Optics and electrooptics of chiral smectic C liquid crystals

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A review is given of optical studies based on diffraction by the supermolecular periodic structure of chiral ferroelectric smectic liquid crystals. Topics discussed include symmetry, physical properties, and electrooptic effects with their possible applications.

INTRODUCTION

The discovery by Meyer *et al.*¹ in 1975 of the ferroelectric properties of chiral smectic C liquid crystals (C^*LCs) led to a revision of many of the ideas about ferroelectricity that had been current until then. In particular, it became clear that it was possible to observe the ferroelectric effect in liquids. However, as is often the case, the resulting interest in C^*LCs was mostly due to the tempting prospect of practical applications: five years after this discovery in thin C^*LC layers, Clark and Lagerwall² achieved electrooptic switching times in the microsecond range. The reduction in electrooptic time constants from the millisecond to the microsecond range meant that the liquid-crystal materials that had been widely and successfully used mostly in displays, became promising as media for optical data processing and the objects of intensive investigation.

The aim of this review is to present a systematic account of electrooptic studies of C^*LCs whose helical supermolecular structure determines their unique optical properties. The optical properties of chiral smectic C liquid crystals are in many ways similar to those of the cholesteric crystals which have been more extensively investigated. There are also qualitative differences between them that become particularly clear when light is incident obliquely to the optic axis.³

In Sec. 1 we consider experimental results on the purely optical properties of C^{*}LCs, namely, Bragg diffraction and directly observed dispersion of eigenwaves.^{4,5}

In the subsequent sections, C^{*}LCs are considered as ferroelectric materials.

In 1978, Pikin and Indenbom employed the Landau model in a thermodynamic description of the physical properties of C^{*}LCs, including the change in their macroscopic structure under the influence of external factors.^{6,7} This model was subsequently extended by $\hat{Z}eks \ et \ al.^8$ in an attempt to develop an adequate description of the detailed behavior of C^{*}LCs near a phase transition, e.g., the temperature dependence of the pitch of the helix and the spontaneous polarization, and also the observed anomalies in the dielectric constants.

Advances in the theoretical description of C^{*}LCs have developed in parallel with experimental studies of their physical studies. Much progress was achieved in overcoming the difficulties in producing C^{*}LCs that can exist in a wide temperature range, have low viscosity, and exhibit high spontaneous polarization. There is now an extensive literature on the practical application of C^{*}LCs in fast light-switching devices, optically controlled transparencies, high-resolution displays with matrix addressing, and so on.

There is considerable current interest in systematic theoretical and experimental descriptions of the electrooptical properties of C^{*}LCs, including their symmetry and basic physical parameters that determine electrooptic polarization. These parameters include viscosity, tilt in a layer, and so on, as well as the experimental conditions for the alignment of C^{*}LCs, cohesion energy, driving field, disposition of polaroids, direction of propagation of light, and so on. We shall devote particular attention to three basic electrooptic effects that are particularly important for applications, namely, the reorientation effect in surfacestabilized structures,² the electroclinic effect near the smectic $A \rightarrow C^*LC$ phase transition⁹ and the deformed helix effect¹⁰ in highly twisted C^{*}LCs. All these effects are examined in Secs. 2 and 3. Section 4 is devoted to practical applications of C^{*}LCs.

1. OPTICAL PROPERTIES

1.1. Bragg reflection and circular dichrolsm. Reflection of plane polarized light

The liquid crystal is intermediate between solid and isotropic phases. The generally accepted classification distinguishes between two classes of liquid crystals, namely, nematic and smectic. Nematic liquid crystals (NLCs) exhibit orientational order: the centers of mass of the individual molecules are randomly distributed in space, but their long axes remain parallel to one another. The structure of smectics, on the other hand, brings them closer to the solid phase and displays additional orientational and layer packing. The liquid-crystal smectic phase exhibits polymorphism, i.e., smectic liquid crystals exist in a number of modifications. We shall confine our attention to two of them. Figure 1 shows two cases of smectic order, namely, smectic A (Fig. 1a) and smectic C (Fig. 1b).

In smectics A, the long axes of the molecules are perpendicular to the smectic layers. Like the nematics, smec-



FIG. 1. Disposition of molecules in smectic (a) and smectic C (b) phases.

tics A are optically uniaxial (the same symmetry, $D_{\infty h}$) with L lying along the optic axis. The optical indicatrix of smectics A is similar to that of nematics.

According to the classification of Sackmann and Demus,¹ the tilted smectic phase is referred to as smectic C. It is optically biaxial and the unit vector L has the following components:

$$L_z = \cos \theta, \quad L_x = \sin \theta \cdot \cos \varphi,$$

$$L_y = \sin \theta \cdot \sin \varphi,$$
(1)

where θ is the tilt of the molecules and φ is the azimuthal angle (Fig. 2).

Saupe¹² concluded on the basis of symmetry considerations that smectics C were biaxial. The first x-ray structure studies were performed by Khistyakov *et al.*^{13,14} and the first optical experiments on the biaxial properties of smectics C were reported in Refs. 15–17.

Early measurements already showed that there were two types of smectic C liquid crystals, namely, type I with a large tilt θ that was independent of temperature (C₁ phase)¹⁸ and type II with small θ and a rapid variation with temperature (C₂ phase).¹⁸ All materials with the C₂ phase exhibit a phase transition to smectic A, but this does not occur for C₁. The C₂ \rightarrow smectic A transition is accompanied by a reduction in the tilt angle to zero, and is a second-order transition. de Vries¹⁹ subsequently showed that there is one further type of smectic C, namely, the C₃ phase in which the tilt θ does not change in the transition to smectic A, and which is a first-order transition.¹⁹

The fact that the smectics C are biaxial can be described schematically as follows (see Fig. 2). Let us sup-



FIG. 3. Optical indicatrix of the smectic C phase.

pose that the smectic layers lie on the x,y plane. The long axis of the molecules is at an angle θ (the tilt angle) to the z direction. The x,z plane is then the plane of symmetry, and the two-fold rotation axis C_2 is perpendicular to the x,zplane and lies in the plane of the smectic layer (the x,yplane). The smectic C phase has the c_{2h} symmetry.

Figure 3 shows the optical indicatrix of the smectic C phase. The dielectric properties of this medium are characterized by a triaxial ellipsoid. In general, the principal values of the permittivity are not equal $(\varepsilon_1 \neq \varepsilon_2 \neq \varepsilon_3)$ and the tilt of the long axis of the ellipsoid may also be somewhat different from the tilt of the molecules.

If the molecules of the smectic C phase are chiral or if chiral molecules are added to the smectic C phase (both mesomorphic and nonmesomorphic), a helical structure is found to arise as shown in Fig. 4. Similarly, the chirality of the molecules in nematics is responsible for the helical supermolecular structure, and the result is the so-called cholesteric liquid crystal (CLC).

The existence of the chiral smectic phase (C^*LC) was first predicted on the basis of a thermodynamic relation by Saupe.¹² The formation of the C^*LC phase in media consisting of a single compound and in mixtures was first demonstrated in Refs. 7 and 20.

From the symmetry point of view, a transition from the smectic C phase to the helical smectic phase is accompanied by a reduction in symmetry, i.e., both the reflection



FIG. 2. Orientation of the director L in a C^{*}LC layer.



FIG. 4. Disposition of molecules in the chiral smectic C phase.

plane and the center of symmetry (point group C_2) are found to vanish. In the case of the C^{*}LC phase, the local dielectric properties are also characterized by a triaxial ellipsoid and the permittivity tensor can be written in the form^{3,21-23}

$$\varepsilon(z) = \begin{pmatrix} \varepsilon_{11} + & \varepsilon_{a} \sin 2\varphi & \varepsilon_{a}' \cos \varphi \\ + \varepsilon_{a} \cos 2\varphi & & \\ \varepsilon_{a} \sin 2\varphi & \varepsilon_{11} - & \varepsilon_{a}' \sin \varphi \\ & -\varepsilon_{a} \cos 2\varphi & \\ \varepsilon_{a}' \cos \varphi & \varepsilon_{a}' \sin \varphi & \varepsilon_{33} \end{pmatrix}, \quad (2)$$

where

$$\varepsilon_{11} = (\varepsilon_1 + \varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta)/2,$$

$$\varepsilon_{33} = \varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta,$$

$$\varepsilon_a = (\varepsilon_1 - \varepsilon_2 \cos^2 \theta - \varepsilon_3 \sin^2 \theta)/2,$$

$$\varepsilon'_a = (\varepsilon_3 - \varepsilon_2) \sin \theta \cdot \cos \theta.$$

It is assumed in the model of the C^{*}LC phase that θ does not change from layer to layer, but φ varies from 0 to 2π , and $\varphi = 2\pi z/P_0$ where P_0 is the equilibrium pitch of the helix.

By analogy with cholesteric liquid crystals, we thus have a spatially modulated structure with the period P_0 . It produces diffraction that must satisfy the Vul'f-Bragg condition

 $m\lambda_0 = 2R\bar{n}\cos\varphi$,

where *m* is the diffraction order, φ is the angle of incidence, \overline{n} is the refractive index of the medium, and *R* is the period which for the C^{*}LC is equal to P_0 .

When light propagates along the axis of the helix of the chiral smectic phase, analysis of theoretical data shows that only the second-order Bragg reflection is produced in this case. The second Bragg order in the chiral smectic case should be analogous to the first order in the cholesteric.^{3,24}

Calculations confirm the presence of additional Bragg orders in the case of obliquely incident light.^{24,25} Theory thus shows that, when light is obliquely incident on a chiral smectic liquid crystal, there should be both secondorder and first-order Bragg reflections, and a qualitative difference between the optical properties of C^{*}LC and CLC is expected precisely for this order.

Selective reflection of visible light by C^{*}LCs remained experimentally unexplored for a long time. This was so because optical studies were mostly confined to materials with a large pitch of the helix $(P_0 < 1 \ \mu m)$.²⁶⁻³⁰

Observations of Bragg reflection became possible only after Gray *et al.*³¹ synthesized a class of chiral smectic liquid crystals, namely, alkyloxyphenyl esters of 4(2methylbutyl) biphenyl-4-carboxylic acid³¹ with selective reflection of visible radiation by cholesteric and smectic phases. It thus became possible to investigate Bragg scattering by the chiral smectic phase, and also compare these results with scattering by cholesteric structures.³²⁻³⁵

Figure 5 shows the temperature dependence of the



FIG. 5. Wavelength at maximum selective reflection by planar chiral smectic C (1) and cholesteric (2) textures at normal incidence of light: $3-CE_3$, 4-90% of CE₃+10% of TDOBAMBCC.

wavelength at maximum selective reflection at normal incidence on planar structures of 4-p-hexyloxyphenyl ester of 4(2-methylbutyl) biphenyl-4-carboxylic acid (CE-3) and a mixture of 90% CE-3+10% TDOBAMBCC (ptetradecyloxybenzylidene n'amino-2-methyl-butyl- α cyanocinnamate). The addition of TDOBAMBCC to CD-3 transforms the chiral smectic C phase into a ferroelectric phase and also extends the temperature range in which it can exist.³⁶

For the smectic phase, λ_0 corresponds to second-order Bragg reflection whereas for the cholesterics, it corresponds to the first-order reflection. The condition $\lambda_0 = P_0 \bar{n}$ is satisfied for both phases, where \bar{n} is the so-called mean refractive index. The authors of Refs. 32–35 were the first to discover and investigate first- and second-order Bragg diffraction by C^{*}LCs. Figure 6 shows the arrangement used to examine the transmission spectrum for circularly polarized light incident at different angles on chiral smectics. Figure 7 shows the experimental results, i.e., the transmitted intensity for left and right circularly polarized light in the first and second orders in the case of laevorotatory CE-3 in the chiral smectic C^{*} phase. Circular dichroism was observed in the second order, but not in the first.

In the chiral smectic phase, the first and second Bragg reflections have the same intensities, whereas in the cho-



FIG. 6. Schematic diagram of an experimental investigation of circular dichroism for obliquely incident light: *1*—light source, 2—monochromator, 3—polarizer, 4—Fresnel biprism, 5—rotating liquid crystal cell, 6—photomultiplier.



FIG. 7. Transmission of left- and right-circularly polarized light (1 and 2, respectively) as a function of wavelength in second order (a; angle of incidence 19.5°) and first order (b; angle of incidence 60°) Bragg reflection.

lesteric, strong diffraction scattering is observed only in the first order.

When a dye with linear dichroic absorption is added to a liquid crystal with helical structure, the latter transforms linear dichroism into circular dichroism, and the observed induced circular dichroism D is given by

$$D = \frac{I_{\rm L} - I_{\rm R}}{I_{\rm L} + I_{\rm R}},$$

where I_L and I_R are the measured light transmission coefficients for left and right polarized radiation, respectively. These coefficients are measured within the absorption wavelength interval of the dye, and the pitch of the helix P_0 is usually greater than the absorption wavelength of the dye, λ_{dye} . However, absorption is suppressed when P_0 and λ_{dye} are equal. The reason for this is that, because the disposition of the molecules is helical, the absorption of light with the diffracted polarization undergoes an abrupt change near the region of selective reflection. On the shortwave side of Bragg reflection, the electric field vector is perpendicular to the long axis of the molecules, i.e., to the absorbing effective oscillators in dyes with positive dichroism.



FIG. 8. Induced circular dichroism at normal incidence in cholesteric (1) and chiral smectic C(2) phases.

Figure 8 shows the induced circular dichroism for both cholesteric and chiral smectic phases.

More complete information about diffraction was obtained by studying the reflection of plane-polarized light.³⁷⁻³⁹

Figure 9 shows the experimental arrangement. The liquid-crystal sample was placed between a flat plate and a hemispherical lens. Light from the source was allowed to pass through the monochromator 1, a polarizer, and a lens, and was collected at the focus of the hemispherical lens 2, which ensured that the beam incident on the liquid crystal layer was parallel. The cell was rotated together with the detector system, and the angles were measured to within 2°. Light from the liquid-crystal cell was reflected by the aluminium mirror 3 into the detector system which consisted of an analyzer and a photodetector 4. This arrangement ensured that small reflection angles could be used. The reflection coefficients were measured for light polarized in the plane of incidence (σ polarization) and at right angles to the plane of incidence (π polarization) in the first and second Bragg orders in the smectic phase. Monomode samples with helical axis perpendicular to the cell surface were produced by a special technique.

Figure 10 shows the reflection coefficients for four combinations of σ and π polarizations at an angle of incidence of 44°.

The wavelength λ_0 corresponds to the selective reflection maximum at normal incidence on the cell. Experimen-



FIG. 9. Schematic diagram of an experimental investigation of obliquely incident plane polarized light: *1*—monochromator, *2*—liquid crystal cell, *3*—aluminum mirror, *4*—photodetector.



FIG. 10. Reflection spectrum for plane polarized light with four combinations of σ and π polarizations in first and second order reflections. *R*—reflection coefficient, λ_0 —wavelength corresponding to maximum reflection at normal incidence, λ —wavelength of incident light.

tal data indicate that, in the first Bragg order, the diffraction of σ -polarized light produces π -polarized light, and *vice versa*. The polarization characteristics of the second Bragg reflection are similar to those observed in cholesterics and, in this case, reflection of any polarization can be observed.

Figure 11 shows the reflection coefficient in the first order as a function of the analyzer position. Light incident at 44° was σ -polarized and the position of the analyzer was varied so that the change $\sigma \rightarrow \pi \rightarrow \sigma$ occurred in a 10° interval. Similar curves were obtained for π -polarized incident light. Figure 12 shows the same characteristics in the second order for angles of incidence of 44°, 25°, and 1.5°.

In the case of Figs. 12a and 12b, the polarizer was arranged in the σ and π positions, respectively. The analyzer was rotated from the π position (0° and 180° for a) to the σ position (90° for a) and from the σ position (0° and 180° for b) to the π position (90° for b). Figure 12 shows a polar plot of the reflection coefficients in which the angles refer to the positions of the analyzer and the radial distance is the reflection coefficient.



FIG. 11. Reflection coefficient as a function of the position of the analyzer in first order reflection. Polarizer in σ position; reflection angle 44°.



FIG. 12. Polarization characteristics of selective reflection for σ and π incident polarizations (a and b, respectively; second order) in polar coordinates at three angles of incidence $(1-44^\circ, 2-25^\circ, \text{ and } 3-1.5^\circ)$.

The wavelength at maximum reflection was determined for the π/π and σ/σ polaroid positions in a preliminary experiment.

Analysis of these experimental characteristics confirms the theoretical predictions reported in Refs. 21–25.

1.2. Determination of the permittivity tensor and direct observation of eigenwave dispersion

To determine the permittivity tensor of C^{*}LCs, we must in general determine the following quantities: the principal values of the permittivity tensor ($\varepsilon_1, \varepsilon_2, \varepsilon_3$), the pitch P_0 of the helix, and the tilt θ of the director. It is shown in Refs. 40 and 41 that these quantities can be found by purely optical methods.

The following expressions relate the measured refractive indices n_{oc} and n_{ec} for waves that are linearly polarized in the plane of incidence and at right angles to it, the refractive indices $n_{\rm R}$ and $n_{\rm L}$ for right and left circularly polarized radiation, the Bragg wavelength λ_0 , i.e., the wavelength at maximum selective reflection, and the required quantities ε_1 , ε_2 , ε_3 , P_0 , θ :

$$\lambda_0 = P_0 \bar{\varepsilon}^{1/2} \,, \tag{3}$$

$$\tilde{\varepsilon} = \frac{n_{\rm R}^2 + n_{\rm L}^2}{2} + \frac{\lambda}{P_0} \left(n_{\rm L} - n_{\rm R} \right) , \qquad (4a)$$

$$\tilde{\varepsilon} = \frac{1}{2} \left(\varepsilon_1 + \frac{\varepsilon_2 \varepsilon_3}{\varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta} \right), \qquad (4b)$$

$$\varepsilon_{a} = \overline{\varepsilon}^{1/2} \left\{ \left[\frac{n_{L}^{2} - n_{R}^{2}}{2\overline{\varepsilon}} + \frac{\lambda}{P_{0}\overline{\varepsilon}} \left(n_{L} + n_{R} \right) \right] - \frac{4\lambda^{2}}{P^{2}\overline{\varepsilon}} \right\}^{1/2}, \quad (5a)$$

$$\varepsilon_{a} = \frac{1}{2} \left(\varepsilon_{1} - \frac{\varepsilon_{2} \varepsilon_{3}}{\varepsilon_{2} \sin^{2} \theta + \varepsilon_{3} \cos^{2} \theta} \right), \qquad (5b)$$

$$n_{\rm oc}^2 = \frac{1}{2} \left(\varepsilon_1 + \varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta \right),$$
 (6)

$$n_{\rm ec}^2 = \varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta , \qquad (7)$$

where $\overline{\epsilon}$ and ϵ_a are the mean value and the anisotropy of the permittivity, respectively. These expressions are obtained by simple transformation of the formulas obtained in Refs. 3, 25, 27, and 39 for the optical properties of chiral



FIG. 13. Schematic illustration of the measurement of refractive indices: 1-source of light, 2-collimator, 3-liquid crystal cell, 4-viewing tube.

smectic C liquid crystals with light propagating along the axis of the helix. We note that (6) and (7) are valid when $P_0 \ll \lambda_0 / \varepsilon_a^{1/2}$, i.e., outside the region of selective reflection.

Simultaneous solution of (3)-(7) yields the following expressions for the required quantities. The pitch of the helix is given by

$$P_0 = \{\lambda (n_{\rm R} - n_{\rm L}) + [\lambda^2 (n_{\rm R} - n_{\rm L})^2 + 2(n_{\rm R}^2 + n_{\rm L}^2)\lambda_0^2]^{1/2}\}$$

$$\times (n_{\rm L}^2 + n_{\rm R}^2)^{-1}$$
 (8)

Next, having calculated $\overline{\varepsilon}$ and ε_a from (4b) and (5b), we have

$$\varepsilon_1 = \overline{\varepsilon} + \varepsilon_a,$$
 (9)

$$\varepsilon_2 = B - (B^2 - A)^{1/2},$$
 (10)

$$\varepsilon_3 = B + (B^2 - A)^{1/2},$$
 (11)

where $A = n_{ec}^2(\overline{\epsilon} - \epsilon_a)$, $B = \frac{1}{2}(2n_{ec}^2 + n_{ec}^2 - \overline{\epsilon} - \epsilon_a)$. Finally,

$$\theta = \arcsin\left(\frac{n_{\rm ec} - \varepsilon_3}{\varepsilon_2 - \varepsilon_3}\right)^{1/2}.$$
 (12)

The problem was thus reduced to the measurement of the five quantities λ_0 , $n_{\rm ec}$, $n_{\rm oc}$, $n_{\rm L}$, $n_{\rm R}$, and study was made of CE-3 and of the mixture CE-3+TDOBAMBCC. The temperature dependence of λ_0 for these mixtures is shown in Fig. 5.

Measurement of the refractive indices presents a problem for both C^{*}LCs and CLCs. Galerne⁴² and Lockhart *et al.*⁴³ have succeeded in measuring the principal values of the refractive index of CLCs (Fig. 13). The difficulties encountered in measurements of *n* for locally biaxial helical structures are discussed in Ref. 44. This is a particularly difficult problem for media for which the pitch of the helix lies in the visible part of the spectrum. As already noted, the propagation of light along the axis of the helix is accompanied by a strong diffractive interaction when the circular polarization of the wave coincides with the twist of the helix. A wave with the opposite circular polarization will not exhibit this interaction, so that the dispersion law is quite different for these two waves.

Figure 14 shows the temperature dependence of the refractive indices $n_{\rm L}$ and $n_{\rm R}$, measured by the wedge method on the G-1.5 goniometer; $n_{\rm oc}$ and $n_{\rm ec}$ were measured on the IRF-22 refractometer. It is clear from the



FIG. 14. Measured temperature dependence of the refractive index of the chiral smectic C phase of CE₃ (open circles) and 90% of CE₃ + 10% of TDOBAMBCC (full points): $a - n_{ec}$ and n_{oc} , $b - n_{R}$ and n_{L} : l - 546 nm, 2 - 577 nm.

figure that successful measurements were made of the refractive indices for both the 'strongly interacting' and 'weakly interacting' waves for different deviations from the Bragg condition, i.e., eigenwave dispersion was directly observed.

These measurements were used in (8)-(12) to calculate the temperature dependence of n_1 , n_2 , n_3 , P_0 , and θ (Fig. 15). It is clear from Fig. 15 that θ is independent of temperature, which is in agreement with the statement made in Ref. 19 that $\partial\theta/\partial T=0$ for smectics from which phase A is absent (they include CE-3).

2. FERROELECTRIC CHARACTERISTICS

2.1. Symmetry and ferroelectricity

The ferroelectric properties of C^*LCs are due to the spontaneous ordering of the permanent dipole moments of the molecules in smectic layers, which corresponds to the polar symmetry group C_2 (Ref. 45). A smectic layer of C^*LC has a single symmetry element, namely, a two-fold rotation axis. This axis lies in the plane of the smectic layer and is perpendicular to the x, z layer (Fig. 2). This plane cannot be a reflection plane because of the chirality of the molecules, so that the axis is a polar axis. Spontaneous polarization is observed when the chiral molecules have a dipole moment perpendicular to their long axis. Figure 16a shows the thermodynamic equilibrium configuration of the long axes of the molecules (the director) of C^*LCs . As the z coordinate is varied (the z axis points along the helix axis



FIG. 15. Calculated temperature dependence of chiral smectic C phase of the liquid crystal CE₃ (open symbols) and a mixture of 90% of CE₃+10% TDOBAMBCC (full symbols): $a-P_0$; $b-n_1$, n_2 , n_3 ; $c-\theta$; $I-\lambda=546$ nm, $2-\lambda=577$ nm.

which is perpendicular to the smectic planes), the C^{*}LC director and the polarization vector P_0 (which is perpendicular to it and points along the C_2 axis lying in the plane of the smectic layer) are found to rotate so that

$$\mathbf{L}(z+P_0) + \mathbf{L}(z) , \qquad (13)$$

$$\mathbf{P}_{\mathrm{s}}(z+P_0)=\mathbf{P}_{\mathrm{s}}(z) ,$$

i.e., the spatial period of rotation is equal to the pitch P_0 of the helix.

It follows from (13) that, in equilibrium, the mean polarization within a C^*LC volume containing a large number of smectic planes must be zero:



FIG. 16. a—Twisting of the director L of C^{*}LC around the helix axis (z axis) perpendicular to the smectic layers. The spontaneous polarization P_s of the smectic C phase is perpendicular to L and the normal to the layers. The angle θ is a measure of the tilt of the director in a layer, φ is the helical twist, and P_0 is the equilibrium pitch of the helix. b—Microscopic packing model for chiral molecules is a C^{*}LC layer (de Gennes' fishes⁴⁵).

$$\langle P_{\rm s} \rangle = \frac{1}{P_0} \int_0^{P_0} P_{\rm s}(\cos q_0 z \cdot \bar{y} - \sin q_0 z \cdot \bar{x}) \mathrm{d}z = 0 \,, \quad (14)$$

where $q_0 = 2\pi/P_0$ is the wave vector of the structure (see Fig. 16).

From the microscopic point of view, the existence of a polar axis in the smectic layer of the C^{*}LC follows from the requirement of densest packing of the chiral molecules (represented in Fig. 16b by the fishes).⁴⁵

The densest packing corresponds to the orientation of the 'fishes' for which their main 'fin' touches the boundary of the smectic layer. In Fig. 16b, the direction of polarization corresponds to the case where the uncompensated dipole moment of each 'fish' points out of the right eye. The polarization P_s of a smectic layer can be calculated from the formula (see Fig. 16b)

$$\mathbf{P}_{\mathbf{s}} = P_{\mathbf{s}}[\mathbf{L} \times \mathbf{z}] . \tag{15}$$

The necessary conditions for the existence of this polarization are: (1) tilted C^{*}LC molecules, i.e., $\theta_c \neq 0$ and (2) chirality of the molecules, which leads to nonuniform rotation around the long axis and nonzero molecular dipole moment that is at right angles to its long axis.

The classical example of the $C^{*}LC$ is p-decyloxybenzylidene p'-amino 2-methyl butyl cinnamate (DOBAMBC)⁴⁵ whose molecule takes the form

$$C_{10}H_{21}O \longrightarrow CH = N \longrightarrow CH = CH - COO - CH_2 - R^{\#}$$
,
 CH_3

where $R^{\#} = C^{\#}H - CH_2 - CH_3$ in which $C^{\#}$ represents an a symmetric optically active carbon atom. The chiral fragment of the molecule $R^{\#}$ and the transverse dipole moment which is due to the ester group —COO— are important elements of the molecule that ensure its tilt and polarization in a layer.

Molecular building is directed toward creating C*LCs with a wide temperature range, low viscosity, and high spontaneous polarization. The most promising approach is not to synthesize individual C^{*}LCs with given molecular shape, but to create multicomponent C^{*}LC mixtures in which the smectic C matrix has low viscosity and is chemically, photoelectrically, and thermally stable as well as being properly oriented; it must also exist in a wide range of temperatures, and the mesogenic (or nonmesogenic) twisting additive must ensure the formation of the ferroelectric helix (see Fig. 16a) and high spontaneous polarization.^{47–49} For example, the C^{*}LC mixture FELIX-001 reported in Ref. 48 exists in the temperature range between 7 °C and 79 °C; its spontaneous polarization is about 10 nC/cm² and its rotational viscosity at room temperature is less than 0.1 poise.

2.2. Physical parameters underlying the electrooptics of chiral smectic C liquid crystals

The basic physical parameters that characterize the electrooptic behavior of C^*LCs are as follows: tilt angle of the director in the layer, pitch of the helix, rotational viscosity of the director, dielectric anisotropy, optical anisotropy, elastic moduli associated with the deformation of the director, flexoelectric polarization associated with the bending of the director in the layers, and cohesion energy between the director and the substrate.

We shall now examine each of these factors in detail.

The tilt of the C^{*}LC director in a layer can vary from a few degrees near the transition to the smectic phase and $\theta \sim 40^{\circ}$ in certain C^{*}LCs (Refs. 50 and 51). The usual objective for electrooptic C^{*}LCs is to achieve tilt angles $\theta \sim 22.5^{\circ}$ in almost the entire temperature range in which the smectic C^{*} phase exists,^{46,51} but in some electrooptic effects the aim is to attain maximum possible values of the tilt angle θ (Refs. 10, 53, and 54) or its modulation depth.⁵⁵ The tilt θ is readily determined from electrooptic data obtained in a sign-changing electric field $\pm E$ (Ref. 50).

The spontaneous polarization of a C^{*}LC is largely determined by the molecular characteristics of its component materials, i.e., the intrinsic ferroelectric smectic C^{*} or the optically active dipolar additive, and can vary between about 1–2 and 220 nC/cm². It has been noted that the magnitude of spontaneous polarization is also a function of the induced dipole-dipole interactions between the molecules, and the degree of ordering of the long axes of the molecules and transverse molecular dipoles.^{56,57} The spontaneous polarization of a C^{*}LC can be measured pyroelectrically by integrating the pyroelectric coefficient $\gamma = dP_s/dt$ with respect to the temperature T (Ref. 56), by measuring changes in capacitance by the Sawyer-Tower method, ^{58,59} or an analogous system with a grounded sample, ^{60,61} and by integrating the time dependence of the repolarization current i_p (Ref. 62 and 63)

$$P_{\rm s} = \frac{1}{2S} \int i_{\rm p} \mathrm{d}\sigma$$

where S is the area of the electrode.

Flexoelectric polarization associated with the bending of the director in smectic layers is an important parameter of C^*LCs (Refs. 6 and 64). It is shown in Ref. 64 that the resultant polarization of C^*LCs is the sum of the components $P_{\parallel}(z)$ and $P_{\perp}(z)$ that are respectively parallel and perpendicular to the C₂ axis in the C^*LC layer. The nonzero values of $P_{\parallel}(z)$ and $P_{\perp}(z)$ are then due to the coupling between the smectic layers, or the flexoelectric effect (Fig. 17):



FIG. 17. a—Total polarization \overline{P} of a C^{*}LC layer, consisting of components P_{\parallel} and P_1 respectively parallel and perpendicular to the C_2 axis. b—Curve 1—total polarization of C^{*}LC. $\langle P_{E}/P_{s} \rangle$ —average along the helix axis (points—experimental), 2—contribution of spontaneous polarization, 3—contribution of flexopolarization, $4-E/E_{u}$ —relative electric field applied to the C^{*}LC (for $E=E_{u}$ the helix is completely unwound: $\varphi=\pi$).⁶⁴

TABLE I. Relative flexoelectric moduli of C^{*}LC (DOBAMBCC⁶⁴).

	$\Delta T = T_{\rm c} - T, ^{\circ}{\rm C}$		
	0,7	2,7	4
$\delta_1 = \frac{\mu_f q_0}{\mu_p}$	5	4	5
$\delta_2 = \frac{\mu'_f q_0}{\mu_p}$	-30	-60	-77
$\delta = \delta_1 - \delta_2$	35	64	82

$$P_{\parallel}(z) = (P_{x}, P_{y}) = (P_{\parallel} \sin \varphi, -P_{\parallel} \cos \varphi),$$

$$P_{1}(z) = (P_{1} \cos \varphi, P_{1} \sin \varphi),$$

$$P_{\parallel} = \chi_{1} \left(\mu_{p} - \mu_{f} \frac{\partial \varphi}{\partial z} \right) \theta,$$

$$P_{1} = \chi_{1} \mu_{f}' \frac{\partial \theta}{\partial z},$$
(17)

where χ_1 is the dielectric susceptibility, μ_p is the piezoelectric modulus, $P_s = \chi_1 \mu_p \theta$ is the spontaneous polarization, and μ_f , μ'_f are the flexoelectric moduli of the C^{*}LC due to the azimuthal (φ) and polar (θ) deformations of the director.

The relative contributions of spontaneous and flexoelectric polarizations to the total polarization of the C⁻LC, averaged along the axis of the helix (the z axis) in fields exceeding the field necessary to unwind the smectic helix, are shown in Fig. 17 (the smectic helix is unwound by the electric field E when the contribution to the energy of the C^{*}LC due to the interaction between the field and the spontaneous polarization exceeds the elastic unwinding energy of the helix). It is clear that the flexoelectric contribution to polarization may exceed the corresponding contribution due to spontaneous polarization and is the dominant factor for high director deformation gradients $\partial \varphi / \partial z$ and $\partial \theta / \partial z$ [see (17)]. The relative values of the flexoelectric coefficients $\delta_1 = \mu_i q_0 / \mu_p$ and $\delta_2 = \mu'_f q_0 / \mu_p$ were estimated for DOBAMBC near the smectic C⁺ \rightarrow smectic A phase transition on the basis of an analysis of the field dependence of the total polarization of the C^{*}LC (Ref. 64). It was shown that $|\delta_2| > |\delta_1|$, i.e., the most significant contribution to polarization near the phase transition is due to the spatial deformation of the polar angle $\partial \theta / \partial z$ and not of the azimuthal angle $\partial \varphi / \partial z$ as had been assumed (Table I).^{65,66} In Table I, $\Delta T = T_c - T$ is the deviation from the temperature T_c of the smectic $A \rightarrow \text{smectic } C^*$ phase transition, $q_0 = 2\pi/P_0$, and P_0 is the pitch of the C[•]LC helix (see Fig. 16).

Rotational viscosity is an important parameter of C^*LCs that determines their response in electrooptics. It is a measure of the dissipation of energy during the orientation of the C^*LC director (see Fig. 16). Symmetry considerations indicate that there are two distinct viscosity coefficients, namely, γ_{θ} and γ_{φ} , which determine the time constants τ_{θ} and τ_{φ} for the reorientation of the C^*LC di-



FIG. 18. Rotational viscosities γ_{θ} and γ_{φ} of smectic phase of DOBAMBCC.⁶⁷

rector in the coordinates θ and φ (Fig. 18). The corresponding simplified dynamic equations take the form^{67,68}

$$\gamma_{\theta} \frac{\mathrm{d}\theta}{\mathrm{d}t} + A\theta = 0, \quad \tau_{\theta} = \frac{\gamma_{\theta}}{A},$$
 (18a)

$$\gamma_{\varphi} \frac{\mathrm{d}\varphi}{\mathrm{d}t} + P_{\mathrm{s}}E\sin\varphi = 0, \quad \tau_{\varphi} = \frac{\gamma_{\varphi}}{P_{\mathrm{s}}E},$$
 (18b)

where t is the time, P_s is the polarization, E is the field strength, $A = 2a(T_c - T)$, and a < 0 is the effective elastic modulus for a change in the tilt angle θ . The viscosity coefficient γ_{φ} is sometimes written in the form⁶⁷⁻⁶⁹

$$\gamma_{\varphi} = \gamma'_{\varphi} \sin^2 \theta, \tag{19}$$

where γ'_{φ} is the rotational viscosity in the coordinate frame coupled to the director. The relation given by (19) shows that $\gamma_{\varphi} \rightarrow 0$ for $\theta \rightarrow 0$, i.e., the rotational viscosity of the C^{*} director γ_{φ} can be made as low as desired by reducing the director tilt in the C^{*}LC layer.

Well away from the ferroelectric phase transition point T_c , we can sensibly confine our attention to the azimuthal φ -deviations of the C^{*}LC director because the θ reorientation of the director relative to the layer normal involves changes in density, which can be neglected within the C^{*} phase. However, near T_c , the angle θ can be varied, e.g., by applying an electric field to the C^{*}LC (electroclinic effect^{9,55}). The quantity γ_{θ} can be determined in the electroclinic effect by measuring the polarization P_s , the tilt θ , and the component of the dielectric susceptibility $\chi_{\theta} = \partial P_s / \partial E$ in accordance with:⁶⁷

$$A = \left(\frac{P_{\rm s}}{\theta}\right)^2 \chi_{\theta}^{-1}, \quad \gamma_{\theta} = \tau_{\theta} A .$$
 (20)

The temperature dependence of the time constant τ_{θ} , polarization $P_{\rm s}$, and dielectric susceptibility χ_{θ} was measured in Ref. 6 by the pyroelectric method.^{56,57} The temperature dependence of the viscosity γ_{θ} of DOBAMBC is shown in Fig. 18.

The rotational viscosity corresponding to the azimuthal angle φ can be determined for a sufficiently strong



FIG. 19. Different methods of measuring the rotational viscosity of the $C^{\bullet}LC$ director. a—Electrical response I(t). b—Repolarization current $i_p(t)$. c—Repolarization current $i_p(t)$ for a triangular electric-field waveform E(t).

applied field E in accordance with equation (18b) (Refs. 67–70). It is shown in Refs. 67 and 69 that it can be estimated from the measured electrooptic response, using the formula

$$\gamma_{\varphi} = P_{s} E \tau_{\varphi}, \qquad (21)$$

$$\tau_{\varphi} = \frac{t_{90} - t_{50}}{\ln \sqrt{5}},$$

where t_{90} and t_{50} are the response times corresponding to the 90% and 50% transmission of the C^{*}LC relative to the maximum (Fig. 19a). The C^{*}LC cell is placed between a polarizer and an analyzer held so as to ensure a monotonic rise in intensity for large values of t (Refs. 67 and 69).

A similar formula for τ_{φ} is proposed in Refs. 68 and 70:

$$\tau_{\varphi} = \frac{t_{90} - t_{10}}{1.8}.$$
 (22)

Values of τ_{φ} determined from (21) and (22) differ by approximately 30%. We note, however, that (22) was ob-

tained numerically for a particular value of the reorientation angle of the director on the surface ($\varphi_0 = 1^\circ$) (Ref. 71) whereas (21) is valid for any φ_0 (Ref. 72).

The viscosity γ_{φ} can be determined from the time dependence of the repolarization current $i_p(t) = dq/dt$ as a function of time (Fig. 19b,c). The following formulas are then used (see Fig. 19b):^{68,70,73}

$$\gamma_{\varphi} = \frac{\tau_{\rm w} P_{\rm s} E}{1.8}, \qquad (23)$$

where τ_w is the half-width at half-height of the repolarization response (see Fig. 19c)

$$\gamma_{\varphi} = \frac{SP_{\rm s}^2 E_{\rm m}}{i_{\rm m}},\tag{24}$$

where S is the area of the electrode, P_s is the polarization, and $i_m(E_m)$ is the maximum repolarization current response in a field E_m .

One way of increasing the electrooptic switching rate in the C^{*}LC is to reduce the viscosity of the C^{*}LC mixture with a simultaneous increase in polarization.⁶ However, it is unlikely that this method will be highly successful as compared with the switching levels achieved so far (~30 μ s at room temperature with $E \sim 15 \text{ V/}\mu$ s; Ref. 74). This follows, firstly, from the fact that an increase in the polarization of C^{*}LC mixtures is usually accompanied by an increase in rotational viscosity⁷⁵ and, secondly, the rise in polarization is accompanied by a rapid rise in the corresponding repolarization current:⁷¹

$$i_{\varphi} \sim \frac{P_{\rm s}}{\tau_{\varphi}} \sim \frac{P_{\rm s}^2}{\gamma_{\varphi}},$$
 (25)

which is highly undesirable in electrooptic displays.

The pitch P_0 of the ferroelectric helix is most readily regulated by varying the concentration of the optically active additive (OAA) in the smectic C matrix. The pitch can be varied between wide limits, say, between 100 and 00.1 μ m by using an OAA with high twisting power, high concentration in the matrix, good orientation in the matrix, and little effect on the temperature range in which the smectic C exists. Moreover, it is desirable for the rotational viscosity of the C^{*}LC to increase with the OAA concentration much more slowly than the corresponding polarization.⁷ One such OAA is Luch-15 with the formula¹⁰

The pitch P_0 of the C^{*}LC helix can be estimated in various ways.^{40,41,44,45,66,77-85} In thick samples ($d > 250 \mu$ m), the pitch ($P_0 < 20 \mu$ m) is determined by measuring the separation between parallel domains in a planar texture when the axis of the helix is parallel to the substrates,^{77,78,81-84} or by determining the deflection β_N of a



FIG. 20. Pitch of helix in 90% of 4-octyloxyresorcylidene-4-dodecylaniline + 10% alkoxysalicylideneaniline based on *l*-menthol. l-n = 2, 2-n = 5.

laser beam with wavelength λ_0 corresponding to the Nth diffraction order^{66,79,82-84} produced by the C^{*}LC helical structure:

$$P_0 = \frac{N\lambda_0}{\sin\beta_N}.$$
 (27)

The pitch can also be found by using the Kano--Grandjean structure in a wedge-shaped cell with the C^*LC helix axis perpendicular to the substrates, in which case P_0 is equal to twice the separation between neighboring disinclinations,^{45,80} and also by using the spectral position of the Bragg reflection maximum for known refractive indices of the C^*LC .^{41,44,85}

The effect of different types of phase transition on the temperature dependence of the pitch of the helix and spontaneous polarization in mixtures of smectic C liquid crystals and optically active additives based on salicylidenanilines. Two types of temperature dependence of the pitch of the helix P_0 were found for chiral-induced smectics. In the first type there is a clear anomaly with a well-defined maximum (Fig. 20, curve 1) in an interval about 10° below the transition to the isotropic phase. The second type of dependence is monotonic and is shown by curve 2 in Fig. 20. The monotonic function $P_0(T)$ is observed when the mixture exhibits the chiral smectic $C \rightarrow$ chiral nematic transition. The anomalous form of $P_0(T)$ is observed when the chiral smectic $C \rightarrow$ smectic A transition is present in the system, and the smectic A can be induced by introducing an optically active compound. However, the presence of the phase transition to smectic A does not necessarily imply a nonmonotonic temperature dependence of the pitch. As far as spontaneous polarization is concerned, its highest values have been observed in systems with an induced smectic A phase and monotonic $P_0(T)$. These characteristics have been explained by assuming that the temperature dependence of the pitch is due to a growth of disinclination loops near the second-order phase transition point and to the presence of a particular surface field that unwinds the helix in chiral materials with strong piezoelectric coupling and correspondingly high spontaneous polarization.

The permittivity of a C^*LC is very dependent on temperature (especially near the transition to the C^* phase) and on the frequency of the applied field. In addition to the usual capacitive methods of measurement^{7,46} there is then the pyroelectric method^{50,57} based on

$$\frac{\partial \gamma}{\partial E} = \frac{\partial}{\partial E} \frac{\partial P}{\partial T} = \frac{\partial}{\partial T} \frac{\partial P}{\partial E} = \frac{\partial \chi}{\partial T}, \qquad (28)$$

where T is the temperature, P the polarization, E the electric field, $\gamma = \partial P / \partial T$ is the pyroelectric coefficient, and $\chi = \partial P / \partial E$ is the dielectric susceptibility.

The dielectric response is defined by

$$\chi = \frac{\varepsilon - 1}{4\pi} = \lim_{E \to 0} \frac{\langle P \rangle}{E}, \qquad (29)$$

where $\langle P \rangle$ is the mean induced polarization which contains contributions of two modes. The soft mode is due to amplitude changes in polarization, i.e., tilt changes in the C^{*}LC layer. This mode is particularly significant near the transition to the C^{*} phase and is responsible for the electroclinic effect.^{9,55} The second mode is associated with changes in the phase of the polarization, i.e., the azimuthal angle φ , and is referred to as the Goldstone mode.

The characteristic time constants and the relaxation frequencies of the permittivities of C^*LCs are determined by constructing the corresponding generalized Cole-Cole diagrams (see Ref. 86-88). The dielectric response of smectic *A* near the phase transition in C^*LC is lower by approximately an order of magnitude than the corresponding response in C^*LC and includes a contribution of only the soft mode; its characteristic relaxation frequencies are given by⁸⁶⁻⁸⁸

$$f_{\rm s} = a(T - T_{\rm c}), \quad T > T_{\rm c},$$

where $a \sim 10-15$ kHz \cdot K⁻¹. In the C^{*}LC phase, the contribution of the soft mode to the permittivity is negligible, and decreases rapidly with distance from the transition point. The characteristic relaxation frequencies are given by the following expressions that is well-known for second-order phase transitions:⁷

$$f_{\rm s} = 2a(T_{\rm c} - T), \quad T < T_{\rm c}$$
.

At the transition point $T = T_c$, the dielectric relaxation frequencies are finite and are determined by the Goldstone mode.^{7,86,88} The characteristic frequencies of the Goldstone mode are $f_G \sim \tau_{C\#}^{-1}$ where $\tau_{C\#}$ is the response time of the C^* director to small perturbations of the helix, $\tau_{C\#} \sim \gamma_{\varphi}/K_{\varphi}q_0^2$, γ_{φ} is the rotational viscosity, $q_0 = 2\pi/P_0$ is the wave vector of the helix, and K_{φ} is the modulus of elasticity for the deformation of the helix. Typical values of Goldstone-mode relaxation frequency are $f_G \sim 100$ Hz-1 kHz (Refs. 46 and 86-98).

As the temperature is reduced below the phase transition point T_c , the dielectric response (29) of the C^{*}LC is found to increase. Estimates^{7,86} show that

$$\chi \sim \frac{P_{\rm s}^2}{F_{\rm v}} \sim \frac{\left(\chi_1 \ \mu_{\rm p} \theta\right)^2}{F_{\rm v}},\tag{30}$$

where $F_v = K_{\varphi} q_0^2/2$ is the elastic bulk energy of the C^{*}LC. It follows from this expression that the temperature dependence of the dielectric susceptibility of the C^{*}LC is actually determined by the temperature dependence of the pitch of the helix:

$$\chi \sim P_0^2(T) , \qquad (31)$$

i.e., it increases with increasing temperature up to a certain steady value. Allowance for the temperature dependence of the flexorelectric contribution to the polarization of the $C^{*}LC$ does not alter the qualitative dependence described by (31) (Ref. 64).

From the practical point of view, it is important to have measurements of the dielectric anisotropy $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ in the frequency range 1-1000 kHz which, for the purposes of the so-called 'dielectric stabilization' of the C^{*}LC (Ref. 48), should be negative. The permittivities ε_{\parallel} and ε_{\perp} were measured in Ref. 46 for planar and homeotropic orientations of the C^{*}LC in the course of slow cooling below the phase transition point T_c in a strong magnetic field. It was found that $\varepsilon_{\parallel} \sim 4$, $\varepsilon_{\perp} \sim 6$, and $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \sim -2$. A relaxation of the soft mode (increase in ε_{\parallel}) was found in the frequency region ~ 20 kHz; the Goldstone mode was responsible for the increase in ε_{\perp} below 5 kHz (Ref. 46).

We now note one further property of C^*LCs that fundamentally distinguishes them from classical nematic liquid crystals in respect of dielectric behavior. The permittivity defined by $\varepsilon = \partial P/\partial E$ is very dependent on the field and may reach 100–1000 or more in fields $E \leq E_u$ (see Fig. 17). This must be taken into account when C^*LCs are used in electrooptic circuits with matched impedances, e.g., photoconductor-LC circuits.⁸⁹

It is also important to note recent data on biaxial dielectrics.^{90,91} Stabilization of ferroelectric liquid crystals with surface-stabilized geometry in an alternating field indicates the presence of significant biaxiality. It is shown in Ref. 90 and 91 that the biaxiality influences the electrooptic characteristics of both chiral and nonchiral smectic C liquid crystals.

As far as optical properties are concerned, these have already been considered in Sec. 1. A more complete account can be found in Refs. 4, 21, 23, 24 and 92. In principle, the C^{*}LCs can be treated to a good approximation as biaxial media although only one of the principal axes of the dielectric tensor, namely, the C2 axis, is clearly defined and is perpendicular to the director and parallel to the plane of the smectic layers⁹³ (see Fig. 16). The C^{*}LCs are mostly looked upon as uniaxial crystals in which one of the axes of the permittivity tensor lies along the director (the refractive index along this axis is n_{\parallel}) and the two other axes (C₂ nd the axis perpendicular to it and to the director) are completely equivalent (the refractive index along these axes is n_{\perp}).^{40,41,43,94} This approximation is validated by direct experiment in which measurements are made of the refractive indices of the C^{*}LC along the principal axes of the optical indicatrix: the biaxiality does not exceed 0.001 and tends to zero as we approach the transition to the smectic A phase. 40,41,43,94

The birefringence $\Delta n = n_{\parallel} - n_{\perp}$ is important in determinations of the electrooptic behavior of C^{*}LCs. It can also be found from electrooptic measurements^{10,50} that rely on the response intensity as a function of the phase factor $\Delta n d/\lambda$ where d is the layer thickness and λ the wavelength. The birefringence Δn can be measured directly with the Berek compensator in a strong stabilizing field that takes the C^{*}LC to a state with a fixed orientation of the director along the layer thickness (uniaxial phase plate).⁴⁶ The dispersion of optical anisotropy is described by the well-known Cauchy rule⁹⁵

$$\Delta n(\lambda) = \Delta n(\infty) + \frac{C}{\lambda^2}.$$

Experiment shows that the dispersion of $\Delta n(\lambda)$ is usually less significant in C^{*}LCs than in nematics. At room temperature, its total range does not exceed 0.01 as the wavelength λ varies across the visible range.

The elastic properties of C^*LCs can be determined in terms of the energy density F_d of distortions in director orientations as follows:

$$F_{\rm d} = \frac{K_1}{2} (\operatorname{div} \mathbf{L})^2 + \frac{K_2}{2} (\mathbf{L} \operatorname{curl} \mathbf{L} - t)^2 + \frac{K_3}{2} ([\mathbf{L} \operatorname{curl} \mathbf{L}] - \mathbf{b})^2, \qquad (32)$$

where the elastic moduli K_1 , K_2 , and K_3 describe different types of deformation as in ordinary nematic liquid crystals and the linear terms $\mathbf{L} \cdot \text{curl } \mathbf{L}$ and $\mathbf{L} \times \text{curl } \mathbf{L}$ remain in the expression for F_b because of the absence of mirror symmetry from C^{*}LCs. The spontaneous twist t and the transverse bending **b** are given by⁹⁶

$$\mathbf{t} = -q_0 \sin^2 \theta , \qquad (33)$$
$$\mathbf{\bar{b}} = q_0 \cos \theta \cdot [\mathbf{L} \times \mathbf{z}] ,$$

where $|q_0| = 2\pi/P_0$ and the sign of q_0 determines the direction of the twist of the helix; $q_0 > 0$ and $q_0 < 0$ determine the right- and left-twisted helix, respectively.

Apart from the volume elastic energy, the free energy of the C^{*}LC must take into account the energy of interaction of the director or the associated polarization P_s of the C^{*}LC with the substrate, which is characterized by the polar and dispersive contributions $W_p = B_p (\mathbf{P} \cdot \vec{v})$ and $W_d = B_d (\mathbf{P} \cdot \vec{v})^2$, where B_p and B_d are the respective rigidities and \vec{v} is the normal to the substrate. Hence the total free energy of elastic deformation of the C^{*}LC is given by

$$F_{\rm y} = \int_{V} F_{\rm d} \mathrm{d}\tau + \int_{S} \left(W_{\rm p} + W_{\rm d} \right) \mathrm{d}\sigma \,, \tag{34}$$

i.e., it consists of the sum of surface and volume integrals. There are at present no reliable methods for estimating the elastic moduli and the cohesion energy of the C^*LC and the substrate although the corresponding phase diagrams have been reported⁹⁶⁻⁹⁹ for different states of the C^*LC as functions of the elastic and surface moduli (helically twisted or uniform). The total free energy F of the C^*LC



FIG. 21. Clark-Lagerwall effect.

is equal to the sum of the elastic energy (34) and the energy of interaction between the C^{*}LC and the electric field E:

$$F = F_{y} + F_{e}, \qquad (35)$$
$$F_{e} = \int_{V} \left[-(\mathbf{P} \cdot \mathbf{E}) - \frac{\varepsilon_{a}}{8\pi} (\mathbf{E} \cdot \mathbf{L})^{2} \right] d\tau,$$

where **P** is the polarization and $\varepsilon_a = (\varepsilon_{\parallel} - \varepsilon_{\perp}) \sin^2 \theta$ is the dielectric anisotropy.

3. ELECTROOPTIC EFFECTS IN C*LCs

3.1. The Clark-Lagerwall effect in surface-stabilized structures

We shall now examine the basic electrooptic effects in C^{*}LCs. The best known is the so-called Clark-Lagerwall effect which is the change in the orientation of the C^{*}LC director L with the sign of the electric field E (Fig. 21). The director is in this case reoriented along the generators of a cone of angle θ whose axis (the z axis) lies along the helix axis of the C^{*}LC that is parallel to the substrate (smectic layers are perpendicular to the substrates), and since the equilibrium direction of polarization is such that $\mathbf{P}_{c} \parallel \mathbf{E}$, the sign change $E \rightarrow -E$ is accompanied by the change $\Delta \varphi = \pi$ in the orientation of the director. The Clark-Lagerwall effect is observed in the so-called surfaceferroelectric stabilized liquid crystal structures (SSFLCs),^{2,10,100} i.e., structures in which the inequality $d \ll P_0$ ensures that the helical structure is energetically unfavorable (i.e., the helix is 'untwisted by the walls') where d is the layer thickness and P_0 is the pitch of the helix.

The change in the azimuthal angle φ in the Clark-Lagerwall effect is described by the equation for the equilibrium of moments, which follows from the condition for minimum free energy (35):

$$\gamma_{\varphi} \frac{\partial \varphi}{\partial t} + K_{\perp} \frac{\partial^2 \varphi}{\partial y^2} = P_{\rm s} E \sin \varphi + \frac{\varepsilon_{\rm a} E^2}{4\pi} \sin \varphi \cdot \cos \varphi \qquad (36)$$

with the boundary conditions

$$\left(K_{\perp} \frac{\partial \varphi}{\partial y} + B_{\rm p} \sin \varphi \pm B_{\rm d} \sin 2\varphi\right)_{y=d,0} = 0, \qquad (37)$$

where K_{\perp} ($K_1 = K_3 = K_4$) is the elastic modulus.

For the usual values of polarization $(P_s \sim 15 \text{ nC/cm}^2)$, control field $(E \sim 10 \ \mu\text{m})$, and directric anisotropy $(|\varepsilon_a| \sim 0.05)$, we have

$$\frac{|\varepsilon_{a}E|}{4\pi} < |P_{s}|, \qquad (38)$$

so that the second term in (36) can be neglected. When (38) is not satisfied, which can be ensured by suitably choosing the C^{*}LC with a high value of $\Delta \varepsilon$ and low value of P_s , the switching time increases without limit in the Clark-Lagerwall effect when $|\varepsilon_s E|/4\pi \sim |P_s|$. The sign of the dielectric anisotropy ε_a is then unimportant.^{71,102-105} Actually, experiment shows that, for negative values of the dielectric anisotropy, $\varepsilon_a < 0$, the slope of the dynamic curve of the C^{*}LC response increases slightly with increasing driving voltage, i.e., there is a reduction in the corresponding switching times.^{103,105} This is important for practical applications in which we have to increase the information capacity of C^{*}LC matrix displays. However, as the voltage is increased further, the total electrooptic response time of the C^{*}LC, which is defined as the time for the intensity to reach 50% of the saturation level,¹⁰⁵ begins to increase, then passes through a maximum for $|\varepsilon_a E|/4\pi \sim |P_s|$, and finally falls again.¹⁰³⁻¹⁰⁵ When $|\varepsilon_a E|/4\pi \gg |P_s|$, the C^{*}LC switching time is evidently determined by the electrooptic effect that is quadratic in E and is the analog of the Frederiks transition.

The actual fields $(\sim 5-15 \text{ V}/\mu\text{m})$ for which the Clark-Lagerwall effect is particularly noticeable are such that the moments associated with elasticity $(\sim K_{\perp} \partial^2 \varphi / \partial y^2)$ and with the anisotropy of permittivity $[(\varepsilon_a E^2/4\pi)\sin\varphi\cos\varphi]$ in (36) can be neglected, in which case the electrooptic switching times can be estimated from the following formula [cf. (21)]:

$$\tau_{\varphi} = \frac{\gamma_{\varphi}}{P_{\rm s}E}.$$
(39)

The measured response-time differences $T_{90} - T_{10}$ (22) and $T_{90} - T_{50}$ (21) differ from τ_{φ} by a factor of the order of unity.

Comparison of the switching times in electrooptic effects in classical nematic liquid crystals, i.e.,

$$\tau_{\rm on}^{\rm (NLC)} \sim \frac{\gamma_1}{\varepsilon_{\rm a} E^2 / 4\pi},$$

$$\tau_{\rm off}^{\rm (NLC)} \sim \frac{\gamma_1}{K\pi^2 / d^2}$$
(40)

 $(\gamma_1 \text{ is the rotational viscosity, } K \text{ is the elasticity, and } d \text{ is the layer thickness}) and in C[*]LC$

$$\tau_{\rm on}^{\rm (C^{\bullet}LC)} \sim \tau_{\rm off}^{\rm c^{\bullet}LC} \sim \tau_{\varphi} = \frac{\gamma_{\varphi}}{P_{\rm s}E}$$

shows that a very high speed of operation can be achieved in the Clark-Lagerwall effect as compared with nematic liquid crystals. Actually, we usually have

$$\tau_{\rm on}^{\rm (NLC)} \lesssim \tau_{\rm off}^{\rm (NLC)}$$

or even

$$\tau_{\rm on}^{\rm (NLC)} \not < \tau_{\rm off}^{\rm (NLC)}$$

(the so-called two frequency relaxation in which the sign of ε_a of the NLC changes with the field frequency⁸⁹ is an exception), since in accordance with (40), the time $\tau_{out}^{(NLC)}$ does not in general depend on the amplitude of the switching field *E*, whereas

$$\tau_{\rm on}^{\rm (C^{\bullet}LC)} = \tau_{\rm off}^{\rm (C^{\bullet}LC)} < \tau_{\rm on}^{\rm (NLC)} .$$
(41)

The validity of (41) can readily be confirmed by considering the usual values of the NLC and C^{*}LC electrooptic switching parameters for $\varepsilon_a \sim 10$, $E \sim 10$ V/µm, $P_s \sim 10$ nC/cm², $\gamma_1/\gamma_{\varphi} = \gamma_1/\gamma'_{\varphi} \sin^2 \theta \sim 1/\sin^2 \theta \sim 9$ (for $\theta = 20^\circ$) we have

$$\frac{\tau_{\text{on}}^{(\text{NLC})}}{\tau_{\text{on}}^{(\text{c}^{*}\text{LC})}} = \frac{\gamma_{1}P_{s}E}{\varepsilon_{a}E^{2}\gamma_{\varphi}/4\pi} > 1.$$
(42)

It is shown in Refs. 106 and 107 that there are two switching regimes in the Clark-Lagerwall effect, separated by the threshold voltage

$$U_{\rm th} \sim \frac{4B_{\rm d}}{P_{\rm s}},\tag{43}$$

where B_d is the rigidity for the dispersive part of the cohesion energy. For $B_d \sim 0.1$ erg/cm² and $P_s \sim 10$ nC/cm², the estimate given by (43) is in agreement with experiment for $U_{\rm th} \sim 4$ V.

When $U < U_{\rm th}$, we observe the motion of the domain walls that separate regions with different directions of polarization, i.e., **P** and $-\mathbf{P}$. The rate at which one domain region is replaced by another determines the switching time. When $U > U_{\rm th}$ (Clark-Lagerwall regime proper), the switching time $\tau_{\varphi} = \gamma_{\varphi}/P_{\rm s}E$ is determined by the reorientation of the director throughout the C^{*}LC. The electrooptic response time of the C^{*}LC is very sensitive to its real structure (type of orientation, the presence of defects, and so on) which will be considered separately.

The total electrooptic response amplitude I of the C^{*}LC in the Clark-Lagerwall regime can be approximately calculated from the formula⁹⁸

$$I = I_0 \sin^2 4\theta \cdot \sin^2 \frac{\Delta \Phi}{2}, \qquad (44)$$

where I_0 is the incident-light intensity, $\Delta \varphi = 2\pi \Delta n d/\lambda$ is the phase delay, and $\delta n = n_{\parallel} - n_1$ is the optical anisotropy of the C^{*}LC. It is clear from (44) that the maximum contrast on switching is observed for $\theta \sim \pi/8(22.5^\circ)$ and $\Delta n d/\lambda = 1/2$, which for $\Delta n \sim 0.125$ and $\lambda \sim 0.5 \ \mu m$ corresponds to $d \sim 2 \ \mu m$. It is shown in Ref. 69 and 72 that a change in the thickness d by $\lambda/8\Delta n$ from its optimum value may produce a significant change in the time depen-



FIG. 22. Time dependence of the electrooptic response for different values of the phase delay $d(n_{\parallel} - n_{\perp})$ in $C^{\bullet}LC$.

dence of the electrooptic response (Fig. 22). Practical quality criteria for electrooptic displays suggest the following more stringent limits: $2 \mu m \pm 10\%$ (Ref. 108).

The disadvantages of the Clark-Lagerwall effect include not only the stringent restrictions on the deviation from the optimum thickness of the C^{*}LC layer and difficulties in producing a defect-free sample, but also obstacles to the realizations of reproducible bistability or optical memory switched by the electric field, as well as stable reproducibility of the voltage-dependent greyness scale. We note that, in the volume switching regime, the transmission of an element is determined by the product of the pulse amplitude U and its duration τ .

When C^{*}LCs are developed for the Clark-Lagerwall effect, high values of P_s are not the prime consideration because they lead to much larger repolarization currents.⁷¹ Actually, if we define the current i_p as the time derivative of charge (the charge being induced by the polarization so that $q = -P_s \cos \varphi$), we find from (36) that

$$i_{\rm p} = \frac{{\rm d}q}{{\rm d}t} = P_{\rm s} \sin \varphi \cdot \frac{{\rm d}\varphi}{{\rm d}t} \sim \frac{P_{\rm s}^2 E \sin^2 \varphi}{\gamma_{\varphi}}, \qquad (45)$$

i.e., the current is proportional to the square of polarization. Moreover, for high values of polarization, the switching process is significantly influenced by the space charge $q=\operatorname{div} \mathbf{P}$ produced during the switching process by the internal field which is reduced by the effect of the switching pulse. Charge phenomena are not fully understood at present, and only certain qualitative estimates are available of the role of these phenomena in C^{*}LC electrooptics.¹⁰⁹⁻¹¹¹

3.2. Deformed helix effect in C*LCs

The deformed helix effect was observed in early experiments on the electrooptic properties of C^*LCs (Refs. 4, 76, and 112), first adequately explained in Ref. 113 and 114. The geometry of the C^*LC cell in which the deformed helix ferroelectric effect (DHFE) is observed and shown in Fig. 23. The polarizer II on the front substrate is at an



FIG. 23. a—Geometry of a C^*LC cell in the deformed helix effect; b—deformation of the current director distribution in a sign-changing electric field.

angle β to the axes of the helix, whilst the analyzer A is perpendicular to the polarizer. The C^{*}LC layers are perpendicular to the substrates, and the layer thickness d is much greater than the pitch P_0 of the helix:

$$d \gg P_0. \tag{46}$$

The light beam with aperture $a \ge P_0$ is parallel to the smectic layers.

The C^{*}LC helix is deformed by the electric field, and the changes that occur are symmetric in the electric field $\pm E$ (see Figs. 23 and 24). The reorientation of the C^{*}LC director is accompanied by a change in the refractive index, i.e., we have birefringence induced by the electric field. The effect occurs right up to fields corresponding to the unwinding of the helix:

$$E_{\rm p} = \frac{\pi^2}{16} \frac{K_{\parallel} q_0^2}{P_{\rm s}},\tag{47}$$

where $K_{\parallel} = K_2$ [see (32)] and $|q_0| = 2\pi/P_0$. The characteristic time constant of the effect in low fields $E \ll E_u$ is independent of the C^{*}LC polarization and the field *E*, and is determined exclusively by the rotational viscosity γ_{φ} of the C^{*}LC and the pitch P_0 of the helix:



FIG. 24. Internal disinclination lines between the helix volume structure and planar adhesion to electrodes for skew-symmetric (a) and symmetric (b) directions of transverse molecular dipoles relative to the normal to the electrodes.

$$\tau_0 \sim \frac{\gamma_{\varphi}}{K_{\parallel} q_0^2} = \frac{\gamma_{\varphi} P_0^2}{K_{\parallel} \pi^2}.$$
(48)

When $E \leq E_u$, the formula given by (48) becomes invalid because the helix becomes highly deformed and its pitch $P_0^{\#}$ rapidly increases: $(P_0^{\#}/P_0)^2 \rightarrow \infty$. According to Ref. 114,

$$\frac{\tau_{\text{off}}}{\tau_0} \sim \left(\frac{P_0^{\#}}{P_0}\right)^2. \tag{49}$$

The time necessary for the helix to return to its original equilibrium state is also found to increase sharply, so that for $E \sim E_u$, for which the helix is almost completely unwound, the time τ_{off} becomes arbitrarily large, i.e., we have structural and optical memory.

However, electrooptic switching is difficult to implement for $E \leq E_u$ because the field dependence of the birefringence $\Delta n(E)$ displays a well-defined hysteresis, especially as E approaches E_u (Refs. 115–117). Moreover, experiment shows that, for $E \leq E_u$, there is practically no hysteresis, and reversible switching of $\Delta n(E)$ and the corresponding light intensity I(E) can readily be achieved.¹⁰

The relative light intensity transmitted by the C^{*}LC sample shown in Fig. 23 can be calculated from the formula^{64,113}

$$\frac{I}{I_0} = \left\langle \left(\sin^2 2\beta + 2\theta \sin 4\beta \cdot \cos \varphi + 4\theta^2 \cos 4\beta \cdot \cos^2 \varphi - \frac{16}{3} \theta^3 \sin 4\beta \cdot \cos^3 \varphi \right) \sin^2 \frac{\Delta \Phi}{2} \right\rangle, \quad (50)$$

where β is the angle between the axis of the helix and the polarizer, θ , φ define the orientation of the C^{*}LC director (θ is the tilt in the layer), $\Delta \Phi = (2\pi d/\lambda)\Delta n(E)$ is the phase delay, and the angle brackets represent averaging over z. If the electric field E is a harmonic function of time ($E = E_0 \cos \omega t$), then according to Refs. 10, 64, and 113

$$\varphi = z' + A \sin z', \quad z' = \frac{z}{P_0},$$
 (51)

$$A = \frac{\pi^2}{16} \frac{E}{E_u} \frac{\cos \omega t + (\omega/\omega_0) \sin \omega t}{1 + (\omega/\omega_0)^2} \,. \tag{52}$$

From (51) we have $\langle \cos \varphi \rangle \sim -A/2$ and $\langle \cos^2 \varphi \rangle \sim 1/2$, and $\langle \cos^3 \varphi \rangle \sim -3A/4$. It then follows from (50) that, when $\sin 4\beta = 1$ ($\beta = \pi/8$, $3\pi/8$), the transmitted intensity is linearly modulated, and the swing of the oscillations is

$$\left|\frac{I(A)}{I_0} - \frac{I(-A)}{I_0}\right|$$
$$= \Delta\left(\frac{I}{I_0(0)}\right) = 2\theta A = \frac{\pi^2}{8} \theta \frac{E}{E_p} \frac{\cos \omega t + (\omega/\omega_0)\sin \omega t}{1 + (\omega/\omega_0)^2}.$$
(53)

The intensity modulation depth is proportional, in the first approximation, to the tilt θ of the C^{*}LC director and to the applied field. This has been confirmed experimentally.¹⁰

When sin $4\beta = 0$ ($\beta = 0$, $\pi/4$, $\pi/2$), the intensity modulation is quadratic in the field. Actually, according to (51)

$$\langle \cos^2 \varphi \rangle \sim \frac{1}{2} \left(1 + \frac{A^2}{2} \right),$$

and the swing of the oscillations is

$$\Delta \left(\frac{I}{I_0}\right) = \left|\frac{I(A)}{I_0} - \frac{I(0)}{I_0}\right|$$
$$= \theta^2 A^2 = \theta^2 \left(\frac{\pi^2}{16} \frac{E}{E_u}\right)^2 \frac{\cos \omega t + (\omega/\omega_0)\sin \omega t}{1 + (\omega/\omega_0)^2},$$
(54)

i.e., it is quadratic in the field, and the oscillations occur at twice the frequency. This has also been confirmed experimentally.¹⁰

In the above two cases of light modulation in the deformed helix effect, the phase factor $\sin^2(\Delta \Phi/2)$ was almost constant and the phase delay could be chosen so that this factor was equal to unity. We note, however, that if the directions of the helix axes are totally random in the C^{*}LC sample, i.e.,

$$\overline{\sin^2 2\beta} = 1/2$$
, $\overline{\sin 4\beta} = 0$, $\overline{\cos 4\beta} = 0$,

where the bar represents averaging over the plane of the substrate, the modulation of the light intensity transmitted by the C^{*}LC is wholly determined by the change in the phase factor $\sin^2(\Delta \Phi/2)$. This factor can be written out in greater detail in accordance with Ref. 64 and 113 and the formula given by (51):

$$\left\langle \sin^2 \frac{\Delta \Phi}{2} \right\rangle \sim \sin^2 \frac{\Delta \Phi_{\max}}{2} - \frac{\sin \Delta \Phi_{\max}}{2} B \left\langle \sin^2 \varphi \right\rangle$$
$$\Delta \Phi_{\max} = \frac{2\pi d}{\lambda} \left(n_{\parallel} - n_{\perp} \right) ,$$

$$B = \frac{\pi dn_{\parallel}}{\lambda} \theta^2 \left(\frac{n_{\parallel}^2}{n_1^2} - 1 \right),$$

$$\langle \sin^2 \varphi \rangle \sim \frac{1}{2} \left(1 - \frac{A^2}{2} \right), \qquad (55)$$

so that in accordance with (50), the swing of the oscillations is

$$\Delta \left(\frac{I}{I_0}\right) = \left|\frac{I(A)}{I_0}\right| - \left|\frac{I(0)}{I_0}\right| = \overline{\sin^2 2\beta} \left\langle \overline{\sin^2 \frac{\Delta \Phi}{2}} \right\rangle$$
$$= \left|\frac{\sin \Delta \Phi_{\max}}{8} BA^2\right|$$
$$= \left|\frac{\sin \Delta \Phi_{\max}}{8} \frac{\pi dn_{\parallel}}{\lambda} \left(\frac{n_{\parallel}^2}{n_{\perp}^2} - 1\right)\right| \theta^2 A^2$$
(56)

and is quadratic in field and frequency, as in the case of (54). However, in addition, it increases more rapidly with increasing phase factor $d\Delta n/\lambda$.

Experimental data^{10,115,117} have confirmed the validity of (50-54) for the electrooptic response in the deformed helix effect. By adding a chiral impurity such as (26) to a wide-temperature low-viscosity smectic C matrix, it has been possible to produce liquid-crystal materials with a high degree of twist ($P_0 \sim 0.3-0.4 \,\mu\text{m}$ at 25°), considerable director tilt in the layer (29-30°), and helix unwinding voltage $U_u \sim 2-3$ V. The switching times for $U \sim 1.5-2$ V and contrast of 100:1 or more were found to be 150-200 μ s (Refs. 10 and 115-117). Obviously, these are not limiting values. The time constants of this effect can be substantially improved by applying narrow, high-amplitude pulses to the C^{*}LC layer as is done, for example, in other electrooptic effects in liquid crystals.⁸⁹

In conclusion, we consider a few of the advantages of the deformed helix effect as compared with the Clark-Lagerwall effect.

1. High speeds are achieved for low driving voltages. This occurs because modulation of birefringence and the associated change in the transmitted-light intensity are due to small deformations of the azimuthal twist angle of the director near the position of equilibrium. The deformation of the C^*LC is achieved in this effect for arbitrarily low values of the voltage, so that the delay time, which can be relatively long in the Clark-Lagerwall effect, is zero in this case.

2. The effect is less sensitive to the treatment applied to the substrates and to variations in thickness around its optimum mean value corresponding to $\sin^2(\Delta \varphi/2) = 1$ (Ref. 10). Experiment and qualitative estimates^{10,113} show that the effective birefringence $\Delta n_{\rm eff}$ is lower in the deformed helix effect by a factor of 1.5 than the value of $\Delta n_{\rm max}$ in the Clark-Lagerwall effect.

3. The effect can be used to reduce the natural greyness scale (that depends exclusively on the voltage amplitude). Moreover, long-term optical memory can be achieved near the unwinding field $E \sim E_u$.

The deformed helix effect can evidently compete with the Clark-Lagerwall effect in applications such as fast light



FIG. 25. Electroclinic effort.

modulators working at low driving voltages, liquid-crystal image converters with optical memory, and so on.

3.3. Electroclinic effect near the smectic $A \rightarrow C^*LC$ transition

The electroclinic effect, i.e., the change in the molecular tilt angle in smectic A near the phase transition to C^{*}LC under the influence of an electric field, was discovered by Garoff and Mayer.⁹ Several subsequent publications were devoted to the investigation of the electrooptic parameters of the effect^{55,118,119} and to the development of new liquid-crystal materials for its applications.^{120,121}

The dependence of the field-induced director tilt on the external electric field in the electroclinic effect is linear^{7,9,55,118,119}

$$\theta = e_{\rm c}E$$
, (57)

where e_{c} is the electroclinic coefficient given by

$$e_{\rm c} = \frac{\chi_{\rm L} \,\mu_{\rm P}}{A},\tag{58}$$

 $P = \chi_1 \mu_p \theta$ is the induced polarization, χ_1 is the susceptibility, μ_p is the piezo-electric modulus, $A = 2a(T_c - T)$, *a* is the effective modulus of elasticity for the change in the tilt angle, and T_c is the temperature at which the transition to the smectic C^{*} phase takes place. According to (58), the electroclinic effect has a singularity at the phase transition point $T = T_c$. The effect, which is also referred to as the soft mode,¹¹⁷ is also found to occur for $T < T_c$, but in the C^{*}LC phase the so-called Goldstone mode is much more noticeable and is due to changes in the azimuthal tilt of the C^{*}LC director in the electric field.

The rate of switching of the director tilt θ in the electroclinic effect is independent of the electric field *E* and is determined exclusively by the rotational viscosity γ_{θ} and elasticity *A* (18a). The corresponding response time

$$\tau_{\theta} = \frac{\gamma_{\theta}}{A} \tag{59}$$

lies in the submicrosecond range.

The geometry of the liquid-crystal cell in which the electroclinic effect is observed in illustrated in Fig. 25. The

optic axis of the sample rotates in the electric field through the angle θ between L(E) and L(0) where L defines the direction of the director. It is shown in Ref. 119 that the light intensity in the electroclinic effect is given by

$$I = I_0 \sin^2 2(\psi_0 + \theta(E)), \qquad (60)$$

where $\psi_0 + \theta(E)$ is the angle between the polarizer and the projection of the director on to the plane of the substrate [we assume that the phase factor $\sin^2(\Delta \varphi/2)$ in (60) is equal to unity]. The intensity modulation responding to (60) for $\theta(0)=0$ is

$$\Delta I = I(E) - I(0)$$

= $I - I_0 \sin^2 2\psi_0 \sim I_0 [2\theta(E) \sin 4\psi_0 + (2\theta(E))^2 \cos 4\psi_0 - \frac{2}{3} (2\theta(e_c))^3 \sin 4\psi_0 + \cdots],$ (61)

i.e., a linear electrooptic response is observed for $\psi_0 = 22.5^{\circ}(\sin 4\psi_0 = 1)$. Substituting $\psi_0 = 22.5^{\circ}$ in (61), together with the value of e_c from (58) and $E = E_0 \sin \omega t$, we obtain¹¹⁹

$$\Delta I = I_0 \cdot 2e_c E_0 \sin \omega t \,. \tag{62}$$

The electroclinic effect is at present the fastest of all the electrooptic effects observed in liquid crystals. It is reported in Refs. 119–121 that the response time achieved with this effect at room temperature (25 °C) does not exceed 600 ms for voltages of about 10–40 V/ μ m and layer thickness $d=2 \mu$ m. The effect can be used in a wide spectral range that includes visible radiation, and the wavelength dependence of transmission can be substantially reduced by using a series of electroclinic cells.¹¹⁹ It is clear from (62) that linear intensity modulation and the corresponding liner greyness scale can be produced with the electroclinic effect.

Optimum light modulation occurs in this effect for $\theta(E) = 11.25^{\circ}$ and considerable efforts will be directed in the near future toward achieving this figure by developers of liquid-crystal materials.¹¹⁷ Another important criterion for the quality of a liquid crystal is the temperature range in which the electroclinic effect exists, and also the degree of polarization induced as a result of this, which is directly proportional to the electroclinic coefficient. At present, the width of the temperature interval achieved in commercially developed liquid-crystal materials is about 20° near room temperature, and the field-induced angle is close to the optimum value of about 11.25° (Refs. 119-121). The electroclinic effect will find applications in inexpensive and compact light switches for frequencies between 100 MHz and 2 MHz, controlled light filters for television cameras, fast image converters based on liquid crystals, and so on.

3.4. Other electrooptic effects in C*LCs

The electrooptic effects in ferroelectric liquid crystals, discussed above, have the most interesting and valuable practical applications. However, to complete the picture, we must consider some certain other electrooptic effects in C^*LCs .

The transient scattering mode effect was first observed in DOBAMBC (16) (Refs. 122 and 123). It involves the scattering of light during the motion of domain walls that separate regions with different polarization directions when the polarization is reversed in a sign-changing electric field. The characteristic response times fall with increasing amplitude of applied voltage, and amount to about 50–100 μ s in high-temperature C*LCs ($T=70-90^{\circ}$ C) with layer thickness $d \sim 3 \mu m$.

Another electrooptic effect that is of practical interest is the C^{*}LC structure transition from the light-scattering untwisted helical state to the transparent state from which the helix is absent.^{124,125} According to (37), the threshold electric field $E_{\rm th}$ for which this type of transition takes place is $E_{\rm th} \sim K_{\parallel} / d^2 P_{\rm s}$. It can therefore be relatively low, i.e., less than 0.5 V/ μ m when the layer thickness and polarization $P_{\rm s}$ are both large.^{124,125}

The scattering of light during the unwinding of the helix is observed without polarizers in sufficiently thick C^*LCs samples (10-75 μ m). The voltage-contrast characteristic exhibits well-defined hysteresis. The response times of high-temperature C^*LCs (DOBAMBC) range from $\sim 500 \ \mu$ s (fast unwinding of the helix) to 50 ms (slow return to the original twisted state). However, the helix relaxation time can be substantially reduced (to 5 ms) by suitably choosing the driving bipolar pulses of different amplitude and duration.

The light-scattering effects observed in Refs. 122–125 during the deformation of the C^{*}LC helix have not as yet been adequately investigated either theoretically or experimentally. There is, for example, no explanation of the correlation between the temperature dependence of the C^{*}LC helix pitch and the scattered-light intensity reported in Ref. 125; the connection between the physical parameters of C^{*}LCs and the characteristics of the above effects such as response time or shape of the hysteresis curve has not been established, and the effects have not been investigated in commercial C^{*}LC mixtures working at room temperature. Nevertheless, these electrooptic effects may well be useful in practice in the creation of polaroid-free liquidcrystal displays, the development of optical memories, and so on.

We note in conclusion, that recent papers have reported a number of new electrooptic properties of C^*LCs that do not fit the above ideas. They include the appearance of a third stable state in surface-stabilized structures with high spontaneous polarization (~100 nC/cm²),¹²⁶ switching associated with the motion of disinclinations between twist states,¹²⁷ and so on.

There is continuing interest in electrooptic effects in the nonchiral smectic C phase (CLC) of the liquid crystal. In addition to the usual (quadratic in the field) Frederiks transition in the smectic C phase, the theory of which is well established,^{4,89,128,129} and which has recently been seen experimentally,^{128,129} a linear electrooptic effect in a CLC has recently been reported in Ref. 130. This effect is preferentially associated with the flexoelectric coupling between the smectic C liquid crystal and the external electric field.

4. PRACTICAL APPLICATIONS OF C*LCs

Chiral smectic liquid crystals are among the most promising LCs with applications in electronics. These applications include high density information displays with matrix addressing,^{53,131-138} fast light switches for electrooptic systems,^{139,140} image converters based on photoconductor-C^{*}LC structures,¹⁴⁰⁻¹⁴⁸ and fast linear arrays of light-valve devices for reprographic and printing technologies.¹⁴⁹⁻¹⁵⁵ We shall now examine each of these applications in greater detail.

The generally adopted method of addressing liquidcrystal displays in which the number of rows is ≥ 8 is the so-called matrix method in which each individual display element (pixel) is in the ON state of signals of different polarity are simultaneously applied to the display row and column that intersect at this particular pixel (Fig. 26). The resulting voltage amplitude (voltage difference between the row and the column) must be sufficient to ensure that the particular pixel can be regarded as being ON. The following conditions must then be satisfied.

1. Steps must be taken to avoid the 'cross-talk effect,' i.e., the voltage applied only to a row (column) must be insufficient to turn on a pixel in the particular row (column).⁸⁹

2. Since the display rows are usually addressed sequentially, the image of the first (and subsequent) rows must persist throughout the time taken to address the entire display (frame time).

3. The time-averaged acting voltage evaluated over many frames and applied to the liquid-crystal layer (i.e., the constant component of the voltage) must be zero in order to avoid electrochemical degradation of the liquid crystal.¹³⁵

Fast linear electrooptic effects (i.e., sensitivity to the sign of the driving field) and the field-switched optical memory make the C^{*}LC very promising for applications in high density information displays, personal computer screens, palmtop television sets, and so on. For example, to produce a standard TV image (625 lines, 25 frames per second), we have to address each display line for not more than 64 μ s. This addressing rate is attainable in ferroelectric liquid crystals even today,¹⁵⁶ which means that the C^{*}LC is one of the most promising liquid crystals (Table II).

Controlled optical bistability is the principle employed in C^{*}LC-based matrix displays capable of handling highdensity information. This means that each pixel must store information written to it throughout the time taken to write the entire frame, and must have two optically different states that are switched by pulses of different polarity. Clearly, a storage time of about 40 ms is necessary if the above television standard is to be maintained, and this is now a practical proposition.¹³⁵

A further important image quality condition for a high density information LC displays is the availability of several levels of greyness (usually ≥ 8) for half-tone production. The first C^{*}LC matrix displays were black and white systems because it had not been possible to produce such half-tones with a simple driving system.^{53,131-134} Subse-



FIG. 26. Matrix addressing of high information density C⁶LC displays: a—general scheme, b—driving pulses for 5τ and 3τ schemes (Refs. 158 and 135, respectively).

quent developments have resulted in improved C^*LC displays either through the use of more sophisticated driving systems and an infrastructure in each pixel, ^{135,137} or by the modification of the electrooptic effect itself.^{10,119}

TABLE II. Row writing rate in matrix-controlled LC display.

LC material (effect)	At present	In the future
C [•] LC	60 μs	10 µs
Nematic LC with	•	
active addressing	20 ms	
Controlled birefringence		
in nematic LC	100 ms	50 ms
Supertwist nematic-		
cholesteric structure ^{*)}	200 ms	50 ms
'Guest-host' effect in supertwist		
nematic-cholesteric structures	300 ms	

[•])Lower row-writing times, down to 75 μs in such structures are reported in Ref. 157.

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We have already mentioned the technological problems encountered in producing a constant gap over a large area $(2\pm0.05 \ \mu\text{m})$ in the Clark–Lagerwall effect) and of achieving reproducible bistability and the absence of defects. These problems have now been successfully solved.^{53,131–138} Much is expected of the new electrooptic effects in C^{*}LCs such as, for example, the deformed helix effect and its modifications.¹⁰

We will give the characteristics of one of the last developments of the color white format of the high informative display on the base of C^*LC^{138} (see Table III).

Figure 26 illustrates the matrix control of a C^{*}LC display capable of handling high-density information (a) and the form of the corresponding driving pulses (b). Lines 1, 2, ... on the display are selected in succession, each occupying 1/n of a frame. At the same time, columns, 1, 2, ... of the matrix receive information pulses that are written into the successive pixels in lines, 1, 2, The resulting signal received by pixel (i,j) at each instant of time is

TABLE III.	Characteristics	of a	high	information	density C	LC color
display.						

Panel size, mm ²	260 × 200		
Size of active region, mm ²	243×182		
Number of pixels in matrix,	639 imes 400		
Pixel size, mm	0.38 imes 0.46		
Method of producing	Mosaic consisting of color		
color image	filters (RGB) with controlled		
	transmission for color production		
	in each pixel		
Multiplexing ratio			
(number of rows written			
per frame)	400:1		
Control voltage, V	30		
Frame rate, Hz	33.3		
Width of control pulses, μs	33.3		
Max. contrast ratio	7:1		
Contrast ratio at 40° to			
normal (viewing angle)	4:1		

determined by subtracting the corresponding voltages supplied to line *i* and column *j*. It is readily seen that, in each frame, the constant component (acting voltage) is zero at each pixel (this is the 5τ scheme of Ref. 158) or at each nonselected pixel (3τ scheme of Ref. 135) if the driving pulses are as illustrated in Fig. 26b. The absence of the 'cross-talk effect' is assured by suitably choosing the dynamic characteristic of the C^{*}LC. A pixel remains in its initial state under a voltage of $\pm V/3(5\tau \text{ scheme})$ or $\pm V/$ $2(3\tau$ scheme) and is switched to state 1 when the voltage is +V and to state 0 when the voltage is -V. The optical memory of the C^{*}LC ensures that the information (optical transmission of the pixels) is retained whilst the entire frame is being written. A detailed discussion of the different types of matrix addressing of C^{*}LC displays capable of handling high density information is given in Ref. 135. Here we merely note that the 3τ addressing scheme is 50% faster than the 5τ scheme, and this produces a corresponding reduction in the required optical memory time (bistability) of the $C^{*}LC$.

The first fast linear arrays consisting of C^{*}LC lightvalve for reprographic systems and printers were developed at the beginning of 1983.¹⁵⁰ The driving systems and the fabrication technology for such linear arrays were subsequently improved by using matrix addressing of groups of elements into which the initial much denser file was divided, and also by increasing the speed of operation and the number of gradations on the greyness scale.^{153,154} Figure 27 shows a simple driving scheme for a linear C^{*}LC array. Zero voltage is applied to the base electrode (or group of electrodes in the case of a matrix). Each light valve is switched to state 1 or 0 by the second of two control pulses, the first being used to cancel the constant component of the voltage applied to the C^{*}LC. If the C^{*}LC has sufficient optical memory, then during the formation of the current linear data file (optical transmission of the valves) one need only address those valves whose optical transmission must be altered. This results in increased speed of operation. Gradations in pixel greyness are produced by the corresponding reduction in the width



FIG. 27. Driving scheme for a light-valve C^{*}LC linear array. τ is the valve switching time.¹⁵⁵

of pulses used to drive the valves at constant pulse amplitude. A special microcomputer is used to drive the $C^{\bullet}LC$ with the linear array in accordance with input data, e.g., the transmission of the copier objective. The parameters of a recent fast $C^{\bullet}LC$ light-valve linear array are listed in Table IV.

Light-valve C^{*}LC linear arrays can be successfully used in electrophotographic printing systems, inexpensive high-speed noncontact high-resolution liquid-crystal printers for personal computers, optical switching elements in target recognition systems, and so on.^{150–155}

Ferroelectric liquid crystals are very promising as optical data processing materials, e.g., for fast switches for optical logic schemes, 74,139,140,159 image converters, optically driven matrix light modulators based on photoconductor-C^{*}LC structures, $^{74,140-148,159,160}$ color filters with controlled transmission, 119,159 and so on.

Speed of operation, switching energy, and size of switching element are the important parameters of C^*LCs for optical data processing systems. Table V compares C^*LCs with solid electrooptic materials used in optoelectronic systems.

It is clear from Table V that low driving voltages and negligible energy dissipation during switching, combined

TABLE IV. Fast linear array of C⁺LC light valves¹⁵³.

Resolution	400 points/inch
	(To points/min)
Effective length of array	260 mm
Number of points	
(light valves in array)	4096
Valve switching time ^{*)}	100 μs
Control voltage	20 B
Multiplexing ratio ^{**)}	8:1
Contrast ratio	4:1
Printing rate ^{***)}	10 lines/min. B4

[•])Max. width of switching pulse (Fig. 27).

***)Faster than 2 ms/arr.

^{**)}Number of valves per matrix addressed group.

TABLE V. Electro-optic effects in C^{*}LCs and several conventional materials.¹⁴⁴

Material		C [*] LC	
Effect	Clark–Lagerwall	Pockels	Кетт
Wavelength, λ , μ s	1	1	1
Thickness, d, µs	2.5	10	10
Pixel size, $a, \mu m$	10	10	10
Refractive index, n	1.5	2.2	2.5
Index anisotropy, Δn	0.2		
e-o coefficient		$30 \cdot 10^{-12} \text{ m/V}$	$3.8 \cdot 10^{-16} \text{ m/V}^2$
Ferroelectric polarization P	350 nC/cm^2		
Permittivity ε		30	5700
Working voltage	30	1600	40
Switching energy, F, J	$2PUa^2$, $21 \cdot 10^{-12}$	$\frac{\varepsilon a \lambda^2}{13 \cdot 10^{-9}}$	$\frac{\varepsilon a^2 \lambda}{2}$, 425 · 10 ⁻¹²
Intrinsic material switching time	2.1 µs	$2n^{6}r^{2}$, 10 ns	$2n^{3}r$, $1 \mu s$
Actual switching time			
(incl. energy dissipation), μ s	2.1	1.3	42

with high speed, place the C^*LCs among the most promising materials or optoelectronics.

One of the most common applications of C^*LCs in optoelectronics is in polarization logic (optical logic gate) that performs various functions in matrix controlled C^*LC arrays (Fig. 28). Light passes through matrix arrays A and B in which each element is a C^*LC cell that can be in one of two states: in the absence of the field (state 0) the polarization of the transmitted light is unaltered, but when the field is present (state 1), the C^*LC cell rotates the plane of polarization by 90° ($\lambda/2$ plate). If a C^*LC element in matrix A rotates vertically polarized light through 90°, whereas an element of matrix B rotates horizontally polarized light by the same amount, then we can readily implement, for example, the logic function $X\tilde{Y} + \tilde{X}Y$ (Fig. 28).



FIG. 28. Polarization logic device (optical logic gate) based on $C^{\bullet}LC$. A and B are matrix arrays in which every pixel is a $C^{\bullet}LC$ cell.

The logic gate operates in the frequency range up to 2 kHz with a contrast of 200:1 or more. Experimental logic gates incorporate 32×32 matrix arrays.¹⁴⁰ Unwanted polarization can be suppressed with efficiency determined in accordance with (44) by the precision with which the angle θ and the phase delay $\Delta \varphi$ can be matched to their optimum values of 22.5° and π , respectively. It amounts to at least 93% in existing devices.

Optically addressable photosensitive liquid-crystal modulators (PLCMs) are widely used as image converters and amplifiers in optoelectronic systems of optical computers and in robotics. The advent of photosensitive structures based on C^{*}LCs has led to an increase in speed of operation by one or two orders of magnitude as compared with traditional nematic (LQs).¹⁴⁰⁻¹⁴⁸

Figure 29 illustrates the overall configuration of a photosensor layer + C^*LC structure. The write beam modulates the photoresistance of the sensor so that the C^*LC layer experiences a spatially inhomogeneous electric field corresponding to the light distribution. This field induces the corresponding changes in the orientation of the C^*LC director, which are recorded optically by the read beam.

Photosensitive liquid-crystal modulators can exploit any of the electrooptic effects in liquid crystals that were



FIG. 29. Photoconductor + C^*LC device: *1*—glass plates, 2—currentconducting plates, 3—photosensitive layer, 4—reflecting mirror, 5— C^*LC layer.

TABLE VI. Characteristics of	photosensitive light modulators.
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Device	Resolving power (at 10% level of maximum), lin/mm	Speed, ms	Sensitivity, mW/cm ²
CdS-nematic	40	15	0,4
Pockels read out modulator	12	< 0,1	50
α-Si-nematic	82	20	0,06
α-SiC*LC	70	0,4	0,25

described above, with planar^{140–148} and homeotropic¹⁶⁰ orientation of the C^{*}LC director on the substrates. Hydrogenized amorphous silicon, α -Si, has recently been used as a photosensor.^{142–145} The photosensor response time is less than 5 μ s, so that the speed of the modulator as a whole is determined by the C^{*}LC. The modulator reported in Ref. 142 has a response time of 400 μ s which is greater by at least an order of magnitude as compared with modulators incorporating nematic liquid crystals. Table VI compares photosensitive modulators and confirms that C^{*}LCs have a very promising future in such structures.¹⁴³

CONCLUSION

We have reviewed the symmetry, structure, and crystal optics of smectic liquid crystals with tilted orientation of layer molecules and spontaneous polarization (ferroelectric liquid crystals, C*LCs). We have examined the basic parameters that determine the behavior of the C*LCs in electric fields and have presented examples of the relation between these parameters and molecular characteristics such as polarization, tilt, viscosity, elasticity, dielectric and optical constants, and so on. Optical properties of the C*LCs were considered separately.

We have also described the main electrooptical effects in thin (1100 μ m) C^{*}LC layers (deformed helix effect, light scattering near the helix unwinding field, switching of uniformly oriented states, the electroclinic effect, and so on).

Examples were presented of practical applications of C^*LCs in light-valve devices, optically controlled transparencies, high information density screens with matrix addressing, and so on. Finally, we considered problems that will have to be solved to ensure extensive applications of C^*LCs in electrooptic liquid-crystal devices.

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