

Anomalous orientation of ferroelectric liquid crystal films in an electric field

P. O. Andreeva, V. K. Dolganov,^{a)} and K. P. Meletov

Institute of Solid-State Physics, 142432 Chernogolovka, Moscow District, Russia

(Submitted 5 August 1997)

Pis'ma Zh. Éksp. Teor. Fiz. **66**, No. 6, 414–418 (25 September 1997)

An anomalous orientation of ferroelectric liquid crystals in an electric field is observed. The tilt planes of the molecules are oriented in a direction parallel to the electric field. The anomalous orientation is observed in freely suspended films above the smectic-C*–smectic-A bulk phase transition temperature. The effect is explained by the appearance of giant flexoelectric polarization, 10^4 times greater than that in bulk liquid-crystal samples, in the film. © 1997 American Institute of Physics. [S0021-3640(97)00918-3]

PACS numbers: 61.30.Gd, 77.84.Nh

Ferroelectric liquid crystals (Sm-C*) have a layered structure, each layer consisting of a two-dimensional liquid with the long axes of the chiral molecules tilted with respect to the normal to the smectic layers.^{1,2} The spontaneous polarization $\mathbf{P}_0$ in a smectic layer is perpendicular to the tilt plane of the molecules ($\mathbf{P}_0$ is parallel to the vector $(\mathbf{z} \times \mathbf{n})$, where $\mathbf{z}$ is the normal to the smectic plane and $\mathbf{n}$ is the director, i.e., the direction of predominant orientation of the long axes of the molecules). The chirality of the molecules causes the tilt plane of the molecules (and, correspondingly, the spontaneous polarization) in neighboring smectic layers to rotate, as a result of which there is no macroscopic polarization in samples which are large compared to the helical pitch. If the sample is smaller in the direction normal to the smectic layer than the helical pitch or if an electric field strong enough to untwist the helix is applied to the crystal, then a ferroelectric liquid crystal has a macroscopic spontaneous polarization $\mathbf{P}_0$. The presence of a spontaneous polarization $\mathbf{P}_0$, the possibility of flexoelectric liquid crystals to be oriented in weak electric fields, and numerous technical applications in this connection arouse great interest in investigations of ferroelectric liquid-crystal structures. We underscore once again that in an electric field the polar axis of the ferroelectric liquid crystal should be oriented in the direction of the field and the tilt plane of the molecules in the smectic layers should be oriented perpendicular to the field. This follows from the symmetry of a ferroelectric liquid crystal and has been confirmed in many experiments.

In the present work it was observed that an abrupt change in the direction of orientation of the molecules occurs in freely suspended films above the temperature of the Sm-C*–Sm-A bulk phase transition. If an electric field orients a ferroelectric film at low temperatures in the same manner as in a bulk sample, then at high temperatures the orientation changes by 90° : The tilt planes of the molecules become oriented in the direction of the field. We attribute the reorientation of the structure to the onset in the film

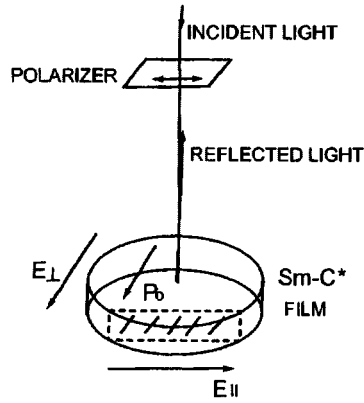


FIG. 1. Relative arrangement of a ferroelectric film and the optical part of the apparatus. The orientation of the molecules in the film is shown for the case when the film is in the low-temperature region of the Sm-C* phase and an electric field $E_{\perp}$ is applied to it. $\mathbf{P}_0$ — ferroelectric polarization vector.

of an anomalously high flexoelectric polarization $\mathbf{P}_f$, directed perpendicular to the spontaneous ferroelectric polarization $\mathbf{P}_0$.

The measurements were performed in the ferroelectric liquid crystal *n*-nonyloxybenzylidene-*n*'-amino-2-methylbutylcinnamate (NOBAMBC), in a bulk sample of which the following sequence of phase transitions occurs: Sm-H* (76 °C)–Sm-C* (91 °C)–Sm-A (116 °C)–I (isotropic liquid). The Sm-C*–Sm-A transition is a second-order phase transition. Some measurements were performed on the flexoelectric liquid crystal *n*-decyloxybenzylidene-*n*'-amino-2-methylbutylcinnamate (DOMAMBC), which forms the same liquid-crystal phases as does NOBAMBC. The films were placed in a 6-mm opening in a glass plate. The planes of the smectic layers in freely suspended films are parallel to the film surface. Optical reflection from the films was measured in the “backward” geometry (Fig. 1). An electric field (3 V/cm) could be applied to the film in two mutually perpendicular directions. The thickness of the films (for $N > 12$ smectic layers) was determined from the spectral dependence of the optical reflection in the Sm-A phase,³

$$I(\lambda) = \frac{(n^2 - 1)^2 \sin^2(2\pi nNd/\lambda)}{4n^2 + (n^2 - 1)^2 \sin^2(2\pi nNd/\lambda)}, \quad (1)$$

where d is the interplanar distance ($d \approx 3.2$ nm in the Sm-A phase of NOBAMBC) and $n = 1.48$ ($\lambda = 630$ nm) is the index of refraction. The spectral reflection curve for thin films is virtually thickness-independent:

$$I(\lambda) \approx N^2 d^2 \pi^2 (n^2 - 1)^2 / \lambda^2. \quad (2)$$

The number of smectic layers in this case was determined from the relative intensity of the reflections for films with a different number of layers $I(N) \sim N^2$. Films with the required thickness were prepared by layer-by-layer thinning by heating above the temperature of the liquid crystal — isotropic phase bulk phase transition.^{4–6}

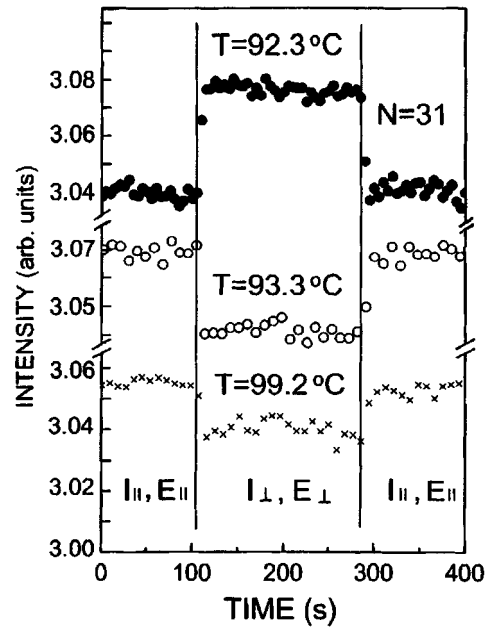


FIG. 2. Optical reflection intensity ($I_{\perp}$, $I_{\parallel}$) for a ferroelectric film ($N=31$) in an electric field applied parallel ($E_{\parallel}$) and perpendicular ($E_{\perp}$) to the direction of polarization of the light ($\lambda = 630$ nm).

The transition into the Sm-A phase in freely suspended films is shifted to higher temperatures with respect to the transition in the bulk sample.⁷⁻⁹ In the present work we measured the optical reflection ($I_{\parallel}$, $I_{\perp}$) for electric fields oriented parallel ($E_{\parallel}$) and perpendicular ($E_{\perp}$) to the plane of polarization of the light in the Sm-C* temperature range and at the transition to the Sm-A phase. This method enabled us to detect an intensity difference of $\sim 10^{-3}$ when the direction of the electric field was switched. The in-plane optical anisotropy is due to the tilting of the long axes of the molecules in Sm-C*. The refractive index $n_0 = n_{\perp}$ in a direction perpendicular to the tilt plane of the molecules is virtually temperature-independent (n_0 is the ordinary index of refraction). The refractive index for the extraordinary ray, $n_e > n_0$, depends on the tilt angle θ of the molecules. Measurement of the reflection for two polarizations is a simple and direct method for determining both the film orientation and the temperature dependence of n_e as well as the polar angle θ in the ferroelectric phase (θ is the order parameter for the Sm-C*–Sm-A phase transition). If the angle θ is not constant in the film, then the intensity of the optical reflection for thin films is determined by the mean-square tilt angle $\overline{\theta^2}/N$ of the molecules (the averaging is over the smectic layers of the film).

The change occurring in the intensity of reflection from the film when the direction of the electric field is switched is qualitatively different at low and high temperatures (Fig. 2, $N=31$). For $T < 92.8$ °C we have $I_{\perp} > I_{\parallel}$, in agreement with the conventional ideas about the direction of the spontaneous polarization in Sm-C*: For $\mathbf{P}_0$ oriented in the direction of the electric field, the larger value of the refractive index n_e and, accordingly,

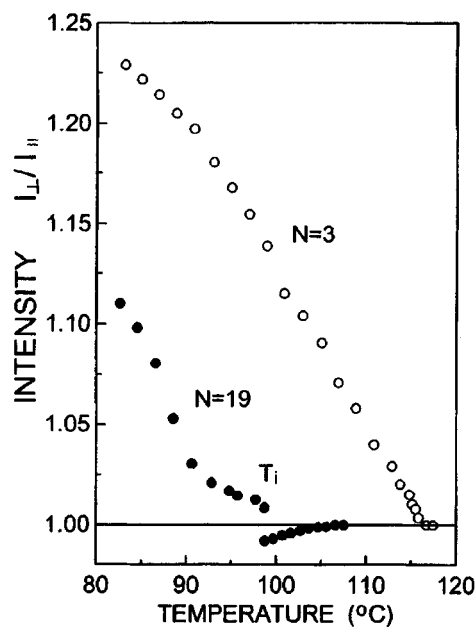


FIG. 3. Temperature dependences of the relative optical reflection intensities $I_{\perp} / I_{\parallel}$ for films 3 and 19 smectic layers thick ($\lambda = 630$ nm).

the larger value of the reflection coefficient $I_{\perp}$ correspond to a direction perpendicular to the field (the tilt plane of the molecules in Sm-C*). At $T_i \approx 92.8$ °C an abrupt change in the reflection intensities occurs for both polarizations: The intensity $I_{\parallel}$ becomes equal to $I_{\perp}$, the value at temperatures $T < T_i$, while $I_{\perp}$ decreases to the value of $I_{\parallel}$ at temperatures $T < T_i$. Above this temperature and up to the transition to the Sm-A phase the reflection intensity decreases when the field is switched $E_{\parallel} \rightarrow E_{\perp}$. This means that the tilt plane of the molecules is oriented in the direction of the field. Figure 3 displays the temperature dependence of the relative reflection intensity $I_{\perp} / I_{\parallel}$ for films with $N = 19$ and $N = 3$. The temperature T_i above which anomalous orientation of the films was observed depends on the film thickness — the higher the temperature, the thinner the film: For films with 12 smectic layers $T_i \approx 104$ °C and for thick films T_i lies close to the temperature of the bulk phase transition ($T_i - T_c \approx 0.3$ °C for $N = 50$). We did not observe anomalous orientation in ultrathin films ($N = 3$, Fig. 3).

It should be underscored that the observed effect is qualitatively different from the reorientation of the direction of the spontaneous polarization by 180° , which has been observed previously in ferroelectric liquid crystals.^{10,11} That reorientation is not specific to thin films and is observed in both films and bulk samples; in addition, the tilt plane of the molecules remains perpendicular to the direction of spontaneous polarization and the electric field. In our case, however, the structure rotates by 90° with respect to the external field.

The decrease of the absolute value $|I_{\perp} / I_{\parallel} - 1|$ with increasing temperature (Fig. 3)

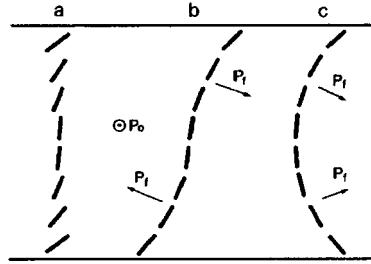


FIG. 4. Orientation of the molecules in a smectic ferroelectric liquid crystal film: S-like orientation of the director (a, b), C-like orientation of the director (c). $\mathbf{P}_0$ — spontaneous ferroelectric polarization, $\mathbf{P}_f$ — flexoelectric polarization.

characterizes the variation of the tilt angle of the molecules with temperature. For $T=82^\circ\text{C}$ the angle θ determined from our data equals 28° for a film with $N=3$ and 21° for $N=19$. A jump in the reflection intensity ($N=19$) occurs at a molecular tilt angle $\theta \approx 6^\circ$. The dependence of θ on the film thickness is related with the surface ordering of the smectic layers.^{7-9,12} Surface ordering is strongest above the bulk phase transition temperature. In this temperature range the angle θ depends strongly on the distance of the smectic layer from the surface.⁷⁻⁹ In our opinion, the variation of the angle θ in the smectic layers could be responsible for the anomalous orientation of the film. Figures 4a and 4b show schematically the orientation of the molecules in the smectic layers of a ferroelectric liquid crystal film. The bending of the director should give rise to a flexoelectric polarization $\mathbf{P}_f$ in the tilt plane of the molecules:¹

$$\mathbf{P}_f = e_1 \mathbf{n}(\nabla \cdot \mathbf{n}) + e_3 (\nabla \times \mathbf{n}) \times \mathbf{n}. \quad (3)$$

Let us compare the spontaneous polarization $\mathbf{P}_0$ and the flexoelectric polarization $\mathbf{P}_f$, induced by bending of the director $\mathbf{n}$, in the temperature range where a transition to anomalous orientation occurs ($N=19$, $\theta \approx 6^\circ$). The ferroelectric polarization $\mathbf{P}_0$ with $\theta=6^\circ$ is of the order of $1 \times 10^{-5} \text{ C/m}^2$ for substances of the NOBAMBC type.¹³ In liquid crystals the flexoelectric constants e_1 and e_3 are typically of the order of 10^{-10} – 10^{-12} C/m .^{2,14} To estimate $\mathbf{P}_f$ we assume the value $e_3=10^{-11} \text{ C/m}$. For the case when the tilt angles of the molecules in the surface layer and at the center of the film differ by $\Delta\theta=0.2 \text{ rad}$ we obtain $\mathbf{P}_f \approx 7 \times 10^{-5} \text{ C/m}^2$.

These estimates show that a flexoelectric polarization $\mathbf{P}_f$ appreciably greater in magnitude than the spontaneous ferroelectric polarization $\mathbf{P}_0$ can arise in a plane perpendicular to $\mathbf{P}_0$. As a result of the much larger bending of the director in a film, the polarization $\mathbf{P}_f$ is 10^4 times greater than the flexoelectric polarization in bulk liquid crystal samples.

In the case of S-shaped bending of the director (Fig. 4b) the direction of $\mathbf{P}_f$ is different at the top and bottom of the film. For a film which is not too thin, the tilt angle of the molecules at the center of the film can become quite small (or zero) above the bulk phase transition temperature. In this case the top and bottom of the film can be oriented independently, and a transition to a C-like orientation of the director (Fig. 4c) with

flexoelectric polarizations directed in the same direction becomes possible. For $\mathbf{P}_f > \mathbf{P}_0$ the C orientation is favored in an electric field, and the $S \rightarrow C$ transition leads to a 90-degree reorientation of the tilt plane of the molecules.

We also observed anomalous orientation in a ferroelectric liquid crystal DOBAMBC. The nonuniform orientational structure of the films that is associated with stabilization of the tilt surface of the molecules and the proximity of the phase transition to the Sm-A, nematic, or isotropic phase is typical for liquid-crystal films. Anomalous reorientation of the structures (caused by transitions of the type $S \rightarrow C$) can be expected to occur in this connection in a wide class of liquid-crystal substances.

We thank E. I. Kats and V. I. Marchenko for helpful discussions. This work was performed with the support the Russian Fund for Fundamental Research (Grant No. 95-02-05343), the State Science and Technology Program "Statistical Physics," and INTAS (Grant No. 94-4078).

^{a)}e-mail: dolganov@issp.ac.ru

¹P.-G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974 [Russian translation, Mir, Moscow, 1977].

²S. A. Pikin, *Structural Transformations in Liquid Crystals* [in Russian], Nauka, Moscow, 1981.

³M. Born and E. Wolf, *Principles of Optics*, Pergamon Press, New York, 1964 [Russian translation, Nauka, Moscow, 1970].

⁴T. Stoebe, P. Mach, and C. C. Huang, Phys. Rev. Lett. **74**, 1384 (1994).

⁵E. I. Demikhov, V. K. Dolganov, and K. P. Meletov, Phys. Rev. E **52**, R1285 (1995).

⁶V. K. Dolganov, E. I. Demikhov, R. Fouret, and C. Gors, Phys. Lett. A **220**, 242 (1996).

⁷S. Heinekamp, R. A. Pelcovits, E. Fontes *et al.*, Phys. Rev. Lett. **52**, 1017 (1984).

⁸S. M. Amador and P. S. Pershan, Phys. Rev. A **41**, 4226 (1990).

⁹Ch. Bahr, C. Booth, D. Fliegner, and J. W. Goodby, Phys. Rev. E **52**, 4612 (1995).

¹⁰N. Mikami, R. Higuchi, T. Sakurai *et al.*, Jpn. J. Appl. Phys., Part 1 **25**, 833 (1986).

¹¹Ch. Bahr, C. Booth, D. Fliegner, and J. W. Goodby, Europhys. Lett. **34**, 507 (1996).

¹²V. K. Dolganov, E. I. Demikhov, R. Fouret, and C. Gors, Zh. Eksp. Teor. Fiz. **111**, 949 (1997) [JETP **84**, 522 (1997)].

¹³B. I. Ostravskii, A. Z. Rabinovich, A. S. Sonin *et al.*, JETP Lett. **25**, 70 (1977).

¹⁴L. M. Blinov, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals*, Wiley, New York, 1983 [Russian original, Nauka, Moscow, 1978].

Translated by M. E. Alferieff