CHAPTER-IV

ELECTRIC PROPERTIES

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4.0 D.C. ELECTRICAL RESISTVITY AND THERMOELECRIC POWER :

INRODUCTION :

Many physical and chemical properties of solids have some sort of relation with the mechanism of the charge transport, which can be understood from measurements of conductivity, Hall coefficient, Thermoelectric power and magnetoresistance. Ferrites are unique magnetic solids which are semiconductors. Their resistivity changes in a very wide range from 10^{-3} ohm cm (magnetite) to 10^{11} ohm-cm (magnesium ferrite) [1].

The d. c. and a. c. conductivity provide valuable information about conduction mechanism in ferrites. The electical properties mainly depend on the method of prepration and presence of impurities, this can be investigated by carrying out the above said expriments.

Verwey et. al. [2] have shown that the condution can be increased by mixing the small amount of foreign oxides as impurities in the high resistivity ferrites. Conduction in ferrites is attributed to a hoping process which obeys the law $\rho = \rho_0 \exp. (\Delta E / KT)$, where ΔE is activation energy. Komar et. al. [3] have observed breaks or discontinuties in the resistivity plots of many ferrites, near the curie temperature. In case of Mn-Ni ferrites verway et. al. (4) have reported the shift of discontinuity towards the higher temperature region as the Mn content of the ferrite increases. Romeijin [5] also has observed such discontinuities in Fe_3O_4 and Mn_3O_4, but on the lower temperature side.

Koops [6] has studied the variation in the resistivity and dielectic constant with frequency and found that the resistivity and dielectric constant fall by large amount at higher frequencies in inhomogeneous material. Many other workers made the electrical conductivity study and found that conduction mechanism can be explained on the basis of polaron hopping model.

Thermoelectric properties are widely used in the interpretation of the conduction mechanism in semiconductors. In ferrites, which mobility is low, thermoelectric power measurement plays an important role in determining the type of charge carrier, The type of charge carriers is directly related to the thermo emf. Another important significance of thermo emf is that it enables one to calculate the value of fermi energy and carrier concntration, which helps in determination of various regions, viz. impurity conduction, impurity exhaustion and intrinsic conduction regions of semiconductor.

4.1 CONDUCTION MECHANISM IN METAL OXIDES :

The conduction in compound semiconductors does not require doping for introducing the localized donor or acceptor levels. In oxides, oxigen non-stoichiometry provides the source of current carriers, many times the O^{2+} ions themselves act as carrier centres. Howeer, in transition metal oxides, the narrow half field d-band counid provide the current carriers by excitation: therefore, many of these metal oxides are semiconductors. In oxides the activation of conduction electrons can be represented by,

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

Where M is divalent transitional metal ion. The energy needed for the formation of ion pairs ($M^{2+}M^{2+}$) and ($M^{3+}M^{1+}$) corrosponds to the gap in density of states.

4.2 CONDUCTION IN FERRITES :

For conduction in ferrites containing most of the Fe ions in trivalent state require a dopant with small percentage of higher valency to give donor centre while dopant of lower valency to provide acceptor centres, when metal to oxygen ratio departs from ideal oxygen vacancies can provide upon the thermal excitation, the trapped electorn to give rise to n- type conductivity in an oxygen - deficient ferrite. Similarly, p- type conductivity has been observed [7,11]. Thus in case of those ferrites showing non-stoichiometry of oxygen extrinsic semi-conduction would prevail throughout the temperature region. In perticular, the charage transport through ferrite is represnted as,

$$M^{2+} O^{2-} Fe^{3+} \longrightarrow M^{3+} O^{2-} Fe^{2+} + Eg \qquad \text{-------}(4.2)$$

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 of spinal lattice. The electrons move from ferrous to ferric ions through the contineous chain of octahedral positions giving rise to high conductivity[1].

In other words conduction mechansism in ferrites is due to the exchange of electron from Fe^{3+} to Fe^{2+} ions in the same octahedral site in the lattice represent ed as

$$Fe^{3+} \longrightarrow Fe^{2+}$$

Electrons and holes are known to move by thermally activated hopping mechanism in ferrite except for the megnetite.

4.3 ELECTRON HOPPING AND POLARONS :

Jonker [12] has onserved in some ferrites that transport properties differ considerably from those of normal semiconductors. as the charge carriers are not free to move through the crystal lattice but jump from ion to ion. It was also noted that in this type of materials (ferrities) the possibility exists the change in valency of a considerable fraction of metal ions and espcially that of iron ions . For this type of conduction ordinary theory based on simple band picture does not apply. Temperature dependence of conductivity can be explained by other mechanism i.e. hopping conduction mechanism.

An electron in the crystal lattice interacts through its electrical charge with the ions or the atoms of the lattice, to create a local deformation of lattice. The deformation further follows the electron at it moves through the lattice, the conduction of electron with a strain field is known as polaron.

The electrostatic interacion between the conduction electron or a hole and the nearby ions may reasult in the displacement ot the ions and hence in polarisation of the surrounding region , so that the carrier become situated at the centre of the polarization potential well. If this well is considered deep enough, the carrier may trapped at a lattice site and its transition to the neighbouring site can be determined by thermal activation. This process has been considered as the ' hopping mechanism ' Heinks and Johnson [13] gave the expression for the mobility of a charge carrier during the hopping process as,

$$\mu_d = (e^2 d^2 \omega_O / KT) \exp(-\Delta E / KT) \quad \ldots\ldots (4.3)$$

Where
d = The distance between the nearest neighbour cations,
ω_O = Vibrational Frequency of the crystal lattice ,
ΔE = Activation energy

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

$$1/2\ \alpha = \frac{\text{deformation Energy}}{h\omega_L} \quad \ldots\ldots (4.4)$$

where

ω_L = longitudinal phonon frequency near zero wave vector

The value of α is high for ionic crystals. the polaron may be called as 'large polaron' when coupling constant possesses the higher values and the ' small polaron' when this value is lower. The effective mass of polaron is greater than the base mass of an electron. Frohlich[14] formulated the interaction Hamiltonian for large polaron. Small polaron formation is favoured 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 hoping mechanism. A strong Experimental evidence has been observed for the existance of small polarons and the hopping process in ferrites [15,16].

4.4 THERMOELECTRIC POWER OR SEEBACK COEFFICIENT:

If the two surfaces of the electrical conducting material are maintained at temperature difference of dT 0°K, then small emf is developed. This is known as seeback effect and the seeback coefficient (α) is defined

$$\alpha = d_V/d_T$$

where,

d_V = emf across the two surfaces
d_T = the temperature difference.

The seeback effect is due to diffusion of electrons or the holes which have more kinetic energy at hotter surface. The semiconductor such as ferrite, contains electrons or holes as charge carriers and exhibit seeback effect.

According to the quantum theory for semiconductors with both types of carriers α can be obtained as,

$$\alpha = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\alpha_n + \sigma_p}$$

where,

$$\sigma_n = n e \mu_p$$

$$\sigma_p = P e \mu_p$$

$$\alpha_n = K / e \, (A_n - E_F \; / K_T)$$

$$\alpha_p = K / e \, (A_p + (E_g + E_F \;) / K_T \;)$$

where n and p are electron and hole densities, μ_n and μ_p are the electron and hole mobilities, E_F is the fermi energy level and E_g is band gap energy. The temperature dependance of the thermo-electric power for the ferrite materials having only one type of charge carriers can be expressed as [17]

$$\alpha = K / e \, (\ln (N_O / n - 1) + e / K_T)] \, a \;\ldots\ldots\ldots\ldots\ldots \; (4.9)$$

where,

K = Boltzman constant

e = electronic charge

N_O = Concentration of trivalent ions on octahedral sites

n = Concentration of Fe^{2+} ions

a = part of activation energy transported by the electrons.

The value of 'a' is zero in case of Mn ferrite [18] and 1 eV for other cases [19]. From the temperature dependance of the seeback coefficient, the sign of charge carriers and their density variation can be determined.

4.5 EXPERIMENTAL

4.5.1 D. C. ELECTRICAL RESISTIVITY :

The experimental set up used for the measurement of d. c. electrical resistivity is shown in fig. 4a. It consists of electrically heated furnace, a digital d. c. microvoltmeter (VMV 15), temperature controlling arrangement and a transistorised power supply unit (TPSU, Type LVA 30/1) to provide the d.c. electric field.

Two probe method is used to measure the resistivity of the sample in the pellet form the experimental circuit diagram is shown in fig. 4 (b) and a special cell in fig. 4 (a). The pellet was pasted with a silver paste and sandwitched between the brass electrodes of the cell. The silver foils were introduced between the brass rods for a good contact. the wire made up of silver was insulated by ceramic beads 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 voltage1 volt for the temperature range 300°K to 850° k. sufficient time was allowed for the sample to attain an equilibrium temperature.

4.5.2 THERMOELECTRIC POWER :

In order to measure seeback coefficient of a sample with temperature variation, the experimental set up used is shown in fig. 4 It consists of an electrically heated furnace, a temperature controller, two digital d. c. microvoltmeters (VMV- 15, Vasavi electronics) a specially designed sample holder and a digital multimeter. For the measurement of thermo - electric power, the samples in the form of pellets coated with thin layer of silver paste for good contact were used . A pellet was put into the sample holder, with necessary connection as shown in fig 4 the sample holder was put into the regulated furnace. For the measurement of thefrmoelectric power, the thermal gradient

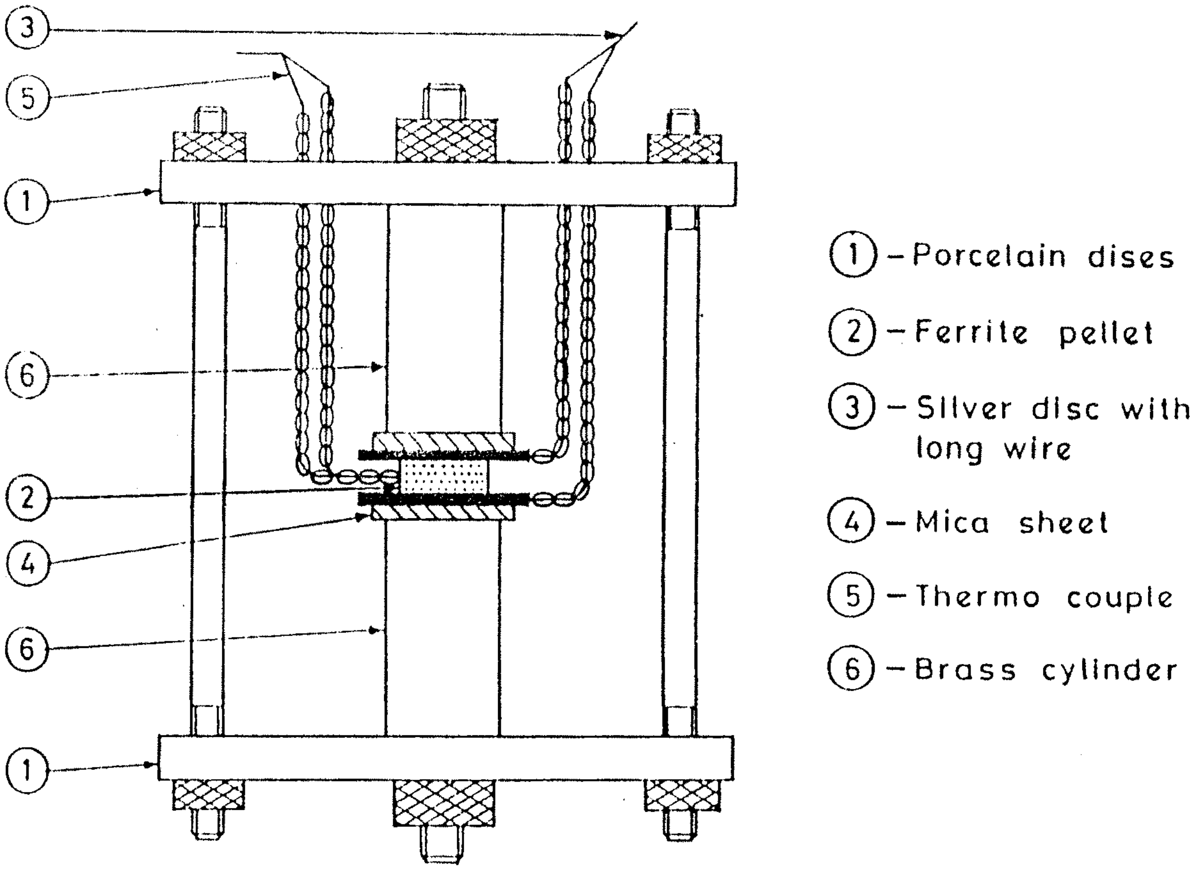


Fig 4.b (b) THE CONDUCTIVITY CELL.

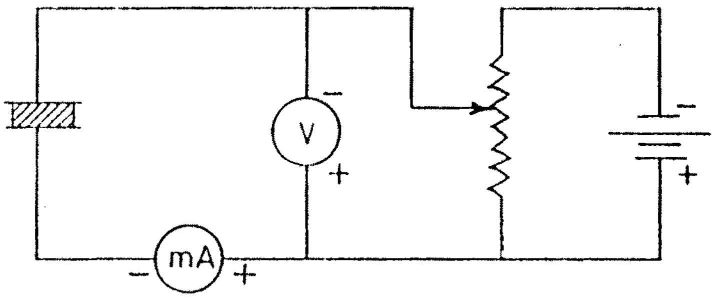
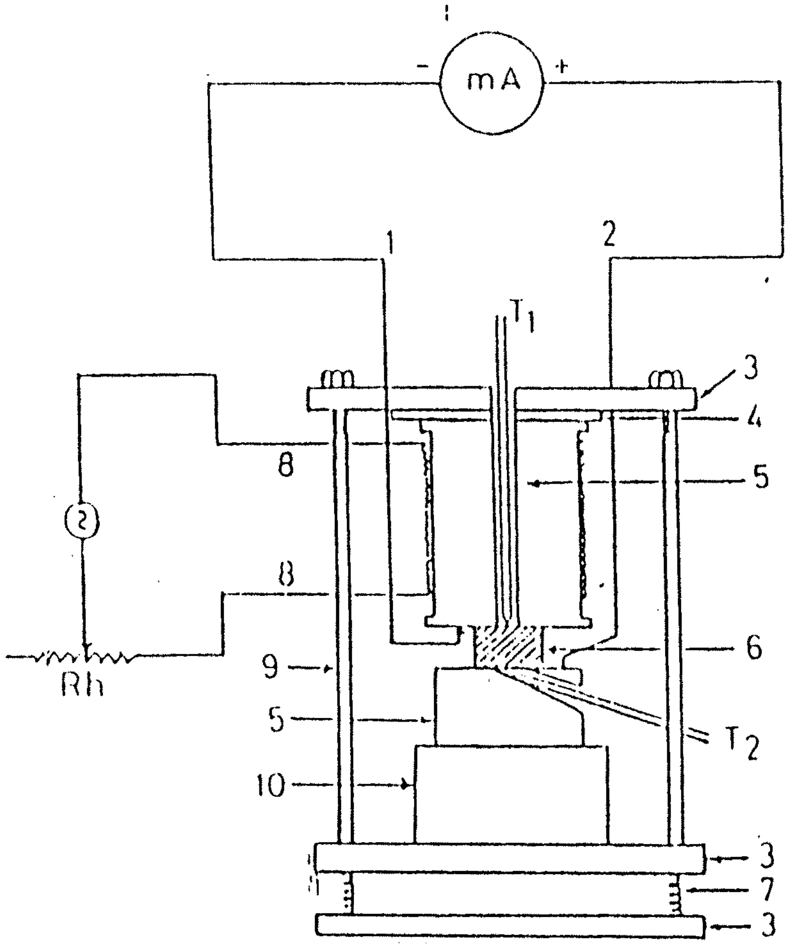


Fig. 4.b (a) CIRCUIT DIAGRAM FOR ELECTRICAL RESISTIVITY.



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. d

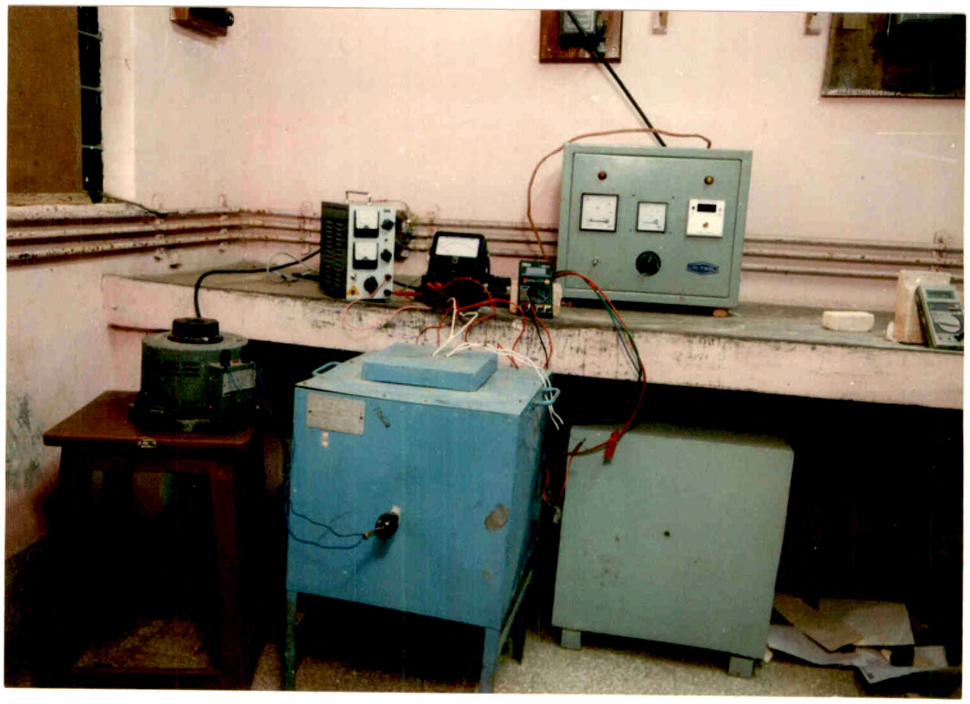


Fig.4a : experimental Set-up of D.C. Resistivity Measurement

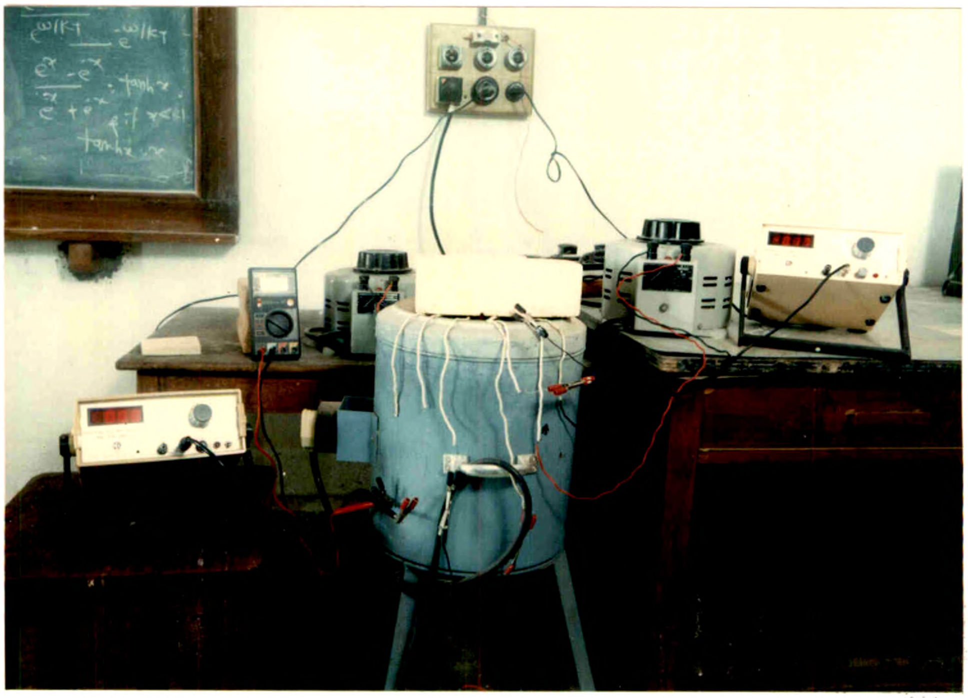


Fig.4c : experimental Set-up of Thermoelectric Power Measurement

($\Delta T = 20\ ^\circ K$) across the sample was obtained with the help of microfurnace attached to one of the electrodes of the sample holder. The thermal gradient was measured by differential chromel - alumel thermocouple. The thermoemf (ΔV) developed across the pellet was measured on digital microvoltmeter by silver electrodes, sufficient time was allowed after applying the thermal gradient ($\Delta T = 20\ ^\circ K$) and the developed thermo emf was measured at different ambient temperatures. The hot end of the sample is connected to positive terminal of microvoltmeter.

4.6 RESULTS AND DISCUSSION:

4.6.1 D.C. CONDUCTIVITY :

FIG 4.1 shows the variation of log ρ Vs $1/T$ for Cu - Mg ferrite system. The plots are linear in nature for all the temperatures suggesting the applicability of the exponential relation of the conductivity . The plots show two distint regions. The first region is from 300° k (R.T) to 450° k and second region is from 450° k to curie temp. Similar regions also have been observed in other ferrite systems [22,23]. According to their analysis 1st region i.e. less than 450° k is attributed to impurities such as grain bounderies, defects, porosity etc. where as second region to poloron hoping. The activation energy calculated by the relation for the second region is given in table 4.1

The activation energies are greater than 1 ev which are much higher than the ionisation energy of electrons or holes: and hence the possibility of band type conduction is ruled out. The extremly low mobility and its exponential temp. dependance are to be expected when the carriers are localized. Here the 'd' electrons are involved in the conduction and their wave functions are less spread out as compared to 's' or 'p' wave functions. Thus there is little overlap between the wave functions on adjacent sites, with the result that the electrons are not free to move through the crystal and most of the time they are localized around the perticular metal ions. This localization effect is aided further by self trapping due to the polarization of the surrounding lattice. In the presence of

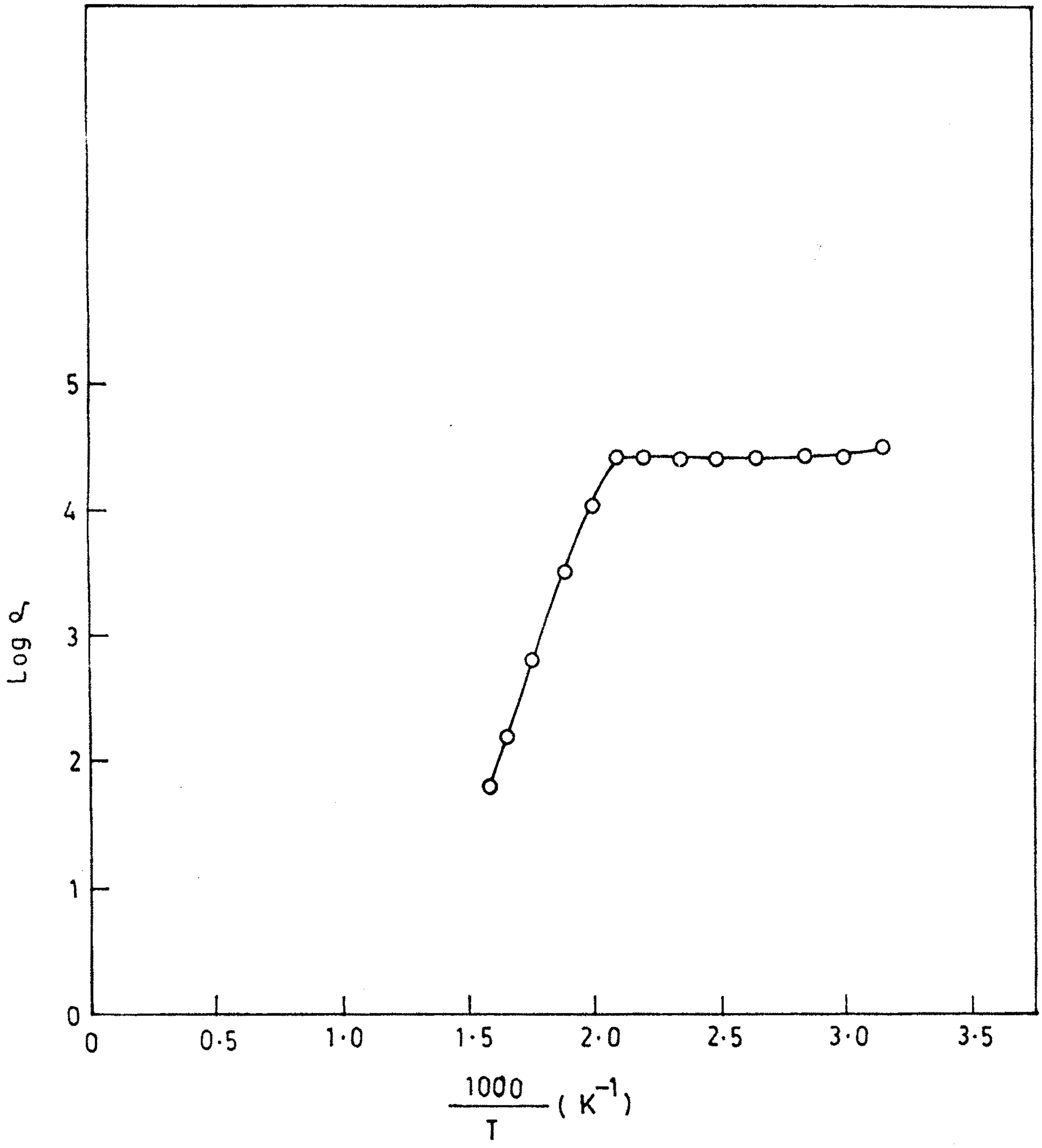


Fig. 4·1(a) – Variation of Log ρ Vs $\frac{1000}{T}$ for $MgFe_2O_4$.

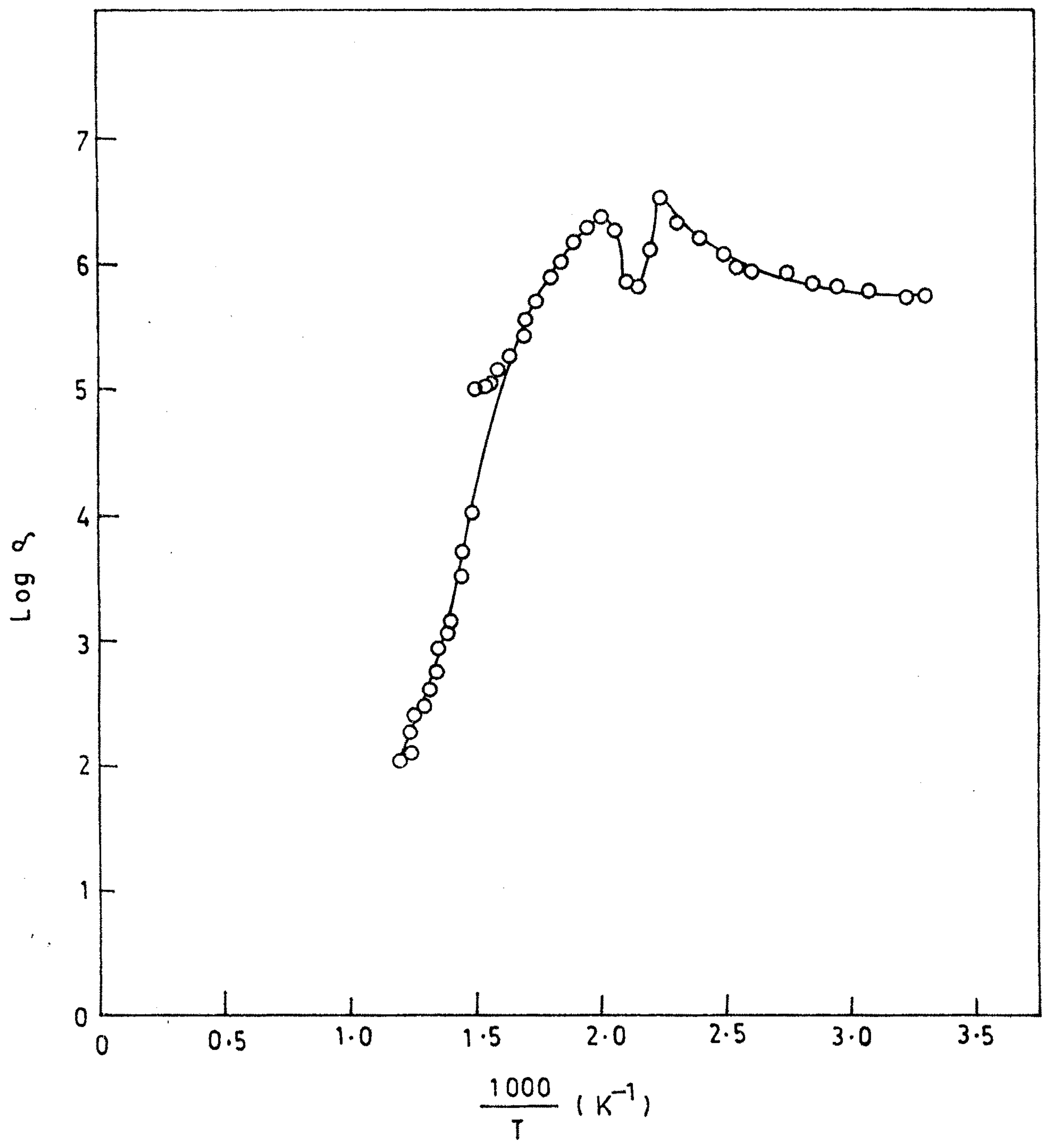


Fig. 4·1 (b) — Variation of Log ρ Vs $\frac{1000}{T}$ for $Mg_{0.7}Zn_{0.3}Fe_2O_4$.

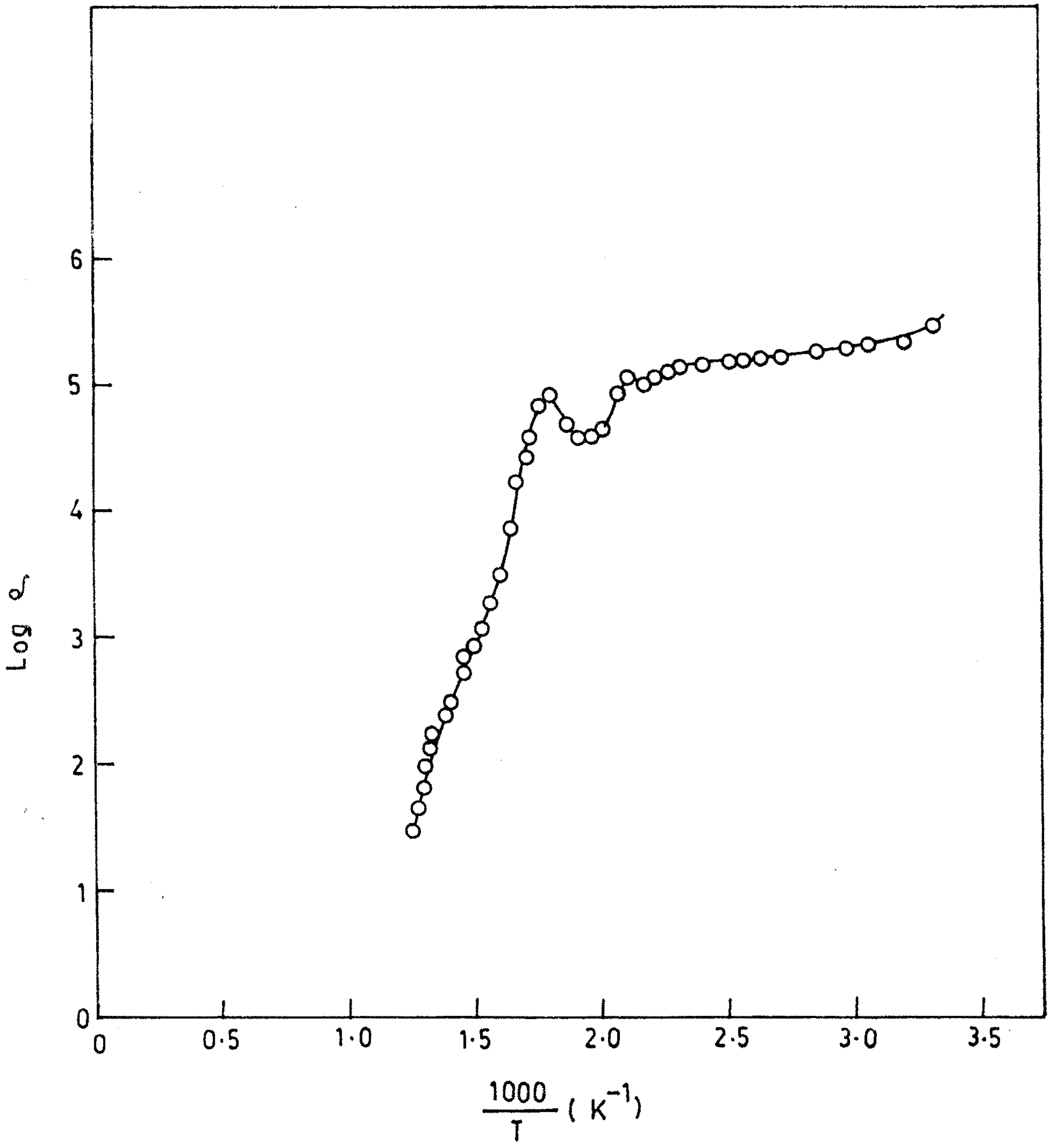


Fig. 4·1(c) – Variation of Log ρ Vs $\frac{1000}{T}$ for $Mg_{0.4}Cu_{0.6}Fe_2O_4$.

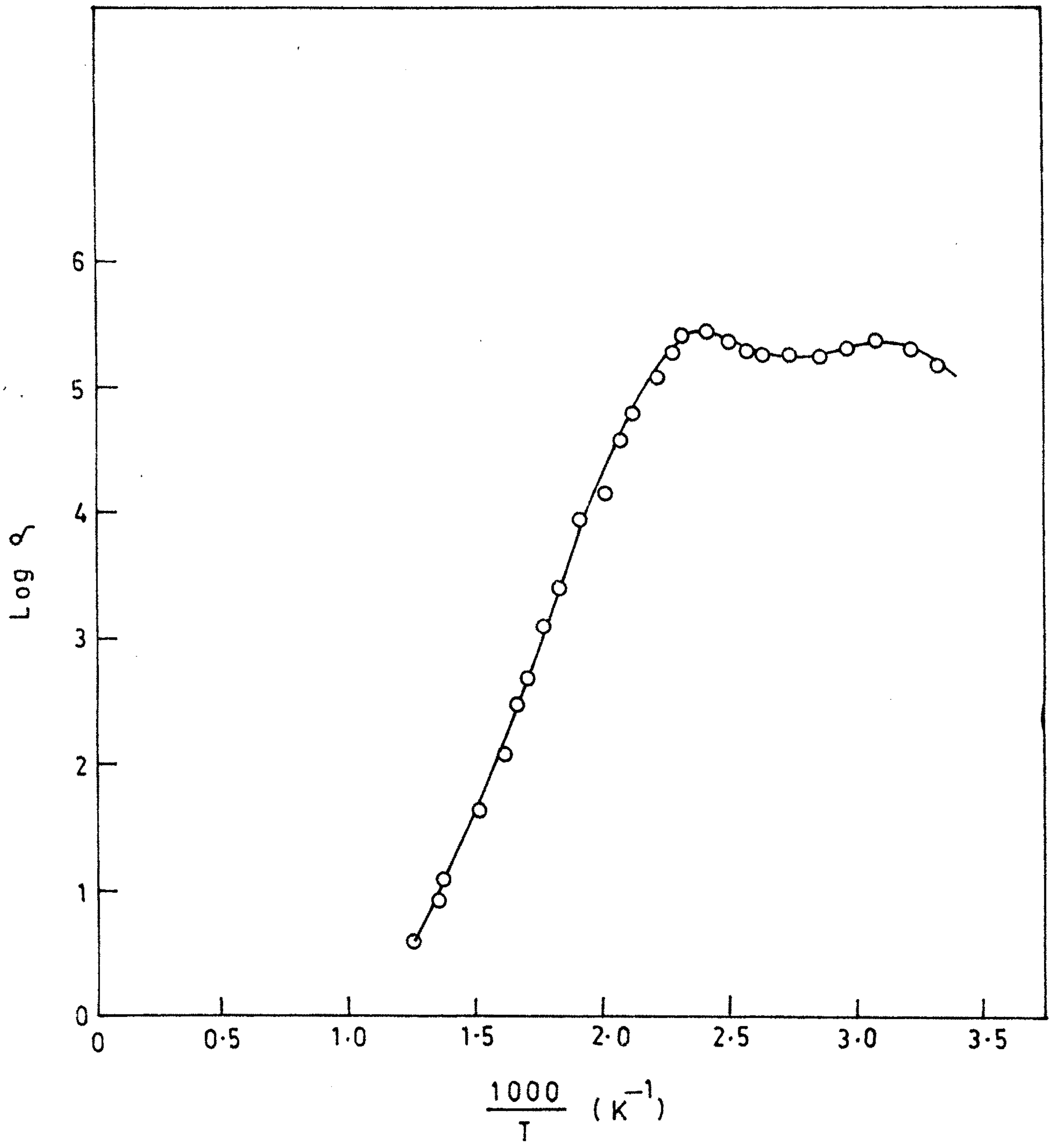


Fig. 4·1(d) — Variation of Log ρ Vs $\frac{1000}{T}$ for $CuFe_2O_4$.

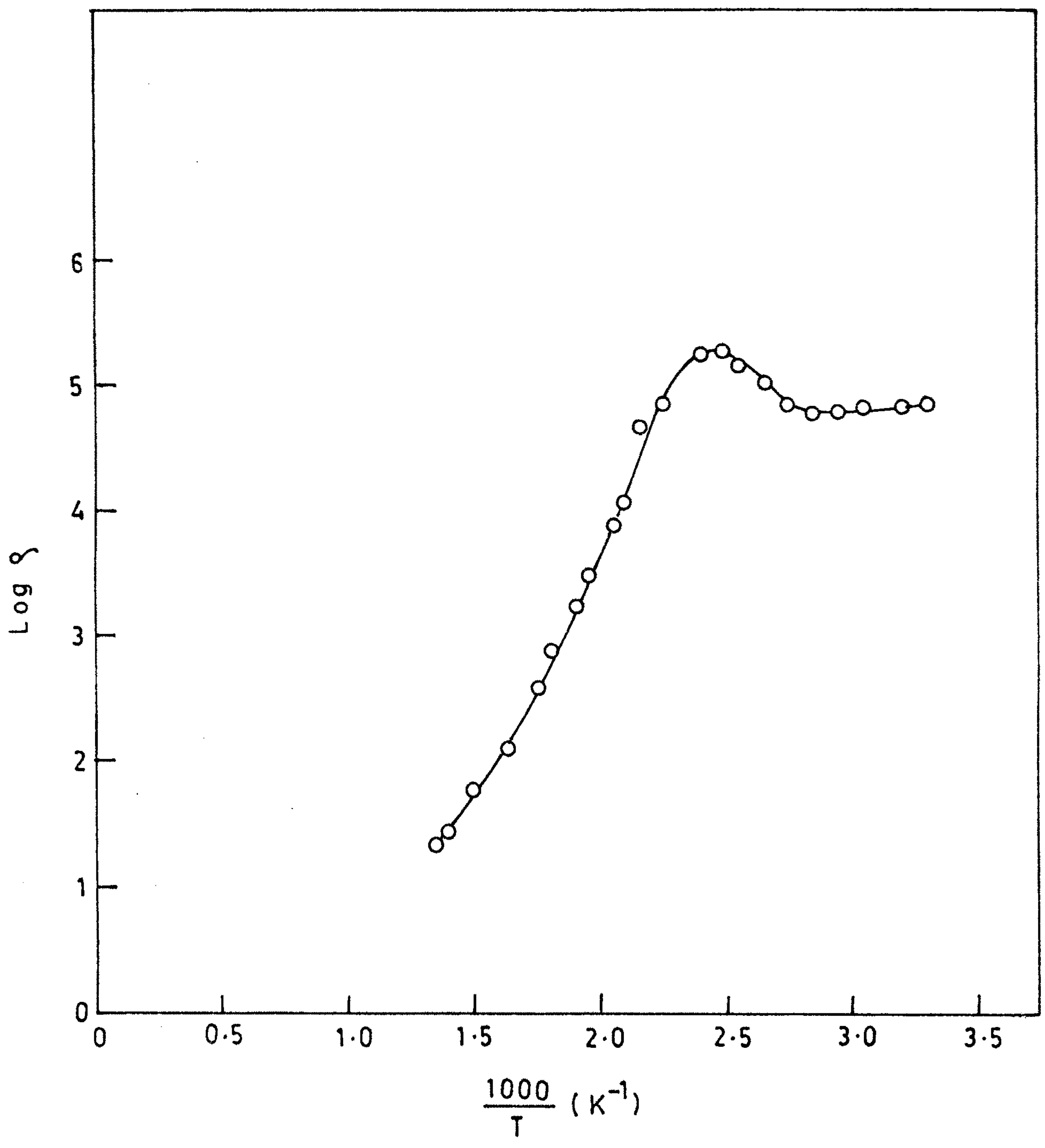


Fig. 4·3(a) — Variation of Log ϱ Vs $\frac{1000}{T}$ for $Cu_{0.7}Zn_{0.3}Fe_2O_4$.

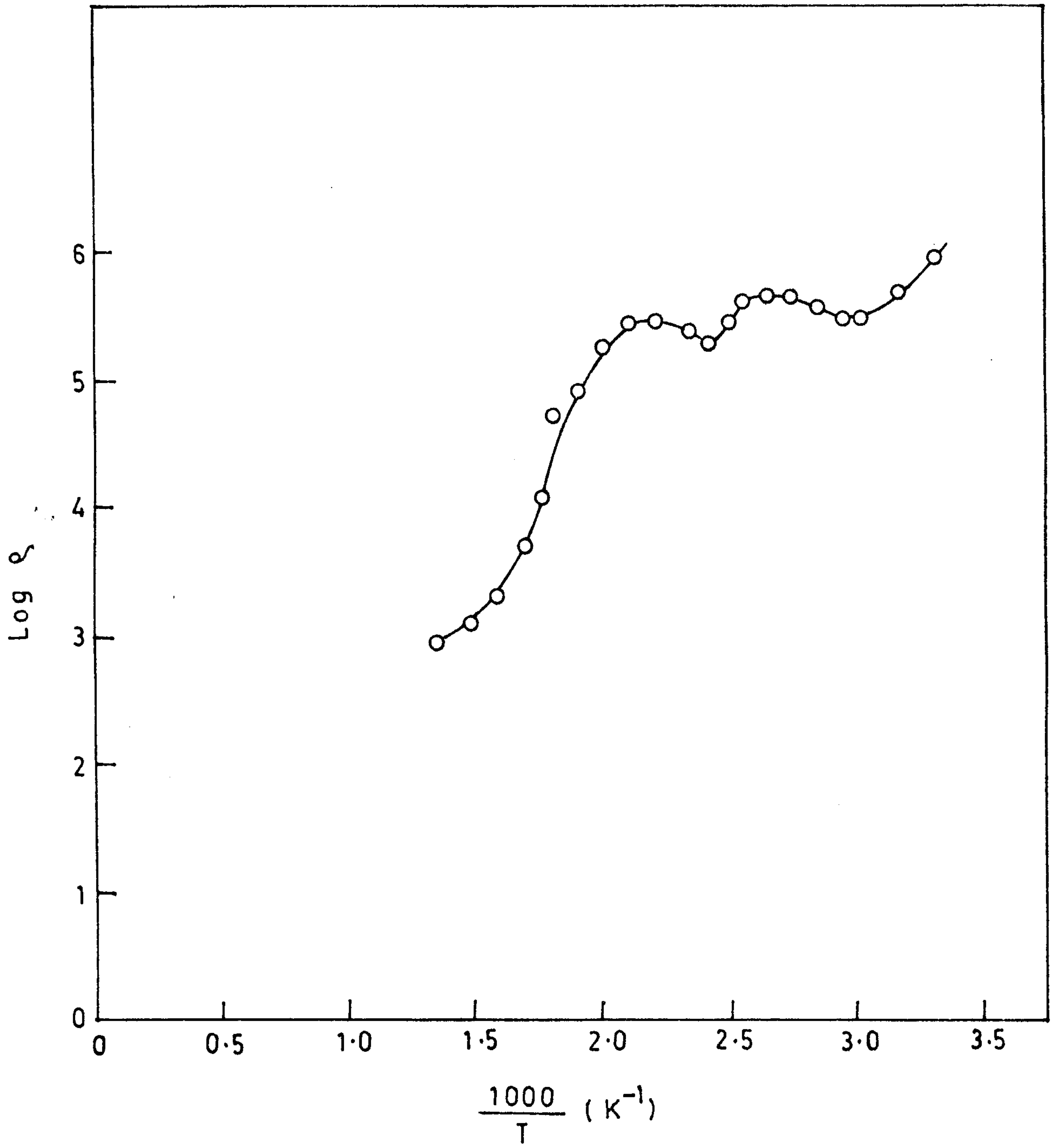


Fig. 4·3(b) – Variation of Log ϱ Vs $\frac{1000}{T}$ for $Cu_{0\cdot4}Zn_{0\cdot6}Fe_2O_4$.

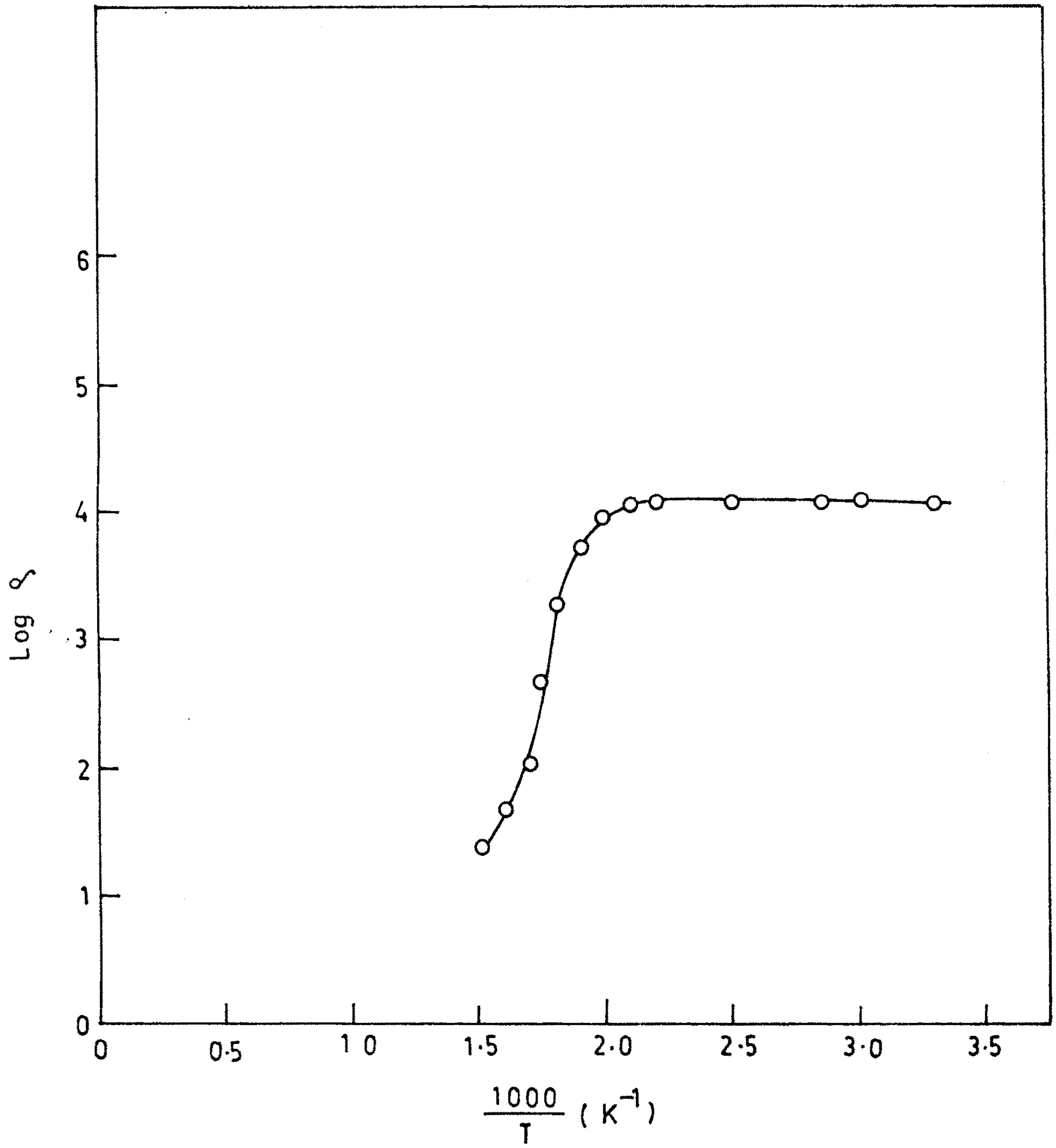


Fig. 4·4(a) – Variation of Log ρ Vs $\frac{1000}{T}$ for $Mg_{0.4}Zn_{0.6}Fe_2O_4$ [chem. ppted.]

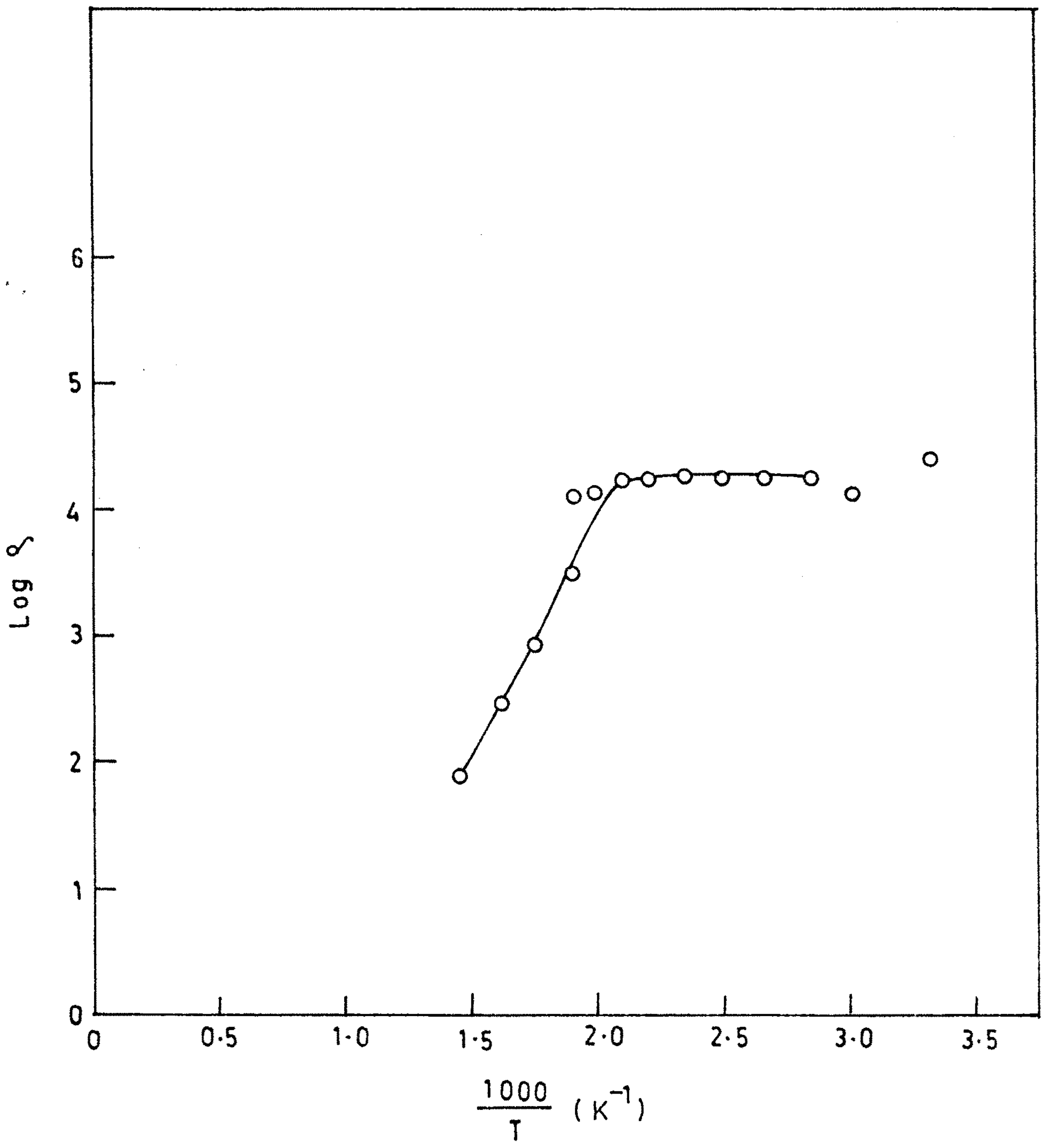


Fig. 4·4(b) – Variation of Log ρ Vs $\frac{1000}{T}$ · for $Mg_{0.4}Zn_{0.6}Fe_2O_4$ [Mixed] .

Table No. 4.1 **Resistivity, Thermo emf and activation energy of ferrite samples sintered at 900°C**

Composition	Resistivity (at 100°C)	Thermo emf		Activation energy E ev
		type	α	
$MgFe_2O_4$	1.616×10^4	n	521	1.0835
$Mg_{.7}Cu_{.3}Fe_2O_4$	8.086×10^5	n	2900	1.4038
$Mg_{.4}Cu_{.6}Fe_2O_4$	1.899×10^5	n	1073	1.3087
$CuFe_2O_4$	2.197×10^5	p	992	1.0391
$Cu_{.7}Zn_{.3}Fe_2O_4$	1.131×10^5	p	200	0.8703
$Cu_{.4}Zn_{.6}Fe_2O_4$	5.448×10^5	n	1457	0.9648
$Mg_{.4}Zn_{.6}Fe_2O_4$ (che. ppted)	1.304×10^4	n	287	0.4966
$Mg_{.4}Zn_{.5}Fe_2O_4$ (mixed)	1.849×10^4	n	586	0.7548

such polarization, whenever the electron jumps from one site to the next, the polarization also shiefts accordingly. Since the change in polarization 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 polaron moves from one impurity centre to another by a thermally activated hopping process and the mobility of carriers increases exponentially with temp.

The fig. 4.4 (a) and 4.4 (b) show the variation of resistivity with temp. for the sample $Mg_{.4}Zn_{.6}Fe_2O_4$ prepared by co-precipitation method and by mixing respectively. It is observed that both the plots show similar behaviour and the resistivity values do not change much . The activation energies calculated are listed in table (4.1)

The careful observation of table 4.1 it is found that the resistivity is large in copper containing ferrites. The high value of resistivity is obtained for the samples with 0.4 copper content in Mg-Cu ferrite and 0.3 copper content in Cu-Zn ferrite.

4.6.2 THERMO EMF

The variation of seebeck coefficient with temp are shown in fig. 4.2. From these plots it is observed that all the samples show n-type behaviour except the $CuFe_2O_4$ which shows p-type behaviour. It is also noted that the absolute value of α decreases with increase in temp. However, the cusp like minima is observed for higher content of copper. The observed variation in seebeck coefficient with temp. obviously indicates the conduction process taking place in the presene of acceptor and donor centres with different relative predominance. These centres are generally observed during sintering process. According to Verwey et al the resistivity of ferrite is due to Fe^{3+} Fe^{2+} transition at B site in spinels which gives n-type behaviour. It has been already reported in the literature that copper ferrite exhibited p type conduction [24] attributed to the appearance of p type carriers due to reduction of Cu^{2+} ions to Cu^{1+} at about 900 °C to 950 °C during the sintering process. Our results are in consistant with the reported

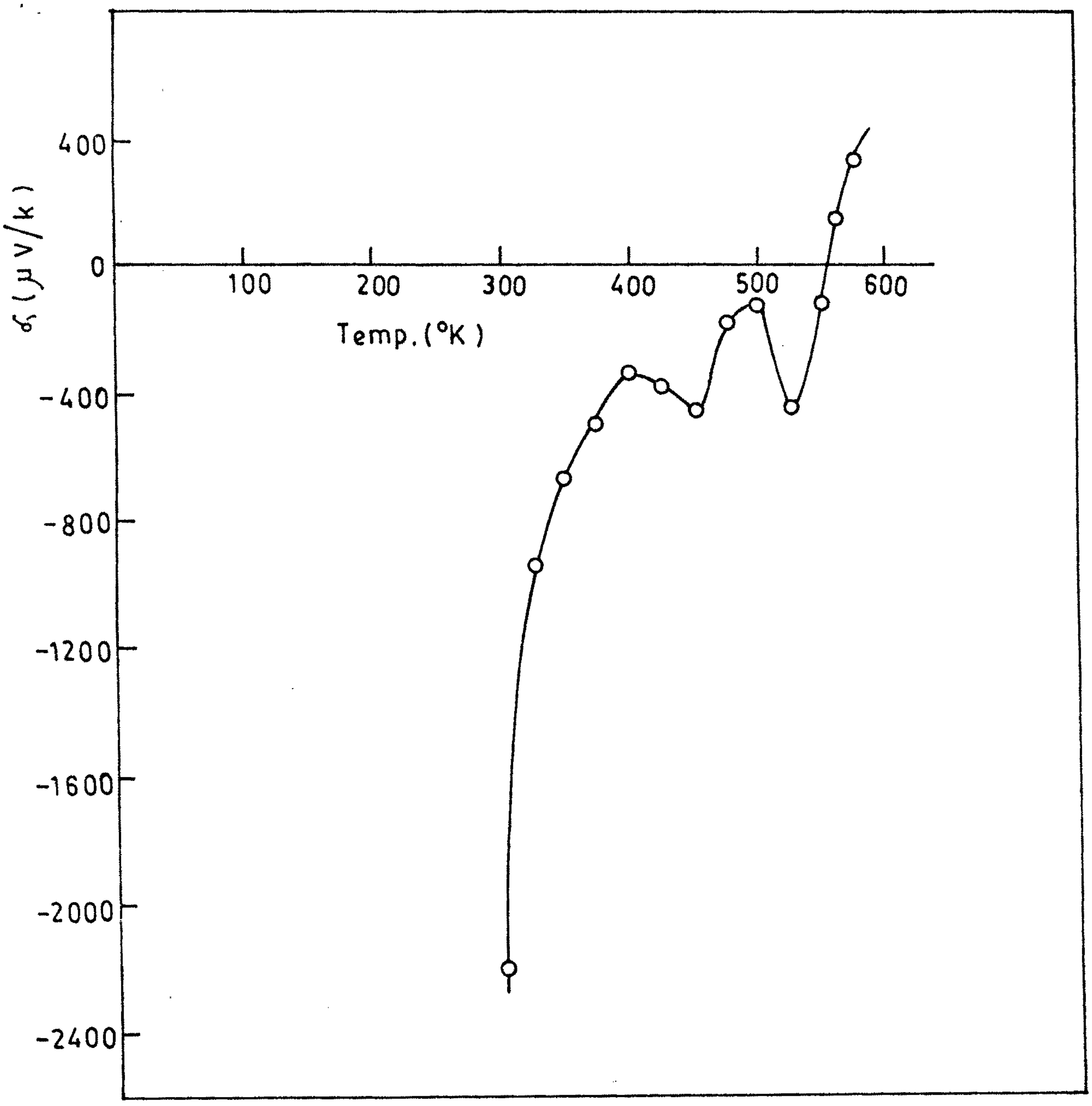


Fig. 4·2 (a) — Variation of α Vs T for $MgFe_2O_4$.

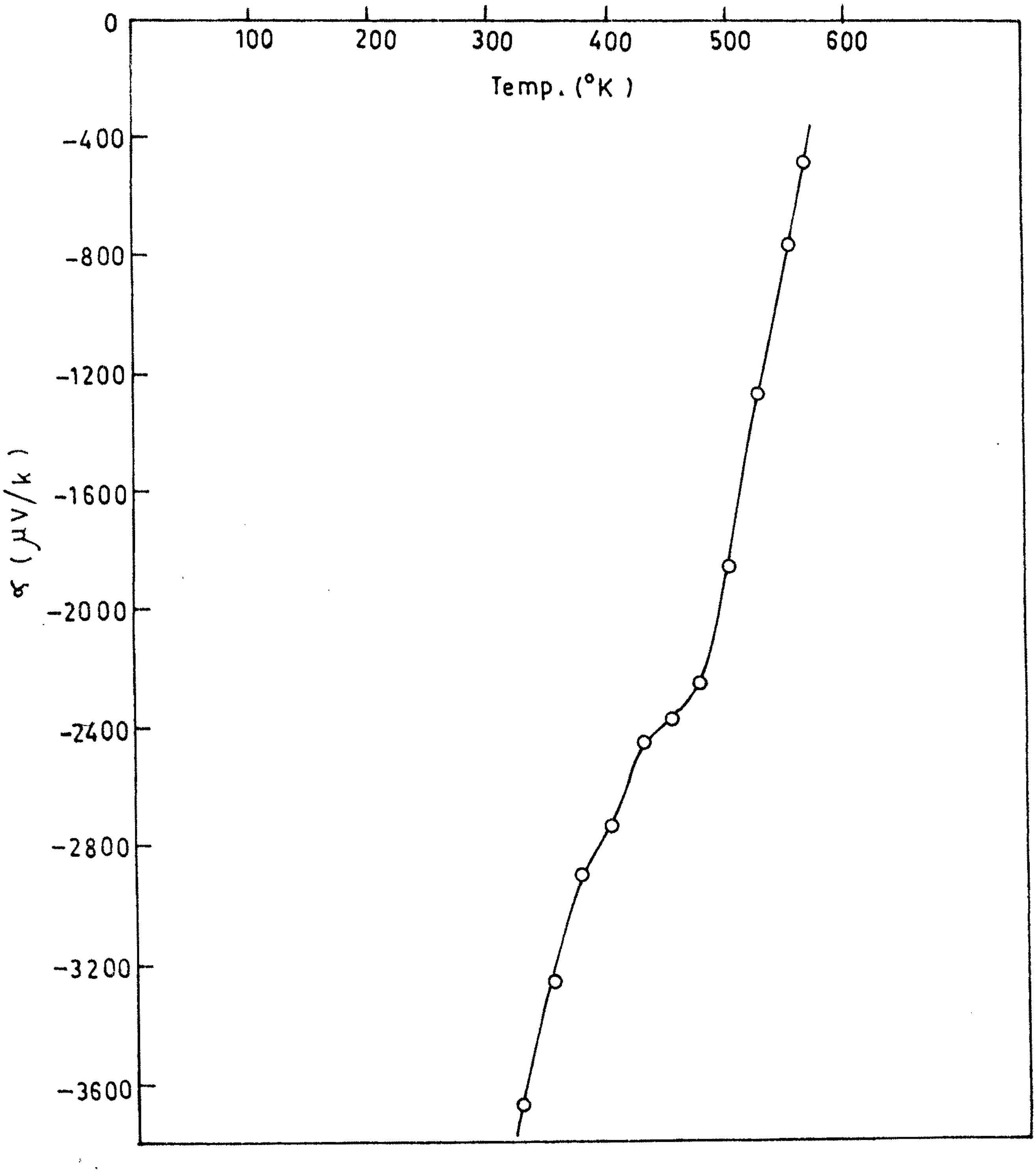


Fig. 4.2 (b) — Variation of α Vs T for $Mg_{0.7}Cu_{0.3}Fe_2O_4$.

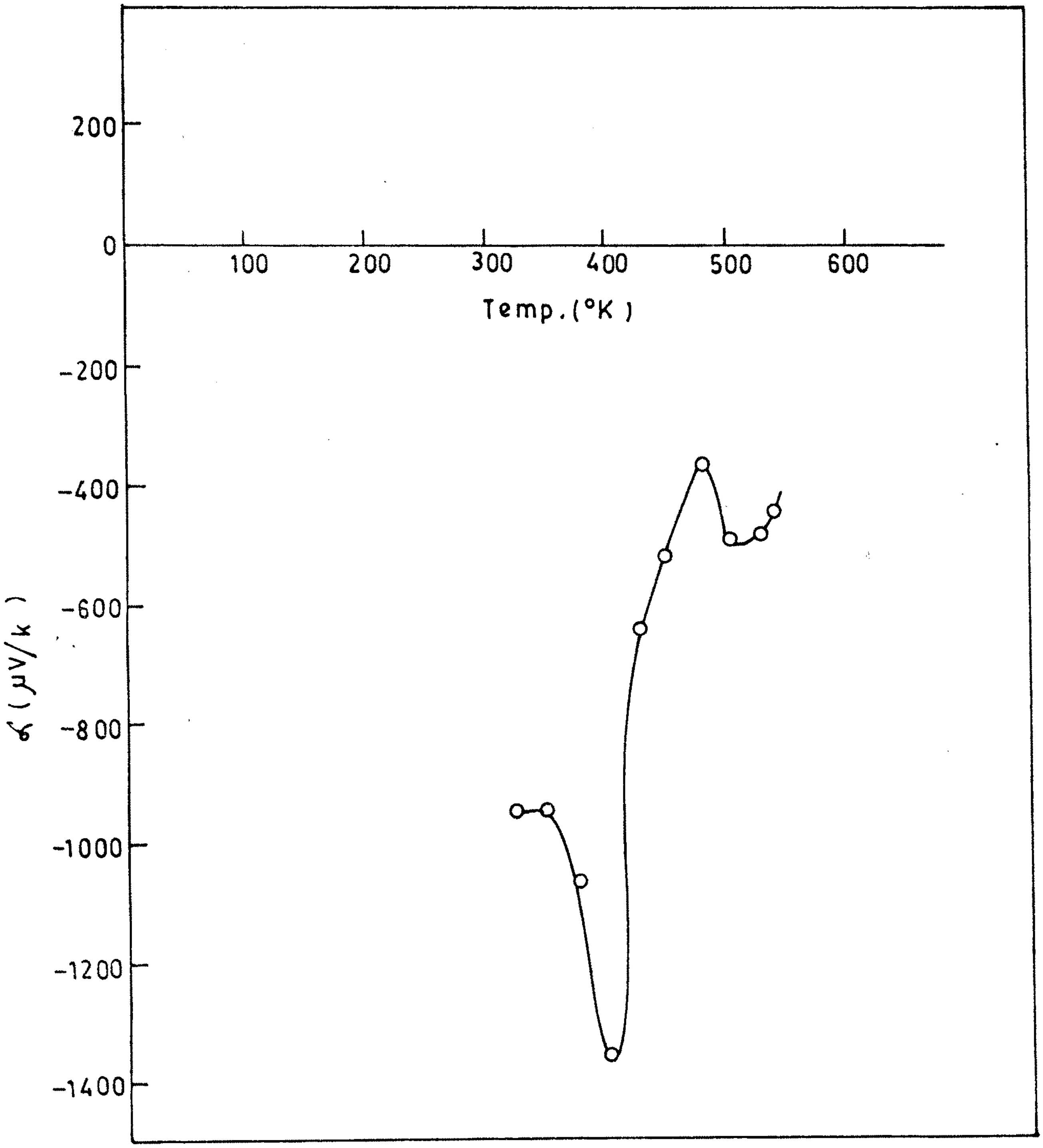


Fig. 4·2 (c) — Variation of α Vs T for $Mg_{0.4}Cu_{0.6}Fe_2O_4$.

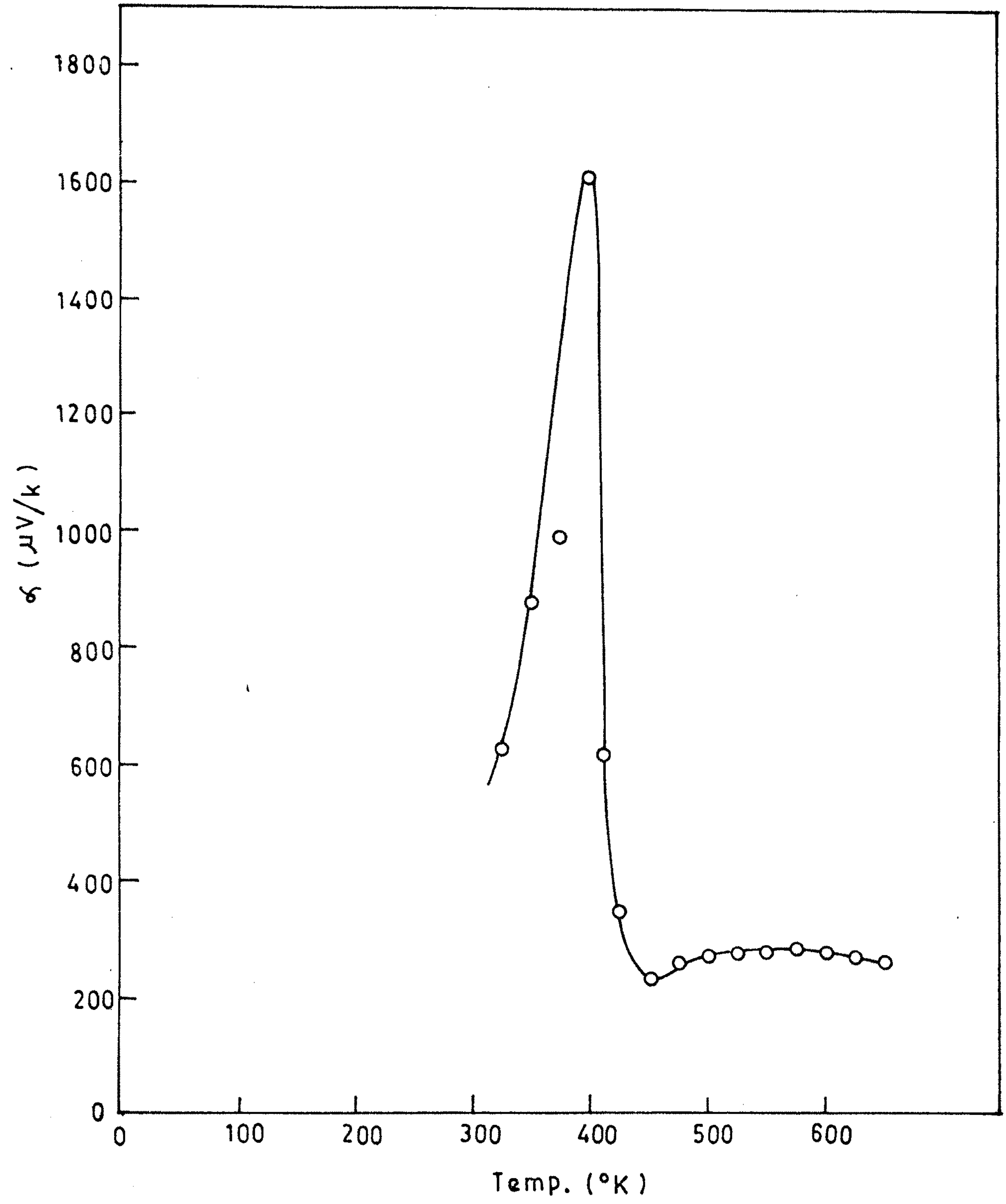


Fig. 4·2(d) — Variation of α Vs T for $CuFe_2O_4$.

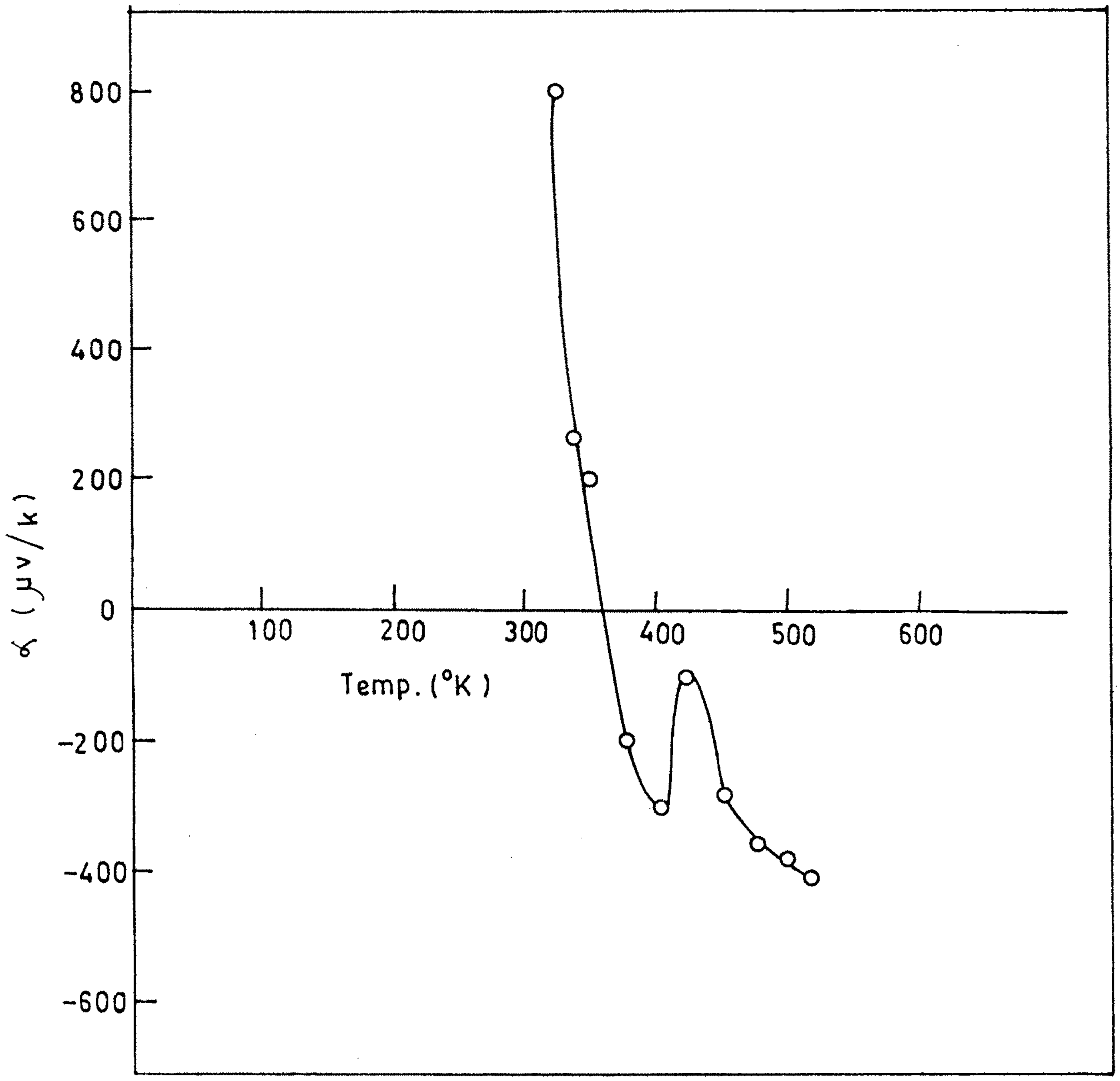


Fig. 4·5(a) – Variation of α Vs T for $Cu_{0.7}Zn_{0.3}Fe_2O_4$.

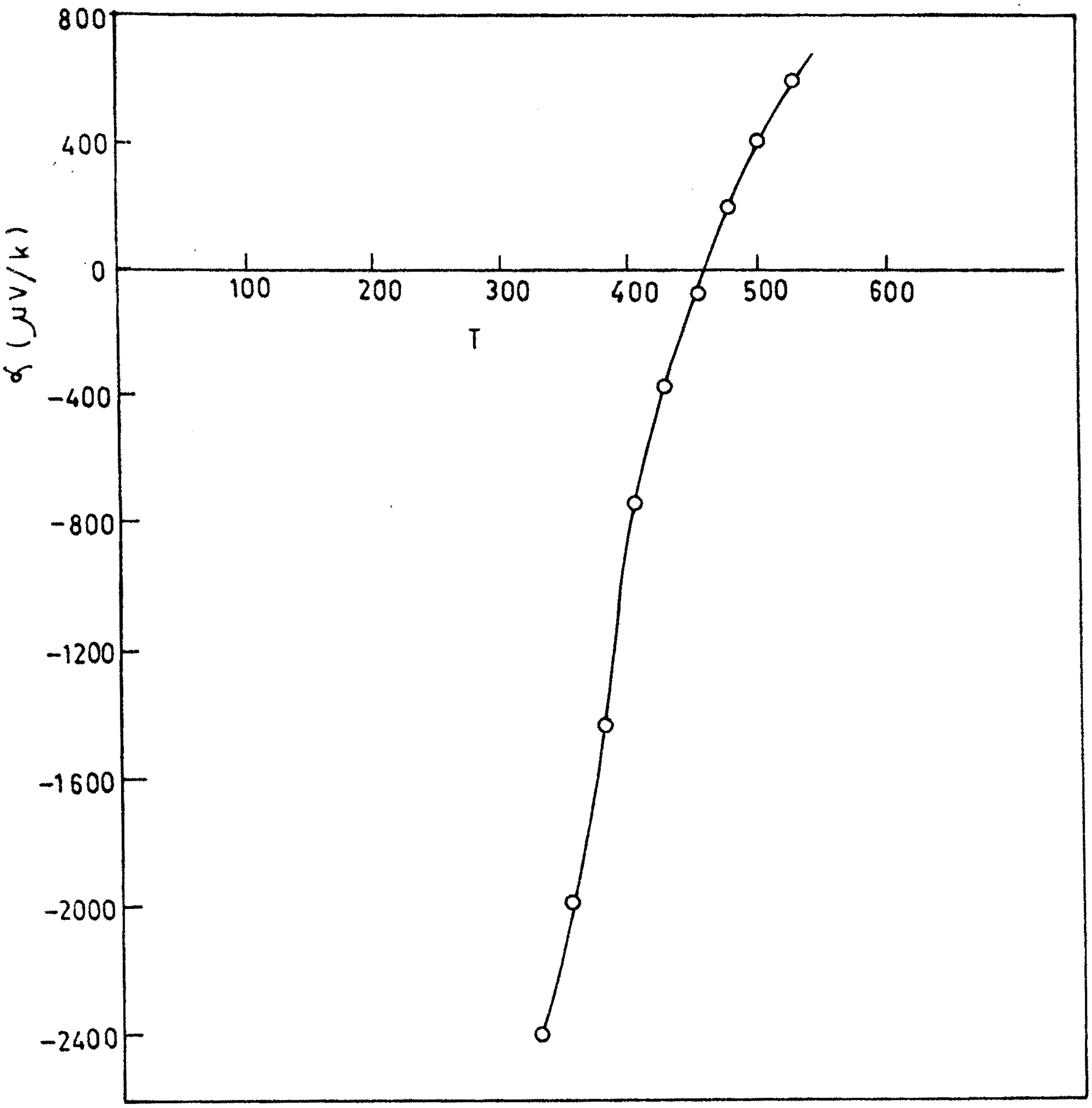


Fig. 4·5(b) — Variation of α Vs T for $Cu_{0.4}Zn_{0.6}Fe_2O_4$.

observations. As the copper content decreases in the system, the samples become p to n type. Therefore the conduction in copper ferrite is predominant with the presence of Cu^{2+} to Cu^{1+} transition, where as it is predominant in remaining samples due to Fe^{2+} to Fe^{3+} transitions.

Fig. 4.5 (a) and (b) show the variation of α Vs T for Cu - Zn series . In Cu - Zn ferrite system, the sample $Cu_{.7}Zn_{.3}Fe_2SO_4$ shows p type behaviour and p to n transition takes place at 350 °K . the $Cu_{.4}Zn_{.6}Fe_2O_4$ sample shows n-type behaviour. The above explaination holds good for this variation.

Good enough at al have discussed the conduction processes at lower temperatures for copper mixed ferrites. According to their analysis there are two temp. regions, one below 200° c, no oxidation process takes place where as above 200 °c to 400°c , There occurs cation exchange and reoxidation processes. In the present study we have observed the small variations in resistivity and thermo emf plots around 150 °c to 200 °c . This variation may be due to reoxidation and cation migration in these ferrites.

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