

Temperature dependence and the "size effect" exhibited by the anchoring energy of a nematic with a planar orientation on a solid substrate

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The method of complete reorientation of the director in a strong electric field from the planar to the homeotropic direction was used to determine the effective energy W^* of anchoring of a nematic crystal 5CB to a solid substrate. The dependences of W^* on the temperature and thickness of a liquid crystal layer were determined for the first time. The room-temperature anchoring energy was found to be $W^* \approx 0.7\text{--}1.2$ erg/cm² for a cell of thickness in the range $d = 39\text{--}3.5\ \mu$. The experimental dependence $W^*(d)$ could be approximated by logarithmic and hyperbolic functions in the case of small and large thicknesses of the layer, respectively.

INTRODUCTION

The interaction of a nematic liquid crystal with a solid substrate can be described by a surface energy W , which generally consists of isotropic and anisotropic parts. The anisotropic part depends on the angles of orientation θ and φ of the director of a nematic liquid crystal relative to the normal to the substrate and relative to some specific "easy orientation" direction in the plane of the substrate. It is assumed that the anchoring energy $W(\theta, \varphi)$, introduced for the director of a sufficiently thick surface layer of a nematic liquid crystal, is independent of the thickness of the layer. In the case when $\varphi = \text{const}$, which will be assumed in the present study, the following expression has been put forward for the function $W(\theta)$ (Refs. 1–3):

$$W(\theta) = \frac{1}{2} W_1 \sin^2(\theta - \theta_0) + \frac{1}{2} \sum_{n=2}^{\infty} W_n \sin^{2n}(\theta - \theta_0), \quad (1)$$

where θ_0 is the initial angle of tilt of the director relative to the plane of the substrate.

The task of experimental determination of the anchoring energy of a nematic liquid crystal layer with the planar orientation ($\theta_0 = 0$) has been tackled by a variety of methods.^{4–8} However, even in the case of low values of θ the energies $W(\theta)$ exhibit a large scatter from 10^{-4} erg/cm² deduced from light scattering experiments⁸ to 1 erg/cm² or more obtained from earlier experiments based on the absence of the thickness dependence of the threshold of the Fréedericksz effect. Moreover, the temperature dependence of the surface (anchoring) energy of a nematic liquid crystal with the planar orientation has not yet been determined experimentally and no studies have been made of the "size effect," i.e., of the possibility that W depends on the thickness of the liquid crystal layer adjoining the solid substrate. Furthermore, the method for the determination of the anchoring energy of a nematic based on the threshold voltage or field intensity in the Fréedericksz effect in electric and magnetic fields, frequently used in the case of the homeotropic orientation of nematic liquid crystals, is ineffective and insensitive to variations of W in the case of the stronger (compared with homeotropic) planar orientation. In fact, this method involves determination of the "extrapolation length" $l = K_{11}/W$, where K_{11} is the Frank constant for longitudinal bending of a liquid crystal, and it represents the

effective increase in the thickness of the liquid crystal layer because of the finite value of the anchoring energy. The value of l is estimated from the difference between the real threshold and the threshold value corresponding to the most rigid anchoring of liquid crystal molecules to the substrate. However, in the planar orientation of a sample this difference between the thresholds is extremely small ($V_{th}^{\infty} - V_{th} \sim 0.01$ V, $H_{th}^{\infty} - H_{th} \sim 0.1$ kG—Ref. 6) and comparable with the error in the determination of the threshold values $V_{th}(H_{th})$ and $V_{th}^{\infty}(H_{th}^{\infty})$.

Moreover, all the experiments carried out in fields equal to or relatively close to the threshold provide an opportunity of estimating only the coefficient W_1 in front of the first term of the expansion of the surface energy function (1) using the approximation of the Rapini potential.¹ Moreover, Young² and Chigrinov⁹ have demonstrated that if the anchoring energy is sufficiently high then in such fields the tilt angle of the director at the substrate-liquid crystal interface is just a few degrees. In other words, the surface region of a liquid crystal, which in the final analysis determines the energy of anchoring of a liquid crystal to a substrate, remains practically undeformed. It would therefore be more interesting to use the Fréedericksz method in strong fields, i.e., in fields much higher than the threshold. It then follows from Eq. (1) that

$$W\left(\theta \rightarrow \frac{\pi}{2}\right) = \frac{W}{2}, \quad W = \sum_{n=1}^{\infty} W_n, \quad (2)$$

and the experimental results give the effective energy of anchoring of a nematic to a substrate^{2,3}

$$W^* = \sum_{n=1}^{\infty} n W_n, \quad (3)$$

where $W^* = W$ in the Rapini-potential approximation. In all probability there should not be a significant difference between W^* and the surface energy W . For example, according to the results of Ref. 4, the values of W^* and W agree to within 10%.

EXPERIMENTAL METHOD

We consider a nematic liquid crystal layer with a positive anisotropy of the permittivity $\Delta\epsilon$ and assume that its orientation is planar in the absence of an external field (Fig. 1a). The application of a sufficiently strong field results in reorientation of the director in the bulk of a liquid crystal

(Fréedericksz effect, Fig. 1b), which increases on further increase in the field intensity. It has been shown theoretically^{2,3,10} that if the energy of anchoring of a nematic to a substrate is finite and the applied voltage or field is sufficiently strong, a complete reorientation of the director to the homeotropic structure takes place and this includes also the surface layers (Fig. 1c). The corresponding value of the "saturation" voltage V_{sat} is related to the effective anchoring energy W^* of a nematic as follows^{2,3}:

$$\text{cth} \left[\frac{\pi}{2} \frac{V_{\text{sat}}}{V_{\text{th}}^{\infty}} \left(\frac{K_{11}}{K_{33}} \right)^{1/2} \right] = \frac{\pi K_{33}}{W^* d} \frac{V_{\text{sat}}}{V_{\text{th}}^{\infty}} \left(\frac{K_{11}}{K_{33}} \right)^{1/2}. \quad (4)$$

Here, K_{33} is the Frank constant in the case of transverse bending and $V_{\text{th}}^{\infty} = \pi(4\pi K_{11}/\Delta\epsilon)^{1/2}$ is the Fréedericksz threshold voltage, corresponding to an infinitely strong anchoring of liquid crystal molecules to the substrate.

Complete reorientation of the director in a strong electric field was first reported in Ref. 4, but it was observed only at one temperature close to the point of bleaching of the investigated liquid crystal ($T_{NI} - T = 0.23^\circ\text{C}$), where the anchoring energy of a nematic and, consequently, the saturation voltage of the structure were found to be fairly low ($W \approx 3.2 \times 10^{-2} \text{ erg/cm}^2$, $V_{\text{sat}} = 100 \text{ V}$ for $d = 56 \mu$). It was pointed out in Ref. 4 that the value of W could not be estimated at lower temperatures because of the rapid rise of V_{sat} , which resulted in breakdown of the investigated samples. When a magnetic field was used, saturation of the structure of a nematic liquid crystal was even more difficult to achieve.¹¹

This method for investigating a nematic with a planar orientation in strong electric fields was applied by us successfully in a wide range of temperatures to the nematic phase range of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) characterized by a transition temperature to the isotropic phase $T_{NI} = 34.75^\circ\text{C}$, employing liquid crystal layers of different thicknesses.

We used apparatus shown as a block diagram in Fig. 2a. Ahrens prisms were used as the polarizer and analyzer. The polarizing power of the apparatus was $k = 5 \times 10^5$. The investigated sample was oriented normally to the incident light beam (of wavelength $\lambda = 0.6328 \mu$) in such a way that the direction of the initial planar orientation of the nematic liquid crystal layer made an angle of 45° relative to the mutually crossed polarizer and analyzer. The signal from a photomultiplier, proportional to the optical transmission of the cell, and the reference signal from a master oscillator were applied to a dual trace oscilloscope with a high input resistance and could be observed simultaneously on the screen.

The thickness of the liquid crystal layer was determined by an interference method from measurements on an empty

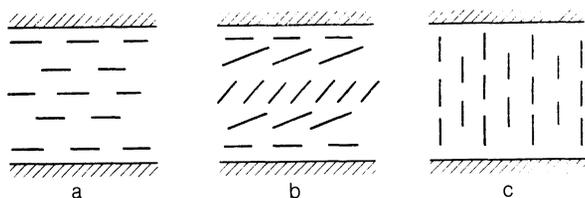


FIG. 1. Distribution of the director in a nematic liquid crystal layer with the planar orientation in the absence of an electric field (a), near the Fréedericksz threshold (b), and in the case of saturation in a strong field (c).

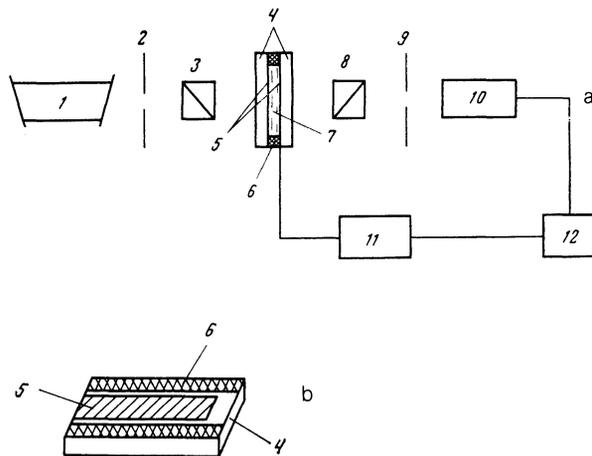


FIG. 2. Block diagram of the apparatus (a) and the symmetry of the electrodes on the substrate (b): 1) LG-52 laser; 2), 9) stops; 3), 8) polarizers; 4) glass plate; 5) transparent current-conducting coating; 6) Teflon spacers; 7) liquid crystal; 10) FEU-79 photomultiplier; 11) GZ-33 ad oscillator; 12) S1-18 oscilloscope.

cell when a light beam was incident at an angle: this was done using the formula $d = \lambda k (\cos\alpha_m - \cos\alpha_{m+k})^{-1/2}$. Here, m and $m+k$ are the angles of incidence corresponding to the m th and $(m+k)$ th interference minima of rays reflected by the upper and lower boundaries of the capillary gap between two glass plates. The value of d was determined to within 1%.

The planar orientation of liquid crystals was set by rubbing the electrodes with dry cotton. The orientation was improved by filling the capillary gap between the rubbed glass plates with a liquid crystal beginning from the end of the cell along the direction of rubbing. The uniformity of the orientation of the liquid crystal was deduced from a uniform darkening of the sample in a polarizing microscope when the polarizing prisms were crossed.

The frequency of the electric field applied to the cell was 1 kHz, which was governed on the one hand by the need to eliminate stray hydrodynamic effects in the bulk of the liquid crystal and, on the other, by the finite orientation relaxation time of the liquid crystal and rapid heating of the sample when the external field frequency was sufficiently high.

Since the saturation value of the electric field was fairly high (at room temperature its peak value was $E_{\text{sat}}^{\text{max}} \sim 3 \times 10^5 \text{ V/cm}$), used in the cells. A current-conducting coating on the glass plates at the points of location of Teflon spacers, which set the thickness of the liquid crystal layer, was etched away as shown in Fig. 2b. This electrode geometry was adopted because usually air bubbles formed at the edges of the insulating spacers during filling of the cell with a liquid crystal. The breakdown strength of air was of the order of 10^4 – 10^5 V/cm , which was considerably less than $E_{\text{sat}}^{\text{max}}$. Under these conditions the voltage was not applied at the points of location of the spacers. Such a procedure made it possible to avoid also the influence of a likely electrostatic charge accumulated on the Teflon, which again resulted in rapid breakdown of a sample.

In some cases a considerable increase of the breakdown voltage of a cell could be achieved by a thin polymer coating (representing an alcohol solution of a phenol formaldehyde polyvinyl butyral resin), deposited on the electrodes before

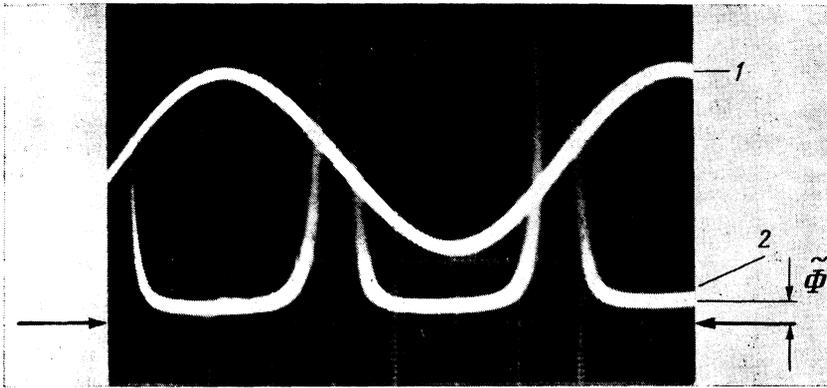


FIG. 3. Photograph of the oscilloscope screen showing the optical transmission of the investigated nematic liquid crystal layer under a saturation voltage: 1) reference signal $E(t)$ from the master oscillator; 2) photomultiplier signal. The arrows demonstrate the level of the photomultiplier signal in the case when the laser beam was not transmitted.

rubbing and probably smoothing out the various microdefects on the substrate surface. The deposited coating had little influence on the energy of anchoring of the investigated nematic liquid crystal to the substrate. This was demonstrated (Fig. 5 below) by the values of W^* obtained for the cells assembled from glasses without a coating. However samples placed between clean glasses broke down when a sufficiently high voltage was applied and this made them unsuitable for our purpose.

EXPERIMENTAL RESULTS AND DISCUSSION

We shall consider the optical response of a liquid crystal cell subjected to a sufficiently strong voltage. Since the deformation of the director in a nematic liquid crystal layer was insensitive to the sign of the external electric field, the optical transmission of the cell varied at a frequency which was twice the frequency of the field $E(t)$ (Fig. 3). At the moments when the field amplitude was maximal the angle of tilt of the director from the initial planar orientation was the largest and this corresponded to the minimum optical transmission of the cell when the polarizer and analyzer were crossed. An increase of the voltage to V_{sat} reduced the optical transmission of the cell at these moments of time to its absolute minimum (signal 2 in Fig. 3) and a further increase in the voltage did not alter the transmission, indicating that the director in the bulk of the liquid crystal was completely reoriented (and this was true also of the surface layers) from the initial planar orientation to the homeotropic direction. In this way it was possible to observe saturation of the Fréedericksz effect on the oscilloscope screen.

For comparison, we identified by arrows in Fig. 3 the level of the signal corresponding to total optical "nontransmission" of the cell, i.e., to the case when the laser beam was stopped completely. The residual signal $\bar{\Phi}$ was due to the finite relaxation time of the director orientation and due to the unavoidable difference of the orientational order parameter of the liquid crystal from unity. Nevertheless, the value of $\bar{\Phi}$ was very small ($\bar{\Phi} \lesssim 7 \times 10^{-3}$ rad) and comparable with the optical transmission of the cell containing 5CB with the homeotropic orientation on both plates (substrates) in the absence of the field. An increase in the thickness of the sample reduced the residual signal and, when the thickness exceeded 30μ , the optical transmission of the cell at peak values of $E(t)$ became zero within the limits of the experimental error.

By way of example, Fig. 4 shows the voltage dependence of the phase lag Φ of the transmitted light wave, measured for a cell which was 30μ thick. We used the relationship¹²

$$J = J_0 \sin^2(\Phi/2), \quad (5)$$

where J_0 and J are respectively, the intensities of the incident and transmitted light. The error in the determination of Φ was 10^{-3} rad. The graph obtained indicated that a complete reorientation of the director in the liquid crystal layer occurred at $V_{\text{sat}} \approx 350$ V.

The values of V_{sat} determined at room temperature for cells of different thicknesses in the range $d = 3.47$ – 38.8μ are plotted in Fig. 5. Samples with the thickness $d > 40 \mu$ exhibited electrohydrodynamic effects when the voltage was sufficiently high and this prevented us from reaching saturation of the liquid crystal structure. It is clear from Fig. 5 that in the range $d > 10 \mu$ the dependence $V_{\text{sat}}(d)$ was linear.

We used Eq. (4) and the measured values of V_{sat} to calculate also the effective surface energy of the investigated nematic liquid crystal in cells of different thicknesses. We substituted the voltage $V_{\text{sat}}^{\text{max}} = 2^{1/2} V_{\text{sat}}$ in Eq. (4), because—as already mentioned—the strongest reorientation of the director occurred at the peak values of the alternating electric field applied to the sample.

The room-temperature values of W^* calculated in this way were of the order 1 erg/cm^2 and they decreased on increase in the thickness of the liquid crystal layer. This dependence is shown in Fig. 5. In the case of small thicknesses

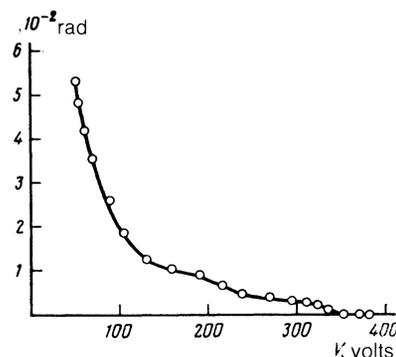


FIG. 4. Voltage dependence of the phase lag of a light wave transmitted by the liquid crystal cell ($d = 30 \mu$, $T = 23^\circ \text{C}$).

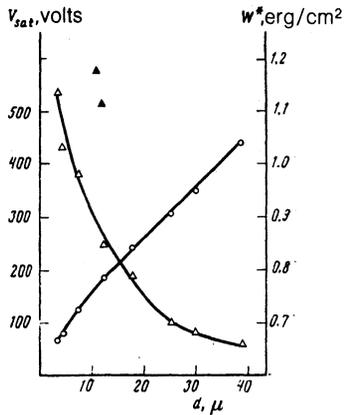


FIG. 5. Dependences of the saturation voltage and of the effective anchoring energy ($T = 23 \pm 1^\circ\text{C}$) on the thickness of the nematic liquid crystal layer: \circ) V_{sat} ; \triangle) W^* ; \blacktriangle) W^* (glass without polymer coating).

($d \lesssim 25 \mu$) the dependence $W^*(d)$ could be approximated by a logarithmic law, whereas in the case of large thicknesses ($d \gtrsim 10 \mu$), it was necessary to use a hyperbolic law (Fig. 6). The overlap of the two regions representing these different approximations was clearly due to the experimental error. Extrapolation of the dependence $W^*(d)$ to the thickness of one liquid crystal monolayer with the planar orientation ($d = 5 \text{ \AA}$) gave $W_0^* \approx 3 \text{ erg/cm}^2$, which was of the same order of magnitude as the difference between the surface stresses in the solid substrate and the nematic liquid crystal.¹³ Extrapolation of this dependence to greater thicknesses gave $W_0^* = 0.57 \text{ erg/cm}^2$, which agreed with the energy of anchoring in a semi-infinite liquid crystal of a substrate. In agreement with Eq. (4), the value of W_0^* was calculated analytically from

$$W_0^* = \left(\frac{K_{33} \Delta \epsilon}{4\pi} \right)^{1/2} E_{\text{sat}}^{\text{max}}, \quad E_{\text{sat}}^{\text{max}} = 2^{1/2} E_{\text{sat}},$$

where the saturation value of the electric field E_{sat} for the investigated structure was determined by the slope of the

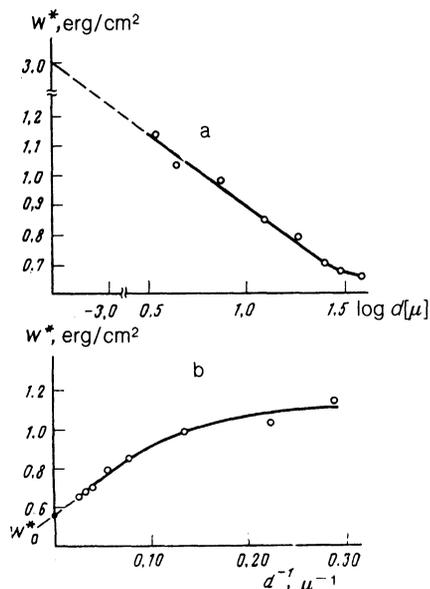


FIG. 6. Dependences of the effective anchoring energy on the thickness of the liquid crystal layer plotted on logarithmic (a) and hyperbolic (b) scales. $T = 23 \pm 1^\circ\text{C}$.

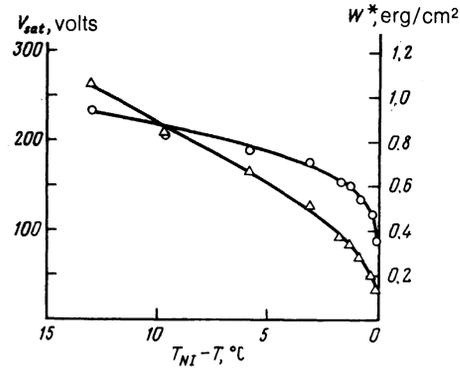


FIG. 7. Temperature dependences of the saturation voltage V_{sat} and of the effective anchoring energy W^* ($d = 13.3 \mu$): \circ) V_{sat} ; \triangle) W^* .

rectilinear part of the dependence $V_{\text{sat}}(d)$ in Fig. 5.

It seemed to us that the value of W_0^* should be regarded as the energy of anchoring of a nematic to a solid substrate in the absence of any other orienting forces acting on a nematic liquid crystal, such as the orienting influence of the second substrate. However, in the case of a nematic liquid crystal layer of finite thickness the director at each point (including the boundary regions) experienced the orienting influence of both confining surfaces and this influence increased on reduction of the distance between them (nonlocality of the director field).

We determined for the first time the temperature dependence of the surface energy of a nematic liquid crystal layer with the planar orientation. We plotted in Fig. 7 the temperature dependences of V_{sat} and W^* determined for a cell of thickness 13.3μ . In these calculations we used the published data on the temperature dependences of the elastic constant K_{33} (Ref. 14) and of the dielectric anisotropy $\Delta \epsilon$ (Ref. 15) of 5CB. It was interesting to note that the dependence $W^*(T)$ of the nematic liquid crystal with the planar orientation was practically identical with the corresponding dependence obtained in Ref. 16 for the homeotropic orientation case. In both cases the anchoring energy varied by a factor of 5–6 in the temperature interval $T_{\text{NI}} - 15^\circ < T < T_{\text{NI}} - 1^\circ\text{C}$. A comparison of the curve $W^*(T)$ obtained here with the temperature dependence of the orientational order parameter S (Ref. 14) yielded a quadratic dependence $W^* \propto S^2$ at low values of S (Fig. 8).

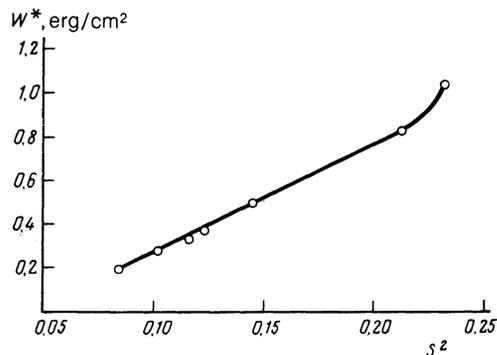


FIG. 8. Relationship between the effective anchoring energy of the nematic liquid crystal with the planar orientation and its orientational order parameter.

CONCLUSIONS

We determined for the first time the temperature dependence of the effective energy of anchoring of a nematic liquid crystal with the planar orientation to a solid surface. Moreover, we found that the anchoring energy depended on the thickness of the liquid crystal layer and this could be explained by nonlocality of the director field, i.e., by the mutual influence of the opposite surface layers.

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¹A. Rapini and M. Papoular, *J. Phys. (Paris)* **30**, Colloq. 4, C4-54 (1969).

²K. H. Yang, *J. Phys. (Paris)* **44**, 1051 (1983).

³H. L. Ong, R. B. Meyer, and A. J. Hurd, *J. Appl. Phys.* **55**, 2809 (1984).

⁴H. Yokoyama and H. A. van Sprang *J. Appl. Phys.* **57**, 4520 (1985).

⁵K. H. Yang, *J. Appl. Phys.* **53**, 6742 (1982).

⁶H. A. van Sprang and R. G. Aartsen, *Mol. Cryst. Liq. Cryst.* **123**, 355 (1985).

⁷L. Komitov and A. G. Petrov, *Phys. Status Solidi A* **76**, 137 (1983).

⁸T. Ya. Marusii, Yu. A. Reznikov, V. Yu. Reshetnyak, M. S. Soskin, and A. I. Khizhnyak, *Zh. Eksp. Teor. Fiz.* **91**, 851 (1986) [*Sov. Phys. JETP* **64**, 502 (1986)].

⁹M. I. Barnik, L. M. Blinov, T. V. Korkishko, B. A. Umanskiĭ, and V. G. Chigrinov, *Zh. Eksp. Teor. Fiz.* **85**, 176 (1983) [*Sov. Phys. JETP* **58**, 102 (1983)].

¹⁰J. Nehring, A. R. Kmetz, and T. J. Scheffer, *J. Appl. Phys.* **47**, 850 (1976).

¹¹K. H. Yang and C. Rosenblatt, *Appl. Phys. Lett.* **43**, 62 (1983).

¹²M. Born and E. Wolf, *Principles of Optics*, 4th ed., Pergamon Press, Oxford (1970).

¹³J. Cognard, *Mol. Cryst. Liq. Cryst. Lett.* **64**, 331 (1981).

¹⁴P. P. Karat and N. V. Mahusudana, *Mol. Cryst. Liq. Cryst.* **36**, 51 (1976).

¹⁵D. A. Dunmur, M. R. Materfield, W. H. Miller, and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.* **45**, 127 (1978).

¹⁶C. Rosenblatt, *J. Phys. (Paris)* **45**, 1087 (1984).

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