

CHAPTER - III

THEORY OF LIGHT PROPAGATION ALONG THE OPTIC AXIS OF A CHOLESTERIC LIQUID CRYSTAL - FILMS OF FINI- TE THICKNESS

INTRODUCTION

The theory developed in the previous chapter is valid for infinitely thick specimens. In practice, measurements are always made only on thin films. The optical properties of thin films may be expected to be slightly different from that of very thick specimens. We shall ^{discuss CS theory and its extension} ~~therefore extend the theory~~ of reflection, circular dichroism and rotatory dispersion to take into account the finite thickness of the film.

Theory of reflection : As before, we calculate the effect of multiple reflections by setting up difference equations similar to Chase formulated by Darwin (1914, 1922). Again, as before, we first regard the liquid crystal to consist of a set of parallel planes P apart and ascribe a reflection coefficient $-iQ$ to each plane for right circularly polarized light at normal incidence. Let T_r and S_r be the complex amplitudes of the primary and the reflected waves at a point just above the plane.

The top most plane is designated by the serial number zero. Neglecting the normal absorption coefficient, which is in fact extremely small in the visible spectrum for most of these compounds (see Ferguson, 1966), the difference equation may be written

$$S_r = -1QT_r + \exp(-i\phi) S_{r+1} \dots\dots\dots(1)$$

$$T_{r+1} = \exp(-i\phi) T_r - 1Q \exp(-2i\phi) S_{r+1} \dots\dots(2)$$

where $\phi = 2\pi ndP/\lambda$. The reflection coefficient is taken to be same on both sides of the plane. Replacing r by $(r-1)$ in (1) and (2)

$$S_{r-1} = -1Q T_{r-1} + e^{-i\phi} S_r \dots\dots\dots(3)$$

$$T_r = \exp(-i\phi) T_{r-1} - 1Q \exp(-2i\phi) S_r \dots\dots(4)$$

Putting (4) in (1)

$$\begin{aligned} S_r &= -1Q \left[\exp(-i\phi) T_{r-1} - 1Q \exp(-2i\phi) S_r \right] + \\ &= 1Q \exp(-i\phi) \left[\frac{S_{r-1} - \exp(-i\phi) S_r}{-1Q} \right] - Q^2 \exp(-2i\phi) S_r + \exp(i\phi) S_{r+1} \end{aligned}$$

Rearranging

$$S_r + \exp(-2i\phi) S_r + Q^2 \exp(-2i\phi) S_r = \exp(-i\phi) S_{r+1} + \exp(-i\phi) S_{r-1}$$

: 3 :

$$S_r \left[\exp(i\theta) + \exp(-i\theta) + Q^2 \exp(-i\theta) \right] = S_{r+1} + S_{r-1}$$

Similarly

$$T_r \left[\exp(i\theta) + \exp(-i\theta) + Q^2 \exp(-i\theta) \right] = T_{r+1} + T_{r-1}$$

$$T_{r+1} + T_{r-1} = y T_r \dots\dots\dots(5)$$

$$S_{r+1} + S_{r-1} = y S_r \dots\dots\dots(6)$$

where $y = \exp(i\theta) + \exp(-i\theta) + Q^2 \exp(-i\theta)$

Suppose that the film consists of n planes, putting

$S_n = 0$ we have from (6)

$$S_{n-2} = y S_{n-1}$$

$$S_{n-3} = y S_{n-2} - S_{n-1} = (y^2 - 1) S_{n-1}$$

$$S_{n-4} = (y^3 - 2y) S_{n-1} \text{ etc.}$$

$$\text{and } S_0 = \left[y^{n-1} - \frac{(n-2)}{1!} y^{n-3} + \frac{(n-4)(n-3)}{2!} y^{n-5} + \dots \right] S_{n-1}$$

$$= f_n(y) S_{n-1} \text{ (say) } \dots\dots\dots(7)$$

Similarly from (2)

$$T_{n-1} = \exp(i\theta) T_n ; \text{ since } S_n = 0$$

$$T_{n-2} = \left[y \exp(-i\theta) - 1 \right] T_n$$

$$T_{n-3} = \left[(y^2 - 1) \exp(-i\theta) - y \right] T_n, \text{ etc.}$$

: 4 :

and

$$T_0 = \left[f_m(y) \exp(i\theta) - f_{m-1}(y) \right] T_m \dots\dots(8)$$

Since from (1)

$$S_{m-1} = -iQ T_{m-1} = -iQ \exp(i\theta) T_m$$

the ratio of the reflected to the incident amplitudes is

$$\frac{S_0}{T_0} = \frac{iQ f_m(y) \exp(i\theta)}{f_m(y) \exp(i\theta) - f_{m-1}(y)} \dots\dots\dots(9)$$

Let us assume a relation in the form $T_{r+1} = x T_r$ so that x satisfies

$$x + 1/x = y = \exp(i\theta) + \exp(-i\theta) + Q^2 \exp(-i\theta) \dots\dots(10)$$

We have seen that the reflection condition is $n_d p = \lambda_0$ or $\theta_0 = 2\pi$ Accordingly we may write

$$\theta = 2\pi \lambda_0/\lambda = \theta_0 + \epsilon \dots\dots(11)$$

where $\epsilon = -2\pi (\lambda - \lambda_0)/\lambda \dots\dots\dots(12)$

which is a small quantity in the neighbourhood of the reflection.

Therefore, from (10)

$$x + 1/x = \exp(i\epsilon) + \exp(-i\epsilon) + Q^2 \exp(-i\epsilon) \dots\dots(13)$$

This suggests that in the neighbourhood of the reflection we may put

$$x = \exp(-\xi) \exp(-i\theta_0) = \exp(-\xi) \dots\dots\dots(14)$$

where ξ is small and may be complex. From (13) and (14)

: 5 :

$$\epsilon \simeq \pm (q^2 - e^2)^{1/2} \dots\dots\dots(15)$$

The series in (7) can be summed as follows: Consider the series

$$\frac{\sin n\theta}{1 - 2x \cos \theta + x^2} = \sin n\theta + \sin 2\theta + x^2 \sin 3\theta + x^{n-1} \sin n\theta + \dots$$

which can be easily verified to be true by multiplying each side by $(1 - 2x \cos \theta + x^2)$

We observe that

$$\frac{\sin n\theta}{\sin \theta} = \text{Coefficient of } x^{n-1} \text{ in } (1 - 2x \cos \theta + x^2)^{-1}$$

that is the coefficient of x^{n-1} in

$$1 + x(2 \cos \theta - x) + x^2 (2 \cos \theta - x)^2 + \dots + x^{n-3} (2 \cos \theta - x)^{n-3} + x^{n-2} (2 \cos \theta - x)^{n-2} + x^{n-1} (2 \cos \theta - x)^{n-1} + x^n (2 \cos \theta - x)^n + \dots$$

Now the coefficient of x^{n-1} in $x^{n-1} (2 \cos \theta - x)^{n-1}$

is $(2 \cos \theta)^{n-1}$; the coefficient of x^{n-1} in x^{n-2}

$(2 \cos \theta - x)^{n-2}$ is the coefficient of x in $(2 \cos \theta)^{n-2} =$

$$-(n-2) (2 \cos \theta)^{n-3}$$

coefficient of x^{n-1} in $x^{n-3} (2 \cos \theta - x)^{n-3}$ is the

coefficient of x^2 in $(2 \cos \theta - x)^{n-3} =$

$$\frac{(n-3)(n-4)(2 \cos \theta)^{n-5}}{1 \cdot 2} ; \text{ and so on}$$

Hence the series is

$$\frac{\sin n \theta}{\sin \theta} = (2 \cos \theta)^{n-1} - (n-2)(2 \cos \theta)^{n-3} + \frac{(n-3)(n-4)}{2!} (2 \cos \theta)^{n-5} - \frac{(n-4)(n-5)(n-6)}{1 \cdot 2 \cdot 3} (2 \cos \theta)^{n-1} + \dots$$

If we put $\theta = i \xi$ $\sin \theta = i \sinh(\xi)$ and $\cos \theta = -i \cosh(\xi)$ substituting in the series expression we had

$$\frac{\sinh(m\xi)}{\sinh(\xi)} = y^{n-1} - \frac{(n-2)}{1!} y^{n-3} + \frac{(n-3)(n-4)}{2!} y^{n-5} \dots \text{(id)}$$

The above series is identical with $f_m(y)$ when

$$y = \exp(+\xi) + \exp(-\xi) = 2 \cosh(\xi)$$

Thus the series in (7) reduces to

$$f_m(y) = \frac{\sinh(m\xi)}{\sinh(\xi)} \dots \dots \dots (17)$$

(See also Gradshteyn and Ryzhik, 1965).

Substituting in (9) we have

$$\frac{S_0}{T_0} = \frac{-iQ \sinh(m\xi)}{\sinh(\xi)} \exp(i\theta) = \frac{\frac{\sinh(m\xi)}{\sinh(\xi)} \exp(i\theta) - \frac{\sinh(m-1)\xi}{\sinh(\xi)}}{-iQ \exp(i\theta)} = \frac{i \exp(i\theta)}{1 \cosh(m\xi) - \cosh(m-1)\xi} \sinh(m\xi)$$

$$= \frac{-1Q \exp(i\epsilon)}{1\epsilon + e^{m\epsilon} + e^{-m\epsilon} - \frac{e^{-m\epsilon} + (e^{m\epsilon} - e^{-m\epsilon})}{e^{m\epsilon} + e^{-m\epsilon}}}$$

$$\frac{S_0}{T_0} = \frac{-1Q \exp(i\epsilon)}{1\epsilon + \cot h(m\epsilon)} \dots\dots\dots(18)$$

$$= \frac{i\epsilon + iQ \cot h(m\epsilon)}{\epsilon^2 + \epsilon^2 \cot h^2(m\epsilon)}$$

$$R = |S_0/T_0|^2 = \frac{Q^2 \epsilon^2 + Q^2 \epsilon^2 \coth^2 m}{(\epsilon^2 + \epsilon^2 \coth^2 m \epsilon)^2} = \frac{Q^2}{\epsilon^2 + \epsilon^2 \coth^2 m \epsilon} \dots(19)$$

for infinitely thick specimen ($m \rightarrow \infty$) this reduces to

$$\frac{S_0}{T_0} = \frac{-Q}{\epsilon + i\epsilon} = \frac{Q}{\epsilon \pm i(Q^2 - \epsilon^2)^{1/2}} \dots\dots(20)$$

when $-Q < \epsilon < Q$ is real and π

$$R_{inf} = |S_0/T_0|^2 = 1$$

The reflection is therefore total within this range.

The spectral width of total reflection turns out

as $(2P \Delta n)/\pi$. We have shown before that

$$Q^2 = Q_0^2 [(\sin \epsilon/\epsilon)]^2$$

in the neighbourhood of reflection. Using (19) and (20)

with the above expression some theoretical reflection curves have been worked out for various values of m and some typical values of the constants.

$$\lambda_0 = 6000 \times 10^{-8} \text{ cm}, P = 4000 \times 10^{-8} \text{ cm}, n_d = 1.5, Q_0 = 0.1$$

$$(i.e. (\Delta n) = 0.075)$$

These are shown in Fig.1 and 2. The reflection curves for $Q_0 = 0.05$ (i.e. $(\Delta n) = 0.0375$), all other parameters remaining the same are shown in Figures 3 and 4.

The theory gives some interesting new results. For specimens with finite film thickness the reflection curves (and hence the circular dichroism curves) should give some secondary maxima along with the principal maximum. As the film thickness is increased the intensity of the principal maximum increases while its width decreases. At the same time the subsidiary secondary maxima increase in number and get closer together. For the very thick specimen the principal and the subsidiary maxima get so much close together that they merge to give a single flat-topped maximum which is also predicted by the previous theory. The width of the total reflection for the very thick specimen is $2P\Delta n/\pi$. For a given n , the peak heights as well as the spacing between the maxima vary with Q (i.e. with Δn). The

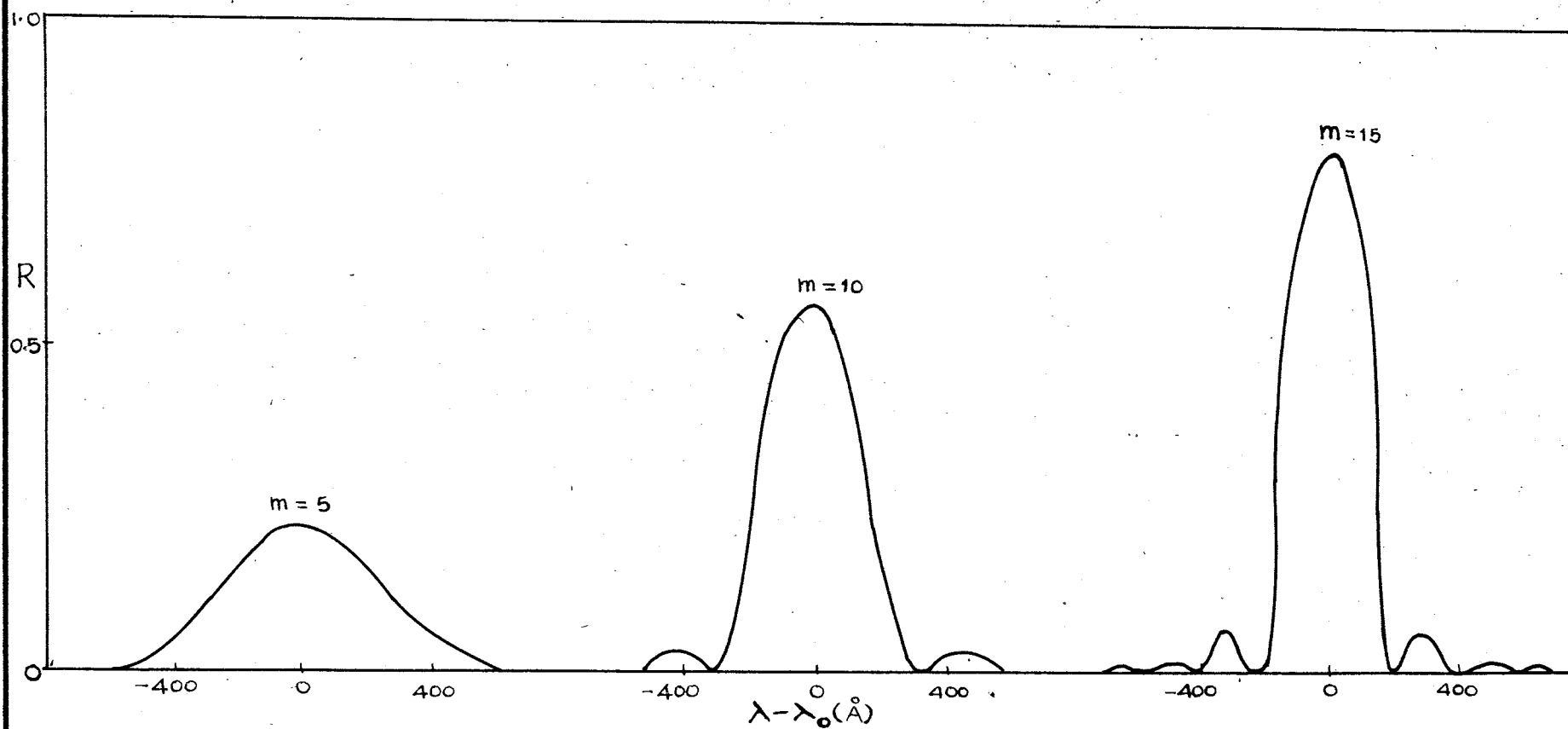


FIG. 1 Theoretical reflection curves for different values of m ($Q_0 = 0.1$).
Film thickness = mP . P is the pitch of the helix.

smaller the reflection coefficient Q , the lesser the peak height and the more spread out the secondary maxima.

Circular dichroism : From (8) we have

$$\frac{T_m}{T_0} = \left[f_m(y) \exp(i\theta) - f_{m-1}(y) \right]^{-1}$$

Using (17) we have

$$\begin{aligned} \frac{T_m}{T_0} &= \left[\exp(i\theta) \frac{\sinh(m\xi)}{\sinh(\xi)} - \frac{\sinh(m-1)\xi}{\sinh(\xi)} \right]^{-1} \\ &\approx \frac{\xi \operatorname{cosech}(m\xi)}{i\theta + \xi \coth(m\xi)} \dots\dots\dots(21) \end{aligned}$$

$$\begin{aligned} \left| \frac{T_m}{T_0} \right|^2 + \left| \frac{S_0}{T_0} \right|^2 &= \frac{Q^2}{\theta^2 + \xi^2 \coth^2 m} + \frac{\operatorname{cosech}^2 m \xi}{\theta^2 + \xi^2 \coth^2 m \xi} \\ &= \frac{Q^2 = Q^2 + \theta^2 + 2\coth^2 m}{\theta^2 + \xi^2 \coth^2 m^2 \xi} = 1 \end{aligned}$$

The Circular dichroism

$$D = \frac{I_1 - I_R}{I_1 + I_R}$$

where I_1 and I_R are the intensities of the transmitted light of for the left and right circular polarizations. Since left circular light is not attenuated by reflection we may put

$$D = \frac{1 - \left| \frac{T_M}{T_0} \right|^2}{1 + \left| \frac{T_M}{T_0} \right|^2} = \frac{R}{2 - R} \dots\dots\dots(22)$$

Since R plotted as a function of wave length exhibits primary and secondary maxima, D plotted as a function of wave length should exhibit primary and secondary maxima similar to the reflection curve except that the peaks will be less pronounced.

Anomalous rotatory dispersion : In the region of normal dispersion the optical rotation per thickness P of the liquid crystal is $1/2(\phi_d - \phi_l)$ and the rotatory power in radians per cm

$$= \frac{1}{2P} (\phi_d - \phi_l) = \frac{-\pi (a) \dots \dots}{4 \lambda^2}$$

where ϕ_d and ϕ_l are the phase retardations for right and left circular light. Here a clockwise rotation as seen along the direction of light propagation is taken as positive.

Near the region of reflection, the dynamical theory predicts that right circular component suffers anomalous phase retardation. Left circular light, on the other

hand exhibits normal behaviour throughout, and as a consequence the rotatory dispersion is anomalous in the vicinity of the reflection.

The phase of the right circular wave can be evaluated from (21). The ratio of the incident to the transmitted amplitudes may be expressed

$$\frac{T_R}{T_0} = A \exp -im(\theta_0 + \psi) = A \exp (-im\psi)$$

$$\text{Where } \tan m\psi = \frac{\epsilon}{\xi \cosh m\xi}$$

The optical rotation per thickness P is

$$\frac{1}{2} (\theta_0 + \psi - \theta_1) = \frac{1}{2} (\theta_0 - \theta_1) + (\psi - \epsilon)$$

Hence the rotatory power in radians per centimeter is

$$\rho = \frac{-\pi (\Delta n)^2 P}{4 \lambda^2} + \frac{(\psi - \epsilon)}{2P} \dots\dots (23)$$

Far away from the region of reflection on either side i.e. when

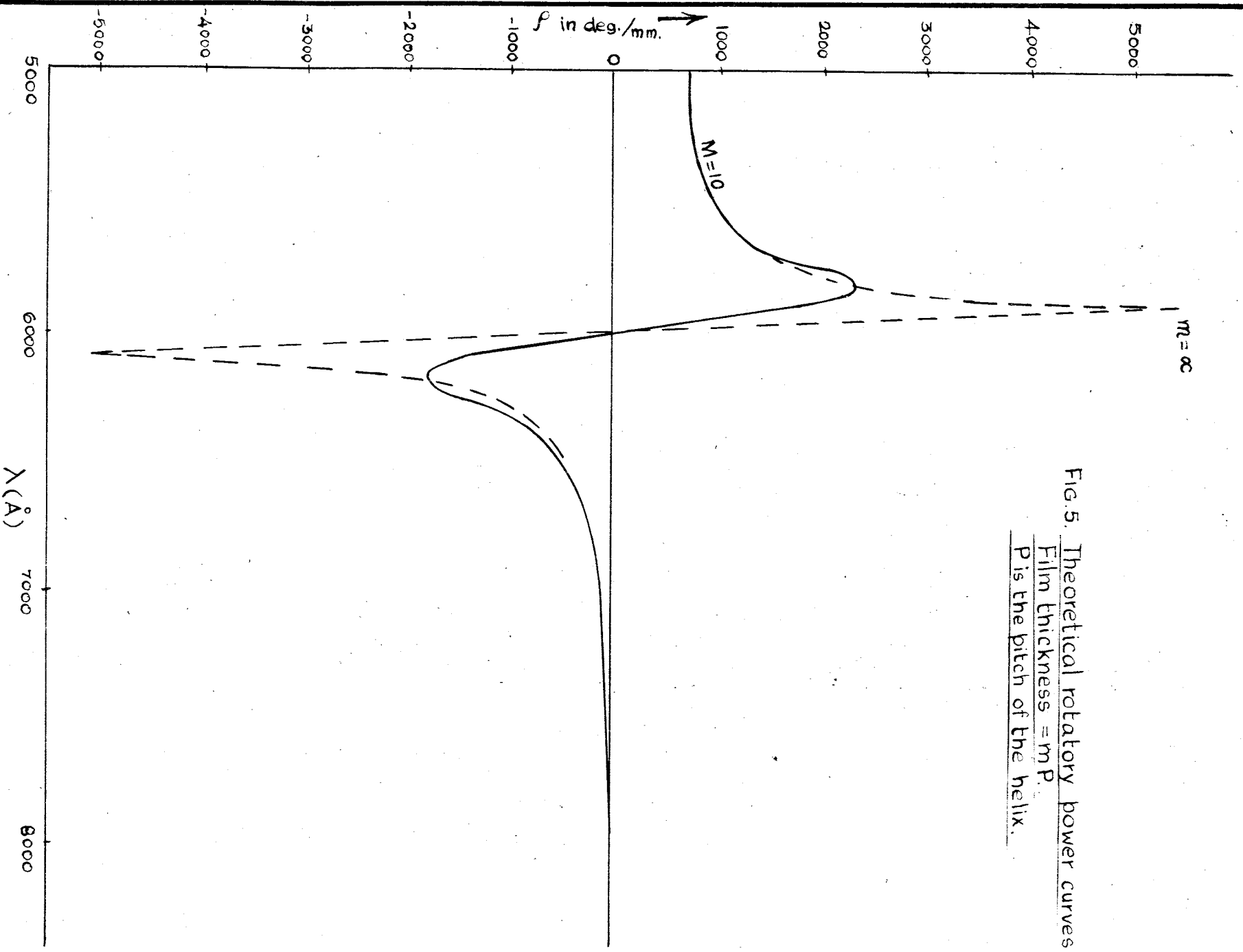
$$\epsilon^2 \gg (Q_0^2 \sin^2 \epsilon / \epsilon^2), \xi = i\epsilon$$

from (14) so that ϵ and the rotatory power reduces to the normal value.

We give some theoretical rotatory dispersion curves for some typical values of the parameters involved;
 $\lambda_0 = 6000 \times 10^{-8}$ cm $P = 4000 \times 10^{-8}$ cm, $n_d = 1.5$,
 $Q_0 = 0.1$ or $(\Delta n) = 0.075$ at $4000\text{\AA}$. The layer birefringence is assumed to vary linearly from 0.1 at $4000\text{\AA}$ to 0.075 at $6000\text{\AA}$ and extrapolated to longer wavelengths. Figs 5 and 6 gives the rotatory power of the right handed structure using the standard sign convention according to which a clockwise rotation as seen by an observer looking at the source of light is taken as positive.

The anomalous rotatory dispersion curve for a film of finite thickness varies smoothly with wavelength and does not show the abrupt changes as in the thick specimen case (Fig.5). In particular the rotatory power at the edge of the reflection band has been blunted out instead of being very sharp as in the case of the very thick specimen. The rotation varies linearly with thickness far away from the region of reflection. However, as we approach the reflection band, the rotation does not vary linearly with thickness, but increases in an abnormal way (see figure 5). This is because the reflection characteristics of the specimen change with the thickness. As the thickness is increased the variations in the

Fig. 5. Theoretical rotatory power curves.
Film thickness = mP .
 P is the pitch of the helix.



rotatory power around the reflection band become more and more pronounced, until finally beyond a certain thickness, the rotatory COWER curves show sharp changes of slope (Fig.6). We see that the observed results in the real experimental situation, namely, the smooth rounded form of the rotatory dispersion curves of Mathieu (1938) and Ferguson (1937) can be easily accounted for by this theory.

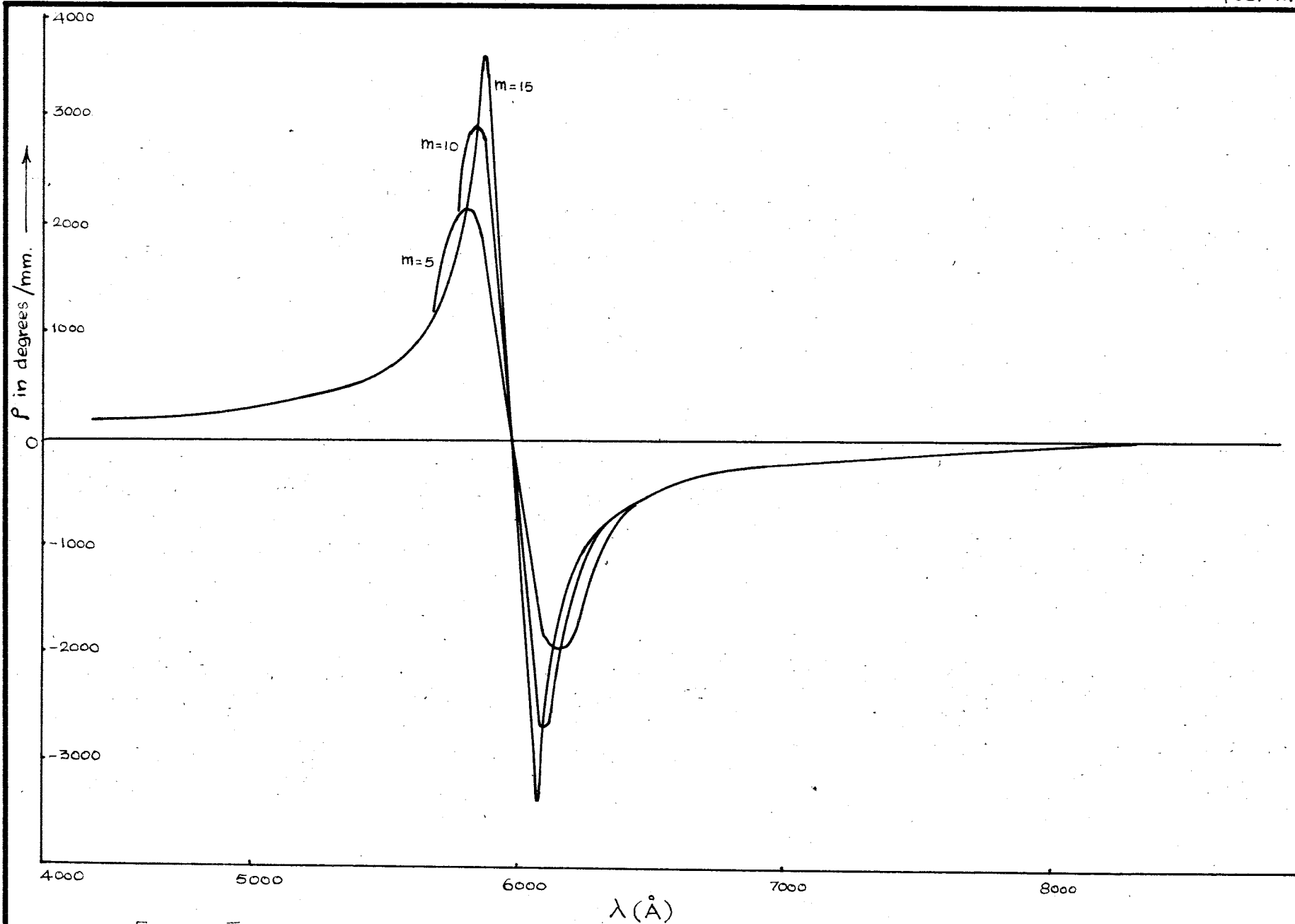


FIG. 6 Theoretical rotatory dispersion curves. (Film thickness = mP . P is the thickness of the helix)