

# New contribution to spontaneous polarization of ferroelectric liquid crystals

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Experiments and theory have shown that a new component of spontaneous polarization exists in chiral smectics *C*, proportional to the cube of the angle of inclination of the molecules and characterized by a small relaxation time.

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1. According to the phenomenological theory,<sup>1</sup> ferroelectricity in liquid crystals has a secondary (pseudointrinsic) nature and arises due to the lowering of symmetry from  $D_\infty$  of the smectic *A* phase, consisting of chiral molecules (*A* \*), to  $C_2$  of the chiral smectic *C* phase (*C* \*). The polarization  $P_s$  in this case is only formally a parameter of the transition  $A^* \leftrightarrow C^*$ , while the physical parameters of the transition are the quadratic combinations of the components of the director

$$(\xi_1, \xi_2) = (n_z n_x, n_z n_y), \quad (1)$$

where  $n_x = \sin\theta \cos\varphi$ ,  $n_y = \sin\theta \sin\varphi$ ,  $n_z = \cos\theta$ ,  $\theta$  is the angle of inclination of the molecular axes from the normal to the surfaces of the smectic layers, and  $\varphi$  is the azimuthal angle of orientation of the director. The electric polarization is caused by spontaneous inclination of molecules due to the piezoelectric effect.

$$(P_x, P_y) \sim (\xi_2, -\xi_1). \quad (2)$$

The piezoelectric polarization (2) of a separate smectic layer is proportional to the angle of inclination of the molecule  $\theta$ :

$$P_c \sim \mu_p \theta, \quad (3)$$

where  $\mu_p$  is the piezoelectric coefficient.

The motion of the director with a change in angle  $\theta$  is accompanied by a rather large ( $10^{-6}$ – $10^{-5}$  s) relaxation time  $\tau_\theta$ , which is estimated in the  $A^*$  phase from the frequency dispersion of the electroclinic effect<sup>2</sup> and the  $C^*$  phase according to the kinetics of the pyroeffect, excited by a short heat pulse.<sup>3</sup> In Ref. 3 it was assumed that the relaxation time  $\tau_\theta$  of the pyroelectric response, characterizing the change in polarization  $P_\theta$  with a change in angle  $\theta$ , is due to slow rotations of molecules around their short axes. The presence of a fast component, apparently related to rotations of molecules around their long axes, in the kinetics of the pyroelectric response of a ferroelectric liquid crystal to a short heat pulse ( $\sim 10^{-8}$  s) was pointed out in the same paper.

In this paper we show that the fast component of the pyroelectric response with relaxation time  $\tau_i \ll 10^{-8}$  s is due to a previously not discussed additional contribution to polarization of the liquid crystal, which in many cases is comparable in magnitude to the piezoelectric contribution. In this case, the phenomenological theory must be supplemented by a new mechanism of dipolar ordering.

2. The additional contribution  $P_i$  to polarization can be attributed to the appearance of ordering along some additional degree of freedom, which the molecules have, for example, along the orientations of the transverse molecular axes. In this case, the order parameter for transverse  $Q' \neq 0$ .

This ordering must arise below the point of the phase transition  $A^* \leftrightarrow C^*$  as a secondary (noncharacteristic) phenomenon and must be characterized by its own relaxation time. In the case of ordering of the short molecular axes, the components of a tensor of rank two, formed by the quadratic combinations of projections of the transverse director  $A^* \leftrightarrow C^*$ , serve a noncharacteristic order parameter<sup>4</sup>:

$$\eta_1 = Q^1(n_x'^2 - n_y'^2), \quad \eta_2 = 2Q'n_x'n_y', \quad (4)$$

where  $n_x' = -\sin \varphi$ ,  $n_y' = \cos \varphi$ . Since the characteristic parameter of the transition  $A^* \leftrightarrow C^*$  is formed by the components (1), while the components of spontaneous polarization transform according to the law (2), the expression for the free energy density contains the invariant

$$\mu_i [(P_y \xi_1 + P_x \xi_2) \eta_1 + (P_y \xi_2 - P_x \xi_1) \eta_2] \approx \mu_i P \theta Q', \quad (\theta \ll 1), \quad (5)$$

where  $\mu_i$  is a phenomenological parameter, determined by the microscopic nature of the interaction of different degrees of freedom of molecules.

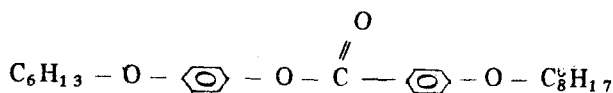
Since  $Q' \sim \theta^2$ ,<sup>4</sup> the additional contribution  $P_i$  to the spontaneous polarization of phase  $C$  must be proportional to

$$P_i \sim \mu_i \theta^3 \quad (6)$$

i.e., the new "fast" component of spontaneous polarization  $P_i$  is characterized not only by a short relaxation time  $\tau_i \ll 10^{-8}$  s, corresponding to rotations of molecules around their long axes, but also by the sharp (cubic) dependence of  $P_i$  on the angle of inclination of molecules  $\theta$ .

3. Using the technique for measuring spontaneous polarization according to the pyroelectric effect, excited by laser heat pulses with different duration,<sup>5</sup> we were able to obtain separately the "slow" and "fast" components of the spontaneous polarization  $P_s$  for the classical liquid crystalline ferroelectric DOBAMBC as well as for ferroelec-

tric liquid crystals based on the nonchiral smectic-C HOPEOOBA (*p*-hexyloxy-phenyl ester *p*'-octyloxybenzoic acid)



doped with a chiral admixture of HOBACPC (*L*-*p*-hexyloxybenzilidene-*p*'-amino-2-cyanopropylcinnamate)

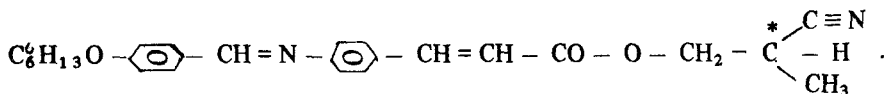


Figure 1 shows the temperature dependences of the pyroelectric coefficient  $\gamma_3 = dP_t/dT$  of DOBAMBC, measured according to the power-voltage sensitivity  $S_t = U_t/Q \sim \gamma_t$  to the gigantic laser pulse with duration  $t_Q \sim 2 \times 10^{-8}$  s ( $U_t$  is the amplitude of the fast component of the pyroelectric response, reproducing the laser pulse (insert in Fig. 1),  $Q$  is the power of the exciting pulse), and of the "fast" component of the spontaneous polarization  $P_t$ , obtained by graphical integration of the curve  $\gamma_t(t)$ .

Figure 2 shows the temperature dependences of the "fast" components of the pyroelectric coefficient  $\gamma_t$  and spontaneous polarization  $P_t$  for the mixture HOPEOOBA + HOBACPC (5 wt.%), as well as of the total polarization  $P_s$  of this mixture, obtained from the pyroelectric response to a "long" free-generation neodymium laser pulse with duration  $t_l \sim 2 \times 10^{-4}$ .

It is clearly evident from Fig. 3 that both for DOBAMBC and for the mixture the "fast" component of the polarization  $P_t$  is proportional to the cube of the angle of inclination of the molecules in agreement with expression (6), while the "slow" component  $P_\theta$ , obtained from the total polarization  $P_s$  by subtracting the "fast" contribution  $P_t$ , is proportional to the angle  $\theta$ , in agreement with the expression for the piezoelectric contribution (3).

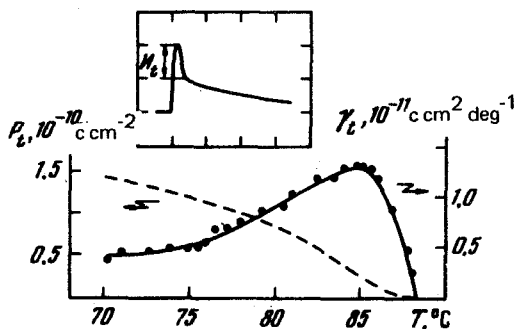


FIG. 1. Temperature dependences of fast contributions to the pyroelectric coefficient ( $\gamma_t$ ) and spontaneous polarization ( $P_t$ ) for DOBAMBC. Insert: Oscillogram of the pyroelectric response of the ferroelectric liquid crystal to a giant laser pulse with duration  $t_Q \sim 2 \times 10^{-8}$  and power  $Q \sim 10^4$  W. The scan is 100 ns/division, the value of division on the vertical axis is 1 mV, and the electrical constant of the amplification circuit is 10 ns.

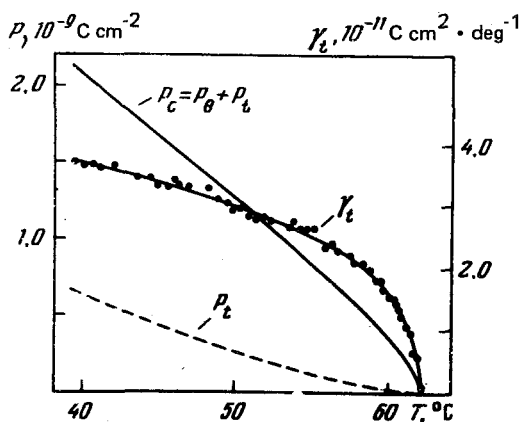


FIG. 2. Temperature dependences of fast contributions to the pyroelectric coefficient ( $\gamma_t$ ) and spontaneous polarization ( $P_t$ ) and total spontaneous polarization ( $P_s$ ) of a nonchiral smectic  $C$  liquid crystal HOPEOBA, doped with the chiral impurity HOBACPC (5 wt.%).

The parameters  $\mu_p$  and  $\mu_t$  for DOBAMBC constituted  $4.3 \times 10^{-4} \text{ C m}^{-2} \text{ rad}^{-1}$  and  $6 \times 10^{-5} \text{ C m}^{-2} \text{ rad}^{-3}$ , respectively. For the mixture HOPEOBA + HOBACPC (5%)  $\mu_p = 2 \times 10^{-4} \text{ C m}^{-2} \text{ rad}^{-1}$ , while  $\mu_t = 3 \times 10^{-4} \text{ C m}^{-2} \text{ rad}^{-3}$ . For DOBAMBC the new contribution  $P_t$  constitutes a small fraction of the piezoelectric contribution  $P_\theta$  ( $P_t \approx 0.03 P_\theta$ ), while the relative contribution of the "fast" component  $P_t$  to spontaneous polarization of the nonchiral smectic  $C$  HOPEOBA, induced by the chiral admixture HOBACPC, is much higher ( $P_t \approx 0.43 P_\theta$ ).

4. By increasing the dipole moment  $p_{\text{mol}}$  in the chiral fragment of the impurity molecules introduced into the nonchiral smectic  $C$  we observed a sharp increase in the relative contribution of the new, "fast" component  $P_t$  in such systems. In this case, the

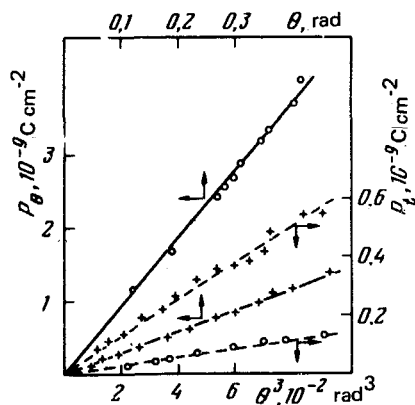


FIG. 3. Solid lines show the dependence of the "slow" component of the spontaneous polarization  $P_\theta(\theta)$  for DOBAMBC (○) and for the mixture HOPEOBA + HOBACPC (+). The dashed lines show the dependence of the "fast" component of the spontaneous polarization  $P_t(\theta^3)$  for DOBAMBC (○) and for the mixture HOPEOBA + HOBACPC (+).

dependence of the polarization  $P_t$ , normalized to the same angle  $\theta$ , on the magnitude of  $p_{\text{mol}}$  is distinctly nonlinear, independent of the choice of the smectic-C matrix.

The new mechanism for dipolar ordering discussed in this paper is apparently also responsible for the nonlinear dependence of the effective dipole moment, calculated per chiral molecular from the spontaneous polarization, on the quantity  $p_{\text{mol}}$  of some liquid crystalline ferroelectrics, as discovered in Ref. 6.

Such a nonlinear dependence of  $P_t$  on the dipole moment  $p_{\text{mol}}$  in a chiral fragment allows us to conclude that the ordering of the transverse molecular axes for large values of  $p_{\text{mol}}$  is caused by the interaction of the transverse component of  $p_{\text{mol}}$  with the local electric field. Of course, this result does not exclude the possibility for the existence of other ordering mechanisms as well.

In conclusion, we thank V. A. Baikalov for help in performing the experiment.

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