CHAPTER - IV

ELECTRICAL CONDUCTIVITY (D.C.)

STUDY ON ELECTRICAL CONDUCTIVITY (D.C.)

4.1 : Introduction :

Ferrites exhibit semiconducting behaviour, having wide range of resistivity. The high resistivity associated with ferrites is beneficial to use them at high frequencies. The studies on conductivity gives a clue on conduction mechanism in ferrites. In this chapter we have presented our studies on d.c. resistivity of the slow cooled $Cu_xNi_{1-x}Fe_2O_4$ series.

4.2 : Conduction In Ferrites :

In the ferrites iron ions with two valence states Fe^{2+} and Fe^{3+} lead to n-type conductivity[1] by exchange of electrons from donor ion Fe^{2+} to Fe^{3+} in the same lattice (Octahedral lattice). This requires a little energy to move an electron. The "electron hopping" model has been proposed[2] for the conduction in transition metal oxides. In this mode of conduction, electrons jump from one lattice site to other under the influence of electric field. The conductivity in the Cu containing ferrites was explained on the basis of above mentioned model by D.Condurache.[3]

The temperature dependence of resistivity in the ferrite is given by,

$$\rho = c \exp \left(\frac{\Delta E}{KT} \right) \quad \ldots\ldots\ldots\ldots \quad (4.2.1)$$

where, c, is the temperature independent constant which depends on the nature of materials,

K, is the Boltzmann constant,

T, is the absolute temperature,

and ΔE, is the activation energy.

The breaks and discontinuties that occur in the log ρ versus $\frac{1}{T}$ plot can be reasoned to several sources. The change in the activation energy at high temperature referred to as ferro-magnetic Curie temperature[4] lead to the strong evidence for the influence of the magnetic ordering upon conductivity[5]. The breaks may also be due to change in the dominant conduction mechanism[6].

The "hopping of polarions" by thermal activation, also contributes to the conduction. The probability of formation of small polarons is more in the solids with large coupling constant and a narrow conduction band. The existence of small polaron and hopping process was confirmed experimentally.[7,8] On the basis of simplified assumptions with suitable approximations[7], energy levels and bands for ferrites have been calculated.

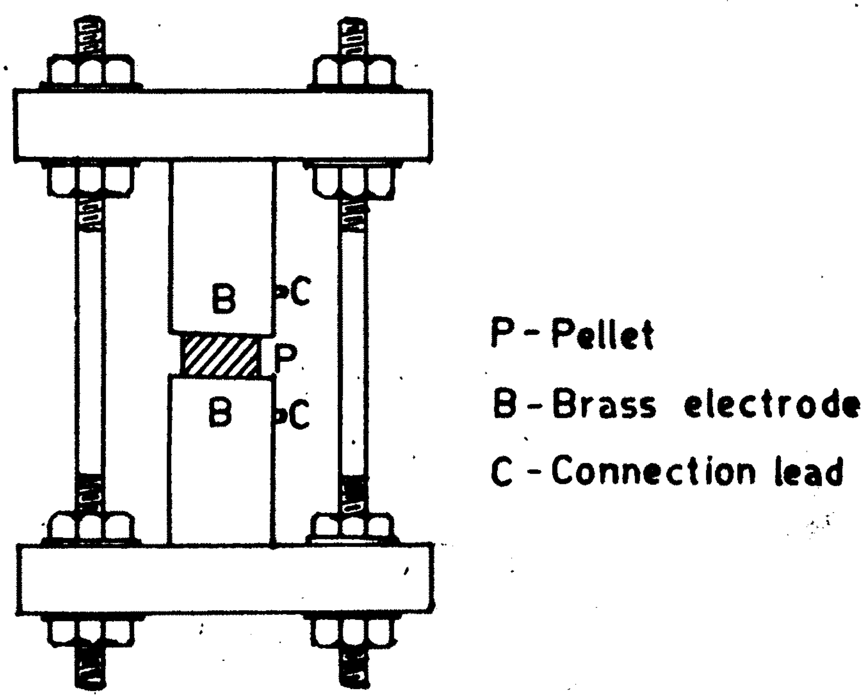
The "two phase polaron" model[8] is made available (in 1975) to explain conduction mechanism. According to Kligner[8] at low temperature the conduction is, via correlated polarons while at high temperature, via non-activated Brownian-like tunneling motion of polarons.

The complexities are associated with the conductivity of ferrites. The interpretation of d.c. conductivity are influenced by different factors like acceptor and doner levels (due to cation and anion vacencies), uncertanity in charge carrier concentration. The different models have been used to discuss various conduction mechanisms by earlier workers.[9-12]

4.3 : Experimental :

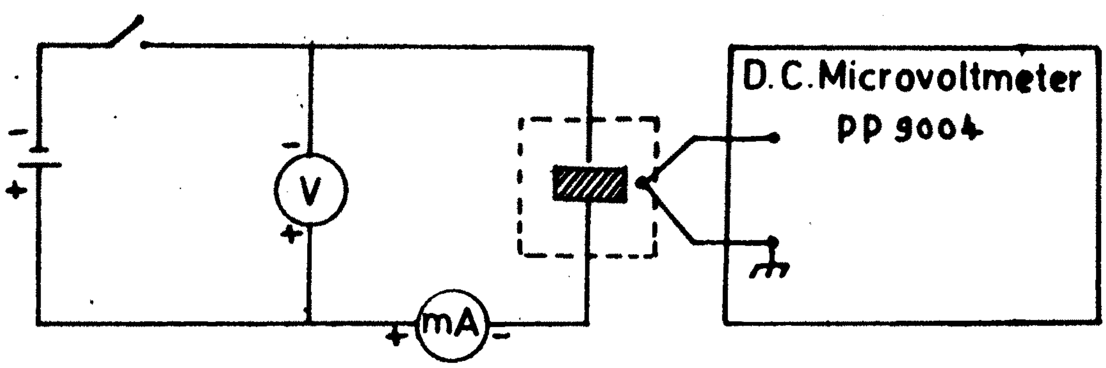
4.3 (a) : Experimental Assembly : For the conductivity measurement specially designed two probe conductivity cell has been fabricated. The block diagram of the conductivity cell is shown in the Fig.4.1(a). It consists of two small cylindrical brass rods which are fitted in the two poreiline discs. The poreiline discs can be held firmely by connecting rods with the help of nuts so as to sandwitch the sample between the two cylindrical rods. The two screws were provided on two brass rods for external connection. The electricially insulated Cu-wires were used for external connections.

The ferrite sample in the form of pellet was sandwitched in between two brass rods. For good ohmic contact silver pest was applied. This entire assembly was then kept in the temperature regulated furnace. The usual chromel-Alumel thermocouple was calibrated and then was used for temperature measurement. A circuit diagram for measurement of d.c. resistivity is shown in Fig.4.1 (b).



Block diagram of pellet holder

Fig. 4.1(a)



A schematic circuit diagram for d.c.conductivity measurements

Fig. 4.1 (b)

4.3 (b) : <u>d.c. Resistivity Measurement</u> : The assembly discussed in the previous sub-section with a circuit diagram was used to measure d.c. resistivity of each sample of slow cooled mixed ferrite series, $Cu_xNi_{1-x}Fe_2O_4$, with x = 0.0, 0.4, 0.6, 0.8 and 1.0; in the disc (i.e. pellet) form of nearly the same thickness. The d.c. electric field was provided by 3 volts and 1.5 volts dry cell. The currents were measured with the help of multimeter from room temperature to 700°C by a temperature interval of 25°C. The resistivity (ρ) was calculated using the relation, $\rho = \frac{V}{I} \times \frac{\pi r^2}{t}$. The plots of log (ρ) versus $\frac{10^3}{T}$ are presented in the Fig.4.2(a) to Fig.4.2(e).

4.4 : <u>Results and Discussion</u> :

The electrical resistivity measurements on $Cu_xNi_{1-x}Fe_2O_4$ ($0 \leq x \leq 1$) have been made by using the set-up and electrical connections explained in the previous sections. In Fig.4.29(a) to Fig.4.2 (f) are given the graphs of log (ρ) versues the $\frac{10^3}{T}$. It can be seen that in the ferrimagnetic region below Curie-temperature the linear nature of the graph has been deviated. This trend of deviation from linearity is found in all the samples including the end members. Recently a similar observation has been reported where it is shown that in the log (ρ) versus $\frac{10^3}{T}$ plot there can exist three regions which arise because of the deviation as we have observed.[13] The authors have attributed these phenomenon to different sources, however,

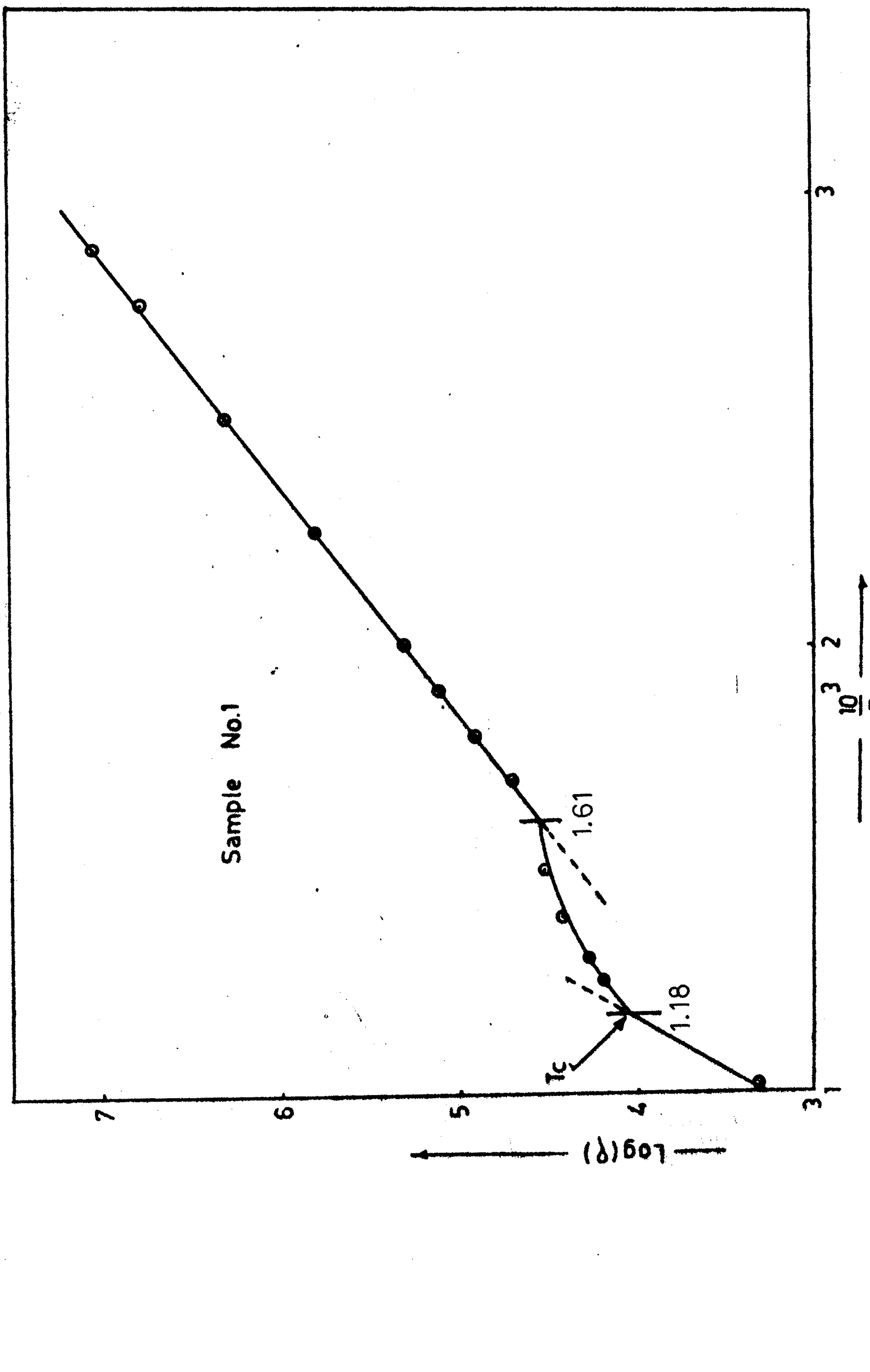


Fig 4.2(a)

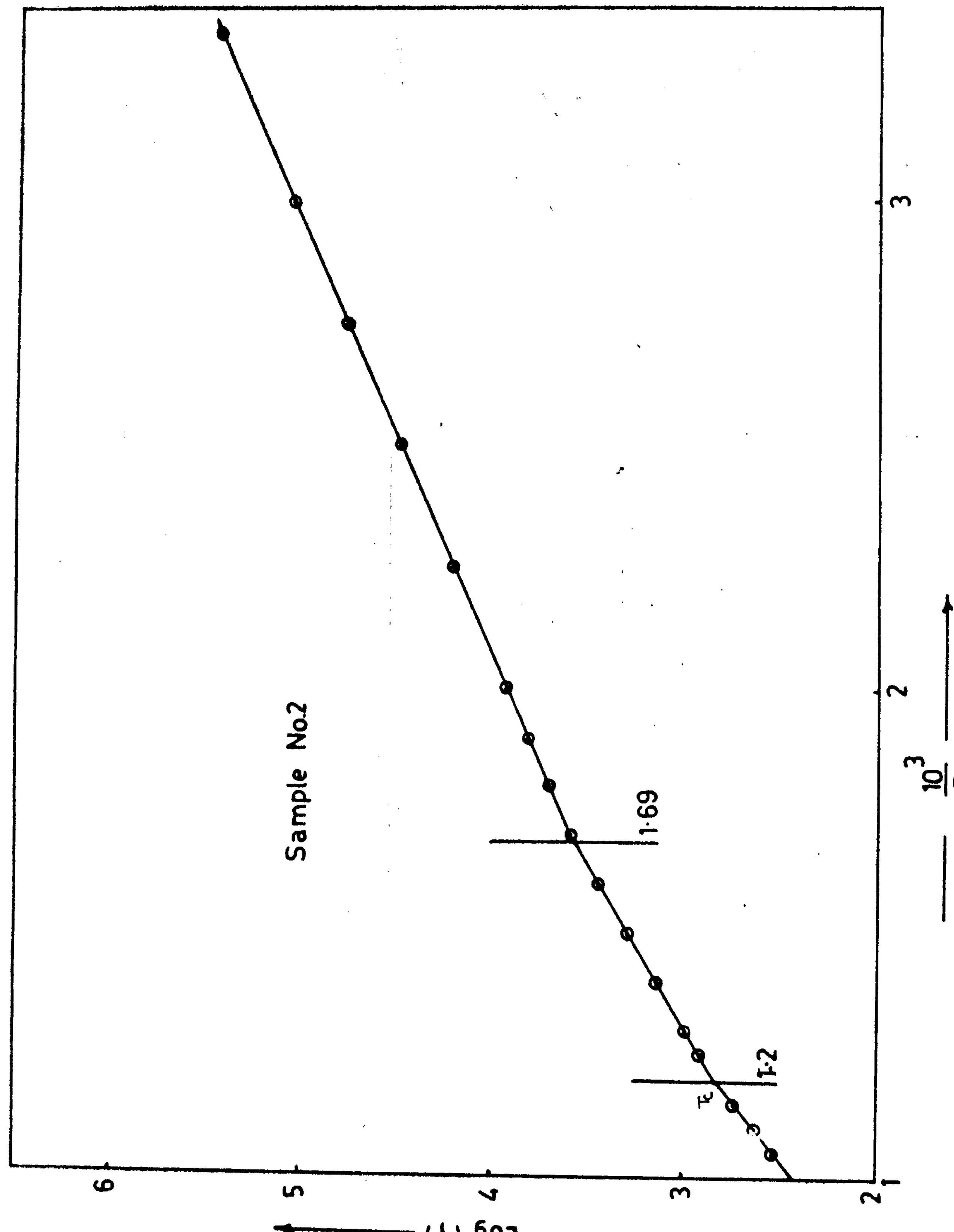


Fig 4·2 (b)

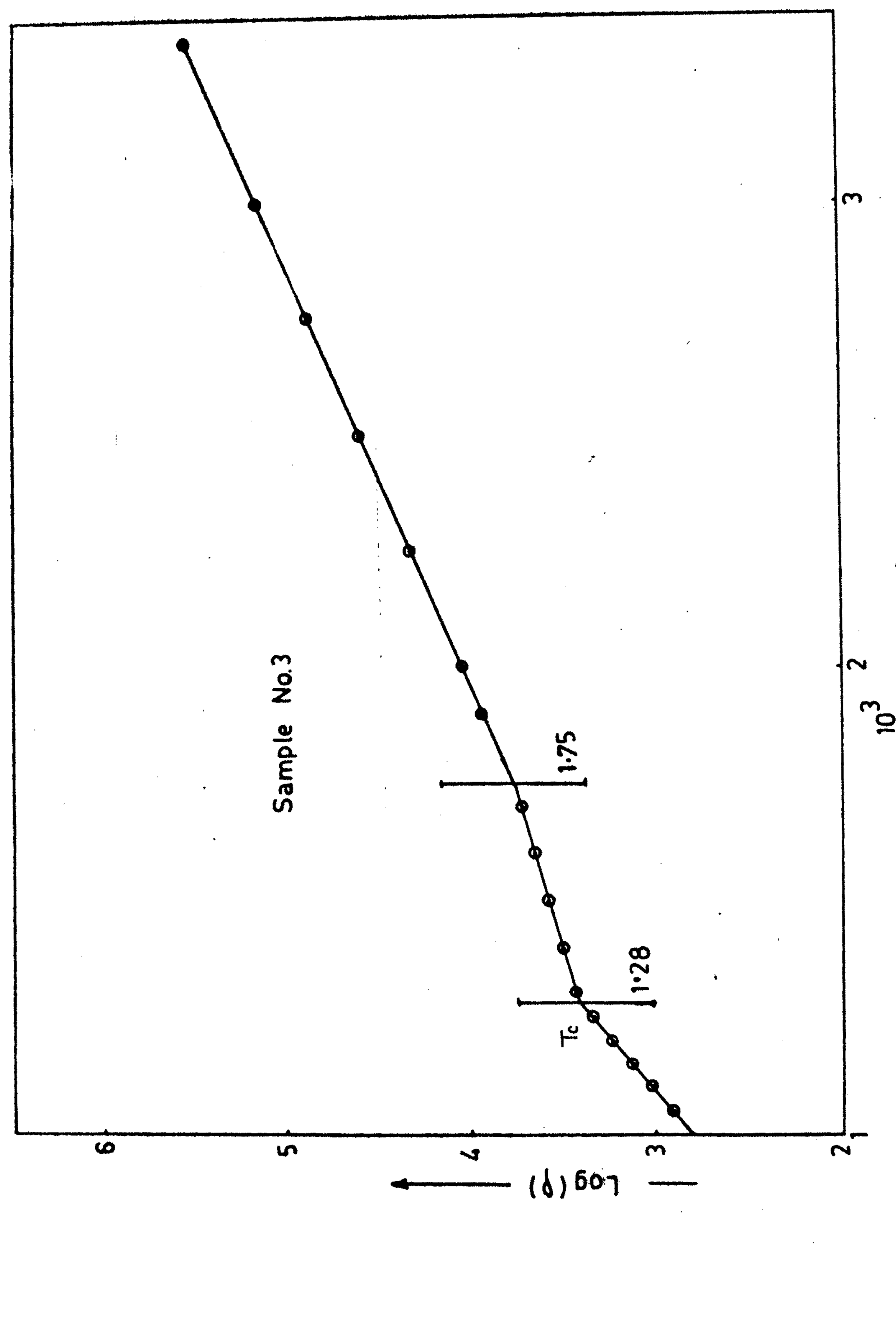


Fig 4·2(c)

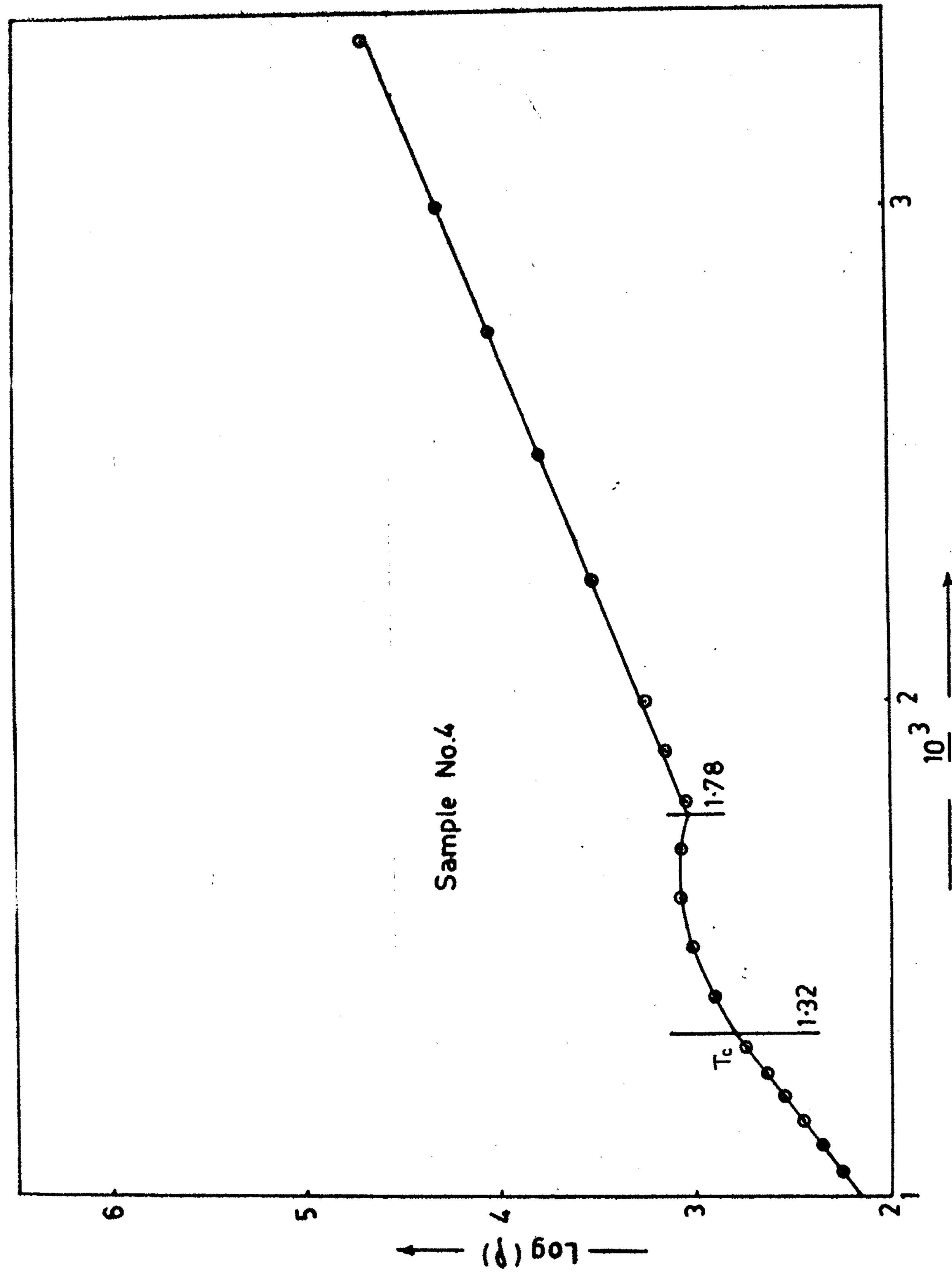


Fig 4·2(d)

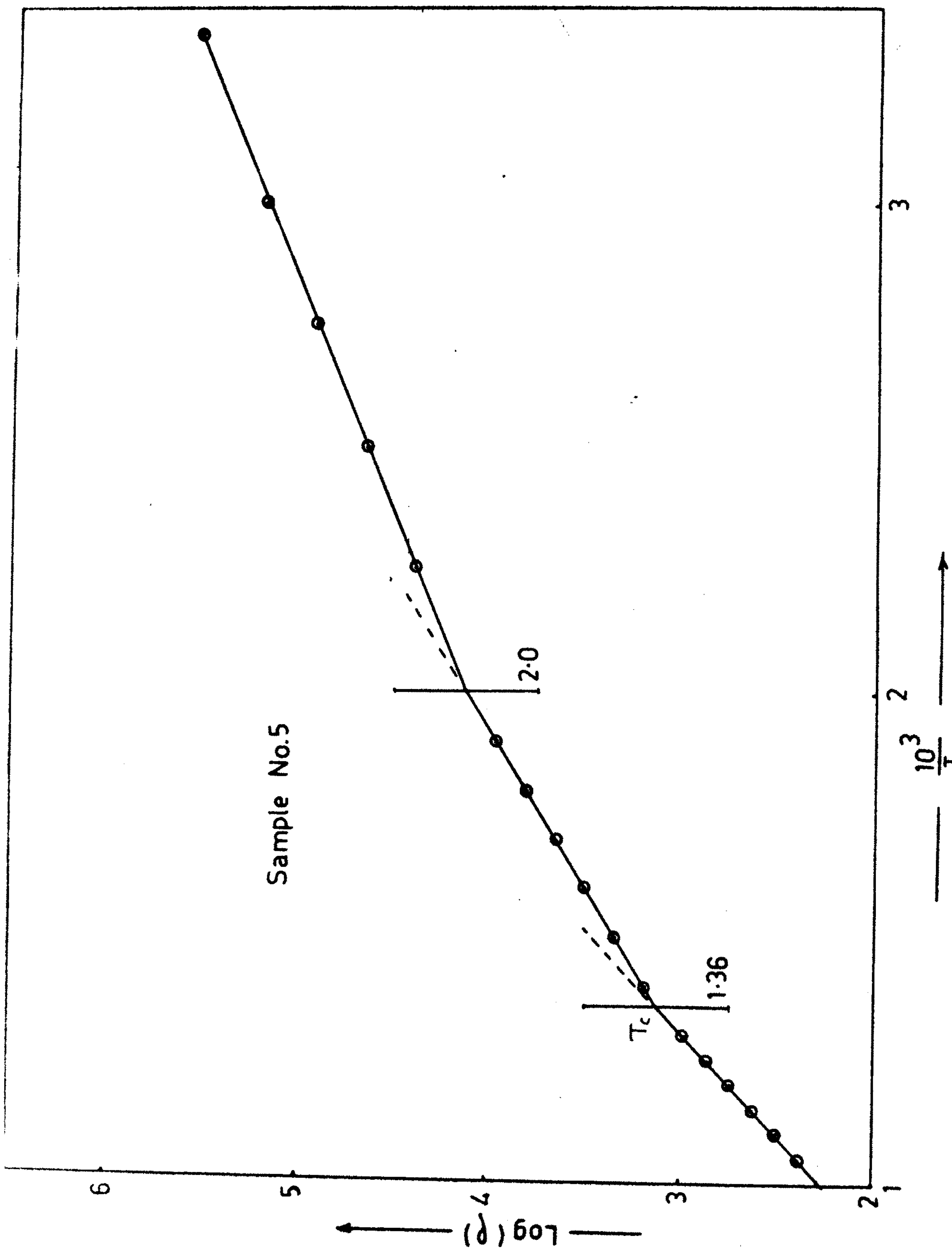


Fig 4.2(e)

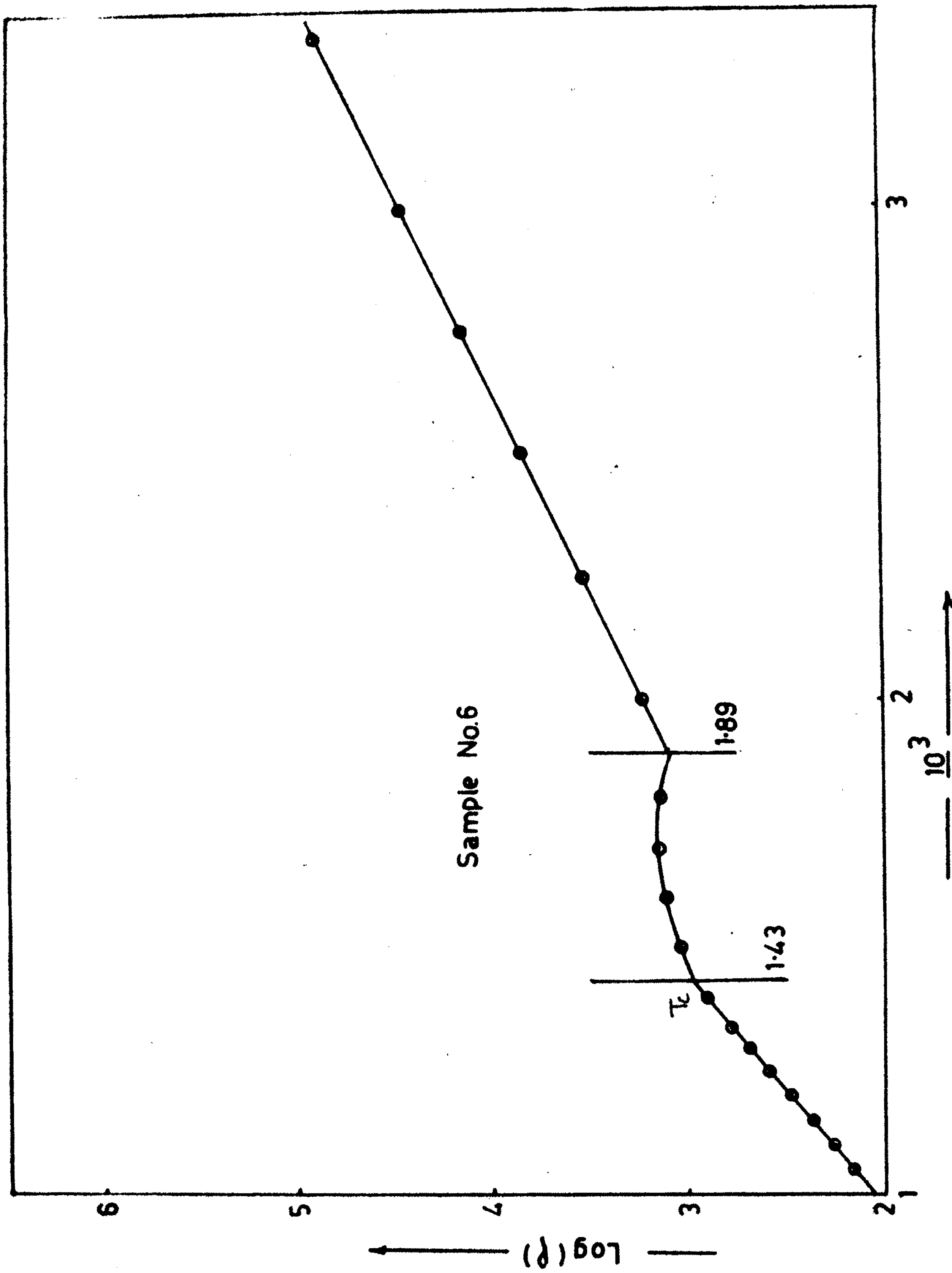


Fig 4.2 (b)

the deviation near and just below the transition temperature (Tc) is attributed to the method of preparation. Ferrites are well known to depend for their behaviour on the physical parameters like denisty, porosity, grain size and the thermal history etc. Therefore, the deviation from the linear nature that we have observed may be attributed mainly to the method of preparation. It can be noted that the physical densities are less than the X-ray densities in this system which can be seen from the table number 2.2. From which it is obvious that, it is mainly the roll of porosity in the samples. There is also a possibility of creation of additional defect levels in the sample at elevated temperature as the magnetic disordering approaches near the Curie temperature (Tc). Further there is also a possibility of developing deficiency of oxygen or excess of oxygen at elevated temperatures, as the experiment is conducted in air, depending on the system. This can be verified by thermogravometric analysis of the sample. A change in slope of the plot, however still indicates the transition temperatures which separate the ferri and para regions and fall very near to Curie temperatures. In Table No.4.1 these "transition temperatures" along with the Curie temperatures experimentally measured are presented. In both Ferri and para magnetic regions the resistivity plot generally obeys the relation.

$$\rho = c \exp \left(\frac{\Delta E}{KT} \right)$$

where C is the temperature dependent constant; ΔE, the activation energy; k, the Boltgmann constant and T, the absolute temperature. The change in the slope therefore indicates the change in activation energy in the two regions. Different explainations are put forth for these transition temperatures where the conductivity mechanism shows a break. Komar and Klimshin[4] have attributed the changes in the activation energies in many ferrites to ferromagnetic Curie temperature of these materials. Fe_3O_4 shows a discontunity at 120°k which is explained as ordering of Fe^{2+} and Fe^{3+} ions on the octahedral B-site.[14] This ordering is also accompanied by Small change in the crystal structure. The activation energy in Ferri and parua magnetic regions are calculated using the relation, $\Delta E = (k)$ (slope of $\log \rho$ Vs $\frac{1}{T}$) and these values are also presented in the same table No.4.1. From this table it can be seen that the activation energy (ΔE) in the ferri and paramagnetic regions decrease with increasing copper-content.

The activation energy is representative of the hopping mechanism either due to electron or polaron in ferrites and when the thermal activation of the sample is sufficient then the conduction can take place by hopping of electrons becomes necessary in ferrites because the B-B distance on the octahedral site is much larger than the sum of the ionic radia of the cations involved. This makes the electron not free to move in the crystal but remains fixed to B-site. In ferrites the conductivity is mainly decided by the availibility of a pair of cations that faciliate hopping process. Therefore, from the

Table No. 4.1 : Data on electrical conductivity in the system $Cu_xNi_{1-x}Fe_2O_4$.

x	Curie Temp.(Tc) in °K, experimentally determined	Transition Temp. from log(ρ) Vs $\frac{10^3}{T}$ Plot	Regions observed for ($\log_e \rho$) Vs $\frac{10^3}{T}$ Plot	Activation Energy ΔE (in e v)	
				Ferri Region	Para Region
0.0	853	847.4	I : Room temp. to 621°K II : 621°K to 847°K III : 847°K to 910°K	0.397	0.826
0.2	838	833.3	I : Room temp. to 591.7°K II : 591.7 to 833.3°K III : 833.3 to 910°K	0.22	0.413
0.4	797	781	I : Room temp. to 571.4°K II : 571.4°K to 781.2°K III : 781.2°K to 910°K	0.22	0.381
0.6	771	757.5	I : Room temp. to 564.9°K II : 564.9°K to 757.5°K III : 757.5°K to 910°K	0.201	0.354
0.8	746	732.2	I : Room temp. to 500°K II : 500°K to 732.2°K III : 732.2°K to 910°K	0.195	0.451
1.0	714	699.3	I : Room temp. to 529.1°K II : 529.1°K to 699.3°K III : 699.3°K to 910°K	0.248	0.381

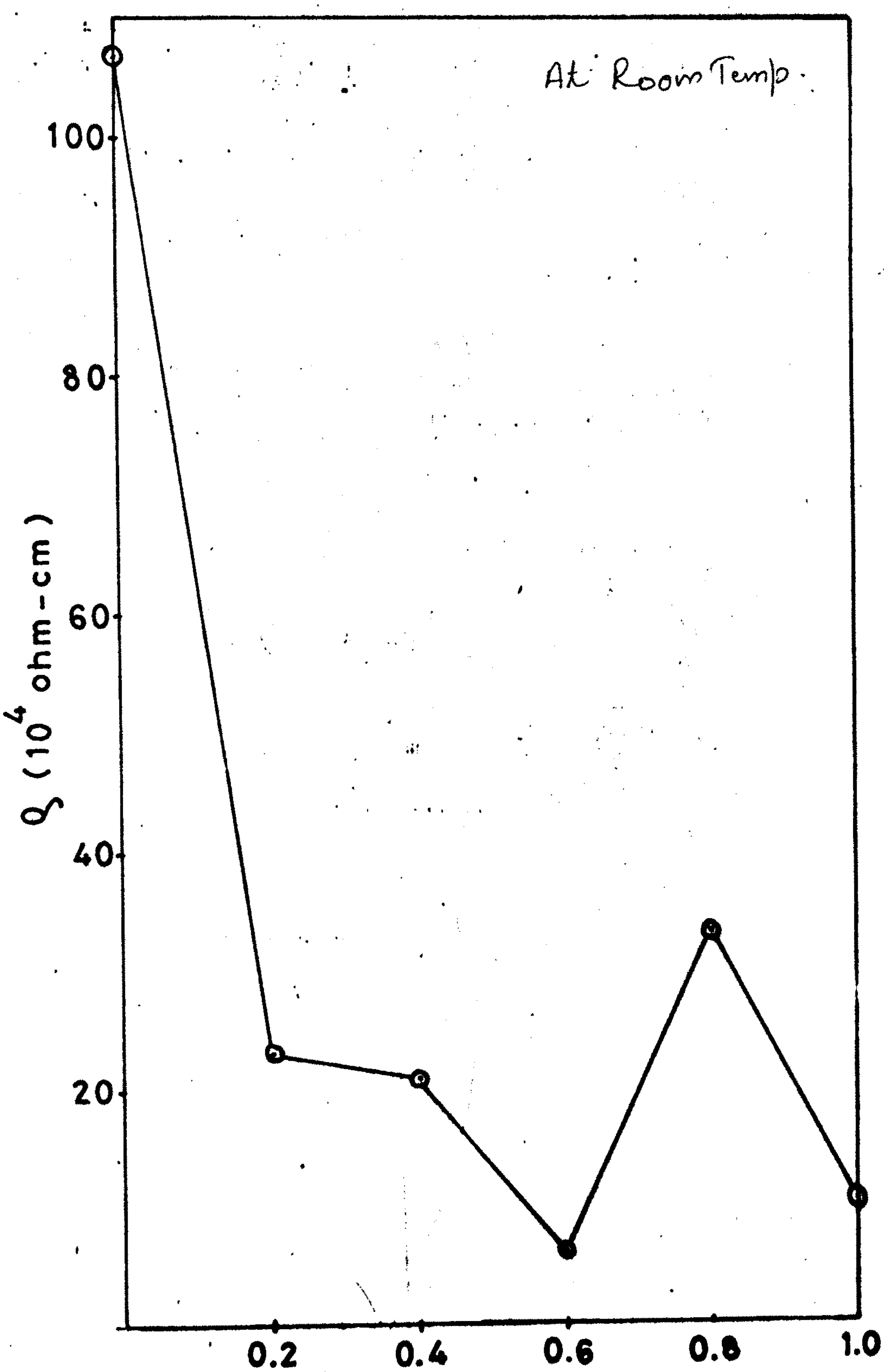


Fig. 4.3

values obtained of activation energies given in table no. 4.1, it can be noted that the decrease of activation energy with increasing copper concentration indicates that hopping process is faciliated from Ni Fe_2O_4 to Cu Fe_2O_4. These values of ΔE are representative of the usual hopping of the form $Fe^{2+} \rightleftarrows Fe^{3+}$ in the present system. In other words it can be said that the diluation of conduction mechanism occurs due to addition of Ni^{2+} on the octahedral B-sites as it has lower affinity for oxygen and can therefore eliminate some forms of conduction.

In fig. 4.3 it can be seen that the resistivity of Ni Fe_2O_4 is maximum at room temperature and goes on decreasing with increasing copper content upto x = 0.6 and beyond that it is once again found to increase and then at x = 1 which is pure $CuFe_2O_4$, it is again minimum. This change in resistivity at room temperature reflects a corresponding change in cation distribution of the system at x = 0.6 where the migration of Cu-ions is enhanced from A to B site. Thus showing that the electrical resistivity data is consistent with the magnetization study on the present system.

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