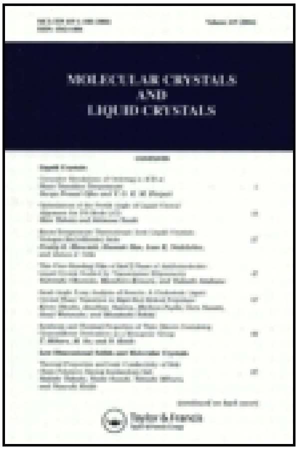

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Twisted Smectic *C* Phase: Unique Optical Properties†

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Abstract—Single-domain samples of cholesteric liquid crystals and of the recently reported twisted smectic *C* phase may have identical optical properties for light incident in the direction of the axis of twist. A single Bragg-reflection band exists for either type of liquid crystal in that case. However, with obliquely incident light the twisted smectic *C* sample would show additional Bragg-reflection bands at optical frequencies intermediate between the bands that would appear in both samples. Examples of computed spectra are given showing the differences that appear as the angle of incidence departs from normal.

1. Introduction

The generally accepted model of the smectic *C* phase in liquid crystals is one in which molecules lie in parallel planes, and in which " directors " of the molecules in any one plane are tilted with respect to the planes in a particular direction. There is now experimental evidence for the existence of a twisted smectic *C* (TSC) phase in which the molecules in adjacent parallel layers are slightly skewed rather than parallel, so that a spiral structure exists with the helical axis normal to the planes of molecules.[1,2,3] A single turn of such a structure is shown schematically in Fig. 1. If it is possible to obtain single domains of such structures that have flat planes over sufficient area to reflect or transmit a well collimated light beam and that have several turns of the spiral structure, then reflection or transmission measurements may be used to verify the existence of the spiral structure. Such measurements would also give the local optical dielectric tensor and the pitch.

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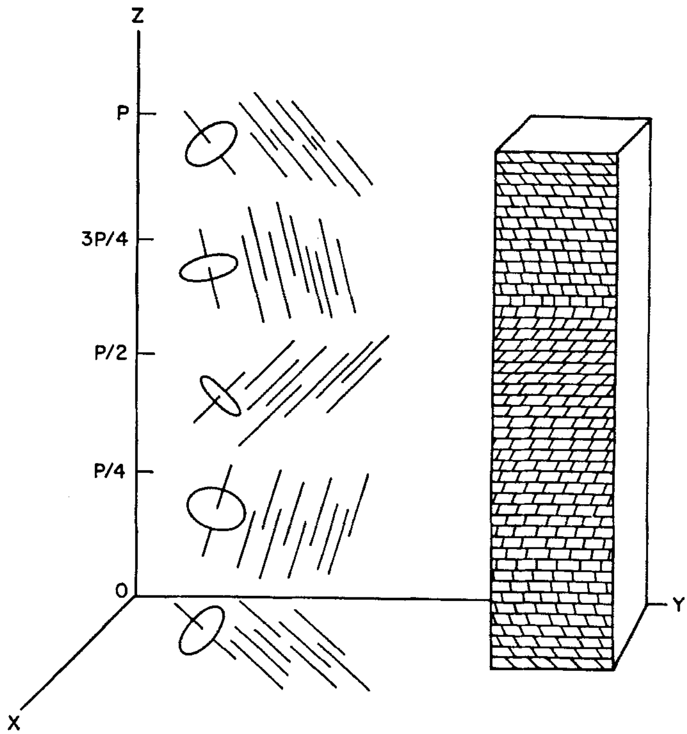

Figure 1. Configuration of twisted smectic C phase, showing direction of directors at four levels in one turn, left, and layers of molecules (lengths exaggerated with respect to pitch), right. Rectangular coordinate system used in equations is illustrated.

We will show that it is necessary to use light that is incident obliquely to the helical axis in order to demonstrate that the " directors ", as defined by the optical dielectric axes, are not parallel to the planes. Many, if not all cholesteric liquid crystals have directors normal to their helical axes. For light incident parallel to the helical axes, no difference would exist between optical properties of such cholesteric liquid crystals and of TSC liquid crystals.

2. Calculation of Reflection and Transmission Spectra

The 4 by 4 matrix method(4,5,6,7) will be used as the basis of the following computation of optical properties of flat single-domain samples of TSC material having surfaces normal to the helical axes.

The optical-frequency-dielectric-tensor at any one point in the liquid crystal has three principal axes, ϵ_1, ϵ_2 and ϵ_3 whose directions with respect to the x, y and z axes in Fig. 1 may be defined by the Euler angles θ, ϕ and ψ shown in Fig. 2. In the model of a TSC sample assumed here, θ and ψ are constant while ϕ is proportional to z. The azimuth ϕ goes through 2π radians in one pitch length, P, as shown in Fig. 1.

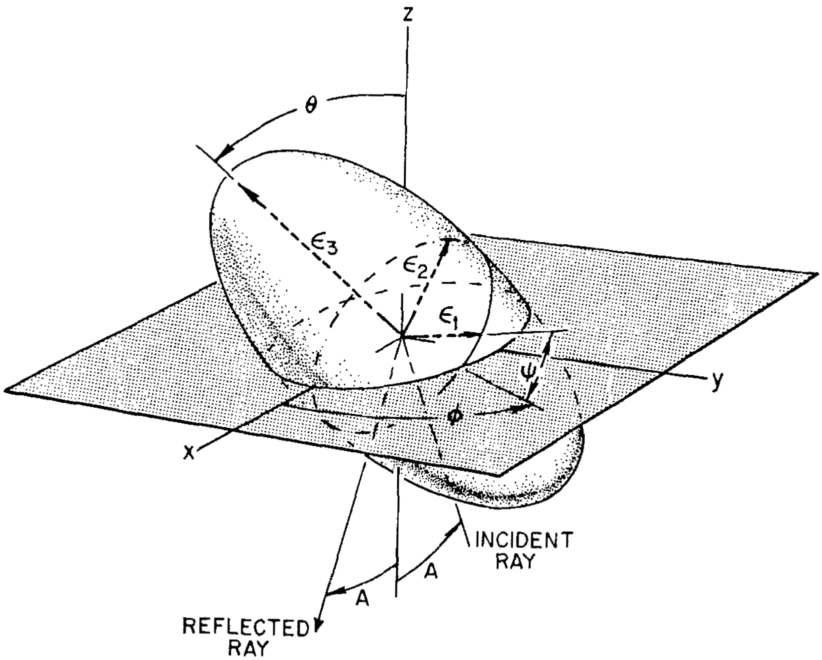

Figure 2. Euler angles of optical dielectric tensor with respect to the rectangular coordinates shown on Figure 1, at some arbitrary value of z.

When the azimuth ϕ is zero the dielectric tensor in the x, y, z coordinate frame may be defined as

$$\bar{\epsilon} = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix}$$

where

$$\begin{aligned}
\epsilon_{11} &= \epsilon_1 \cos^2 \psi + \epsilon_2 \sin^2 \psi \\
\epsilon_{12} &= (\epsilon_1 - \epsilon_2) \sin \psi \cos \psi \cos \theta \\
\epsilon_{13} &= (\epsilon_1 - \epsilon_2) \sin \psi \cos \psi \sin \theta \\
\epsilon_{22} &= (\epsilon_1 \sin^2 \psi + \epsilon_2 \cos^2 \psi) \cos^2 \theta + \epsilon_3 \sin^2 \theta \\
\epsilon_{23} &= (\epsilon_1 \sin^2 \psi + \epsilon_2 \cos^2 \psi - \epsilon_3) \sin \theta \cos \theta \\
\epsilon_{33} &= (\epsilon_1 \sin^2 \psi + \epsilon_2 \cos^2 \psi) \sin^2 \theta + \epsilon_3 \cos^2 \theta.
\end{aligned}$$

It was recently shown[6,8] that in one cholesteric liquid crystal mixture, $\theta = \pi/2$ and $\epsilon_1 = \epsilon_2$. In that case ⁻ i ; diagonal with $\epsilon_{11} = \epsilon_{22}$. We believe that $\bar{\epsilon}$ has these properties in all or nearly all cholesteric liquid crystals. In any case, we believe that $\psi = 0$ in all cholesterics. If so, $\bar{\epsilon}$ is always diagonal for cholesterics. In the TSC phase we expect none of the tensor elements to be zero, in general.

When ϕ is not zero we may write the optical dielectric tensor in the x, y, z coordinate frame as

$$\bar{\bar{\epsilon}} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix}$$

where

$$\begin{aligned}
\epsilon_{xx} &= [(\epsilon_{11} + \epsilon_{22}) + (\epsilon_{11} - \epsilon_{22}) \cos 2\phi - 2\epsilon_{12} \sin 2\phi]/2 \\
\epsilon_{yy} &= [(\epsilon_{11} + \epsilon_{22}) - (\epsilon_{11} - \epsilon_{22}) \cos 2\phi + 2\epsilon_{12} \sin 2\phi]/2 \\
\epsilon_{xy} &= [(\epsilon_{11} - \epsilon_{22}) \sin 2\phi + 2\epsilon_{12} \cos 2\phi]/2 \\
\epsilon_{xz} &= \epsilon_{13} \cos \phi - \epsilon_{23} \sin \phi \\
\epsilon_{yz} &= \epsilon_{13} \sin \phi + \epsilon_{23} \cos \phi \\
\epsilon_{zz} &= \epsilon_{33}.
\end{aligned}$$

Maxwell's equations for plane waves in anisotropic media stratified in the z-direction may be written in the 4 by 4 matrix form[7]

$$\frac{\partial}{\partial z} \begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_x \end{pmatrix} = \frac{i\omega}{C} \begin{pmatrix} \Delta_{11} & \Delta_{12} & \Delta_{13} & 0 \\ \Delta_{21} & \Delta_{11} & \Delta_{23} & 0 \\ 0 & 0 & 0 & 1 \\ \Delta_{23} & \Delta_{13} & \Delta_{43} & 0 \end{pmatrix} \begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_x \end{pmatrix}$$

where C is the velocity of light, ω is its frequency and

$$\Delta_{11} = -\frac{v_x}{C}\frac{\epsilon_{xz}}{\epsilon_{zz}}$$

$$\Delta_{21} = \epsilon_{xx} - \frac{\epsilon_{xz}^2}{\epsilon_{zz}}$$

$$\Delta_{12} = 1 - \left(\frac{v_x}{C}\right)^2 \cdot \frac{1}{\epsilon_{zz}}$$

$$\Delta_{13} = -\frac{v_x}{C}\frac{\epsilon_{yz}}{\epsilon_{zz}}$$

$$\Delta_{23} = \epsilon_{xy} - \frac{\epsilon_{xz}\epsilon_{yz}}{\epsilon_{zz}}$$

$$\Delta_{43} = \epsilon_{yy} - \frac{\epsilon_{yz}^2}{\epsilon_{zz}} - \left(\frac{v_x}{C}\right)^2.$$

Here, v_x is the x-component of the velocity of the incident light in vacuum if all optical surfaces are parallel. (If light strikes the liquid crystal from within a prism the definition of v_x is more complicated and $v/_xC$ may be greater than unity.) We have assumed that ordinary optical activity and magneto-optic effects are negligible in this formulation. Ordinary optical activity in real samples, which persists in the isotropic phase, is always several orders of magnitude smaller than the more or less similar effect caused by long-range helical structure in twisted liquid crystal phases. Inserting the ϕ-dependent expressions for the $\bar{\epsilon}$ tensor into the expressions for the Δ_{ij} terms, we get

$$\Delta_{11} = \frac{-v_x}{C\epsilon_{33}}(\epsilon_{13}\cos\phi - \epsilon_{23}\sin\phi)$$

$$\Delta_{13} = \frac{-v_x}{C\epsilon_{33}}(\epsilon_{13}\sin\phi + \epsilon_{23}\cos\phi)$$

$$\Delta_{12} = 1 - \frac{1}{\epsilon_{33}}\left(\frac{v_x}{C}\right)^2$$

$$\Delta_{21} = \left[\left(\frac{\epsilon_{11}-\epsilon_{22}}{2} - \frac{\epsilon_{13}^2-\epsilon_{23}^2}{2\epsilon_{33}}\right)\cos 2\phi - \left(\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}}\right)\sin 2\phi\right]$$
$$+ \left(\frac{\epsilon_{11}+\epsilon_{22}}{2} - \frac{\epsilon_{13}^2+\epsilon_{23}^2}{2\epsilon_{33}}\right)$$

$$\Delta_{43} = -\left[\left(\frac{\epsilon_{11}-\epsilon_{22}}{2} - \frac{\epsilon_{13}^2-\epsilon_{23}^2}{2\epsilon_{33}}\right)\cos 2\phi - \left(\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}}\right)\sin 2\phi\right]$$
$$+ \left(\frac{\epsilon_{11}+\epsilon_{22}}{2} - \frac{\epsilon_{13}^2+\epsilon_{23}^2}{2\epsilon_{33}}\right) - \left(\frac{v_x}{C}\right)^2$$

$$\Delta_{23} = \left[\left(\frac{\epsilon_{11} - \epsilon_{22}}{2} - \frac{\epsilon_{13}^2 - \epsilon_{23}^2}{2\epsilon_{33}}\right) \sin 2\phi + \left(\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}}\right) \cos 2\phi\right].$$

Note that only Δ_{11} and Δ_{13} are periodic in ϕ alone; all other terms have 2ϕ periodicity and/or constants. Also note that Δ_{11} and Δ_{13} are zero when $v_x = 0$, and that they are always zero if $\epsilon_{13} = \epsilon_{23} = 0$, as in a cholesteric.

The Δ_{ij} terms may be rewritten in the shorter, general form

$$\Delta_{11} = -\frac{v_x}{C} A_1 \cos(\phi + \alpha)$$

$$\Delta_{13} = -\frac{v_x}{C} A_1 \sin(\phi + \alpha)$$

$$\Delta_{12} = 1 - \frac{1}{\epsilon_{33}} \left(\frac{v_x}{C}\right)^2$$

$$\Delta_{21} = A_2 \cos(2\phi + \beta) + A_3$$

$$\Delta_{43} = A_2 \cos(2\phi + \beta) + A_3 - \left(\frac{v_x}{C}\right)^2$$

$$\Delta_{23} = A_2 \sin(2\phi + \beta).$$

In this notation A_1 is always zero for a cholesteric. A_1 is not involved for either liquid crystal structure when light is normally incident, since v_x is then zero.

Without doing any numerical calculations we can see from the foregoing results that the fundamental periodicity of cholesteric liquid crystals is 2ϕ. The well known " normal " Bragg reflection band in such liquid crystals is characteristic of a periodic structure with period equal to half the pitch. The same is true of the TSC structure when v_x is zero. However, for obliquely incident light v_x is not zero, and while the basic period is always half the pitch for cholesterics, terms of period equal to the full pitch appear in the 4 by 4 matrix for the TSC structure. Hence, a Bragg reflection band at about twice the wavelength of the " normal " band should make its appearance when light is obliquely incident on a TSC structure but not when on a cholesteric.

For normally incident light, only the normal band appears in either structure. This fact was first shown to be true for cholesterics by Oseen[9] and by DeVries.[10] For obliquely incident light, bands appear at all higher order harmonics of the normal band in cholesterics.(6,11) In the TSC structure, all higher harmonics of the full pitch band also appear with obliquely incident light. The odd-order members of this additional set of bands are a unique feature of the TSC structure. The even-ordered members occur near the same wavelengths as the normal band and its harmonics, and cause distortion of those bands.

Figure 3 shows reflectance spectra computed for a cholesteric and for a TSC sample having like spectra for normally incident light. Each structure is assumed to have ten full turns, with ϕ equal to zero at the two surfaces (see Fig. 2). The parameters used in the computation are given in Table 1. For simplicity we have neglected

TABLE 1 Parameters used directly or indirectly to generate Fig. 3

	TSC	Both	Cholesteric
ϵ_0		2.3	
ϵ_1		2.0	
ϵ_2		2.0	
ϵ_3	3.0		2.4
θ	45°		90°
ψ		0°	
α		90°	
β		0°	
A_1	−0.2		0
A_2		−0.2	
A_3		2.2	

to include the effects of optical dispersion or absorption in the calculations, although both may show marked effects in real experiments.(8) The parameters used are very roughly what one might expect in a TSC sample of some compound similar to para-azoxyanisol confined between glass prisms or hemispheres,(6,8) using visible light. The cholesteric with the same normal incidence spectrum is considerably less optically anisotropic. In each graph the abscissa is the ratio of the pitch of the structure to the vacuum wavelength of the light. The ordinate measured upward from the zero line is the reflectance that would be measured through a polarizing analyzer oriented so that it transmits π polarized light; i.e., light with its electric field in the plane of the incident and reflected

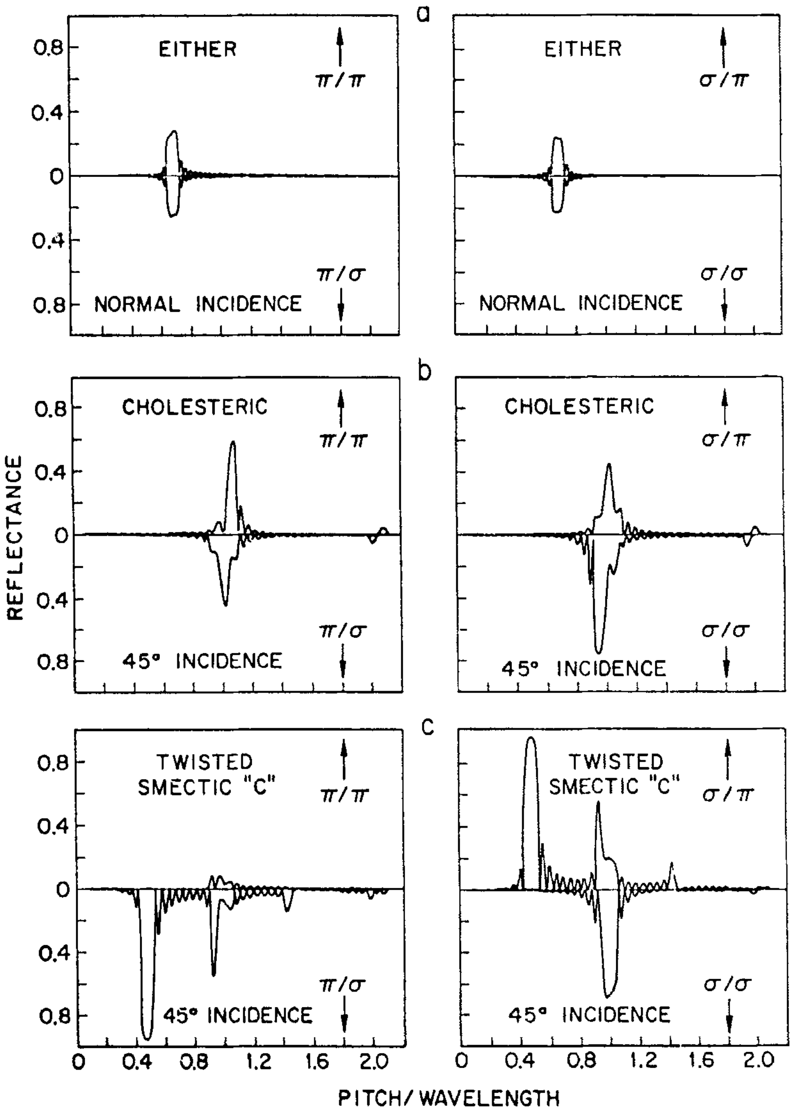

Figure 3. Computed reflectance vs. pitch/wavelength for plane polarized incident light in π (left) and σ (right) orientation, observed through a plane-polarizing analyzer in π orientation (up from zero axes) and σ orientation (down), (a) for normal incidence on either liquid crystal ($A = 0$), (b) oblique incidence ($A = 45°$) on cholesteric, and (c) on TSC liquid crystal.

beams. The ordinate measured downward is the reflectance that would be measured through an analyzer oriented for transmission of σ polarized light; i.e., that with its electric field parallel to the sample surface. The figures on the left are for π-polarized incident light, and those on the right are for σ-polarized incident light. (Data for crossed polarizer and analyzer were not presented in Refs. 6 and 8.)

Figure 3a shows the single "normal" Bragg reflection band in the reflection spectrum of a cholesteric or a TSC structure with normally incident light.

Figure 3b and c shows the unlike reflection spectra of the two different liquid crystal structures for light incident at 45° from normal to the surface. The angle of incidence is to be measured inside an isotropic dielectric medium of optical dielectric constant ϵ_0, whose flat surface would support one surface of the liquid crystal sample. The opposite surface of the sample is also assumed to lie against a thick piece of the same dielectric medium.

An interesting and unexpected feature may be observed in the computed reflection spectra of the TSC structure with obliquely incident light. Observe the extra reflection bands arising from terms of period equal to the pitch, P. When π-polarized light is incident, the reflected light is σ-polarized in these bands, and conversely, when σ-polarized light is incident, π-polarized light is reflected. Almost no perturbation occurs in the very low reflection of light polarized in the same direction as the incident light. We thought this might be an accidental feature characteristic of the particular angle of incidence, number of turns or choice of θ and ψ. However, spectra computed when each of these parameters was changed separately still showed the same peculiar characteristics. We are unable to give a convincing intuitive argument for this very odd result. Its observation would be a striking verification of the existence of the TSC structure, as well as a verification of the correctness of the computations.

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