

CHAPTER - V

*THEORY OF LIGHT PROPAGATION NORMAL TO THE OPTIC AXIS OF A CHOLESTERIC LIQUID CRYSTAL

INTRODUCTION :

We have so far investigated theoretically and experimentally the propagation of light along the optic axis of the cholesteric liquid crystals. The general agreement between theory and experiment confirm that the model that has been assumed is essentially correct. In this chapter we shall consider the propagation of light at right angles to the optic axis.

When light is incident normal to the screw axis of an homogeneous specimen of cholesteric liquid crystal, some interesting effects are observed. If the incident beam is parallel, diffraction patterns are formed on a distant screen somewhat similar to those produced by an optical grating. These patterns were observed by Sockmann, Meiboom, Snyder, Meixner and Dietz (1968). If the specimen is observed through a microscope, alternate dark and (relatively) bright bands are seen. When the microscope is moved either closer or further away from the specimen, there is a reversal in the pattern that is, the dark region becomes bright and the brighter region dark. These were first observed by Robinson and Ward (private communication). We shall now discuss the theory of light propagation normal to the screw axis and explain these effects in some detail.

* This theory is developed by Chandrasekhar and Chandrasekhar Prasad

Theory :

Figure (2B) in Chapter I is a schematic diagram of helical structure showing the principal axes of the successive layers rotated about OZ. We shall suppose that the principal refractive indices of each layer are n_1 and n_2 (n_1 greater than n_2).

Let a plane wave be incident along OX. Clearly a wave with electric vector polarised parallel to OZ has the refractive index same for all layers, equal to n_2 and is therefore transmitted wholly as the ordinary ray. The wave will thus appear to encounter no inhomogeneities in the medium. On the other hand, the wave with electric vector polarized parallel to OX i.e. perpendicular to OZ will encounter a refractive index which varies periodically from n_1 to n_2 along the Z direction. A plane wavefront polarized parallel to OX will therefore, suffer periodic changes in amplitude, as was first demonstrated by Wood (1934), due to the fact that parallel rays acquire a slight curvature, when travelling in a medium in which the gradient of the refractive index is normal to the direction of propagation. Thus, the amplitude and phase of the emergent wave front will vary along OZ with a periodic $P/2$ - half the pitch of helical structure and will give rise to diffraction effects. The phenomenon is analogous to the diffraction

of light by ultrasonic waves and can be solved by applying the theory of Raman and Nagendra Nath (1935).

The variation of the refractive index will cause some parts of the wave front to move faster than the other and the wave front will acquire corrugation and the emergent wave front may be expressed as

$$\Psi = \phi(y, z) \exp(2\pi i Yt)$$

where $\phi(y, z)$ is given by a Fourier's series in the form

$$\phi(y, z) = \sum_{-\infty}^{\infty} f_p(y) \exp(2\pi i p z / \Delta)$$

where $\Delta = P/2$

The diffraction from such a wavefront will evidently give rise to maxima at angles

$$\sin^{-1}(n \lambda / \Delta), \quad n = 0, 1, 2, 3, \dots$$

where λ is the wavelength of light and n half the p th of helix. To evaluate the Fourier coefficients and hence the intensities of the diffraction maxima in the general case is rather a complex problem, and we therefore, have to resort to an approximate solution.

The variation of the refractive index with twist for the electric vector polarized parallel to OX is given by the well known relation.

$$1/n_z^2 = \frac{\sin^2 \alpha}{n_1^2} + \frac{\cos^2 \alpha}{n_2^2} \dots\dots\dots(1)$$

(see Ramachandran and Ramaseshan (1961)). But this cannot be directly used without difficulty in the derivation of the theory. So we shall evaluate a simple expression as follows :

Let the ellipsoid OA OB with Centre 'O' be the optical indicatrix of the material at some point z along the Z axis, and OX be the direction of propagation of the extraordinary ray which has its electric vector in the plane of the paper Figure (1). The lengths OA and OB represent the principal refractive indices of material n_1 and n_2 . The refractive index for an extraordinary ray propagated along OX is given by OE which is the length of the diameter conjugate to OA. Consider the rectangular axes ξ and η . Let the equation of OA be

$$\eta = m_1 \xi \dots\dots\dots(2)$$

Fig.1 : Optical indicatrix of the material at a point z where $m_1 = \tan \theta = \tan 2\pi z/p$ and that of OE, $\eta = m_2 \xi \dots\dots\dots(3)$

Since $n_1^2 = 2\pi$ and $n_2^2 = P$, we have $\beta = 2\pi/P$ and β at a distance 'Z' along the Z axis is $(2\pi z/p)$. The condition for these lines to be conjugate diameters of the ellipsoid is

$$\frac{\xi^2}{n_1^2} + \frac{\eta^2}{n_2^2} = 1 \dots\dots\dots(4)$$

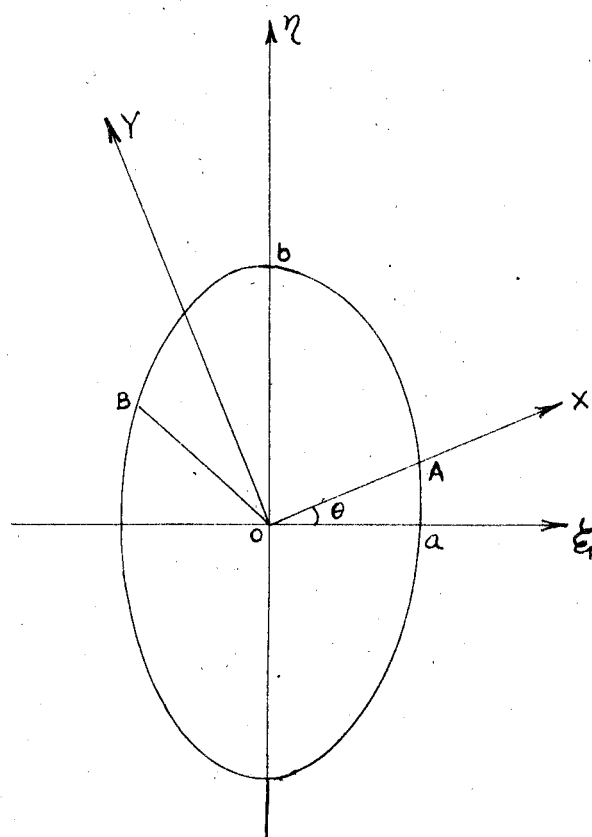


FIG. 1 Optical indicatrix of the material at a point z along the Z axis.

i.e., $m_1 m_2 = -b^2/a^2$ (from Analytical Geometry), using the value of $m_2(3)$ turns out as

$$\eta = \frac{-n_2^2 \xi}{n_1^2 m_1^2} \dots\dots(5)$$

By combining (4) and (5) the coordinates of B turn out as

$$\xi = \frac{n_1^2 m_1^2}{(n_1^2 m_1^2 + n_2^2)^{1/2}} \text{ and } \eta = \frac{n_2^2}{(n_1^2 m_1^2 + n_2^2)^{1/2}}$$

The length of OB is

$$(\xi^2 + \eta^2)^{1/2} = \left[\frac{n_1^4 m_1^2 + n_2^4}{n_1^2 m_1^2 + n_2^2} \right]^{1/2} \dots\dots(6)$$

It can be simplified by taking advantage to the fact that n_1 and n_2 are very nearly equal by putting $n_1 = n_2 + (\Delta n)$ and expanding (6) in powers of (Δn) and neglecting the terms of the order $(\Delta n)^2$ and higher we get

$$\begin{aligned} n_2 &= n_1 - (\Delta n) \cos^2 2\pi z/P \\ &= n_1 - (\Delta n) \frac{\cos 4\pi z/P - 1}{2} \\ &= 1/2 (n_1 + n_2) - 1/2 (n_1 - n_2) \cos 2\pi z/\Delta \end{aligned}$$

It can as well be taken as

$$n_z = 1/2 (n_1 + n_2) - 1/2 (n_1 - n_2) \sin 2\pi z/\Delta \quad (7)$$

The error between (7)' and (1) is quite small. For example with $n_1 = 1.8$ and $n_2 = 1.5$ the maximum error in $n_z = 0.15$ per cent; with $n_1 = 1.8$ and $n_2 = 1.5$ it is 1.2 per cent with ($n_1 = 2$) and $n_2 = 1.5$ is 3.5 per cent.

Now according to the model n_z changes discontinuously on passing from one layer to the next, but as discussed in the theory of light incident parallel to the optic axis the angle between the principal axes of the successive molecular layers in the helical structure is only of the order of 10^{-2} radians or less, so that to a good approximation (1) may be taken to be continuously varying function. One further approximation made is that the curvature of the ray in the medium and consequent changes of the amplitude are negligible. If only the first few orders of diffraction are of interest, this approximation is valid when (λ/Λ) is small (Roman and Nagendra Nath, 1936). After passing through a cell of thickness L , the transmitted wave at a height z will be given by

$$\Psi = \exp \left[2\pi i \gamma (t - n_z L/c) \right]$$

The diffracted amplitude along a direction making an angle θ with respect to the direct beam will be proportional to

$$\int_{-d}^d \exp \left[\frac{2\pi i}{\lambda} \left\{ z \sin \theta + L/2 (n_1 - n_2) \sin \left(\frac{2\pi z}{\Lambda} \right) \right\} \right] dz$$

where $2d$ is the width of the beam along the z axis. Therefore the term involving $(n_1 + n_2)/2$ does not contribute anything to

the corrugation of the wave front along the Z axis. So it is neglected. Putting

$$u = 2\pi/\lambda; \quad b = 2\pi/\Delta; \quad v = \pi L \left[(n_1 - n_2)/\lambda \right]$$

the real and imaginary parts of the Integral turn out respectively as

$$I_1 = \int_{-d}^d \left[\cos(uz \sin \theta) \cos(v \sin bz) - \sin(uz \sin \theta) \sin(v \sin bz) \right] dz$$

and

$$I_2 = \int_{-d}^d \left[\sin(uz \sin \theta) \cos(v \sin bz) + \cos(uz \sin \theta) \sin(v \sin bz) \right] dz$$

Now we have the standard expansions

$$\begin{aligned} \cos(v \sin bz) &= 2\sum' J_{2r}(v) \cos(2rbz) \\ \sin(v \sin bz) &= 2\sum J_{2r+1}(v) \sin((2r+1)bz) \quad (\text{see} \\ &\quad \text{Watson, 1944}) \end{aligned}$$

where the summations extend from zero to infinity and indicates that the coefficient of J_0 is half that of the other terms.

We obtain

$$\begin{aligned} I_1 &= 2\sum' J_{2r}(v) \int_{-d}^d \cos(uz \sin \theta) \cos(2vBz) dz \\ &\quad - 2\sum J_{2r+1}(v) \int_{-d}^d \sin(uz \sin \theta) \sin((2r+1)bz) dz \end{aligned}$$

Using the transformation of products into sums or differences

$$\begin{aligned} 2 \cos A \cos B &= \cos(\text{sum}) + \cos(\text{difference}) \\ 2 \sin A \sin B &= \cos(\text{difference}) - \cos(\text{sum}) \end{aligned}$$

We have

$$\begin{aligned}
 I_1 &= E' J_{2r}(v) \int_{-d}^d \left[\cos \left\{ (u \sin \theta + 2rb) z \right\} + \cos \left\{ (u \sin \theta - \right. \right. \\
 &\quad \left. \left. 2 \pm b) z \right\} \right] dz \\
 &+ E J_{2r+1}(v) \int_{-d}^d \left[\cos \left\{ (u \sin \theta + \overline{2r+1} b) z \right\} - \cos \left\{ (u \sin \theta - \right. \right. \\
 &\quad \left. \left. \overline{2r+1} b) z \right\} \right] dz \\
 &= 2d E' J_{2r}(v) \left[\frac{\sin \left\{ (u \sin \theta + 2rb) d \right\}}{(u \sin \theta + 2rb) d} + \right. \\
 &\quad \left. \frac{\sin \left\{ (u \sin \theta - 2 \pm b) d \right\}}{(u \sin \theta - 2 \pm b) d} \right] \\
 &+ 2d E J_{2r+1}(v) \left[\frac{\sin \left\{ (u \sin \theta + \overline{2r+1} b) d \right\}}{u \sin \theta + \overline{2r+1} b \cdot d} - \right. \\
 &\quad \left. \frac{\sin \left\{ (u \sin \theta - \overline{2r+1} b) d \right\}}{(u \sin \theta - \overline{2r+1} b) \cdot d} \right] \dots (8)
 \end{aligned}$$

$$\begin{aligned}
 I_2 &= Q E' J_{2r}(v) \int_{-d}^d \sin In? \sin \theta) \cos (2rbz) dz \\
 &+ 2 E J_{2r+1}(v) \int_{-d}^d \cos (u \sin \theta) \sin (\overline{2r+1} bz) dz
 \end{aligned}$$

Using the formulations : $2 \sin A \cos B = \sin (\text{sum}) + \sin (\text{difference})$

$2 \cos A \sin B = \sin (\text{sum}) - \sin (\text{difference})$

and simplifying in the previous way the diffraction integral

I_2 turns out as zero.

We see that the magnitude of each individual term in (8) attains its highest maximum (the other maxima being negligibly small compared to the highest) when its denominator vanished. Also we see that when any one of the terms is maximum all the others have negligible values as the numerator of each cannot exceed unity and the denominator is some integral nonvanishing multiple of b which is sufficiently large. So the maxima of the magnitude of (8) corresponds to the maxima of diffraction occur when

$$u \sin \theta + 2rb = 0$$

or when

$$u \sin \theta \pm (2r + 1) b = 0$$

that is

$$u \sin \theta \pm nb = 0 \quad \dots\dots(9)$$

'n' is an odd or even positive integer. The equation (9) gives the directions in which the magnitude of the amplitude is maximum which corresponds also to the maximum of the intensity. Substituting for u and b , the condition for maximum may be expressed more generally as

$$\sin \theta = \pm n \lambda / \Delta \quad \dots\dots(10)$$

The magnitudes of the various components in the directions given by (10) can be calculated if we know

$$J_n(x) \text{ or } J_n \left(\pi L \frac{n_1 - n_2}{\lambda} \right)$$

Thus, the relative intensities of the m^{th} component to the n^{th} component i.e., the ratio of the intensities of the m^{th} and n^{th} orders is

$$\frac{J_m^2(v)}{J_n^2(v)}$$

where

$$v = \pi L (n_1 - n_2) / \lambda$$

In the isotropic case $(\Delta n) = n_1 - n_2 = 0$

In the case all the other orders vanish except the zero component for

$$J_m(0) = 0 \text{ for all } m \neq 0 \text{ and } J_0(0) = 1$$

Comparison with experiment :

Diffraction patterns :

Diffraction patterns were reported in cholesteric liquid crystals by Meiboom, et al. (1968). In fact these authors has pointed out the similarities between the phenomenon and the diffraction by ultrasonic waves. In their experiment, a laser beam was sent at right angles to the optic axis of a liquid crystalline mixture of cholesteryl chloride and cholesteryl myristate which was placed in a magnetic field. In vary strong fields in plane and thus the screw axis aligns parallel to the field. The sample was heated by a stream of hot nitrogen gas and was allowed to align for about four to five hours. This magnetically aligned crystal exhibited periodically varying refractive

index and acted as an optical grating. When the beam of Helium-Nitrogen Laser (63128 Å) was directed on the sample perpendicular to the field, diffraction patterns were observed (Fig.2). (Sackmann etc. (1968), R.W. Wood 1934).

The cholesteryl chloride and the cholesteryl myristate have helical structures of opposite senses, so that the pitch of the liquid crystalline mixture could be altered by the changing the temperature. Thereby the positions of the diffraction spots also shifted accordingly. The diffraction maxima were strongly polarized with the electric vector perpendicular to the screw axis; as it to be expected. Perfect polarization could not be achieved because of some depolarization due to scattering. No intensity measurements have been reported by them. At a certain temperature, there occurred an exact compensation of the two opposite screw structure and the sample became nematic with $P = \infty$, then all the molecules are parallel to one another and perpendicular to the magnetic field. Under these circumstance only the central spot was present.

We now evaluate the relative intensities of the diffraction maxima for some typical values of the parameters involved. Sackmann, et al (1968)

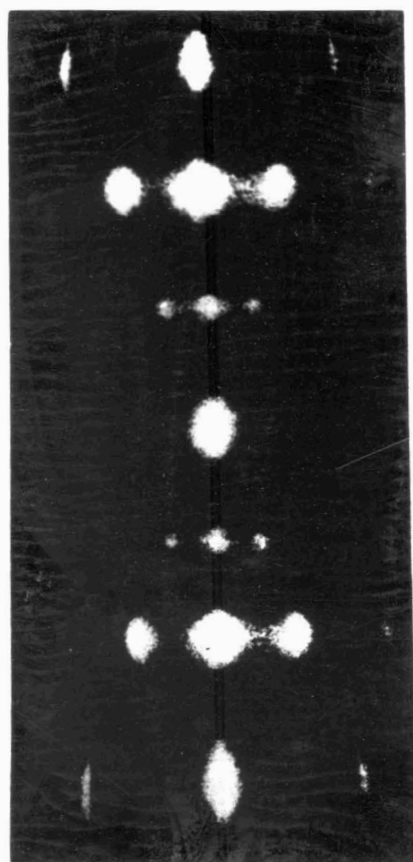
used a cell of thickness $L = 0.025$ cms and Helium-Neon Laser beam (6328 Å). The layer birefringence Δn in cholesteric liquid crystal usually lies in the range 0.005 to 0.3. Substituting these values of L , $(\)$ and $n_1 - n_2$ in the expression for intensities of diffraction pattern and using the well known expansion

$$J_n(v) = \left(\frac{v}{\pi}\right)^{1/2} \left[\cos(v - n\pi/2 - \pi/4) \left\{ 1 - \frac{(4n^2 - 1^2)(4n^2 - 3^2)}{2! (8v)^2} + \frac{(4n^2 - 1^2)(4n^2 - 3^2)(4n^2 - 5^2)(4n^2 - 7^2)}{4! (8v)^4} + \dots \right\} - \sin(v - n\pi/2 - \pi/4) \left\{ \frac{(4n^2 - 1^2)}{1! (8v)} - \frac{(4n^2 - 1^2)(4n^2 - 3^2)(4n^2 - 5^2)}{3! (8v)^3} + \dots \right\} \right] \quad (Watson, 1944)$$

the relative intensities of the zero first and second order maxima have been plotted. There are shown in Figures 3 and 4 for a few values of $n_1 - n_2$ ranging from 0.005 to 0.25 which correspond to v ranging from 6.2 to 310.3. The calculations illustrate the pronounced changes which can be seen in the intensity distribution under different experimental conditions.

We also notice from the figure that the relative intensities of the diffraction maxima will not lead to

3568



31

36°

39°

42°

46°

49°

53°

Figure 1. Diffraction pattern of a 1.75:1 by weight ratio

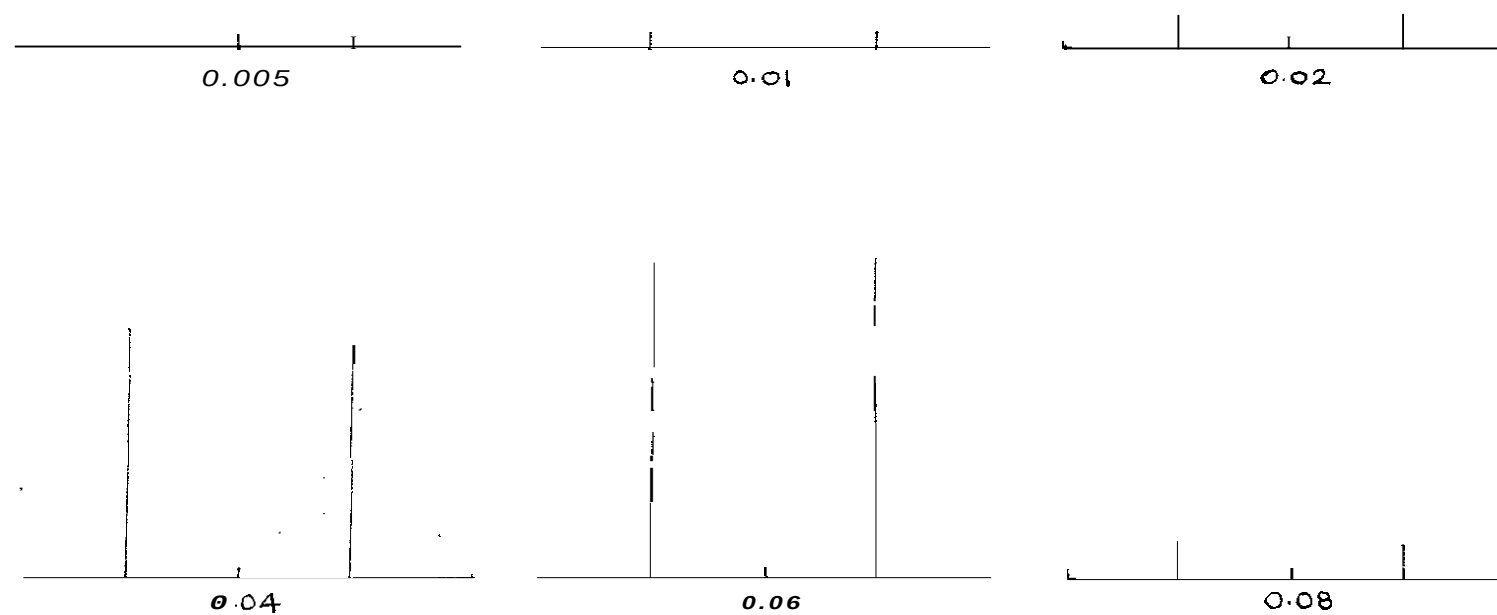


FIG. 3. Relative intensities of the zero, first and second order maxima for different values of Δn

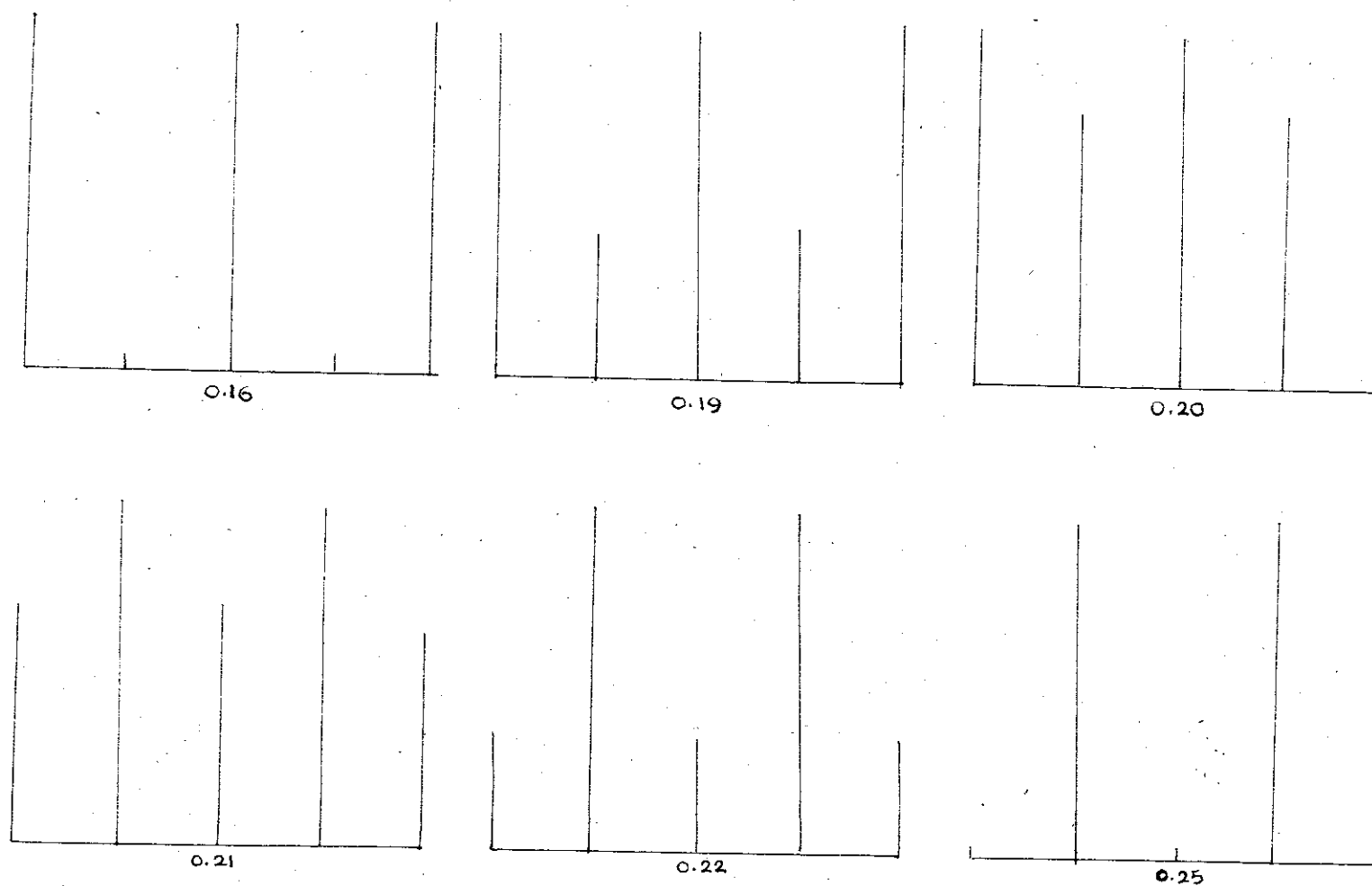


FIG. 4. Relative intensities of the zero, first, second order maxima for different value of (Δn) .

an unambiguous experimental determination of $n_1 - n_2$. But by an experiment with two different thicknesses and under same experimental conditions ($n_1 - n_2$) can be determined.

A focussing periodicity in poly-γ-benzyle-L-glutamate liquid crystalline solutions.

As described in Chapter I, Robinson and co-workers (1957, 1958, 1961, and a private communication) discovered that certain polypeptides dissolved in organic solvents adopted the cholesteric structure, usually of very large pitch 100 μ above a certain concentration. These authors observed that when these homogeneously aligned specimens are viewed through a microscope at right angles to the optic axis, a series of equidistant parallel dark lines (with spacings of the order of 0.1 to 0.001 μ m) interspersed with lighter lines, running perpendicular to the helical (or optic) axis are seen, when the light was polarized with the electric vector perpendicular to the helical axis. The distance between the adjacent dark (or bright) lines was $P/2$. The lines vanished when the electric vector was related so as to be parallel to the helical axis. It has been further observed (Ward, 1957, private communication) that when the light was polarized with the electric vector perpendicular to the helical

axis, and the microscope was racked slowly upwards (or down wards) the lines at first become blurred and were then replaced by a similar set of lines displaced side ways along the helical axis by $P/4$. On racking the microscope a little further the lines again become blurred and finally replaced by a set of equivalent to the original one. This sequence could be repeated several times and the repeat period was substantially constant. The author has described this effect as a 'focussir periodicity'.

The focusing periodicity may be explained in terms of the model discussed earlier. In deriving the theory, we assumed the incident beam to be prefectly parallel and neglected any deviations in the path of the rays on traversing the medium. On the other hand *if* there is a very slight divergence in the beam, the rays will be deviated, as was demonstrated by some beautiful experiments of R.W. Wood (1934) with the following set up.

A glass trough 50 cms. long by 10 cms. high and 2 cms., wide with plate glass ends *is* filled to the depth of 3 cms. with plate glass ends, is filled to the depth of 3 cms with a strong solution of alum. On this is floated a layer of water containing 10 % of alcohol, which is very much lighter than the alum

solution, though having about the same refractive index. A mixture of glycerine and 85 per cent alcohol has a much higher refractive index, but a specific gravity intermediate between these two liquids, consequently it is possible by means of a glass siphon, drawn down to a small aperture which is bent in a horizontal direction, to introduce a layer of it between the alum solutions and the supernatant water. The three solutions were previously acidified with sulphuric acid, and rendered fluorescent with sulphate of quinine in order that the paths of the rays could be followed. By cautious stirring the diffusion of the layers into each other can be assisted, and we have as a result, a medium in which the refractive index increases from the surface towards the sodium plane, and then decreases from this plane towards the bottom,

Now, if a very narrow beam of light from an arc-lamp, made parallel by means of a condensing lens, be thrown obliquely into one end of the trough, it will be seen to traverse the liquid in the form of a most beautiful blue wave, the curvature of which varies with the angle at which the ray enters. A ray of light travelling in a sine curve is shown in Fig. 5(a and b). (~~Fig. 5(a and b) showing the path of a ray of light travelling in a sine curve.~~).

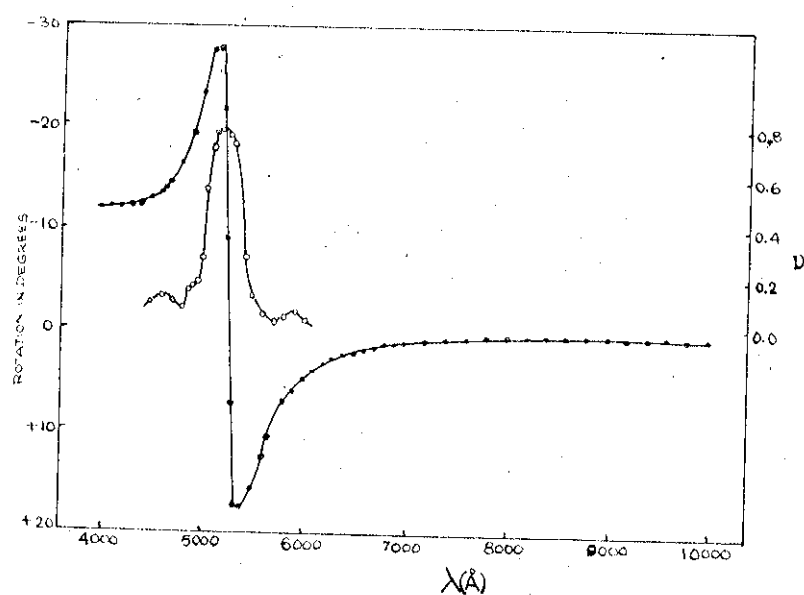


FIG.5 Circular dichroism and rotatory dispersion of cholesteric cinnamate at 177°C. Thickness $\sim 3\mu$.

The alternate convergence and divergence of rays, and the successive foci was obtained by allowing a nearly parallel bundle of rays to enter on end of the through in a horizontal direction. A

~~photograph of this phenomenon is given above (page 15).~~

From Wood's experiments it is obvious that when a slightly divergent beam is incident normal to the optic axis of a cholesteric liquid crystal, there will be in the field of view planes in which the beam will be in focus interlaid by planes in which it will be out of focus interlaid by planes in which it will be out of focus. This therefore explains the focussing periodicity observed by Robinson and Ward.

APPLICATIONS OF CHOLESTERIC LIQUID CRYSTALS.

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