

Chapter 4

OPTICAL STUDIES IN COPPER PHTHALOCYANINE COBALT PHTHALOCYANINE AND LEAD PHTHALOCYANINE THIN FILMS

4.1. Introduction

For probing the band structure in semiconductors, one of the most direct methods is the optical absorption studies. We can determine the energy gap of the material as well as determine whether the valence band and conduction band extrema occur at the same or different points in the k -space knowing the frequency dependence of the absorption processes such as fundamental absorption, free carrier absorption, excitonic absorption and impurity absorption. Electrons can be excited from the valence band to the conduction band with the absorption of a photon of energy equal to the band gap of the material. In phthalocyanines, the absorption coefficient is of the order of 10^5 to 10^6 cm^{-1} . Rapid drop in the absorption coefficient on the high energy side of the absorption band leads to the band edge in semiconductors.



The metallophthalocyanines belong to the point group D_{4h} and the electronic structure of metal phthalocyanines was described by Gouterman and coworkers.^{1,2} Charge transfer and electroabsorption studies of metal phthalocyanine by Yoshida³ et. al. suggested the effect of hybridisation between intramolecular excitations. Our understanding of the electrical behaviour of CuPc, CoPc and PbPc has improved somewhat, although the problems associated with the validity of application of band models in common with many organic semiconductors, still needs clarification. This chapter deals with the optical characterisation of CuPc, CoPc and PbPc films.

4.2. Theory

Absorption is a phenomenon of fundamental interest because of its relation to the dynamics of the electrons and ions of the medium under the influence of electromagnetic radiation. From the frequency dependence of the absorption, one can determine the energy gap of the material. When the energy of the incident photon is greater than that of the band gap ($h\nu > E_g$) the absorption coefficient ' α ' is given by⁴

$$\alpha = \frac{A}{h\nu} \left\{ (h\nu - E_g)^{1/2} + \frac{\pi}{2} B - B \arcsin \left[\frac{h\nu - E_g}{h\nu - E_g + B^2} \right]^{1/2} \right\} \quad 4.2.1$$

where $B^2 = \frac{(C_c + C_v)^2}{4(b_c + b_v)}$. Here the constants $b_c, b_v > 0$ and $C_c, C_v \geq 0$



For $h\nu - E_g \leq B^2$ equation 4.2.1 simplifies to

$$\alpha = \frac{A}{h\nu 3B^2} (h\nu - E_g)^{3/2} \quad 4.2.2$$

For $h\nu - E_g \gg B^2$ equation 4.2.2. becomes

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^{1/2} \quad 4.2.3$$

where A is a constant

When the energy of the incident photon exceeds the band gap (E_g) of the material, an electron is excited from the valence band to the conduction band. There are two types of transitions - direct and indirect. Transition involving photons only is direct and transition involving photon and phonon is indirect. A direct vertical optical transition near the fundamental absorption edge in a semiconductor is shown schematically in Figure 4.2.1. The valence band maximum and conduction band minimum appear at the same point in the Brillouin zone at $k = 0$. The direct band gap is estimated from equation 4.2.3. The procedure consists of plotting α^2 versus $h\nu$ and extrapolating the linear region of the curve to the energy axis; the intercept being identified as the band gap.

When transition requires a change in both energy and momentum, a double transition process is required because photon

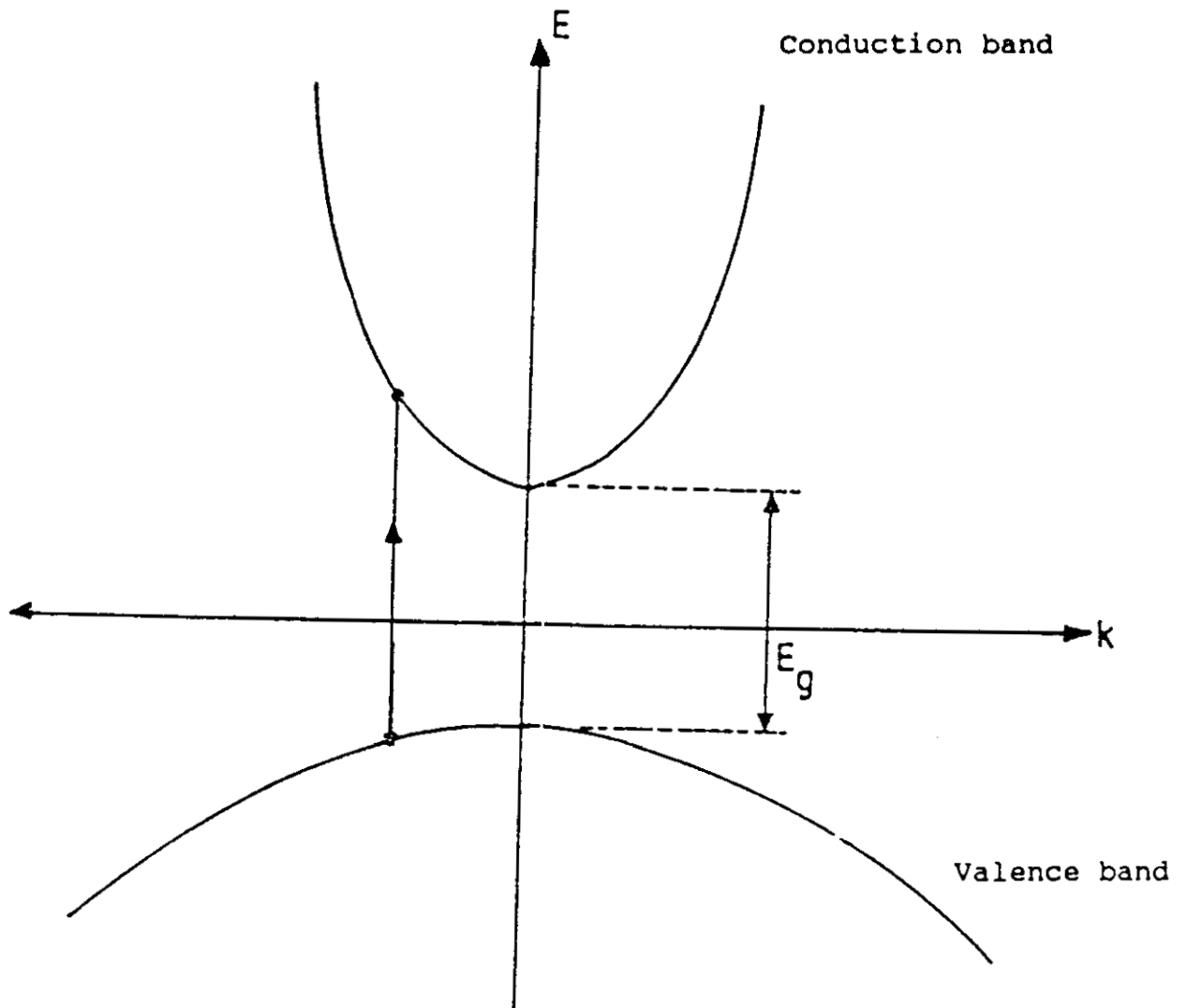


Figure 4.2.1 : Direct transition from valence band to conduction band

cannot provide change in momentum. For overcoming this, emission or absorption of phonons occurs. Momentum is conserved through a phonon interaction resulting in an indirect transition as shown schematically in Figure 4.2.2. The indirect band gap is determined from the relation

$$\alpha = (h\nu - E_g)^2 \quad 4.2.4$$

There is a shift in the band gap towards higher energy for the film having higher carrier density. This shift is due to the filling of states near the bottom of the conduction band and is known as Burstein Moss^{5,6} shift and is illustrated in Figure 4.2.3. The shift is given by the relation

$$E_g = E_{g_0} + \Delta E_g^{BM} \quad 4.2.5$$

where E_{g_0} is the intrinsic band gap and ΔE_g^{BM} is the BM shift. The shift is related to the carrier density as

$$\Delta E_g^{BM} = \frac{\pi^2 \hbar^2}{2m^*} (3N/\pi)^{2/3} \quad 4.2.6$$

where m^* is the reduced effective mass.

The plot of α^2 versus $h\nu$ for direct allowed transition, $\alpha^{2/3}$ versus $h\nu$ for direct forbidden transition, $\alpha^{1/2}$ versus $h\nu$ for indirect allowed transition and $\alpha^{1/3}$ versus $h\nu$ for indirect forbidden transition will lead to straight lines. By extrapolating these lines to $\alpha = 0$, one can determine the corresponding band gap of a material.



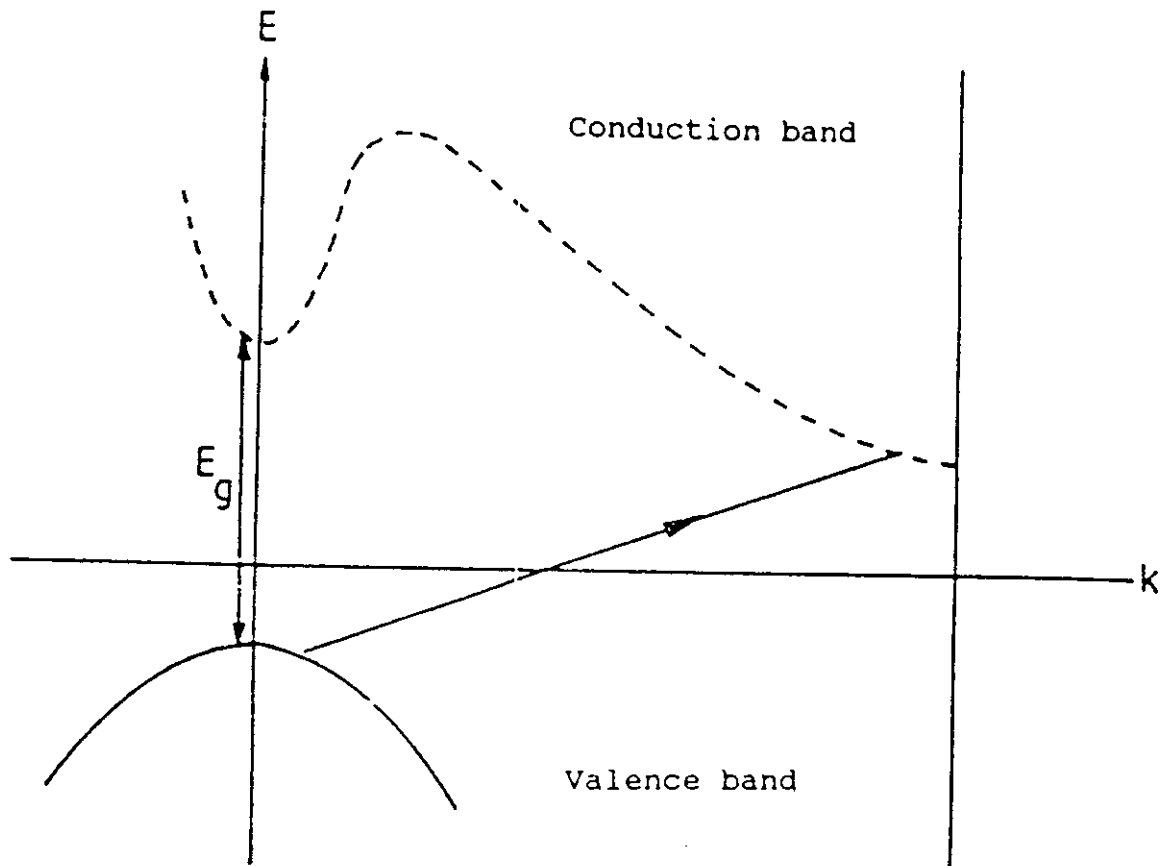


Figure 4.2.2 : Indirect transition from valence band to conduction band

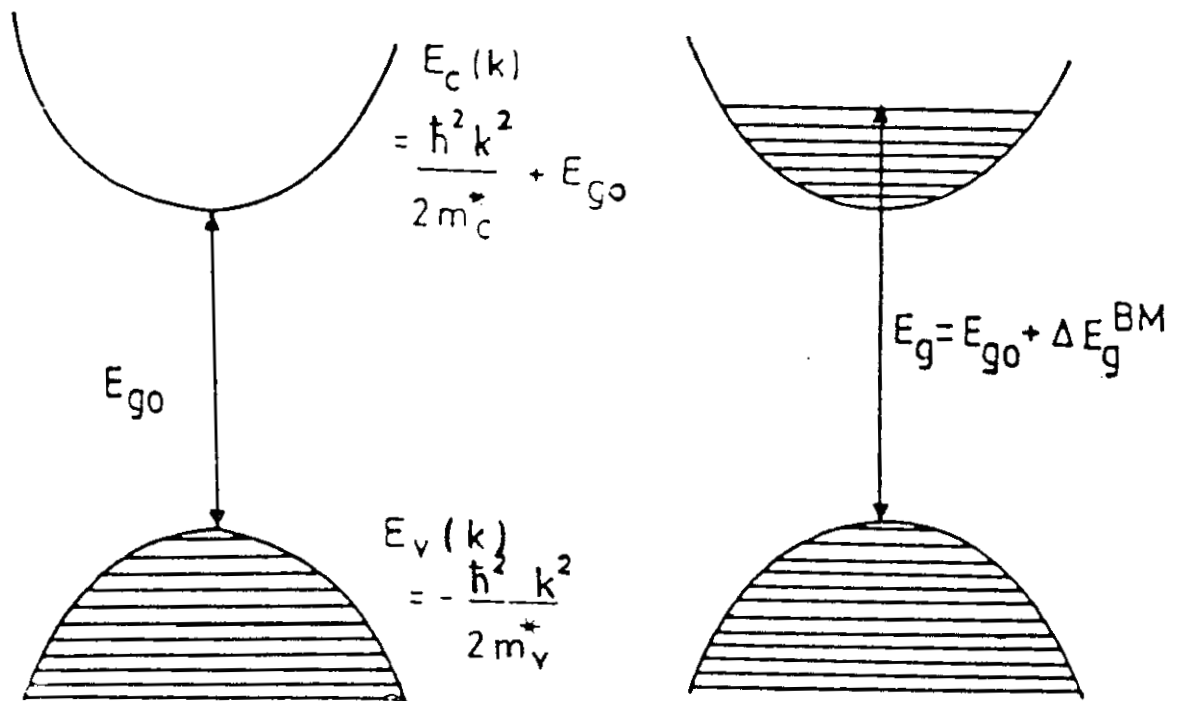


Figure 4.2.3: Illustration of Burstein Moss shift.

It can be seen that a careful and systematic study of optical data can yield a wealth of information regarding the material. It includes the band gap of the material and the relative positions of the conduction and valence band maxima in k space. The functional dependence of absorption coefficient on photon energy near a transition can tell whether the transition is allowed or forbidden. The nature of transition can give information about the electronic states from which the transition takes place and this in turn helps to get the band structure of the semiconducting material.⁷

4.3. Experiment

Commercially available copper phthalocyanine, cobalt phthalocyanine and lead phthalocyanine (CuPc, CoPc, PbPc) powders (98% pure) supplied by Aldrich Company INC., WI, are used as the source materials for the preparation of thin films. The films are prepared at a base pressure of 10^{-5} Torr by vacuum sublimation of the materials from a molybdenum boat using resistive heating technique. The details of preparation are discussed in section 2.14 of Chapter 2. The rate of evaporation is kept 10–15 nm/minute. Visible, ultraviolet and near infrared absorption spectra of CuPc, CoPc and PbPc films are recorded using Shimadzu 160A spectrophotometer. The Spectro-photometer consists of a Spex Minimate monochromator (containing a 50 W quartz



halogen lamp illuminating a diffraction grating of 900 lines/nm) interfaced to a computer which can scan the spectrum from 350nm to 1100 nm in steps of 10nm.

Films are prepared at various substrate temperatures from 50°C to 300°C. Optical absorption spectra are recorded for the films of CuPc, CoPc and PbPc evaporated at different substrate temperatures and the spectra analysed to study the effect of substrate temperature on the band gap and trapping levels. Substrate temperature is measured by a copper–constantan thermocouple attached to the substrate.

Post evaporation annealing is carried out for CuPc, CoPc and PbPc films prepared at room temperature. The post evaporation annealing is carried out in a furnace whose temperature is controlled by a controller cum recorder. The annealing time is two hours. The absorption spectra are recorded and analysed to obtain the effect of annealing on the band gap of the material.

4.4. Results and Discussion

Figures 4.4.1, 4.4.2. and 4.4.3. show the percentage transmission versus wavelength for CuPc, CoPc and PbPc thin films of thicknesses 1800Å, 3460 Å and 2250 Å respectively. The peak occurs at 478 nm for CuPc film. For CoPc and PbPc films the peaks are at 470 nm and



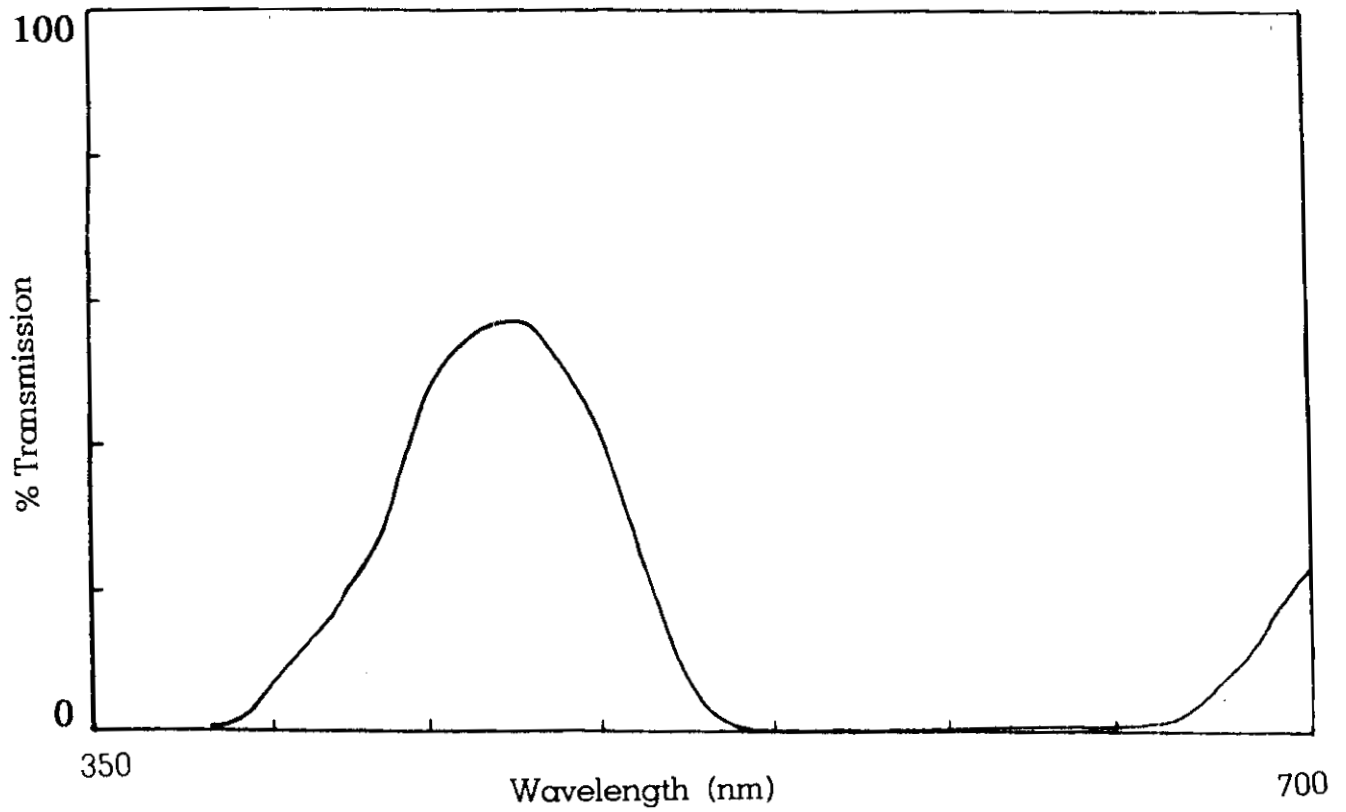


Figure 4.4.1: Percentage transmission versus wavelength spectrum of CuPc film of thickness 1800 Å

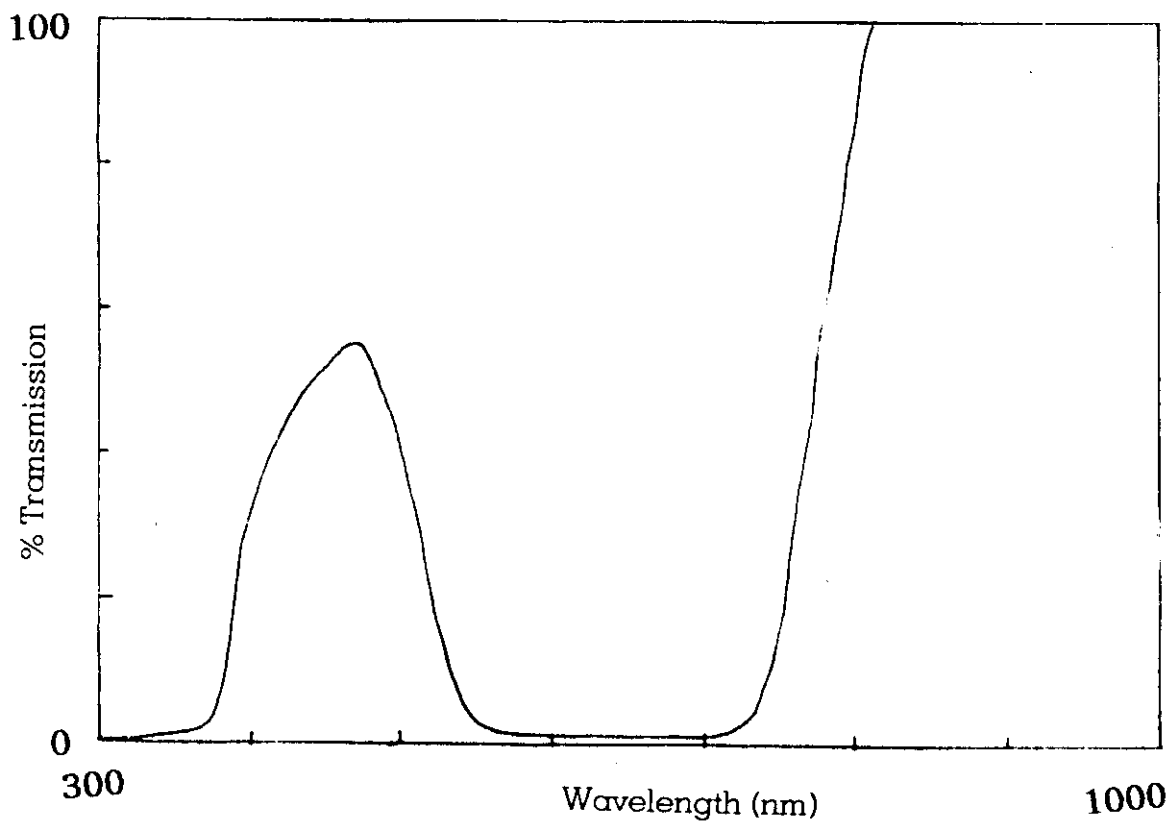


Figure 4.4.2: Percentage transmission versus wavelength spectrum of CoPc film of thickness 3460 Å

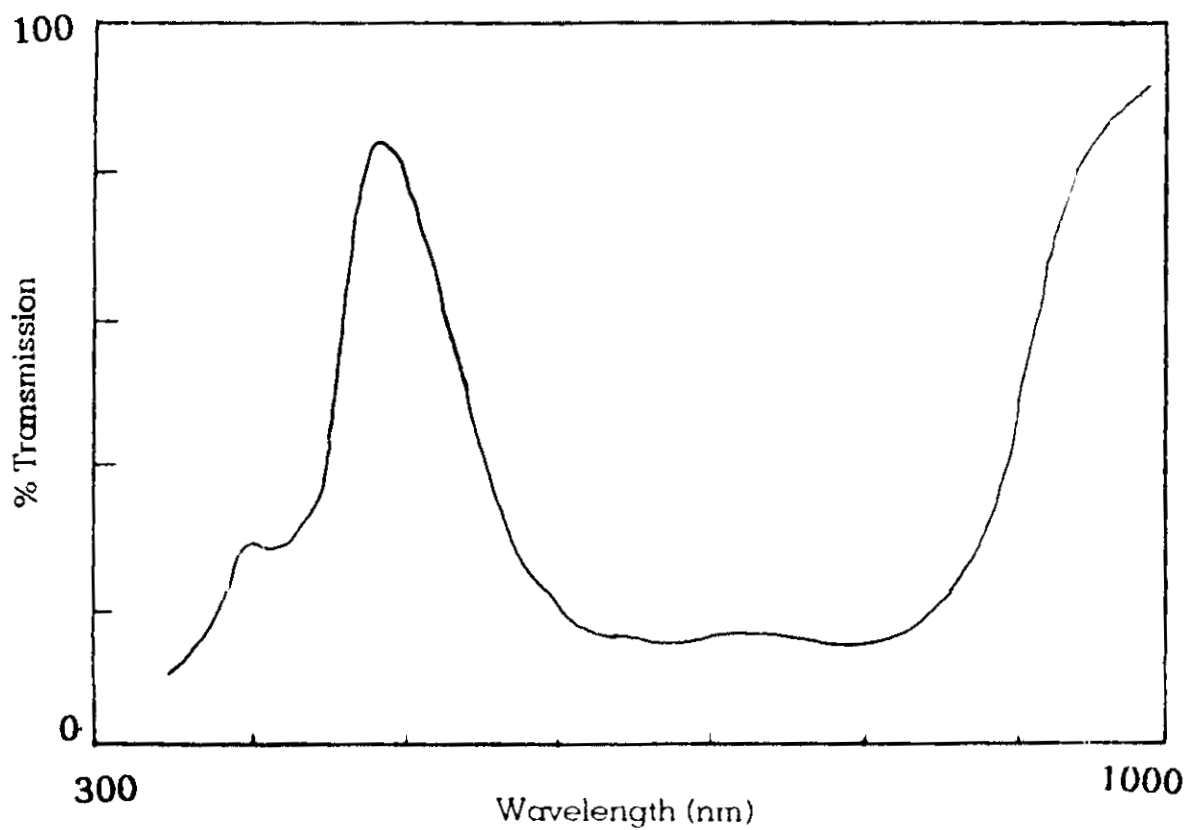


Figure 4.4.3: Percentage transmission versus wavelength spectrum of PbPc film of thickness 2250 Å

517 nm respectively. The low energy side of the transmittance spectrum shows absorption which decreases slowly with increase in photon energy. The high energy side of the transmission spectrum shows a sharp absorption edge.

To obtain information about direct or indirect interband transitions, the fundamental absorption edge is analysed within the one electron theory of Bardeen.⁸ Schmeisser et. al.⁹ show evidence for the absorption band at low energies. The absorption coefficient ' α ' is related to the photon energy ' $h\nu$ ' by¹⁰

$$\alpha = \alpha_0(h\nu - E_g)^n \quad 4.4.1$$

where E_g is the optical band gap and $n = 1/2$ for direct allowed transitions. In the case of CuPc, CoPc and PbPc films, the absorption coefficient $\alpha \geq 10^3 \text{ cm}^{-1}$ and the transitions are direct allowed transitions.

Figures 4.4.4, 4.4.5 and 4.4.6 give the plot of α^2 versus $h\nu$ for CuPc, CoPc and PbPc films. Extrapolation of $\alpha^2=0$ near the absorption edge gives the band gap energy. For CuPc we obtain the optical band gap is obtained as 2.71 eV¹¹ as shown in Figure 4.4.4. Schmeisser et. al.⁹ have predicted the optical band gap of CuPc to be higher than 2.42 ± 0.02 eV which is in agreement with the present value of 2.71 eV. CoPc also exhibits a similar transition spectrum. We have obtained the optical

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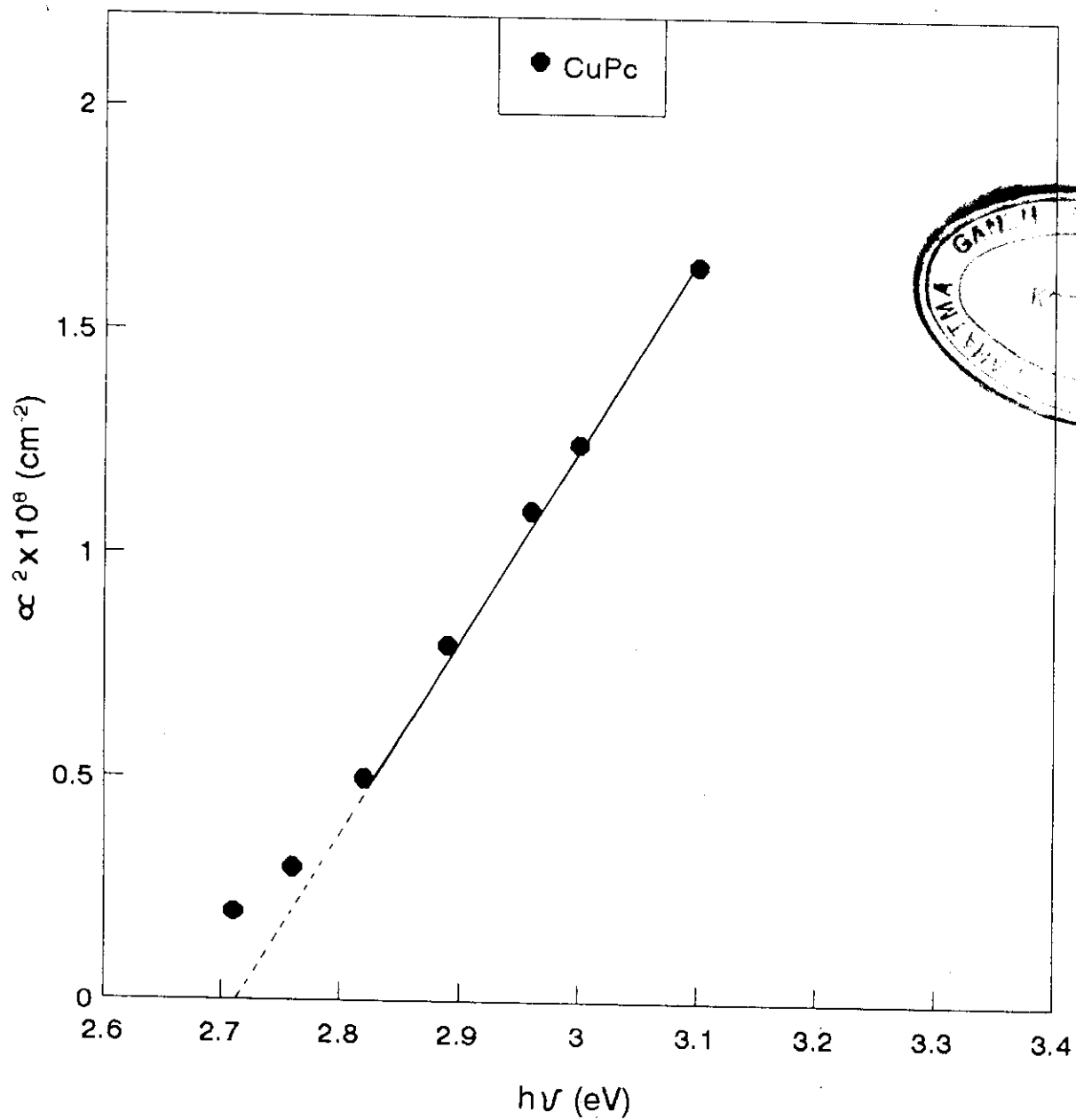


Figure 4.4.4 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å prepared at room temperature

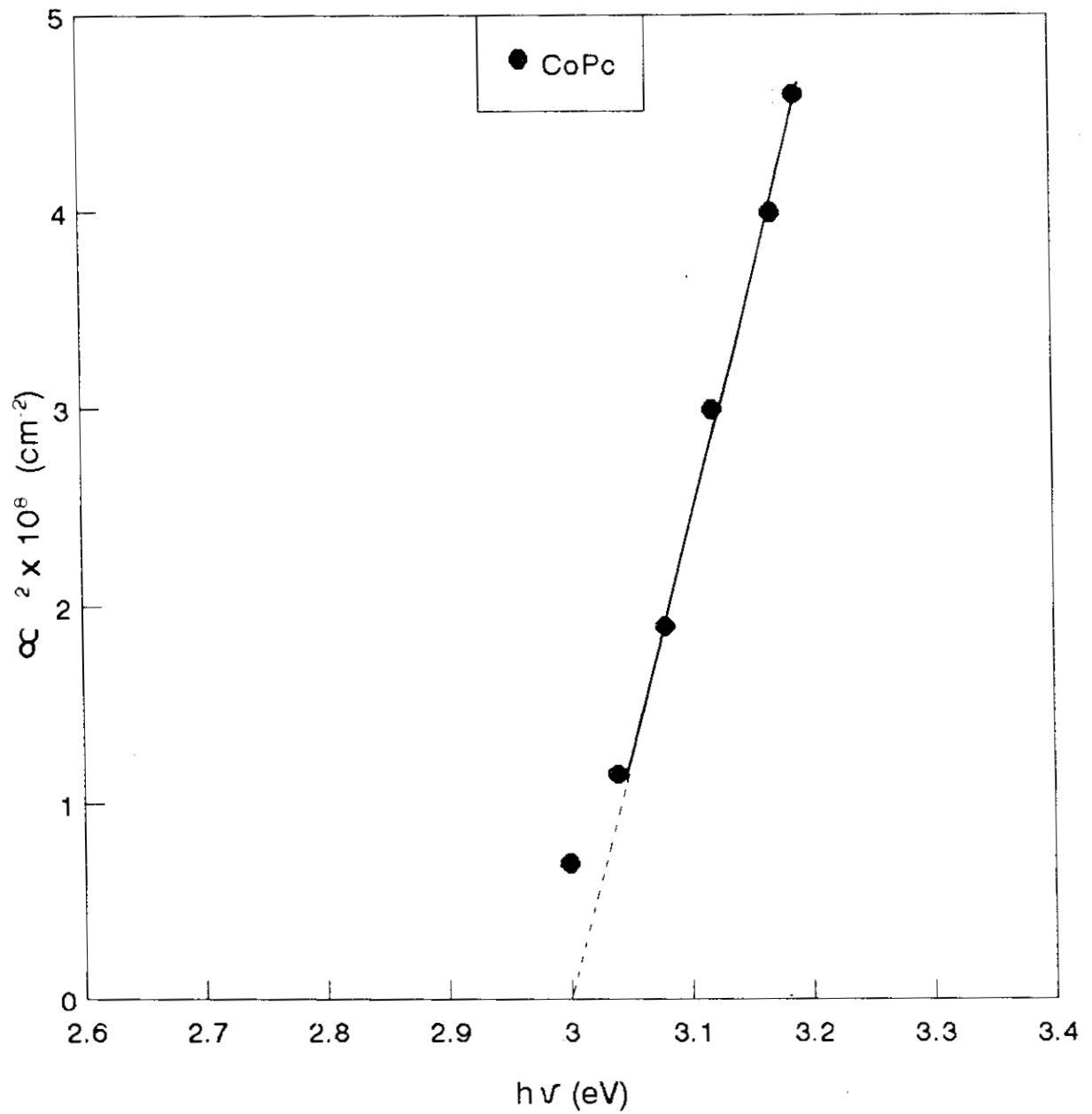


Figure 4.4.5 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å prepared at room temperature

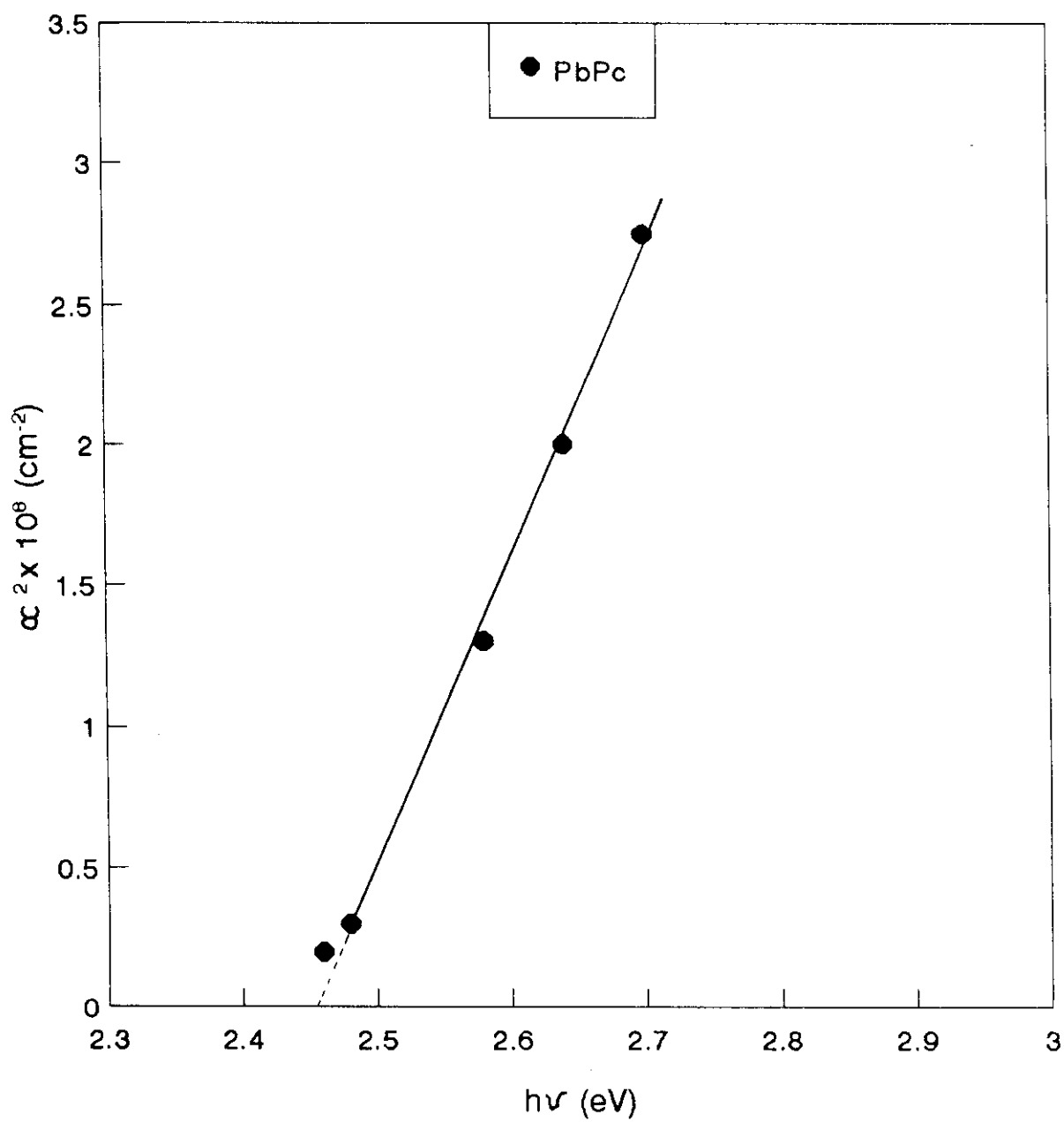


Figure 4.4.6 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å prepared at room temperature

band gap as 3.0 eV from Figure 4.4.5. For PbPc films in addition to the transmission maximum at the absorption edge, there is an additional peak as given in Figure 4.4.3. From the α^2 Versus $h\nu$ plot given in Figure 4.4.6, the optical band gap is determined as 2.46 eV. Collins et. al.¹⁰ have obtained the band gap of PbPc films as 2.42 eV. In all these cases the direct electronic transitions from $\pi - \pi^*$ orbits in the 300–450 nm range result in Soret transitions (B band) which give the absorption edge. Okei¹² suggested a model where electronic conduction is due to a charge transfer from sP_z mixing orbit to the π electron system of the macrocyclic ring of phthalocyanine. The consistency of the present results in terms of agreement with other materials adds support to the band model consideration to be appropriate for phthalocyanine thin films.

Percentage transmission versus wavelength spectra are recorded for CuPc, CoPc and PbPc thin films for different substrate temperatures as given in Figures 4.4.7, 4.4.8 and 4.4.9 respectively. An additional peak in the 640–670 nm range which was originally absent at room temperature is observed for CoPc films as the substrate temperature increases from 50°C to 300°C. Position of the new peak remains the same whereas the height of the peak progressively increases as the substrate temperature increases. Figures 4.4.10, 4.4.11 and 4.4.12 give



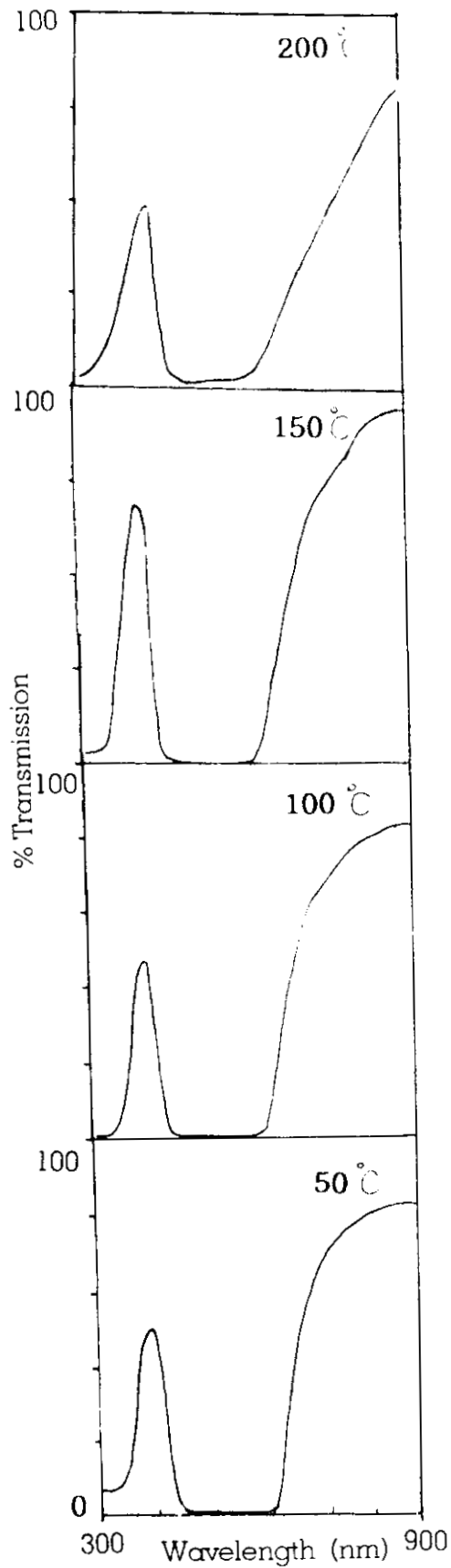


Figure 4.4.7: Percentage transmission versus wavelength spectrum of CuPc film prepared at $T_s = 50, 100, 150$ and 200°C .

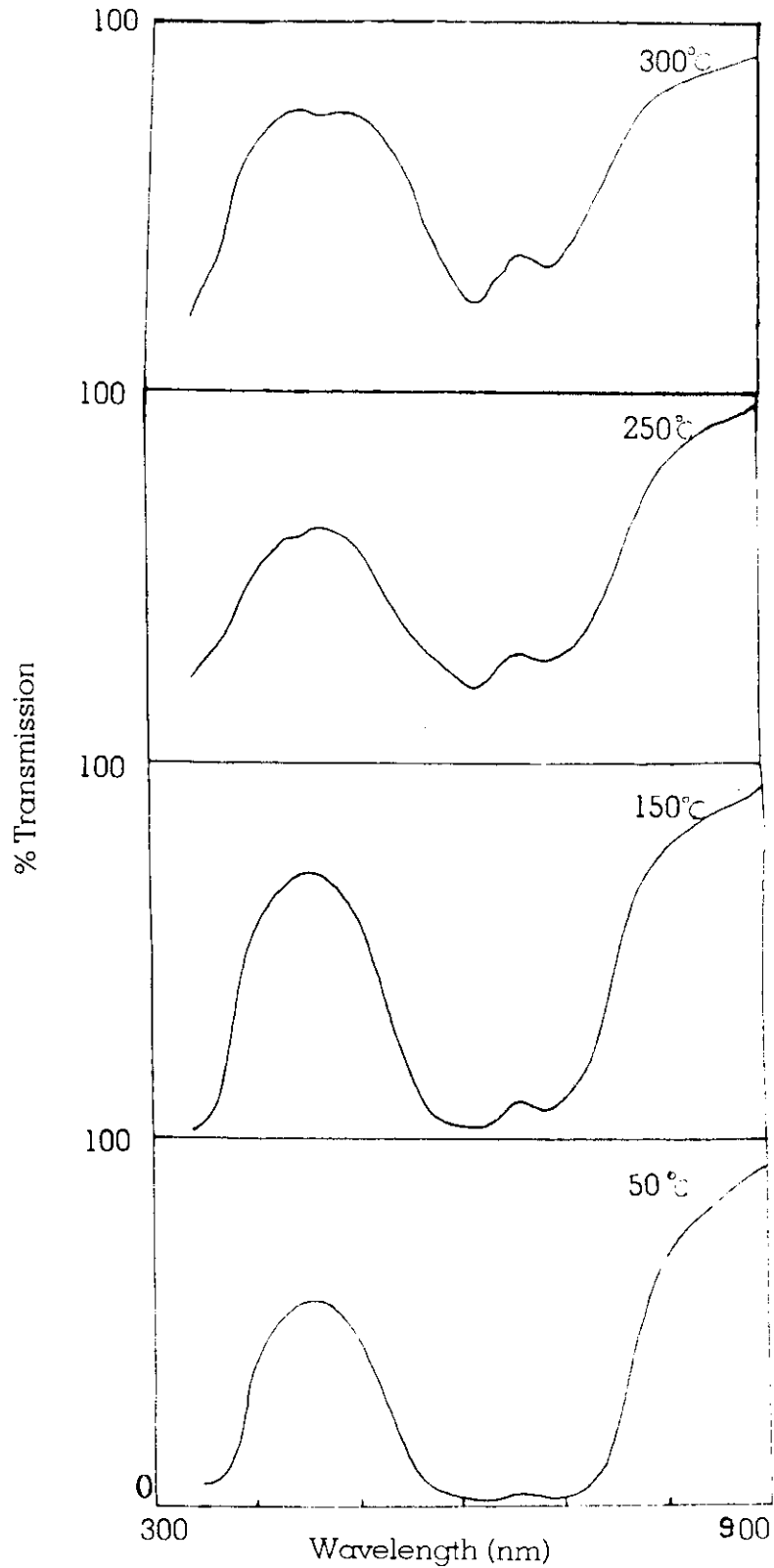


Figure 4.4.8: Percentage transmission versus wavelength spectrum of CoPc film prepared at $T_s = 50, 150, 250$ and 300°C .

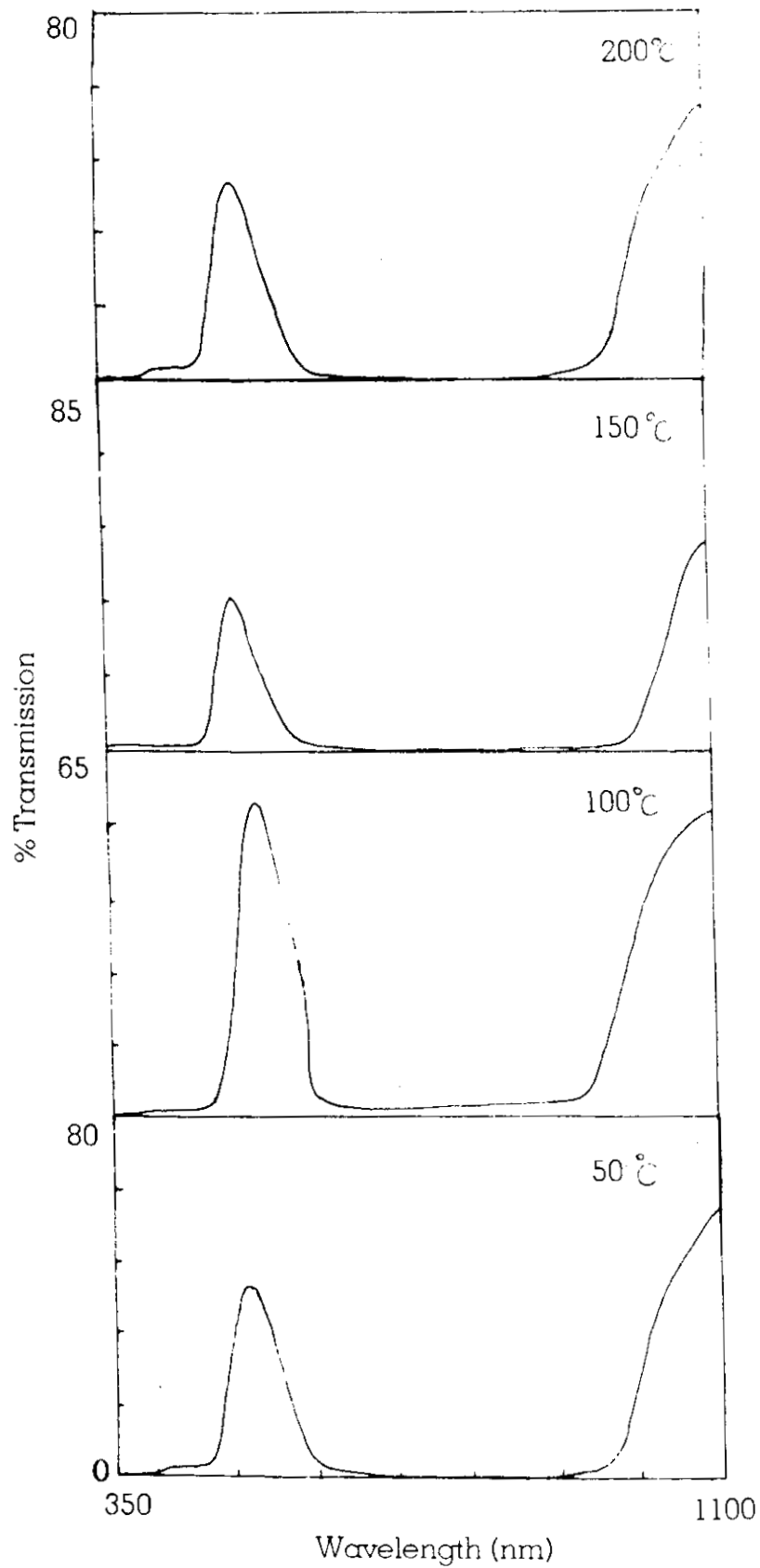


Figure 4.4.9: Percentage transmission versus wavelength spectrum of PbPc film prepared at $T_s = 50, 100, 150$ and 200°C .

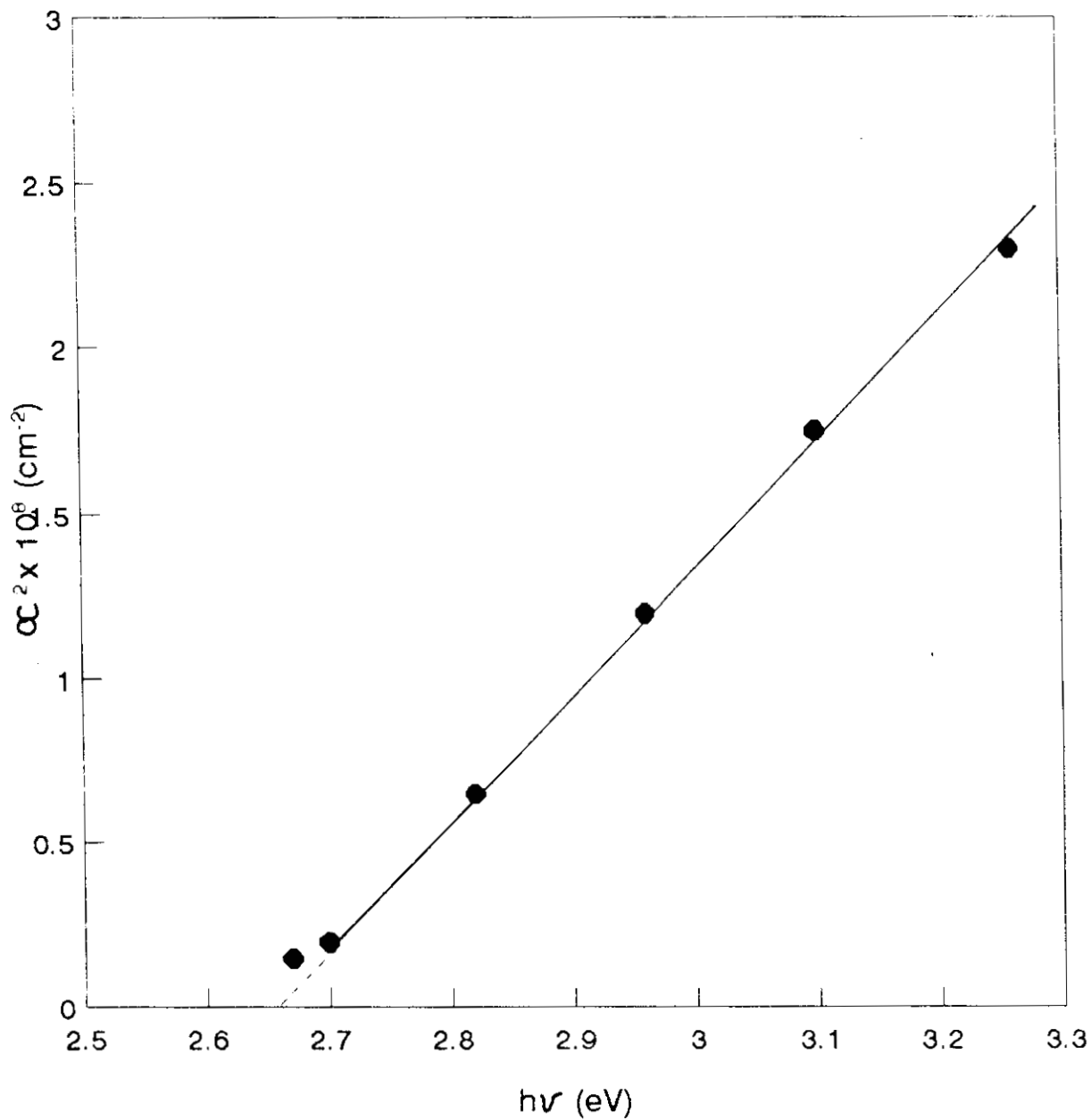


Figure 4.4.10 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å prepared at $T_s = 50$ °C

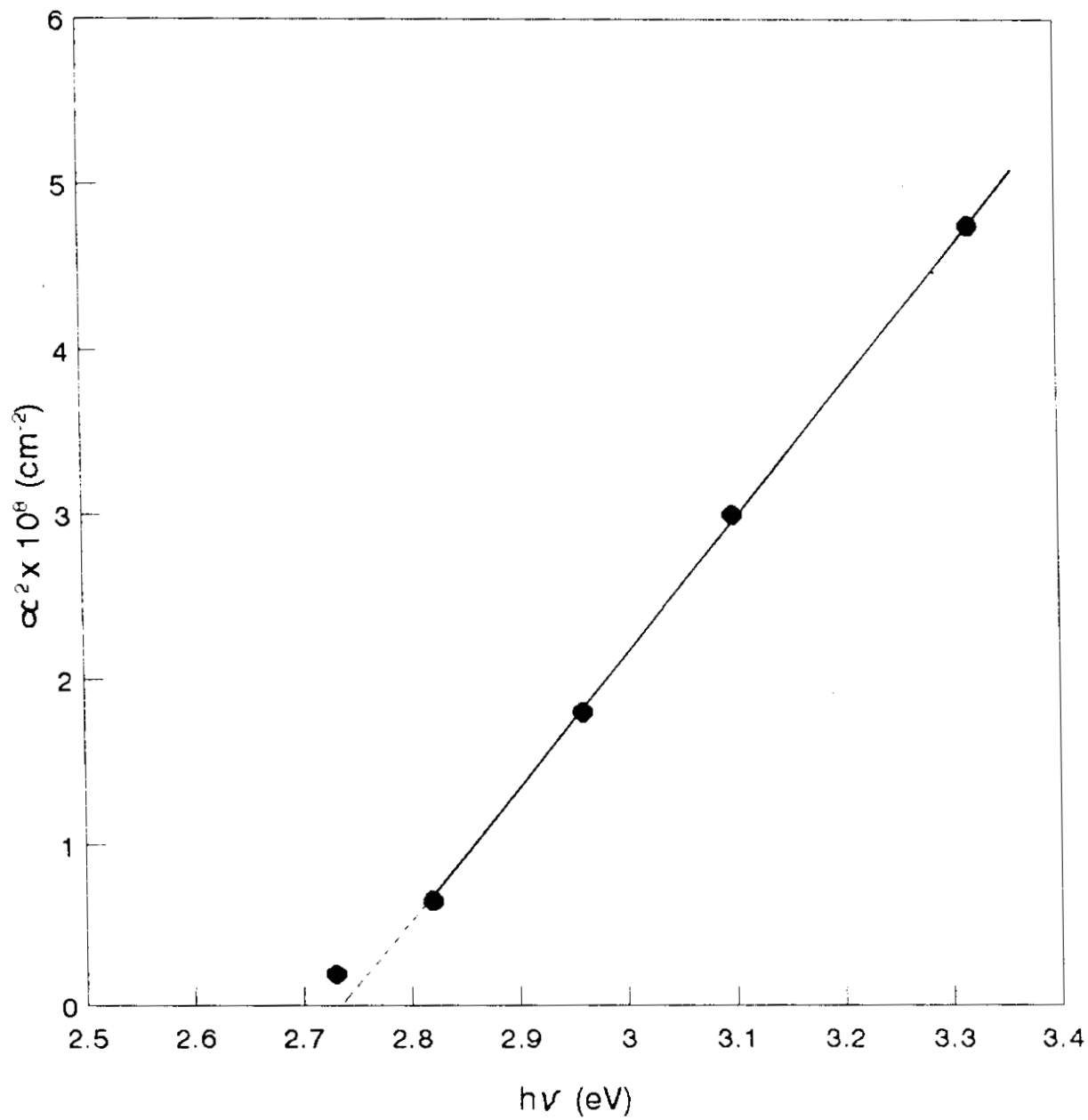


Figure 4.4.10 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å prepared at $T_s = 100^\circ\text{C}$



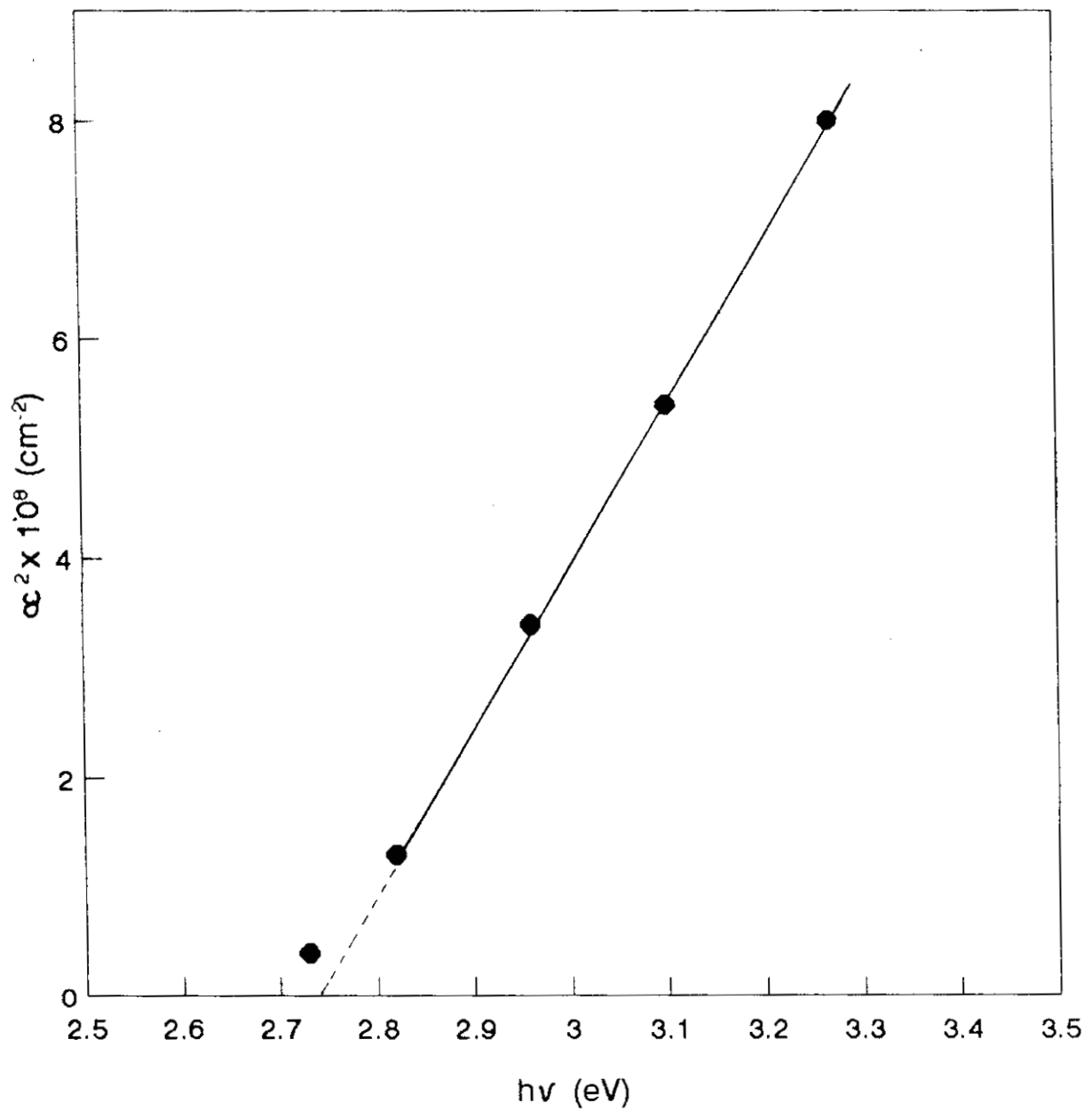


Figure 4.4.10 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å prepared at $T_s = 150^\circ\text{C}$

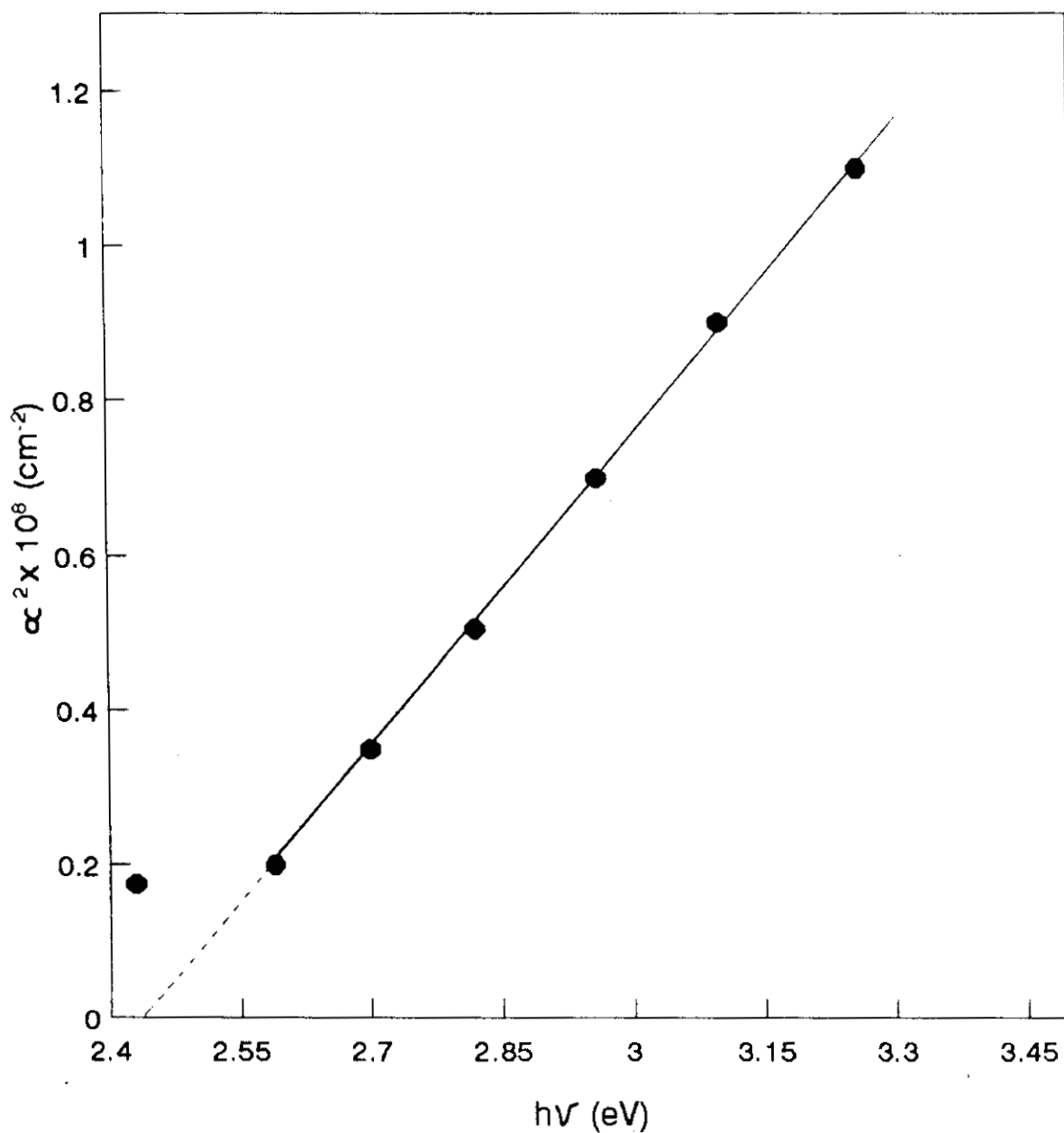


Figure 4.4.10 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å prepared at $T_s = 200^\circ\text{C}$

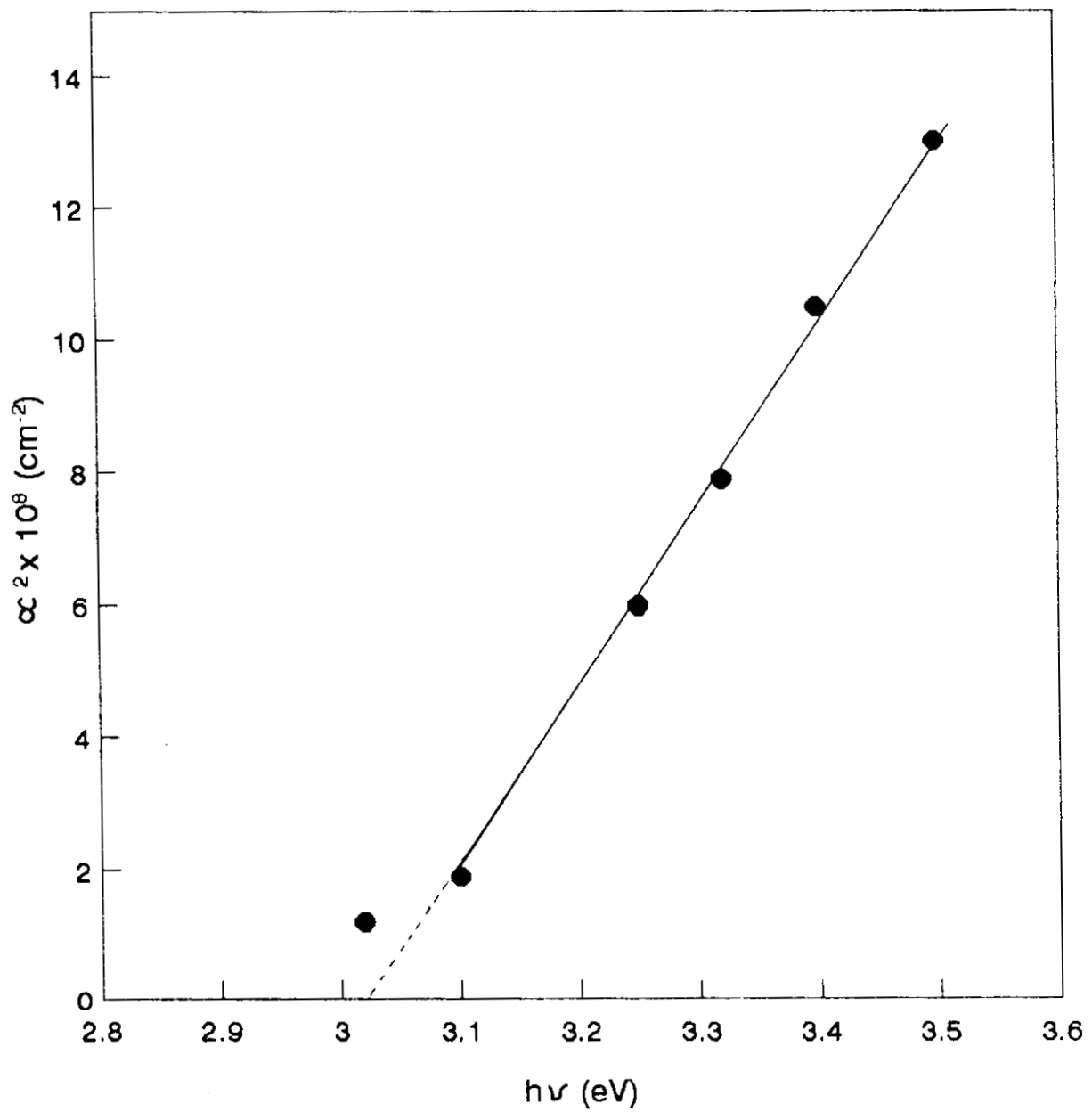


Figure 4.4.11 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å prepared at $T_s = 50^\circ\text{C}$

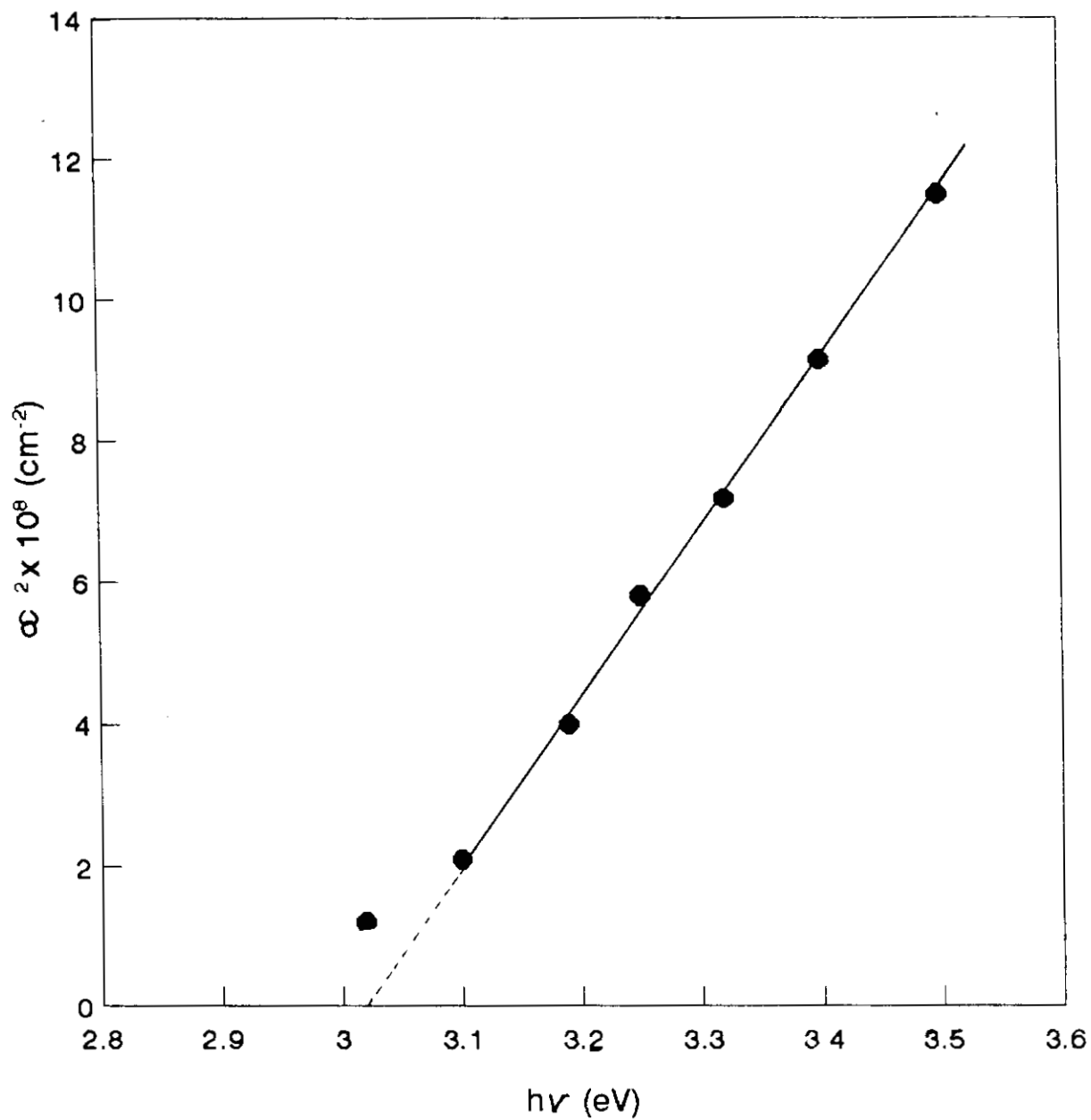


Figure 4.4.11 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å prepared at $T_s = 150^\circ\text{C}$

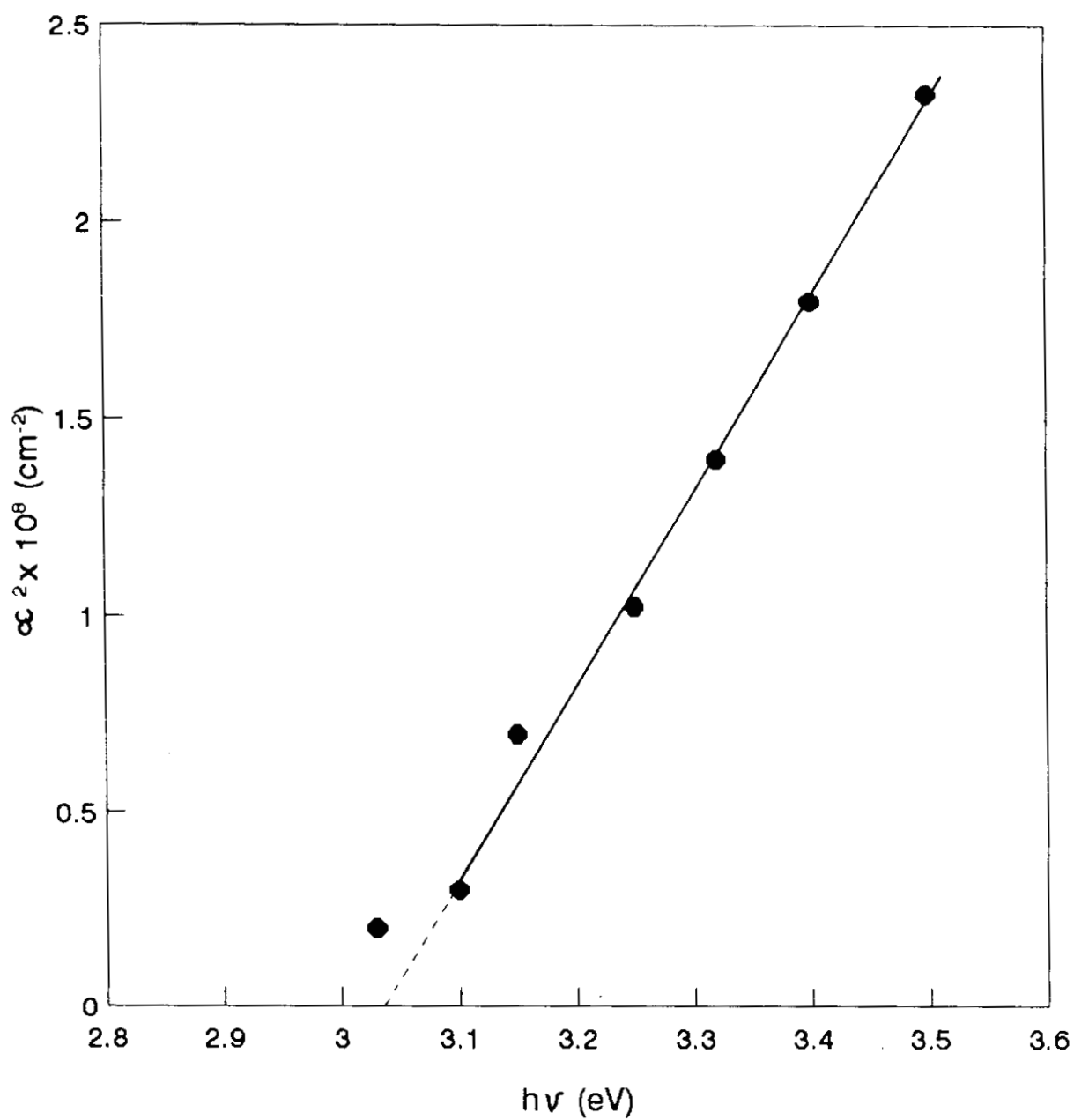


Figure 4.4.11 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å prepared at $T_s = 250^\circ\text{C}$



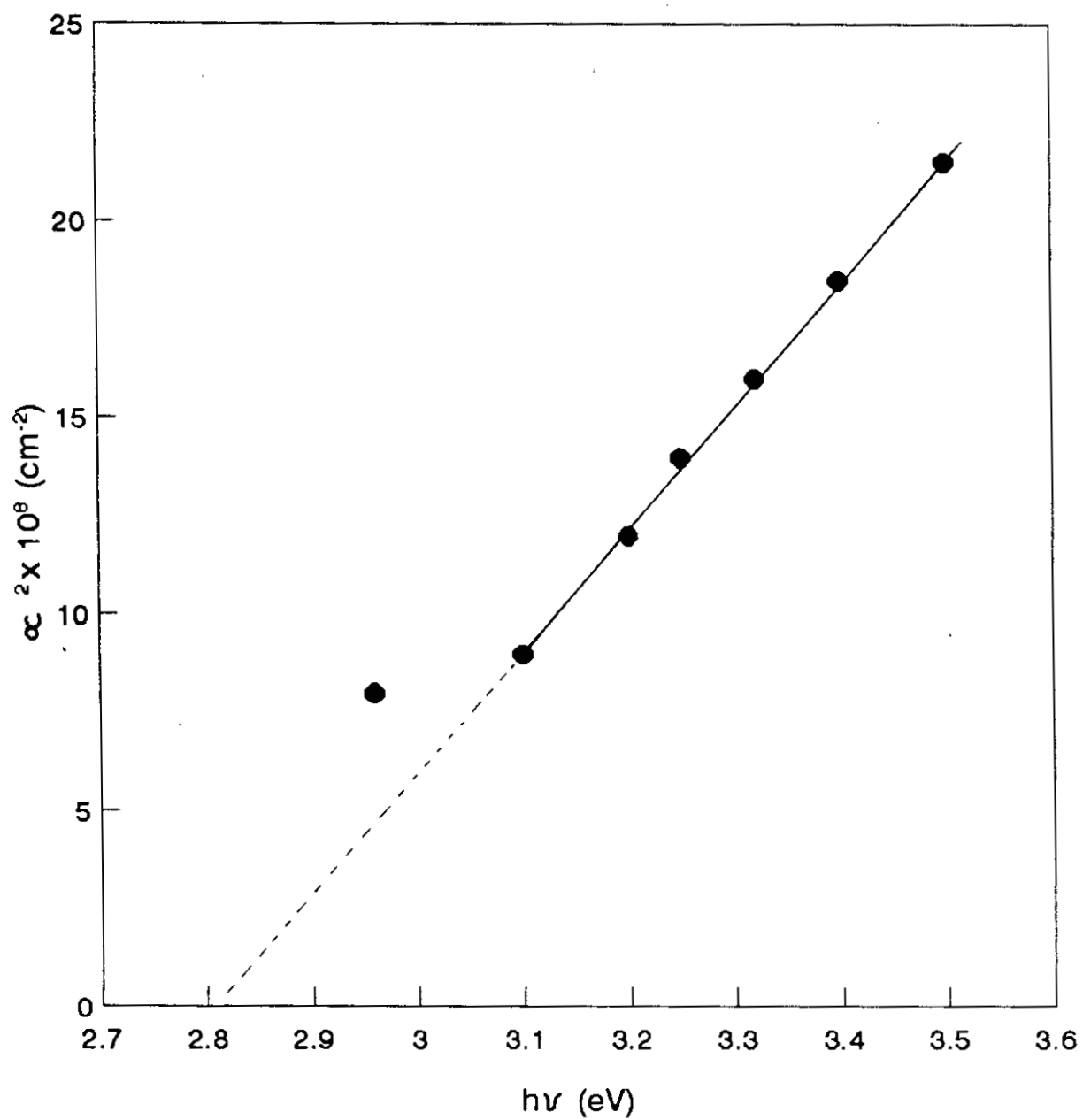


Figure 4.4.11 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å prepared at $T_s = 300^\circ\text{C}$



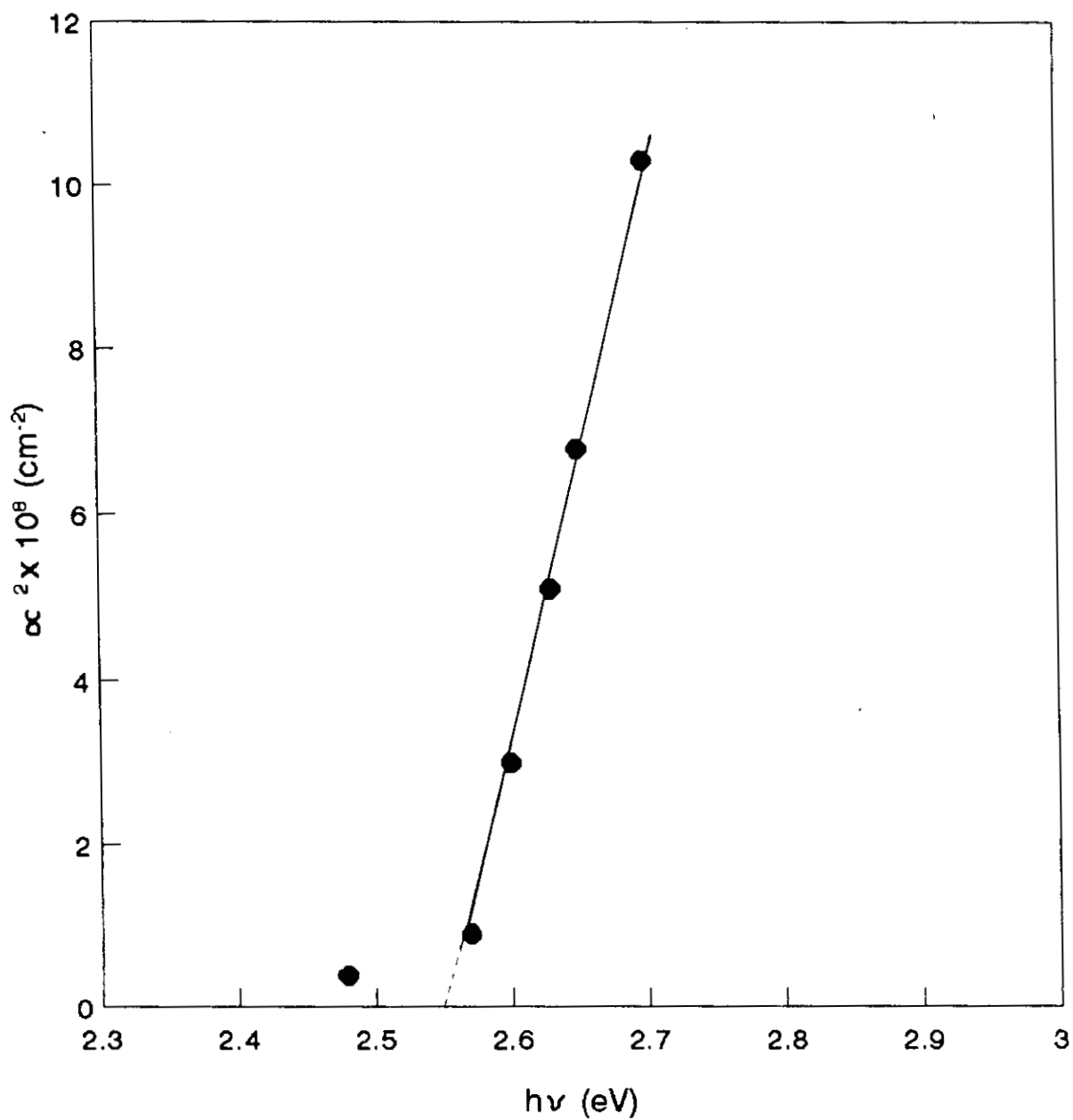


Figure 4.4.12 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å prepared at $T_s = 50^\circ\text{C}$



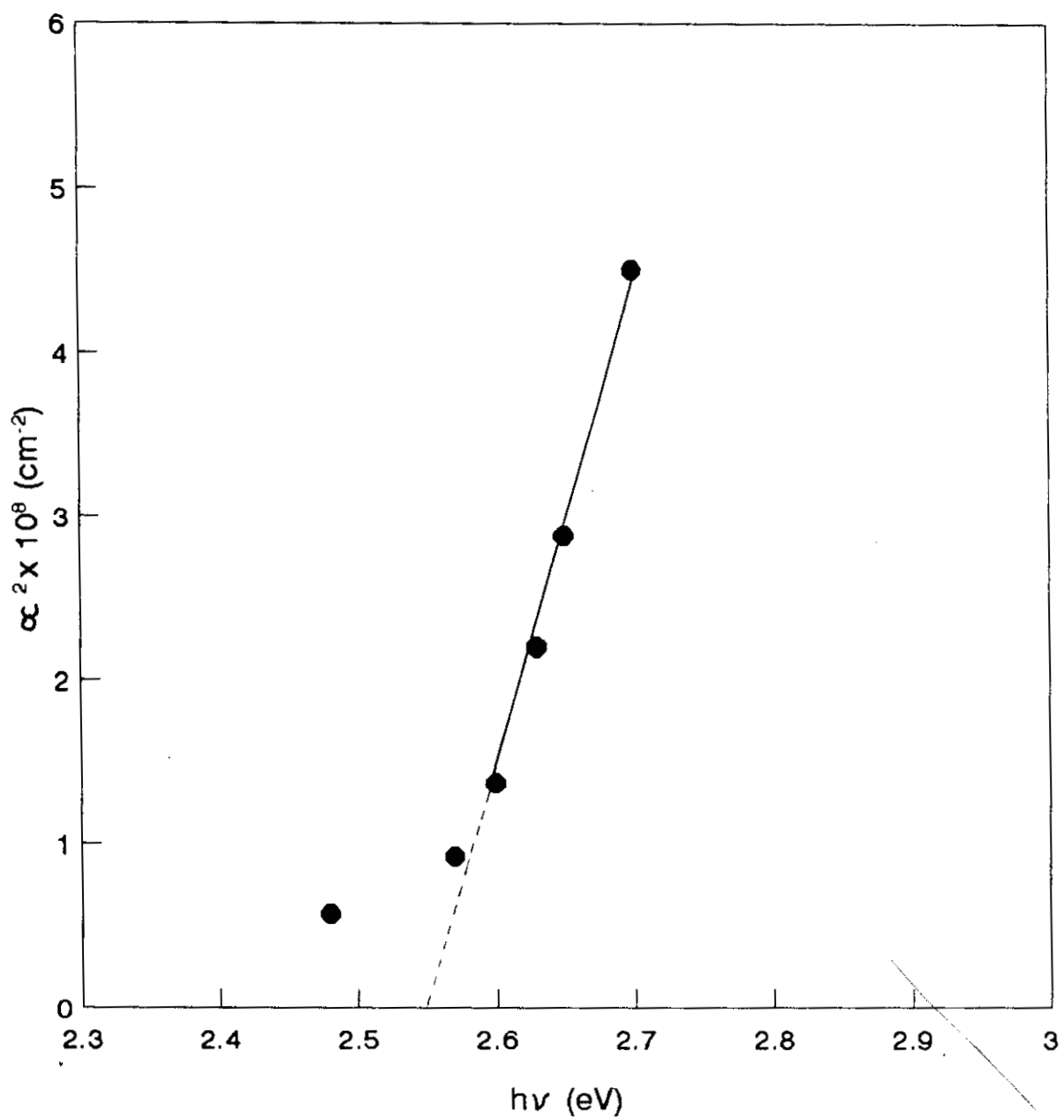


Figure 4.4.12 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å prepared at $T_s = 100^\circ\text{C}$

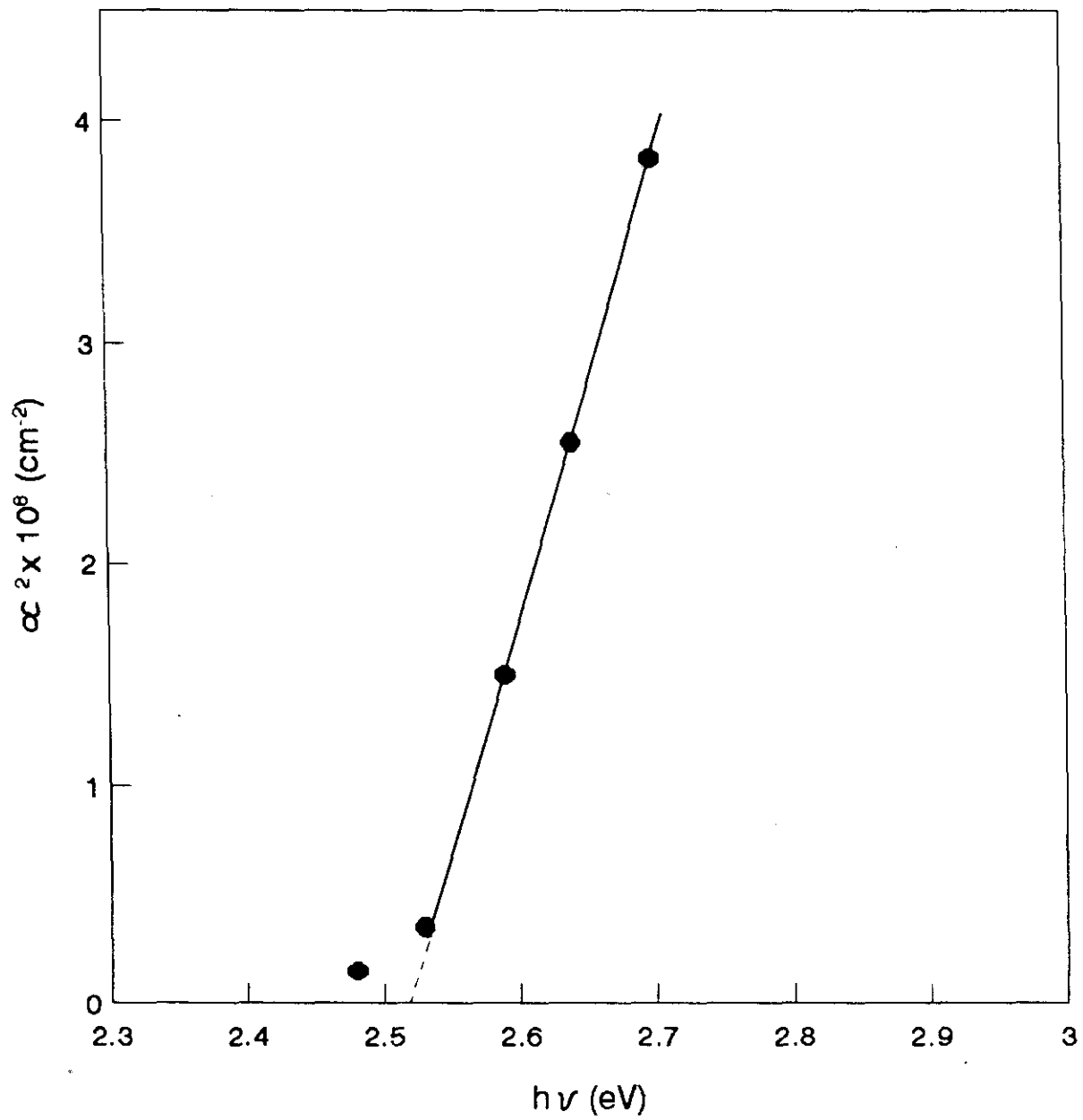


Figure 4.4.12 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å prepared at $T_s = 150^\circ\text{C}$

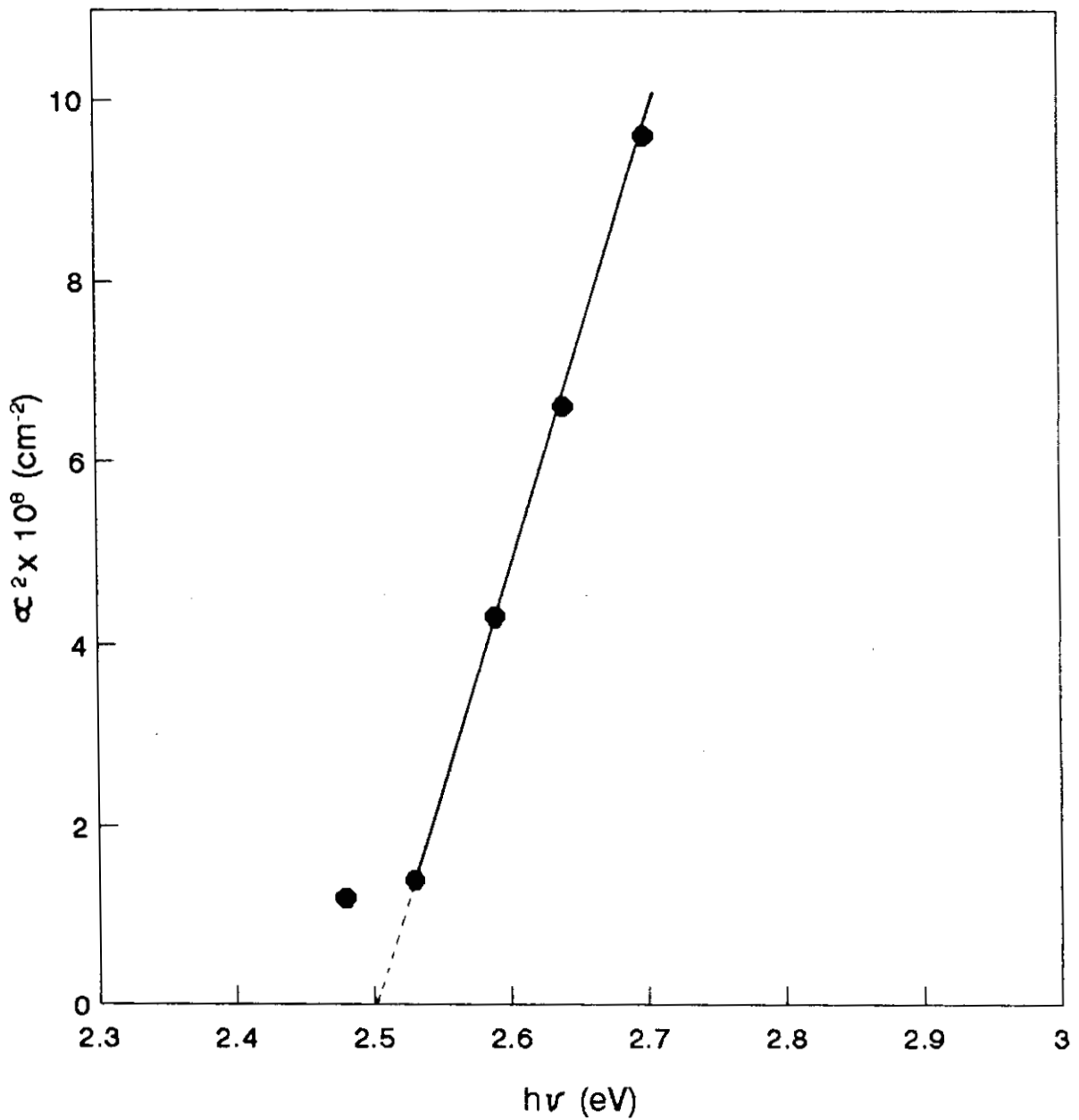


Figure 4.4.12 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å prepared at $T_s = 200^\circ\text{C}$



the plots of α^2 versus $h\nu$ at absorption edge region for CuPc, CoPc and PbPc thin films respectively. The extrapolation of $\alpha^2 = 0$ gives the band gap. The same procedure has been used to get the trap level energy at the lower energy regions of the spectrum. The M-shaped shoulder region in Figure 4.4.8 is attributed to the Q-band in the 600–750 nm range. This is explained as the charge transfer from the highest occupied molecular orbit (HOMO) to the lowest unoccupied molecular orbit (LUMO) in the Q-band.¹³ The UV-visible spectrum of phthalocyanines originates from molecular orbitals within the aromatic 18π electron system and from overlapping orbitals within the central metal atom.¹⁴

The optical band gap and the trapping energy level for CuPc, CoPc and PbPc films at different substrate temperatures are collected in Table 4.4.1. The band gap remains constant upto a substrate temperature of 150°C for CuPc films and it decreases at 200°C. Optical band gap changes from 3.0 eV to 2.81 eV for CoPc films as the substrate temperature changes from 30°C to 300°C. For CuPc and CoPc there is a marked decrease in the band gaps at 200°C and 300°C respectively. Nevertheless the value for the energy band gap remains constant throughout the temperature range for PbPc film. The Q band transitions



in CuPc, CoPc and PbPc give rise to the trap level. There is little variation in the trap energy levels for CuPc, CoPc and PbPc as the substrate

Table 4.4.1: Band Gap and Trap Energy Level for CuPc, CoPc and PbPc Films at Different Substrate Temperatures.

Material	Substrate temperature (°C)	Trap energy Level (eV)	Band gap (eV)
CuPc	30	1.55	2.71
	50	1.57	2.67
	100	1.52	2.73
	150	1.57	2.73
	200	1.55	2.43
CoPc	30	1.61	3.00
	50	1.60	3.03
	100	1.61	3.02
	250	1.62	3.03
	300	1.59	2.81
PbPc	30	1.21	2.46
	50	1.23	2.56
	100	1.22	2.55
	150	1.25	2.52
	200	1.24	2.50

temperature is varied. The variation in band gap energy for CuPc and CoPc films at substrate temperatures of 200°C and 300°C respectively is marked which can be attributed to a phase change for CuPc between 150°C and 200°C and for CoPc, between 250 and 300°C Hoshi et. al.¹⁵ have reported that if higher temperature substrates are used, the phthalocyanine admolecule mobility is high and islands of normal bulk crystal structure are formed. The additional peaks in the transmission spectrum 4.4.8 for CoPc films in Q band are explained as follows. The



molecules will be under tensile stress due to the constraint imposed by the substrate and this affects the electronic structure resulting in additional peaks.

Figures 4.4.13, 4.4.14, 4.4.15 are the percentage transmission versus wavelength for CuPc, CoPc and PbPc thin films for different annealing temperatures. Figures 4.4.16, 4.4.17, 4.4.18 give the plots of α^2 versus $h\nu$ near the absorption edge for CuPc, CoPc and PbPc films respectively. The optical band gap and trap level for CuPc, CoPc and PbPc films for different annealing temperatures are obtained using the same procedure described earlier and given in Table 4.4.2. As

Table 4.4.2: Band Gap and Trap Energy Level for CuPc, CoPc and PbPc at Different Annealing Temperatures

Material	Annealing temperature (°C)	Trap energy level (eV)	Band gap (eV)
CuPc	30	1.55	2.71
	50	1.55	2.69
	100	1.55	2.70
	150	1.55	2.69
	200	1.55	2.45
CoPc	30	1.61	3.00
	50	1.61	3.08
	150	1.60	3.02
	250	1.63	3.02
	300	1.61	2.87
PbPc	30	1.21	2.46
	50	1.23	2.50
	100	1.25	2.45
	150	1.24	2.50
	200	1.22	2.48

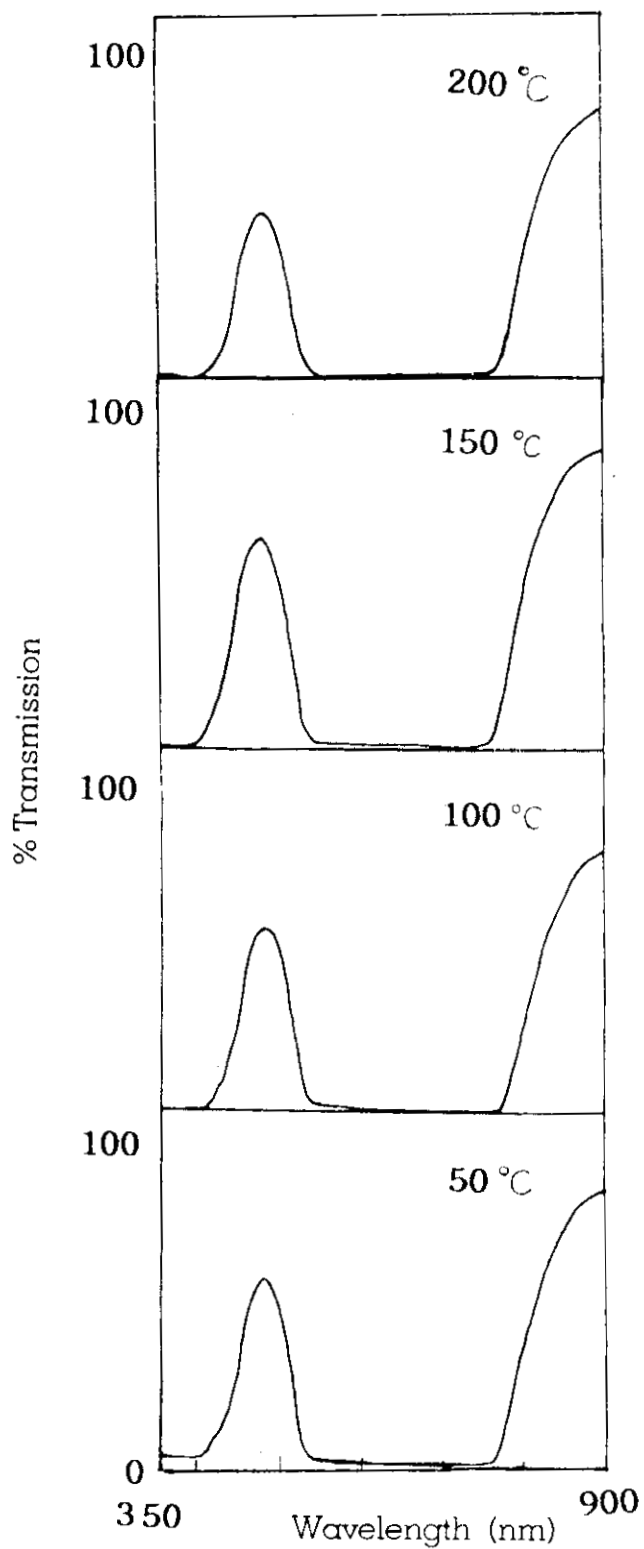


Figure 4.4.13: Percentage transmission versus wavelength spectrum of CuPc film annealed at $T_a = 50, 100, 150$ and 200°C .

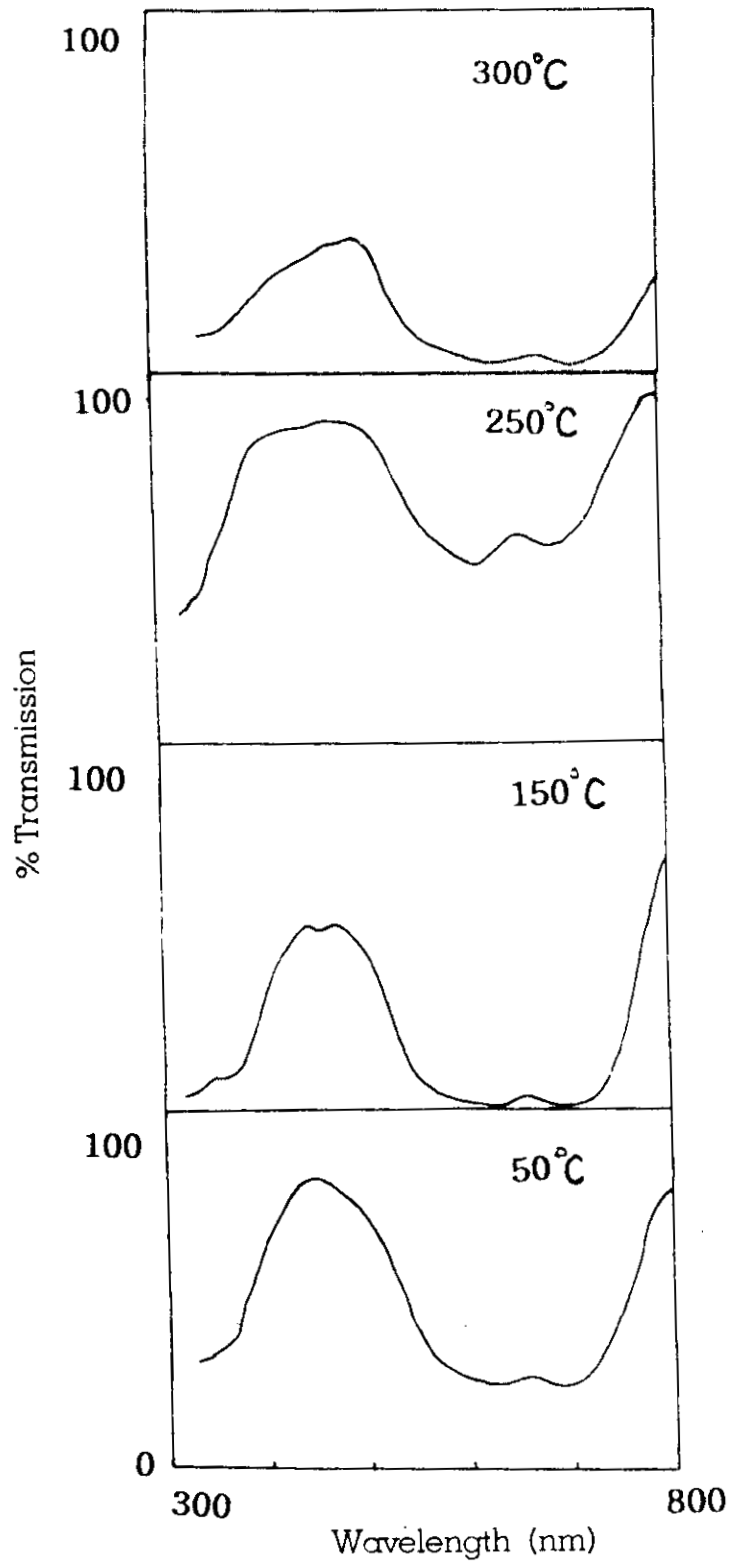


Figure 4.4.14: Percentage transmission versus wavelength spectrum of CoPc film annealed at $T_a = 50, 150, 250$ and 300°C .

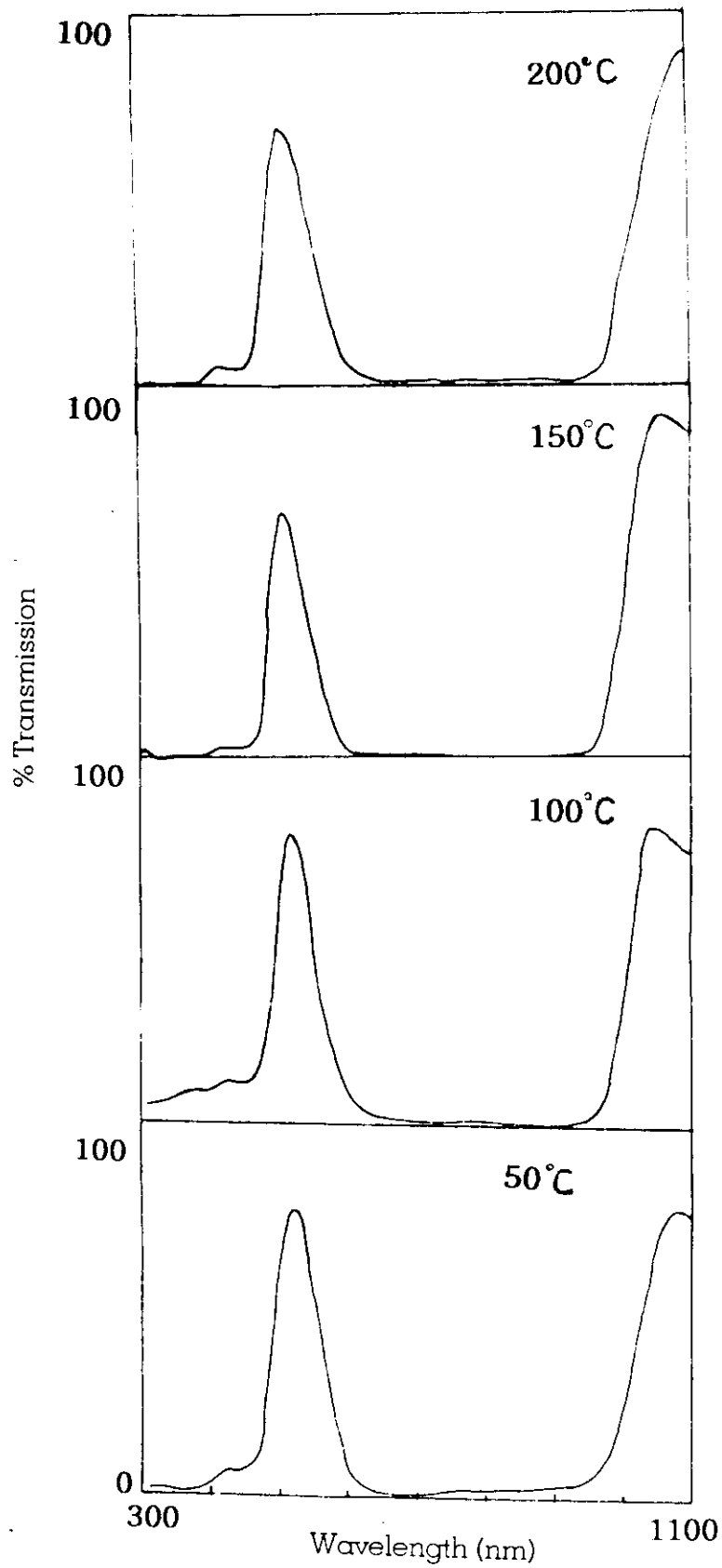


Figure 4.4.15: Percentage transmission versus wavelength spectrum of PbPc film annealed at $T_a = 50, 100, 150$ and 200°C .

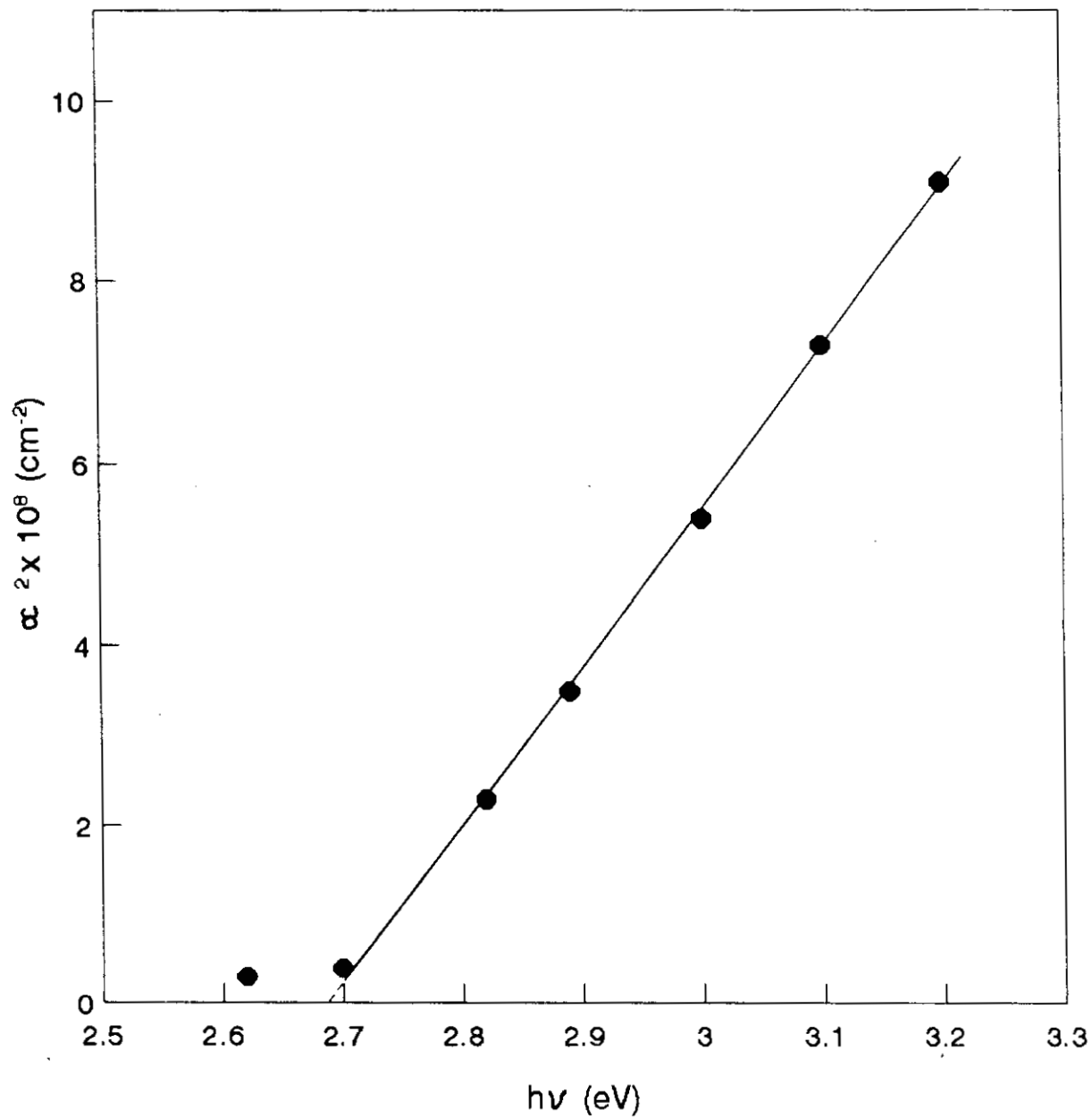


Figure 4.4.16 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å annealed at $T_a = 50^\circ\text{C}$

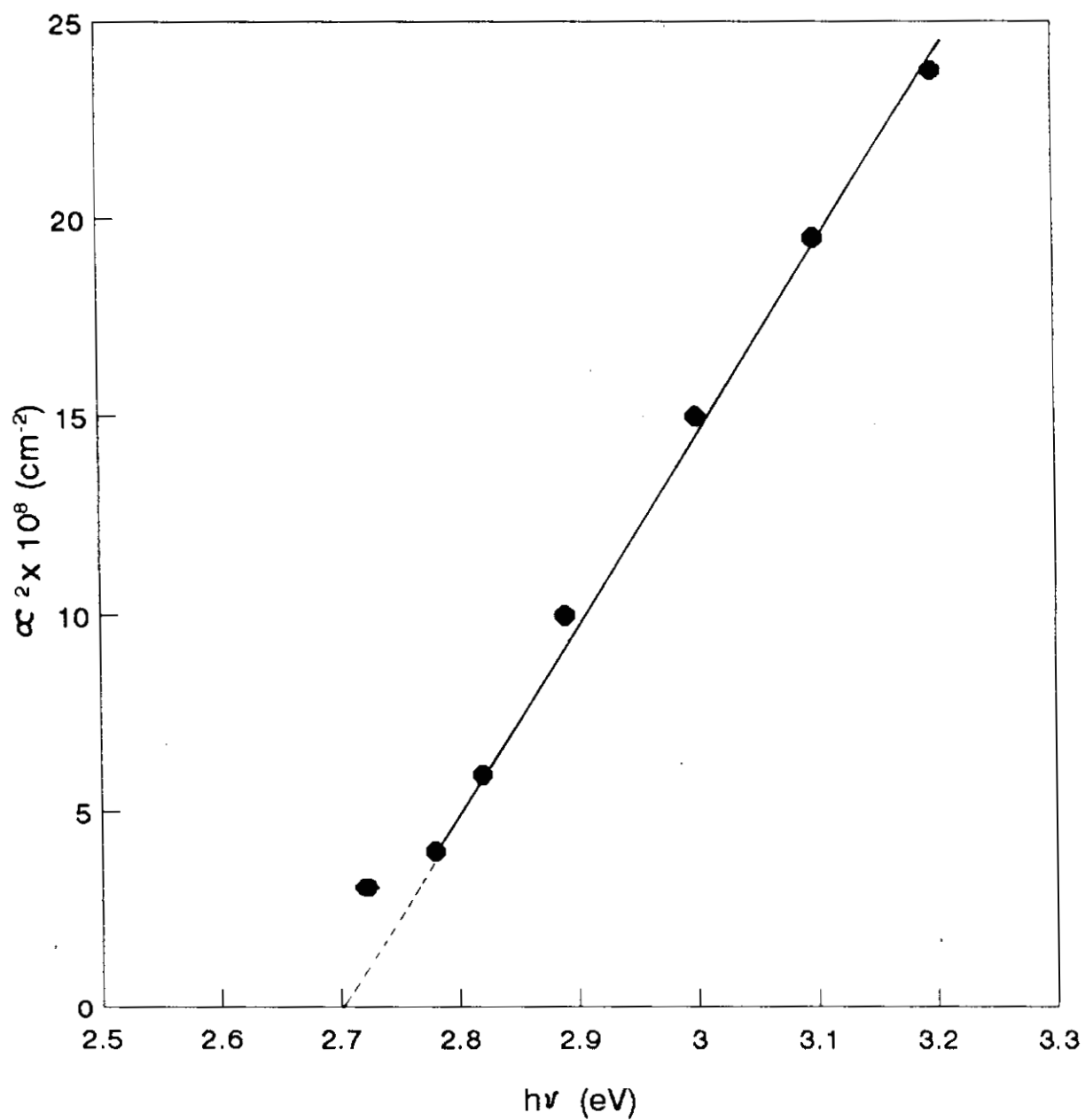


Figure 4.4.16 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å annealed at $T_a = 100^\circ\text{C}$



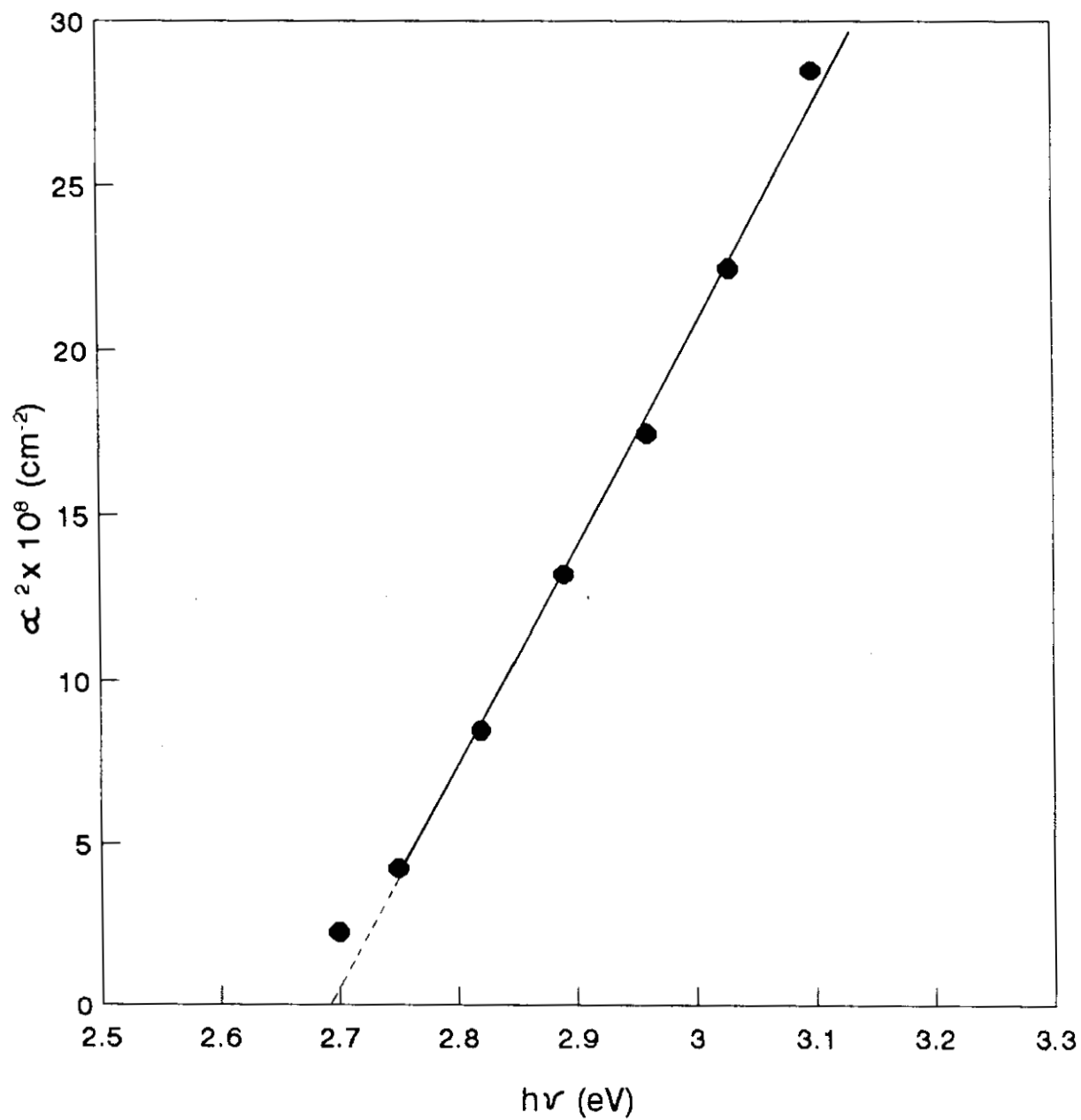


Figure 4.4.16 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å annealed at $T_a = 150^\circ\text{C}$



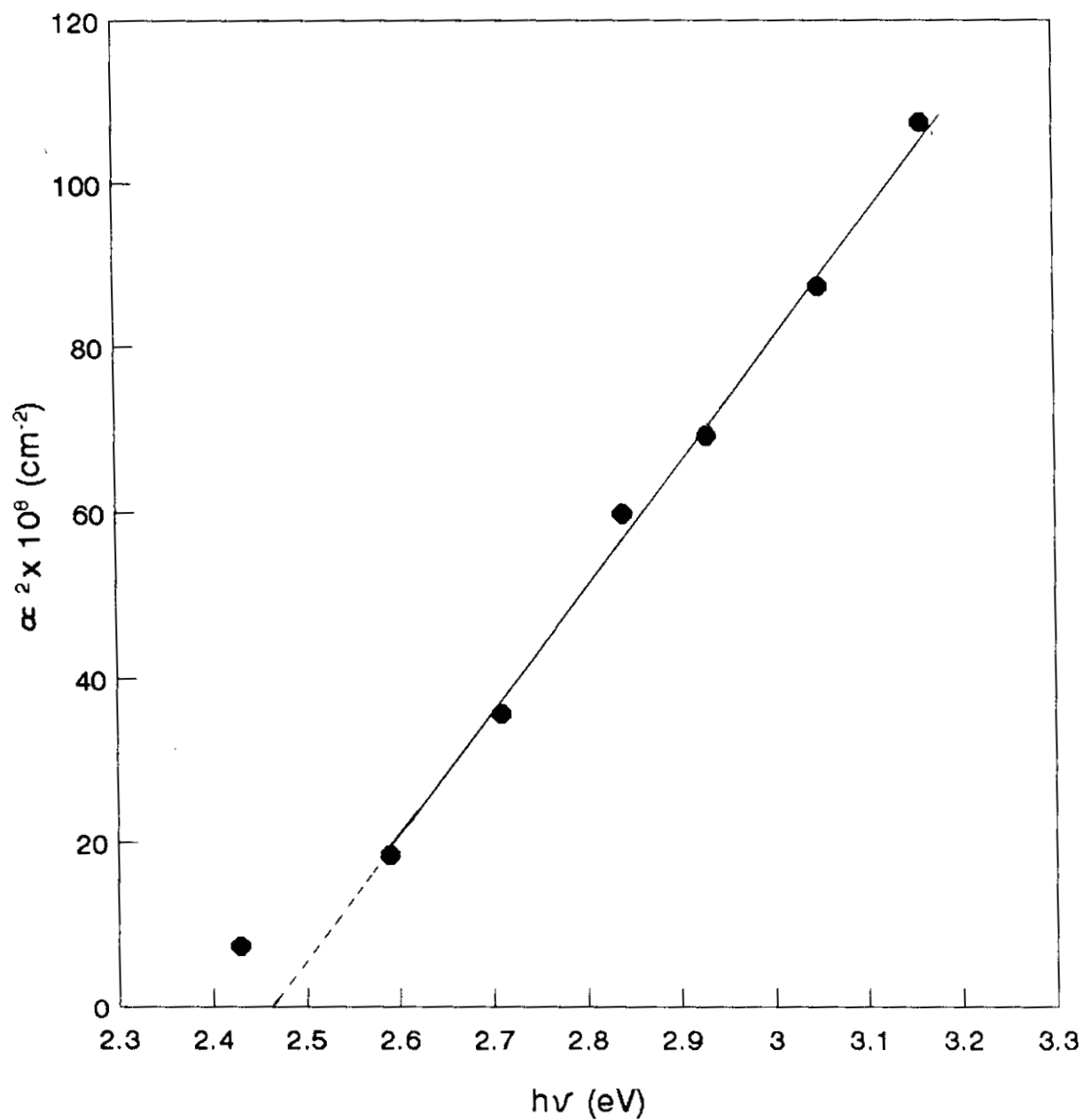


Figure 4.4.16 Plot of α^2 vs $h\nu$ for CuPc film of thickness 1800 Å annealed at $T_a = 200^\circ\text{C}$

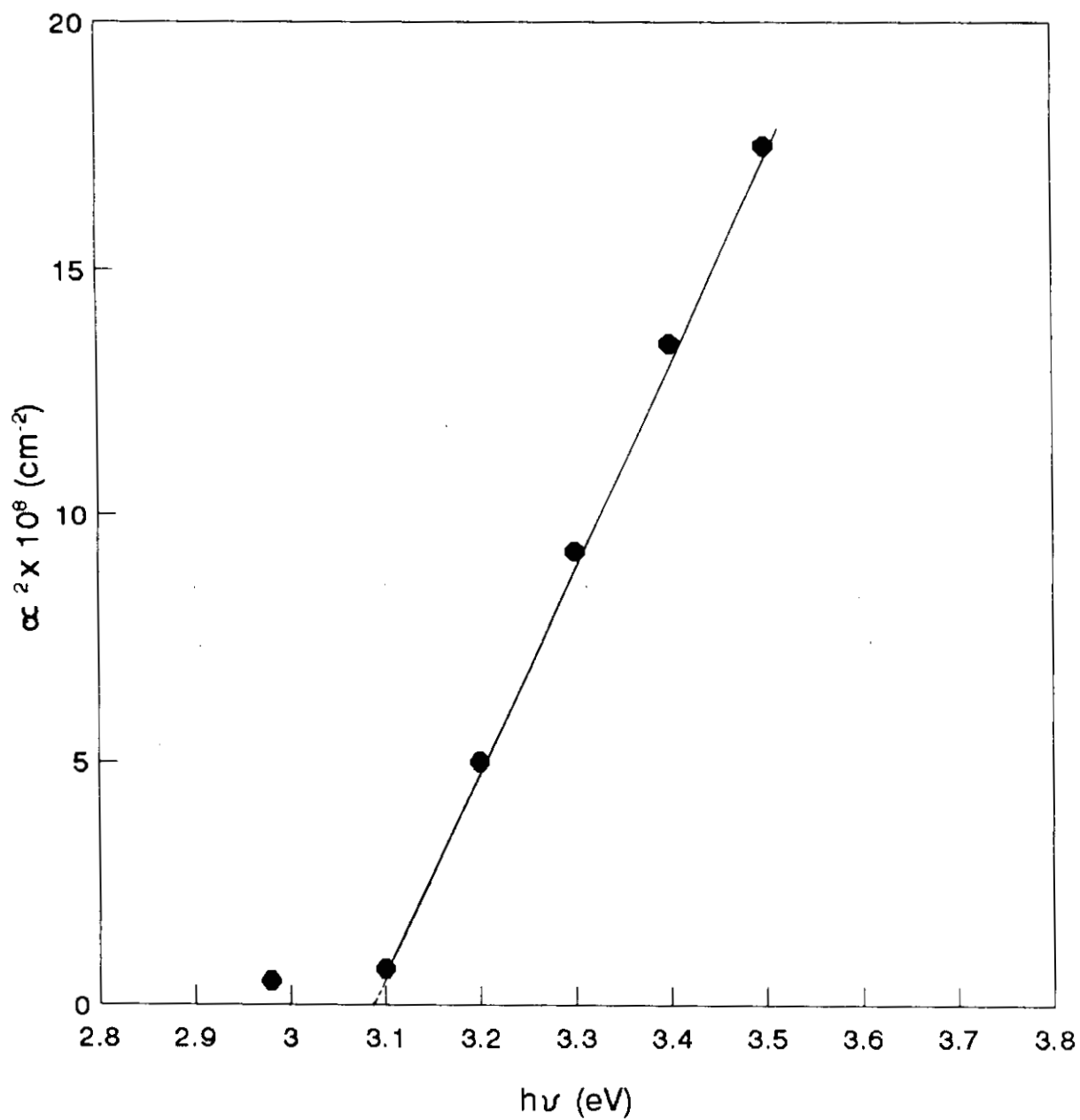


Figure 4.4.17 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å annealed at $T_a = 50^\circ\text{C}$

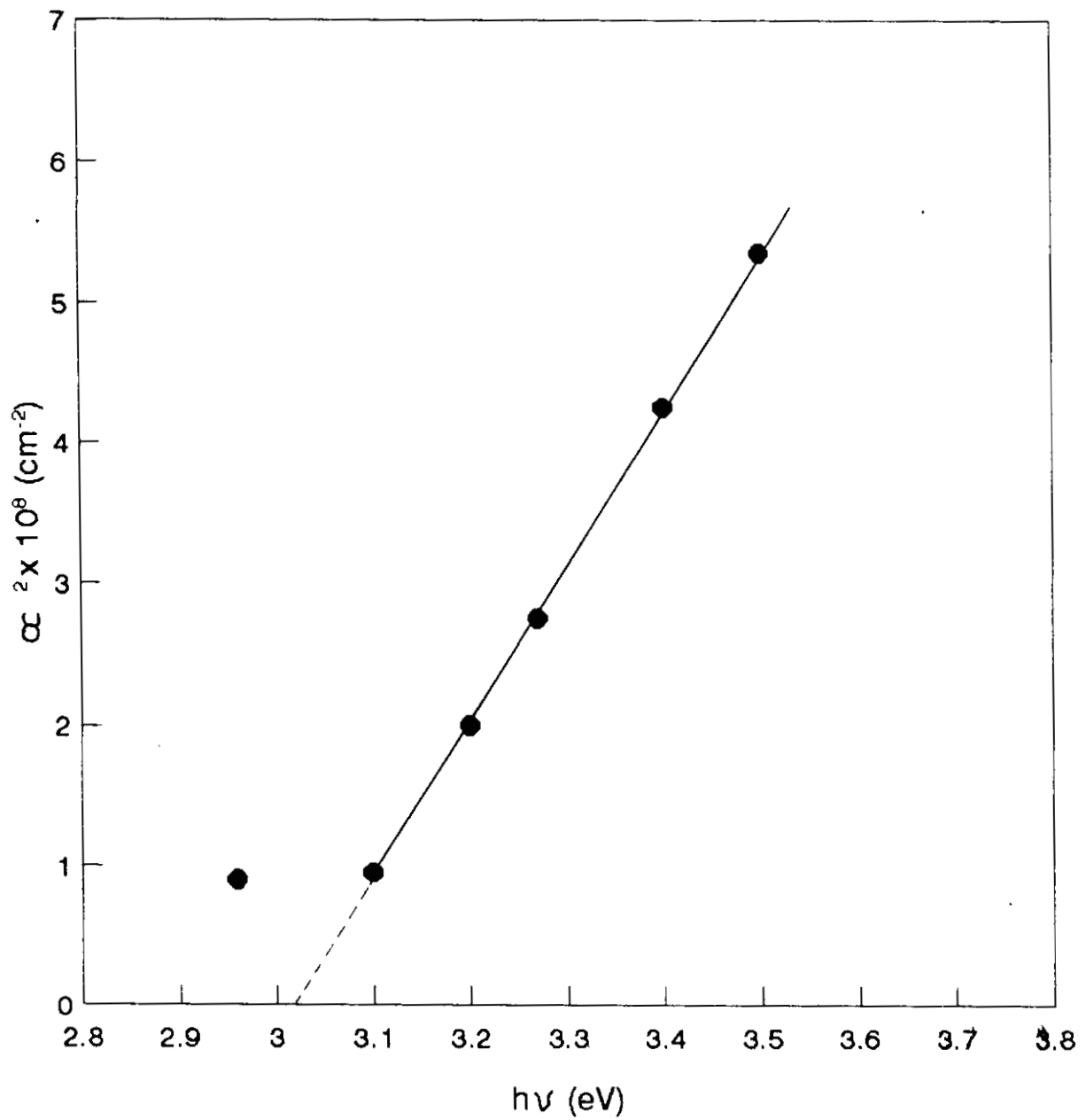


Figure 4.4.17 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å annealed at $T_a = 150^\circ\text{C}$



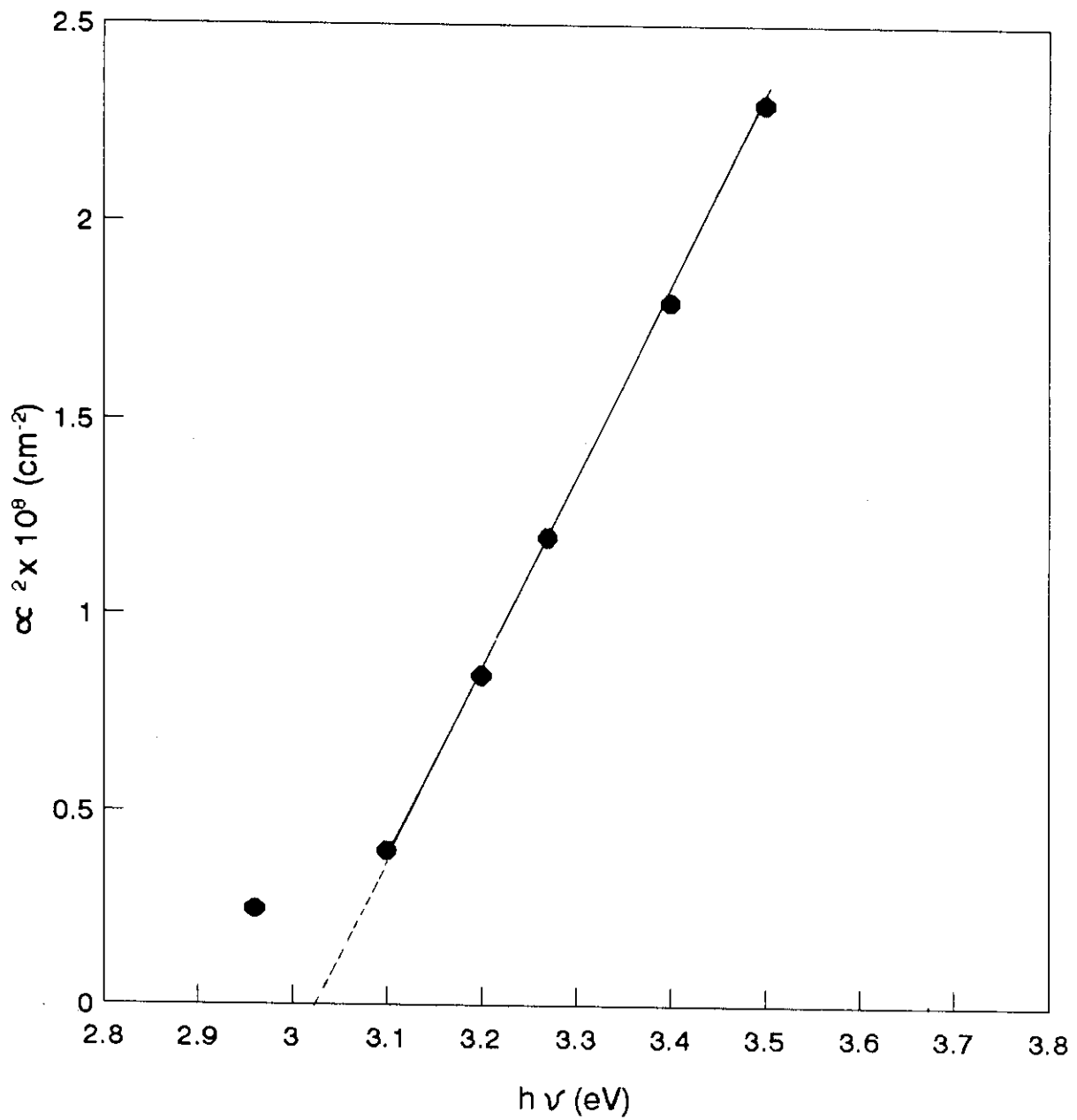


Figure 4.4.17 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å annealed at $T_a = 250^\circ\text{C}$

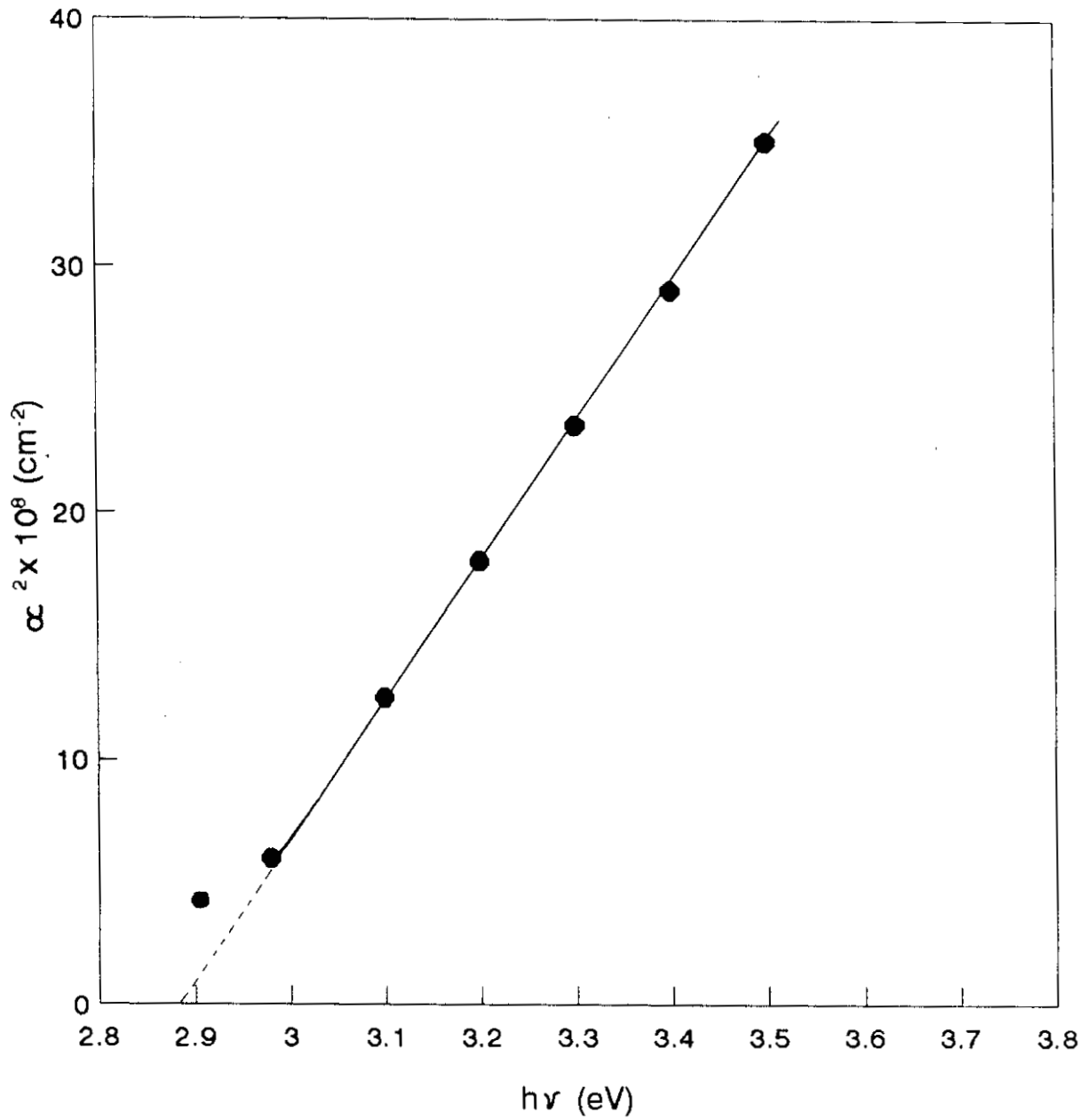


Figure 4.4.17 Plot of α^2 vs $h\nu$ for CoPc film of thickness 3460 Å annealed at $T_a = 300^\circ\text{C}$



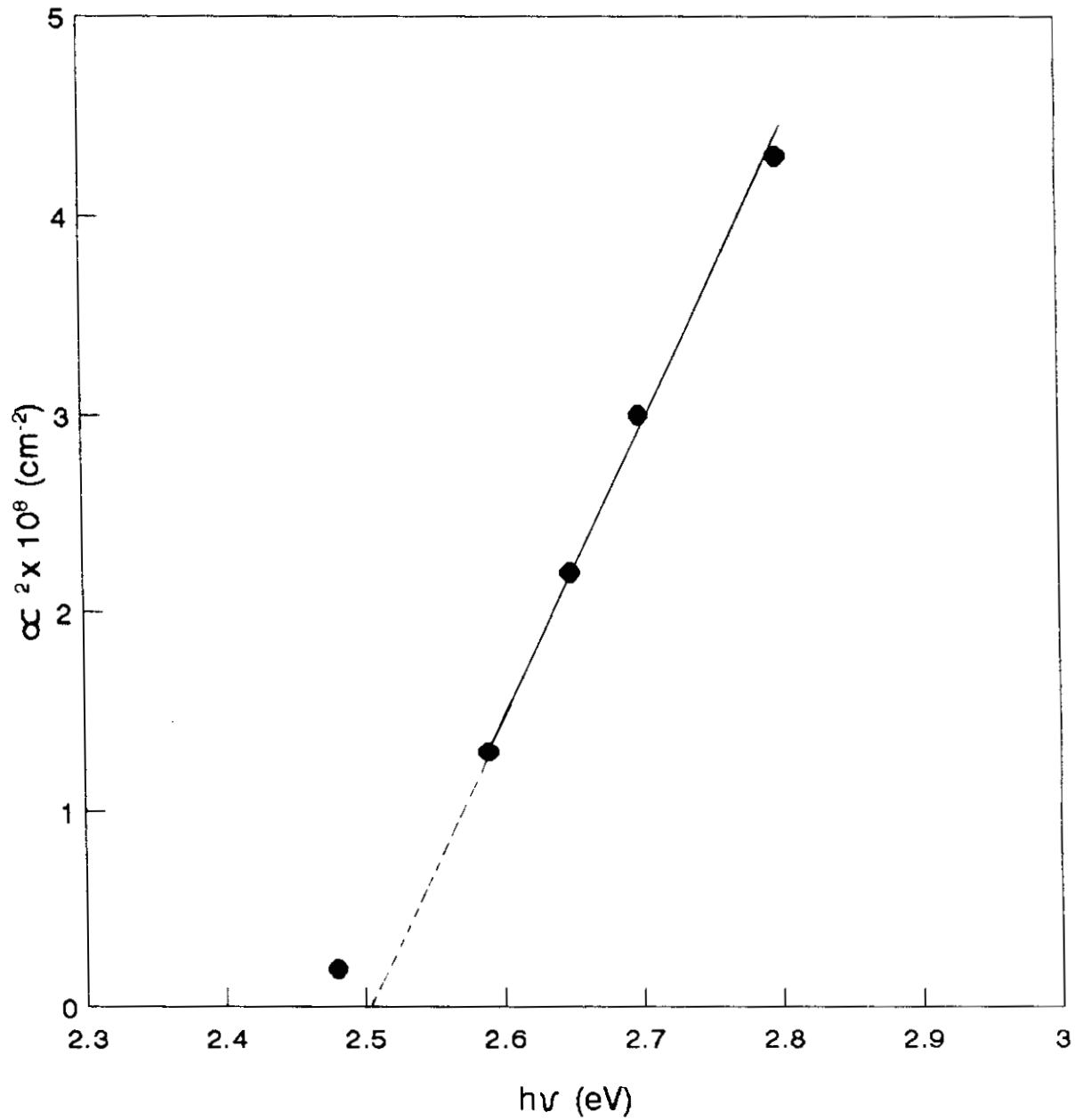


Figure 4.4.18 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å annealed at $T_a = 50^\circ\text{C}$

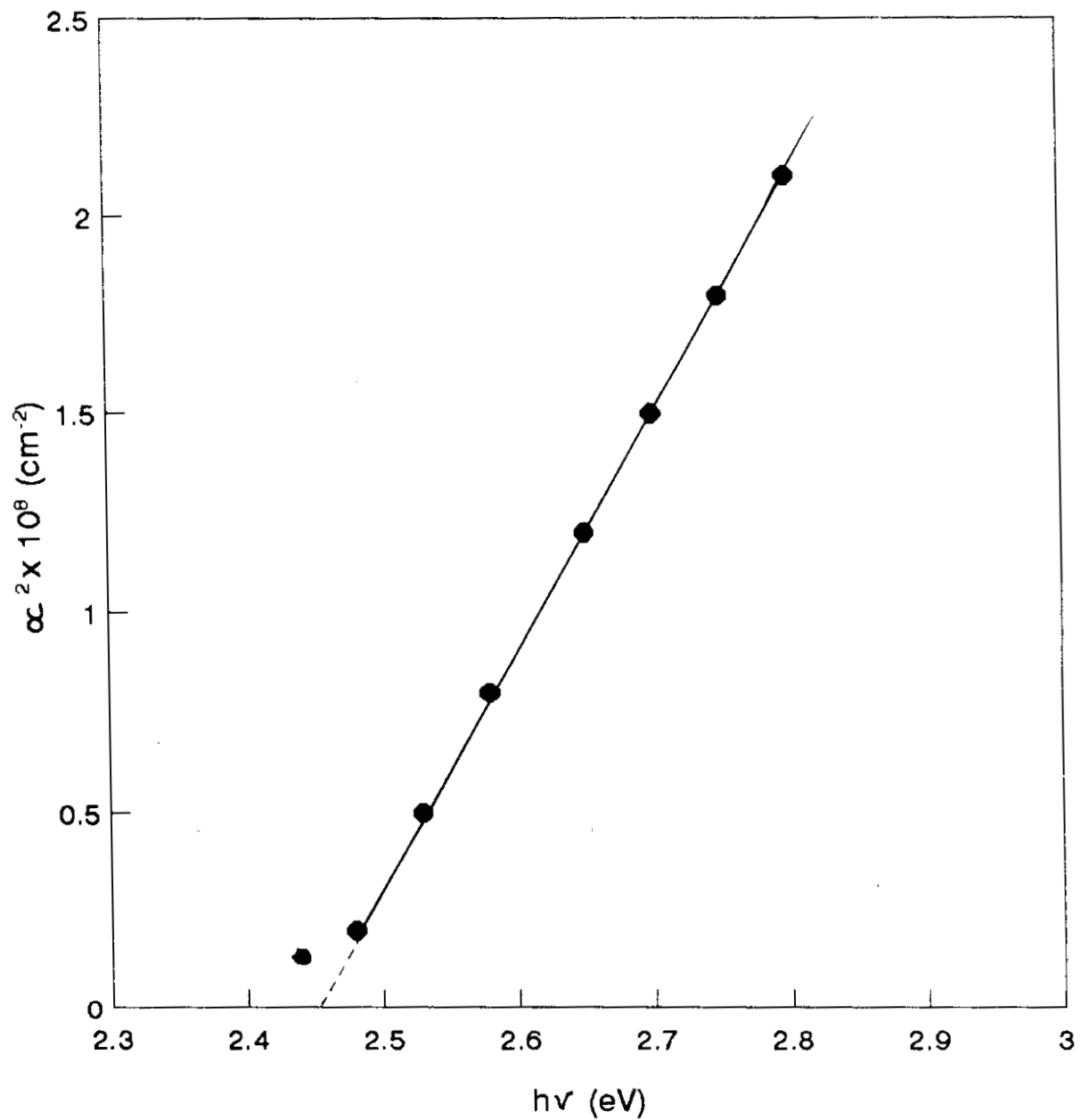


Figure 4.4.18 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å annealed at $T_a = 100^\circ\text{C}$

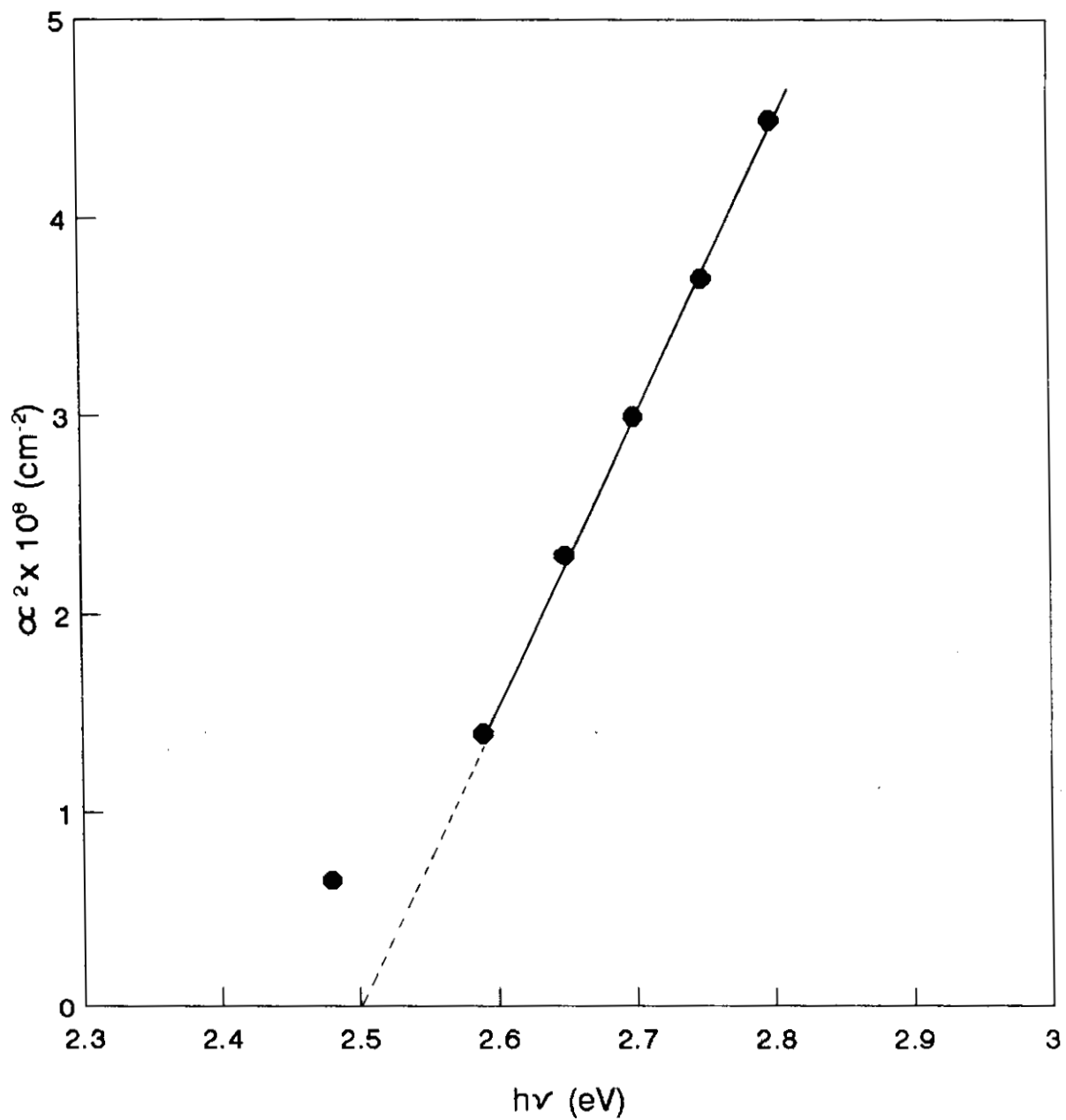


Figure 4.4.18 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å annealed at $T_a = 150^\circ\text{C}$



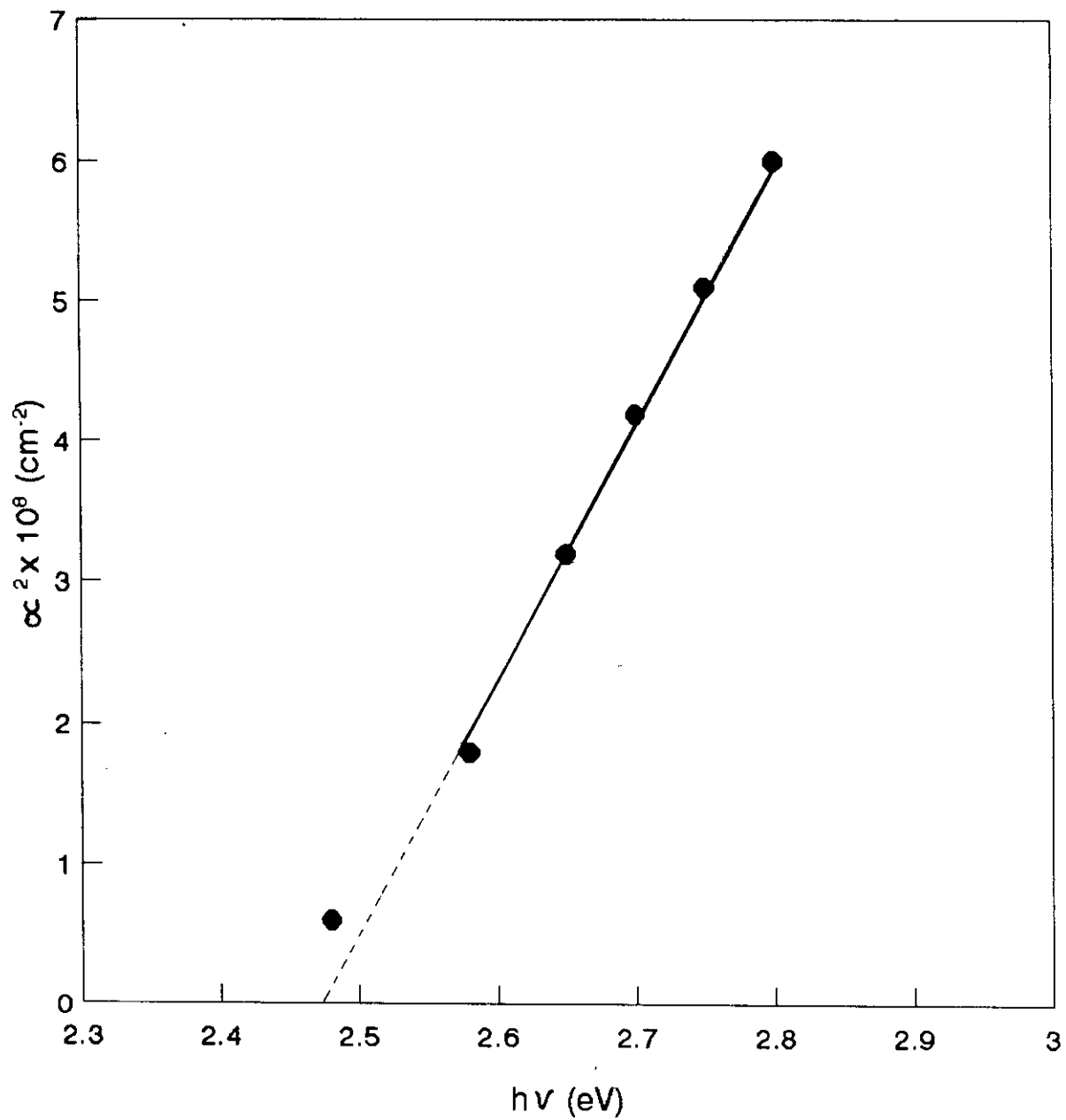


Figure 4.4.18 Plot of α^2 vs $h\nu$ for PbPc film of thickness 2250 Å annealed at $T_a = 200^\circ\text{C}$

the annealing temperature is increased the optical band gap for CuPc decreases from 2.71 to 2.45 at 200°C, but the trap level at 1.55 is found to be unaffected. The absorption edge analysis of CoPc films annealed upto 250°C shows little change in the band gap. At 300°C, the band gap decreases to 2.87 eV. The trap level at 1.61 eV remains constant in this case also. For PbPc films it is seen that there is no marked variation in the band gap energy and trap energy as the annealing temperature is changed. For CuPc and CoPc the pseudomorphic layers formed at room temperatures are in metastable states and can be destroyed by thermal activation such as annealing. When the layers are destroyed, the phthalocyanine units are free to migrate across the surface and form larger crystallite islands. The relatively strong interaction between admolecule and substrate may cause some distortion in the electronic surface of phthalocyanine molecule through a charge transfer interaction. Alternatively it could be due to the occurrence of forbidden transitions due to symmetry breaking in the pseudomorphic layers. The central metal atoms can influence the film properties. The optical band gap of lead phthalocyanine is unaffected by the substrate temperature and annealing temperature is seen from Table 4.4.1 and 4.4.2. This may be due to the high atomic weight of central atom. The central lead atom in PbPc is not in the same plane but lies over the phthalocyanine ring.



4.5. Conclusion

Optical characterisation of the CuPc, CoPc and PbPc films were carried out at room temperature and at different substrate temperatures. Post evaporation annealing is carried out for CuPc, CoPc and PbPc films and uv-visible spectra recorded and band edge analysed to obtain the optical band gap. The optical band gap for CuPc and CoPc films remain constant upto 150°C and 250°C respectively. Even though the band gap energy abruptly falls above this temperature, trap level is unaffected. This fall in band gap energy is attributed to phase transition. The annealing temperature as well as substrate temperature is found to have no considerable effect on the band gap and the trap levels for PbPc films.

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