[1]One has in mind, of course, the growth as a result of the phase transition, and not of the motion of the interphase boundary along with the liquid in the laboratory system of the coordinates.

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Investigation of the nature of homotropic orientation of nematic liquid crystal molecules, and the possibility of applying it in modulation spectroscopy

A. N. Chuvyrov and A. N. Lachinov

Physics and Mathematics Division with Computational Center, Bashkir Affiliate, USSR Academy of Sciences
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The electroreflection method has been used to investigate the spontaneous polarization of nematic liquid crystals (NLC) as a function of the orientation of the molecules. It is found that electroreflection in a NLC–semiconductor system is observed only with homotropic orientation of the molecules. The existence of the phenomenon of electroreflection is considered in its dependence on various conditions; the fixed bias, the frequency and amplitude of the modulating field, the temperature of the specimen, and the form of the modulating signal. An explanation of the observed phenomena is given from the point of view of the polar structure of the NLC. A theoretical analysis of electroreflection is made on the basis of a bipolar model of the NCL. Good verification is obtained of the experimental results and of the observed electrooptical effects of the first to sixth orders. A new technique of modulation spectroscopy, using nematic liquid crystals, is proposed.

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It is known that under certain boundary conditions it is possible, in thin layers of nematic liquid crystals (NLC), to attain homotropic orientation of the molecules.[1] Homotropic layers have been obtained and investigated[2] that originated spontaneously in specimens of a thickness less than a certain critical value during the phase transition from the isotropic phase to the nematic; their nature was associated with the polar structure of the NLC. But so far there is no direct experimental confirmation of such a structure. In the present paper, therefore, a direct test is made of the presence of polarity, and a comprehensive investigation of it is made in a homotropically orientated NLC by the method of electroreflection from a semiconductor–nematic liquid crystal boundary; also, the possibility of application of NLC for investigation of electroreflection (the Franz-Keldysh effect) is clarified. The essence of this method in the present case was as follows.

It is known that the change of the reflection coefficient of a semiconductor placed in an electric field is determined by the change of the imaginary part ϵ_i and real part ϵ_r of the permittivity. In a field of intensity E, the changes of these quantities are respectively[3]

$$\Delta\epsilon_i(\omega, E) = \frac{B\theta^{1/2}}{\omega^2} F\left(\frac{\omega_g - \omega}{\theta}\right), \quad \Delta\epsilon_r(\omega, E) = \frac{B\theta^{1/2}}{\omega^2} G\left(\frac{\omega_g - \omega}{\theta}\right), \quad (1)$$

and the change of the reflection coefficient is

$$\Delta R/R = \alpha(\omega)\Delta\epsilon_i + \beta(\omega)\Delta\epsilon_r, \quad (2)$$

where ω is the frequency of the light, $\theta = E^2/2\mu^*$; μ^* is the effective mass, $B = 2|P_{cv}n|^2(2\mu^*)^{3/2}$, $P_{cv}(k)$ is the matrix element of the momentum P between the Bloch functions of the conduction band and of the valence band for the vector k, n is the unit vector along the field, $\alpha(\omega) = \partial \ln R/\partial \epsilon_i$, and $\beta(\omega) = \partial \ln R/\partial \epsilon_r$. The functions $F[(\omega_g - \omega)/\theta]$ and $G[(\omega_g - \omega)/\theta]$ are expressed in terms of the Airy functions $Ai(x)$ and $Bi(x)$ and the unit step function $H(x)$:

$$F\left(\frac{\omega_g - \omega}{\theta}\right) = \pi\left[Ai'^2\left(\frac{\omega_g - \omega}{\theta}\right) - \left(\frac{\omega_g - \omega}{\theta}\right)Ai^2\left(\frac{\omega_g - \omega}{\theta}\right) - \left(\frac{\omega - \omega_g}{\theta}\right)^{1/2}H\left(\frac{\omega - \omega_g}{\theta}\right)\right],$$

$$G\left(\frac{\omega_g - \omega}{\theta}\right) = \pi\left[Ai'\left(\frac{\omega_g - \omega}{\theta}\right)Bi'\left(\frac{\omega_g - \omega}{\theta}\right) - \left(\frac{\omega_g - \omega}{\theta}\right) \cdot Ai\left(\frac{\omega_g - \omega}{\theta}\right)Bi\left(\frac{\omega_g - \omega}{\theta}\right) - \left(\frac{\omega_g - \omega}{\theta}\right)^{1/2}H\left(\frac{\omega_g - \omega}{\theta}\right)\right]. \quad (3)$$

The value of the field $E = \partial\phi/\partial z$ at the surface of the semiconductor in the semiconductor–NLC system is determined by the volume distribution of dipole moment $\mu(z)$; see Fig. 1 (following Ref. 2, we shall suppose that $\mu(\pm\sigma/2) = \mu_0$ and $\mu(0) = 0$). The value of the potential in
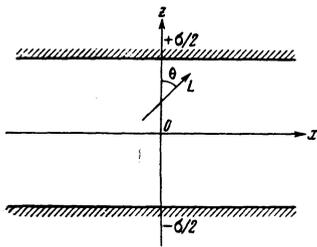
FIG. 1. Geometry of a layer of nematic liquid crystal with homotropic orientation of the molecules.

such a layer is[4]

$$+\frac{1}{4\pi\varepsilon_0}\int_{\varphi=\varphi_0}|\mu(z)|\nabla'\left(\frac{1}{r-r'}\right)\cos\theta\,dv. \quad (4)$$

Here the primes denote that the coordinates pertain to the source of the field, the dipoles. From this expression it follows that a change of the angle between the dipole moments and the z axis leads to a change of the potential at the surface of the semiconductor and determines the value of the electroreflection effect. This angle exactly coincides with the angle of rotation of the director; thus the problem of determining the potential reduces to the calculation of the motion of the director in an electric field.

It must be noted that because of the experimental difficulties of recording electroreflection spectra, fields ~10^5 - 10^6V/cm will usually be necessary; therefore in the absence of polarization of the NLC, fields ~10^3V/cm are small for observation of this phenomenon in the experiments described below. On the other hand, electroreflection spectra can be excited by a low voltage because of the potential drop at the electric double layer near the surface of the semiconductor, since the liquid crystal is a weak electrolyte (the conductivity of the NLC used ~$10^{-12}\Omega^{-1}cm^{-1}$). Therefore electroreflection spectra were investigated with planar orientation of the molecules and in a semiconductor—isotropic melt system, and a comparison was also made with results obtained by the electrolytic method (the electrolyte was a 0.1 normal solution of KOH). Apparently one can assume an influence of still a third mechanism of the electroreflection effect in a semiconductor—NLC system: change of the contact difference of potential by the electric field.

EXPERIMENTAL METHOD

The measurements of electroreflection were made according to the scheme described by Cardona et al.[5] As source of monochromatic radiation, a monochromator SPM-2 was used; scanning of the spectrum was accomplished by external drive of a recorder G1B1. A photoelectric mirror attachment to the monochromator was constructed; it permitted measurements in the range 0.2–1 μm. Its construction provides for making measurements of the modulation spectra both in the transmitted and in the reflected light. In measurement in the reflected light, the angle of incidence is 10°. For recording the spectrum, use was made of photomultipliers of types FÉU-39 (0.2–0.8 μm) and FÉU-83 (0.7–1.2 μm). At the photomultiplier, a constant level of input signal was maintained through the change of the

voltage at the diodes, by means of a system similar to that used in Ref. 5. The variable signal was amplified by a selective amplifier U2-6, then entered a voltage converter V9-2 and, after amplification by a constant-current microvoltmeter V2-11, was recorded by the recorder G1B1. A reference voltage at the voltage converter was provided from a frequency synthesizer, which made it possible to obtain a voltage of frequencies that were multiples of the fundamental frequency of the voltage supplied to the cell. The source of the field was a generator G3-33 or G5-6A; frequency control was accomplished with a frequency meter Ch3-32. For heating the specimen, a double thermostat UT-20 was used.

The cell was a plane capillary, formed by glass with a transparent conducting coating of SnO_2 and a surface of semiconductor Ge. The thickness of the capillary was 10–25 μm and was set by the thickness of the mica gaskets between the semiconductor and the transparent electrode. The NLC used in the work were methoxybenzylidene butylaniline (MBBA), with negative dielectric anisotropy $\Delta\varepsilon \sim -1.5$, and p'-cyanophenyl ester of para-heptylbenzoic acid (CPEHBA), with positive dielectric anisotropy $\Delta\varepsilon \sim 19$, and also mixtures of these.

The method of obtaining planar layers was the same as before.[6] Homotropic layers, in specimens with thicknesses less than a certain critical value d_{cr} (~22 μm for MBBA, ~100 μm for CPEHBA), originated spontaneously upon heating of planarly oriented NLC to the isotropic phase and subsequent cooling to the nematic state. At specimen thicknesses above the critical, the planar orientation was retained after the phase transition.[1] The orientation of the molecules was monitored with a reflection polarization mocroscope MP-6, by analysis of the polarization of a parallel beam of light transmitted through the transparent electrode and the NLC and reflected by the surface of the germanium. The presence of a homotropic orientation was evidenced by the absence of double refraction, since a homotropic layer of NLC is similar to a uniaxial crystalline plate cut perpendicular to the optic axis. A sample with planar orientation of the molecules is similar to a crystalline plate cut parallel to the optic axis, which was registered by the occurrence of double refraction. The orientation of the molecules and the chemical bonds at the semiconductor—NLC surface were monitored by infrared spectroscopy of attenuated total internal reflection (ATIR). 48-fold ATIR elements were made from germanium. The sample was enclosed in a capillary of thickness 10–25 μm, formed by the plate of the ATIR element and glass with a metallized coating. The differences of orientation of the molecules manifested themselves in the ATIR spectra in a change of intensity of the absorption bands of infrared radiation. The angle of orientation with respect to the surface was determined from Fresnel's formulas. All the experimental results described below were verified for other systems also, for example GaAs-NLC, FeS_2-NLC, Si-NLC, etc.

INVESTIGATION OF NEMATIC LIQUID CRYSTALS WITH NEGATIVE DIELECTRIC ANISOTROPY

We shall discuss the results of investigation of electroreflection at the frequencies of various harmonics.

The measurements were made in the region of the peaks E_1 and $E_1 + \Delta_1$. In all the spectra obtained, these singularities were clearly resolved. The electroreflection spectrum for the first harmonic is shown in Fig. 2. The size of the peak $E_1 + \Delta_1$ is larger than of E_1. Apparently this is due to the fact that in germanium, oscillations at $E_1 + \Delta_1$ are not caused solely by the Franz-Keldysh effect. The amplitude of these oscillations varies linearly with increase of the field (Fig. 3). This result indicates the presence of polarity of the liquid crystal and is a consequence of this linear electro-optic effect (the Pockels effect).

The largest electroreflection effect was observed at the doubled frequency (Fig. 2). In this case the values of the peaks E_1 are larger than of $E_1 + \Delta_1$; this agrees with results obtained by the electrolytic method.[3] The amplitude of the oscillations is proportional to the square of the applied voltage (Fig. 3). The best resolution of the spectra could be attained with minimum value of the modulating field ~250 mV. It then became clear that the peak E_1 is split into two peaks and that the peak $E_1 + \Delta_1$ also has a complicated structure (Fig. 4). The possibility of such splitting was pointed out be Cardona.[3]

In the investigation of higher harmonics, the third, fourth, fifth, and sixth harmonics were detected. The signals of higher-order harmonics could not be resolved. The general form and character of the dependence of these harmonics on the wavelength of the light do not differ from the first and second harmonics, but the intensity ratios are: $(\Delta R/R)_\Omega$: $(\Delta R/R)_{2\Omega}$: ... : $(\Delta R/R)_{6\Omega}$ = 1: 22: 0.04: 0.12: 0.004: 0.006. When the frequency of the field on the cell was increased to 300 Hz, the value of $\Delta R/R$ for all the harmonics fill abruptly to zero.

Because the character of the behavior of the electroreflection spectra is the same for different harmonics, we shall discuss in more detail the results of investigation of the features of the first and second of them. First, to make the nature of these harmonics more precise, we shall consider the influence on the electroreflection spectra of the constant field, the bias. On ap-
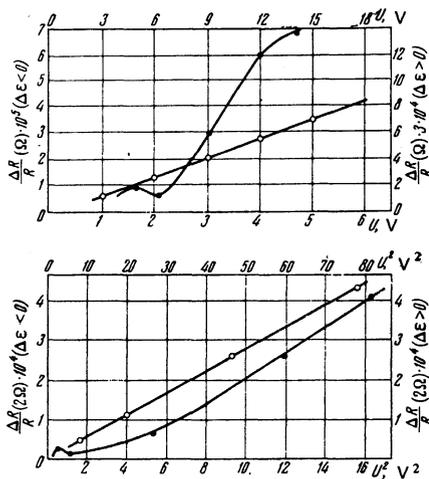
FIG. 3. Variation of the amplitude of oscillation of peak E_1 with value of the modulating field: O, NLC with $\Delta\epsilon < 0$, $T = 300$ K; ●, NLC with $\Delta\epsilon > 0$, $T = 323$ K.

plication of a constant bias to the specimen, the character of the electroreflection changes, depending on the polarity of the bias. In contrast to the electrolytic method, the amplitude of the oscillations increases when the semiconductor is biased positively with respect to the transparent electrode. Change of the bias from 0.8 to 2 V causes an increase of the effect by a factor 1.5. Negative bias has a slight effect on the electroreflection, diminishing its intensity. The different effect of positive and negative biases is due to the fact that in an electric field, the molecules tilt differently, depending on the field direction. With positive bias, the angle between the field direction and the director decreases; with negative, it increases. In the first case, this leads to an increase of the discontinuity of potential at the LC-semiconductor surface; in the second, to a decrease. Starting from this, one can determine the orientation of the dipoles in a homotropic layer with respect to the surface of the layer: the dipoles orient themselves with the negative end toward the surface.

In the case of the linear effect, the influence of a constant bias is opposite, although not so clearly manifested. Negative bias increases the amplitude of the electroreflection insignificantly. Increase of a positive bias leads to collapse of the oscillations, and electroreflection is practically unobservable at a value of the bias equal to 3 V.

Thus with respect to the character of the influence of a constant bias on the electroreflection spectra, the method that uses liquid crystals is closer to a strong-field method than to an electrolytic method. This is also confirmed by measurements of the effect in unipolar pulsed fields, whose electroreflection spectra coincided
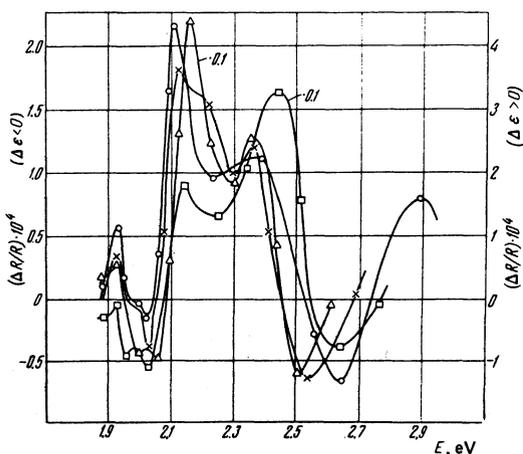
FIG. 2. Electroreflection spectra of germanium. Nematic liquid crystal with $\Delta\epsilon < 0$ at $T = 300$ K: □, first harmonic, $U = 4$ V; O, second harmonic, $U = 4$ V. Nematic liquid crystal with $\Delta\epsilon > 0$ at $T = 323$ K: △, first harmonic, $U = 6$ V; ×, second harmonic, $U = 6$ V.
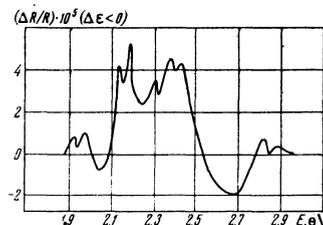
FIG. 4. Electroreflection spectrum of germanium at voltage 0.25 V, $T = 300$ K, $\Delta\epsilon < 0$.

with those obtained in sinusoidal fields. In the case of an electrolyte, application of the pulse method leads to a smearing out of the peaks and to a change of the ratio between them (Fig. 5).

RESULTS OF INVESTIGATION OF NEMATIC LIQUID CRYSTALS WITH POSITIVE DIELECTRIC ANISOTROPY

From the point of view of the Oseen-Frank continuum theory, without allowance for the bipolar model, in a NLC with homotropic orientation of the molecules and with positive dielectric anisotropy, upon application of a field along the orientation of the director, there should be no deformational effects; furthermore, with arbitrary random inclination of the director it will be restored to the original orientation. But direct optical polarization investigations of the effect of an electric field on a system consisting of a semiconductor and a homotropically oriented NLC showed the presence of deformation of the layer at sufficiently low voltages, ~0.2–0.3 V. A manifestation of this fact is the appearance in the sample plane of a system of spherules (Fig. 6). Change of the polarity of the constant voltage leads to disappearance of the spherules and appearance of them at the other electrode. Raising of the voltage to 7–8 V leads to the onset of electrohydrodynamic instability.

In the investigation of the semiconductor—nematic liquid crystal system with positive dielectric anisotropy, electroreflection effects were also observed, but only of the first to fourth orders. Higher harmonics could not be resolved. The largest amplitude of the oscillations was observed at the second harmonic; it was five times higher than the oscillations of the first harmonic and two orders of magnitude higher than the oscillations of the third and fourth harmonics. This result is similar to that for a liquid crystal with $\Delta\epsilon < 0$.

The existence of harmonics in electroreflection indicates that the field in the semiconductor—NLC transitional layer varies in an asymmetric manner, in contrast to the influencing field. The amplitude of the oscillations at the double frequency is proportional to the square of the applied field, but at field intensities ~$6\cdot10^3$ V/cm a departure from the quadratic dependence occurs: the increase of the oscillation amplitude abruptly slows down, and at fields ~$3\cdot10^3$ V/cm a dip is observed. At the frequency of the applied field, the amplitude of the oscillations is proportional to that field, but deviations from linearity are also observed at the fields indicated above. In the case of NLC with $\Delta\epsilon < 0$, such deviations at low voltages for the first and second harmonics were not observed (Fig. 3).
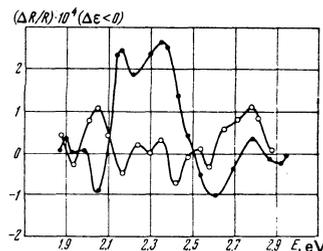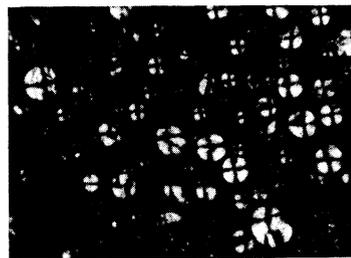
FIG. 6. Spherules that appear under the influence of a constant electric field in a system consisting of a semiconductor and a homotropically oriented NLC with positive dielectric anisotropy.

Figure 7 shows the amplitude-frequency characteristic of the electroreflection for a NLC with $\Delta\epsilon>0$. In contrast to NLC with $\Delta\epsilon < 0$, the oscillation amplitude decreases abruptly with increase of the frequency from 20 to 500 Hz; with further increase of the frequency to 20 kHz, the change of amplitude occurs more slowly. When $\Delta\epsilon < 0$, the decrease of the amplitude to zero occurs in the interval from 100 to 300 Hz. A parallel investigation of light transmission for a polarizer—liquid crystal—analyzer system showed agreement of the frequency dependences of the electroreflection and of the transmission. From analysis of this result, it could be supposed that the reflection at frequencies above 300–500 Hz is due to a change of the degree of ordering S of the molecules, caused by the external electric field.

We shall discuss the results of investigation of the electroreflection of a semiconductor—NLC system as a function of temperature. The results are shown in Fig. 8. In the case of NLC with $\Delta\epsilon > 0$, with increase of temperature the oscillation amplitude of the electroreflection increases up to the temperature of the phase transition. There then occurs an abrupt decrease of the amplitude, in accordance with the degree of transition of the liquid crystal to the isotropic phase. For NLC with $\Delta\epsilon < 0$, no significant change of the oscillation amplitude occurs on increase of temperature: a slight increase is observed, and at the phase-transition temperature the oscillation amplitude decreases to zero. Such different behavior of the electroreflection for different signs of $\Delta\epsilon$ apparently indicates that in the phase-transition region, the electroreflection mechanisms are different in these cases: when $\Delta\epsilon > 0$, the increase of amplitude is due to a change of the degree of ordering S, and the maximum change of S, at the phase transition, coincides with the maximum amplitude of oscillation; when $\Delta\epsilon < 0$, the principal contribution to the electrore-

FIG. 5. Electroreflection spectra of germanium on application of a pulsed field to the liquid crystal (●) and to an electrolyte (○); 300 K, $\Delta\epsilon < 0$.
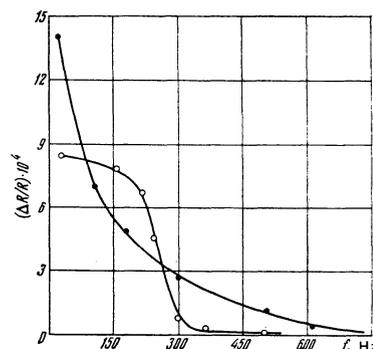
FIG. 7. Amplitude-frequency characteristic of electroreflection for NLC with $\Delta\epsilon > 0$ (●) and with $\Delta\epsilon < 0$ (○); $\lambda = 580$ nm.
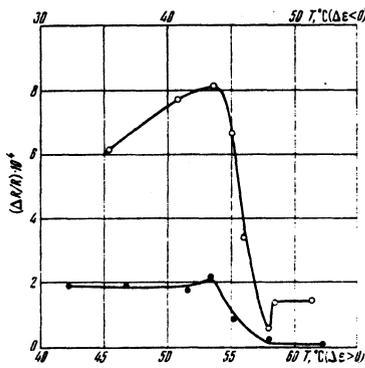
FIG. 8. Temperature variation of oscillation amplitude for NLC with $\Delta\epsilon > 0$ (●) and with $\Delta\epsilon < 0$ (○).

flection process is made by deformational phenomena, and therefore the intensity of the electroreflection depends little on the temperature over the temperature range in which the given NLC exists. The insignificant increase up to the phase-transition temperature is obviously due to the insignificant change of the degree of ordering S and correspondingly of $\mu(z)$. A slight manifestation of the electroreflection effect is observed in the isotropic phase, but in the vicinity of the phase transition: $\Delta T \sim 10$–20 °C. This is apparently due to the existence of NLC nuclei with polar structure.

The conclusion that there is a contribution to the electroreflection from a mechanism connected with the degree of ordering of the molecules is supported by measurements in low-frequency pulsed fields, with pulse duration about 15 μsec. Electroreflection was observed in this case, and its intensity was quite high. In measurement in fields with a longer pulse duration, ~20 μsec, an increase of the electroreflection was found for pulses of negative polarity with respect to the semiconductor. This is apparently due to orientation of the dipole moments in CPEHBA with the negative end toward the semiconductor. We note that in the regime of electrohydrodynamic instability in NLC, both with $\Delta\epsilon < 0$ and with $\Delta > 0$, the electroreflection spectra are smeared out, and at higher voltages they disappear.

THEORETICAL ANALYSIS OF THE ELECTRO-REFLECTION EFFECT, WITHIN THE FRAMEWORK OF THE BIPOLAR MODEL OF A HOMOTROPICALLY ORIENTED LIQUID-CRYSTAL LAYER

As was pointed out above, the calculation of the electroreflection spectra reduces to the determination of the angle of rotation of the director by the electric field. This problem can be solved within the framework of linear NLC mechanics.[7] But the formulation of the problem is different for NLC with $\Delta\epsilon < 0$ and with $\Delta\epsilon > 0$. The difference is as follows. First, in NLC with $\Delta\epsilon < 0$ it is necessary to take into account the occurrence of the Frederiks effect, which manifests itself in a reorientation of the molecules at fields above a certain critical value and begins at the middle of the specimen. Therefore the problem of calculating the motion of the director is one-dimensional. At fields below the critical, $U < U_0$, and also in NLC with $\Delta\epsilon > 0$, this problem is three-dimensional, since because of the cylindrical symmetry of the NLC, reorientation of the molecules is possible in various directions with retention of the cylindrical symmetry.

We consider the first case: the electroreflection ef-

fect in NLC with $\Delta\epsilon < 0$ and above the Frederiks threshold. In the solution of the problem, we shall consider the liquid crystal incompressible and shall neglect dissipation of energy. Then the system of equations that described the motion of the centers of inertia and of the continuum of directions of the molecules has the form

$$\rho \frac{\partial v_i}{\partial t} = \frac{\partial \sigma_{ik}}{\partial x_k} + \rho f_i, \tag{5}$$

$$\frac{\partial \mu_{ik}}{\partial x_k} - \sigma_{nm}\varepsilon_{imn} + \rho m_i = 0, \quad \text{div } v = 0, \tag{6}$$

where

$$\sigma_{(ik)}^- = a_1\dot{e}_{ik} + \tfrac{1}{2}(\dot{e}_{in}L_nL_k + \dot{e}_{nk}L_nL_i) + (a_3L_iL_k + a_4\delta_{ik})L_nL_m\dot{e}_{nm}$$
$$+ (a_4L_iL_k + a_5\delta_{ik})e_{nm} + \tfrac{1}{2}a_6(L_kL_ne_{sin} + L_iL_ne_{skn})(\tfrac{1}{2}\text{rot } v - \Omega),$$

$$\sigma_{(ik)}^- = \tfrac{1}{6}a_6(\dot{e}_{kn}L_nL_i - \dot{e}_{in}L_nL_k)$$

$$- \tfrac{1}{2}[2a_7\varepsilon_{sik} + a_8(L_kL_ne_{sin} + L_iL_me_{smk})](\tfrac{1}{2}\text{rot } v - \overline{\Omega});$$

$$\mu_{ik}^+ = \mu_{ik}^0 + d_{1212}(r_{ik}^+ - r_{ik} + L_iL_k) + d_{1122}(\delta_{ik} - L_iL_k)r_{nm}^+$$
$$+ d_{1221}(r_{ki}^+ - r_{ks} + L_iL_i) + d_{1313}r_{is}^+ L_iL_k,$$

$$r_{ik}^+ = L_i(\partial L_m/\partial x_k)\varepsilon_{inm}, \quad \varepsilon_{ik} = \dot{e}_{ik} - (\tfrac{1}{2}\text{rot } v - \dot{\Omega})_s \varepsilon_{sik},$$

$$\dot{e}_{ik} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right),$$

$$a_1 = 2\eta_1 - \eta_5, \quad a_2 = 2(\eta_3 - \eta_5 - 2\eta_1) - \eta_4, \quad a_3 = \eta_1 - \eta_2 - \eta_3 + \eta_7 + \eta_8 - 2\eta_6,$$
$$a_4 = \tfrac{1}{2}(2\eta_1 - \eta_2 - \eta_3 + \eta_4 - 2\eta_5 + 2\eta_6 - 2\eta_7),$$
$$a_6 = \eta_2 - \eta_5, \quad a_8 = \eta_4 - 2\eta_5, \quad a_9 = \eta_9, \quad a_{10} = \eta_{10} - \eta_9.$$

Here $\sigma_{(ik)}^-$ and $\sigma_{[ik]}^-$ are the symmetric and antisymmetric parts of the viscoelastic stress tensor, ρ is the density of the mesophase, d_{iklm} is the elastic-constant tensor, L_i is the director $\eta_1, \ldots, \eta_{10}$ are the coefficients of viscosity, and v and Ω are the linear and angular velocities of the mesophase.

With allowance for the geometry of the problem being solved, the equations of motion of the continuum of long axes and of centers on inertia of the molecules take the simpler form:

$$d_{33}\frac{\partial^2 L}{\partial z^2} - \eta_1\frac{\partial L}{\partial t} + \eta_1\frac{\partial v}{\partial z} - L\left[\mu(z)E_0\cos\Omega t + \frac{\Delta\epsilon}{4\pi}E_0^2\cos^2\Omega t\right] = 0, \tag{7}$$

$$\rho\frac{\partial v}{\partial t} - \eta_3\frac{\partial^2 v}{\partial z^2} + \eta_1\frac{\partial^2 L}{\partial z\,\partial t} = 0$$

under the following boundary conditions:

$$L|_{z=\pm 0} = 0, \quad v|_{z=\pm 0} = 0 \quad \text{as} \quad t \to \infty. \tag{8}$$

We shall seek solutions in the form of series:

$$L = \sum_{-\infty}^{\infty} A_m e^{i\cdot 2mpz}, \quad v = \sum_{-\infty}^{\infty} B_m e^{i\cdot 2mpz}. \tag{9}$$

To find the coefficients A_m and B_m, we expand the function $\mu(z)$ as a Fourier series:

$$\mu(z) = \sum_{n=1}^{\infty} c_n \cos 2npz + c_0 ; \tag{10}$$

on substituting (9) in (7), we have

$$-m^2 p^2 d_{13} A_m - \eta_4 \frac{\cdot \, dA_m}{dt} + \eta_1 imp B_m - c_0 A_m E_0 \sin \Omega t$$

$$-\frac{\Delta \varepsilon}{4\pi} E_0^2 \sin \Omega t A_m - E_0 \sin \Omega t \sum_{n=1}^{\infty} c_n (A_{m+n} + A_{m-n}) = 0, \qquad (11)$$

$$\rho \frac{dB_m}{dt} + \eta_3 m^2 p^2 B_m - i\eta_1 mp \frac{dA_m}{dt} = 0. \qquad (12)$$

From (11) and (12), we have the following equation for finding the coefficients A_m:

$$\frac{\eta_4}{m\eta_1} \frac{d^2 A_m}{dt^2} + \left(\frac{d_{13}}{\eta_1} m + c_0 E_0 \sin \Omega t + \frac{\eta_4}{\eta_1 m} - \eta_1 - \frac{\Delta \varepsilon}{4\pi \eta_1} E_0^2 \sin^2 \Omega t \right) \frac{dA_m}{dt}$$

$$- \left(\frac{c_0}{\eta_1} \Omega \cos \Omega t - \frac{\Delta \varepsilon}{4\pi \eta_1} E_0^2 \sin 2\Omega t + \frac{d_{13}}{\eta_1} m + \frac{c_0}{\eta_1} E_0 \sin \Omega t \right.$$

$$\left. + \frac{\Delta \varepsilon}{4\pi \eta_1} E_0^2 \sin \Omega t \right) A_m + \sum_{n=1}^{\infty} \frac{c_n}{\eta_1} E_0 (\sin \Omega t + \Omega \cos \Omega t)(A_{m+n} + A_{m-n})$$

$$+ \sum_{n=1}^{\infty} \frac{c_n}{\eta_1} \frac{d(A_{m+n} + A_{m-n})}{dt} E_0 \sin \Omega t = 0; \qquad (13)$$

since

$$\sum_{n=1}^{\infty} c_n (A_{m+n} + A_{m-n}) = \sum_{n=1}^{\infty} c_{n+m} A_m, \qquad (14)$$

we have, on summing (13) over m,

$$\frac{d^2 A_m}{dt^2} + g_m \frac{dA_m}{dt} + d_m A_m = 0; \qquad (15)$$

$$g_m = \frac{m^2 \eta_1^2}{\eta_4} + \frac{d_{13}}{\eta_4} m^2 + \frac{\eta_1}{\eta_4} c_0 E_0 \sin \Omega t - \frac{\Delta \varepsilon}{4\pi \eta_4} E_0^2 \sin^2 \Omega t$$

$$+ \sum_{n=1}^{\infty} \frac{1}{\eta_4} c_{n+m} E_0 \sin \Omega t,$$

$$d_m = - \frac{c_0}{\eta_4} m\Omega \cos \Omega t - \frac{\Delta \varepsilon}{4\pi \eta_4} mE_0^2 \sin 2\Omega t + \frac{d_{13} m^2}{\eta_4} + \frac{c_0}{\eta_4} m\Omega E_0 \sin \Omega t$$

$$+ \frac{\Delta \varepsilon}{4\pi \eta_4} mE_0^2 \sin^2 \Omega t + \sum_{n=1}^{\infty} \frac{c_{n+m}}{\eta_4} m(\sin \Omega t + \Omega \cos \Omega t).$$

On setting

$$d_m = \rho^2 f_m(t) + l_m(t), \qquad f_m(t) = \frac{m}{4\pi \eta_4} E_0 \sin 2\Omega t + \frac{mE_0^2}{4\pi \eta_4 \Omega} \sin^2 \Omega t,$$

$\rho = (\Delta \varepsilon \omega)^{1/2}$, and $A_m = \exp[\rho \int U_m(t)dt]$, we get

$$\rho U_m' + \rho^2 U_m^2 - \rho^2 f_m - l_m + \rho g_m U_m = 0. \qquad (16)$$

We shall seek a solution of this equation in the form

$$U_m = \begin{cases} \sum_{v=0}^{\infty} U_{mv}(t)\rho^{-v} & \text{for} \quad \rho > 1 \\ \\ \sum_{v=0}^{\infty} U_{mv}(t)\rho^{v} & \text{for} \quad \rho < 1 . \end{cases} \qquad (17)$$

We get the following values for the coefficients U_m:

$$U_0 = -[f(t)]^{1/2} \neq 0, \quad U_1 = -U_0'/2U_0, \quad U_2 = (g - U_1' - U_1^2)/2U_0,$$

$$U_{v+1} = -\frac{1}{2U_0} \left(U_0' + f_m U_v + \sum_{p=1}^{v} U_p U_{v+1-p} \right) \quad \text{for} \quad v \geq 2.$$

The principle of superposition of electric fields enables us to represent (9) in a more obvious form, satisfying the boundary conditions and exactly coinciding with (9) in the interval $[-\sigma/2, \sigma/2]$:

$$L \approx \sum_{m=1}^{\infty} A_m \cos \frac{mpz}{2} . \qquad (18)$$

Then for small $L = L_0 + L_1$ we have from (4)

$$E|_{z=\sigma} = \frac{d\varphi}{dz}$$

$$= \frac{1}{8\pi \varepsilon_0} \int_{-\sigma/2}^{\sigma/2} |\mu(z)| \frac{d}{dz'} \frac{1}{(z-z')^2} \left[1 - \frac{L^2}{2!} + \frac{L^4}{4!} - \ldots \right] dz' = E_0 + E_{10}. \qquad (19)$$

Here E_0 is the field determined by the static deformation of the orientational ordering of the molecules, and E_{10} is a field that varies with time. With allowance for the smallness of the field E_{10}, we get according to (1)–(3)

$$\frac{\Delta R}{R} \approx \alpha(\omega)\Delta \varepsilon_i + \beta(\omega)\Delta \varepsilon_r + \left[\alpha(\omega) \frac{\partial \Delta \varepsilon_i}{\partial E_{10}} + \beta(\omega) \frac{\partial \Delta \varepsilon_r}{\partial E_{10}} \right] E_{10}$$

$$\sim \alpha(\omega)\Delta \varepsilon_i + \beta(\omega)\Delta \varepsilon_r + \left[\alpha(\omega) \frac{\partial \Delta \varepsilon_i}{\partial E} + \beta(\omega) \frac{\partial \Delta \varepsilon_r}{\partial E} \right]$$

$$\times (M_1 \cos \Omega t + M_2 \cos 2\Omega t + M_3 \cos 3\Omega t + \ldots), \qquad (20)$$

where $M_1, \ldots, M_n, \ldots$ are the corresponding integrals (19).

Thus the reflected signal contains various harmonics of the signal acting on the liquid crystal. The intensity of the harmonics depends to a significant degree on the frequency Ω of the field and on the dielectric anisotropy $\Delta \varepsilon$. In agreement with experiment, it follows from (10), (17), and (20) that with increase of the value of the dielectric anisotropy the higher harmonics decrease, but the second harmonic is always more intense than the others. On the other hand, increase of the frequency leads to decrease of the intensity of the harmonics to zero.

We consider electroreflection in a NLC system with $\Delta \varepsilon < 0$ (when $U < U_0$) and $\Delta \varepsilon > 0$. The equation of state of mesophase for this case will have the form

$$(d_{1122} + d_{1221}) \frac{\partial}{\partial y} \left(\frac{\partial L_x}{\partial y} - \frac{\partial L_y}{\partial x} \right) + d_{1212} \Delta L_x + d_{1313} \frac{\partial^2 L_x}{\partial z^2}$$

$$+ \frac{1}{2}(\eta_3 + \eta_4 - \eta_2) \frac{\partial v_x}{\partial z} + (\eta_3 - \eta_2) \frac{\partial L_x}{\partial t} + aL_y = 0,$$

$$-(d_{1122} + d_{1221}) \frac{\partial}{\partial x} \left(\frac{\partial L_x}{\partial y} - \frac{\partial L_y}{\partial x} \right) + d_{1212} \Delta L_x + d_{1313} \frac{\partial^2 L_y}{\partial z^2}$$

$$+ \frac{1}{2}(\eta_3 + \eta_4 - \eta_2) \frac{\partial v_y}{\partial z} + (\eta_3 - \eta_2) \frac{\partial L_x}{\partial t} + aL_x = 0; \qquad (21)$$

$$\rho \frac{dv_x}{dt} = \eta_1 \Delta v_x + \eta_7 \frac{\partial}{\partial x} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right)$$

$$+ \frac{\partial}{\partial z} \left[\eta_3 \frac{\partial v_x}{\partial z} + \frac{1}{2}(\eta_3 + \eta_4 - \eta_2) \frac{dL_x}{dt} \right],$$

$$\rho \frac{dv_y}{dt} = \eta_1 \Delta v_y + \eta_7 \frac{\partial}{\partial y} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right)$$

$$+ \frac{\partial}{\partial z} \left[\eta_3 \frac{\partial v_x}{\partial z} + \frac{1}{2}(\eta_3 + \eta_4 - \eta_2) \frac{dL_y}{dt} \right], \qquad (22)$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}, \qquad a = \mu(z)E_0^2 \cos \Omega t + \frac{\Delta \varepsilon}{4\pi} E_0^2 \cos^2 \Omega t.$$

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On multiplying the equation for the y component by i and summing the equations for the x and y components of the director and of the velocity, we have

$$-(d_{1122}+d_{1221})\frac{\partial^2 \hat{L}}{\partial x\,\partial y}+(d_{1122}+d_{1221}+d_{1212})\frac{\partial^2 \hat{L}}{\partial x^2}+d_{1212}\frac{\partial^2 \hat{L}}{\partial y^2}$$

$$+d_{1313}\frac{\partial^2 \hat{L}}{\partial z^2}+\frac{1}{2}(\eta_3+\eta_4-\eta_2)\frac{\partial v}{\partial z}+(\eta_3-\eta_2)\frac{\partial \hat{L}}{\partial t}+aL=0,$$

$$\rho\frac{dv}{dt}=\eta_1\Delta\hat{v}+\eta_1\frac{\partial}{\partial x}\left(\frac{\partial\hat{v}}{\partial x}+\frac{\partial\hat{v}}{\partial y}\right)$$

$$+\frac{\partial}{\partial z}\left[\eta_3\frac{\partial v}{\partial z}+\frac{1}{2}(\eta_3+\eta_4-\eta_2)\frac{dL}{dt}\right], \tag{23}$$

$$L=L_x+iL_y,\quad \hat{v}=v_x+iv_y.$$

Hence

$$L\sim\exp[i(k_x x+k_y y)], \tag{24}$$

where k_x and k_y are the respective wave vectors of the spherule structure.

The further solution of (23) is analogous to the one-dimensional problem; therefore we shall not discuss it. It follows from (24) that in a NLC with $\Delta\epsilon>0$, or with $\Delta\epsilon<0$ and $U<U_0$, the electroreflection is different at different points of the semiconductor surface and depends on the coordinates in the following manner: $\Delta R/R \sim \exp\times[i(k_x x+k_y y)]$. Otherwise the character of the electroreflection is the same as in the one-dimensional problem.

One can suppose that all the electroreflection phenomena described are due to the presence of an electric double layer on the liquid crystal–semiconductor boundary, and may liken the liquid crystal itself to a weak electrolyte. But in observation of longitudinally oriented layers (from which homotropically oriented layers were subsequently obtained) and of an isotropic melt outside the phase-transition region, electroreflection spectra could not be observed, although the presence of a double layer does not exclude this. But because of the small impedance of the Helmohltz layer in comparison with the liquid crystal, the voltage drop across it is small. Also small, apparently, is the contribution to the electroreflection from the NLC-semiconductor contact difference of potentials, a contribution that is determined by the position of the Fermi level in the NLC and that changes in the presence of reorientation of the molecules by the electric field at the semiconductor-NLC surface; but investigation of the effect of a field by the BTIR method showed absence of such reorientation near a germanium surface in fields up to 10^4 V/cm.

Thus the reported experimental and theoretical investigations of the electroreflection effect in a semiconductor-NLC system support the polar-structure model of a NLC with homotropic orientation of the molecules. The spontaneous homotropic orientation is apparently due to occurrence of a polar structure, as a result of which the total energy of the thin film of NLC decreases by the amount

$$\frac{\epsilon_\parallel}{4\pi}\int_V E_{in}^2\,dV,$$

where E_{in} is the internal field, and where V is the volume occupied by the NLC; that is, this state of the system is energetically more advantageous. On the other hand, from the results of the reported investigations there follows a possibility of applying liquid crystals to the purposes of modulation spectroscopy; the proposed HOLC (homotropically oriented liquid crystals) method is not inferior and in some cases is apparently superior to a number of known methods. The merits of this method include the possibility of observing electroreflection at various harmonics, the large magnitude of the signal, simple preparation of the crystal, a high degree of reproducibility of the experimental results, and absence of etching of the specimen (this is expecially valuable in investigation of thin films).

With respect to the quantity of singularities, the electroreflection spectrum with application of liquid crystals does not fall short of the electrolytic method, but even has additional oscillations, which (Fig. 2) gradually attentuate and are apparently due to Airy oscillations. These singularities are not due to the character of electro-optical phenomena in liquid crystals, since the latter lead only to a shift of the general level of the signal and, in the regime of electrohydrodynamic instability of the NLC, to their disappearance. At the same time, the change of the transmission spectra of a liquid crystal placed in an electric field showed absence of any modulation singularities of the spectrum.

In conclusion, we note that in principle the effect considered above, which appears to be inherently electroreflection, can be caused by a magnetic field, mechanical shear, or periodic heating of the liquid crystal.

[1)]Additional investigations of about 50 different NLC showed that spontaneous homotropic orientation is characteristic of NLC with asymmetric molecules.

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