CHAPTER III
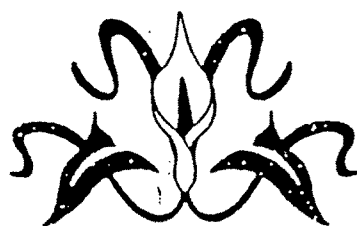
CHAPTER III

ELECTRICAL PROPERTIES

3.1 INTRODUCTION

There are a great number of applications for which electrical conduction properties are important (1). Semiconductor materials are used for many specialized applications, such as resistance, heating elements, semiconductor devices such as rectifiers, photocells. transistors, thermistors, detectors and moudulators have become an important part of modern electronics. An equally important applications of oxides are as electrical insulators, porcelains and glasses used for low and high voltage insulation.

The electrical conducting properties mainly depends on the method of preperation and presence of impurity. Electrical comduction being a Kinetic phenomenon, will be discussed with regard to it's temperature dependence. For thermistor applications the temperature dependence represents the materials sensitivity to temperature change

In general electical conducting in high temperature materials is a function of temperature and composition (non-stoichiometry and impurities),irrespective of the type of conduction, In some cases grain boundaries can significantly influence electrical properties.

3.2   DC CONDUCTIVITY

In oxide oxygen non-stoichiometry provides the source of current carriers, many times the ion themselves. However, in transition metal oxides,

the narrow half filled d-band could provide the current carriers by excitation, therfore many of the metal oxides are semiconductors. In general the spinel oxide crystal structure may be conviniently regarded in terms of oxygen ions.

The electric currrent density j is defined as a charge transported through a unit area in a unit time. If the number of charge particles per unit volume is n and they have a drift velocity of v and a charge per particle ze. where z is valence and e be the electronic charge, then the electrical current density is given by

$$j_i = n_i z_i eV.$$

The electrical conductivity σ is defined by the relation ship $\sigma = j / e$

If E is the electic field strength, taking any field into account. (2)

Consequently $\sigma_i = (n_i z_i e) V / E$ ----------(3.1)

The drift velocity is directly proportional to the locally acting electric firld strength, and the ratio is defined as mobility.

$$\mu_i = V_i / E_i \qquad \text{----------(3.2)}$$

The conductivity then, is the product of the concentration and mobility of charge carriers

$$\sigma_i = (n_i z_i e) \mu_i \qquad \text{--------(3.3)}$$

Sometimes it is desirable to employ an absoute mobility B, defined as the drift velocity per unit of applied force. This is given by

$$B_i = V_i / F_i = V_i / Z_i eE \qquad \text{-------(3.4)}$$

In terms of the absolute mobility the conductivity is given by

$$\sigma_i = n_i z_i{}^2 e^2 B \qquad \text{------------(3.5)}$$

When we consider, the effect of variables such as composition, structure and temperature on electrical conductivity, we are concerned with there two separate contributors, the concentration of charge carriers and their mobility. If we consider the charge carriers as initially having a random movement with an average drift velocity of zero, the equation of motion resulting from the application of a steady average external force F = ZeE, is

$$m \quad (dv/dt + v/\tau) = F = ZeE \qquad \text{----------(3.6)}$$

When m is mass of particle. In the absence of external forces,

$$dv/dt + v/\tau = o \qquad \text{-----------(3.7)}$$

and by integrating,

$$V(t) = Vo \exp (- t/\tau) \qquad \text{----------(3.8)}$$

Where τ is characteristic relaxation time governing the time required to reach equilibrium. In equation (3.6) the first term describe inertial effects, when v is time dependant, once the inertial effects have diedout (dv/dt = 0)

we have,

$$V = Ze \tau E/m \qquad \text{----------(3.9)}$$

and by comparison with equation 3.1

$$e = nz^2e^2\tau/m \qquad \text{-----------(3.10)}$$

That is the charge transported is proportional to the charge density (Zen), the accelration of charge is given field (proportional ro Ze/m) and τ corresponding to the time that these forces act on the charge between collisions and random motion.

3.3 THERMOELECTRIC POWER

Hall effect and thermoelectric properties are widely use in semiconductors. The interpretation of Hall effect is more straight forward. However in case of low mobility materials such as oxides thermoelectric power measurment is the only alternative about p or n-type conduction. Another important significance of thermoemf is that it enables one to calculate the fermi energy and carriers concentration (3).

When the two surfaces of electrically conducting materials are mentioned at different temperatures (ΔT) they develop a potential (ΔV) then the sebeck coeffcient can be given as

$$\alpha = \Delta V / \Delta T \qquad \text{----------(3.11)}$$

The sebeck effect may be thought of as a diffussion process. The electrons or holes at hot end have higher kinetic energy as compared to that at cold end. Hence electric field is produced across the sample.

According to the Quantum theory, for semiconductors with both types of carriers, α is given by

$$\alpha = (\alpha_n \sigma_n + \alpha_p \sigma_p) / (\sigma_n + \sigma_p) \qquad \text{----------(3.12)}$$

Where

$$\sigma_n = n_e \mu_n \text{ and } \sigma_p = p_e \mu_p \qquad \text{----------(3.13)}$$

$$\alpha n = (k / e) (A_n - E_f / KT) \qquad \text{----------(3.14)}$$

and $\qquad \sigma p = (k / e) [A_p + (E_g + E_f) / KT) \qquad \text{----------(3.15)}$

Where n and p are the electron and hole densities,

μ_n and μ_p are the electron and hole mobilities,

E_f is the fermi energy and

E_g is the band gap energy.

From the temperature dependence of the sebeck coefficient, the sign of charge carriers and their mobility variation can be calculated.

3.4 EXPERIMENTAL

The DC electrical conductivity is measured with two probe method. The sample is used in the form of pellet. To assure good ohmic contact, silver paste is sandwiched between two silver foils. The specially designed conductivity cell is used and is shown in Fig (3.1). The low voltage is applied across the sample and corresponding current through the sample is measured. The complete assembly is then placed into the furnace. The temperature of furnace is measured with calibrated chromel - alumel thermocouple. The resistivity of sample is measured at various temperatures. The experimental set up is shown in the photograph Fig (3.2).

The resistivity (ρ) was calculated by using the relation

$$\rho = \pi r^2 \, V \, / \, t.I \qquad \text{------------(3.16)}$$

Where t is the thickness of the pellet,

   r is the radius of the pellet and

   I is current through the sample.

Initially, the surface of pellet was coated with silver paste for good ohmic contact. The pellet was put into the sample holder and then kept into the regulated furnace for the measurement of thermoelectric power. A schematic diagram with necessary connections is shown in Fig 3.3. For the
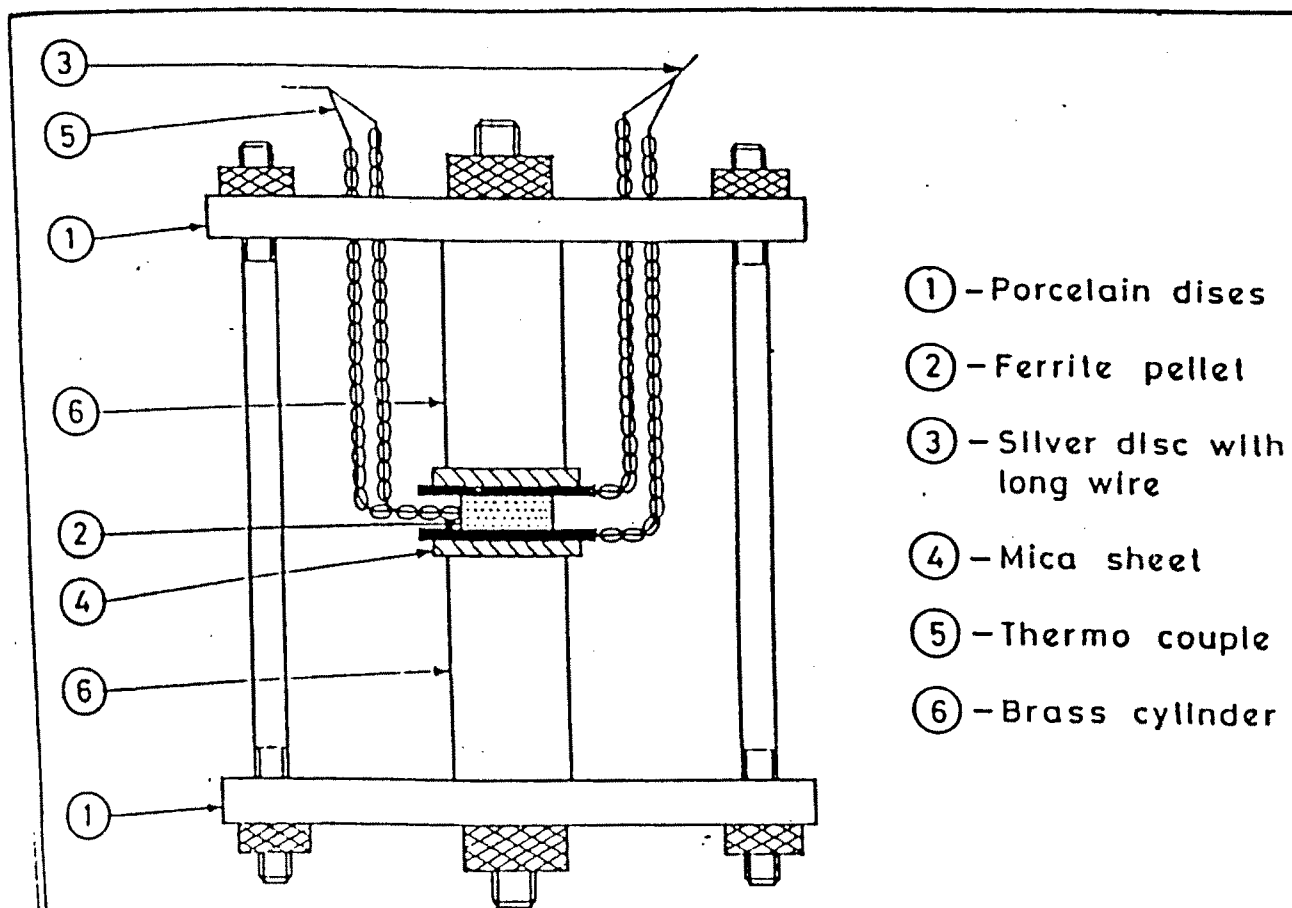
1 —Porcelain dises

2 —Ferrite pellet
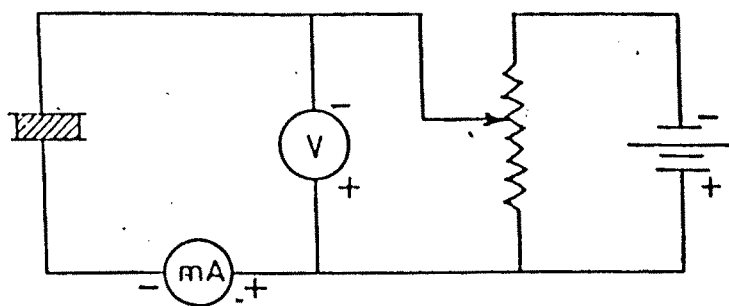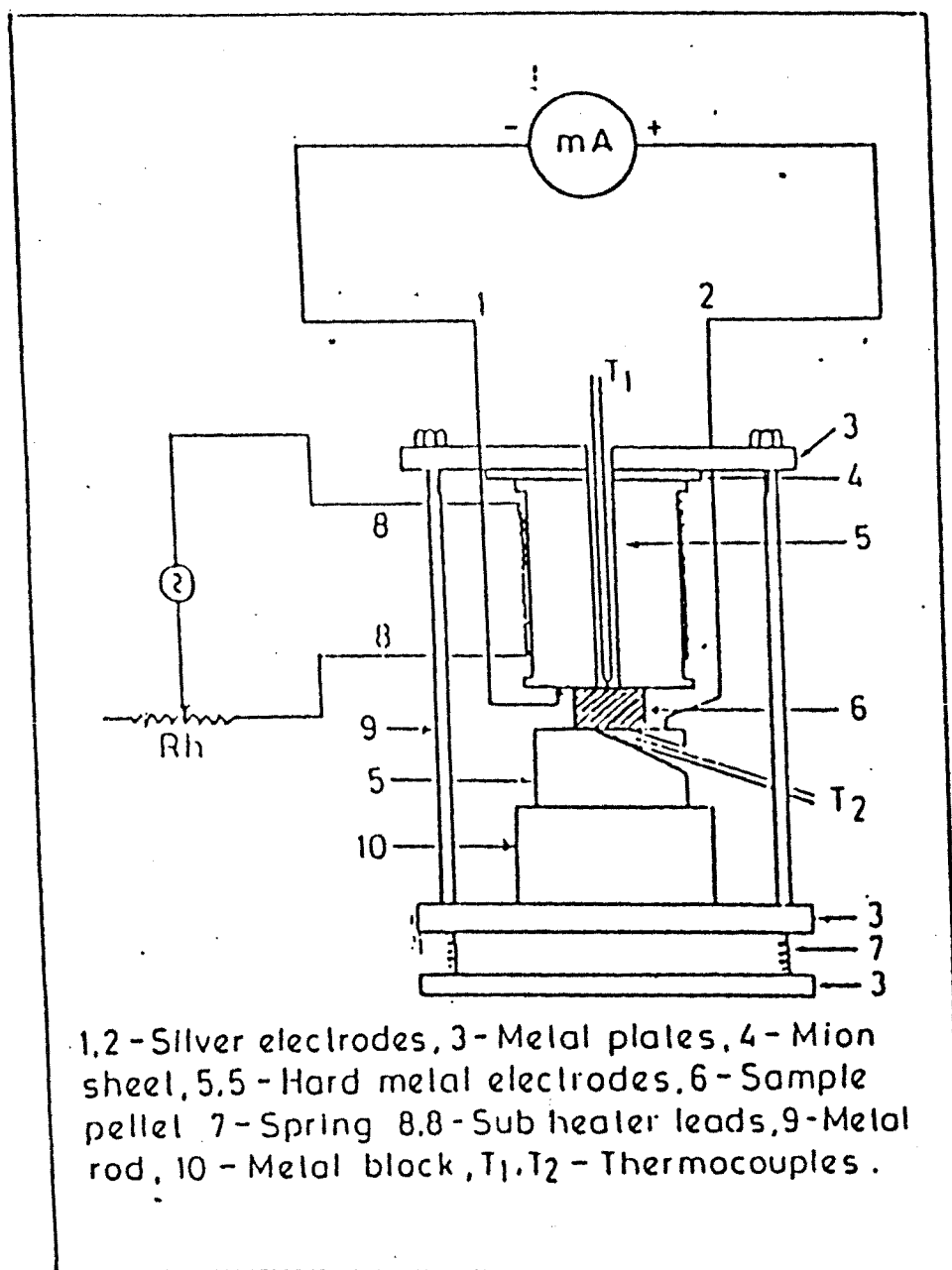
3 —Silver disc with
    long wire

4 —Mica sheet

5 —Thermo couple

6 —Brass cylinder

Fig. 3·1(a) THE CONDUCTIVITY CELL.

Fig. 3·1(b) CIRCUIT DIAGRAM FOR ELECTRICAL
           RESISTIVITY.

1,2 - Silver electrodes, 3 - Metal plates, 4 - Mion sheet, 5,5 - Hard metal electrodes, 6 - Sample pellet 7 - Spring 8,8 - Sub heater leads, 9 - Metal rod, 10 - Metal block, T_1, T_2 - Thermocouples.

— Scematic diagram of experimental set-up for the measurment of thermoelectric power.

FIG. 3.3
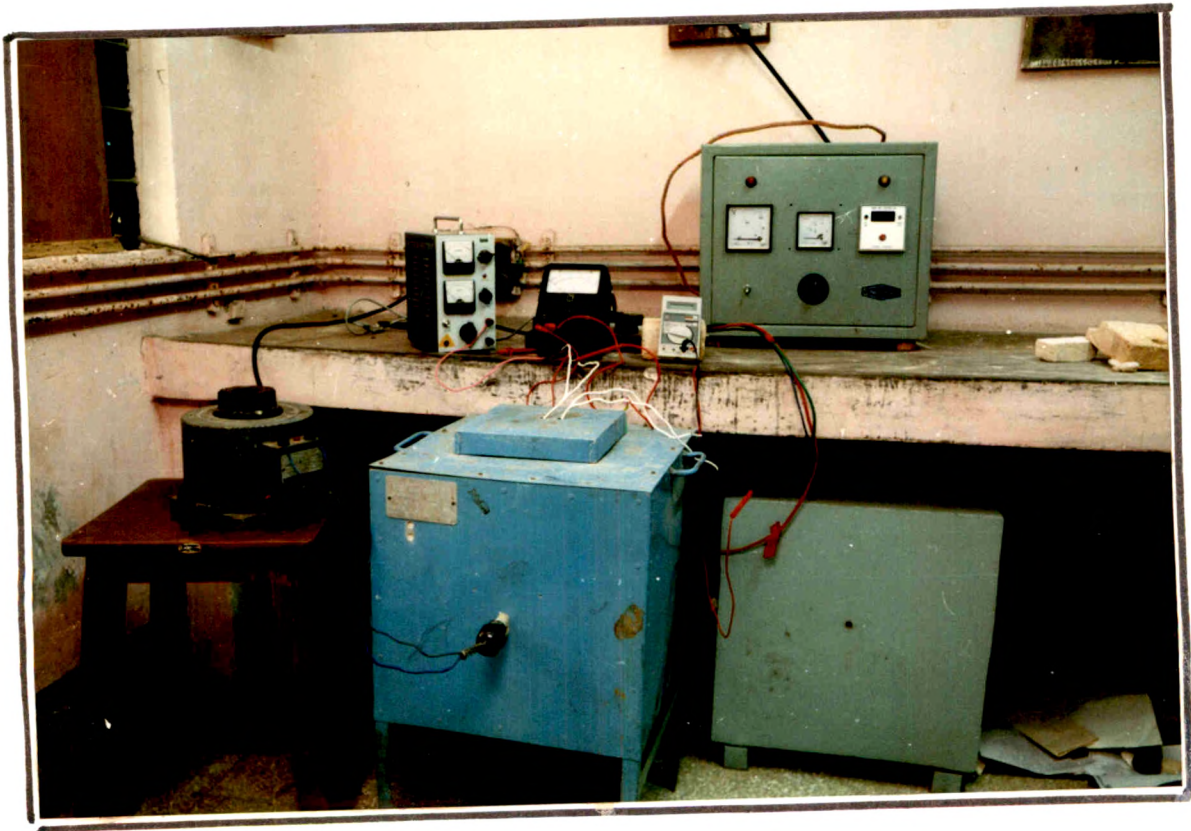
Fig. 3.2 Experimental set up for the measurement of D.C. electrical resistivity.
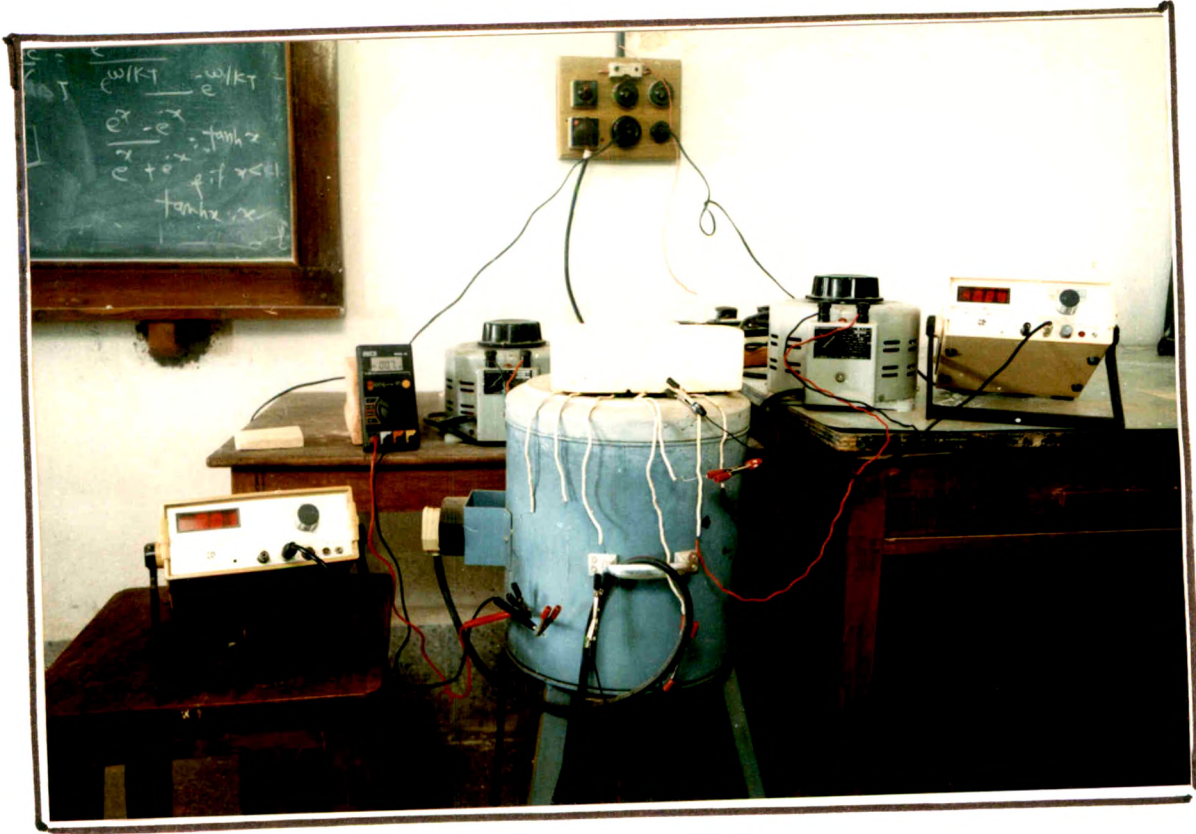
Fig. 3.4 Experimental set up for the measurement of Thermoelectric power.

measurement of thermoelectric power, the temperature differnce of 20^0 C across the pellet was maintained with the help of a small heater attached to one of the electrodes of the sample holder. The thermoemf (Δv) developed across the pellet was measured on a degital d.c microvoltmeter. Sufficient time was allowed to attain the thermal equillibrium before recording the thermo emf. The sample was then heated by keeping the temperature differnce of 20^0C and the devloped thermo emf was measured at different temperatures.

In the measurement of Δv, the microvoltmeter gives a positive reading by connecting the positive terminal to hot end of the sample. This happens in the case of n-type charge carriers. This situation reverses when the charge carriers are of p-type. The thermoelectric power was determed by using the relation.

$$\alpha = \Delta V/\Delta T \qquad \text{-----------(3.17)}$$

Where ΔV is thermoemf and

ΔT is the temperature difference across the pellet.

The experimental set up is shown in Fig(3.4)

3. 5 RESULTS AND DISCUSSION

The electrical conduction In solids is generally determined by two parameters; carriers concentration n(the number of carrier of charge q per unit volume), and carrier mobility μ. In terms of n and μ the electrical conductivity σ, can be expressed as

$$\sigma = nq\mu \qquad \text{-------(3.18)}$$

For solids more than one type of charge carrier the electrical conductivity is the sume of the partial conductivity σi, of all the charge carriers, electrons, holes, cations and anions, and can be expressed as

$$\sigma = \sum \sigma i$$

$$= \sum n_i\, q_i\, \mu_i \qquad \text{-------(3.19)}$$

The overall conductivity can neither electronic, ionic or a mixture of the two depending on the relative magnitude of the product of n_i and μ_i of all carriers. In predominently ionic compounds such as oxides charge transport is, in principle, characterized by both ionic and electronic counduction. Often one type of charge carrier dominates the charge transport, but transition to the other type of conduction may occur at certain temperatures and / or atmospheres as a result of charge in composition or stoichiometry of the solids(4)

In equation (3.18) both the carrier concentration and mobility can contribute to the temperature dependence of electrical conduction. For materials with a band gap, both processes may be thermally activated and therefore the temperature dependence of electrical conduction can generally be described by an Arrhenious type equation.

$$\sigma = \sigma_o \exp(-Q/kT) \text{ -----------(3.20)}$$

Where Q is activation energy of electrical conduction and σ_o is the pre-exponential factor. For oxide materials in particular, intrinsic conductivity is only observed with high purity samples at high temperatures.
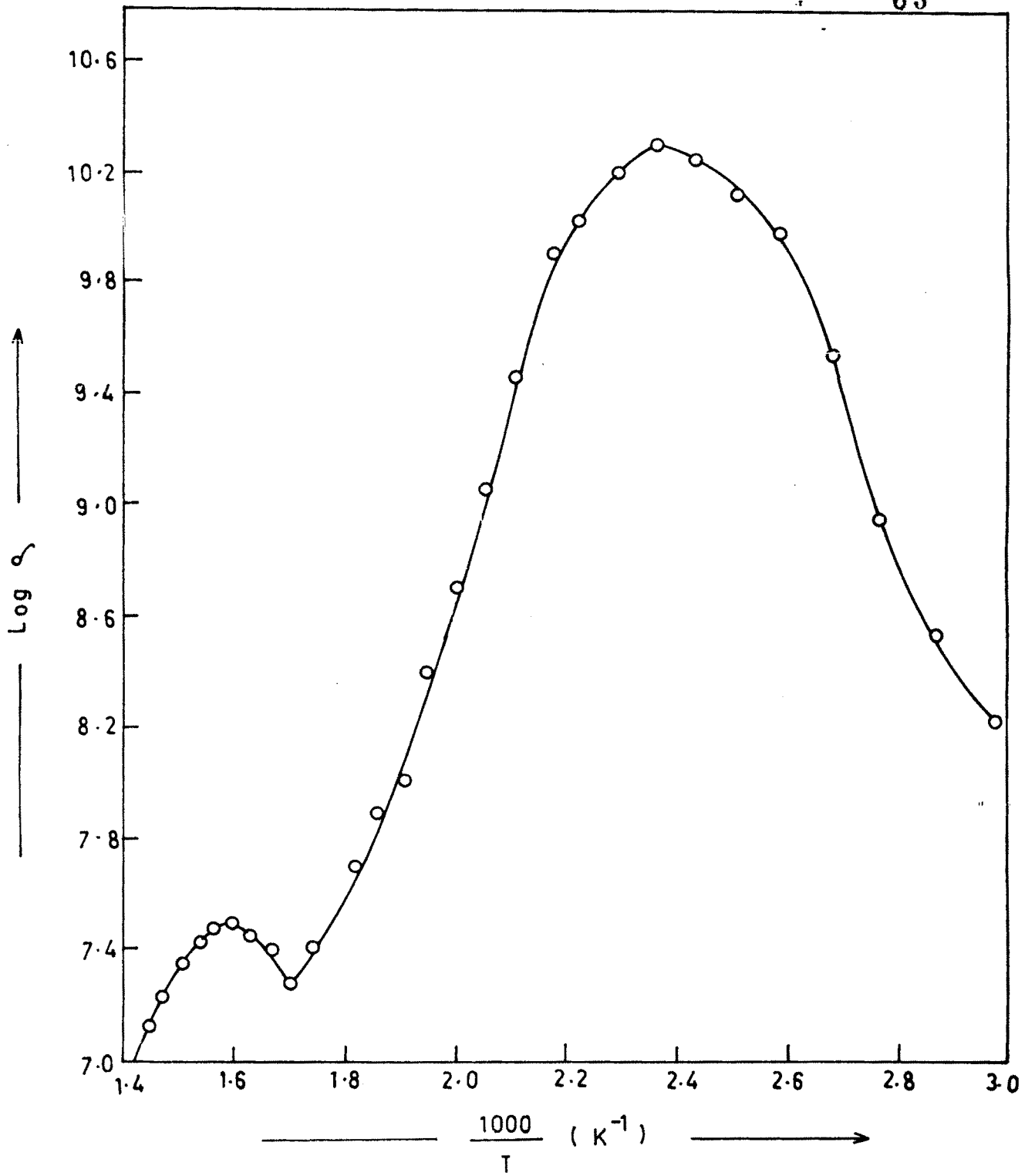
Fig. 3.5 — Variation of Log ρ Vs $\dfrac{1000}{T}$ (K^{-1}) for $Ce_2 Ti_2 O_7$.
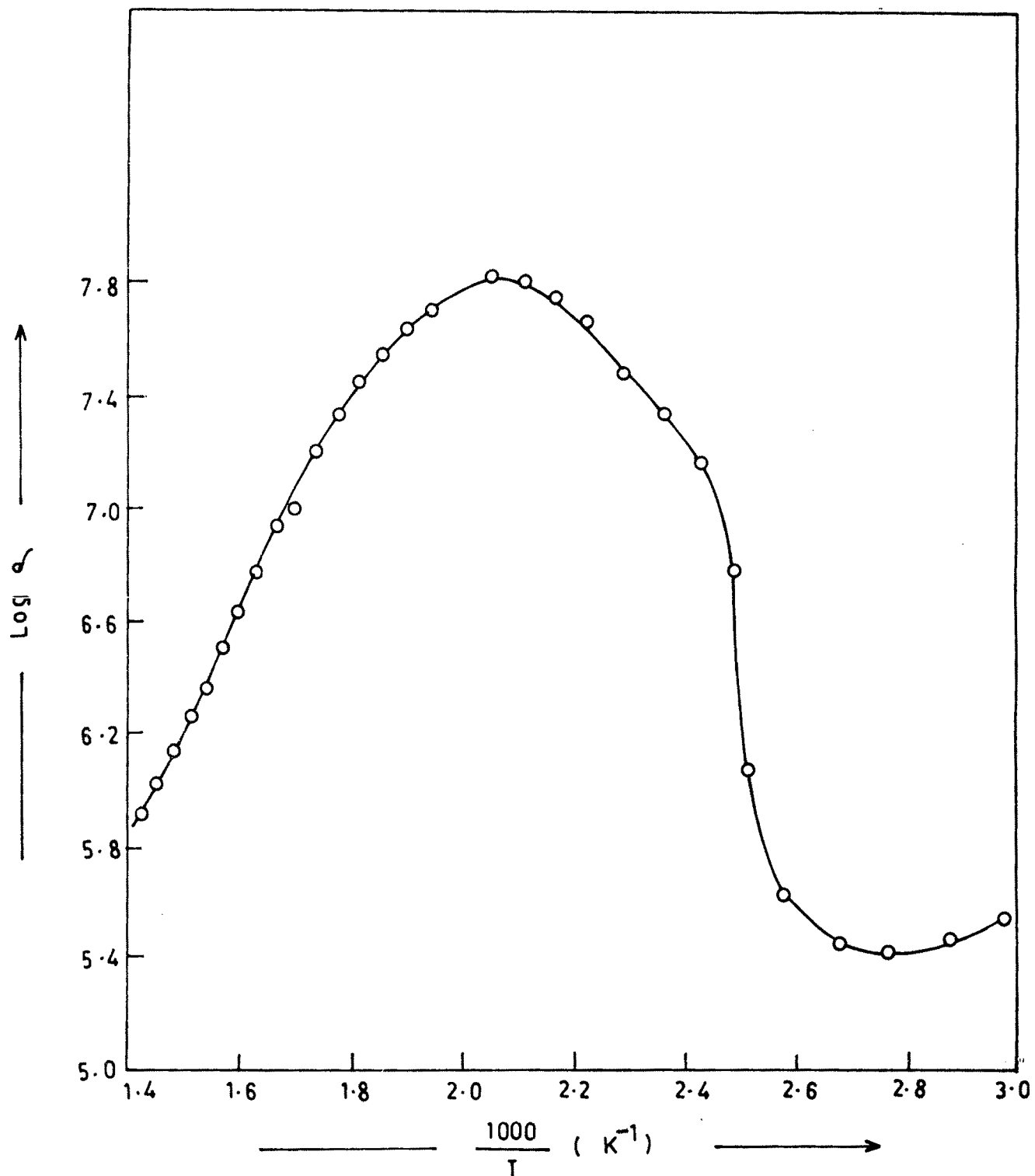
Fig. 3·6 — Variation of Log ϱ Vs $\dfrac{1000}{T}$ for $Ce_2 Sn_2 O_7$.
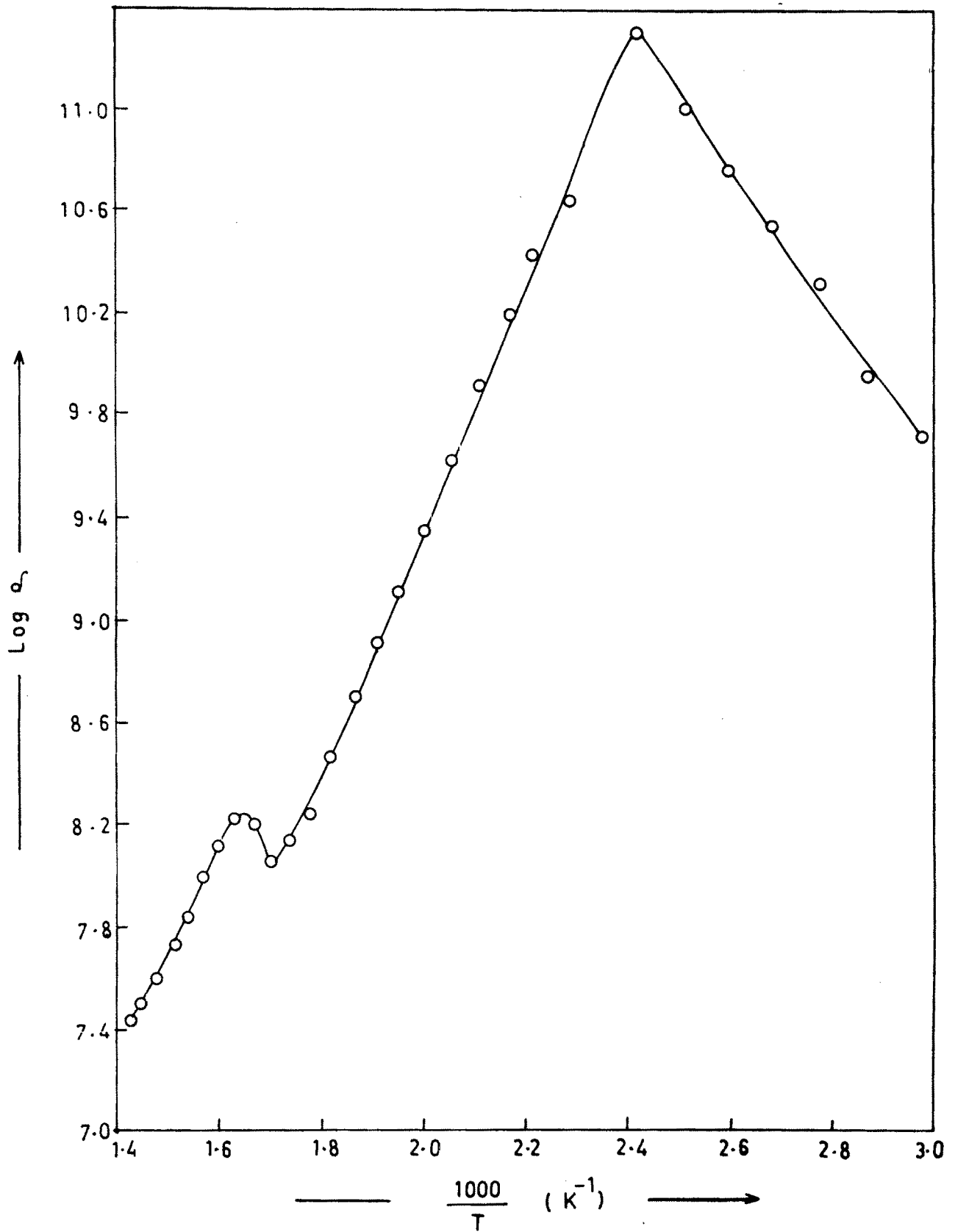
Fig. 3-7 — Variation of Log ρ Vs $\dfrac{1000}{T}$ for $Y_2Ti_2O_7$.
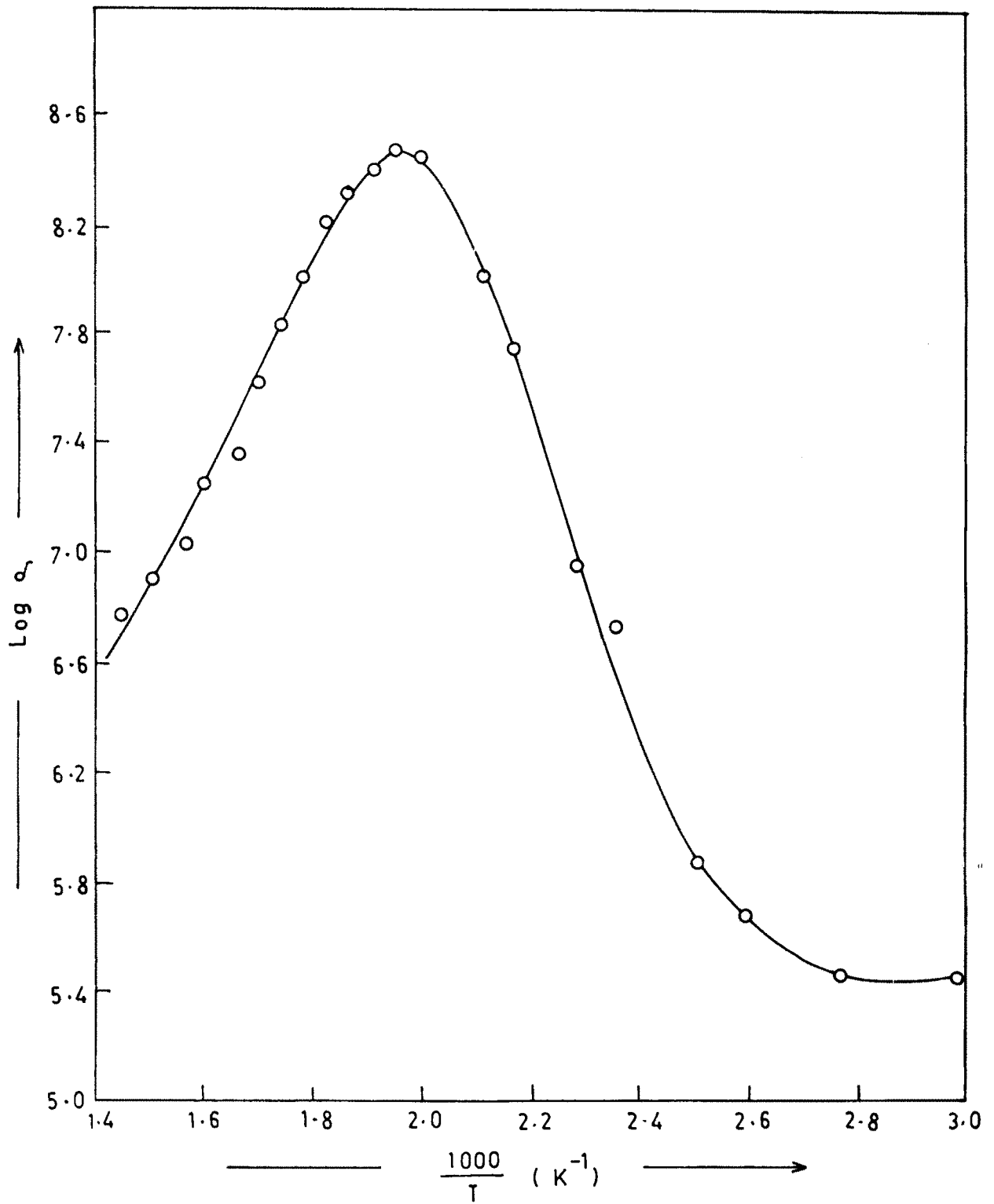
Fig. 3·8 — Variation of Log ρ Vs $\dfrac{1000}{T}$ for $Y_2 Sn_2 O_7$.
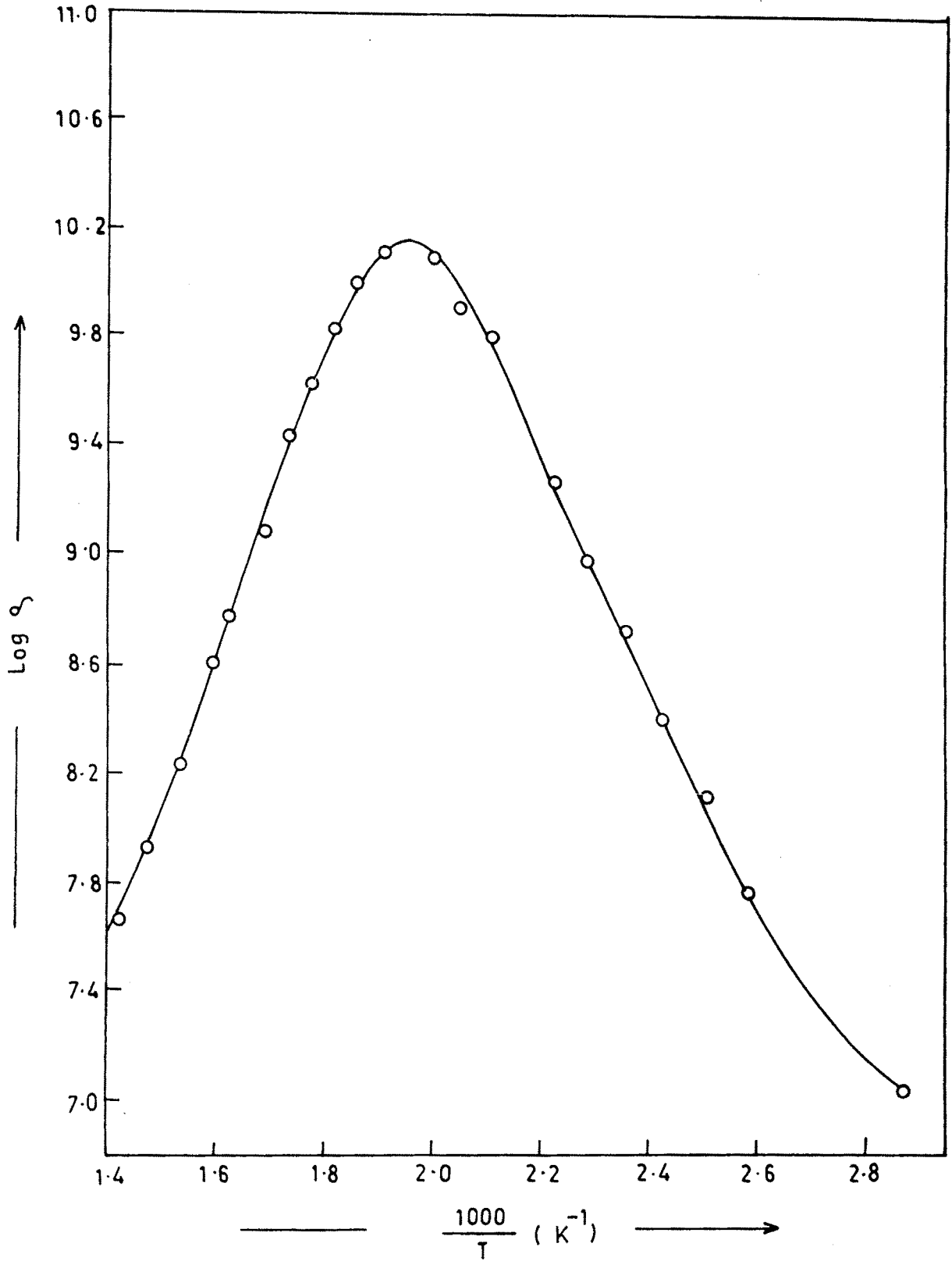
Fig. 3·9 — Variation of Log ϱ Vs $\frac{1000}{T}$ for $Sm_2 Ti_2 O_7$.
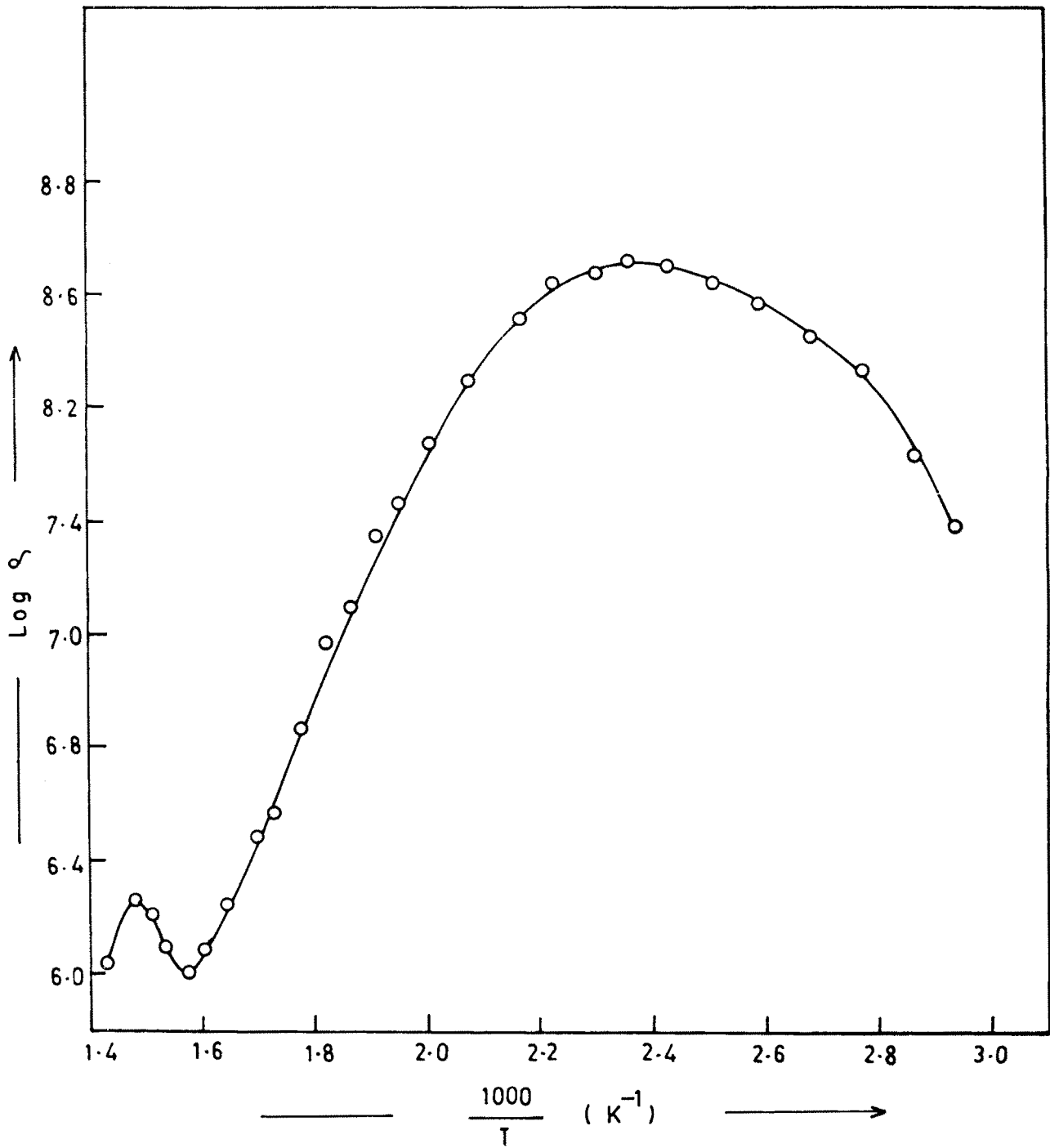
Fig. 3.10 — Variation of Log ρ Vs $\dfrac{1000}{T}$ for $Sm_2 Sn_2 O_7$.

The plot of logρ Vs (1000/T) are shown in the Fig (3.5 to 3.10) The value of ρ has been found to increase with temperatures at about 400^0 k maximum. At temperatures exceeding this particular temperatures, the variation of resistivity follows a typical semiconductor behaviour. The variation of resistivity with temperature can be attributed to ionic drift current due to electrons in the conduction bands. The present results indicates that the contribution from ionic drift current is predominent in this anolomous region. For an ionic conductor where the movement of ions takes place by the transport of lattice defects. The temperature dependence of electrical conductivity is determined by the effect of concentration and mobility as charge carriers. It should be noted however, that in case of intrinsic ionic conduction, Q in equation (3.20) is the sum of formation energy of defect and the migration energy. The overall transport property of a compound may depend on the type and concentration of defects contributing to electrical conduction both of which, however can vary with temperatures. In general the overall transport properties of oxides are determined by the defects formed in response to both impurities and influenced by both the temperature and oxygen pressure.

The plots of variation of thermo emf with temperature is shown in Fig 3.11 to 3.13 It is observed that all the samples show n-type semiconduction and n-to p- transition occurs around 450^0 to 550^0 k. All these compounds exhibited p-type semiconduction above 450^0 k temperature. The variation of α with temperature shows cusp like behavior before n to p transition It is already stated, that in oxides the charge transport is in principle,
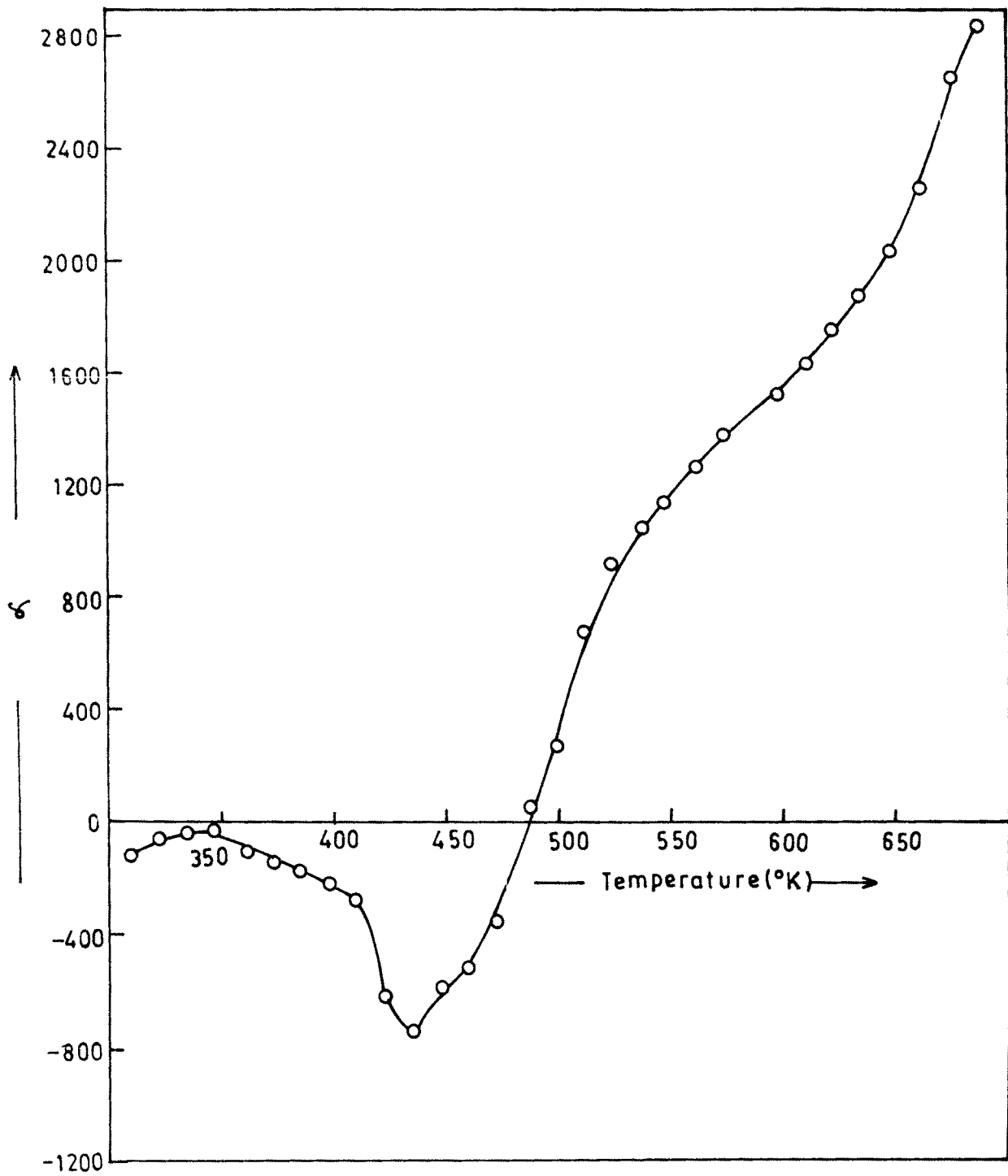
Fig. 3·11 — Temperature variation of Thermoelectric power for $Ce_2Sn_2O_7$.
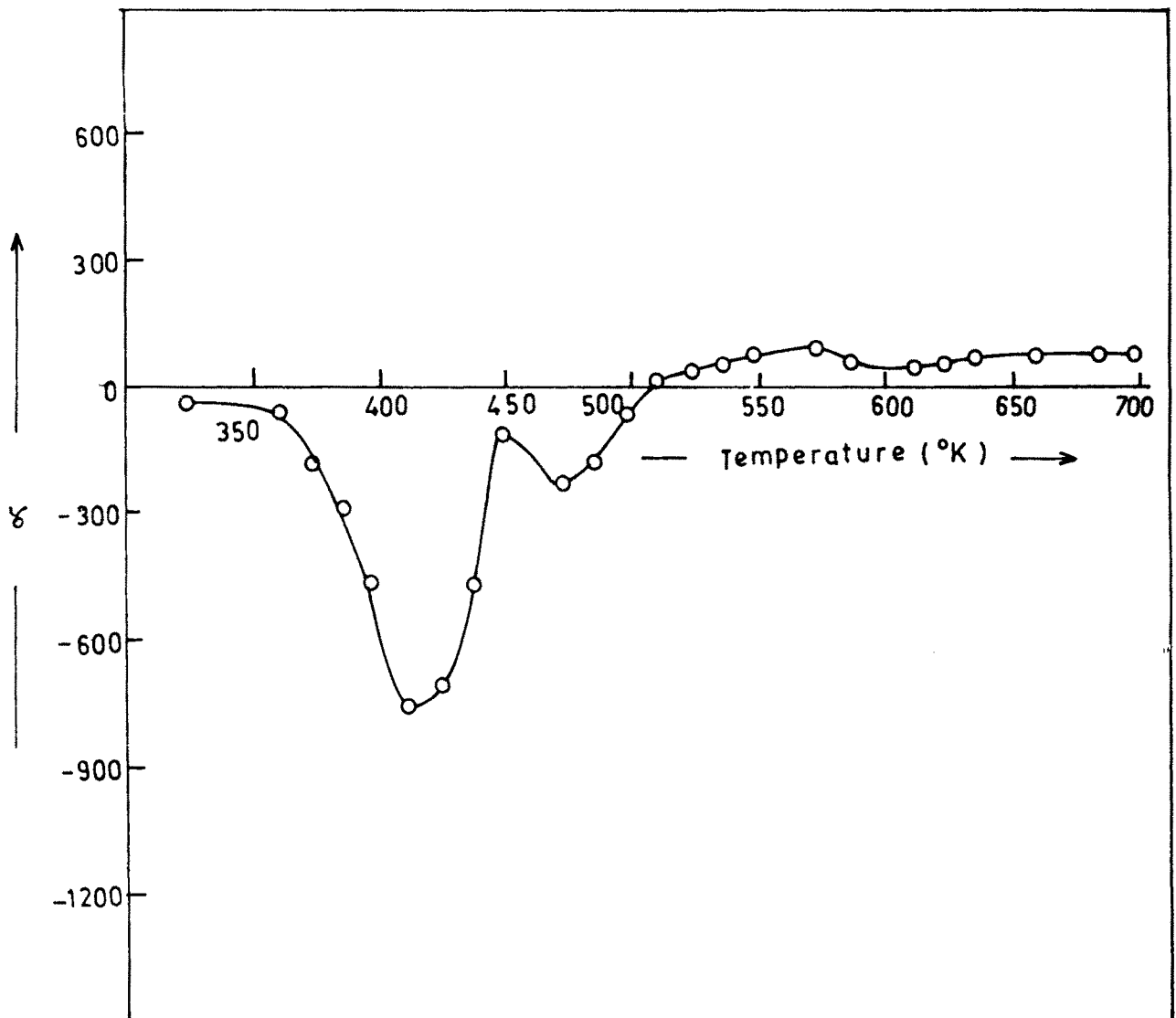
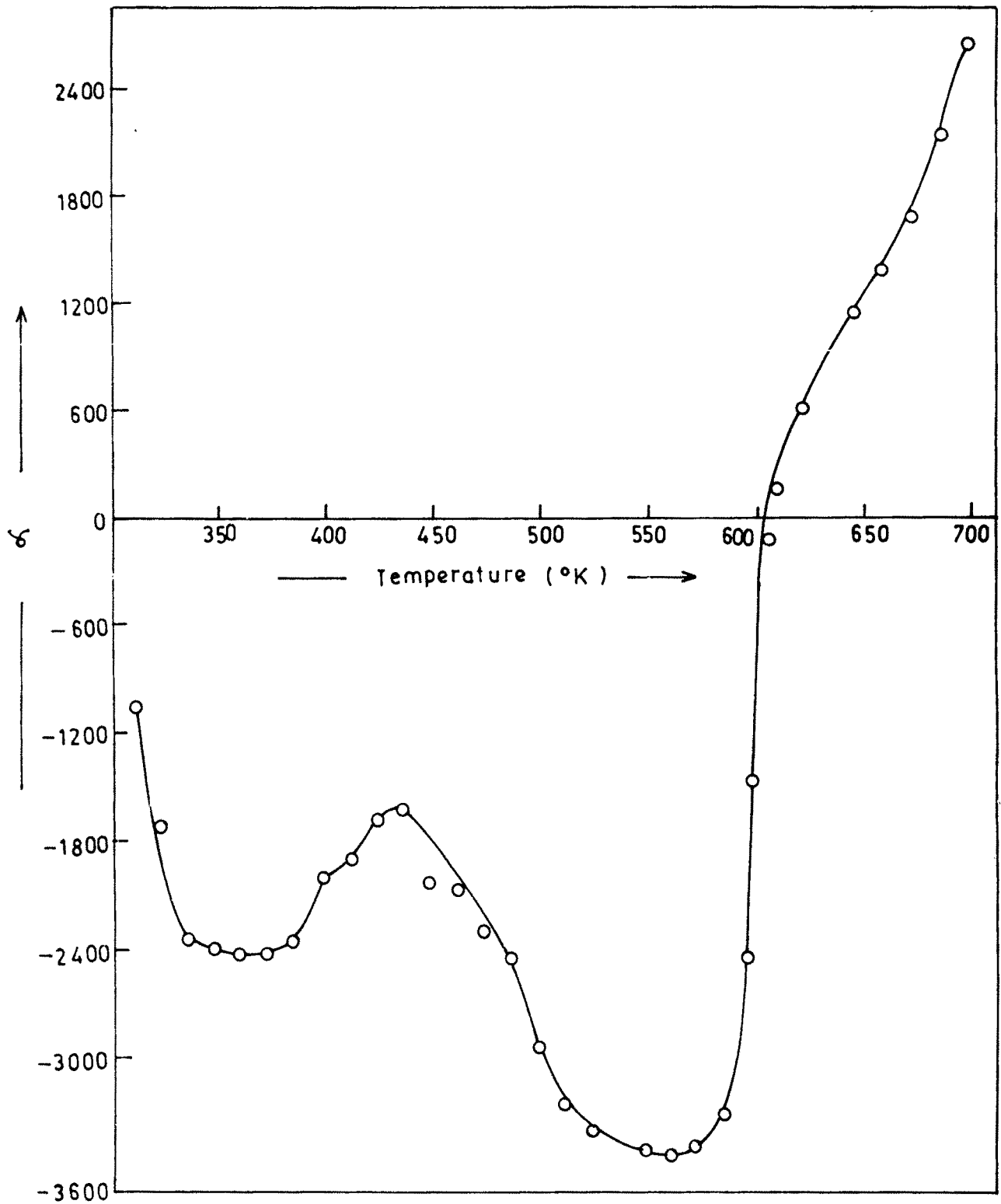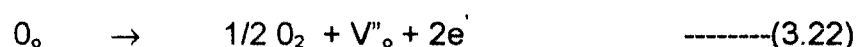Fig. 3·12 — Temperature variation of Thermoelectric power for $Y_2 Ti_2 O_7$

Fig. 3·13 — Temperature variation of Thermoelectric power for $Y_2 Sn_2 O_7$

characterized by both ionic and electronic conduction,often one type of charge carriers dominates the charge transport but transition to other type of conduction may occur at certain temperature and / or atmospheres as a result, a change in composition or stoichiometry of the solids. In pyrochlores depending on the type of the substituent ion as well as temperature and oxygen pressure interaction with atmosphere can take place according to either of the following reactions.

$$V''_o + 1/2\ O_2 \quad \rightarrow \quad O_o + 2h^{\cdot} \qquad \text{--------(3.21)}$$

$$O_o \quad \rightarrow \quad 1/2\ O_2 + V''_o + 2e^{'} \qquad \text{--------(3.22)}$$

and hence under certain conditions p or n-type electronic defects exists in these solids. Hence the observed variations for the present system may due to oxygen concentration in the material.

T. Van. Dijk et al (5) reported that, if the oxygen vacancies are completely ordered in stoichiometric materials, vacancies are changed into non-occupied structural sites. The concentration of mobile species then varies strongly immediately around the stoichiometric composition, while it is mainly determined by the intrinsic defect equillibria of the pyrochlore structure. Non- stoichiometric compositions can be considered as stoichiometric compounds doped with one of the end members of the binary system. This causes introduction of extrinsic defects in the oxygen sublattice. Both effects mentioned above will influence the conductivity.

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