CHAPTER-III: RESISTIVITY STUDIES

3.1 INTRODUCTION

Ferrites are semiconductors by nature and have a large range of variation in resistivity. As the Ferrites possess high resistivity they are used in high frequency operation which exhibit large eddy current losses. The studies on conductivity provide useful data from the application point of view as well as from the point of view of understanding the mechanism of conduction. In this chapter the studies on resistivity of $Xn_xMg_{1-x}Fe_2O_4$ samples, slow cooled and quenched from 800°C, in the temperature range of 300°K to 873°K have been presented. A brief survey of conductivity models is given and results are explained on their basis.

3.2 Survey of Conductivity Models

In Ferrites Fe^{+2} ions are present among Fe^{+3} ions which lead to the n-type conductivity[1] at temperature which are high enough so that extra electron on the Fe^{+2} ion can move through the crystal. The resistivity ρ can be written as -

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

where e = electronic charged, n_e and n_h are concentrations of mobile carriers, μ_e and μ_e are the mobilities of carriers.

The temperature dependence of resistivity in many cases is given by

$$\rho = C\exp\left[\frac{\Delta E}{KT}\right]$$

where C = temperature independent constant which depends upon the nature of the material. K is Boltzman constant. T = absolute temperature. ΔE = Activation energy.

Breaks and discontinuities that occur in the log σ Vs $\frac{1}{T}$ plots can be ascribed to several sources. Komar and Klivshin[2] have observed changes in the activation energies for conduction which occur at high temperature in several ferrites and correlate with Ferromagnetic curie temperatures of the ferrites. This offers a solid evidence for influence of magnetic ordering upon conductivity in ferrites.[3] The breaks may also be due to change in dominant conduction mechanism.[4] For the transition metal oxides the model of electron hopping has been proposed.[5] In this model electrons jump from one lattice site to another. On the basis of this model D. Condurache[6] has explained the conductivity of Cu containing ferrites.

An additional element has been introduced in the theory of electrical conductivity by "The hopping of Polarons", by thermal activation.[7] 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 function between neighbouring metal ions is relatively small. There is a strong experimental proof for the existence of small polarons and the hopping process.[7-8] The energy levels and the bands for ferrites have been calculated only after making a number of simplifying assumptions and using suitable approximations.[7]

Klinger has explained the conduction mechanism in magnetite like solids using two phase polaron model.[8] He has concluded that at low temperature the conduction is via thermally activated motion of strongly correlated polarons; and at high temperature via weakly hopping motion or a non-activated Brownian like tunnelling motion of polarons.

The conductivity of ferrites presents many complexities. The interpretation of DC resistivity in polycrystalline materials becomes rather involved due to presence of grain boundaries; giving rise to additional scattering. The cation or anion vacancies may be responsible for acceptor and donor level and the number charges 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 DC conductivity data. Besides the anions and cation vacancies may also contribute a component of ionic conductivity to the DC conductivity of the sample.[9] Various conduction mechanisms based on different models for donor levels have been given by different workers.[9-12]

3.3 D.C. Conductivity Cell

The cell for the measurement of DC 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 periferies, to ensure uniform pressure and good electrical contact between silver discs and pellet.

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

3.4 D.C. Resistivity Measurement

The measurement of the resistance of the pellet was done by a digital multimeter. The resistance was measured from room temperature upto 600°C at an interval of 25°C. The dimensions of each pellet were measured, the resistivity at various temperatures was determined and the graphs of log $\rho \longrightarrow \frac{1}{T}$ were plotted. These plots are shown in figures.

The activation energies ΔE were then determined from these graphs.

3.5 Result and Discussion

Figures 3.2, 3.3, 3.4 and 3.5 represent the variation of log Vs $\frac{10^3}{T}$ for the slow cooled ferrite system $Zn_xMg_{1-x}Fe_2O_4$, and Figures 3.6, 3.7, 3.8, 3.9, 3.10 and 3.11 represent the variation of log ρ against $\frac{10^3}{T}$ for the quenched samples of

$Zn_xMg_{1-x}Fe_2O_4$ ferrite. This variation is for the temperature range from 300°K to 873°K. The variation of resistivity exhibits the linear relationship suggesting that the variation of resistivity is governed by the relation $\rho = \rho_0 \exp\left(\frac{\Delta E}{KT}\right)$ where

ρ = resistivity of material at temperature T.

ρ_0 = resistivity of the material at 0°K.

ΔE = activation energy

K = Boltzman constant.

T = Absolute temperature.

The breaks and discontinuities that occur log ρ Vs $\frac{10^3}{T}$ plots can be attributed to several sources. Komar and Klirshin[2] have observed changes in the activation energies for conduction which occurs 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.[13] The breaks may also be due to change in conduction mechanism.[5] Recently Ghani *et al.*[14] have shown more than one break in the temperature variation of resistivity in case of Ni-Zn 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.

In Table 3.1 the values of ΔE in eV, values of curie temperatures obtained from experiment, indicated by log ρ Vs $\frac{10^3}{T}$

plots and computed values using theoretical formula are presented. Theoretical values of T_c are evaluated using Gillio's expression.[15]

Gillio has given the cation distribution for a general spinel system.

$M_{3-m}Fe_mO_4$ $(o < m < 3)$ as

$$Fe_{m\lambda}\ M_{(1-m\lambda)}\ [Fe_{(1-\lambda)m}\ M_{2-(1-\lambda)m}]O_4 \qquad (1)$$

where M represents non-magnetic ion and λ is cation distribution coefficient.

For our present system m = 2 and hence formula (1) becomes as

$$Fe_{2\lambda}M_{1-2\lambda}\ [Fe_{2(1-\lambda)}M_{2\lambda}\ ]O_4 \qquad (2)$$

Gillieo has also given the expression for T_c as

$$T_c = \frac{3\lambda(1-\lambda)\ f\ (\lambda m)\ g(\lambda m)\ mT_Q}{2[(1-\lambda)\ f(m\lambda) + \lambda g(\lambda m)]} \qquad (3)$$

For general ferrite

$$Fe_{xm}\ M_{1-xm}[Fe\ (1-x)_m M_2 - (1-x)_m]O_4$$

Gilleo's expression for curie point is

$$T_c(^oK) + \frac{3x\ (1-x)\ f(xm)\ g(xm)\ mT_Q}{2[(1-x)\ f(xm) + xg(xm)]}$$

$$f(xm) = 1-(1-xm)^5\ (1 + 5xm)$$

$$g(xm) = 1 - [1 - \tfrac{1}{2}m\ (1-x)\ ]^{11}[1 + \tfrac{11}{2}m\ (1-x)\ ]$$

T_o = constant.

T_o = 962°K with cation distribution

$$[\ Mg_{0.1}\ Fe_{0.9}\ ]^{A}\ [\ Mg_{0.9}\ Fe_{1.1}\ ]^{B}O_4$$

We have evaluated the constant T_o assuming that all Mg ions occupy B-sites, and the theoretical values of T_c = 450°C T_o = 874°K. Larois et al.[16] have suggested a method to determine curie temperatures of ferrites. We have modified this method and experimentally determined the values of curie temperature of our samples. This method is already described. A detectable change in the slope of log ρ Vs $\frac{10^3}{T}$ plots for various compositions is also seen. If ρ is mostly determined by number of hopping processes, assuming the role of scattering phenomenon and mean free path to be minimal, this change in the slope indicates the change in activation energy ΔE. These temperatures where the change occurs nearly coincides with T_c.

The conductivity in Ferrites has been associated to the presence of ions of a given element in more than one valence state in general.[17] These ions having the valence states get distributed randomly over the crystallographically equivalent sites. The high conductivity of Fe_3O_4 has been attributed to the presence of both Fe^{+2} and Fe^{+3} ions[18] on identical sites (B-sites). The electrons move from divalent iron ions to the trivalent iron ions within the octahedral positions and the transition does not cause a change

in the energy state of the crystal i.e.,

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

The values of ΔE to cause usual electron hopping are of the order of 0.2 eV and less.[19]

From Table 3.1 it is seen that the values of ΔE in ferrimagnetic region are in excess of 0.2 suggesting that the conductivity process in these ferrites is governed by hopping of polarons. Further it is seen that with the addition of zinc in the system $Zn_xMg_{1-x}Fe_2O_4$, no definite trend is exhibited by the ΔE values. However, the trend of compositional variation of ΔE in slow cooled and quenched samples is similar with the difference that the values of ΔE are lowered on quenching the samples.

In the Ferrites having the spinel structure, the B-B distances are smaller than A-A and A-B distances. Even then B-B distance is more than the sum of ionic radii of the cations involved indicating a little or no overlap between d-d-wavefunction of ions on adjacent octahedral sites. This gives rise to a situation in which 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 of current carriers. The temperature dependence of electrical conductivity in such a case involves less temperature dependent, concentration of carriers and mostly associated with

the temperature dependent mobility. The mechanism of the hopping process itself involves occasional excitation by lattice vibration of the carriers with high degree of probability. Heikes and Johnstan have given the mobility hopping process as

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

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 variations due to local surroundings on the other.

In solids with the large coupling constants and narrow conduction bond small, polarons 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 processes.[7,8] The energy levels and bond per ferrite have been calculated only after making a number of simplifying assumptions, and using suitable approximations.[7] Of late Klinger has explained the conduction mechanism in magnetite like solids, using two phase polaron model. He has concluded that at low temperature 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. This can be attributed to the effect of magnetic ordering in the conduction process.[3] According to strict theoretical consideration the anomalous changes in the activation energy occur at the disordered temperature. In Fig. 3.12 the compositional variation of ΔE is shown. It is seen that on quenching the ΔE values show a considerable reduction. However, trend of variation of ΔE in quenched samples tends to be little more regular than that exhibited by slow cooled samples. In Fig. 3.12 the compositional variation of T_c for the slow cooled and quenched samples is shown. It is seen that the T_c values show decrease with the addition of zinc in the Ferrites, also on quenching T_c values are considerably reduced. The theoretical T_c values are quite larger than the values of T_c in the slow cooled samples. The theoretical values of T_c have been calculated assuming cation distribution to be of the form -

$$(Fe_1)^A \ (Mg_1Fe_1)^B \ O_4$$

$MgFe_2O_4$ is a partially inverted ferrite. The change in the T_c values in the slow cooled samples indicates that there may be some cation migration from B site to A site, leading to the observed reduction in T_c. The same argument can be applied to the quenched samples which show further reduction in the values of T_c. Figures 3.13 and 3.14 show compositional variation of resistivity for the slow cooled and quenched samples of $Zn_xMg_{1-x}Fe_2O_4$ system. In case of slow cooled samples the resistivity decreases with the addition of zinc which is in one to one correspondence with the

trend exhibited by T_c values.

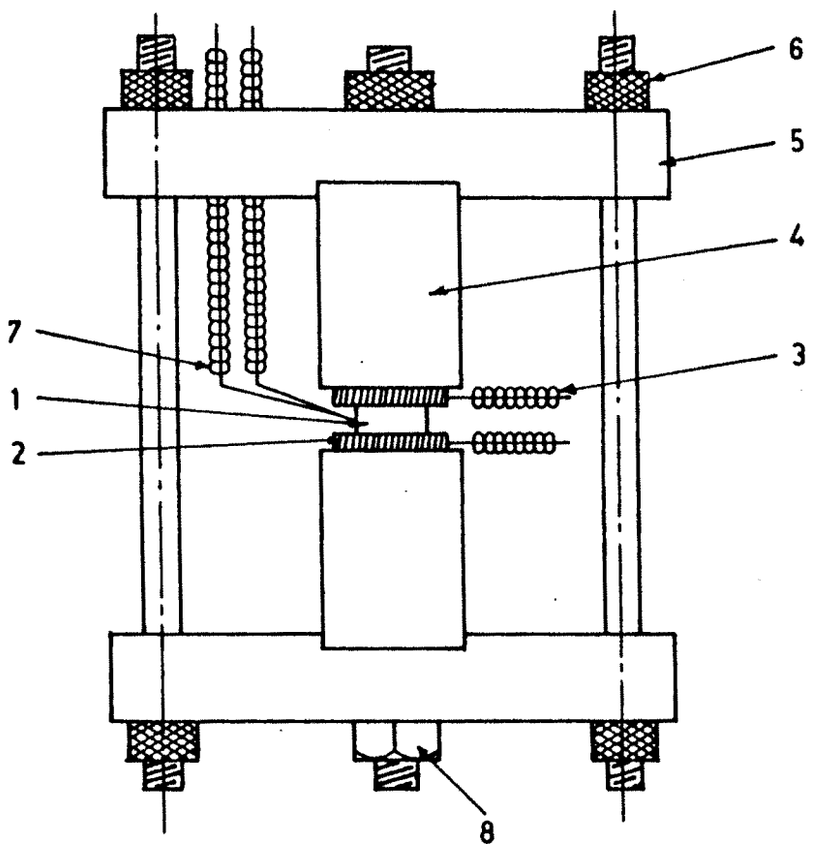
A quenched sample also shows the similar behaviour for the content of zinc beyond 50 per cent. However, for the content of zinc corresponding to x=0 to x=0.6, the resistivity shows an increasing trend. The increase in resistivity may be attributed to hopping of polaros with the addition of zinc. The compositional variation of resistivity and magnetisation in case of quenched samples also bear one to one correspondence which indicates that the resistivity of the ferrites is influenced by magnetic ordering.

The conductivity of ferrites present many complexities. The interpretation D.C resistivity in polycrystalline materials 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 or donor level and 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 DC conductivity data. Besides the anion or cation vacancies may also contribute a component of ionic conductivity to the DC conductivity of the samples.[5] Various conduction mechanisms based on different models for the donor levels have been given by different workers.[9-12]

Table 1.1: Values of ΔE, Curie temps. for $Mg_xZn_{1-x}Fe_2O_4$ system

History	Samples	ΔE values in eV		Curie temperatures in °C		
		Para	Ferri	Experimental	Theoretical	From log $\frac{1}{T}$ graphs.
Slow-cooled	$MgFe_2O_4$	0.992	0.3637	482	450	420
	$Zn._2Mg._8Fe_2O_4$	0.496	0.682	375	419	350
	$Zn._4Mg._6Fe_2O_4$	0.506	0.314	282	325	175
	$Zn._6Mg._4Fe_2O_4$	0.434	0.3156	145	162	125
	$Zn._8Mg._2Fe_2O_4$	-	-	-	-	-
	$ZnFe_2O_4$	-	-	-	-	
Quenched from 800°C	$MgFe_2O_4$	0.496	0.25	435	-	393
	$Zn._2Mg._8Fe_2O_4$	0.372	0.29	340	-	275
	$Zn._4Mg._6Fe_2O_4$	0.48	0.3273	245	-	203
	$Zn._6Mg._4Fe_2O_4$	0.396	0.192	120	-	115°
	$Zn._8Mg._2Fe_2O_4$	-	-	-	-	-
	$ZnFe_2O_4$	-	-	-	-	-

THE CONDUCTIVITY CELL



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

Fig.3·1

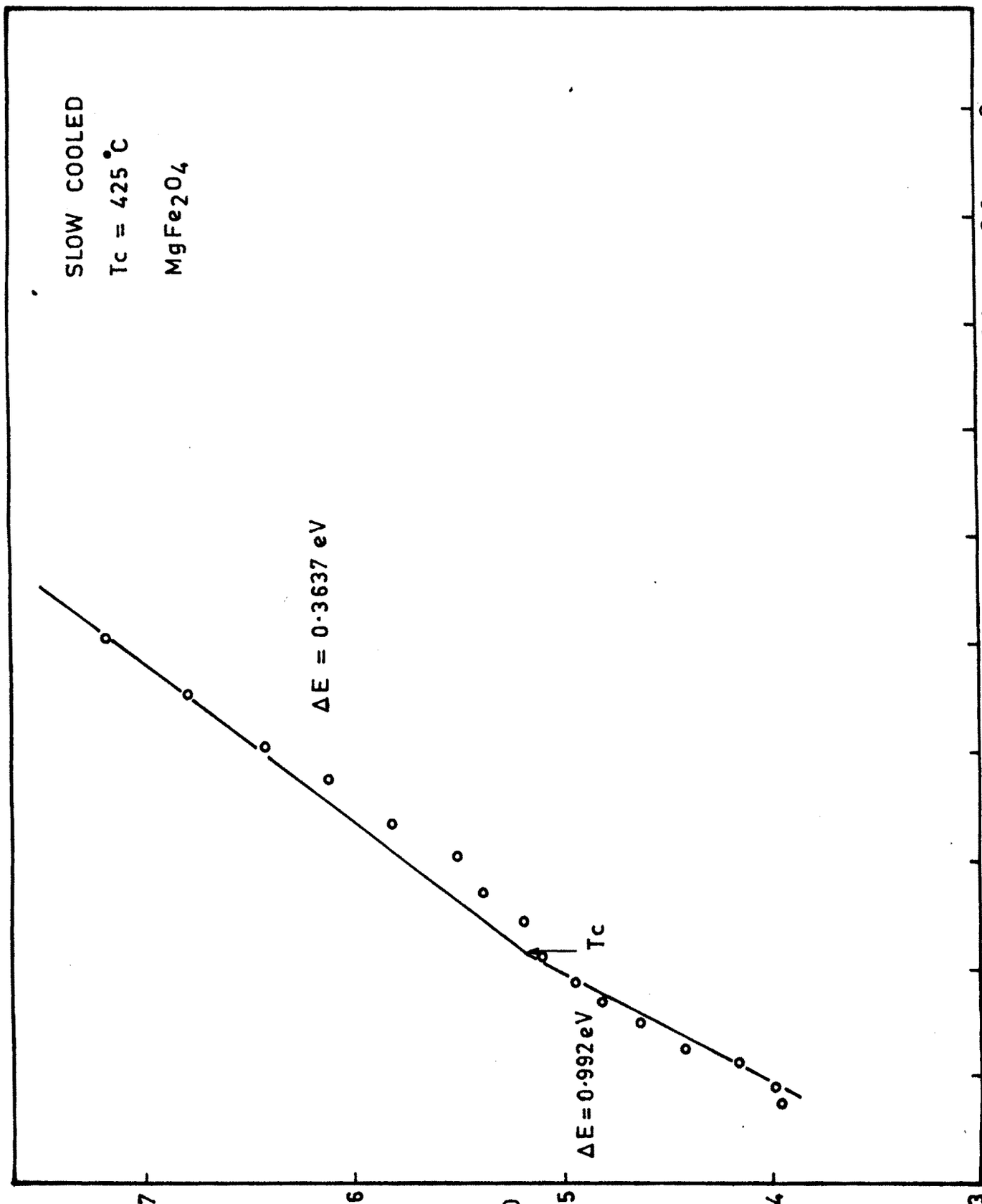

SLOW COOLED
Tc = 425 °C
MgFe2O4
ΔE = 0·3637 eV
ΔE = 0·992 eV
Tc
Log10 e
1/T
7
6
5
4
3
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3

Fig. 3·2

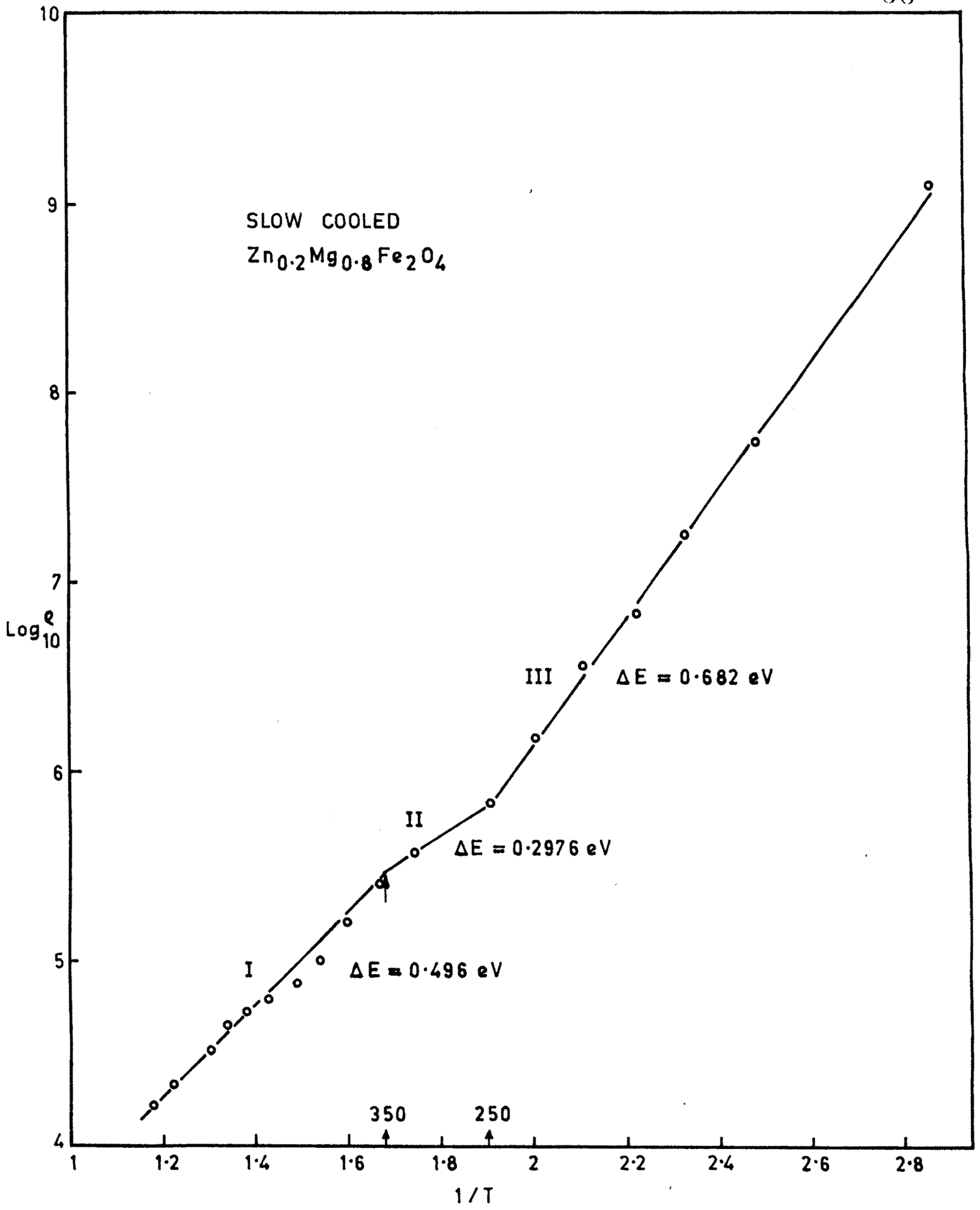

SLOW COOLED
$Zn_{0.2}Mg_{0.8}Fe_2O_4$
$\log_{10}\rho$
1/T
I
II
III
ΔE = 0·496 eV
ΔE = 0·2976 eV
ΔE = 0·682 eV
350
250
10
9
8
7
6
5
4
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8

Fig. 3·3

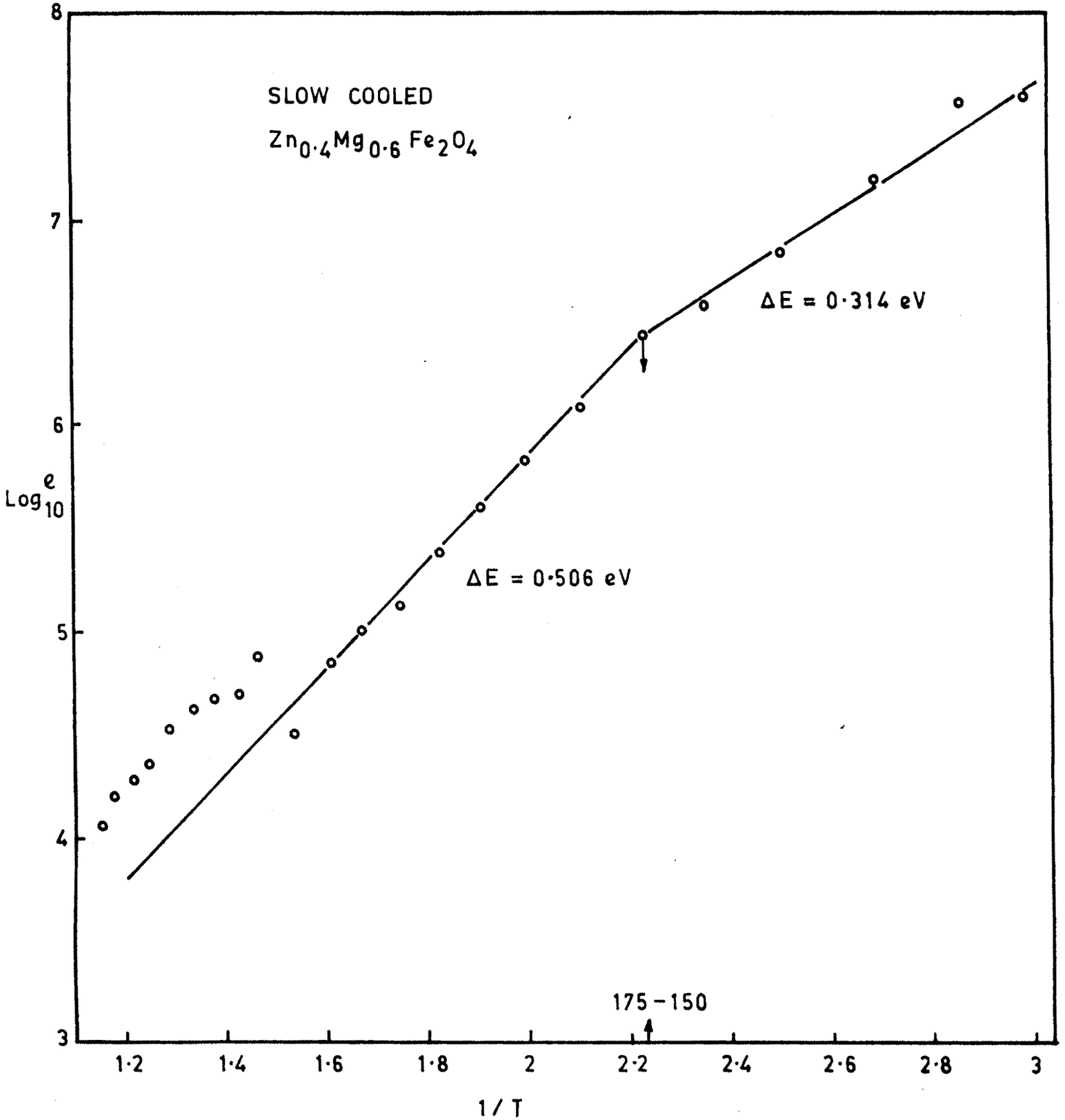

SLOW COOLED
$Zn_{0.4}Mg_{0.6}Fe_2O_4$
ΔE = 0·314 eV
ΔE = 0·506 eV
175 – 150
Log_{10}^{e}
1/T
8
7
6
5
4
3
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3

Fig. 3·4

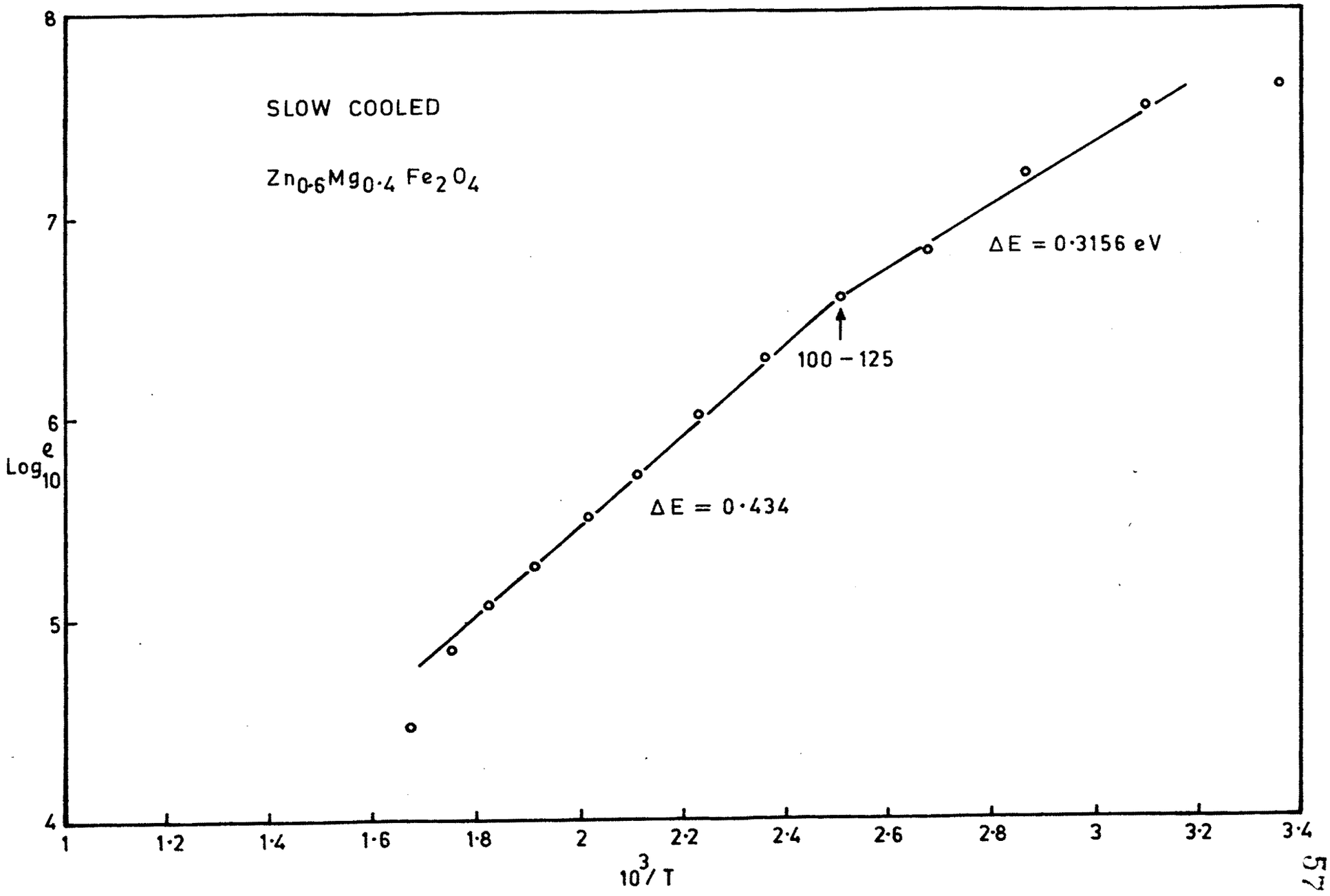

SLOW COOLED
$Zn_{0.6}Mg_{0.4}Fe_2O_4$
ΔE = 0·3156 eV
100 – 125
ΔE = 0·434
$\log_{10}^{e}$
$10^3/T$
8
7
6
5
4
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
3·2
3·4

Fig. 3·5

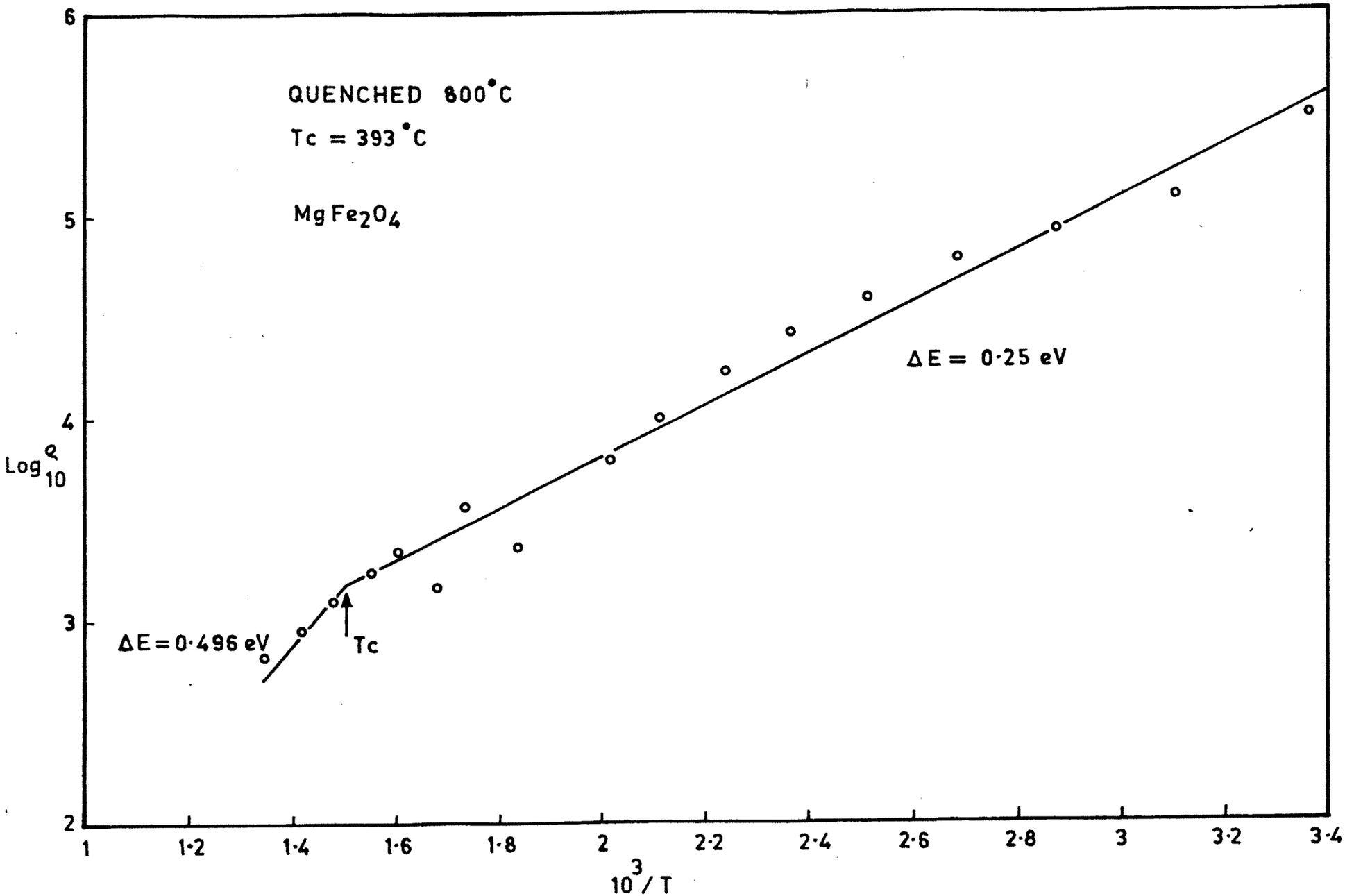

QUENCHED 800°C
Tc = 393 °C
Mg Fe2O4
ΔE = 0·25 eV
ΔE = 0·496 eV
Tc
Log10 ρ
10^3 / T
6
5
4
3
2
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
3·2
3·4

Fig. 3·6

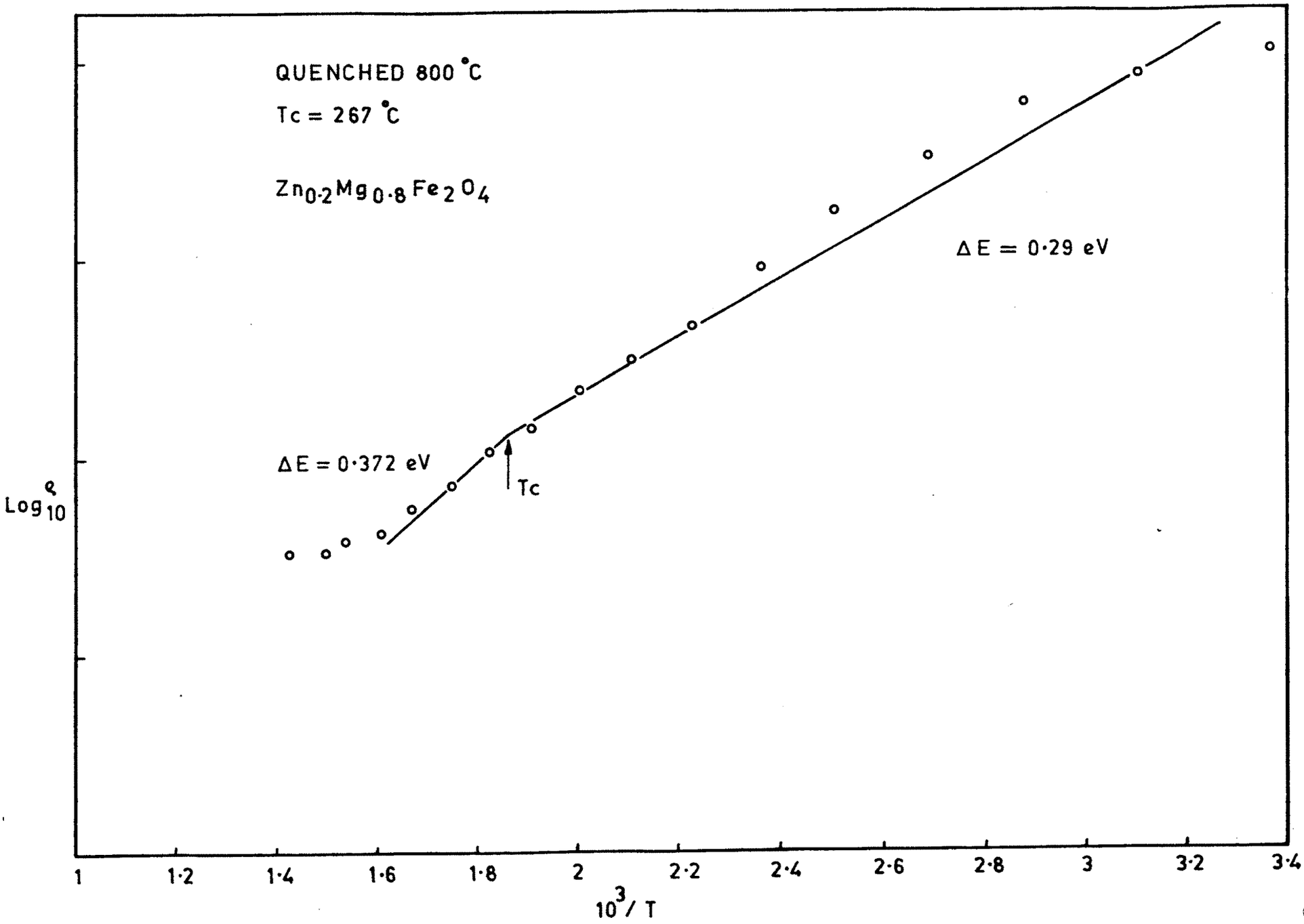

QUENCHED 800 °C
Tc = 267 °C
$Zn_{0.2}Mg_{0.8}Fe_2O_4$
ΔE = 0·29 eV
ΔE = 0·372 eV
Tc
ρ
Log_{10}
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
3·2
3·4
$10^3/T$

Fig. 3·7

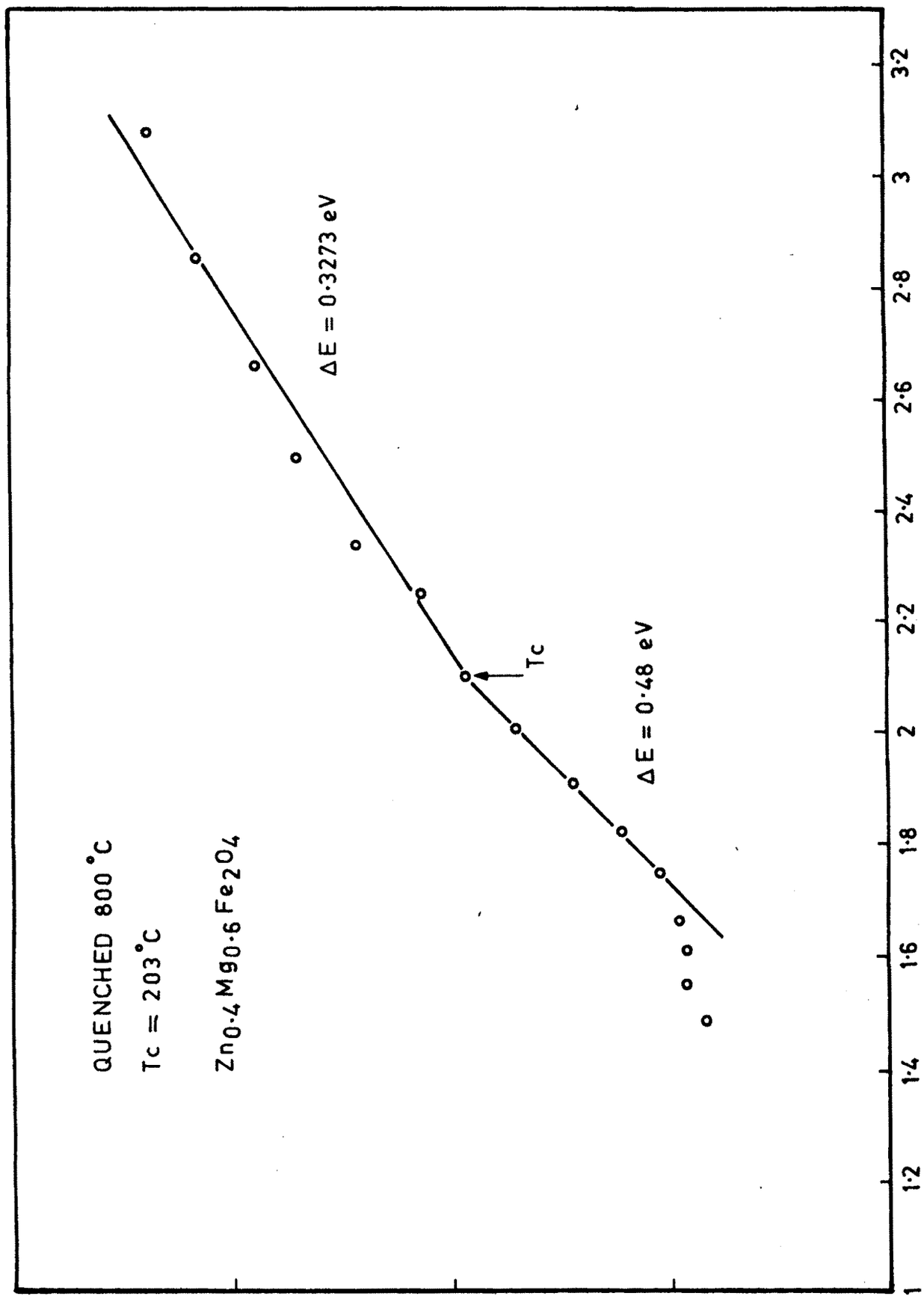

QUENCHED 800 °C
Tc = 203 °C
Zn0·4Mg0·6Fe2O4
ΔE = 0·3273 eV
ΔE = 0·48 eV
Tc
Log10 σ
10^3/T
6
5
4
3
2
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
3·2

Fig. 3·8

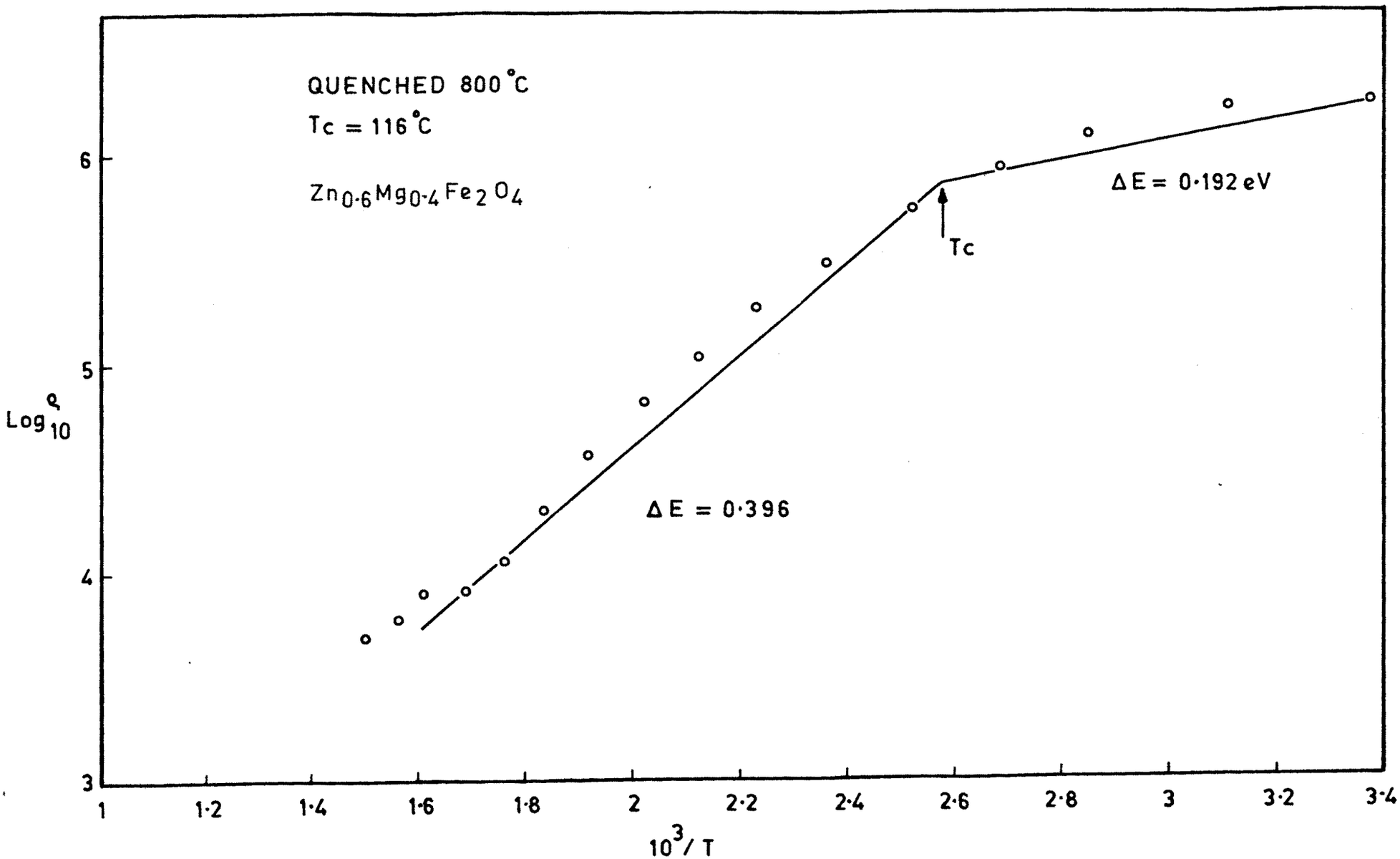

QUENCHED 800 °C
Tc = 116 °C
$Zn_{0.6}Mg_{0.4}Fe_2O_4$
ΔE = 0·192 eV
Tc
ΔE = 0·396
$Log_{10}\rho$
6
5
4
3
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
3·2
3·4
$10^3/T$

Fig. 3·9

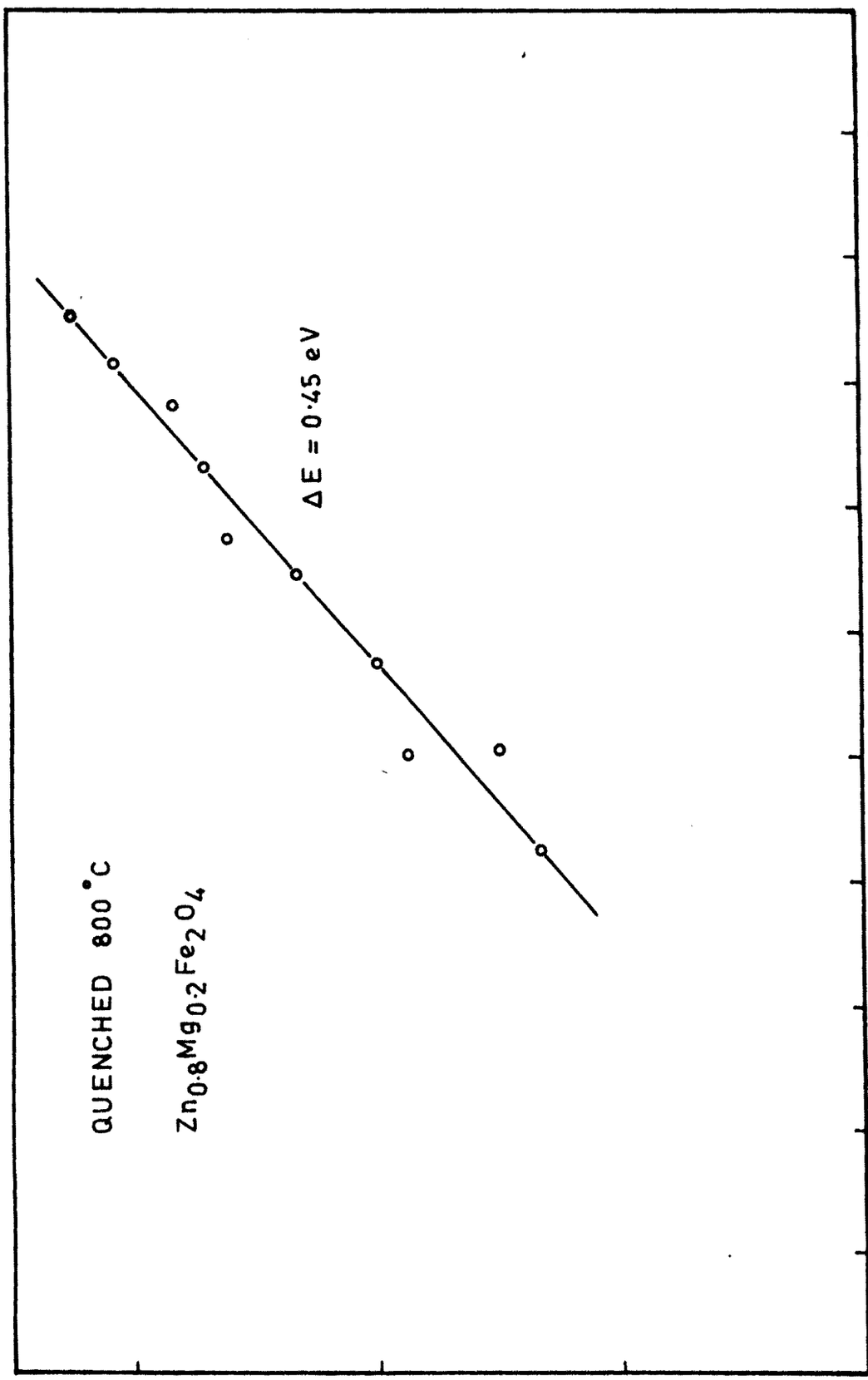

QUENCHED 800 °C
$Zn_{0.8}Mg_{0.2}Fe_2O_4$
ΔE = 0·45 eV
$\log_{10}\sigma$
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3
$10^3/T$

Fig. 3·10

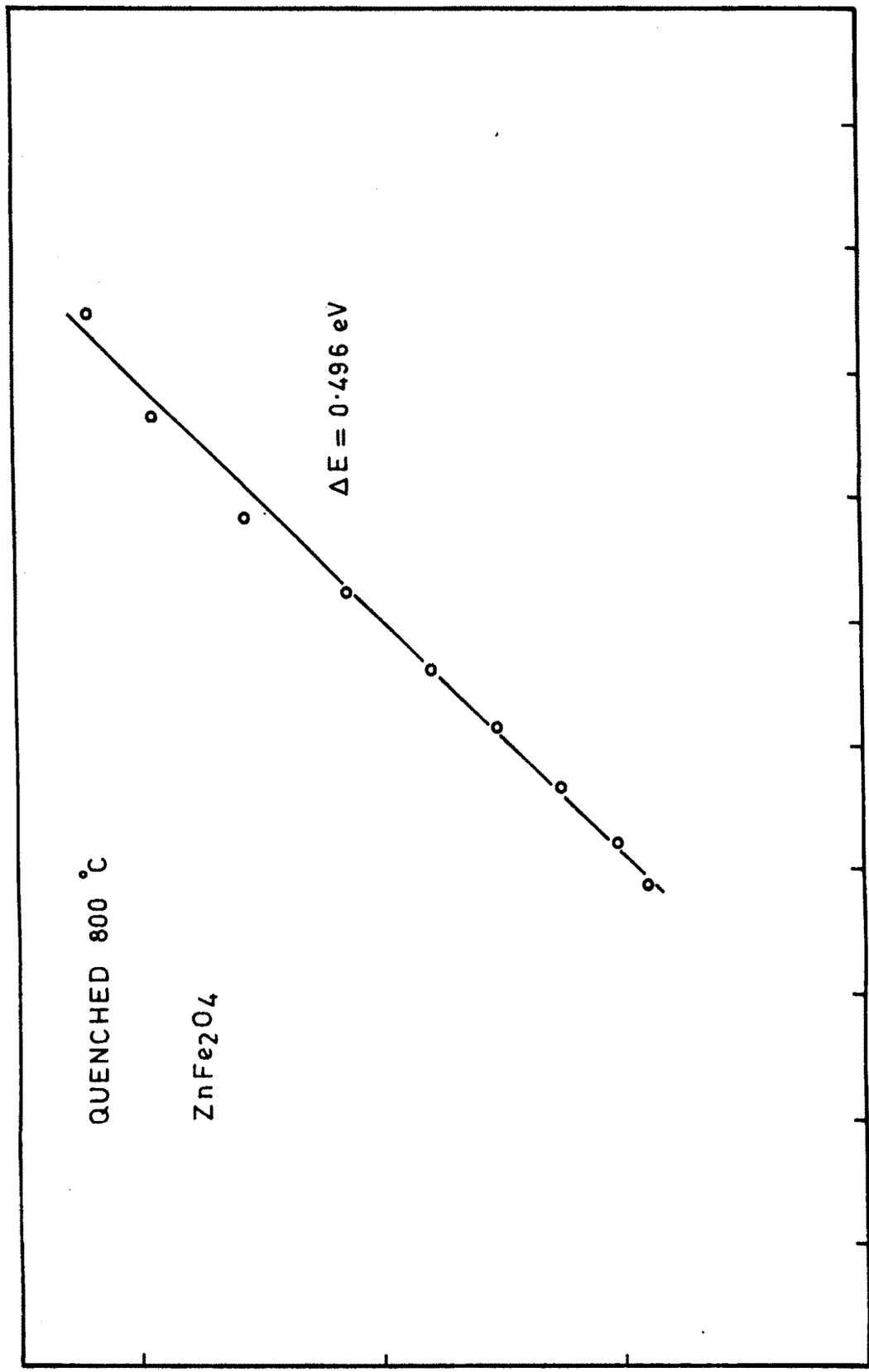

QUENCHED 800 °C
ZnFe2O4
ΔE = 0·496 eV
Log10 ρ
10^3/T
6
5
4
3
1
1·2
1·4
1·6
1·8
2
2·2
2·4
2·6
2·8
3

Fig. 3·11

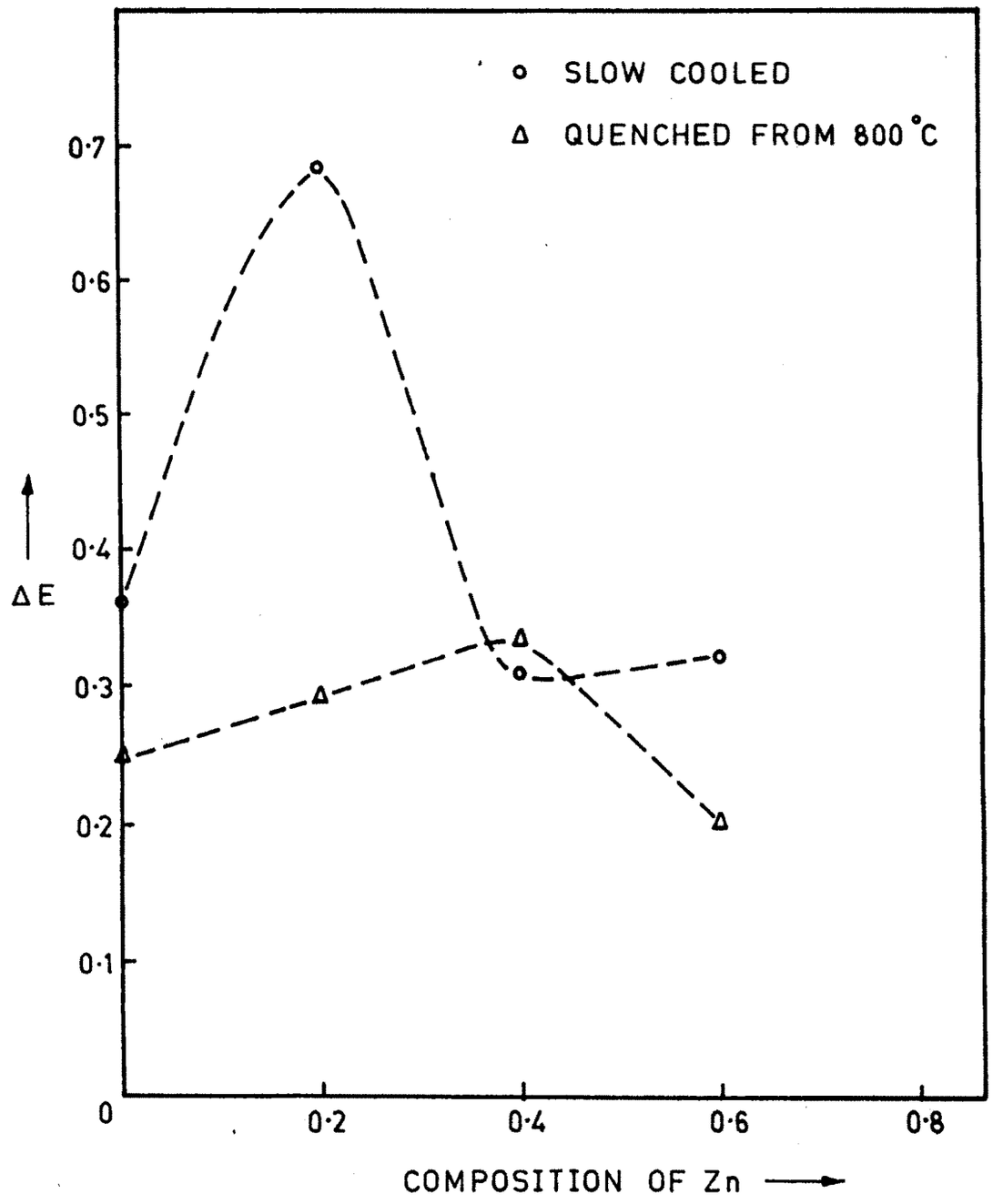

SLOW COOLED
QUENCHED FROM 800 °C
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
ΔE
0·2
0·4
0·6
0·8
COMPOSITION OF Zn

Fig. 3·12

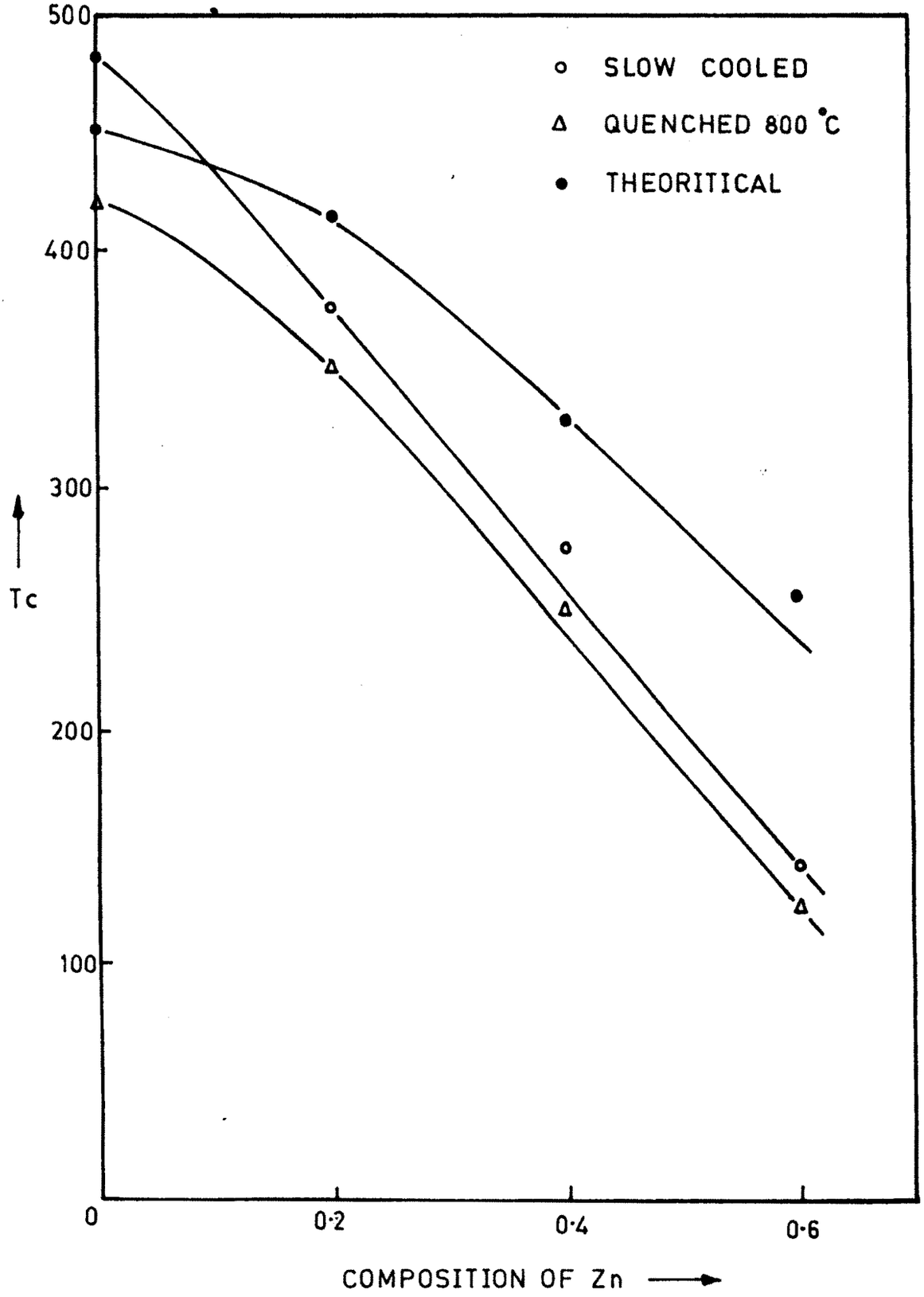

500
400
300
200
100
0
Tc
SLOW COOLED
QUENCHED 800 °C
THEORITICAL
0·2
0·4
0·6
COMPOSITION OF Zn

Fig. 3·13

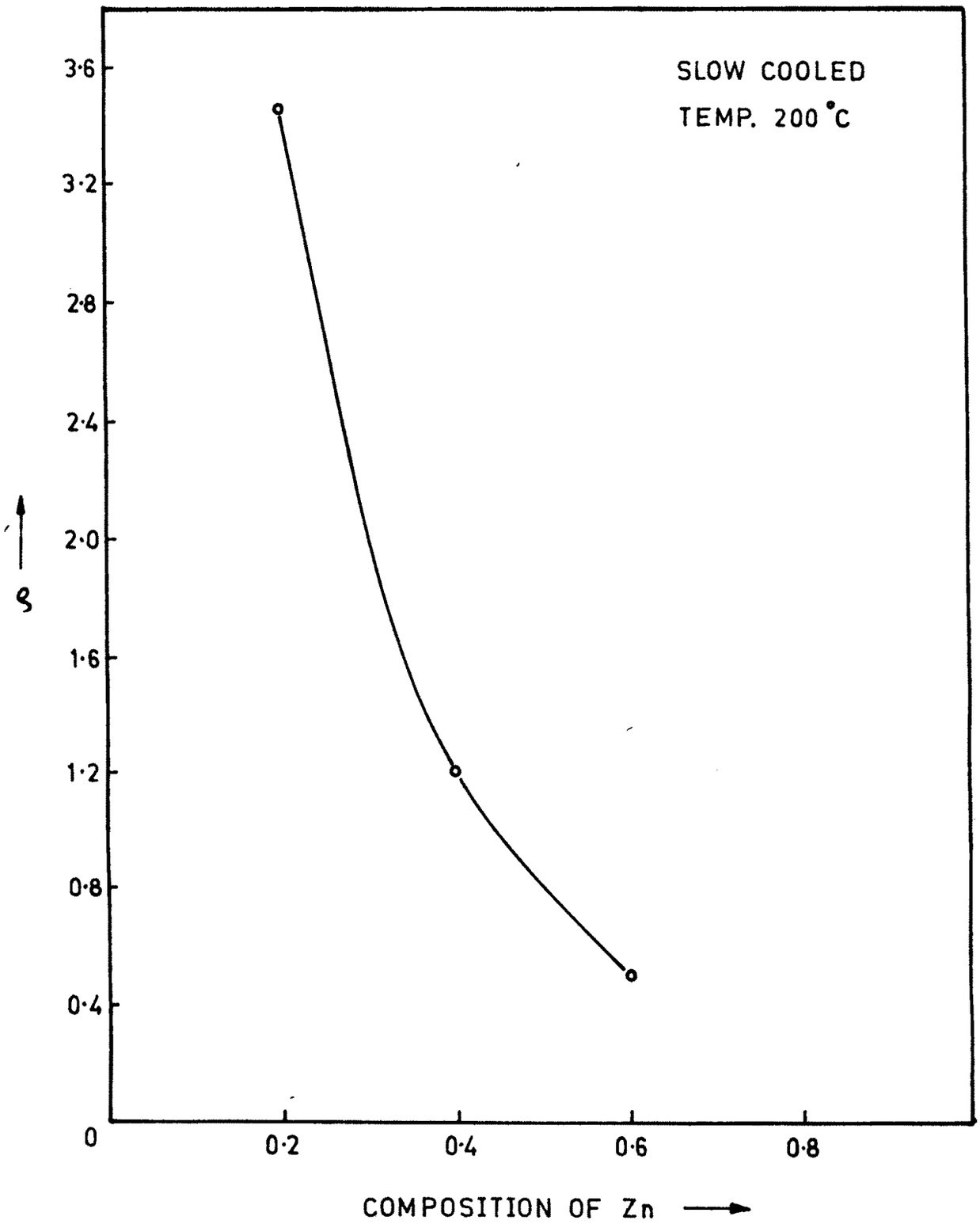

SLOW COOLED
TEMP. 200 °C
3·6
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
ρ
0·2
0·4
0·6
0·8
COMPOSITION OF Zn

Fig. 3·14

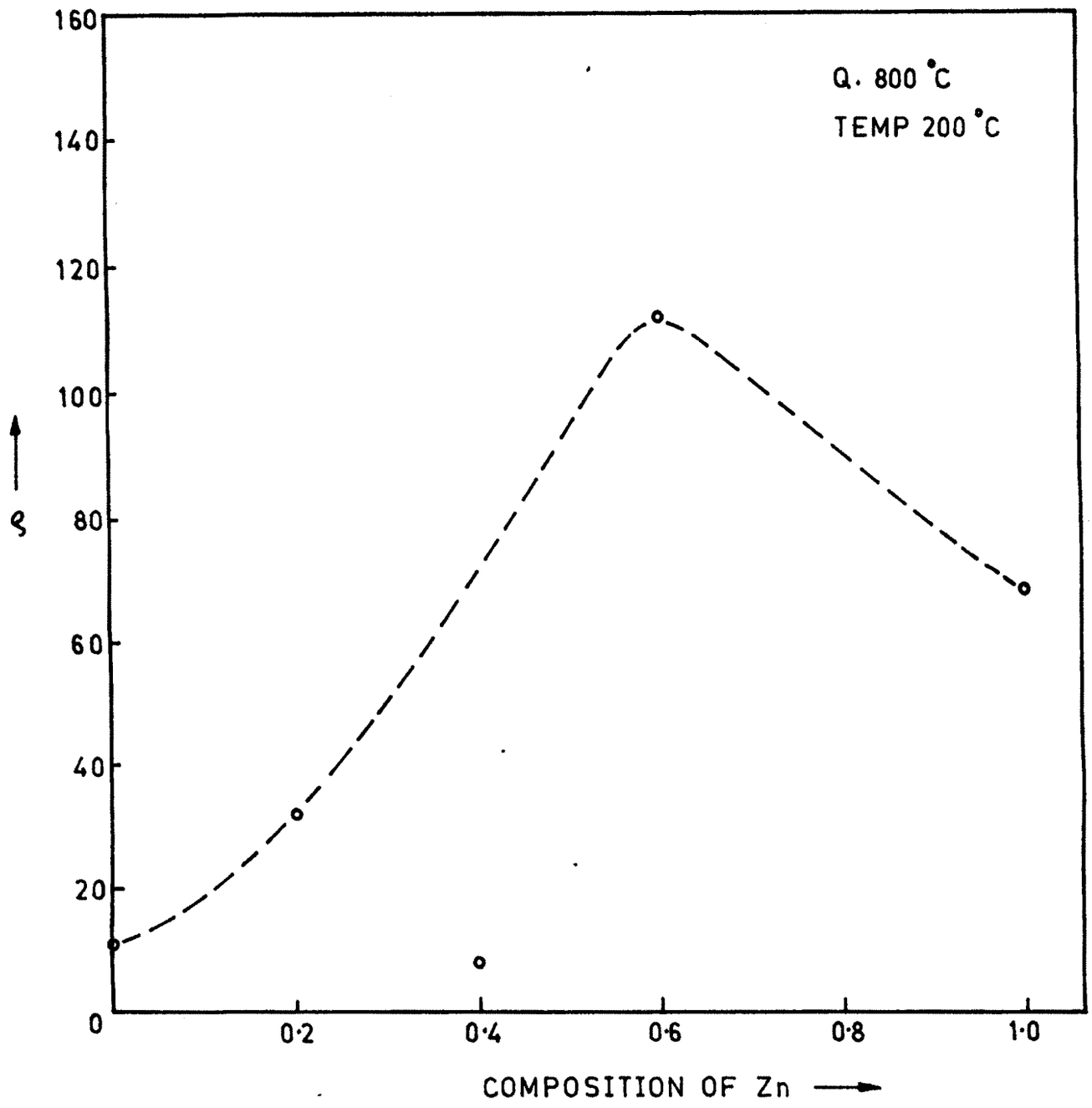

160
140
120
100
80
60
40
20
0
ρ
Q. 800 °C
TEMP 200 °C
0·2
0·4
0·6
0·8
1·0
COMPOSITION OF Zn

Fig. 3·15

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