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CHAPTER - I I I

RESISTIVITY STUDIES

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### 3.1 Introduction

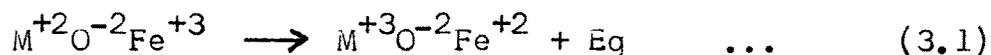
Ferrites are semiconductors by nature and have a large range of variation in resistivity from  $10^{-3}$  ohm cm to  $10^{+9}$  ohm cm. Due to their high resistivity the ferrites find preference over metals and alloys in high frequency operation, which exhibit large eddy current losses. The studies on conductivity furnish a useful data from the application point of view and also in understanding the mechanism of conduction. The low resistivity in  $\text{Fe}_3\text{O}_4$  is due to the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the crystallographically equivalent sites<sup>1</sup>. Conduction in ferrites is attributed to hopping process. [Komar et al.<sup>2</sup> have observed breaks and discontinuities in  $\log \rho$  versus  $1/T$  plots for many ferrites. This discontinuity occurs near Curie temperature and the segments refer different conduction mechanisms. Verwey et al.<sup>3</sup> have observed such discontinuities in Mn-Ni ferrites and that these discontinuities shifted towards higher temperature as Mn content is increased. Anamolous results showing different values of resistivity were obtained in Ni ferrites<sup>4</sup>. Van Uietret<sup>5</sup> observed low resistance before and after grinding for Zn-Ni ferrites. He attributed this change to Zn which voltalizes during heat treatment and encourages the formation of  $\text{Fe}^{2+}$  ion on the surface.]

The conduction mechanism in ferrites is due to exchange of electrons from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in the same (octahedral) lattice. This requires little energy to move an electron. Under the

influence of electric field these extra electrons can be considered to constitute the conduction current by hopping from one site to the other. Recently Klinger<sup>6</sup> has stated that hopping of polarons is the main conduction mechanism ~~in~~ in ferrites. He has suggested two phase mechanism<sub>7</sub> for hopping of polarons. Parker et al.<sup>7</sup> have measured resistivity of nonstoichiometric Zn and Ni ferrites and observed discontinuities in the resistivity plots. The observed temperatures of these discontinuities are lower and lower than the Curie temperature for more and more iron content. Recently Ghani et al.<sup>8</sup> have observed more than two breaks in the log  $\rho$  versus  $1/T$  plots for Cu-Ni ferrites.

### 3.2 Survey of Conduction Models

In simple ferrites where all the Fe ions are trivalent the transport of electrons may be represented by



where  $E_g$  the activation energy which may reflect the difference between third ionisation potential of  $Fe^{+3}$  and  $M^{+3}$  ions in the solid. Jonker<sup>9</sup> has studied the ferrite  $Co_xFe_{3-x}O_4$  and predicted qualitatively the above stated mechanism.

Ionic state of the cations in an ionic crystal gives some insight into the effect of impurities on electrical properties. In so far as the ionisation potential of  $O^{-2}$  ion is the dominant term, substitution upto 1 % or so of the cations of another element; of the same valency should have little effect upon

the conductivity. If the dopant has higher valency, it will contribute donor centers, if it has lower valency, it will provide acceptor centers.

Analogous considerations may apply to cations of mixed valency in ferrites which result from a departure from the ideal metal to oxygen ratio. An oxygen ion valency will contribute two extra electrons to the 3 d band. If these extra charges are detached from their vacancies by thermal agitation, n-type conductivity is induced in oxygen deficient and p-type conductivity in oxygen excess materials. Some oxides are very difficult to prepare homogeneously with a stoichiometric anion to cation ratio. Extrinsic semiconduction may then prevail throughout the temperature region amenable to electrical measurements. In such cases it may still be possible to infer the activation energy of intrinsic conduction samples from which extrinsic effects have been suppressed by introduction of compensating impurities. This was first demonstrated by Van Uietret<sup>5</sup> in  $\text{NiFe}_2\text{O}_4$  by replacing 1 to 2 % Fe by Mn or Co. Electrons donated by oxygen vacancies will fill the impurity levels in preference to iron conduction levels. Mixed valency state will be confined to the impurity element if its local concentration exceeds twice that of oxygen vacancies. This technique is based on the assumption that impurity band conduction is absent and the allowed impurity concentrations indicate that the cation wave functions do not extend significantly beyond nearest neighbour distance in the B lattice. Electrons and holes are

known to move by thermally activated hopping mechanism except for pseudometallic composition region close to magnetite. Elwell et al.<sup>10</sup> have calculated intrinsic activation energy by applying Van Uieterts consideration to materials which have been prepared under different conditions of oxidation.

### Electron Hopping And Polarons

Another co-relation may also play a role in determining the mechanism of charge transport. The electrostatic interaction between a conduction electron or hole and nearby ions may result in a displacement of the latter and hence in polarization of the surrounding region. So the carrier becomes situated at the centre of the polarization potential well. If this well is deep enough, a carrier may be trapped at a lattice site and its transition to a neighbouring site may be determined by thermal activation. This has been described by hopping mechanism. The electron takes part in a diffusion process by jumps from one lattice site to another. The thermal activation process is encountered in ionic diffusion and ionic conductivity. The mobility<sup>11</sup> is given by the following expression

$$\mu = \frac{ed^2\nu}{KT} \exp\left(\frac{-q}{KT}\right) \dots \quad (3.2)$$

where  $d$  = distance between nearest neighbours.

$\nu$  = frequency of vibration.

$q$  = activation energy for hopping process.

This has been used by many authors in the discussion of

conductivity. With the development of polaron theory it has become evident that equation (3.2) represents a special case of much more complicated relationship between mobility  $\mu$  and a parameter of ionic lattice.

For realistic model for the calculation of mobility, knowledge of approximate spatial extent of the potential well is required. If the potential well extends over many lattice units in the crystal, the excess charge may be considered to interact with a dielectric continuum and this model has been employed by Frohlich<sup>12</sup> to formulate interaction <sup>Hamiltonian</sup> for large polarons. He gave the parameter, known electron phonon coupling constant, for the discussion of polarons. For small polarons, the well is confined to a volume comparable to the ionic volume. It is self evident that for small polarons, the interaction between the individual near neighbour ions is important. The actual polaron size can be inferred from consideration of the free energy. Small polaron formulation is favoured in solids which combine a large coupling constant with a narrow conduction band.

At sufficiently low temperature a small polaron should behave as a particle moving in a very narrow band. At high temperatures small polaron motion may result from the absorption of one or more phonons and this process is essentially the hopping mechanism. If the time of tunnelling of the excess charge from one ion to the next, is less than the time  $\tau$  between

successive hopping transitions, small polaron conduction will be the dominant transport mechanism. There is a strong experimental evidence for the existence of small polarons and for the hopping process.<sup>13</sup>

In ferrites  $\text{Fe}^{2+}$  ions are present among  $\text{Fe}^{3+}$  ions which lead to the n-type conductivity<sup>14</sup> at temperatures which are high enough so that extra electron on the  $\text{Fe}^{2+}$  ion can move through the crystal. The resistivity  $\rho$  can be written as

$$\rho = [ e(n_e \mu_e + n_h \mu_h) ]^{-1} \dots \quad (3.3)$$

where  $e$  is the electronic charge  $n_e$  and  $n_h$  are concentrations of mobile carriers and  $\mu_e$  and  $\mu_h$  are the mobilities of carriers.

The temperature dependence in many cases is given by

$$\rho = C \exp [ \Delta E / KT ] \dots \quad (3.4)$$

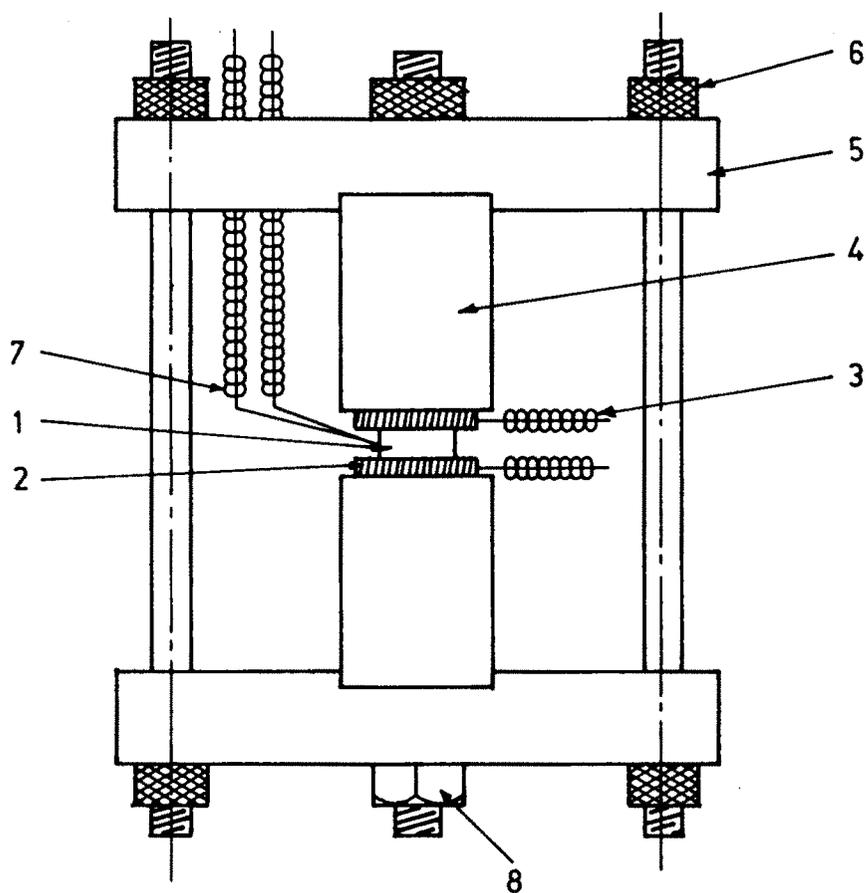
where 'C' is a temperature independent constant which depends upon the nature of the material, 'K' is Boltzmann constant and 'T' is absolute temperature. Breaks and discontinuities that occur in the  $\log \rho$  versus  $1/T$  plot can be ascribed to several sources. Komar and Klivshin<sup>2</sup> have observed changes in the activation energies for conduction which occur at high temperature in several ferrites and correlate with the ferromagnetic Curie temperatures of the ferrites. This offers a strong evidence for the influence of magnetic ordering upon

conductivity in ferrites<sup>15</sup>. The breaks may also be due to change in the dominant conduction mechanism<sup>16</sup>. For transition metal oxides, the model of electron hopping has been proposed<sup>17</sup>. In this model, electrons jump from one lattice site to another. On the bases of this model D. Condurache<sup>18</sup> has explained the conductivity of copper containing ferrites. Recently Ghani et al.<sup>8</sup> have studied the temperature dependence of d.c. resistivity ( $\rho$ ) and thermoelectric power ( $\alpha$ ) for some compositions of mixed Cu-Ni ferrites. The plots showed three different regions. The differentiation between these three regions was done in view of change in activation energy ( $\Delta E$ ) and the behaviour of  $\alpha$ . According to them, the conduction in the first region is due to impurity charge carriers. In the second region the conduction is greatly affected by the phase transition from tetragonal to cubic phase. In the third region a hopping mechanism of conduction is suggested.

### 3.3 D.C. Conductivity Cell

The cell for the measurement of D.C. conductivity consisted of two silver discs about 1 cm in diameter and 0.5 mm in thickness electrically connected to silver wires. The pellet was placed between these two silver discs and the assembly was held between two thick brass cylinders fixed to porcelain discs. These discs were tightly held by three screws symmetrically situated along their periferies to ensure uniform pressure and good electrical contact between silver discs and the pellet.

## THE CONDUCTIVITY CELL



- 1 Ferrite specimen ( pellet ).
- 2 Silver discs .
- 3 Silver wires with porcelain beads .
- 4 Brass cylinders .
- 5 Porcelain discs .
- 6 Holding screws .
- 7 Chromel Alumel thermocouple .
- 8 Screws holding the brass blocks to porcelain discs .

Fig. 3-1

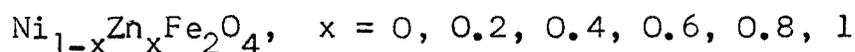
The conductivity cell, thus prepared was placed in a temperature regulated furnace. A chromel-alumel thermocouple was used along with a digital multimeter of least count 0.1 mV to measure the temperature accurately. Fig.No.3.1 shows this arrangement.

#### 3.4 D.C. Resistivity Measurement

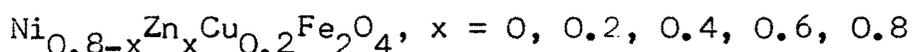
The measurement of resistance of the pellet was done by a digital multimeter. The resistance was measured from room temperature upto 710°C at an interval of 25°C. The dimensions of each pellet were measured and the resistivity  $\rho$  at various temperatures was determined and the graphs of  $\log \rho$  versus  $1/T$  were plotted. These plots are shown in figures (Fig.No.3.2 to 3.12). The activation energies  $\Delta E$  were then determined from these graphs.

#### 3.5 Results and Discussion

The variation of  $\log \rho$  versus  $10^3/T$  has been studied for the ferrites



forming the series A and



forming the series B

in the temperature range from 300°K to 1000°K. Figures 3.2 to 3.12 show these plots. The variation of resistivity exhibits

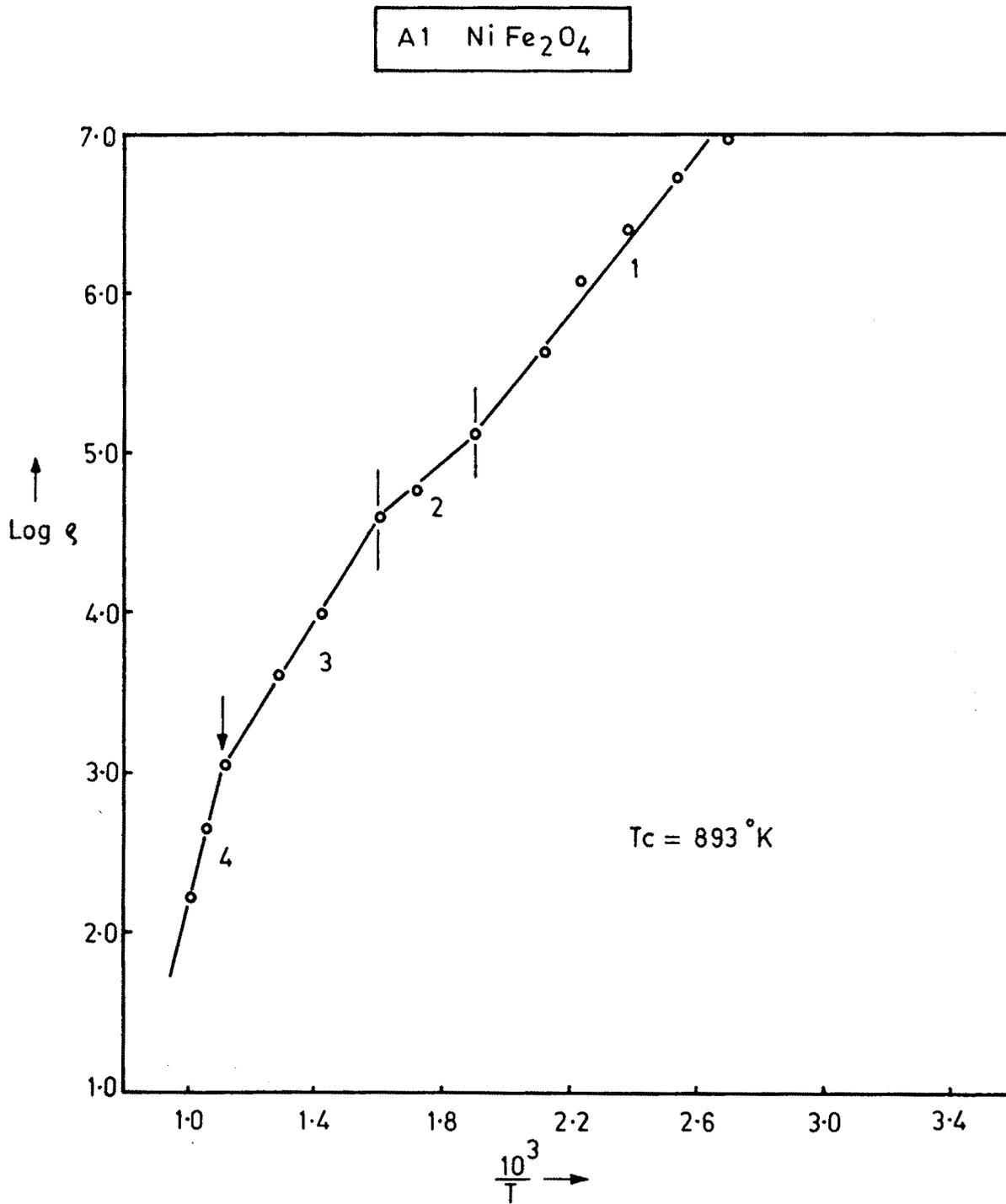


Fig. 3·2

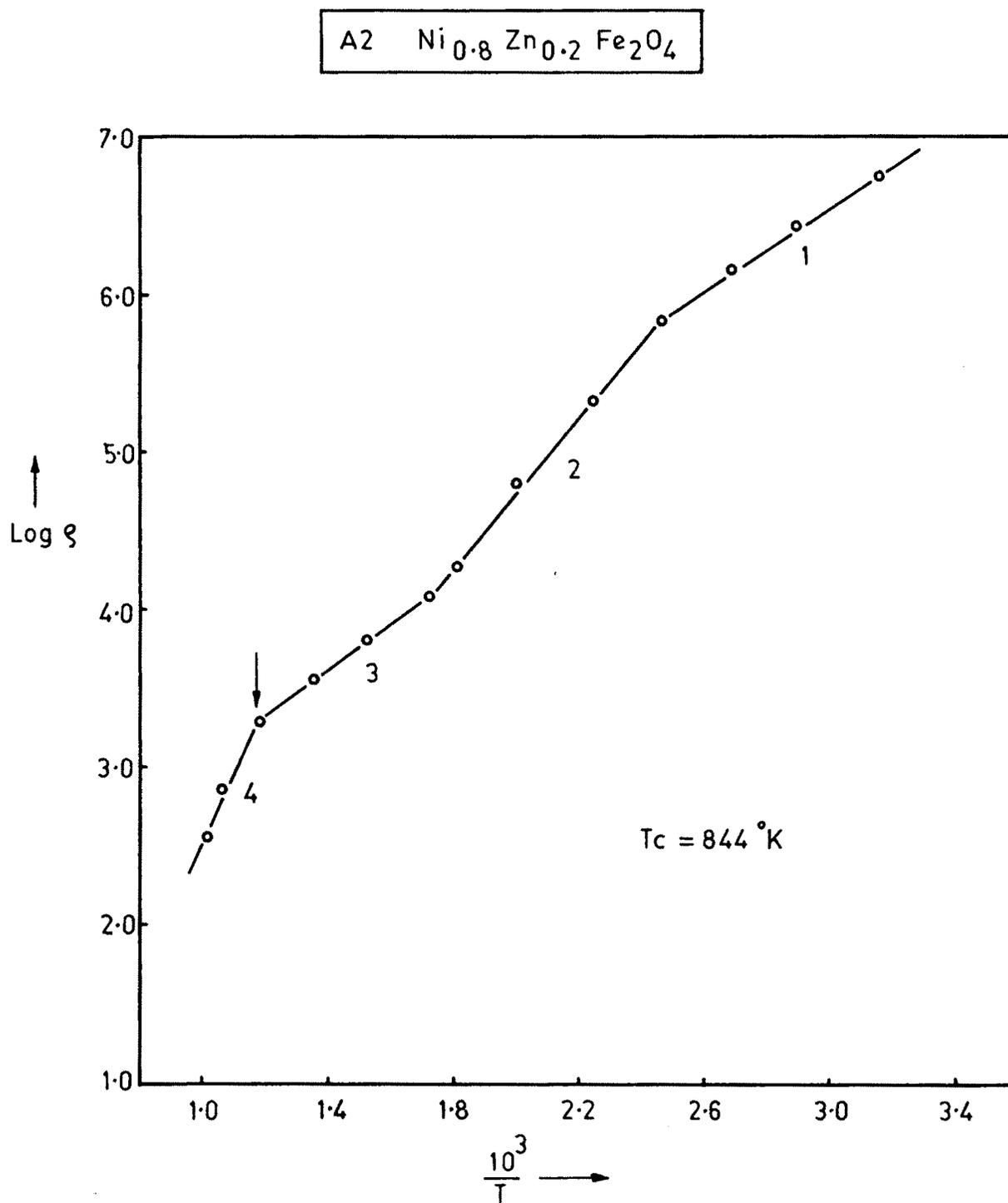


Fig. 3-3

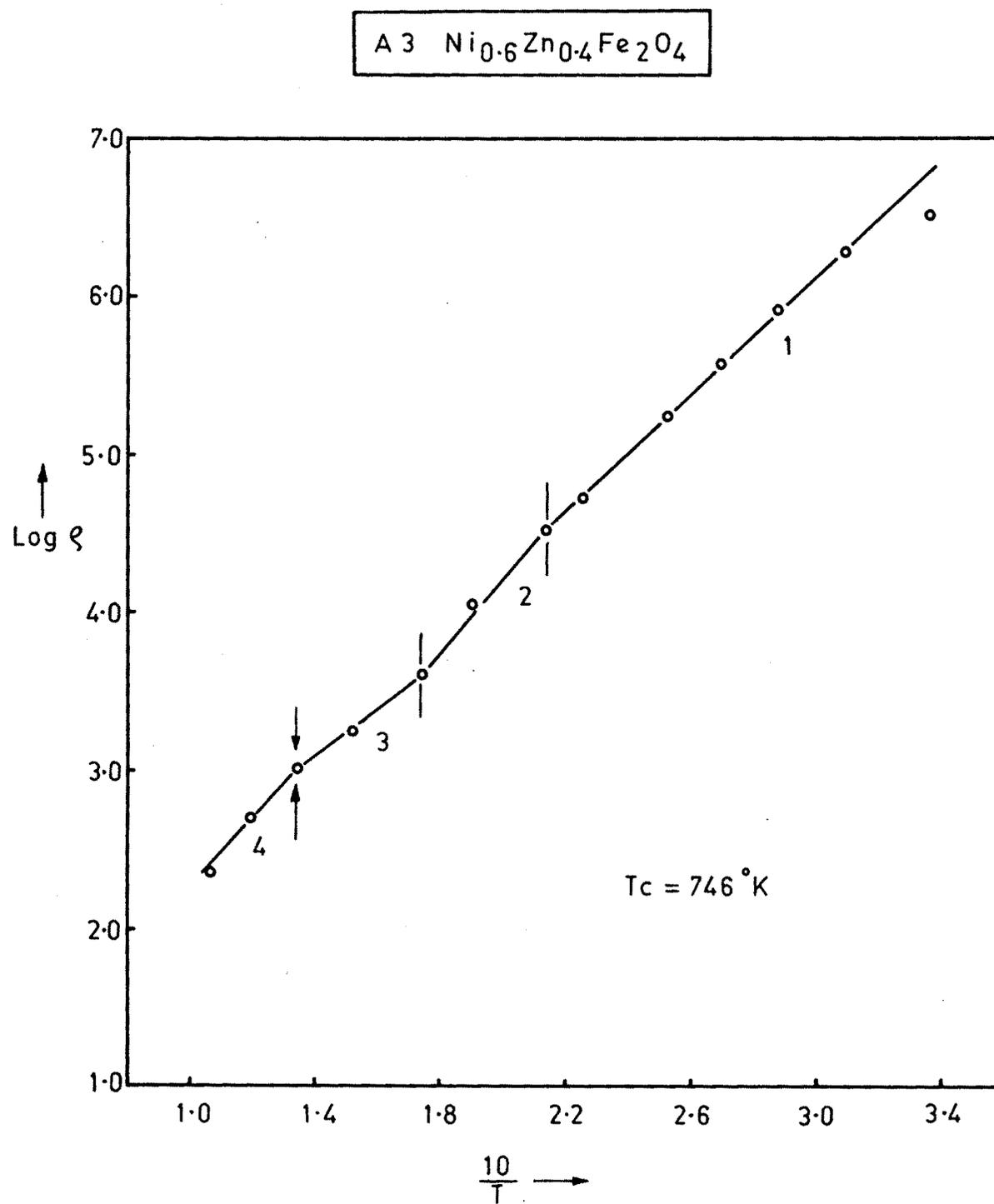


Fig. 3-4

A4 Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2</sub>O<sub>4</sub>

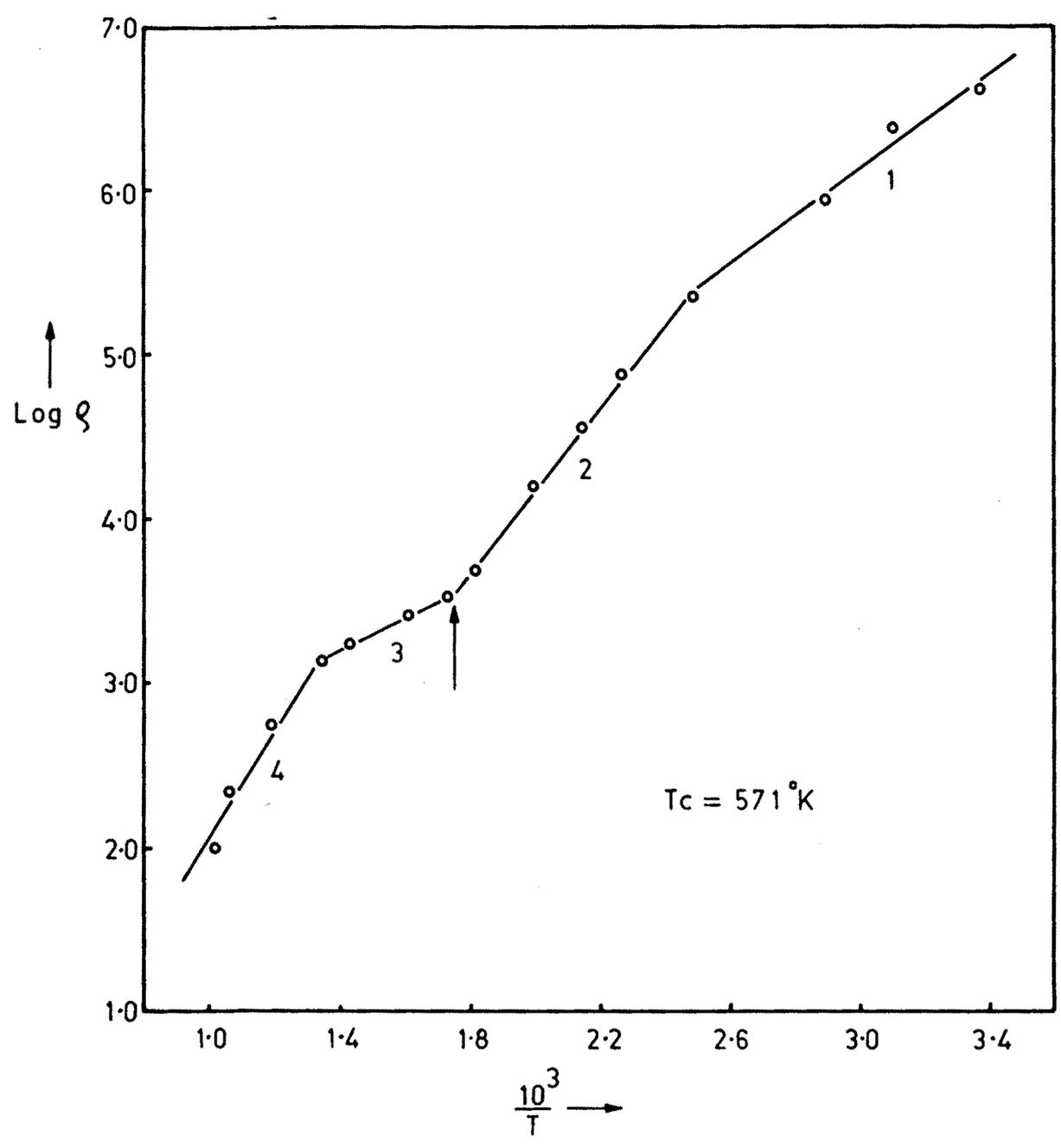


Fig. 3-5

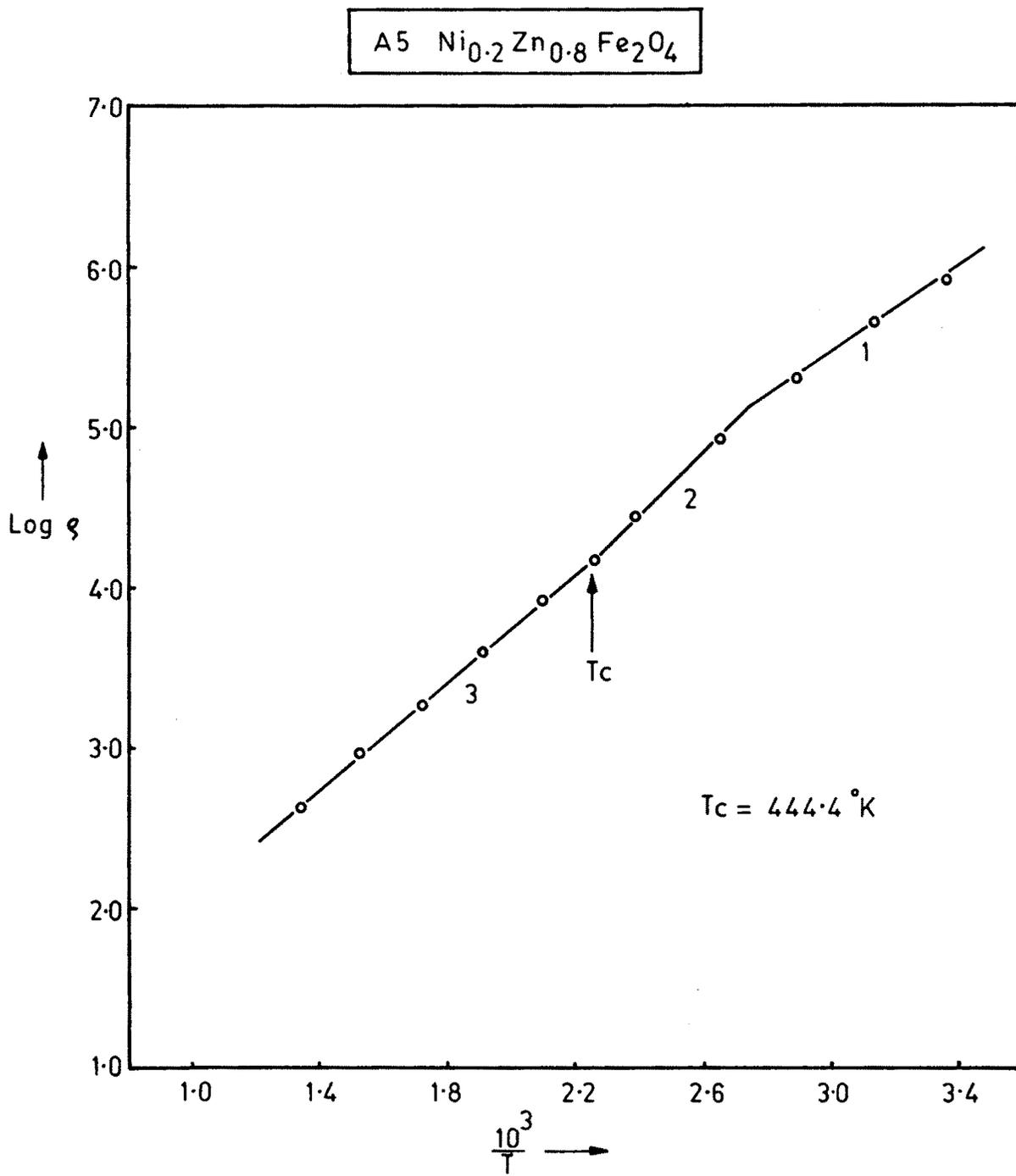


Fig. 3-6

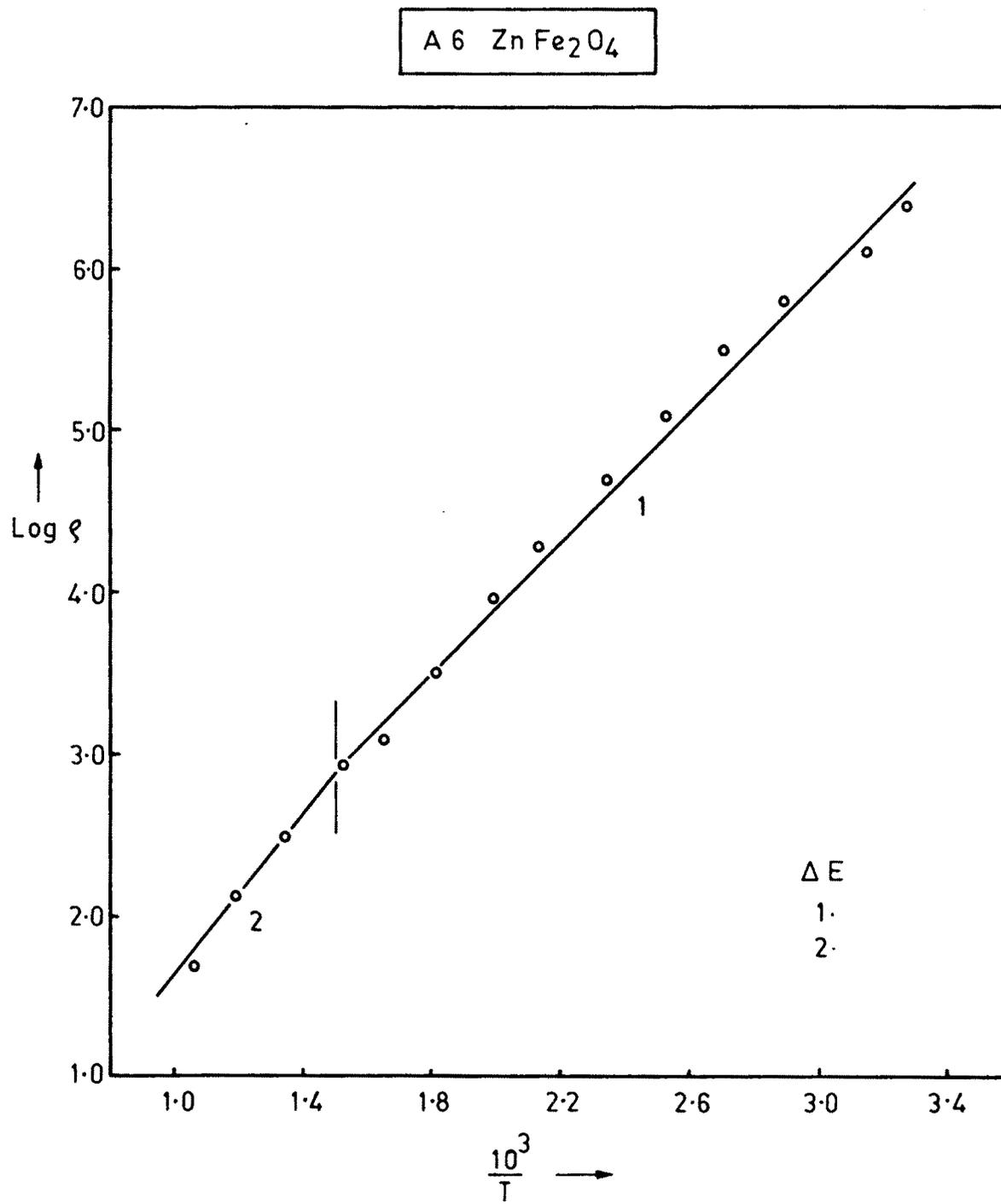


Fig. 3.7

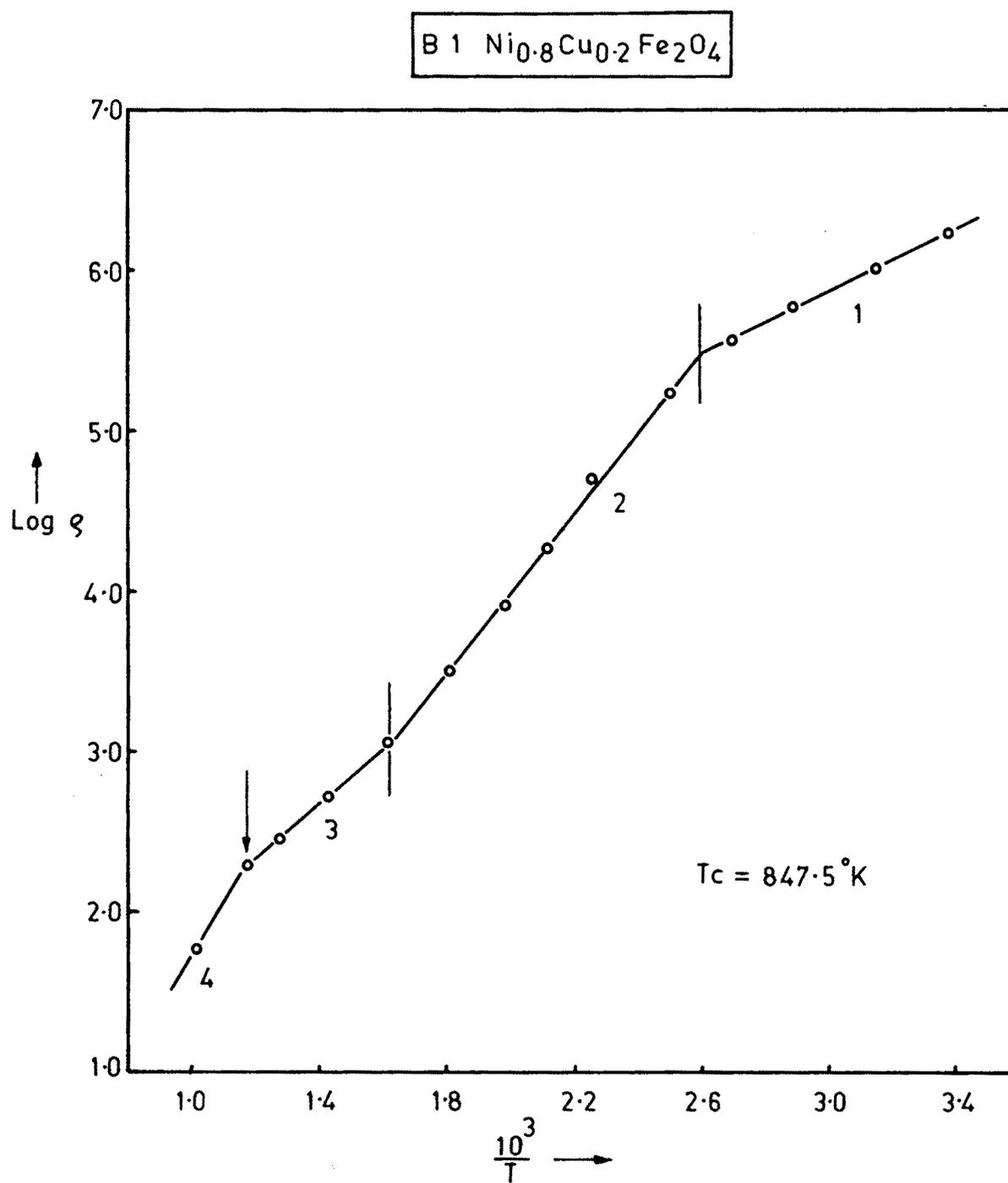


Fig. 3·8

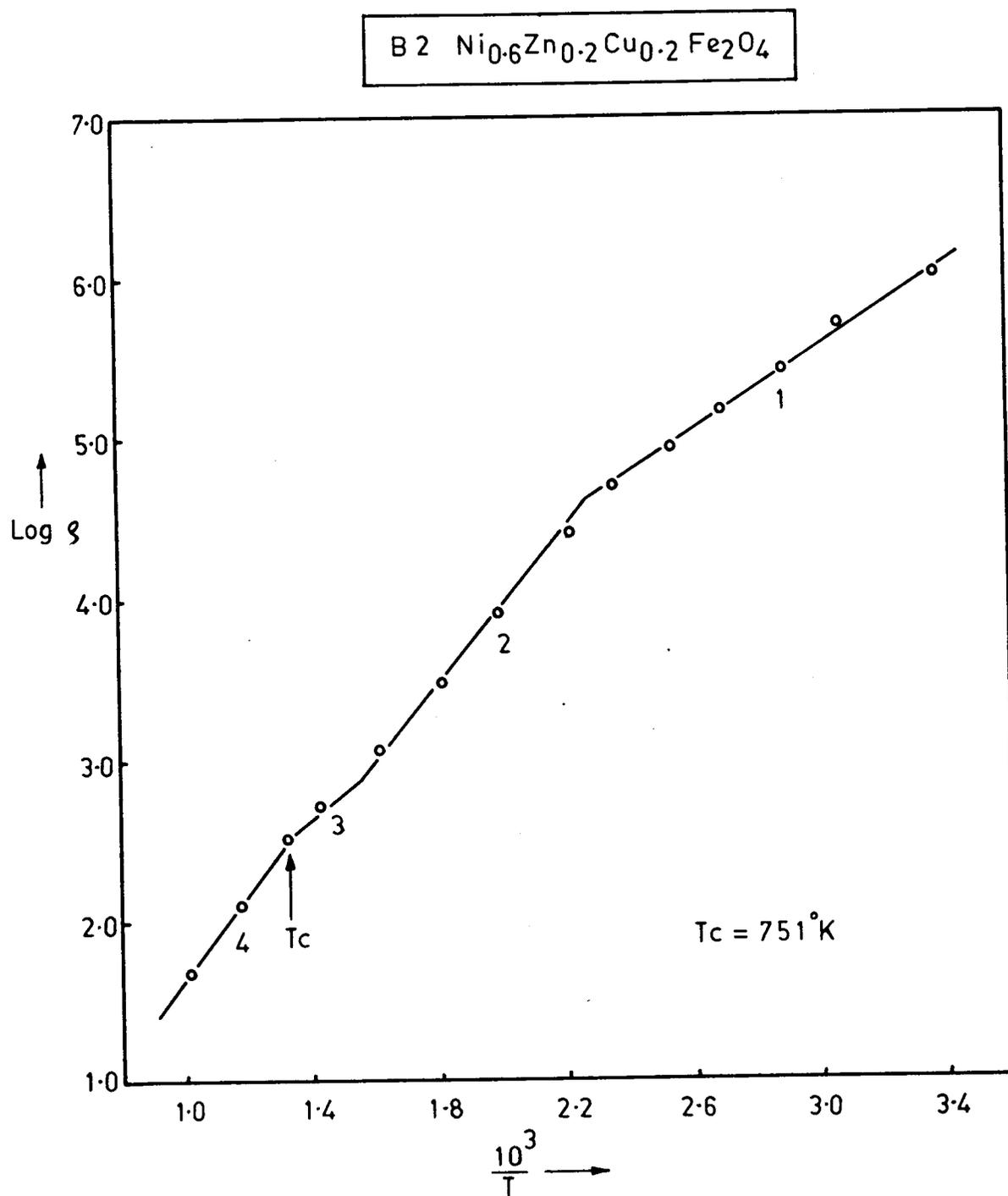


Fig. 3-9

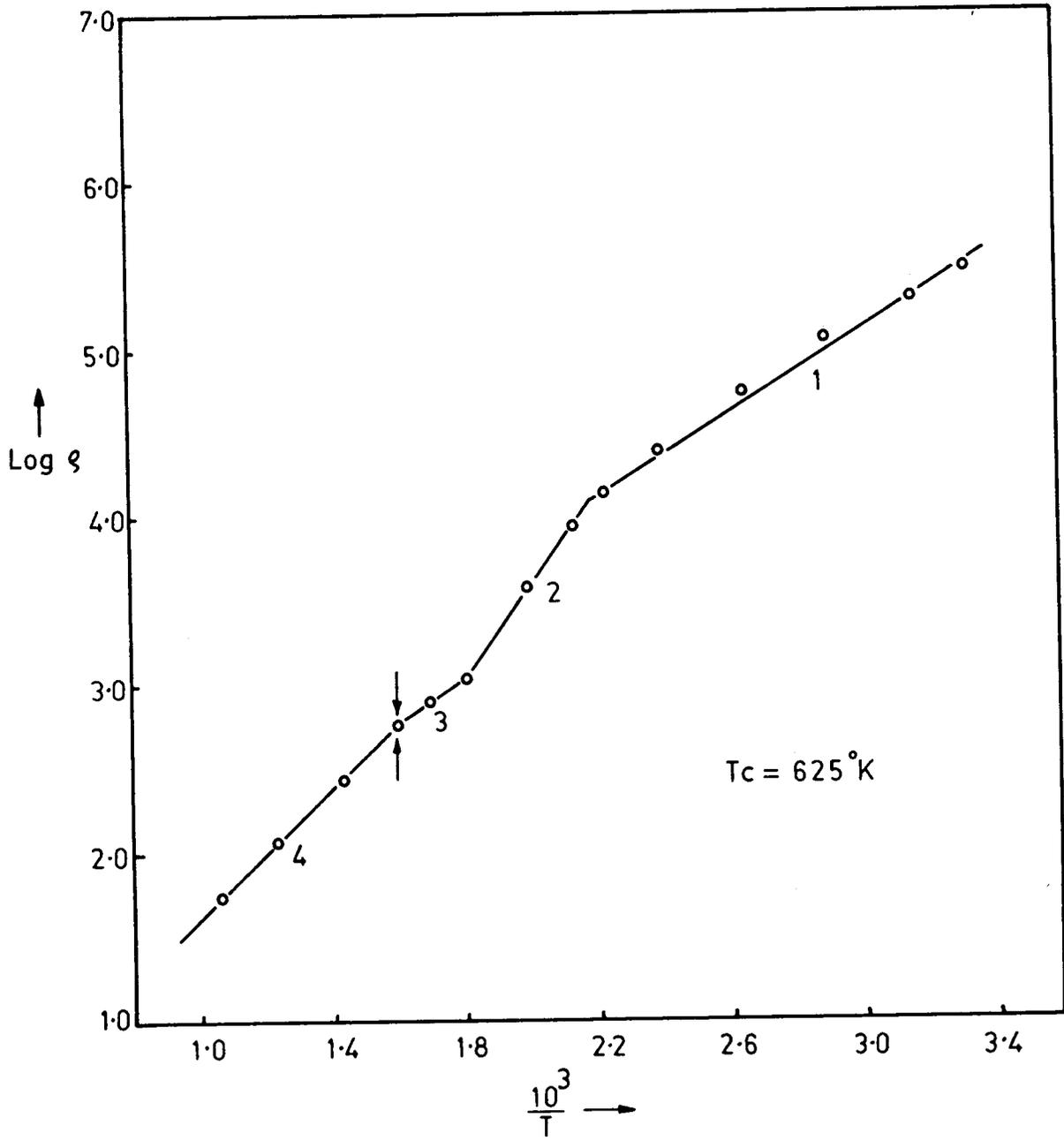
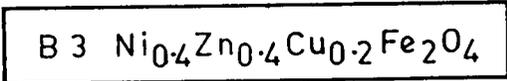


Fig. 3-10

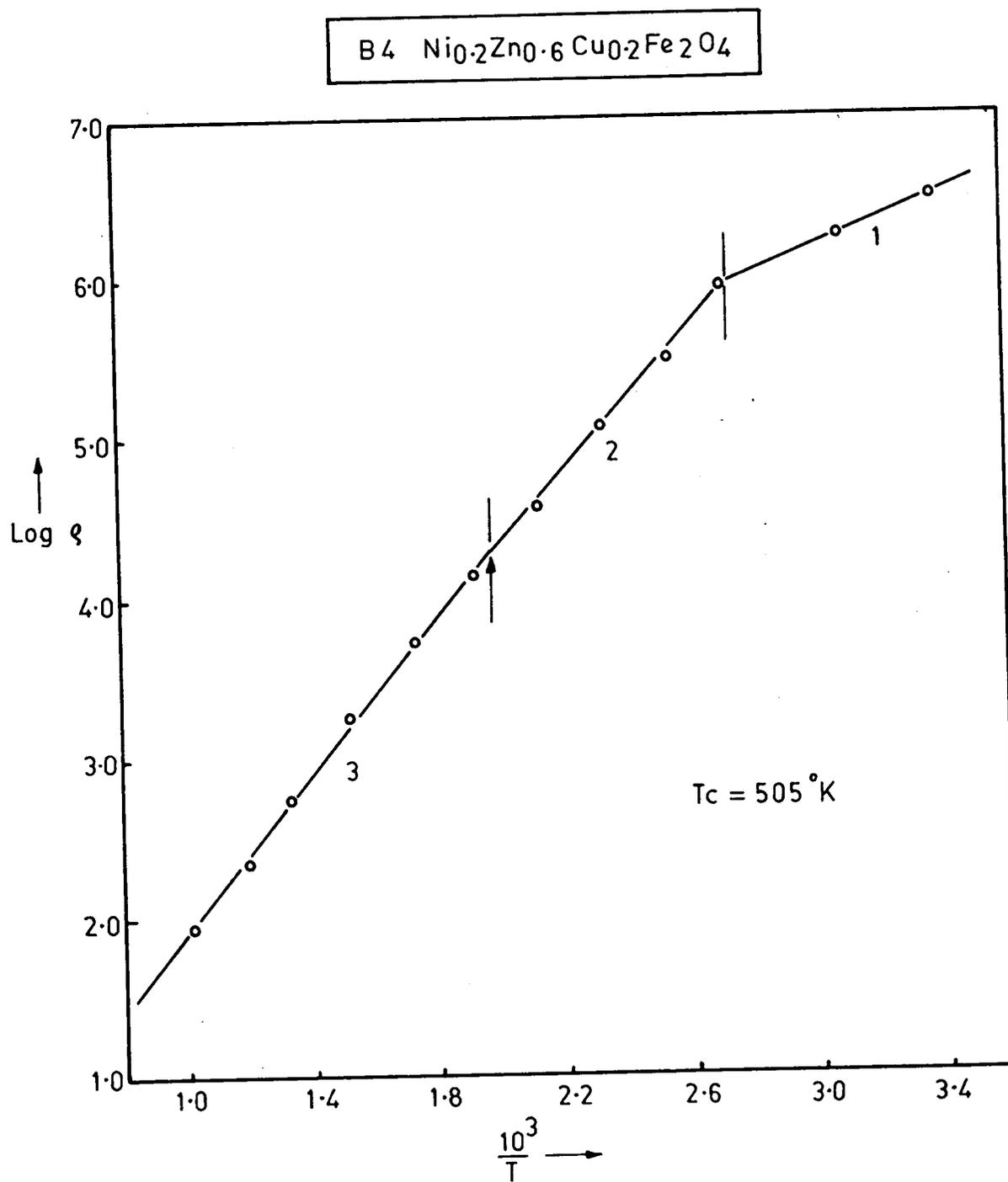


Fig.3.11

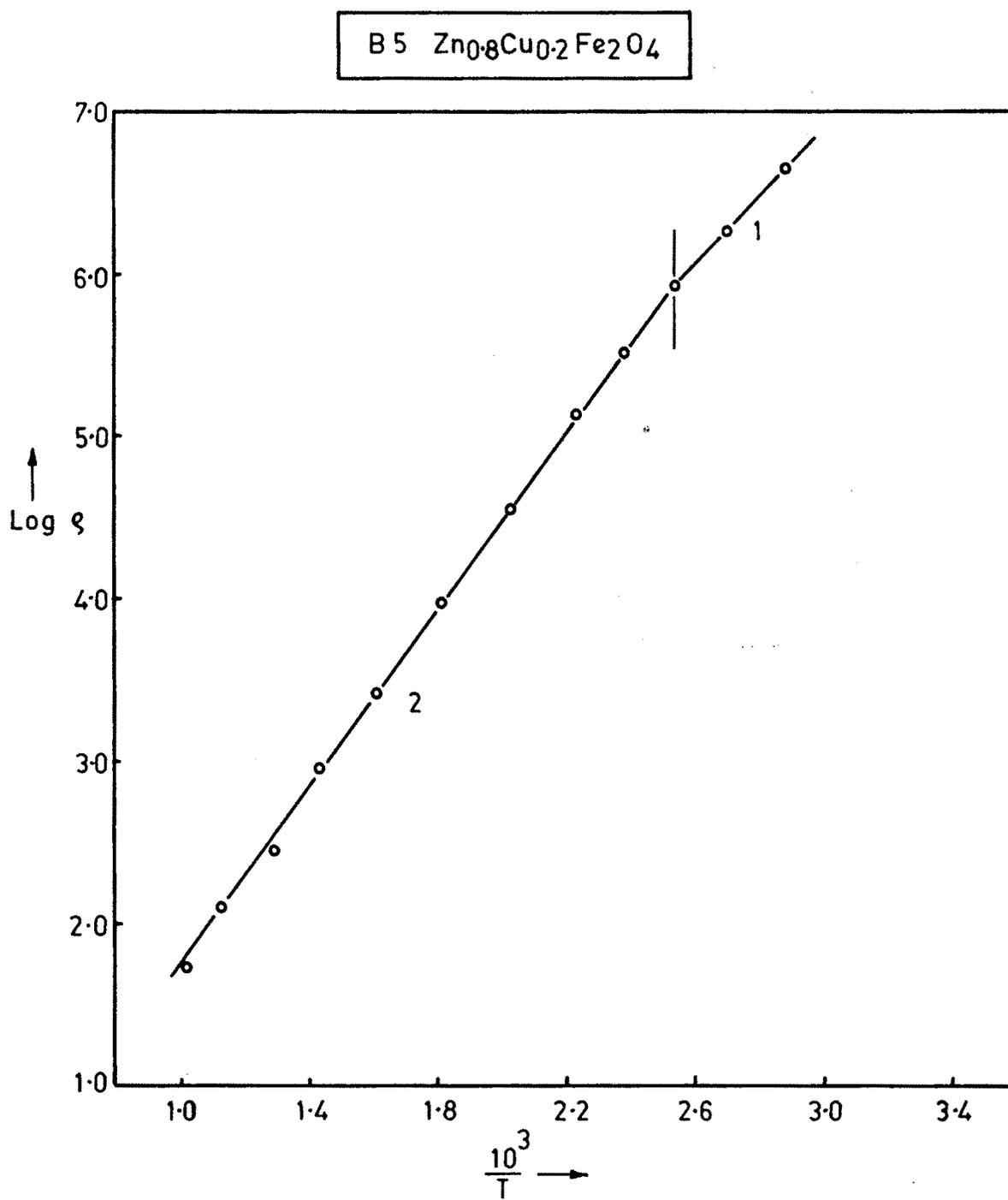


Fig. 3·12

two trends. For the samples  $A_1, A_2, A_3, A_4$ , four regions are seen with three breaks indicated by arrows (The break is indicated by an arrow corresponding to the Curie temperature). For the samples  $A_5$  and  $A_6$  only two regions are seen with only one break. Similar trend is exhibited by the series of samples B. Samples  $B_1$  and  $B_3$  show four regions with three breaks and  $B_2, B_4$  three regions with two breaks while  $B_5$  showing only one break and with two regions.

All the plots of  $\log \rho$  versus  $10^3/T$  exhibit a linear relationship suggesting that the resistivity obeys a relation

$$\rho = \rho_0 \exp. (\Delta E/KT) \quad \dots \quad (3.5)$$

where  $\rho$  = Resistivity of the material at temperature T

$\rho_0$  = Resistivity at  $0^\circ\text{C}$

$\Delta E$  = Activation energy,

K = Boltzmann constant

T = Absolute temperature

Relation (3.4) is the same as (3.3) with the only change, that the temperature independent constant C is replaced by  $\rho_0$ .

The breaks and discontinuities that occur in  $\log \rho$  versus  $10^3/T$  plots can be attributed to several sources. Komar and Klivshin<sup>2</sup> have observed changes in the activation energies for conduction which occur at high temperature in several ferrites and correlated with the ferromagnetic Curie temperature of the ferrites. This offers a solid evidence for the influence of

magnetic ordering upon conductivity in ferrites<sup>16</sup>. The breaks may also be due to change in conduction mechanism<sup>17</sup>. Recently Ghani et al<sup>8</sup> have shown more than one break in the temperature variation of resistivity in case of Cu-Ni ferrites. They have attributed the conduction mechanism in the first region to presence of impurities, in the second region to the phase transition from tetragonal to cubic and in the third region to magnetic ordering change.

A detectable change in the slope of the  $\log \rho$  versus  $10^3/T$  plots for various compositions has been observed. This change in the slope indicates the change in the activation energy. Table (3.1) shows these changes in the activation energy in the four different regions. It is clearly seen that the activation energy goes on changing, being maximum in the region at highest temperature and minimum in the region at low temperatures. The low values of  $\Delta E$  in region one (at low temperatures) mean less activation for the conduction electron. It may well be attributed to the impurity conduction which is generally observed in the ferrites at low temperature. In the region two characterised by slightly more values of  $\Delta E$  the conductivity may be influenced either due to the phase transition as suggested by Ghani et al. or may be due to some impurity phases present in the ferrites and formation of some undetected phases at that temperature as discussed in 2.2.

Table No. 3.1

Ferrite	Composition	Activation energy $\Delta E$ (eV) Region			
		1	2	3	4
A <sub>1</sub>	NiFe <sub>2</sub> O <sub>4</sub>	.4899	.3386	.6455	1.351
A <sub>2</sub>	Ni <sub>0.8</sub> Zn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.2648	.4766	.2979	.8341
A <sub>3</sub>	Ni <sub>0.6</sub> Zn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	.3664	.4668	.2327	.4519
A <sub>4</sub>	Ni <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	.2880	.5030	.1906	.4807
A <sub>5</sub>	Ni <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	.2648	.3904	.3297	
A <sub>6</sub>	ZnFe <sub>2</sub> O <sub>4</sub>	.3976	.4866		
B <sub>1</sub>	Ni <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.1887	.4866	.3526	.5363
B <sub>2</sub>	Ni <sub>0.6</sub> Zn <sub>0.2</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.2402	.4766	.3078	.5114
B <sub>3</sub>	Ni <sub>0.4</sub> Zn <sub>0.4</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.2391	.4567	.2532	.2863
B <sub>4</sub>	Ni <sub>0.2</sub> Zn <sub>0.6</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.1588	.4567	.4916	
B <sub>5</sub>	Zn <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	.3313	.5363		

Table No. 3.2

Ferrite	Composition	$T_c$ by expt. $^{\circ}\text{K}$	$T_c$ by graph $^{\circ}\text{K}$
A <sub>1</sub>	NiFe <sub>2</sub> O <sub>4</sub>	907	893
A <sub>2</sub>	Ni <sub>0.8</sub> Zn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	805	844
A <sub>3</sub>	Ni <sub>0.6</sub> Zn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	698	746
A <sub>4</sub>	Ni <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	553	571
A <sub>5</sub>	Ni <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	473	444
A <sub>6</sub>	ZnFe <sub>2</sub> O <sub>4</sub>	-	
B <sub>1</sub>	Ni <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	868	846
B <sub>2</sub>	Ni <sub>0.6</sub> Zn <sub>0.2</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	766	751
B <sub>3</sub>	Ni <sub>0.4</sub> Zn <sub>0.4</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	644	625
B <sub>4</sub>	Ni <sub>0.2</sub> Zn <sub>0.6</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	482	505
B <sub>5</sub>	Zn <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	-	

The breaks in the conductivity separating regions three and four in case of samples  $A_1, A_2, A_3, A_4, B_1, B_3$  and two and three in case of samples  $B_2$  and  $B_4$  give a temperature which nearly coincides with the Curie temperature suggesting a magnetic ordering change taking place in the samples. The change in the activation energy in the two regions indicates that the magnetic ordering has effect on the conductivity.

The plots of  $\log \rho$  versus  $1/T$  show linear variation of  $\log \rho$  with  $1/T$  which is a characteristic of the semiconducting materials. The resistivity can be written as

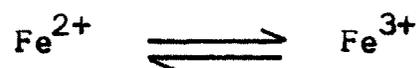
$$\rho = e (n_e \mu_e + n_p \mu_p)$$

where  $n_e$  and  $n_p$  are the concentrations of mobile carriers and  $e$  is the electronic charge.

The electrical resistivity, the change in activation energy at Curie point and the relationship of activation energy with the composition can be explained and discussed only in the light of the mechanisms of the hopping of polaron process which has been successfully employed to explain the conduction mechanisms in ferrites<sup>19</sup>. Therefore, the polaron hopping, although thermally activated in both the temperature regions appears to have lower activation energy in the magnetic region below Curie temperature. This is bound to be the case as the polaron in the case of ferrite does not significantly

involve the strain in ionic lattice as in the case of other ionic solids due to the fact that the d-electrons constitute the polaron. The cooperative behaviour would be the characteristic of such a polaron giving rise to lower activation energy. However, the clear explanation of these and the lower temperature conductivity need further detailed analysis<sup>20</sup> and studies.

The conductivity in ferrites has been associated to the presence of ions of a given element in more than one valance state in general<sup>21</sup>. These ions having the valence state get distributed randomly over the crystallographically equivalent sites. The high conductivity of  $\text{Fe}_3\text{O}_4$  has been attributed to the presence of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions<sup>22</sup> on identical sites (B site). The electrons move from divalent iron ions to the trivalent iron ions within the octahedral positions and the transitions do not cause a change in the energy state of the crystal i.e.



The values of  $\Delta E$  to cause usual electron hopping are of the order of 0.2 eV and less<sup>23</sup>.

In the ferrites having the spinel structure, the B-B distances are smaller than A-A and A-B distances. Even then the B-B distance is more larger than the sum of ionic radii of the cations involved, indicating a little or no overlap between d-d

wave functions of 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 a hopping process. The result of the conduction by hopping process is large effective mass and low mobility to current carriers. The temperature dependence of electrical conductivity in such a case involves less of temperature dependent concentration of carriers and mostly associated with the temperature dependant mobility. The mechanism of the hopping process itself involves occasional excitation by lattice vibration of the carriers with high degree of probability. Heikes and Johnston<sup>24</sup> have given mobility of hopping process as

$$\mu = \frac{ed^3\nu}{KT} \exp \left( - \frac{q}{KT} \right)$$

Thus, mobility which is a central factor deciding the activation energy depends on the phonon spectrum of the crystal on one hand and shows local variation due to local surroundings on the other.

The values of  $\Delta E$  from table 3.1 indicate that the hopping process due to polaron is favoured in case of our ferrites. The theory of conductivity has been explained on the hopping of polarons due to thermal activation<sup>25</sup>.

In solids with large coupling constant and a narrow conduction band small polaron formation is more probable. In

oxides of iron group of metals the overlap of 3-d wave functions between neighbouring metal ions is relatively small. There is a strong experimental proof for the existence of small polarons and the hopping process<sup>26,27</sup>. The energy levels and bands for ferrites have been calculated only after making a number of simplifying assumptions and using suitable approximations<sup>26</sup>. Of late Klinger has explained the conduction mechanism in magnetite like solids using two phase polaron model<sup>27</sup>. He has concluded that at low temperatures the conduction is via thermally activated motion of strongly correlated polarons and at high temperatures via weakly activated hopping motion or a non activated Brownian-like tunneling motion of polarons.

The activation energy in the paramagnetic region is found to be more than that for ferrimagnetic region (Table 3.1). This can be attributed to the effect of the magnetic ordering in the conduction process<sup>15</sup>. According to strict theoretical considerations the anomalous changes in the activation energy occur at the disordered temperature.

The compositional variation of resistivity has been shown in the figures 3.13 and 3.14, for the temperatures 373<sup>o</sup>K and 714<sup>o</sup>K for the samples of series A ( $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ) and B ( $\text{Ni}_{0.8-x}\text{Zn}_x\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ ). Similar trend in the variation is exhibited by these samples at the two temperatures indicated. For Ni-Zn ferrites (Series A), first the resistivity decreases with the increase in the Zn content. For the sample,  $\text{Ni}_{0.4}$

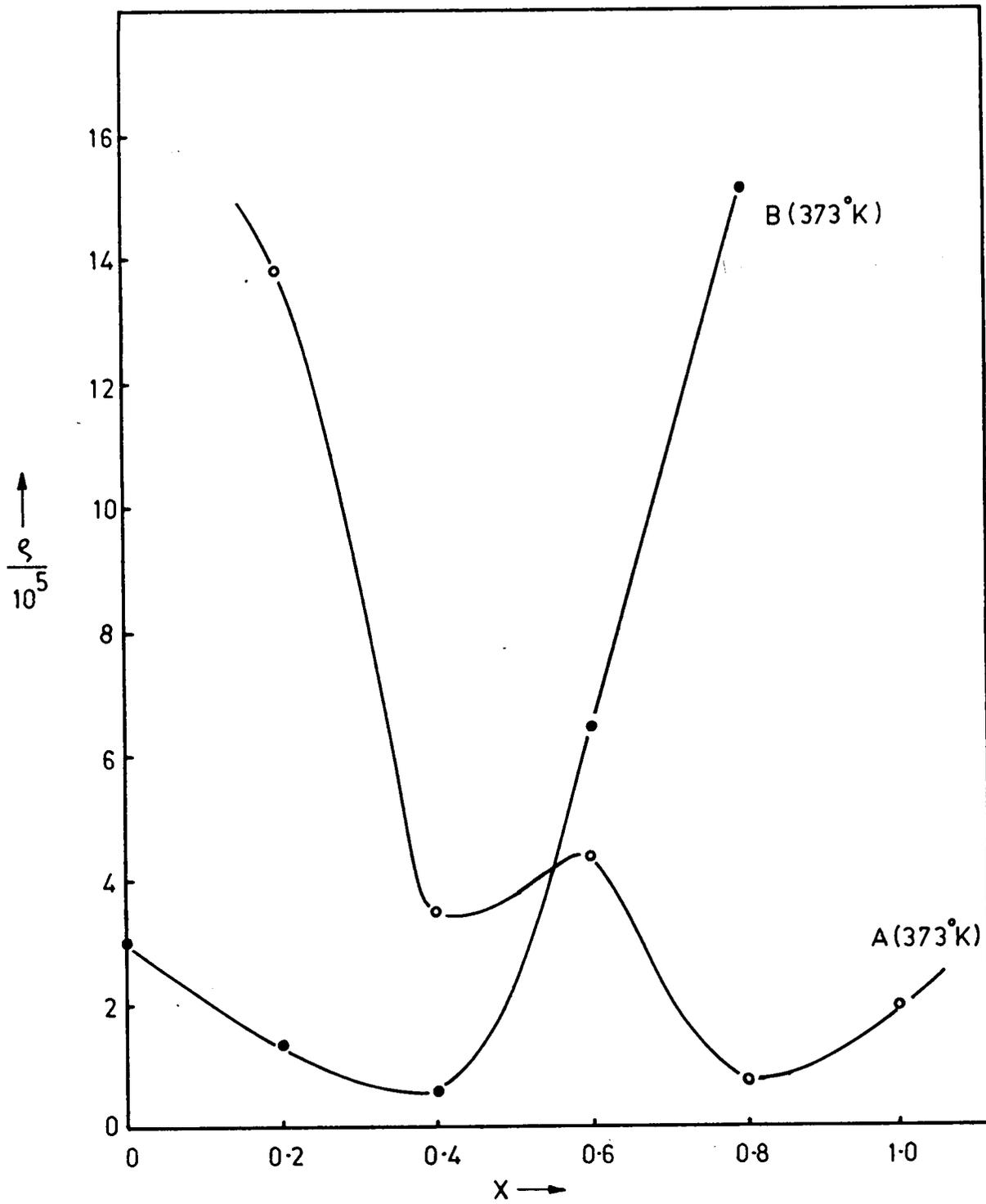


Fig. 3-13 PLOT OF  $\xi$  vs X AT 373°K

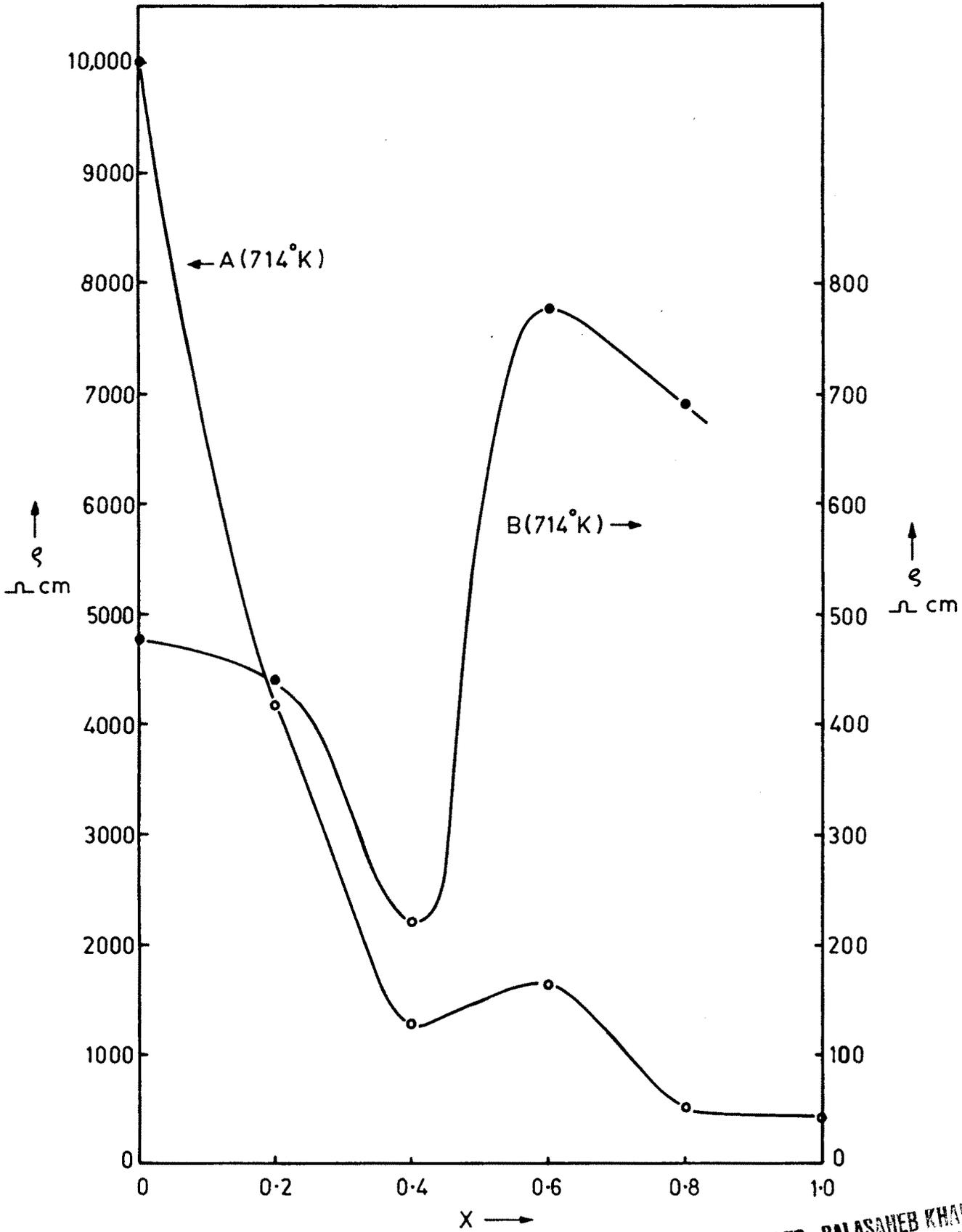


Fig. 3-14: PLOT OF  $\xi - X$  AT  $714^{\circ}\text{K}$

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$Zn_{0.6}Fe_2O_4$  the resistivity shows slight increase and decrease in value for the sample  $Ni_{0.2}Zn_{0.8}Fe_2O_4$ . For  $ZnFe_2O_4$  the value of  $\rho$  shows again an increasing trend.  $\rho$  is found to be maximum for Ni ferrite and minimum for  $Ni_{0.2}Zn_{0.8}Fe_2O_4$ . This trend is repeated at  $714^\circ K$ . For Ni-Zn ferrite series containing copper (i.e. Series B) almost similar trend can be seen, in compositional variation of resistivity at  $373^\circ K$  and  $714^\circ K$ . The resistivity shows two regions. In the first region a decreasing trend with the increase in the Zn content upto 40 % of zinc is revealed, while the resistivity is on the increase beyond 40 % content of zinc in the samples.

*Saturation magnetization*  
 The compositional variation of resistivity and the compositional variation of  $M_s$  (Fig. 4.1) bear one to one correspondence indicating the role of magnetic ordering in influencing the resistivity of the ferrite samples. This statement is corroborated by the fact that there is a decrease in  $T_c$  with increasing zinc content. Guillauds and Gorter have given compositional variation of  $M_s$  for series of ferrites<sup>28,29</sup>. The magnetization behaviour of the zinc containing ferrites has been explained on the basis of three sub-lattice model by Yafet and Kittel<sup>30</sup>. Recently Srivastava et al.<sup>31</sup> have used three sub-lattice model to determine exchange constants in spinel ferrites.

The variation of lattice parameter with the content of zinc shows a linear increase from  $8.33 \text{ \AA}$  in case of nickel

ferrite to  $8.44 \text{ \AA}^0$  in case of zinc ferrite. This increase is due to the more ionic radii ( $0.83 \text{ \AA}^0$ ) for zinc than that of  $\text{Ni}^{2+}$  ( $0.73 \text{ \AA}^0$ )<sup>32</sup>. This indicates that the unit cell dimension goes on increasing with the addition of zinc. The decrease in  $\rho$  can be attributed to the more room available for the polaron hopping on the B sites upto 40 % content of zinc. Beyond 40 % content of zinc there is more and more weakening of A-B interactions leading to the dominant non-magnetic behaviour of the sample. As a result of the phase transition the conduction is also modulated which has shown an interesting trend with the increase of zinc content.

An interesting behaviour is exhibited by the Ni-Zn ferrite with the addition of copper. The peak in the variation of  $\rho$  that is observed for 60 % content of zinc in NiZn ferrite disappears with the addition of copper. Copper is a Jahn-Teller ion. This deviation may be attributed to the effect of Jahn-Teller ion on the ground states of  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  ions in spinel ferrites<sup>33</sup>.

The variation of  $\log \rho$  versus  $1/T$  has shown more <sup>than</sup> one break for the 40 % content of zinc, however, the samples of Ni-Zn ferrite and Ni-Zn ferrite containing copper with 60 % and more zinc content show only one break. This can be explained on the magnetic ordering change taking place in the samples due to excessive addition of zinc.

The conductivity of ferrites presents many complexities. The interpretation of D.C. resistivity in polycrystalline material becomes, rather involved, due to the presence of grain boundaries, giving rise to additional scattering. The cation or anion vacancies may be responsible for acceptor and donor levels and the number of charge carriers may remain uncertain in a ferrite sample, especially when it has undergone a unique heat treatment. This presents additional complexities from the point of view of interpretation of d.c. conductivity data. Besides the anion or cation vacancies may also contribute a component of ionic conductivity to the D.C. conductivity of the sample<sup>34</sup>. Various conduction mechanisms based on different models for the donor levels have been given by different workers<sup>34-37</sup>.

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