Piezoelectric and flexoelectric effects in ferroelectric liquid crystals

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Flexoelectric and piezoelectric effects in ferroelectric liquid crystals (FLCs) have been studied. It is shown that nonlinear electromechanical coupling is determined by a local flexoelectric effect. Dependence of the parameters of nonlinearity of the flexoelectric effect on the parameter of phase transition from a paraelectric phase to a polar phase has been studied. Dependencies of flexoelectric and piezoelectric coefficients on the frequency of the mechanical vibrations have been studied.

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I. INTRODUCTION

For many years liquid crystal science has been growing, especially in recent decades, due to applications in the electronic display industry [1–3]. The discovery of ferroelectric behavior in a chiral smectic liquid crystal originated the research and development of new types of materials termed ferroelectric liquid crystals (FLCs) [3–5]. Undoubtedly, electro-optical effects in FLCs and high-speed devices do not exhaust all of the potential applications of such materials. During the last decade, the electromechanical effect in FLCs was intensively studied [6]. The presence of a piezoelectric effect in FLCs potentially enables the extension of the field of application of FLCs. Liquid crystalline ferroelectrics are also the subject of interest for basic research since they represent pseudointrinsic ferroelectrics with electromechanical coupling.

According to theoretical and experimental data, the possibility of the appearance of piezoelectric behavior in FLC depends on the symmetry of a paraelectric phase [7], i.e., the nonpolar phase of a ferroelectric which exists at higher temperatures above the Curie point. In accordance with the Curie law, loss of a center of inversion occurs upon transition from a paraelectric phase to a polar phase, and a crystal can acquire piezoelectric properties. The possibility of obtaining of such piezoelectric properties depends on the relationship between symmetry properties of paraelectric and ferroelectric phases. According to the Curie principle, initiation of piezoelectric properties is possible when a group of symmetry elements of a polar phase constitutes the subgroup of a paraelectric phase. Introduced for proper ferroelectrics, this principle could be also extended to nonintrinsic ferroelectrics. However, the possibility of its application to pseudointrinsic ferroelectrics has not been studied at all.

Many intrinsic and nonintrinsic ferroelectrics possessing translational ordering also possess the piezoelectric effect. However, for pseudointrinsic ferroelectrics, the flexoelectric effect is also possible [8], which is inherent for polar dielectrics that possess orientational ordering further to translational ordering. According to the existing theories, two types of flexoelectric effects are possible for FLCs [9–11]. The first type of effect is related to the presence of a helicoidal structure in a FLC where a homogeneous component of a spontaneous polarization occurs upon deformation of the helicoidal structure [9,10]. The other type of effect relates to the deformation of the director field in the smectic layers and leads to the variation of the dipole distribution within the smectic layer [11]. Both effects are accompanied with the appearance of a dipole moment in the bulk of a sample. The piezoelectic effect occurs as a result of a disturbance of the translational ordering accompanied with a variation of a director tilt angle in the smectic layer.

At the beginning of this work it was experimentally shown that the electromechanical coupling in FLCs is dynamic, i.e., polarization occurring at static deformations disappears for a few milliseconds [12]. It was revealed that in certain FLCs electromechanical coupling is nonlinear; however, causes for such nonlinearity have not been determined [13].

In this work, experimental results concerning determination of the contributions of the flexoelectric and piezoelectric effects to the electromechanical coupling are presented for the first time. In order to extract the contributions of the effects to the electromechanical coupling, separation by relaxation time scale was used. This approach is based on the fact that a large-scale flexoelectric effect is characterized in a larger relaxation time scale as compared with the relaxation time scale for the deformation of director in the smectic layer, as was shown in dielectric studies of the Goldstone mode [14].

II. EXPERIMENT

Experiments were carried out on the induced ferroelectric liquid crystal compositions. Each composition used comprises an achiral smectic *C* host and a chiral guest (CG). Chemical structures of the FLC components are shown in Table I.

Compounds **2** and **3** were commercially available (Kharkov plant of the chemicals). Compound **8** was obtained by a similar method as described in Ref. [15]. Other compounds under study were synthesized according to the corresponding works: **1** [16]; **4–6** [17]; **7** [18]; *E* isomer of compound **9** [19,20].

Each FLC composition possesses its own distinct set of properties such as spontaneous polarization (P_S), tilt angle of molecules in smectic layers (θ), rotational viscosity (γ_φ), phase sequence, and phase transition temperatures, which will be specified below.

Composition **I** contains 24.8 wt% CG **7** in a host **1**. The phase sequence and transition temperatures are as

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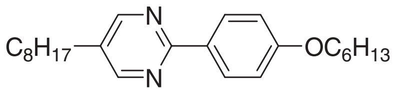
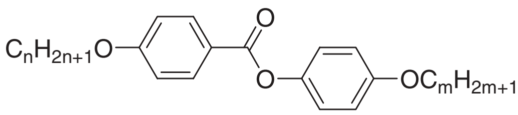
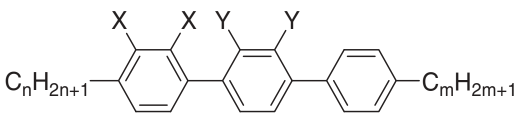
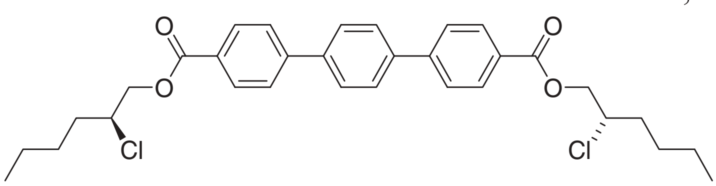
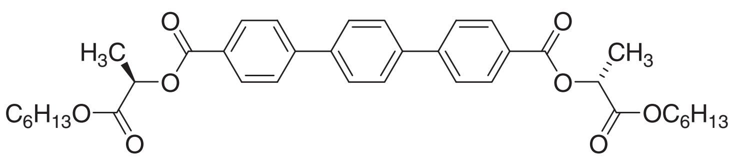
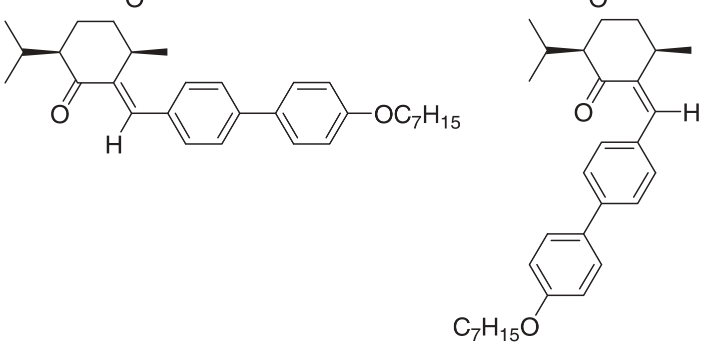
TABLE I. Chemical structures of the FLC components.

		**1**
	m = 6, n = 8	**2**
	m = 6, n = 10	**3**
	n = 5, m = 7, X = F, Y = H	**4**
	n = 5, m = 7, X = H, Y = F	**5**
	n = 7, m = 5, X = F, Y = H	**6**
		**7**
		**8**
 ~1 : 9		**9**

follows:

$$\text{Iso} \underset{80.5}{\longrightarrow} \text{two-phase region Iso,}$$
$$\text{Sm}A^* \underset{77.5}{\longrightarrow} \text{Sm}A^* \underset{54}{\longrightarrow} \text{Sm}C^* \underset{<20}{\longrightarrow} \text{Cr},$$

where Iso is the isotropic phase; SmA^* is the smectic A phase comprising CG molecules; SmC^* is the chiral smectic C phase; Cr is the crystal phase. Characteristic values of ferroelectric parameters of the composition **I**, such as spontaneous polarization (P_S) = −27.6 nC/cm^2, smectic tilt angle (θ) = 21°, and rotational viscosity (γ_φ) = 0.3 P were obtained at temperature (ΔT) 20° below SmA^*→SmC^* phase transition.

Composition **II** contains 17.4 wt% CG **8** in liquid crystal (LC) host **2**. The phase sequence and transition temperatures are as follows:

$$\text{Iso} \underset{87}{\longrightarrow} \text{BP} \underset{86.4}{\longrightarrow} N^* \underset{74}{\longrightarrow} \text{Sm}C^* \underset{42}{\longrightarrow} \text{Cr},$$

where BP is a blue phase, and N^* is the cholesteric phase. Characteristic FLC parameters of the composition **II** at ΔT = 20 °C are $P_S = -50$ nC/cm^2, $\theta = 28°$, $\gamma_\varphi = 0.51$ P.

Composition **III** is the eutectic mixture of 25%, 50%, and 25% of compounds **4**, **5**, and **6**, respectively, to which 15.5 wt% of CG **9** is added. CG **9** is the photostationary mixture of E and Z isomers which was obtained from pure E isomer [19] by irradiation with nonfiltered light of a mercury lamp DRSh-120 for 1 h, as was described in Ref. [20].

The phase sequence and transition temperatures for composition **III** are

$$\text{Iso} \underset{106}{\longrightarrow} N^* \underset{66}{\longrightarrow} \text{Sm}A^* \underset{59}{\longrightarrow} \text{Sm}C^* \underset{<20}{\longrightarrow} \text{Cr}.$$

Characteristic FLC parameters of the composition at ΔT = 20 °C are $P_S = 28$ nC/cm^2, $\theta = 29.8°$, $\gamma_\varphi = 0.48$ P.

Composition **IV** is the eutectic equimolar mixture of compounds **2** and **3** as nonchiral host to which 14 wt% of CG **8** is added. The composition has the following phase transition temperatures:

$$\text{Iso} \underset{88}{\longrightarrow} N^* \underset{71}{\longrightarrow} \text{Sm}A^* \underset{59}{\longrightarrow} \text{Sm}C^* \underset{<20}{\longrightarrow} \text{Cr}.$$

Characteristic ferroelectric parameters of the composition at ΔT = 20 °C are $P_S = -50$ nC/cm^2, $\theta = 28°$, $\gamma_\varphi = 0.51$ P.

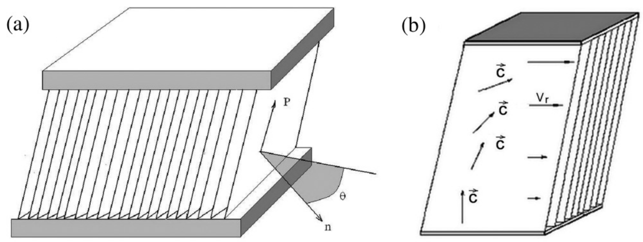


FIG. 1. Experimental geometry of studies of the piezoelectric (a) and flexoelectric (b) effects.

Composition **V** is prepared on the base of the same nonchiral host as composition **IV** by adding 9.85 wt% of CG **8**. Temperature of the second-order phase transition SmA^*→SmC is 65 °C. P_S value for the composition is 22.5 nC/cm^2 at 30 °C.

A FLC was placed in a cell consisting of two plane parallel glasses coated with transparent ITO electrodes. The surface area of the cell plates was about 4 cm^2. The specified cell thickness was set in the range from 24 to 33 μm by using glass rod spacers of the corresponding diameter. Planar alignment of a FLC sample was obtained using an orienting layer of a polyimide coating by a known method [21]. The cell construction allows small shifts of the upper plate by means of sealing with flexible silicon glue.

Figure 1 shows cell geometry which enables the measurement of the piezoelectric coefficient [Fig. 1(a)] and the flexoelectric coefficients [Fig. 1(b)] according to the theoretical works [9–11]. Studies of the piezoelectric response were carried out at the conditions where the deformation vector coincides with the normal to the smectic layers [Fig. 1(a)]. As a result of such deformation, some decrease of the layer thickness occurs and consequently the tilt angle of the director in the smectic layers increases. In order to study flexoelectric effects, shear deformation along the smectic layers was applied [Fig. 1(b)]. Measurements at different frequencies were carried out in order to study local and large-scale flexoeffects. It is necessary to affect the sample with a frequency greater than the relaxation frequency of the Goldstone mode such that the helicoids do not have enough time to respond to the external field $\vec{c}$.

III. RESULTS AND DISCUSSION

Dependencies of the electric response of a sample on the amplitude of the mechanical shear along the normal to the smectic layers (direct piezoelectric effect) and of the amplitude of the mechanical shear on the electric-field strength (inverse piezoelectric effect) were studied. Results of these studies for the direct piezoelectric effect are shown in Fig. 2. It is seen that the direct piezoelectric effect is linear as well as the inverse piezoelectric effect.

We have also carried out a dielectric study of the FLCs and determined the Goldstone-mode frequency. From Fig. 3 one can see that for compositions **II** and **III** the Goldstone mode is 700 Hz. Thus, by using frequencies more than 700 Hz we can exclude the influence of helix deformation on the electromechanical coupling.

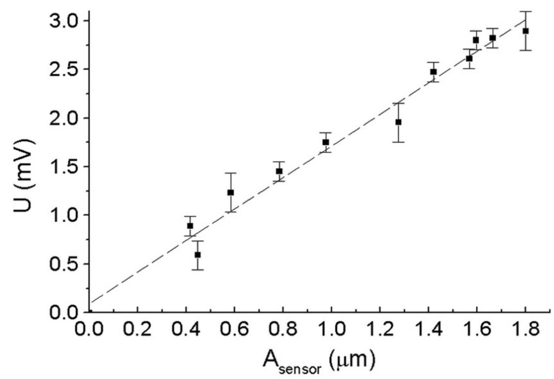


FIG. 2. The dependence of the amplitude of electric response of the FLC sample on the amplitude of the mechanical shear of the upper cell plate along the normal to the smectic layers, (composition **I**, T = 20 °C, $f = 4.6$ kHz).

We have studied the dependencies of the electric response of the FLC sample on the amplitude of the mechanical shear of the upper cell plate along the smectic layers at different frequencies. As can be seen from Fig. 4, the electromechanical coupling increases with the increase of frequency.

The experimental data have low reproducibility under the Goldstone-mode frequency (Fig. 4). It could be due to the fact that the electromechanical coupling coefficient at low frequencies is low and therefore the contribution to the electromechanical coupling from helix deformation should be also low. The experimental data coincide with theory [10] where the large-scale effect is not considered. Thus, the electromechanical coupling is realized more effectively by means of local deformation, at least in the studied FLCs.

Investigation of the dependence of flexoelectric coefficients on frequency has shown that two ranges could be assigned (Fig. 5): the nonlinear range (from 0 up to 1200 Hz) and the linear range (over 1200 Hz).

The linear nature of the dependence of the flexoelectric coefficients is predicted by the model offered in Ref. [12]. According to this model, the value of polarization of the sample of a FLC is given by the following ratio:

$$P = \varsigma \frac{\partial V}{\partial z} = \varsigma \frac{\omega A}{d}, \tag{1}$$

where ς is a coefficient which depends on the viscoelastic properties of a FLC, A is the amplitude of mechanical vibrations, d is the thickness of the sample, and ω is the cyclic frequency of mechanical vibrations of the cell.

Frequency dependence of the coefficients could also be obtained from the theory stated in Ref. [13]. According to this theory, the performance of the electromechanical coupling is determined by the velocity gradient of the cell plates along the thickness of the sample. When the vibration frequency increases, the vertical velocity gradient V_y also increases (see Fig. 1) thus leading to the enhancement of the electromechanical coupling. Let us suppose that the deformation of a FLC is described by the following ratio:

$$u = A(z)\sin(\omega t), \tag{2}$$

where $A(z)$ is the deformation amplitude, z is the distance from the stationary cell plate, ω is the cyclic frequency of

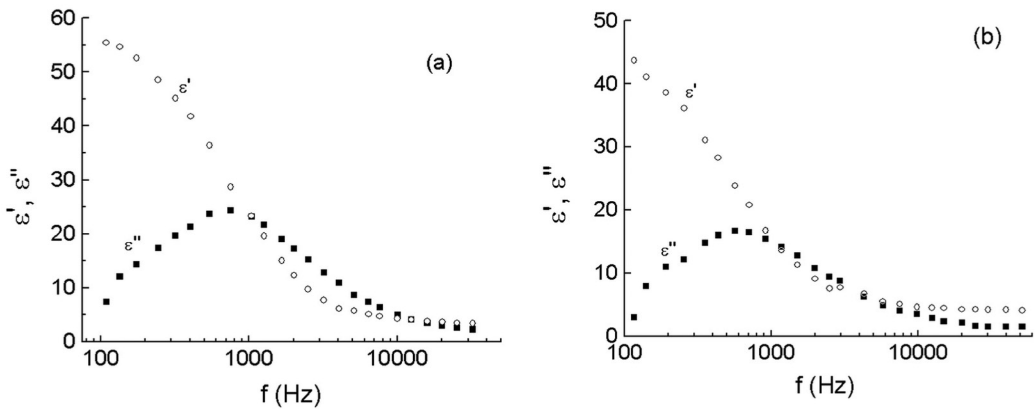


FIG. 3. Dependencies of real and imaginary components of the dielectric permittivity on the frequencies; composition **II** (a), composition **III** (b).

the deformation, and t is time. Then the velocity of the displacement of a FLC $[V(z,t)]$ could be written as

$$V(z,t) = \omega A(z)\cos(\omega t). \tag{3}$$

According to the theory in Ref. [13], the polarization value is proportional to the frequency gradient:

$$P \approx \text{grad}[V(z,t)]\,. \tag{4}$$

Therefore, the polarization is proportional to the frequency of vibrations:

$$P \approx \omega\cos(\omega t)\text{grad}[A(z)]\,. \tag{5}$$

Thus, it is follows from Ref. [13] that the linear dependence of the electromechanical coupling on frequency occurs so that this theory adequately describes experimental data obtained at frequencies over 1200 Hz. For the frequencies below 1200 Hz disagreements between the theory and the experiment are revealed which consist in noticeable deviation from linearity. The frequency range where nonlinear dependence of the flexoelectric coefficients is observed coincides with the frequency range where the two types of flexoelectric effect occur. It seems that simultaneous occurrence of the two types of effect results in the nonlinear frequency dependence of the flexoelectric coefficients. In the frequency range from 700 to 1200 Hz the deformed spiral does not have enough time to relax. This leads to the reduction of the contribution from the large-scale relaxation to the electromechanical coupling. In the frequency range over 1200 Hz this contribution is not present; thus the frequency dependence of the flexoelectric coefficients becomes linear.

When measuring the flexoelectric coefficients in the different FLCs, it was discovered that in certain materials a nonlinear response is observed. Investigations were made in order to reveal the parameter specifying nonlinearity of the flexoelectric response. In Fig. 6 the results of the study of the inverse flexoelectric effect for the compositions with different values of the θ angle are shown. It can be seen that the greater the value of the smectic tilt angle the stronger the nonlinearity of the flexoelectric effect is observed. For the direct flexoelectric effect, nonlinear coupling between the amplitude of the mechanical shear and the electric response of a sample is also revealed.

We supposed that not only piezoelectric but also flexoelectric effect is possible under deformations applied along the normal to the smectic layers. These assumptions are based on the following considerations. In a FLC sample, a helicoid exists due to the correlations in the orientation of the director in the adjacent smectic layers. These correlations result from dispersion interactions between molecules constituting the layers. When the layers are shifted relative to each other,

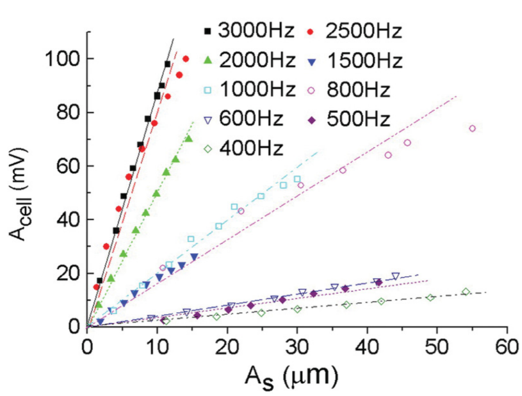


FIG. 4. (Color online) The dependence of the amplitude of the electric response of the FLC sample on the amplitude of the mechanical shear of the upper cell plate at different frequencies (composition **V**).

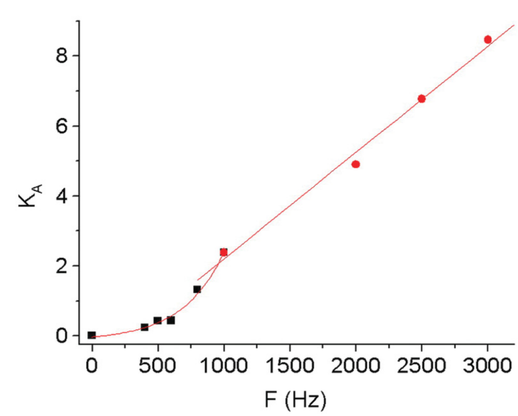


FIG. 5. (Color online) Frequency dependence of the flexoelectric coefficients for the mixture **V**.

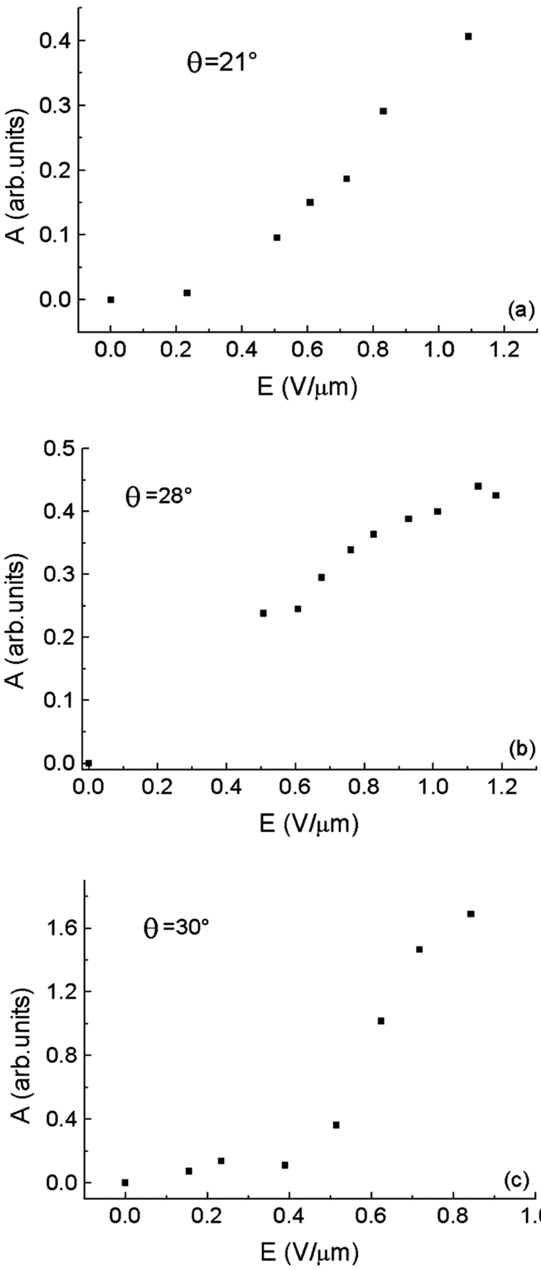


FIG. 6. Dependence of the amplitude of the mechanical oscillations (A) on the electric-field strength (E) for various FLC compositions: (a) composition **I** ($T = 34\,^{\circ}$C), (b) composition **IV** ($T = 68.6\,^{\circ}$C), (c) composition **III** ($T = 23\,^{\circ}$C).

the correlation between them breaks which leads to the distortion of the director field within the smectic layer, i.e., cross-coupling between layer deformations and deformations of the director occurs (see Fig. 7). To restore the correlation between layers, time not less than the relaxation time of the Goldstone mode is required. If the deformation frequency exceeds the frequency of the Goldstone mode for a material, then the flexoelectric effect must occur.

In accordance with our experimental data, a response is linear when deformation occurs along the normal to the smectic layers which means that there is no contribution from nonlinear flexoelectric effect. Thus, our assumptions appear to be mistaken.

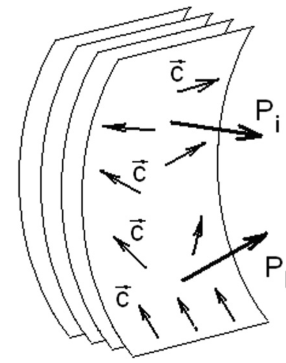


FIG. 7. Deformation of a layered structure along the normal to the smectic layers (P).

We found the Nakagawa theory [22] to be much closer to the actual conditions. This theory takes account of dipole-dipole interactions between smectic layers which do not allow occurrence of the flexoelectric effect in such geometry.

Coupling of the flexoelectric effect and spontaneous polarization was studied (Fig. 8). Contribution of the flexoelectric effect to the repolarization process is well known from experimental data:

$$I \sim P_S \frac{\partial \phi}{\partial t} \sin \phi. \tag{6}$$

According to Eq. (6), temperature dependence of the electric response of a FLC should be directly proportional to $P_S(T)$. However, as can be seen from experimental data (Fig. 8), coupling between electric response and spontaneous polarization is nonlinear.

We have tried to obtain electromechanical transformation with the aid of the piezoelectric effect and with maximum exclusion of the contribution from the flexoelectric effect. In these experiments the sample was subjected to the flexural strain of a layered structure. It was supposed that such deformation is accompanied with the variation of the molecular tilt angle in a smectic layer without distortion of the director field in the plane of the layer.

Results of these studies are presented in Fig. 9. It is seen from the figure that the coupling is accompanied with a marked

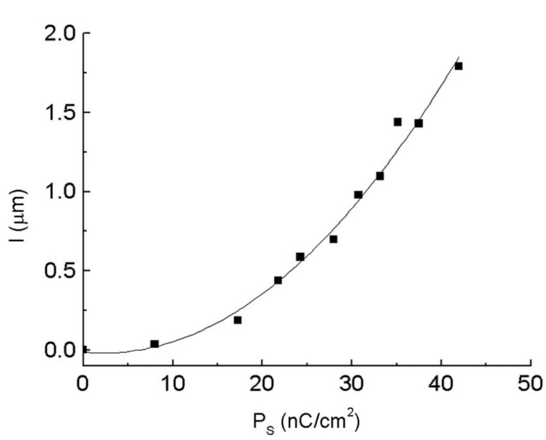


FIG. 8. Dependence of electric response of the sample on the spontaneous polarization with constant shear deformation along smectic layers ($f = 3.95$ kHz) for the composition **II**.

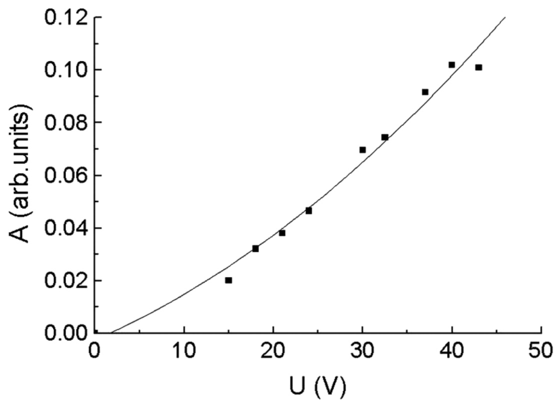


FIG. 9. Dependence of the amplitude of the electric response on the strain generating deformation of the sample when studying local deformation (composition **I**, T = 20 °C, $f = 4$ kHz).

deviation from linearity, obviously due to the significant maintenance of the contribution from the flexoelectric effect in such geometry.

The next problem is investigation of the soft mode effect on the piezoelectric effect. At the beginning of these investigations, the electroclinic effect occurring near the Curie point was known. Smectic tilt angle of the director is changed under the electric field. In fact, this effect is the reverse piezoelectric effect under fixed boundary conditions. It was revealed that in the Curie point effectiveness of piezoelectric coupling reaches a maximum [23].

We have proceeded with these investigations to study the direct piezoelectric effect in FLCs possessing different polymorphism. In Fig. 10 results of the investigations for two FLCs possessing first- and second-order phase transitions are respectively shown. For the FLC with the first-order phase transition effectiveness of the coupling gradually increases from the Curie point with the decrease of temperature (Fig. 10, line 1). For the FLC with the second-order phase transition maximal effectiveness is observed at the Curie point (Fig. 10, line 2). The nature of this effect is obscured so far.

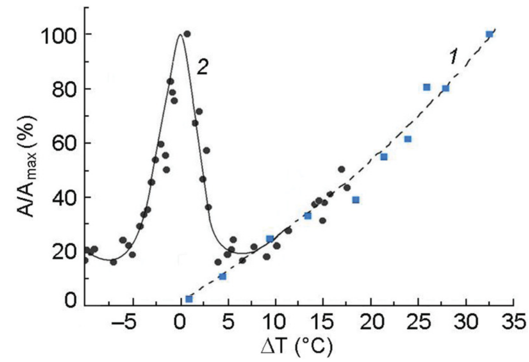


FIG. 10. (Color online) The temperature dependence of the electric response of the FLC sample under the shear deformation: 1, composition **II**, $f = 3.95$ kHz; 2, composition **III**, $f = 4$ kHz.

IV. CONCLUSIONS

Investigations of the flexoelectric and piezoelectric effects in FLCs have shown that nonlinear electromechanical coupling is determined by local flexoelectric effect. Quantitative characteristics of the nonlinearity of the flexoelectric effect are determined by the value of the parameter of the phase transition from paraelectric phase to polar phase.

We have also found the piezoelectric and flexoelectric coefficients to depend on the frequency of mechanical vibrations. Their functional relationship with the frequency is obtained. Electroclinic effect near SmA^*→SmC^* phase transition enhances the efficiency of the electromechanical transformation in the SmC^* phase.

ACKNOWLEDGMENT

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