Investigation of the flexoelectric effect in MBBA

A. S. Vasilevskaya, A. V. Kaznacheev, and A. S. Sonin

All-Union Research Institute for Physical Optics Measurements
(Submitted 27 March 1983)
Zh. Eksp. Teor. Fiz. **85**, 943–947 (September 1983)

The dependence of the induced birefringence on the intensity of the electric field in flexoelectric deformation of a homeotropically oriented MBBA sample is investigated. It is shown that a deviation of this dependence from quadratic takes place and its sign depends on sample thickness and temperature. A method is proposed for calculating the interaction energy from the experimentally determined inflection point E_c on the plot of the induced birefringence vs the electric field intensity. It is shown that allowance for W leads to a correct value of the flexoelectric coefficient. The influence of the negative effective surface energy on the flexoelectric effect is considered.

PACS numbers: 77.60. + v, 78.20.Jq

The flexoelectric effect of a homeotropic MBBA layer in a transverse electric field was investigated theoretically and experimentally in Refs. 1 and 2. It was shown there that the director orientation angle is a linear function of the electric field intensity. Such a variation of the director orientation leads to birefringence that depends quadratically on the field intensity. The theoretical investigations in these papers did not take into account the anisotropy of the dielectric constant and the energy of the adhesion of the nematic to the boundary surfaces.

In later papers[3,4] were formulated boundary conditions that take the surface energy of the nematic and the surface polarization into account. In this case, solution of the problem of flexoelectric deformation of a homeotropic nematic layer with negative dielectric anisotropy shows that deviations of the dependence of the induced birefringence on the electric field intensity from quadratic are possible.

We report here an attempt to observe this deviation in experiment and to investigate its features. The object chosen for the investigation was a nematic MBBA liquid crystal with negative dielectric anisotropy. To obtain a homeotropic layer, the glass bearing surfaces of the measuring cells were treated with an aqueous solution of decyltrimethylammonium bromide. The homeotropic orientation was monitored against a conoscopic picture with a polarization microscope. A transverse electric voltage was applied to aluminum-foil electrodes that served simultaneously as the liners between the bearing glasses of the measuring cells. The distance between electrodes was 1 mm and the thickness of the homeotropic layer ranged from 15 to 180 μm.

The induced birefringence $\bar{\Delta}n$ was measured by a polarization-optical method. The light source was a laser with emission wavelength 0.63 μm. A PDS-021 automatic x-y recording potentiometer determined the intensity of the light passing through the optical system as a function of the electric field intensity E. These results were used to calculate the dependence of $\bar{\Delta}n$ on E. In the temperature measurements the sample temperature was thermostatically maintained within ~0.1 °C.

Before measuring the birefringence, we obtained for each sample, under a microscope, the threshold electrohydrodynamic-instability voltage. All our results were obtained in below-threshold fields, in which this instability did not yet set in.

We investigated the dependences of the induced birefringence on the electric field intensity at various sample thicknesses d. The results of these measurements for several thicknesses at a 20 °C are shown in Fig. 1. A characteristic feature of these dependences is the deviation from a quadratic law. The sign of the deviation depends on the sample thickness. As can be seen from Fig. 1, there exists a certain critical thickness at which the deviation from the quadratic law reverses sign. Also dependent on the sample thickness is the field intensity at which this deviation appears.

The temperature dependences of the birefringence on the field intensity were investigated for a sample 90 μm thick (Fig. 2). The measurement results show that deviations from the quadratic law are observed in the entire temperature interval from 20 °C to the point of transition into the isotropic phase. The sign of the deviation depends on the temperature.

Some of the results can be interpreted within the framework of Ref. 4, according to which we have for symmetric boundary conditions

$$\theta=(e_2+p)E\left(W\,\mathrm{sh}\frac{d}{2\xi}+\frac{K_3}{\xi}\,\mathrm{ch}\frac{d}{2\xi}\right)^{-1}\mathrm{sh}\frac{z}{\xi}, \qquad (1)$$

where θ is the angle of orientation of the director relative to the z axis which is normal to the layer, e_2 and K_3 are the flexoelectric coefficient and the elastic constant of the longitudinal bending, $\xi=E^{-1}(4\pi K_3/|\varepsilon_a|)^{1/2}$ is the electric-co-

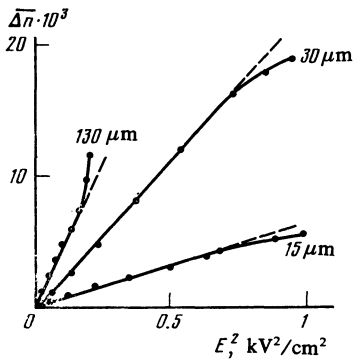

FIG. 1. Dependence of induced birefringence on the square of the electric field intensity for samples of various thicknesses at 20 °C.

 0038-5646/83/090548-03$04.00 © 1984 American Institute of Physics

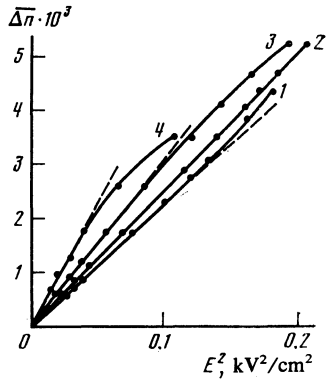

FIG. 2. Dependence of induced birefringence on the square of the electric field intensity for a sample 90 μm thick at temperatures: 1—20.9, 2—24.2, 3—28.5, 4—34.2 °C.

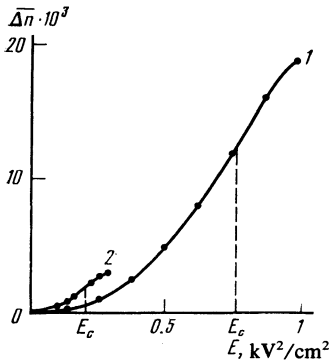

FIG. 3. Dependence of induced birefringence on the electric field intensity for the samples: 1—$d = 30$ μm, $t_{NI} - t = 16$ °C; 2—$d = 90$ μm, $t_{NI} - t = 4.5$ °C.

herence length, d is the layer thickness, ε_a is the anisotropy of the dielectric consant, W is the surface energy, and p is the surface polarization.

Using (1), we can calculate the induced birefringence:

$$\overline{\Delta n} = \frac{1}{4d} n_0 \left(1 - \frac{n_0^2}{n_e^2}\right) \left(\frac{e_2+p}{K_3}\right)^2 E^2 \xi^3 \left(\operatorname{sh}\frac{d}{\xi} - \frac{d}{\xi}\right) \times \left\{\operatorname{ch}^2 \frac{d}{2\xi}\left[1 - \frac{2\xi}{d_c}\operatorname{th}\frac{d}{2\xi}\right]^2\right\}^{-1}, \quad (2)$$

where $d_c = 2K_3/W$, and n_0 and n_e are respectively the ordinary and extraordinary refractive indices.

To analyze (2), we consider the case $d < \xi$. It is realized in fields $E < d^{-1}(4\pi K_3/|\varepsilon_a|)^{1/2}$. For an MBBA sample 100 μm thick the intensity of these fields is less than 300 V/cm. When this condition is satisfied all the hyperbolic functions in (2) an be expanded in powers of $x = d/\xi$. As a result we obtain for $\overline{\Delta n}$, accurate to first order in x, the expression

$$\overline{\Delta n} \approx \frac{1}{24} n_0 \left(1 - \frac{n_0^2}{n_e^2}\right) \left(\frac{e_2+p}{K_3}\right)^2 \frac{E^2 d^2}{(1+\beta)^2} \left[1 - x^2 \frac{6+\beta}{30(1+\beta)}\right], \quad (3)$$

where $\beta = d/d_c$. In contrast to Ref. 2, account is taken in (3) of the surface polarization p, which introduces a correction to the quantity e_2, and of the finite energy, contained in β, of the adhesion of the nematic to the boundary surface.

Since $x \propto E$, expression (3) yields a negative deviation from the quadratic law. This explains qualitatively the deviation from quadratic for thin samples ($d < 60$ μm, Fig. 1) and thick ones ($d > 60$ μm) at high temperatures (Fig. 2). Since $x^2 \propto |\varepsilon_a|$, we can conclude from (3) that this type of deviation is connected with the dielectric stabilization of the layer.

By investigating the deviations from the quadratic $\overline{\Delta n}(E)$ dependence we can determine the anisotropic part of the adhesion energy and calculate correctly the flexoelectric coefficient e_2 at finite W. Figure 3 shows plots of $\overline{\Delta n}(E)$ at different concentrations of the aqueous solutions of CTAB used to treat the glass surfaces, and at different sample thicknesses. This figure shows clearly the inflection points of E_c in the $\overline{\Delta n}(E)$ plots; these points are determined by the condition

$$\left.\frac{d^2\overline{\Delta n}}{dE^2}\right|_{E=E_c} = 0. \quad (4)$$

Using (3) and (4) we obtain an expression

$$E_c^2 = 20\pi K_3(1+\beta)/|\varepsilon_a| d^2(6+\beta), \quad (5)$$

that allows us to calculate β and W from the measured ε_a, K_3, d, and E_c. Typical calculations for two samples are given in Table I. The difference between the values of W obtained in the two cases is due to the different concentrations of the CTAB solutions used to treat the bearing surfaces. From the quadratic part of the $\overline{\Delta n}(E)$ dependence we determined the value of $e_2 + p$ at $W = 0$ and $W \neq 0$ (see Table I). It follows from the results that the degree of treatment of the bearing surfaces does not influence the determined $e_2 + p$ if W is taken into account in the calculation.

Experiments[8,2] yielded respectively for $e_2 + p$ the values 3×10^{-4} and 3.7×10^{-5} dyn$^{1/2}$, which differ by an order of magnitude. In the first reference they used pure glass surfaces, and in the second the surfaces were covered with an aqueous solution of lecithin. In neither case was the energy W taken into account in the estimate of the flexoelectric coefficient. As can be seen from Table I, neglect of this energy leads to an order-of-magnitude difference between the values of $e_2 + p$. Since this difference is most significant at high energies W, it is obvious that its neglect in Ref. 2 is inadmissible.

TABLE I.

Sample no.	d, μm	$(t_{NI}-t)$, °C	E_c, V/cm	K_3, dyn [5]	$\lvert\varepsilon_a\rvert$ [6]	β	W, erg/cm²	$n_0(1-n_0^2/n_e^2)$ [7]	$(e_2+p)_{W\neq 0}$, dyn$^{1/2}$	$(e_2+p)_{W=0}$, dyn$^{1/2}$
I	30	16	760	$7.8\cdot10^{-7}$	0.65	7.19	$3.74\cdot10^{-3}$	0.477	$7.21\cdot10^{-4}$	$8.8\cdot10^{-5}$
II	90	4.5	220	$4.7\cdot10^{-7}$	0.5	6.44	$6.72\cdot10^{-4}$	0.41	$1.6\cdot10^{-4}$	$2.48\cdot10^{-5}$

To explain the deviations of $\overline{\Delta n}(E)$ of thick samples ($d > 60\,\mu$m) from quadratic we consider the flexoelectric effect with a negative effective surface energy $\tilde{W}$ that leads to spontaneous destruction of the homeotropic nematic layer at $d > d_c = 2k_3/|\tilde{W}|$.

We write down the balance equation and the boundary condition for the flexoelectric effect with $W < 0$, using the single-constant approximation

$$K\frac{d^2\theta}{dz^2} - \frac{|\varepsilon_a|}{8\pi}E^2 \sin 2\theta = 0, \tag{6}$$

$$K\frac{d\theta}{dz} - \frac{1}{2}|\tilde{W}_1|\sin 2\theta + E(e_1 \sin^2\theta - e_2\cos^2\theta) - p_1 E\cos\theta = 0, \quad z = \frac{d}{2},$$

$$K\frac{d\theta}{dz} + \frac{1}{2}|\tilde{W}_2|\sin 2\theta + E(e_1 \sin^2\theta - e_2\cos^2\theta) + p_2 E\cos\theta = 0, \quad z = -\frac{d}{2}. \tag{7}$$

Let us introduce simplifying assumptions that do not influence the qualitative result of this problem. We put $|\varepsilon_a| = 0$, $p_1 = p_2 = 0$, and $|\tilde{W}_1| = |\tilde{W}_2| = |\tilde{W}|$. The solution of (6) takes then the form

$$\theta = \theta_0 z.$$

To determine θ_0 we use the boundary conditions (7) written accurate to third order of smallness in $\theta_0 d$. This is necessary to describe the solution at $d \sim d_c = 2K/|\tilde{W}|$. As a result we obtain an equation for $a = \theta_0 d$:

$$a^3 + 6\left(\frac{E}{E_1}\right)a^2 + 6\left(\frac{d_c}{d} - 1\right)a - 6\frac{E}{E_2} = 0, \tag{8}$$

where

$$E_1 = 2|\tilde{W}|/(e_1+e_2), \quad E_2 = |\tilde{W}|/2e_2.$$

Putting $|\tilde{W}| \sim 10^{-4}$ erg/cm^2 and $e \sim 10^{-4}$ dyn$^{1/2}$ we obtain $E_1 \sim E_2 \sim 300$ V/cm.

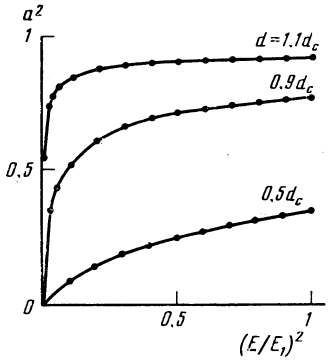

FIG. 4. Dependence of a^2 on $(E/E_1)^2$.

The solution of (8) under the assumption $E_1 = E_2$ is shown in Fig. 4. Since $\overline{\Delta n} \sim \theta_0^2 \sim a^2$, it is obvious that the use of $W < 0$ also leads to negative deviation of $\overline{\Delta n(E)}$ from quadratic. Allowance for the anisotropy of the dielectric constant only enhances this effect. Consequently, the approach considered does not explain the deviations from the quadratic law for thick samples.

It is possible that these deviations are due to inhomogeneity of the field along the z axis, which leads to a joint action of the surface and bulk flexoelectric effects.

[1]W. Helfrich, Phys. Lett. **35A**, 393 (1971).
[2]D. Schmidt, M. Schadt, and W. Helfrich, Zs. Naturforsch. **27**, 277 (1972).
[3]J. Prost and P. S. Pershan, J. Appl. Phys. **47**, 2298 (1976).
[4]A. Derzhanski, A. G. Petrov, and M. D. Mitov, J. Phys. (France) **39**, 273 (1978).
[5]W. H. de Jeu, W. A. Claassen, and A. M. Spruyit, J. Mo. Cryst. Liq. Cryst. **37**, 269 (1976).
[6]D. Diguet, F. Rondelez, and G. Durand, Compt rend. **271B**, 954 (1970).
[7]R. Chang, Mol. Cryst. Liq. Cryst. **30**, 155 (1975).
[8]W. Haas, J. Adams, and J. B. Flannery, Phys. Rev. Lett. **25**, 1326 (1970).

Translated by J. G. Adashko