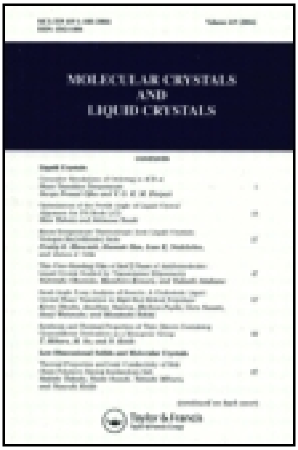


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Dielectric Anomaly Near the Transition from the Smectic A* to Smectic C* Phase and Visco-Elastic Properties of Ferroelectric Liquid Crystals

E. P. Pozhidayev [b] , L. M. Blinov [a] , L. A. Beresnev [a] & V. V. Belyayev [b]

[a] Institute of Crystallography, USSR Acad. Sci., 117333, Leninsky prosp. 59, Moscow, USSR
[b] Organic Intermediates & Dyes Institute, Moscow, USSR

Version of record first published: 17 Oct 2011.

To cite this article: E. P. Pozhidayev , L. M. Blinov , L. A. Beresnev & V. V. Belyayev (1985): The Dielectric Anomaly Near the Transition from the Smectic A* to Smectic C* Phase and Visco-Elastic Properties of Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals, 124:1, 359-377

To link to this article: http://dx.doi.org/10.1080/00268948508079488

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 359–377
0026-8941/85/1244-359/$20.00/0

The Dielectric Anomaly Near the Transition from the Smectic A* to Smectic C* Phase and Visco-Elastic Properties of Ferroelectric Liquid Crystals†

E. P. POZHIDAYEV,‡ L. M. BLINOV,§ L. A. BERESNEV§ and
V. V. BELYAYEV‡

§*Institute of Crystallography, USSR Acad. Sci., 117333 Leninsky prosp. 59, Moscow, USSR*
‡*Organic Intermediates & Dyes Institute, Moscow, USSR*

(*Received July 19, 1984*)

A pyro-electric technique is developed which allows the measurement of the dielectric response near the A^*-C^* phase transition in ferroelectric liquid crystals. The temperature dependence of the elastic modulus $K_\theta(T)$ corresponding to the molecular tilt in smectic layers is calculated from the experimental data. Direct pyro-electric measurements of the relaxation time for the spontaneous polarization P_s and the data on $K_\theta(T)$ allow us to calculate the temperature behaviour of the twist-viscosity $\gamma_t(T)$ for the smectic C^* phase. The curves $\gamma_t(T)$ are compared for the smectic C^* and the nematic phase of the same compound and the dependence of the twist viscosity on the molecular tilt angle in the C^* phase is investigated. The results of the dielectic measurements are discussed in terms of the mean-field approximation.

INTRODUCTION

Experimental data on viscous and elastic properties of the smectic C^* phase are rather scare and contradictory. The temperature be-

---

†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

haviour of the elastic modulus K_2 and the twist viscosity γ_1 in the chiral smectic C^* phase has been studied.[1] The elastic modulus was shown to be two orders of magnitude less than typical values for the nematic phase. The values of γ_1 for the nematic and achiral smectic C phase have been compared[2] and were shown to be of the same order of magnitude. The temperature behaviour of the γ_1 coefficient in the C-phase far below the phase transition, as well as in the nematic phase, is described by the Arrenius law:

$$\gamma_1(T) \sim \exp \frac{V}{k_B T} \tag{1}$$

where V is an activation energy, and k_B is Boltzman's constant.

Most experimental data on elastic moduli for the chiral smectic C^* phase were obtained using the Landau expansion for free energy

$$F = \frac{1}{2} a\theta^2 + \frac{1}{4} B\theta^4 + \frac{1}{2} K_2 q^2 \theta^2, \tag{2}$$

where $a = a'_o(T - T_c)$, $a'_o > 0$, B and K_2 are the elastic moduli, T_c is the A^*-C^* transition temperature and q is a wave vector for the helical structure. However, the application of the mean-field (MF) approximation to the A^*-C^* transition is the problem to be solved. The calorimetric measurements and the investigation of the tilt angle, as a function of temperature,[3,4] seem to agree with the MF approximation which allows the coefficients a'_o and B in eq. (2) to be determined. The coefficient a'_o has also been calculated from the measurement of the electroclinic effect in the smectic A^* phase.[5] The values a'_o for a classical ferroelectric liquid crystal DOBAMBC obtained in references 3 and 5 have the same order of magnitude.

On the other hand, the measurements of heat capacity, dielectric permittivity and the field-induced untwisting of the helix performed in references 6–8 have cast some doubts on the applicability of the MF approximation. Formally used Eq. 2 gives a'_o values two or three orders of magnitude less than those from references 3 and 5.

The aim of the present paper is to investigate the dielectric susceptibility and visco-elastic properties near the smectic C^* phase transition using a unified approach based on the modified pyro-electric technique. In calculating the elastic and viscosity coefficients we only used experimental data and strict thermodynamical equalities which are true for any model description of the A^*-C^* phase transition.

RELATIONSHIP BETWEEN THE DIELECTRIC SUSCEPTIBILITY AND THE ELASTIC MODULUS OF THE *C**-PHASE

Let us consider the simplest case when the helical structure of a liquid crystalline ferroelectric is untwisted by an exernal electric field E. Under such a condition ($E > E_c$ where E_c is the critical untwisting field) it is necessary to consider only the elastic modulus K_θ which is referred to the tilt of molecules in smectic layers. If θ is an equilibrium value for the tilt angle then for $E \gg E_c$ this angle would change by an amount $\theta_1 \ll \theta$ for the electroclinic effect. The corresponding contribution to the free energy density is a quadratic function of the deformation:

$$W_1 = \frac{1}{2} K_\theta \, \theta_1^2. \tag{3}$$

The equation (3) may be considered as a definition of the elastic modulus K_θ. Let us try to relate K_θ to the dielectric susceptibility of the C^*-phase. We use a linear relationship between the spontaneous polarization P_s and the tilt angle θ, i.e.

$$P_s = \alpha\theta, \tag{4}$$

where α is a temperature independent coefficient. When the tilt angle changes in an external field the additional term $P_e(E,T)$ appears to be caused by the electroclinic effect:

$$P = \chi_\infty E + \alpha(\theta + \theta_1) = \chi_\infty E + P_s(T) + P_e(E,T) \tag{5}$$

Here, χ_∞ is the apolar temperature independent part of the susceptibility.

The steady-state value of θ_1 is determined by an equality of two terms, namely, the energy of interaction of the "electroclinic polarization" P_e with the electric field (this term may be written in the form $W_e = 1/2 \, P_e E$) and the elastic energy W_1 which is due to the change in angle by θ_1. Therefore

$$P_e E = K_\theta \theta_1^2 = \frac{P_e^2 K_\theta}{\alpha^2}, \tag{6}$$

that is

$$P_e = \frac{\alpha^2 E}{K_\theta} \tag{7}$$

In eq. (7) the only temperature dependent parameters are K_θ and P_e. After the substitution of Eq. 7 into Eq. 5 and differentiation(5) over temperature one can find the dependence of the pyro-electric coefficient ($\gamma \equiv \partial P/\partial T$) on electric field

$$\gamma(T,E) = \gamma_0(T) - \frac{\alpha^2 E}{K_\theta^2} \cdot \frac{\partial K_\theta}{\partial T} \tag{8}$$

where $\gamma_0(T) = \frac{\partial P_s}{\partial T} = \alpha \frac{\partial \theta}{\partial T}$ is the field-independent part of the pyroelectric coefficient which is due to the spontaneous polarization. Taking into account a definition of the dielectric susceptibility $\chi = \partial P/\partial E$ we have

$$\frac{\partial \gamma}{\partial E} \equiv \frac{\partial}{\partial E}\left(\frac{\partial P}{\partial T}\right) \equiv \frac{\partial}{\partial T}\left(\frac{\partial P}{\partial E}\right) \equiv \frac{\partial \chi}{\partial T}. \tag{9}$$

After differentiation of (8) with respect to the electric field and having regard to Eq. (9) we obtain

$$\frac{\partial \gamma}{\partial E} \equiv \frac{\partial \chi}{\partial T} = -\frac{\alpha^2}{K_\theta^2} \frac{\partial K_\theta}{\partial T}. \tag{10}$$

Integrating Eq. 10 results in the relationship between the elastic modulus and the dielectric susceptibility:

$$K_\theta = \frac{\alpha^2}{\chi(T) - \chi_\infty} = \frac{\alpha^2}{\chi_T}, \tag{11}$$

where $\chi_T = \chi(T) - \chi_\infty$ is a temperature dependent part of the susceptibility. Therefore, the temperature behaviour of the modulus K_θ can be investigated from experimental data on the temperature dependencies of χ_T, P_s and θ $\left(\text{note that } \alpha = \frac{P_s(T)}{\theta(T)}\right)$.

As will be shown below it is difficult to obtain accurate values of K_θ far from the C^*-A^* phase transition since the χ_T values decrease sharply with decreasing temperature. Hence, it is convenient to relate χ_T values to the equilibrium pyro-electric coefficient $\gamma_0 = \partial P_s/\partial T = \alpha\partial\theta/\partial T$ which can be measured with high accuracy over the whole temperature range of the smectic C^* phase. The heat capacity ΔC_θ which is due to the spontaneous molecular tilt θ and corresponding elastic energy W_θ is defined as

$$\Delta C_\theta = -T\frac{\partial^2 W_\theta}{\partial T^2}. \tag{12}$$

Under the condition $W_1 \gg W_\theta$ Eq. (3) for elastic modulus may be rewritten in the form

$$K_\theta = +\frac{\partial^2 W_\theta}{\partial\theta^2}, \tag{13}$$

and using a definition of the pyro-electric coefficient and relationships (4) and (12) we have:

$$\left|\Delta C_\theta\right| = +\frac{T}{\alpha^2}\left(\delta_0^2\frac{\partial W_\theta}{\partial\theta^2} + \frac{\partial\gamma_0}{\partial\theta}\cdot\frac{\partial W_\theta}{\partial\theta}\right). \tag{14}$$

Since in equilibrium $\partial\gamma_0/\partial\theta \equiv 0$ and $\partial W_\theta/\partial\theta = 0$ it follows from Eqs. (13), (14) and (11) that

$$K_\theta = \frac{\alpha^2\Delta C_\theta}{\gamma_0^2\, T}, \tag{15}$$

and

$$\chi_T = \frac{\gamma_0^2\, T}{\Delta C_\theta}. \tag{15'}$$

EXPERIMENTAL TECHNIQUE

The pyro-electric technique for measuring the dielectric susceptibility is based on Eq. (9). The derivative $\partial\chi/\partial T$, at a given temperature, can be determined from the experimental dependence of the pyro-electric coefficient on a *d.c.* electric field at this temperature. Our experiments were carried out for a completely untwisted helix ($E >$

E_c), therefore, all the effects resulting from the distortion of the helix were excluded. Under such a condition one can only observe a relaxation process due to the change in the tilt of molecules with characteristic time $\tau_f \approx 10^{-6}$ s (i.e., the soft mode)[9] and in order to measure the steady-state values of the pyro-electric coefficient and corresponding steady-state values for $\partial\chi/\partial T$ one should use rather long heat pulses. To this effect we used infra-red light pulses from a Nd-glass laser in the normal mode regime having a total (envelope) duration of $\tau_p \approx 2.10^{-4}$ S.

The volume absorption of light (wavelength $\lambda = 1.06$ μm) in a sample was provided by dissolving small amounts (0.2% wt/wt) of a dye in a liquid crystal. The experimental data were obtained on a classical ferroelectric liquid crystal DOBAMBC (p-decyloxybenzylidene-p′-amino-2-methylbutyl cinnamate) with the planar molecular

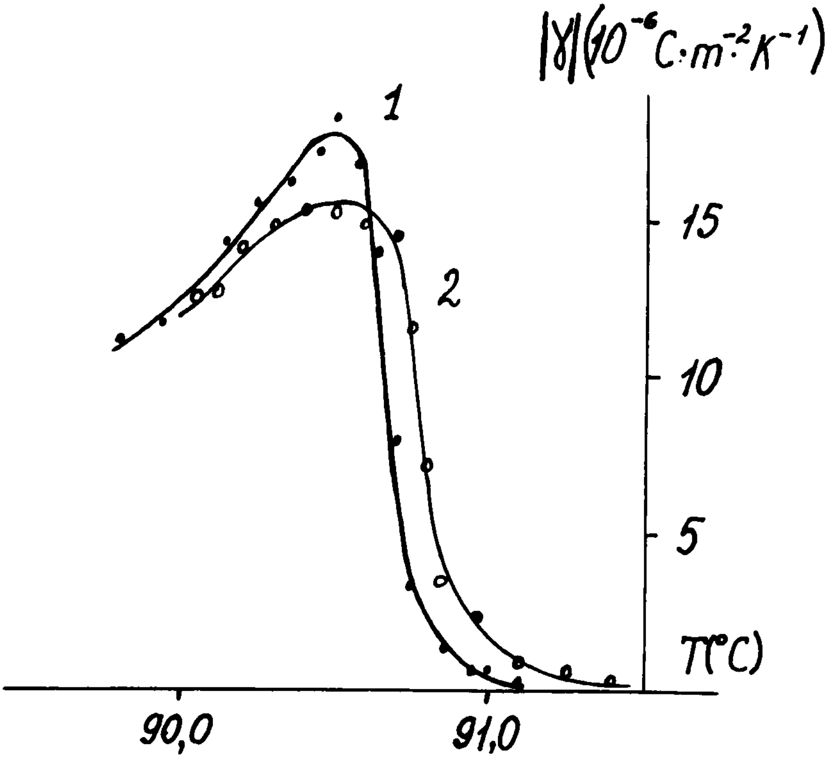
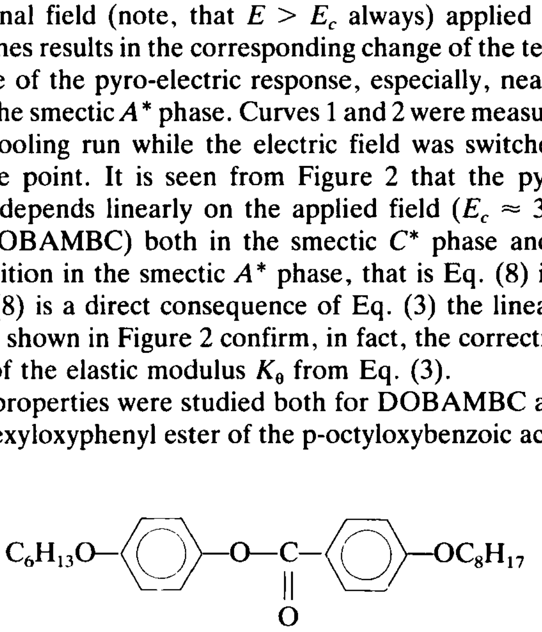


FIGURE 1 Temperature behaviour of the pyro-electric coefficient of DOBAMBC near the A^*-C^* phase transition for applied electric fields $E = 0.5{\cdot}10^6$ V·m^{-1} (curve 1) and $1.5{\cdot}10^6$ V·m^{-1} (curve 2).

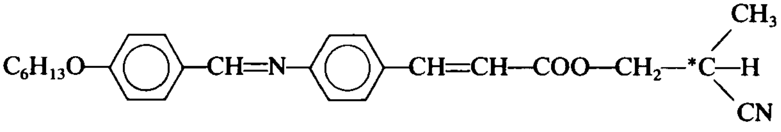
orientation. The thickness of the liquid crystal layer was 110 μm so the mass of a sample did not exceed $5 \cdot 10^{-3}$ g. The temperature rise during the heat pulse action never exceeded 0.02°C. The temperature dependence of $\partial\chi/\partial T$ was measured during a sample cooling run at a rate of 10^{-4} °C/s. Temperature was measured with an accuracy of ±0.025°C.

Figure 1 illustrates the principle of our measurements. A change in an external field (note, that $E > E_c$ always) applied parallel to smectic planes results in the corresponding change of the temperature dependence of the pyro-electric response, especially, near the transition into the smectic A^* phase. Curves 1 and 2 were measured during the same cooling run while the electric field was switched at each temperature point. It is seen from Figure 2 that the pyro-electric coefficient depends linearly on the applied field ($E_c \approx 3 \cdot 10^5$ V $\cdot$ m^{-1} for DOBAMBC) both in the smectic C^* phase and near the phase transition in the smectic A^* phase, that is Eq. (8) is fulfilled. Since Eq. (8) is a direct consequence of Eq. (3) the linear dependencies $\gamma(E)$ shown in Figure 2 confirm, in fact, the correctness of the definition of the elastic modulus K_θ from Eq. (3).

Viscous properties were studied both for DOBAMBC and for the achiral p-hexyloxyphenyl ester of the p-octyloxybenzoic acid (HOPE OOBA)



doped with a chiral additive (5% wt/wt) 4-p-hexyloxy-benzylidene-p′-amino-2-cyanopropyl cinnamate



The latter mixture (mixture I) has not only the smectic C^* and A^* phases but also a nematic phase which allows a comparison of the temperature behaviour of the twist-viscosity γ_1 in different phases.

In the nematic phase the twist viscosity γ_1 was calculated from the director relaxation time for a homogeneously oriented layer distorted by an electric field.[10] To enhance the accuracy of these measurements the nematic phase of HOPE OOBA was doped with 3% wt/wt of 5-

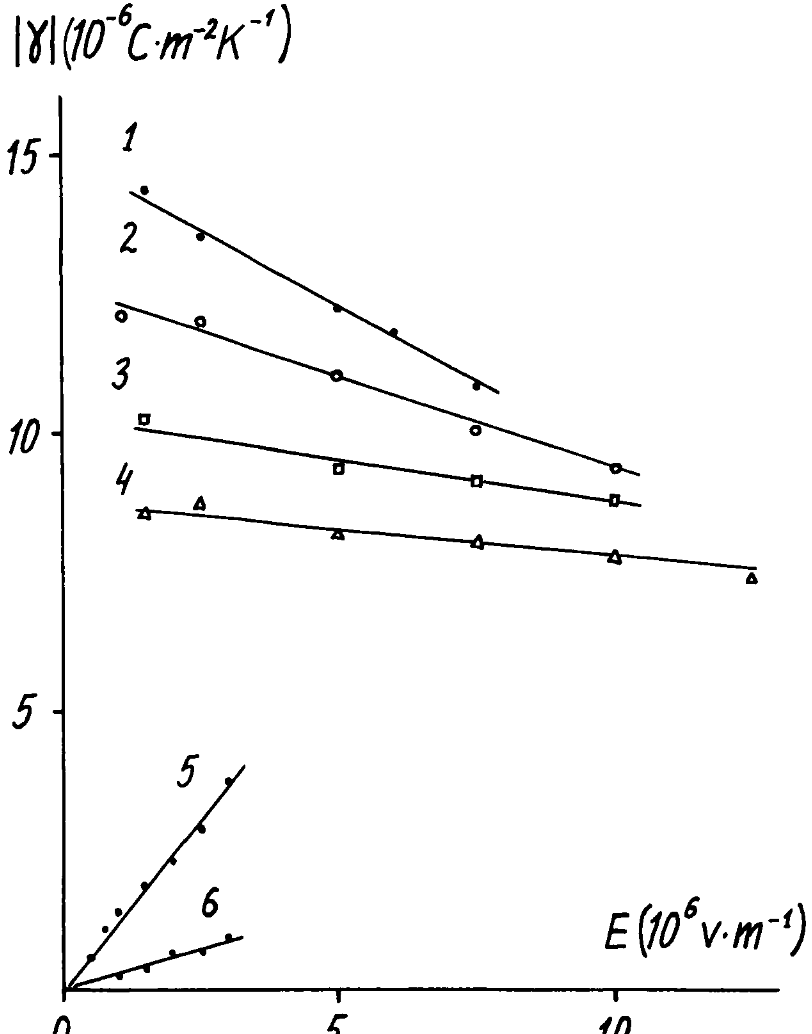
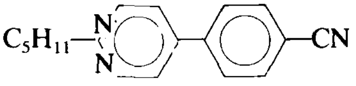


FIGURE 2 Field dependencies of the pyro-coefficient of DOBAMC at $E \gg E_c$ and temperatures 90.2°C (1), 90.05°C (2), 89.8°C (3), 89.6°C (4) in the C^* phase and $T = 91.0$°C (5) and 91.4°C (6) in the A^*-phase.

p-pentyl-2-(4-cyanophenyl)-pyrimidine



(mixture II). In both mixtures (I and II) the impurity concentrations were adjusted to obtain almost identical phase transition sequences:

$$C_r \xleftarrow{39°\mathrm{C}} S_c \xleftarrow{62°\mathrm{C}} S_A \xleftarrow{68°\mathrm{C}} N \xleftarrow{89°\mathrm{C}} I$$

Moreover, for such small concentrations the viscous properties of both mixtures were essentially indistinguishable from those of a pure matrix.[11]

The relaxation of the perturbation θ_1 in the tilt angle θ of the smectic C^* phase after switching off the external field can be described by equation

$$\gamma_1 \frac{\partial \theta_1}{\partial t} = -K_\theta \theta_1. \tag{16}$$

The corresponding relaxation time $\tau_f = \gamma_1/K_\theta$, as a function of temperature, could also be measured by our pyro-electric technique if one uses short (giant) pulses of the same Nd-glass laser working in the Q-switched regime with the pulse duration $\tau_p \approx 2 \cdot 10^{-8}$ S. The temperature behaviour of the relaxation time for the soft mode (τ_f) was investigated under the same sample cooling conditions.

The viscosity coefficient γ_1 in the smectic C^* phase was calculated from Eq. (16) using Eq. (11):

$$\gamma_1 = \tau_f K_\theta = \frac{\tau_f \cdot \alpha^2}{\chi_T} = \frac{\tau_f P_s^2}{\chi_T \theta^2}. \tag{17}$$

EXPERIMENTAL RESULTS

Figure 3 shows the temperature behaviour of the derivative $\partial\chi/\partial T$ and the corresponding integrated value of the temperature dependent part of the dielectric susceptibility χ_T measured at field strength $E = 2 \cdot 10^6\ \mathrm{V \cdot m^{-1}}$. The pyro-electric technique automatically separates the term χ_T from the temperature independent background χ_∞. Using

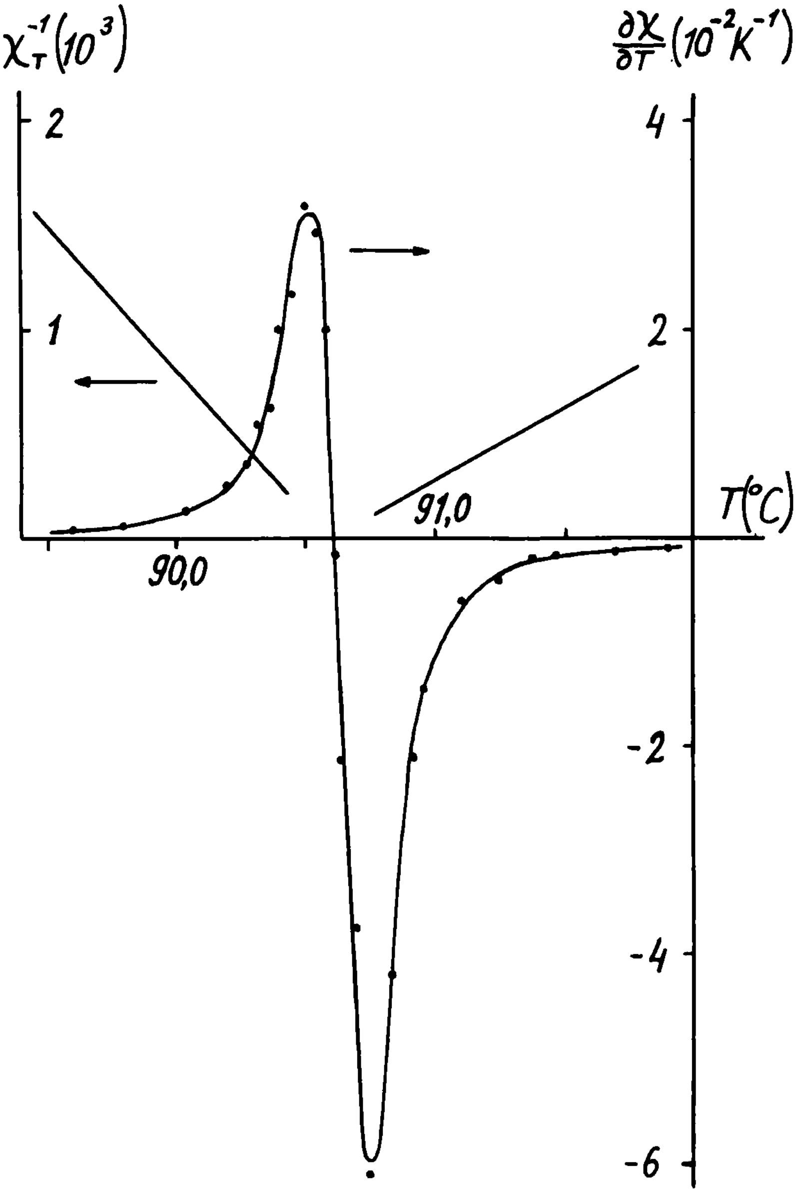


FIGURE 3 Temperature dependencies of the derivative $\partial\chi/\partial T$ and the temperature dependent part of the dielectric susceptibility χ_T for DOBAMBC at $E > E_c$.

the indentity $\partial\chi/\partial T \equiv \partial\chi_T/\partial T$ and graphically integrating the function $\partial\chi/\partial T$ over temperature one can find the maximum value for χ_T corresponding to the phase transition point. The value $\chi_T^{\max}$ is as small as $1.2 \cdot 10^{-2}$ compared to a background value of $\chi_\infty \approx 0.28$.[6] This comparison characterizes the sensitivity of our measurements.

We define the phase transition temperature T_c using the condition $\partial\chi/\partial T = 0$. Virtual errors may result from both the finite rate of sample cooling and the spatial inhomogeneity of the laser emission absorbed. In any case, T_c found from the condition above and T_c taken from visual observations of the twisting process under a microscope at $E = 0$ coincide with an accuracy of ±0.05°C. The region of the smearing of the phase transition peak in Figure 3 has a width of the order of 0.3°C. Outside this region the derivative $|\partial\chi/\partial T|$ decreases in accordance with a power law, Figure 4. The value $\partial\chi/\partial T$ in the C^*-phase could be measured with accuracy of ±15% for $(T_c - T) < 1.5$°C. Errors increase with further decreasing temperatures for a marked decrease in the magnitude of $\partial\chi/\partial T$.

The temperature dependence of modulus K_θ can be calculated from Eq. (11) using data for χ_T from Figure 3 and $\alpha \approx 9 \cdot 10^{-5}\ \mathrm{C \cdot m^{-2}}$ for DOBAMBC.[12] To calculate $K_\theta(T)$ over a wider temperature range we should use the same curve χ_T, relationships (11), (15), and (15'), and the temperature dependence of the pyro-electric coefficient shown in Figure 5 on the double logarithmic scale. First of all we should calculate the heat capacity term ΔC_θ from Eq. (15') and data of Figures 3 and 5. In the temperature range $0.2°\mathrm{C} \leqslant T_c - T \leqslant 1.6°\mathrm{C}$ $\Delta C_\theta \approx 3.1 \cdot 10^5\ \mathrm{J \cdot m^{-3}\,K^{-1}}$ and is independent of temperature. This figure nearly coincides with a heat capacity jump at the A-C transition point measured with an adiabatic calorimeter,[8] i.e. $\Delta C \approx 2.5 \cdot 10^5\ \mathrm{J \cdot m^{-3}\,K^{-1}}$.

According to Eq. (15') the product $\Delta C_\theta \cdot \chi_T$ can be measured over the whole range of the smectic C^* phase. At the same time, in the limited range $0.2° \leqslant T_c - T \leqslant 2°\mathrm{C}$ it is possible to determine separately χ_T which has a strong temperature dependence and ΔC_θ which is temperature independent. There is no physical reason to expect such a temperature dependence of ΔC_θ with further decreasing temperature. Therefore, we assume ΔC_θ to be a reference constant and calculate the temperature behaviour of the elastic modulus $K_\theta(T)$ from Eq. (15). The result is given in Figure 6 together with experimental relaxation times τ_f and a twist viscosity curve calculated with the help of Eq. (17).

A direct comparison of temperature curves for viscosity γ_1 and the spontaneous polarization P_s shows that with decreasing temperature

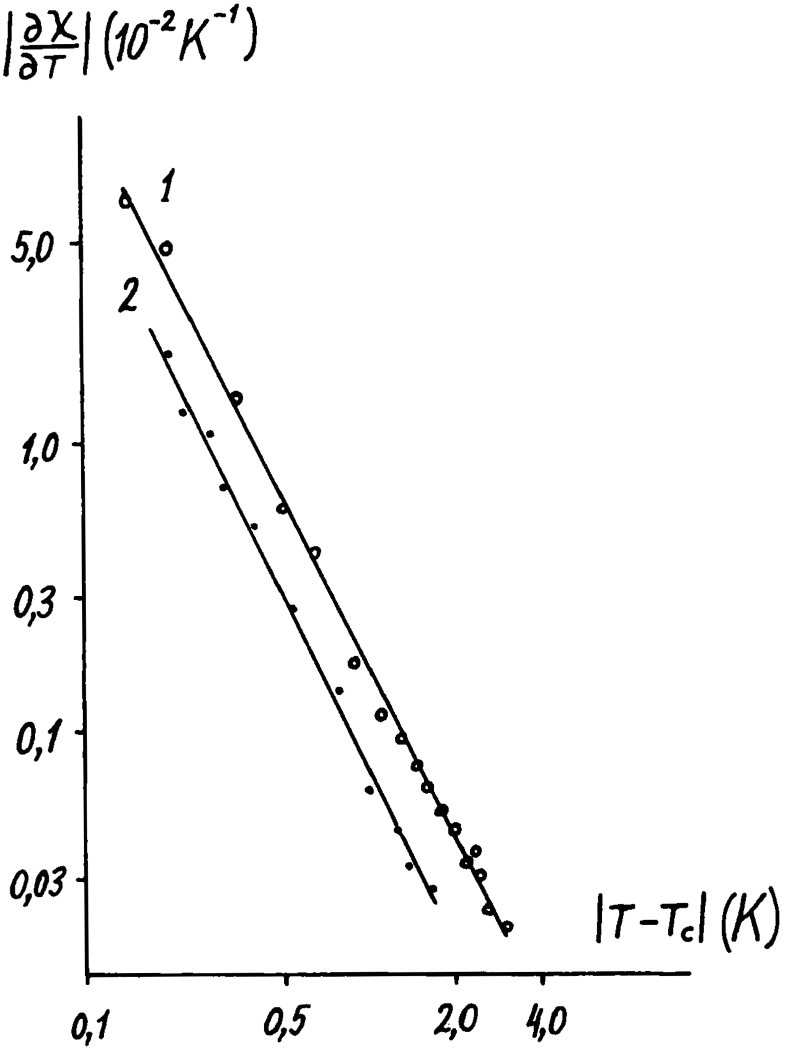


FIGURE 4 Temperature curves for $|\partial\chi/\partial T|$ of DOBAMBC on a log-log scale ($E > E_c$).

γ_1 increases faster than P_s. This result can account for the marked retardation of the electro-optical response of a ferro-electric liquid crystal with decreasing temperature.[13]

The temperature-viscosity curve for various liquid crystalline phases of mixtures I and II (that is, in fact, of HOPE OOBA) is given in Figure 7 on the logarithmic scale. It is seen that, far from the phase

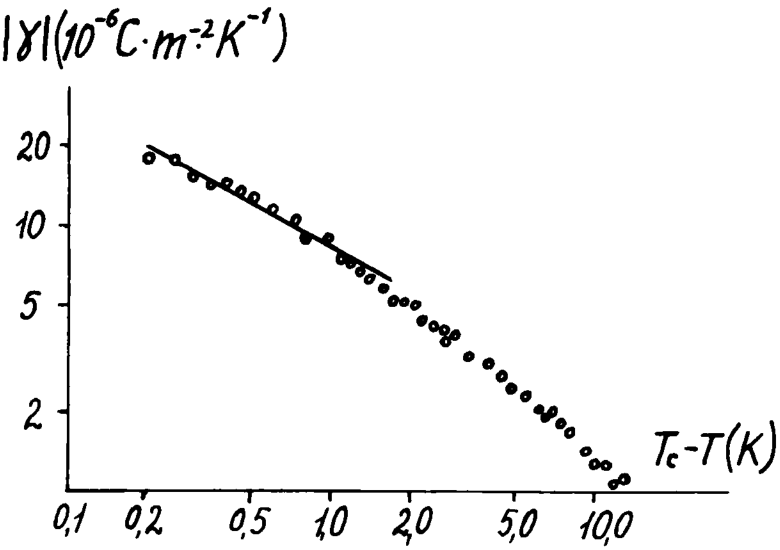


FIGURE 5 Temperature dependence of the pyro-coefficient of DOBAMBC on the log-log scale; $E \approx (0.3\text{–}0.5)\cdot 10^6$ V·m^{-1}.

transitions where the order parameters of the nematic and smectic C^* phases depend slightly on temperature, the dependence $\gamma_1(T)$ in the C^* phase is close to the $\gamma_1(T)$ curve of the nematic phase extrapolated into the smectic C^* temperature range. The corresponding activation energies V calculated from Eq. (1) and data of Figure 7 are 0.78 ± 0.06 eV and 0.74 ± 0.04 eV for the nematic and the smectic C^* phases, respectively. This result shows that the lamellar structure of the smectic C^* phase has no serious effect on molecular motion and the twist viscosity coefficient. In this respect our results are in contrast with those of reference 2 where the activation energy markedly decreases at the transition from the nematic into the smectic C phase.

DISCUSSION

According to the semi-phenomenological theory for the twist viscosity[14] the dependence of γ_1 on θ (i.e., the angle which is the order parameter of the smectic C phase) has the following form:

$$\gamma_1 = A \sin^2\theta \exp \frac{\mu \cdot \sin^2\theta}{k_B T}, \qquad (18)$$

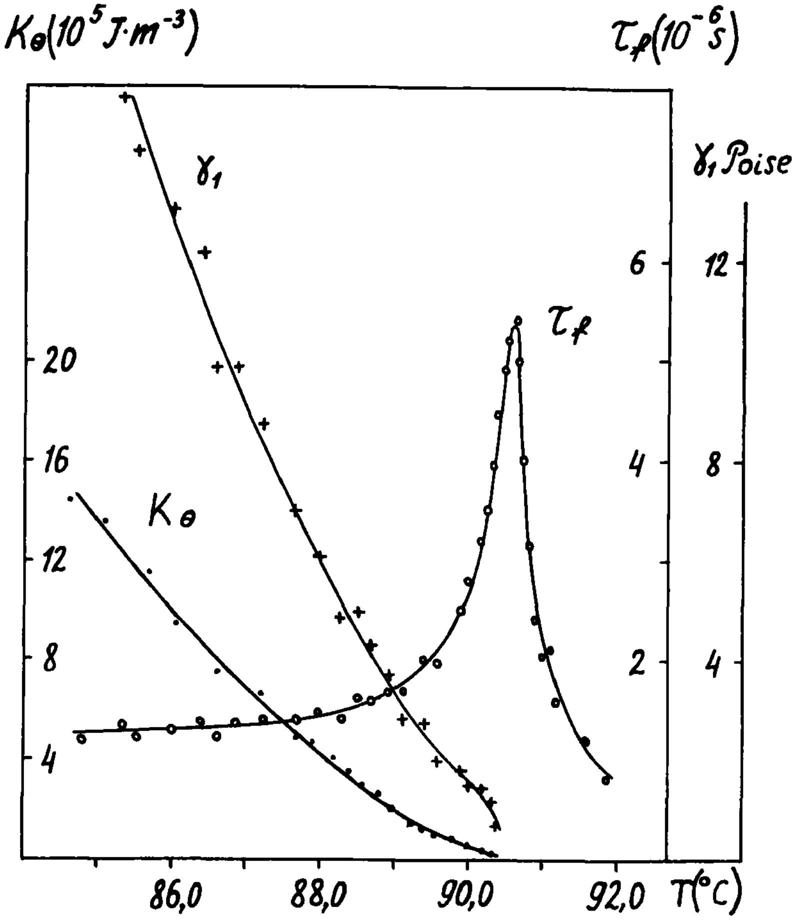


FIGURE 6 Temperature behaviour of the elastic modulus K_θ, relaxation time for the spontaneous polarization τ_f and twist viscosity coefficient γ_1 for the C^* phase.

where $\mu \cdot \sin^2 \theta$ is an energy barrier between two molecular orientations (θ and $-\theta$) and A is a constant. In contrast to (18) for the chiral smectic C^* phase, at the $T = T_c$, the coefficient γ_1 is small but finite (according to our estimations, $\gamma_1 \approx 0.2 - 0.5\ P$ at $T = T_c$ for DOBAMBC) since the elastic modulus and relaxation time are finite. Nevertheless, because of the sharp increase in $\gamma_1(T)$ on going away from the transition, Figure 6, our experimental data may be approximated by Eq. (18) for $T_c - T > 0.5$°C, Figure 8 (curve 1). However, Eq. (18) does not agree with experimental data on $\gamma_1(\theta)$ for mixture I. In the latter case, the experimental curve is better described by

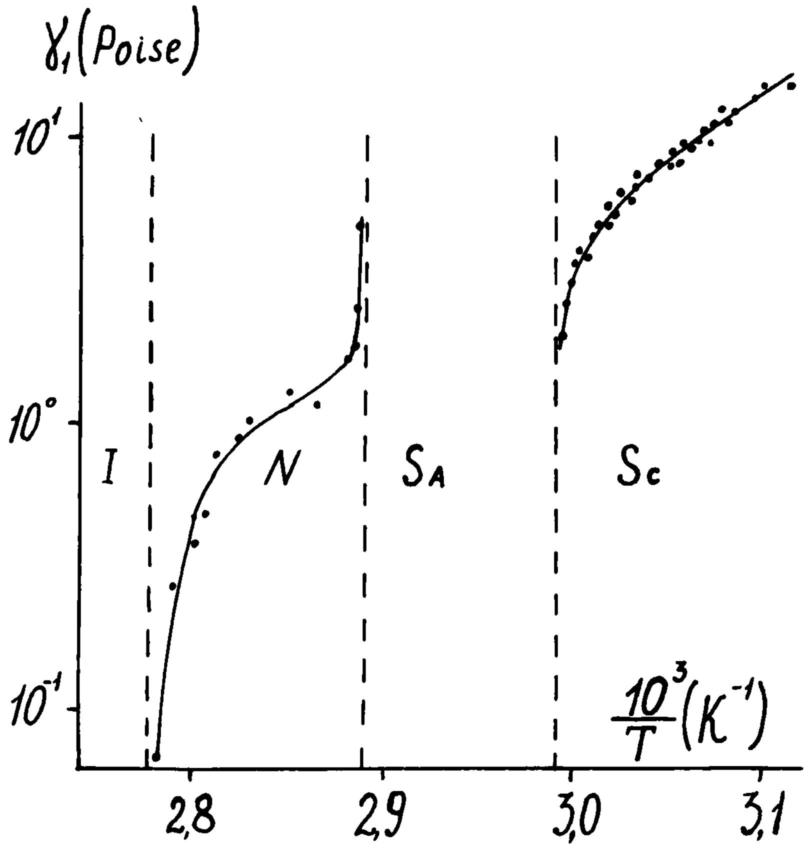


FIGURE 7 Temperature behaviour of the twist viscosity coefficient in the nematic and smectic C^* phase of doped HOPE OOBA.

the empirical equation

$$\gamma_1 = A \sin\theta \exp\frac{\mu \sin^2\theta}{k_B T} \tag{19}$$

This result is in accordance with the fact that the temperature retardation of the electro-optical effect for mixture I is much weaker than for other substances. This example shows that the switching rate of displays based on ferro-electric liquid crystals, which is governed by the ratio P_s/γ_1, can in principle, be improved by a proper choice of a liquid crystalline material.

Now let us discuss the possibility of using the mean-field approximation for the determination of the parameters of a liquid crystal. If we exclude from consideration the smearing region in the vicinity of the A-C phase transition the temperature dependence of $\partial\chi/\partial T$ in Figure 4 would be approximated by the power-law relationship

$$\left|\frac{\partial\chi}{\partial T}\right| = \sigma|T - T_c|^{-\delta}, \qquad (20)$$

where σ is a constant, and δ is a critical exponent. The constant δ_A calculated from (20) and the experimental data for the smectic A phase is two times greater than the corresponding constant σ_c for the C^*-phase (more exactly $\sigma_A/\sigma_c = 2, 1$ see Figure 4). Thus, the so-called "rule of two" which should be fulfilled in the mean-field approximation takes place. The values for critical exponents for the A^*- and C^*-phases ($\delta_A = 1.97 \pm 0.07$, $\delta_c = 2.02 \pm 0.11$) also agree with this approximation.

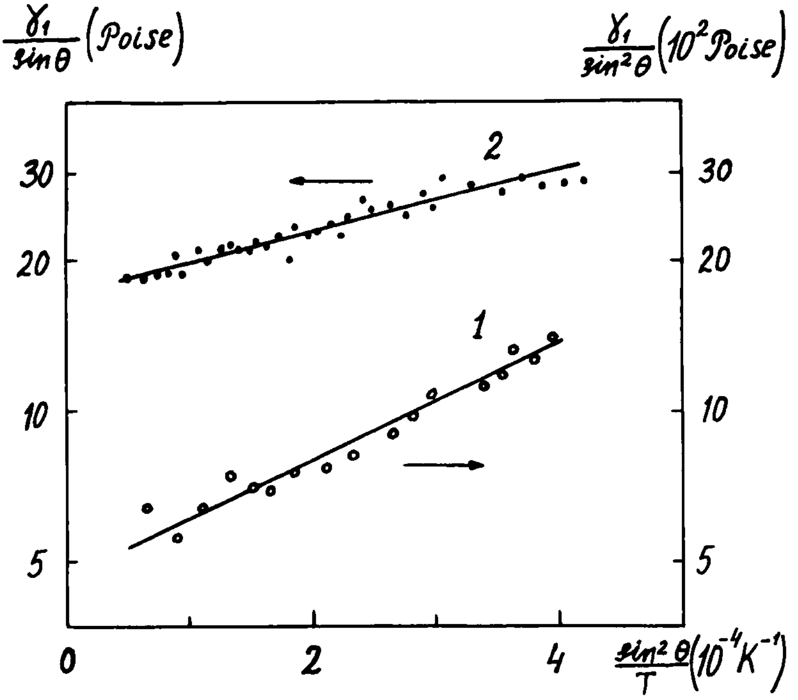


FIGURE 8 The twist viscosity γ_1 as a function of the tilt angle θ for DOBAMBC (curve 1) and mixture I (curve 2).

It follows from the expansion (2) for $E > E_c$ that[15]

$$\chi_T = \begin{cases} \alpha^2[a'_o\,(T - T_c)], & T > T_c \\ -\alpha^2\,[2a'_o\,(T - T_c)], & T < T_c. \end{cases} \tag{21}$$

The data of Figure 4 are well approximated by Eq. (21). So, one can calculate the parameter $a'_o \approx 5 \cdot 10^4\ \mathrm{J \cdot m^{-3}\,K^{-1}}$. This result agrees well with the data of reference 3 and has the same order of magnitude as reported in reference 4. It follows from (11) and (21) that modulus K_θ defined above for the C^*-phase may be related to the phenomenological parameters of the mean-field theory:

$$K_\theta = -2a'_o\,(T - T_c). \tag{22}$$

Needless to say Eqs. (21) do not hold for the whole temperature range of the smectic C^* phase. The same is also true for the approximation of the pyro-electric coefficient by a power law. For example, the curve of $\gamma(T)$ in Figure 5 can be approximated by the function $\gamma \sim (T_c - T)^{\beta-1}$ with $\beta = 0.48 \pm 0.05$ in the range $0.2°\mathrm{C} \leqslant T_c - T \leqslant 1.4°\mathrm{C}$ (β is the critical exponent for the spontaneous polarization, $P_s \sim (T_c - T)^\beta$). This exponent decreases to $\beta = 0.32 \pm 0.05$ with a broadening of the interval of approximation up to $T_c - T = 10°\mathrm{C}$. The latter explains different β-values obtained in earlier papers.[16,17]

Nevertheless there still remains the possibility of calculating the $K_\theta(T)$ dependence over a wider temperature range. To this end, one should expand the free energy to include higher terms,[3,4] i.e.

$$F = \frac{1}{2}a\theta^2 + \frac{1}{4}B\theta^4 + \frac{1}{6}c\theta^6. \tag{23}$$

In this approximation the spontaneous polarization is written as follows:[18]

$$P_s \approx \alpha\left(-\frac{a}{B}\right)^{1/2}\left(1 + \frac{ac}{B^2}\right)^{1/2},\ a = a'_o\,(T - T_c). \tag{24}$$

One can calculate parameters B and c from the temperature dependence of P_s (e.g. $B \approx 1.3 \cdot 10^6\ \mathrm{J \cdot m^{-3}}$, $c \approx 1.9 \cdot 10^6\ \mathrm{J \cdot m^{-3}}$ for

DOBAMBC). Using Eq. (11) and the approximate equation for χ_T, i.e.

$$\chi_T^{-1} \approx -2\alpha^2 a \left(1 - \frac{ac}{B^2}\right), \tag{25}$$

it is possible to calculate $K_\theta(T)$. The resulting dependence agrees well with the curve shown in Figure 6. Therefore, the phenomenological theory is again confirmed.

In conclusion, the modified pyro-electric technique allowed us to study the temperature behaviour of the dielectric susceptibility, elastic modulus K_θ, and twist viscosity γ_1 for a ferro-electric liquid crystal DOBAMBC using only general thermodynamic equations. As a result, it was shown, independently, that the mean-field theory is a good approximation for description of the A^*-C^* phase transition within a temperature deviation up to 1°C. The allowance made for higher terms of the phenomenological expansion of free energy provides an adequate description of the experimental data within the range $T_c - T$ up to 10°C.

Acknowledgment

The authors would like to thank Dr. V. G. Chigrinov, Dr. M. A. Osipov and Prof. S. A. Pikin for numerous helpful discussions.

References

1. W. Kuczynski, *Ber. Bunsenges Phys. Chem.*, **85**, 3, 324 (1981).
2. S.Meiboom and R. C. Hewitt, *Phys. Rev. Letters*, **34**, 18, 1146 (1975).
3. T. Carlsson and J. Dahl, *Mol. Cryst. Liq. Cryst.*, **95**, 373 (1983).
4. C. C. Huang and J. M. Viner, *Phys. Rev. A.*, **25**, 6, 3385 (1982).
5. S. Garroff and R. B. Meyer, *Phys. Rev. Lett.*, **38**, 848 (1977).
6. B. I. Ostrovsky, A. Z. Rabinovich, A. S. Sonin, and B. A. Strukov, *Zh. Eksp. Teor. Fiz.*, **74**, 1748 (1978).
7. B. I. Ostrovsky, S. A. Pikin, and V. G. Chigrinov, *Zh. Eksp. Teor. Fiz.*, **77**, 1631 (1977).
8. B. I. Ostrovsky, *Doct. Thesis*, Moscow, 1980.
9. L. A. Beresnev, L. M. Blinov, and E. B. Sokolova, *Zh. Eksp. Teor. Fiz.*, **28**, 340 (1978).
10. V. G. Chigrinov, M. F. Grebenkin, *Kristallografiya*, **20**, 1240 (1975).
11. M. F. Grebenkin, V. A. Seliverstov, L. M. Blinov, and V. G. Chigrinov, *Kristallografiya*, **20**, 984 (1975); V. V. Belyayev, and M. F. Grebenkin, *Vth Conf. of Soc. Countries on Liquid Crystals*, Odessa, 1983 (Abstracts, C-25).
12. E. P. Pozhidayev, L. A. Beresnev, L. M. Blinov, and S. A. Pikin, *Zh. Eksp. Teor. Fiz.*, **37**, 73 (1983).

13. L. A. Beresnev, L. M. Blinov, V. A. Baikalov, E. P. Pozhidayev, G. V. Purvanetskas, and A. I. Pavluchenko, *Mol. Cryst. Liq. Cryst.*, **89**, 3, 27 (1972).
14. A. C. Diogo, A. F. Martins, *Liq. Cryst. One and Two Dimens. Order.*, Eds. W. Helfrich and G. Hepke, (Springer-Verlag, Berlin, 1980), p. 108.
15. S. A. Pikin and V. L. Indenbom, *Ferroelectrics*, **20**, 151 (1978).
16. B. I. Ostrovsky, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova, *Zh. Eksp. Teor. Fiz.*, **25**, 80 (1977).
17. B. I. Ostrovsky, A. Z. Rabinovich, A. S. Sonin, and E. L. Sorkin, *Ferroelectrics*, **24**, 309 (1980).
18. R. Blinc and B. Žeks, *Ferroelectrics and Antiferroelectrics*, Moscow, Mir, 1975 (in Russ.).