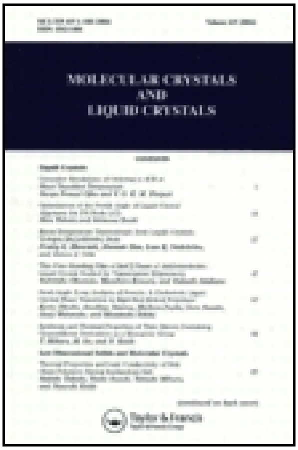

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An Experimental Study of the Anomalous Transmission (Borrmann Effect) in Absorbing Cholesteric Liquid Crystals

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An Experimental Study of the Anomalous Transmission (Borrmann Effect) in Absorbing Cholesteric Liquid Crystals

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It has been shown previously that in analogy with the Borrmann effect in X-ray diffraction from crystals there is an anomalous increase in the transmitted intensity near the Bragg reflection band in an absorbing cholesteric liquid crystal. In this communication detailed experimental studies of this effect carried out on thin films of mixtures of cholesteryl nonanoate and *p*-azoxyanisole of different concentrations are reported. Numerical calculations based on the dynamical theory of reflection are also presented. The theoretical curves of circular dichroism versus wavelength are in qualitative agreement with the experimentally observed features.

1 INTRODUCTION

Borrmann[1] discovered that there is an enhancement of the intensity of transmission of X-rays when a perfect crystal is set for Bragg reflection. A similar phenomenon has been predicted and established experimentally in absorbing cholesteric liquid crystals.[2,3] The difference in the latter case is that the polarization of the wavefield and the linear dichroism of the molecules play a significant role. The physical origin of the effect in cholesterics may be explained as follows. Consider left circular light at normal incidence (i.e., propagating along the helical axis) on a cholesteric film of the same handedness. At the reflection band, standing waves are set up inside the medium due to the interference between the primary and the reflected circularly polarized waves. We shall suppose that the linear birefringence and linear dichroism of the molecules are both positive. The phase of the reflected wave with respect to the primary wave varies from π to 0 starting from the shorter wavelength edge of the reflection band to the longer wavelength edge. Hence the electric vector in the medium makes an angle $\pi/2$ with respect to the director on the shorter wavelength side and along the director on the longer wavelength side, thus experiencing minimum and maximum absorption respectively at the two edges of the reflection band. As a result there occurs an anomalous increase of the transmitted intensity on the shorter wavelength side which is over and above the normal attenuation due to Bragg reflection. That such an enhancement in the transmitted intensity occurs has been verified experimentally. The present paper reports a more detailed experimental study and a comparison with the predictions of the theory.

2 EXPERIMENTS

The experiments were conducted on thin films of cholesteryl nonanoate in which was dissolved small quantities of *p*-azoxyanisole (PAA). The solute molecules arrange themselves in a helical fashion in the cholesteric structure. PAA has a strong linearly dichroic band around 0.36 μm. Pure cholesteryl nonanoate is left handed and has a Bragg reflection band at 0.36 μm at 88.5°C. This temperature decreases slightly with increasing concentration of PAA. The experimental procedure consisted of adjusting the sample temperature so that the reflection band of the cholesteric mixture coincided (as closely as possible) with the absorbing band at 0.36 μm.

The sample was taken between two optically flat fused silica plates and by careful displacement of the plates well oriented plane texture cholesteric was obtained. In all the experiments the sample thickness was fixed using a mylar spacer of thickness 0.25 mils ($\approx$ 6.4 μm).

A parallel beam of intense white light from an iodine-quartz lamp was passed through a circular polarizer and the sample. The transmission spectrum was recorded photographically using a quartz spectrograph (Hilger E 498.306/49645). The spectra for left and right circularly polarised light were recorded on the same photographic plate under identical conditions. Microdensitometer tracings were then obtained for the developed plates and the relative intensities were evaluated using previously calibrated relative intensity-density curves for the source spectrum. The relative intensities thus evaluated give a measure of the transmission coefficient of the sample. The constant of proportionality involved in the relative intensity was eliminated by calculating the circular dichroism defined as

$$D = \frac{\sqrt{I_L} - \sqrt{I_R}}{\sqrt{I_L} + \sqrt{I_R}} \tag{1}$$

where I_L and I_R are transmitted intensity for left and right circularly polarised light respectively.

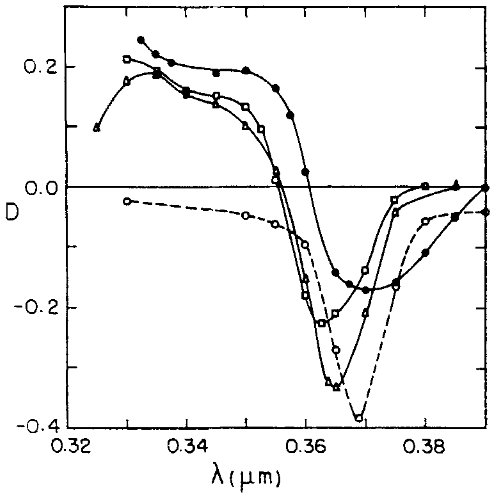

FIGURE 1 Experimental curves of circular dichroism as a function of wavelength for mixtures of cholesteryl nonanoate and PAA. (a) non-absorbing (0% PAA), --○--○--○--; (b) absorbing (1) 0.98% PAA —△—△—△—△—; (2) 1.76% PAA —□—□—□—; (3) 3.78% PAA —●—●—●—.

Figure 1 shows experimental curves of *D* as a function of wavelength for 0, 0.98, 1.76 and 3.78% PAA (by weight) concentration. The curves show the following features:

a) In absorbing cholesterics, *D* changes sign at the lower wavelength side of the reflection band, whereas for the non-absorbing cholesterics (0% PAA) *D* is always negative.

The change of sign in *D* for the absorbing case is due to the anomalous transmission of the left circularly polarised light which is enhanced at the lower wavelength side and attenuated at the higher wavelength side of the reflection band. The right circularly polarised light suffers only the normal attenuation.

b) With increase in the concentration of PAA the magnitude of the negative peak decreases while the positive side shows an increasing trend.

c) The half width of the negative peak increases with increasing PAA concentration.

3 COMPARISON WITH THEORY

The theory of the Borrmann effect in cholesterics has been discussed on the basis of the rigorous Oseen–de Vries model[2] as also from the point of view of the dynamical theory of X-ray diffraction.[3] The two approaches yield results in close agreement. The latter treatment is simpler and will be followed in the present calculations.

For left circularly polarized light incident normally on a thin film of absorbing left handed cholesteric, the dynamical theory leads to the equation

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

where T_r and T_{r+1} are the complex amplitudes of the primary wave just above the rth and $(r + 1)$th planes respectively. $\hat{x}$ is the phase factor and is given by

$$\hat{x} = \exp(-i\hat{\xi})\exp(-i\varphi_0) \tag{2}$$

where

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

$$\varphi_0 = 2\pi$$

$$\hat{e} = \frac{2\pi(\hat{\mu}_L P - \lambda)}{\lambda}$$

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

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

$$\Delta\hat{\mu} = \hat{\mu}_1 - \hat{\mu}_2; \quad \hat{\mu} = \tfrac{1}{2}(\hat{\mu}_1 + \hat{\mu}_2)$$

$$\mu_1 = n_1 - ik_1; \quad \hat{\mu}_2 = n_2 - ik_2.$$

n_1, n_2 are the principal refractive indices and k_1, k_2 are the principal absorption coefficients of the medium parallel and perpendicular to the director and P is the pitch of the cholesteric. All the parameters with a roof ($\hat{}$) are complex quantities. The real and imaginary part of $\Delta\hat{\mu}$ gives the birefringence Δn and the linear dichroism Δk respectively of the molecules.

The phase change of the right circularly polarized light in travelling a distance P is given by

$$\hat{\varphi}_R = \frac{2\pi\hat{\mu}_R P}{\lambda} \tag{3}$$

where

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

The wave vectors $\hat{K}_L$ and $\hat{K}_R$ for the respective waves are given by Eqs. (2) and (3),

$$\hat{K}_L = \frac{2\pi + \hat{\xi}}{P}$$

$$\hat{K}_R = \frac{2\pi \hat{\mu}_R}{\lambda}.$$

The imaginary parts of $\hat{K}_L$ and $\hat{K}_R$ give the attenuation of the respective waves in the absorbing cholesteric medium.

The transmitted intensities are given by

$$I_L = \left| \frac{1}{\exp(i\hat{e}) \cdot \dfrac{\sinh m\hat{\xi}}{\sinh \hat{\xi}} - \dfrac{\sinh(m-1)\hat{\xi}}{\sinh \hat{\xi}}} \right|^2 \tag{4}$$

$$I_R = |\exp(-m\hat{\varphi}_R)|^2 \tag{5}$$

where m = number of pitches in the sample thickness.

Using Eqs. (4), (5) and (1) the theoretical values of D versus wavelength can be calculated. The absorption coefficients of the cholesteryl nonanoate + PAA mixture around 0.36 μm were assumed to be only due to that of PAA. Maier and Saupe[4] have measured the molecular extinction coefficient ε for PAA in the isotropic phase ($\bar{\varepsilon}$) and in the nematic phase for the electric vector polarized perpendicular to the director ($\varepsilon_\perp$). The maxima of absorption in the two cases are at 0.34 and 0.355 μm respectively. ε is related to the absorption coefficient k by the general equation

$$k = 2.303\ \varepsilon c \lambda / 2\pi$$

where c = concentration of PAA, λ = wavelength of light.

The absorption profiles could be fitted approximately to a Gaussian of the form

$$k = k_{\max} \cdot \exp\left[-\left(\frac{\lambda - \lambda_{\max}}{\Delta\lambda} \right)^2 \right].$$

Using the experimental values of $\bar{\varepsilon}$ and $\varepsilon_\perp$ along with the above expressions, $k = \frac{1}{2}(k_1 + k_2)$ and $\Delta k = k_1 - k_2$ could be calculated as a function of wavelength and concentration. The other parameters used in the calculations are $P = 0.24\ \mu$m, $\lambda_0 = nP = 0.36\ \mu$m [i.e., $n = (n_1 + n_2/2) = 1.5$], $m = 25$ and $\Delta n = 0.07$. The dispersion of n and Δn, as well as the dependence of k and Δk on temperature were neglected. Theoretical curves of D for a few typical values of k and Δk are presented in Figure 2.

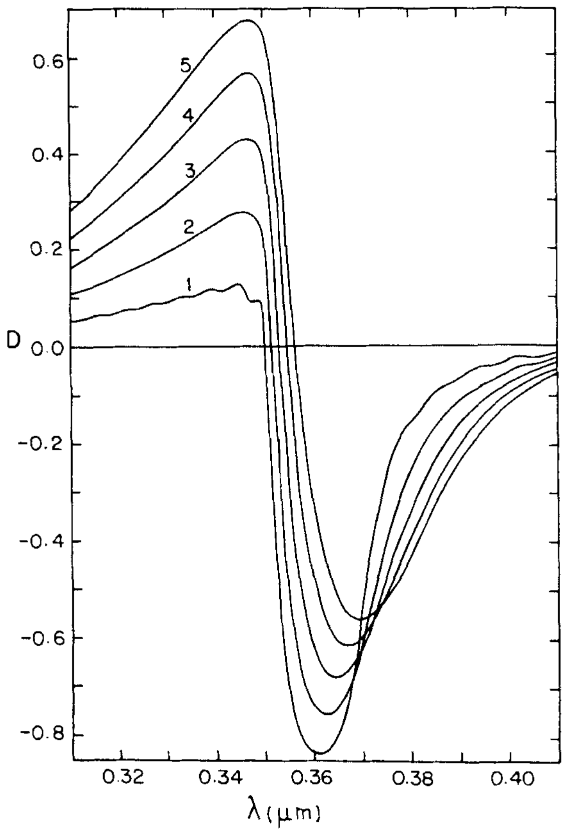

FIGURE 2 Theoretical curves of circular dichroism as a function of wavelength for a few values of k and Δk.

1) $k = 0.0125$, $\Delta k = 0.0157$ (1% PAA)
2) $k = 0.0250$, $\Delta k = 0.0314$
3) $k = 0.0375$, $\Delta k = 0.0471$
4) $k = 0.0500$, $\Delta k = 0.0628$
5) $k = 0.0625$, $\Delta k = 0.0785$.

Considering the experimental difficulty in adjusting reflection band to coincide exactly with the absorption maximum of the mixture and taking into account the various approximations involved in the numerical calculations, it is gratifying that there is qualitative agreement between experiment and theory. In particular the prediction that with increasing concentration of PAA, the positive peak in the circular dichroism curve should increase in magnitude and the negative peak should decrease in magnitude but increase in half width is borne out by experiments.

Acknowledgements

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