CHAPTER-III

ELECTRICAL CONDUCTIVITY IN COPPER-COBALT FERRITES

INTRODUCTION

The ferrites are the ferrimagnetic oxides, having resistivity in the range of 10^{-3} ohm-cm to 10^{11} ohm-cm[1] depending on chemical composition, nature of constituent ions and heat treatment. Electrical conductivity in ferrites is the subject of many investigations since Snoek produced these spinel ferrites. The high resistivity in comparison with that of magnetic metal is the main asset of ferrites for application at microwave frequencies. The transport mechanism can be investigated with the help of electrical studies such as conductivity, thermoelectric power and magneto resistance. The order of magnitude of conductivity greatly influences dielectric and magnetic behaviour of ferrites. Hence this created considerable interest in the electrical conductivity and frequency dependent dielectric behaviour of ferrites[2,3,4].

It has been reported that high conductivities are due to the presence of both ferrous (Fe^{3+}) and ferric (Fe^{2+}) ions on equivalent sites[5]. Koops[6] studied the electrical conductivity of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ fired under different conditions and showed that conductivity largely depends on preparation technique. The deficiency of iron gives rise to lower conductivity while the excess of iron gives rise to higher conductivity. Hence the material behaves as P-type for iron deficiency and n-type for excess iron. Jonker[7] studied series of cobalt ferrites and established two regions of conductivity. One region was of low conductivity caused by Co^{2+} and Co^{3+} ions while the other region was of high conductivity caused by Fe^{2+} and Fe^{3+} ions. Further he was able to show that the first region was p-type and latter region was n-type semiconductor respectively. When the valency of the doped ions differs from that of ions in the ferrites some of the ions are forced to change their valence state, resulting in the increase of conductivity.

Parker et al[8] studied the effect of dopping of cobalt and manganese in nickel ferrite and observed the increase in conductivity with increasing concentration of both cobalt and manganese. Jefferson[9] studied the conductivity and Seebeck constant for ferrites containing copper. The electrical and magnetic properties of ferrites containing copper were studied by Rezlescu et al[10]. Ahmad et al[11] reported that the conductivity in copper-zinc ferrite was due to small radius polarons while domain wall resonance in copper ferrite was studied by Srinivasan[12] attributing the resonance to hopping process.

Mazen[13] studied the mechanism of conduction in copper ferrite on the basis of both band picture and hopping model. According to the band picture, the temperature dependence of conductivity is mainly due to the variation of concentration of charge carriers with temperature, while in the hopping model, the change of their mobility with temperature is considered to constitute the current by jumping from one ion to next ion.

3.1 CONDUCTION MECHANISM

Generally oxide crystals are described in terms of the lattice of oxygen ions with relatively small number of metal ions, occupying the intersticial positions. Though the bonding in transition metal oxides is predominently ionic the electrical conductivity is decided by the electrons with 'd' like wave functions and most probably the impurity states.

In the crystalline field of the solid, the levels are split up into triplet and doublet states. The triplet states lie below the doublet and oxides are expected to be metallic conductors, atleast, above antiferromagnetic temperature[14]. Below Neel temperature, the exchange forces give rise to further splitting of 3d band. However the oxides behave as semiconductors at all temperatures and possess excess intrinsic activation energy that could be expected by exchange splitting. Therefore the conventional band theory fails to account for the electrical transport properties in oxides.

3.1.a Conduction in Oxides

The majority of the transition metals oxides are semiconductors and their electrical conductivity is given by the equation

$$= \frac{A}{T^{B-1}} \quad \exp\left(\frac{-B}{KT}\right) \qquad \text{- - - - - - - - - -} \quad (3.1)$$

Where A and B (1 or 2) are constants. The activation energy ranges upto 1.5 ev and very much smaller values are encountered at sufficiently low temperature. For an oxide of composition MeO, the activation of a conduction electron may be represented by

$$O^{2-}\ Me^{2+}\ O^{2-}\ Me^{2+}\ O^{2-}\ \text{---}\ O^{2-}\ Me^{1+}\ O^{2-}\ Me^{3+}\ O^{2-}\ \text{----}(3.2)$$

where Me = Transition metal ion.

The energy necessary for the relation of Me^{3+} and Me^{1+} ion pairs corresponds to the energy gap in the density of states. On the basis of electron correlation, one has to consider the following terms for the contribution to activation energy.

1) The difference between ionization energy and electron affinity of the free Me^{2+} ion
2) The difference in energy of the two configurations, represented in equation (3.2)
3) The difference in stabilization of crystal field of above configuration
4) The polarization energy of the surrounding crystal lattice.

The first and second terms are opposite in sign and play a dominent part in the contribution to activation energy while the third term contributes very little (about one or two ev). Whereas the fourth term is predominent over the third term and contributes few ev to activation energy. A somewhat similar consideration may be thought to estimate the activation energy for impurity conduction. The polarization term has an important effect on the mobility of charge carriers and also upon the holes and electrons that are loosely bound to the impurity centres.

3.1.b Conduction in Ferrites

The mechanism of electron transport in metal oxides does not apply to the simple ferrites where all iron ions are trivalent. The transport may be represented by

$$Me^{2+}\ O^{2-}\ Fe^{3+} \text{ --- } Me^{3+}\ O^{2-}\ Fe^{2+} + Eact \quad \text{- - - - -} \quad (3.3)$$

where Eact = Activation energy.

The activation energy corresponds to the difference between third ionization potential of Fe^{3+} and Me^{3+} ions in the solid.

The spinel type crystal structure of ferrites contain comparatively large number of oxygen ions and small number of metal ions in the intersticial spaces. Ferric (Fe^{2+}) and ferrous (Fe^{3+}) ions are at the same octahedral sites (B) in spinel structure. The conduction takes place when electrons move from divalent iron ions to trivalent iron ions. The conduction in ferrites is assumed to be related to d-electrons and the direct electron motion between Fe^{2+} ions and Me^{2+} ions is neglected, due to small tunneling amplitude of d-electrons. In a stoichiometric compound, the ferrous ions are created by thermal activation according to the relation

$$M_B^{2+} + Fe_B^{3+} \rightleftarrows M_B^{3+} + Fe_B^{2+} + Eg \quad \text{- - - - -} \quad (3.4)$$

Where B denotes octahedral sites and M denotes divalent metal ion such as Ni, Co, Cu, Mn, Mg etc. Eg is the energy required to transfer the electron from M_B^{2+} to Fe_B^{3+} and vice-versa. For e.g. the presence of nickel on octahedral sites of spinel structure favours the conduction mechanism as

$$Ni^{2+} + Fe^{3+} \rightleftharpoons Ni^{3+} + Fe^{2+} \quad ----- \quad (3.5)$$

This explains the predominent conduction mechanism in nickel-zinc ferrites.

Ghani[15] and others reported three distinct regions of conduction in Cu-Ni ferrites. They attributed the conduction in first region to impurity charge carriers. The conduction in second region was accounted by the phase transition from tetrahedral to cubic phase. Whereas they suggested hopping mechanism for third region. The addition of nickel with increasing percentage in copper ferrite did not affect the first region. However it caused the disappearance one or both of the other regions, depending upon the method of preparation.

Ferrites are semiconducting oxide magnetic materials. Hence one can think of conduction mechanism in terms of holes and electrons. The electrical charge transport occurs by migration of charge carriers under the external potential difference. Electrons are the common charge carriers in most of the semiconductors. The electron deficiency or vacancy is called a hole which behaves as a positive charge having the mass and velocity equal to that of electron. Hence the conductivity can be written as

$$\sigma = e (n_e M_e + n_h M_h) \qquad ----- \quad (3.6)$$

where e = charge of electron

n_e = concentration of mobile electrons

n_h = concentration of mobile holes

M_e = mobility of electrons

M_h = mobility of holes

The temperature dependence of conductivity is given by the equation

$$\sigma = \sigma_o \exp. \left(- \frac{E_g}{KT} \right) \qquad ----- \quad (3.7)$$

where E_g = activation energy

K = Boltzmann constant

T = absolute temperature

σ_o = temperature independent constant.

In ferrites, the mobility is found to be much smaller (10^{-3} to 10^{-7} $cm^2/v.sec$) than that of semiconductors

(10 to 10^4 cm^2/v.sec). This made Heikes and Johnston[16] to propose the hopping electron model of Verwey[17] for the conduction mechanism in ferrites.

3.1.c Electron hopping and polarons

The electron interacts with the ions of the lattice creating a local deformation of the latter. This tends to follow the electron as it moves through the lattice. In many cases the lattice deformation increases the effective mass of electron, as it partially drags the ion along with it. The effect is more pronounced due to strong coulomb interaction in ionic crystals such as ferrites. The combination of electron and the strain field is called as polaron. The strength of lattice interaction is measured by electron-phonon coupling constant defined as

$$\frac{1}{2}\alpha = \frac{\text{deformation energy}}{hw} \qquad ----- \quad (3.8)$$

where w = longitudinal phononon frequency.

The displacement of lattice causes the polarization of the surrounding region and electron gets trapped at the centre of the potential well. When the well is deep enough, the electron may be trapped at the lattice site and its transition to the neighbouring sites may be governed by thermal activation. Due to thermal activation lattice is set into periodic vibrations which are quantised into phonons.

The coupling constant determines the nature of polarons. The polaron is said to be large one when coupling constant possesses higher value. Such polarons are found in ionic crystals. Whereas polaron is said to be small when coupling constant possesses small value. These polarons are found usually in covalent crystals. At high temperatures conduction is due to the diffusion of electrons by jumps from one site to next one in anology to the thermal activation processes accounted in ionic diffusion and ionic conductivity[18,19]. Thus hopping mechanism contributes to the conductivity at high temperatures. While at low temperatures electrons tunnel slowly through the crystal giving rise to the observed conductivity. The conductivity largely depends upon the mobility of the charge carriers. The expression for mobility of the charge carrier involving lattice vibration and jump length[20] is given by the equation

$$M = \frac{e^2 d^2 w}{KT} \quad \exp\left(- \frac{E_g}{KT}\right) \quad ----- \quad (3.9)$$

where d = distance between the nearest neighbouring sites i.e. jump length

e = charge of electron

W = phonon frequency

E_g = activation energy for hopping process.

At sufficiently low temperatures polaron behaves as a particle moving in a narrow band. Whereas at high temperatures small polaron motion results by the absorption of one or more phonons. Therefore the process is essentially a hopping mechanism. When the tunneling time is less than the time for successive hopping transition conduction by small polarons becomes predominent. There is a strong experimental evidence for small polarons and hopping mechanism[21]. Kawai[22] and others observed the hopping type mechanism in the ferrimagnetic region of Mn-Zn single crystal ferrites.

3.2 ACTIVATION ENERGY

It is the energy gap between the lowest conduction and highest valence band. This view is true provided the semiconducting material is pure and in the form of a single crystal. However this is rarely found in polycrystalline oxide semiconductors. The presence of impurities creates trap levels and localised states[23] and super exchange theory requires activation of electrons for their migration. The

Bloch wave functions are not suitable for the description of electrons localised on specific cations. Hence conventional band theory fails to account for the conduction properties in ferrites. Therefore the idea of band gap of semiconductors should be discarded and new concept of activation energy is introduced for oxide semiconductors.

Instead of conduction band and valence band, some descrete conducting states, separated by forbidden non-conducting states are assumed to exist in oxide semiconductors. Under such a condition certain minimum energy is necessary for an electron to take a jump from lower state to higher state. The potential barrier of the two states must be overcome for conduction to take place. Hence charge carriers do not cross the barrier unless they are activated by some external agent. The kinetic theory of heat suggests that the energy is imparted to the charge carriers to just creep the barrier and to make the conduction possible. This is known as " thermal activation " and minimum energy required for charge carriers to drift from low conducting state to the high conducting state may be taken as a measure of activation energy. Activation is effected by making use of other forms of energy such as optical wave energy or electric or magnetic fields.

3.3 TEMPERATURE DEPENDENCE OF RESISTIVITY

Like the semiconductors, the resistivity of ferrites is very sensitive to temperature. The diffusion of charge carriers from one state to other state is possible only when their energy exceeds the certain minimum energy called activation energy. As per Boltzmann statistics, if the height of the barrier is ΔE carrier having sufficient energy can cross the barrier in a fraction of $\left(\exp -\frac{\Delta E}{KT} \right)$ of time[24]. The thermal lattice vibrations constantly give rise to phonons and electron hops between the pairs of states either by absorption or by emission of phonon each time. In this way transport of charge carriers is achieved by thermally activated hopping process through interaction with phonons. On this basis, the temperature dependence of resistivity is represented by the expression

$$\rho = C \exp \left(- \frac{\Delta E}{KT} \right) \qquad ----- \qquad (3.10)$$

where C = temperature dependent constant

K = Boltzmann constant

T = absolute temperature

E = activation energy

For ferrites, constant (C) is replaced by another temperature independent constant (ρ_0)

$$\therefore \rho = \rho_0 \exp \left(- \frac{\Delta E}{KT} \right) \qquad ----- (3.11)$$

taking logarithms on both sides, we get

$$\log_e \rho = \log_e \rho_0 - \frac{\Delta E}{KT} \qquad ----- (3.12)$$

This represents the equation of a straight line. However the graph of $\log \rho$ vs $\frac{1}{T}$ represents a break at the Curie temperature. It is due to the transition from the paramagnetic region to ferrimagnetic region. Komar and Klivshin[25] used the slope of such a graph to calculate the activation energy.

3.4 EXPERIMENTAL TECHNIQUE

The conductivity was measured by the two probe method on compressed and sintered pellets of about 1 cm in diameter and 0.2 cm in thickness, with the experimental set up shown in Fig.3.1. The measurements were carried out with the help of a special conductivity cell, fabricated in the workshop of the physics department of Shivaji University, Kolhapur.

The cell consists of two brass cylindrical rods fitted in two porcelain discs. The fitting screws were used to keep the assembly of discs and rods firmly. The screws

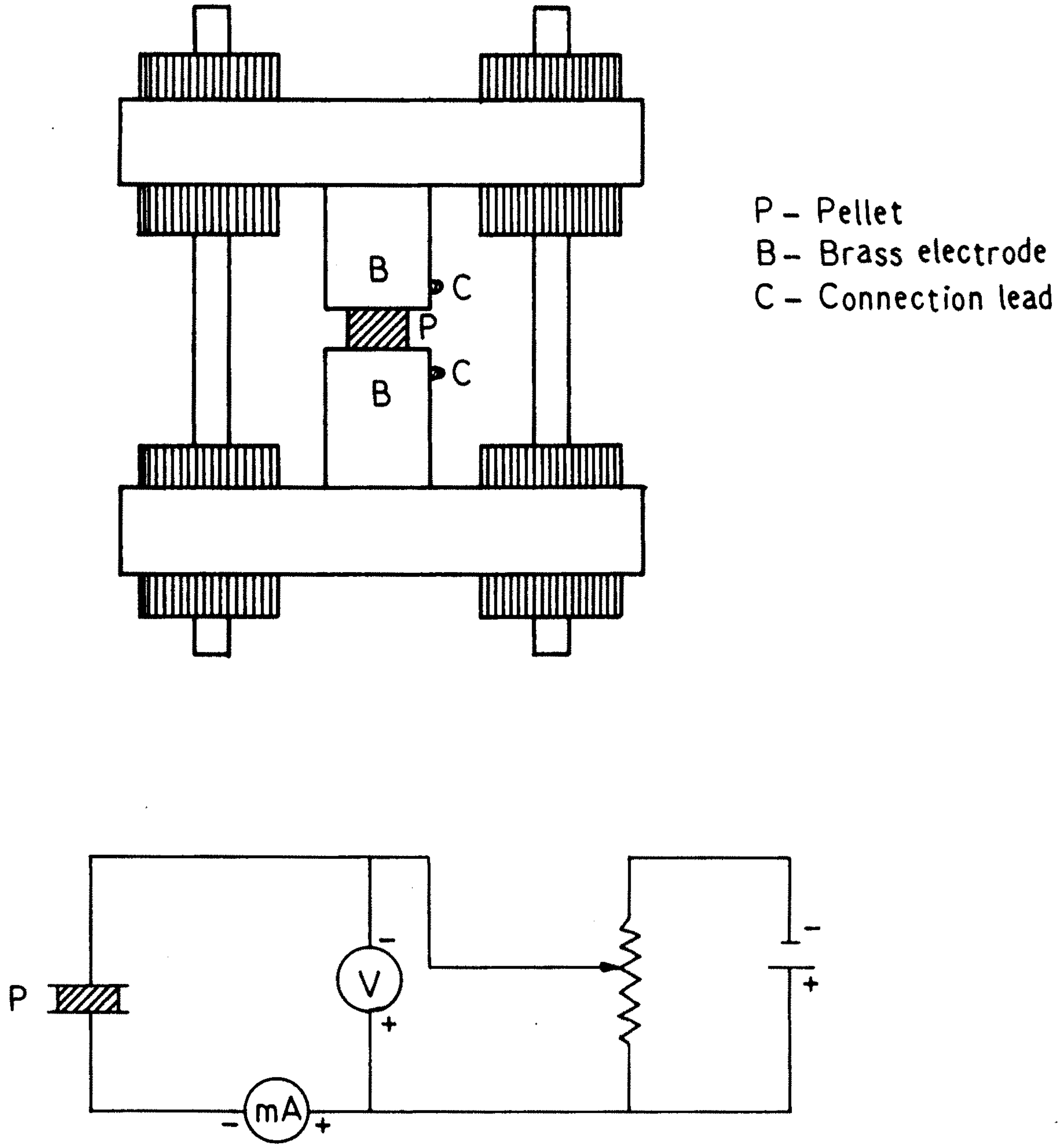

Fig.3.1 Sample holder and circuit diagram for electrical resistivity

provided on the rods were used for external contact with the help of silver leads, insulated from each other by ceramic beads. To have the good ohmic contact, the pellet was polished and silvered on opposite faces and sandwitched between the rods (Fig.3.1). The entire assembly was kept inside the temperature regulated furnace. The calibrated chromel-alumel thermo-couple was used to measure the temperature of pellet accurately by keeping its tip very close to the sample. The actual experimental set up is shown in the photograph of Fig.3.2. The d.c. voltage of about 2 volts was applied across the pellet through transistorised power supply unit (TPSU). Whereas thermo emf was measured with digital multimeter and the current with electronic multimeter.

The temperature of the furnace was gradually increased from room temperature to 750°C and corresponding current was measured for every change of 1 milivolt in thermo emf for each sample. Then the resistance of the pellet was calculated by Ohm's Law.

$$R = \frac{V}{I} \qquad \text{-----} \qquad (3.13)$$

where V = voltage across the pellet in volts

Fig. 3·2 EXPERIMENTAL SET UP FOR D.C. RESISTIVITY MEASUREMENT.

I = current through the pellet in amps while resistivity was calculated by the formula

$$\rho = \frac{R.A}{h} \qquad ----- \qquad (3.14)$$

where A = area of cross section of a pellet

h = height of a pellet.

Lastly, the plots of log ρ versus $\frac{10^3}{T}$ were plotted (Fig.3.3 to 3.8) for various compositions mentioned earlier to calculate the activation energy and to determine Curie temperature.

3.5 RESULTS AND DISCUSSION

3.5.a Curie temperature and Activation Energy

The electrical resistivity was measured on $Cu_x Co_{1-x} Fe_2O_4$ with x = 0, 0.4 and 1.0, from room temperature to 750°C by experimental set up shown in Fig.3.1. The variation of resistivity with respect to temperature is shown in Fig.3.3 to 3.8. The change in slope is markedly observed in all the three ferrites. Such a change is either due to Curie temperature[25] or change in conduction mechanism[26]. It is observed that in both the regions the resistivity obeys the relation (3.11) and decreases with rise in temperature. This indicates the semiconducting nature of

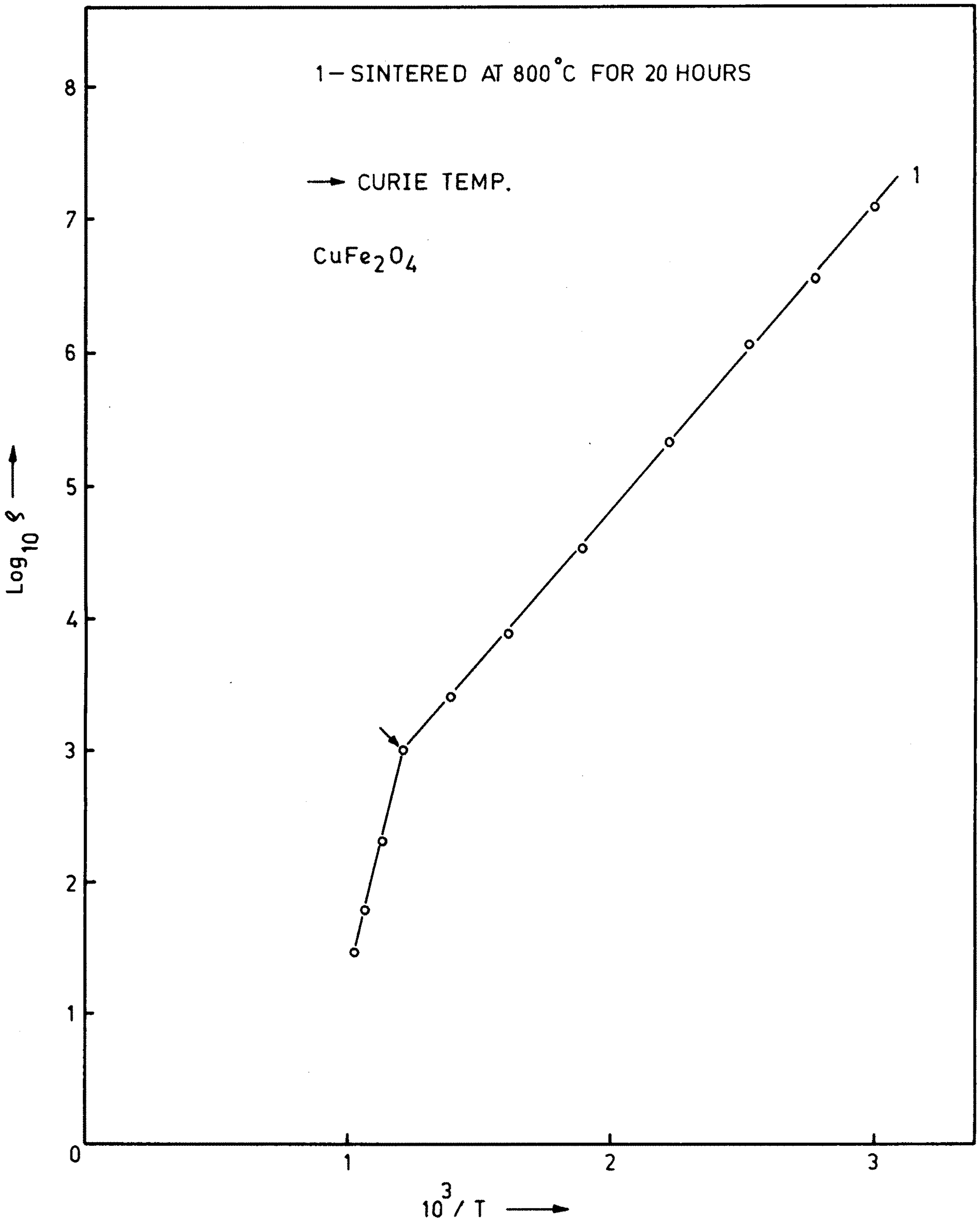

Fig. 3·3 $\text{Log}_{10}\,\varrho$ vs $10^3/T$

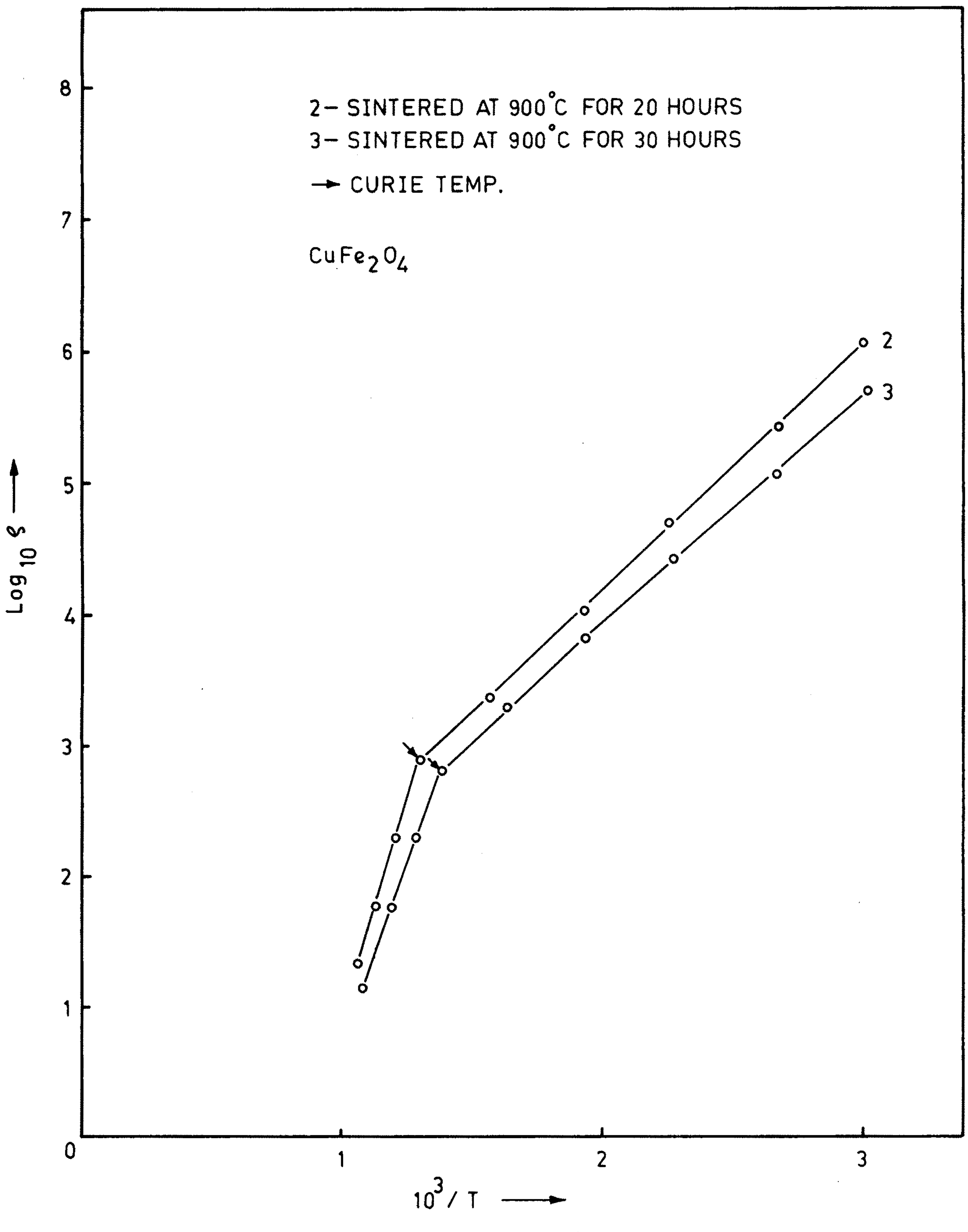

Fig. 3·4 Log$_{10}$ ϱ vs 10^3/T

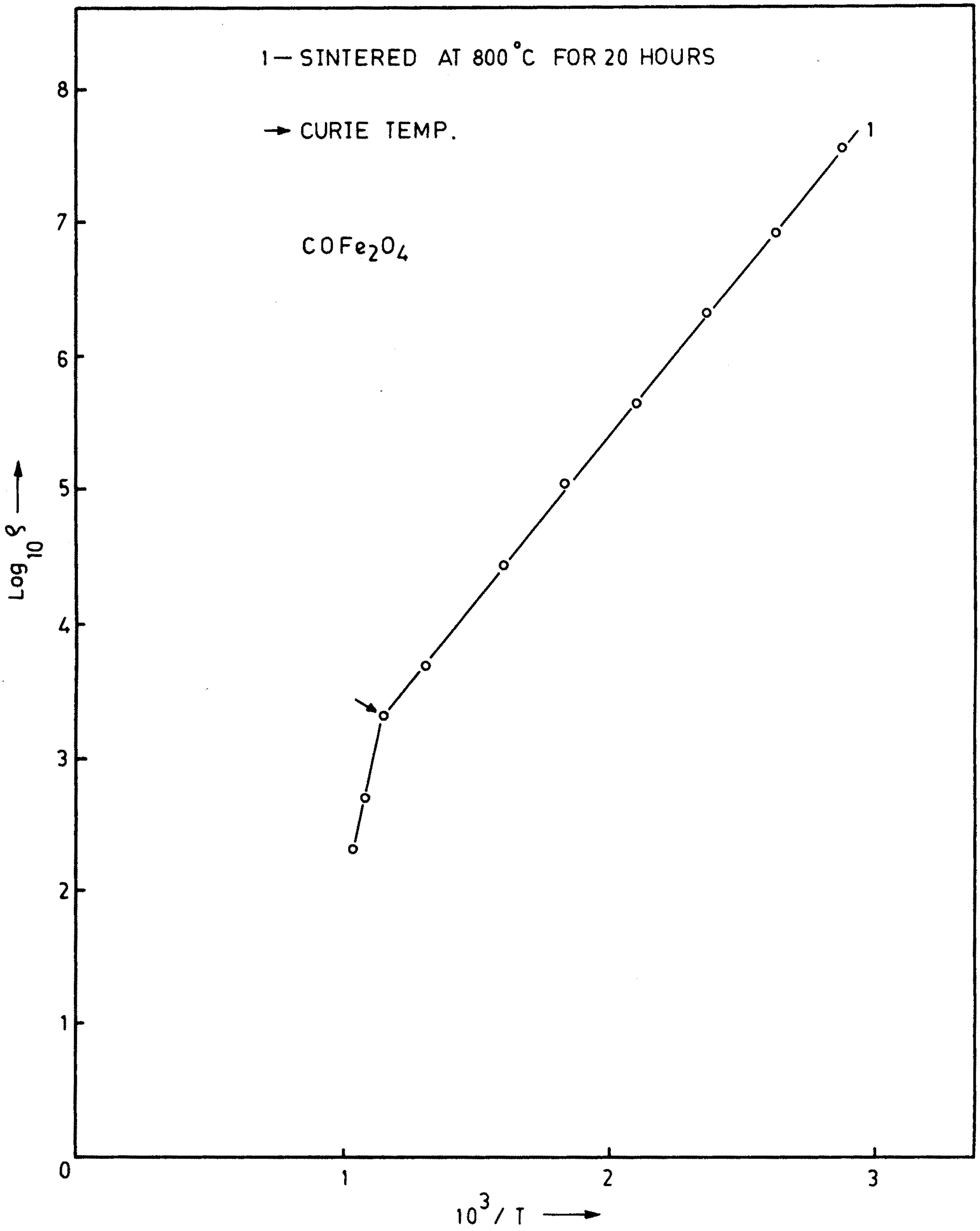

Fig. 3·5 $Log_{10} \varrho$ vs $10^3/T$

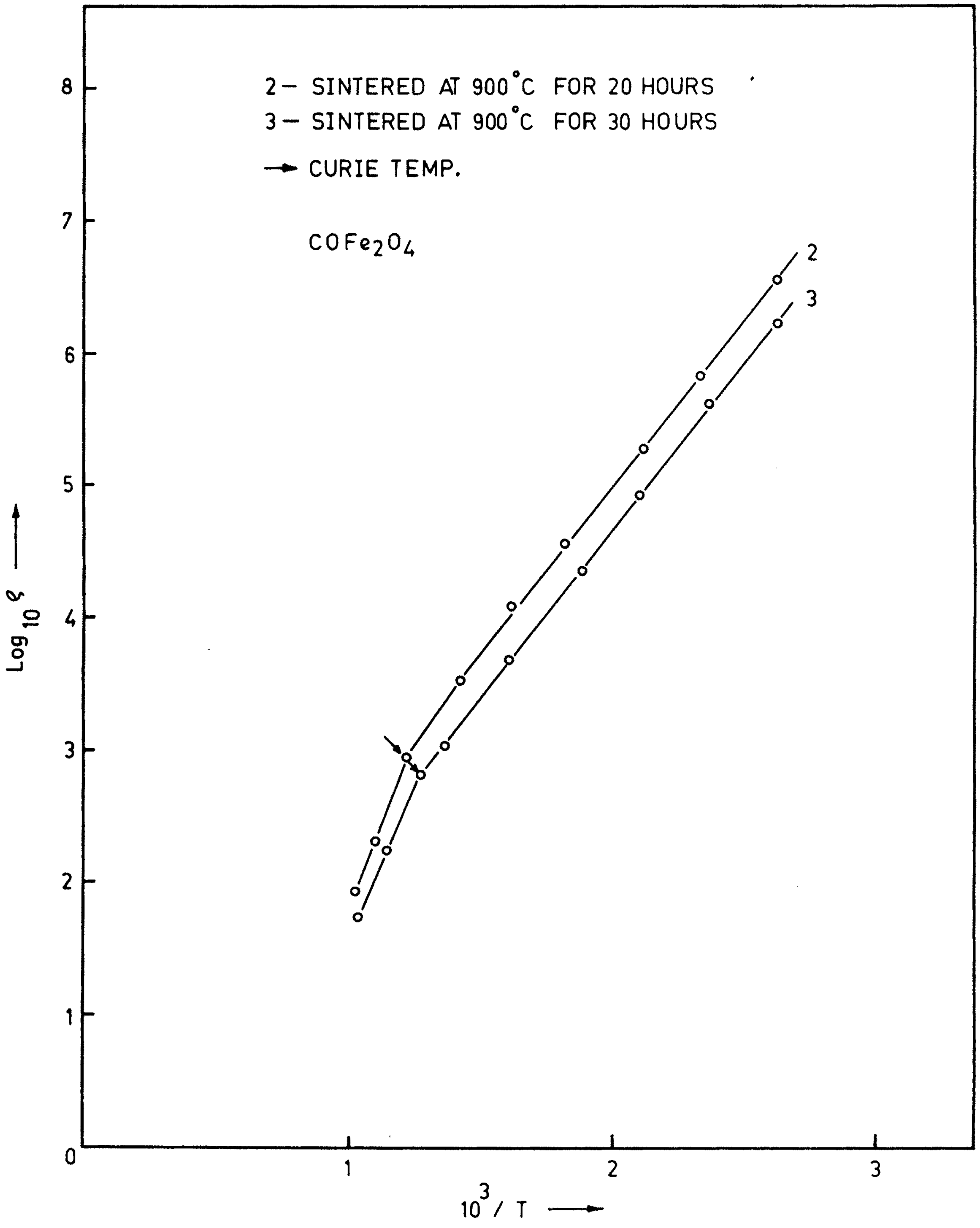

Fig. 3·6 $\text{Log}_{10}\,\varrho$ vs $10^3/T$

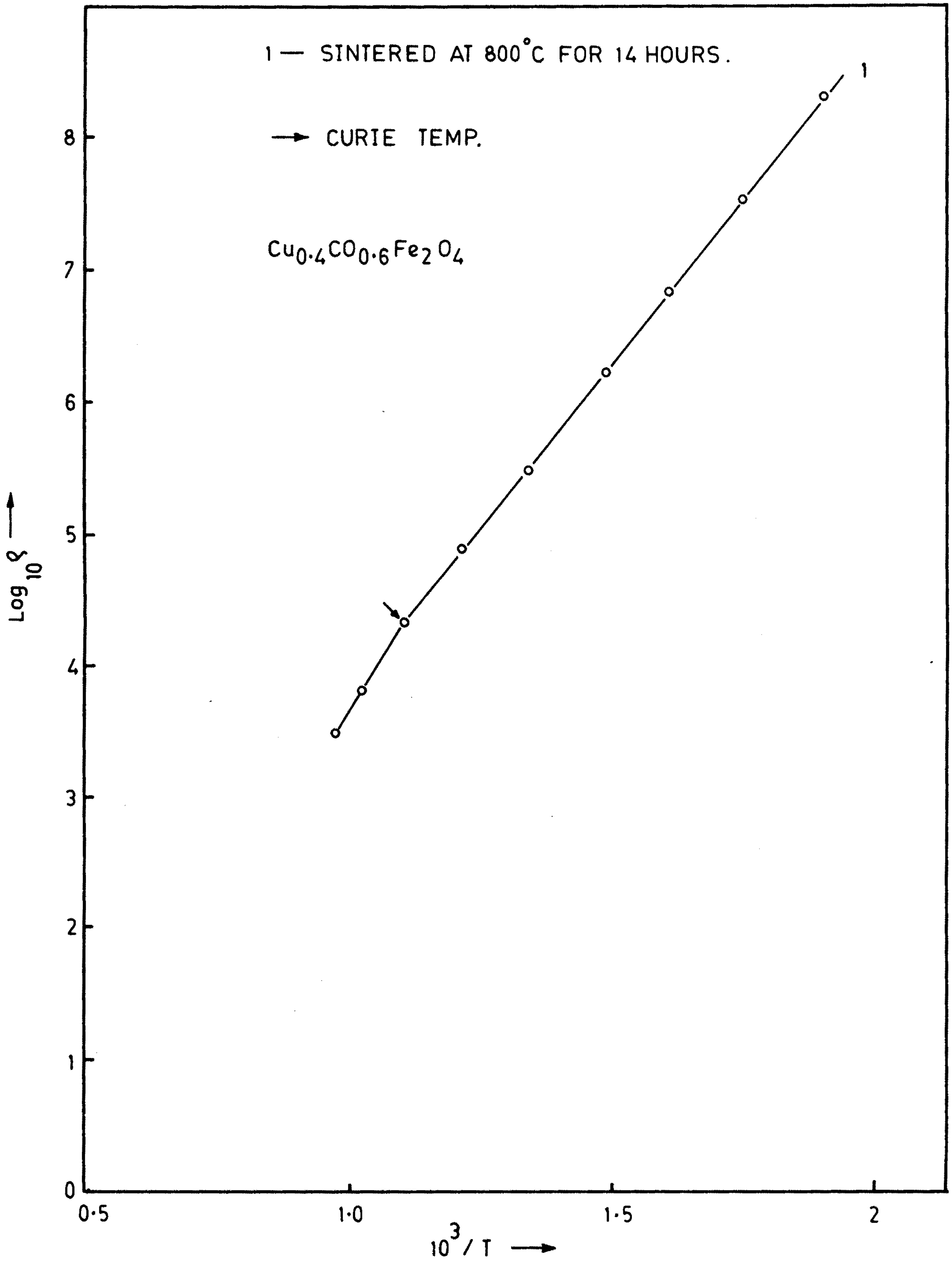

Fig. 3·7 Log$_{10}$ ρ vs $10^3/T$

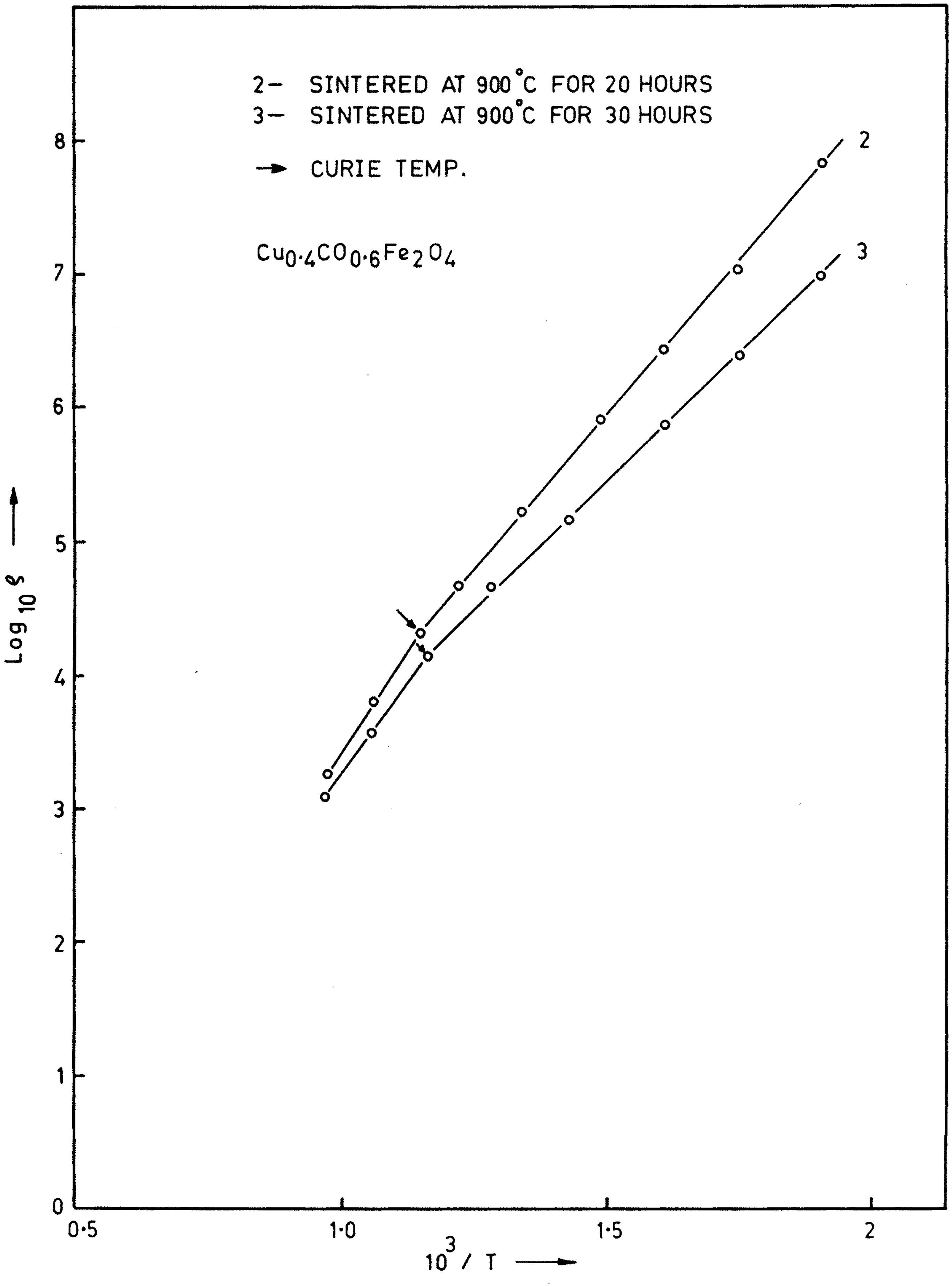

Fig. 3·8 $Log_{10}\rho$ vs $10^3/T$

ferrites under study.

The activation energies are calculated from the slopes of the paramagnetic and ferrimagnetic region and tabulated in table 3.1 along with sintering temperature and time and Curie temperatures. From the table it is evident that the activation energy for paramagnetic region is greater than that of ferrimagnetic region. Graphically observed Curie temperatures agree well with the reported values[27,28].

In all the three ferrites, there is a change in slope of resistivity with temperature variation. Smit and Wijn[27] pointed out that the change in slope can be attributed to two parallel conductivity mechanisms with different activation energies. Our results are in good agreement with this conclusion. Similarly Ivkhin et al[29] had shown theoretically that the change in slope occurs in a straight-line while crossing the Curie temperature. However different explanations are given for the transition temperature at which conductivity mechanism shows the break. The electrical conductivity of Co-Zn ferrite was studied by Satyanarayan and Raman Murthy[30] as a function of composition and temperature. They explained the conductivity in terms of hopping mechanism by measuring Seebeck coefficient. The plots of log ρ versus $\frac{1}{T}$ were almost straight-line and showed a transition near Curie temperature. They observed higher activation energy in paramagnetic region than that of ferrimagnetic region.

The change in slope indicates[25] the magnetic transition. The distance between the octahedral sites is much greater than the sum of radii of cations. As a result of this electrons will not be free to move in a crystal but remain fixed to B site. However, the conduction is due to the activation of states on account of change in cation valency i.e. $Fe^{2+} \dashrightarrow Fe^{3+}$ hopping mechanism. The discontinuity is explained on the ordering of Fe^{2+} and Fe^{3+} ions on the octahedral sites[31] accompanied by a small change in crystal structure. The lowering of activation energy is attributed to the effect of spin ordering[14,32]. In otherwords the change in slope at Curie temperature is mainly due to spin disordering of electrons[33]. Therefore this strongly insists that there is some predominent change in conduction mechanism due to magnetic phase transition.

Two phase polaron model was used by Klinger[34] to explain the conduction mechanism. At low temperature, the conduction is via magnetically correlated polarons, whereas above Curie temperature conduction is via Brownian like tunneling motion of polarons.

The presence of cobalt on octahedral sites favours the conduction mechanism of $Co^{2+} + Fe^{3+} \rightleftarrows Co^{3+} + Fe^{2+}$ type in cobalt-copper ferrite. Parker et al[8] studied the electrical conductivity of $NiFe_2O_4$ ferrite with a small substitution of cobalt and established two valence states of cobalt.

Broese Van Groenou[20] pointed out that the presence of Fe^{2+} ions amidst the Fe^{3+} ions gives rise to n-type conductivity at sufficiently high temperature due to movement of extra electron on Fe^{2+} ion moving through the crystal. A similar situation exists for Co^{3+} and Cu^{3+} ions in $CoFe_2O_4$ and $CuFe_2O_4$ respectively. In these cases the deviating valency is higher than that originally present (Co^{2+}, Cu^{2+}) and p-type conduction is found.

Thus in iron excess ferrites, Fe^{2+} concentration is appreciable and predominent conduction is due to hopping of electrons from Fe^{2+} to Fe^{3+} ions leading to n-type conductivity with relatively low activation energy (Table 3.1). Such behaviour is found in case of $CuFe_2O_4$ ferrite. Whereas the low conductivity in $CoFe_2O_4$ is due to deficiency of iron leading to p-type conductivity with relatively large activation energy (Table 3.1).

TABLE 3.1

Activation energy and Curie temperature of $Cu_xCo_{1-x}Fe_2O_4$ ferrite.

Sample	Sintering temperature and time in °C/hrs	Activation Energy in ev.		Curie temperature in °C
		paramagnetic region	ferrimagnetic region	
$CuFe_2O_4$	800, 20	1.5889	0.4495	521.5
"	900, 20	1.3407	0.3641	482.3
"	900, 30	0.9647	0.3371	451.6
$CoFe_2O_4$	800, 20	1.72	0.4937	589.1
"	900, 20	1.03	0.4824	546.7
"	900, 30	0.9269	0.4804	520.7
$Cu_{0.4}Co_{0.6}Fe_2O_4$	800, 14	1.2863	1.004	543.4
"	900, 20	1.1350	0.8970	493.3
"	900, 30	1.022	0.7363	473.3

The lowest conductivity in $Cu_{0.4}Co_{0.6}Fe_2O_4$ with relatively largest activation energy (Table 3.1) may be attributed to electron-hole compensation[35].

The dependence of resistivity of various spinel ferrites upon firing temperature has been studied by Long Kla Tien and Shouwa Channg-Chuang Wei[36]. They noticed maximum conductivity in the ferrites fired at 1300°C and classified the conductivity into two types as deficient and excess impurity by the valence controlled action. Besides these two actions they suggested two other mechanisms namely grain boundary and structure distortion which can affect the resistivity of ferrites considerably. Such behaviour is found in all the three samples studied in the present case (Fig. 3.3 to 3.8).

However in either case of ferrites, the presence of single phase is found by X-ray diffraction patterns to confirm the idea that the conductivity in ferrites is an intrinsic nature of single phase spinel structure rather than the other phases.

3.5.b Effect of Porosity and Sintering Temperature

Figures 3.3 to 3.8 represent the plots of $\log_{10} \rho$ versus $\frac{10^3}{T}$ of the samples sintered at different temperature and time.

In all the cases it is observed that the plots of higher sintering temperature and time lie below the plots of lower sintering temperature and time. This reveals the fact that the resistivity decreases with increase in sintering temperature and time. Table 3.1 represents the various activation energies of samples sintered at different sintering temperature and time. From the table it is observed that activation energy decreases with increase in sintering temperature and time. However curie temperature generally shifts towards lower temperature side, on increasing firing temperature/time. This is due to the fact that a sample having higher grain size favours easy transition between ferro and para regions. The porosity for each sample for each sintering temperature/time is calculated and tabulated in Table 3.2 along with resistivity at 250°C. From the table it is observed that resistivity decreases with firing temperature/time.

The above results can be explained on the basis of microstructural changes during heat treatment. The electrical properties like conductivity, eddy current losses etc are mainly governed by heat treatment during preparation process.

TABLE 3.2

Porosity and Resistivity of $Cu_x\ Co_{1-x}\ Fe_2O_4$ Ferrite.

Sample	Sintering temperature and time °C/hrs.	Actual density (da) grams/c.c.	X-ray density (dx) grams/c.c.	Porosity $=\frac{dx-da}{dx}$	Resistivity at 250°C
$Cu\ Fe_2O_4$	800, 20	3.9834	5.6510	0.2951	33.11 KΩcm
"	900, 20	4.3283	5.6510	0.2341	13.18 KΩcm
"	900, 30	4.5732	5.6510	0.1904	2.19 KΩcm
$Co\ Fe_2O_4$	800, 20	3.5897	5.2900	0.3219	173.8 KΩcm
"	900, 20	4.0211	5.2900	0.2399	70.79 KΩcm
"	900, 30	4.2242	5.2900	0.2016	23.44 KΩcm
$Cu_{0.4}Co_{0.6}Fe_2O_4$	800, 14	3.5585	5.3488	0.3347	275.4 MΩcm
"	900, 20	3.6880	5.3488	0.3105	97.72 MΩcm
"	900, 30	3.7892	5.3488	0.2916	10.23 MΩcm

The d.c. electrical resistivity, dielectric constant loss etc depend upon extrinsic parameters such as purity of starting material, stoichiometry, surface condition and sintering temperature, physico-chemical history, porosity, density, grain size, chemical inhomogeneity etc. Electrical conductivity also depends upon cation distribution. Polycrystalline ferrites show higher resistivity in presence of pores, grain boundries and other compounding agents including substitutional and impurity ions.

Porosity increases the resistivity markedly and the presence of pores filled with air provides insulating path to electrons resulting in high resistivity. Such a behaviour is observed in the present samples (Table 3.2). It is reported that the average grain size increases with sintering temperature[37]. Similar phenomenon is revealed by the micrographs of the samples of Fig. 5.1 to 5.6. As sintering temperature/time increases grain size increases and porosity decreases. This results in higher conductivity in the samples as a consequence of decrease in resistivity.

Oxygen stoichiometry also plays crucial part in the conductivity of ferrites. An oxygen ion vacancy contributes two extra electrons to 3-d band. When these extra electrons get detached from their vacancies by thermal agitation, n-type of conductivity is predominent in oxygen deficient material. While p-type conductivity is predominent in oxygen excess material[8].

Heat treatment during the preparation process changes the electrical properties of polycrystalline ferrites due to rapid oxygen dissociation at high sintering temperature. This leads to the formation of small amount of divalent ion during sintering and causes the ferrites to possess high conductivity. The presence of air gaps between the grains results in the formation of inhomogeneous dielectric structure[38]. This greatly affects the d.c. and a.c. conductivity of ferrites and hence conduction mechanism in ferrite is largely dependent on porosity. Therefore smaller the porosity greater will be the grain size and higher will be the conductivity.

The pore density decreases due to densification at higher sintering temperatures[27a]. The micrographs (Fig.5.1 to 5.6) indicate the low porosity in a matrix of large-sized grains in a ferrites sintered at higher temperature for a longer time. This causes the decrease in resistivity (Table 3.2) and increase in conductivity. Therefore it can be emphasized that one of the factors for higher conductivity in ferrites is the increase in average grain size and decrease in pore concentration during the heat treatment.

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