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ON THE OPTICAL PROPERTIES OF VACUUM-DEPOSITED LEAD SULPHIDE FILMS

KHAIRY A. MADY, HAMMAM R. MOUSTAFA*, SIHAM Y. GIRGIS and HODA A. MADY*

Physics Department, National Research Centre, Dokki, Cairo, Egypt

** Faculty of Science, Al-Azhar University (Girls Branch), Nasr City, Cairo, Egypt*

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The optical constants of vacuum-deposited PbS films were determined from transmission measurements in the spectral ranges 2.5—40 μm and 200—800 nm following two computational procedures. The analysis of the data revealed a direct energy gap of 0.41 eV and an indirect gap of 0.37 eV. The spectral behaviour of the refractive index exhibited a peak associated with the rapid change in the absorption edge. The values of the real and imaginary parts of the refractive index are in suitable agreement with published work on single crystals. The high frequency dielectric constant was found to be 17.2.

1. Introduction

The optical properties of semiconductors are among the most important sources of information on the band structure. The optical properties of PbS in the spectral region of the fundamental absorption edge have been measured at room temperature several times. Transmission, absorption and reflected measurements have been undertaken for single crystal specimens[1-4], chemically-deposited films[5] and epitaxial films[6-9]. It seems to be established that the direct energy gap is about 0.41 eV and the indirect gap is 0.37 eV.

The dispersion of the refractive index of PbS near the fundamental absorption edge indicated a maximum near the absorption edge[10,11]. The double reflection

of vacuum-deposited layers was attributed to their porosity and oriented distribution of crystallites[12]. The refractive index of synsetized films, by oxygen treatment, was found to be about 2 compared with a value of about 4 for the pure sulphide[13]. This was attributed to the formation of a film of $PbO \cdot PbSO_4$ surrounding the PbS crystallites.

The effect of the deposition rate on the microstructure of thin vacuum-deposited PbS films showed that by lowering the deposition rate single crystalline PbS layers could be grown on cleaved surfaces of rock-salt[14,15]. Hence, it seems interesting to investigate the optical properties of such films.

2. *Experimental and computational techniques*

Bulk material of PbS was prepared chemically from pure ingredients of lead acetate and dimethylthiocyanide solutions. Thin films were deposited by conventional thermal evaporation technique in about 10^{-6} Pa vacuum on thin cleaved single crystals of NaCl, KBr and CaF_2. The film thickness and the rate of deposition were determined interferometrically. Optical transmission measurements were conducted using a Beckman 4220 multiple-beam spectrophotometer in the range 2.5 μm—40 μm and a Beckman spectrophotometer in the range 200 nm—800 nm.

The optical constants of PbS films were determined in the intrinsic absorption region by applying Tubbs method[16] by solving the relation:

$$T = \frac{16\, n_1 n_3 (n_2^2 + K_2^2)}{[(n_1 + n_2)^2 + K_2^2]\,[(n_3 + n_2)^2 + K_2^2]} \exp\left[-4\pi K_2 d/\lambda\right] \qquad (1)$$

where n_1, n_2 and n_3 are the refractive indices of the surrounding medium, the PbS film and the substrate, respectively, and K_2 is the extinction coefficient, d is the film thickness and λ is the wavelength of light. This relation is valid when $4\pi K_2 d \gg \lambda$.

In the weakly absorbed region a modified interference method was applied by frequent use of convenient nomograms and the application of successive approximations in order to improve the calculations[17,18]. The effect of the substrate on the measurements was also allowed to improve the accuracy. A brief account about the method is given in the Appendix together with useful nomograms.

3. *Results and discussions*

The spectral behaviour of the percent transmission of thin PbS films in the infrared region from 2.5 μm to 40 μm (4000 cm^1 to 250 cm^{-1}) is shown in Fig. 1 as a function of film thickness.

The spectral behaviour of the absorption coefficient $\alpha = 4\pi K/\lambda$, where K is the absorption index, is shown in Fig. 2 near and above the absorption edge.

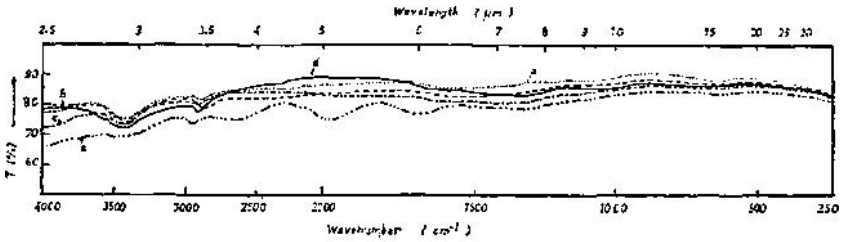

Fig. 1. Spectral behaviour of the percentage transmission of PbS films in the infrared region. Film thicknesses; (a) 50 nm, (b) 60 nm, (c) 70 nm, (d) 90 nm and (e) 100 nm.

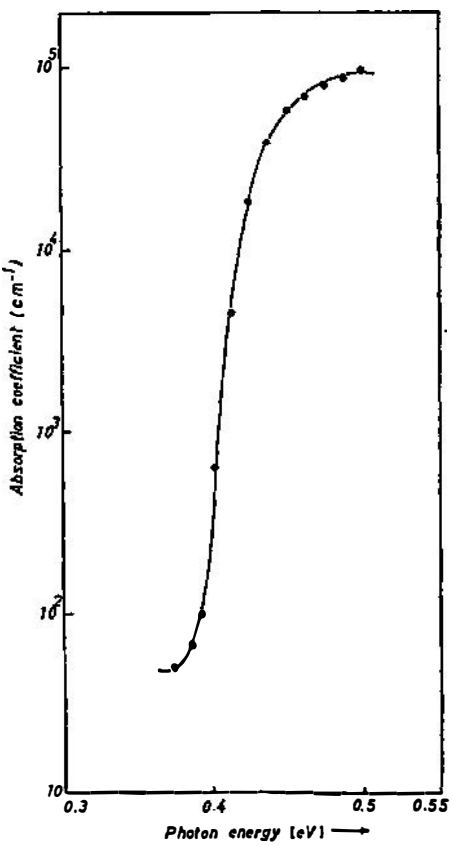

Fig. 2. Spectral behaviour of the absorption coefficient at the absorption edge of PbS.

The analysis of the absorption coefficient near and above the absorption edge gives information about the energy band structure of the material. Thus, plotting α^2

versus photon energy, $h\nu$, gave a straight line (Fig. 3) indicating an allowed direct transition described by[19]

$$\alpha = \frac{A}{h\nu}(h\nu - E_g^d)^{1/2}. \tag{2}$$

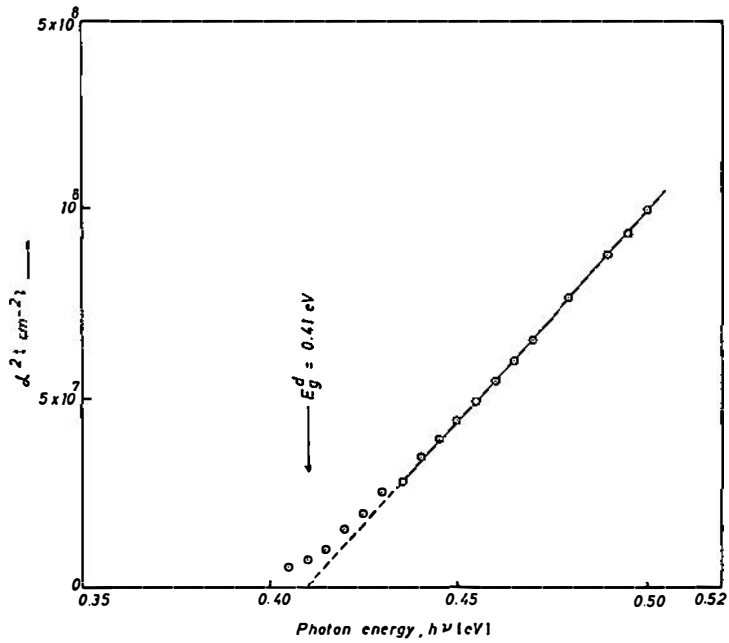

Fig. 3. The square of the absorption coefficient versus photon energy.

Extrapolating the straight line to zero absorption gives the value $E_g^d = 0.41$ eV. On other hand, plotting $\alpha^{1/2}$ versus $h\nu$ gave a straight line (Fig. 4) described by[19],

$$\alpha = \frac{A'}{h\nu}(h\nu - E_g')^2 \tag{3}$$

with the value $E_g' = 0.37$ eV. The determined values of the energy gaps are in good agreement with published work[3,6,7], and with known band structure calculations[20].

The refractive index, n, of PbS films in the spectral range 0.1 eV to 0.5 eV is represented in Fig. 5. A peak appears in the refractive index which is associated with the rapid change in the absorption coefficient in the fundamental absorption edge. The energy gap E_g^d is at a somewhat lower energy than the position of the peak. The absorption edge of a semiconductor is usually a region of very rapidly rising absorption. It is a direct consequence of the dispersion relation, between

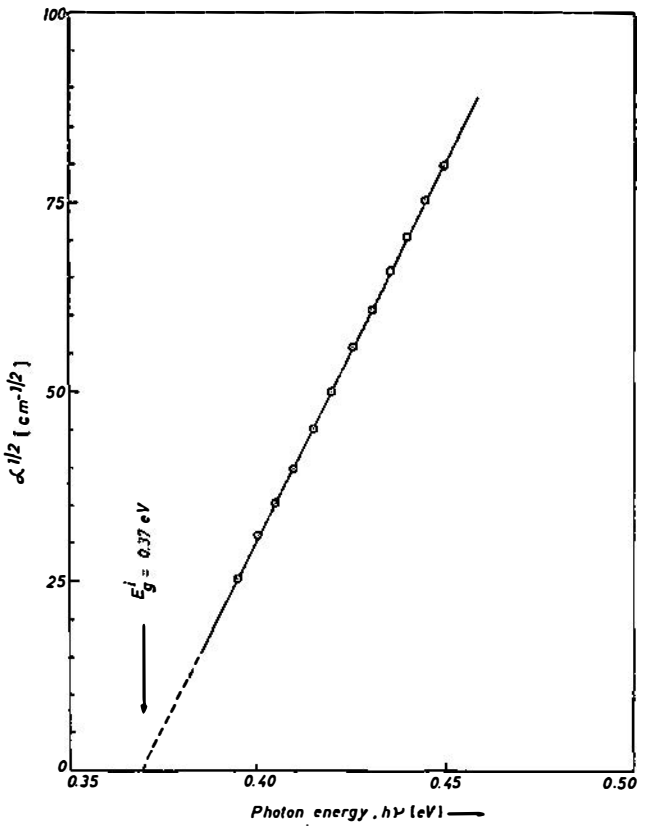

Fig. 4. The square-root of the absorption coefficient versus photon energy.

the real and imaginary parts of the complex index of refraction that this rapid rise in absorption will lead to structure in the index of refraction near the photon energy of the absorption edge.

An estimate of the contribution of the absorption edge region to the dispersion of the index could be expressed by[21]

$$\Delta n(E) \approx (\hbar c/\pi) \int_0^{E_s} \alpha(E') (E'^2 - E^2)^{-1} \, dE' \tag{4}$$

where E_s is an arbitrary energy separating the region near the edge from the high energy region.

The conventional absorption edge arising from allowed direct transitions between the conduction and valence bands is simply described by:

$$\alpha(E) = 0, \qquad E < E_g \tag{5a}$$

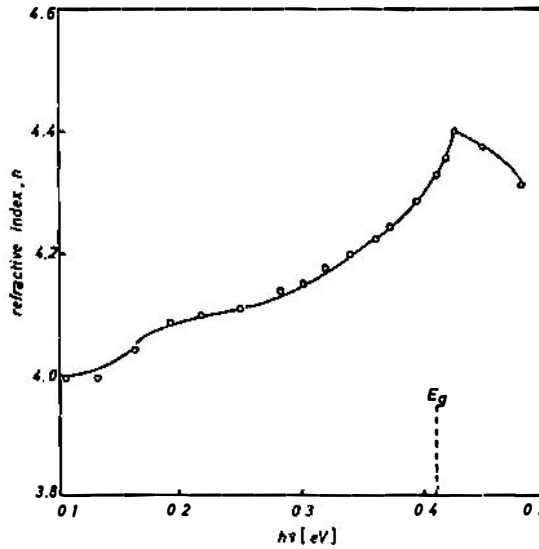

Fig. 5. Spectral behaviour of the refractive index of PbS films in the range from 0.1 eV to 0.5 eV.

$$\alpha(E) = B(E - E_g)^{1/2}\,[1 - (E - E_g)/(E_s - E_g)^{-1}],\ E_g < E < E_s. \tag{5b}$$

If we let $E_s \to \infty$, we find from Eq. (4) that

$$\Delta n(E) = (\hbar cB/2E)\,[(E_g + E)^{1/2} - (E_g - E)^{1/2}],\ E < E_g \tag{6a}$$

$$\Delta n(E) = (\hbar cB/2E)\,(E_g + E)^{1/2},\quad E > E_g. \tag{6b}$$

Thus, it appears that there is a peak in the index of refraction at the absorption.

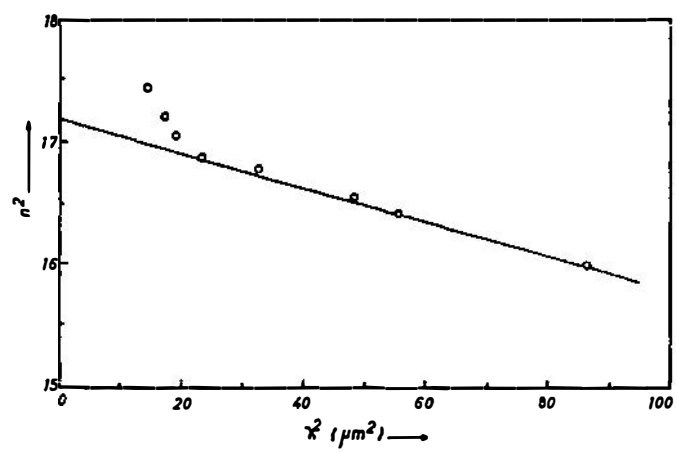

Fig. 6. n^2 versus λ^2.

The high frequency dielectric constant, ε_∞, of PbS could be determined from the spectral behaviour of the index of refraction. Two procedures have been followed. The first was to extrapolate the free carrier and lattice dispersion to infinite energy. This was done by plotting n^2 versus λ^2 and extrapolating the long wavelength linear region to zero wavelength which yields $n_0^2 = \varepsilon_\infty$, as shown in Fig. 6. The second procedure[22] was to assume that the high frequency properties of lead sulphide could be treated as a single oscillator at wavelength, λ_0, and apply

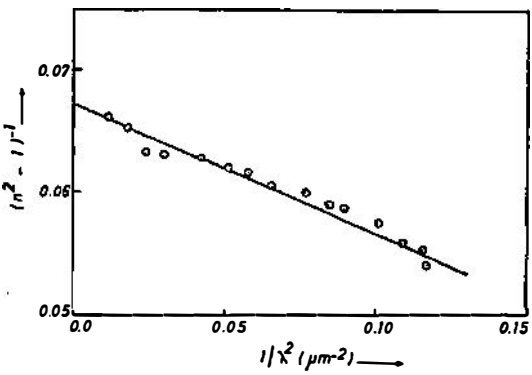

Fig. 7. $(n^2 - 1)^{-1}$ versus $1/\lambda^2$.

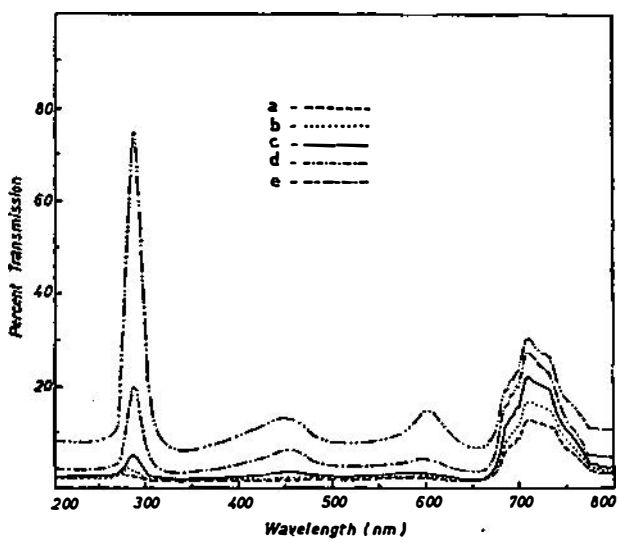

Fig. 8. Spectral behaviour of the transmission of PbS films in the range from 200 nm to 800 nm Film thickness: (a) 50 nm, (b) 60 nm, (c) 70 nm, (d) 85 nm and (e) 90 nm.

the simple classical dispersion relation[23]. If n_0 is the refractive index of an empty lattice at infinite wavelegth, the index will vary as

$$\frac{n_0^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 . \tag{7}$$

The λ_0 and n_0 have been evaluated from plots of $(n^2 - 1)^{-1}$ versus λ^{-2} for PbS (Fig. 7). The values of ε_∞ obtained from the first and second procedures are 17.2 and 15.82, respectively, in suitable agreement with the values 17.4 and 16.9, respectively, reported by Zemel et al.[10].

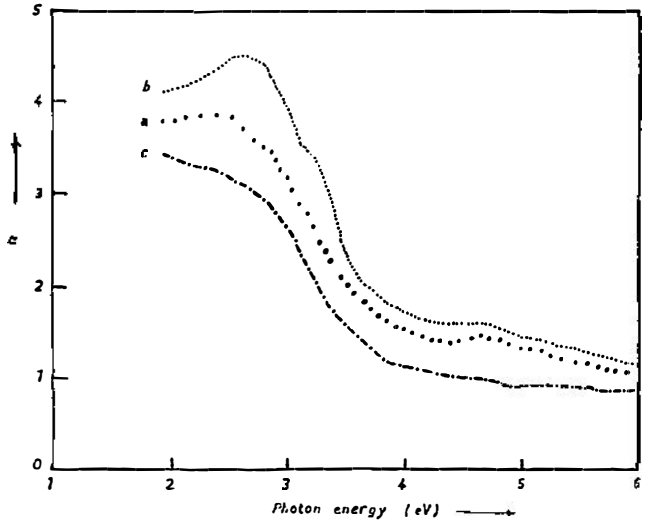

Fig. 9. Spectral behaviour of the refractive index of PbS films in the range from 200 nm to 800 nm. (a) Present work, (b) Refs. 2, 8 and 9 and (c) Ref. 4.

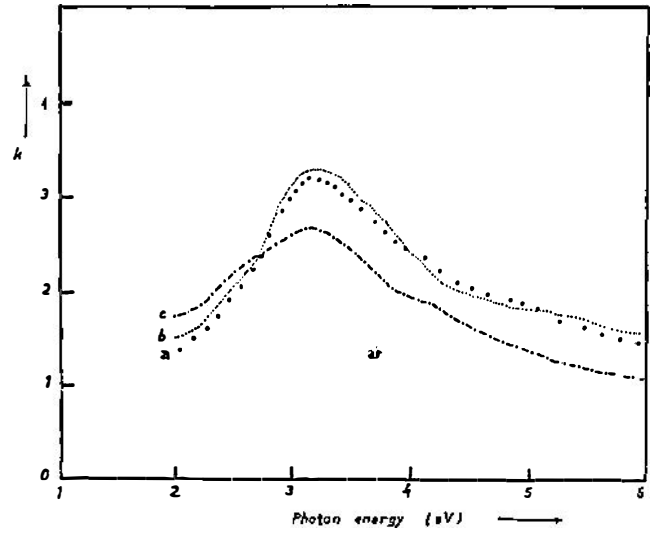

Fig. 10. Spectral behaviour of the absorption index of PbS films in the range from 200 to 800 nm. (a) Present work, (b) Refs. 2, 8 and 9, and (c) Ref. 4.

Transmission measurements were made on five selected PbS films ranging in thickness from 30 nm to 60 nm. The spectral behaviour of the transmission in the range 200 nm to 800 nm, for such films is shown in Fig. 8. The transmission spectra are characterized by the appearance of maxima in the transmission near 720 nm, 600 nm, 450 nm and 280 nm. The intensity of the peaks at 600, 450 and 280 nm decrease on increasing the film thickness and disappear completely in the transmission spectra of thick films. However, the transmission peak at 600 nm always appear in the transmission spectra of PbS films, and thus it can be taken as a characteristic peak for PbS films.

The refractive index, n, and the absorption index K, of PbS films determined from the transmission spectra according to the method mentioned before are represented in Figs. 9 and 10, which are in reasonable agreement with previous work.

4. *Appendix*

Assume a thin weakly absorbing layer with unknown refractive index ($\bar{n}_2 = n_2 - iK_2$, $K_2 \ll 1$) deposited onto a thick plane-parallel substrate of refractive index n_3 and the surrounding media are air ($n_1 = n_4 = 1$). Allowing for the interference of light beams undergoing multiple reflections, the transmission coefficient, T_0, of the uncoated substrate of thickness $h_3 \gg \lambda$ using spectrophotometers with medium resolving power, is given by[17]

$$T_0 = \frac{3n_3}{n_2^2 + 1}. \tag{A.1}$$

The transmission coefficient of the same substrate coated with a weakly absorbing film is given by[17]

$$T_{extr} = \frac{16\, n_2^2\, n_3}{(n_2+1)^3\,(n_2^2+n_2)\,e^{\gamma_2} - (n_2-1)^3\,(n^2-n_2)\,e^{-\gamma_2} + (-1)^m \cdot 2\,(n_2^2-1)\cdot(n_3^2-n_2^2)}. \tag{A.2}$$

In case of complete absence of absorption ($\gamma_2 = 0$) the extreme value, T_{extr}, is denoted by T^0_{extr} where

$$T^0_{extr} = T_0 = \frac{2\, n_3}{n_3^2 + 1}, \quad \ldots \quad m \text{ even} \tag{A.3}$$

$$T^0_{extr} = \frac{4\, n_2^2\, n_3^2}{(n_2^2 + 1)\,(n_3^2 + n_2^2)}, \qquad m \text{ odd.} \tag{A.4}$$

Expression (A.2) could be rewritten, for an odd value of m expanding $e^{\pm\gamma_2}$ into a series with terms involving up to the second powers of γ_2, in the form:

$$T_{extr} = T^0_{extr}\left[\left(1 - A\,\gamma_2 + \left(A^2 - \frac{B}{2}\right)\gamma^2\right]. \tag{A.5}$$

where T^0_{extr} is given by formula (A.4) and

$$A = \frac{(n_3^2 + n_2)(n_2 + 1)^3 + (n_3^2 - n_2)(n_2 - 1)^3}{4(n_2^2 + 1)(n_3^2 + n_2^2)},$$

$$B = \frac{(n_3^2 + n_2)(n_2 + 1)^3 - (n_3^2 - n_2)(n_2 - 1)^3}{4(n_2^2 + 1)(n_3^2 + n^2)}.$$

The first approximation for n_2 is obtained by applying expression (A.4) or the corresponding nomogram (Fig. A.1), which serves also for the determination of n_3 from the transmission coefficient of the uncoated substrate.

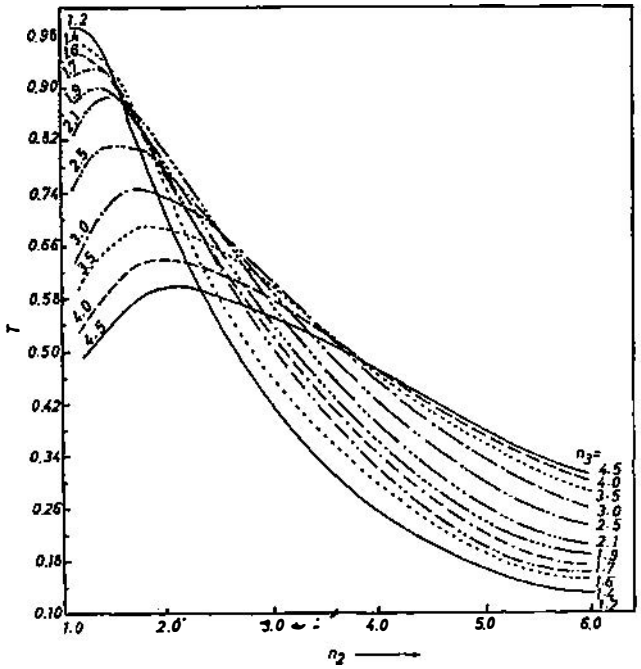

Fig. A1. Nomogram for the determination of the refractive indices of nonabsorbing substrates and layers.

The first approximation for γ_2 for even values of m is obtained from expression (A.2) or the corresponding nomogram (Fig. A.2). For each value of n_3 there should be a separate nomogram relating T_{extr} at λ_m with n_2 and γ_2. The first approximation for n_2 obtained above is used here.

To proceed from the first approximation to the second and from the second to the third, etc., one uses expression (A.5) and the nomogram for A and $[A^2 - (B/2)]$ (Figs. A.3 and A.4). Substituting the values of A and $[A^2 - (B/2)]$, corresponding to the previous approximation for n_2, and the first approximation for γ_2 into the right side of expression (A.5) and the experimental value of T_{extr}

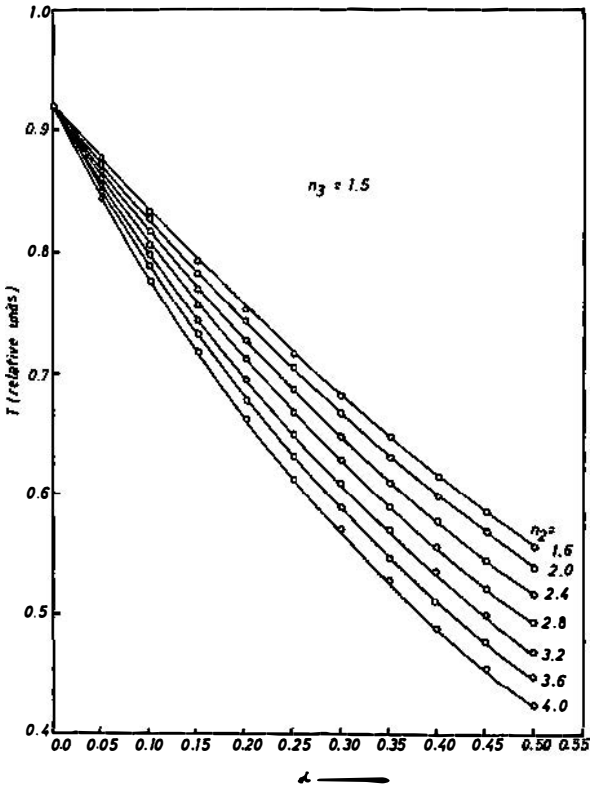

Fig. A2. Nomogram for the determination of the absorption coefficient of a layer on a substrate with refractive index ($n_3 = 1.5$). (N. B.: similar nomograms could be plotted for other values of n_3).

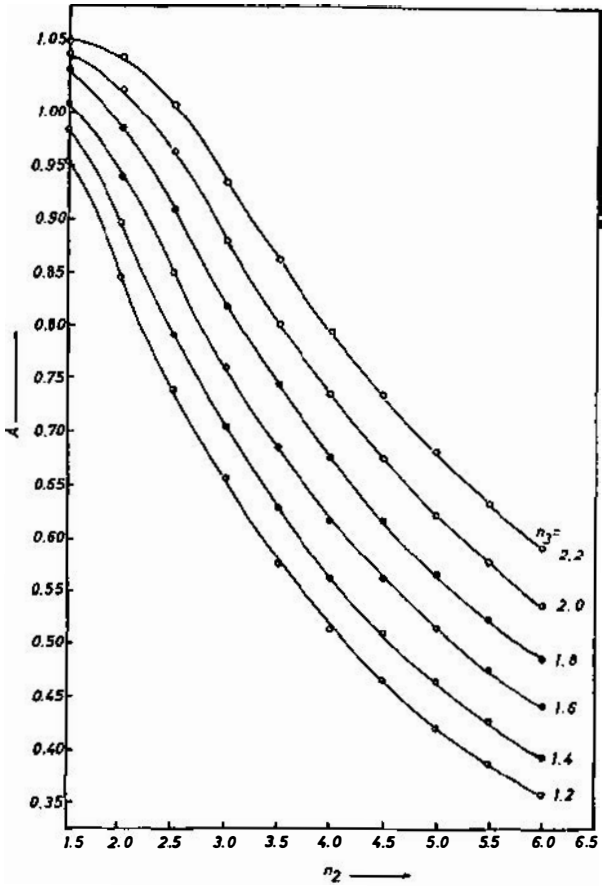

Fig. A3. Nomogram for the determination of the coefficient *A*.

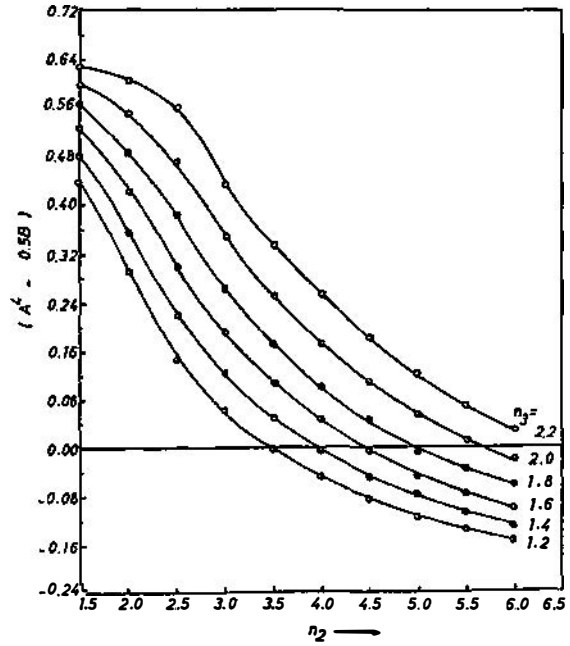

Fig. A4. Nomogram for the determination of the coefficient $[A^2 - (B/2)]$.

into the left side, one obtains a new value of T^0_{extr}. On application of the nomograms (Fig. A.1) this value yields the next approximation for n_2 and the next approximation for γ_2 is obtained from the nomograms (Fig. A.2). This cycle may be repeated as many times as necessary.

When the final values of n_2 and γ_2 are found K_2 is given from:

$$K_2 = \frac{2 n_2 \gamma_2}{m \pi}.$$

The order of interference, m, is

$$m = \frac{\lambda_{m+1}}{\lambda_m - \lambda_{m+1}}$$

where λ_m and λ_{m+1} are the wavelengths of two adjacent extreme points.

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OPTIČKE KONSTANTE VAKUUMSKI-DEPONIRANIH FILMOVA OLOVO SULFIDA

KHAIRY A. MADY, HAMMAM R. MOUSTAFA+, SIHAM Y. GIRGIS

i HODA A. MADY+

Physics Department, National Research Centre, Dokki, Cairo, Egypt

+Faculty of Science, Al-Azhar University (Girls Branch), Nasr City, Cairo, Egypt

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Optičke konstante vakuumski-deponiranih filmova PbS određene su na osnovi mjerenja u spektralnim intervalima 2,5—40 μm i 200—800 nm, pomoću dviju računskih procedura. Analiza podataka ukazuje na direktni energetski procijep od 0,41 eV i indirektni procijep od 0,37 eV. Spektralno ponašanje indeksa loma pokazuje vrh koji je pridružen brzoj promjeni apsorpcionog ruba. Vrijednost realnog i imaginarnog indeksa loma su u slaganju sa objavljenim rezultatima za monokristale. Visokofrekventna dielektrična konstanta je 17,2.