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Anomalous transmission (Borrmann effect) in absorbing cholesteric liquid crystals

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Abstract. The celebrated Borrmann effect is an anomalous increase in transmitted x-ray intensity when a crystal is set for Bragg reflexion. In this paper, it is shown that a similar effect occurs in absorbing cholesteric liquid crystals in the vicinity of the reflexion band. However, in contrast to the x-ray case, the polarization of the wave field and the linear dichroism of the molecules play an essential part.

Numerical computations are presented, based on the general theory of reflexion and transmission by oriented cholesteric films. They illustrate the role of dichroism and sample thickness in determining the magnitude of the effect.

The existence of the effect is established by experimental studies on cholesteryl nonanoate mixed with small quantities of *p*-azoxyanisole or *n*-*p*-methoxybenzylidene-*p*-phenylazoaniline. When the reflexion band is adjusted to overlap with the strongly dichroic band of the solute molecules, the transmission spectrum exhibits the features predicted by theory.

Introduction

The optical properties of a cholesteric liquid crystal are well described by the model of Oseen[1]. Locally the molecular axes are, on the average, aligned parallel to a fixed direction as in a nematic, so that this is a principal axis of the local dielectric ellipsoid. As we move along the z axis, this direction of preferred alignment (the director) rotates in the x–y plane, sweeping out an angle qz in a distance z. The pitch p is defined as the distance along z in which the director rotates through 2π; thus $p = 2\pi/q$. The components of the dielectric tensor are periodic functions of position. Many of the features of wave propagation in periodic structures which were first studied in the context of x-ray diffraction by crystals can be observed in cholesterics in the optical range of wavelengths since their periodicity is of this order. The selective reflexion of one circular polarisation in a band of frequencies, the extinction of that wave within the medium and the anomalous dispersion of the optical rotatory power in this frequency region are well known experimental facts which have been discussed theoretically by de Vries[2] and Chandrasekhar and Srinivasa Rao[3]; the latter authors have emphasized the analogy with the dynamical theory of x-ray diffraction.

This paper concerns another striking phenomenon which can occur in an absorbing periodic medium – the Borrmann effect[4, 5]. First discovered for x-rays incident on highly perfect crystals, this effect consists of an (intuitively) unexpected increase in the transmitted intensity near the Bragg reflexion setting, which is precisely where a decrease in transmission is expected. Hence the name "anomalous transmission". This is a consequence of the standing wave nature of the disturbance within the medium when the incident frequency is in the reflection band, as will be explained in detail in section 1, which also presents the features special to the cholesteric medium. Section 2 describes claculations based on the theory of reflexion and transmission by plane parallel cholesteric films which has been described in the previous paper[6]. These show the feasibility of observing the effect under suitable conditions. Section 3 presents the results of preliminary experiments on the transmission of light of both circular polarisations by films of cholesteryl nonanoate to which a small amount ($<5\%$) of dichroic molecule such as *p*-azoxyanisole (PAA) or *n*-*p*-methoxybenzylidene-*p*-phenylazoaniline (MBPAA) had been added. The curves giving circular dichroism as well as transmitted intensity as a function of wavelength near the reflexion band indeed show the predicted features.

1. Nature of the waves in the cholesteric medium and a qualitative discussion of the Borrmann effect

An exact solution of the normal incidence problem is given in the papers by Kats[7] and Nityananda[8]. The medium is described by a dielectric tensor with principal values ε_a and ε_b and principal axes rotating through an angle of 2π in the x–y plane per pitch p traversed along z. The solution of Maxwell's equations under these conditions is given by a combination of two circular waves with opposite sense and wave vectors differing by $2q$. Naturally, there are two such solutions for a given direction of propagation, which would reduce to a pure left circular wave and a pure right circular wave in the limit $\varepsilon_a - \varepsilon_b \rightarrow 0$. We call these the left and right dominant solutions. In the range of wavelengths near the reflexion band which is of interest here, the amplitude of the dominant component is never less than that of the other component, justifying the name. Further, one of the two solutions (the right dominant for a right handed cholesteric) becomes strongly mixed, near the reflection band. That is, if we write it as a superposition of a right circular wave $\exp(iK_1 z)$ and a left circular wave $d \exp[i(K_1 - 2q)z]$ then the coefficient d becomes of the order of 1 for wavelengths near the reflexion band (figure 1 *a*). If we fix the value of z, thereby studying the electric field at one point in the medium, the two circular components add to give an elliptic vibration. The direction of the major axis of this ellipse is the direction in which the two circular waves add (figure 1 *b*). When the coefficient d has an absolute value of 1, the resultant vibration is linearly polarised. As we change z, the relative phase of the two circular components changes by $2qz$. The resultant elliptic vibration therefore changes in azimuth by qz, but has the same ellipticity. Indeed, in a co-ordinate system rotating at the same rate as the director, we have a fixed elliptic vibration as was pointed out by de Vries[2]. This is important for what follows. Away from the reflexion band, the coefficient d is small and we have almost a circular vibration. On the long wavelength side of the reflection band, we obtain an ellipse with major axis along the direction of greater principal dielectric constant

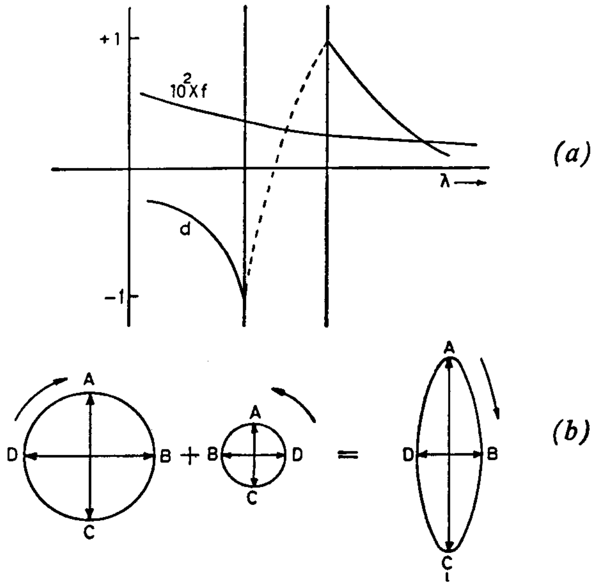


Figure 1 (*a*) The coefficients *d* and *f* which determine the mixed character of the normal waves as functions of wavelength. The dotted part of the curve for *d* is meant to indicate that $|d|$ remains 1 within the reflection band, while the phase varies from 180° to 0: that is, *d* moves along the semicircle of unit radius in the upper half of the complex plane, varying from -1 to $+1$ as the wavelength increases from one edge of the reflection band to the other.

(*b*) Combination of two opposite circular waves to give an elliptic vibration with the same sense as the stronger circular wave and azimuth along the direction in which the electric vectors of the two circular waves are parallel. A B C and D represent four successive states of the vibration separated by 90° in phase or a quarter of a period in time.

say ε_a. Since the electric vector is now sampling a direction with greater polarisability, it is natural that the effective refractive index for the wave is greater. On the short wavelength side of the reflexion band, the major axis of the ellipse is directed along the axis with lower principal dielectric constant ε_b. We expect that the effective refractive index would now be less than the average for the medium. The dispersion curve (wave vector **K** as a function of frequency ω) plotted in figure 2, confirms this physical picture. Within the reflexion band the wave is linearly polarised with the azimuth rotating at the same rate as the director and making a fixed angle to it. As we decrease the wavelength, going through the reflexion band, this angle changes from 0 to 90° as the phase of the complex number d varies from 0 to 180° (figure 1). The second normal wave is only weakly mixed. If we write it as a superposition of a left circular wave $\exp(iK_2 z)$ and a right circular wave $f \exp[i(K_2 + 2q)z]$, then f remains small and shows no remarkable variation near the Bragg reflexion (figure 1 a). For qualitative purposes, we can think of this wave as a pure left circular wave which sees only the average medium and has a refractive index $\bar{n}$, and a simple linear dispersion relation (figure 2) $\omega = (c/\bar{n})k$. We call this the 'indifferent' normal wave. The polarisation behaviour of the normal waves is summarised in figure 3.

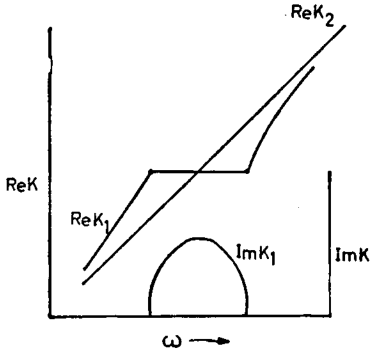


Figure 2 The dispersion relation (wave vector K as a function of frequency ω) for the two normal waves. K_2 is real, while K_1 has an imaginary part which is separately shown.

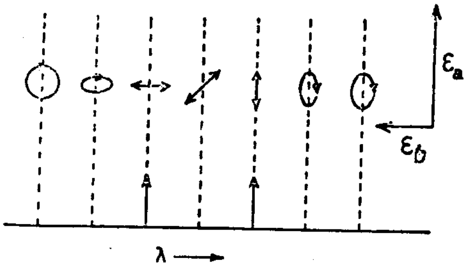


Figure 3 Polarisation of the normal wave as a function of wavelength.

The above description is valid for a non-absorbing cholesteric medium. However, we can assess the effects of dichroism (that is, a different imaginary part for ε_a and ε_b) by assuming that the polarisation behaviour of the normal waves remains qualitatively unchanged. Taking the imaginary part of ε_a to be greater (that is, the more polarisable axis is also the axis of greater absorption) - we see immediately that the attenuation of the first normal wave will be greater than the average on the long wavelength side of the reflexion band since it will be sampling more of the ε_a axis, and it will be less than the average on the short wavelength side of the reflexion band. Hence right circular incident light, which couples to this normal wave, should undergo more absorption on the long wavelength side of the band and less on the short wavelength side.

This effect is over and above the extinction of the right circular wave which occurs even in the absence of absorption. Qualitatively, we expect enhanced transmission of the right circular wave on the short wavelength side. This is the Borrmann effect. The reduced absorption in this case is a consequence of the polarisation being at right angles to the highly absorbing axis. For x-rays in crystals the reduced absorption follows from the amplitude of the electric field being small at the absorbing sites (figure 4). Both these are due to the standing wave nature of the disturbance in the medium, and both depend on the relative phase of the primary and Bragg reflected waves (the position of the modes in the x-ray case, the polarisation of the linear vibration in the liquid crystal). Since these phases vary continuously (by 180°) as we pass through the Bragg reflection band, the optimum conditions for the Borrmann effect are fulfilled at only one wavelength — in our example at one edge of the reflexion band.

Figure 4 A qualitative picture of the Borrmann effect in x-rays. The nodes of the standing wave coincide with the atomic positions giving minimum absorption.

2. Numerical calculations on absorbing cholesterics

Using the formulae of the previous paper[6] the transmission coefficients of a plane parallel cholesteric slab were calculated as functions of wavelength near the Bragg reflexion for each circular polarisation incident on it. To correspond to the experimental practice, the total transmitted intensity was calculated as the sum of that in the two polarisations, although, predominently, only the incident circular polarisation is present. The results are also presented in the form of circular dichroism D as a function of wave length, where

$$D = \frac{\sqrt{I_+} - \sqrt{I_-}}{\sqrt{I_+} + \sqrt{I_-}}$$

I_+ and $I-$ are the transmitted intensities for the + and – circular polarisations. These curves should be compared with the corresponding curves for a non-absorbing cholesteric presented in the previous paper[6]. The pitch p and principal refractive indices n_b and n_a have been chosen to be 3571 Å; 1·4 and 1·47 respectively as for the non-absorbing case. The dichroism Δk has been given the values 0·006, 0·03 and 0·06 successively. Here it is assumed that n_b remains real ($n_b = 1{\cdot}4$) and $n_a = 1{\cdot}47 + i\,\Delta k$ The dichroism has the same sign as the birefringence, *i.e.*, the more absorbing axis of the molecule is taken to be the same as the more polarisable axis.

A plot of the reflection coefficient as a function of wavelength is given for $\Delta k = 0{\cdot}006$ in figure 5. When compared to the non-absorbing case, it shows asymmetry. This is analogous to the asymmetry of the reflexion as a function of angle which Prins[9] calculated for x-rays incident on an absorbing perfect crystal. The reflection coefficient is higher on the short wavelength side and falls off towards longer wavelengths.

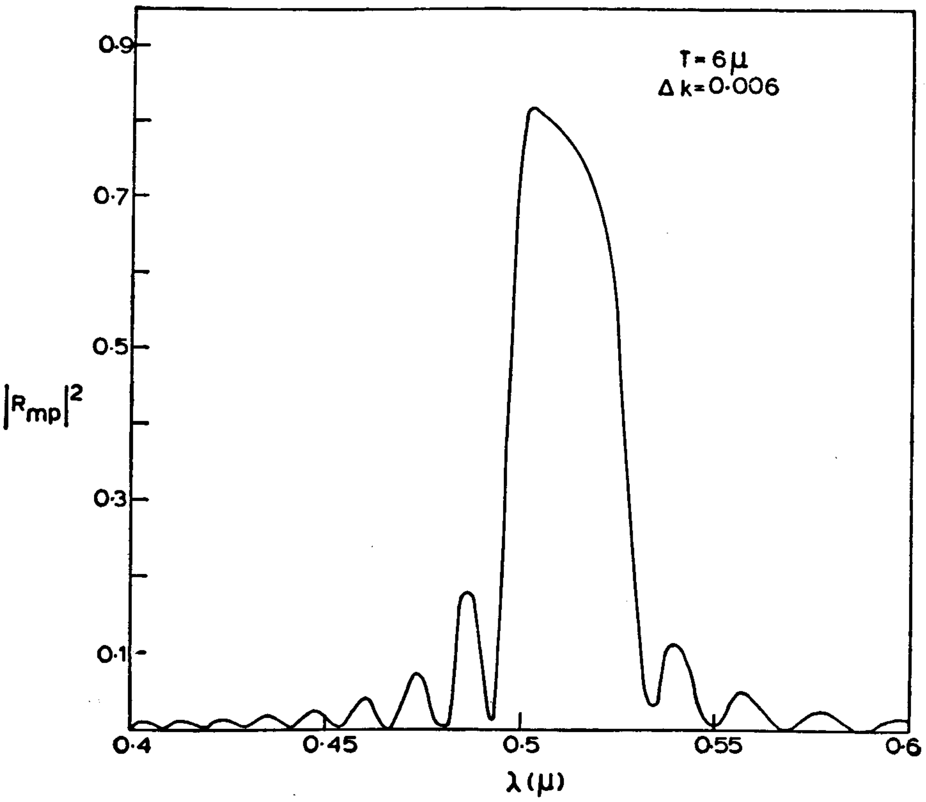


Figure 5 Intensity of reflexion with change in the sense of circular polarisation for an absorbing cholesteric. Thickness $T = 5.6\,\mu$ dichroism $\Delta k = 0.006$.

Figure 6 *a* shows the transmitted intensity for the two circular polarisations, and figure 6 *b* the circular dichroism for $\Delta k = 0{\cdot}006$. The curves

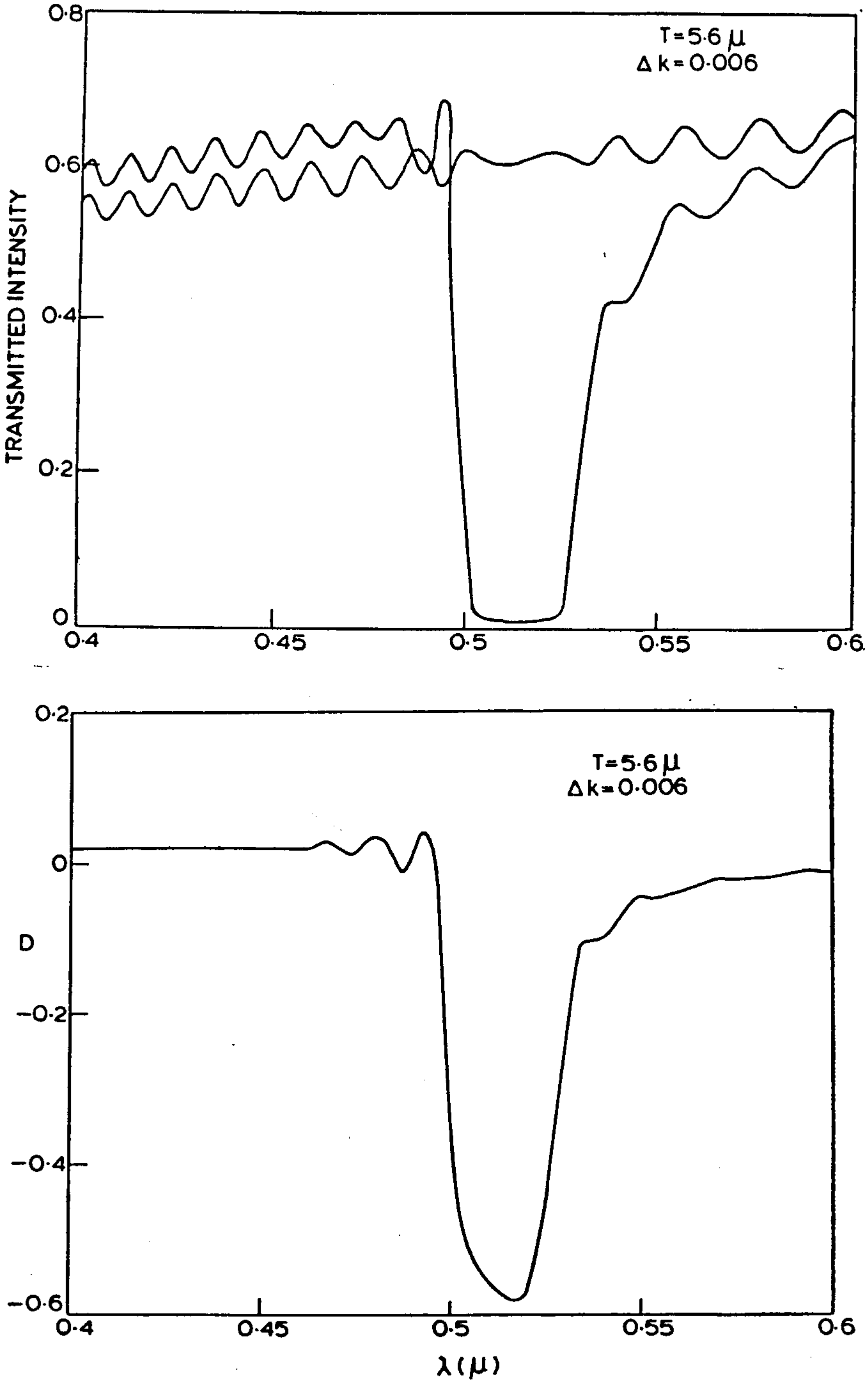


Figure 6 (*a*) Transmitted intensity, and (*b*) circular dichroism as function of wavelength.
$T = 5.6\,\mu$, $\Delta k = 0.006$.

are noticeably asymmetric, and the circular dichroism has changed sign on the short wavelength side so that the right circular polarisation which is cut down in the Bragg reflexion is actually enhanced on this side. By itself this does not constitute the Borrmann effect since there is a circular dichroism at short wavelengths which can be predicted from the Mauguin[10] formula for rotation by making Δn complex and it has the right sign. However, this is expected to fall off with increase in wavelength; while

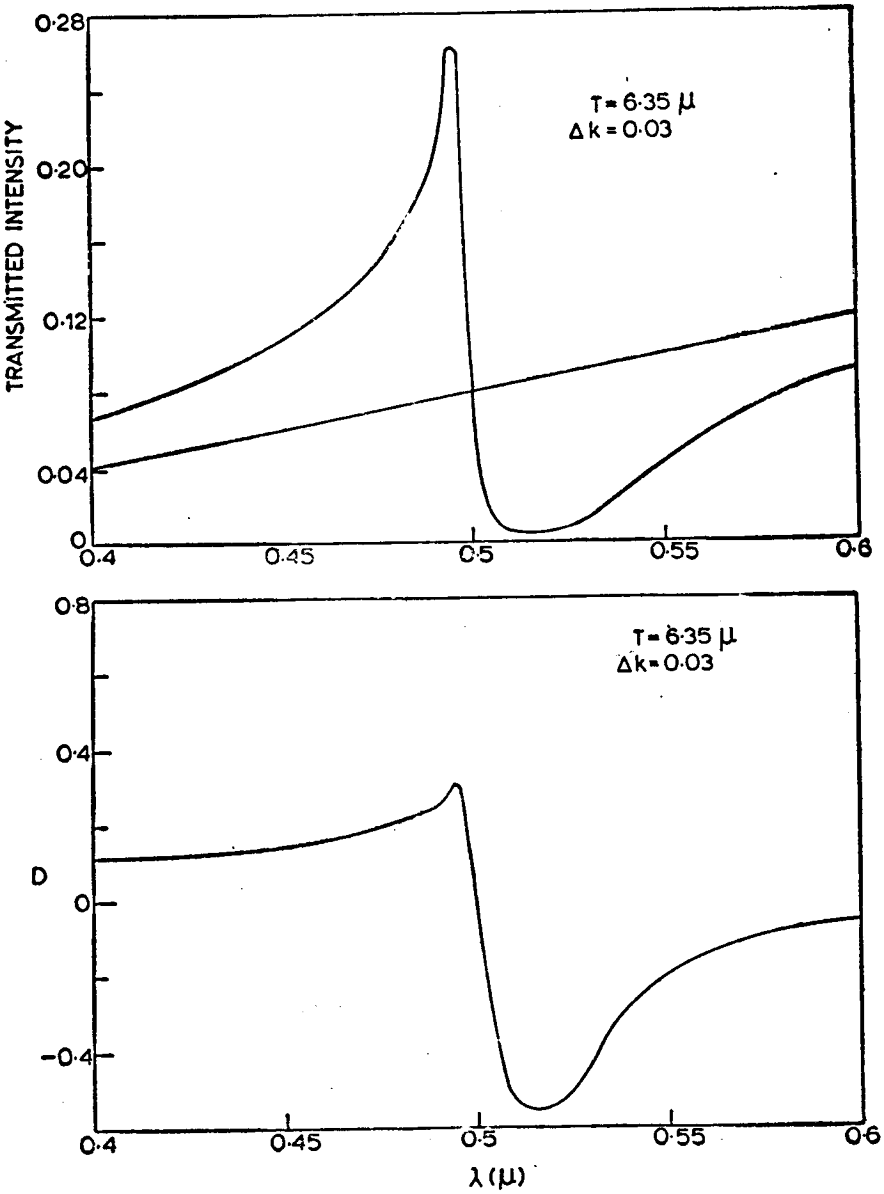


Figure 7 (*a*) Transmitted intensity, (*b*) Circular dichroism
$T = 6.35\mu$, $\Delta k = 0.03$.

the arguments of section 1 suggest that the transmission of right circular light should show a well defined maximum near the short wavelength edge of the reflexion band. This is brought out clearly in figures 7 *a* and 7 *b* which show the transmission coefficients and D for $\Delta k = 0{\cdot}03$. This is even clearer in figures 8 *a* and 8 *b* which are for $\Delta k = 0{\cdot}06$. We also note

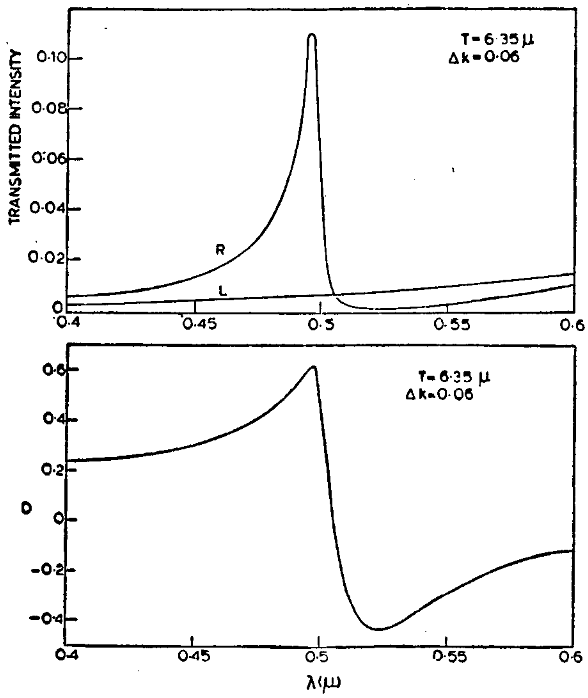


Figure 8 (*a*) Transmitted intensity, (*b*) Circular dichroism $T = 6.35\,\mu$, $\Delta k = 0.06$.

the opposite effects on the long wavelength side, *viz.*, the transmission of right circular light remains low for at least 500 Å beyond 5140 Å (which was the centre of reflexion band in the non-absorbing case). This is to be expected from the qualitative arguments of section 1 – in this wavelength region the major axis of the ellipse is along the more absorbing axis of the molecules (figure 3).

The broadening and asymmetry of the circular dichroism curve has implications for optical rotation as well. We expect the zero crossing of the optical rotation to shift to longer wavelengths. This effect can be seen in figures 9 *a*, *b* and *c* which show the calculated optical rotation as a function of wavelength for $\Delta k = 0{\cdot}006$, $0{\cdot}015$ and $0{\cdot}03$.

3. Experiments

The experiments were carried out on thin samples of cholesteryl nonanoate with small percentages of PAA or MBPAA added. The former gives a

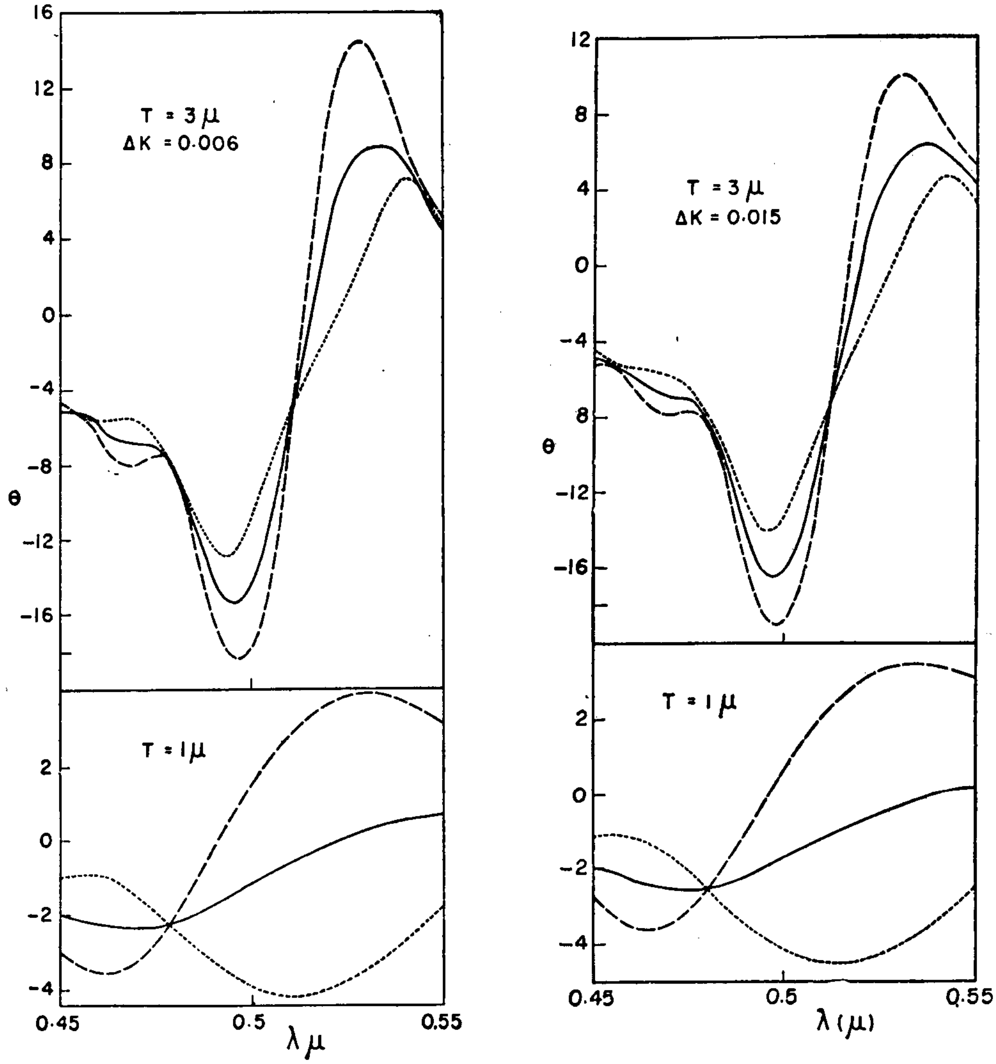


Figure 9 Optical rotation for incident linear polarisation along the director (dashed curve) and perpendicular to it (dotted curve). (*a*) $\Delta k{=}0.006$, (*b*) $\Delta k = 0.015$.

band of linear dichroism (Δk) at about 3500 Å and the latter at about 3800 Å. They were well oriented in the plane texture and the wavelength of the Bragg reflexion could be controlled by using the temperature dependence of the pitch. The basic technique was to photograph the spectrum of a continuum source (tungsten lamp) through a circular polariser and the given sample. This is done for each circular polarisation separately and the transmitted intensity as a function of wavelength inferred from a microdensitometer trace of the developed photographic plate. Several exposures of the tungten lamp source without any liquid crystal sample interposed were taken for calibration purposes. The

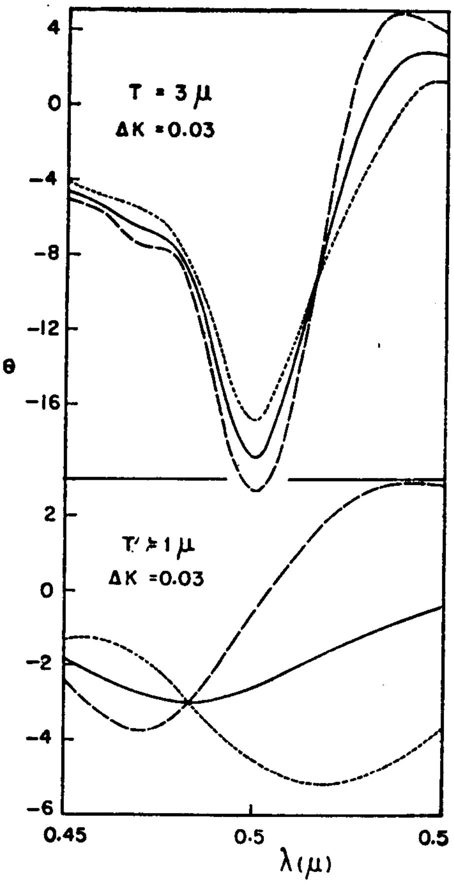


Figure 9 c Optical rotation for incident linear polarisation along the director (dashed curve) and perpendicular to it (dotted curve). $\Delta k = 0.03$.

intensity obtained from these calibration curves is in arbitrary but fixed units. It is proportional to the transmission coefficient of the sample at that wavelength. The circular dichroism, which requires only the ratio of the transmission coefficients for the two circular polarisations, is independent of this undetermined factor of proportionality.

The raw microdensitometer traces for non-absorbing sample are shown in figure 10a. The two traces do not cross, showing that the circular dichroism does not change sign. Figure 10b shows the two traces for 2·45% PAA (by weight) in cholesteryl nonanoate. For this composition, we roughly estimate the maximum Δk to be 0·03. The Bragg reflection is at about 3550 Å, as is seen by the dip in the transmission for right circular light. At shorter wavelengths, the transmission has actually risen above that for left circular light. Figure 10c shows the transmission coefficients (in arbitrary units) and figure 10d the circular dichroism for the same sample. Figure 11 shows the results of a similar experiment on 4·25% MBPAA the Bragg reflection being at about 4020 Å.

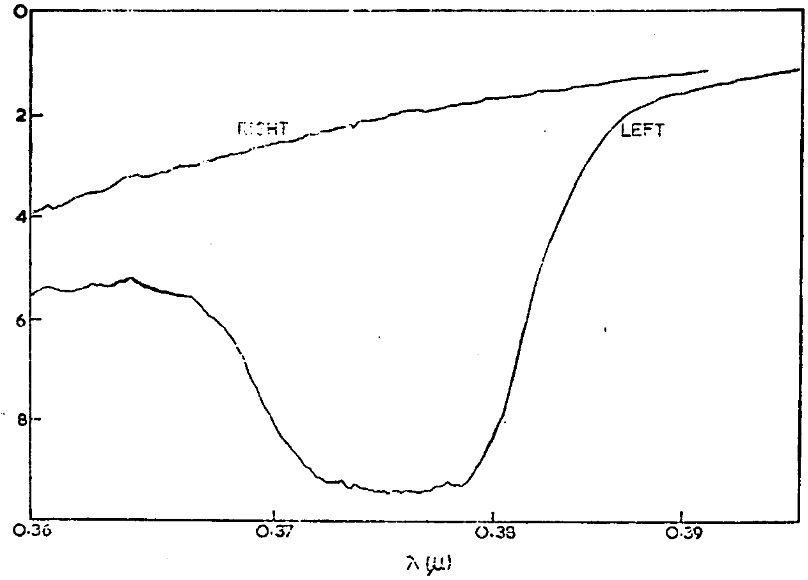
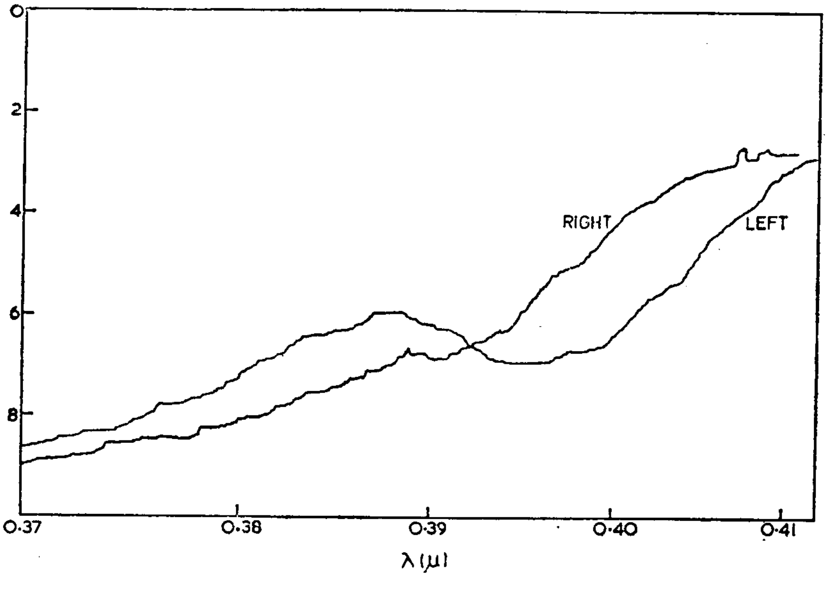
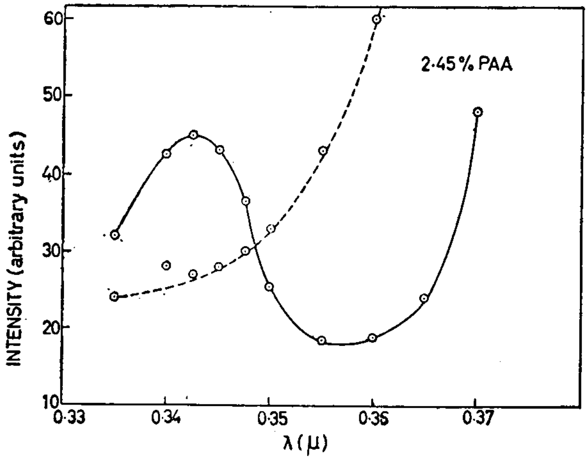


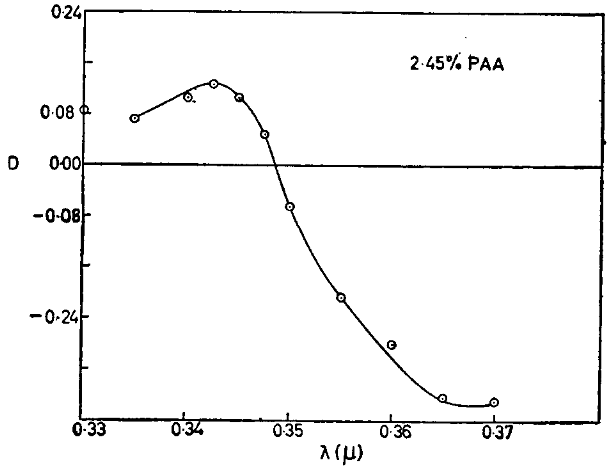
Figure 10 (*a*) Raw microdensitometer traces for a non-absorbing sample showing qualitatively the behaviour of the transmitted intensity as a function of wavelength for the two circular polarisations.



(*b*) Microdensitometer traces for the two circular polarisations.



(*c*) Transmitted intensity for the two circular polarisations (arbitrary units). The dashed line is for right circular polarisation and the solid line for left circular.



(*d*) Circular dichroism. Sample : 2.45% PAA in cholesteryl nonanoate $T = 6.35$ μ.

In interpreting the experimental dichroism curves one must recall that the linear dichroism Δk is a function of wavelength[11] showing a maximum and falling off on either side. Since the experimental dichroism curves depend critically on the relative position of the reflexion band and the band of dichroism, we do not expect the resemblance to the theoretical curves of section 2, computed for constant Δk, to be very close. However, the curves do show the maximum at shorter wavelengths which falls off at longer wavelengths, characteristic of the Borrmann effect.

Conclusions

The cholesteric liquid crystal, having a periodicity of the same order as the wavelength of light, shows optical effects analogous to those studied in x-ray diffraction. The Borrmann effect has been observed in such a system for the first time, and shows the features expected from theory.

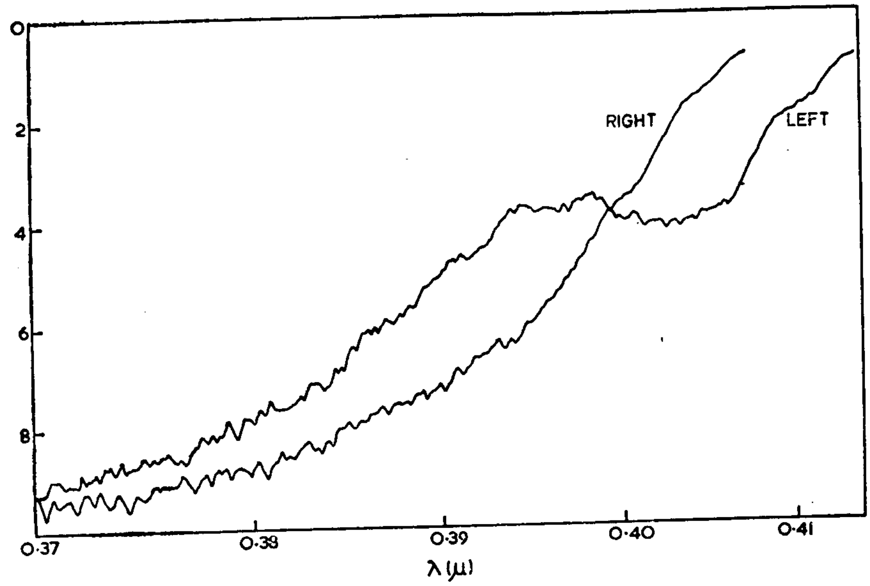
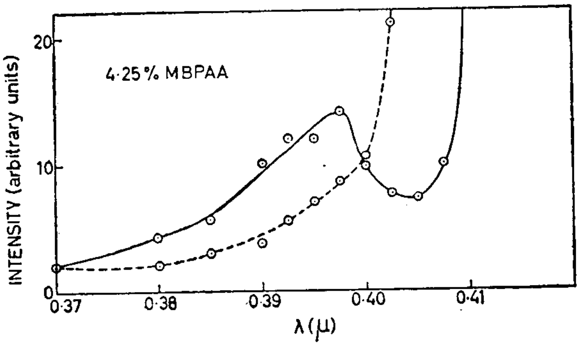
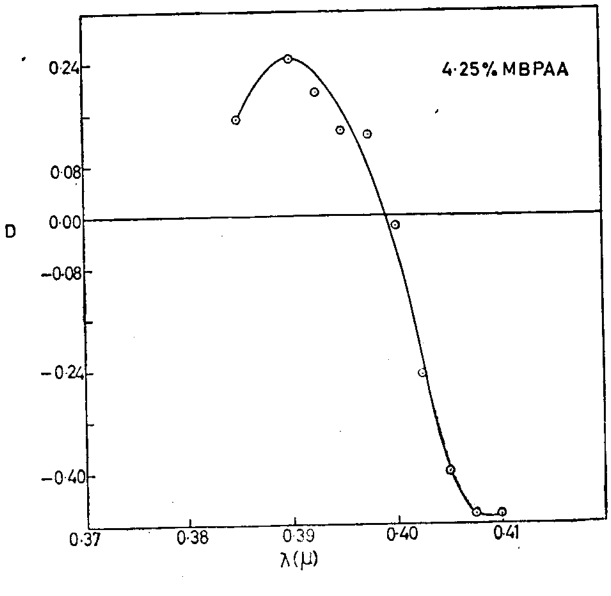


Figure 11 (*a*) Microdensitometer traces.



(*b*) Transmitted intensity in arbitrary units. The dashed line is for right circular polarisation and the solid line for left circular.



(*c*) Circular dichroism. Sample : 4.25% MBPAA in cholesteryl nonanoate $T = 6.35\ \mu$.

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DISCUSSION

Darbari : How did you measure the thickness of the sample ?

Nityananda : The thicknesses quoted are the nominal thicknesses of the spacers which may be accurate to about 3 or 5%. In the present experiments it is assumed that the sample thickness is the same as that of the spacers.

Billard : In transparent materials if the refractive index is purely imaginary we do not have attenuated waves but only an evanescent oscillation. In a plate you have the optical tunnel effect.

Nityananda : I agree – the extinction of the normal wave in the Bragg reflection is analogous to the attenuation of the evanescent wave in the rarer medium.

Rustichelli : Do you think that, in analogy to x–ray or neutron anomalous transmission, the light anomalous transmission could be used to get information on defects in cholesteric liquid crystals ?

Nityananda : It is possible, however, in liquid crystals conventional optical observation also reveals the disclinations, etc.

Rustichelli : The dynamical theory of x–ray or neutron diffraction foresees an angular amplification of the order of 10^4 – 10^5 for the diffracted beam inside a perfect crystal in a plane geometry. Do you think that such an effect will exist also for light in cholesteric liquid crystals with possibilities of useful applications?

Nityananda : I am not familiar with angular amplification, but there is a full analogy with the x-ray dynamical theory, which Ranganath* will be talking about, and we should investigate this.

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* Chandrasekhar S, Ranganath G. S. and Suresh K. A., this Conference.