Existence of a Critical Tilt Angle for the Optical Properties of Chiral Smectic Liquid Crystals

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The optical properties of single-domain chiral smectic liquid crystals have been theoretically studied as a function of the tilt angle. It is shown that structures with a particular value $\theta_{\rm rev}$ of the tilt angle, which depends only on the principal values of the local dielectric tensor, have very peculiar behavior. In passage through $\theta_{\rm rev}$ a reversal of the polarization states of the eigenfunctions and a drastic change of many optical properties occur.

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The growing interest in the chiral smectic-C phase and the discovery of new chiral liquid-crystal phases[1] have recently stimulated the study of the optical properties of helical periodic structures that are more complex than the cholesteric ones.[2–4] In Ref. 3 it has been shown that the polarization states of the optical Bloch waves propagating in locally uniaxial structures are generally smooth functions of the tilt angle, except at an angle $\theta_{\rm rev}$, where an inversion or a drastic change of polarization occurs. In this Letter a full explanation of this interesting feature is given, and the dependence of $\theta_{\rm rev}$ on the other optical parameters is explicitly found. Furthermore, the same study is extended to locally biaxial structures, which more closely correspond to the actual smectic liquid crystals.

As usual for chiral C smectics,[5] the liquid crystal is considered a locally biaxial medium, with a spatially uniform rotation of the dielectric tensor ϵ around a z axis, which is normal to the smectic layers. Let $\pi/2$, $\theta-\pi/2$, and θ be the angles between the principal axes 1, 2, and 3 for ϵ and z, $\epsilon_1, \epsilon_2, \epsilon_3$ the corresponding principal values, and θ the tilt angle of the structure.[6] The model describes cholesteric liquid crystals in the limiting case $\theta=\pi/2$ and homogeneous anisotropic crystals in the case $\theta=0$ and $\epsilon_1=\epsilon_2$. In the latter case the eigenfunctions of the Maxwell equations, which are generally Bloch waves, reduce to the ordinary and extraordinary plane waves propagating in homogeneous media.

By making use of the 4×4 matrix method,[7] one easily obtains[5] from Maxwell's equations

$$\frac{d}{dz}\begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_x \end{pmatrix} = i\frac{\omega}{c}\begin{pmatrix} M\sin qz & \Delta_{12} & -M\cos qz & 0 \\ a_0+a_1\cos 2qz & M\sin qz & a_1\sin 2qz & 0 \\ 0 & 0 & 0 & 1 \\ a_1\sin 2qz & -M\cos qz & b_0-a_1\cos 2qz & 0 \end{pmatrix}\begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_y \end{pmatrix}, \tag{1}$$

where $q=2\pi/p$ (p is the helix pitch), qz is the angle between the 1 axis of the dielectric tensor and the x axis, and

$$a_0=\frac{\epsilon_1}{2}+\frac{\epsilon_2\epsilon_3}{2\epsilon_{33}},\quad a_1=\frac{\epsilon_1}{2}-\frac{\epsilon_2\epsilon_3}{2\epsilon_{33}},$$
$$b_0=a_0-m^2,\quad \Delta_{12}=1-m^2\epsilon_{33}^{-1},$$
$$M=m(\epsilon_2-\epsilon_3)\epsilon_{33}^{-1}\cos\theta\sin\theta, \tag{2}$$
$$\epsilon_{33}=\epsilon_2\sin^2\theta+\epsilon_3\cos^2\theta.$$

Here $m=K_xc/\omega$, where K_x is the component of the light wave vector orthogonal to the z axis. For light entering the sample through a surface perpendicular to the z axis,

$$m=n_i\sin\theta_i,$$

where θ_i is the incidence angle and n_i the refractive index of the external medium.

If the z-dependent part of the 4×4 matrix is considered as a perturbation, the unperturbed solutions of Eq. (1) are the σ- and π-polarized plane waves which correspond to the ordinary and extraordinary waves of a homogeneous crystal, and their wave vectors have z components given by

$$K_\sigma=(\omega/c)(b_0)^{1/2},\quad K_\pi=(\omega/c)(\Delta_{12}a_0)^{1/2}. \tag{3}$$

This is a very crude approximation. However, it should be noticed that the actual eigensolutions of Eq. (1) are in general reasonably well approximated by the unperturbed ones, except in the following two cases.

(1) Near the Bragg reflection peaks, where a

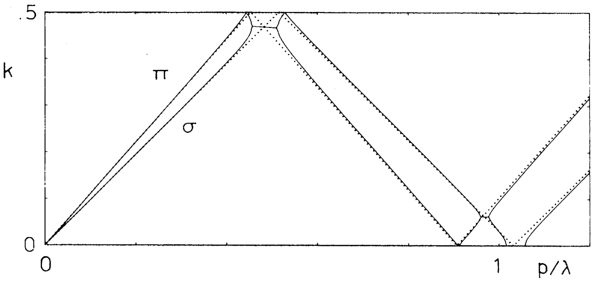

FIG. 1. Exact (solid lines) and approximate (dotted lines) dispersion curves. $\epsilon_1=\epsilon_2=2$, $\epsilon_3=3$, $\theta=30°$, $\theta_i=45°$ in glass ($n_i=2.3$), p = helix pitch, λ = light wavelength, $k=K_z/q$. The approximate K_z values are given by Eq. (3); for the exact ones see Ref. 9.

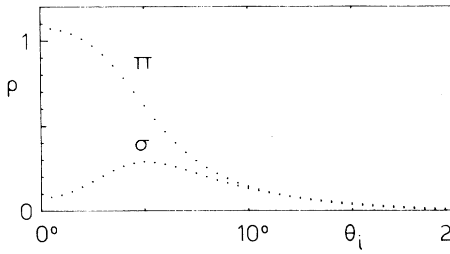

FIG. 2. Normalized differences between approximate and exact wave vectors vs θ_i for $\theta=30°$, $p/\lambda=0.6$, $\epsilon_1=\epsilon_2=2$, $\epsilon_3=3$; $\rho=\Delta K/(K_{1z}-K_{2z})$, where K_{1z} and K_{2z} are the exact eigenvalues of Eq. (1) and ΔK is the difference between the approximate and the exact eigenvalue of each eigenfunction.

better approximation is obtained by a superposition of forward and backward waves. We recall that in addition to the Bragg peaks associated with each eigensolution (referred to in the following as type B), a further series of reflection peaks is present (type C), which is common to both eigensolutions.[8] In Fig. 1 the exact and approximate values of K are compared. The frequency range includes the first two reflection bands, and a reduced Brillouin-zone scheme is used.[9] A good agreement of the K values is indicative of a fairly good agreement between the eigensolutions.

(2) Near a degeneration point of the unperturbed solutions, i.e, when $K_\sigma=K_\pi$. By taking into account Eqs. (2) and (3), this condition can be written

$$m^2(a_0-\epsilon_{33})=0.$$

This equation shows that degeneration can occur in two distinct and very different cases.

(a) At normal incidence of light, where $m=n_i\sin\theta_i=0$. Figure 2 shows that for the parameter values given in the caption the approximation fails for $\theta_i<10°$.

(b) If $a_0=\epsilon_{33}$, i.e., if

$$2(\epsilon_2\sin^2\theta+\epsilon_3\cos^2\theta)^2-\epsilon_1(\epsilon_2\sin^2\theta+\epsilon_3\cos^2\theta)-\epsilon_2\epsilon_3=0. \tag{4}$$

This case will be considered in more detail. In fact the tilt angle which satisfies Eq. (4) is to be identified with the angle $\theta_{\rm rev}$, where a reversal of the polarization states of the eigenfunctions occurs. One has

$$\cos^2\theta_{\rm rev}=\tfrac{1}{2}+\{-(3+\delta'+\delta'')+[(3+\delta'+\delta'')^2-8(\delta'+\delta''+\delta'^2)]^{1/2}\}(8\delta')^{-1}$$
$$=\tfrac{1}{3}-\tfrac{4}{27}\delta'-\tfrac{1}{6}\delta''/\delta'+\tfrac{1}{27}\delta''+\tfrac{1}{54}\delta''^2/\delta'+O(\delta'^2)+O(\delta''^2), \tag{5}$$

where

$$\delta'=(\epsilon_3-\epsilon_2)(\epsilon_3+\epsilon_2)^{-1},$$

$$\delta''=2(\epsilon_2-\epsilon_1)(\epsilon_3+\epsilon_2)^{-1}.$$

In both cases (a) and (b), better unperturbed approximations are the elliptically polarized waves obtained by a suitable superposition of the σ- and π-polarized plane waves considered before.

Some very significant differences between cases (a) and (b) of degeneration are to be stressed. The one of most practical interest is that condition (a) can be obtained for any chiral structure by simply changing the incidence angle, whereas condition (b), which involves only the parameters ϵ_i and θ which characterize the smectic structure, is satisfied by specific smectic liquid crystals. For locally uniaxial media, $\delta''=0$, and Eq. (5) gives for $\theta_{\rm rev}$ a value which is always close to the value of 56° given in Ref. 3. More precisely, $\theta_{\rm rev}=54.7°$ in the limiting case $\delta'=0$, and 56.6° in the highly anisotropic case $\delta'=0.2$. This means that $\theta_{\rm rev}$ practically depends only on the local biaxiality of the structure. In particular $\theta_{\rm rev}$ does not depend on the light frequency (which can appear only indirectly through the parameters ϵ_i for very dispersive media) and on the incidence angle θ_i. The fact that an inversion of the polarization states of the eigenfunctions occurs in the neighborhood of a tilt angle which is practically independent of the frequency of the incidence angle, and, for locally uniaxial structures, of the anisotropy, was first noticed in Ref. 3. The present approach gives a full explanation of it. In particular the independence of θ_i is not obvious. An intuitive argument is the following. The unperturbed solutions are the same as those in a homogeneous uniaxial crystal whose principal refractive indices n_o and n_e are suitable average values of the dielectric tensor components. For given values of $\epsilon_1, \epsilon_2, \epsilon_3$ such average values depend only on θ. The inversion angle is the one which gives $n_e = n_o$, and in this case $K_\pi = K_\sigma$, independent of θ_i.

A further difference between cases (a) and (b) lies in the extension of the nearly degenerate region, which can be evaluated by comparing the amplitudes $M\omega/c$ and $a_1\omega/c$ of the perturbing terms with the difference $K_\sigma - K_\pi$. Actually in case (a) the degeneration of the unperturbed solutions occurs as a function of the angle of incidence θ_i, and the quantity $K_\sigma - K_\pi$ is not a very sensitive function of θ_i near $\theta_i = 0$, because of the fact that its derivative is zero at this point. On the contrary, in case (b), where the degeneration occurs as a function of the tilt angle θ, the quantity $K_\sigma - K_\pi$ monotonically changes with θ near θ_{rev}. In fact

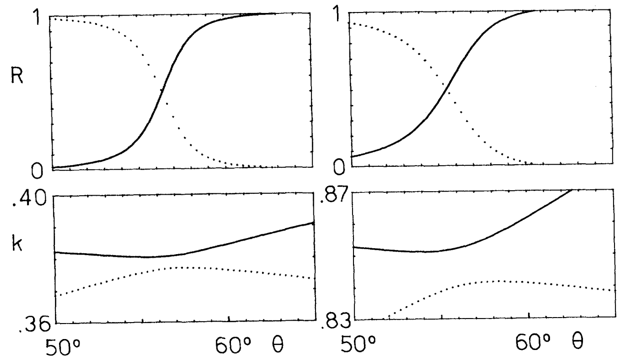

FIG. 3. Polarization states (upper plots) and exact dispersion curves (lower plots) vs θ for $\epsilon_1 = \epsilon_2 = 2$, $\epsilon_3 = 3$, $\theta_i = 60°$, $p/\lambda = 0.35$ and 0.70 (left-hand and right-hand sides, respectively; the first Bragg peak is at $p/\lambda = 0.48$); $R = P_z^\pi / P_z$, where P_z is the z component of the Poynting vector and P_z^π is the contribution to P_z arising from the π components of the electromagnetic field. The two eigensolutions are represented, respectively, by solid and dotted lines.

$$\left[\frac{d(K_\sigma - K_\pi)}{d\theta}\right]_{\theta=\theta_{\text{rev}}} = \left(\frac{\omega}{c}\right)^2 m^2(\epsilon_3 - \epsilon_2)[(\epsilon_1\epsilon_{33} + 2\epsilon_2\epsilon_3)(2\epsilon_{33}^3 K_\sigma)^{-1}\sin\theta\cos\theta]_{\theta=\theta_{\text{rev}}}$$

$$\approx \frac{\omega}{c} m^2 \delta' (\bar{\epsilon} - m^2)^{-1/2}[2 - \delta''(2\delta')^{-1}]^{1/2} \neq 0,$$

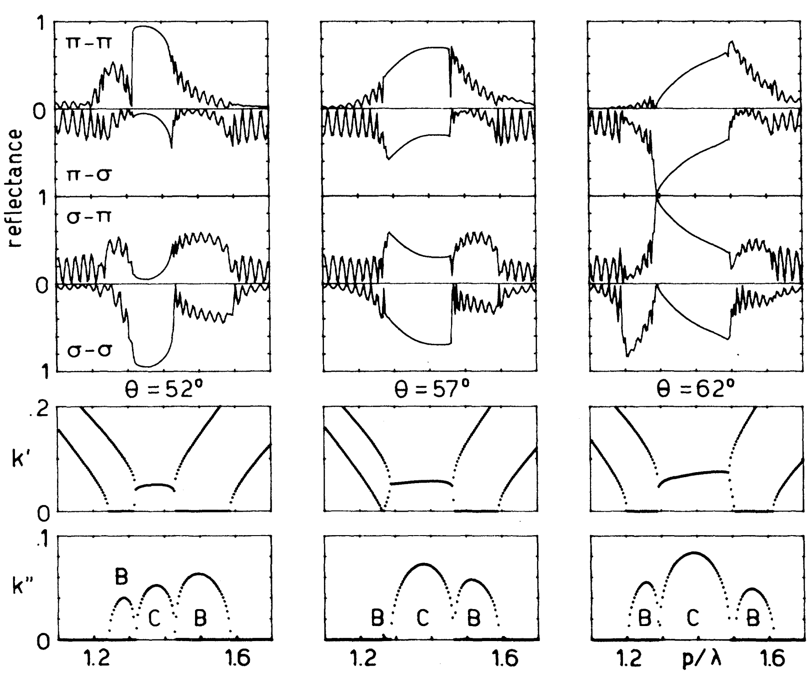

FIG. 4. Reflectance spectra and exact dispersion curves vs p/λ at the second-order Bragg reflection band for $\epsilon_1 = \epsilon_2 = 2$, $\epsilon_3 = 3$, corresponding to $\theta_{\text{rev}} = 56.6°$. Plots refer to $\theta = 52°$, 57°, and 62°, respectively, for a sample 24 pitches thick and for $\theta_i = 60°$; k' and k'' are the real and imaginary parts of K_z/q; π-π, π-σ, σ-π, and σ-σ refer to the polarizer and analyzer settings.

where $\bar{\epsilon}$ is the mean value of $\epsilon_1, \epsilon_2, \epsilon_3$. As a consequence, very small variations of θ near θ_{rev} correspond to great variations of the eigensolutions. As far as the polarization states of the eigensolutions are concerned, a very drastic change occurs. This is shown in Fig. 3, where a parameter R, which gives the relative amplitude of the π and σ components of the exact eigenfunctions, is plotted versus θ for two frequency values and for $\theta_i = 45°$. A full inversion of the polarization states occurs in a θ interval of few degrees around θ_{rev}, which can therefore be considered a very critical tilt angle.

The inversion of the polarization states of the eigenfunctions gives rise to an inversion of many important optical properties. In order to illustrate this point the reflectance spectra as functions of the frequency at the second-order Bragg reflection band have been plotted for three values of θ in the neighborhood of θ_{rev} (Fig. 4). The band is a triplet whose lateral peaks correspond to the B-type instabilities of the two eigenfunctions, while the central peak corresponds to a C-type instability, which involves both eigenfunctions. Let us consider for instance the B-type instability which gives rise to the left-hand side peak. It appears to be nearly absent for $\theta = \theta_{rev}$, whereas it gives rise to a π-polarized reflected wave for $\theta < \theta_{rev}$, and to a σ-polarized one for $\theta > \theta_{rev}$. The opposite occurs for the other B-type instability. The drastic change in the shape of the central peak, where total reflection always occurs, should also be noticed.

Structures having a tilt angle $\theta \approx \theta_{rev}$ may be of some practical interest. We recall that one of the most important properties of the cholesteric liquid crystals is their apparent rotatory power. This occurs where the eigenfunctions are nearly left and right circularly polarized, respectively, a fact which is related to the degeneration of the unperturbed solutions discussed in (a). By considering that a smectic structure with a tilt angle $\theta \approx \theta_{rev}$ has nearly degenerate unperturbed solutions at any incidence angle, we can guess that such a structure could be of some interest with respect to its rotatory power. A further reason for interest comes from the fact that the optical properties of these structures strongly depend on their tilt angle. A small change of this angle, due for instance to an external field or to a temperature variation, can be easily detected by optical methods.

[1]For a review, see G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals* (Leonard Hill, Glasgow and London, 1984).

[2]I. Abdulhalim, L. Benguigui, and R. Weil, in Abstracts of the Tenth International Liquid Crystal Conference, York, 15–21 July 1984 (unpublished), E11; J. W. Doane, *ibid.*, E55; S. W. Shiaynovsky, *ibid.*, E62.

[3]C. Oldano, P. Allia, and L. Trossi, in Abstracts of the Tenth International Liquid Crystal Conference, York, 15–21 July 1984 (unpublished), E60.

[4]H. Takezoe, to be published.

[5]D. W. Berreman, Mol. Cryst. Liq. Cryst. **22**, 175 (1973).

[6]The extension to the case where none of the axes is orthogonal to z is straightforward, but all the equations become rather involved.

[7]D. W. Berreman, J. Opt. Soc. Am. **62**, 502 (1972).

[8]C. Oldano, E. Miraldi, and P. Taverna Valabrega, Phys. Rev. A **27**, 3291 (1983).

[9]Eigenfunctions and eigenvalues of Eq. (1) have been obtained by the method of Ref. 3. The eigenvalues can be more easily computed by diagonalization of the 4×4 transfer matrix obtained when Eq. (1) is integrated over one pitch.