Flexoelectric effect and polarization properties of chiral smectic *C* liquid crystal

B. I. Ostrovskiĭ, S. A. Pikin, and V. G. Chigrinov

Crystallography Institute, USSR Academy of Sciences
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We investigate the role of piezoelectric and flexoelectric phenomena that occur in chiral smectic *C* liquid crystals ($\tilde{C}$). It is shown that the distortion of the helicoidal oreintational structure of $\tilde{C}$ by an electric field is due to periodic perturbations of the distribution of both the azimuthal angle $\varphi(z)$ and the inclination angle $\Theta = \Theta_0 + \Theta_1(z;E)$ of the molecules relative to the normal to the smectic layers. The spatial distributions of $\varphi(z)$ and $\varphi_1(z)$ in fields $0 < E < E_u$ (E_u is the untwisting field of the $\tilde{C}$ helix) and the ensuing dependences of the macroscopic polarization $\langle P \rangle$ on the field were obtained by numerical means. It follows from the calculations that spatial modulation of the angle $\Theta_1(z)$ at $E < E_u$ together with the flexoelectric effect lead to appreciable changes of $\langle P \rangle$ compared with the mean value $\langle \cos\varphi(z;E) \rangle$. An attempt is made to estimate the principal material constants of the *C* phase of the liquid crystal DOBAMBC (*d*-*p*-decyloxybenzilidine-*p*′-amino-2-methylbutyl-cinnamate) from a comparison of the experimental and theoretical results on the behavior of the $\tilde{C}$ phase near its point of transition into the chiral smectic *A* phase. The influence of the boundary conditions on the properties of the $\tilde{C}$ phase is considered.

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1. INTRODUCTION

It is known that an electric field produces in liquid crystals flexoelectric deformations that lead to the appearance of a macroscopic polarization due to the fact that molecules with anisotropic shape have a dipole moment.[1-3] These properties are possessed by nematic as well as smectic phases, and in the case of the chiral smectic-*C* liquid crystals ($\tilde{C}$) the flexoeffect connected with the spontaneous orientational deformation $d\varphi/dz = q$ makes a definite contribution to the spontaneous polarization of the material.[3] In the absence of an electric field **E** the polarization in the $\tilde{C}$ phase, averaged over the volume, is zero. When an field **E** is applied a macroscopic polarization is produced in the plane of the smectic layer and is proportional to the applied field. The macroscopic polarization $\langle P \rangle$ in the $\tilde{C}$ phase is due to distortions of the helicoidal orientational structure produced by both the piezoeffect and the flexoeffect. A distinction must be made here between two types of distortion. The first is due to perturbation of the distribution of the azimuthal angle $\varphi(z) - \varphi_0(z)$ [$\varphi_0(z) = q_0 z$] at a uniform distribution of the angle of inclination θ_0 of the molecules relative to the crystal axis z. The second is due to the periodic perturbation $\theta_1(z)$ of the inclination angle $\theta = \theta_0 + \theta_1(z)$ with the period (pitch) $p = 2\pi/q$ unperturbed. Obviously, this distinction between the distortions is meaningful only if they are small.

The contribution of the distortions of the first type and of the corresponding piezoelectric effect to the dielectric susceptibility was considered in preceding papers.[3,4] We note that, owing to the piezoeffect, the deformations of the second type also contribute to the value of χ in the $\tilde{C}$ phase. The flexoeffect can cause macroscopic polarization of the $\tilde{C}$ phase only if periodic deformations of the second type are caused by the field. Physically the situation here is similar to the flexoeffect in a nematic crystal, where the modulated orientational structure contains two types of distortion: $\varphi(z)$ and $\theta(z)$.[2] In the present paper we investigate the roles of the piezo- and flexoeffects in the polarization phenomena that occur in chiral smectic liquid crystals, and attempt to estimate the fundamental parameters of these substances on the basis of a comparison of the theoretical results and the experimental data on the behavior of *C* near the point of the phase transition of *C* into the chiral smectic *A* phase (A^*).[5,6]

2. BEHAVIOR OF HELICOIDAL STRUCTURE IN ELECTRIC FIELD

The polarization properties of *C* near the phase transition point are described within the framework of the phenomenological theory of ferroelectricity of this phase in Refs. 3 and 4. According to this theory the density of the free energy F in an electric field **E** is given by

$$F = a\theta^2 + b\theta^4 + \frac{1}{2} g \left(\frac{\partial\theta}{\partial z}\right)^2 + \frac{1}{2} K\theta^2 \left(\frac{\partial\varphi}{\partial z}\right)^2 + \lambda\theta^2 \frac{\partial\varphi}{\partial z} + \frac{1}{2\chi}(P_x^2 + P_y^2) - (P_x \sin\varphi - P_y \cos\varphi)\left(\mu_1 - \mu_2 \frac{\partial\varphi}{\partial z}\right)\theta - \mathbf{PE}, \quad (1)$$

where $a = a'(T - T_0)$; $b > 0$; K and g are the elastic moduli; χ is the dielectric susceptibility and is assumed here to be isotropic; μ_1 and μ_2 are the piezoelectric moduli, and λ is the chirality parameter, which is usually small and can also expressed as a series in powers of $\theta^2 \ll 1 : \lambda = \lambda_0 + \lambda'\theta^2 + \ldots$.

The ferroelectric phase $\tilde{C}$ is characterized by a finite inclination of the director by an angle θ to the crystal z axis and by a helicoidal twisting of the polarization P around the z axis, corresponding to an inhomogeneous distribution of the components of the transition parameter

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$\xi_1 = {}^1/_2 \sin 2\theta \cos\varphi, \quad \xi_2 = {}^1/_2 \sin 2\theta \sin\varphi.$

At $E=0$ it follows from (1) that the minimum free energy corresponds to the distributions $\theta(z)=\text{const}$, $\varphi(z) = \varphi_0(z) = q_0(z)$, where $2\pi/q_0$ is the pitch of the helicoid and depends in general on the temperature:

$$q_0 = q_c + q'\theta^2 + q''\theta^4 + \ldots, \quad q_c = -(\lambda_0 + \chi\mu_1\mu_2)/\tilde{K}, \quad \tilde{K} = K - \chi\mu_2^2. \tag{2}$$

The phase-transition point T_c corresponds to vanishing of the coefficient

$$\tilde{a} = a - {}^1/_2\chi\mu_1^2 - {}^1/_2\tilde{K}q_c^2, \tag{3}$$

of the angle θ, and of the polarization P.

At $\mathbf{E} \neq 0$ we have $\varphi(z) \neq \varphi_0(z)$ and $\theta(z) \neq \text{const}$, if the modulus $g \neq \infty$. Assuming that the electric field $\mathbf{E}$ is parallel to the y axis, we obtain by minimizing F with respect to P_x and P_y

$$P_x = \chi\theta\left(\mu_1 - \mu_2\frac{\partial\varphi}{\partial z}\right)\sin\varphi, \quad P_y = \chi E - \chi\theta\left(\mu_1 - \mu_2\frac{\partial\varphi}{\partial z}\right)\cos\varphi. \tag{4}$$

Substituting (4) in (1) and minimizing F with respect to $\varphi(z)$ and $\theta(z)$, we arrive at the following system of equations for φ and θ:

$$\begin{gathered}\tilde{K}\theta_0^2\frac{\partial^2\varphi}{\partial z^2} + \chi E\left(\mu_1\theta_0\sin\varphi - \mu_2\frac{\partial\theta_1}{\partial z}\cos\varphi\right) = 0,\\ -4\tilde{a}\theta_1 - g\frac{\partial^2\theta_1}{\partial z^2} + \tilde{K}\theta_0\left(\frac{\partial\varphi}{\partial z} - q_0\right)^2 + \chi E\left(\mu_1 - \mu_2\frac{\partial\varphi}{\partial z}\right)\cos\varphi = 0,\end{gathered} \tag{5}$$

where

$$\theta = \theta_0 + \theta_1, \quad 2\tilde{a} + 4b\theta_0^2 = 0, \quad |\theta_1| \ll \theta_0.$$

Since the value of the untwisting field of the helicoid $[\varphi(z) = \text{const}]$ is of the order of $E_u \sim K\theta_0 q_0^2/\chi\mu_1$, we get at $E \approx E_u$ the value $\theta_1 \sim \tilde{K}q_0^2\theta_0/|\tilde{a}|$ in the $\tilde{C}$ phase. Therefore if the inequality

$$\frac{\mu_2 q_0}{\mu_1}\frac{q_0^2\tilde{K}}{|\tilde{a}|} \ll 1$$

is satisfied we can write Eqs. (5), at all fields up to $E \approx E_u$ in the simplified form:

$$\begin{gathered}\tilde{K}\theta_0^2\frac{\partial^2\varphi}{\partial z^2} + \chi E\mu_1\theta_0\sin\varphi = 0,\\ 4\tilde{a}\theta_1 + g\frac{\partial^2\theta_1}{\partial z^2} - \chi E\left(\mu_1 - \mu_2\frac{\partial\varphi}{\partial z}\right)\cos\varphi = 0.\end{gathered} \tag{6}$$

At $E \ll E_u$ Eqs. (6) are valid at all values of the parameters.

The first equation of (6) describes the distortion of the helicoid in the electric field, with $\varphi(z) = \varphi_0(z)$ at $E=0$. This problem is similar to that of the deformation of the cholesteric helix.[7] Using the known solution, we get

$$E_p = \frac{\pi^2}{16}\frac{q_0^2\tilde{K}\theta_0}{\chi\mu_1}. \tag{7}$$

The intermediate distributions of $\varphi(z)$ at $0 < E < E_u$ were obtained in the present study numerically. Substituting the function $\varphi(z)$ obtained in this manner in the second equation of (6) we can find the particular solution $\theta_1(z)$ in the form

$$\theta_1(z) = \frac{1}{2}\left(-\frac{g}{\tilde{a}}\right)^{1/2}\chi E\int_0^z\left(\mu_1 - \mu_2\frac{\partial\varphi}{\partial u}\right)\cos\varphi \operatorname{sh} 2\left(-\frac{\tilde{a}}{g}\right)^{1/2}(z-u)\,du, \tag{8}$$

where $\tilde{a} < 0$ at $T < T_c$. To obtain a periodic solution $\theta_1(z)$ having the period of the inhomogeneous part of the second equation of (6) we must add to (8) the corresponding solutions of the homogeneous part of this equation, i.e., the functions

$$C_\pm \exp\left[\pm 2(-\tilde{a}/g)^{1/2}z\right].$$

At $E \ll E_u$ the periodic solution $\theta_1(z)$ takes the form

$$\theta_1(z) = \frac{\chi E(\mu_1 - \mu_2 q_0)}{4\tilde{a} - gq_0^2}\cos q_0 z, \tag{9}$$

and the function $\varphi(z)$ is given by[7]

$$\varphi(z) = q_0 z + \frac{\chi\mu_1 E}{\tilde{K}q_0^2\theta}\sin q_0 z. \tag{10}$$

With the aid of (4), (9), and (10) we obtain the macroscopic mean polarizations $\langle P_y\rangle$ at $T < T_c$:

$$\langle P_y\rangle = (\chi + \delta\chi)E, \quad \delta\chi = \frac{\chi^2}{2}\left[\frac{\mu_1^2}{\tilde{K}q_0^2} + \frac{(\mu_1 - \mu_2 q_0)^2}{gq_0^2 - 4\tilde{a}}\right]. \tag{11}$$

We note that at $T > T_c$ the value of $\delta\chi$ is[3]

$$\delta\chi = \chi^2\mu_1^2/(\tilde{K}q_c^2 + 2\tilde{a}). \tag{12}$$

At $E \approx E_u$ it is convenient to seek the solution $\theta(z)$ in the form

$$\theta = \theta_0(T)[1 + \eta(z;E)], \quad |\eta| = |\theta_1/\theta_0| \ll 1.$$

The function $\eta(z;E)$ is the periodic solution of the equation

$$g\frac{d^2\eta}{dz^2} + A\eta = \frac{\chi E}{\theta_0}\left(\mu_1 - \mu_2\frac{d\varphi}{dz}\right)\cos\varphi, \quad A = -4\tilde{a}. \tag{13}$$

Changing to the dimensionless variables

$$\begin{gathered}x = z/p, \quad r = g/\tilde{K}, \quad S^2 = 4\pi^2\varkappa^2 A/gq_0^2 > 0,\\ h = \mu_2 q_0/\mu_1, \quad C = \pi^4 k^2\varkappa^2/F_2^2(k)r\end{gathered} \tag{14}$$

and taking into account the relations

$$\frac{\chi E\mu_1}{\tilde{K}\theta_0} = \frac{q_0^2\pi^2 k^2}{4F_2^2(k)}, \quad \varkappa = \frac{p}{p_0} = \frac{1}{\pi^2}F_1(k)F_2(k),$$

where a change of the electric field E from $E=0$ to $E = E_u$ corresponds to a change of the parameter k from $k=0$ to $k=1$, and $F_1(k)$ and $F_2(k)$ are elliptic integrals of the first and second kind, we obtain from (13)

$$d^2\eta/dx^2 - S^2\eta = CF(x), \tag{15}$$

where

$$F(x) = \left(1 - \frac{h}{2\pi\varkappa}\frac{d\varphi}{dx}\right)\cos\varphi$$

is a periodic function with unity period.

The periodic solution of (15) was obtained by two methods corresponding to the asymptotic relations $S^2 \ll 1$ and $S^2 \gg 1$. In the case $S^2 \ll 1$ it is convenient to rewrite the periodic solution (15) in the form

$$\bar{\eta} = \frac{C}{S}\int_0^x F(u)\operatorname{sh}S(x-u)\,du + C_1\operatorname{sh}\varkappa x + C_2\operatorname{ch}\varkappa x, \tag{16}$$

where

$$C_1 = \frac{C}{2S}\left[\int_0^1 F(u)\operatorname{ch}S(x-u)\,du + \frac{\operatorname{sh}S}{(1-\operatorname{ch}S)}\int_0^1 F(u)\operatorname{sh}S(x-u)\,du\right],$$

$$C_2 = \frac{C}{2S}\left[\int_0^1 F(u)\operatorname{sh}S(x-u)\,du + \frac{\operatorname{sh}S}{(1-\operatorname{ch}S)}\int_0^1 F(u)\operatorname{ch}S(x-u)\,du\right].$$

If $S^2 \gg 1$, a numerical calculation in accord with (15) entails great difficulties and an asymptotic expansion in powers of $1/S^2$ must be used:

$$\eta=-C\left(\frac{F(x)}{S^2}+\frac{d^2F}{dx^2}\frac{1}{S^4}+\frac{d^4F}{dx^4}\frac{1}{S^6}+\dots\right). \tag{17}$$

The obtained value of the axial perturbation is the starting point for the determination of the average polarization $\langle P\rangle$ of the smectic layer:

$$\langle P\rangle=-\chi\mu_1\theta_0(T)\left[\langle\cos\varphi(x)\rangle+\langle\eta(x)F(x)\rangle\right], \tag{18}$$

where $\langle\dots\rangle$ denotes averaging over the helicoid period $0 \leq x \leq 1$.

The polarization was determined numerically from (18) in the following manner. Given the electric field $0 \leq E \leq E_u$ we determined the induced helix pitch and the azimuthal distribution $\varphi(x)$ satisfying the relation

$$x=\int\limits_0^{\varphi/2}(1-k^2\sin^2u)^{-1/2}\frac{du}{F_1(k)}. \tag{19}$$

Depending on the value of the parameter S^2, the value of $\varphi(x)$ was substituted in (16) and (17) to determine the axial perturbation $\eta(x)$ (Fig. 1).

The polarization $\langle P\rangle$ was determined from (18) by numerical integration with respect to x from $x=0$ to $x=1$. At $E=E_u$ the values of $|\eta|$ and $\langle P\rangle$ are of the order of

$$|\eta|\sim\frac{C(k=1)}{S^2}\approx\frac{\pi^2}{16}\frac{\tilde{K}q_0^2}{A},$$
$$\langle P\rangle\sim\chi\mu_1\theta_0\left(1+\frac{\pi^2}{16}\frac{\tilde{K}q_0^2}{A}\right). \tag{20}$$

Figures 2 and 3 show the dependences of the relative polarization $\langle P\rangle/\chi\mu_1\theta_0$ on the field E, calculated by the method described above. A characteristic feature of these dependences is the nonmonotonic character of the curves near $E=E_u$ as $T\to T_c$. It is seen that at a ratio $g/\tilde{K}\gg 1$ there is a pronounced maximum near $E=E_u$, which decreases with decreasing temperature, and on the $\langle P\rangle$ (E) curve there are produced in succession a minimum and a flex that goes over into a monotonic dependence at $T_c-T\approx 15-20$ K. At $g/\tilde{K}\approx 1$ the $\langle P\rangle$ (E) curves remain nomonotonic, but the indicated maximum is weakly pronounced.

We emphasize that the contribution of the distortion $\theta_1(z)$ to $\langle P\rangle(E)$ is particularly significant as $T\to T_c$ and corresponds to an anomalous increase of the susceptibility in the vicinity of the phase-transition point. We note also that the slopes of the indicated curves on

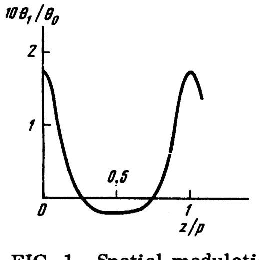

FIG. 1. Spatial modulation of the relative angle θ_1/θ_0 in the $\tilde{C}$ phase: $E/E_p=0.98$, $g/\tilde{K}=25$, $T_c-T=0.5$°C.

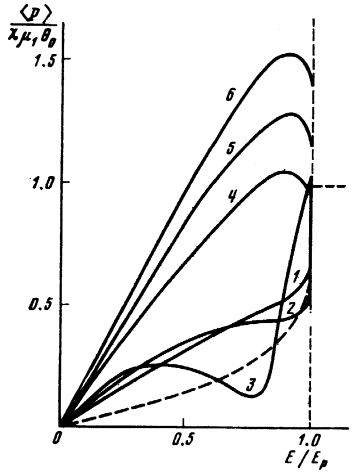

FIG. 2. Dependence of the relative macroscopic polarization $\langle P\rangle/\chi\mu_1\theta_0$ in the $\tilde{C}$ phase on the ratio E/E_u at the temperatures T_c-T°C: 1) 11; 2) 12; 3) 4; 4) 1.0; 5) 0.7; 6) 0.5 ($g/\tilde{K}=25$, $\mu_2q_0/\mu_1=14$, $a'=2.5\cdot10^2$; the dashed line corresponds to the field dependence of $\langle\cos\varphi(z;\ E/E_p)\rangle$.

Figs. 2 and 3 are proportional as $E\to0$ to the susceptibility correction calculated analytically from Eq. (11).

3. COMPARISON WITH EXPERIMENT

We compare first the expressions (11) and (12) for the dielectric susceptibility with the measured dielectric constant ε of the chiral smectic liquid crystal *d-p*-decyloxybenzilidene-*p'*-amino-2-methybutyl-cinnamate (DOBAMBC).[5,6] The dependences of ε on the temperature and on the frequency of the measuring field were obtained with rather thick $\tilde{C}$ samples ($d\approx 50-150$ μm) in a planar orientation (the helicoid z axis is in the electrode plane). In the experiment we determined the dielectric-tensor component $\varepsilon_{yy}=\varepsilon_\perp$, connected with the polarization P_y produced along the y axis under the influence of the field E_y

$$\varepsilon_\perp=\varepsilon_\infty+4\pi P_y/E_y, \tag{21}$$

where ε_∞ is the dielectric constant due to displacements of the induced dipoles in the measuring field.

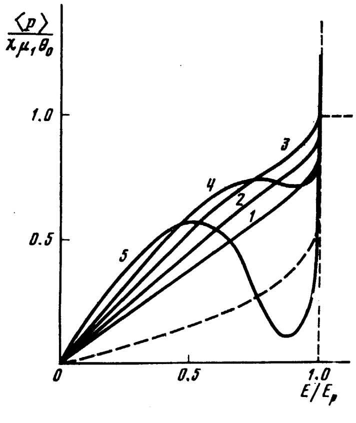

FIG. 3. Dependence of the relative macroscopic polarization $\langle P\rangle/\chi\mu_1\theta_0$ in the $\tilde{C}$ phase on the ratio E/E_u at the temperatures T_c-T°C: 1) 22; 2) 9; 3) 4; 4) 1.6; 5) 1.2 ($g/\tilde{K}=1$, $\mu_2q_0/\mu_1=5$, $a'=2\cdot10^2$; the dashed line is a plot of $\langle\cos\varphi(z;\ E/E_p)\rangle$.

The investigations were made in weak measuring fields $E_{\sim}$ [$E_{\sim}/E_p(T \approx T_c) \approx 10^{-1}$], i.e., in precisely the region where the analytic expression (9)–(11) are valid. The expression for the static dielectric constant $\varepsilon_{\perp 0}$ can be written with the aid of (11) in the form

$$\varepsilon_{\perp 0}=\varepsilon_{\infty}+2\pi\chi^2\left[\frac{\mu_1^2}{\tilde{K}q_0^2}+\frac{(\mu_1-\mu_2q_0)^2}{gq_0^2-4\tilde{a}}\right]. \quad (22)$$

Figure 4 shows the temperature dependence of the value of $\varepsilon' = \varepsilon_{\perp 0} - \varepsilon_{\infty}$, previously obtained[6] by extrapolating the plots of $\varepsilon'(f; T - T_c)$ into the frequency region $f = 0$. Using the data of Fig. 4 and the known temperature dependence of the helix pitch $p_0(T - T_c)$ in DOBAMBC,[5,6] we can estimate the quantities that enter in (14). We note that a value that agrees with experiment can be obtained for the anomaly $\varepsilon'(T - T_c)$ from (14) provided that the flexoelectric effect makes a substantial contribution to the onset of the macroscopic polarization ($\mu_2 q_0 \gtrsim \mu_1$). In the opposite case ($\mu_2 q_0 \ll \mu_1$) one should expect the relations $\varepsilon'(T - T_c) \sim p_0^2(T - T_c)$, and $\varepsilon'(T \approx T_c)/\varepsilon'(T \ll T_c) \approx 4$, whereas it follows from Fig. 4 that the last mentioned ratio is close to two.

Starting from the relation $g \geq \tilde{K}$ between the elastic constants of DOBAMBC and putting $\tilde{K} \sim 5 \cdot 10^{-6}$–$2.5 \cdot 10^{-5}$,[8] we obtain the region of permissible values of a' and g in which (14) describes best the temperature dependence of ε':

$$a'/g \leqslant 2 \cdot 10^7, \quad \tilde{a}=a'(T-T_c).$$

Figure 4 shows plots of $\varepsilon'(T - T_c)$ based on (14) for certain permissible sets of values of the parameters a', g, and $\tilde{K}$ and of the ratio $\mu_2 q_0/\mu_1$. The best agreement between the experimental and theoretical $\varepsilon'(T - T_c)$ is reached in those cases when the quantities μ_1 and $\mu_2 q_0$ are of the same order ($\mu_2 q_0/\mu_1 \approx 1$–$5$). Some discrepancies between the experimental and theoretical curves can be due to the weak temperature dependences of the material constants χ, $\tilde{K}$, and g near the point of the $A^* \leftarrow \tilde{C}$ phase transition.

In accord with (12), the anomaly of the dielectric constant in the A^* phase at $T \approx T_c$ is determined mainly by the value of the elastic energy $\tilde{K}q_c^2$. Comparing the expressions for ε' in the phase $\tilde{C}(\varepsilon'_C)$ in the region of the monotonic increase of the helicoid with ε' in the phase A^* at $T \approx T_c(\varepsilon'_A)$ we get

$$\frac{\varepsilon_C'}{\varepsilon_A'}\approx\frac{q_c^2}{q_0^2}\left[1+\left(\frac{\mu_2q_0}{\mu_1}\right)^2\frac{\tilde{K}}{g-4\tilde{a}/q_0^2}\right]. \quad (23)$$

The numerical estimates for various ratios $g/\tilde{K}$, $\mu_2 q_0/\mu_1$, and q_c/q_0 yield for (23) values $\varepsilon'_C/\varepsilon'_A \approx 10 - 10^2$, which agree with the experimental results.[8]

We note that Garoff and Meyer[9] obtained for a' an estimate much higher than ours ($a' \approx 10^2 - 10^3$). This may be due to the fact that they estimated a' from the relaxation time τ of the angle θ in the A^* phase. The value of τ is calculated, strictly speaking, from the formula

$$\tau=\gamma_1/(2\tilde{a}+\tilde{K}q_c^2),$$

where γ_1 is the viscosity. Garoff and Meyer,[9] however, do not take into account the term $\tilde{K}q_c^2$ in the expression for τ, thus incurring an appreciable error due to the strong increase of q_0 at $|T - T_c| < 1°$.

Starting from the experimental data, we estimate from the temperature dependences[5,6] of $\varepsilon_{\perp 0}(T)$, $\theta(T)$, $P_s(T)$, $q_0(T)$, $E_u(T)$ the principal material parameters of DOBAMBC:

$$\begin{gathered}\chi\mu_1\approx P_s/\theta_0\approx 15-25 \text{ e cgs esu} \quad \tilde{K}=K-\chi\mu_2^2\approx 10^{-5} \text{ dyn}\\ \chi=(\varepsilon_\infty-1)/4\pi\approx 0.2\div 0.3, \quad a'\approx 2\div 5\cdot 10^2 \text{ cgs esu/deg}\\ \mu_2q_0/\mu_1\approx 1\div 5, \quad |\mu_1|\approx 75-90 \text{ cgs esu} \quad |\mu_2|\approx 10^{-2} \text{ cgs esu}\\ |\lambda|\leqslant|\chi\mu_1\mu_2|\approx 0.1 \text{ cgs esu}\end{gathered} \quad (24)$$

The condition $\theta_1/\theta_0 < 1$, as shown by calculations, is violated at $T_c - T \approx 1°$. An estimate of θ_1 by the formula

$$\theta_1=\chi\mu_1E/(2\tilde{a}+\tilde{K}q_c^2), \quad (25)$$

which is valid for the A^* phase,[3] yields at $T = T_c$ the value $\theta_1 \approx 0.5 - 1.0°$ V/cm, and $p_c = (1 - 2) \times 10^{-4}$ cm. A qualitative plot of $\theta(T)$ at constant E is shown in Fig. 5.

Since $\theta_1(E) \neq 0$, the temperature dependences of the molecule inclination angle and of the spontaneous polarization P_s measured in a field $E \approx E_u$ differ slightly from the functions $\theta_0(T)$ and $P_s \sim \chi\mu_1\theta_0$. This leads to a certain renormalization of the critical exponent β calculated from the functions $\theta(T, E_u)$ and $P_s(T, E_u)$ compared with the exponent for the modulus of the order parameter $\theta_0 \sim (T_c - T)^\beta$. However, since the increment connected with θ_1 is comparable with the errors of the measurements of θ and P_s at $T \approx T_c$,[5,6] the changes of the

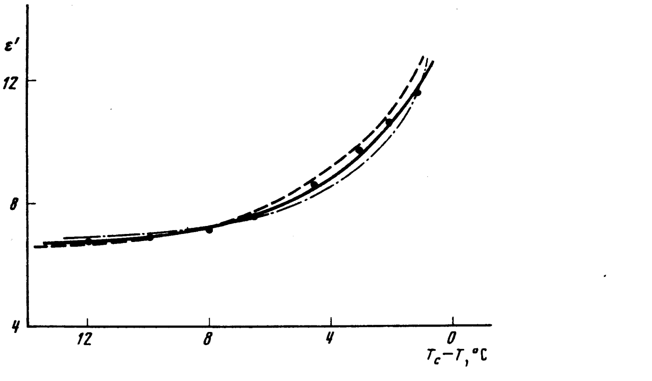

FIG. 4. Temperature dependences of the static dielectric constant $\varepsilon' = \varepsilon_{\perp 0} - \varepsilon_0$ at $E \ll E_p$, $\varepsilon_\infty = 4.8 \mp 0.2$; points—experimental value for the chiral smectic crystal DOBAMBC.[5,6] Theoretical calculations by Eq. (11): dashed—$a' = 1.6 \cdot 10^2$, $\tilde{K} = 10^{-5}$, $g = 10^{-5}$, $\mu_2 q_0/\mu_1 \approx 4$; solid—$a' = 1.6 \cdot 10^2$, $\tilde{K} = 5.10^{-6}$, $g = 10^{-5}$, $\mu_2 q_0/\mu_1 \approx 5$; dash-dot—$a' = 2 \cdot 10^2$, $\tilde{K} = 5 \cdot 10^{-6}$, $g = 2.5 \cdot 10^{-5}$, $\mu_2 q_0/\mu_1 \approx 8$.

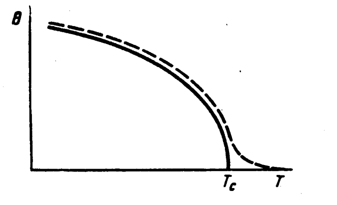

FIG. 5. Qualitative temperature dependences of the inclination angle of the molecules in the $\tilde{C}$ and A^* phases. Solid line—$\theta = \theta_0(T)$ at $E = 0$, dashed line—$\theta = \theta_0(T) + \theta_1(T)$ at constant E.

critical exponent, as shown by calculations, do not exceed the β confidence interval.

The foregoing numerical calculation of the field dependence of $\langle P\rangle$ has shown that a small spatial modulation of the angle θ_1 at $E<E_u$, joingly with the flexoelectric effect, leads to appreciable changes of the macroscopic polarization $\langle P\rangle$ compared $\langle P_0\rangle=\chi\mu_1\theta_0\langle\cos\varphi\rangle$ (Figs. 2 and 3). This effect can be observed if the measured values of P_s in the field $E<E_u$ corresponds to rigorously defined states of the helical structure of $\tilde{C}$ deformed by the electric field. Let us examine the extent to which the capabilities of a real experiment correspond to this condition.

The measurements of P_s in the $\tilde{C}$ phase were made mainly by a repolarization method[5,10-13] that makes it possible to obtain a repolarization oscillogram in which the amplitude of the vertical deflection is proportional to P_s and the linear components of the conductivity and capacitance of the samples are compensated for. The repolarization frequency f is chosen such that the time of one cycle is too short for leakage due to the conductance of the samples to occur[14] $1/f\leq\tau_0$ (typical time constants of $\tilde{C}$ samples are $\tau_0=10^{-1}-10^{-2}$ sec and determine the minimal repolarization frequency, $f>10$ Hz). The oscillogram of the repolarization of $\tilde{C}$ takes the form of a hysteresis curve with saturation in the field region $E\geq E_u$. The values of the macroscopic polarization in the saturation region correspond to a completely untwisted state of the helical structure of $\tilde{C}$. The intermediate sections of the oscillogram $(E/E_u<1)$, however, do not correspond to the polarization of a partially deformed helicoid, because of the large (1 – 2 sec) times τ of relaxation from the homogeneous to the helicoidal state $(\tau\gg 1/f)$. For the same reason, and also because sample-texture defects, the $P_s(E)$ plot exhibits hysteresis even though for the continuous symmetry group of the helicoidal $\tilde{C}$ this should be a reversible function. In the ideal case of nonconducting $\tilde{C}$ at slow reorientation, $P_s(E)$ is apparently fully reversible. Other methods of measuring P_s (pulsed[15] and pyroelectric[16]) also yield values of P_s corresponding to the homogeneous state of $\tilde{C}(E\geq E_u)$.

We discuss now the influence of the boundary conditions on the considered properties of the $\tilde{C}$ phase. Assume that the $\tilde{C}$ layer is bounded along the y axis, has a thickness d, and the molecules are rigidly pinned to the solid surface, where $\theta=0$. In this case it is necessary to add to (1) the term

$$g_\parallel(\partial\theta/\partial y)^2,$$

which corresponds to the energy of the elastic distortions in the surface layer. With increasing distance from the solid surface, the value of $\theta(y)$ tends to the value of θ_0 in a sufficiently thick layer. In the absence of a field, the minimum of F corresponds to the function $\varphi(z)=qz$ at all y and to the function $\theta(y)$ that satisfies the equation

$$-g_\parallel\frac{\partial^2\theta}{\partial y^2}+2\tilde{a}\theta+4b\theta^3=0 \qquad (26)$$

with boundary conditions $\theta(0)=\theta(d)=0$. The value of the angle θ at the center of the layer at $y=d/2$ is

$$\theta(d/2)\approx\theta_0(1+4g_\parallel/\tilde{a}d^2), \qquad (27)$$

if $g_\parallel\ll|\tilde{a}|d^2$.

Thus, the foregoing results are valid for sufficiently thick samples and for temperatures not too close to the transition point. Substituting in (27) the material constants of the $\tilde{C}$ phase of DOBAMBC, $g_\parallel\approx 10^{-5}$, $\tilde{a}=a'(T-T_c)$, $a'=2\cdot 10^2$, we find that the deviations of $\theta(d/2)$ from θ_0 become significant for samples of thickness $d\approx 50$ μm at $|T_c-T|<0.1°$, but for samples with $d\approx 10$ μm already at $|T_c-T|<1°$.

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