Pramāṇa, Suppl. No. 1, 1975, pp. 341–352

Dynamical theory of reflexion from cholesteric liquid crystals

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Abstract. The analogy between the optical phenomena exhibited by cholesterics and the diffraction of x-rays from perfect crystals is emphasized and some of its consequences are discussed. Difference equations similar to those formulated by Darwin in his dynamical theory lead to simple analytical expressions for the reflexion coefficient, rotatory power and circular dichroism which are shown to be in good agreement with the results of the rigorous electromagnetic treatment. An extension of the theory to absorbing systems at once yields the relevant formulae for the Borrmann effect in cholesterics. It is pointed out that this simple approach should be sufficient for most practical calculations.

Introduction

The reflexion of light from cholesteric liquid crystals at normal incidence can be treated as analogous to the diffraction of x-rays from perfect crystals[1]. As the dynamical theory of x-ray diffraction and its applications are now understood quite thoroughly this approach may prove to be useful in elucidating the optical behaviour of cholesterics and in looking for new optical analogues of certain well established x-ray effects. An example of a new phenomenon reported recently is the Borrmann effect in cholesterics[2].

The aim of this paper is to review the results of the dynamical theory of reflexion from cholesterics and to compare them with the predictions of the rigorous electromagnetic treatment[3–5]. It is shown that calculations based on the dynamical theory are sufficiently accurate for most practical purposes.

Kinematical theory of reflexion

We regard the cholesteric structure as a pile of very thin birefringent (quasi-nematic) layers with the principal axes of the successive layers turned through a small angle β. Such a system can, in general, be replaced by a rotator and a retardation plate for light propagating normal to the layers[6]. However, for wavelengths comparable to the pitch P of the helical structure and for sample thicknesses which are not too small (say > 10 P) the system can be treated to a very good approximation as a pure rotator. Under such circumstances, the normal waves may be assumed to be circularly polarized, *i.e.*, right and left circular light travel without change of form, but at slightly different velocities. The refractive indices for the two components are respectively[1]

$$\mu_R = \mu - \frac{(\Delta\mu)^2 P}{8\lambda}$$

$$\mu_L = \mu + \frac{(\Delta\mu)^2 P}{8\lambda}$$

and the rotatory power in radians per unit thickness

$$\rho = -\frac{\pi(\Delta\mu)^2 P}{4\lambda^2} \qquad (1)$$

where $\Delta\mu = (\mu_1 - \mu_2)$ is the layer birefringence, $\mu = \frac{1}{2}(\mu_1 + \mu_2)$.

When the wavelength of the light in the medium is cqual to the pitch, reflexion of one of the circular components takes place and, contrary to usual experience, the reflected wave has the same sense of circular polarization as that of the incident wave. This will be clear from the following simple argument. We shall suppose that the principal axes of the first layer are along OX, OY of a cartesian coordinate system and that the structure is right-handed, *i.e.*, β is positive. Let right circular light given by $D_0 = \left[\begin{smallmatrix}1\\ i\end{smallmatrix}\right]$ referred to OX, OY be incident along OZ. To calculate the reflexion coefficient at the boundary between the $(\nu+1)$th and $(\nu+2)$th layers, we resolve the incident light vector along the principal axes of the $(\nu+1)$th layer which are inclined at an angle $(\nu+1)\beta$ with respect to OX, OY. The resolved components are

$$\begin{bmatrix}\xi\\ \eta\end{bmatrix} = \begin{bmatrix}1\\ i\end{bmatrix} \exp[i\{(\nu+1)\beta - \varphi_{\nu+1}\}],$$

where $\varphi_{\nu+1} = 2\pi\mu_R(\nu+1)p/\lambda$, p being the thickness of each layer. At the boundary, the ξ vibration emerges from a medium of refractive index μ_1 and the η vibration from a medium of refractive index μ_2. If ξ' and η' refer to the principal axes of the $(\nu+2)$th layer, then the reflected components are[7]

$$\begin{bmatrix}\xi'\\ \eta'\end{bmatrix} = -\frac{\beta\Delta\mu}{2\mu}\begin{bmatrix}i\\ 1\end{bmatrix} \exp[i\{(\nu+1)\beta - \varphi_{\nu+1}\}]$$

$$= -iq\begin{bmatrix}1\\ -i\end{bmatrix} \exp[i\{(\nu+1)\beta - \varphi_{\nu+1}\}],$$

where $|q| = \beta\Delta\mu/2\mu$. We make the approximation here that $\sin\beta \approx \beta$, since β is assumed to be very small ($\sim 10^{-2}$ radian). On reflexion a very slight ellipticity is introduced in the transmitted beam, but we shall neglect this in the present discussion. Transforming back to OX, OY, the reflected wave on reaching the surface of the liquid crystal will be

$$\begin{bmatrix} X \\ Y \end{bmatrix} = -iq \begin{bmatrix} 1 \\ -i \end{bmatrix} \exp[i\{(2\nu+3)\beta - 2\varphi_{\nu+1}\}],$$

which represents a *right circular* vibration travelling in the negative direction of OZ. Clearly the phase difference between this wave and that reflected at the boundary between the first and second layers is $[2(\nu\beta - \varphi_\nu)]$. When $\lambda = \mu_R P$, we have $2\pi\mu_R p/\lambda = \beta$ and $\varphi_\nu = \nu\beta$ (since $np = P$ and $n\beta = 2\pi$, where n is the number of layers per turn of the helix). Hence the phase factor $\exp[2i(\nu\beta - \varphi_\nu)]$ becomes unity irrespective of the value of ν, and there results a strong interference maximum. On the other hand, for a left-handed structure, β is negative and $(\nu\beta - \varphi_\nu)$ does not vanish when $\lambda = \mu_R P$. Therefore the waves from the different layers will not be in phase and the vibration will be transmitted practically unchanged.

Using the kinematical approximation the reflexion coefficient per turn of the helix is then

$$-iQ = -inq = -i\pi\Delta\mu/\mu, \qquad (2)$$

Dynamical theory of reflexion

The complete solution of the problem has to take into account the effect of multiple reflexions. This can be done by setting up different equations closely similar to those used by Darwin[8] in his dynamical theory of x-ray diffraction. For the purposes of this theory, let us regard the liquid crystal as consisting of a set of parallel planes spaced P apart. Each plane therefore replaces the n birefringent layers per turn of the helix of pitch P. We ascribe a reflexion coefficient $-iQ$ per plane for right circular light at normal incidence. Assuming the kinematical approximation for the n layers, Q is given by (2).

Let T_r and S_r be the complex amplitudes of the primary and reflected waves at a point just above the rth plane, the topmost plane being disignated by the serial number zero. Neglecting absorption, the difference equation may be written as

$$S_r = -iQT_r + \exp(-i\varphi)S_{r+1} \qquad (3)$$

$$T_{r+1} = \exp(-i\varphi)T_r - iQ\exp(-2i\varphi)S_{r+1}, \qquad (4)$$

where $\varphi = 2\pi\mu_R P/\lambda$. The reflexion coefficient is here taken to be the same on both sides of the plane. Replacing r by $(r-1)$ in (3) and (4), substituting and simplifying, we obtain

$$T_{r+1} + T_{r-1} = yT_r \tag{5}$$

$$S_{r+1} + S_{r-1} = yS_r \tag{6}$$

where

$$y = \exp(i\varphi) + \exp(-i\varphi) + Q^2 \exp(-i\varphi). \tag{7}$$

Suppose that the film consists of m planes. Putting $S_m = 0$, we have from (6)

$$S_{m-2} = yS_{m-1},$$

$$S_{m-3} = yS_{m-2} - S_{m-1} = (y^2 - 1)S_{m-1},$$

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

and

$$S_0 = [y^{m-1} - \frac{(m-2)}{1!} y^{m-3} + \frac{(m-4)(m-3)}{2!} y^{m-5} - \ldots] S_{m-1}$$

$$= f_m(y) S_{m-1} \text{ (say)} \tag{8}$$

Similarly, from (4), (5) and (7)

$$T_{m-1} = \exp(i\varphi) T_m$$

$$T_{m-2} = [y \exp(i\varphi) - 1] T_m$$

$$T_{m-3} = [(y^2 - 1)\exp(i\varphi) - y] T_m, \text{ etc.,}$$

and

$$T_0 = [f_m(y)\exp(i\varphi) - f_{m-1}(y)] T_m \tag{9}$$

Since from (3),

$$S_{m-1} = -iQT_{m-1} = -iQ\exp(i\varphi)T_m,$$

the ratio of the reflected to the incident amplitude is

$$\frac{S_0}{T_0} = -\frac{iQf_m(y)\exp(i\varphi)}{f_m(y)\exp(i\varphi) - f_{m-1}(y)} \tag{10}$$

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

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

We have seen that the reflexion condition is $\mu_R P = \lambda_0$ or $\varphi_0 = 2\pi$. Accordingly we may write

$$\varphi = 2\pi\lambda_0/\lambda = \varphi_0 + \varepsilon,$$

where $\varepsilon = -2\pi(\lambda - \lambda_0)/\lambda,$

which is a small quantity in the neighbourhood of the reflexion. Therefore,

$$x + \frac{1}{x} = \exp(i\varepsilon) + \exp(-i\varepsilon) + Q^2 \exp(-i\varepsilon) \qquad (11)$$

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

$$x = \exp(-\xi)\exp(-i\varphi_0) = \exp(-\xi) \qquad (12)$$

where ξ is small and may be complex. From (11) and (12),

$$\xi = \pm (Q^2 - \varepsilon^2)^{1/2} .$$

When

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

the series in (8) is given by

$$f_m(y) = \frac{\sinh m\xi}{\sinh \xi} . \qquad (13)$$

substituting in (10) and simplifying

$$\frac{S_0}{T_0} \approx \frac{-iQ\exp(i\varepsilon)}{i\varepsilon + \xi\coth m\xi}, \qquad (14)$$

or

$$R = \left|\frac{S_0}{T_0}\right|^2 = \frac{Q^2}{\varepsilon^2 + \xi^2\coth^2 m\xi}. \qquad (15)$$

From (9) and (13)

$$\frac{T_m}{T_0} = \left[\exp(i\varepsilon)\frac{\sinh m\xi}{\sinh\xi} - \frac{\sinh(m-1)\xi}{\sinh\xi}\right]^{-1}$$

$$\approx \frac{\xi\,\mathrm{cosech}\, m\xi}{i\varepsilon + \xi\coth m\xi} \qquad (16)$$

Thus

$$\left|\frac{T_m}{T_0}\right|^2 + \left|\frac{S_0}{T_0}\right|^2 = 1.$$

For a thick specimen, $m = \infty$,

$$\frac{S_0}{T_0} = -\frac{Q}{\varepsilon + i\xi} \qquad (17)$$

when $-Q < \varepsilon < Q$, ξ is real

$$R = \left|\frac{S_0}{T_0}\right|^2 = 1.$$

The reflexion is total within this range. The spectral width of total reflexion $\Delta\lambda = Q\lambda/\pi \approx Q\lambda_0/\pi$. Using (2) $\Delta\lambda = P\Delta\mu$, in agreement with the de Vries theory[3].

Illustrative curves of R as a function of wavelength are shown in figure 1. The parameters chosen for the calculation are $\mu = 1{\cdot}5$, $\Delta\mu = 0{\cdot}07$, $P = 3330$ Å. The thick specimen gives the well-known flat topped curve of the dynamical theory, while the thin film gives a principal maximum accompanied by subsidiary fringes, which have been observed experimentally[9, 10]. The figure also shows the values computed from the exact theory of Nityananda[5,11]. In the latter computations, the external isotropic medium (external to the cholesteric specimen) is assumed to have a refractive index of 1·5, so that the contribution of the ordinary Fresnel reflexion coefficient at the cholesteric/isotropic interface is eliminated.

Anomalous rotatory dispersion

If reflexions are neglected, the optical rotation per thickness P of the liquid crystal is $\frac{1}{2}(\varphi_R - \varphi_L)$ and the rotatory power is given by (1). Near the region of reflexion, the right circular component suffers anomalous phase retardation and, 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.

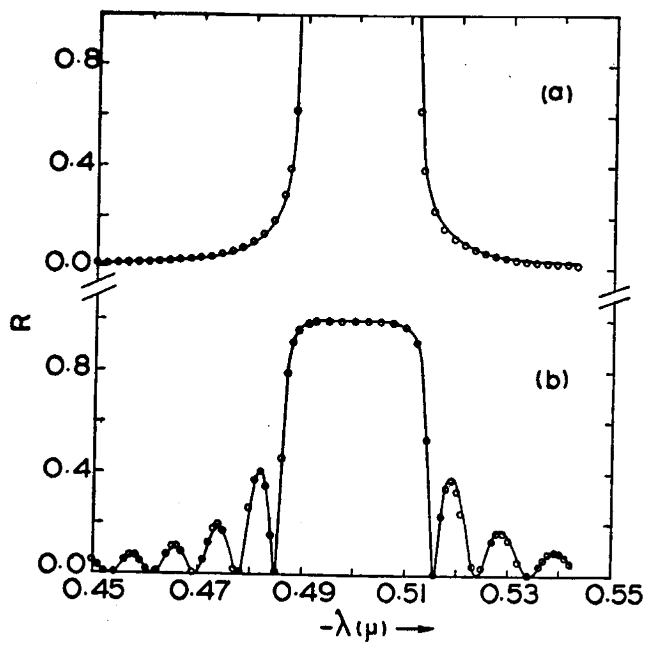

Figure 1 Reflexion coefficient R *versus* wavelength λ in the non-absorbing case: (*a*) semi-infinite medium, (*b*) film of thickness 25P. Curves are derived from the dynamical theory; circles represent values computed from the exact theory[5,11].

Thick specimen

According (12),

$$T_{r+1} = x\, T_r,$$

where

$$x = \exp(-\xi)\exp(-i\varphi_o)$$

$$\xi = \pm (Q^2 - \varepsilon^2)^{1/2}$$

$$\varphi_0 = \varphi_R - \varepsilon = 2\pi.$$

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

$$\chi \approx \xi/2.$$

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

$$\alpha = \tfrac{1}{2}(\varphi_0 - \varphi_L) = \frac{\pi P}{\lambda}(\mu_R - \mu_L) + \frac{\pi(\lambda - \lambda_0)}{\lambda} = -\frac{n\gamma^2}{2\beta} + \frac{\pi(\lambda - \lambda_0)}{\lambda}.$$

Here $\gamma = \pi p\,(\Delta\mu)/\lambda$. Therefore the rotatory power

$$\rho = -\frac{\pi(\Delta\mu)^2 P}{4\lambda^2} + \frac{\pi(\lambda - \lambda_0)}{P\lambda}, \qquad (18)$$

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

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

$$\alpha = \tfrac{1}{2}\left[(\varepsilon^2 - Q^2)^{1/2} + \varphi_0 - \varphi_L\right]$$

$$= -\frac{n\gamma^2}{2\beta} - \frac{\varepsilon}{2}\left[1 - \left(1 - \frac{Q^2}{\varepsilon^2}\right)^{1/2}\right]$$

Hence the rotatory power

$$\rho = -\frac{\pi(\Delta\mu)^2 P}{4\lambda^2} + \frac{\pi(\lambda - \lambda_0)}{P\lambda}\left[1 - \left(1 - \frac{Q^2}{\varepsilon^2}\right)^{1/2}\right] \qquad (19)$$

Thin film

For a thin film the phase of the right circular wave can be evaluated from (16):

$$\frac{T_m}{T_0} = A \exp [-im(\varphi_0 + \phi)]$$

where $\tan m\phi = \dfrac{\varepsilon}{\xi \coth m\xi}$

The optical rotation for thickness P is

$$\tfrac{1}{2}(\varphi_0 + \phi - \varphi_L) = \tfrac{1}{2}[(\varphi_R - \varphi_L) + (\phi - \varepsilon)]$$

and the rotatory power

$$\rho = -\frac{\pi (\Delta\mu)^2 P}{4\lambda^2} + \frac{(\phi - \varepsilon)}{2P}.$$

Figures 2 and 3 show some typical calculations based on the above equations. It will be seen that the reflexion, circular dichroism and rotatory power predicted by this theory agree very closely with those of the electromagnetic treatment[5].

Absorbing systems : The Borrmann effect

Suppose now that the birefringent layers are also linearly dichroic. Let us assume that the principal axes of linear birefringence and linear

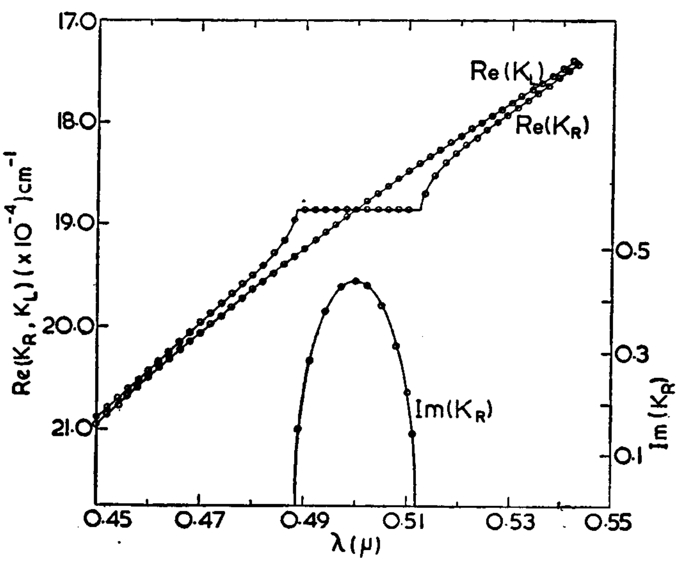

Figure 2 The wave vectors K_R and K_L of the normal waves as functions of λ in a semi-infinite non-absorbing medium. Curves are derived from the dynamical theory; circles represent values computed from the exact theory[5].

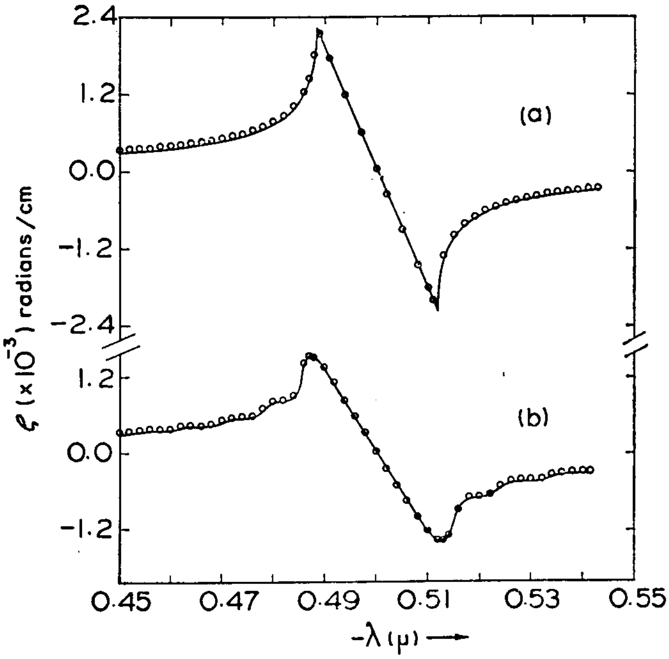

Figure 3 Rotatory power ρ *versus* λ in the non-absorbing case: (*a*) semi-infinite medium, (*b*) film of thickness 25P. Curves are derived from the dynamical theory; circles represent values computed from the exact theory[5,11].

dichroism are the same. If $\hat{\mu}_1$ and $\hat{\mu}_2$ be the principal complex refractive indices of each layer, then the reflexion coefficient $\hat{Q}$ and the phase retardation $\hat{\varphi}$ per pitch also become complex:

$$\hat{Q} = \pi \frac{\Delta\hat{\mu}}{\hat{\mu}}$$

$$\hat{\varphi}_R = \frac{2\pi}{\lambda}\hat{\mu}_R P = \frac{2\pi}{\lambda}\hat{\mu}P - \frac{\pi(\Delta\hat{\mu})^2P^2}{4\lambda^2}$$

$$\hat{\varphi}_L = \frac{2\pi}{\lambda}\hat{\mu}_L P = \frac{2\pi}{\lambda}\hat{\mu}P + \frac{\pi(\Delta\hat{\mu})^2P^2}{4\lambda^2}$$

Here

$$\Delta\hat{\mu} = \hat{\mu}_1 - \hat{\mu}_2 \qquad \hat{\mu}_1 = \mu_1 - ik_1$$

$$\hat{\mu} = \tfrac{1}{2}(\hat{\mu}_1 + \mu_2) \qquad \hat{\mu}_2 = \mu_2 - ik_2$$

k_1 and k_2 are the principal absorption coefficients.

All the equations obtained for non-absorbing media are still valid for absorbing systems except that $\hat{Q}$, $\hat{\varphi}_R$ and $\hat{\varphi}_L$ replace Q, φ_R and φ_L respectively. For example, for the thick specimen, the reflexion coefficient R for the right circular wave, the optical rotatory power $\hat{\rho}$ (which is now complex), the wave vectors $\hat{K}_R$ and $\hat{K}_L$ are given by

$$R = \left| \frac{\hat{Q}}{\hat{\varepsilon} \pm (\hat{\varepsilon}^2 - \hat{\xi}^2)^{1/2}} \right|^2$$

$$\hat{\rho} = -\frac{\pi(\Delta\hat{\mu})^2 P}{4\lambda^2} + \frac{\pi(\lambda - \hat{\mu}_R P)}{P\lambda}\left[1 - \left(1 - \frac{\hat{Q}^2}{\hat{\varepsilon}^2}\right)^{1/2}\right]$$

$$\hat{K}_R = \frac{2\pi + \hat{\xi}}{P} \qquad \hat{K}_L = \frac{(2\pi\hat{\mu}_L)}{\lambda} \qquad (21)$$

Here

$$\hat{\varepsilon} = \frac{2\pi}{\lambda}(\hat{\mu}_R P - \lambda)$$

$$\hat{\xi} = \pm(\hat{Q}^2 - \hat{\varepsilon}^2)$$

Figure 4 shows the dependence R, ρ (the real part of $\hat{\rho}$), and the imaginary parts of $\hat{K}_R$ and $\hat{K}_L$ on wavelength. Here $k = \frac{1}{2}(k_1 + k_2) = 0.02$,

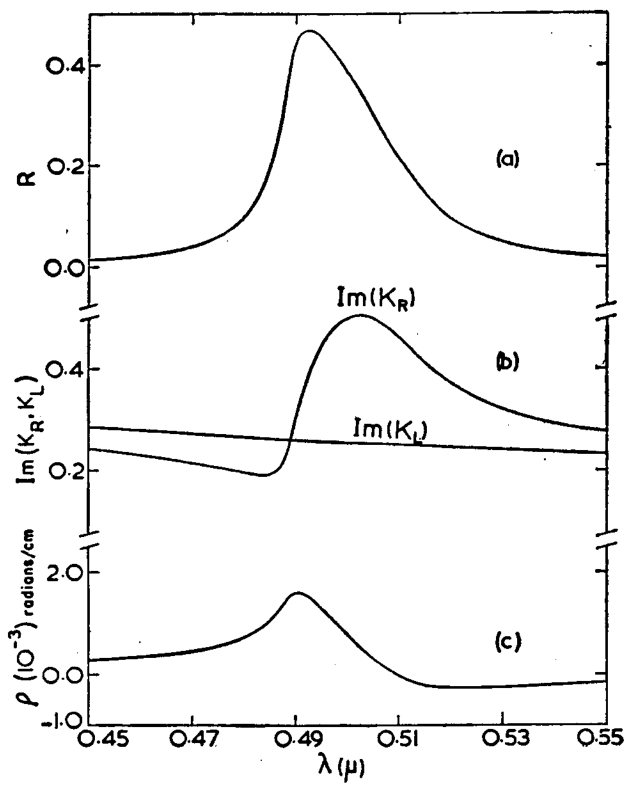

Figure 4 (*a*) Reflexion coefficient *R*, (*b*) imaginary parts of $\hat{K}_R$ and $\hat{K}_L$, (*c*) rotatory power ρ, plotted as functions of λ for an absorbing semi-infinite medium.

and $\Delta k = (k_1 - k_2) = 0.028$. The interesting result is obtained that on the shorter wavelength side $\mathrm{Im}(K_R)$ is less than $\mathrm{Im}(\hat{K}_L)$, *i.e.*, the right circular wave is less attenuated than the left circular wave, whilst on the longer wavelength side the opposite is true. To observe this effect thin films have to be used.

The transmission coefficients T_R and T_L for the right and left circular waves through an absorbing cholesteric film of thickness mP are given by

$$T_R = \left| \frac{\hat{\xi} \operatorname{cosech} m\hat{\xi}}{i\hat{\varepsilon} + \hat{\xi} \coth m\hat{\xi}} \right|^2 ,$$

$$T_L = |\exp(-m\hat{\varphi}_L)|^2 \qquad (22)$$

The theoretical dependence of T_R and T_L on wavelength are shown in figure 5, for both the non–absorbing and the absorbing cases for a film thickness of 25 P. The structure being right–handed the right circular component is reflected, and hence in the non–absorbing film ($k = \Delta k = 0$), T_R is always less than T_L. On the other hand, in the absorbing case, T_R shows an enhanced value on the short wavelength side of the reflexion band, which is the analogue of the Borrmann effect. It can be shown that T_L will exhibit an anomalous increase for a left-handed structure (*i. e.*, negative β) and also that the peak transmission will occur on the long wavelength side of the reflexion if Δk is negative. These results are found to be in good quantitative agreement with the rigorous treatment of the phenomenon by Nityananda *et al*[2].

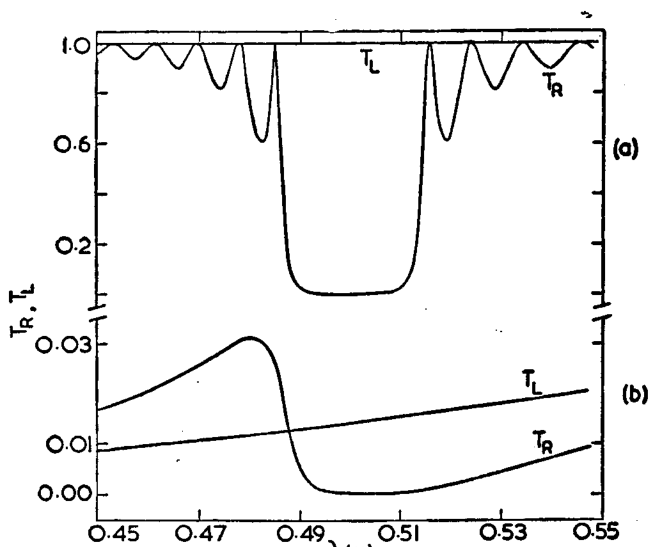

Figure 5 Transmission coefficients T_R and T_L for right and left circular waves for a film of thickness 25P (*a*) non-absorbing, (*b*) absorbing. The enhanced transmission for the right circular component in (*b*) is the analogue of the Borrmann effect.

Concluding remarks

We have shown that the dynamical model yields results in conformity with the more detailed electromagnetic theories. However, the simple treatment presented here has certain limitations. Firstly, it is developed for small ε and therefore does not hold good far away from the reflexion band. Secondly, it is strictly valid only for integral values of the pitch; and thirdly, it fails when the film thickness is very small (or when the extinction length is of the order of a pitch) as the assumption that the normal waves are circularly polarized is then no longer justified. These limitations can be removed by including the effect of multiple reflexions within the n layers per turn of the helix, which has been neglected in this discussion. The simple difference equations then become matrix difference equations and the resulting solutions can be shown to be fully equivalent to those of the rigorous treatment[5]. However, the calculations presented in previous sections indicate that this more elaborate formulation of the theory is probably not necessary for most practical problems.

Acknowledgements

We are grateful to R Nityananda and U D Kini for providing the numerical results computed from the exact theory.

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