undergo total internal reflection. According to (11), (15), (22), and (23), we have for  $\tau_1 = \tau_2$ 

$$\xi_{1} = -\frac{4m_{\parallel}m_{\perp}Q_{1}}{(m_{\parallel}+m_{\perp}Q_{1})^{2}}(1-Q_{1}),$$

$$\xi_{2} = \frac{4m_{\parallel}m_{\perp}Q_{2}}{(m_{\perp}+m_{\parallel}Q_{2})^{2}}(Q_{2}-1);$$

$$Q_{1,2} = \left[1 \mp \left(\frac{m_{\parallel}}{m_{\perp}}-1\right)\frac{r^{2}}{q_{1,2}^{2}}\right]^{1/2}.$$
(24)

We recall that by hypothesis  $m_{\parallel} > m_{\perp}$ . Therefore  $\xi_2 \neq 0$ for all r and q, whereas  $\xi_1 \neq 0$  only for those values of the quasimomentum for which  $(m_{\parallel}/m_{\perp}-1) \cdot (r^2/q^2) < 1$ (see above). We note that  $\xi_1$  and  $\xi_2$  are of opposite signs, whence it follows that the electromechanical force density in the two crystallites also has opposite signs (Fig. 3). Calculation of  $\langle \xi_1 \rangle$  and  $\langle \xi_2 \rangle$  for arbitrary  $m_{\parallel}/m_{\perp}$  (see (26)) is possible only by numerical integration. We shall restrict ourselves to calculation of the limiting values for  $m_{\parallel}/m_{\perp} \gg 1$  and for  $m_{\parallel} \approx m_{\perp}$ . If  $m_{\parallel} \gg m_{\perp}$ , then

$$\langle \xi_1 \rangle \approx -\frac{1}{15} (m_\perp/m_\parallel)^4, \langle \xi_2 \rangle \approx m_\perp/m_\parallel, \qquad (25)$$

and for  $m_{\parallel} \approx m_{\perp}$ ,

$$\langle \xi_1 \rangle \approx -10^{-2} \left(\frac{\Delta m}{m}\right)^{1/h}, \quad \langle \xi_2 \rangle \approx 0.7 \left(\frac{\Delta m}{m}\right)^{1/h}, \qquad (26)$$

$$\Delta m = m_{\parallel} - m_{\perp}, \ m = m_{\parallel} \approx m_{\perp}.$$

The estimate of  $\langle \xi_s \rangle$  shows that the electromechanical force density, as was to be expected, is smaller in the case of a specular boundary than in the case of a diffuse one.

The sensitivity of  $\mathcal{F}(z)$  to the electronic energy spectrum of the metal should be noted. The electromechanical forces naturally have their maximum value on a diffuse crystallite interface ( $\mathcal{F}_{surf}$ ). It is convenient to express this force (see (13)) in terms of the current density. On omitting dimensionless factors (usually close to unity), we get

$$\mathcal{F}_{surf} \approx j p_F / e$$
,

whence  $\mathcal{F}_{surf} [dyn/cm^2] \approx j [A/cm^2]$ . In some experiments the current density reaches  $\approx 10^6 A/cm^2$ ; in such cases  $\mathcal{F}_{surf} \approx 10^6 dyn/cm^2$ .

- <sup>1)</sup>In the case of two different metal specimens with diffusely scattering surfaces, the boundary conditions would coincide with (5).
- <sup>1</sup>V. B. Fiks, Ionnaya provodimost' v metallakh i poluprovodnikakh (Ionic Conduction in Metals and Semiconductors), Nauka, 1969.
- <sup>2</sup>O. A. Troitskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 10, 18 (1969) [JETP Lett. 10, 11 (1969)].
- <sup>3</sup>V. I. Spitsyn, O. A. Troitskii, V. G. Ryzhkov, and A. S. Kozyrev, Dokl. Akad. Nauk SSSR 231, 402 (1976).
- <sup>4</sup>K. M. Klimov, G. D. Shnyrev, and I. I. Novikov, Dokl. Akad. Nauk SSSR 219, 323 (1974) [Sov. Phys. Dokl. 19, 787 (1975)].
   <sup>5</sup>W. M. Kuntanich, The Flore Team File 50, 2116 (1976).

<sup>5</sup>V. M. Kontorovich, Zh. Eksp. Teor. Fiz. **59**, 2116 (1970) [Sov. Phys. JETP **32**, 1146 (1971)].

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## The electrotropic cholesteric-nematic transition and the storage effect based on it

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The threshold, contrast, and time characteristics of the cholesteric-nematic phase transition induced by an electric field have been studied in compensated mixtures of cholesteric liquid crystals with nematic-liquidcrystal admixtures (up to 10%). A storage effect has been observed which consists in the prolonged preservation of the homeotropic orientation of the molecules near the cholesteric-nematic transition temperature. Judging by the principal electro-optical parameters, the investigated system surpasses the well-known nematic-cholesteric system in which the storage effect is due to texture transformations under conditions of dynamic scattering of light.

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The twistedness of the hypomolecular structure determines the unusually strong optical activity of the cholesteric liquid crystal (CLC). In this case the plane of polarization of polarized light passing through the CLC may rotate either clockwise or anticlockwise, depending on the structure of the individual molecules of the cholesteric compound. By mixing in definite concentration proportions dextro- and levo-rotatory CLC, we can compensate the optical activity.<sup>[1]</sup> The compensation occurs at a definite—for each mixture—temperature  $T_{c-n}$ , at which the mixture acquires the characteristic properties of a nematic liquid crystal (NLC), i.e., at which the cholesteric-nematic phase transition occurs. As we approach the phase-transition temperature, the helix pitch of the cholesteric mixture increases and becomes infinitely large at  $T_{c-n}$  (this corresponds to the structure of a nematic compound). The neutralization of the rotatory power is observed not only in a mixture of two CLC with opposite directions of rotation of the plane of polarization, but also in a mixture of a dextrorotatory CLC with a NLC, as well as in a three-component mixture of a compensated cholesteric compound and a nematic compound.

If we apply a constant or a low-frequency alternating electric field to a cell containing a two-component compensated mixture, then at  $T_{c-n}$  and in its vicinity the molecules are easily aligned perpendicularly to the surfaces of the electrodes, forming a homotropic nematic structure. A necessary condition for this electric-field induced (electrotropic) cholesteric-nematic phase transition to occur is that the value of the anisotropy in the permittivity of the mixture should be positive.<sup>[2]</sup> After the field is switched off, the molecules relax to the initial planar state. But if to the compensated mixture we add a definite quantity of a NLC, then the molecules of the nematic compound will hinder the relaxation of the cholesteric molecules, and the homotropic orientation will be preserved for some time after the field has been switched off. Thus, a storage effect based on the electrotropic cholesteric-nematic transition can obtain in the three-component compensated mixture.

In spite of the fact that a number of theoretical<sup>[3,4]</sup> and experimental<sup>[5-10]</sup> investigations have been devoted to the study of compensated CLC, no paper has so far been published in which the storage effect due to the above-described phenomenon is considered in detail. The aim of the present paper is to investigate the indicated effect.

As the cholesteric components, we chose a compensated mixture of dextrorotatory cholesteryl chloride (CC) and levorotatory cholesteryl laurate (CL); a eutectic mixture of p-methoxybenzylidene-p'-n-butyl aniline (MBBA) and p-ethoxybenzylidene-p'-n-butyl aniline (EBBA) served as the nematic component. The cholesteric phase, in both the CC-CL mixture and the threecomponent compound, formed only upon cooling from the isotropic melt, i.e., it was monotropic. Therefore, in the course of the preparation all the samples were heated to a temperature somewhat higher than the critical temperature of the transition into the isotropic liquid; they were thoroughly mixed in this state and then cooled to the experimental temperature.

The measurements were performed on an electro-optical apparatus constructed on the basis of a binocular polarizing microscope. To one of the tubes of the microscope was attached a photomultiplier, the signal from which was fed to recorders. Such a system allowed us to directly observe the changes in the textures of the liquid crystal and at the same time record the corresponding optical characteristics of the sample. The cell with the sample was placed in a thermostat, which was



FIG. 1. Variation of the critical temperature of the cholesteric-nematic transition (the curve 1) and that of the transition into the isotropic liquid state (the curve 2) of compensated CLC mixtures with the NLC concentration.

fixed on the stage of the microscope. The thermostatic control was realized to within  $\pm 0.5$  °C.

The cholesteric-nematic transition temperature was determined from the change in light transmission by the cell in crossed polaroids. In this case the transmission  $T_{\rm c-n}$  changed by a factor of several tens. To attain maximum contrast, we used thin (~8  $\mu$ ) samples, and the surfaces of the electrodes were covered with a layer of lecithin, which facilitated the homotropic orientation of the molecules.

The neutralization of the rotatory power in the CC-CL mixture occurred when the CL content was between 32 and 38% by weight. For this concentration interval the  $T_{o-n}$  lay in the region of existence of the mesophase and moved toward the region of higher temperatures as the CL content was increased. The NLC was added to the compensated mixture in amounts of up to 10% by weight, and, as it was increased, the  $T_{o-n}$  also shifted monotonically toward the region of higher temperatures (Fig. 1). In this case the critical temperature for the transition into the isotropic liquid virtually remained unchanged.

Let us note that an increase in the NLC and levorotatory CLC contents in the compensated mixture has a similar effect on  $T_{c-n}$ . It should also be noted that a mixture of a NLC and a small quantity of a cholesteric compound is always levorotatory, irrespective of the sign of the optical activity of the CLC itself. A comparison of these factors indicates that a NLC, an optically inactive material, behaves in mixtures with twisted structures like an optically active levorotatory element. It is well known<sup>[11]</sup> that the screw sense of a cholesteric structure is connected with the distinctive features of the structure of the CLC molecule, namely, with the length, d, of its side radical. For d < 2.08 Å there is formed a dextrorotatory structure, while for d > 2.08 Å a levorotatory structure is formed. Therefore, it can be assumed that the orientation of the NLC molecules in a compensated mixture is equivalent to an increase in the length of the side radical of the cholesteric molecule.

The induced cholesteric-nematic transition in a threecomponent mixture occurs at a definite threshold voltage potential,  $U_{\rm thr}$ , of the constant or low-frequency alternating electric field. The quantity  $U_{\rm thr}$  depends on the temperature of the sample and the thickness of the



FIG. 2. The temperature dependence of the threshold voltage potential  $U_{\text{thr}}$  (the curves 1, 2) and of the switching-on time  $\tau_{\text{sw}}$  (the curve 3) of the electrotropic cholesteric-nematic transition. The sample thickness: 1), 3) 8  $\mu$ ; 2) 32  $\mu$ . The switching-on time was measured for U = 50 V. The arrows on the right and on the left mark the transitions respectively into the isotropic-liquid and solid-crystal states.

layer under investigation. In Fig. 2 we show the temperature dependences of  $U_{\rm thr}$  for a compensated mixture containing 4% of a NLC. A sample of this concentration proportion is suitable for investigation, since its  $T_{\rm c-n}$  ( $\approx 39$  °C) lies in the middle of the existence interval for the mesophase. Near  $T_{\rm c-n}$  the quantity  $U_{\rm thr}$  has its smallest value, which decreases with decreasing layer thickness.

It should be noted that, in thin samples, the molecules of the mixture can, at temperatures near  $T_{\rm c-n}$ , spontaneously align themselves perpendicularly to the electrode surface without the application of a field (the segment *AB* of the curve 1). A similar phenomenon in two-component compensated mixtures has been named the self-orientation effect.<sup>[9]</sup> The spontaneous orientation of the molecules occurs in cells with electrodes whose surfaces are covered with lecithin, or are, in general, not specially treated. But if the treatment of the surfaces is such as to prescribe a planar orientation, then the spontaneous alignment of the molecules is not observed, and  $U_{\rm thr}$  can be determined in the entire mesophase region.

For a fixed voltage potential the switching-on time of the induced cholesteric-nematic transition has its minimum value near  $T_{c-n}$  and increases with increasing  $\Delta T$ = $|T - T_{c-n}|$  (the curve 3). An increase in the applied voltage potential leads to a decrease in the switching-on time. It should be noted that the switching-on time of the cholesteric-nematic transition is considerably shorter than the rise time of the dynamic-light-scattering effect.<sup>[12]</sup> Accordingly, for the system with a memory



FIG. 3. Temperature dependence of the memory-preservation time  $t_s$  for a cell with untreated electrode surfaces (the curve 1) and with electrode surfaces grated in one direction (the curve 2). The sample thickness was 15  $\mu$ .





FIG. 4. The spontaneous erasure of the memory produced as a result of the electrotropic cholesteric-nematic transition (the curve 1) and the texture transformation in the dynamiclight-scattering regime (the curve 2).

under consideration, this time is shorter than the switching-on time for the well-known NLC-CLC memory system,<sup>[13]</sup> in which the confocal texture arising as a result of the turbulent motion in the dynamic-scattering regime is preserved.

After the applied voltage potential is siwtched off, the molecules of the three-component mixture for some time remain aligned perpendicularly to the electrode surfaces, i. e., storage of the established texture occurs. In the present case the preservation time for the homeotropic orientation of the molecules can be called the storage time,  $t_s$ . As we approach the transition temperature,  $t_s$  increases sharply (Fig. 3), and at  $T_{c-n}$  the storage can last for an infinitely long time. For a cell with untreated electrode surfaces (the curve 1),  $t_s$  is longer than in the case of planar orientation of the molecules (the curve 2).

The contrast, K, of the cell during the entire  $t_s$  virtually does not change, and the spontaneous erasure of the memory occurs as a rapid return to the original structure (Fig. 4, curve 1). In the same figure we show the curve of spontaneous memory erasure for the NLC-CLC system (the curve 2).<sup>[13]</sup> The contrast, K, of such a system is significantly lower, and decreases noticeably in the first few seconds after the switching off of the voltage potential.



The sharp threshold for the electrotropic cholesteric-

FIG. 5. Dependence of the memory-preservation time on the grid bias at a temperature of 33° C (the curve 1) and at 28° C (the curve 2). The sample thickness was 8  $\mu$ .



FIG. 6. Dependence of the memory-preservation time on the applied voltage potential (the curve 1) and on the time,  $t_h$ , the sample is kept under the influence of the voltage potential (the curve 2);  $T = 46^{\circ}$  C. For the curve 1)  $t_h = 15$  sec; for 2) U = 250 V.

nematic transition allows us to apply to the cell in addition a constant, or an alternating (f < 3 kHz), grid bias  $U_b$ . In this case the storage time increases sharply, starting from some value of  $U_b$  (Fig. 5). The application of a  $U_b$  whose strength is close to  $U_{\rm thr}$  allows us to increase  $t_s$  by three to four orders of magnitude. As  $\Delta T$  decreases, the magnitude of the voltage potential  $U_b$  necessary for the attainment of the same  $t_s$  decreases substantially. At a fixed temperature the voltage potential  $U_b$  is directly proportional to the sample thickness. The erasure of the memory in the considered case is accomplished simply by switching off  $U_b$ .

The storage time depends on the strength of the exciting voltage potential and on the time this potential acts on the sample (Fig. 6). As the applied voltage potential is increased,  $t_s$  monotonically increases with a tendency toward saturation. An increase in the time interval during which the sample is kept under the influence of the voltage potential (the holdup time) at first leads to quite a sharp increase in  $t_s$ , which subsequently stabilizes. Such a behavior of  $t_s$  is due to the specific nature of the storage mechanism in question. The effect under consideration is connected with near-surface phenomena in the cell. After the voltage potential has been switched off, the molecules in the near-surface layers remain aligned perpendicularly to the electrode surfaces owing to the elastic forces of the interaction with the material of the backing. The near-surface molecules strive to maintain in the perpendicular direction the molecules of the deeper-lying layers. At the same time the re-establishment of the cholesteric structure occurs in the volume, which leads to the destruction of the ordering. As  $T_{c-n}$  is approached, the forces of the interaction between the molecules in the cholesteric layers weaken, the re-establishment of the structure proceeds slowly, and  $t_s$  increases accordingly. It is clear that  $t_s$  is directly determined by the number of molecules aligned perpendicularly in the near-surface layers. This connection is confirmed by the nature of the observed dependences of  $t_s$  on temperature, the strength of the exciting voltage potential, and the duration of the application of this potential to the sample.

- <sup>1</sup>G. Friedel, Ann. Phys. (Paris) 18, 273 (1922).
- <sup>2</sup>P. G. De Gennes, Solid State Commun. 6, 163 (1968).
- <sup>3</sup>P. N. Keating, Mol Cryst. Liq. Cryst. 8, 315 (1969).
- <sup>4</sup>S. Chandrasekhar, G. S. Rangaanath, U. D. Kini, and K. A. Suresh, Mol. Cryst. Liq. Cryst. 24, 201 (1973).
- <sup>5</sup>E. Sackmann, S. Meiboom. L. C. Snyder, A. E. Meixner,
- and R. E. Dietz, J. Am. Chem. Soc. **90**, 3567 (1968). <sup>6</sup>H. Baessler and M. M. Labes, Phys. Rev. Lett. 21, 1791 (1968).
- <sup>7</sup>H. Baessler and M. M. Labes, J. Chem. Phys. **51**, 1846 (1969).
- <sup>8</sup>H. Baessler, T. M. Laronge, and M. M. Labes, J. Chem. Phys. **51**, 3213 (1969).
- S. Sato and M. Wada, Jpn. J. Appl. Phys. 11, 1566 (1972).
- <sup>10</sup>S. Sato and M. Wada, Jpn. J. Appl. Phys. 11, 1752 (1972).
- <sup>11</sup>L. B. Leder, J. Chem. Phys. 55, 2649 (1971).
- <sup>12</sup>E. Jakeman and E. P. Raynes, Phys. Lett. A39, 69 (1972).
   <sup>13</sup>G. H. Heilmeier and J. E. Goldmacher, Proc. IEEE 57, 34 (1969).

Translated by A. K. Agyei.