiltonian for large polaron. Small polaron formation is favored in solids which combine a large coupling constant with narrow conduction band. At higher temperatures small polaron motion might involve the absorption of one or more phonons, leading to the hopping mechanism. A strong experimental evidence has been observed for the existance of small polarons and the hopping process in ferrites (9, 10).

4.5 Experimental

The d.c. electrical measurements of different samples were carried out in the temperature range from room temperature to 700° K by conventional probe method. Resistivity of ferrite samples in the form of pellets of about 1.5 cm diameter and 0.2 to 0.3 cm thickness was measured by two probe method. The conductivity cell is shown in fig 4.1 and the necessary circuit diagram is shown in fig 4.2. The photograph of the experiment set up is depicted in Fig. 4.3.

The pellet was polished and pasted with a silver paste and sandwiched between the brass electrodes of the cell. The silver foils were introduced between the brass rods for a good ohmic contact.The two probes are made out by silver wires which are insulated with ceramic beads

③ – Porcelain dises
⑤

①

⑥

②
④

⑥

①
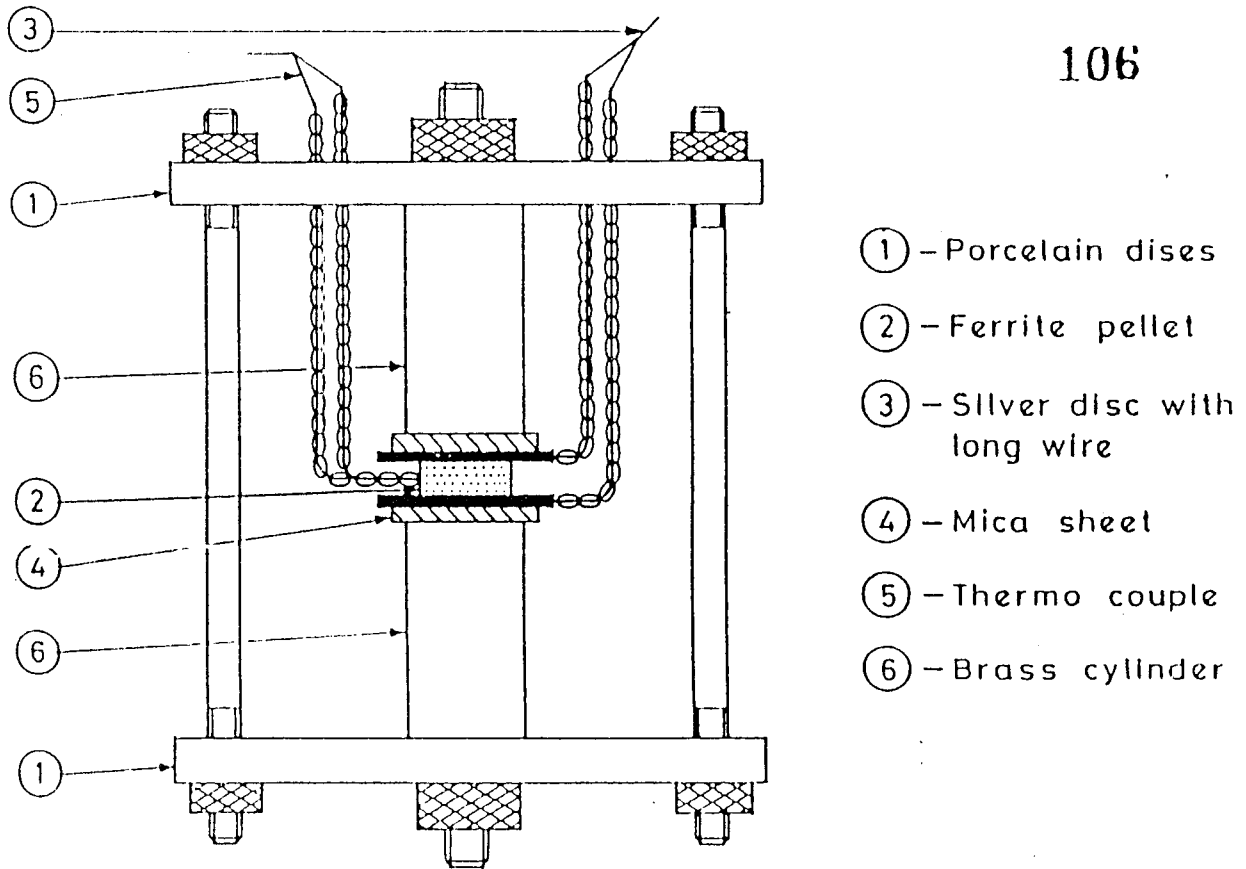
① – Porcelain dises

② – Ferrite pellet

③ – Silver disc with long wire

④ – Mica sheet

⑤ – Thermo couple

⑥ – Brass cylinder
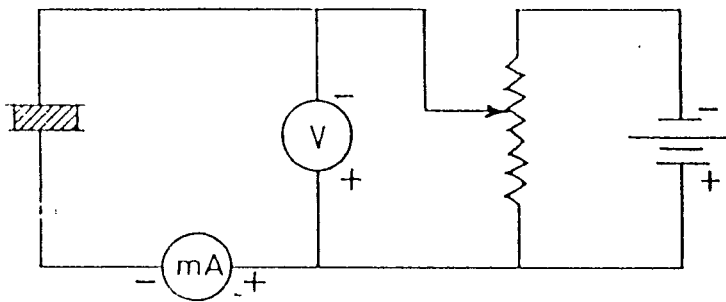
Fig.4.1   THE CONDUCTIVITY CELL .

Fig. 4.2 , CIRCUIT DIAGRAM FOR ELECTRICAL
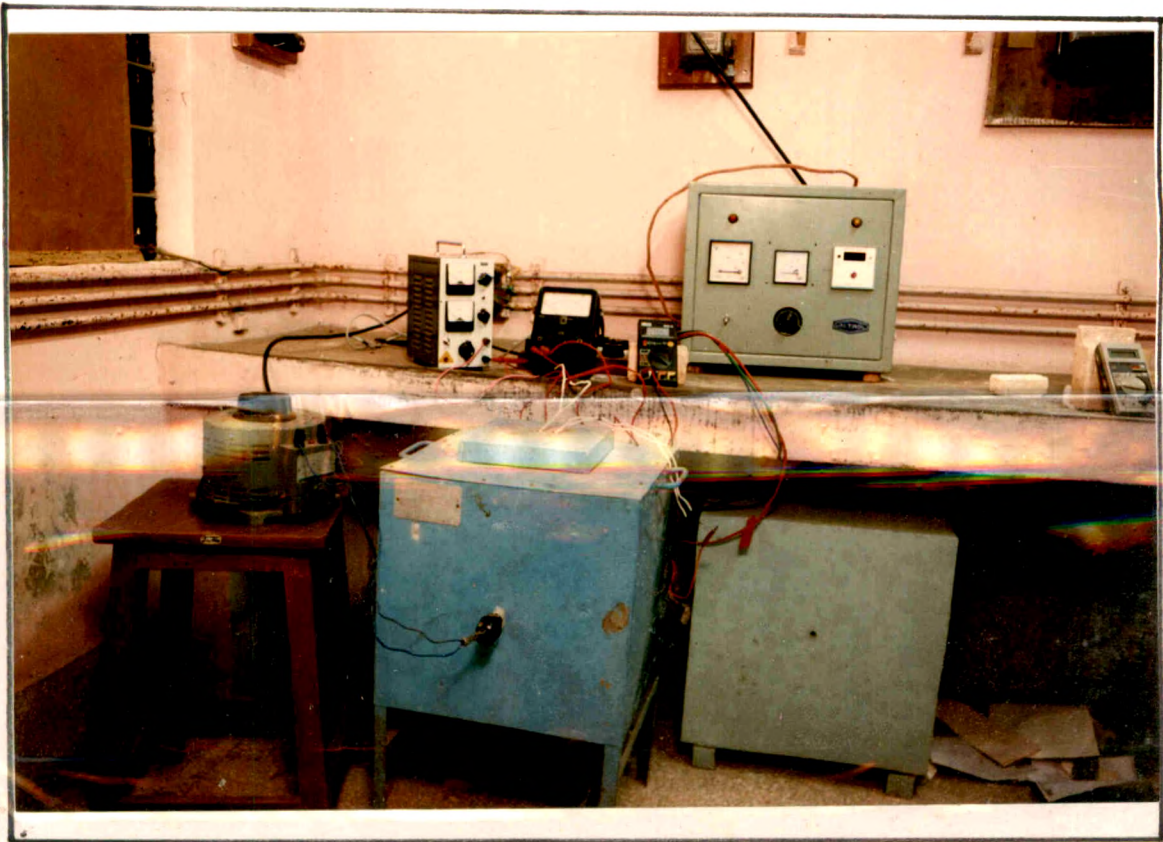RESISTIVITY .

Fig.4.3 : Experimental set up of D.C.Resistivity Measurement.

and connected to the brass electrodes. The entire cell was then kept in the temperature controlled furnace. A calibrated chromel-Alumel thermocouple was used to measure the temperature of the furnace by keeping the junction near to the sample. Resistivity measurements were carried out by measuring the current at constant voltage 5 volt for the temperature range 300 - 700° K.

Resistivity was calculated from the formula

$$\int = \frac{R\,A}{t} = \frac{\Pi\,r^2}{t}\,R$$

Where A = area of cross section of the pellet.

t = thickness of the pellet.

Curie temperature and activation energy were determined by plotting log $\int$ versus 10^3 / T for all the samples.

4.6 Results and Discussion

The plots of log $\int$ versus 10^3/T for present samples are shown in Fig. 4.4.

The activation energy corresponding to ferrimagnetic and paramagnetic regions of different samples are calculated using the equation

$$\int = \int_o\ Exp\ (\Delta E/KT) \qquad \ldots 4.1$$

where ΔE is the activation energy.

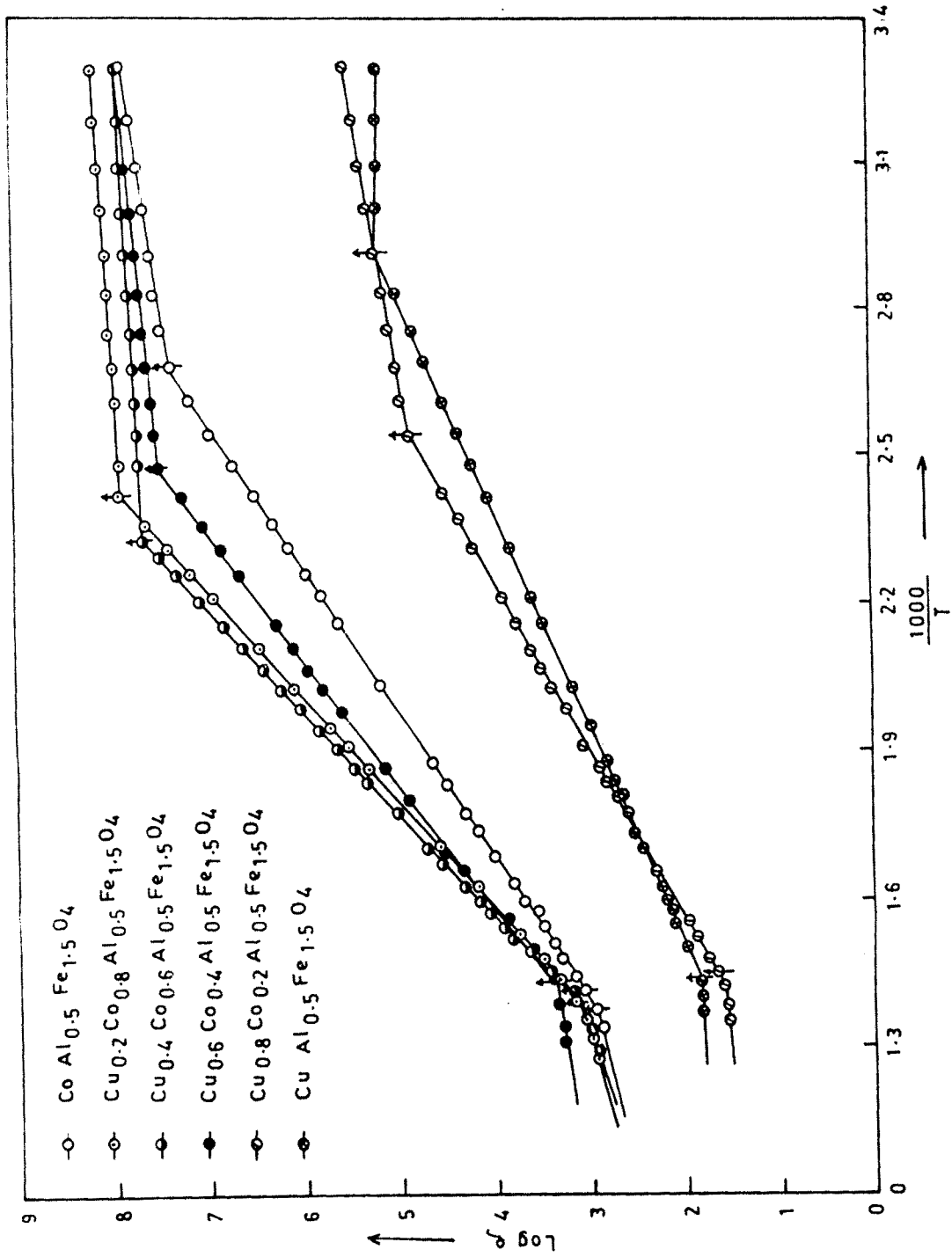By plotting the graph, log $\int$ against 10^3/T the value of ΔE is determined as

Fig.4.4 : Variation of log ρ vs 1000/T

Legend:
- $Co\ Al_{0.5}\ Fe_{1.5}\ O_4$
- $Cu_{0.2}\ Co_{0.8}\ Al_{0.5}\ Fe_{1.5}\ O_4$
- $Cu_{0.4}\ Co_{0.6}\ Al_{0.5}\ Fe_{1.5}\ O_4$
- $Cu_{0.6}\ Co_{0.4}\ Al_{0.5}\ Fe_{1.5}\ O_4$
- $Cu_{0.8}\ Co_{0.2}\ Al_{0.5}\ Fe_{1.5}\ O_4$
- $Cu\ Al_{0.5}\ Fe_{1.5}\ O_4$

$$\Delta E = 2.303 \times 1000 \times K \times Slope \quad ... \ 4.2$$

where K is Boltzman constant.

The activation energies calculated are presented in Table 4.1. The plot is linear in nature and the slopes are changing at different temperatures. The activation energies of different regions are calculated by using the relation 4.2. From the plots it is observed that, each sample shows three distinct regions with two breaks. The first break is indicated by T_1 represents the characteristic temperature and the second break T_2 represents nearly the curie temperature.

Ghani et al (11) have distinguished three regions on the basis of change in activation energy. Komar and Klivshin (3) have observed the changes in slopes of conductivity plots near curie temperature. They have suggested that this change is due to magnetic transition i.e from paramagnetism to ferrimagnetism. Verway et al (2) have also observed such breaks in Mn-Zn ferrites. Ghani et al have observed three region in Cu-Ni ferrites. The present studied samples also show three distinct regions. Ghani et al have suggested that the I^{st} region is due to impurities IInd to phase transition and third to magnetic ordering, other workers (12 to 17) have suggested the I region to impurities and II and III to polaron hopping.

From the table it is observed that the activation
energy in Ferri region is higher than those of para
region. This itself suggests that magnetic interaction
will not affect the conduction process. Similar results
are observed in other ferrites (18, 19). From
conductivity measurement it is found that curie
temperature also decreases with increase in copper
content. The curie temperature obtained form the
reistivity measurement and from a.c. susceptibility
studies are in good agreement with each other.

For the present system the activation energy for
first region in less than 0.2eV which suggests that the
conduction in this region may be due to impurities. The
activation energy in second region is greater than 0.6 eV
which is very much higher than the activation energy
required for Fe^{2+} Fe^{3+} transition. Therefore the
conduction in this region may be due to polaron hopping.
Polaron hopping model has been used successfully to
discuss the conduction phenomenon in ferrite (11).

In ferrites having spinel structure, the B-B
distances are smaller than A-A and A-B distances. When B-
B distance is much larger than the sum of ionic radii of
the cations involved it gives rise to a situation in
which the electrons are not free to move through the
crystal but remain fixed on B site necessiating a hopping

process. However in addition to magnetic ordering there are other factors which affect the resistivity such as surface states, internal barrier, inhomogeneities, impurities, inclusions, porosity.

Table 4.1

Activation energy and Curie temperature for the system $Cu_x Co_{1-x} Al_{0.5} Fe_{1.5} O_4$ samples

Composition	E_I	E_{II}	E_{III}	$T_I °K$	$T_{II} °K$
$CoAl_{0.5}Fe_{1.5}O_4$	0.145	0.68	0.55	373	743
$Cu_{0.2}Co_{0.8}Al_{0.5}Fe_{1.5}O_4$	0.073	0.99	0.77	415	730
$Cu_{0.4}Co_{0.6}Al_{0.5}Fe_{1.5}O_4$	0.052	0.99	0.23	429	723
$Cu_{0.6}Co_{0.4}Al_{0.5}Fe_{1.5}O_4$	0.120	0.77	0.26	403	715
$Cu_{0.8}Co_{0.2}Al_{0.5}Fe_{1.5}O_4$	0.160	0.49	—	393	703
$CuAl_{0.5}Fe_{1.5}O_4$	—	0.45	0.36	343	693

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