

## Chapter 3

### ELECTRICAL CONDUCTIVITY STUDIES IN COPPER PHTHALOCYANINE, COBALT PHTHALOCYANINE AND LEAD PHTHALOCYANINE THIN FILMS

#### 3.1. Introduction

The phthalocyanines are organic semiconductors, whose electrical properties have considerable importance owing to their potential application in electronic devices<sup>1,2</sup> and sensor systems.<sup>3-5</sup> The electronic transport in phthalocyanines shows ohmic conduction at low voltages and space charge limited conduction at high voltages.<sup>6-8</sup> Discrete trap levels located below the conduction band edge is dominated either by an exponential trap distribution<sup>9</sup> or by a uniform trap distribution.<sup>10</sup> The difference in crystal structures of phthalocyanines gives rise to different electrical properties. Wiksne and Newkirk<sup>11</sup> and Eley and Parfitt<sup>12</sup> have reported sharp differences in the electrical conductivities of  $\alpha$  and  $\beta$  polymorphs of phthalocyanine. In this chapter we report the studies on the evaporation of thin films of copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and lead phthalocyanine (PbPc) and the measurement of their electrical



conductivity as a function of film thickness, substrate temperature and post deposition annealing.

### 3.2. Theory

The semiconducting properties are brought about by thermal excitation, impurities, lattice defects and nonstoichiometry. A highly purified semiconductor exhibits intrinsic conductivity. In the temperature range at which the intrinsic conductivity is exhibited, the electrical properties of the crystal are not modified by impurities. In semiconductors as the temperature is increased from absolute zero, electrons are thermally excited from the valence band to the conduction band. The vacant sites left behind in the valence band viz. holes and the electrons in the conduction band contribute to the electrical conductivity. The conductivity  $\sigma$  due to electrons and holes is

$$\sigma = (n e \mu_e + p e \mu_h) \quad 3.2.1$$

where  $n$  and  $\mu_e$  are the carrier concentration and mobility of the electrons and  $p$  and  $\mu_h$  are the corresponding quantities for the holes. In an intrinsic semiconductor, the number of electrons is equal to the number of holes. The expression for carrier concentration is given by

$$n_i = N_c \exp E_F / k_B T \quad 3.2.2$$

$$p_i = N_v \exp - (E_F + E_g) / k_B T$$



where  $N_c$  and  $N_v$  are the density of states in the conduction band and valence band,  $E_g$  is the forbidden energy gap,  $k_B$  and  $T$  are the Boltzmann's constant and absolute temperature respectively.

$N_c$  and  $N_v$  are given by

$$\begin{aligned} N_c &= 2(2\pi m_e^* k_B T / h^2)^{3/2} \\ N_v &= 2(2\pi m_h^* k_B T / h^2)^{3/2} \end{aligned} \quad 3.2.3$$

where  $m_e^*$  and  $m_h^*$  are the effective masses of the electrons and holes respectively. Since  $n_i = p_i$

$$\begin{aligned} n_i = p_i &= 2(2\pi k_B T / h^2)^{3/2} (m_e^* m_h^*)^{3/2} \exp(-E_g / 2k_B T) \\ &= A \exp(-E_g / 2k_B T) \end{aligned} \quad 3.2.4$$

where  $A$  is a constant.

If we assume that the variation of mobility of the electrons and holes in an electric field with temperature is small, then conductivity  $\sigma$ , which is proportional to the number of carriers has a variation of the form

$$\sigma = \sigma_0 \exp(-E_g / 2k_B T) \quad 3.2.5$$

where  $\sigma_0$  is a constant. Such an exponential variation of electrical conductivity is known for semiconductors. Multiple donor levels exist within the forbidden energy gap and deeper levels can be frozen out as the temperature is increased.

Conductivity in phthalocyanines is due to both hopping of holes and charge transport via excited states. In such a case, the conductivity is given by



$$\sigma = A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T) + C \exp(-E_3/k_B T) + \dots \quad 3.2.6$$

where  $E_1$  is the intrinsic energy gap and  $E_2, E_3$ , the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band.<sup>13</sup> A, B, C are constants.

The conductivity ' $\sigma$ ' of a film of resistance ' $R$ ', length ' $l$ ' breadth ' $b$ ' and thickness ' $t$ ' is given by

$$\sigma = l/Rbt \quad 3.2.7$$

### 3.3. Experiment

Powdered samples of CuPc, CoPc and PbPc (98% pure) obtained from Aldrich corporation INC., WI. are used as the source materials. Pre-cleaned glass substrates of dimension 7.5 x 2.5 x 0.01 cm are used as substrates for evaporation. The cleaning process of the substrate is discussed in detail in section 2.12 of Chapter 2. CuPc is evaporated onto glass substrates with pre-evaporated high purity silver electrodes, at a base pressure of  $10^{-5}$  Torr by resistive heating from a molybdenum boat as per the procedure described in section 2.14 of Chapter 2. The optimum rate of evaporation is adjusted to be 10–15 nm per minute. CoPc and PbPc are also evaporated onto glass substrates by vacuum sublimation with an evaporation rate of 10–15 nm/minute using the resistive heating technique to obtain the films.



For electrical conductivity measurements ohmic electrode contacts are made on CuPc, CoPc and PbPc thin films. Normally contacts are either ohmic or nonohmic. Ohmic contact introduces negligible impedance to the flow of current.<sup>14</sup>

Thin film of CuPc of thickness 2260 Å is mounted over the sample holder of the conductivity cell shown in Figure 2.20.1 of Chapter 2. The temperature of the film is varied using a heater circuit and measured by a copper–constantan thermocouple. Resistance of the film is measured at regular intervals of 5K using a programmable Keithley electrometer (model no.617) by the two probe technique shown in Figure 2.21.1(a) of Chapter 2. The electrical conductivity is obtained using equation 3.2.7. Electrical conductivity measurements are carried out both in air and vacuum for CuPc, CoPc and PbPc films for different thicknesses. Thicknesses of the films have been measured by Tolansky's multiple beam interference technique described in section 2.17 of Chapter 2.

The electrical conductivity measurements have also been made for CuPc films evaporated at different substrate temperatures. The conductivity studies are made in vacuum of  $\leq 10^{-3}$  Torr using the conductivity cell. The electrical conductivity measurements are also done for CoPc and PbPc thin films prepared at different substrate temperatures.



CuPc, CoPc and PbPc films evaporated onto glass substrates kept at room temperature are annealed in air for one hour at different annealing temperatures. The electrical conductivity has been measured for CuPc, CoPc and PbPc films for different annealing temperatures.

### **3.4. Results and Discussion**

The hot probe method is adopted to detect the type of majority carriers. The distribution of thermal velocities in a small region of the film depends on the temperature at that region. In the hot probe method, charge carriers near the hot end have higher velocities than at the cold end which produces an electric field. This field is positive if the carriers are electrons and negative if the carriers are holes. CuPc, CoPc and PbPc thin films are found to be p-type semiconductors from the hot probe measurements.

Silver and aluminium are used as the contact electrodes. The distance between the electrodes is kept at 2.5 mm. Copper strands of diameter 0.8 mm are fixed onto the films by means of the colloidal suspension of silver in a medium of aqua or alkadag.

#### **3.4.A Dependence of Film Thickness**

The resistance of CuPc film has been measured in the temperature range 300 – 500K using a programmable Keithley



electrometer. A biasing voltage of 5V is selected and applied onto the sample. All the measurements are carried out in a dynamical vacuum of  $10^{-3}$  Torr. The electrical conductivity  $\sigma$  is calculated using equation 3.2.7 knowing the length, breadth and thickness of the film. A graph is plotted with  $\ln \sigma$  along the y - axis and  $1000/ T$  along the x-axis. Figure 3.4.1 gives the  $\ln \sigma$  versus  $1000/ T$  plot for CuPc films of thicknesses 2261, 2877, 3802 and 5058 Å. From the slope of the graph the activation energy is determined. The activation energy is determined within an accuracy of  $\pm 0.01$  eV in all the subsequent measurements. The activation energy for CuPc is 1.49 eV for thickness 2261 Å. The activation energy for CuPc is collected in Table 3.4.1 for different thicknesses. Aoyagi et. al.<sup>15</sup> have reported an activation energy of 1.98 eV for CuPc single crystals. Hamann<sup>16</sup> have reported an activation energy of 1.96 eV for CuPc thin films. From the present study, it is seen that the activation energy decreases with increase in film thickness. Delacote et. al.<sup>17</sup> have predicted variation in activation energy for CuPc with change in thickness. Figure 3.4.2 gives the plot of  $\ln \sigma$  versus  $1000/ T$  for CoPc of thin films of thicknesses 1465, 4658, 7324

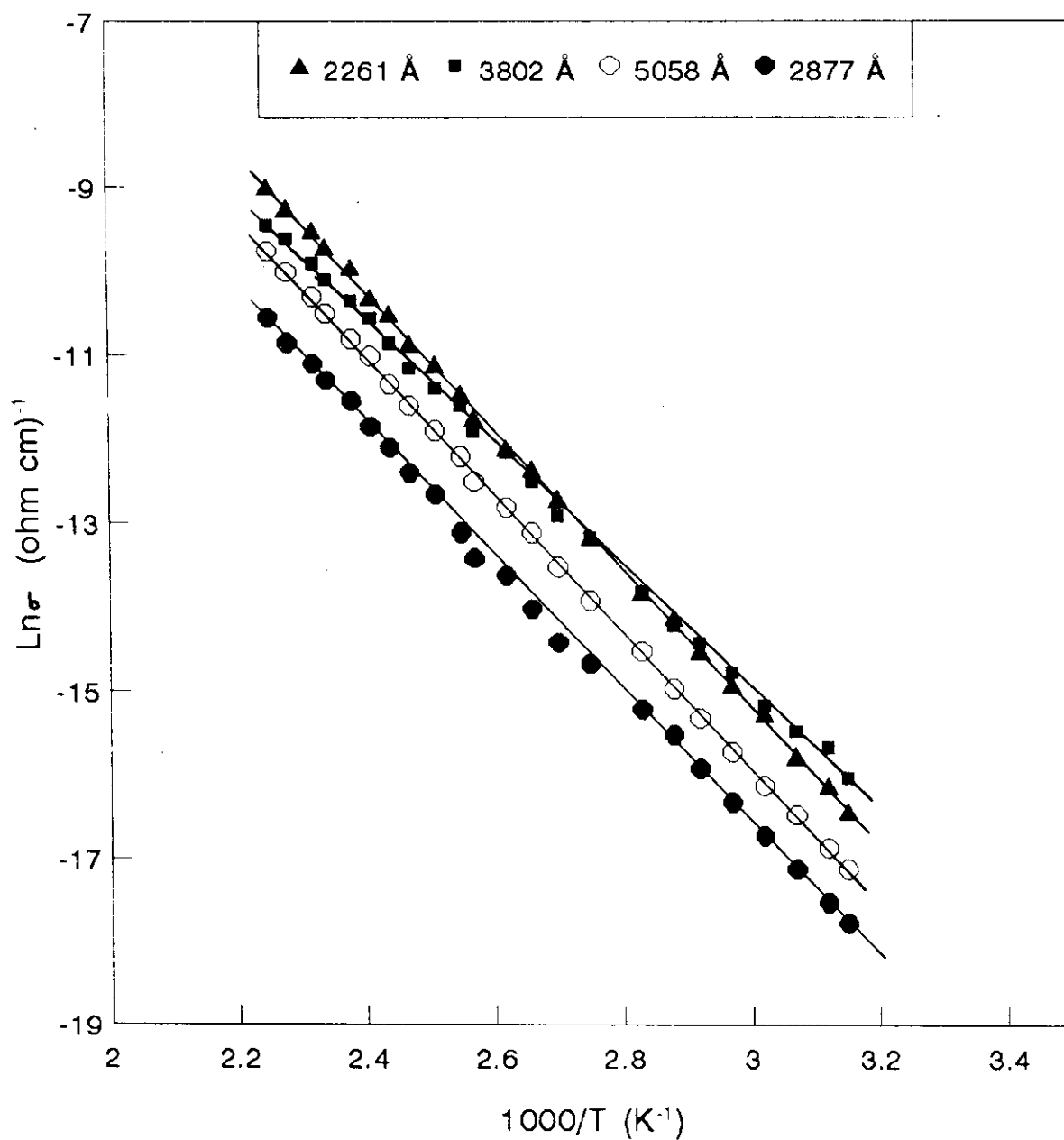


Figure 3.4.1 Plot of  $\text{Ln}\sigma$  vs  $1000/T$  for CuPc film of thickness 2261, 2877, 3802 and 5058 Å



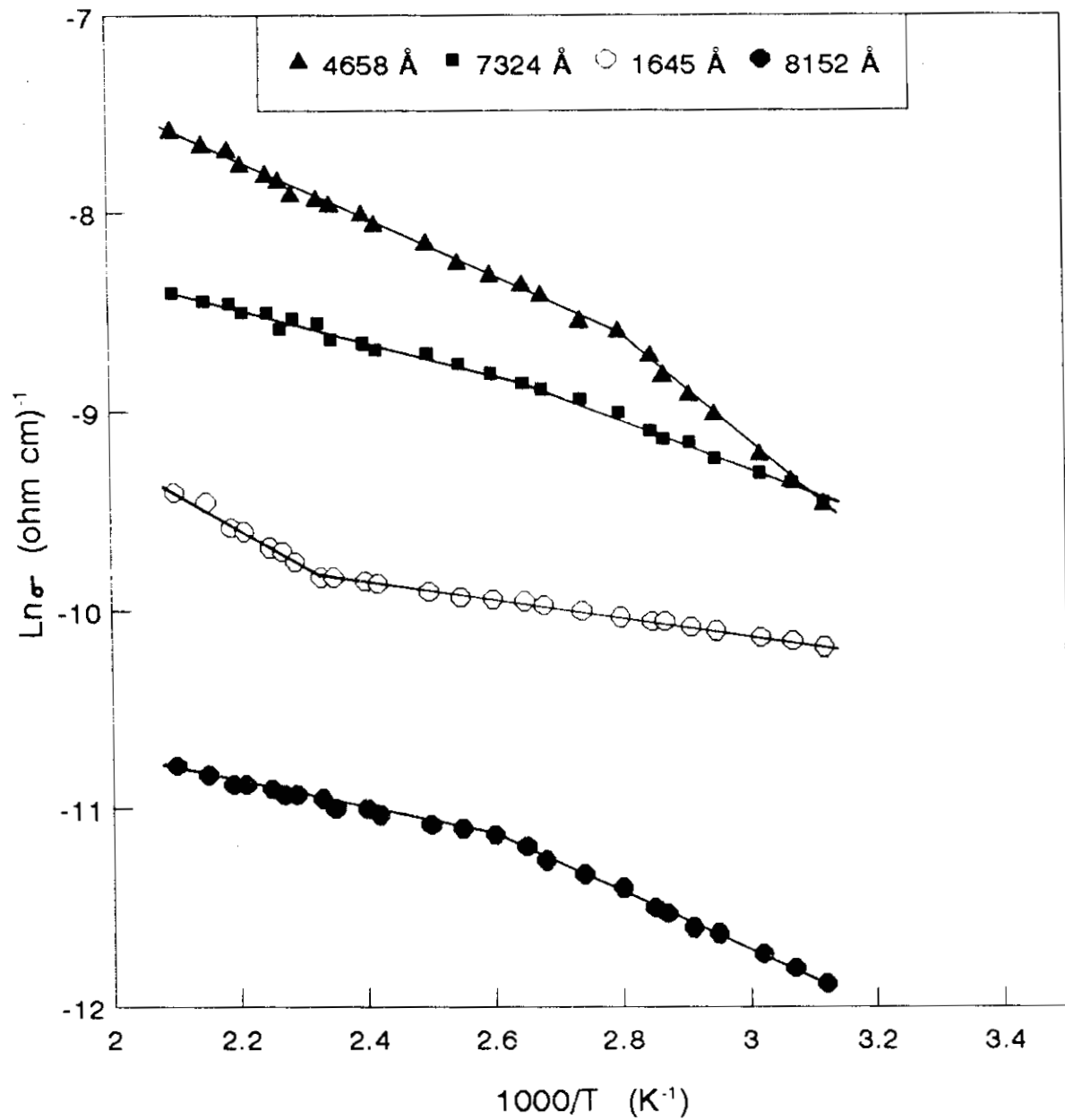


Figure 3.4.2 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for CoPc film of thickness 1645, 4658, 7324 and 8152 Å

and 8152 Å. There are two linear regions in all the graphs. From the slope of the linear portions the values of the activation energy are determined. The value of the activation energy obtained is 0.24 eV and 0.14 eV for CoPc film of thickness 1465 Å. Table 3.4.1 gives the activation energy for CoPc films of different thicknesses. For CoPc films also the activation energy  $E_1$  is found to decrease with increase in film thickness. Shihub and Gould<sup>18</sup> have reported an activation energy of 0.54 eV for CoPc films. Gould and Hassan<sup>19</sup> report 0.3 eV as the activation energy for CoPc films from their a.c. conductivity studies.

Figure 3.4.3 gives the plot of  $\ln \sigma$  versus  $1000/T$  for PbPc films of thicknesses 1440, 2837, 4251 and 5490 Å. There are three slopes for the graphs. The activation energies are determined from the slopes of the linear regions of the graphs and collected in Table 3.4.1. Unlike in CuPc and CoPc, PbPc films give three activation energies  $E_1$ ,  $E_2$  and  $E_3$ . As in the case of CuPc and CoPc, the activation energy  $E_1$  decreases with increase in thickness for PbPc thin films also. The values of the activation energy for PbPc are not compared with; as the same are not available in literature.

The steady state transport properties in phthalocyanines are controlled by the presence and energy distribution of carrier sites. In the case of CuPc, the traps exist in thin films either as a single energy level



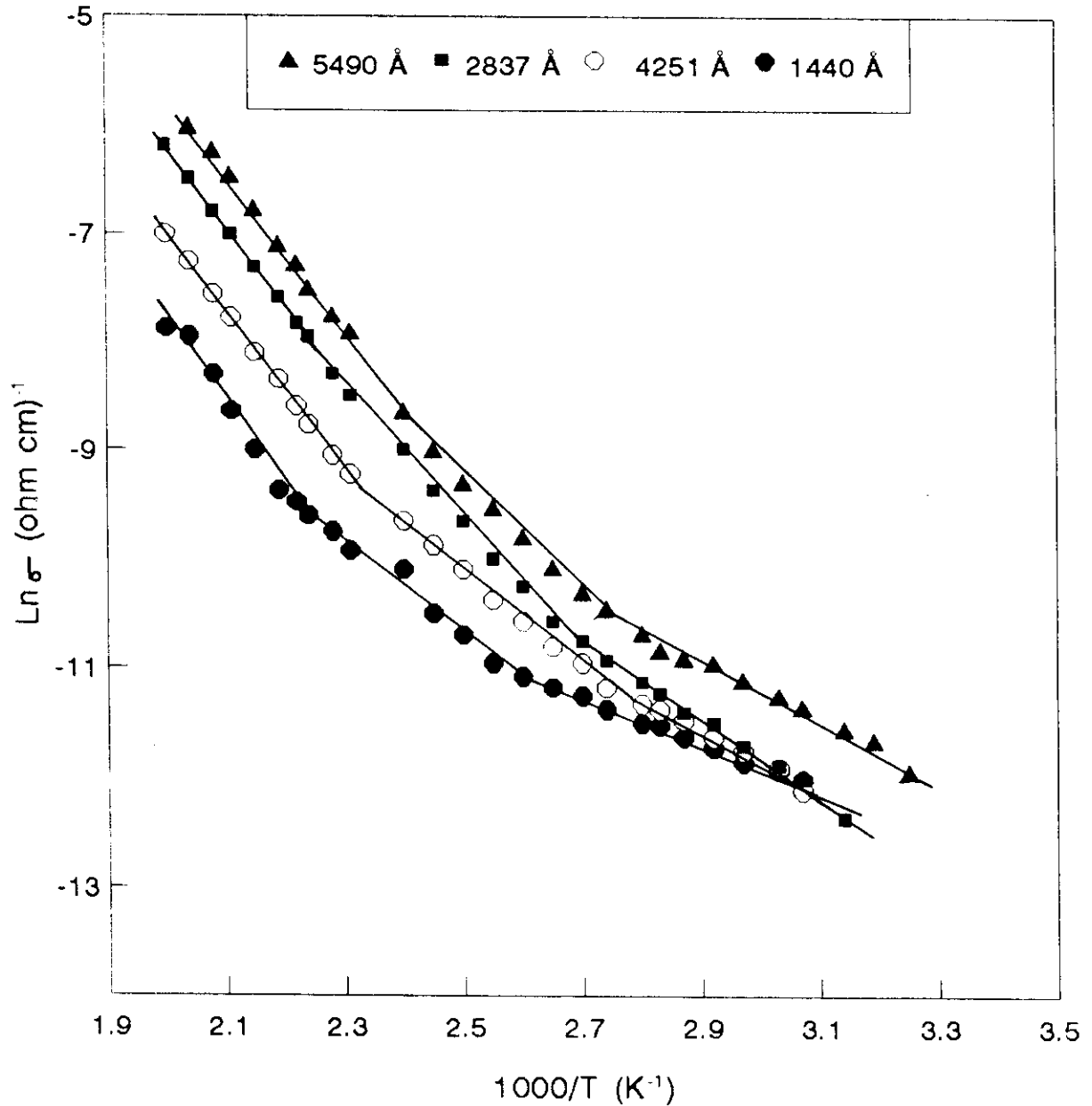


Figure 3.4.3 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for PbPc film of thickness 1440, 2837, 4251 and 5490 Å

or as a quasicontinuous energy distribution which is exponential in nature. It is suggested that the metal 3d orbitals provide an out-of-plane interaction with antibonding orbitals of nitrogen atoms in molecules situated in parallel planes above and below it.<sup>20</sup> Thus the central Cu metal atom adds another bridge for intermolecular charge transfer. Riehl and Bäessler<sup>13</sup> confirm more than one activation energy in aromatic compounds.  $E_1$  arises from the intrinsic charge carriers and  $E_2$  and  $E_3$  depend on the extrinsic conduction due to impurity scattering.

**Table 3.4.1: Activation Energy for CuPc, CoPc and PbPc Thin Films for Different Thicknesses of the Film**

Material	Thickness (Å)	Activation energy (eV)		
		$E_1$	$E_2$	$E_3$
CuPc	2261	1.49	—	—
	2877	1.45	—	—
	3802	1.39	—	—
	5058	1.36	—	—
CoPc	1645	0.24	0.14	—
	4658	0.23	0.03	—
	7324	0.15	0.08	—
	8152	0.11	0.05	—
PbPc	1440	0.68	0.38	0.17
	2837	0.64	0.45	0.29
	4251	0.62	0.39	0.24
	5490	0.57	0.46	0.25

In the extrinsic conduction region the charge carriers move by hopping along with the ions or electrons.<sup>21</sup> The intrinsic region gives 0.68 eV and the extrinsic regions give 0.38 eV and 0.17 eV as activation energy for PbPc film with thickness 1440 Å.

### 3.4.B Dependence of Substrate Temperature

To study the effect of substrate temperature on the conduction mechanism, thin films of CuPc, CoPc and PbPc are prepared at substrate temperatures of 50, 100, 150 and 200°C. Electrical connections are made with air dry silver paste. Resistance is measured at regular intervals of 5K using the programmable Keithley electrometer from 300K to 500K. Electrical conductivity  $\sigma$  is obtained using equation 3.2.7. Plots of  $\ln \sigma$  versus  $1000/T$  are made and are given in Figures 3.4.4, 3.4.5 and 3.4.6 for CuPc, CoPc and PbPc thin films respectively. In all the cases there are two linear regions; corresponding to two activation energies  $E_1$  and  $E_2$ .  $E_1$  is the activation energy at higher temperatures and  $E_2$  that at lower temperatures. From the linear portions of the graphs activation energies are calculated. Table 3.4.2 give the activation energy at different substrate temperatures for CuPc, CoPc and PbPc thin films. It is seen that as the substrate temperature increases, the activation energy  $E_1$  decreases for CuPc, CoPc and PbPc. Shihub and Gould<sup>18</sup> have reported the activation energy for CuPc from their a.c. conductivity



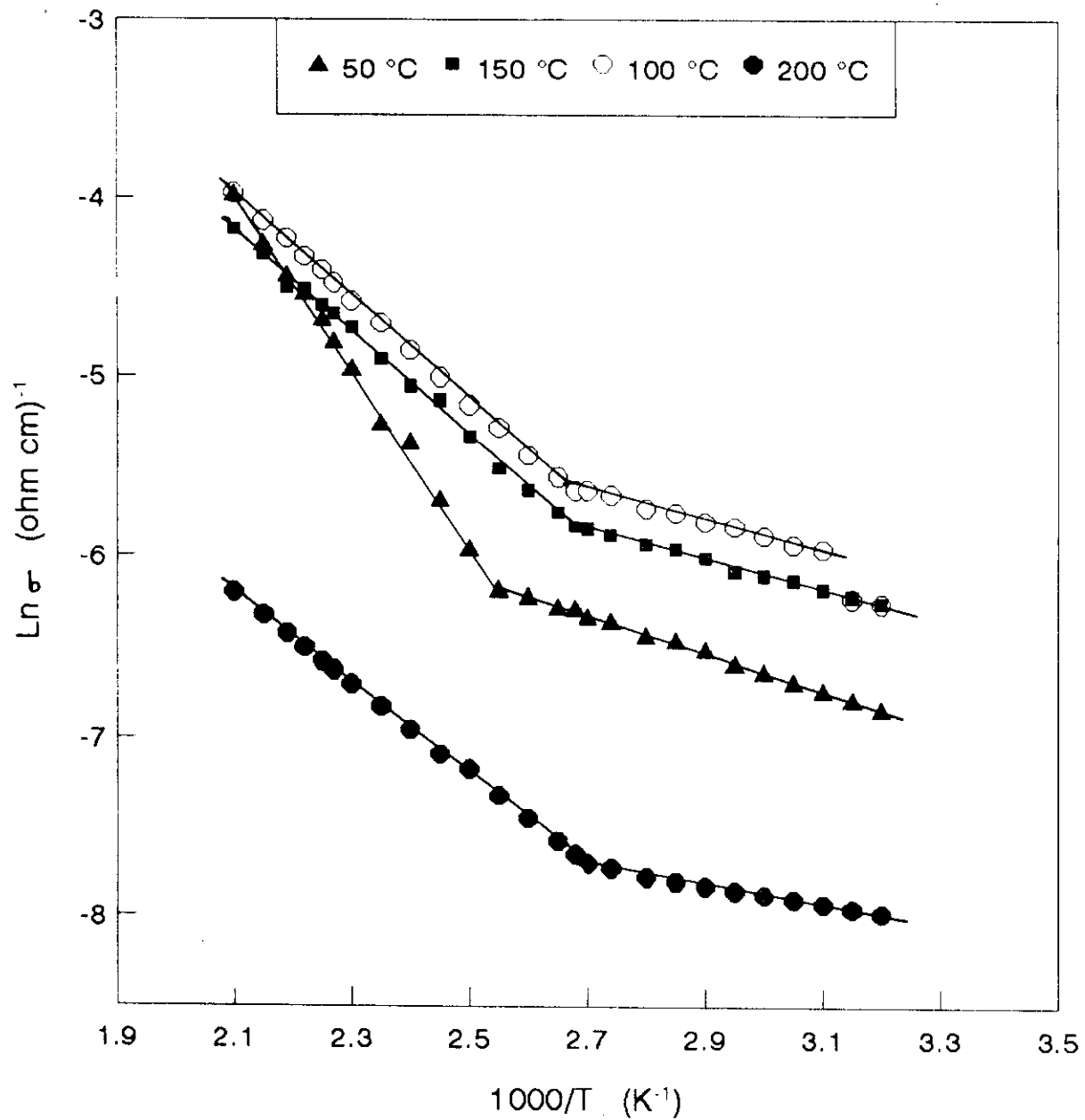


Figure 3.4.4 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for CuPc films of thickness 4100 Å evaporated at  $T_s = 50, 100, 150$  and  $200$  °C

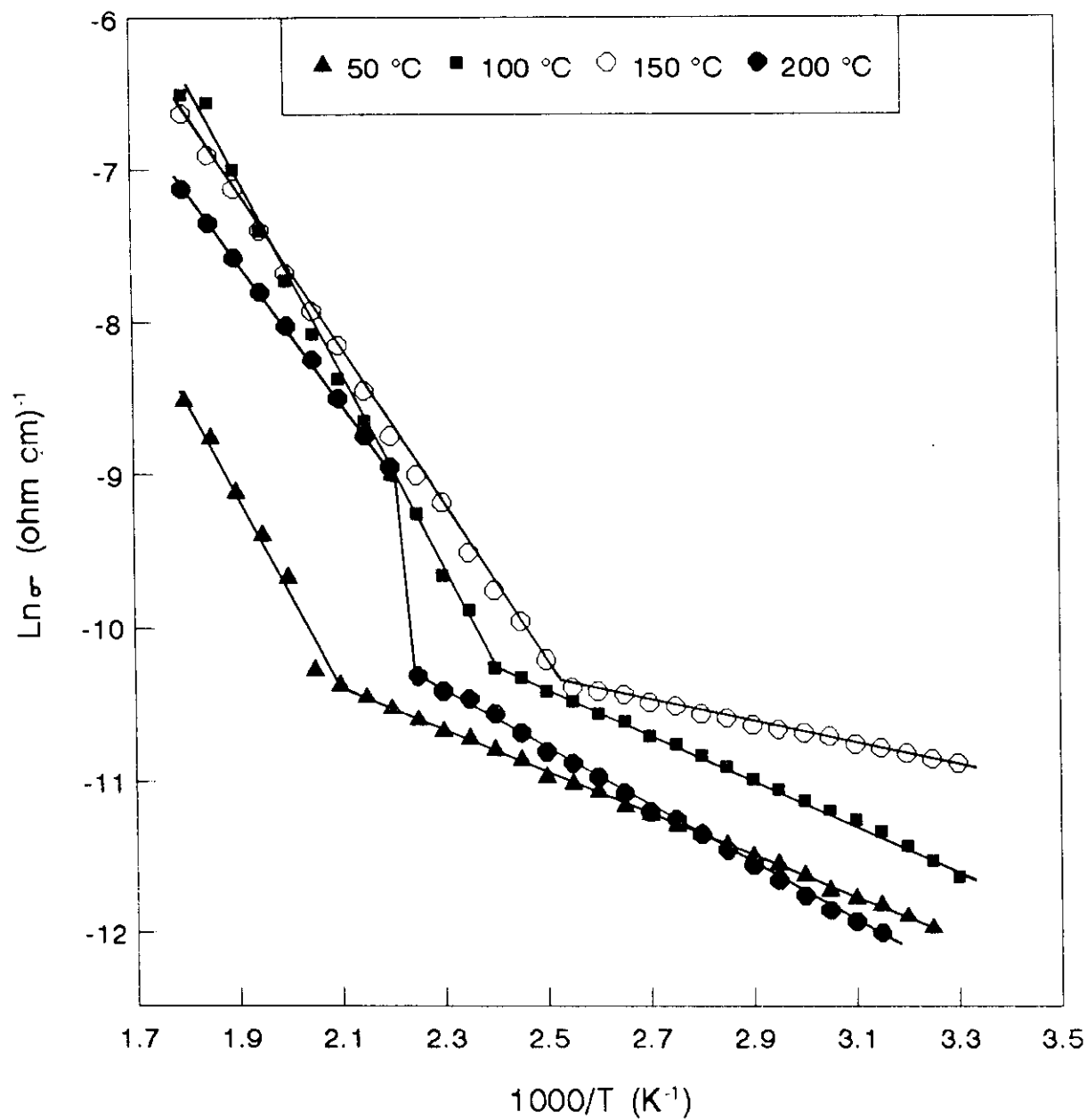


Figure 3.4.5 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for CoPc films of thickness 2900 Å evaporated at  $T_s=50, 100, 150$  and  $200$  °C

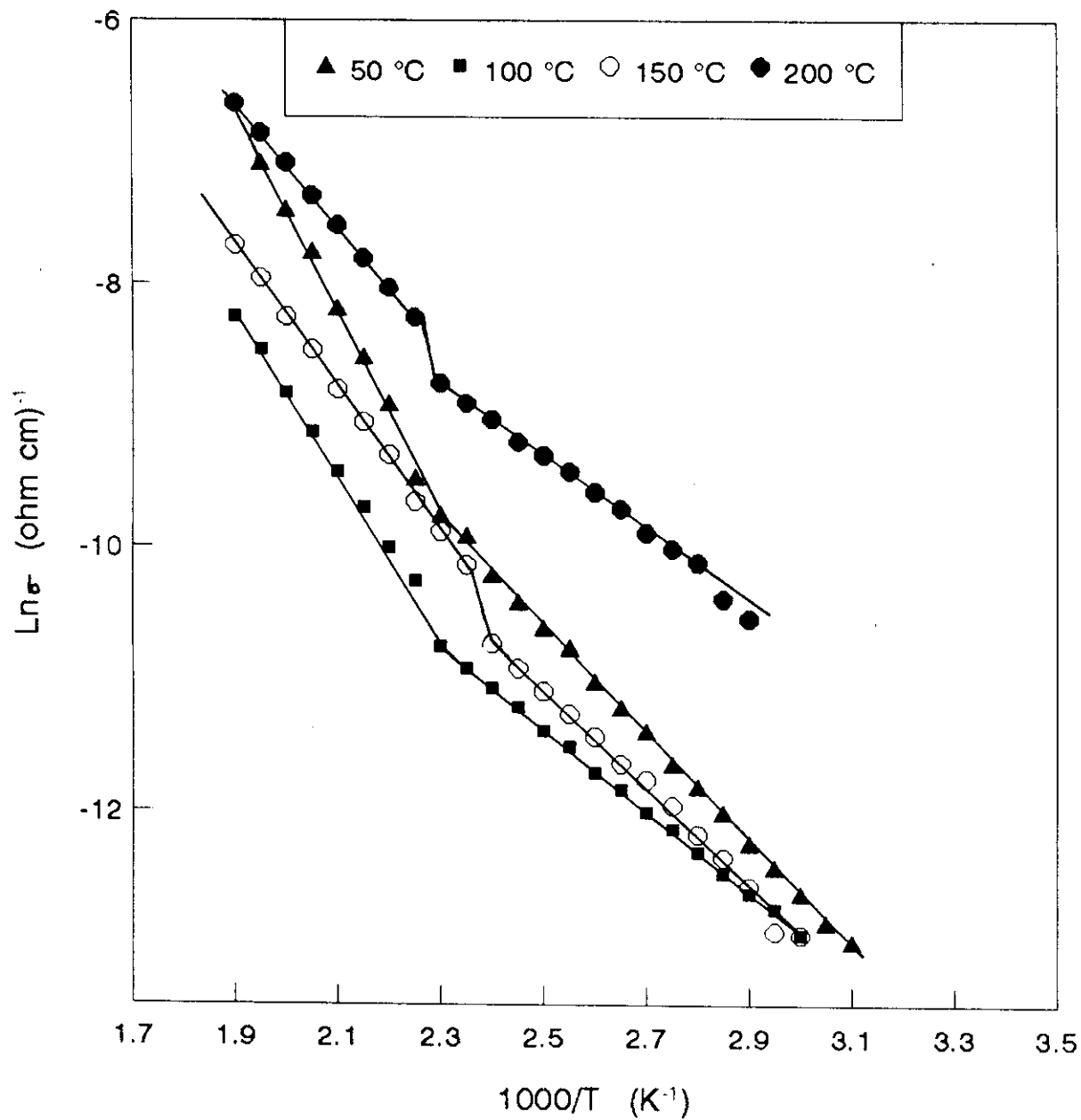


Figure 3.4.6 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for PbPc films of thickness 3150 Å evaporated at  $T_s=50, 100, 150$  and  $200$  °C



**Table 3.4.2: Activation Energy for CuPc, CoPc and PbPc Thin Films for Different Substrate Temperatures**

Material	Substrate temperature (°C)	Activation energy (eV)	
		$E_1$	$E_2$
CuPc	50	0.42	0.12
	100	0.30	0.14
	150	0.28	0.19
	200	0.26	0.08
CoPc	50	0.59	0.16
	100	0.54	0.12
	150	0.44	0.10
	200	0.39	0.03
PbPc	50	0.66	0.35
	100	0.51	0.27
	150	0.47	0.38
	200	0.40	0.29

studies. These results can also be interpreted in terms of hopping through a band of localised states at lower temperature and by free conduction at higher temperatures. The values reported by Shihub and Gould is 0.6 eV and 0.4 eV for CoPc. Hassan and Gould<sup>8</sup> obtained much lower values of 0.3 eV and 0.1 eV for CuPc at substrate temperature 423 K.

### 3.4.C Dependence of Annealing Temperatures

Thin films of CuPc, CoPc and PbPc prepared at room temperature have been annealed at 50, 100, 150 and 200°C. Annealing is carried out in air for a period of one hour. Ohmic contacts are given and electrical connections are made using air dry silver paste. D.C. electrical

conductivity measurements are made in the 300–500K range. The resistances are measured at regular intervals of 5K using Keithley electrometer. Electrical conductivity ' $\sigma$ ' is obtained using equation 3.2.7. Plots are made with  $\ln \sigma$  along y-axis and  $1000/T$  along x-axis and given in Figures 3.4.7, 3.4.8 and 3.4.9 for CuPc, CoPc and PbPc respectively. The activation energy is calculated from the slopes of the linear regions of the graphs. Two activation energies are obtained for CuPc films except at an annealing temperature of 200°C, whereas CoPc and PbPc have three activation energies. The activation energy for CuPc, CoPc and PbPc thin films for different annealing temperatures are collected in Table 3.4.3.

**Table 3.4.3: Activation Energy for CuPc, CoPc and PbPc for Different Annealing Temperatures**

Material	Annealing temperature (°C)	Activation energy (eV)		
		$E_1$	$E_2$	$E_3$
CuPc	50	0.63	0.15	—
	100	0.50	0.11	—
	150	0.42	0.10	—
	200	0.38	0.29	0.09
CoPc	50	0.59	0.23	0.08
	100	0.60	0.37	0.05
	150	0.75	0.42	0.14
	200	0.86	0.54	0.17
PbPc	50	0.49	0.30	0.14
	100	0.50	0.40	0.18
	150	0.53	0.39	0.09
	200	0.62	0.32	0.20



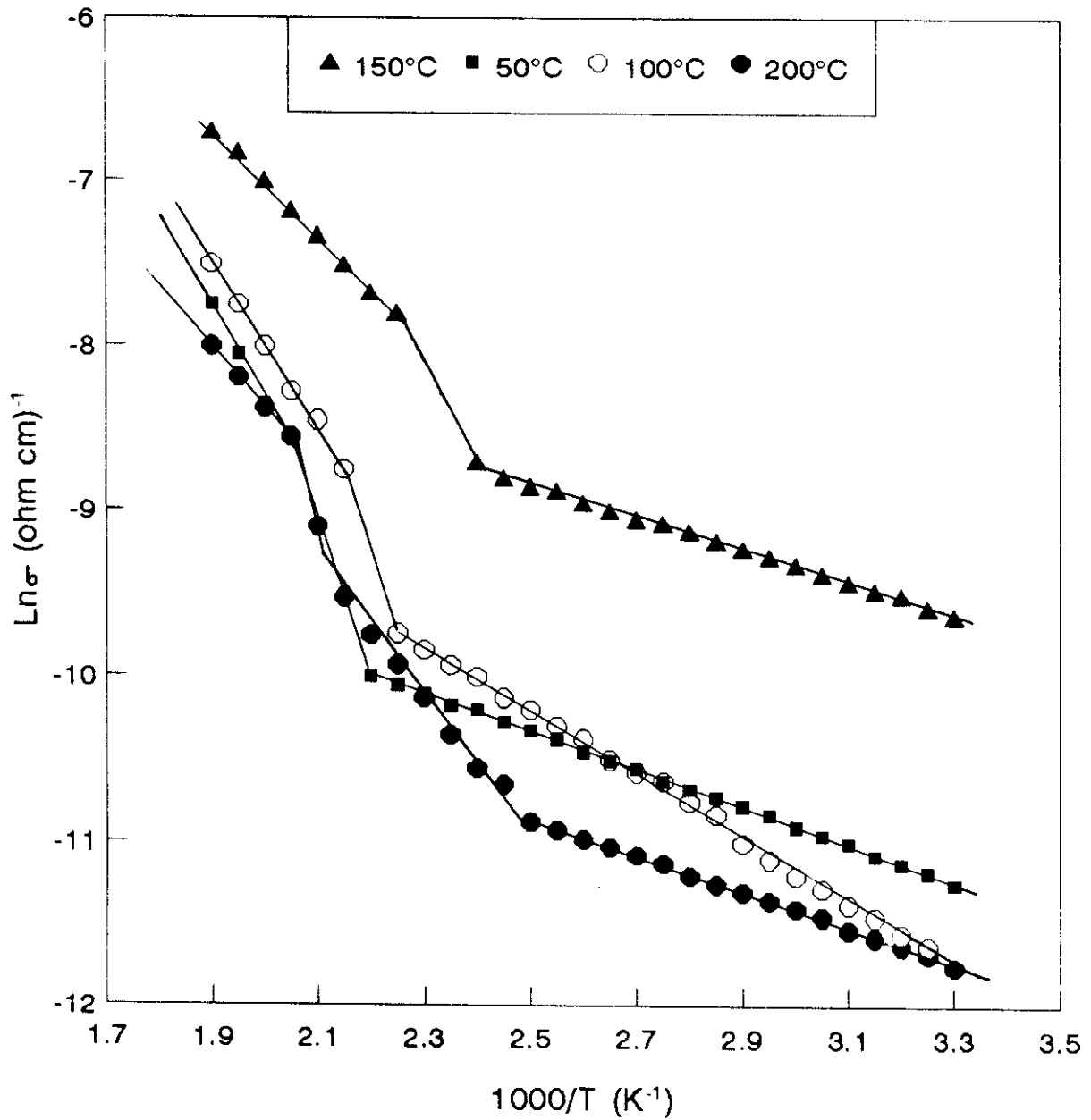


Figure 3.4.7 Plot of  $\text{Ln}\sigma$  vs  $1000/T$  for CuPc films of thickness 4100 Å annealed at  $T_a=50, 100, 150$  and  $200^\circ\text{C}$

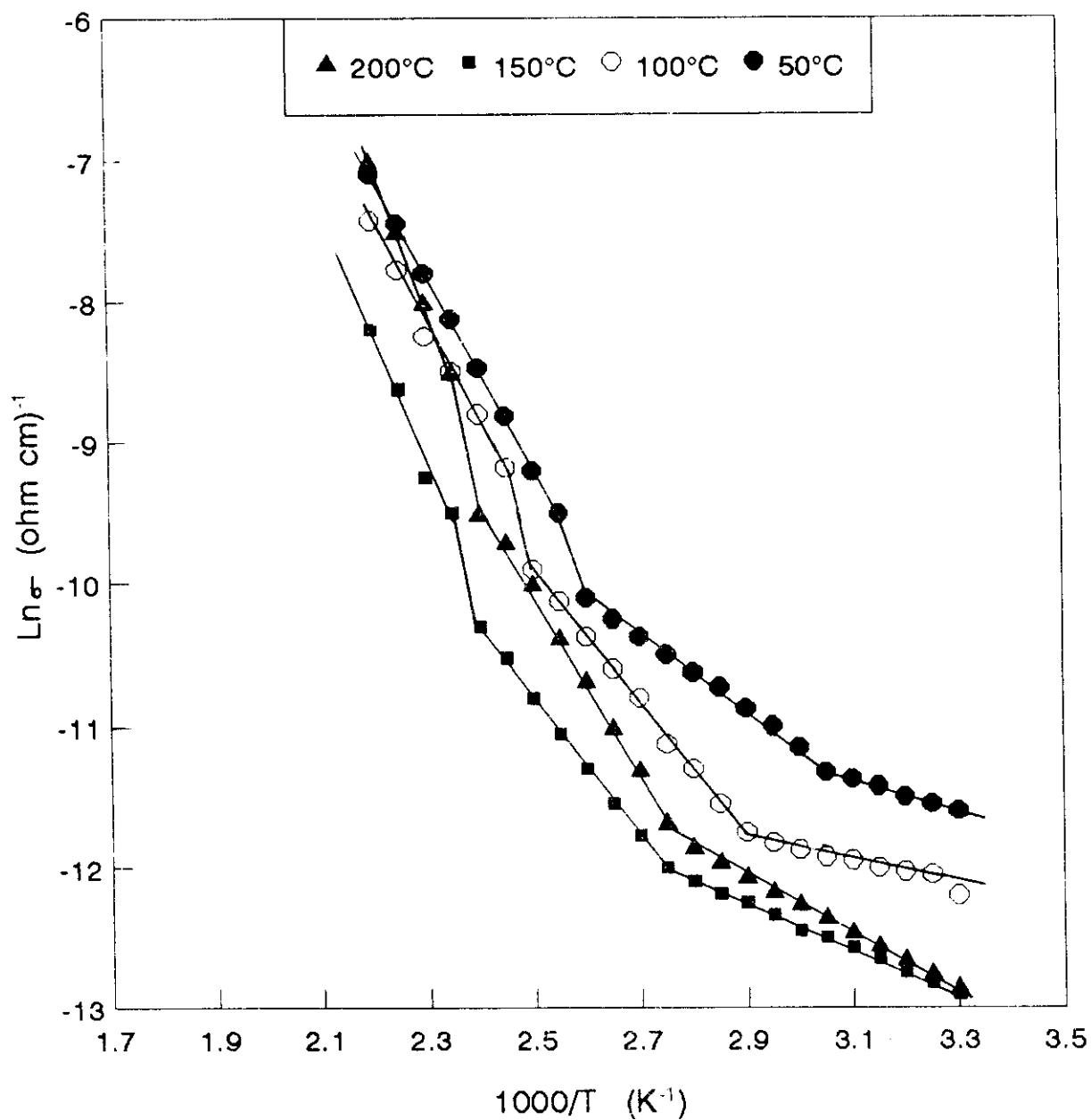


Figure 3.4.8 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for CoPc films of thickness 2900 Å annealed at  $T_a=50, 100, 150$  and  $200^\circ\text{C}$

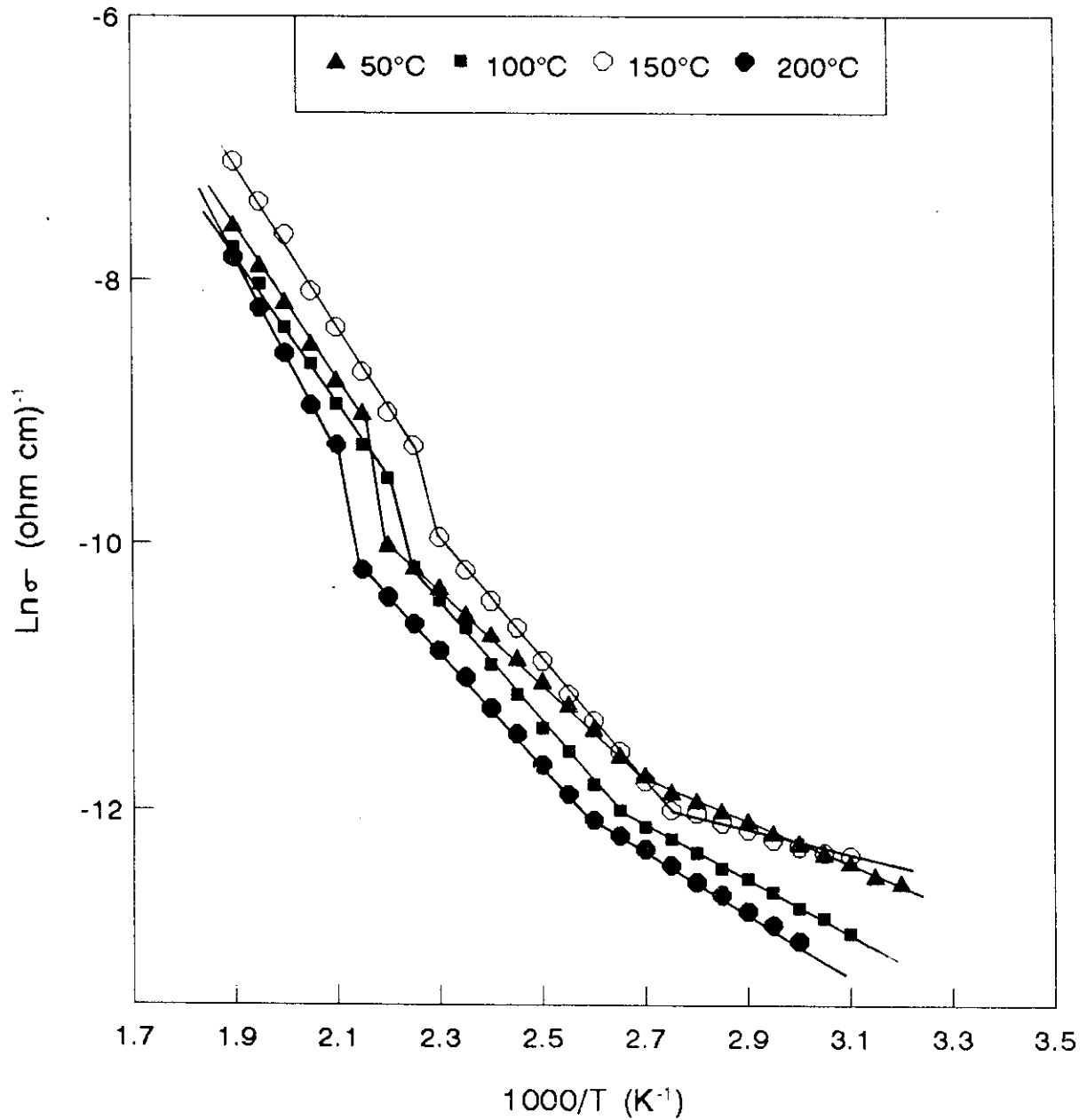


Figure 3.4.9 Plot of  $\text{Ln } \sigma$  vs  $1000/T$  for PbPc films of thickness 3150 Å annealed at  $T_a=50, 100, 150$  and  $200^\circ\text{C}$

As the annealing temperature increases the activation energy  $E_1$  increases for CoPc and PbPc films. For CuPc films the activation energy is 0.63 eV and 0.15 eV at 50°C and it reduces to 0.38 eV, 0.29 eV and 0.09 eV at 200°C. Sussmann<sup>22</sup> have reported that the distribution of trapping sites is altered by annealing. Oxygen causes distribution of the trap levels altered by annealing, giving two activation energies. CoPc and PbPc have three activation energies which increase with increase in annealing temperatures. On annealing in air, the exponential trap distribution is re-established, confirming that additional oxygen impurities are responsible for the modified behaviour.<sup>23</sup> Shihub and Gould<sup>18</sup> have reported that annealing decreases the density of defects thereby changing the electrical conductivity and conduction mechanism.

Electrical conductivity measurements of the room temperature evaporated CuPc, CoPc and PbPc films are done both in air and in vacuum. Resistance is measured at intervals of 5K from 300–450K using the programmable Keithley electrometer. The electrical conductivity is obtained using equation 3.2.7 for CuPc, CoPc and PbPc films. The conductivity in air is 2 to 3 times higher than that in vacuum for all the materials. The conductivity changes are due to the creation or recombination of holes on the surface of the film. Dahlberg and Musser<sup>24</sup> argue that this effect is due to the presence of oxygen in an



undissociated form above the central metal atom in the phthalocyanine ring. The effect of gases on the electrical conductivity of phthalocyanines is well described by Gutmann and Lyons<sup>25</sup>, Meier<sup>26</sup> and by Gutmann et. al.<sup>27</sup> They have investigated the effects of oxygen on thin films of phthalocyanines as it helps to understand the process involved in photosynthesis (as chlorophyll resembles phthalocyanines structurally) and the effect of low molecular hydrocarbons and toxic gases, on the electrical conductivity of phthalocyanines.

### 3.5. Conclusion

The conjugation structure of phthalocyanine is the essential condition leading to intrinsic conductivity. Molecular interactions in phthalocyanines are due to van der Waal's type forces and they maintain molecular properties. It is observed that as the film thickness increases, the activation energy  $E_1$  decreases for CuPc, CoPc and PbPc thin films. CuPc is intrinsic in nature whereas CoPc and PbPc exhibit extrinsic conductivity. As the substrate temperature is increased, the activation energy  $E_j$  is decreased for CuPc, CoPc and PbPc films. The activation energies are due to majority carriers and the trapping levels (created by the impurities). On annealing CuPc films except at 200°C two activation energies have been observed which decrease with the increase in annealing temperature. CoPc and PbPc thin films have



three activation energies which increase with increase in annealing temperature.

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