A New Method for Investigating the Refractive Index and the Thickness of Thin Interference Films on Glass*

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If plane polarized light falls on lead glass the surface of which had been chemically changed to be covered with an interference film, the reflected light is in general elliptically polarized. If, however, the path difference of reflected rays from the air-film boundary and from the film-glass boundary is $2n_0d\cos r+\frac{1}{2}\lambda=k\lambda$, where k gives the order of the maximum, the first maximum for $k=1$ being $d(n_0^2-\sin^2\varphi)^{\frac{1}{2}}=\frac{1}{4}\lambda$, and where n_0 is the refractive index of the film, d its thickness, φ the angle of incidence, r the angle of refraction and λ the wave-length of the monochromatic light, then the reflected light is plane polarized. For this angle of incidence, φ, the plane of polarization of the reflected plane polarized light will be the same as if the polarized light were reflected from an ideal surface of glass (not covered with a film). From the angle between the plane of polarization of the analyzer and the plane of incidence the refractive index of the glass, n, can be calculated according to the formula deduced from Fresnel's relations: $n^2=\sin^2\varphi[1+\mathrm{tg}^2\varphi\,\mathrm{tg}^2(\psi+45°)]$, where φ is the angle of incidence, ψ the angle between the plane of polarization of the analyzer and the plane of incidence (the angle between the plane of polarization of the polarizer and the plane of incidence is 135°). We can calculate the refractive index, n_0, and thickness, d, of the surface film from the formula for the maxima if we determine two angles of incidence, φ_1 and φ_2 for two different wave-lengths. The refractive index of the film, n_0, is given by the formula:

$$n_0=\left(\frac{\lambda_1^2\sin^2\varphi_2-\lambda_2\sin^2\varphi_1}{\lambda_1^2-\lambda_2^2}\right)^{\frac{1}{2}}.$$

The results of the measurements are given in tables.

In a previous paper[1] artificial surface films on glass were studied for the first time. The present communication is concerned with the results of a study proposed in that paper of the elliptical polarization of light reflected from such thin films on glass. As these results are in good accord with those obtained with similar films by K. B. Blodgett[2] and described in the paragraph "etching of glass" of her paper published in this journal, and were besides this obtained quite independently, their communication may not be out of place here.

Thin films are formed on certain kinds of lead glass by action of dilute sulphuric acid. The surface of the glass is thereby covered with a dust of lead sulphate which can be easily removed. The sulphuric acid penetrates only to a certain depth, and on a soft lead glass a thin, but very hard, superficial film is formed, which is, as the measurement of its refractive index shows, substantially a film of quartz glass.

The object of the present paper is the description of a new method for measuring the refractive index and the thickness of these interference films on glass; it is thus a supplement to the present author's previous paper, as well as to that by K. B. Blodgett already quoted, with which he became acquainted only after completion of his experiments.

Apparatus

The polarimetric measurements of the refractive index and of the thickness of the superficial film on glass were made with a Fuess (Berlin) polarization spectrometer. Focal length of the collimator and telescope object-lenses is 180 mm (diameter 18 mm). The circle of the spectrometer has a diameter of about 165 mm, the smallest division being 10 minutes of arc. With a lens 10 seconds of arc can be read on a vernier. In front of the collimator is placed a polarizer and similarly an analyzer in front of the telescope (see the schematic diagram in Fig. 1). The polarizer and analyzer (Glan-Thomson's Nicols, square section 14×14 mm) are placed in a rotating circle (diameter about 130 mm); the circles are divided in 15 minutes of arc. With a lens 30 seconds of arc can be read on a vernier. The rotating circles of the analyzer and polarizer can be moved either by hand or by means of

* A preliminary notice on the present investigation has been presented before the Česká akad. Praha, December 15, 1939.
[1] Stornik české vysoké škely technické v Brně 12, 45 (1938); Kolloid Zeits. 86, 288 (1939).
[2] K. B. Blodgett, Phys. Rev. 55, 391 (1939).

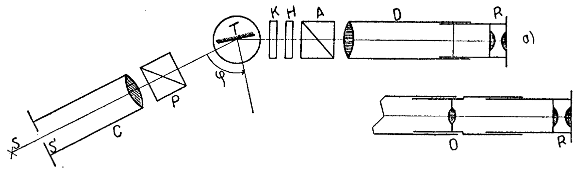

FIG. 1. The sketch of the polarization spectrometer. S the source of monochromatic light, S' the slit, C the collimator, P the polarizer, T the rotating table, K the compensator, D Nakamura's double-plate, A the analyzer, D the telescope, R eyepiece for measurements in a dark field (a) and the telescope O with eyepiece R (for measurements in half-shade (b)).

micrometric screws for fine adjustment. In front of the analyzer is placed the circle of the compensator with a similar outfit as the polarizer or analyzer. The Sénarmont's compensator (a quarter-wave mica plate) is placed so that it is possible to put it in an oriented position in front of the analyzer and to take it out again. Between the analyzer and the compensator Nakamura's double-plate of quartz is placed in a fixed position for half-shade measurements.

As a source of monochromatic light a sodium vapor discharge tube emitting wave-length 5893A or a mercury high pressure lamp with a special green filter for monochromatic light of wave-length 5461A was used. Both sources were manufactured by Philips, Eindhoven.

The polarimetric measurements can be made in two ways. In the first, a dark field in the telescope is used. The telescope is to be focused on the slit (or to infinity) of the collimator. The analyzer is rotated until the image of the slit vanishes on the dark background, the Nicols being crossed. In the second method, the measurements are made in half-shade. Nakamura's double-plate is placed in front of the analyzer, the eyepiece of the telescope being replaced by a telescope focused on the boundary-line of the double-plate. The analyzer is rotated until both halves of the double-plate are equally shaded.

When studying polarized light with a weak ellipticity by the half-shade method Sénarmont's compensator is the most suitable one. The measurement is made as follows:[3] Sénarmont's compensator is at first not introduced, so that the rays of light pass directly into the Nakamura's plate and into the analyzer. The analyzer is rotated until we get half-shade. This adjustment of the analyzer is made easily if the ratio of the semi-axes of the ellipse is less than $\frac{1}{10}$. In this position the plane of vibration of the analyzer is perpendicular to the semi-major axis of the ellipse, indicating thus the angle, χ, between the semi-major axis and the plane of incidence. This plane is given by the axis of the collimator and that of the telescope. Then the Sénarmont's compensator is oriented so that its directions of vibration coincide with the directions of the semi-axes of the ellipse, that is with the direction of vibration of the analyzer, is put in front of the analyzer.

The half-shade is thus destroyed, and with plane polarized light we have to rotate the analyzer through a certain angle, γ, to get the half-shade again (Fig. 2). This angle indicates the so-called ellipticity $\lg\gamma = b/a$, which is equal to the ratio of the semi-axes of the ellipse.

Sénarmont's compensator is placed so that at positive ellipticity, that is, when the light vector describes an ellipse in the positive direction, the analyzer is rotated in the positive direction. This is to the left when we look into the telescope. At negative ellipticity the analyzer is rotated in the opposite direction. The angle of the polarizer is at 45°. In the fundamental position the data read on the circles of the analyzer and compensator are nearly the same—the difference being only a few minutes. Thus the adjustment of the compensator is made very easy.

By measuring the angle, χ, between the semi-major axis of the ellipse and the plane of incidence, and the angle γ giving the ellipticity of light, the light vector describing the ellipse is completely determined. Because in the formulae for optical constants there is usually given the

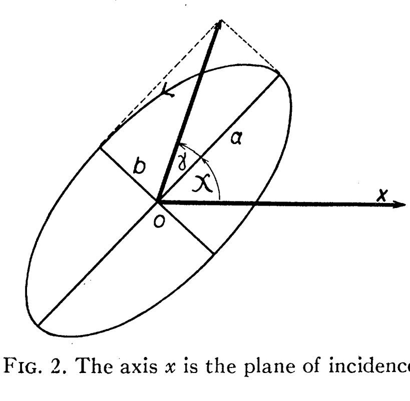

FIG. 2. The axis x is the plane of incidence.

[3] Geiger-Scheel, *Handbuch der Physik* (Berlin, 1928), Vol. 19, p. 955.

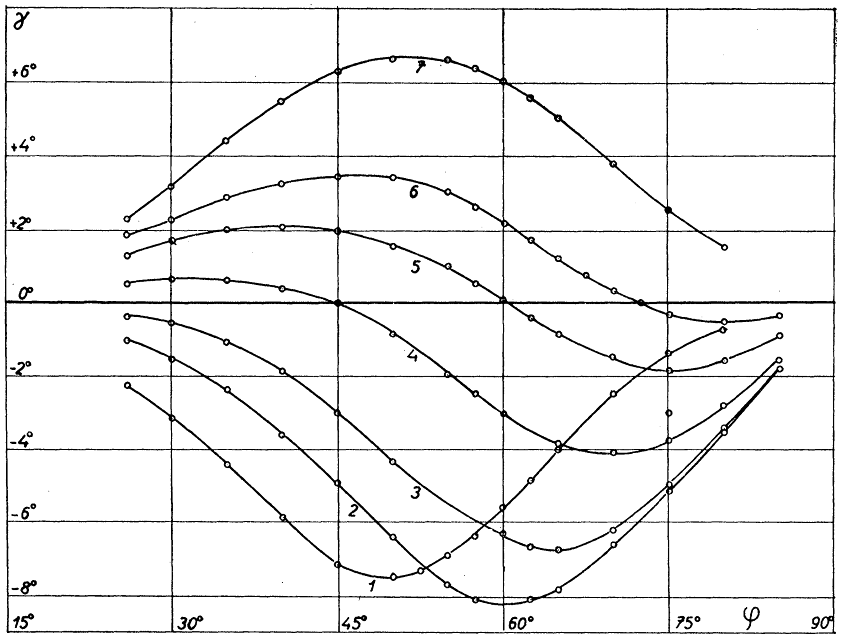

FIG. 3. The angle γ indicating the ellipticity as a function of the angle of incidence φ. The curves were obtained for white-blue (1), white-yellow (2), yellow (3), yellow-brown (4), red (5), purple (6), and blue (7).

ratio of the amplitudes, $\mathrm{tg}\,\psi$, and the phase difference, Δ, the ψ and Δ are calculated from the formulae

$$\cos^2\psi = \cos^2\gamma\cos^2\chi, \tag{1}$$

$$\mathrm{tg}\,\Delta = \mathrm{tg}^2\gamma/\sin^2\chi. \tag{1'}$$

THE MEASUREMENTS

The plane of polarization of the polarizer includes with the plane of incidence an angle of 135°. Thus many errors in measurement are eliminated, especially the systematic error in adjustment of the compensator, if the directions of vibration of the compensator do not coincide exactly with the semi-axes of the ellipse. When plane-polarized light falls on glass covered with a thin interference film, the reflected light is in general weakly elliptically polarized—the light vector describing a very narrow ellipse approaching a straight line. Fig. 3 represents graphically the dependence of the angle γ indicating the ellipticity on the angle of incidence, φ. The curves were obtained for the following interference colors: white-blue, white-yellow, yellow, yellow-brown, red, purple, and blue. Fig. 3 gives the best idea about the course of those curves for various interference colors of the film. Fig. 4 gives similarly the dependence of the angle χ between the semi-major axis of the ellipse and the plane of incidence on the angle of incidence, φ, for the same yellow-brown, interference color (curve 4). The curve 0 corresponds to the ideal surface of glass without the superficial film.

In Fig. 3 attention is called to the curves, which turn from positive values to negative ones, in other words, to those angles of incidence, where the ellipticity or the angle γ is zero. At this angle of incidence the reflected light is strictly plane polarized. With the color corresponding to a greater thickness of the film in white light (from yellow-brown to red and to purple) these points are shifted to greater angles of incidence. Note in Fig. 4 the angle of incidence corresponding in Fig. 3 to the angle of incidence for zero ellipticity. At this angle of about 45° for zero ellipticity the experimental curve touches the curve corresponding to the ideal surface of glass without the film, or the reflecting glass covered with the film behaves in the same way as glass without any such film.

The angle of incidence for the zero ellipticity has the following significance: the rays of light reflected on the air-film boundary and on the film-glass boundary meet at this angle of incidence in the same phase—or this angle of incidence determines the maximum of reflected

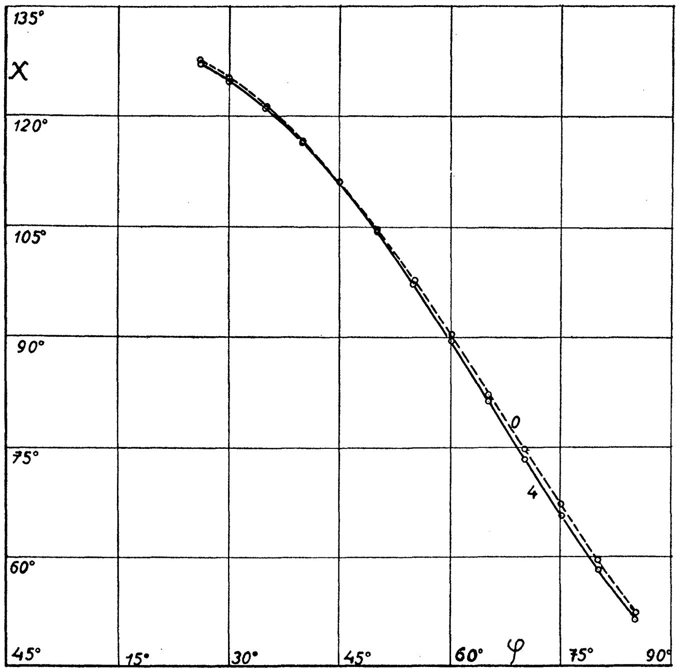

FIG. 4. The angle χ between the semi-major axis of the ellipse and the plane of incidence as a function of the angle of incidence φ. The curve O is calculated for the ideal surface of glass without film; (4) is the experimental curve for yellow-brown color. The angle between the plane of polarization of the polarizer and the plane of incidence is 135°.

monochromatic light of the wave-length λ used. The condition for this maximum on a film of the refractive index n_0 and the thickness d, if the angle of refraction in the film is r, is

$$2n_0d\cos r+\tfrac{1}{2}\lambda=k\lambda, \tag{2}$$

where k is the order of the maximum. The additional term $\frac{1}{2}\lambda$ on the left side of Eq. (2) is connected with the change of phase into the opposite one for the case of reflection on a medium with a greater refractive index.

For the first-order maximum ($k=1$)

$$2n_0d\cos r=\tfrac{1}{2}\lambda. \tag{3}$$

Taking instead of the angle of refraction, r, the angle of incidence, φ, we have

$$\cos r=(n_0{}^2-\sin^2\varphi)^{\frac{1}{2}}/n_0$$

and

$$d(n_0{}^2-\sin^2\varphi)^{\frac{1}{2}}=\tfrac{1}{4}\lambda. \tag{4}$$

If the angle of incidence corresponds to zero ellipticity of the reflected light—the reflected light being then strictly plane polarized—the film behaves as a plate with a path difference equal to λ for the first-order maximum. (The actual path difference in the volume is $\frac{1}{2}\lambda$ but an additional $\frac{1}{2}\lambda$ must be introduced because of the change of phase for a reflection on a medium of greater refractive index.) Such a superficial film has no influence upon the plane polarized light reflected on the unchanged surface of the glass.

The plates with a path difference λ, 2λ, $3\lambda\cdots$ are made usually of a doubly refracting material such as mica or quartz. If n_0 and n_e denote the two refractive indices of the ordinary and extraordinary rays, the thickness d of the plate with path difference λ is given by the relation

$$(n_0-n_e)d=\lambda. \tag{5}$$

Such a plate with path difference λ has no influence when it is placed between the reflecting surface and the polarizer (or the analyzer). In the doubly refracting plate the ray is divided into two rays which after passing through the plate combine and interfere with a certain path difference. The thin film on glass behaves quite similarly if the path difference of the light reflected on the air-film and on the film-glass boundary is λ for the first-order maximum or 2λ, $3\lambda\cdots$ for higher orders. Such films have no influence upon plane polarized light reflected on the unchanged surface of the glass. The angle between the plane of polarization of the plane polarized light and the plane of incidence is the same as if the plane polarized light were reflected from an unchanged surface of glass without a film. In addition to Eq. (4) which may relate to the angle of incidence for zero ellipticity, we have also the formula for the refractive index of glass n deduced from Fresnel's relations:

$$n^2=\sin^2\varphi[1+\mathrm{tg}^2\varphi\ \mathrm{tg}^2(\psi+45°)], \tag{6}$$

where ψ is the angle between the plane of polarization of the analyzer and the plane of incidence. We assume that this angle between the plane of polarization of the polarizer and the plane of incidence is 135°. The value of the refractive index of the glass, n, calculated from formula (6) is identical with that obtained by the method of minimum deviation.

If the angle of incidence for zero ellipticity is measured only for one wave-length, e.g., for the sodium line $\lambda=5893$A, only the refractive index of the glass, n, can be calculated from formula (6). If, however, the refractive index of the film, n_0, is known, it is possible to calculate from the formula (4) also the thickness, d, of the film. Because the refractive index of the film, n_0, is not known usually, it is necessary to determine for two wave-lengths λ_1 and λ_2 the angles of incidence, φ_1 and φ_2 for zero ellipticity. Then we have for the wave-length λ_1

$$d(n_0^2-\sin^2\varphi_2)^{\frac{1}{2}}=\lambda_1/4 \tag{7}$$

and for the wave-length λ_2

$$d(n_0^2-\sin^2\varphi_2)^{\frac{1}{2}}=\lambda_2/4. \tag{8}$$

TABLE I. *Measurements of the reflection of the sodium line and mercury line from the film on glass. The mean of the values of n_0 given in column 4 is 1.462 ± 0.002.*

Investigated Surface No.	φ_1	φ_2	n_0	d(A)	n_0d(A)
1 1st meas.	30°00′	46°01′	1.465	1073 ± 1	1568 ± 1
1 2nd meas.	30°00′	45°53′	1.459	1072 ± 1	1567 ± 1
2 1st meas.	30°25′	46°17′	1.463	1079 ± 1	1570 ± 1
2 2nd meas.	30°31′	46°19′	1.461	1075 ± 2	1571 ± 1
3 1st meas.	35°00′	49°50′	1.461	1095 ± 2	1602 ± 1
3 2nd meas	34°49′	49°47′	1.465	1095 ± 2	1601 ± 1
4	35°36′±7′	50°23′±5′	1.463 ± 0.007	1106 ± 2	1606 ± 1
5	38°38′±7′	52°57′±4′	1.463 ± 0.007	1114 ± 2	1629 ± 1
6	41°59′±6′	55°54′±6′	1.461 ± 0.008	1133 ± 2	1657 ± 1

The refractive index of the film is then

$$n_0\left(\frac{\lambda_1^2\sin^2\varphi_2-\lambda_2^2\sin^2\varphi_1}{\lambda_1^2-\lambda_2^2}\right)^{\frac{1}{2}}. \tag{9}$$

The thickness of the film, d, may be calculated according to one of the formulae (7) and (8).

With regard to dispersion the refractive index of the film calculated according to formula (9) is the mean of the refractive indices of the film for the wave-lengths λ_1 and λ_2. The measurements summarized in Tables I and II were made for the sodium line $\lambda_1=5893$A and mercury green line $\lambda_2=5461$A. The temperature of the room changed between 18°–20°C.

TABLE II. *Data on films which show colors when white light is incident on the film. Measurements are made for $\lambda=5893A$, and the value of n_0 is taken as 1.462 ± 0.002. The mean of the value of n given in column 5 is 1.7390 ± 0.0003. This is to be compared with the value of n obtained by the method of minimum deviation which is 1.7393 ± 0.0001.*

Investigated Surface No.	Color	φ	$\psi+45°$†	n	d(A)	n_0d(A)	n_0d*(A)
1	yellow-brown	45°00′	66°00′	1.7385	1151 ± 2	1683 ± 1	1680
2		45°14′	65°44′	1.7393	1153 ± 2	1685 ± 1	
3	red	59°35′	45°47′	1.7386	1248 ± 3	1824 ± 1	2450
4		60°21′	44°37′	1.7392	1253 ± 3	1832 ± 1	
5	purple	70°25′	28°54′	1.7392	1318 ± 3	1927 ± 2	2570
6		72°03′	26°22′	1.7390	1327 ± 3	1940 ± 2	

* According to the literature.
† The angle of the polarizer is 135°.

Column 1 gives the number of the measured surface. At a perpendicular incidence of white light on the reflecting surface covered with an interference film one sees when observing the vertically reflected light, a yellow-brown interference color. Surface No. 1 shows the lightest shade. Columns 2 and 3 give the measured angles of incidence for zero ellipticity, φ_1, for the sodium line $\lambda_1=5893$A, and φ_2, for the mercury green line $\lambda_2=5461$A.

The angles of incidence, φ_1 and φ_2, for zero ellipticity were determined by interpolation. In the neighborhood of the angle of incidence for zero ellipticity, the angle γ indicating the ellipticity is determined for 3 to 4 angles of incidence, e.g., for 27.5°, 30.0°, 32.5°, and 35.0°. If, for example, for the angle of incidence $\varphi=30.0°$ the ellipticity is zero, the angle indicating the ellipticity is positive for $\varphi=27.5°$, whereas it is negative for $\varphi = 32.5°$. Then the dependence of the angle γ on the angle of incidence, φ, is represented graphically, and the angle of incidence for zero ellipticity determined from this graph by interpolation. The angles γ indicating the ellipticity are reproducible to 0.5, this being also the smallest division, which we can read by means of the vernier on the circle of the compensator. To this error of measurement in the angle of incidence for zero ellipticity corresponds a maximum error $7'$ for the sodium line (at smaller angles of incidence it is larger) and up to $6'$ for the mercury green line. Note the measurements on surfaces Nos. 4, 5, and 6. With the surfaces Nos. 1, 2, 3 two independent series of measurements were made on the same reflecting surface, from which the reproducibility of the measurements by this method can be well estimated.

The refractive index of the film, n_0, calculated according to the formula (9) is given in column 4. The exactness of the measurement of the refractive index is about 0.5 percent as can be judged from the results obtained on surfaces Nos. 4, 5, and 6. If the measurements are made on several surfaces, we can reduce this error to 0.2 percent.

The mean value of the refractive index n_0 measured for $\lambda_1 = 5893\text{A}$ and $\lambda_2 = 5461\text{A}$ corresponds to the refractive index of fused quartz. K. B. Blodgett in her communication gives an approximate value of 1.46 for the refractive index of this film. According to Landolt-Börnstein,[4] the refractive index of fused quartz is 1.4585, for $\lambda = 5893\text{A}$ and 1.4607 for $\lambda = 5330\text{A}$, the mean being 1.4595. This result is an important criterion for the chemical composition of the thin superficial film on the glass, formed artificially by chemical treatment. The thin film is of fused quartz. This was to be expected from the chemical point of view. The lead atoms have been extracted from the surface layer of the glass and precipitated by sulphuric acid in the form of lead sulphate.

Column 5 gives the thicknesses of the film, d, and finally column 6 gives the optical paths, n_0d, which are from an optical point of view more important.

Table II gives the results of measurements on surface films, which show at perpendicular incidence of white light and perpendicular reflection a yellow-brown, red and purple color. The measurements were made only for sodium light $\lambda = 5893\text{A}$. The refractive index of the film is known from measurements given in Table I; $n_0 = 1.462 \pm 0.002$.

Column 1 gives again the number of the measured surface. For each of the three mentioned colors two surfaces showing approximately the same interference color were measured. Column 2 gives again the interference color. Column 3 gives the angles of incidence, φ, for zero ellipticity of the reflected light, and column 4 the angle ψ between the plane of polarization of the analyzer and the plane of incidence corresponding to the mentioned angle of incidence, φ. Column 5 gives the values of the refractive index of the glass, n, calculated by formula (6). Below the table the refractive index of the glass measured by the method of the minimum deviation is given for comparison. The value of the refractive index of glass obtained by reflection agrees with that from refraction of light within the limits of experimental error.

Column 6 gives the thicknesses of the interference films, d, and column 7 the optical paths n_0d. Finally, column 8 gives, for purpose of comparison, the thicknesses, n_0d, of the air-layer according to Müller-Pouillet,[5] which, at perpendicular incidence of white light and when observing the light reflected perpendicularly, would show the same interference colors (as far as it is possible to compare the interference colors). For the yellow-brown color the results are in good accord. There is a striking difference in the values of the optical paths for the red and purple colors, where the results given by the present author are substantially lower. It is worth mentioning that the difference of optical paths for the red and the purple color is in both instances the same. It is to be noted that Newton originally estimated the thickness of the air-layer for the red color lower than is given in the above-mentioned *Lehrbuch der Physik*.[5] (See, also, a paper by A. Rollet.[6]) Also according to the experimental curves, the values given by the present author are correct;

[4] Landolt-Börnstein, *Handbuch der Physik* (Berlin, 1923), Table II, p. 915.

[5] Müller-Pouillet, *Lehrbuch der Physik*, tenth edition (Braunschweig, 1909), "Optik," p. 744.

[6] A. Rollet, Akad. Wiss. Wien, **3**, No. 77, 177 (1878), see especially pp. 229 and 230.

values mentioned heretofore in the literature are too high.

It would be a useful task to measure by this method the thicknesses of thin interference surface films by using maxima not only of the first order, but mainly those of higher orders. Films on glass offer only limited possibilities in this respect since they give only maxima of the first and partially of the second order. More suitable for this study would be monomolecular films as produced and studied by K. B. Blodgett, for it is possible to lay these monomolecular layers on each other to any thickness.

In conclusion some practical consequences following from the study of physical properties, such as refractive index and thickness, of films on lead glass may be mentioned. By an optical method this superficial film was identified as a film of quartz glass. This thin, but very hard film of quartz glass can give good protection against mechanical damage to the soft lead glass (for example, of lenses). Another question is, whether the vessels of various types of lead glass, for example dishes, can be dangerous to life or not owing to chemical reaction with an acid. Finally, thin surface films on glass may be used in practice for producing glass articles showing iridescent colors.

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A Direct Comparison on a Crystal of Calcite of the X-Ray and Optical Interferometer Methods of Determining Linear Thermal Expansion

Evidence of Differences Among Calcite Crystals*

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Measurements by the x-ray and optical interferometer methods on the same specimen of calcite gave values for the coefficient of linear expansion which agree within the limit of measurement. Comparison of these results with data for other crystals of calcite shows that there is a significant difference in the expansion of different crystals. The spacing between the (211) [((100))] planes is also measurably different.

In a recent determination of the thermal dilatation of calcite, Weigle and Saïni,[1] using an x-ray powder method, obtained coefficients for the expansion along the two principal crystallographic axes which were approximately 20 percent lower than those obtained by Benoit,[2] whose data, obtained by means of an optical interferometer, have hitherto been regarded as among the best available. This discrepancy, which is many times greater than the combined experimental error, indicates either that the two methods do not give comparable results or that there is a significant difference in the expansion of different crystals of calcite. As measurements of the dilatation of sodium nitrate by the same x-ray method[3] had given values in satisfactory agreement with data obtained by means of the interferometer,[4] it seemed likely that the discrepancy with calcite was due to a difference in the specimens tested, a view which is supported by the difference in density among calcite crystals observed by DeFoe and Compton.[5]

* A preliminary note describing these results has been given by Saïni, Compte rendu des Séances, Société de physique et d'histoire naturelle de Genève **52**, 108 (1935).

[1] J. Weigle and H. Saïni, Helv. Phys. Acta **7**, 257 (1934).

[2] J. R. Benoit, Trav. Bur. Int. Poids et Mesures **6**, 190 (1888).

[3] H. Saïni and A. Mercier, Helv. Phys. Acta **7**, 267 (1934).

[4] J. B. Austin and R. H. H. Pierce, Jr., J. Am. Chem. Soc. **55**, 661 (1933).

[5] O. K. DeFoe and A. H. Compton, Phys. Rev. **25**, 618 (1925).