Sci. Annals, Fac. Phys. & Mathem., Uuiv. Thessaloniki, **13**, 85 (1973)

DETERMINATION OF OPTICAL CONSTANTS IN LAYERED COMPOUNDS

By

A. P. LAMBROS and N. A. ECONOMOU

(Physics Department, University of Thessaloniki)

(Received 9.6.1973)

Abstract: *A method is proposed for deriving the optical constants of either layered or epitaxially grown crystals from Fabry - Perot interference fringes. Only transmission measurements at normal incidenee are required. As an example, the method has been applied to the layered structure compound* $SiTe_2$.

1. INTRODUCTION

Considerable interest has recently been raised on the optical properties of layer semiconducting compounds. These compounds crystallize in a layered structure, with the bonding between layers of the Van der Waals type, while that within each layer is predominantly covalent. The usual method for determining the optical constants of these materials has been a separate determination of the optical absorption constant and the reflectivity. However the anisotropy of these crystals and the accurate determination of the reflectivity introduce difficulties. The discussion though of the reflection and absorption spectra in the region of the absorption edge is impossible without the precise knowledge of the extinction coefficient k(λ) and the index of refraction n(λ), especially when the details of the absorption edge are sought.

In the case of crystals with parallel faces that may be considered as optical flats, the sample acts as a Febry-Perot etalon, so that interference fringes appear either in transmitted or reflected light. From these fringes it is possible to obtain the main optical characteristics of the crystal and also to determine the thickness rather accurately. The method is applicable in the case of crystals of layered structure, where optical perfect faces can be produced through cleavage, and also in the case of epitaxially grown crystals.

In the present paper we present a modification of the method proposed mainly by Hazelwood [1] for the calculation of the optical constants from the modulation of transmitted light due to interference effects.

2. TRANSMISSION SPECTRA OF SPECIMENS BOUNDED BY PERFECT PARALLEL FACES

Let us consider a crystal of thickness d and a complex refractive index $N = n + ik$. For normal incidence of light a fraction of the intensity is transmitted while the rest is reflected. The fractional transmitted light defines the transmittance of the crystal e.g. the ratio of the transmitted intensity to the incident, $T = T(\lambda, n, k, d)$. If the crystal is bounded by perfect parallel faces, the light undergoes multiple reflections[2] so that the transmitted intensity is the result of the interference of a large number of coherent rays.

The phase difference between the transmitted and the incident ray is

$$\delta = \frac{3\pi}{\lambda} nd\cos\varphi \tag{1}$$

while the amplitude of the transmitted ray is

$$t = t_1 t_2 e^{-i\delta} (1 - r_1 r_2 e^{-2i\delta})^{-1} \tag{2}$$

where t_1 and t_2 are the transmittivity the upper and the lower faces respectively and r_1 and r_2 the corresponding reflectivities. For crystals free from substrates, $r_1 = r_2 = r$ and $t_1 t_2 = 1 - r^2$, the transmitted intensity becomes

$$t = (1 - r^2) e^{-i\delta} (1 - r^2 e^{-2i\delta})^{-1} \tag{3}$$

The transmitted energy T is equal to the product of the transmitted amplitude multiplied by its complex conjugate,

$$T = t \cdot t^* = \frac{(1 - r^2)^2}{1 - 2r^2\cos 2\delta + r^4} \tag{4}$$

In the above equation no absorption effects have been considered. Taking these into account, equation (4) becomes

$$T = \frac{(1 - R^2)\ (1 + k^2/n^2)}{\left(e^{\frac{4\pi k}{\lambda} d} - Re^{-\frac{4\pi k}{\lambda} d}\right)^2 + 4R\sin^2(\delta + \psi)} \tag{5}$$

where the parameters R and ψ have the values

$$R = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2} \qquad \psi = \frac{2k}{n^2 + k^2 - 1} \tag{6}$$

The parameter R is known as the reflectance of the crystal.

From the above results it is obvious that for a given wavelength the transmittance is a function of the thickness, while for constant thickness the transmittance is a function of wavelength. In fig. 1a the variation of the transmittance with the thickness is presented for the case of the layered compound $SiTc_2$, while in fig. 1b the variation of the transmittance with the wavelength is presented for the same compound[3].

3. DETERMIHATION OF THE FRINGE ORDER, THE THICKNESS AND THE REAL PART OF THE REFRACTIVE INDEX

The condition for a maximum in the transmittance pattern, for normal incidence, results from equation (5) and requires that the phase difference is an integral multiple of π,

$$\delta = j\pi \qquad (j = 0, 1, 2 \ldots\ldots) \tag{7}$$

or from equation (1)

$$j\lambda = 2nd$$

To determine the fringe order j and the real part of the refractive index, the thickness of the crystal is needed[4]. For two consequent fringes lying in the longer wave length part of the spectrum the following condition is satisfied

$$\begin{aligned} j\lambda_1 &= 2n(\lambda_1)d \\ (j+1)\lambda_2 &= 2n(\lambda_2)d \end{aligned} \tag{8}$$

Assuming that in this part of the spectrum the refractive index does not vary appreciable, so that

$$n(\lambda_1) = n(\lambda_2)$$

a probable value of the fringe order is obtained by solving the simultaneous equartions (8) for j

$$j = \frac{\lambda_2}{\lambda_1 - \lambda_1} \tag{9}$$

Thus we are able to assign a tentative order on all the observed fringes. Plotting the value $j(\lambda)$ vs λ we obtain a straight line which in-

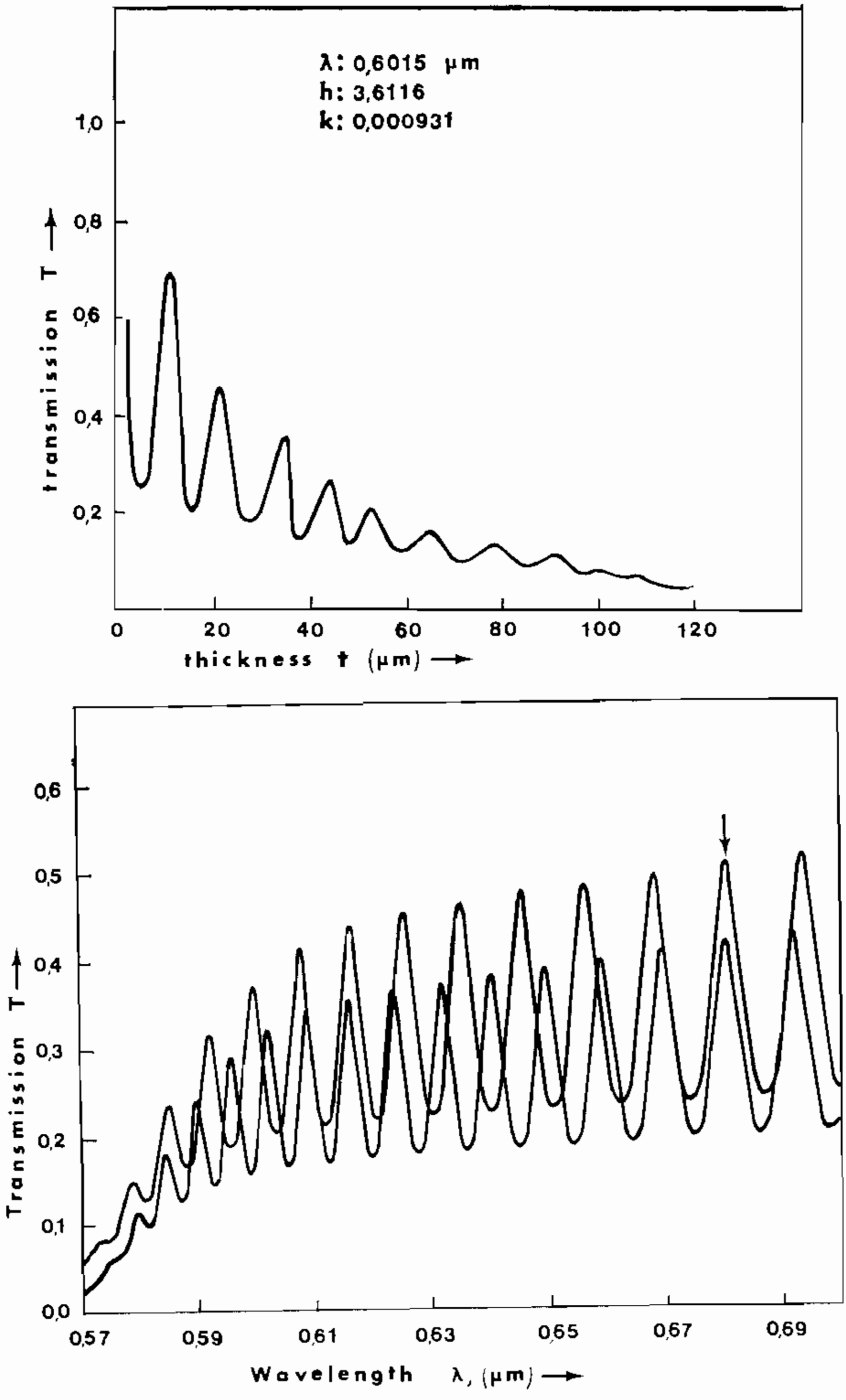


Fig. 1

a) The variation of the transmittance with the thickness for a layered structure compound ($SiTe_2$).

b) The variation of the transmittance with warelength for two different crystal hticknesses (the arrow indicates coinciding maxima).

dicates the variation of the real part of the refractive index, which must be known for a definite ordering.

The above difficulty is removed in the case where the spectra of two crystals are simultaneously analysed. In the spectrum of the first crystal, one fringe is chosen arbitrarily as the zero order one. With this zero order fringe as a reference it is possible to enumerate the consecutive fringes. If, for a certain fringe, the obtained arbitrary order is $J_1(\lambda)$, this would be related to the true order $j_1(\lambda)$ by the following relation

$$j_1(\lambda) = J_1(\lambda) + A_1$$

so that for the fringes in the two spectra the following relation exists between true and arbitrary order

$$\begin{aligned} j_1(\lambda) &= J_1(\lambda) + A_1 = \frac{2d_1 n(\lambda)}{\lambda} \\ j_2(\lambda) &= J_2(\lambda) + A_2 = \frac{2d_2 n(\lambda)}{\lambda} \end{aligned} \qquad (10)$$

where A_1 and A_2 are integral numbers to be determined. Dividing the above equations by parts the result

$$\frac{j_1(\lambda)}{j_2(\lambda)} = \frac{J_1(\lambda) + A_1}{J_2(\lambda) + A_2} = \frac{d_1}{d_2} \qquad (11)$$

indicates that between $J_1(\lambda)$ and $J_2(\lambda)$ exists a linear relationship. Thus plotting $J_1(\lambda)$ vs $J_2(\lambda)$ a straight line is obtained with a slope equal to d_1/d_2 with an intersect determined by A_1 and A_2.

The above two methods are satisfactory in the case of thin crystals with fringes that have orders smaller than 50. For thick crystals the real order of the fringes may exceed 100 and a graphical solution of the equation (11) is rather inaccurate. We have used the following method to determine the real order of the fringes for thick crystals.

Let us assume that in the spectra of two crystals A and B, two fringes have maxima at the same wavelength. These fringes are assigned as zero order fringes and with these as a reference we enumerate the rest. Since in this case $J_1(\lambda) = J_2(\lambda) = 0$ it follows that

$$\frac{j_1(\lambda)}{j_2(\lambda)} = \frac{A_1}{A_2} = \frac{d_1}{d_2} \qquad (12)$$

If there is a second wavelength at which the maxima of the fringes in the two spectra coincide, from equation (11) we obtain

$$\frac{j_1(\lambda')}{j_2(\lambda')} = \frac{J_1(\lambda')+A_1}{J_2(\lambda')+A_2} = \frac{d_1}{d_2} \tag{13}$$

Therefore

$$\frac{J_1(\lambda')+A_1}{J_2(\lambda')+A_2} = \frac{A_1}{A_2} \tag{14}$$

from which

$$\begin{aligned} J_1(\lambda') &= \varkappa A_1 \\ J_2(\lambda') &= \varkappa A_2 \end{aligned} \tag{15}$$

where $\varkappa$ is an integral with a value 0 for the arbitrary defined as zero order fringes, 1 for the first coinciding maxima etc...

For the first coinciding maxima

$$\begin{aligned} A_1 &= J_1(\lambda') = j_1(\lambda') \\ A_2 &= J_2(\lambda') = j_2(\lambda') \end{aligned} \tag{16}$$

thus the real order of the arbitrary as zero defined fringe is determined. This result is verified either by using coinciding fringes with a $\varkappa$ of larger order or by using the spectra of different samples.

It is easily deduced from equations (12) and (16) that if the thickness of one sample is known, the corresponding values of the thicknesses of the other samples can be found.

4. DETERMINATION OF THE IMAGINARY PART OF THE REFRACTIVE INDEX

The transmittance T, expressed by equation (5), is a function of the parameters d, λ, n, k. When d and n are determined independently, as in the previous section, the transmittance is a function of the imaginary part of the refractive index, e.g. $T = T(k)$.

In order to determine the value of k we have used the following method which is based on calculating the real value by successive approximations. The starting value is obtained from the well known equation

$$\frac{I}{I_0} = T = e^{-\frac{4\pi k}{\lambda}d}$$

so that

$$k = \frac{\lambda d}{4\pi} \ln \frac{1}{T} \tag{17}$$

For m samples of known thicknesses we may obtain a set of transmittance values

$$\begin{matrix} d_1 & d_2 & d_3 & d_4 \ldots\ldots d_m \\ T_1 & T_2 & T_3 & T_4 \ldots\ldots T_m \end{matrix} \qquad (18)$$

Now since we may express

$$T = T(n, k) \qquad (19)$$

the transmittance converges to the point (n , k), the real values of the optical constants. Expanding T(n, k) in Taylor series around the point (n , k)

$$T(n, k) = T(n_0, k_0) + \frac{n-n_0}{1!} \frac{\partial T(n, k)}{\partial n}\Big|_{n_0, k_0} + \frac{(k-k_0)}{1!} \frac{\partial T(n, k)}{\partial k}\Big|_{n_0, k_0} +$$

$$+ 2(n-n_0)(k-k_0) \frac{\partial^2 T(n, k)}{\partial n \partial k}\Big|_{n_0, k_0} + \ldots\ldots \qquad (20)$$

and having neglected higher order terms the final result is

$$(n-n_0) \frac{\partial T}{\partial n}\Big|_{n_0, k_0} + (k-k_0) \frac{\partial T}{\partial k}\Big|_{n_0, k_0} = T - T(n_0, k_0) \qquad (21)$$

If the following substitutions are made

$$n-n_0 = x \qquad\qquad k-k_0 = \psi$$

$$\frac{\partial T}{\partial n}\Big|_{n_0, k_0} = A \qquad \frac{\partial T}{\partial k}\Big|_{2_0, k_0} = B \qquad T - T(n_0, k_0) = C \qquad (22)$$

equation (22) is expressed as

$$Ax \times B\psi = C \qquad (23)$$

so that the whole set of measurements form the following set of simultaneous equations

$$\begin{aligned} A_1 x + B_1 \psi &= C_1 \\ A_2 x + B_2 \psi &= C_2 \\ \ldots\ldots&,\ldots\ldots \\ A_m x + B_m \psi &= C_m \end{aligned} \qquad (24)$$

Applying least square analysis the set of equations (24) reduce to the following

$$\begin{aligned} [AA]x + [AB]\psi &= [AC] \\ [AB]x + [BB]\psi &= [BC] \end{aligned} \qquad (25)$$

where the bracketed coefficients are equal to

$$\begin{aligned} [AA] &= A_1^2 + A_2^2 + \ldots\ldots\ldots + A_m^2 \\ [AB] &= A_1B_1 + A_2B_2 + \ldots\ldots + A_mB_m \\ [AC] &= A_1C_1 + A_2C_2 + \ldots\ldots + A_mC_m \\ [BB] &= B_1^2 + B_2^2 + \ldots\ldots\ldots + B_m^2 \\ [BC] &= B_1C_1 + B_2C_2 + \ldots\ldots + C_mC_m \end{aligned}$$

By solving equation (25), the values of n and k are determined. If these values are used to further refine the results by the substitution

$$\begin{aligned} n_0' &= n_0 + x \\ k_0' &= k_0 + \psi \end{aligned} \qquad (26)$$

a better set of values is obtained. This calculation may be repeated until the uncertainity of the calculated value is less than

$$\begin{aligned} x &\leqq 0{,}001 \\ \psi &\leqq 0{,}00001 \end{aligned} \qquad (27)$$

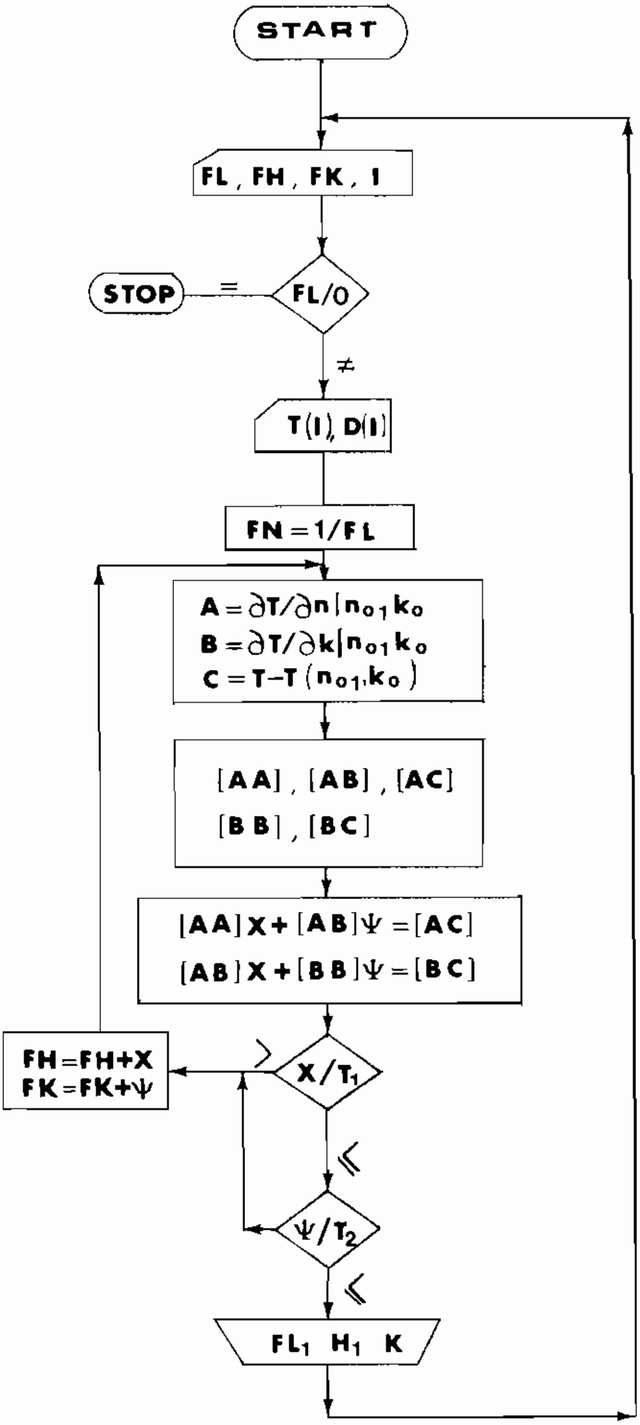
These calculations may be performed using the flow chart presented in figure 2.

In the case that the value of n is determined accurately (section 3) the above procedure is reduced considerably in labour, or it may be used as a further check of the results.

5. DISCUSSION

The final check of the above mentioned procedures in calculating the optical constants was made on $SiTe_2$. This compound crystallizes in a layered structure with a structure of the CdJ_2 type and lattice parameters as determined by Weiss and Weiss [5] a = 4.28, c = 6.71 A. Dne to its structure $SiTe_2$ is a highly anisotropic material. The results presented here refer only to light incident parallel to the crystal c axis. The crystals are also highly reactive especially in humid atmosphere.

In figure 3 the results of the absorption coefficient calculated by the proposed method are compared to the results obtained previously



$FL = \lambda$
$FH = n_o$
$FK = k_o$
$FN = \frac{1}{\lambda}$
$H = n$
$K = k$

Fig. 2
Flow chart for determing the values of n and k.

by Rau and Kannewurf[6] who used the usual procedure (equation 17). The agreement is satisfactory, while as it is easily deducted the fine details of the spectrum are missing from the results of Rau et al, a fact that points out the superiority of the proposed method.

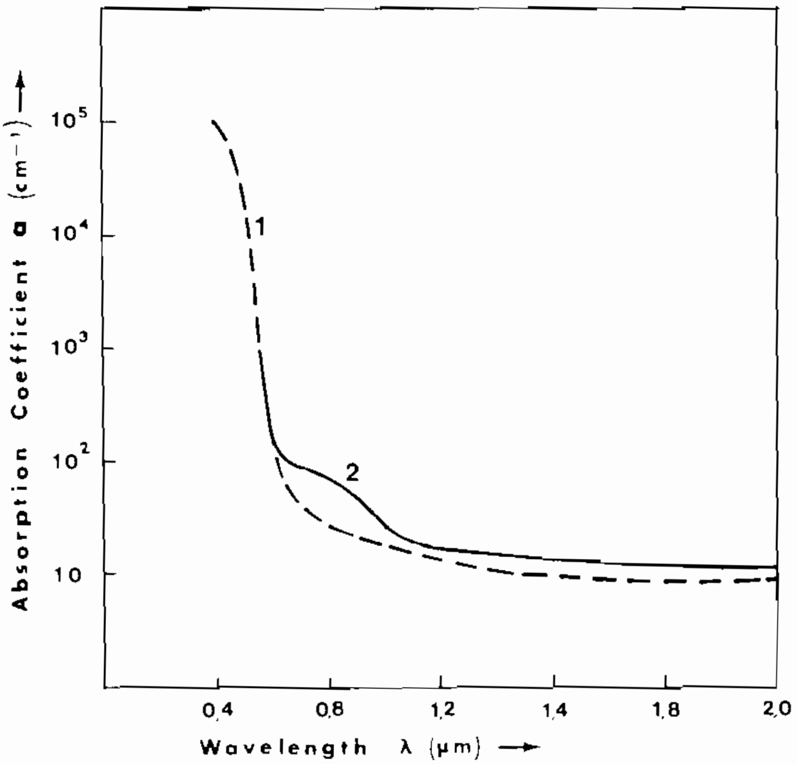


Fig. 3

The absorption coefficient vs wavelegth of silicon ditelluvide, according to the present method (dotted line represents the measurements by the usual procedure [6]).

Acknoledgments

The authors would like to acknowledge the financial support received through the National Hellenic Research Foundation and the ESSO-PAPPAS Co for one of them (A.P.L.).

REFERENCES

1. R. A. Hazelwood : Thin Solid Films 6, 329 (1970).
2. T. S. Moss : Optical Properties of Semiconductors, Butterworth, London (1961)
3. A. P. Lambros and N. A. Economou : Phys. Stat. Solidi, 57, 793 (1973)
4. W. J. Choyke and L. Patric : J. Opt. Soc. Am. 58, 377 (1968).
5. A. Weiss and A. Weiss : Z. Anorg. Chem. 273, 126 (1953).
6. J. W. Ran and C. R. Kannewurf : J. Phys. Chem. Solids 27, 1097 (1966).

ΠΡΟΣΔΙΟΡΙΣΜΟΣ ΟΠΤΙΚΩΝ ΣΤΑΘΕΡΩΝ ΕΙΣ ΦΥΛΛΟΜΟΡΦΟΥΣ ΕΝΩΣΕΙΣ

Ὑπὸ

Α. Π. ΛΑΜΠΡΟΥ καὶ Ν. Α. ΟΙΚΟΝΟΜΟΥ
(Ἐργαστήριον Β΄ Ἕδρας Φυσικῆς, Πανεπιστημίου Θεσσαλονίκης)

ΠΕΡΙΛΗΨΙΣ

Προτείνεται μέθοδος ὑπολογισμοῦ τῶν ὀπτικῶν σταθερῶν κρυστάλλων ποὺ παρουσιάζουν ἀπολύτως παραλλήλους ἐπιφανείας. Τοιαῦται περιπτώσεις συναντῶνται εἰς κρυστάλλους μὲ φυλλόμορφον δομήν, ὁπότε αἱ σχισμογενεῖς ἐπιφάνειαι εἶναι ἀπολύτως παράλληλοι ἢ εἰς ὑμένια ἀναπτυχθέντα ἐπιταξιακῶς. Αἱ ὀπτικαὶ σταθεραὶ προκύπτουν δι᾽ ἀναλύσεως τῶν κροσσῶν συμβολῆς τύπου Fabry-Perot, οἱ ὁποῖοι ὑφίστανται εἰς τὸ φάσμα ἀπορροφήσεως λόγω τῶν πολλαπλῶν ἀνακλάσεων ποὺ ὑφίσταται τὸ φῶς. Ἡ μέθοδος ἀποτελεῖ ἐπέκτασιν τῆς μεθόδου τοῦ Hazelwood, διὰ τὴν περίπτωσιν κρυστάλλων, ἔνθα ἡ τάξις τῶν κροσσῶν ὑπερβαίνει τὸν ἀριθμὸν 50. Ἡ μέθοδος ἐφαρμόζεται διὰ τὸν προσδιορισμὸν τῶν ὀπτικῶν σταθερῶν τοῦ $SiTe_2$, τὸ ὁποῖον εἶναι φυλλόμορφον ὑλικόν. Τὰ ἀπαιτούμενα δεδομένα προκύπτουν ἐκ μετρήσεων μόνον τῆς διαφανείας τοῦ κρυστάλλου διὰ φῶς προσπίπτον καθέτως πρὸς τὴν ἐπιφάνειαν. Διαπιστοῦται ἡ ὑπεροχὴ τῆς μεθόδου ἔναντι τῶν κλασσικῶν τοιούτων, καθ᾽ ὅτι ἀποκαλύπτει τὴν λεπτὴν ὑφὴν εἰς τὸ φάσμα τῶν τιμῶν συντελεστοῦ ἀπορροφήσεως.