lar spin configurations, $\theta<\pi/2$, at low temperatures, as well as the different slopes of $H_r^c(T)$ and $H_r^a(T)$, are connected with the large magnitudes of the second- and fourth-order anisotropy constants measured by us and the strong dependence of these constants on temperature.

In conclusion, we consider it our pleasant duty to express our thanks to A. K. Gapeev for carrying out the x-ray spectral analysis of the compositions of the investigated samples and to A. K. Zvezdin and V. M. Matveev for fruitful discussions.

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Threshold piezoelectric instability in a liquid crystal

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The threshold characteristics of a new type of piezoelectric instability in a finite-thickness nematic layer are calculated as a function of the frequency of the applied electric field.

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1. As is well known,[1] a peculiar piezoelectric effect exists in nematic liquid crystals, caused by the linear coupling between the electric polarization and the orientation of the strains of the mesophase. The corresponding contribution to the free energy of a liquid crystal, placed in an external electric field **E**, can be expressed in the following form by starting out with the symmetry properties of the mesophase in the following manner:

$$\delta\mathcal{F}=-\int[e_1(\mathbf{En})\,\mathrm{div}\,\mathbf{n}+e_2\mathbf{E}(\mathbf{n}\nabla)\mathbf{n}]\,d^3\mathbf{r}, \tag{1}$$

where **n** is the "director" of the liquid crystal, and e_1 and e_2 are the piezomoduli. By minimizing the total free energy $\mathcal{F}=\mathcal{F}_0+\delta\mathcal{F}$, where

$$\mathcal{F}_0=\frac{1}{2}\int\left[K_{11}(\mathrm{div}\,\mathbf{n})^2+K_{22}(\mathbf{n}\,\mathrm{rot}\,\mathbf{n})^2+K_{33}[\mathbf{n}\,\mathrm{rot}\,\mathbf{n}]^2-\frac{\varepsilon_a}{4\pi}(\mathbf{En})^2\right]d^3\mathbf{r}, \tag{2}$$

K_{jj} are the elastic moduli, and ε_a is the dielectric anisotropy, Meyer has shown that a periodic distribution $\mathbf{n}(\mathbf{r})$ is produced in an unbounded liquid crystal by an electric field. Here, if the director **n** in the unperturbed state is parallel to the x axis and the field **E** is directed along the z axis (Fig. 1), the angle of inclination θ of the director **n** to the x axis in the xz plane is given by the expression[1]

$$\theta=e_1Ex/K_{11} \tag{3}$$

at $e_2=-e_1$, $K_{11}=K_{33}$, and $\varepsilon_a=0$. We note that in the given case the effect is not a threshold one and that the angle θ changes by an amount π at a distance $x_0=\pi K_{11}/e_1E$, i.e., a domain picture periodic along the x axis and parallel to the y axis should appear. This effect was generalized in the work of Dmitriev[2] to the case of finite values of the dielectric anisotropy ε_a. In particular, it was shown that this type of instability can take place only upon satisfaction of the following inequality:

$$|\varepsilon_a|<e_1^2\pi^3/K_{11}. \tag{4}$$

We note that the absence of a threshold in the effect considered above is connected with the unboundedness of the medium. In the liquid-crystal layer of finite thickness, the role of the boundary conditions at the solid surfaces is decisive, and generally such a piezoeffect should have a threshold character. The distribution (3)

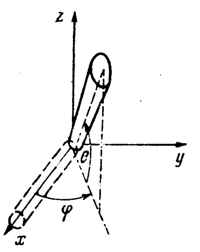

FIG. 1. Perturbations of the molecular orientation.

is characterized by a large amplitude of the inclination of the director, which, at a finite layer thickness, will lead to the appearance of declinations; thus, the formation threshold of such a structure must obviously be quite large. Such an instability has not been observed experimentally at the present time.

2. In the present article it is shown that the piezoelectric coupling between the field and the orientation strains can cause an instability of a different type. The new instability, which arises in a nematic layer of finite thickness at some threshold stress is characterized by small deviations of the director from the x axis in two planes: at the angle θ in the xz plane and at the angle φ in the xy plane (Fig. 1). Here a periodic picture of domains parallel to the x axis is formed along the y axis. We emphasize that the boundary conditions in the given problem are taken into account exactly. We consider the case of small strains of the layer $|\varphi|$, $|\theta| \ll 1$. In this case, we have $n_x \approx 1$, $n_y \approx \varphi$, $n_z \approx \theta$, $E_x = 0$, $E_y = 0$, $E_z = E$, $\varphi = \varphi(y, z)$, $\theta = \theta(y, z)$. By minimizing the quantity $\mathscr{F} = \mathscr{F}_0 + \delta\mathscr{F}$ with respect to φ and θ, where for simplicity, the elastic moduli are set equal: $K_{11} = K_{22} = K$, we obtain the equations for the stationary orientation structure of the liquid crystal:

$$\begin{gathered}\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2}-\frac{e^*E}{K}\frac{\partial\theta}{\partial y}=0,\\ \frac{\partial^2\theta}{\partial y^2}+\frac{\partial^2\theta}{\partial z^2}+\frac{e^*E}{K}\frac{\partial\varphi}{\partial y}+\frac{\varepsilon_a E^2}{4\pi K}\theta=0,\end{gathered} \tag{5}$$

where $e^* = e_1 - e_2$. Taking into account the boundary conditions $\varphi = \theta = 0$ at $z = \pm d/2$, where d is the thickness of the layer, we find the solutions of Eqs. (5) in the form

$$\theta=\theta_0\cos(qy)\cos(\pi z/d),\quad \varphi=\varphi_0\sin(qy)\cos(\pi z/d). \tag{6}$$

Substituting (6) in (5), we obtain (from the requirement of nontriviality of the quantities θ_0 and φ_0) the dispersion equation that connects the field intensity E with the wave number q, and is of the form

$$E^2=\left(\frac{K}{e^*}\right)^2\frac{[q^2+(\pi/d)^2]^2}{q^2+\mu[q^2+(\pi/d)^2]}, \tag{7}$$

where $\mu = (\varepsilon_a K/4\pi e^{*2})$. The threshold of the occurrence of the considered instability is determined by the minimum $E = E_c$ at $q = q_c$ on the curve $E(q)$, described by Eq. (7). Minimizing $E(q)$, we get

$$E_c=\frac{2\pi K}{|e^*|(1+\mu)d},\quad q_c=\frac{\pi}{d}\sqrt{\frac{1-\mu}{1+\mu}}. \tag{8}$$

It is seen from (8) that the instability can arise only if the condition $|\mu| < 1$ is satisfied or

$$|\varepsilon_a|<4\pi e^{*2}/K, \tag{9}$$

which is similar to the condition (4). Setting $\varepsilon_a = 0$, $K \sim 10^{-6}$ dyn, $|e^*| \sim 10^{-4}$ esu,[3] we get the estimate for $V_c = E_c d \sim 20$ V.

3. A similar piezoelectric instability exists both at constant and at alternating fields. In the latter case, the threshold field E_c depends on the frequency of the field ω. In the approximation considered, starting with the general equation of motion of the director,[3] we can easily obtain equations for the functions (6) with nonstationary amplitudes $\theta_0(t)$ and $\varphi_0(t)$:

$$\frac{\partial\varphi_0}{\partial t}+A\varphi_0=B\theta_0,\quad \frac{\partial\theta_0}{\partial t}+(A+\delta A)\theta_0=B\varphi_0, \tag{10}$$

where

$$A=\frac{K}{\gamma_1}\left[q^2+\left(\frac{\pi}{d}\right)^2\right],\quad \delta A=-\frac{\varepsilon_a E^2(t)}{4\pi\gamma_1},\quad B=\frac{e^*E(t)q}{\gamma_1},$$

$\gamma_1 = \alpha_3 - \alpha_2$ is the coefficient of shear viscosity.

It is simplest to analyze the frequency dependence of the threshold for the formation of piezoelectric domains in the case of a meandering external periodic field of the form:

$$E(t)=\begin{cases}E, & t_0\le t<t_0+T/2,\\ -E, & t_0+T/2\le t<t_0+T,\end{cases}$$

where $T = 2\pi/\omega$. Correspondingly, in the right side of Eqs. (10), the quantity B changes sign at every half period. It is then seen that periodic solutions $\theta_0(t)$ or $\varphi_0(t)$ exist in the set of Eqs. (10), changing sign with each half period:

$$\theta_0(t+T/2)=\theta_0(t),\quad \varphi_0(t+T/2)=-\varphi_0(t), \tag{11a}$$

$$\theta_0(t+T/2)=-\theta_0(t),\quad \varphi_0(t+T/2)=\varphi_0(t). \tag{11b}$$

Estimating the solutions $\theta_0(t)$ and $\varphi_0(t)$ in the form

$$\theta_0(t)=c_1e^{\lambda_1 t}+c_2e^{\lambda_2 t},\quad \varphi_0(t)=c_3e^{\lambda_1 t}+c_4e^{\lambda_2 t}, \tag{12}$$

where the solutions of the characteristic equation (λ_1, λ_2) are given by the expressions

$$\lambda_{1,2}=-A-{}^1/_2\delta A\pm[{}^1/_4(\delta A)^2+B^2]^{1/2}, \tag{13}$$

and substituting (12) in (11), we obtain the following dispersion equations, which determine the dependence $E(q)$:

$$(\lambda_1+A)\,\mathrm{th}\left(\frac{\lambda_1T}{4}\right)=(\lambda_2+A)\,\mathrm{th}\left(\frac{\lambda_2T}{4}\right), \tag{14a}$$

$$(\lambda_1+A)\,\mathrm{th}\left(\frac{\lambda_2T}{4}\right)=(\lambda_2+A)\,\mathrm{th}\left(\frac{\lambda_1T}{4}\right). \tag{14b}$$

Introducing dimensionless quantities

$$\varkappa=\left(\frac{qd}{\pi}\right)^2,\quad v=\frac{|e^*|Ed}{2\pi K},\quad \Omega=\frac{\gamma_1 d^2}{\pi^2TK},$$

we rewrite Eqs. (14) as

$$\pm\frac{\mu v}{(\mu^2v^2+\varkappa)^{1/2}}=\mathrm{sh}\left[\frac{1}{\Omega}\left(\frac{1+\varkappa}{2}-\mu v^2\right)\right]\Big/\,\mathrm{sh}\left[\frac{v}{\Omega}\sqrt{\mu^2v^2+\varkappa}\right]. \tag{15}$$

4. Analysis of Eqs. (15) shows that a solution of the form (11a) is possible only at $\mu > 0(\varepsilon_a > 0)$. The solution (11b) is possible only at $\mu < 0(\varepsilon_a < 0)$. In the limiting case of low frequencies $\omega(\Omega \ll 1)$ the Eqs. (15) have the solutions (7) and (8), in which the sign of μ uniquely determines the amplitudes of $\theta_0(t)$ and $\varphi_0(t)$ according to

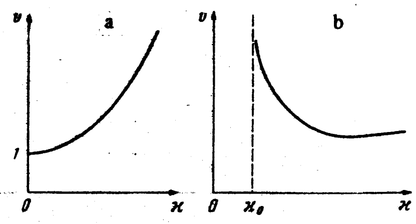

FIG. 2. Qualitative dependence of the electric field on the wave vector of a modulated structure: a—Fréedericsz effect; b—threshold piezoelectric instability, $\varkappa_0 = |\mu|/(1-|\mu|)$.

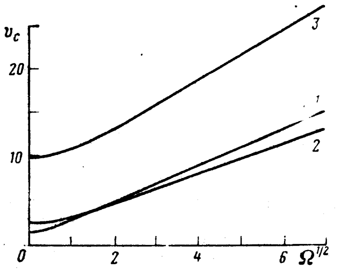

FIG. 4. Dependence of the threshold field on the frequency, calculated at different values of the parameter μ: $\mu = -0.01$ (curve 1); -0.5 (curve 2); -0.9 (curve 3).

(11). We note that at $\mu > 1$ and $\Omega \ll 1$, the solution (7) remains valid; however, the quantity $E(q)$ has a minimum

$$E_0 = \frac{\pi}{d}\sqrt{\frac{4\pi K}{\varepsilon_a}} \tag{16}$$

at $q=0$ (Fig. 2a). This effect of the generation of an orientation strain that is uniform relative to x, y (the Fréedericsz effect) is in fact independent of the piezoelectric properties of the liquid crystal.

At high frequencies $\omega(\Omega \gg 1)$ and $\mu > 0(\varepsilon_a > 0)$, the Fréedericsz effect is realized only at a constant threshold value of the field E_0. In the case $\mu < 0$ and $\Omega \gg 1$, an instability of the type (11b) arises at the threshold field $E_c(\omega)$; it is strongly dependent on the frequency. It is not difficult to establish this fact if the inequality $(1-|\mu|) \ll 1$ is satisfied. In fact, assuming satisfaction of the inequalities

$$v^2 \gg \Omega, \quad \mu^2 v^2 \gg \varkappa$$

and carrying out the corresponding expansions in (15), we find

$$v^2 = \frac{\Omega}{|\mu|}\left(1+\frac{\varkappa}{4|\mu|\Omega}\right)\frac{\varkappa}{(1-|\mu|)\varkappa-|\mu|} \tag{17}$$

A plot of $v(\varkappa)$ is shown qualitatively in Fig. 2b. The minimum of the right side in the expression (17) is achieved at the value $\varkappa = \varkappa_c$ if $|\mu| \lesssim 1$:

$$\varkappa_c = \frac{|\mu|}{1-|\mu|} + \left[\left(\frac{\mu}{1-|\mu|}\right)^2 + \frac{4\mu^2\Omega}{1-|\mu|}\right]^{1/2}. \tag{18}$$

It is seen from (18) that the wave vector of the resultant structure q_c depends weakly on the frequency $\omega \sim \Omega$;

$$\frac{dq_c}{\pi} = \varkappa_c^{1/2} = \begin{cases} [2|\mu|/(1-|\mu|)]^{1/2}, & \Omega \ll (1-|\mu|)^{-1}, \\ [4\mu^2\Omega/(1-|\mu|)]^{1/4}, & \Omega \gg (1-|\mu|)^{-1}. \end{cases} \tag{19}$$

Since, according to (19), the quantity $\varkappa_c \ll \Omega$ at $\Omega \gg 1$, then the expression for the threshold value of v_c can be written with the aid of (17) in the form

$$v_c^2 \approx \frac{\varkappa_c\Omega}{|\mu|[(1-|\mu|)\varkappa_c-|\mu|]} = \begin{cases} 2\Omega/|\mu|(1-|\mu|), & \Omega \ll (1-|\mu|)^{-1}, \\ \Omega/|\mu|(1-|\mu|), & \Omega \gg (1-|\mu|)^{-1}. \end{cases} \tag{20}$$

Thus, according to (20), the threshold voltage $V_c \sim v$ has the following qualitative dependence of the parameters of the material, the thickness of the layer and the frequency of the applied field:

$$V_c \sim 4d[\gamma_1\omega/(|\varepsilon_a|(1-|\mu|))]^{1/2}. \tag{21}$$

The functions of $v(\varkappa)$ calculated numerically for different values of the parameter Ω are plotted in Fig. 3. Figure 4 shows the results of numerical calculations of the dependence $v_c(\Omega)$ for different values of the parameter $|\mu|$. Both figures are in qualitative agreement with the conclusions drawn above.

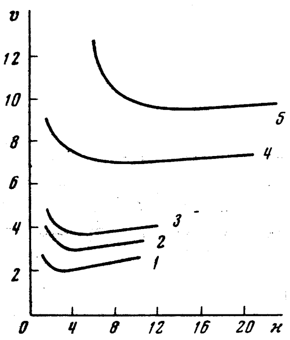

FIG. 3. Dependence of the electric field on the wave vector, calculated at different values of the relative frequency: $\Omega = 0.1$ (curve 1); 1 (curve 2); 2 (curve 3); 10 (curve 4), 20 (curve 5).

5. The new type of piezoelectric instability should be observed in layers of finite thickness in nematic and smectic liquid crystals with negative anisotropy of the dielectric permittivity and planar orientation of the molecules on the bounding surfaces. Korn's law for the frequency dependence of the corresponding threshold field must be satisfied at frequencies higher than the reciprocal of the structural relaxation time ($\Omega > 1$) in contrast with the similar law in the case of the so-called dielectric regime,[3] where this law is valid at frequencies higher than the reciprocal of the relaxation time of the volume charge. The spatial period of the arising structure depends relatively weakly on the frequency ($\sim \omega^{-1/4}$) in contrast to the dielectric regime ($\omega^{-1/2}$).

In substances with positive anisotropy of the dielectric permittivity, the effect can only exist in a narrow range of frequencies ($\Omega < 1$), smaller than the reciprocal of the structural relaxation time. Here the threshold characteristics depend weakly on the frequency and are practically the same as the expressions (8).

The geometry of the forming "domain structure," which differs radically from that normally observed, can serve as an indication of the presence in the material of significant piezoelectric constants. Inhomogeneous structures possessing the geometry described above have been observed in a number of studies.[4] Unfortunately, however, the nature of these phenomena remains unclear. It is desirable to search for the above effect in liquid crystals of the type investigated in Ref. 5, in which Williams domains cannot exist because of the change of the sign of the anisotropy of the conductivity or viscosity.[6]

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