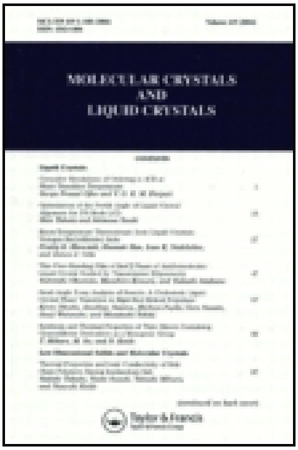

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Reflection and Transmission by Single-Domain Cholesteric Liquid Crystal Films: Theory and Verification†

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Abstract—We have developed a fast and essentially exact numerical technique for computing propagation, reflection and transmission of light by a flat layer of any linear optical medium in which the dielectric tensor varies only in a direction normal to the surfaces. Using this technique with Oseen's spiraling-dielectric-tensor model of a single domain in a cholesteric liquid crystal, we predicted triplet Bragg reflection bands of both first and higher orders for light incident obliquely on thin films, similar to the triplet bands that Taupin predicted by a different technique for semi-infinite samples. We have observed the first and second order Bragg reflection bands for light incident at 45 degrees on single-domain cholesteric films between two glass prisms. The films used were mixtures of 4,4′-Bis(n-hexyloxy)azoxybenzene, which is nematic at about 100 °C, and dextro-4,4′-Bis(2-methylbutoxy)azoxybenzene which is asymmetric and causes the cholesteric spiral twist in the mixture. Adjustment of parameters in a general spiraling ellipsoid model to fit the data shows that the dielectric ellipsoids of such films are approximately prolate spheroids with the major axis normal to the spiral axis, as hypothesized by Oseen and Taupin. In mixtures having a pitch of 0.764 microns, for example, the two unlike principal values of the dielectric tensor are approximately 3.060 and 2.430 for blue light around the second order triplet. Additional Bragg reflection bands, which we predicted if no major axis of the dielectric ellipsoid were parallel to the spiral axis, were not observed.

1. Mathematical Technique

We have used a 4 × 4 matrix formulation of the electromagnetic wave equations in stratified media to compute the reflectance and transmittance of single-domain cholesteric liquid crystal films.⁽¹⁾ Our technique is basically equivalent to the 4 × 4 matrix technique first described by Teitler and Henvis,⁽²⁾ and applied by them to

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finite layers of homogeneous anisotropic media. We have found that the method can easily be extended to the numerical solution of problems involving media with continuously varying anisotropic dielectric properties.

Prior to our publication,⁽¹⁾ Taupin⁽³⁾ found an entirely different technique for computing some of the optical properties of certain models of single domain cholesteric liquid crystals with obliquely incident light using truncated infinite matrices. Recently Dreher *et al.*⁽⁴⁾ have found propagation eigenvalues for oblique rays in such crystals using a single fourth-order differential equation. We believe the generality and simplicity of the 4 × 4 matrix technique makes it a useful alternative to Taupin's method or the method of Dreher *et al.* for computing optical properties of cholesteric liquid crystals.

2. Propagation in Stratified Media

When stratified, nonmagnetic, dielectric media carry electromagnetic waves of the form

$$\psi(z) \exp(ikx - i\omega t),$$

Maxwell's equations can be reduced to the matrix form

$$\frac{\partial}{\partial z}\begin{bmatrix} E_x \\ iH_y \\ E_y \\ -iH_x \end{bmatrix} = \frac{\omega}{c}\begin{bmatrix} \left(-i\dfrac{kc\epsilon_{xz}}{\omega\epsilon_{zz}}\right) & \left[1 - \dfrac{1}{\epsilon_{zz}}\left(\dfrac{kc}{\omega}\right)^2\right] & \left(-i\dfrac{kc}{\omega}\dfrac{\epsilon_{yz}}{\epsilon_{zz}}\right) & 0 \\ \left(-\epsilon_{xx} + \dfrac{\epsilon_{xz}^2}{\epsilon_{zz}}\right) & \left(-i\dfrac{kc}{\omega}\dfrac{\epsilon_{xz}}{\epsilon_{zz}}\right) & \left(\dfrac{\epsilon_{xz}\epsilon_{yz}}{\epsilon_{zz}} - \epsilon_{xy}\right) & 0 \\ 0 & 0 & 0 & 1 \\ \left(\dfrac{\epsilon_{xz}\epsilon_{yz}}{\epsilon_{zz}} - \epsilon_{xy}\right) & \left(-i\dfrac{kc}{\omega}\dfrac{\epsilon_{yz}}{\epsilon_{zz}}\right) & \left[\dfrac{\epsilon_{yz}^2}{\epsilon_{zz}} - \epsilon_{yy} + \left(\dfrac{kc}{\omega}\right)^2\right] & 0 \end{bmatrix}\begin{bmatrix} E_x \\ iH_y \\ E_y \\ -iH_x \end{bmatrix}$$

or

$$\frac{\partial}{\partial z}\psi(z) = \frac{\omega}{c}\,\mathscr{D}(z)\psi(z).$$

We shall call $\mathscr{D}(z)$ the differential propagation matrix. When $\mathscr{D}(z)$ does not vary appreciably over an interval h, an integral of this equation is

$$\begin{aligned}\psi(z+h) &= \mathbf{P}(z,h)\psi(z) = \exp[\mathscr{D}(z)(h\omega/c)]\psi(z) \\ &= [\mathbf{1} + \mathscr{D}(z)(h\omega/c) + \mathscr{D}(z) : \mathscr{D}(z)(h\omega/c)^2/2! + \ldots]\psi(z).\end{aligned}$$

We shall call $\mathbf{P}(z, h)$ the local propagation matrix.

Now consider larger intervals of length $l = mh$, where the total variation of $\mathscr{D}(z)$ is large over l, but small over each of the m subintervals, h. We may write a general propagation matrix $\mathbf{F}(z, l)$ such that

$$\psi(z + l) = \mathbf{F}(z, l)\psi(z).$$

An obvious approximation for $\mathbf{F}(z, l)$ is

$$\mathbf{F}(z, l) \approx \mathbf{P}(z + l - h, h) : \mathbf{P}(z + l - 2h, h) : \ldots \mathbf{P}(z + h, h) : \mathbf{P}(z, h).$$

However, for most practical problems another approximation for $\mathbf{F}(z, l)$ converges faster. From the symmetry of the physical problem we know that

$$\mathbf{P}(z, h) = \mathbf{P}^{-1}(z, -h) \approx \mathbf{P}^{-1}(z + h, -h).$$

If this expression is substituted for alternate terms in the preceding product series for $\mathbf{F}(z, l)$, we obtain the following more symmetrical expansion, assuming the number of subintervals, m, is even.

$$\mathbf{F}(z, l) \approx \mathbf{P}(z + l - h, h) : \mathbf{P}^{-1}(z + l - h, -h) : \ldots \mathbf{P}(z + h, h) : \mathbf{P}^{-1}(z + h, -h).$$

If ϵ is periodic with period l, then

$$\mathscr{D}(z + l) = \mathscr{D}(z),$$

$$\mathbf{P}(z + l, h) = \mathbf{P}(z, h)$$

and

$$\psi(z + Nl) = \mathbf{F}(Nl)\psi(z).$$

$$= \mathbf{F}^{N}(l)\psi(z)$$

3. Computing Reflectance and Transmittance

Let the subscript i denote incident, r reflected and t transmitted field components for beams in isotropic media separated by a flat stratified layer of thickness T. Let the first medium, which contains the incident and reflected rays, have optical dielectric constant ϵ_1, and let the last medium have optical dielectric constant ϵ_2. Let the angle of incidence within the first medium be θ_1 (see Fig. 1). Snell's law gives

$$\epsilon_1^{1/2} \sin \theta_1 = \epsilon_2^{1/2} \sin \theta_2.$$

The following 6 relations are easily obtained from Maxwell's equations

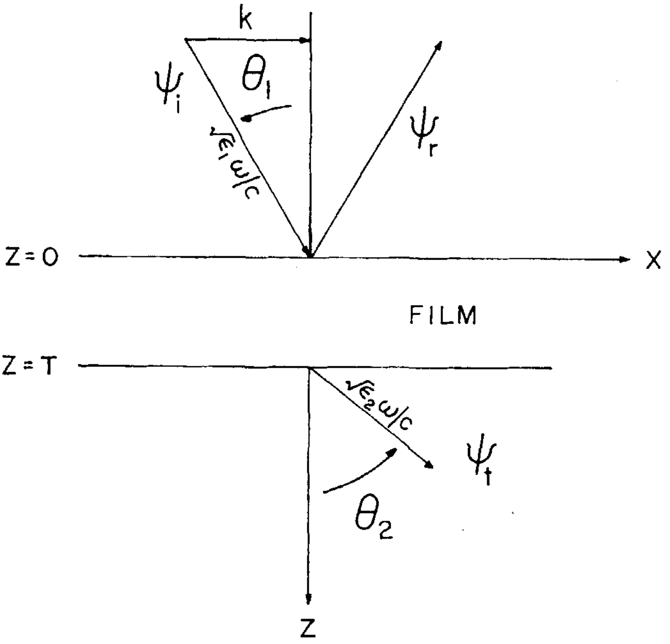

Figure 1. Illustration of variables used in computing the reflectance and transmittance of a stratified film of thickness T.

in isotropic media

$$
\begin{aligned}
(H_y/E_x)_i &= -(H_y/E_x)_r = \epsilon_1^{1/2}/\cos\theta_1 \\
(H_x/E_y)_i &= -(H_x/E_y)_r = \epsilon_1^{1/2}\cos\theta_1 \\
(H_y/E_x)_t &= \epsilon_2^{1/2}/\cos\theta_2 \\
(H_x/E_y)_t &= \epsilon_2^{1/2}\cos\theta_2
\end{aligned}
$$

Matching fields at the layer surfaces gives the matrix equation

$$\psi_t(T) = \mathbf{F}(T)\,(\psi_i(0) + \psi_r(0))$$

which can now be expressed as 4 linear equations in 6 field variables, such as E_{xi}, E_{yi}, E_{xr}, E_{yr}, E_{xt} and E_{yt}. Given E_{xi} and E_{yi}, we can compute the remaining 4, which give reflectance and transmittance of the combined layer and two interfaces.

4. Optical Model of a Cholesteric Liquid Crystal

A very simple optical model of a perfectly ordered cholesteric liquid crystal was first studied by Oseen⁽⁵⁾ and later by Hl. de

Vries.(6) They only investigated light propagated normal to the x, y plane. A slight generalization of their model, which appears to describe correctly the samples of real liquid crystals that we studied, is given by the following dielectric tensor.

$$\boldsymbol{\varepsilon} = \begin{bmatrix} \bar{\epsilon} + \delta \cos 2\beta z & \delta \sin 2\beta z & 0 \\ \delta \sin 2\beta z & \bar{\epsilon} - \delta \cos 2\beta z & 0 \\ 0 & 0 & \epsilon_3 \end{bmatrix}$$

The value of ϵ_3 was irrelevant to Oseen and de Vries' investigations because they only found solutions for normally incident light. Taupin(3) recently described theoretical solutions for light obliquely incident on semi-infinite samples, assuming that $\epsilon_3 = \bar{\epsilon} - \delta$, which appears to be at least approximately the correct relationship for our samples.

Our model gives a differential propagation matrix

$$\mathscr{D}(z) = \mathscr{D}_0 + \mathscr{D}_2(z),$$

where

$$\mathscr{D}_0 = \begin{bmatrix} 0 & 1 - (kc/\omega)^2/\epsilon_3 & 0 & 0 \\ -\bar{\epsilon} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -\bar{\epsilon} + (kc/\omega)^2 & 0 \end{bmatrix}$$

and

$$\mathscr{D}_2(z) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ -\delta \cos 2\beta z & 0 & -\delta \sin 2\beta z & 0 \\ 0 & 0 & 0 & 0 \\ -\delta \sin 2\beta z & 0 & +\delta \cos 2\beta z & 0 \end{bmatrix}$$

In this model, dielectric ellipsoids spiral about the z axis with pitch $2\pi/\beta$, but the period of the periodic $\mathscr{D}(z)$ matrix is $l = \pi/\beta$ (see Fig. 2). If the ellipsoids were tilted, $\boldsymbol{\varepsilon}$ would have no zeros and $\mathscr{D}$ would contain sin (βz) and cos (βz) terms, so that the period would be $l = 2\pi/\beta$. We found solutions for this case. Additional strong Bragg reflection bands corresponding to the longer fundamental period appear in this case. These additional bands were not observed

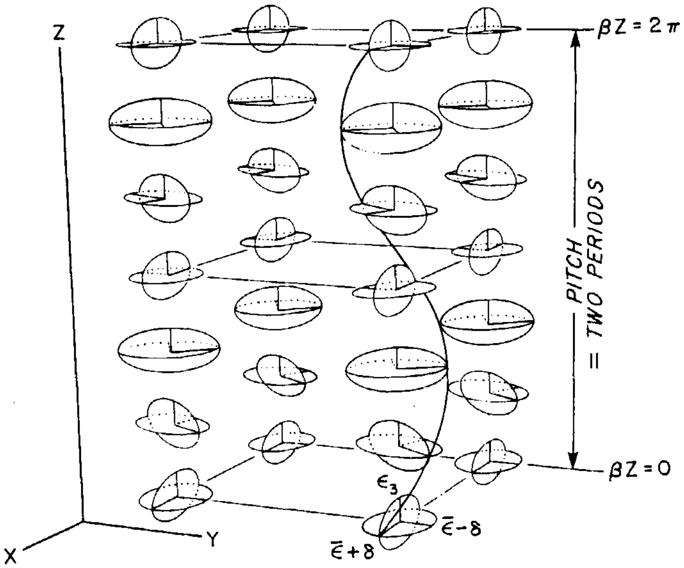

Figure 2. Spiraling dielectric ellipsoids in Oseen's optical model of a cholesteric liquid crystal.

experimentally. Hence the dielectric ellipsoids must not be tilted in our sample.

If the alternating product series expression is used to compute $\mathbf{F}(l)$, a rather rough approximation for $\mathbf{P}(z, h)$ may be used without introducing excessive cumulative errors in $\mathbf{F}$. With the generalized Oseen model, a satisfactory approximation is

$$\mathbf{P}(z, h) \approx \mathbf{P}_0(h) + (h\omega/c)\,\mathscr{D}_2(z).$$

The z-independent term $\mathbf{P}_0(h)$ is the propagation matrix corresponding to the invariant part, $\mathscr{D}_0$, of the differential propagation matrix. It may be written in the following exact, closed form.

$$\mathbf{P}_0(h) = \begin{bmatrix} \cos(abh\omega/c) & (a/b)\sin(abh\omega/c) & 0 & 0 \\ (-b/a)\sin(abh\omega/c) & \cos(abh\omega/c) & 0 & 0 \\ 0 & 0 & \cos(vh\omega/c) & (1/v)\sin(vh\omega/c) \\ 0 & 0 & (-v)\sin(vh\omega/c) & \cos(vh\omega/c) \end{bmatrix}$$

where

$$a = [1 - (kc/\omega)^2/\epsilon_3]^{1/2}$$
$$b = (\bar{\epsilon})^{1/2}$$

and

$$v = [\bar{\epsilon} - (kc/\omega)^2]^{1/2}$$

We computed the reflectance spectrum for obliquely incident plane wave radiation interacting with a system obeying Oseen's optical model. Figure 3 (bottom) shows the first and second order Bragg reflection bands that we predicted for certain principal values of the dielectric tensor.

5. Experiment

A straightforward experiment to verify our calculations would be to measure the reflectivity of a single domain in a cholesteric liquid crystal where the helicoidal axis is uniformly perpendicular to the film surface over the whole area of the light beam. To our knowledge, there have been no prior reflectivity studies made on single-domain cholesteric liquid crystal systems.

The cholesteric films that Fergason(7) and Adams, Haas, and Wysocki(8) used in their optical experiments were not single domain systems. To explain the reflectivity of these films Fergason(7) assumed a distribution in orientation of small Bragg scattering domains embedded in a matrix of constant refractive index. Experiments of Adams, Haas, and Wysocki(8) have shown that there is also a variation in the Bragg spacing, making it impractical to measure the distribution in orientation of these domains. Without knowledge of this orientational distribution, only qualitative comparison of experiments with the single-domain optical theories of Oseen,(5) de Vries,(6) and others(3,4,9) can be made.

We have used a single-domain cholesteric film in which the helicoidal axis is uniformly perpendicular to the film surface over regions of a square centimeter or more. Our cholesteric film is a binary mixture of non-mesomorphic dextro-4,4′-Bis(2-methylbutoxy)azoxybenzene (2 MBAB) and nematic 4-4′-Bis(*n*-hexyloxy)azoxybenzene.(10) We can vary the pitch of the resulting cholesteric mesophase from infinity to 0.24 μ by increasing the mole fraction of 2 MBAB in the mixture from 0 to 85%, which is the upper limit for

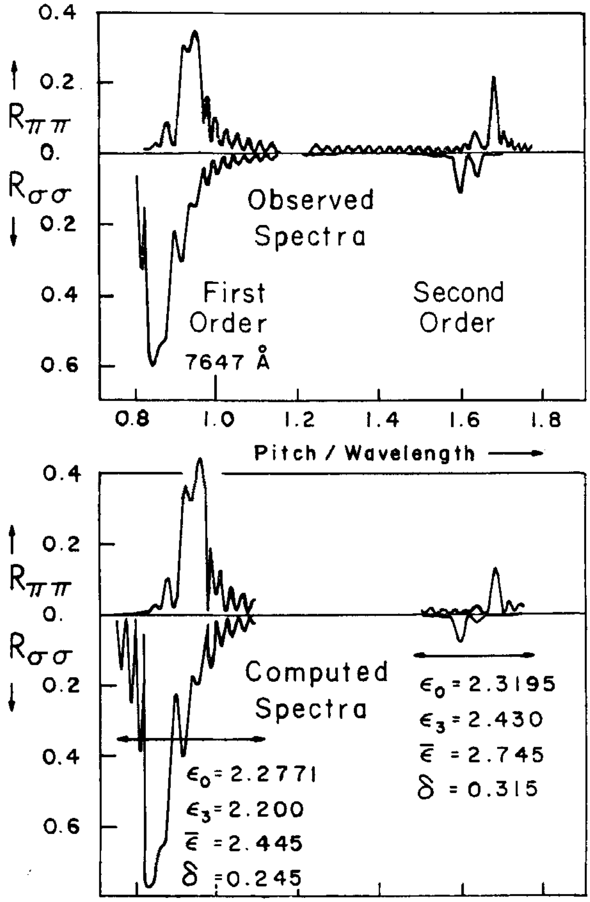

Figure 3. First and second order reflectance spectra of a cholesteric liquid crystal film 15 pitch lengths or 11.47 μ thick, confined between two glass prisms of optical dielectric constant ϵ_0. Light beam is incident at 45 degrees. Polarizer and analyzer were parallel to the plane of incidence for $R_{\pi\pi}$ and normal to it for $R_{\sigma\sigma}$ measurements. Mole fraction of 2 MBAB is 0.45 and temperature is 88 °C. Small oscillations are interference fringes from the two film-prism interfaces.

the existence of a pure cholesteric phase. The pitch shows only a small temperature dependence, decreasing only a few tenths of a percent for each centigrade degree increase in temperature. The mesomorphic range depends upon the fraction of 2 MBAB in the mixture, but all ranges fall between 42 and 130 °C.

The experimental arrangement that we used for measuring Bragg reflection from this cholesteric film is shown in Fig. 4. We directed an obliquely incident, plane-polarized, monochromatic beam of parallel light at the liquid crystal film contained between the faces of two 36 × 25 × 25 mm right angle glass prisms. We observed that the reflected light from the film always emerged at the specular angle. The reflected beam passed through an analyzer and was focused on a photomultiplier detector. We measured the reflected intensities for both sigma and pi polarized radiation. For pi polarized radiation both the polarizer and analyzer were oriented so that the electric field vector of the radiation passing through them would be in the plane defined by the incident and reflected beam. The polarizer and analyzer were rotated 90 degrees from this position for sigma polarized radiation. The analyzer was needed because it eliminated the dependence of detector sensitivity on polarization. We compared the reflected intensities with 100% reflection values that we measured in a separate experiment by using only the lower prism so the light beam would be totally internally reflected.

We made permanent spacers for the sample by evaporating chromium at three spots on the lower prism face, electroplating a thicker layer of gold on them and then polishing the gold to the desired thickness. The sample thickness was determined at the time of the experiment by measuring the wavelengths of a series of interference minima observed at normal incidence within an air bubble trapped in the film. We calculated the cholesteric pitch by measuring the spacing of the Grandjean-Cano(11,12) discontinuities produced by placing some of the sample between a convex lens surface of known curvature and a flat glass plate, both of which had been rubbed in one direction with lens tissue to insure a well-oriented sample.

We defined the molecular orientation at the surfaces of the liquid crystal film by rubbing the prisms on lens tissue in the x-direction. (See Fig. 4.) We introduced the sample in its isotropic phase between the heated glass prisms and then allowed the system to cool until the sample passed to its cholesteric phase. The desired temperature was held within a degree centigrade or so by means of a simple thermostatic oven arrangement. Before starting the reflection measurements we sheared the film by moving the upper prism back and forth several times in the x direction to obtain the Grandjean plane texture.

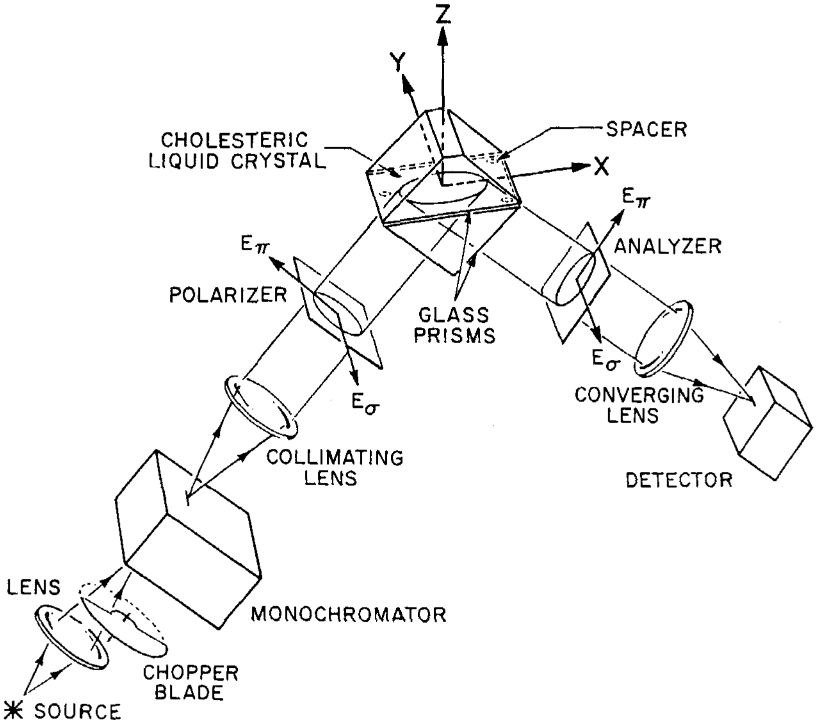

Figure 4. Apparatus for measuring reflectance of oblique rays by a liquid crystal film.

Our sample contained two or three parallel Grandjean discontinuities about 1 cm apart because it was slightly wedge-shaped. We took reflectivity measurements over a single domain region of uniform pitch by positioning a mask so that only light reflected from a $2 \times \frac{1}{2}$ mm rectangular area half way between two discontinuities and parallel to them was allowed to strike the detector.

The measured reflectivity curves for our cholesteric system are shown in Fig. 3 (top).

6. Conclusions

The mathematical method outlined here was used to generate reflectance spectra for liquid crystal films having the known thickness and pitch of our samples. By adjusting $\bar{\epsilon}$, δ and ϵ_3 we were able to fit frequencies of variations in reflectance quite closely. (See Fig. 3, top.) The method can easily be used for models with dielectric tensors that vary in a more complicated way. Our experimental data did not show additional Bragg reflection bands or other spectral features that we predicted if the principal axis ϵ_3 were not parallel to the z axis. We found that $\epsilon_3 \approx \bar{\epsilon} - \delta$; that is, that the dielectric tensor ellipsoid is (at least approximately) a prolate spheroid, as assumed by Taupin.(3) Our computations show that the second order Bragg reflection band for an oblate spheroid would be much less symmetric about the central component of the band (which is common to both π and σ polarized radiation) than that computed for a prolate spheroid.

We are in doubt as to whether the discrepancy between the computed and the measured intensities shown in Fig. 3 is significant. The first order Bragg reflection band appears to be somewhat weaker and the second somewhat stronger than predicted. Altering the initial and final azimuth of the dielectric ellipsoid or its principal values only made the fit worse. Assuming an error in pitch measurement did not help either. Thin regions near the surfaces with anomalous dielectric properties might account for the discrepancy. However, there might have been an experimental error due to difficulty in getting the same alignment of the sample and reference beams.

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