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Optical Rotatory Power of a Cholesteric Liquid Crystal for Obliquely Incident Light Using Multiple Scaling

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The axis of polarization of light propagating through a cholesteric liquid crystal rotates with the angular rotation per distance traversed termed rotatory power. The rotation is due to the helical array of the molecules rather than due to the individual molecules as is found, for instance, with light being propagated through a sugar solution. The De Vries model for rotatory power of a cholesteric liquid crystal is generalized using multiple scaling theory to include light traveling at an oblique angle to the pitch axis. The resulting expression is tested experimentally using a mixture of cholesteryl oleyl carbonate and cholesteryl chloride.

I INTRODUCTION

The axis of polarization of light propagating through a cholesteric liquid crystal rotates with the angular rotation per distance traversed termed rotatory power. The rotation is due to the helical array of the molecules rather than due to the individual molecules as is found, for instance, with light being propagated through a sugar solution.

In 1951 H. De Vries[1] developed a theory for the propagation of light along the helical axis of a cholesteric liquid crystal. He obtained expressions for both the rotatory power and reflection intensities as a function of the wavelength of the incident light. His expression for the rotatory power reduced to the result that Mauguin[2] had obtained much earlier for the limit when the cholesteric pitch was much greater than the wavelength. This expression has been generalized theoretically by Chandrasekhar and Rao[3] to regions of wavelength closer to the reflection band and has been verified experimentally by Robinson,[4] Cano and Chatelain,[5] Baessler, Laronge and

Labes,[6] Chandrasekhar and Shashidara,[7] and Teucher, Ko and Labes.[8] De Vries' results for reflection intensities at normal incidence have been generalized to include oblique angles by Dreher, Meier and Saupe,[9] Taupin[10] and Berreman and Scheffer.[11] However, there has apparently been no generalization of the expression for the rotatory power to include light incident at an oblique angle.

In Section II we show how the method of multiple scaling can be used with Maxwell's equations to obtain the rotatory power at oblique angles. In Section III we present experimental results which support the theoretical expression derived in Section II.

II THEORETICAL DEVELOPMENT

Let the pitch axis of the cholesteric lie along the z direction so the director has components

$$n_x = \cos qz$$

$$n_y = \sin qz$$

with $q = 2\pi/P$ where P is the pitch. The dielectric tensor in the cholesteric may be represented by

$$\varepsilon = \begin{pmatrix} \bar{\varepsilon} & 0 & 0 \\ 0 & \bar{\varepsilon} & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix} + \Delta\varepsilon \begin{pmatrix} \cos 2qz & \sin 2qz & 0 \\ \sin 2qz & -\cos 2qz & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

with $\bar{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$ and $\Delta\varepsilon = (\varepsilon_1 - \varepsilon_2)/2$.

For light incident in the xz plane Maxwell's equations can be written as[12]

$$\frac{d^2F_1}{d\alpha^2} + g^2F_1 + \eta g^2(F_1 \cos 2\alpha + F_2 \sin 2\alpha) = 0 \tag{2}$$

$$\frac{d^2F_2}{d\alpha^2} + h^2F_2 - \eta k^2(F_2 \cos 2\alpha - F_1 \sin 2\alpha) = 0 \tag{3}$$

where the electric field is

$$E_1 = F_1(\alpha)e^{imx - i\omega t} \tag{4}$$

$$E_2 = F_2(\alpha)e^{imx - i\omega t} \tag{5}$$

and

$$\alpha = qz \tag{6}$$

$$\eta = \frac{\Delta\varepsilon}{\bar{\varepsilon}} \tag{7}$$

$$k^2 = \frac{\bar{\varepsilon}\omega^2}{q^2c^2} \tag{8}$$

$$g^2 = \frac{\bar{\varepsilon}}{q^2}\left(\frac{\omega^2}{c^2} - \frac{m^2}{\varepsilon_3}\right) \tag{9}$$

$$h^2 = \frac{\bar{\varepsilon}}{q^2}\left(\frac{\omega^2}{c^2} - \frac{m^2}{\bar{\varepsilon}}\right) \tag{10}$$

with c being the speed of light in a vacuum.

Assuming $\varepsilon_2 = \varepsilon_3$ we can write

$$h^2 = g^2 + \eta\frac{m^2}{q^2} + \eta^2\frac{m^2}{q^2} + \cdots \tag{11}$$

The approximate form for h^2 as expressed in Eq. (11) gives an error in h^2 of less than 1% for light in the cholesteric propagating at 45° to the pitch axis taking 0.05 for the value of η. For the sample we used we found η to be approximately 0.04 in value. Since the index of refraction, n, was approximately 1.45 the direction of light propagation on the air side of the cholesteric-air interface might be 90° with less than a 1% error in this approximate expression for h^2. We will use the method of multiple scaling[13] to obtain solutions for F_1 and F_2. We expand the derivatives in powers on η:

$$\frac{\partial}{\partial\alpha} = \frac{\partial}{\partial\alpha_0} + \eta\frac{\partial}{\partial\alpha_1} + \eta^2\frac{\partial}{\partial\alpha_2} + \cdots \tag{12}$$

$$F_1 = U_0 + \eta U_1 + \eta^2 U_2 + \cdots \tag{13}$$

$$F_2 = V_0 + \eta V_1 + \eta^2 V_2 + \cdots \tag{14}$$

We may now substitute Eq. (6)–(14) into Eq. (2) and (3) and equate terms of the same power in η. To zero order we have:

$$\frac{\partial^2 U_0}{\partial\alpha_0^2} + g^2 U_0 = 0 \tag{15}$$

$$\frac{\partial^2 V_0}{\partial\alpha_0^2} + g^2 V_0 = 0 \tag{16}$$

from which we obtain:

$$U_0 = A(\alpha_1, \alpha_2)e^{ig\alpha_0} \tag{17}$$

$$V_0 = B(\alpha_1, \alpha_2)e^{ig\alpha_0} \tag{18}$$

To first order from Eq. (2) and (3) we have

$$\frac{\partial^2 U_1}{\partial \alpha_0^2} + g^2 U_1 = -\left[\frac{2\,\partial^2 U_0}{\partial \alpha_0\, \partial \alpha_1} + g^2(\cos 2\alpha_0)U_0 + g^2(\sin 2\alpha_0)V_0\right] \quad (19)$$

$$\frac{\partial^2 V_1}{\partial \alpha_0^2} + g^2 V_1 = -\left[\frac{2\,\partial^2 V_0}{\partial \alpha_0\, \partial \alpha_1} - k^2(\cos 2\alpha_0)V_0 + k^2(\sin 2\alpha_0)U_0 + \frac{m^2 V_0}{q^2}\right] \quad (20)$$

Substituting Eq. (17) and (18) into Eq. (19) and (20) we obtain

$$\frac{\partial^2 U_1}{\partial \alpha_0^2} + g^2 U_1 = -2ig\frac{\partial A}{\partial \alpha_1} e^{ig\alpha_0} - \frac{g^2 A}{2}\left[e^{i(g+2)\alpha_0} + e^{i(g-2)\alpha_0}\right]$$
$$- \frac{g^2 B}{2i}\left[e^{i(g+2)\alpha_0} - e^{i(g-2)\alpha_0}\right] \quad (21)$$

$$\frac{\partial^2 V_1}{\partial \alpha_0^2} + g^2 V_1 = -\left[2ig\frac{\partial B}{\partial \alpha_1} + \frac{m^2 B}{q^2}\right]e^{ig\alpha_0} + \frac{k^2 B}{2}\left[e^{i(g+2)\alpha_0} + e^{i(g-2)\alpha_0}\right]$$
$$- \frac{k^2 A}{2i}\left[e^{i(g+2)\alpha_0} - e^{i(g-2)\alpha_0}\right] \quad (22)$$

To avoid an infinite solution for U_1 and V_1 we must have

$$\frac{\partial A}{\partial \alpha_1} = 0 \quad (23)$$

$$2ig\frac{\partial B}{\partial \alpha_1} + \frac{m^2 B}{q^2} = 0 \quad (24)$$

We conclude that

$$A(\alpha_1, \alpha_2) = A'(\alpha_2) \quad (25)$$

$$B(\alpha_1, \alpha_2) = B'(\alpha_2)e^{im^2\alpha_1/2gq^2} \quad (26)$$

Therefore, the component with x–z polarization sees a slightly different index of refraction than the component with y polarization. We can now solve for U_1 and V_1:

$$U_1 = \frac{g^2}{2}\left[(A - iB)\frac{e^{i(g+2)\alpha_0}}{4(g+1)} - (A + iB)\frac{e^{i(g-2)\alpha_0}}{4(1-g)}\right] \quad (27)$$

$$V_1 = \frac{k^2}{2}\left[(-B - iA)\frac{e^{i(g+2)\alpha_0}}{4(g+1)} + (-B + iA)\frac{e^{i(g-2)\alpha_0}}{4(1-g)}\right] \quad (28)$$

To second order Eq. (2) and (3) are

$$\frac{\partial^2 U_2}{\partial \alpha_0^2} + g^2 U_2 = -\left(\frac{\partial^2}{\partial \alpha_1^2} + 2\frac{\partial^2}{\partial \alpha_0\,\partial \alpha_2}\right)U_0 - 2\frac{\partial^2 U_1}{\partial \alpha_0\,\partial \alpha_1} - g^2(\cos 2\alpha_0)U_1 - g^2(\sin 2\alpha_0)V_1 \tag{29}$$

$$\frac{\partial^2 V_2}{\partial \alpha_0^2} + g^2 V_2 = -\left(\frac{\partial^2}{\partial \alpha_1^2} + 2\frac{\partial^2}{\partial \alpha_0\,\partial \alpha_2}\right)V_0 - 2\frac{\partial^2 V_1}{\partial \alpha_0\,\partial \alpha_2} - \frac{m^2 V_1}{q^2} - \frac{m^2 V_0}{q^2} + k^2(\cos 2\alpha_0)V_1 - k^2(\sin 2\alpha_0)U_1 \tag{30}$$

Using the solutions for U_0, U_1, V_0, V_1 together with Eq. (29) and (30) we find to avoid infinite solutions of U_2 and V_2 we must have:

$$\frac{\partial A}{\partial \alpha_2} + \frac{g(k^2+g^2)A}{16i(1-g^2)} + \frac{g^2(k^2+g^2)B}{16(1-g^2)} = 0 \tag{31}$$

$$\frac{\partial \mathrm{B}}{\partial \alpha_2} + \left[\frac{k^2(k^2+g^2)}{16ig(1-g^2)} + \frac{m^2}{2igq^2} - \frac{m^4}{8ig^3q^4}\right]B - \frac{k^2(k^2+g^2)A}{16(1-g^2)} = 0 \tag{32}$$

If we let

$$a = \frac{g^4+k^4+2g^2k^2}{32(1-g^2)g} + \frac{m^2}{4gq^2} - \frac{m^4}{16g^3q^4} \tag{33}$$

and

$$b = \sqrt{\left[\frac{g^4-k^4}{32g(1-g^2)} - \frac{m^2}{4qg^2} + \frac{m^4}{16g^3q^4}\right]^2 + \frac{k^2g^2(g^2+k^2)^2}{16^2(1-g^2)^2}} \tag{34}$$

then the solutions for A and B are

$$A = (A_1 \sin b\alpha_2 + A_2 \cos b\alpha_2)e^{ia\alpha_2} \tag{35}$$

$$B = (B_1 \sin b\alpha_2 + B_2 \cos b\alpha_2)e^{ia\alpha_2} \tag{36}$$

We have a typical solution being composed of both an A (x-z polarized) and a B (y polarized) wave each oscillating sinusoidally, out of phase with each other. For an incident A wave we have

$$A = A_2 \cos b\alpha_2 e^{ia\alpha} \tag{37}$$

$$B = B_1 \sin b\alpha_2 e^{ia\alpha_2} \tag{38}$$

The rotatory power in the z direction, R_0, is clearly $\eta^2 bq$. The rotatory power, R, in the direction of motion is

$$R = \frac{g\eta^2 bq}{k} \tag{39}$$

We can substitute $g = k\cos\theta'$ where θ' is the angle between the z axis and the direction of the light ray in the sample to obtain

$$R = \frac{q\eta^2 k^4 \cos\theta'}{2}\sqrt{\frac{\cos^2\theta'(1+\cos^2\theta')^2}{64(1-k^2\cos^2\theta')^2} + \psi^2} \tag{40}$$

where

$$\Psi = \frac{\cos^4\theta' - 1}{16k\cos\theta'(1-k^2\cos^2\theta)} - \frac{\sin^2\theta'}{2k^3\cos\theta'} + \frac{\sin^4\theta'}{8k^3\cos^3\theta'} \tag{41}$$

For $\theta' = 0$ we have

$$R_0 = \frac{\eta^2 k^4 q}{8(1-k^2)} \tag{42}$$

which agrees with the De Vries[1] result for rotatory power.

III EXPERIMENT

To test the validity of the derived expression for rotatory power we have used a mixture of cholesteryl oleyl carbonate (COC) and cholesteryl chloride (CCl). We obtained the COC from Aldrich Chemical Co., lot number 111107. The Hawaii Liquid Crystal Group has used numerous purification schemes on COC with the usual result that small crystals formed about one or two days after the purification. It has been reported[14] that the presence of the crystals are an indication of purity. We have found, however, by filtering the COC with the temperature just above the cholesteric-isotropic transition the crystals could be removed indefinitely. The CCl was obtained from Eastman Kodak Co. and was recrystalized twice.

Alignment was induced by rubbing the cleaned glass slides in one direction with parallel positioning of the slides maintained by two 70 μm spacers. The nP value of the sample was measured to be 717 $\pm$ 1 nm where P is the pitch and n the index of refraction. For this measurement a monochrometer was attached to a polarization microscope in the reflection mode. Measuring refracting angles the index of refraction of the sample was found to be 1.45 $\pm$ 0.05.

To measure the rotation of the plane of polarization a helium-neon laser was used as indicated in Figure 1. Care was taken in maintaining the sample in a horizontal position to avoid gravitational flow which would alter the alignment. The signal from the photomultiplier after amplification was fed to a boxcar integrator in the signal averaging mode. The average signal was applied to the y axis of an x-y plotter. The x axis was controlled by an

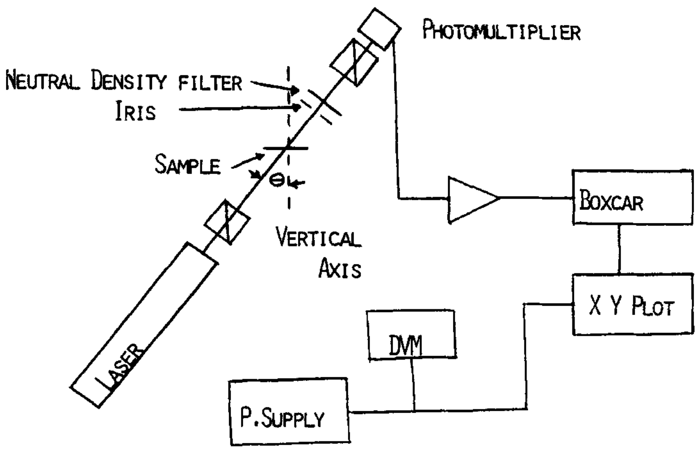

FIGURE 1 Diagram of the experiment.

independent power supply which was advanced as the analyzer was rotated. The light after transmission through the sample is elliptically rather than linearly polarized. However, the ratio of the light intensities for the analyzer parallel and perpendicular to the long elliptic axis was found to be greater than twelve to one for all incident angles. To find the rotation of the long axis which we take to be the rotation of polarization of the light it was found more accuracy could be attained by measuring the rotation of the minimum light intensity as a function of analyzer position. We define θ to be the angle the light ray makes outside the sample with the pitch axis. The results for the relative rotation, $R/R_0 \cos\theta'$, versus θ are found in Figure 2. Combining Eq. (40)–(42) we have the theoretical expression for relative rotatory power:

$$\frac{R}{R_0} = 4\cos\theta'(1-k^2)\sqrt{\frac{\cos^2\theta'(1+\cos^2\theta')^2}{64(1-k^2\cos^2\theta')^2}+\psi^2} \tag{43}$$

where

$$\sin\theta = n\sin\theta' \tag{44}$$

The relative rotation is the right side of Eq. (43) divided by $\cos\theta'$. The solid line in the graph of Figure 2 is not a best fit of this expression. Rather, since both k (1.14) and n (1.45) have been measured we can simply plot the right side of Eq. (43) divided by $\cos\theta'$ as a function of θ. The solid line in Figure 2 is the result. Within the uncertainties of our measurements the experimental results are in agreement with the theory. Using Eq. (42) η is found to be small as was assumed in the derivation, $\eta = 0.038 \pm 0.003$.

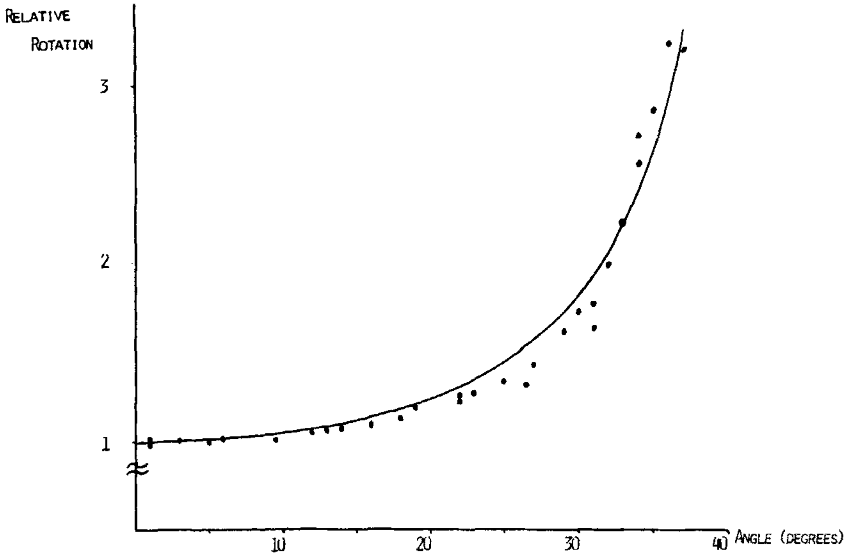

FIGURE 2 Graph of the relative rotation of the polarization axis vs. θ, the angle the incident light from outside the sample made with the pitch axis. The solid line is not a best fit to the data but the theoretical plot of Eq. (43) using the measured values of n and k.

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