

Ferroelectric liquid crystals

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A review is given of practically all the theoretical and experimental results on ferroelectric liquid crystals based on chiral smectics with molecular tilt. The symmetry aspects of the problem are examined, and the fundamentals of the phenomenological theory are discussed. The microscopic approach to the description of the dipolar ordering in tilted smectics is set forth, and several molecular models are considered. The critical behavior of a liquid crystal at the second-order transition between the smectic A and smectic C phases is also discussed. Considerable space is devoted to considering the relationship between the actual structure of the molecules and the size of the spontaneous polarization and to discussing the behavior of ferroelectric liquid crystals in various external fields. Data are presented on the physical parameters of the known liquid-crystal ferroelectrics. The article concludes with a discussion of the possibilities for practical application of ferroelectric liquid crystals.

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1. INTRODUCTION. THE LIQUID-CRYSTAL AND FERROELECTRIC STATES

Over the sixty-year history of the physics of ferroelectricity and the almost one-hundred-year history of the physics of liquid crystals these two scientific disciplines have accumulated an enormous conceptual baggage which has been the subject of a voluminous literature. We shall mention here only the recent monographs of Refs. 1–9. Until 1975 these two fields of knowledge developed practically independently, although there had been repeated attempts to arrive at a theoretical understanding of whether liquid or liquid crystal ferroelectrics could exist.

From the time of the classical studies by Born in the

early part of the century it has been known that nematic liquid crystals and also certain smectic phases (A, B, and C), like ordinary isotropic liquids, lack a spontaneous polarization because they have a center of inversion. If, however, the liquid crystal is in contact with a solid surface, it becomes possible for polarization to be induced in a thin surface layer whose thickness is determined by the elastic properties of the mesophase. The change with temperature of this induced polarization gives rise, for example, to a pyroelectric current in an external circuit if the liquid crystal and the bounding surfaces form a capacitor.

Another situation which can look like a manifestation of ferroelectricity arises when the free charges in such a layered structure form a double layer near conducting sur-

faces in contact with the liquid crystal or isotropic liquid. Here a change in temperature causes a change in the density of surface charge and produces a current in an external circuit which is experimentally similar to a pyroelectric current.

Still another spurious manifestation of ferroelectricity in sandwich structures is due to the nonlinearity of the voltage-current characteristics of the conducting-surface contacts with the liquid crystal or liquid. In this case an experiment to detect the polarization-reversal currents in an alternating electric field could find hysteresis loops, for example.

In these cases, of course, one cannot speak of ferroelectricity in the sense that the term is understood for solid ferroelectrics. Ferroelectrics are usually understood to be solid crystals which in a certain temperature interval have a spontaneous polarization (or dipole moment per unit volume) which is reversible or reorientable by an external electric field or external stress.⁴

The term liquid crystal usually refers to all the intermediate phases (mesophases) between isotropic liquids and solid crystals with three-dimensional translational ordering. The absence of long-range order in one or two measurements, as we shall see, does not preclude the possibility that a spontaneous polarization will arise in a certain temperature interval.

In 1975, R. B. Meyer (USA) showed that dipolar ordering should arise in smectic C or H phases of liquid crystals which consist of optically active (chiral) molecules (such phases are sometimes denoted by an asterisk, S_C^* or S_H^*). This approach stimulated the chemical research at the University of Orsay (France) which culminated in the discovery of a liquid-crystal ferroelectric.^{10,11}

It should be particularly emphasized that according to the symmetry conditions proposed by Meyer, spontaneous polarization can arise not only in the thermotropic liquid-crystal phases S_C^* and S_H^* but also in any other system having a layered structure, tilt, and chirality of the constituent molecules. Systems of this kind could include, for example, solid layered structures, lyotropic liquid crystals, and also many biological objects (biomembranes of animal cells, protein molecules, etc.).

The theoretical and experimental study of the spontaneous polarization in thermotropic liquid crystals is therefore important not only for the physics of liquid crystals or ferroelectricity but apparently also for comprehending the microscopic nature of certain mechanisms in life processes.

The present review is intended to elucidate from a unified point of view all the available information on the structure and properties of liquid-crystal ferroelectrics. Since Meyer's discovery there have been almost two hundred papers published on this subject. The theoretical aspects of the problem have been elucidated by S. A. Pikin and co-workers in a monograph,⁸ a review article,¹² and a number of papers.^{13,30-32,57} Some experimental results have been presented in the reviews by Meyer¹¹ and by G. Durand and Ph. Martinot-Lagarde.¹⁴

For our subsequent discussion of ferroelectric mesophases it will be expedient to start off from the physics of

liquid crystals (rather than ferroelectrics), since all known liquid-crystal ferroelectrics have a spontaneous polarization arising not as a result of the dipole-dipole (static) interaction but as a side effect of intermolecular interactions of other kinds (the dispersive and steric interactions, in particular). The spontaneous polarization is not the order parameter of the ferroelectric transition as is characteristic of improper ferroelectrics, but it is proportional to the true order parameter. For this reason S. A. Pikin and V. L. Indenbom have classified the known liquid-crystal ferroelectrics as pseudo-proper. It is not ruled out, however, that ferroelectric mesophases of other types will also be discovered.

2. DIPOLAR ORDERING IN LIQUID CRYSTALS

a) The structure of liquid crystals and the symmetry of the ferroelectric phase

To remind the reader of the terminology, let us briefly list the main types of liquid-crystal structures.^{8,9,12}

Let us suppose that we have an isotropic melt of an organic material whose molecules are rod-shaped and have mirror symmetry (the point symmetry group of the isotropic phase is K_h). Then upon cooling the material can pass through a sequence of phases as shown in Fig. 1: Nematic, with point symmetry group $D_{\infty h}$, smectic A (of the same point symmetry but with a density which is periodic along z), smectic C (symmetry C_{2h}), and more-highly ordered phases (smectic B, C, H, etc.). Smectic C is characterized by a tilt angle θ of the vector specifying the predominant molecular orientation (the director) with respect to the normal to the smectic layers.

Let us now start from an isotropic melt of molecules which lack mirror symmetry; such molecules are called chiral (from the Greek "cheiros," meaning "hand"), and the melt has symmetry K . The sequence of phases usually observed (others are possible) upon cooling of the material is shown in Fig. 2. In this figure an asterisk denotes a chiral phase and a tilde (e.g., \tilde{C}_2) denotes a structure having a spatially periodic modulation which is incommensurate with the period of the lattice in the case of the smectic phases. The isotropic phase now goes over to a cholesteric phase with the

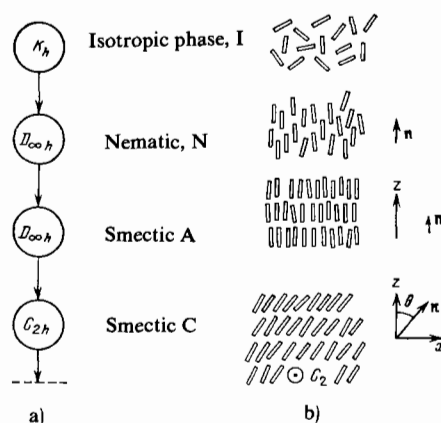


FIG. 1. Schematic of the phase transitions usually observed in materials with mirror-symmetric molecules. a) Symmetry point groups, b) packing of molecules; n is the director.

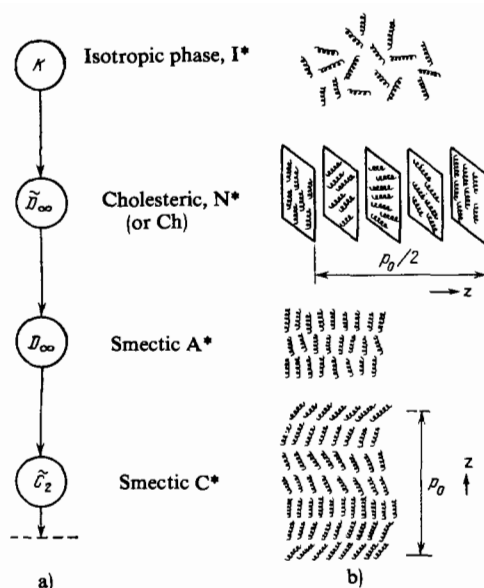


FIG. 2. Schematic of phase transitions for materials with mirror-asymmetric (chiral) molecules. a) Symmetry groups, b) packing of molecules; p_0 pitch of the modulated structure.

same local symmetry as the nematic phase, but without a center of inversion. Over large spatial intervals, however, the cholesteric phase is a helix with pitch p_0 hundreds and thousands of times greater than the dimensions of the molecules. The director has components $n_x = \cos\varphi$, $n_y = \sin\varphi$, $n_z = 0$, where the z direction coincides with the axis of the helix.

As the temperature is lowered the cholesteric undergoes a transition to the mirror-asymmetric unmodulated smectic A^* and then to smectic C^* whose macroscopic structure is again modulated at scale dimensions $p_0 \sim 1 \mu\text{m}$ and larger. One of these angles, as in the unmodulated smectic C , is the constant (along z) tilt angle θ describing the inclination of the director to the z axis. The other is the azimuthal angle φ , which has period p_0 :

$$\begin{aligned} n_x &= \sin\theta \cos\varphi; \\ n_y &= \sin\theta \sin\varphi; \\ n_z &= \cos\theta. \end{aligned} \quad (1)$$

The structure of a helical smectic C^* liquid crystal is shown in Fig. 3. Let us examine one of the smectic layers. In

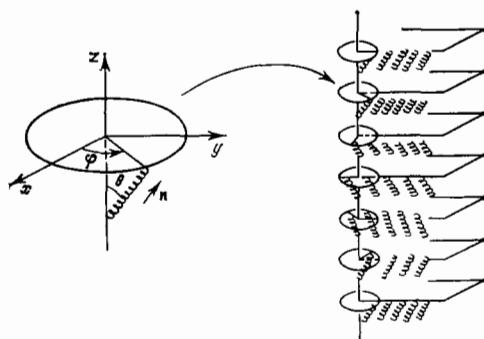


FIG. 3. Structure of the helical smectic C^* and the definition of the angles θ and φ .

the mirror-symmetric smectic C phase (Fig. 1) there is a mirror plane (the plane of the figure, zx) and a two-fold rotation axis C_2 , which is perpendicular to the zx plane and lies in the plane of the smectic layer. In a chiral smectic phase the mirror plane is lost, but the C_2 axis is preserved locally in each smectic layer (it is perpendicular to the plane zn containing the molecular axes). Consequently, the C_2 axis in the case of the chiral smectic C^* phase is a polar axis which admits the existence of a spontaneous polarization along it. As one goes along the helical axis z , this polar axis swings around in accordance with the change in the azimuthal angle φ of the director.

b) Dipolar ordering

What we have said above has no direct bearing on whether or not the molecules forming the liquid crystal have permanent dipoles. Real molecules have rather large static dipole moments, reaching 5 D and higher [1 debye (D) = 10^{-18} cgs esu]. It is possible in principle for a ferroelectric state to form in a liquid crystal on account of the direct interaction of the permanent dipoles with one another. The phenomenological theory of such a phase transition for an ensemble of molecules with dipole moments parallel to the long axes has been considered by Khachatryan.¹⁶ By minimizing the free energy (which is the sum of the elastic energy and the energy of the dipole-dipole interaction) of the nematic, Khachatryan showed that the resulting phase cannot be homogeneous, but is twisted. The spontaneous polarization P has components only in the plane perpendicular to the twist axis, so that the ferroelectric is similar, on the whole, to a cholesteric liquid crystal with a pitch proportional to $P^{-2/3}$.

This type of ferrophase has not been observed in experiment. Also unconfirmed are the many experimental results on the detection of ferroelectric properties in nematic liquid crystals through the piezoelectric and pyroelectric effects, polarization-reversal currents, and optical second-harmonic generation. The last method is apparently the most sensitive, but it is based on the widespread belief that the second-harmonic generation of light is possible only in the absence of a center of inversion. It has been shown,^{17,18} however, that second-harmonic generation can also occur in centrosymmetric liquid crystals on account of a quadrupolar (and not dipolar) interaction of the light with the molecular ensemble.

In all ferroelectric liquid crystals studied to date the dipolar ordering results from an ordering of the short molecular axes which is not due to the presence of dipole moments. Let us explain what we have said. Suppose we have a chiral smectic C^* phase formed by nondipolar molecules. Then, on account of the steric and other interactions between the chiral molecules,¹³ the average $\langle \cos\psi \rangle$ over the smectic layer acquires a nonzero value (ψ is the orientation angle of the short molecular axes with respect to, for example, the perpendicular to the tilt plane of the molecules). This means that the rotation of the chiral molecules about their long axes is no longer completely free; one of the short axes of the molecule spends a somewhat longer time at the azimuth corresponding to the polar axis of the smectic layer (Fig. 4). The

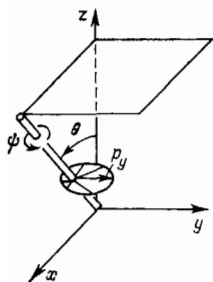


FIG. 4. Directionality diagram for the short axis of a molecule rotating about its long axis in a smectic C* layer.

values of the order parameters $\langle \cos \psi \rangle$ for the short molecular axes, as measured directly by nuclear magnetic resonance in the smectic C phase of the now classical liquid crystal ferroelectric *L*-*n*-decyloxybenzylidene-*p*'-amino-2-methylbutylcinnamate (DOBAMBC), were of the order of $5 \cdot 10^{-2}$ (Ref. 19).

If the molecule has a dipole moment d_l directed along the same short axis which undergoes the ordering, the smectic layer will acquire an uncompensated dipole moment $d_l \langle \cos \psi \rangle$ or, in other words, a macroscopic spontaneous polarization P_y (see Fig. 4). From one layer to the next the polarization vector will swing around together with the polar axis. If the helical structure of the ferroelectric is not disrupted, the average polarization over the volume turns out to be zero.

True, the role of the molecular dipoles in the formation of the spontaneous polarization of the smectic layer in the chiral phase C* is not fully understood, and, in addition to the improper (or pseudoproper) mechanism described above there can also be important contributions from the dipole-dipole forces and from interactions of the permanent-dipole-induced-dipole type (see Sec. 5).

c) Simplest phenomenological theory of the transition to the ferroelectric phase

The phenomenological theory of liquid crystal ferroelectrics is an extension of the Landau theory of phase transitions²⁰ in the form proposed by V. L. Ginzburg for solid ferroelectrics.²¹ This theory is presented in its most complete form in the monograph by Pikin.⁸ First, however, we shall discuss a simplified version which preserves the main features.

Let us first consider the uniaxial case, i.e., a phase transition from an isotropic liquid to a nematic or smectic A phase. In the absence of an external field the free-energy density of an ensemble of rod-shaped molecules with permanent dipole moments directed along the long molecular axes can be expanded into the series.

$$F = F_0 + \frac{1}{2} a(T) S^2 + \frac{1}{4} b S^4 + \frac{1}{2} c P^2 - d S P^2 + \dots; \quad (2)$$

where F_0 is the free-energy density of the isotropic phase, $S = (1/2)(3\cos^2\psi - 1)$ is the nematic order parameter (ψ is the angle between the molecular axis and the director), $a = a'(T - T_0)$, where T_0 is the temperature of the transition in question, P is the polarization, and a' , b , c , and d can be considered independent of temperature.

Minimizing F , we obtain

$$\begin{aligned} \frac{\partial F}{\partial S} &= aS + bS^3 - dP^2 = 0, \\ \frac{\partial F}{\partial P} &= cP - 2dSP = 0. \end{aligned} \quad (3)$$

One of the solutions, which is stable for $T > T_0$, is the isotropic phase ($P = 0$, $S = 0$), and another, stable for $T < T_0$, describes a nonferroelectric nematic phase ($P = 0$, $S = \sqrt{-a(T)/b}$). The third solution, corresponding to $P \neq 0$, $S = c/2d$, does not give a free energy minimum, and so a ferroelectric nematic with a homogeneous orientation cannot occur, in agreement with the results obtained in Ref. 16.

We can now consider the biaxial case, which is realized at the transition from the smectic A* phase with point symmetry D_∞ to the smectic C* phase with symmetry C_2 . Let us set aside for now the helical structure of the chiral C* phase and for simplicity assume this phase to be spatially homogeneous. This assumption is admissible because helical twist is in principle not a necessary condition for the appearance of a spontaneous polarization (we shall give examples later). Near the temperature T_c of the transition from the smectic A* phase to the smectic C* phase, the free-energy density can be expanded in a series in powers of the angle $\theta = \mathbf{e} \times \mathbf{n}$ describing the molecular tilt with respect to the normal \mathbf{e} to the smectic planes and the polarization component $P_l = \mathbf{P}$ lying in the smectic layer:

$$F = F_A + a(T) |\theta|^2 + b |\theta|^4 + \frac{1}{2\chi} |P|^2 - \mu_p \theta P + \dots; \quad (4)$$

here F_A describes the elastic energy of the initial, smectic A* phase, and the coefficient $a(T) = a'(T - T_0)$ is the elastic modulus for deviations of the molecules from the normal to the smectic layers; this coefficient describes the "pure" transition A* → C* (without allowance for the polarization) that would occur at temperature T_0 if, for example, the molecules did not have a dipole moment. The inverse susceptibility $1/\chi = 1/\chi(T - T'_0)$ describes a "pure" ferroelectric transition (at temperature T'_0) that is not allied to the formation of the C phase. The piezoelectric coefficient μ_p and the parameter b can be treated as constants.

The equilibrium values of the tilt angle θ_0 and polarization P are obtained from the minimization conditions $\partial F / \partial \theta = 0$ and $\partial F / \partial P = 0$ as

$$\theta_0 = \sqrt{-\frac{2a - \mu_p^2 \chi}{4b}}, \quad (5)$$

$$P = \mu_p \chi \theta_0. \quad (6)$$

The spontaneous polarization displays a characteristic proportionality to the tilt angle of the molecules in the C* phase, i.e., the smectic C order parameter (we have a pseudoproper ferroelectric).

d) Generalization to helical phase

Formula (4) for the expansion of the free energy does not describe a number of experimental facts. First of all, one should incorporate the helicity of the smectic C* phase, and then, in addition to the piezoelectric term $-\mu_p \theta \cdot \mathbf{P}$ which couples the molecular tilt angle with the spontaneous polarization of the homogeneous phase, one should include the

flexoelectric contribution to the spontaneous polarization, which is due to the spatial (z) dependence of the azimuthal angle φ .

The most complete form of the phenomenological theory of Pikin and Idenbom^{8,23} incorporates the helicity of the ferroelectric phase by introducing on the right-hand side of the expression for F a Lifshitz invariant²⁰ of the form

$$\lambda \sin^2 \theta \partial \varphi / \partial z. \quad (7)$$

Then, assuming that the degree of ordering S of the long axes of the molecules is constant and the tilt angle θ is small, and considering only those distortions of the structure which leave the polarization vector in the plane of the smectic layer, we obtain the following expression for the free energy density:

$$F = F_A + a\theta^2 + b\theta^4 + \frac{1}{2\chi_\perp} P^2 - \mu_p P \theta + \lambda \theta^2 \frac{\partial \varphi}{\partial z} + \mu_f P \theta \frac{\partial \varphi}{\partial z} - PE + \dots, \quad (8)$$

where the sum of the first five terms is analogous to expression (4) (the vector notation is dropped), while the flexoelectric contribution due to the change in the angle φ with the coordinate z , $\varphi(z) = q_0 z$, is given by the term with coefficient μ_f . The last term takes into account the influence of the external field.

By minimizing the free energy (8) we can obtain a formula for the wave vector of the helix as a function of θ :

$$q_0 = q_c + q'\theta^2 + q''\theta^4 + \dots, \quad q_c = -\frac{\lambda + \chi_\perp \mu_p \mu_f}{K}. \quad (9)$$

In the expression for q_c (the wave vector at the transition point), χ_\perp corresponds to the susceptibility in the direction perpendicular to the director, and $K = K_{33} - \chi_\perp \mu_f^2$ is the "nematic" elastic modulus for longitudinal bending, renormalized by the flexoelectric effect [in Eq. (8) this modulus is included in the quantity F_A]. The temperature of the transition from the C* to the A* phase is given by the expression

$$T_c = T_0 + \Delta T = T_0 + \frac{1}{2a} (\chi_\perp \mu_p^2 + K q_c^2), \quad (10)$$

where T_0 is the temperature of the transition from the smectic A to the nonferroelectric C phase.

Below the transition point the tilt angle θ_0 depends on the temperature through the renormalized parameter $a^* = a - (\mu_p^2 \chi_\perp / 2) - (K q_0^2 / 2)$, and near the transition we have

$$\theta_0 = -\sqrt{-\frac{a^*}{2b}}, \quad (11)$$

while the spontaneous polarization is

$$|P| = \chi_\perp |\mu_p - \mu_f q_0| \theta. \quad (12)$$

Qualitatively similar temperature dependences $\theta_0(T)$ and $P(T)$ are also found in the phenomenological theory developed for the helical C* phase by Michelson *et al.*²⁴ without allowance for the flexoelectric contribution. Nonclassical values are obtained for the critical exponent in (11), viz. $\beta = 0.37$ instead of 0.5, if fluctuations of the order parameter are taken into account.²⁵ The influence of solid boundaries on the A*→C* transition temperature was considered in Ref. 26; it was found (in agreement with experiment) that the

value of T_c decreases by several degrees as the layer thickness is decreased.

On the whole, formulas (10)–(12) are confirmed by experiment. As to the temperature dependence of the pitch, the experimental data require the assumption of a negative value of the coefficient q'' in (9). The microscopic approach developed in Ref. 13 is able to satisfy this condition.

e) Dynamics of the polarization

The dynamics of the fluctuations of the tilt angle θ and spontaneous polarization P on both sides of the smectic A*↔smectic C* phase transition point was first considered by Blinc²⁷ for a one-dimensional model corresponding to expansion (4), i.e., without allowance for the helical structure of the C* phase (with a wave vector $q_0 = 0$). The initial Landau-Khalatnikov equations (see Ref. 28) with the characteristic coefficients Γ_1 and Γ_2 for the tilt angle and polarization, respectively ($\Gamma_1 \ll \Gamma_2$)

$$\frac{\partial \theta}{\partial t} = -\Gamma_1 \frac{\partial F}{\partial \theta}, \quad \frac{\partial P}{\partial t} = -\Gamma_2 \frac{\partial F}{\partial P} \quad (13)$$

are written for the fluctuating variables $\theta = \theta_0 + \delta \theta$ and $P = P_0 + \delta P$ and analyzed separately for the smectic A* ($T > T_c$, $P_0 = \theta_0 = 0$) and smectic C* ($T < T_c$, $P_0, \theta_0 \neq 0$) phases.²²

For the smectic A* phase equations (13) correspond to the degenerate (with respect to right-hand and left-hand rotations) rotation of the molecules about their long axes in combination with the precession of these axes about the normal to the layers. As a result, there are two relaxation times for the coupled quantities θ and P . One of these times,

$$\tau_- = \frac{\Gamma_1 \mu_p^2 \chi_\perp^2 + \Gamma_2}{2\Gamma_1 \Gamma_2 a' (T - T_c)}, \quad T > T_c, \quad (14)$$

corresponds to fluctuations of P and θ in phase with each other. It is this soft mode that is responsible for the onset of ferroelectric order at the transition point $T \rightarrow T_c$. Taking into account that $\Gamma_2 \gg \Gamma_1 = 1/\gamma_1$, where γ_1 is the coefficient of viscosity, we obtain $\tau_- = \gamma_1 [2a'(T - T_c)]^{-1}$. The other solution

$$\tau_+ = \frac{\chi_\perp}{\Gamma_2 + \Gamma_1 \mu_p^2 \chi_\perp^2}, \quad T > T_c, \quad (15)$$

corresponds to the rapid ($\tau_+ \approx \chi_\perp / \Gamma_2$) damping of the out-of-phase fluctuations of the polarization and tilt angle. At the transition point this (stiff) mode, unlike (14), does not exhibit critical behavior.

In the smectic C* phase ($T < T_c$) a new fluctuational mode appears, recovering the broken symmetry (the Goldstone mode). This mode corresponds to motion of the molecules about the normal to the smectic layers along the surface of a cone at a constant angle θ_0 . Such a motion requires no expenditure of energy; the orientation fluctuations $\delta \theta_x$ and δP_x are in phase with each other ($P = P_y$, $\delta \theta_y = \delta P_y = 0$), and the corresponding relaxation rate is

$$\frac{1}{\tau_1} = 0. \quad (16)$$

Besides the Goldstone mode there is a branch corresponding to out-of-phase orientational fluctuations $\delta \theta_x$ and δP_x with a relaxation time $\tau_2 = \tau_+$ [see (25)] and two

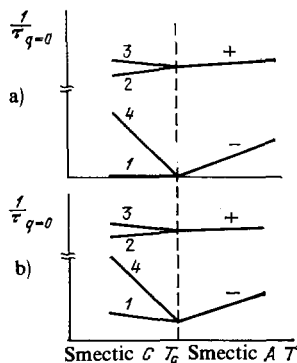


FIG. 5. Temperature dependence of the relaxation time of the fluctuational modes with zero wave vector for the smectic A \leftrightarrow smectic C phase transition in the homogeneous approximation (a) and for a helical ferroelectric (b).

branches describing amplitude changes in the parameters $\theta = \theta_y$ and $P = P_y$ ($\delta\theta_x = \delta P_x = 0$, $\delta\theta_y, \delta P_y \neq 0$); these changes are in phase (τ_4) and out of phase (τ_3) with each other, respectively.

The in-phase amplitude fluctuations of the tilt angle and polarization (τ_4) represent the soft mode for the low-temperature phase.

Figure 5a shows a diagram of all the fluctuation branches corresponding to the simplest expansion (4). The theory has been generalized²⁹ to the case of a helical ferroelectric with allowance for the flexoelectric contributions on the basis of expansion (8). In this case the picture shown in Fig. 5a remains completely valid for fluctuations of P and θ with wave vectors corresponding to the equilibrium pitch of the helix, $q = q_0$. For the Goldstone mode this means that it is only for those fluctuations in the orientation of θ and P which have a period equal to the pitch of the helix that there is no energy requirement. For homogeneous distortions with $q = 0$ the corresponding relaxation times in the C* phase turn out to be finite (see Fig. 5b):

$$\tau_1 = \frac{\gamma_1}{Kq_0^2}. \quad (17)$$

The time τ_1 characterizes the slow damping of perturbations of the azimuthal angle φ at a constant tilt angle $\theta = \theta_0$, i.e., it describes the recovery of the disrupted helical structure.

The soft modes at the transition point also have finite relaxation times:

$$\tau_{-}|_{q=0} = \gamma_1 [2a'(T - T_c) + Kq_0^2]^{-1}, \quad T > T_c, \quad (18)$$

$$\tau_{+}|_{q=0} = \gamma_1 [4a'(T_c - T) + Kq_0^2]^{-1}, \quad T < T_c. \quad (19)$$

The times τ_{-} and τ_{+} correspond to relaxation of the molecular tilt angle in the A* and C* phases, respectively.

3. MICROSCOPIC APPROACH

a) Interaction potential of the molecules in the ferroelectric phase

One of the problems in the microscopic theory is to evaluate the phenomenological coefficients of expansions (4) and (8) by proceeding from the molecular characteristics. Such a theory was developed recently by Osipov and Pi-

kin,^{13,30-32} The theory proceeds from the fact that ferroelectricity is observed only in materials which consist of chiral molecules. At the same time, the thermodynamic characteristics of the smectic C phase are practically independent of whether or not it is a chiral phase. In particular, the temperature of the transition from the C (or C*) phase to the A (or A*) phase is almost independent of the chirality. Consequently, the ferroelectric ordering of the short molecular axes can be treated as a small correction to the overall smectic C order in the position of the long molecular axes. This correction is due precisely to the chirality of the molecules.

It is thus assumed that smectic C order (i.e., a layered structure with the long axes of the molecules tilted with respect to the normals to the layer) is already present on account of intermolecular interactions which are not due to the chirality of the molecules. Such interactions might include static interactions of the permanent-dipole-induced-dipole type,³³ which do not require a mandatory hindering of the rotation of the molecules about their long axes (in accordance with experiment for the nonchiral C phase³⁴). Next, the molecules are given an "admixture" of chirality in the form of a certain distortion of the molecular structure, and one then treats the interaction of the chiral molecules without assuming that they are cylindrically symmetric. Without yet specifying the type of intermolecular interaction but proceeding solely from symmetry considerations, Osipov and Pikin³⁰⁻³² write the interaction energy of the chiral molecules i and j (Fig. 6) in the simplest form

$$W = -v (\mathbf{a}_i \cdot \mathbf{u}_{ij}) (\mathbf{a}_j \times \mathbf{u}_{ij} \cdot \mathbf{b}_i), \quad (20)$$

which corresponds to an ideal orientational order and satisfies the following requirements¹³: a) the interaction potential is even with respect to the directions of the long axes $\mathbf{a}_i, \mathbf{a}_j$, as it must be, since the two directions along the long molecular axes in the C phase are equivalent; b) the interaction potential is odd with respect to the directions of the short axes \mathbf{b}_i and \mathbf{b}_j and thus describes the required ferroelectric ordering; c) the potential changes sign upon spatial inversion and so corresponds to chiral molecules; d) the potential is even in the direction of the intermolecular vector \mathbf{u}_{ij} and therefore contributes to the ground-state energy (although only a small amount, in accordance with the experimental thermodynamic characteristics of the chiral C* phase).

Potential (20) is fundamentally different from the potential of the form $V^* = J \mathbf{a}_i \cdot \mathbf{a}_j (\mathbf{a}_i \times \mathbf{a}_j \cdot \mathbf{u}_{ij})$ that was used in Ref. 35. This latter potential describes the interaction of chiral, but cylindrically symmetric (on account of the rotation) molecules and can be used only to calculate the helical pitch of the smectic C* phase. The ordering of the short axes is not taken into account by this potential, and so all the

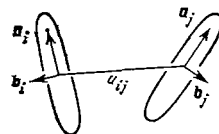


FIG. 6. Interaction of two molecules having preferred longitudinal ($\mathbf{a}_i, \mathbf{a}_j$) and transverse ($\mathbf{b}_i, \mathbf{b}_j$) axes.

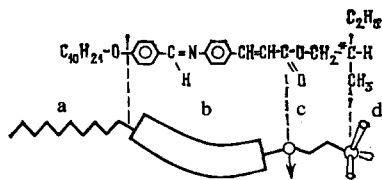


FIG. 7. Structural formula of the DOBAMBC molecule (top) and the corresponding model structure (bottom).

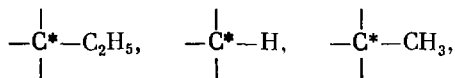
ferroelectric effects contained in potential (20) drop out of consideration.

b) Molecular models

Figure 7 shows the structural formula and layout of the molecule of the compound DOBAMBC, mentioned above, which has a ferroelectric smectic C* phase. It is for this compound that the bulk of the experimental information on ferroelectric liquid crystals has been obtained. The DOBAMBC molecule contains the following fragments of fundamental importance (from left to right): a long alkoxy tail "a" which together with a rigid lath-shaped part "b" is responsible for the formation of the nonchiral smectic C phase; the transverse dipole moment of the



group "c," relatively flexibly connected with the central fragment "b"; and an asymmetric carbon atom C which, with a right-handed or left-handed vector triplet of the bonds



(which have different lengths) forms a chiral center "d." This chiral center is responsible for the ordering of the short molecular axes in the chiral C* phase, and the attendant ordering of the dipoles "c" gives rise to spontaneous polarization. The flexibility of the bond between the chiral center "d" and the dipole "c," resulting from intramolecular rotations of both "c" and "d" about the single "b-c" and "c-d" bonds, causes the polarization to be smaller than it would otherwise be.

The microscopic theory of the C* phase takes the actual shape of the molecules into account only partially: It is assumed³⁰⁻³² that the molecules have a curved lath-shaped form with (or without) a transverse dipole moment and with a chiral fragment at the end of the molecule. The corresponding interaction models are illustrated in Fig. 8. The

possibility of intramolecular rotations is completely ignored here, and for this reason a number of experimental laws which depend on the relative position of the dipole "c" and chiral center "d" have dropped out of consideration.

The interaction model considered in Ref. 32 (Fig. 8a) approximates the chiral center of molecule *i* by an additional fragment (vector o_i) whose center of mass is located a distance m_i off the longitudinal axis of the molecule. The vector triplet a_i, m_i, o_i creates a chirality of the molecule as a whole. To simplify the treatment the second molecule *j* is assumed to be nonchiral, but with a curved banana-shaped form which models the bending of the rigid fragment of the DOBAMBC molecules (see Fig. 7). This bending is characterized by an angle ϵ . It is important to note that the presence of a permanent electric moment is not assumed for either molecule, but it is a purely steric interaction that is being considered.

A second model, which was considered in Ref. 30, is illustrated in Fig. 8b. The chiral molecule *i* is modeled by the same shape as in the previous case, but the second molecule *j* is assumed to be unbent but having a transverse static dipole moment $d = d_1 b_j$. This dipole can interact with the quasi-dipole moment of fragment o_i of molecule *i* (for molecule *i* on the whole, this is an octupole moment).

As was shown in Ref. 13, the steric interaction potential for the first model and the dipole-octupole interaction potential for the second model, satisfy the general expression (20). A third model, also leading to a potential of the form (20), considers the dispersion interaction between a chiral and a banana-shaped molecule.³¹ Such an interaction can be important only in the case when the chirality is due to a special shape of the polarizing skeleton of the molecule (Fig. 8c) and not simply to the presence of an asymmetric "tail." Then the dispersion interaction of the combined dipole-dipole and quadrupole-quadrupole type leads to the necessary form of the potential. The model illustrated in Fig. 8c can be important in considering compounds consisting of cholesterol derivatives introduced into a smectic C matrix.

Using all three interaction models shown in Fig. 8 in the molecular field approximation, Osipov¹³ calculated the free energy *F* of the chiral smectic C* phase. The general form of *F* corresponds to the phenomenological expansion in (8), and so the phenomenological coefficients μ_p, λ , and μ_r in (8) are expressed in terms of microscopic characteristics which reflect the bending (the angle ϵ), dipolarity (moment *d*), chirality (the angles between the long axes and the chiral fragments of the molecule), and dimensions of the molecules, and also the intermolecular distances. The results are rather general and describe both one-component smectic C* phases

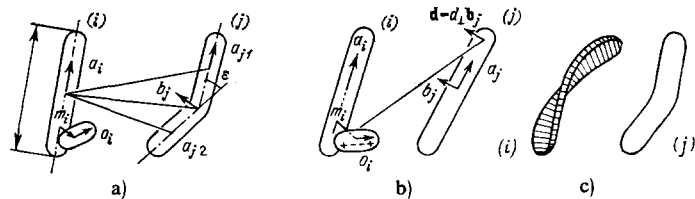


FIG. 8. Models of intermolecular interactions. a) Steric interaction of chiral (*i*) and banana-shaped (*j*) nondipolar molecules; b) dipole-octupole interaction of chiral (*i*) and dipolar (*j*) molecules; c) dispersion interaction of chiral (*i*) and banana-shaped (*j*) nondipolar molecules.

and also the behavior of impurities (chiral or dipolar) in smectic matrices (nonchiral or chiral).

However, the theory does not incorporate the changes in the confirmation of the molecules—in particular, the internal rotations of the individual molecular fragments. This rules out the possibility of establishing correlations between the size of the polarization and the location of the dipole in the molecule and complicates the calculation of the molecular constants (ϵ , d , etc.) from polarization measurements.

4. SMECTIC A-SMECTIC C PHASE TRANSITION AND THE CRITICAL BEHAVIOR OF THE PHYSICAL PARAMETERS

a) Thermodynamic parameters

In expanding the free energy of the smectic C phase in a series in the order parameters, we earlier proceeded from the idea that such an expansion is possible because we are dealing with a second-order phase transition. Experiment does in fact show³⁶ that the heats of transition for the transitions between the smectic A phase and the (nonchiral) smectic C phase, as determined by differential scanning calorimetry, are very small. Moreover, in differential scanning calorimetry one can easily mistake the integrated thermal effect due to the specific-heat anomaly for the heat of transition. Therefore, the A \leftrightarrow C transition is most likely of second order. The chiral interactions do not alter this picture, as is confirmed by the circumstance that the temperatures of the transition from the A phase to the C phase for the chiral state of DOBAMBC and its racemate (a compensated mixture of right-handed and left-handed isomers) differ by less than 1°C (Ref. 10). This corresponds to expression (10) if the parameter α' is of the order of 10^2 – 10^3 cgs esu.

Direct measurements of the specific heat c_p near the temperature of the ferroelectric transition $A^* \leftrightarrow C^*$ in DO-BAMBC have revealed³⁷ a small anomaly which can be interpreted in terms of a second-order transition. The critical exponents characterizing the divergence of the specific heat at temperatures above and below the transition point are difficult to determine in this case.³⁸ Similar behavior of the specific heat is characteristic of other materials as well.³⁹

b) Molecular tilt angle and the spontaneous polarization

The phase transition from the smectic A to the non-chiral C phase has been studied quite a lot in recent years. The order parameter in the C phase can be written in the form

$$\theta = \theta_0 e^{i\varphi}, \quad (21)$$

where θ_0 is the tilt of the molecules with respect to the normal to the smectic layer, and the angle φ characterizes the orientation of the projection of the director onto the plane of this layer. Such a form of the order parameter is formally analogous to the wave function of superfluid helium, which is the order parameter of the transition to the superfluid phase.⁵

The helium analogy predicts that the tilt angle θ_0 will have a power-law temperature dependence $\theta_0 \sim (T_c - T)^\beta$ with critical exponent $\beta \approx 0.35$, while mean field theory gives $\beta = 0.5$ [formula (11)]. The experimental data obtained for

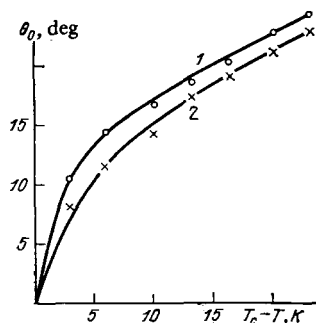
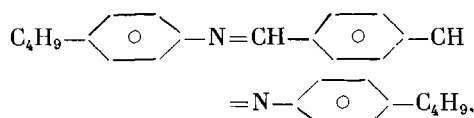


FIG. 9. Temperature dependence of the molecular tilt angle in TBBA as obtained by optical (1) and x-ray (2) methods.⁴²

nonchiral smectic phases by NMR,⁴⁰ optical,^{40,41} and x-ray⁴¹ methods shows a considerable spread in the value of the exponent β (0.4–0.5). Figure 9 shows the results of measurements of $\theta(T)$ by optical and x-ray methods⁴² for a single material, terephthal-bis-butylaniline (TBBA; $\beta = 0.5$):



In the same study the value $\beta = 0.5$ was obtained for three nonchiral smectics C. Materials whose molecules have longer alkyl tails than TBBA exhibit a systematic difference between the values of the angle θ_0 obtained from the optical and x-ray measurements ($\theta_0^{\text{opt}} > \theta_0^{\text{x-ray}}$). This indicates that the simple representation of the molecules as a rigid rod (Fig. 10a) must be re-examined. It would be much more acceptable to approximate the molecule by the zigzag structure shown in Fig. 10b. The corresponding phenomenological theory of the C phase was worked out in Ref. 43.

The ordering of the short molecular axes and transverse dipoles (if such there be) in the ferroelectric C phase does not affect the tilt angle θ_0 of the longitudinal molecular axes, at least in a first approximation. Therefore, one expects the same temperature dependence $\theta_0(T)$ for chiral ferroelectric phases as for nonchiral phases. Unfortunately, the experimental data on $\theta_0(T)$ are still very scanty. Data have been obtained only for DOBAMBC and several mixtures, and the critical exponents have, as a rule, been difficult to find because of the uncertainty in the location of the phase transition point itself.

The function $\theta(T)$ that was obtained for DOBAMBC in Ref. 38 can be approximated by the power-law function

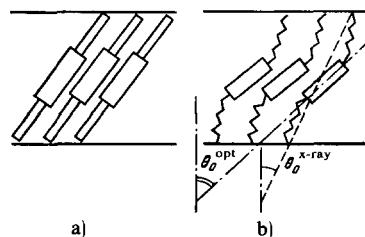


FIG. 10. Possible packing of molecules in the C phase.⁴² a) Rigid-rod model, b) zigzag model.

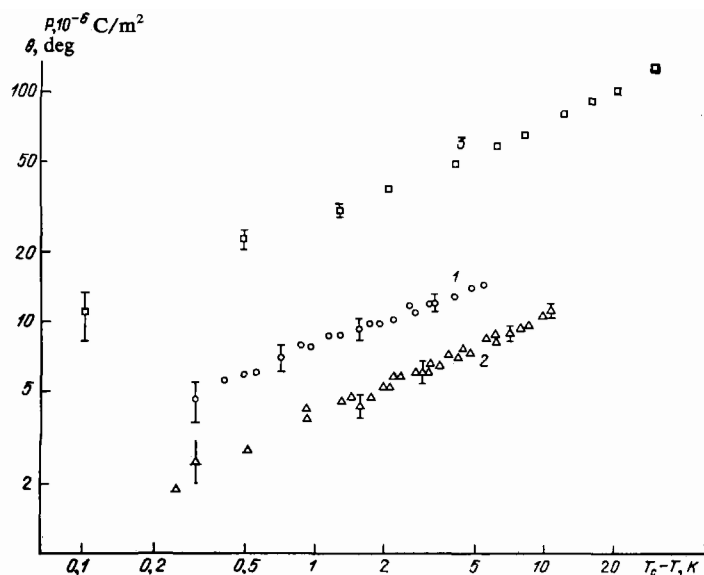


FIG. 11. Temperature dependences of the molecular tilt angle in MBOPDOB (1) and of the spontaneous polarizations in MBOPDOB (2) and in a binary mixture of a nonchiral smectic C with a chiral impurity (3).

$\theta_0 \sim (T_c - T)^\beta$, where $\beta = 0.31 \pm 0.05$. This figure is close to the value predicted by analogy with helium, although, as we mentioned earlier, a small shift in T_c has a strong effect on the value of β , and the chemical stability of DOBAMBC leaves something to be desired. The temperature dependence of the polarization can be written in an analogous form, but the exponent β comes out different: $\beta = 0.37 \pm 0.1$. Recall that the phenomenological theory of Landau, which is actually a mean field theory, predicts the same value $\beta = 0.5$ for the exponent in both $\theta_0(T)$ and $P(T)$ [see formulas (6), (11), and (12)]. Allowance for fluctuations lowers β to 0.37 (Ref. 25).

A difference between the exponents β for θ_0 and P , while at odds with the simple theory, is expected for the zigzag model shown in Fig. 10b. In fact, the polarization depends on the steric shape of the chiral center and on the size of the transverse dipole moment of the DOBAMBC molecule, which is shown in Fig. 7. The value and temperature dependence of the tilt angle of these fragments should differ from the tilt angle of the rigid central core of the molecule, which is what was measured optically in Ref. 38. Unfortunately, for DOBAMBC there are no data on the angle $\theta_0(T)$ from the x-ray experiment, so that one cannot even say which of the angles, θ_0^{opt} or $\theta_0^{\text{x-ray}}$, is larger in this case.

Besides DOBAMBC, the critical exponents have been determined for other compounds having $A^* \leftrightarrow C^*$ transitions.³⁹ For example, the chemically stable material *d*-4-(2-methylbutoxy)-phenyl 4'-decyloxybenzoate has $\beta = 0.35 \pm 0.06$ for the tilt angle and $\beta = 0.43 \pm 0.05$ for the spontaneous polarization (Fig. 11).⁴⁴ The value $\beta = 0.4 \pm 0.05$ has also been measured in esters of benzoic acid derivatives.⁴⁵

It is thus seen that for individual materials the exponent β usually lies in the range 0.3 – 0.5, while in mixtures formed by the introduction of chiral impurities into a nonchiral smectic C matrix, the values of β obtained by the authors are generally greater than 0.4 [a typical $P(T)$ curve for a mixture of this type is shown in Fig. 11] and in several cases even exceed 0.5.

Let us mention the methods of measuring the spontaneous polarization. The value of P given by equation (12) is the spontaneous polarization of an individual smectic layer. It contains two terms, with the flexoelectric contribution ($-\mu_r q_0 \theta$) being due entirely to the helical structure. In practice, the methods used so far have only been able to measure the total (volume-averaged) polarization, which has a non-zero value only in an untwisted (if only partially) helix. At the present time the two most reliable methods of measuring P are: a) the classical Sawyer-Tower⁴⁶ method of polarization reversal, and b) the pyroelectric method.⁴⁷ The latter has the obvious advantage that it permits studying the spontaneous polarization not only in the C phase but also in the lower-temperature phases, and can also be used to study the dynamics of the polarization.^{48–49} Other, less accurate methods based, for example, on measuring the polarization-reversal currents⁵⁰ or the critical field for the untwisting of the helix¹⁰ also yield only the value of P due to the piezoelectric contribution $\langle P \rangle = \chi_1 \mu_p \theta_0$. For the piezoelectric modulus of DOBAMBC we have in order of magnitude $\mu_p = 120$ cgs esu ($P \approx 4 \cdot 10^{-5}$ C/m² = 24 cgs esu, $\theta_0 \approx 0.5$ rad, $\chi_1 \approx 0.2$). For measuring the flexoelectric contribution it is necessary to make a careful analysis of the value of the polarization of a partially untwisted helix⁵¹ (see Secs. 6b and 6c) or to develop new methods capable of detecting the spatial dependence $P(z) = P \sin q_0 z$.

c) Dynamics of the tilt angle

According to the theory of Blinc and Žekš,²⁹ the relaxation of the tilt angle for a homogeneous ($q = 0$) orientational deformation of the smectic A^* phase ($T > T_c$) or smectic C^* phase ($T < T_c$) is described by expressions (18) and (19), which predict critical behavior for both relaxation times, with exponents $\gamma = 1$. At the transition point both τ_- and τ_+ should remain finite if we are dealing with a helix which is not untwisted.

Experimentally, the critical behavior of the molecular

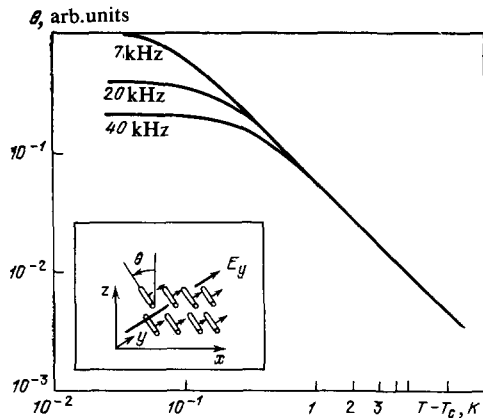


FIG. 12. Temperature dependence of the molecular tilt angle induced in a smectic A* phase by fields of various frequencies.⁵² The inset shows the experimental geometry.

tilt angle has been studied by two methods. In the ferroelectric phase one can change the angle θ by means of a thermal pulse and observe the subsequent relaxation of the polarization by monitoring the pyroelectric response on an oscilloscope.⁴⁸ In the smectic A* phase, in which the equilibrium value of the tilt angle is $\theta_0 = 0$, one can cause the molecules to be deviated by an angle $\theta(E)$ by applying an external field along the surface of the smectic layers.⁵² Let us first discuss the experiments on the smectic A* phase, i.e., for $T > T_c$.

Let z be the normal to the smectic layers and y be the direction of the external electric field E . If the molecules have a transverse dipole moment d_{\perp} , then the field induces a partial orientation [proportional to $\exp(-d_{\perp}E/kT)$, where k is the Boltzmann constant] of the transverse dipoles, i.e., causes an ordering of the short molecular axes. For non-chiral molecules the yz plane would remain a mirrorplane even with the field. If, on the other hand, the molecules are chiral, the reflection symmetry is broken, and the directions $+x$ and $-x$ become nonequivalent. As a result, the molecules acquire a coordinated tilt in the xz plane (see the inset in Fig. 12). This so-called electroclinic effect is the inverse of the effect wherein spontaneous polarization arises upon tilting of the molecules. The temperature dependence of the angle $\theta(E)$ in DOBAMBC was studied in detail in Ref. 52, and the results are shown in Fig. 12.

If one ignores the helicity of the low-temperature phase, then the angle θ is divergent at $T \rightarrow T_c$ because of the critical temperature dependence of the modulus $a = a'(T - T_c)$:

$$\theta = \frac{\mu_p \chi_{\perp}}{2a} E. \quad (22)$$

Here the "electroclinic" coefficient μ_p is the same as the piezoelectric coefficient. Allowance for the helical structure of the C* phase removes the divergence,⁸

$$\theta = \frac{\chi_{\perp} \mu_p}{2a^* + Kq_c^2} E, \quad (23)$$

but the term Kq_c^2 comes into play only in the immediate proximity of the transition temperature. For $T - T_c > 0.02$ K (Ref. 52) the behavior (23) goes over to (22), and the experiment yields the critical exponent γ . The value obtained for this exponent from the data shown in Fig. 12 is 1.1; this

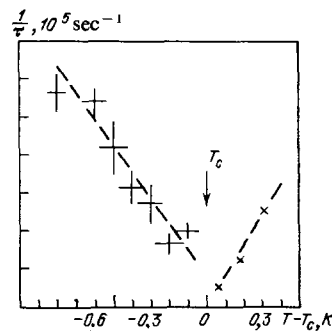


FIG. 13. Soft modes in the smectic A* and smectic C* phases. The right-hand part ($T > T_c$) was obtained from the electroclinic-effect data,⁵² the left-hand part ($T < T_c$) from the dynamics of the pyroelectric response.⁴⁸

figure lies between the mean-field prediction $\gamma = 1$ and the value $\gamma = 1.315$ predicted by the helium analogy.

The same exponent γ should also occur in the expression for the soft-mode relaxation time, equation (18). Data on $\tau_{-}(T)$ were not given explicitly in Ref. 52, but one can obtain three values on the temperature scale from the frequencies indicated in Fig. 12; we find the results shown on the right-hand side of Fig. 13. For the exponent γ at $T > T_c$ we can obtain only a rough estimate: $\gamma \approx 1$.

The left-hand side of Fig. 13 shows a plot of the data of Ref. 48. A short laser pulse was used to change the temperature of a DOBAMBC sample, thereby altering the equilibrium angle $\theta_0(T)$ in the ferroelectric phase. The increment $-\Delta\theta_0$ corresponded to a polarization increment $-\Delta P$, which relaxed after the thermal pulse had ended. The relaxation of the polarization was observed by monitoring the pyroelectric signal on an oscilloscope, and the relaxation time τ_4 [Eq. (19)] was read directly off the screen. Near the transition the value of τ_4 was 1–6 μ sec. In the pyroelectric experiment the helix was untwisted by a weak electric field ($q_0 = 0$), so that one would expect a pure divergence of τ_4 as $T \rightarrow T_c$, in accordance with (19). The experimental curves in Fig. 13 are in fact close to the predicted curves for $q_0 = 0$ (see Fig. 5a). However, the critical exponent evaluated in Ref. 48 for the C phase, $\gamma = 0.67 \pm 0.1$, is lower than the prediction of mean field theory.

The experiment of Ref. 53 also detected a deviation from the behavior $\theta^2 \sim E^2$ predicted by equation (22). The exponent x for the experimental curves of the birefringence as a function of the field, $\Delta n(E) \sim \theta^2(E) \sim E^x$, varied from 1.7 to 1 as the temperature was raised and the distance from the phase transition point was increased. This discrepancy was attributed⁵³ to a possible field-induced biaxiality of the tilted phase [expression (22) was obtained under the assumption of a uniaxial medium]. It is possible that the biaxiality is also reflected in the value of the critical exponent.

The critical behavior of the spontaneous polarization near the transition between two ferroelectric phases in the liquid crystal L-4-hexyloxybenzylidene-4'-amino-2-chloropropylcinnamate (HOBACPC) was studied in Ref. 24 by a pyroelectric method. It was possible to determine the critical exponents for the soft-mode relaxation time on both sides of the phase transition; the two values turned out to be equal:

$\gamma = 1.0 \pm 0.1$. Such a dynamics of the polarization indicates that the transition should be classified as second order. And since the size of the polarization in this material is determined by the "tail" part of the molecules, where the chlorine atom forms a part of the chiral center, the transition studied in Ref. 54 is evidently due to a structural rearrangement of the "tails" of the molecules.

d) Pitch of the helix and the flexoelectric effect

We have seen that the phenomenological theory of the ferroelectric phase gives a rather good description of the general features of the behavior of the molecular tilt angle, the polarization, and the polarization relaxation time as functions of temperature, although the critical exponents by no means always agree with the predictions of molecular field theory. This is not surprising, since the ferroelectric ordering in the present case is due not to the long-range dipole-dipole forces but to interactions of a different sort (steric, dispersional, etc.) with substantially shorter ranges.

The matter of the temperature dependence of the helical pitch is much more complicated. Typical experimental curves for DOBAMBC and its homolog TDOBAMBC (which has a $C_{14}H_{29}O$ — chain instead of $C_{10}H_{21}O$ —) are shown in Fig. 14. A characteristic feature of the $p_0(T)$ curves for thick cells (curves 1 and 2) is the presence of a sharp peak near the point of the transition from the A^* to the C^* phase. In thinner cells (curves 1' and 2') this peak is leveled off by the influence of the solid surfaces bounding the layer, which tend to untwist the helix. The phenomenological theory does not predict critical behavior for $p_0(T)$. According to Eq. (9) the pitch remains finite at the transition: $p_c = 2\pi/q_c$. In order to describe its nonmonotonic temperature dependence (see Fig. 14) one must assume that $q'' < 0$. Such a behavior of the helix cannot be described on the basis of the model developed for cholesteric liquid crystals in Ref. 56. The explanation of the observed behavior is closely related to the theory of the flexoelectric effect of the smectic C^* phase.⁵⁷

The flexoelectric effect, i.e., the appearance of polarization as a result of an orientational deformation of a liquid crystal, can arise in a nonchiral or chiral smectic C for the same reasons as in a nematic phase. Two microscopic causes of the flexoelectric effect have been established for nema-

tics.^{6,8} According to Meyer's model⁵⁸ the polarization arises upon a longitudinal or transverse bending deformation of a nematic phase consisting of banana-shaped or pear-shaped dipolar molecules (in the first case the effect is due to the transverse component d_\perp of the molecular dipole moment; in the second case, to the longitudinal component d_\parallel). In Prost's model⁵⁹ the molecules need not have an asymmetric shape and a dipole moment, but they must have a quadrupole moment (as is always the case for the elongated molecules of liquid crystals).

These same two mechanisms can also play a role in a smectic C. In addition, the flexoelectric coefficient contains a substantial contribution from the dipole-quadrupole mechanism, which is absent in the case of nematic liquid crystals.⁵⁷ In a chiral phase C^* the flexoelectric contribution to the polarization is due to the natural twist of the helix, i.e., to the gradient $d\varphi/dz$. In this case the helical pitch itself depends on the flexoelectric coefficient [Eq. (9)]. It was shown in Ref. 57 that the behavior of the pitch as a function of temperature is governed solely by the steric interactions of banana-shaped molecules. The shape of the molecules here is specified by their length L , diameter D , and the "banana angle" ε shown in Fig. 8a.

A statistical calculation¹³ shows that the flexoelectric coefficient μ_f appearing in the phenomenological expression [Eq. (9)] for the wave vector of the helix depends in a non-monotonic manner on the molecular tilt angle θ_0 , which in turn depends on the temperature. As the difference $T_c - T$ increases, the coefficient μ_f first increases sharply (in proportion to $\sqrt{1 + \theta_0/\varepsilon}$) and then begins to fall off at a relatively slow rate. This is precisely the behavior of the pitch p_0 according to both Eq. (9) and experiment. The maximum pitch is reached at $\theta_0 = D/6L$ (for molecules which are approximately ellipsoids of rotation). This corresponds to the DOBAMBC experiment if one sets $L/D \approx 6$. Without allowance for the flexoelectric effect one can explain only the decay of the helical pitch on the low-temperature side of the peak.⁶⁰ The theory of Ref. 57 also explains the oscillations of the maximum value of the pitch with changing homolog number if one takes into account the oscillations in the "banana angle" for molecules with different lengths of the alkyl chain (the even-odd effect).¹³

The features of the ferroelectric phase transition in two-dimensional systems, e.g., freely suspended liquid-crystal films one or two monomolecular layers thick, were considered theoretically in Ref. 61.

5. MOLECULAR AND STRUCTURAL ASPECTS

a) Magnitude of the spontaneous polarization

In spite of the extremely short history of research on ferroelectricity in liquid crystals, in some respects the mechanism which gives rise to the spontaneous polarization in these materials is even better understood than in the traditional crystalline ferroelectrics. This is because of the rich possibilities of varying the organic molecules by means of directed chemical synthesis in the liquid-crystal case. Let us summarize the necessary conditions for the appearance of

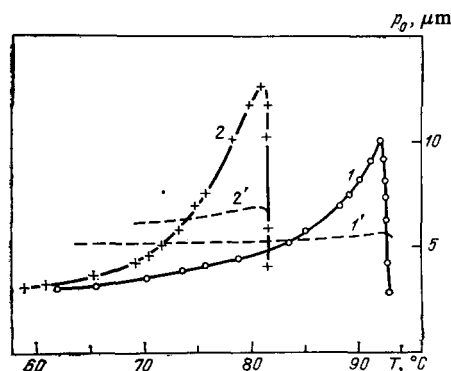


FIG. 14. Temperature dependence of the pitch of the helix in the ferroelectric C^* phase of DOBAMBC (1, 1') and TDOBAMBC (2, 2') for layers 200 μm (1, 2) and 20 μm (1', 2') thick (data of the present authors).

Compound	Abbreviation	T_c	$P, C/m^2$ ($T_c - T = 5 K$)	θ_0 ($T_c - T = 5 K$)	$P/\theta_0, C/m^2$	
$C_6H_{13}-O-\text{C}_6\text{H}_4-O-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)-\text{CH}_2-$	D-4-n-hexyloxyphenyl 4'(2-methylbutyl) carboxylate	HOPMBCO	76 °C	—	—	$\sim 0^*$
$C_{10}H_{21}-O-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)-\text{H}$	D-4-[2-methylbutoxy]phenyl 4-decyloxybenzoate	MBOPDOB	52 °C	$4 \cdot 10^{-6}$ [Ref. 49]	15° [Ref. 39]	$1.5 \cdot 10^{-5}$
$C_{10}H_{21}-O-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)-\text{H}$	L-4-decyloxybenzylidene-4'-amino-2-methylbutylcinnamate	DOBAMBC	90 °C	$3 \cdot 10^{-5}$ [Refs. 49, 64]	19° [Ref. 46]	$9 \cdot 10^{-5}$
$C_6H_{13}-O-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{C}(\text{Cl})(\text{CH}_3)-\text{H}$	L-4-hexyloxybenzylidene-4'-amino-2-chloropropylcinnamate	HOBACPC	74 °C	$1.5 \cdot 10^{-4}$ [Ref. 49]	10° [Ref. 66]	$8.5 \cdot 10^{-4}$
$C_6H_{13}-O-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{C}(\text{CN})(\text{CH}_3)-\text{H}$	L-4-hexyloxybenzylidene-4'-amino-2-cyanopropylcinnamate	HOBACyPC	—	—	—	$[2 \cdot 10^{-3}]^{**}$

* Based on private communication from G. S. Chilaya reporting that an external electric field does not affect the helical structure of this compound.

** We estimated P/θ_0 for HOBACyPC, which does not have a smectic C* phase, by extrapolating from experiments on mixtures of HOBACyPC with nonferroelectric smectics C (Ref. 65).

* Based on private communication from G. S. Chilaya reporting that an external electric field does not affect the helical structure of this compound.

** We estimated P/θ_0 for HOBACyPC, which does not have a smectic C* phase, by extrapolating from experiments on mixtures of HOBACyPC with nonferroelectric smectics C (Ref. 65).

polarization and see how they are realized in experiment (see Fig. 7).

First, it is necessary that the material be able to form a smectic phase with a spontaneous molecular tilt. This condition can be realized by choosing molecules with long alkyl tails (the number of carbon atoms in the tails can be varied from, say, 6 to 15).⁶² The presence of small transverse dipole moments in the central part of the molecule promotes the formation of a tilted phase.^{33,63}

Second, the molecule should contain a chiral fragment, lowering the symmetry of the tilted smectic phase from C_{2h} to C_2 . The chiral fragment arises because of an asymmetric carbon atom, which is denoted by an asterisk for the compounds listed in Table I. Finally, one should have as large a transverse dipole moment d_\perp as possible, since this dipole moment contributes to the spontaneous polarization through the piezoelectric and flexoelectric coefficients μ_p and μ_f in formula (12). The theory does not specify the position of the dipolar group in the molecule, but assumes only that this dipole is rigidly connected to the chiral fragment. Such a situation is by no means always realized in experiment.

Table I gives values of the spontaneous polarization (divided by the tilt angle θ_0 for liquid-crystal ferroelectrics whose molecules differ in the position of the dipole moment d_\perp .^{49,64} In the first three materials the dipole moment $d_\perp \approx 2.5-3$ D is due to the $-\text{C}=\text{O}$ group, which is located at different distances from the chiral center. In HOPMBCO the dipolar group is separated from this center by the biphenyl fragment, which is characterized by a practically free rotation of the benzene rings about the single bond joining them. There is thus no correlation between the direction of d_\perp and the configuration of the chiral center, and, conse-

quently, the polarization is negligible. For MBOPDOB such a correlation begins to appear, since the dipole group is located somewhat closer to the chiral center, and the polarization increases. This tendency is even stronger in the classical material DOBAMBC, for which P/θ_0 is 6 times as large as in the preceding compound.

The introduction of a dipolar group (a chlorine atom, $d_\perp \approx 2$ D) directly into the chiral fragment increases the ratio P/θ_0 by another order of magnitude (HOBACPC). Finally, replacing the chlorine atom in the chiral fragment by a nitrile group $-\text{C}\equiv\text{N}$ (HOBACyPC, $d_\perp \approx 4$ D) increases the polarization still further. In the last case the estimate of P/θ_0 is an indirect one: It was obtained by extrapolating from measurements of P in mixtures,⁶⁵ since HOBACyPC in pure form does not form a smectic C* phase. We thus see that the polarization is in fact determined by the magnitude and position of the transverse molecular dipole.

Data are also available⁶⁷ on the dependence of P on the length of the alkyl chain for homologs of the ester shown in the second line of the table. At the same value of the reduced temperature ($T_c - T = 10^\circ\text{C}$) the value of P decreases monotonically by about a factor of 2.5 as the number of carbon atoms in the chain is increased from 7 to 10. A similar trend is observed in other classes of materials.⁶⁴ The apparent reason for this behavior is that the molecules have a zigzag shape (see Fig. 10), so that a lengthening of the tails leads to a decrease in the effective tilt angle θ_0 , which is the quantity that determines the polarization [Eq. (12)].

Data on the spontaneous polarization in the tilted smectic H* phase that arises in certain materials upon cooling of the C* phase can be obtained from piezoelectric-effect measurements (Fig. 15).⁴⁹ The sharp peaks of the piezoelectric coefficient $\gamma(T) = dP(T)/dT$ correspond to a sharp increase

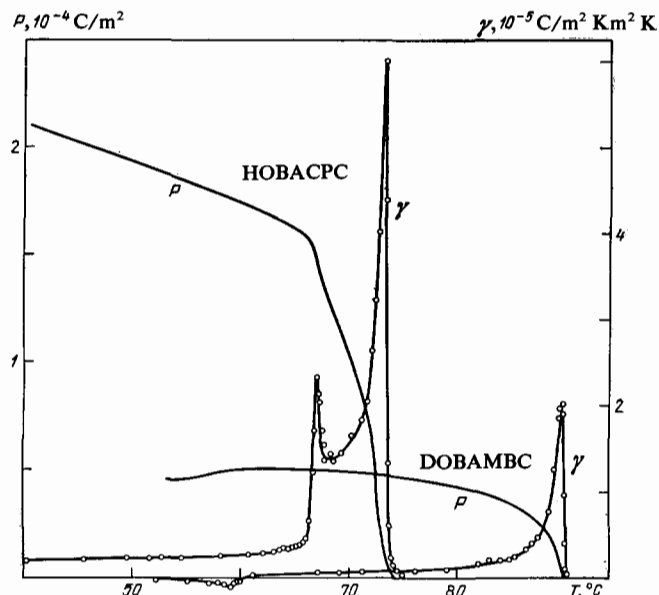


FIG. 15. Temperature dependence of the pyroelectric coefficient and spontaneous polarization of HOBACPC and DOBAMBC in the C* and H* phases.

in the polarization. The increase in the polarization of HOBACPC at the temperature of the transition from the C* phase to the H* phase is apparently due to a sharply enhanced hindering of the rotation of the chiral fragment (which also contains the dipolar group) upon the transition to a phase with translational ordering in the plane of the smectic layers. At the lowest temperatures the polarization reaches $2 \cdot 10^{-4} \text{ C/m}^2$ (60 cgs esu). For DOBAMBC the transition to the H* phase is accompanied not by an increase but by a decrease in the value of P . This suggests that although the rotation of the chiral center tends to become hindered as the temperature is lowered, the motion of the dipolar —C=O group can remain weakly coordinated with this rotation.

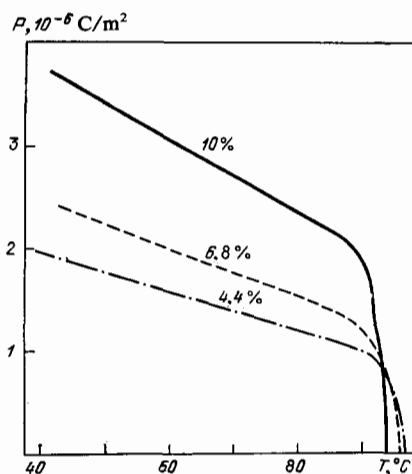


FIG. 16. Temperature dependence of the spontaneous polarization of 4-nonyloxybenzylidene-4'-amino-pentylcinnamate (NOBAPC) doped with the chiral impurity L-4-decyloxybenzylidene-4'-amino-2-cyanopropylcinnamate (DOBACyPC) at various concentrations.

The influence of the molecular structure on the pitch of the helix in the C* phase and on the elastic modulus K was considered by Aliev and Aslanov,⁶⁹ who investigated the homologous series of the same ester (the second row in Table I) and also that of the salicylideneanilines. As one goes to longer alkyl chains the pitch of the helix increases (by about a factor of 3 as n changes from 8 to 11 in the ester series). This tendency is easily explained in the microscopic approach expounded in Sec. 3. In fact, lengthening the molecule without changing the chiral fragment actually lowers the "specific contribution" of this fragment to the total asymmetry of the molecular shape (the fragment becomes more remote from the geometric center of the molecule), and this leads to a weakening of the interactions responsible for the twist of the C* phase. As was shown in Ref. 69, the elastic modulus K also tends to increase with increasing length of the alkyl chain. The simultaneous growth of p_0 and K as functions of n is in agreement with the phenomenological expression (9).

b) Impurity-induced polarization

The necessary conditions for spontaneous polarization can be realized not only in one-component chemical compounds but also in binary (and more complex) mixtures. Here a sort of "division of labor" among the various components becomes possible. For example, the host may have a tilted, but not chiral, smectic phase, while the dipolar impurity molecules provide the chirality of structure necessary for ferroelectricity. From a practical standpoint it greatly simplifies matters if the materials responsible for the formation of the smectic phases can be synthesized separately from the dipolar chiral compounds, which need not be liquid-crystalline. The possibility of such a "division of labor" is implied by the microscopic picture of the genesis of the polarization.¹³ The introduction of a chiral impurity into a smectic C matrix causes a twisting of its structure, with the wave vector of the helix being approximately proportional to the concentration of the impurity, in analogy with how the cholesteric phase arises upon the addition of a chiral impurity to a nematic liquid crystal.

Experimentally, polarization (extremely weak, $P \leq 1.5 \cdot 10^{-6} \text{ C/m}^2$) induced by a chiral impurity in a C phase was first observed by Kuczynski and Stegemeyer.⁷⁰ Substantially higher values $P \approx 1.5 \cdot 10^{-5} \text{ C/m}^2$ have since been obtained⁴⁹ by introducing chiral impurities having large dipole moments into a smectic C. Figure 16 shows how the polarization increases as impurity molecules containing a dipolar —CN group directly in their chiral fragment are introduced into a nonferroelectric liquid crystal.⁶⁵ The resultant spontaneous polarization is influenced by a number of factors: the molecular structure of the impurity (the strength of the dipole and its proximity to the chiral fragment), the impurity concentration, the tilt angle of the host molecules, and the conformity in length of the impurity and host molecules. With an eye to all these factors, we recently succeeded in producing an "extrinsic" (impurity) ferroelectric liquid crystal with a polarization in the C* phase of $P = 2.2 \cdot 10^{-4} \text{ C/m}^2$, higher than the record polarization for pure liquid-crystal ferroelectrics (Fig. 17)⁷¹; the mixture involved has a wide

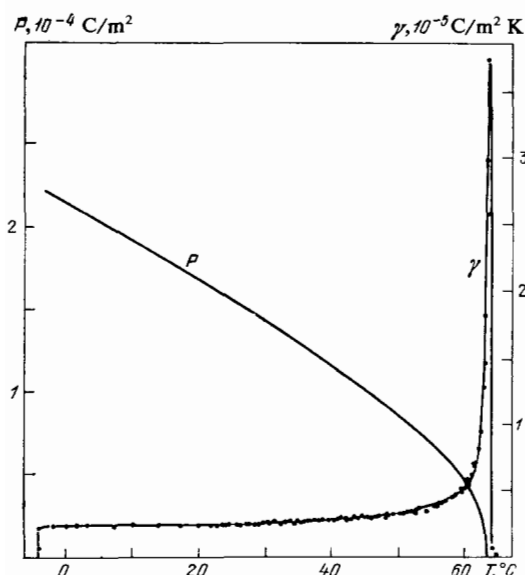


FIG. 17. Maximum values obtained⁷¹ for the pyroelectric coefficient and spontaneous polarization.

existence region of the C* phase (from -4 to 60°C), an important consideration for practical applications. Figure 18 shows how the effective dipole moment of the chiral molecules, $d_{\text{eff}} = d_1 \langle \cos\psi \rangle$, which is responsible for the spontaneous polarization and is proportional to the ferroelectric order parameter, grows with increasing molecular dipole moment d_1 . It is clearly seen that d_{eff} has a nonlinear dependence on d_1 , implying that the parameter $\langle \cos\psi \rangle$ increases with increasing d_1 . Consequently, the ordering of the short molecular axes, which determines $\langle \cos\psi \rangle$, is not, strictly speaking, independent of the strength of the molecular dipole, as is assumed in the models of improper ferroelectrics.

The introduction of small (up to 10%) concentrations of dipolar (nonchiral) molecules into the ferroelectric C phase of DOBAMBC has an insignificant effect on the size of the polarization.⁶⁴ Strong dilution of ferroelectric liquid crystals by nonchiral impurities causes the spontaneous polarization to vanish.⁷² Ionic impurities cause an appreciable screening of the polarization.⁴⁹

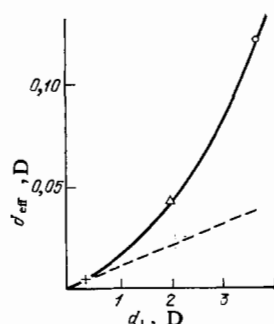


FIG. 18. Nonlinear behavior of the effective dipole moment (divided by the angle θ) of the smectic C* phase as a function of the molecular dipole moment.

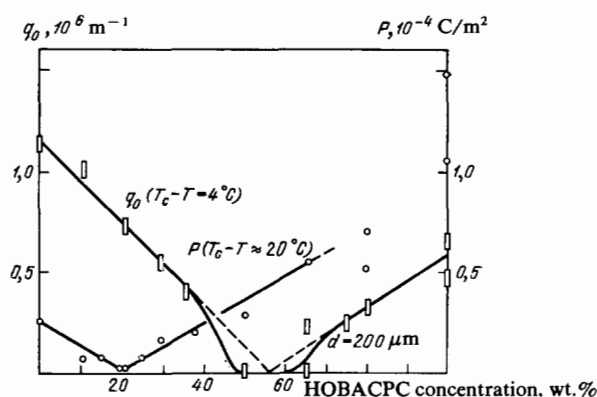


FIG. 19. Compensation of the helical structure and the vanishing of the polarization in a mixture of levorotatory DOBAMBC and dextrorotatory HOBACPC.

c) Nonhelical ferroelectrics

By mixing two ferroelectric liquid crystals having chiralities of opposite sign (left-handed and right-handed) one can compensate the twist and obtain a homogeneous ferroelectric phase.⁷³ Here the spontaneous polarization has a non-zero value (Fig. 19). This occurs because the pitch of the helix and the polarization are due to different microscopic mechanisms. The pitch of the helix is completely determined by the interaction of the chiral molecules with one another or with the matrix, while the polarization is due to the steric (e.g., banana-like) shape of the molecules and to their dipole moment. A strict compensation of the twist and the polarization occurs only in a racemic mixture of right-handed and left-handed molecules of the same chemical compound.

One can see two "magic" points in Fig. 19. At one of them (HOBACPC concentration $c = 55\%$ in a mixture with DOBAMBC) the helix is untwisted ($q_0 = 0$) but the polarization is finite ($P_c = 4 \cdot 10^{-5} \text{ C/m}^2$ for $T_c - T = 20^\circ\text{C}$), while at the other point ($c = 20\%$) the situation is reversed—the pitch has a finite value ($q_0 = 8 \cdot 10^5 \text{ m}^{-1}$, $p_0 = 2\pi/q_0 = 8 \mu\text{m}$) but the polarization of the homogeneously oriented, untwisted C* phase is zero. For thick cells the compensation of the twist occurs at a single, completely determinate ratio of the components ($c = 55\%$). In this case the volume spontaneous polarization in the smectic C* phase persists for tens of minutes after removal of the external polarizing field (which here serves not to untwist the helix but to "force" the polycrystalline structure into a single domain). As the thickness d of the cell decreases, a certain range of concentrations appears in which the helix is untwisted.

d) Polymorphism of ferroelectric phases

Practically all the research that has been done on ferroelectric effects in liquid crystals has been done on the compounds DOBAMBC (and its several homologs) and HOBACPC, which have only smectic C* and H* phases. Binary mixtures can exhibit a richer polymorphism of the ferroelectric phases.⁶⁵ Figure 20 shows the temperature dependence of the pyroelectric coefficient for the compound NOBAPC (the same as in Fig. 16) doped with dipolar chiral impurities of HOBACPC and HOBACyPC. While the initial com-

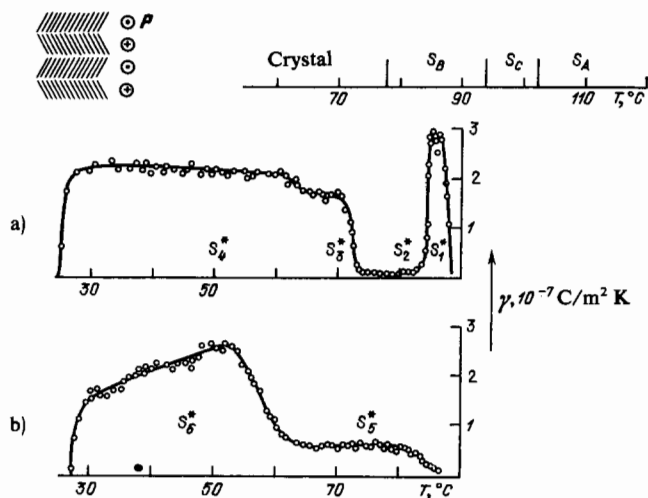


FIG. 20. Temperature dependence of the pyroelectric coefficient for NOBAPC doped to 20% with the chiral impurities HOBACPC (a) and HOBACyPC (b). At the upper right is the sequence of phase transitions in pure NOBAPC, and the upper left-hand corner shows the antiferroelectric herring-bone packing of the molecules.

pound (see the scale at the top of Fig. 20) displays a transition from a smectic C phase to an orthogonal B phase as the temperature is lowered, in the mixture with HOBACPC there are at least four pyroelectric phases. The dependence of the polarization on the external electric field in one of these phases is reminiscent of that of an antiferroelectric.⁶⁵ The possibility of antiferroelectricity is not ruled out in phases with the herring-bone packing discussed in Ref. 74. An antiferroelectric phase of this type is fundamentally different from a smectic A with antiparallel packing of polar molecules in adjacent layers.⁷⁵

e) Possibility of ferroelectricity in living fibers and the asymmetry of biological molecules

There are certain experimental data which indicate that the living fibers exhibit ferroelectric properties (e.g., the pyroelectric effect⁷⁶), but the possible microscopic mechanism for the dipolar ordering has remained unclear.

On the other hand, investigators have long been interested in the fact that most biological molecules exhibit asymmetry (i.e., chirality). To this day neither the meaning of this phenomenon nor its function in the molecular mechanisms of life processes has been fully explained.¹²⁵

In Ref. 78 we called attention to the possibility of ferroelectricity in living fibers at the cell membrane level, reasoning from the analogy between the molecular structure of biomembranes and the structure of a ferroelectric liquid crystal formed by a smectic C phase containing chiral impurity molecules (see Sec. 5b). The chirality of the biological molecules which enter into the composition of biomembranes (e.g., cholesterol molecules) automatically satisfies one of the necessary conditions for inducing a spontaneous polarization. The analog of the smectic C phase in membranes is the bilayer lipid structure, in which, as recent studies show,⁷⁷ the lipid molecules can be tilted with respect to the normal to the membrane surface. Such a tilt can develop,

at least locally, and can also be induced by external influences, as, for example, when bending-deformation waves propagate through the membrane.

By symmetry considerations a spontaneous polarization is possible not only at the level of the multicomponent structure of cell membranes but also at the level of the nucleic-acid and protein molecules, whose helical structure contains all the necessary symmetry elements for the emergence of a polar direction described by a polar axis C_2 which is perpendicular to the long axis of these molecules and undergoes a continuous precession as one goes along the long axis.

To estimate the polarization which can be induced in membranes by biological molecules, we used smectic C liquid crystals to model the conditions which could occur in biomembranes. It was found that all the asymmetric biological molecules tested (cholesterol, phenoxymethylpenicillin, erythromycin, etc.), when introduced into a smectic C, induced an appreciable polarization $P = 10^{-6} - 10^{-5}$ C/m² at chiral-molecule concentrations of 1–6 wt.%. Extrapolation of the estimates suggests that a polarization $P \sim 10^{-4}$ C/m² can be induced by cholesterol, for example, in natural biomembranes.

The direct detection of polarization in biomembranes, with the polarization vector lying (according to our ideas) in the plane of the membrane, would occasion a serious reinterpretation of a number of physical mechanisms responsible for such important processes as the propagation of excitation over membranes, ionic transport, the long-range interaction between enzymes, and so forth.

f) Two-dimensional systems

Optical and electrooptical studies of thin films of ferroelectric liquid crystals have been reported in a series of papers by R. Meyer and co-workers.^{79–81} They studied freely suspended films consisting of only a few ($N = 2-8$) smectic layers. Ellipsometric measurements⁷⁹ showed that the tilt angle of the molecules to the normal of the smectic layer increases with decreasing number of smectic layers (Fig. 21,

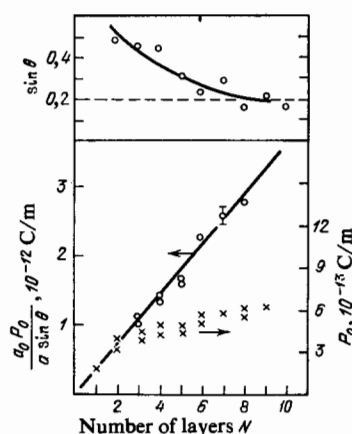


FIG. 21. Molecular tilt angle θ and the spontaneous polarization P_0 of a thin DOBAMBC film as functions of the number of smectic layers. The crosses denote the normalized value of the polarization; the slope of the straight line corresponds to the volume value of P .

top). The spontaneous polarization, also shown in Fig. 21, was determined from measurements of the intensity of the light-scattering from the freely suspended film as a pulsed external field was switched on and off.⁸⁰ As the number of layers decreased, the measured polarization of the film as a whole (P_0) decreased (Fig. 21, bottom). At the same time the values of the polarization divided by the product of the angle times the layer thickness coincides with the value of P/θ_0 in the volume. This is indicated by the linear dependence of $a_0 P_0/a \sin \theta$ on the number of layers (a_0 and $a = a_0 \cos \theta$ are the thickness of the smectic layer in the bulk sample and in the freely suspended film, respectively).

In Ref. 80 the values of the "two-dimensional" elastic moduli and viscosity coefficients were also determined. The dynamics of defects in thin ferroelectric films ($N = 3$), which simulate the behavior of ideal two-dimensional systems, was studied in Ref. 81.

6. BEHAVIOR IN EXTERNAL FIELDS

a) Optical properties

In the absence of external fields a smectic C* liquid crystal is a set of optically biaxial monomolecular layers in which the direction of the optic axis gradually swings around in going from one layer to the next, so that the macroscopic structure is a helix. The helical structure as a whole is uniaxial, with the optic axis coinciding with the axis of the helix. This last fact has been established by conoscopic studies.^{10,82}

For the theoretical description of the optical properties of the helical structure of the smectic C* phase one introduces a locally biaxial dielectric tensor, which rotates as one goes along the normal to the smectic planes.^{83,84} The optical properties of the helical structure for light incident along the helical axis are completely analogous to those of a cholesteric liquid crystal⁸⁵ if one introduces effective refractive indices for the ordinary and extraordinary waves. The smectic C* structure rotates the plane of polarization of light, possesses a selective reflection in the second diffraction order, has characteristic structural defects in the form of Grandjean fringes, etc. For light at oblique incidence the selective scattering of the light has an important distinction from that of cholesteric liquid crystals, viz., in the smectic C*, owing to its polar structure, the first order of Bragg reflection turns out to be allowed when the wavelength of the reflection maximum in the medium corresponds to $\lambda_m = 2p_0$. This occurs because in the smectic C* a rotation of the director by an angle of 2π corresponds to a physically identical state, while in a cholesteric this occurs for a rotation by only π (because of the equivalence of the director directions \mathbf{n} and $-\mathbf{n}$). The optical properties of the helical structure of smectics C* were studied experimentally in Refs. 87 and 88. For a smectic C* belonging to the class of esters of carboxylic acid having small helical pitches,⁸⁹ a single selective-reflection maximum is observed in the visible region of the spectrum at normal incidence of the light, while at oblique incidence there are two. When dyes are introduced into a smectic matrix one can observe a diffractive decrease in the absorption of light near the reflection fringes (the Borrmann effect).

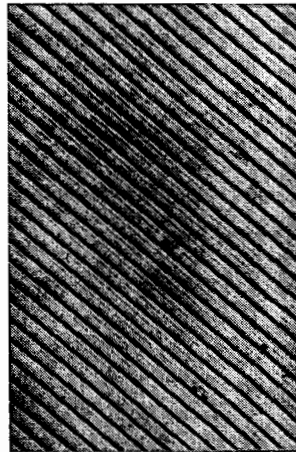


FIG. 22. Stripe domains in a chiral smectic C* phase for a planar orientation of the molecules at the walls.⁹⁰ the distance between adjacent stripes (in this case $16 \mu\text{m}$) is equal to the pitch of the helix.

Experimentally, especially in electrooptical studies, one often deals with thin layers of a smectic C* sandwiched between two glass plates. As a rule, the plates have been finished so as to provide a planar orientation of the molecules of the liquid crystal on their surfaces. In this case the axis of the helix lies in the plane of the layer, and the interaction with the boundaries gives rise to various structural defects in the form of stripes,⁹⁰ walls and networks,⁹¹ toroidal domains,⁹² etc.

Of greatest interest to us are the stripe domains (Fig. 22), since they are separated by a distance exactly equal to the pitch of the helix and can be used to easily monitor the untwisting of the helix in external fields. The scattering of light by the periodic structures of a smectic C* in the absence of field was studied theoretically and experimentally in Ref. 93.

Smectic C* liquid crystals have interesting nonlinear optical properties. In particular, their polar symmetry admits second harmonic generation. Experiments done on DOBAMBC have shown⁹⁴ that the nonlinear susceptibility $\chi^{(2)}$ responsible for the generation effect is small, in agreement with the small value of the ferroelectric order parameter $\langle \cos \psi \rangle$.¹²⁶ Interestingly, the periodic structure of the still twisted helix makes it possible to arrange a phase synchronism of the generated wave of second harmonic light in certain directions.

b) Dielectric response and the untwisting of the helix by an electric field

In nonferroelectric liquid crystals one observes a wide variety of different electrooptic effects due to the quadratic interaction of the electric field with the anisotropy of the dielectric permittivity of the medium.^{6,95} In the expression for the free energy of a liquid crystal this interaction corresponds to a term of the form $-\Delta\epsilon E^2/4\pi$, where $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, and the subscripts \parallel and \perp refer to the local direction of the longitudinal molecular axes. Quadratic effects remain in the case of a ferroelectric liquid crystal, but now there is an additional, linear interaction of the field with

the polarization [a term of the form $\mathbf{P} \cdot \mathbf{E}$ in expression (8)]. For the sake of simplicity let us right now discuss only the linear interaction, since this is the dominant interaction in fields which are not too strong. For example, at typical field strengths corresponding to the untwisting of the helix, $E = 10^5$ V/m = 3 cgs esu, and at a polarization of $P \approx 10^{-4}$ C/m² = 30 cgs esu, the linear contribution outweighs the quadratic contribution ($P \gg \Delta \epsilon E$) all the way up to values $\Delta \epsilon \approx 10$.

The imposition of an electric field on the helical structure of a ferroelectric smectic C* causes the transverse molecular dipoles to orient themselves along the field direction, and this in turn causes the molecules to swing around the normal to the smectic layers along the surface of a cone. The new orientation is incompatible with the presence of the helical structure, and the helix therefore untwists. The energy expended on such an untwisting amounts to Kq_0^2 . In simple models of this effect it is assumed that the angle θ_0 remains constant during the untwisting,¹⁴ but the change in θ_0 , especially at temperatures close to T_c , should really be taken into account. Evidence supporting this position comes from x-ray measurements of the thickness of the smectic layers during the untwisting of the helix by an external field⁹⁶ and also from the field dependence of the pitch of the helix.⁹⁷

A theory of the steady-state response of a helical smectic C* to an external electric field at small angles θ_0 was developed by Ostrovskii, Pikin, and Chigrinov (see Refs. 12 and 51). Let us assume that the field E is directed perpendicular to the axis of the helix. Minimizing expression (8) for the free energy, we find that strong fields correspond to a homogeneous state of orientation, i.e., an untwisted helix. The critical untwisting field

$$E_0 = \frac{\pi^2}{16} \frac{q_0^2 K \theta_0}{\chi_{\perp} \mu_p} \quad (24)$$

depends on the same renormalized elastic modulus $K = K_{33} - \chi_{\perp} \mu_f^2$ as before [see (9)]. The flexoelectric coefficient μ_f does not appear explicitly in expression (24), since the critical field by definition corresponds to the final stage of the untwisting, $q_0 \rightarrow 0$, when the flexoelectric contribution to the polarization has already vanished.

The dielectric response corresponding to weak fields $E \ll E_c$, on the contrary, does contain a flexoelectric term, since the helical structure is still present. If we allow not only for the field dependence of the azimuthal angle $\varphi(z, E)$ but also for that of the tilt angle $\theta(z, E)$, then we obtain the following formula for the zero-frequency dielectric permittivity^{8,98}:

$$\epsilon_{\Delta}(\omega=0) = \epsilon_{\Delta}(\omega=\infty) + 2\pi\chi_{\Delta}^2 \left[\frac{\mu_p^2}{Kq_0^2} + \frac{(\mu_p - \mu_f^* q_0)^2}{g_{\parallel} q_0^2 - 4a^*} \right]. \quad (25)$$

In Eq. (25) the elastic modulus g_{\parallel} is the coefficient in front of the gradient $(\partial\varphi/\partial z)^2$ in the expansion of the elastic part of the free energy (8), while the modulus a^* , which appears in (11), is the renormalized (with allowance for the helical structure and the piezoeffect) modulus a of the ordinary smectic C phase; this modulus is responsible for the deviation of the molecules from the normal to the layer.

The flexoelectric coefficient $\mu_f^* = \mu_f - \mu_f' \neq 0$ takes into account the contributions to the free energy from both $\partial\varphi/\partial z$

and $\partial\theta/\partial z$ (the coefficients μ_f and μ_f' , respectively).⁸ The last circumstance makes expression (25) different from that obtained in Ref. 99.

Formula (25) reflects the contribution to the dielectric response from two components. The first term describes the "twisting-untwisting" of the helix, i.e., the Goldstone mode discussed in Sec. 2. The contribution of this term increases with increasing pitch of the helix because the increase in the pitch brings the wave vector of the helix ($q_0 \rightarrow 0$) into coincidence with that of the external field ($q = 0$). The second term corresponds to the soft mode and exhibits a critical dependence on temperature for $q_0 \rightarrow 0$. In real smectic C* phases the wave vector of the helix does not go to zero at the transition point ($q_0 \rightarrow q_c$ at $T \rightarrow T_c$), and the dielectric response is therefore not divergent at $T = T_c$. This conclusion agrees with the results of Ref. 24.

The Goldstone and soft modes are most easily distinguished by observing the frequency dependence of the dielectric response. The first of these modes has a long relaxation time, determined by the viscoelastic characteristics of the helix [Eq. (17)], while the second is characterized by a small time τ_4 which exhibits a critical dependence on temperature and reflects the rapid damping of the molecular tilt angle θ from the normal to the smectic layer [Eq. (19)].

The frequency dependence $\epsilon(\omega)$ in the ferroelectric phases has been measured experimentally in a number of studies.^{64,100-104} The results of the most careful measurements of ϵ for DOBAMBC in the low-frequency region are given in Ref. 100, while the dispersion of ϵ in the high-frequency region was observed in Ref. 64. The results of these two studies are combined in Fig. 23 (the values of ϵ in the range 10–10⁴ Hz from Ref. 100 join easily with the values of ϵ in the range 10³–10⁷ Hz from Ref. 64). One can clearly see the relaxation of the Goldstone mode at frequencies up to 10³ Hz; this contribution vanishes when the helix is untwisted by an external field $E > E_c$. From the relaxation time $\tau_1 = 4 \cdot 10^{-4}$ sec in DOBAMBC at 83 °C one can determine the ratio $\gamma_1/K = \tau q_0^2$ using Eq. (17), since the values of q_0 are known from independence measurements of the helical pitch ($q_0 \approx 8 \cdot 10^3$ cm⁻¹). The ratio $\gamma_1/K = 2.5 \cdot 10^4$ sec/cm² agrees with the value $\gamma_1/K = 4.5 \cdot 10^4$ sec/cm² determined independently in Ref. 82. Consequently, at the characteristic values $K \approx 10^{-6}$ dyn required for agreement with the thresh-

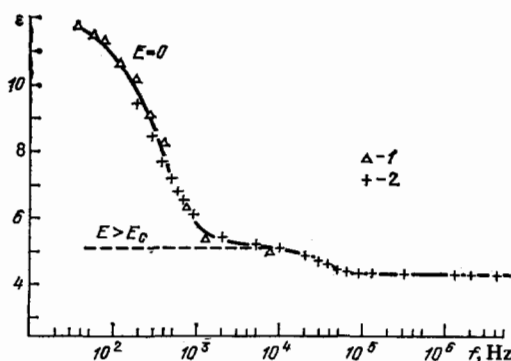


FIG. 23. Frequency dispersion of the dielectric susceptibility of DOBAMBC at $T_c - T \approx 15$ K [data of Refs. 38 (1) and 64 (2)].

old for the untwisting of the helix (see below), the coefficient of viscosity is $\gamma_1 \approx (2-5) \cdot 10^{-2}$ P.

The dispersion at frequencies of around 10^5 Hz corresponds to the soft relaxation mode of the molecular tilt angle. The corresponding relaxation times τ agree with the results of independent measurements based on the relaxation of the pyrosignal (Fig. 13). Using the curves in Fig. 13, one can estimate the coefficient a' in formulas (18) and (19). Far from the transition (for $|T_c - T| \gtrsim 5$ K) we can neglect the terms Kq_c^2 and Kq_0^2 , and assuming $\gamma = 3 \cdot 10^{-2}$ P, we obtain $a' \approx 10^4$ erg/cm³K in the smectic A* phase and $a' = 7.5 \cdot 10^3$ erg/cm³K in the smectic C* phase. In view of the fact that these values were obtained by completely different experimental methods, the agreement of the results can be considered very good.

A quantitative processing of the temperature and frequency curves of the dielectric susceptibility can in principle yield the constants μ_p and μ_f^* appearing in (25) as well. However, the strong temperature dependence of the wave vector of the helix greatly complicates such estimates. In particular, the data of Ref. 100 were used⁸ to deduce the relation $\mu_f^* q_0 \gg \mu_p$, i.e., it was thought that the flexoelectric contribution to the dielectric susceptibility is dominant at low frequencies. At the same time, unsuccessful attempts to evaluate the flexoelectric contribution by an optical method during the field-induced untwisting of the helix¹⁴ suggest that $\mu_f q_0 \leq 0.1 \mu_p$. Granted, the method used in Ref. 14 derives from the incorrect premise that the critical field for the untwisting of the helix depends on the flexoelectric coefficient through the polarization. The flexoelectric contribution to the polarization can in principle be detected by measuring the polarization for a partially untwisted helix.⁵¹ The point is that for an undistorted helical structure the average value of the polarization over the sample is $\langle P \rangle = 0$. As the helix is untwisted the polarization no longer averages out completely, and a nonzero value $\langle P \rangle = \langle P_p + P_f \rangle \neq 0$ appears. In addition to the piezoelectric contribution P_p , this value also includes a flexoelectric contribution P_f so long as the structure remains inhomogeneous. For $E > E_c$ the helix is untwisted, and $\langle P \rangle \equiv P_p$. The field dependence of the averaged polarization for DOBAMBC at $E \leq E_c$ was calculated numerically in Ref. 51, and the results are shown in Fig. 24 for various temperatures. For this calculation it was assumed that $\mu_f q_0 \approx 5 \mu_p$ (in accordance with Ref. 100), and the elastic moduli g and K were assumed equal. The non-monotonicity of the curves of the reduced polarization as a function of the reduced field is due to the flexoelectric contribution, which should be manifested particularly clearly near the phase transition (curve 5 corresponds to $T_c - T = 1.2$ K). The theoretical curves can be compared with the field dependence of the sample-averaged pyroelectric coefficient of DOBAMBC at $T_c - T \approx 1^\circ\text{C}$ (Ref. 64). The monotonic behavior of $\langle \gamma_{\max}(E) \rangle$ reflects the monotonic behavior of $\langle P(E) \rangle$ and thus indicates that the flexoelectric contribution to the spontaneous polarization is small. This result is also confirmed by the simple shape of the hysteresis loop in Sawyer-Tower measurements of the polarization.^{44,104}

We have managed to obtain¹²⁷ a direct estimate of the flexoelectric contribution to the spontaneous polarization in

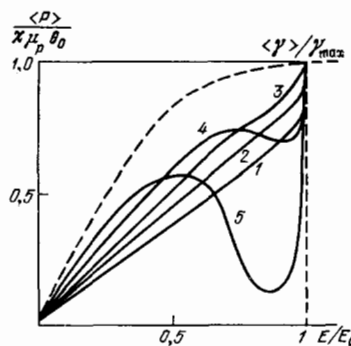


FIG. 24. Theoretical curves of the sample-averaged spontaneous polarization for a partially untwisted helix at various temperatures. Solid curves: 1) $T_c - T = 22$ K, 2) 9 K, 3) 4 K, 4) 1.6 K, 5) 1 K. The experimental (dashed) curve shows the reduced value of the sample-averaged pyroelectric coefficient for $T_c - T = 1$ K.

a mixture of the ferroelectric liquid crystals DOBAMBC and HOBACPC (this mixture forms a nonhelical liquid ferroelectric; see Sec. 5c). Here, in addition to the "magic" points described in Sec. 5c there is a third "magic" point at which the piezoelectric and flexoelectric contributions compensate each other in the absence of external influences. In our experiment this point corresponded to the vanishing of the linear (in the field) electrooptic modulation of a wide (≈ 1 mm) light beam passing through a thick (200 μm) cell at an amplitude of the low-frequency (40 Hz) control voltage that is much smaller than the voltage corresponding to the untwisting of the helix.

After using the results of the electrooptic measurements to determine the impurity concentration at which the piezoelectric and flexoelectric contributions cancel (23.4 wt. % HOBACPC), we separately measured the "pure" piezoelectric polarization P_p in this mixture by a pyroelectric technique, eliminating the flexoelectric polarization P_f by untwisting the helix in an external electric field greater than the untwisting field. The measured value of P_p is approximately equal in size to the "eliminated" flexoelectric polarization: $P_p \approx P_f = \chi_1 \theta_0 q_0 \mu_f$. For $T_c - T$ between 1 and 5°C we obtained for the flexoelectric coefficient the value $\mu_f = 0.6 \cdot 10^{-10}$ C/m [$T_c - T = 5^\circ\text{C}$, $P_f = P_p = 0.25 \cdot 10^{-5}$ C/cm², $\theta_0 \approx 13^\circ = 0.23$ rad, $q_0 = 0.71 \cdot 10^6$ m⁻¹, $\chi_1 = 0.28$ (Ref. 103)]. An estimate of the piezomodulus μ_p for a mixture containing 55% HOBACPC ($q_0 = 0$) from the curve of P_p as a function of the concentration (Fig. 19) for $T_c - T = 10^\circ\text{C}$ gives the value $\mu_p = (2-3) \cdot 10^{-4}$ C/m². Naturally, changing the concentration of the components leads to variations in μ_p .

Extrapolation of the results of our measurements for DOBAMBC to $T_c - T = 5^\circ\text{C}$ gives the following relation for the flexoelectric and piezoelectric contributions to the spontaneous polarization in this widely known material: $\mu_f q_0 = (0.1-0.2) \mu_p$. For HOBACPC one has $\mu_f q_0 \approx (0.02-0.03) \mu_p$.

Thus the flexoelectric contribution to the spontaneous polarization of chiral smectics is apparently important only for highly twisted helical liquid crystals having a twist pitch of less than 5 μm and consisting of molecules whose chiral fragment has a small dipole moment (≈ 1 D).

The experimental values^{64,97,100} of the threshold field for the untwisting of the helix lie in the range between $4 \cdot 10^4$ to $5 \cdot 10^5$ V/m for temperatures $T_c - T \approx 0.2$ K and 20 K, respectively. These values are in good agreement with formula (24). For example, for DOBAMBC at $T_c - T \approx 20$ K, with $p = 2\pi/q_0 = 4 \mu\text{m}$, $\theta_0 \approx 0.5$, $K \approx 10^{-6}$ dyn, $\chi_1 \approx 0.2$, and $\mu_p \approx 120$ cgs esu, we get $E_c \approx 3$ cgs esu = 10^5 V/m.¹

The dependence of the sample-averaged spontaneous polarization on the external electric field was calculated in Ref. 105 with allowance for the quadratic term $\Delta\epsilon E^2$ but under the simplifying condition $\theta_0 = \text{const}$. Because of the competition between the untwisting effect of the linear term PE and the stabilizing effect of the quadratic interaction, the process of untwisting is complicated by the attendant formation of special defects: walls. Observation of the walls provides yet another way of estimating the flexoelectric coefficient.

The dynamics of the untwisting of the helix in an external electric field applied perpendicular to the axis of the helix was studied in Ref. 106. In the simplest model it was assumed that the angle θ_0 remains constant during the untwisting and that the polarization includes only the piezoelectric contribution. In this case the balance equation for the moments (elastic, viscous, and field-polarization interaction) is formally analogous to the corresponding equation for cholesteric liquid crystals⁶:

$$K\theta_0 \frac{d^2\varphi}{dz^2} - \gamma_1\theta_0 \frac{d\varphi}{dt} + \chi_1\mu_p E \sin \varphi = 0. \quad (26)$$

For small fields $E \ll E_c$ this equation is solved analytically, while for large fields $E \gtrsim E_c$ it is solved numerically.⁵¹ The relaxation times of the field-deformed helix for $E \ll E_c$ correspond to the Goldstone mode: $\tau_1 = \gamma_1/Kq_0^2$. With increasing field we have $q_0(E) \rightarrow 0$, and a critical divergence of the relaxation time is observed for $E \rightarrow E_c$. The behavior predicted by equation (26) is confirmed by experiment.¹⁰⁶

c) Electrooptic effects

The electrooptic effects observed in ferroelectric liquid crystals can be arbitrarily divided into two unequal groups. The first group might include the wide range of effects that are due in some way to the helical structure of the smectic C* phase and to the different changes of its external form (texture) in an applied electric field. The second group might include the effects, few in number but important in practice, associated with the reorientation of the director in the untwisted helical structure, i.e., in the homogeneous state.

The helical structure of the smectic C* phase strongly rotates the plane of polarization of light incident along the axis of the helix. This rotation depends noticeably on the magnitude of the external field.⁵³ Strong electrooptic effects also accompany the untwisting of the helix for light incident perpendicular to the axis of the helix. In this case one should observe a directed diffraction of the light¹⁰⁷ if the pitch of the helix is sufficiently small, $p_0 < 1 \mu\text{m}$, and corresponds to wavelengths in the visible region of the spectrum. For pitches $p_0 \gtrsim 1 \mu\text{m}$ the optical transmission of the cells turns out to depend on the field only in the sample-averaged sense (if the width of the light beam is larger than the pitch) be-

cause the untwisting of the helix is accompanied by a coordinated rotation of the optic axes of the individual parts of the helical structure. The corresponding linear (in the field) electrooptic effect was observed in Refs. 107–111. In Ref. 108 it was first shown that a liquid ferroelectric can have three stable states: for $E = 0$ and for $\pm E$ at $|E| > E_c$.

In the category of textural changes in an electric field we might also include the appearance of domain patterns, which was observed in Refs. 96 and 111. The region of field frequencies in which domains arise coincides with the region of the soft-mode relaxation of the dielectric susceptibility (see Fig. 23). In nematic liquid crystals the formation of different domain structures is highly typical of the frequency range in which $\epsilon(\omega)$ exhibits relaxation.⁶ It could be that these effects in the ferroelectric phases are also due to the same mechanisms (hydrodynamic or dielectric).¹¹²

The reorientation of the optic axis of a homogeneous (untwisted) structure was studied in Refs. 113 and 114. In both cases very thin (microns¹¹⁴ or even fractions of a micron¹¹³ thick) layers of a smectic C phase were used. The cells consisted of two glass plates with transparent SnO₂ electrodes deposited on their inner surfaces. When the electrodes were finished in such a way that the liquid-crystal molecules lay parallel to the walls and in a vertical orientation (Fig. 25), the helix was held in an untwisted state by surface forces. Such an untwisting of the helix was mentioned previously in our discussion of nonhelical ferroelectrics (see Fig. 19). Depending on the polarity of the static field applied to the transparent electrodes, the spontaneous polarization vector became oriented either along the light beam or counter to it. Accordingly, the long axes of the molecules were oriented at an angle of $\pm \theta$ to the left or right of the vertical. For a suitable choice of analyzer and polarizer directions, reversing the polarity of the field led to a practically 100% modulation of the light beam. The time required for reorientation of the optic axis was inversely proportional to the field strength, reaching fractions of a microsecond¹¹³ in HOBACPC at a temperature $\sim 68^\circ\text{C}$ and a cell thickness of $1.5 \mu\text{m}$ and reaching hundreds of microseconds^{71,114} in mixtures having a ferroelectric phase at room temperature, at a cell thickness of $6 \mu\text{m}$.

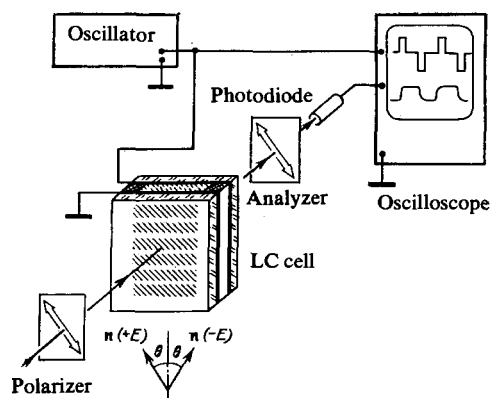


FIG. 25. Geometry of experiment for observing the electrooptic switching of an untwisted C* phase.

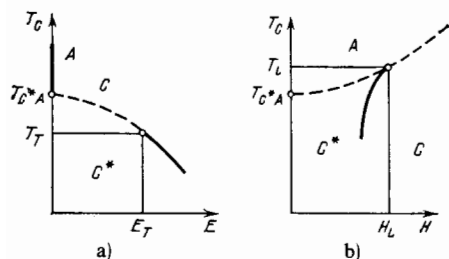


FIG. 26. Temperature-external-field phase diagrams demonstrating the presence of a tricritical point T_T (a) and a Lifshitz point T_L (b). The solid curves correspond to first-order phase transitions, the dashed curves to second-order transitions.

d) Tricritical and Lifshitz points

Let us now discuss the influence of external fields on the temperature of a transition between smectic phases. Here the form of the interaction (linear or quadratic) between the field and liquid crystal turns out to be extremely important.

Let $T_c = T_{C^*A}$ be the temperature of the second-order phase transition between the twisted smectic C^* phase and the smectic A phase at zero field (Fig. 26). A static electric field causes a molecular tilt in the high-temperature phase, thereby causing a transition to a homogeneous (untwisted) C phase. In the high-temperature phase a weak field causes only a certain deformation of the helical structure. According to Ref. 115, the temperature of the second-order transition between the helical C^* phase and the field-induced C phase becomes somewhat lower as E increases (Fig. 26a). At the same time, we know that the untwisting of the helix in a strong field $E = E_c$ corresponds to a first-order transition from the C^* to the C phase. Consequently, at a certain point on the $T_c(E)$ phase diagram the second-order transition line goes over to a first-order transition line (the solid curve), i.e., there is a tricritical point T_T on the $T_c(E)$ curve. The location of this point, according to Ref. 115, is given by the relation $T_T \approx T_{C^*A} - 0.3\Delta T$, where ΔT is given by Eq. (10).

Let us now suppose that a magnetic field rather than an electric field is applied to the original material. The magnetic field interacts with the molecular ensemble through the diamagnetic anisotropy (a quadratic term $\Delta\chi H^2$ in the free energy). It does not cause a coordinated tilt of the molecules in the smectic A (there is no electroclinic effect). The $T_c(H)$ phase diagram therefore has a somewhat different appearance (Fig. 26b). According to Ref. 116, T_c increases with increasing field, with the transition to the smectic A from the C^* phase remaining second order. A strong field untwists the helix in the C^* phase [on account of the quadratic interaction; this process corresponds to a first-order transition (the solid curve in Fig. 26b)]. In fields exceeding the critical field the transition from the homogeneous C phase to the A phase is, as before, a second-order transition. Consequently, there is a triple point T_L where the lines of the first-order and second-order transitions come together. In the present case we are dealing with a special variety of triple point, separating disordered phase (A, with $\theta_0 = 0$), a homogeneously ordered phase (C, with $\theta_0 = \text{const}$, $\varphi = \text{const}$), and a spatially modulated phase (C^* , with $\theta_0 = \text{const}$, $\varphi = q_0 z$). Such a triple point is called a Lifshitz point. According to Ref. 116,

$$T_L = T_{C^*A} + 3\Delta T.$$

A Lifshitz point is also expected to occur in the case of a high-frequency ($\omega \gg \tau_1^{-1}$) electric field interacting with the molecular orientation through the dielectric anisotropy (energy $\sim \Delta\epsilon E^2$).

The main features of the phase diagrams shown in Fig. 26a, b agree with those of the experimental diagrams obtained in Refs. 128 and 117. However, in both cases an inverse transition to a twisted (though deformed) C^* phase is observed at certain values of the fields E and H . A theoretical approach to this phenomenon was developed in Ref. 129.

Still another interesting effect due to the joint action of a static electric field and a magnetic field was predicted theoretically in Ref. 118. If the fields E and H act along the normal (z) to the smectic layers of an A phase formed by molecules having reflection symmetry, then the E field removes the mirror plane parallel to xy and the H field removes the other mirror plane, parallel to z . As a result, the symmetry of the phase is lowered from D_∞ to C_∞ . As the temperature is lowered the new phase should undergo a transition to a helical structure having a wave vector proportional to the product EH .

e) Thermal effects and flow-induced polarization

The heating or cooling of a chiral smectic C^* phase leads to a change in the magnitude of the spontaneous polarization; such a change can be detected by measuring the current in an external circuit. This (pyroelectric) effect, which was first observed in ferroelectric liquid crystals by Yu *et al.*,¹¹⁹ is characterized by a pyroelectric coefficient $\gamma \equiv dP/dT$. The pyroelectric coefficient has a maximum near the phase transition temperature (see Figs. 15 and 17) and can reach a value⁵⁴ of $6 \cdot 10^{-5}$ C/m²K, a typical value for solid film pyroelectrics. Allakhverdiv *et al.*¹²⁰ observed the inverse pyroelectric effect, i.e., the evolution of heat when an electric field is applied to a ferroelectric liquid crystal. The size of this (electrocaloric) effect depends on the temperature and can be used to calculate the pyroelectric coefficient and, thence, the spontaneous polarization.

The nonzero value of the sample-averaged polarization of a twisted smectic C^* phase can also be obtained by deforming the helical structure by a shear flow.^{82,121,122} In the initial state the smectic layers (xy planes) are parallel to the bounding surfaces, and the liquid crystal forms an optically active planar texture with helical axis parallel to z . Motion of the upper plate relative to the lower plate along the y axis deforms the helix and gives rise to a voltage along the x axis. The value of this voltage can be used to calculate the spontaneous polarization. The values of P obtained for DO-BAMBC and HOBACPC ($6 \cdot 10^{-5}$ and 10^{-4} C/m², respectively; Ref. 122) are in agreement with the values obtained by the pyroelectric method ($4 \cdot 10^{-5}$ and $1.5 \cdot 10^{-4}$ C/m², respectively; Refs. 49 and 64). This is yet another piece of evidence that the flexoelectric contribution to P is not the predominant one, since the measurements of Ref. 122 were made on a slightly deformed helical structure which would still support a flexoelectric effect.

The values of some of the physical parameters of DO-

BAMBC at temperature $T_{CA} - T = 5$ K ($\approx 87^\circ\text{C}$) are: $\mu_p = (4-5) \cdot 10^{-4}$ C/m², $\mu_t \approx 0.6 \cdot 10^{-10}$ C/m, $|\lambda_o| = 6 \cdot 10^{-5}$ J/m², $\chi_\perp = 0.23$, $K = (5-7) \cdot 10^{11}$ N, $q_c \sim 3 \cdot 10^6$ m⁻¹, $a' = 10^3$ J·m³/K, $\gamma = 3 \cdot 10^{-3}$ Pa·sec.

7. CONCLUSION. POSSIBLE PRACTICAL APPLICATIONS OF LIQUID-CRYSTAL FERROELECTRICS

In summing up, one can say that the most important features of the ferroelectric state in liquid crystals are at the present time satisfactorily explained by both the phenomenological and microscopic theories. The bulk of the experimental data is for the rather high-temperature smectic C* phases of the compounds DOBAMBC and HOBACPC, although fundamentally new results (Sec. 5) have recently been obtained for low-temperature mixtures as well. There is very little information in the literature for other ferroelectric phases (H*, G*, etc.).

Of greatest interest from a practical standpoint are the electrooptic properties of the smectic C* phases. In comparison with the now traditional nematic materials, smectics C* provide a fundamentally faster response (response times of milliseconds and microseconds over a wide range of temperatures, including room temperature^{113,114}). The fast response make these materials promising candidates for use in a wide variety of devices for controlling light beams, e.g., optical shutters and light modulators, controlled transparencies in optical information-processing systems, matrix displays, flat television screens, etc. The wide exploitation of ferroelectric liquid crystals is being held back by the inadequate selection of materials and the underdeveloped technology for fabricating optically homogeneous liquid-crystal layers.

The use of ferroelectric liquid crystals as media for pyroelectric and piezoelectric elements, i.e., in the traditional sphere of application of ferroelectrics, is also of great interest, since liquid-crystal (for practical purposes, liquid) media permit the fabrication of rather sizable devices of arbitrary shape. At the present time, however, there is no information on the use of ferroelectric liquid crystals in devices of this sort.

The second-order phase transitions between the chiral smectic C* and homogeneous smectic A* phases exhibit almost no latent heat of transition. This circumstance makes smectic C* materials promising for use in devices for visualizing thermal effects. This principle has been used, for example, in the recording of information by a heating laser beam,^{123,124} which is of interest in creating peripheral devices for computers (plotters, for example). The shift of the temperature of the ferroelectric phase transition as a function of impurity concentration may be used to detect radiolysis products and, consequently, to construct detectors of ionizing radiation.

Finally, the absence of a center of inversion in liquid crystal ferroelectrics makes these materials extremely promising for us in nonlinear-optics devices. These materials feature a high radiation resistance, since light-induced defects in liquid-crystal media tend to heal up.

In conclusion, the achievements to date in the physics of liquid-crystal ferroelectrics permit a very optimistic view of

the prospects for exploiting the properties of these materials in modern technology.

- ¹V. G. Vaks, *Vvedenie v mikroskopicheskuyu teoriyu segnetoelektrikov* [Introduction to the Microscopic Theory of Ferroelectrics], Nauka, Moscow (1973).
- ²I. S. Zheludev, *Osnovy segnetoelektricheskosti* [Principles of Ferroelectricity], Nauka, Moscow (1973).
- ³R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics*, North-Holland, Amsterdam (1974).
- ⁴M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford (1977).
- ⁵P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1974).
- ⁶L. M. Blinov, *Elektro- i magnitooptika zhidkikh kristallov*, Nauka, Moscow (1978) [Electro-Optical and Magneto-Optical Properties of Liquid Crystals, Wiley, New York (1983)].
- ⁷S. Chandrasekhar, *Liquid Crystals*, Cambridge Univ. Press (1977).
- ⁸S. A. Pikin, *Strukturnye prevrashcheniya v zhidkikh kristallakh* [Structural Transformations in Liquid Crystals], Nauka, Moscow (1981).
- ⁹S. A. Pikin and L. M. Blinov, *Zhidkie kristally* [Liquid Crystals], Nauka, Moscow (1982).
- ¹⁰R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris) Lett.* **36**, L-69 (1975).
- ¹¹R. B. Meyer, *Mol. Cryst. Liq. Cryst.* **40**, 33 (1977).
- ¹²S. A. Pikin and V. L. Indenbom, *Usp. Fiz. Nauk* **125**, 251 (1978) [Sov. Phys. Usp. **21**, 487 (1978)].
- ¹³M. A. Osipov, Author's abstract of candidate's dissertation, Moscow State University (1982).
- ¹⁴G. Durand and Ph. Martinot-Lagarde, *Ferroelectrics* **24**, 89 (1980).
- ¹⁵A. P. Levanyuk and D. G. Sannikov, *Usp. Fiz. Nauk* **112**, 561 (1974) [Sov. Phys. Usp. **17**, 199 (1974)].
- ¹⁶A. G. Khachatryan, *Phys. Lett.* **51**, 103 (1975); *J. Phys. Chem. Solids* **36**, 1055 (1975).
- ¹⁷G. A. Lyakhov and Yu. P. Svirko, *Zh. Eksp. Teor. Fiz.* **80**, 1307 (1981) [Sov. Phys. JETP **53**, 669 (1981)].
- ¹⁸N. M. Shtykov, L. M. Blinov, A. M. Dorozhkin, and M. I. Barnik, *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 142 (1982) [JETP Lett. **35**, 171 (1982)].
- ¹⁹R. Blinc, A. Levstik, I. Musevic, J. Pirs, and B. Zeks, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 1, Tbilisi (1981), p. 143.
- ²⁰L. D. Landau and E. M. Lifshitz, *Statisticheskaya Fizika*, 2nd ed., Nauka, Moscow (1964) [Engl. Transl. Statistical Physics, Pergamon Press, Oxford (1966)], Sec. 139.
- ²¹V. L. Ginzburg, *Usp. Fiz. Nauk* **38**, 490 (1949); *Fiz. Tverd. Tela* (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1961)].
- ²²R. Blinc, *Ferroelectrics* **14**, 603 (1976).
- ²³V. L. Indenbom, S. A. Pikin, and E. B. Loginov, *Kristallografiya* **21**, 1093 (1976) [Sov. Phys. Crystallogr. **21**, 632 (1976)].
- ²⁴A. Michelson, L. Benguigui, and D. Cabib, *Phys. Rev.* **16**, 394 (1977).
- ²⁵S. Trimper, *Phys. Status Solidi B* **82**, K75 (1977).
- ²⁶S. A. Pikin and K. Yoshino, *Jpn. J. Appl. Phys.* **20**, L557 (1981).
- ²⁷R. Blinc, *Phys. Status Solidi B* **70**, K29 (1975).
- ²⁸E. M. Lifshitz and L. P. Pitaevskii, *Fizicheskaya Kinetika*, Nauka, M., 1979 [Physical Kinetics, Pergamon Press, Oxford (1981)], Sec. 101.
- ²⁹R. Blinc and B. Zeks, *Phys. Rev. A* **18**, 740 (1979).
- ³⁰M. A. Osipov and S. A. Pikin, *Kristallografiya* **26**, 263 (1981) [Sov. Phys. Crystallogr. **26**, 147 (1981)].
- ³¹M. A. Osipov and S. A. Pikin, *Zh. Tekh. Fiz.* **52**, 158 (1982) [Sov. Phys. Tech. Phys. **27**, 109 (1982)].
- ³²M. A. Osipov and S. A. Pikin, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 1, Tbilisi (1981), p. 147.
- ³³B. W. van der Meer and G. Vertogen, *J. Phys. (Paris)* **40**, Colloq. C3-222 (1979).
- ³⁴J. Seliger, V. Sagar, and R. Blinc, *Phys. Rev. A* **17**, 1149 (1978).
- ³⁵B. W. van der Meer and G. Vertogen, *Phys. Lett. A* **74**, 239 (1979).
- ³⁶G. W. Smith and Z. G. Garland, *J. Chem. Phys.* **59**, 3214 (1973).
- ³⁷B. I. Ostrovskii, S. A. Taraskin, B. A. Strukov, A. Z. Rabinovich, A. S. Sonin, and N. I. Chernova, *Fiz. Tverd. Tela* (Leningrad) **19**, 3686 (1977) [Sov. Phys. Solid State **19**, 2153 (1977)].
- ³⁸B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and S. A. Taraskin, *Ferroelectrics* **20**, 189 (1978).
- ³⁹B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, and E. L. Sorkin, *Ferroelectrics* **24**, 309 (1980).
- ⁴⁰R. Wise, D. Smith, and W. Doane, *Phys. Rev. A* **7**, 1366 (1973).

- ⁴¹T. R. Taylor, J. L. Fergason, and S. L. Arora, *Phys. Rev. Lett.* **25**, 722 (1970).
- ⁴²R. Bartolino, J. Doucet, and G. Durand, *Ann. Phys. (Paris)* **3**, 389 (1978).
- ⁴³A. Wulf, *Mol. Cryst. Liq. Cryst.* **56**, 123 (1979).
- ⁴⁴M. V. Loseva, B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova, *Pis'ma Zh. Eksp. Teor. Fiz.* **28**, 404 (1978) [*JETP Lett.* **28**, 374 (1978)].
- ⁴⁵N. N. Shereshovets, A. I. Komyak, and A. A. Min'ko, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 2, Tbilisi (1981), p. 123.
- ⁴⁶B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova, *Pis'ma Zh. Eksp. Teor. Fiz.* **25**, 80 (1977) [*JETP Lett.* **25**, 70 (1977)].
- ⁴⁷L. A. Beresnev, L. M. Blinov, and Z. M. Elashvili, *Pis'ma Zh. Tekh. Fiz.* **4**, 225, 931 (1978) [*Tech. Phys. Lett.* **4**, 92 (1978)].
- ⁴⁸L. A. Beresnev, L. M. Blinov, E. B. Sokolova, *Pis'ma Zh. Eksp. Teor. Fiz.* **28**, 340 (1978) [*JETP Lett.* **28**, 314 (1978)].
- ⁴⁹L. A. Beresnev and L. M. Blinov, *Ferroelectrics* **33**, 129 (1981).
- ⁵⁰Ph. Martinot-Lagarde, *J. Phys. (Paris)* **38**, L17 (1977).
- ⁵¹B. I. Ostrovskii, S. A. Pikin, and B. G. Chigrinov, *Zh. Eksp. Teor. Fiz.* **77**, 1615 (1979) [*Sov. Phys. JETP* **50**, 811 (1979)].
- ⁵²S. Garoff and R. B. Meyer, *Phys. Rev. Lett.* **38**, 848 (1977); *Phys. Rev. A* **19**, 338 (1979).
- ⁵³H. Takezoe, K. Furuhashi, T. Nakagiri, A. Fukuda, and E. Kuze, *J. Appl. Phys.* **17**, 1219 (1978).
- ⁵⁴L. A. Beresnev, L. M. Blinov, and G. B. Purvanetskias, *Pis'ma Zh. Eksp. Teor. Fiz.* **31**, 37 (1980) [*JETP Lett.* **31**, 34 (1980)].
- ⁵⁵J. Doucet, P. Keller, A. M. Levelut, and P. Porquet, *J. Phys. (Paris)* **39**, 548 (1978).
- ⁵⁶G. S. Chilaya, and L. N. Lisetskii, *Usp. Fiz. Nauk* **134**, 279 (1981) [*Sov. Phys. Usp.* **24**, 496 (1981)].
- ⁵⁷M. A. Osipov and S. A. Pikin, *Zh. Eksp. Teor. Fiz.* **80**, 2380 (1981); **82**, 774 (1982) [*Sov. Phys. JETP* **53**, 1245 (1981); **55**, 458 (1982)].
- ⁵⁸R. B. Meyer, *Phys. Rev. Lett.* **22**, 918 (1969).
- ⁵⁹J. Prost and J. P. Marcerou, *J. Phys. (Paris)* **38**, 315 (1977).
- ⁶⁰B. W. van der Meer and G. Vertogen, *Phys. Lett. A* **74**, 239 (1979).
- ⁶¹R. A. Pelcovits and B. I. Halperin, *Phys. Lett. B* **19**, 4614 (1979).
- ⁶²G. W. Gray and J. W. Goodby, *Ann. Phys. (Paris)* **3**, 123 (1978).
- ⁶³W. H. de Jeu, *J. Phys. (Paris)* **38**, 1265 (1977).
- ⁶⁴L. M. Blinov, L. A. Beresnev, N. M. Shtykov, and Z. M. Elashvili, *J. Phys. (Paris)* **40**, Colloq. C3-269 (1979).
- ⁶⁵L. A. Beresnev, L. M. Blinov, V. A. Baikalov, E. P. Pozhidayev, G. V. Purvanetskias, and A. I. Pavluchenko, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 2, Tbilisi (1981), p. 28; *Mol. Cryst. Liq. Cryst.* **89**, 327 (1982).
- ⁶⁶Ph. Martinot-Lagarde, *J. Phys. (Paris)* **37**, Colloq. C3-129 (1976).
- ⁶⁷M. V. Loseva, B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, and N. I. Chernova, *Fiz. Tverd. Tela (Leningrad)* **22**, 938 (1980) [*Sov. Phys. Solid State* **22**, 551 (1980)].
- ⁶⁸G. W. Gray, *Mol. Cryst. Liq. Cryst.* **63**, 3 (1981).
- ⁶⁹D. F. Aliev and M. A. Aslanov, *Fiz. Tverd. Tela (Leningrad)* **23**, 3712 (1981) [*Sov. Phys. Solid State* **23**, 2160 (1981)].
- ⁷⁰W. Kuczynski and H. Stegemeyer, *Chem. Phys. Lett.* **70**, 123 (1980).
- ⁷¹L. A. Beresnev, E. P. Pozhidayev, L. M. Blinov, A. I. Pavluchenko, and N. B. Étingen, *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 430 (1982) [*JETP Lett.* **35**, 531 (1982)].
- ⁷²H. Matsumura, *Mol. Cryst. Liq. Cryst.* **49**, 105 (1978).
- ⁷³L. A. Beresnev, B. A. Baikalov, L. M. Blinov, E. P. Pozhidayev, and G. V. Purvanetskias, *Pis'ma Zh. Eksp. Teor. Fiz.* **33**, 553 (1981) [*JETP Lett.* **33**, 536 (1981)].
- ⁷⁴I. G. Chistyakov, L. S. Shabyshev, R. I. Jarenov, and L. A. Gusakova, in: *Liquid Crystals* (ed. by G. H. Brown), Part II, Gordon and Breach, London (1969), p. 813.
- ⁷⁵L. Benguigui and F. Hardouin, *J. Phys. (Paris)* **42**, Lett. L-381 (1981).
- ⁷⁶S. B. Lang, *Ferroelectrics* **34**, 3 (1981).
- ⁷⁷V. G. Ivkov and G. N. Berestovskii, *Dinamicheskaya struktura lipidnogo bisloya* [Dynamic Structure of Lipid Bilayers], Nauka, Moscow (1981).
- ⁷⁸L. A. Beresnev, L. M. Blinov, and E. I. Kovshev, *Dokl. Akad. Nauk SSSR* **265**, 210 (1982).
- ⁷⁹R. Pindak, R. Pelkovits, and R. B. Meyer, *Bull. Am. Phys. Soc.* **23**, 353 (1978).
- ⁸⁰C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978); C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).
- ⁸¹R. Pindak, C. Y. Young, R. B. Meyer, and N. A. Clark, *Phys. Rev. Lett.* **45**, 1193 (1980).
- ⁸²P. Pieranski, E. Guyon, P. Keller, L. Liebert, and M. Kuczynski, *Mol. Cryst. Liq. Cryst.* **38**, 633 (1977).
- ⁸³D. Berreman, *Mol. Cryst. Liq. Cryst.* **22**, 175 (1973).
- ⁸⁴V. A. Belyakov, V. E. Dmitrienko, and V. P. Orlov, *Usp. Fiz. Nauk* **127**, 221 (1979) [*Sov. Phys. Usp.* **22**, 63 (1979)].
- ⁸⁵O. Parodi, *J. Phys. (Paris)* **36**, Colloq. C1-325 (1975).
- ⁸⁶D. Taupin, E. Guyon, and P. Pieranski, *J. Phys. (Paris)* **39**, 406 (1978).
- ⁸⁷G. S. Chilaya, S. N. Aronishidze, and M. N. Kushnirenko, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 1, Tbilisi (1981), p. 382.
- ⁸⁸S. N. Aronishidze, M. N. Kushnirenko, and S. G. Chilaya, *Zh. Tekh. Fiz.* **52**, 157 (1982) [*Sov. Phys. Tech. Phys.* **27**, 107 (1982)].
- ⁸⁹G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.* **37**, 189 (1976).
- ⁹⁰M. Brunet and C. Williams, *Ann. Phys. (Paris)* **3**, 237 (1978).
- ⁹¹M. Brunet and O. Parodi, *J. Phys. (Paris)* **43**, 515 (1982).
- ⁹²A. Perez, M. Brunet, and O. Parodi, *J. Phys. (Paris)* **42**, 1559 (1981).
- ⁹³A. Garoff, R. B. Meyer, and R. Barakat, *J. Opt. Soc. Am.* **68**, 1217 (1978).
- ⁹⁴A. N. Vtyupin, V. P. Ermakov, B. I. Ostrovski, and V. G. Shabanov, *Phys. Status Solidi B* **107**, 397 (1981).
- ⁹⁵L. M. Blinov, *Usp. Fiz. Nauk* **114**, 67 (1974) [*Sov. Phys. Usp.* **17**, 658 (1975)].
- ⁹⁶I. G. Chistyakov, L. K. Vistin, Z. B. Rajabova, and S. P. Chumakova, in: *Advances in Liquid Crystals: Research and Applications* (ed. by L. Bata), Pergamon Press; Akademiai Kiadó, Budapest (1980), p. 493.
- ⁹⁷K. Kondo, Y. Sato, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.* **20**, L871 (1981).
- ⁹⁸S. A. Pikin, *Mol. Cryst. Liq. Cryst.* **63**, 181 (1981).
- ⁹⁹Ph. Martinot-Lagarde and G. Durand, *J. Phys. (Paris)* **41**, Lett. L-43 (1980).
- ¹⁰⁰B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, and B. A. Strukov, *Zh. Eksp. Teor. Fiz.* **74**, 1748 (1978) [*Sov. Phys. JETP* **47**, 912 (1978)].
- ¹⁰¹A. Levstik, B. Zeks, I. Levstik, R. Blinc, C. Filipic, *J. Phys. (Paris)* **40**, Colloq. C3-303 (1979).
- ¹⁰²J. Hoffmann, W. Kuczynski, and J. Malecki, *Mol. Cryst. Liq. Cryst.* **44**, 287 (1978).
- ¹⁰³D. S. Parmar and Ph. Martinot-Lagarde, *Ann. Phys. (Paris)* **3**, 275 (1978).
- ¹⁰⁴K. Yoshino, T. Uemoto, and Y. Inuishi, *Jpn. J. Appl. Phys.* **16**, 571 (1977).
- ¹⁰⁵V. E. Dmitrienko and V. A. Belyakov, *Zh. Eksp. Teor. Fiz.* **78**, 1568 (1980) [*Sov. Phys. JETP* **51**, 787 (1980)]; *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 1, Tbilisi (1981), p. 417.
- ¹⁰⁶B. I. Ostrovski, A. Z. Rabinovich, and V. G. Chigrinov, in: *Advances in Liquid Crystals: Research and Applications* (ed. by L. Bata), Pergamon Press; Akademiai Kiadó, Budapest (1980), p. 469.
- ¹⁰⁷B. I. Ostrovskii and V. G. Chigrinov, *Kristallografiya* **25**, 560 (1980) [*Sov. Phys. Crystallogr.* **25**, 322 (1980)].
- ¹⁰⁸B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, and B. A. Strukov, *Fiz. Tverd. Tela (Leningrad)* **21**, 917 (1979) [*Sov. Phys. Solid State* **21**, 537 (1979)].
- ¹⁰⁹K. Yoshino, T. Uemoto, K. G. Balakrishnan, S. Yanagida, and Y. Inuishi, *Tech. Rep. Osaka Univ.* **27**, 427 (1977).
- ¹¹⁰L. K. Vistin, S. P. Chumakova, and Z. B. Rajabova, in: *Advances in Liquid Crystals: Research and Applications* (ed. by L. Bata), Pergamon Press; Akademiai Kiadó, Budapest (1980), p. 483.
- ¹¹¹I. G. Chistyakov, L. K. Vistin, S. P. Chumakova, and Z. B. Radzhabova, *Kristallografiya* **25**, 643 (1980) [*Sov. Phys. Crystallogr.* **25**, 372 (1980)].
- ¹¹²L. M. Blinov, *J. Phys. (Paris)* **41**, Colloq. C1-417 (1979).
- ¹¹³N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
- ¹¹⁴L. A. Beresnev, V. A. Baikalov, and L. M. Blinov, *Zh. Tekh. Fiz.* **52**, 2109 (1982) [*Sov. Phys. Tech. Phys.* **27**, 1296 (1982)].
- ¹¹⁵A. Michelson and D. Cabib, *J. Phys. (Paris)* **38**, Lett. L-321 (1977).
- ¹¹⁶A. Michelson, *Phys. Rev. Lett.* **39**, 464 (1977).
- ¹¹⁷I. Mušević, B. Žekš, R. Blinc, Th. Rasing, and P. Wyder, *Phys. Rev. Lett.* **48**, 192 (1982).
- ¹¹⁸A. Michelson, *Phys. Lett. A* **60**, 29 (1977).
- ¹¹⁹L. J. Yu, H. Lee, C. S. Bak, and M. M. Labes, *Phys. Rev. Lett.* **36**, 388 (1976).
- ¹²⁰G. R. Allakhverdov, I. A. Kleinman, and A. Z. Rabinovich, *Fourth International Conference of Socialist Countries on Liquid Crystals*, Vol. 2, Tbilisi (1981), p. 14.
- ¹²¹P. Pieranski, E. Guyon, and P. Keller, *J. Phys. (Paris)* **36**, 1005 (1975).
- ¹²²L. Petit, P. Pieranski, and E. Guyon, *C. R. Acad. Sci. B* **284**, 535 (1977).

- ¹²³A. N. Nesrullaev, A. Z. Rabinovich, and A. S. Sonin, *Zh. Tekh. Fiz.* **50**, 2468 (1980) [*Sov. Phys. Tech. Phys.* **25**, 1445 (1980)].
- ¹²⁴A. N. Nesrullaev, A. Z. Rabinovich, and A. S. Sonin, E. B. Shelepin, *Kvantovaya Electron. (Moscow)* **7**, 2578 (1980) [*Sov. J. Quantum Electron.* **10**, 1505 (1980)].
- ¹²⁵S. G. Galaktionov, *Asimmetriya biologicheskikh molekul* [Asymmetry of Biological Molecules], Vysheishaya Shkola, Minsk (1978); V. A. Kizel', *Usp. Fiz. Nauk* **131**, 209 (1980) [*Sov. Phys. Usp.* **23**, 277 (1980)].
- ¹²⁶M. I. Barnik, L. A. Beresnev, L. M. Blinov, and N. M. Shtykov, *Proc. Fifth International Conf. of Socialist Countries on Liquid Crystals*, Vol. 1, Part 2, Odessa (1983), p. 24.
- ¹²⁷L. A. Beresnev, B. A. Baikalov, and L. M. Blinov, *Proc. Fifth International Conf. of Socialist Countries on Liquid Crystals*, Vol. 2, Part 1, Odessa (1983), p. 7.
- ¹²⁸K. Kondo, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L-43 (1983).
- ¹²⁹M. Yamashita and H. Kimura, *J. Phys. Soc. Jpn.* **52**, 1509 (1983).

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