

CHAPTER - III

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ELECTRICAL PROPERTIES

3.1 INTRODUCTION: -

There are a great number of applications for which electrical 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 modulators) have become an important part of modern electronics. Equally important applications of oxides are as electrical insulators, porcelains and glasses used for low and high voltage insulation.

The electrical properties mainly depend on the method of preparation and presence of impurity. Electrical conduction being a kinetic phenomenon will be discussed with regard to its temperature dependence. For thermistor applications the temperature dependence represents the materials sensitivity to temperature change.

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

3.2 DC CONDUCTIVITY: -

In oxides oxygen non-stoichiometry provide 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 carries by excitation,

therefore many of the metal oxides are semiconductors. In general the spinel oxide crystal structure may be conveniently regarded in terms of oxygen ions.

The electric current 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 , they have a drift velocity v and charge per particle ze . Where z is valency and e is the electronic charge, then the electrical current density is given by

$$j_i = n_i z_i e v \quad (3.1)$$

The relation who gives the electrical conductivity (σ) is

$$\sigma = j/E. \quad (3.2)$$

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

$$\sigma_i = (n_i z_i e) v / E \quad (3.3)$$

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

$$\mu_i = v_i / E_i \quad (3.4)$$

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

$$\sigma_i = (n_i z_i e) \mu_i \quad (3.5)$$

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

$$B_i = v_i / F_i \quad (3.6)$$

$$B_i = v_i / z_i e E \quad (3.7)$$

In terms of the absolute mobility the conductivity is given by

$$\sigma_i = (n_i z_i^2 e^2) B_i \quad (3.8)$$

When we consider the effect of variables such as composition, structure and temperature on electrical conductivity, we are concerned with their two separate contribution i.e. 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

$$F = ZeE, \quad \text{is}$$

$$m (dv/dt + v/\tau) = F = ZeE \quad (3.9)$$

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

$$dv/dt + v/\tau = 0 \quad (3.10)$$

and by integrating

$$V(t) = V_0 \exp(-t/\tau) \quad (3.11)$$

where τ is characteristic relaxation time governing the time required to reach equilibrium. In equation (3.9) the first term describe inertial effects, when v is time dependant, once the inertial effects have died out ($dv/dt = 0$)

We have

$$V = ze\tau E/m \quad (3.12)$$

And by comparison with equation 3.1

$$E = nz^2 e^2 \tau/m \quad (3.13)$$

That is the charge transported is proportional to the charge density (Zen), the acceleration of charge in given field (proportional to 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 used in semiconductors. The interpretation of Hall effect is more straightforward. However in case of low mobility materials such as oxides, thermoelectric power measurement is the only alternative about p or n-type conduction. Another important significance of thermoelectric power is that it enables one to calculate the Fermi energy and carrier concentration (3).

When the two surfaces of electrically conducting material are maintained at different temperatures (ΔT) they develop a potential (ΔV) then the Seebeck coefficient can be given as

$$\alpha = \Delta V / \Delta T \quad (3.14)$$

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

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

$$\alpha = (\alpha_n \sigma_n + \alpha_p \sigma_p) / (\sigma_n + \sigma_p) \quad (3.15)$$

$$\sigma_n = n_e \mu_n \quad \text{and} \quad \sigma_p = p_e \mu_p \quad (3.16)$$

$$\sigma_n = (k/e) (A_n - E_f / KT) \quad (3.17)$$

$$\sigma_p = (k/e) [A_p + (E_g + E_f) / KT] \quad (3.18)$$

where, n and p are the electron and hole densities, μ_n and μ_p are the electron and hole mobilities and E_f is the Fermi energy and E_g is the band gap energy.

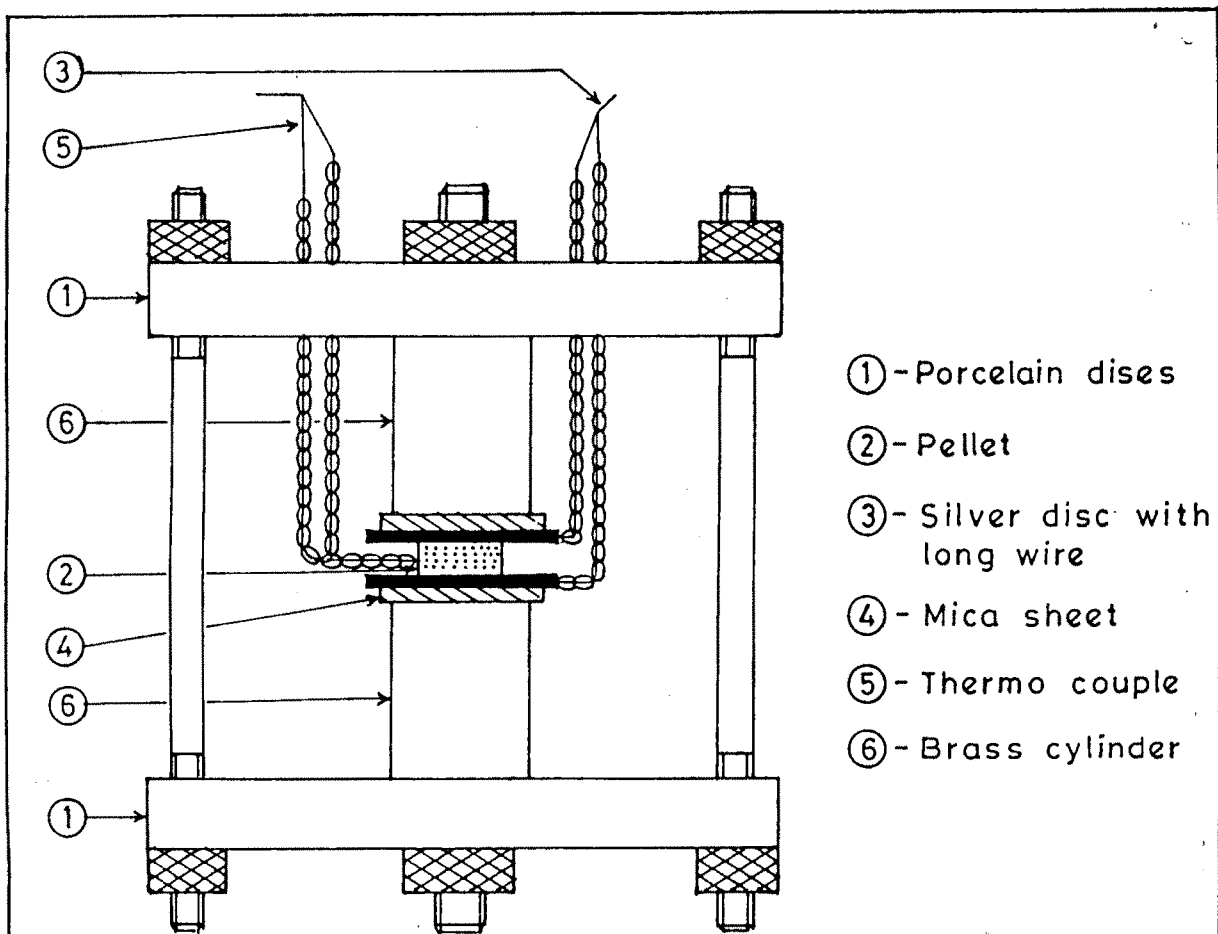


Fig.3.1 (a): - THE CONDUCTIVITY CELL .

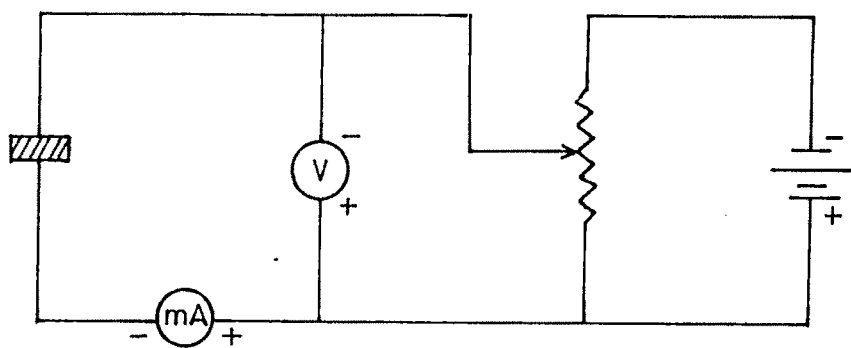


Fig. 3.1(b): -CIRCUIT DIAGRAM FOR ELECTRICAL RESISTIVITY.



Fig. 3.2: - Experimental set up for the measurement of d.c electric resistivity.

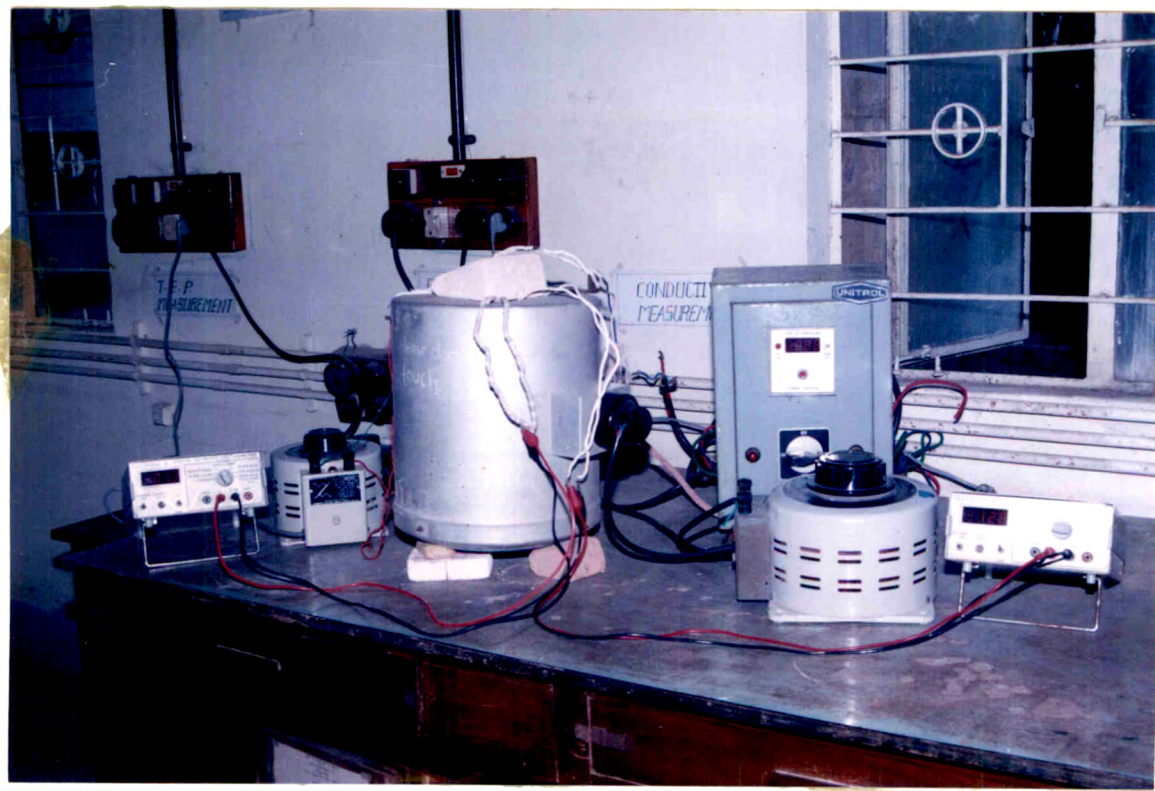


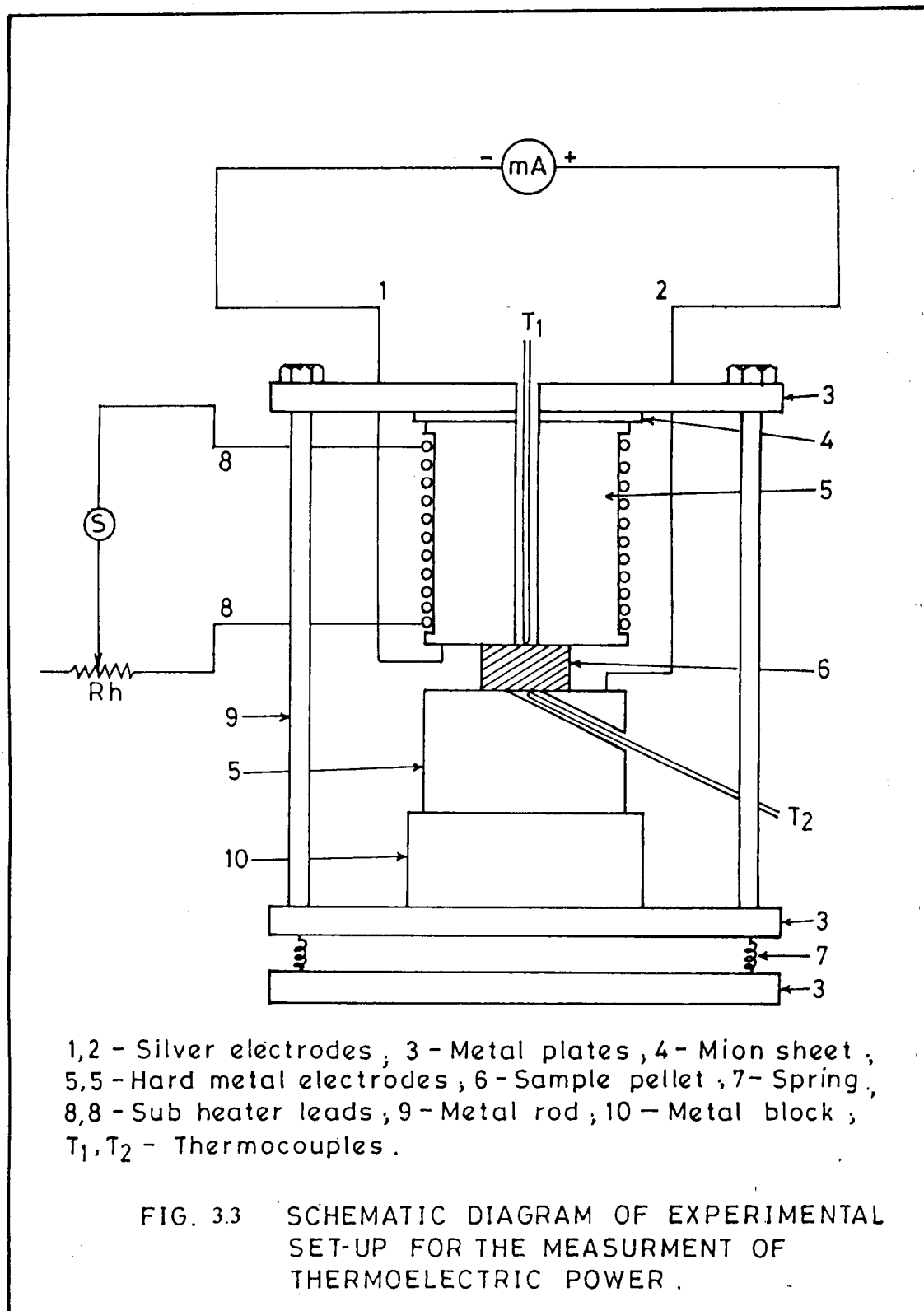
Fig. 3.4: - Experimental setup for the measurement of thermoelectric powder.

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

3.4 EXPERIMENTAL: -

The d.c. electrical conductivity is measured with two probe method. The sample is used in the form of pellet. To ensure good ohmic contact, silver paste is coated on the surfaces of the pellet. The specially designed conductivity cell is used and is shown in Fig 3.1a. The circuit used for measurements of electrical resistivity is also shown in fig3.1b. Then the sample is sandwiched between two silver foils and fixed the cell. 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.

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 measurement of thermoelectric power, the temperature difference of 20°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 digital d.c. microvoltmeter. Sufficient time was allowed to attain the thermal equilibrium before recording the thermo emf. The sample was then heated by keeping the temperature difference of 20°C and the developed thermo



emf was measured at different temperatures. Experimental set up is shown in the Fig. 3.4

In the measurement of ΔV if the microvoltmeter gives a positive reading by connecting the positive terminal to hot end of the sample, then the charge carriers are n-type. This situation reverses when the charge carriers are of p-type. The thermoelectric power or Seebeck coefficient was determined by using the relation.

$$\alpha = \Delta V / \Delta T \quad (3.19)$$

where, ΔV is thermoemf and ΔT is the temperature difference across the pellet.

3.5 RESULTS AND DISCUSSION: -

The electrical conduction in solids is generally decided by parameters, namely carrier concentration n (the number of carrier of charge per unit volume) and carrier mobility. The electrical conductivity can be expressed as

$$\sigma = n q \mu \quad (3.20)$$

where, n is carrier concentration, q charge of each carrier and μ carrier mobility.

In case of solids having more type of charge carriers the electrical conductivity is sum of the conductivity due to all type of charge carriers. For example, the electrical conductivity σ of the solids is sum of the conductivities due to charge carriers as holes, electrons, cations and anions.

$$\begin{aligned} \sigma &= \sum \sigma_i \\ \sigma &= \sum n_i q_i \mu_i \end{aligned} \quad (3.21)$$

The over all conductivity can either electronic, ionic or a mixture of two depending upon the relative magnitude of the product of n_i and μ_i of all the carriers. In case of ionic compounds such as oxides, charge transport is in principle, characterized by both ionic and electronic conduction. Often one type of charge carrier dominates for the charge transport. But transition to the other type of conduction may occur at certain temperature and/or atmospheres as a result of change in composition or stoichiometry of the solids (4).

In equation (3.21) 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 Arrhenious type equation.

$$\sigma = \sigma_0 \exp(-E / kT) \quad (3.22)$$

where, E is activation energy of electrical conduction and

σ_0 is the electrical conductivity at absolute zero (or σ_0 is also known as pre-exponential factor).

For oxide materials in particular, intrinsic conductivity is only observed with high purity samples at high temperatures.

The variation of $\log \rho$ Vs $1000/T$ are shown in fig 3.5 to 3.10. From the graph it is seen that ρ is constant or stable up to 450K for the sample with $x = 0.0$ and 0.2 anomaly is observed $x = 0.4$ to $x = 1.0$. For these sample the conductivity increases and maximum near to 450K. Above 450 K the variation of resistivity with temperature, follows a typical semiconductor behavior. The

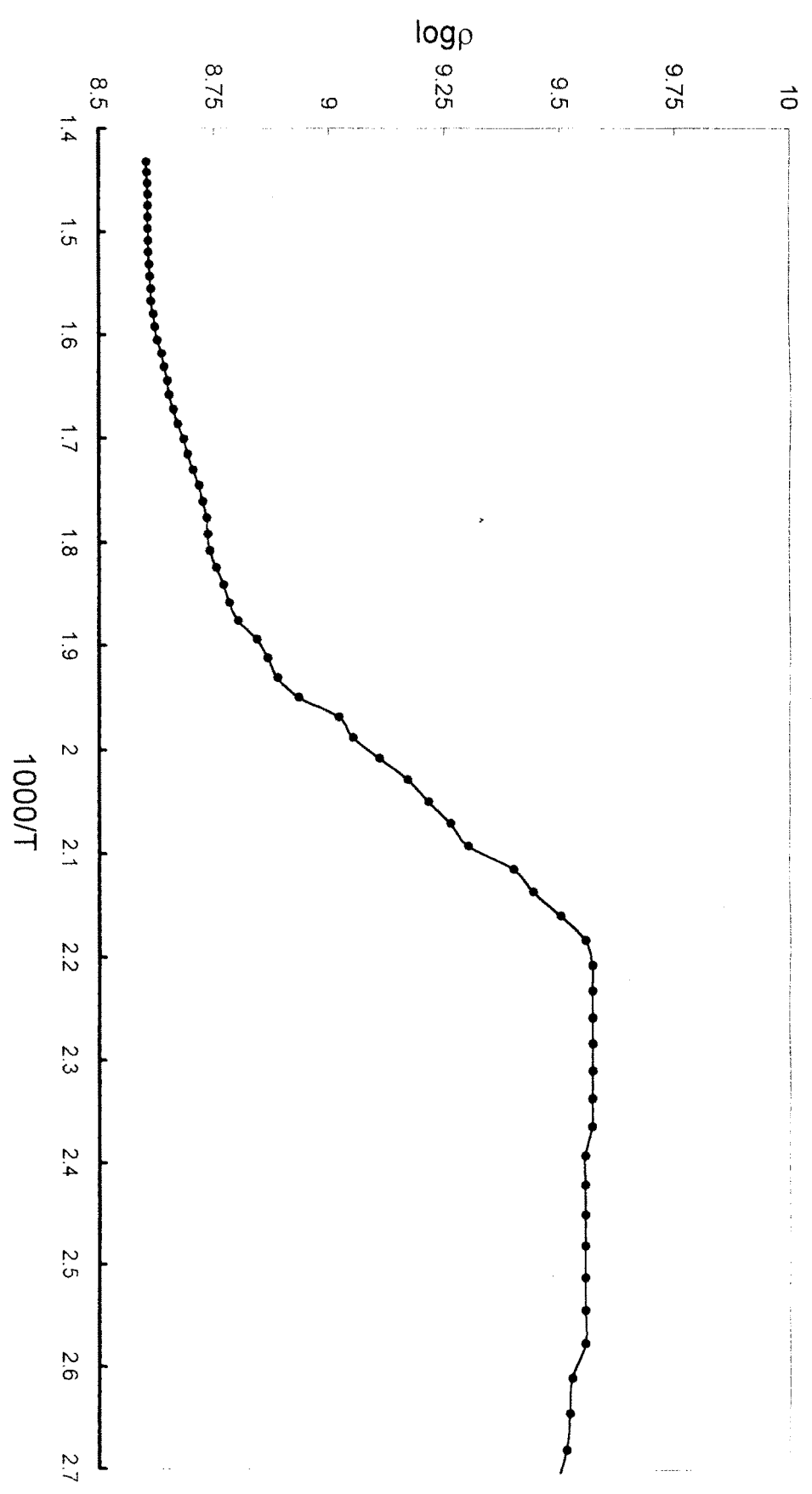


Fig 3.5 :- Variation of $\log p$ with temperature for $X=0.0$

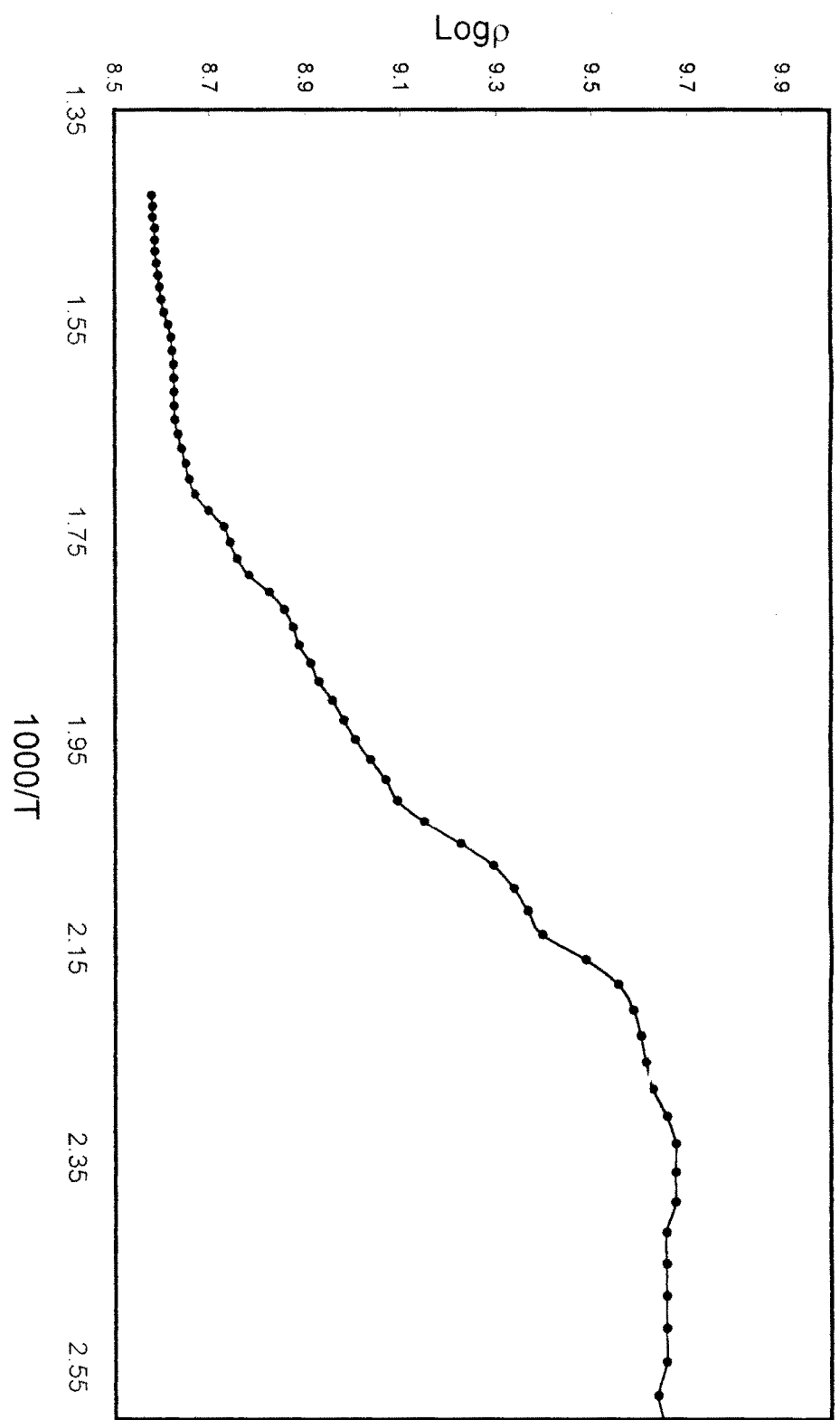


Fig 3.6:- Variation of log p with temperature for x= 0.2

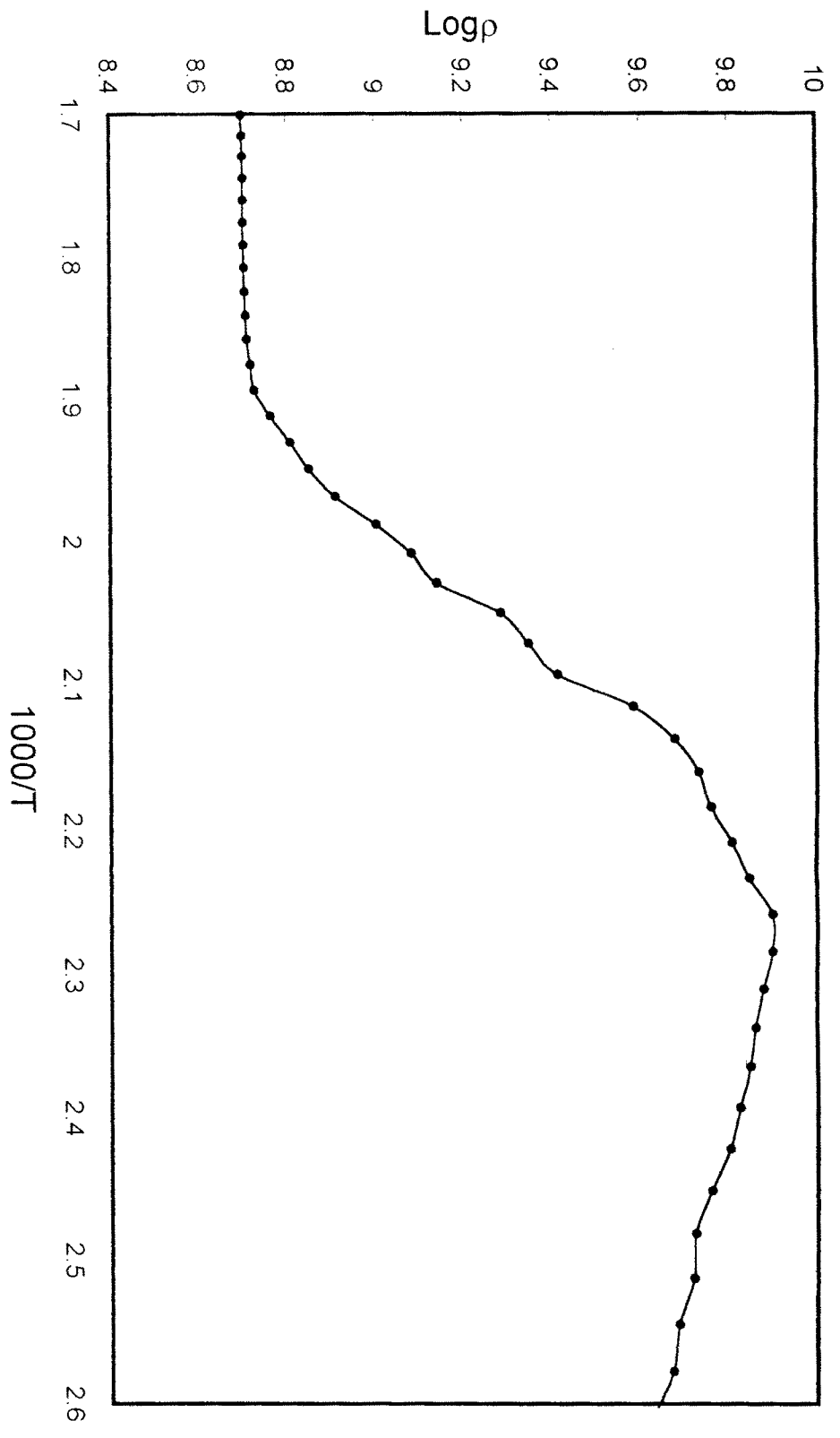


Fig 3.7 Variation of log p with temperature for x = 0.4

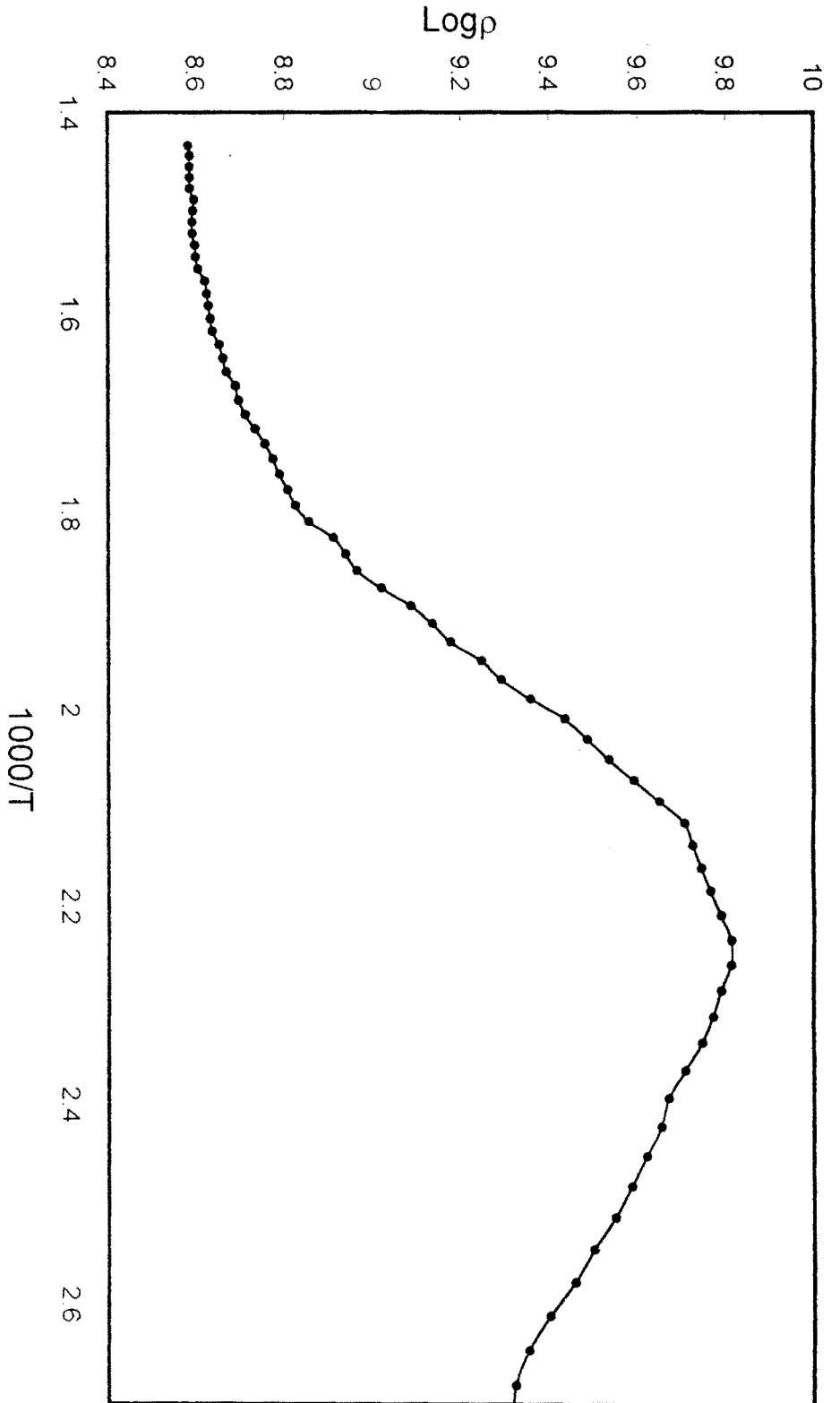


Fig 3.8:- Variation of log p with temperature for x=0.6

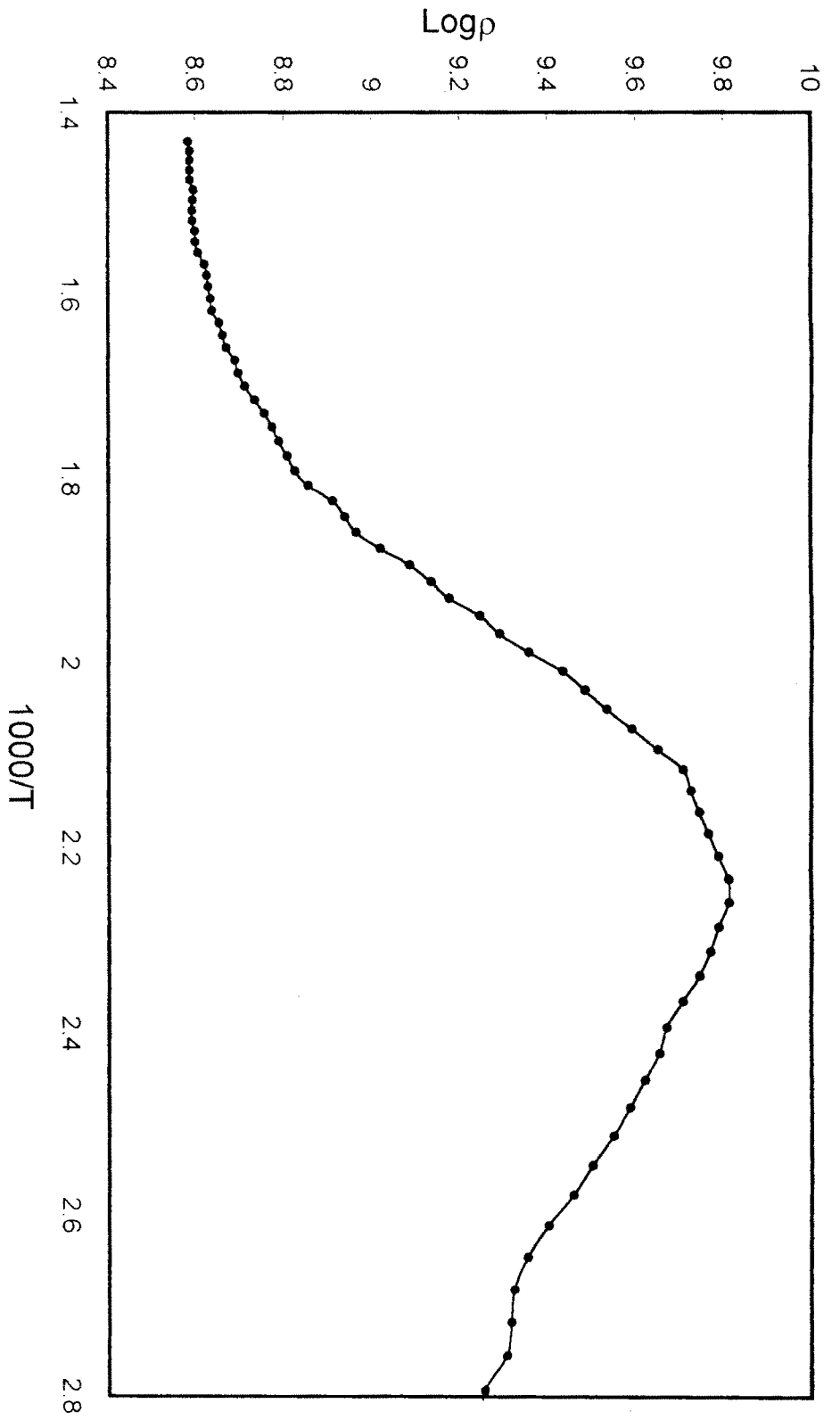


Fig 3.9 Variation of log p with temperature for x=0.8

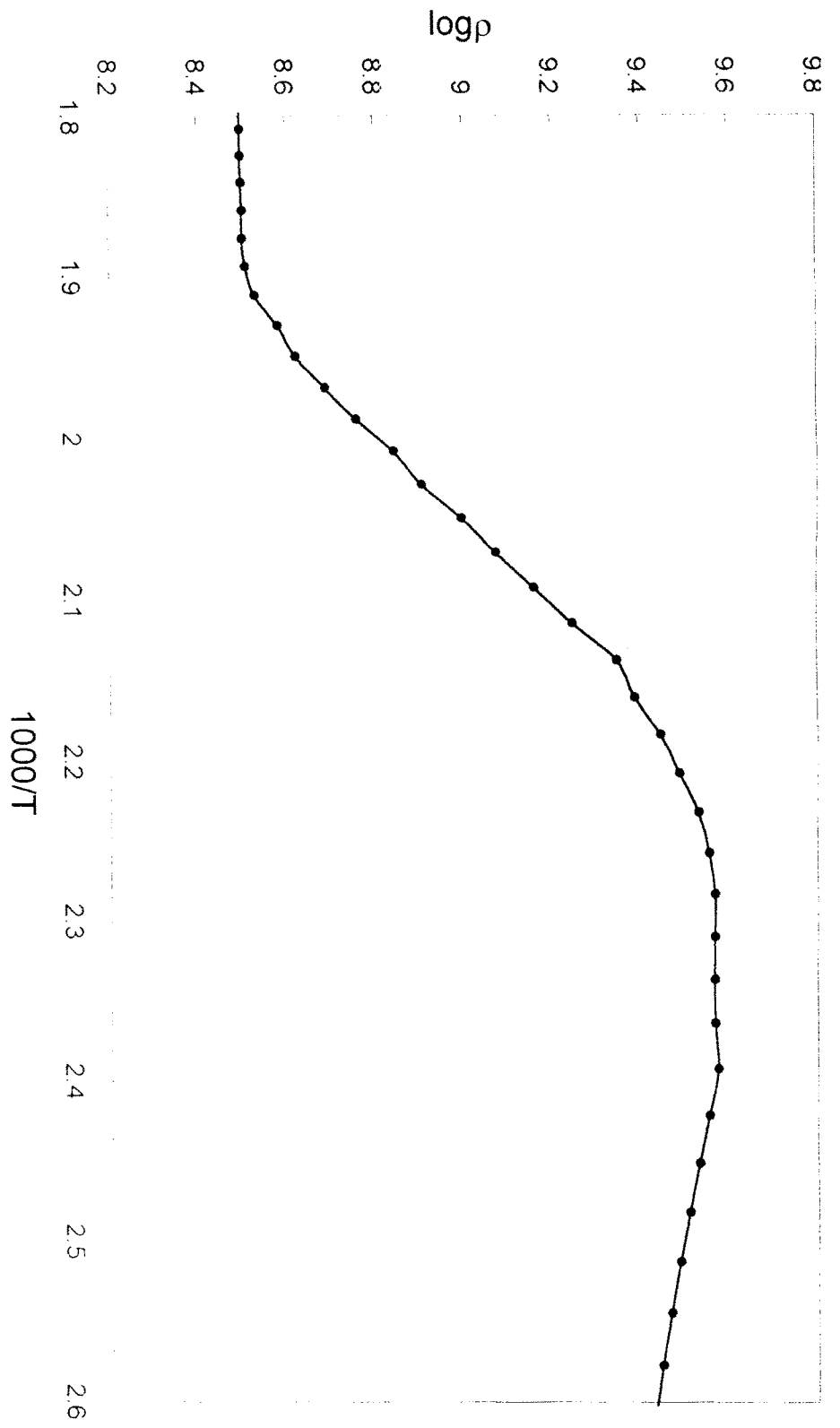


Fig 3.10:- Variation of log p with temperature for x = 1

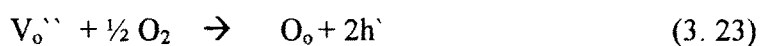
variation of resistivity with temperature can be attributed to ionic drift current due to electrons in the conduction bands. The present results indicate that the contribution from ionic drift current is predominant in this anomalous region. For an ionic conductor where the movement of ions takes place by the transport of lattice defects, the effect of concentration and mobility of charge carriers determine the temperature of dependence of electrical conductivity. It should be noted that in case of intrinsic ionic conduction, E in equation 3.22 is a sum of the formation energy of defect and migration energy. The overall transport property of a compound may depend on the type and concentration of defect contributing to electrical conduction both of that however can vary with temperature.

Table 3.1 :- Activation energy of all the compositions

Composition (x)	Activation Energy (eV)
0.0	0.2079
0.2	0.3436
0.4	0.3919
0.6	0.5376
0.8	0.6279
1	0.6452

In general overall properties of oxides are determined by the defects formed in response to both impurities and influenced by both the temperature and oxygen pressure. Activation energies for all compositions are calculated and are shown in table 3.1. Table 3.1:- Activation energy of all the compositions

Fig 3.11 to 3.13 shows a variation of TEP with temperature. It is observed that all the sample shown n-type behavior. The CUSP in α Vs T curve shows near to 450–500 K. Above 500 K the absolute α value decreases and n-p transition takes place around 650-700K. The conductivity plots also show change in slope near to 650-750K. Anomalous behavior of ρ near to the temperature of CUSP in the α . It is already stated that in oxides, the charge transport is in principle, 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 upon the type substituent ions as well as temperature and oxygen pressure interaction with atmosphere can take place according to either of the following reactions.



Under certain conditions p or n type electronic defects exist in these solids. Hence observed variations for the present system may be 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, then cationic vacancies are changed into non-occupied structural sites. The concentration of mobile species then varies strongly immediately around the stiochiometric composition, while it is mainly determined by the intrinsic defect equilibria of the pyrochlore

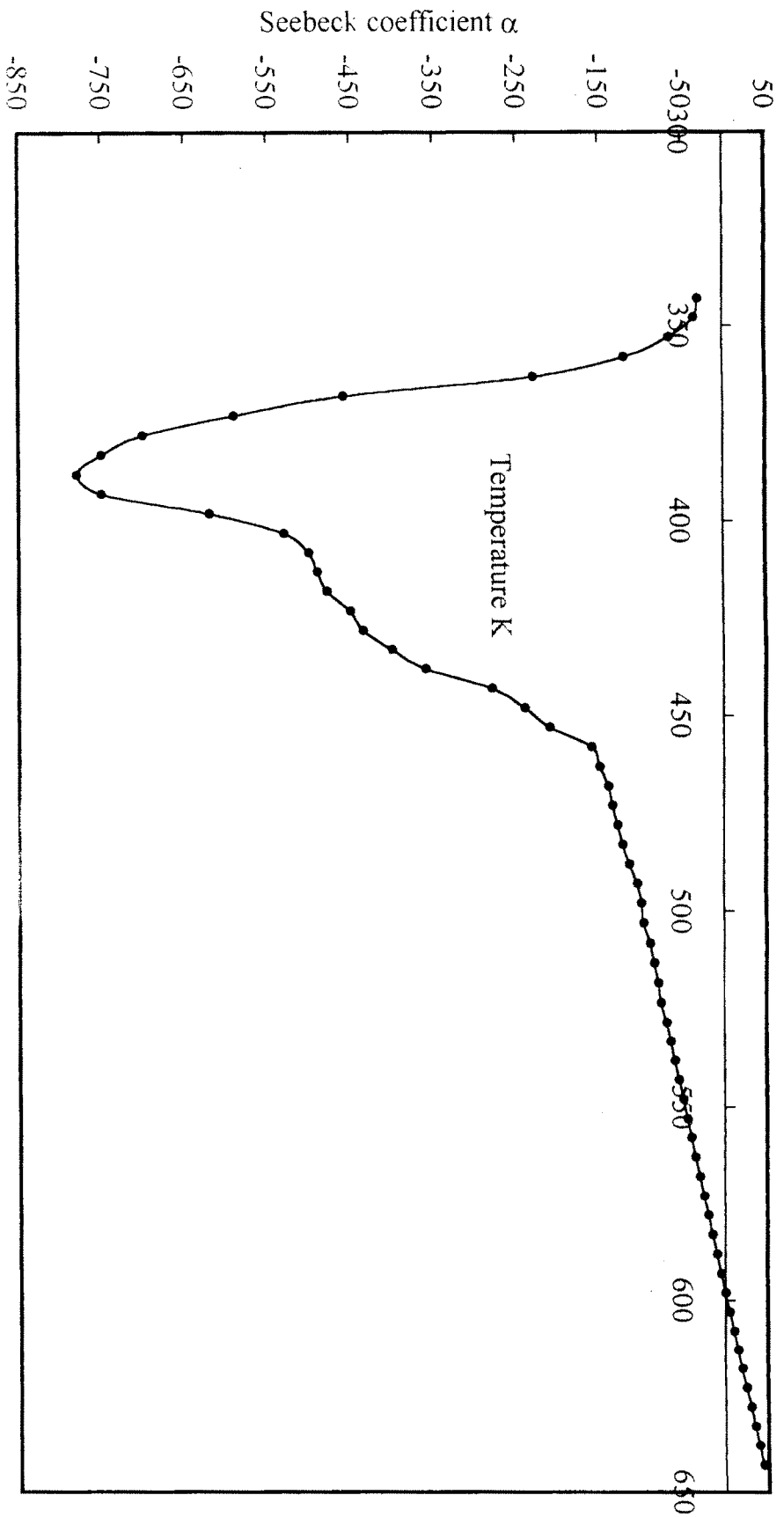


Fig 3.11:- Variation of TEP with temperature for $x=0.0$

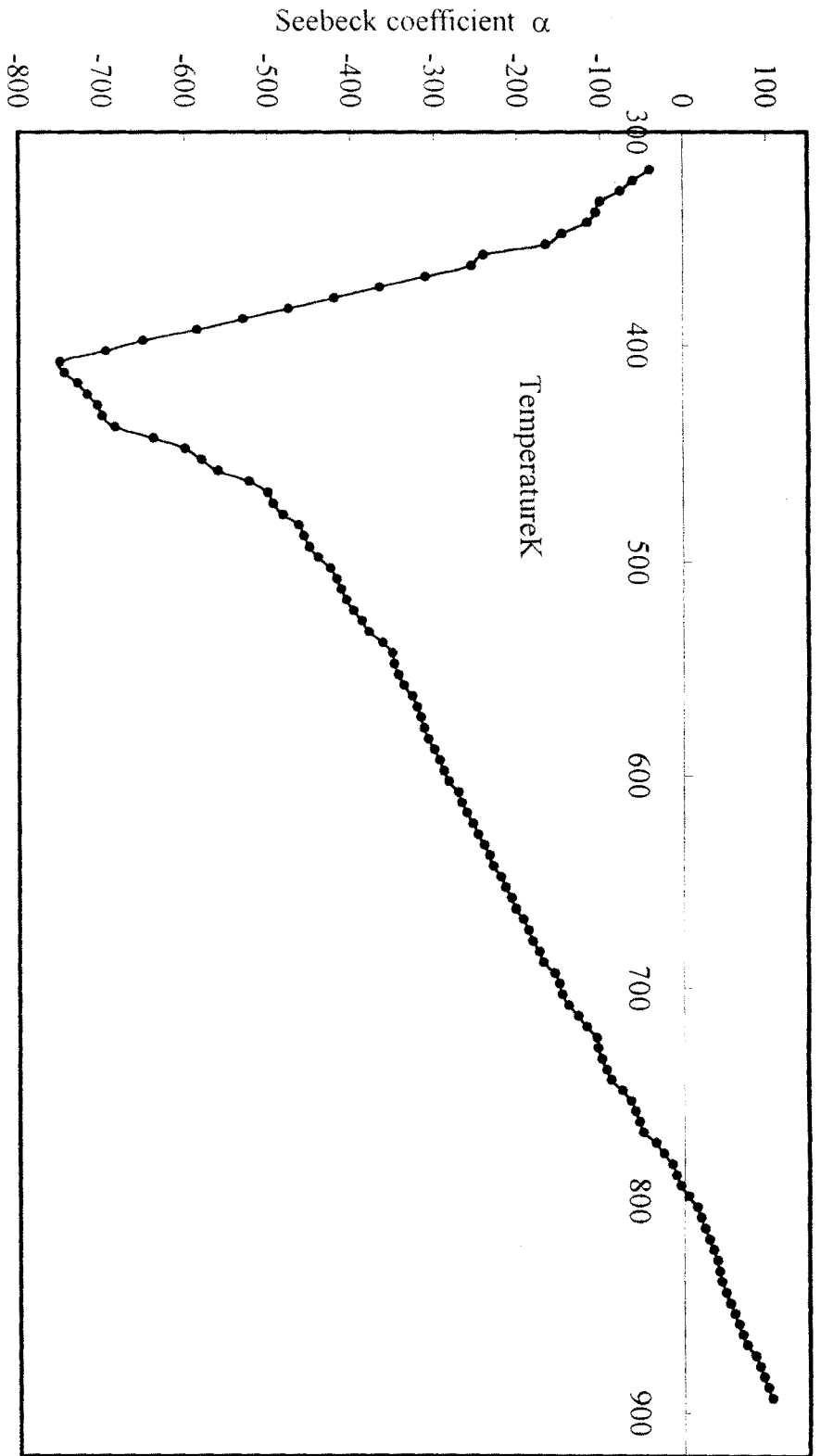


Fig 3.12 Variation of TEP with temperature for $x = 0.4$

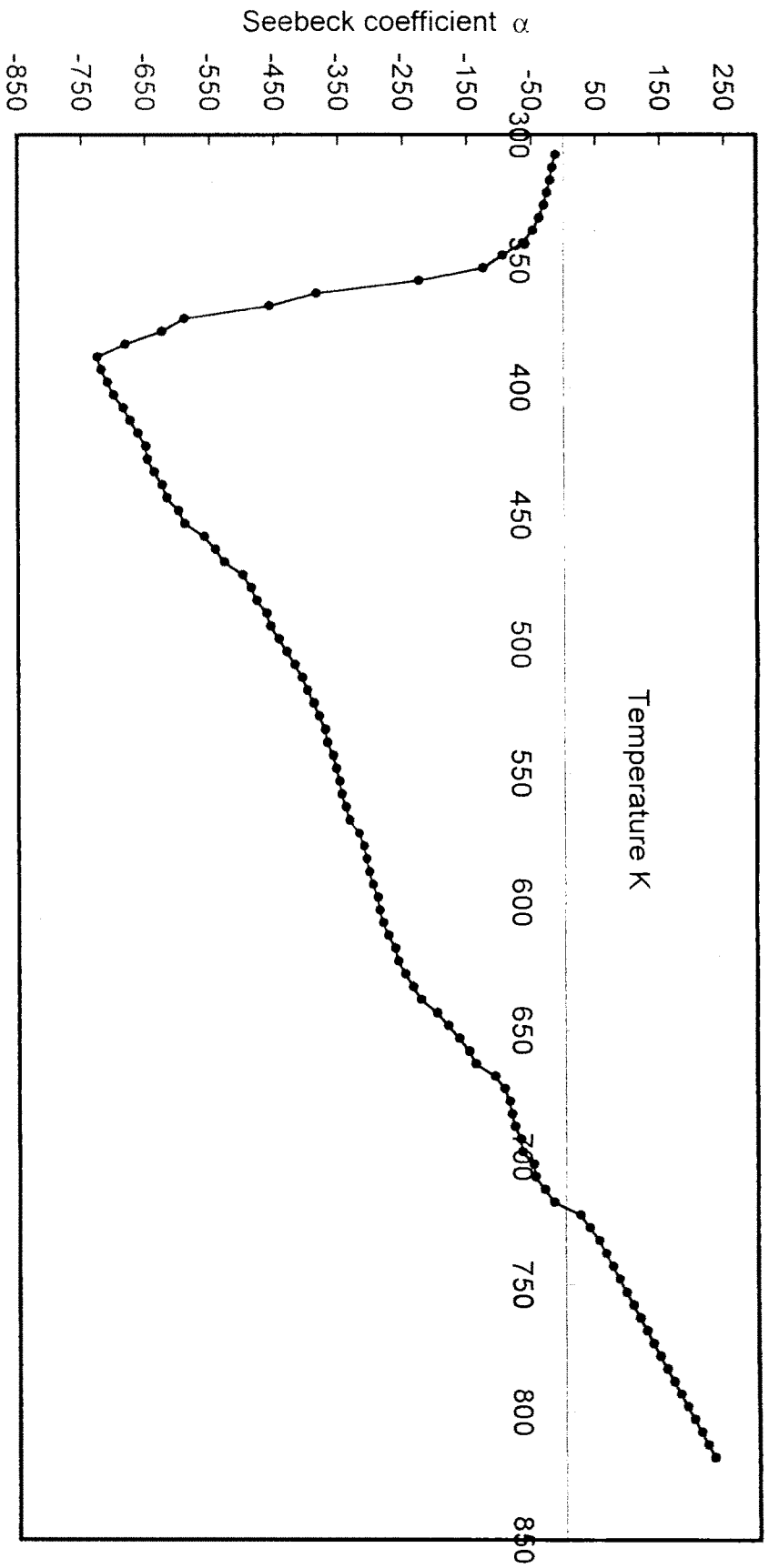


Fig 3. 13 :-Variation of TEP with temperature for x=0.6

structure. Non-stoichiometric compounds 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 sub-lattice. Both effects mentioned above will influence the conductivity.

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