CHAPTER-IV

ELECTRICAL PROPERTIES

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4.1 INTRODUCTION :

Ferrites are the magentic substances wich are semiconductors by nature. Their resistivity can very from $10^{-3}\ \Omega$ cm (magnetite) to $10^{11}\ \Omega$ cm (Magnesium ferrite) [1].The high resistivity ferrites find preference over metals and alloys in the high frequency operation which exhibit large current losses . The electricaly conducting properties mainly depend on the method of preparation and the presence of impurities. From theoretical point of view the mechanism of charge transport is of prime importance and this can be investigated from the experimental study on d.c. and a.c. conductivity, thermoelectric power, magneto-resistance and Hall effect.

4.2 CONDUCTION MECHANISM IN METAL OXIDES :

In case of an oxide of composition MO the activation of conduction electron is represented by,

$$O^{2-}\ M^{2+}\ O^{2-}\ M^{2+}\ O^{2-} \rightleftarrows O^{2-}\ M^{1+}O^{2-}\ M^{3+}\ O^{2-} \qquad ......(4.1)$$

where M is 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 states. There are following additional factors contributing to activation energy

1) The difference between ionisation energy and electron affinity of the free M^{2+} ion.

2) The difference in madelung energy of the configurations (M^{2+} M^{2+}) and (M^{3+} M^{1+}).

3) The difference in crystal field stabilisation energy of the above configurations.

4) Energies of polarisation of the surrounding crystal lattice.

4.3 CONDUCTION IN FERRITES:

The charge transport through ferrites is represented as,

$$M^{2+}\,O^{2-}\,Fe^{3+} \rightarrow M^{3+}\,O^{2-}\,Fe^{2-} + Eg \qquad ....(4.2)$$

where Eg, the activation energy, may reflect the difference between third ionization potentials of Fe^{3+} and M^{3+} ions in solids. The low resistivity in Fe_3O_4 was found to be due to the presence of both Fe^{2+} and Fe^{3+} ions in the octahedral B-sites. The conduction mechanism in ferrites is due to the exchange of electrons between Fe^{3+} and Fe^{2+} ions in the same octahedral site in the lattice and is represented as,

$$Fe^{3+} + e^{-1} \rightleftarrows Fe^{2+} \qquad ....(4.3)$$

4.4 ELECTRON HOPPING AND POLARONS :

An electron in the crystal lattice interacts through its charge with the ions or the atoms of the lattice and creates a local deformation of the lattice. The deformation then follows the electron as it moves through the lattice. The combination of electron together with its strain field is known as a polaron. The electrostatic interaction between a conduction electron or a hole and the nearby ions may result in the displacement of the ions and hence, in the polarisation of surrounding region, so that the carrier becomes situated at the center of a polarisation potetial well. When this well is considered to be deep enough, the carrier may be trapped at a lattice site and its transition to the neighboring site can then be determined by thermal activation. This process has been considered as the hopping mechanism. An expersions has been derived by Heikes and Johnson [2] for the mobility

$$\mu = \frac{ed^2 \nu}{kT} \exp \frac{(-\Delta E)}{kT} \qquad \ldots\ldots\ldots(4.4)$$

where, d is the distance between nearest neighbors , ν is the frequency of vibration of crystal lattice and ΔE is the activation energy. If the well could be cosnidered as a volume comparable to the ionic volume, for which interactions between the individual neighboring ions are important, then the small polaron model could be used. Small polaron formation is favoured in solids which combine a large coupling constant with a narrow conduction band. At low temperatures small polaron behaves as a particle moving in a narrow conduction band, and at high temperatures a small polaron is created by absorption of one or more thermal phonons, and there is subsequent hopping of this polaron. There is sound experimental proof for the existance of polarons and their hopping [3-4].

4.5 THERMOELECTRIC POWER

The Seebeck effect may be thought of as a diffusion process. The electrons or holes, from 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 semiconductor with both types of carriers, Seebeck coefficient (α) is given by,

$$\alpha \qquad \frac{(\alpha_n \ \sigma_n + \alpha_p \sigma_p)}{(\sigma_n + \sigma_p)} \qquad ....(4.5)$$

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

$$\alpha_n = (k/e)\,[A_n - E_F/kT) \qquad ....(4.6)$$

$$\alpha_n = (k/e)\,[A_p + (Eg + E_F)/kT] \qquad ....(4.7)$$

where n and p are the electron and hole densities, μ_n and μ_p are electron and hole mobilites, E_F is the Fermi energy and Eg is the band gap energy.

For a partially filled band the Seebeck coefficient varies linearly with temperature.

$$\alpha n = - \frac{\pi^2 k^2}{3e} \ T \ \left[\frac{d \ln \sigma (E)}{dT} \right]_{E = E_F} \qquad ....(4.8)$$

where $\sigma(E)$ refers to the value of the conductivity for a specimen in which the fermi level is at E. The term "dln σ (E)/dT" can be approximated according to whether the fermi energy is temperature dependent or not. The temperature dependance of the thermoelectric power for the ferrite material having one type of charge carriers can be expressed as [5].

$$\alpha = \frac{k}{e} \ [\ln (\frac{No}{n} - 1) + \frac{e}{kT}]a \qquad ....(4.9)$$

where No is the concentration of trivalent ions on the octahedral sites, n is the concentration of Fe^{2+} ions, the term 'a' is the part of activation energy transported by the electrons and T is the absolute temperature. The value of 'a' is zero in the case of Mn ferrites [6] and $\approx$ 1 eV in other cases [7].

4.6 EXPERIMENTAL :

4.6(a) D.C. ELECTRICAL CONDUCTIVITY :

A conducting cell and circuit diagram for the measurement of resistivity of samples are shown in Fig.4.1(a) and Fig.4.1(b), respectively. Initially, silver paste was applied on the surfaces of pellet for good ohmic contact. The pellet was sandwiched tightly in between brass rods with the help of screws. The conductivity cell was then placed in a temperature regulated furnace. A calibrated Alumel-chromel thermocouple was used to measure the temperature of the furnace. The resistivity of was pellet determined by measuring the current at constant voltage, from room temperature to above Curie temperature. The resistivity (σ) was calculated by using the relation,

$$\rho = \frac{\pi r^2}{t} \; \frac{V}{1} \qquad \ldots(4.10)$$

where r is the radius and t is the thickness of the pellet.

4.6(b) THERMOELECTRIC POWER :

The pellet coated with silver paste was put into sample holder and then kept into the regulated furnace for the measurement of thermoelectric power. A schematic diagram with necessary connections is shown in Fig.4.2. For the

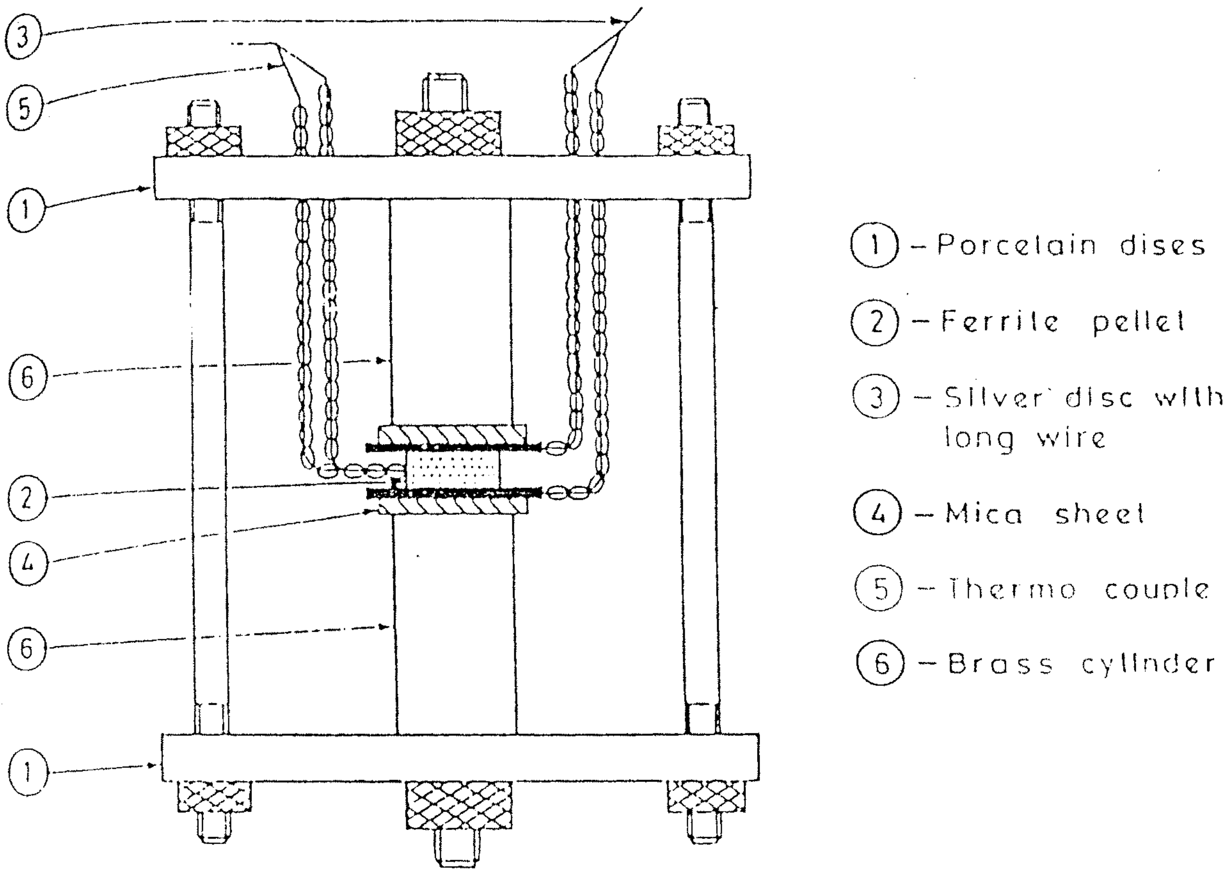


Fig. 4·1(a)— THE CONDUCTIVITY CELL.

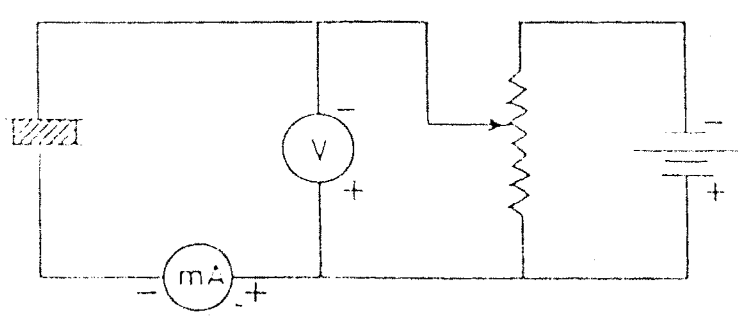
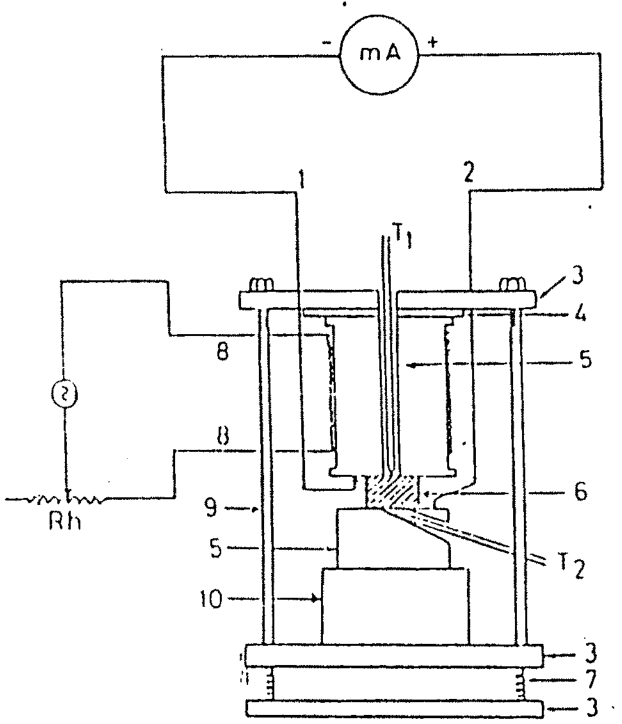


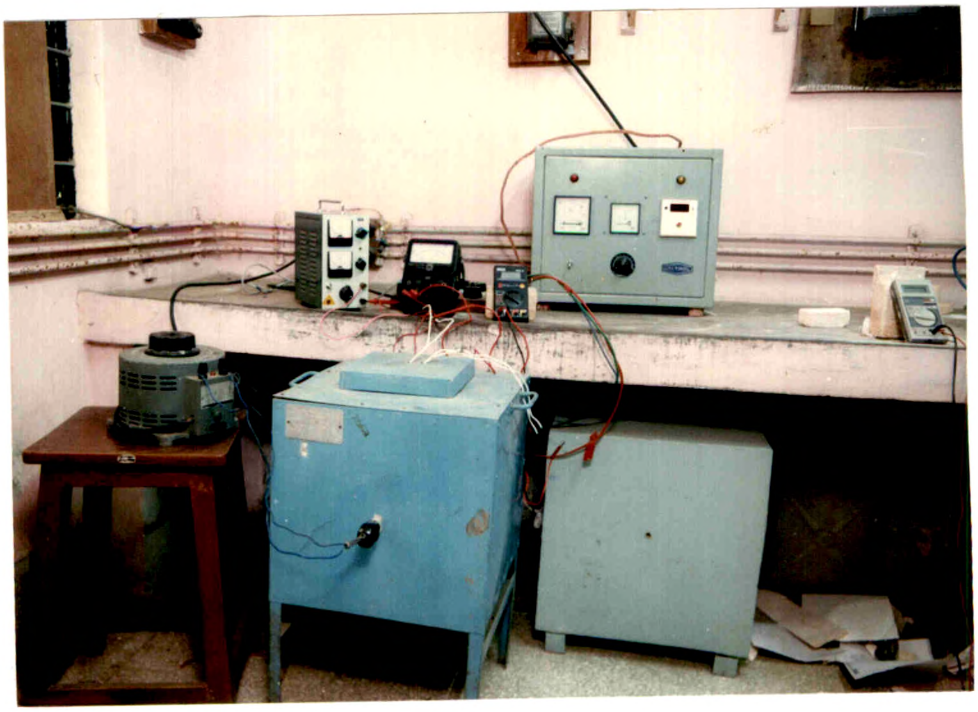
Fig. 4·1(b) — CIRCUIT DIAGRAM FOR ELECTRICAL RESISTIVITY.



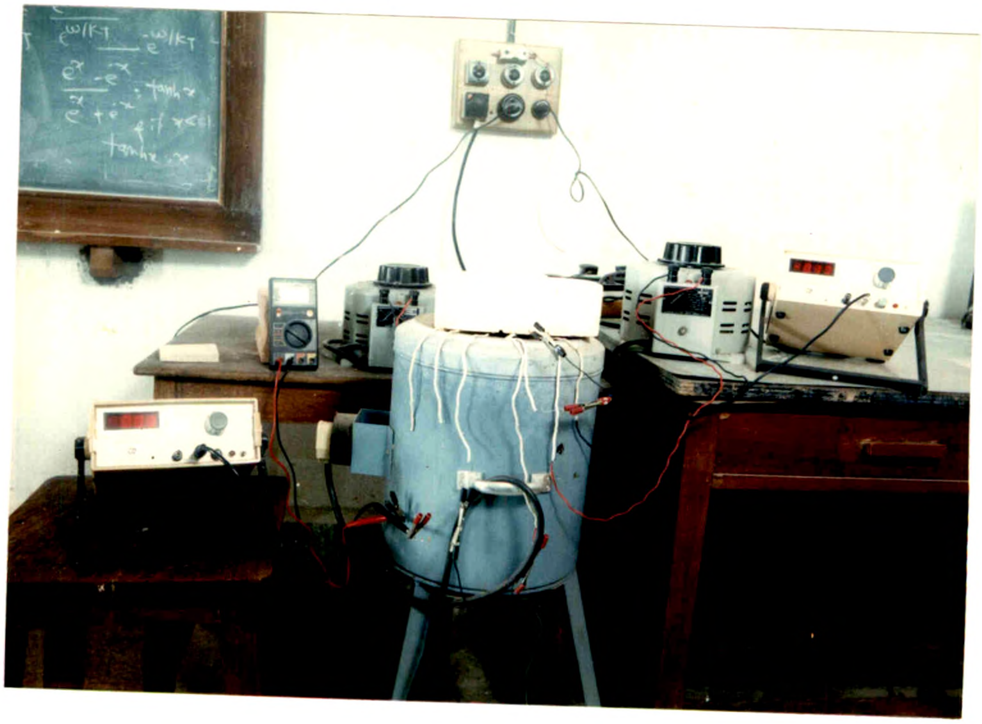
1,2 - Silver electrodes, 3 - Metal plates, 4 - Mion sheet, 5.5 - Hard metal electrodes, 6 - Sample pellet 7 - Spring 8.8 - Sub heater leads, 9 - Metal rod, 10 - Metal block, T_1, T_2 - Thermocouples.

- Scematic diagram of experimental set-up for the measurment of thermoelectric power.

FIG. 4.2



EXPERIMENTAL SETUP OF DC-CONDUCTIVITY MEASUREMENT



EXPERIMENTAL SETUP OF THERMO-EMF MEASUREMENT

measurement of thermoelectric power, a temperature difference 20 K was maintained across the pellet with the help of a small heater attached to one of the electrodes of the sample holder. The thermo emf (ΔV) developed across the pellet was measured on a digital d.c. microvoltmeter. Sufficient time was allowed to attain the thermal equilibrium before recording the thermo emf . The sample was then heated in the furnace by maintaining the temperature difference of 20 K and the thermo emf was measured at different temperatures.

The Seebeck coefficient at different furnace temperatures was calculated by,

$$\alpha = \left(\frac{dv}{dT}\right)_T$$

Where dv is the observed thermo emf and dT is the temperature difference across the pellet.

4.7 RESULTS AND DISCUSSION :

The variation of log ρ versus 1/T is shown in Fig.4.3 a,b. For lower concentration of Cr i.e. x = 0,0.2,0.4, the value of ρ increases with temperature upto 450 K. As the temperature exceeds a particular value the resistivity follows a typical semiconductor behaviour. For higher contants of Cr, the resistivity decreases with increase of temperature similar to that of a semiconductor behaviour.

The anomalous behaviour in ferrites was observed by number of workers [8]. According to their analysis this variation can be attributed to ionic drift current, current due to electron hopping and current due to electrons in conduction. The ionic drift current increases the resistivity. Therefore the conduction below 450 K is due to ionic drift current.

Copper ferrites having tetragonal structure show tetragonal to cubic transition near 500 K. The resistivity plot of these ferrites also show a transition [9]. It is also noted that the Cu ferrite having cubic structure shows a cubic to tetragonal transition at about the same temperature, but requries diffusion process. Also in mixed Cu ferrites the intersite cation distribution and cation exchange reaction have been found to be facile above 200 K and in between 300 K to 400 K there occur intersite cation exchange and reoxidation. Considering these facts, the observed anomalous region for higher contents of Cr may be of complex conduction process.

The resistivity plot shows three regions. Number of workers have observed three regions for mixed ferrites [10]. In region one of low temperature, conduction process is of extrinsic type, which may be due to impurities, ions etc. It is intrinsic type at high temperature which may be attributed to polaron hopping.

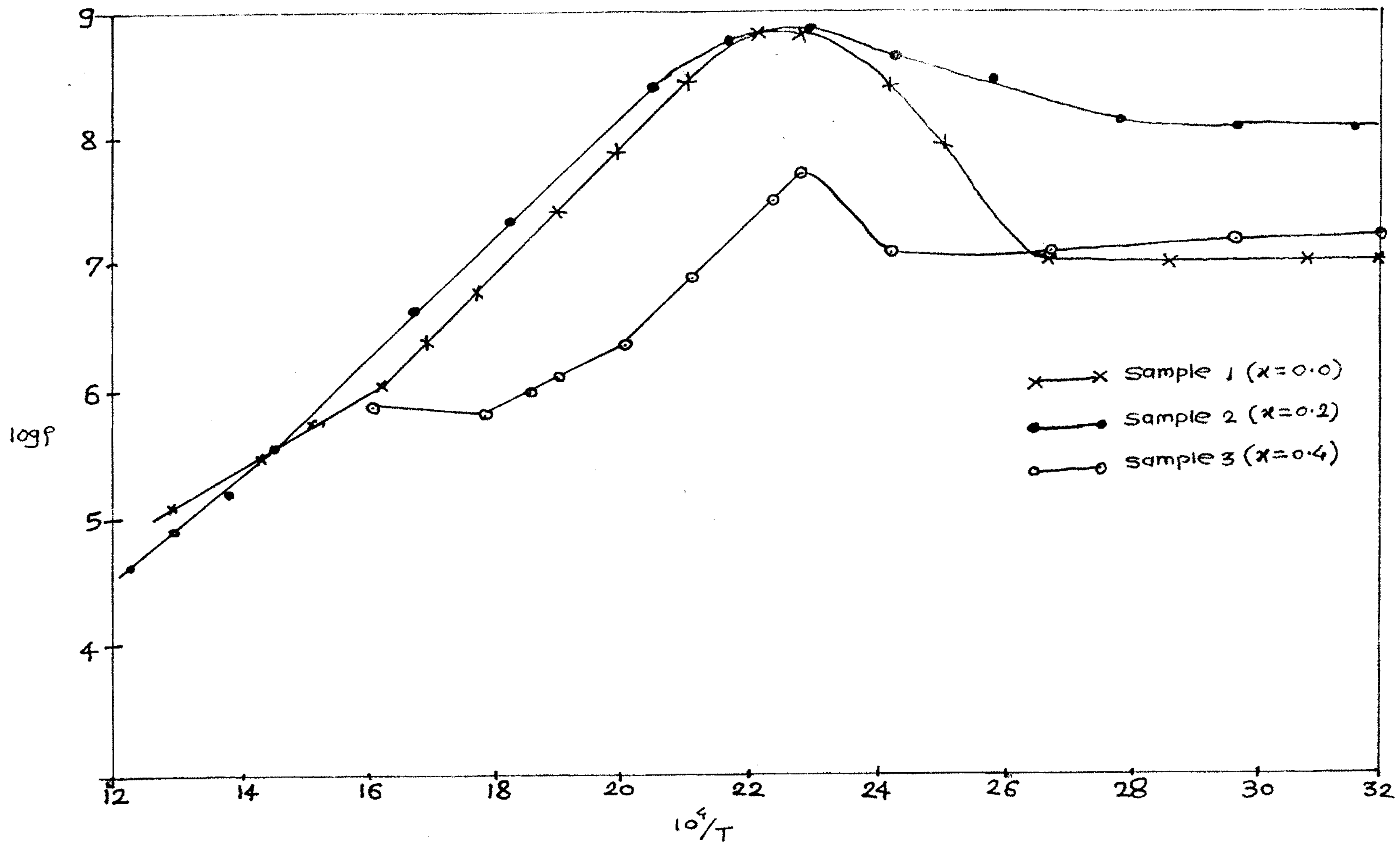
In ferrites having spinel structure the B-B distances are smaller than A-A and A-B distances. However, B-B distance is much longer than the sum of ionic radii of cations involved, indicating little or no overlap between d wave functions of the ions on adjacent octahedral sites. This gives rise to a situation in which the electrons are not free to move through the crystal, but remain fixed on B-sites necessitating the hopping process to increase effective mass and impart low mobility to current carriers.

The variation of Seebeck coeffieint with temperature is shown in Fig.4.4 a,b. From these plots, it is observed that, the absolute value of thermo-emf increases upto around 450 K and then decreases and remains consant for further increase of temperature. The temperature at which the thermoemf shows a maxima is nearly same as that of the first region (anomalous region) observed in resistivity. This is attributed to the impurity conduction. All the samples show n type behaviour. The room temperature thermoemf decreases with increase of Cr content. This may be due to the reduction in Fe content in the system.

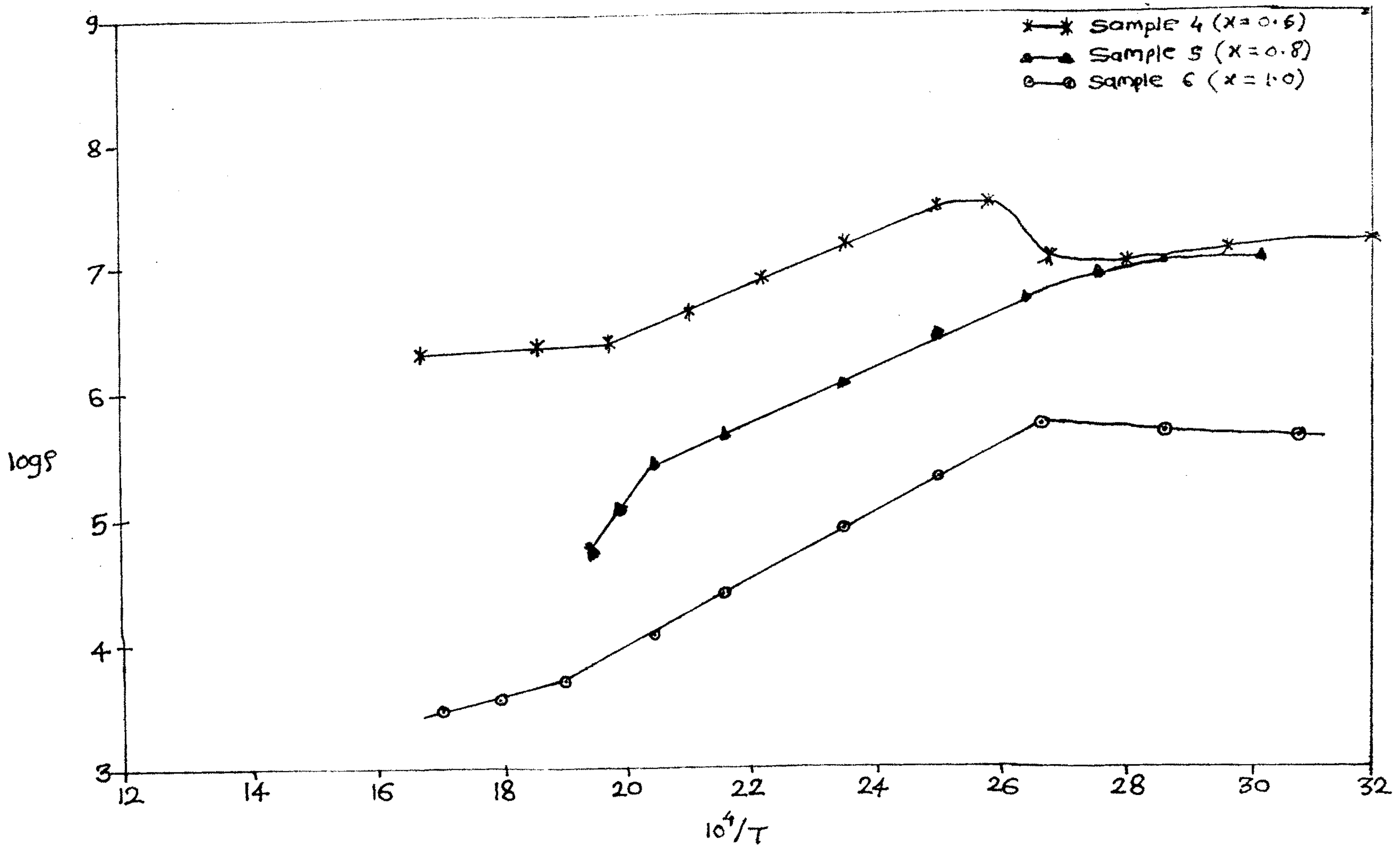
The activation energies in the para region and ferriregion are calculated by using relation $\rho = \rho_o e^{-E/kT}$ and are noted in the table 4.1. It is observed that the resistivity, thermoemf and activation energies in general show a decreasing trend with increase of Cr content. It is also observed that, the activation energy in ferro region is greater than that in para region. Similar resutls have been observed by Van Vitert,et al [11].

Baszsynski,et al [12] attributed the higehr value of activation energy in ferri region to the lowering of the generation of currnet carriers due to magnetic ordering. While Murthy, et al [13] link the change in activation energy to the change in conduction mechanism.

The activation enegies calculated from log ρ versus 1/T curves are greater than 0.45 eV which is much larger than the ionisation energy of electrons or holes and hence the possibility of band type conduction is ruled out. The extremely low mobility and it's exponential temperature dependance are to be expected when the carriers are localised. Here, the 'd' electrons are involved in

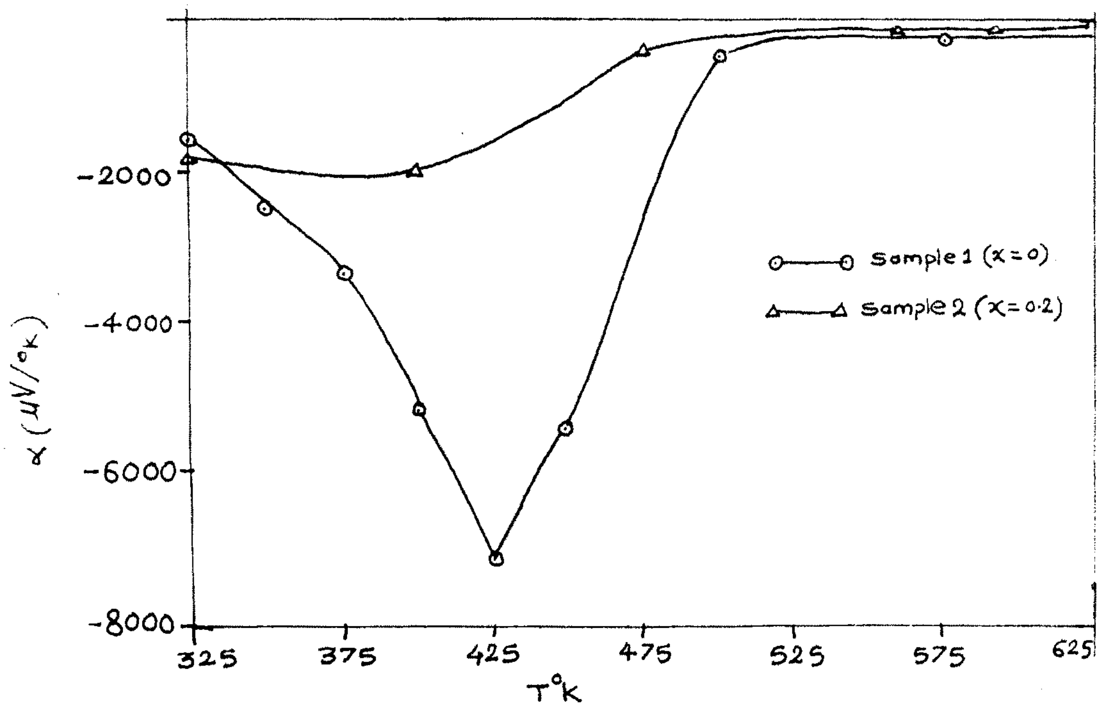


4.3(a) The Variation of log ρ with 1/T for Ferrites of Composition $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$ (x=0.0,0.2,0.4)

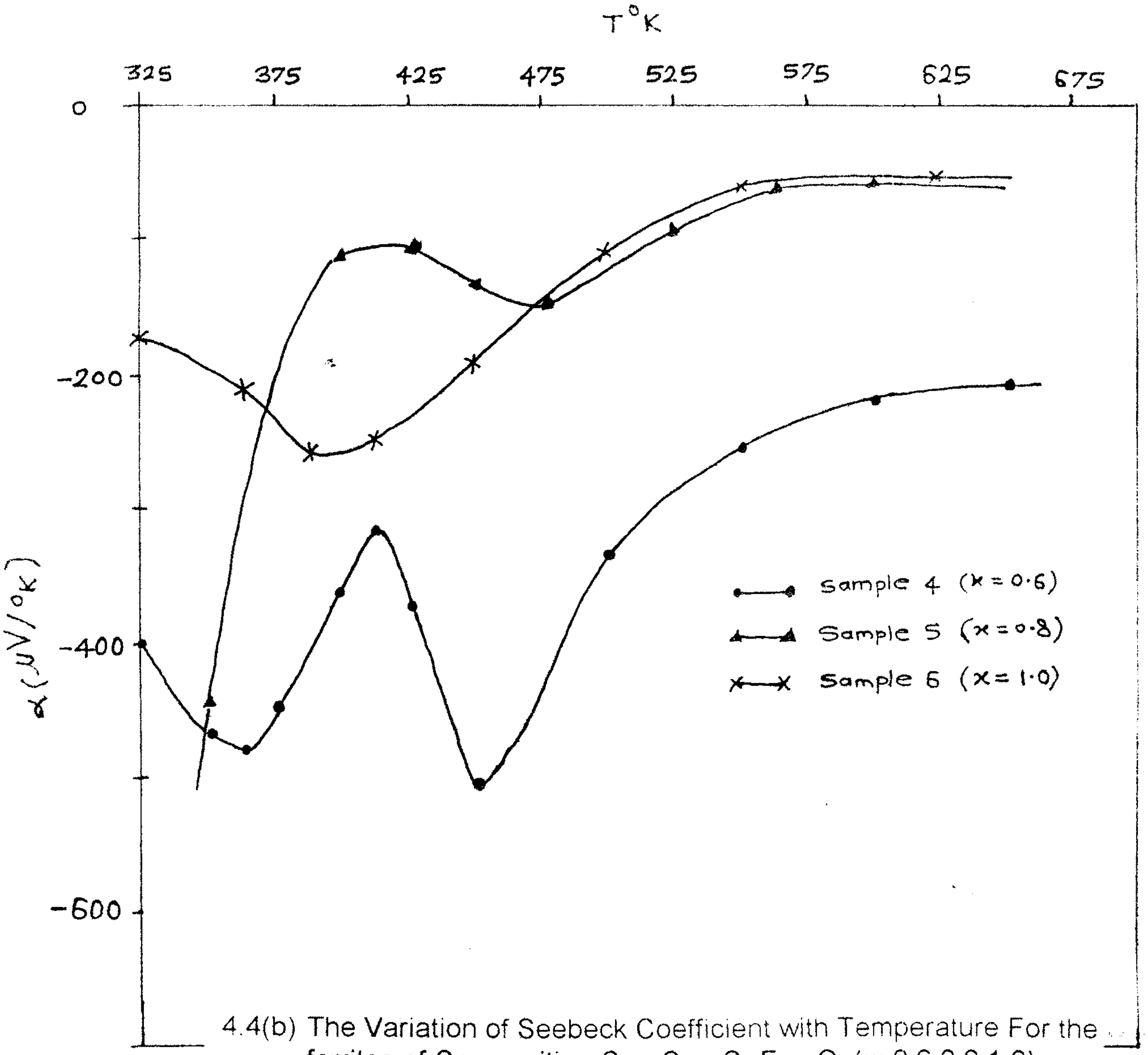


4.3(b) The Variation of log ρ with 1/T for Ferrites of Composition $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$(x=0.6,0.8,1.0) the conduction and their wave functions are less spread out as compared to the S or P wave fucntions. Thus there is little overlap between the wave functions of the adjacent sites, with the result that the electrons are not free to move through the crystal and most of the time they are localised around the particular metal ions. This localisation effect is aided further by self trapping due to the polarisation of the surrounding lattice. In the presence of such polarisation whenever the electron jumps from one site to the other, the polarisation also shifts accordingly. Since the change in polarisation involves the motion of heavy ions the electronic mobility becomes a thermally activated process. Hence, the only possibility left is conduction via the small polaron hopping mechanism. In hopping type conduction the small polarons moves from one impuirity centre to another by a thermally activated hopping process and the mobility of carriers increases exponentially with temperature.

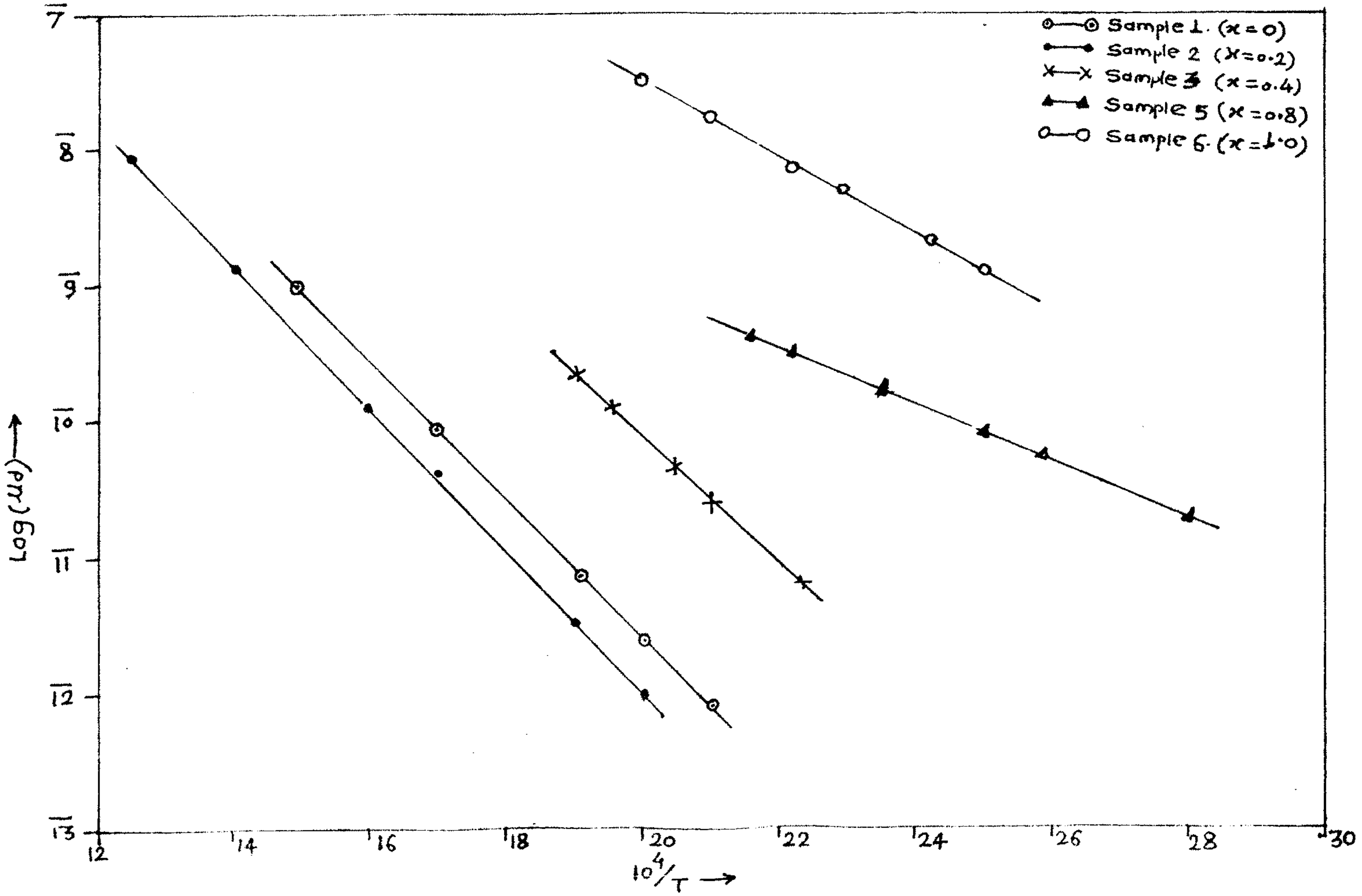
The mobility μ_d was calculated using the results for both α and ρ at different temperatures for all the compositions. The plotsof log , μ_d versus 1/T ($400 < T < T_c$) are shown in Fig.4.5 . This clearly shows that, the drift mobility μ_d increases linearly with temperature. Consequently it is concluded that, the change in resistivity depends on mobility. The activation energies from mobility were calculated and are noted in Table.4.1 . In these samples, in the region above 450 K the thermoemf is almost constant indicating that concentration n is constant. Therefore activation energies derived from conductivity and from mobility are expected to be equal. From table 4.1 it is clear that, the both these activation energies are equal which confiirms the conduction mechanism in these ferrites is based on hopping process. The hopping mechanism is also supported by the fact that, the temperature dependance of μd is positive and that the values of μ are much smaller than 10^{-4} M^{3} S^{-1} V^{-1} . Electrical conduction based on hopping by poalron have been reported for same oxides [14].



4.4(a) The Variation of Seebeck Coefficient with Temperature For the ferrites of Composition $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$ (x=0.0,0.2)



4.4(b) The Variation of Seebeck Coefficient with Temperature For the ferrites of Composition $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$ (x=0.6,0.8,1.0)



4.5 The Variation of log μ_d with 1/T for Ferrites of Composition $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$

Table 4.1 : The Compositional variationof resistivity ,seebeck coefficient , transition temperature and activation energies of $Cu_{0.5}Co_{0.5}Cr_xFe_{2-x}O_4$ System

X	at 500 K		Transition Temp. from conductivity		Activation energies by conductivity		Activation energies by mobility eV
	ohm-cm	uV/°C	T_1 K	T_2 K	E_F eV	E_p eV	
0.0	8.47×10^7	520	444	614	1.035	0.579	1.0276
0.2	14.80×10^7	335	444	689	1.031	0.834	1.0187
0.4	2.66×10^6	332	441	498	1.029	0.3046	0.9934
0.6	2.86×10^6	285	392	508	0.397	0.0754	0.3517
0.8	1.07×10^5	99	345	488	0.44	0.6215	0.4138
1.0	7.99×10^3	110	375	526	0.5421	0.2343	0.552

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