CHAPTER – III

ELECTRICAL CONDUCTIVITY

3.1 INTRODUCTION

The reason that spinel ferrites play a useful role in many magnetic applications is that the electrical conductivity (σ) is low in comparison with the magnetic metals. For applications at microwave frequencies even a value of $\sigma = 10^{-6}$ $ohm^{-1}cm^{-1}$ may be prohibitively large because of eddy current damping. Ferrites, having a wide range of resistivity varying from 10^{-3} ohm cm to 10^{11} ohm cm [1], have much smaller conductivity. Hence they find preference over metals in high frequency operations. Conductivity studies give useful data for application purposes. It also gives a clue to conduction mechanism in ferrites. The order of magnitude of conductivity greately influences dielectric and magnetic behaviour of ferrites. Since it is important to control conductivity in ferrites, many researchers have taken much interest in the study of electrical conductivity and frequency dependent dielectric behaviour of ferrites[2,3,4].

3.2 CONDUCTIVITY MODELS AND CONDUCTIVITY IN FERRITES

In many transition metal oxides one finds a small value of σ if vacancies (cations or anions) or impurities are not present. These imperfections can give rise to deviating

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valency states of the transition metal ions. In ferrites the presence of Fe^{2+} amidst the Fe^{3+} ions gives rise to n-type conductivity[5]if the temperature is high. A similar situation exists for Ni^{3+} in $NiFe_2O_4$ or Co^{3+} in $CoFe_2O_4$. In these cases the deviating valency is higher than the one originally present (Ni^{2+} , Co^{2+}) and p-type conductivity is found. The presence of imperfections also gives rise to magnetic relaxation effects. Relaxation and conductivity might be related to the same atomic processes.

As ferrites are oxide semiconductors by nature their conductivity σ , can be written as

$$\sigma = e\,(n_e\mu_e + n_h\mu_h) \qquad \ldots(3.1)$$

where e = electronic charge,

$n_e(n_h)$ = concentration of mobile electrons(holes),

and $\mu_e(\mu_h)$ = mobility of electrons(holes).

The temperature dependence of σ can be expressed by

$$\sigma = \sigma_0 \exp\left[\frac{-E_a}{KT}\right] \qquad \ldots(3.2)$$

where K is Boltzmann's constant and E_a is the activation energy.

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The break or discontinuities that occur in the plots of $\log_{10} \rho \longrightarrow (10^3/T)$ can be ascribed to several reasons. Komar and Klivshin [6] have observed breaks and changes in activation energy at high temperatures in several ferrites and have correlated these temperatures with the magnetic Curie temperatures of the ferrites. This offers an evidence for the influence of magnetic ordering upon conductivity in ferrites [7]. The breaks may also be due to changes in dominent conduction mechanisms [8].

In broad band semiconductors the value of μ is large (10 to 10^4 $cm^2/V.$ sec). In transition metal oxides μ has been found to be much smaller and frequently strongly temperature dependent. For the latter case the model of the hopping electron has been proposed [9]. In this model electrons take part in a diffusion process by jumps from one lattice site to another. In analogy with the thermal activation processes encountered in ionic diffusion and ionic conductivity [10,11], the following expression for mobility can be given

$$\mu = l_i^2 \, e f_o \, (KT)^{-1} \exp\left[\frac{-q}{KT}\right] \qquad \ldots(3.3)$$

where $\mu = \mu_e$ or μ_h depending on charge carrier type,

l_i= the jump length,

f_o= frequency, characteristic of lattice vibrations,

and q = activation energy for the hopping process.

In the theory of electrical conductivity of ferrites a new concept of hopping of polarons by thermal activation has been used [11]. There is strong experimental proof for the existence of polarons and the hopping process [11,12]. Klinger has explained the conduction mechanism in magnitite like solids using two phase polaron model [12].

In spinels, charge carriers can be introduced by forming mixed crystals of a ferrite and Fe_2O_4. In a perfect stoichiometric compound Fe^{2+} ions can be produced by thermal activation of the reaction ;

$$Me_B^{2+} + Fe_B^{3+} \rightleftharpoons Me_B^{3+} + Fe_B^{2+} + E_g \qquad ...(3.4)$$

where the index B denotes the B-sites. Me can be Mn, Co, or Ni and E_g is the energy involved for transfer of an electron from Me^{2+} to Fe^{3+}, E_g is called the band gap. The conduction takes place when electrons move from divalent iron ions to trivalent iron ions.

3.3 PROBLEMS OF CONDUCTIVITY IN FERRITES

The subject of conductivity in ferrites suffers from a number of problems. In polycrystalline materials the nature of the grain boundary as a source of resistance, inhibits the interpretation of many DC measurements. AC measurements on

Li-doped Nio have shown [13] that the mobility is much larger than originally concluded from DC results.

A second source of uncertainity in the interpretation is the presence of cation or anion vacancies. These impurities may act as acceptors or donors, thereby compensating the original doping. The number of charge carriers is then uncertain. Moreover extra conduction processes are possible. Various conduction mechanisms based on different models for the donor levels have been given by different workers [14,15,16,17].

3.4 CONDUCTION BY POLARONS

The charge of the electron in a crystal lattice interacts with the charge of the ions and atoms of the lattice creating local deformation of the lattice. This follows the electron as it moves through the lattice. The combination of electron and the strained field is called as 'Polaron'. The strength of the lattice interaction is measured by electron phonon coupling constant defined by

$$\frac{1}{2}\alpha = \frac{\text{deformation energy}}{\hbar\omega} \qquad \ldots. (3.5)$$

where ω = longitudinal phonon frequency.

The displacement of the lattice causes the polarisation of the surrounding region and the electron gets trapped at the

centre of potential well. Transition of electron to the neighbouring sites may be governed by thermal activation. At high temperature, conduction is due to the diffusion of electrons by jumps from one site to the next in analogy to the thermal activation process accounted in ionic diffusion and ionic conduction [10 , 11].

Thus at high temperature, conductivity in ferrites is contributed by hopping mechanism; while at low temperature electrons tunnel slowly through the crystal giving rise to the observed conductivity. The conductivity largely depends on the mobility of the charge carriers.

When tunneling time is less than the time for successive hopping transition, conduction by small polarons (those with small coupling constant) becomes predominent. Kawai et al. [18] have observed the hopping type maechanism in the ferroma gnetic region of Mn-Zn single crystal ferrites.

3.5 ACTIVATION ENERGY

Because of the complexities of the structure present in the ferrites, band theory cannot give full explanation of the conduction properties of ferrites. Therefore, the idea of 'band gap' which is used for semiconductors has been replaced by the new concept of 'energy of activation' in case of ferrites.

It is assumed that discrete conducting states separated by forbidden non-conducting states exist instead of conduction band and valence band. Some minimum energy is required for an electron to jump from lower state to the higher state. conduction can occur only when carriers are able to cross the poten tial hill between the two states. Therefore they need to be 'activated' by some external energy. According to the kinetic theory of heat, if the energy imparted to the particles is just sufficient to overcome the potential barrier conduction can take place. This is called as ' thermal activation' and the minimum energy needed for the current carriers to pass from low conducting state to high conducting state is defined as the 'energy of activation'. Activation can also be caused by using other forms of energy such as light, electric field or magnetic field.

3.6 TEMPERATURE DEPENDENCE OF RESISTIVITY

Ferrites being semiconducting oxide materials their resistivity is very sensitive to temperature. Charge carries can diffuse from one state to other state only if their energy exceeds activation energy. According to Boltzmann statistics, if the height of the potential hill is ΔE, carriers having sufficient energy can cross the barrier in a fraction $\exp\left[\frac{-\Delta E}{KT}\right]$ of time [19]. The thermal lattice vibrations

constantly give rise to phonons, and electron hops between the pairs of states either by absorption or emission of a phonon each time. Thus transport of charge carriers is achieved by thermally activated hopping process through interaction with phonons. On the basis of this the temperature dependence of resistivity can be expressed as

$$\rho = \rho_0 \exp\left[\frac{\Delta E}{KT}\right] \qquad \ldots(3.6)$$

where ρ_0 = temperature independent constant,

K = Boltzmann constant,

T = Absolute temperature

and ΔE = activation energy.

Equation 3.6 can be written as

$$\log_e \rho = \log_e \rho_0 - \frac{\Delta E}{KT} \qquad \ldots (3.7)$$

This represents a straight line. But experiments have shown that the plot of $\log_e \rho$ versus $(1/T)$ shows a break at the Curie temperature. This is attributed to the transition from paramagnetic region to ferrimagnetic region. The slope of such a graph is used to calculate the activation energy [6].

3.7 EXPERIMENTAL

Resistivity of ferrite samples in the form of pellets of about 1cm diameter and 0.2 – 0.3 cm thickness was measured by two probe method. The conductivity cell, electrical circuit

and the experimental set up used for resistivity measurement are shown in Figs. 3.1 and 3.2.

The conductivity cell consists of two copper rods, of about 1cm diameter and 2cm length, fitted in two porcelain discs. For external contact, each copper rod was electrically connected to a copper wire using the screws provided on it. The opposite faces of the pellet were polished and silvered to ensure good electrical contact with the copper rods. The pellet was held sandwitched between copper rods. Fitting screws were used to keep the assembly of discs and rods firmly.

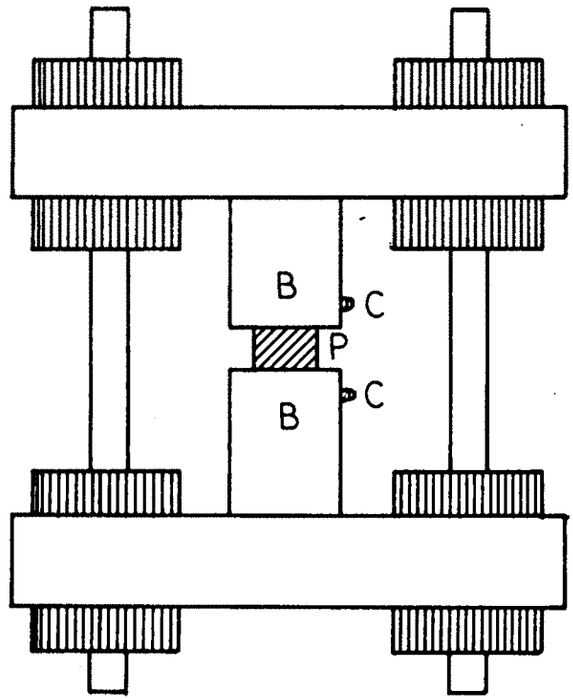
The conductivity cell was placed in an electrically heated furnace. A calibrated Cromel-alumel thermocouple was used along with a digital multimeter to measure temperature of the pellet accurately by keeping its tip very close to the pellet. DC voltage of 2 volts was applied across the pellet; and the current through the pellet was measured using an electronic multimeter at different temperatures with an interval of $25^{\circ}C$ between room temperature and $700^{\circ}C$. This process is repeated for each sample.

Resistance of the pellet was calculated by using Ohm's law

$$R = \frac{V}{I} \qquad \ldots(3.8)$$

where V = voltage across the pellet,

I = current through the pellet.



P – Pellet
B – Brass electrode
C – Connection lead

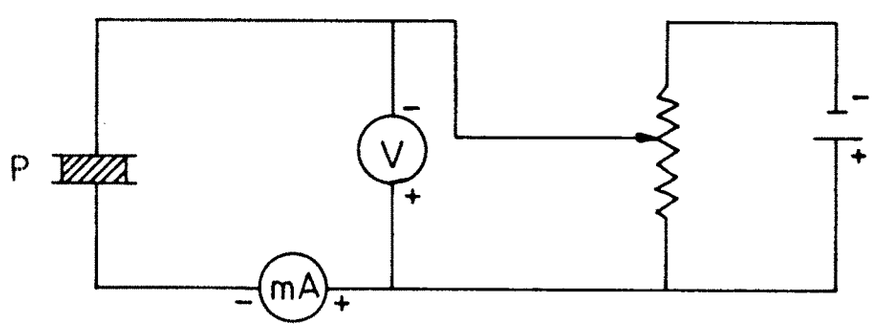


Fig.3.1 Sample holder and circuit diagram for electrical resistivity

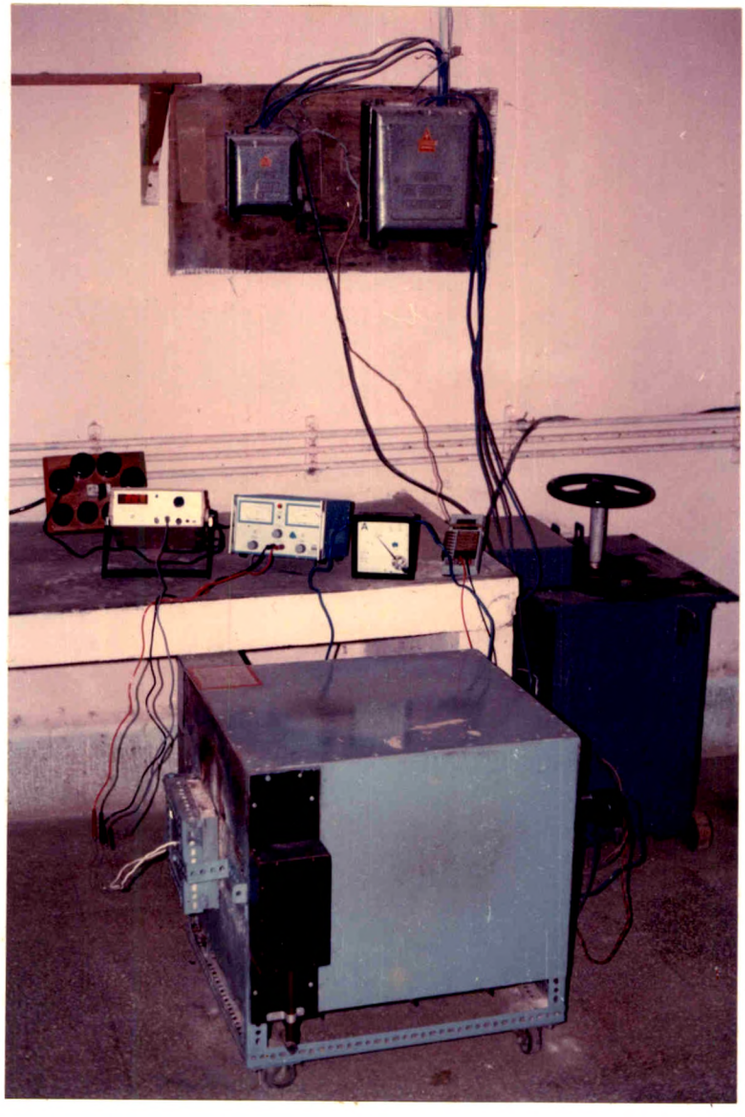


Fig. 3·2 – Experimental set up for electrical resistivity measurement.

Resistivity was obtained from the formula

$$\rho = \frac{RA}{t} \qquad \ldots(3.9)$$

where A = area of cross section of the pellet,

t = thickness of the pellet.

Curie temperature and activation energy were determined by plotting $\log_{10} \rho$ versus $\left[\frac{10^3}{T} \right]$ for all samples.

3.8 RESULTS AND DISCUSSION

3.8.1 *COMPOSITION DEPENDENCE OF ELECTRICAL CONDUCTIVITY*

The electrical resistivity was measured on $Co_xZn_{1-x}Fe_2O_4$ system with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0, between RT and 700°C using the electrical circuit and the experimental set up shown in figures 3.1 and 3.2. The plots of $\log_{10} \rho$ versus $\left(\frac{10^3}{T} \right)$ for all the samples are given in figures 3.3 to 3.8. The plots are linear and show breaks or change in slope at certain temperatures which agree well with Curie temperature of the corresponding samples. No break is observed in the case of $Co_{0.2}Zn_{0.8}Fe_2O_4$ as here the transition temperature is less than room temperature. The

break is also not observed in the case of $ZnFe_2O_4$ as it is non-magnetic.

In Table 3.1 the electrical measurement data such as resistivity at 100°C, transition (Curie) temperatures and activati on energy for different $Co_xZn_{1-x}Fe_2O_4$ compositions sintered at 900°C for two sintering times are presented.

From Figure 3.9, it can be seen that the transition point in the plots $\log_{10} \rho$ vs ($10^3/T$) is shifting towards higher temperature side with the increase of Co concentration ie.with decreasing concentration of Zn (Also see Fig. 3.10). This behaviour is expected to be due to the increasing number of A-B interactions resulting with the decreasing Zn concentration. Satyamurthy et. al have pointed out that a quantitative expression for this variation would involve the various sublattice magnetizations in a complicated way. It can also be seen that the conductivity (at 100°C) is increasing with the increase of Cobalt concentration. This may be due to the presence of large number of Cobalt ions (which can show the Co^{2+} to Co^{3+} mechanism) in the samples. Our observation is in agreement with the result reported by Rezlescu et al. [20] who found in case of Li-Zn ferrites that the resistivity decreased (or conductivity increased) with the decreasing Zn concentration.

3.8.2 *TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY*

Plots of $Log_{10}\ \rho$ vs $\left[\frac{10^3}{T}\right]$ that the resistivity (ρ) obeys the relation $\rho = \rho_0 \exp\left[\frac{\Delta E}{KT}\right]$. This indicates the semiconducting nature of our ferrites.

Activation energies are calculated from the slopes of ferrimagnetic and paramagnetic regions of the curves, and presented in Table 3.1 along with the sintering temperature and time, and Curie temperatures for different compositions. From this table it is evident that the activation energy for paramagnetic region is greater than that for ferrimagnetic region. Graphically observed transition (Curie) temperatures agree well with the reported values. [21].

Irkhin and Turov [22] have developed a theoretical explanation for the existence of kink at the Curie temperatures. They have shown that the change in slope of the straight line occurs while passing through the Curie temperature. This point separates the upper ferrimagnetic region from the lower parama gnetic region as the spin-spin interaction vanishes due to thermal vibrations. The change in slope indicates the change in activation energy in two regions. Our results of activation energy are in agreement with the above thory. Similar results have been observed for manganese, Li-Ni and Mn-Mg ferrites [23, 24, 25].

It should be noted that activation energy varies from 0.2 eV to 0.55 eV, and that a high activation energy is accompanied by a low conductivity as was shown by Smit and Wijn [26].

Different explanations are given for transition temparature at which conductivity machanism shows a break. According to Komar and Klivshin [6] the change in slope of the plot $\log_{10} \rho$ vs $\left[\frac{10^3}{T} \right]$ dicates a magnetic transition. The B-B distance on the octahedral sites is much greater than the sum of atomic radii of the cations. The result is that the elect- rons are not free to move in the crystal but remain fixed to B-sites. Verwey has shown that the conduction takes place due to activation of states involving cations of changing valence i.e. $Fe^{2+} \Longleftrightarrow Fe^{3+}$ and vice versa which is hopping mechanism. Discontinuity is explained as ordering of Fe^{2+} and Fe^{3+} ions on octahedral B-sites [27]. The lowering of activation energy is attributed to the effect of spin ordering [7, 28]. In short the change in slope is due to disordering of electron spins at that temperature i.e. the Curie temperature [29]. These breaks suggest that there is some predominent change in the conduction mechanism due to magnetic phase transition.

Two phase polaron model was used to explain conduction mechanism by Klinger [12]. According to him at low temperature the conduction is via magnetically correlated polarons whereas above Curie temperature conduction is via Brownian like tunneling motion of polarons.

Iudin [30] considered a ferrite as a lattice of classical magnetic dipoles submerged in a dielectric continuum. From an analysis of the electrical conductivity of such a model he showed that the line obtained by plotting $\log_{10}\rho$ vs $\left[\frac{10^3}{T}\right]$ must have a break at the Curie point as the activation energy in the ferrimagnetic region is less than that in paramagnetic region. This conclusion is in agreement with the experimental results obtained in the present investigation.

The presence of Cobalt on octahedral sites favours the conduction mechanism of $Co^{2+} + Fe^{2+} \Longleftrightarrow Co^{3+} + Fe^{2+}$ type in Co - Zn ferrites. Parker et al. [31] studied the electrical conductivity of $NiFe_2O_4$ with small substitution of Cobalt and established two valence states of Cobalt.

In our ferrites, the presence of single phase is found by X-ray diffraction pattern to confirm the idea that the conductivity in ferrites is of intrinsic nature of single phase spinel structure rather than other phases.

3.8.3 *EFFECT OF POROSITY AND SINTERING TIME/TEMPERATURE ON ELECTRICAL CONDUCTIVITY*

Naik and Powar [32] have studied the effect of sintering temperature on conductivity of Ni-Zn ferrites. Pujar [33] has reported the effect of sintering temperature on Co-Zn ferrites. They have concluded that resistivity of ferrites decreases with increase in the sintering temperature for their samples.

In the present work we have studied the effect of sintering time on conductivity of our samples. From figures 3.3 to 3.8 it can be seen that the plots for samples corresponding to higher sintering time [30 hrs] lie below the plots for lower sintering time [15 hrs]. This reveals that the resistivity decreases with increase in sintering time. Table 3.1 shows activation energies of samples sintered at 900°C for 15 hrs and 30 hrs respectively. It is observed that the activation energy decreases with increasing sintering time. There is little difference in transition temperatures of samples in two sintering cases, and the two transition temperatures are nearly equal to the Curie temperature of the sample. When sintering time is increased the transition point shifts slightly towards lower temperature side. The porosity is reduced at higher sintering time for all samples(Table 3.1) and resistivities are considerably decreased as the sintering time is increased.

The observed changes in resistivity behaviour of samples can be explained on the basis of microstructural changes brought in by sintering conditions. The pores invariably introduce the insulating or the impending paths to the electrons. In otherwords, pores offer extrinsic contribution to the activation energy. At higher sintering time/temperature, it is obvious that there is densification or less porosity. The reduction in activation energy may be attributed to the reduction in number of pores due to densification. Due to reduced number of pores, the individual grains become larger and come closer, thus increasing effective area of grain to grain contact. The resistivity is inversely proportional to the cross sectional area of the conductor and at higher sintering time/temperature, the total resistance of the matrix may decrease. Reduction in resistivity or increase in conductivity is the consequence of reduction in activation energy.

It is reported that the average grain size increases with increase in sintering temperature and time [34]. This is clearly revealed in the micrographs of our samples (Figs. 5.7 and 5.8). As sintering time or temperature or both increase average grain size increases and porosity decreases. This results in higher conductivity in the samples as a consequence of decrease in porosity.

TABLE - 3.1

Conductivity data of $Co_xZn_{1-x}Fe_2O_4$ samples sintered at 900°c, for 15 and 30 hrs.

S.No.	Composition	Sintering time hrs.	Resistivity at 100°C ρ_{100} ($X10^5$) ohms cm	Curie Temparature in °C From Conductivity data	Curie Temparature in °C Literature Value (Ref.35)	Activation Energy Ferri region (eV)	Activation Energy Para region (eV)
1	$CoFe_2O_4$	15	4.18	533	515	0.310	0.55
		30	1.27	521		0.297	0.519
2	$Co_{0.8}Zn_{0.2}Fe_2O_4$	15	5.5	402.6	389	0.290	0.440
		30	2.1	393.6		0.276	0.397
3	$Co_{0.6}Zn_{0.4}Fe_2O_4$	15	6.58	282	275	0.262	0.342
		30	2.6	267.5		0.248	0.313
4	$Co_{0.4}Zn_{0.6}Fe_2O_4$	15	6.8	150.7	137	0.236	0.283
		30	3.1	145		0.227	0.262
5	$Co_{0.2}Zn_{0.8}Fe_2O_4$	15	12.5		25		0.242
		30	4.5				0.238
6	$ZnFe_2O_4$	15	23.1	-	-	-	0.222
		30	7.1	-	-	-	0.208

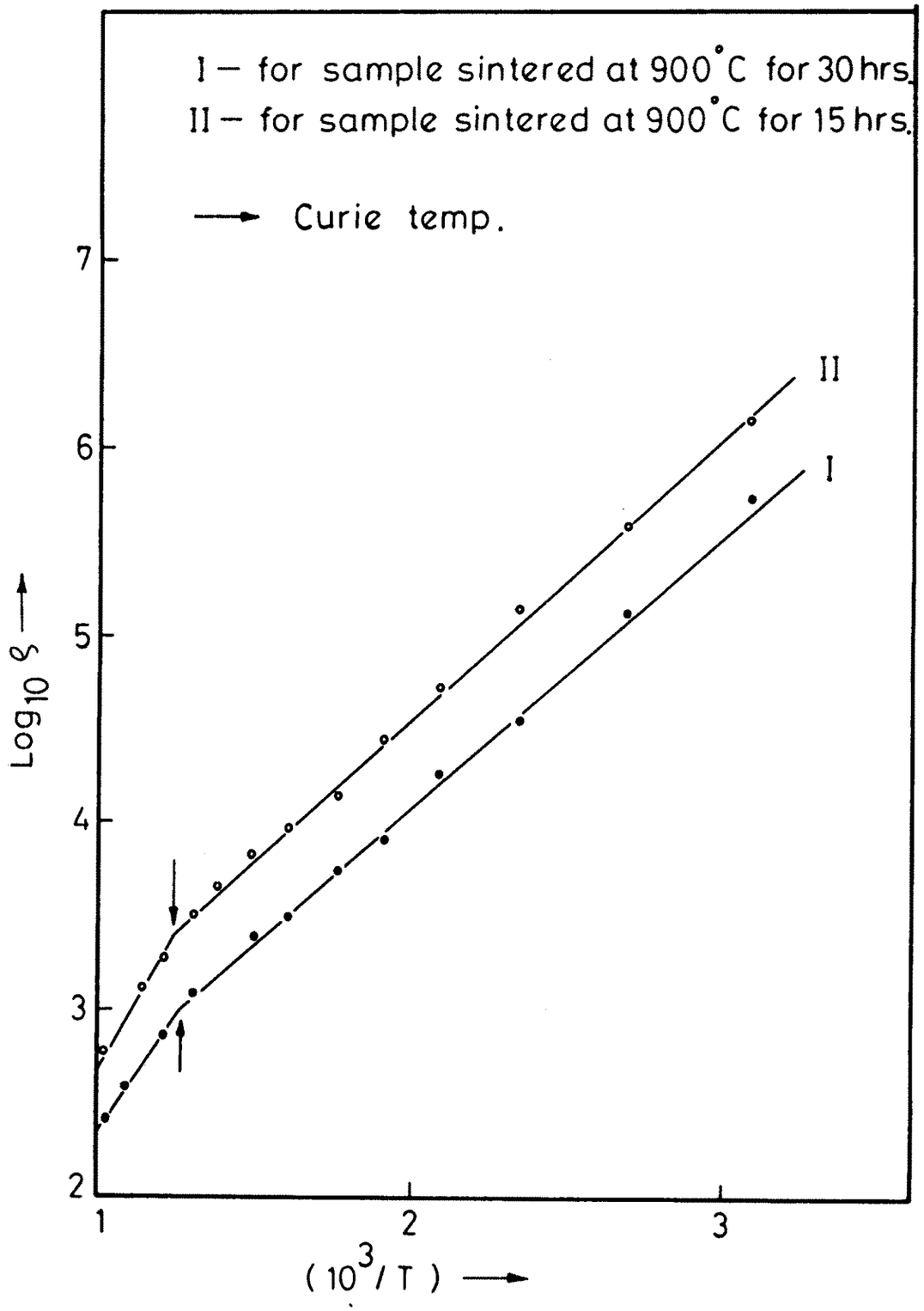


Fig. 3·3 – $Log_{10}\rho$ vs $(10^3/T)$ for $CoFe_2O_4$.

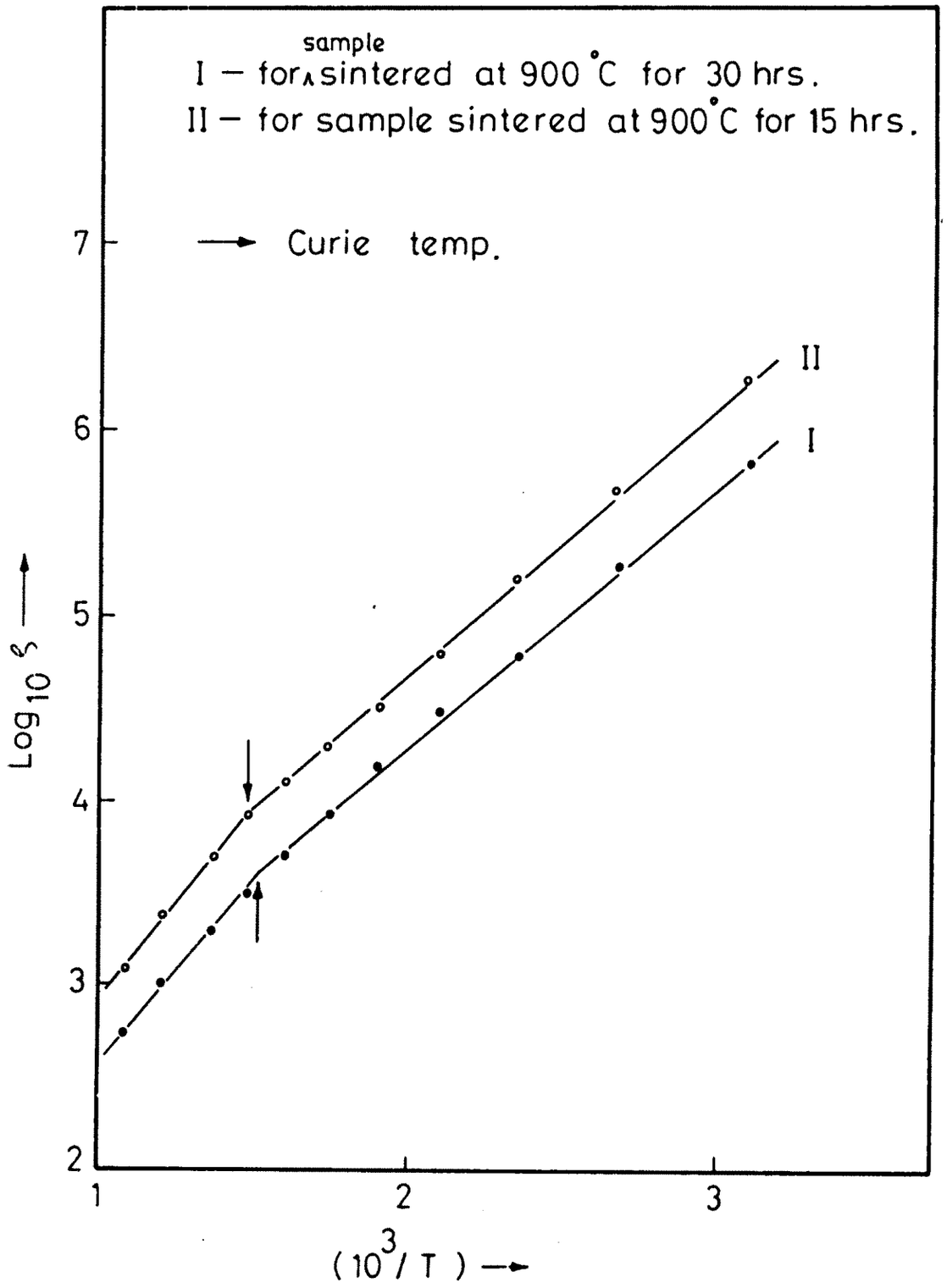


Fig. 3·4 – $Log_{10}\rho$ vs ($10^3/T$) for $Co_{0.8}Zn_{0.2}Fe_2O_4$

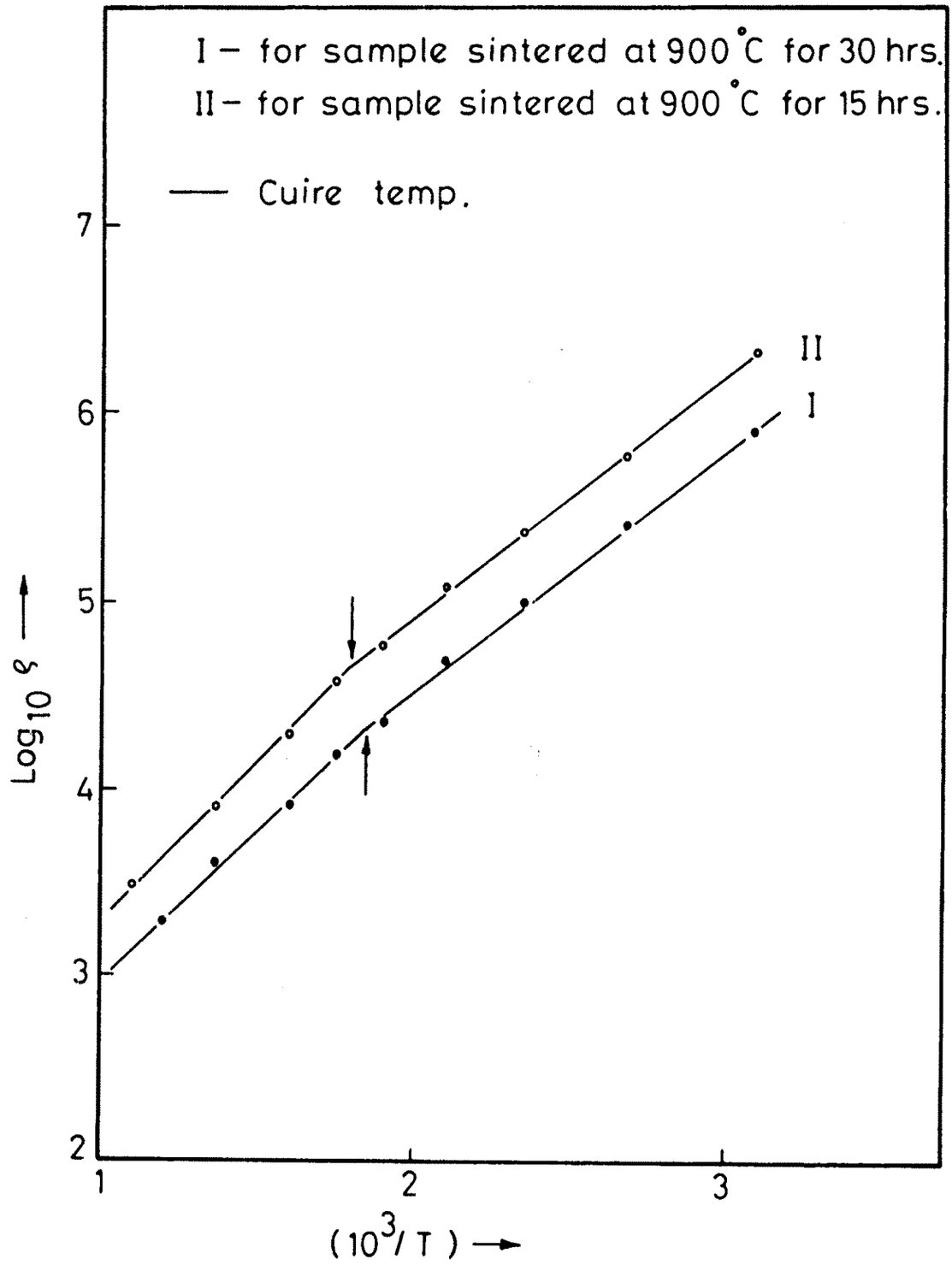


Fig. 3·5 – $Log_{10} \rho$ vs $(10^3/T)$ for $Co_{0.6}Zn_{0.4}Fe_2O_4$.

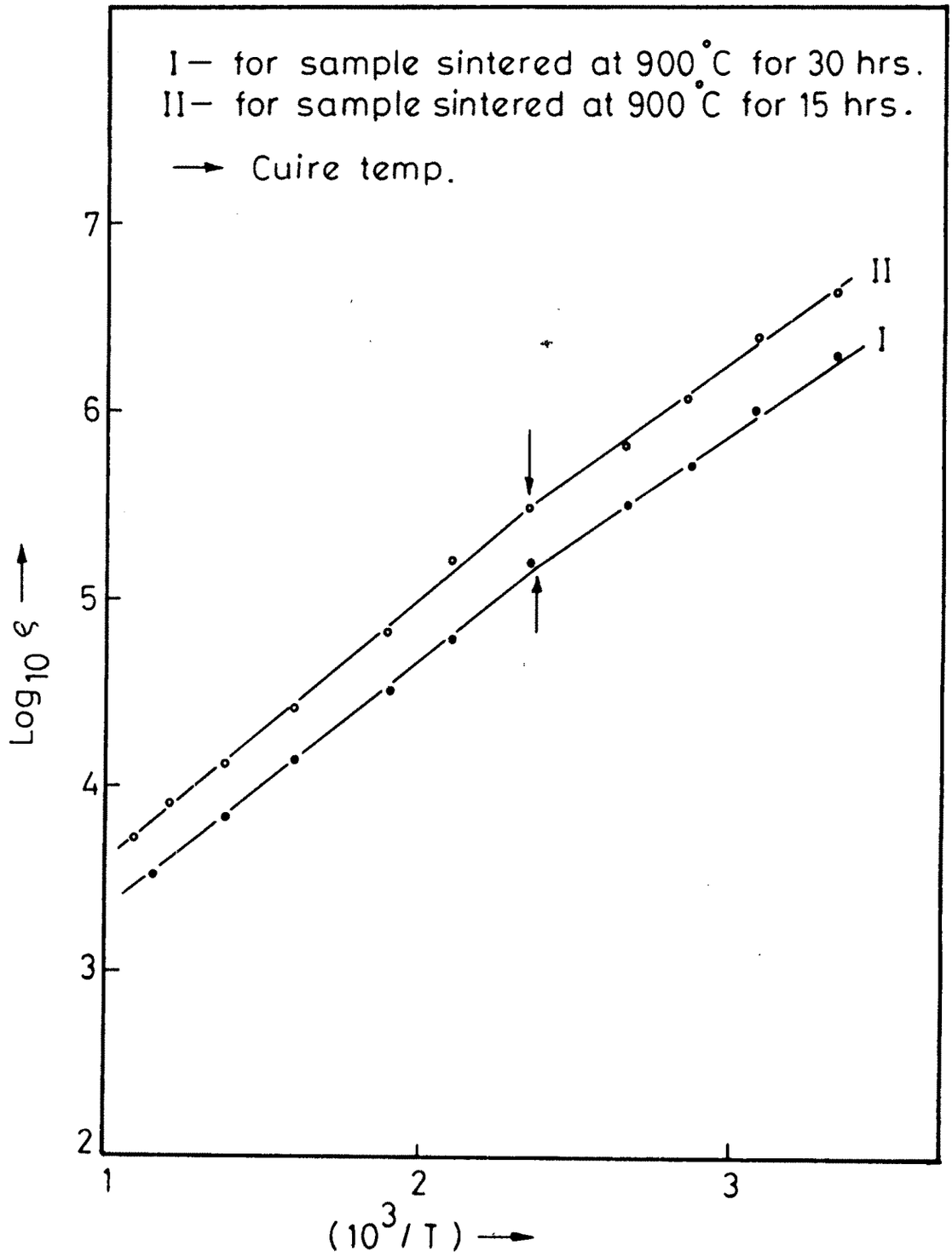


Fig. 3·6 – $Log_{10}\,\rho$ vs $(10^3/T)$ for $Co_{0.4}Zn_{0.6}Fe_2O_4$.

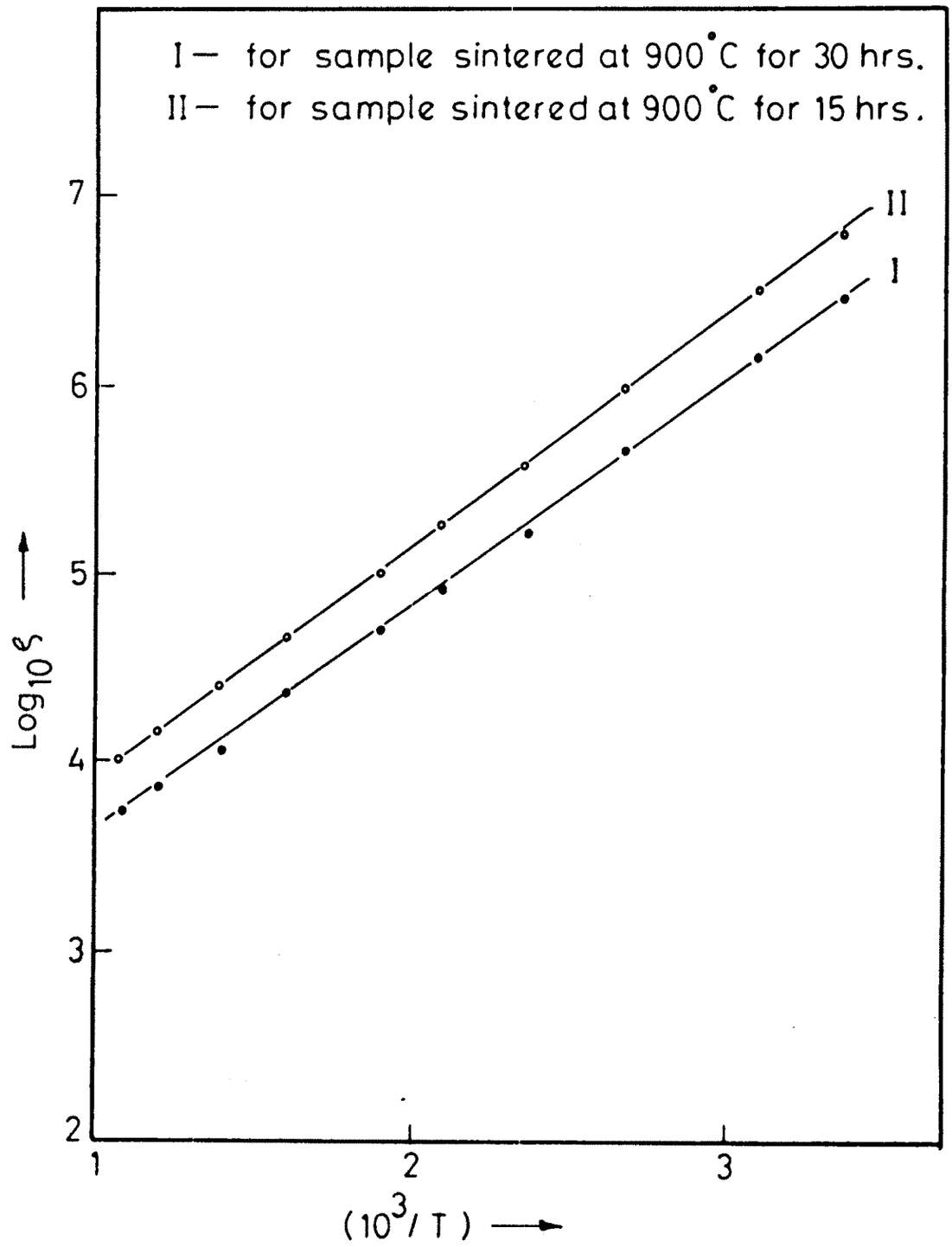


Fig.3·7- $Log_{10}\rho$ vs $(10^3/T)$ for $Co_{0.2}Zn_{0.8}Fe_2O_4$.

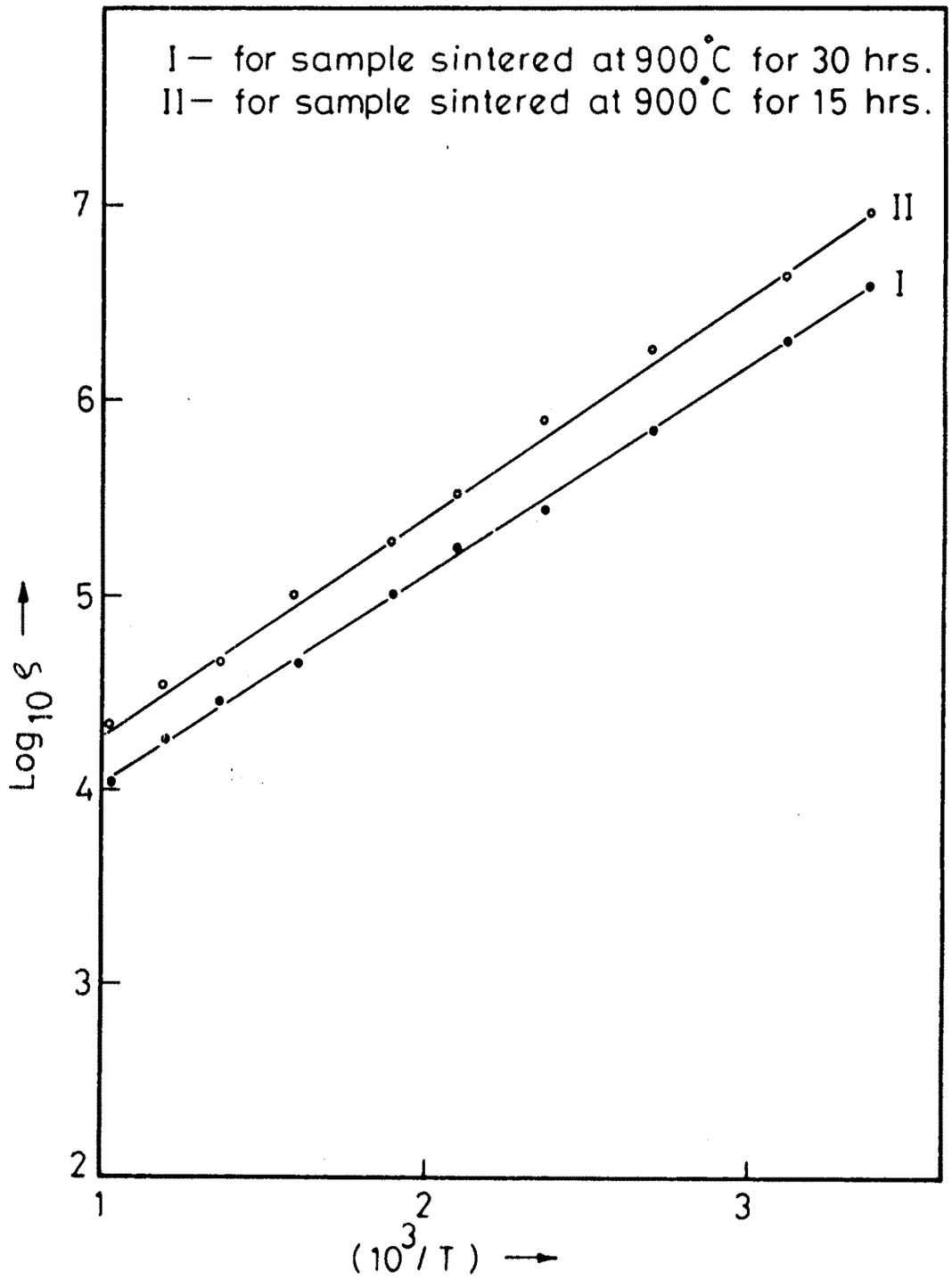


Fig. 3·8 – Log_{10} ρ vs $(10^3/T)$ for $ZnFe_2O_4$.

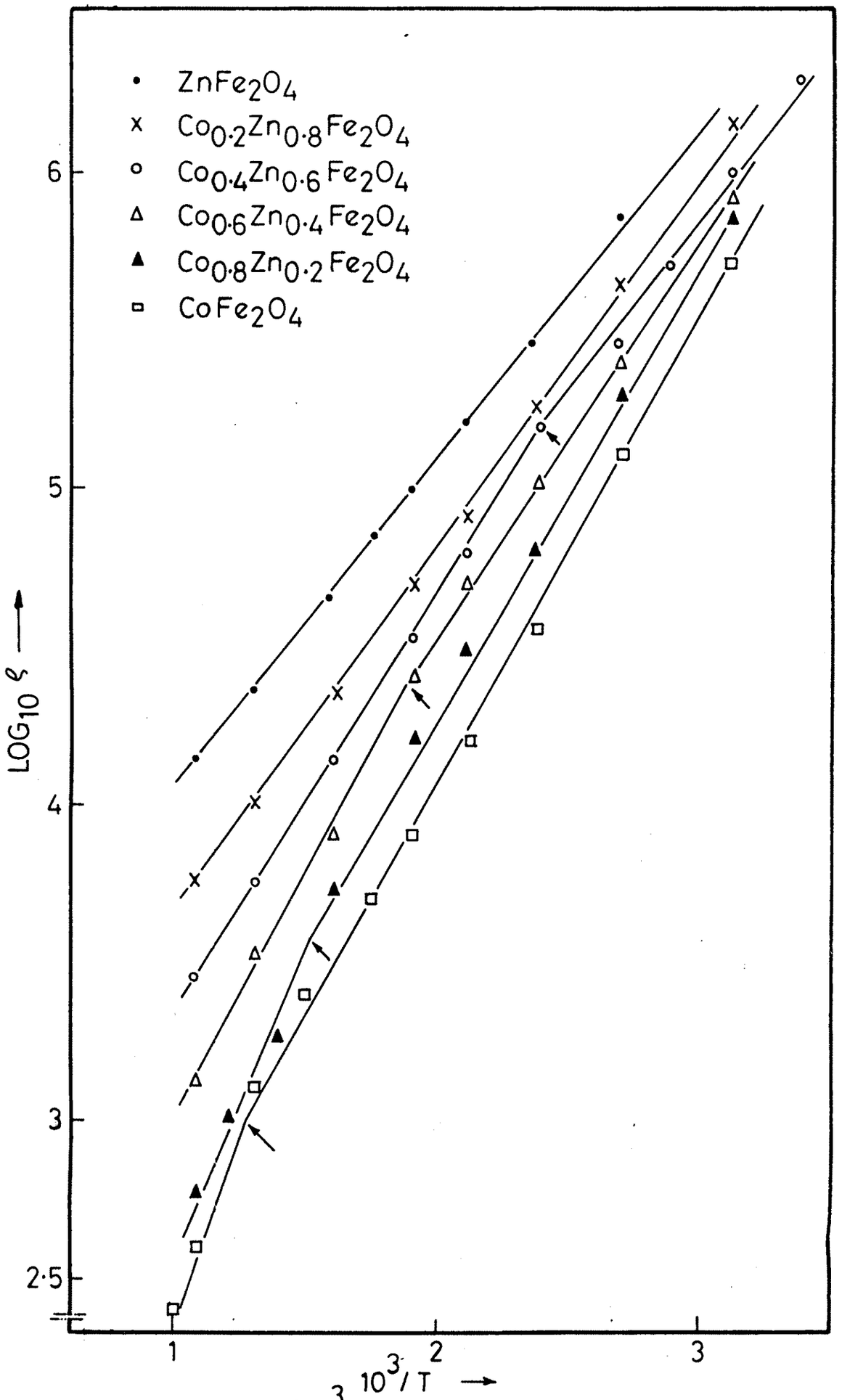


Fig. 3·9 - $Log_{10}\rho$ vs ($10^3/T$) Plots for $Co_xZn_{1-x}Fe_2O_4$ ferrites sintered at 900°C for 30 hrs.

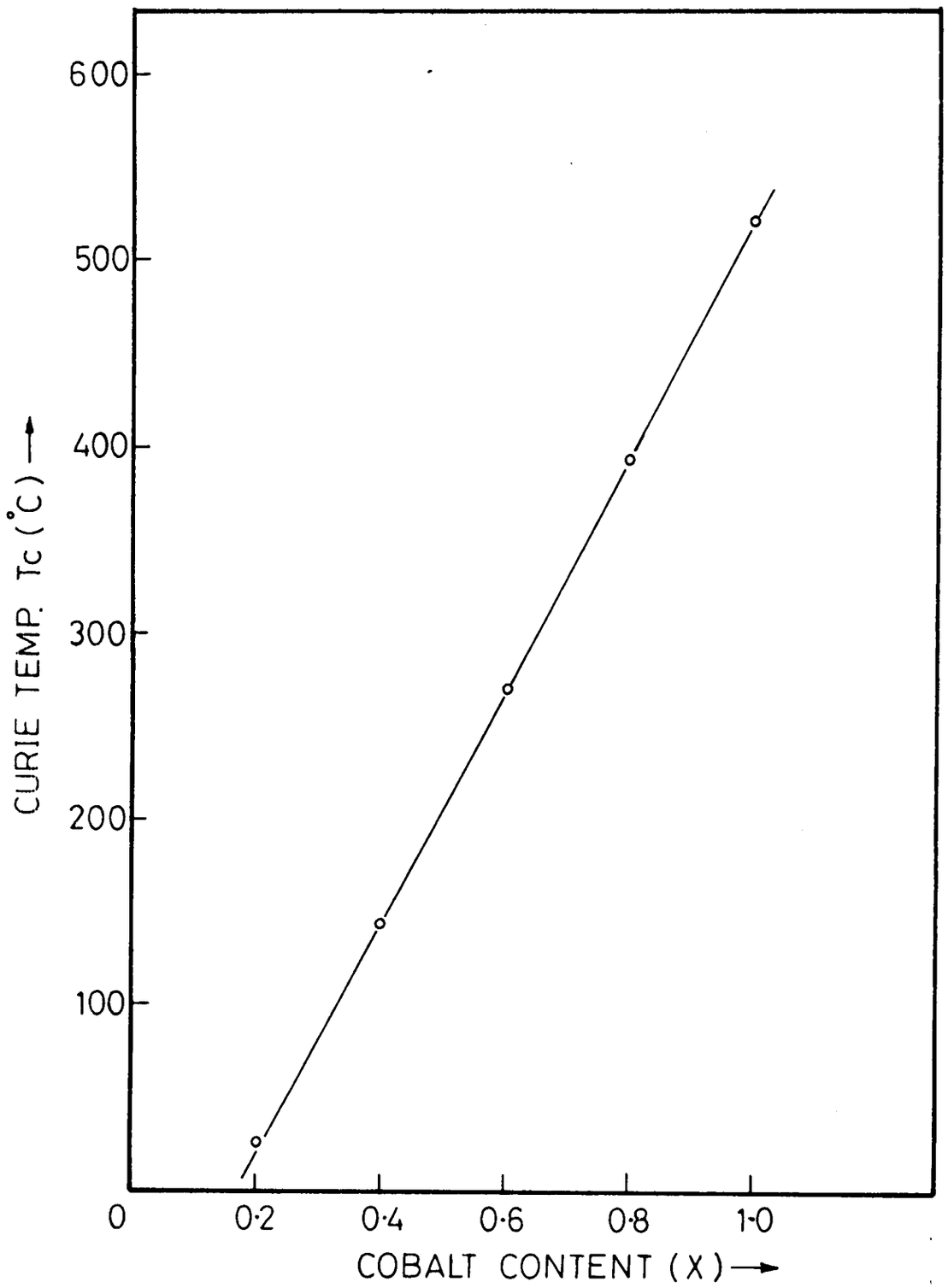


Fig. 3·10 – Variation of cuire temp. with Cobalt content in the $Co_xZn_{1-x}Fe_2O_4$ ferrites sintered at 900°C for 30 hrs.

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