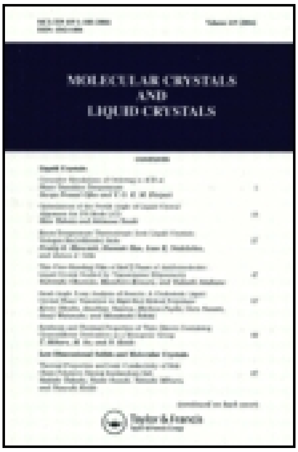

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Surface Polarization: Possible Sources and Main Characteristics

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SURFACE POLARIZATION: POSSIBLE SOURCES AND MAIN CHARACTERISTICS

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Abstract The experimental investigation of surface polarization by modulation spectroscopy of electro-reflection from the nematic liquid crystal-semiconductor interface and capacitance modulation spectroscopy of direct piezoeffect in nematics has been carried out. The models of surface polarization with induced polar order parameter have been suggested.

Keywords: surface polarization, polar order parameter, electro-reflection, nematic liquid crystals, modulation spectroscopy

INTRODUCTION

It is well known that in the close vicinity of interfaces the structure and properties of a nematic liquid crystal (NLC) differ considerably from the bulk ones. In particular, near the boundary surface a polar layer may appear. Note, that, in general, two different sources of surface polarization seem to exist. The first one is the symmetry breaking of NLC near the boundary: if the two ends of NLC molecules have a different chemical affinity with the boundary, a surface polar order parameter exists and hence $P_s \neq 0$ is expected[1-4]. Furthermore, the surface polarization may be caused by the difference between the surface-induced scalar order parameter and the bulk one ; this leads to the so-called order-electric polarization[5,6]. The second reason is the selective ions adsorption[7,8] : if the adsorption energy of the boundary for the positive ions, for instance, is lower than for the negative ones, then the positive ions will migrate on the surface and give rise to a surface field E_s. This is equivalent to the surface polarization, normal to the boundary.

The surface polar layer was detected in experiments on the electro-reflection of light from the NLC-semiconductor interface[9-11], the direct piezoelectric effect in NLC[12,13] and the optical second harmonic generation at the NLC-glass interface[14].

ELECTRO-REFLECTION MEASUREMENTS

We consider the results of investigation of the molecular ordering in thin surface NLC-layers by the electro-reflection technique. When putting in contact the NLC and the semiconductor, under an applied a.c. electric field the variation of molecular orientation induces the changes of the surface states of the semiconductor and its optical properties in the region of the interband peculiarities. These changes may be detected using high-sensitivity modulation spectroscopy. The experimental details have been described previously[9-11]. Our experiments were performed with the semiconductor of n-type Ge in the region of well known doublet E_1, $E_1+\Delta_1$ near the fundamental absorption edge (2.1-2.35 eV)[15]. We have used NLC MBBA (p-methoxybenzylidene-p-n-butylaniline), BHAOB (n-butyl-n-heptanoilazoxybenzene) with $\varepsilon_a<0$ and OCB (octyl-cyano-biphenyl), HBACPE (n-heptylbenzonoic acid n-cyanophenyl ester), NPOOB (4-nitrophenyl-4-n- octyloxybenzoate) with $\varepsilon_a>0$. All NLC used show a spontaneous homeotropic orientation at the Ge-substrate, that was controlled by polarized microscope. The experimental set-up and the sandwich cell constructions for the different ways of generating of electro-reflection (electro, thermo, magneto, piezomodulation) are shown at Fig.1. The NLC have been inserted between Ge and upper glass plates separated by mylar spacers. The NLC layer thickness was 15 μm and a.c. voltage for electro-reflection modulation was $U\leqslant 4.5$V of frequency f=79Hz. Directly measured magnitude of electro-reflection $\Delta R/R$ was registered on the modulation frequency f and on the double frequency 2f in the range of modulation singularities of Ge E_1, $E_1+\Delta_1$. In according to Franz-Keldysh effect, $\Delta R/R$ must be proportional to E_s^2, where E_s is an electric field on the surface of semiconductor[15].

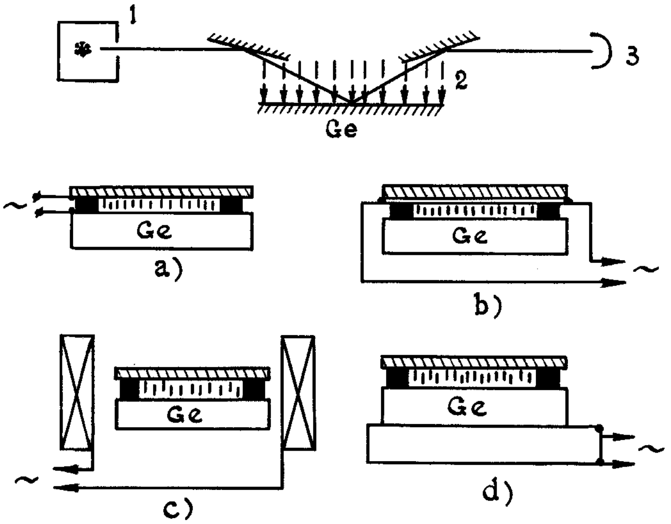

FIGURE 1. The experimental set-up: 1-monochromator; 2-NLC cell; 3-photodiode. a), b), c), d) - cell constructions.

We have detected the existence at the same time of the first and the second harmonics of ΔR/R, that seems to be connected with a non-symmetrical variation of the surface field under alternative external modulation. Experimental dependencies of electro-reflection amplitude vs applied a.c. voltage are given at Fig.2.

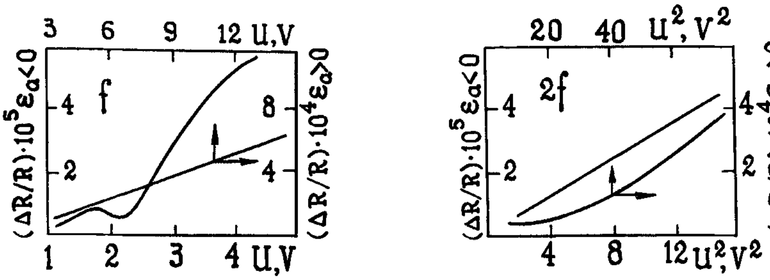

FIGURE 2. The dependencies of electro-reflection amplitude vs applied a.c. voltage.

From the data $\Delta R/R = kE_s^2$, where k depends only on Ge properties and has been determined in modulation spectroscopy experiments using electrolyte method[15], the magnitudes of effective electric field E_s in the NLC layer near the boundary has been obtained for various NLC. To estimate the effective thickness of polar layer δ, the electro-reflection measurements were made with the different thickness h of dielectric interlayer on the semiconductor surface. This interlayer is to depress the influence of NLC surface polar layer field on the semiconductor. Ge was covered by GeO_2 dielectric film with controlled thickness h. Results of the experiment are shown in Fig.3. $U_\delta = E_s \delta$ and δ calculated from the obtained data are given in Table 1, where the permanent dipole moments of NLC molecules are also given.

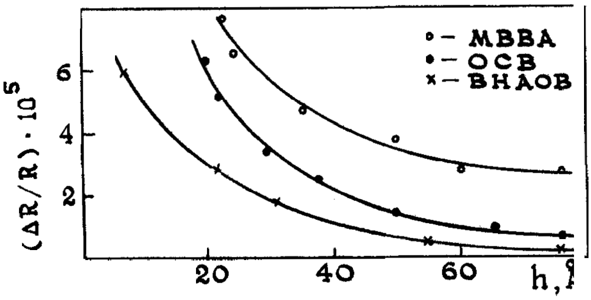

FIGURE 3.

Table 1 Some physical parameters for NLC studied.

NLC	μ (D)	U_δ (V)	δ (A)
MBBA	1.5	0.55	300
BHAOB	3.1	0.30	60
HBACPE	2.2	0.55	30
OCB	4.9	0.80	160
NPOOB	4.1	0.45	40

PIEZOELECTRIC RESPONSE MEASUREMENTS

The polar layer parameters and their temperature behavior were studied by use of the capacitance modulation spectroscopy. Namely, the electrical response of NLC layer under the periodic acoustic bend or shear perturbation of one boundary was detected (Fig.4). In these experiments the NLC cell with glass substrates covered by conducting Cr film was used. An electro-dynamical modulator allows to generate the oscillations of thin (100 μm) glass substrate in the range 20-20000 Hz with controlled amplitude. In the case of bend deformation on both the glass plates of NLC cell the spontaneous homeotropic orientation takes place. The planar orientation of NLC in the shear deformation measurements has been obtained by rubbing of glass substrates. The first ($U_{1\omega}$) and the second ($U_{2\omega}$) harmonics of the electrical response were measured. $U_{2\omega}$ is independent on the thickness of NLC layer d.

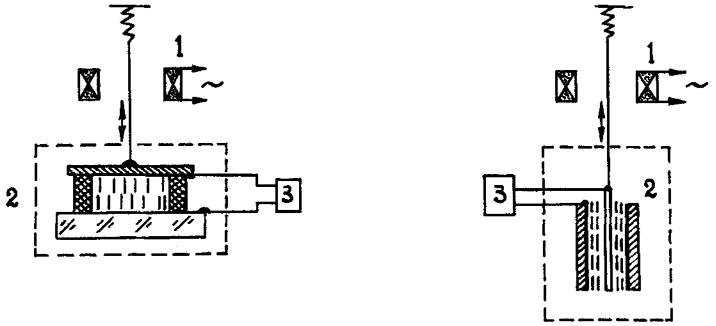

FIGURE 4. The experimental set-up: 1-electrodynamical modulator; 2-NLC cell in the oven; 3-selective amplifier.

It follows that $U_{2\omega}$ formation is caused by the surface instabilities in NLC in the close vicinity of the perturbing substrate. It has been established, that the piezoelectric response of NLC strongly depends on the electric field (Fig.5). When the applied d.c. voltage increases, $U_{2\omega}$ grows up markedly for NLC both with $\varepsilon_a<0$ and $\varepsilon_a>0$. It is connected with the gain in molecular orientational polarization which is induced by the surface polar layer.

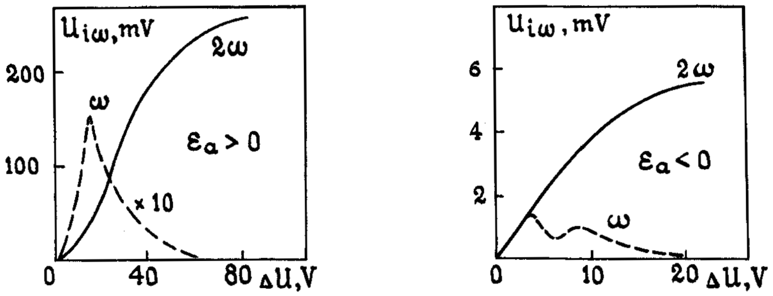

FIGURE 5. The dependencies of $U_{1\omega}$ and $U_{2\omega}$ vs applied d.c. voltage.

The temperature dependencies of $U_{1\omega}$, $U_{2\omega}$ have attracted more interest. The alternating voltage $U_{2\omega}$ is a result of the orientational disturbance of the polar layer[12]:

$$U_{2\omega} \simeq \int_0^d P(z,t)dz \simeq P_s\delta\langle\theta_s^2\rangle \mathrm{Cos}2\omega t ,$$

where $\langle\theta_s^2\rangle$ is an average square of director declination angle near the oscillating substrate. $U_{2\omega}(T)$ and the data on the temperature behavior of the $\langle\theta_s^2\rangle$ [13] allow to calculate the voltage step on the surface polar layer $U_\delta = P_s\delta$ (Fig.6). These data are in a good agreement with the results of electro-reflection measurements (Table 1).

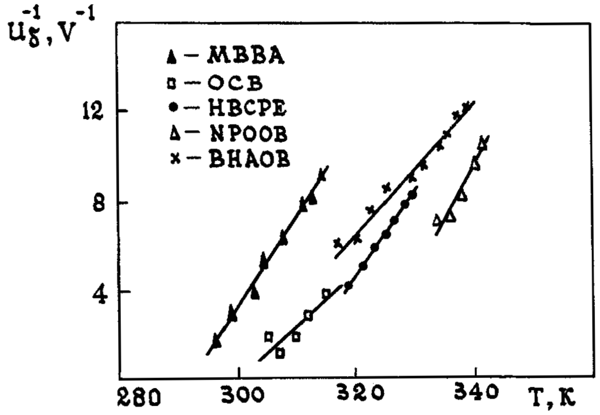

FIGURE 6. The temperature dependencies of the inverse voltage across the surface polarization layer.

MODELS OF SURFACE POLARIZATION AND DISCUSSION

When NLC molecules have a permanent dipole $\mu \simeq 3-6D$, the dipole-dipole interaction compares with the dispersion one, and should be taken into account in investigations of polar properties of NLC[16,17]. Now, we consider the model of a polar layer near the boundary of NLC in the mean field approximation. Except the scalar order parameter $S_2=\langle P_2(\mathrm{Cos}\theta)\rangle$, we introduce the polar ordering parameter $S_1=\langle P_1(\mathrm{Cos}\theta)\rangle$, where $P_n(.)$ denotes the Legendre polynomials; θ is the angle between the direction of ordering and orientation of the long molecular axis ; $\langle . \rangle$ denotes thermodynamical average. Let the plane layer of NLC with homeotropic orientation have the interface with the solid substrate at $z=0$ (OZ axis is normal to the boundary surface). Let us imagine, that in the first approximation S_2 is independent from z and $S_1(z)$ is a smooth function of z. Then, expanding $S_1(z)$ in series up to second order, one has for the interaction energy[12] :

$$U(\theta,z)=-[K_1S_1+K_3d^2S_1/dz^2]P_1(\mathrm{Cos}\theta)-K_2S_2P_2(\mathrm{Cos}\theta), \qquad (1)$$

where the constant in the Maier-Saupe energy is equal $K_2=4.48k_BT_c$ [18] ; $K_1=4/3\pi N\mu^2 \simeq k_BT_c$; $K_3 \simeq 5R^2K_1$; $R \simeq 20-40A$ is an average length of a dipole-dipole interaction. The self-consistent equations can be written as :

$$S_1=I^{-1}\int_{-1}^{1}P_1(\mathrm{Cos}\theta)\exp[-U/k_BT]d(\mathrm{Cos}\theta),$$

$$S_2=I^{-1}\int_{-1}^{1}P_2(\mathrm{Cos}\theta)\exp[-U/k_BT]d(\mathrm{Cos}\theta), \qquad (2)$$

$$I=\int_{-1}^{1}\exp[-U/k_BT]d(\mathrm{Cos}\theta),$$

where the interaction energy is given by eq.(1). From the numerical calculations of (2), approximate solution has been found :

$$K_1S_1+K_3d^2S_1/dz^2=\alpha TS_1,$$

$$S_1(z)=S_1^0\exp[-\lambda z], \quad \lambda=[K_3/(\alpha T-K_1)]^{1/2}, \qquad (3)$$

where coefficient α is calculated from the self-consistently (2); S_1^o is the polar order parameter at the substrate. The temperature dependence of $S_1(z)$ is shown at Fig.7.

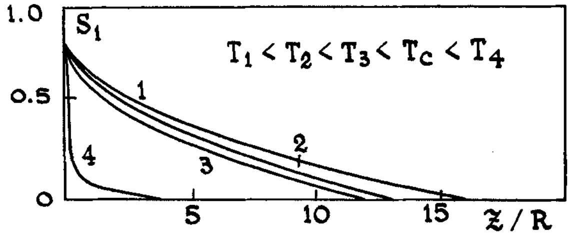

FIGURE 7. $S_1(z)$ dependencies for different temperatures.

The surface polar layer thickness is $\delta=\lambda^{-1}\simeq5-10R$ and, consequently, for $S_1^o\neq0$ the nematic ordering provides a polar layer near the boundary with a thickness of $\delta\simeq200-300A$. This value depends on the parameters of interaction energy (1) and may differ for various NLC. After the NLC-isotropic liquid phase transition the thickness of the polar layer decreases sharply over a distance $\delta\simeq R$. One restriction of this model is the absence of connection between the surface polar order parameter S_1^o and characteristics of NLC-substrate interaction potential. As a consequence, we can not conclude over the temperature dependencies of S_1^o and δ.

Next, we consider the model of surface polarization in the framework of Landau-de Gennes theory[18]. Taking into account the interaction of constant dipole moments of LC molecules with each other and coordinate dependence of $S_1(z)$, the total free energy of NLC layer per unit area can be written as

$$F = \int_0^d [\phi(S_2)+\tfrac{1}{2}aS_1^2+\tfrac{1}{2}g(dS_1/dz)^2]dz + f(S_1^o) , \qquad (4)$$

$$\phi(S_2) = \tfrac{1}{2}AS_2^2 - \tfrac{1}{3}BS_2^3 + \tfrac{1}{4}CS_2^4 ,$$

where $\phi(S_2)$ corresponds to the free energy density in

Landau-de Gennes nematic model; $A=A_o(T-T_*)$; $a=a_o(T-T_o)$; $A_o>0$; $a_o>0$; $g>0$; $B>0$; $C>0$ and the term $f(S_1^o)$ characterizes the interaction of NLC with the substrate. Minimizing (4) with respect to S_1 and S_2 we obtain for the nematic phase at the range $T_o<T<T_c$:

$$S_1(z) = S_1^o \exp[-(a/g)^{1/2}z] , \qquad (5)$$

$$S_2=(B/2C)[1+(1- 4AC/B^2)^{1/2}] ,$$

where $T_c=T_*+B^2/4A_oC$ is the NLC-isotropic liquid transition temperature. Then, for the total free energy we shall have

$$F = \int_{S_1^o}^{o} (ag)^{1/2}S_1dS_1+f(S_1^o) = \frac{1}{2}(ag)^{1/2}(S_1^o)^2+f(S_1^o) ,$$

where in eq.(4) we neglect the term $\phi(S_2)$ which is independent on S_1 and S_1^o. It is reasonable to suggest that the surface interaction energy $f(S_1^o)$ is $f=-kS_1^o$, where $k>0$ characterizes the interaction between the substrate and dipole moment of LC molecules. The equilibrium value of S_1^o is determined from the condition $dF/dS_1^o=0$:

$$S_1^o= k/(ag)^{1/2}= k/[a_og(T-T_o)]^{1/2} . \qquad (6)$$

From eq.(5) the temperature dependence of the effective thickness of the polar layer δ may be found

$$\delta = (g/a)^{1/2}= [g/a_o(T-T_o)]^{1/2} . \qquad (7)$$

By using eqs.(6),(7) we obtain the temperature dependence of the voltage across the surface polarization layer U_δ , which is measured experimentally :

$$U_\delta = P_s\delta \simeq S_1^o\delta = k/a_o(T-T_o) .$$

Thus, models based on the existence of surface polar layer in NLC can explain the results of the electro-reflection and piezoelectric response measurements discussed above.

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