Mr J.R.Luyten performed the diagonalization of the field gradient tensors with the help of the Telefunken TR4 Computer of the 'Rekencentrum' of the University. Dr P.Bennema helped in growing the single crystals. Mr S.Postma constructed the crystal holder.

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Optical Rotatory Power of Liquid Crystals

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A theory of the very high rotatory power exhibited by cholesteric liquid crystals is developed by the use of the Jones calculus for optical systems. The calculations are based on the model proposed by de Vries in which the liquid crystal is regarded as built up of a large number of thin birefringent layers arranged helically. When light is incident normal to the layers, *i.e.* along the screw axis, selective reflexion of one of the circularly polarized components takes place and the rotatory dispersion in the neighbourhood of the region of reflexion is anomalous. The reflexion curve and the amplitude attenuation factor, $\exp(-\xi)$, for circularly polarized light at normal incidence are derived as functions of wavelength by setting up difference equations closely similar to those formulated by Darwin in his dynamical theory of X-ray diffraction. Within the range of total reflexion, ξ is real, primary extinction occurs and the medium is highly circularly dichroic. The spectral width of the reflexion and the primary extinction coefficient predicted by theory compare favourably with the experimental values. Outside the region of total reflexion, ξ is imaginary and opposite in sign on opposite sides of the reflected band. This is responsible for the reversal of the sign of the rotation on crossing the band. The anomalous part of the rotation is a direct measure of the phase of the primary wave given by the dynamical theory.

Introduction

Friedel (1922) discovered that a certain class of liquid crystals, which he named 'cholesteric', have optical rotatory powers of the order of several thousands of degrees per millimetre. The very large rotation is associated with some other equally remarkable optical properties. When white light is incident on the surface of the liquid crystal, selective reflexion takes place over a small region of the spectrum, the wavelength of maximum reflexion varying with angle of incidence in accordance with Bragg's law. At normal incidence, the reflected light is circularly polarized; one circular component is totally reflected over a spectral range of some 200 Å, whilst the other passes through unchanged. Further, contrary to usual experience, the reflected wave has the same sense of circular polarization as that of the incident wave.

In the neighbourhood of the region of reflexion, the rotatory dispersion is anomalous and the sign of the rotation opposite on opposite sides of the reflected band. The behaviour is therefore similar to that of an optically active molecule in the vicinity of an absorption. The anomalous rotatory dispersion around the reflecting region was first observed by Stumpf (1910) in amyl cyanobenzylideneaminocinnamate and later verified by Mathieu (1938, 1957) in a number of derivatives of cholesterol.

A model for the molecular structure of the cholesteric liquid crystal was proposed by de Vries (1951) in an attempt to explain these unusual optical properties. He assumed the structure to be built up of a large number of thin birefringent layers with the principal axes of the successive layers turned through a small angle. He took the molecules in each layer to lie with their long axes approximately parallel to one another. Thus the structure may be looked upon as a nematic arrangement on which is superimposed an n-fold screw axis at right angles to the long axes of the molecules, n being a large number. The rotatory power of this type of structure but with a much larger pitch had, in fact, been worked out previously by Mauguin (1911) using the Poincaré sphere to interpret the optical rotation produced by rotating the cover glass over a nematic liquid crystal. But Mauguin's calculations are not valid when the pitch of the helix is comparable to the wavelength of light. It was correctly pointed out by de Vries that a helical arrangement of birefringent layers would give rise to selective reflexion of circularly polarized light at normal incidence when the pitch is equal to the wavelength of light in the medium and, moreover, that the sense of the circular polarization would be unaltered by reflexion. However, his theory of the rotatory power is an essentially phenomenological one and does not explicitly take into account the molecular structure proposed by him, except in so far as to postulate that the 'principal' dielectric constants twist round continuously in the form of a helix. The theory leads to the formula for the rotatory power

$$\varrho = -\frac{2\pi}{P}\,\frac{\alpha^2}{8\lambda'^2(1-\lambda'^2)}\,, \tag{1}$$

where P is the pitch of the helix, $\alpha=(\varepsilon_1-\varepsilon_2)/2\varepsilon$, ε_1 and ε_2 are the principal dielectric constants of the untwisted structure, $\varepsilon=\frac{1}{2}(\varepsilon_1+\varepsilon_2)$, $\lambda'=\lambda/\varepsilon^{1/2}P$ and λ is the wavelength in vacuum. Thus, according to the formula, the rotatory power should increase rapidly as the wavelength approaches the critical wavelength of reflexion $\lambda_0(=\varepsilon^{1/2}P)$, change sign on the other side of the reflexion and then decrease in magnitude uniformly. Although the theory would appear to have explained the phenomenon broadly, the physical principles underlying the calculations are not at all clear (see also Chatelain, 1954); in particular, the interesting question of why reflexions should cause a reversal in the sign of rotation still remains obscure.

In this paper, we give a theory of the optical rotatory power of cholesteric liquid crystals using the molecular model proposed by de Vries. (As we shall see later, the systematic investigations of Robinson (1961) leave little doubt that this model is essentially correct.) It is shown by the dynamical theory that the effect of multiple reflexions is responsible for the anomalous rotatory dispersion. The variation of the rotatory power in the immediate vicinity of the reflected band predicted by this theory is significantly different from that given by de Vries's formula.

Normal rotatory dispersion

We now proceed to calculate the optical rotation produced by a helically arranged pile of birefringent layers, neglecting at first the effect of reflexions. Each layer is supposed to be only a few Å thick. Since the pitch of the helix is assumed to be comparable to the wavelength of light, each turn of the helix will consist of several hundred layers, and the angle β between adjacent layers will be of the order of 10^{-2} radian. The question arises whether such thin layers may be looked upon as birefringent plates. But it is well known that when an electromagnetic wave passes through a sheet of isotropic scattering material, it acquires an additional phase of $-q_0$, where $-iq_0$ is the complex amplitude scattered by the layer in the exact forward direction when a plane wave of unit amplitude falls on it (see, *e.g.* James, 1954). This is equivalent to ascribing a refractive index to the layer. The argument may obviously be extended to anisotropic scatterers as well.

We define a quantity γ which represents half the phase difference between waves polarized along the two principal axes after passing through the layer of thickness p, *i.e.*

$$\gamma = \frac{\pi}{\lambda}(\mu_1-\mu_2)p\,. \tag{2}$$

Judging from the available data on nematic liquid crystals, the birefringence $(\mu_1-\mu_2)$ may be taken to be approximately in the range 0·1 – 0·3. Thus γ is 10^{-3} or less, *i.e.* an order of magnitude smaller than β.

We now apply the Jones calculus to such a system, assuming that light is incident normal to the layers, *i.e.* along OZ. Let the principal axes of the first layer be inclined at an angle β with respect to the axes OX, OY. If the Jones retardation matrix with respect to the principal axes is

$$\mathbf{G} = \begin{pmatrix} e^{i\gamma} & 0 \\ 0 & e^{-i\gamma} \end{pmatrix},$$

where γ is defined by (2), the retardation matrix with respect to OX, OY is

$$\mathbf{J}_1 = \mathbf{SGS}'\,,$$

where

$$\mathbf{S} \equiv \mathbf{S}(\beta) = \begin{pmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{pmatrix},$$

and $\mathbf{S}'=\mathbf{S}^{-1}$ is the transpose of $\mathbf{S}$ so that $\mathbf{SS}'=\mathbf{S}'\mathbf{S}=\mathbf{E}$, the unit matrix (Jones, 1941; Hurwitz & Jones, 1941; see also Ramachandran & Ramaseshan, 1961).

Now, if $\mathbf{D}_0$ is the complex two-dimensional column vector with respect to OX, OY representing the incident light, the emergent light vector after passing through the layer is

$$\mathbf{D}_1 = \mathbf{J}_1 \mathbf{D}_0 ,$$

where, as we are interested only in the state of polarization of the emergent beam, we neglect a factor $\exp(i\eta)$, $\eta = \pi(\mu_1+\mu_2)p/\lambda$. Let $\mathbf{D}_1$ be now incident on a second birefringent layer whose principal axes are inclined at 2β with respect to OX, OY. The Jones matrix for this layer is

$$\mathbf{S}(2\beta)\mathbf{G}\mathbf{S}'(2\beta) = \mathbf{S}^2\mathbf{G}\mathbf{S}'^2 ,$$

and the emergent vector is

$$\begin{aligned}\mathbf{D}_2 &= \mathbf{S}^2\mathbf{G}\mathbf{S}'^2\mathbf{D}_1 = \mathbf{S}^2\mathbf{G}\mathbf{S}'^2\mathbf{S}\mathbf{G}\mathbf{S}'\mathbf{D}_0\\ &= \mathbf{S}^2(\mathbf{G}\mathbf{S}')^2\mathbf{D}_0 = \mathbf{J}_2\mathbf{D}_0 ,\end{aligned}$$

where $\mathbf{J}_2 = \mathbf{S}^2(\mathbf{G}\mathbf{S}')^2$ is the appropriate Jones matrix for this system of two layers. In general, if we have a pile of n layers, where the principal axes of the mth layer are inclined at $m\beta$ with respect to OX, OY $(m = 1, 2, \ldots n)$, the Jones matrix for the pile is evidently

$$\mathbf{J}_n = \mathbf{S}^n(\mathbf{G}\mathbf{S}')^n .$$

We now proceed to an explicit evaluation of $\mathbf{J}_n$. Applying a result from the theory of matrices (Abelès, 1950; see Appendix), which has also been used by Born & Wolf (1959) in discussing light propagation in periodically stratified media,

$$(\mathbf{G}\mathbf{S}')^n = \frac{\sin n\theta}{\sin\theta}\mathbf{A} - \frac{\sin(n-1)\theta}{\sin\theta}\mathbf{E} , \tag{3}$$

where

$$\mathbf{A} = \mathbf{G}\mathbf{S}' = \begin{pmatrix} e^{i\gamma} & 0 \\ 0 & e^{-i\gamma}\end{pmatrix}\begin{pmatrix}\cos\beta & \sin\beta \\ -\sin\beta & \cos\beta\end{pmatrix}$$

and

$$\cos\theta = \cos\beta\cos\gamma . \tag{4}$$

Now the factor $\mathbf{A}$ in (3) is the effect of a single layer. Therefore, as far as the total effect of n layers is concerned, n being large, we may, without sensible error, put $\mathbf{A} \simeq \mathbf{S}'$, *i.e.* $\exp(i\gamma) \simeq 1$ in $\mathbf{A}$. Further, since θ and β are also small, though of an order of magnitude greater than γ, we may take $\sin\theta \simeq \sin\beta \simeq \beta$; $\cos\theta \simeq \cos\beta \simeq 1$. We then have on simplification

$$(\mathbf{G}\mathbf{S}')^n \simeq \begin{pmatrix}\cos n\theta & \sin n\theta \\ -\sin n\theta & \cos n\theta\end{pmatrix} .$$

Hence

$$\begin{aligned}\mathbf{J}_n = \mathbf{S}^n(\mathbf{G}\mathbf{S}')^n &\simeq \begin{pmatrix}\cos n\beta & -\sin n\beta \\ \sin n\beta & \cos n\beta\end{pmatrix}\begin{pmatrix}\cos n\theta & \sin n\theta \\ -\sin n\theta & \cos n\theta\end{pmatrix}\\ &= \begin{pmatrix}\cos n(\beta-\theta) & -\sin n(\beta-\theta) \\ \sin n(\beta-\theta) & \cos n(\beta-\theta)\end{pmatrix} .\end{aligned} \tag{5}$$

Thus the effect of n layers is to produce a rotation of the incident vector through an angle $\alpha = n(\beta-\theta)$ in the positive direction. Since β and γ are small, we have from (4)

$$\theta^2 \simeq \beta^2 + \gamma^2 .$$

Therefore,

$$\begin{aligned}\alpha &= n\{\beta - (\beta^2+\gamma^2)^{1/2}\}\\ &\simeq -n\gamma^2/2\beta .\end{aligned} \tag{6}$$

If n is the number of layers per turn of the helix of pitch P, $n\beta = 2\pi$ and $np = P$.

Substituting for γ from (2) in (6), the optical rotation/pitch

$$\alpha = -\frac{\pi(\mu_1-\mu_2)^2P^2}{4\lambda^2} .$$

Thus the rotatory power in radians per unit length is

$$\varrho = -\frac{\pi(\mu_1-\mu_2)^2P}{4\lambda^2} . \tag{7}$$

The negative sign indicates that the sign of the rotation is opposite to that of the helical twist of the structure. This formula is the same as that derived by Mauguin (1911) using the Poincaré sphere and rolling cone method. It may also be shown to be equivalent to (1) when $\lambda'^2 \ll 1$ (Robinson, 1961).

The most detailed verification of (7) is due to Robinson (1961) who found that solutions of some polypeptides in organic solvents, *e.g.* poly-γ-benzyl-L-glutamate (PBLG) in dioxan, methylene chloride, chloroform *etc.*, spontaneously adopted the cholesteric mesophase above a certain concentration. Under suitable conditions, the solutions exhibited equi-spaced alternate bright and dark lines when observed through a microscope. The lines may be interpreted as a view of the structure at right angles to the screw axis so that the periodicity of the lines is equal to half the pitch of the screw. Robinson confirmed this interpretation by observations between crossed polaroids and also by the use of a quartz wedge. The retardation plotted against distance in a direction at right angles to the lines had an oscillating value, as is indeed to be expected from the structure. The pitch for any given polypeptide depended on factors such as concentration, solvent, temperature *etc.* When viewed along the screw axis no lines were seen, but a very high optical rotatory power was present. The rotation in every solution, with P ranging from 10–200μ, was found to be proportional to $1/\lambda^2$. Robinson substituted the values of ϱ and P in (7) and calculated the layer birefringence $(\mu_1-\mu_2)$ per volume fraction of the polypeptide in solution. The birefringence was remarkably constant despite the widely varying values of ϱ and P. He then prepared a solution with equal quantities of the D and L forms (PBDG and PBLG), which too, under certain conditions, adopted the spontaneously birefringent phase, only, in this case, it was not the twisted cholesteric structure but the untwisted nematic structure. He was therefore able to measure the birefringence directly and the value agreed well with that calculated from the rotatory dispersion formula. The experiments of Robinson show quite conclusively that this model is an accurate representation of the structure of the cholesteric liquid crystal.

Dynamical theory of reflexion

The results of the theory discussed in the previous section show that the liquid crystal behaves as if it had circular birefringence; in other words, right and left circular vibrations travel without change of form but at slightly different velocities. We shall now give a simple interpretation of how, under certain conditions, reflexion of one of the circularly polarized components takes place. Let right circular light given by $\mathbf{D}_0=\binom{1}{i}$, referred to OX, OY, be incident normally on the surface of the liquid crystal. We shall suppose that the structure is right handed, *i.e.* β is positive. After passing though m molecular layers, each of thickness p, the light vector will be $\mathbf{D}_0 \exp(-i\varphi)$, where $\varphi=2\pi m\mu_d p/\lambda$, μ_d being the refractive index for right circular light and λ the wavelength in vacuum. To calculate the reflexion at the boundary between the mth and $(m+1)$th layer, we resolve the light vector along the principal axes of the mth layer, which are inclined at an angle $m\beta$ with respect to OX, OY. The resolved components will be given by

$$\begin{pmatrix}\cos m\beta & \sin m\beta\\ -\sin m\beta & \cos m\beta\end{pmatrix}\begin{pmatrix}1\\ i\end{pmatrix}\exp(-i\varphi)$$
$$=\begin{pmatrix}1\\ i\end{pmatrix}\exp[i(m\beta-\varphi)]\,. \qquad (8)$$

Since the principal axes of the $(m+1)$th layer are rotated slightly with respect to those of the mth layer, one of the components of (8) will, on emerging from the mth layer, meet a 'rarer' medium, whereas the other component will meet a 'denser' medium. Thus one component will get reflected without any change of phase and the other with a change of phase of π. As a consequence, the sense of the circular polarization remains the same after reflexion. Referred to the principal axes of the mth layer, the reflected wave on reaching the surface will be

$$\begin{pmatrix}1\\ -i\end{pmatrix}\exp[i(m\beta-2\varphi)]\,, \qquad (9)$$

neglecting a factor representing the reflexion coefficient of the layer. Transforming back to OX, OY, (9) becomes

$$\begin{pmatrix}\cos m\beta & -\sin m\beta\\ \sin m\beta & \cos m\beta\end{pmatrix}\begin{pmatrix}1\\ -i\end{pmatrix}\exp[i(m\beta-2\varphi)]$$
$$=\begin{pmatrix}1\\ -i\end{pmatrix}\exp[2i(m\beta-\varphi)]\,, \qquad (10)$$

which is a right circular wave propagated along the negative direction of OZ. When $\lambda=\mu_d P$, $2\pi\mu_d p/\lambda=\beta$, or $\varphi=m\beta$, since $np=P$ and $n\beta=2\pi$, where n is the number of molecular layers per turn of the helix. The phase factor $\exp[2i(m\beta-\varphi)]$ in (10) then becomes unity irrespective of the value of m, and the waves reflected by the successive layers will all cooperate to give rise to a strong interference maximum. On the other hand, if the structure is left handed, *i.e.* β is negative, $(m\beta-\varphi)$ does not vanish when $\lambda=\mu_d P$. Therefore, the reflected waves from the different layers will not be in phase and the vibration will be transmitted unchanged.

It has been assumed in (9) and (10) that the reflexion coefficients for the two linearly polarized components are the same. This may not be quite true and it is possible that right circular light acquires a slight ellipticity after reflexion from a single layer. However, if the amplitudes of the waves reflected by the different layers of the helical structure are added, the resultant reflected wave will evidently be circularly polarized.

The complete solution of the problem has to take into account the effect of multiple reflexions. We may do so by setting up difference equations in a manner closely similar to that used by Darwin (1914) in his dynamical theory of X-ray diffraction. Such a procedure is valid because, as we have said earlier, circularly polarized vibrations travel in the medium without change of form and the interference of multiply reflected waves with one another and with the primary wave can be evaluated directly.

For the purposes of this theory, we regard the liquid crystal as consisting of a set of parallel planes spaced at a distance P apart. Each plane therefore replaces the n molecular layers per turn of the helix of pitch P. We ascribe a reflexion coefficient $-iQ$ to each plane for circularly polarized light at normal incidence. Clearly, $-iQ$ represents the over-all effect of the reflexions from the n molecular layers, and is related to $-iq$, the reflexion coefficient of a single molecular layer, in exactly the same way as the structure factor F of a crystal is related to the scattering factor f of an atom. Since Darwin's theory can be applied to any crystal merely by substituting F for f, our model should be adequate for deducing the reflexion characteristics of the liquid crystal. However, unlike in the X-ray case where the reflexion curve is usually derived as a function of the Bragg angle, we work it out here as a function of the wavelength.

We shall suppose, as before, that the structure is right handed and that right circular light is incident normally. Let T_r and S_r be the complex amplitudes of the primary and reflected waves respectively at a point just above the rth plane. (The topmost plane is designated by the serial number zero.) We then write the difference equations, suitably modified to the optical case, assuming that absorption is negligible (see, *e.g.*, James, 1954):

$$S_r=-iQT_r+\exp(-i\varphi)S_{r+1} \qquad (11)$$
$$T_{r+1}=\exp(-i\varphi)T_r-iQ\exp(-2i\varphi)S_{r+1}\,, \qquad (12)$$

where $\varphi=2\pi\mu_d P/\lambda$ and μ_d is the refractive index for right circularly polarized light. The reflexion coefficient is here taken to be the same on both sides of the plane. Replacing r by $r-1$ in (12), and using (11) and (12) we obtain

$$T_{r+1}+T_{r-1}$$
$$=[\exp(i\varphi)+\exp(-i\varphi)+Q^2\exp(-i\varphi)]T_r\,. \qquad (13)$$

We assume a solution in the form

$$T_{r+1} = xT_r\,, \tag{14}$$

where x is independent of r. Hence x must satisfy

$$x + \frac{1}{x} = \exp(i\varphi) + \exp(-i\varphi) + Q^2 \exp(-i\varphi)\,. \tag{15}$$

Substituting for T_{r+1} from (14) in (12), and using (11) we get

$$S_{r+1} = \frac{x - \exp(-i\varphi)}{x\exp(-i\varphi) - \exp(-2i\varphi) - Q^2\exp(-2i\varphi)}\, S_r\,. \tag{16}$$

From (15) and (16), we have

$$S_{r+1} = xS_r\,. \tag{17}$$

As we have seen earlier, the reflexion condition is $\mu_d P = \lambda_0$, or $\varphi_0 = 2\pi$. Let us put $\varphi = 2\pi\lambda_0/\lambda = 2\pi + \varepsilon$, where

$$\varepsilon = -2\pi(\lambda - \lambda_0)/\lambda\,, \tag{18}$$

which is a small quantity in the neighbourhood of the reflexion. We have, therefore, from (15)

$$x + \frac{1}{x} = \exp(i\varepsilon) + \exp(-i\varepsilon) + Q^2\exp(-i\varepsilon)\,. \tag{19}$$

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

$$x = \exp(-\xi)\exp(-i\varphi_0) = \exp(-\xi)\,, \tag{20}$$

where ξ is small and may be complex. From (19) and (20) we have

$$\xi \simeq \pm(Q^2 - \varepsilon^2)^{1/2}\,. \tag{21}$$

Using (17), (11) and (21), and putting $r = 0$, we obtain the ratio of the reflected to the incident amplitudes:

$$\frac{S_0}{T_0} = -\frac{Q}{\varepsilon \pm (\varepsilon^2 - Q^2)^{1/2}}\,. \tag{22}$$

When $-Q < \varepsilon < Q$, (22) may be expressed as

$$\frac{S_0}{T_0} = -\frac{Q}{\varepsilon \pm i(Q^2 - \varepsilon^2)^{1/2}}\,, \tag{23}$$

and hence

$$R = |S_0/T_0|^2 = 1\,.$$

The reflexion is therefore total within this range. Outside this range, the reflexion decreases rapidly and symmetrically on either side. It will be seen from (18) that when $\lambda > \lambda_0$, ε is negative, and so the negative value of the square root in the denominator of (22) has to be taken because R can never exceed unity. Similarly when $\lambda < \lambda_0$, the positive value has to be taken.

Spectral width of total reflexion and primary extinction

The range of total reflexion extends from $\varepsilon = +Q$ to $-Q$, *i.e.* from $\lambda_0 - Q\lambda/2\pi$ to $\lambda_0 + Q\lambda/2\pi$. The spectral width of the reflexion is therefore $Q\lambda/\pi \simeq Q\lambda_0/\pi$.

In the solution of the difference equations, we have assumed that the amplitude of the primary beam is changed by a factor $\exp(-\xi)$ on passing from one plane to the next. Within the range of total reflexion $Q^2 > \varepsilon^2$, so that ξ is real and primary extinction takes place. To evaluate the extinction coefficient we first calculate the mean value of ξ within the totally reflecting range,

$$\bar{\xi} = \frac{1}{Q}\int_0^Q (Q^2 - \varepsilon^2)^{1/2} d\varepsilon = \pi Q/4\,.$$

The intensity falls by a factor $\exp(-2\bar{\xi})$ on passing through a thickness P, or by $\exp(-\pi Q/2P)$ per unit length.

Outside the region of total reflexion, ξ is imaginary and primary extinction vanishes.

We shall now use these results to make numerical estimates of the theoretically expected magnitudes of the spectral width of the total reflexion and the primary extinction. Taking $\lambda_0 = 5600$ Å, $P = 3500$ Å and $Q = 0{\cdot}05$, the width of the reflexion turns out to be 90 Å and the extinction coefficient $\pi Q/2P = 2{\cdot}24 \times 10^3$. Thus the intensity is reduced to about 1/1000 of its incident value after passing through a thickness of 31 microns.

These values compare quite favourably with the experimental data. The width of the reflexion has been reported by Mathieu (1938, 1957) to be about 200 Å in some cholesteric liquid crystals. He has also remarked that within this range, unpolarized light becomes almost perfectly circularly polarized after traversing a thickness of a few tens of microns. Considering that our calculations are for the ideally perfect case, the agreement with experiment may be regarded as an excellent confirmation of the theory.

Anomalous rotatory dispersion

We have seen earlier that in the region of normal dispersion, the optical rotation per thickness P of the liquid crystal is given by

$$\alpha = \frac{1}{2}(\varphi_d - \varphi_l) = \frac{\pi P}{\lambda}(\mu_d - \mu_l) = -\frac{n\gamma^2}{2\beta}\,,$$

where φ_d, φ_l are the phase retardations and μ_d, μ_l the refractive indices for right and left circular vibrations. (In conformity with the convention adopted in the theory, a clockwise rotation as seen along the direction of propagation of light is taken as positive. This is contrary to normal usage.) In the region of reflexion, the dynamical theory shows that the right circular component suffers an additional phase retardation and also, under certain circumstances, attenuation as it travels through the medium. Left circular light, on the other hand, exhibits normal behaviour throughout, and as a consequence the rotatory dispersion is anomalous around the reflecting region. We shall now investigate the anomalous dispersion in detail.

Case I. *Region of total reflexion*

According to (20), the amplitude of the right circular wave as it passes from one plane to the next is given by

$$T_{r+1}=xT_r\,,$$

where

$$x=\exp(-\xi)\exp(-i\varphi_0)\,,$$
$$\xi=(Q^2-\varepsilon^2)^{1/2}\,,$$
$$\varphi_0=\varphi_d-\varepsilon=2\pi\mu_d P/\lambda+2\pi(\lambda-\lambda_0)/\lambda\,.$$

Inside the totally reflecting range, ξ is real and therefore the medium becomes highly circularly dichroic. If very thin films are employed, the emergent light is elliptically polarized. It is readily seen that the ellipticity χ produced per thickness P is given by

$$\tan\chi=\frac{1-\exp(-\xi)}{1+\exp(-\xi)}=\tanh\xi/2\,,$$

or

$$\chi\simeq\xi/2\,.$$

The azimuth of the major axis of the ellipse after passing through a thickness P is

$$\alpha=\frac{1}{2}(\varphi_0-\varphi_l)=\frac{\pi P}{\lambda}(\mu_d-\mu_l)+\frac{\pi(\lambda-\lambda_0)}{\lambda}$$
$$=-\frac{n\gamma^2}{2\beta}+\frac{\pi(\lambda-\lambda_0)}{\lambda}\,.$$

Therefore the rotatory power

$$\varrho=-\frac{\pi(\mu_1-\mu_2)^2P}{4\lambda^2}+\frac{\pi(\lambda-\lambda_0)}{P\lambda}\,, \qquad (24)$$

which is valid within the range $\lambda_0-Q\lambda/2\pi<\lambda<\lambda_0+Q\lambda/2\pi$.

Case II. *Outside the region of total reflexion*

Outside the totally reflecting range, $\xi=i(\varepsilon^2-Q^2)^{1/2}$ and may be positive or negative depending on whether ε, given by (18), is positive or negative. Therefore,

$$\alpha=\tfrac{1}{2}[(\varepsilon^2-Q^2)^{1/2}+\varphi_0-\varphi_l]$$
$$=-\frac{n\gamma^2}{2\beta}-\frac{\varepsilon}{2}\left[1-\left(1-\frac{Q^2}{\varepsilon^2}\right)^{1/2}\right]$$
$$=-\frac{n\gamma^2}{2\beta}+\frac{\pi(\lambda-\lambda_0)}{\lambda}\left[1-\left(1-\frac{Q^2}{\varepsilon^2}\right)^{1/2}\right].$$

Hence the rotatory power

$$\varrho=-\frac{\pi(\mu_1-\mu_2)^2P}{4\lambda^2}+\frac{\pi(\lambda-\lambda_0)}{P\lambda}\left[1-\left(1-\frac{Q^2}{\varepsilon^2}\right)^{1/2}\right]. \qquad (25)$$

Discussion

To facilitate comparison with experiment, we shall rewrite (24) and (25) using the standard sign convention according to which a clockwise rotation as seen by an observer looking at the source of light is taken to be positive. When

$$\lambda_0-Q\lambda/2\pi<\lambda<\lambda_0+Q\lambda/2\pi\,,$$
$$\varrho=\frac{18(\mu_1-\mu_2)^2P}{4\lambda^2}-\frac{18(\lambda-\lambda_0)}{P\lambda}\,; \qquad (26)$$

when

$$\lambda<\lambda_0-Q\lambda/2\pi\,,\ \text{or}\ \lambda>\lambda_0+Q\lambda/2\pi\,,$$

$$\varrho=\frac{18(\mu_1-\mu_2)^2P}{4\lambda^2}-\frac{18(\lambda-\lambda_0)}{P\lambda}\left[1-\left(1-\frac{Q^2}{\varepsilon^2}\right)^{1/2}\right], \qquad (27)$$

where ϱ is expressed in degrees per millimetre.

Fig. 1 shows the reflexion curve for right circular light calculated from the dynamical theory with $Q=$ 0·05. As discussed earlier, with this value of Q the spectral width of the total reflexion turns out to be about 90 Å. Fig. 2 shows the corresponding rotatory dispersion curve given by (26) and (27) taking $\lambda_0=$ 5600 Å, $P=3500$ Å (or $\mu_d=1{\cdot}6$) and $\mu_1-\mu_2=0{\cdot}15$. The assumption has been made that $\mu_1-\mu_2$ is independent of wavelength. The sign of the rotatory power changes twice on passing from one side of the reflecting region to the other in a manner closely analogous to the rotatory dispersion of a molecule around an optically active absorption band. The two wavelengths corresponding to zero rotatory power occur at $\lambda>\lambda_0$, one inside the region of circular dichroism and the other outside. These results appear to be at variance with the predictions of de Vries's theory. Far away from the region of reflexion on either side, *i.e.*, when $\varepsilon^2\gg Q^2$, the second term in (27) becomes small and the rotatory dispersion approaches the normal value. A

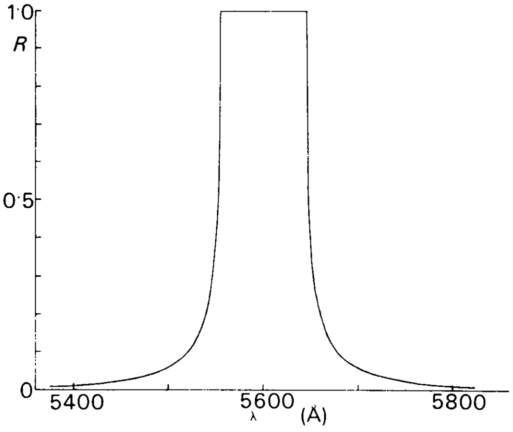

Fig. 1. Reflexion curve for right circular light.

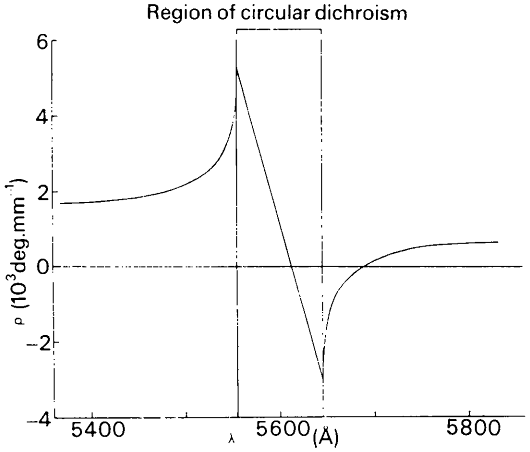

Fig. 2 Anomalous rotatory dispersion in region of reflexion.

comparison of these curves with those given by Mathieu (1957) shows that the theoretical relationship between reflexion, circular dichroism and anomalous rotatory dispersion is in general agreement with observations.

It is a noteworthy fact that the phenomenon brings out clearly certain aspects of the dynamical theory which are not so easily demonstrable in the X-ray case. For example, the circular dichroism in the totally reflecting range is a striking proof of the effect of primary extinction, and similarly, the anomalous rotatory power is direct evidence of the variation of the phase of the primary wave in the region of multiple reflexions.

APPENDIX

In order to obtain an explicit expression for $\mathbf{J}_n$, we evaluate $\mathbf{A}^n$ where

$$\mathbf{A}=\mathbf{GS}'(\beta)=\begin{pmatrix} e^{i\gamma}\cos\beta & e^{i\gamma}\sin\beta \\ -e^{-i\gamma}\sin\beta & e^{-i\gamma}\cos\beta \end{pmatrix}=\begin{pmatrix} a & b \\ c & d \end{pmatrix},\ \text{say.}$$

We observe that $\mathbf{A}$ is unimodular, *i.e.*

$$ad-bc=1\ . \tag{A1}$$

We give here a direct method of determining $\mathbf{A}^n$ for an arbitrary unimodular matrix $\mathbf{A}$, whereas the method due to Abelès (1950) depends on the Lagrange–Sylvester interpolation formula. The characteristic equation

$$|(\mathbf{A}-\lambda\mathbf{E})|\equiv\lambda^2-\lambda(a+d)+1=0$$

yields the eigenvalues exp $(\pm i\theta)$, where

$$\cos\theta=\frac{a+d}{2}\ . \tag{A2}$$

Evidently, $\begin{pmatrix} -b \\ a-e^{i\theta} \end{pmatrix}$ and $\begin{pmatrix} -b \\ a-e^{-i\theta} \end{pmatrix}$ may be taken as the eigenvectors belonging respectively to the eigenvalues $e^{i\theta}$ and $e^{-i\theta}$. Hence, with

$$\mathbf{T}=\begin{pmatrix} -b & -b \\ a-e^{i\theta} & a-e^{-i\theta} \end{pmatrix},$$

we have

$$\mathbf{T}^{-1}\mathbf{AT}=\mathbf{\Lambda}=\begin{pmatrix} e^{i\theta} & 0 \\ 0 & e^{-i\theta} \end{pmatrix}$$

and

$$\begin{aligned}\mathbf{A}^n&=(\mathbf{T\Lambda T}^{-1})^n=\mathbf{T\Lambda}^n\mathbf{T}^{-1}\\ &=\begin{pmatrix} -b & -b \\ a-e^{i\theta} & a-e^{-i\theta} \end{pmatrix}\begin{pmatrix} e^{ni\theta} & 0 \\ 0 & e^{-ni\theta} \end{pmatrix}\\ &\times\begin{pmatrix} \dfrac{a-e^{-i\theta}}{\Delta} & \dfrac{b}{\Delta} \\ -\dfrac{a-e^{i\theta}}{\Delta} & -\dfrac{b}{\Delta} \end{pmatrix},\end{aligned}$$

where

$$\Delta=\det\mathbf{T}=-2ib\sin\theta\ .$$

Thus

$$\mathbf{A}^n=\frac{1}{\sin\theta}\times\begin{pmatrix} a\sin n\theta-\sin(n-1)\theta & b\sin n\theta \\ -\dfrac{\sin n\theta(a^2-2a\cos\theta+1)}{b} & \sin(n+1)\theta-a\sin n\theta \end{pmatrix}. \tag{A3}$$

Using $(A1)$, $(A2)$ and the relation

$$\sin(n+1)\theta+\sin(n-1)\theta=2\sin n\theta\cos\theta\ ,$$

we rewrite the elements of the second row of $(A3)$ and obtain

$$\begin{aligned}\mathbf{A}^n&=\frac{\sin n\theta}{\sin\theta}\begin{pmatrix} a & b \\ c & d \end{pmatrix}-\frac{\sin(n-1)\theta}{\sin\theta}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\\ &=\mathrm{U}^{(z)}_{n-1}\mathbf{A}-\mathrm{U}^{(z)}_{n-2}\mathbf{E}\ ,\end{aligned} \tag{A4}$$

where $\mathrm{U}^{(z)}_n=\dfrac{\sin(n+1)\theta}{\sin\theta}$ is the Tschebychev polynomial of the second kind in $z=\cos\theta$.

The expression $(A4)$ is applicable to our problem with

$$\cos\theta=\frac{a+d}{2}=\cos\beta\cos\gamma\ .$$

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