Orienting effect of an electric field on nematic liquid crystals

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An electric field applied to a layer of a nematic liquid crystal with positive anisotropy of the dielectric constant orients the molecules in the layer in the direction of the field. The aim of the present work is to study the reorientation of the molecules and their relaxation to the original state. This is performed by recording the phase shift of the laser light beam due to birefringence of the oriented liquid crystal film. The experimental dependences of the phase shift on the applied voltage and the field switch-off time are obtained. The threshold nature of the reorientation and the mentioned dependences are analyzed theoretically. The orientation effect is employed in various applications in phase-regulating and light-valve devices.

INTRODUCTION

The great attention presently paid to liquid crystals is due to the extensive possibilities of their practical utilization in various branches of technology, particularly for optical information processing. So far, no acceptable materials have been found for controlled transparencies serving as phase converters of information. Of interest in this connection are oriented films of nematic liquid crystals, in which an entire ensemble of molecules can be synchronously reoriented under the influence of an electric field, thus causing phase changes in coherent light passing through the crystal[1,2]. This effect is the subject of the present paper.

We consider a single-crystal layer of nematic mesophase made up of flat glass substrates with transparent electrodes, and having a preferred optical axis lying in the plane of the layer. The optical indicatrix which determines the value of the refractive indices of the obtained uniaxial-crystal plate is an ellipsoid of revolution about the principal symmetry axis OO[3]

$$\frac{n_x^2}{n_e^2}+\frac{n_y^2}{n_o^2}+\frac{n_z^2}{n_o^2}=1. \tag{1}$$

If the light polarization vector **E** is perpendicular to the optical axis of the crystal, then the refractive index for the vector is equal to n_0. If the direction of **E** coincides with the optical axis OO, the refractive index is equal to n_e. The characteristic difference $n_e - n_0$ for liquid crystals is appreciable, on the order of 0.3. In the general case, for a polarization vector lying in the principal plane of the crystal, the refractive index is determined by the major semiaxis of the ellipse in the indicatrix section perpendicular to the normal to the wave front

$$n=\frac{n_o n_e}{(n_o^2\cos^2\theta+n_e^2\sin^2\theta)^{1/2}} \tag{2}$$

where $90°-\theta$ is the angle between the optical axis and the normal to the wave front.

In an electric field (see Fig. 1), the molecule axes of the liquid crystal with positive anisotropy of the dielectric constant assume a certain angle $\theta(z)$ relative to the initial orientation (in the plane of the substrates), with the exception of the molecules adjacent to the electrodes of the thin boundary layer, so that $\theta_{\max} = \theta(L/2)$ and $\theta(0) = \theta(L) = 0$, where L is the thickness of the liquid-crystal film, and the value of $\theta_{\max}$ $(0 \le \theta_{\max} \le 90°)$ is determined by the applied electric field. In this case, if the polarization vector **E** makes an angle φ with the principal plane of the crystal, then passage of light through the liquid-crystal film produces between the ordinary and extraordinary rays a phase difference amounting to

$$\Phi=\frac{2\pi}{\lambda}\left[\int\limits_0^L\frac{n_o n_e\,dz}{(n_o^2\cos^2\theta(z)+n_e^2\sin^2\theta(z))^{1/2}}-n_oL\right]. \tag{3}$$

The intensity of the light registered behind an analyzer that is crossed with respect to **E** is

$$I=I_0\sin^2 2\varphi\sin^2(\Phi/2), \tag{4}$$

where I_0 is the intensity of the incident light.

Turning on (turning off) the electric field leads to a reorientation of the molecules and to a corresponding change in the phase delay of the light:

$$\Delta\Phi=\frac{2\pi}{\lambda}\left[n_eL-\int\limits_0^L\frac{n_o n_e\,dz}{(n_o^2\cos^2\theta(z)+n_e^2\sin^2\theta(z)^{1/2}}\right], \tag{5}$$

accompanied by a change in the intensity I. At a field intensity sufficient to rotate the molecules by $\theta = 90°$, the layer of the liquid crystal becomes isotropic for light propagating along the z axis, and the birefringence vanishes. The analyzer will then transmit the largest number of maxima (minima) of intensity, as determined by the relation $m = \Delta\Phi/2\pi$. This number does not depend on whether the analyzer is crossed relative to the polarization vector of the light or is parallel to it, but zero intensity is established after the field is turned on in the former case, and maximum intensity in the latter case.

A change of the intensity (phase delay) can also be registered by observing the interference of the light reflected from both surfaces of the glass plates in contact with the liquid crystal, in which case the vector **E** should lie in the principal plane of the crystal[1]. The

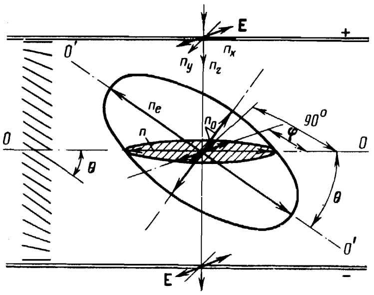

FIG. 1. Distribution of the molecule axes in a liquid-crystal layer acted upon by an electric field.

interference method of registration is twice as sensitive, because of the double passage of the light through the liquid-crystal layer. At the same time, the polarization method of observing the orienting action of the electric field on the liquid-crystal molecules is preferrable because of the lower loss of light, the easier tuning, and the closer approach to the actual application conditions.

It should be noted that for liquid crystals with negative anisotropy of the dielectric constant and homotropic arrangement of the molecules relative to the light propagation direction, the considerations advanced above concerning the change of the birefringence in the electric field are valid in practice[4]. The effect of the electric field consists in this case of increasing the birefringence (formula (3) can be used to determine the phase delay), and is analogous to removal of the electric voltage from the electrodes for a layer of liquid crystal with positive dielectric anisotropy.

EXPERIMENTAL CONDITIONS

The orienting action of the electric field was investigated using the following nematic liquid crystals with positive dielectric-constant anisotropy:

No. 1—4'ethoxybenzylidene-4-aminobenzonitrile;

No. 2—4'-butoxybenzylidene-4-aminobenzonitrile;

No. 3—Mixture of substances No. 1 and No. 2 in a ratio 1 :1;

No. 4—Mixture of metoxybenzal-p'-n-butylaniline with substance No. 1 in a ratio 6 :1.

The characteristics of these substances are listed in the table, and the values of the refractive indices for them, measured by an interference procedure[5], are indicated for the central section of the temperature interval in which the nematic mesophase exists. The oriented single-crystal films of the liquid crystals with thickness ~10 μ were produced in the usual manner by filling a capillary gap between previously rubbed-in substrates with a current-conducting layer having a resistance 20—30 Ω for a square of side 1 cm and a transmission ~90% at the wavelength 0.63 μ. The two substrates were rubbed-in in the same direction.

Characteristic of substance	Temperature interval, °C	Refractive indices*	
		n_e	n_o
№ 1	103—113	1.84	1.47
№ 2	63—104	1.82	1.47
№ 3	50—90	1.80	1.47
№ 4	20—65	1.78	1.50

*Measurement accuracy 1%.

The setup for measuring the orienting action of the electric field on nematic liquid crystals is shown in Fig. 2. Emission from an He-Ne laser 1 with wavelength $\lambda = 0.63\ \mu$, after passing through polarizer 2, collimator 3, and a 50% mirror, enters a cell with the liquid crystal (7, 8, 9), placed in a thermostat 6. Both methods of recording the orientation order in the liquid crystal were used. In the polarization method, the optical axis of the crystal made an angle of 45° with the polarization vector of the incident radiation, and analyzer 10 and photomultiplier 11 were placed behind the cell. In the interference method, the vector E was in the principal plane of the crystal and the intensity was likewise measured with photomultiplier 4. Both a dc voltage from battery 16 and a pulsed voltage from a generator (13 or 15) were applied to the crystal. A special amplifier circuit made it possible to turn on a sinusoidal voltage (frequencies $10^3 - 2 \times 10^5$ Hz) from generator 12; this voltage was turned off during the time when the field pulse from generator 13 was applied. The photomultiplier signals were registered with a PDS-021 automatic recorder and an S1-17 oscilloscope.

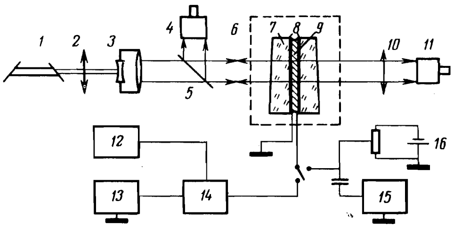

FIG. 2. Experimental setup for the study of the orienting action of an electric field on nematic liquid crystals: 1—laser, 2, 10—polarizers, 3—collimator; 4, 11—photomultipliers; 5—beam splitter, 6—thermostat, 7—glass substrates, 8—transparent current-conducting film, 9—liquid crystal, 12—sound generator (GZ-33), 13—pulse generator (G5-6A); 14—amplifier, 15—shifted-pulse generator (G5-7A), 16—dc voltage source.

EXPERIMENTAL RESULTS

Figure 3 shows a typical dependence of the change of the intensity on the applied voltage for light registered ahead of the analyzer (curve 1) and behind it (curve 2); the analyzer is crossed with respect to the polarization vector of the incident light. In Fig. 3a, the transmission T is given for a crystal film No. 1 of thickness ~10 μ with the voltage increasing slowly (12 V in 60 sec), while Fig. 3b shows the same for a voltage decreasing at the same rate. The reorientation of the molecules has a certain threshold, as is particularly clearly seen in Fig. 3b. The strong attenuation of the light at a voltage U exceeding the threshold value ($U_{thr} = 2.0$ V) is due to the fact that the position of the molecules in the layer becomes unstable at U_{thr}, causing a rapid inhomogeneous reorientation of the molecule and a loss of the single-crystal character of the film, accompanied by scattering of the light. Curves 2 show distinct transmission maxima due to the decrease of the phase delay of the light in the electric field. The phase shift between two neighboring maxima is 2π. The curves for the remaining substances are similar.

The transmission curves were used to plot the phase delay of the transmitted light as a function of the applied voltage (Fig. 4, curves 1—4). The initial value of

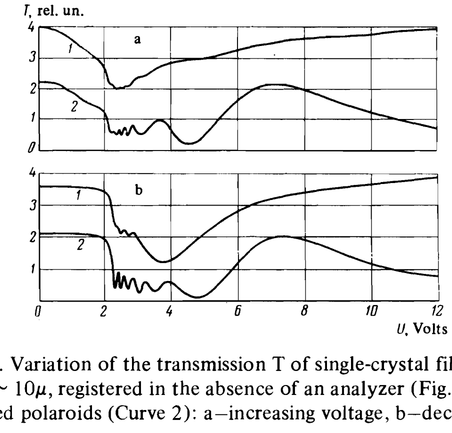

FIG. 3. Variation of the transmission T of single-crystal film No. 1 of thickness ~ 10μ, registered in the absence of an analyzer (Fig. 1) and behind crossed polaroids (Curve 2): a—increasing voltage, b—decreasing voltage.

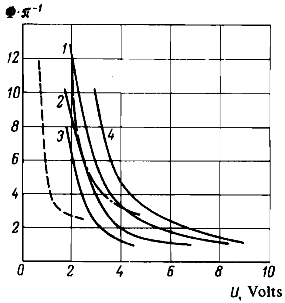

FIG. 4

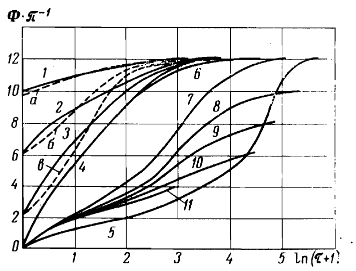

FIG. 5

FIG. 4. Phase difference between the ordinary and extraordinary rays vs. the voltage on the liquid-crystal film (thickness ~ 10 μ). The solid curves 1–4 show the experimental plots for substances Nos. 1–4 (see the table), while the dashed and dash-dot lines correspond to an approximate calculation for crystal No. 1.

FIG. 5. Change of the phase delay of light following relaxation of the molecules of liquid crystal No. 1 (layer thickness ~ 10 μ, temperature ~ 110°C): in the case of curves 1-5, there is no bias voltage U_b and the duration τ_p of the rectangular voltage pulses ($U_p = 50$ V) is respectively 0.02, 0.028, 0.038, 0.2, and 2.0 msec; for curves 6-11, U_b is respectively 1.8, 2.1, 2.7, 3.0, 3.3, and 3.5 V at pulse parameters $U_p = 50$ V and $\tau_p = 0.2$ msec; the dashed lines a, b, and c show the calculated course of the relaxation of the phase delay for θ_{max} equal to 30, 60, and 89°, respectively.

Φ is determined by the values of n_e and n_o in the temperature interval in which the nematic phase exists and by the thickness of the liquid-crystal film, and while the formula $\Phi = 2\pi L(n_e - n_o)\lambda^{-1}$ holds true within the scatter of the values of these parameters. The threshold voltage U_{thr} for the reorientation of the molecules did not exceed 3 V for the investigated crystals. The curve characterize the high sensitivity of the change in the phase delay to the applied electric field. For the sections with the largest slope, the rate of this change reaches 7π per volt. From the behavior of the phase delay with increasing voltage one can assess the change in the thickness of the transition boundary layer; at 10 V, for example, it is of the order of 0.5 μ.

When a pulsed electric field was applied, the molecules were completely reoriented in a position with $\theta = 90°$ within the time on the order of 200 μsec at a rectangular-pulse amplitude 50 V. An intensity minimum was observed in this case in crossed polaroids. The relaxation of the molecules to the initial state with $\theta = 0$ is a much slower process. The relaxation time amounts usually to tens (for crystal No. 1) and hundreds of milliseconds (for crystal No. 4), and depends on the temperature of the material in the interval of the existence of its mesophase. If the molecules are given an initial orientation $\theta \neq 0$ by applying a constant potential difference to the electrodes (a bias voltage U_b), the relaxation time increases somewhat with increasing U_b. This is due primarily to lengthening of the last stage of the relaxation, during which the maximum phase delay is established. When the bias voltage reaches U_{thr}, the rate of relaxation change of the phase delay decreases jumpwise during all stages of the relaxation time, since the electric field balances the elastic forces that tend to restore the initial single-crystal state of the layer. The amplitude of the relaxation maxima of the transmission decreases as a result of scattering of the light by the aforementioned instabilities. Further increase of the bias voltage leads to a restoration of the amplitude of the maxima, and then to a reduction in their number. The reason for the latter is that when $U_b > U_{thr}$ the dsistribution of the molecule axis in the layer is characterized by a smaller value of the phase delay. As a result of the decrease in the reorientation angle, the relaxation time decreases and at U_b on the order of 7 V, when turning the field pulse on (off) changes the phase delay by only π, it amounts to approximately 0.4 msec for crystal No. 1. This behavior of the liquid-crystal layer in the course of relaxation was exhibited by all the investigated substances. Inhomogeneities of the film led only to a blurring of the indicated main features. Application of an alternating bias U_b instead of a dc bias did not change the character of the relaxation.

Figure 5 shows a plot of the phase difference between the ordinary and extraordinary rays against the time when the molecules of crystal No. 1 relax to a state determined by the value of the bias voltage. The instant of time $\tau = 0$ corresponds to turning off the field pulse. The family of curves 1–6 in the figure corresponds to relaxation at $U_b < U_{thr}$, while curves 7–11 correspond to U_b increasing to 3.5 V. The region of unstable equilibrium lies in the interval between curves 6 and 7, for which the values of U_b differ by only 0.3 V. The solid curves 1–5 describe the relaxation process in the absence of a bias voltage for the case $0 < \theta_{max} < 90°$. The maximum deviation angle was decreased in this case by reducing the duration of the rectangular voltage pulses. It is also seen from Fig. 5 that at the duration of these pulses (on the order of 2 msec), which greatly exceeds the value needed to orient the molecules with $\Phi = 0$, the relaxation time increases substantially as a result of the decrease of the relaxation rate during its initial stage. For several dozen seconds after the action of such pulses, the character of the slow relaxation remains in force also when short electric pulses (~ 0.2 msec) are applied. This is evidence of the strong influence of pulses with high field energy on the process of orientation packing of molecules at $\theta = 90°$, which proceeds without a change in phase delay.

COMPARISON WITH THEORY

The orientation changes produced by the electric field in the director d, which determines the direction of the optical axes of the molecule, can be considered theoretically. At small distortions of the spatial distribution of d, the free energy of a liquid crystal in an electric field $\mathscr{E}$ is given by[6]

$$F = -\frac{1}{2}\int\left\{K_{11}(\operatorname{div}\mathbf{d})^2 + K_{22}(\mathbf{d}\operatorname{rot}\mathbf{d})^2 + K_{33}[\mathbf{d}\times\operatorname{rot}\mathbf{d}]^2 - \frac{\varepsilon_a}{4\pi}(\vec{\mathscr{E}}\mathbf{d})^2\right\}dv, \qquad (6)$$

where K_{ii} is the elastic constant and $\epsilon_a = \epsilon_\parallel - \epsilon_\perp > 0$ is the anisotropy of the dielectric constant.

According to the geometry of the problem, the change of the orientation of d takes place in the xz plane, with $d_x = \cos\theta(z)$ and $d_z = \sin\theta(z)$. For a qualitative description of the considered phenomena we assume that $K_{11} = K_{33} = K$. In this case the Euler equation corresponding to the functional (6) takes the form

$$\frac{d^2\theta}{dz^2} + \frac{a}{2}\sin 2\theta = 0, \quad a = \frac{\varepsilon_a\mathscr{E}^2}{4\pi K}. \qquad (7)$$

The solution of Eq. (7) determines the angle of inclination θ_{max} of the director d at the center of the layer, as a function of the field

$$\frac{L}{2}=\int\limits_0^{\theta_{max}}\frac{d\theta}{(C+{}^1/_2 a\cos 2\theta)^{1/2}}. \qquad (8)$$

Minimizing F with respect to the constant C, we obtain ultimately with the aid of (8)

$$\frac{1}{2}a^{1/2}L=\int\limits_0^{\theta_{max}}\frac{d\theta}{(\sin^2\theta_{max}-\sin^2\theta)^{1/2}}. \qquad (9)$$

Substituting in (9), for crystal No. 1, the values $\epsilon_a = 14$[7], $K = 7\times 10^{-7}$ dyne, and $L = 10\ \mu$, we rewrite (9) in the form

$$U\approx E(\theta_{max})\ [\mathrm{V}], \qquad (10)$$

where E is a Jacobi elliptic integral of the first kind. It follows from (10) that the change of the orientation of the director in a liquid-crystal layer occurs at voltages exceeding the threshold value $U_{thr} \approx 0.75$ V. The discrepancy with the experimental result ($U_{thr} = 2$ V) can be attributed to the assumption that the elastic moduli are equal and to the lack of data concerning their values. The order-of-magnitude agreement, however, is good.

The inhomogeneous distribution of the director over the thickness of the layer $\theta(z)$ at a given U is described by the formula

$$\left(\frac{a}{2}\right)^{1/2}z=\int\limits_0^{\theta(z)}\frac{d\theta}{(\cos 2\theta-\cos 2\theta_{max})^{1/2}} \qquad (11)$$

which follows from (7)–(9). The course of the theoretical dependence of the phase delay Φ on the voltage is shown in Fig. 4 by a dashed line. The value of Φ was calculated from formulas (3) and (11). It is seen from Fig. 4 that there is qualitative agreement with experimental curve 1. By substituting in (3) and (11) the value $K \sim 10^{-5}$ dyne, which is obtained from the experimental value $U_{thr} = 2$ V, we get the theoretical $\Phi(U)$ plot shown by the dash-dot line. Comparison with the experimental curve 1 points to anisotropy of the elastic constants of the investigated liquid crystal.

Let us estimate the transients occurring when the electric field is turned on (off). In our approximation, they are described by the equation[6]

$$K\frac{\partial^2\theta}{\partial z^2}=\gamma_1\frac{\partial\theta}{\partial t}, \qquad (12)$$

where the viscosity coefficient is $\gamma_1 \approx 0.03\ \mathrm{g\text{-}cm^{-1}sec^{-1}}$. The initial condition for (12) is

$$\theta(z)\,|_{t=0}=\theta(z) \qquad (13)$$

(see (11)). The boundary conditions for (12) are

$$\theta\,|_{z=0}=\theta\,|_{z=L}=0. \qquad (14)$$

The solution of (12) under conditions (13) and (14) is

$$\theta(z,t)=\frac{2}{L}\int\limits_0^L\sum_{m=1}^{\infty}\theta(z')\sin\frac{\pi mz'}{L}\sin\frac{\pi mz}{L}\exp\left[-\frac{\pi^2m^2}{L^2}\frac{K}{\gamma}t\right]dz'. \qquad (15)$$

With the aid of (15) and formula (3) we calculated the time variation of the phase delay Φ when the electric field is turned off. The results of the numerical calculation for θ_{max} equal to 30, 60, and 89° are shown in Fig. 5 by the dashed lines a, b, and c. A comparison with the experimental curves 1–5 shows qualitative agreement. The difference between the relaxation times is due to the fact that we used in the calculations approximate (in order of magnitude) viscosity and elastic coefficients for the liquid crystals.

CONCLUSION

The described method of controlling birefringence serves as a basis for a number of technical applications of oriented liquid-crystal films. As shown earlier[1], it is possible to produce high-speed phase and amplitude modulation of a light beam by using low control voltages. Oriented films can be successfully used in phase-regulating devices whose necessary characteristic is high sensitivity of the phase response to the action of an electric field. The difficulties connected with maintaining constant film thickness and constant refractive indices can be easily overcome, especially by using bias voltages and liquid crystals in which the mesophases exist in a large temperature interval.

The orientational distribution of the molecules established in the liquid-crystal layer by the electric field can be fully determined, as follows from the present paper, from the phase delay of the light passing through the film. Therefore optical observation methods can yield reliable information on the occurring orientational processes and the internal parameters of the medium. Thus, for example, the elastic moduli of a liquid crystal can be calculated from experimental data on the threshold voltage and on the change of the birefringence in an electric field. The relaxation behavior of the phase delay as a function of the time can yield more exact information on the viscosity coefficients than other known methods. It should be noted here that the theoretical description of the corresponding characteristics must take into account the anisotropy of the internal parameters of the mesophase.

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