S. A. Pikin and M. A. Osipov. *Ferroelectricity in liquid crystals.* At the present time no limitations in principle are known forbidding the appearance of ferroelectric ordering in an isotropic liquid. However such ferroelectric substances have not been discovered as yet. At the same time, as was predicted by Meyer in 1975 a spontaneous polarization must arise in the so-called smectic C* liquid crystals (LC) whose structure is shown in Fig. 1.

In smectic C* LC there exist both an orientational and a one-dimensional translational order, and the direction of the predominant orientation of the long axes of the molecules defined by the unit director-vector **n** is inclined at an angle θ with respect to the normal **e** to the smectic layers. If the molecules of such a LC are chiral then in the system only a polar axis of the second order remains which lies in the plane of the smectic layer perpendicular to the vectors **n** and **e** (Fig. 1a). It is along this polar axis that the spontaneous polarization arises, and this was confirmed experimentally in 1975. At the present time hundreds of ferroelectric LC have been synthesized, and the maximum polarization attains values of 10^{-7} C/cm^2.

The chirality of the molecules of the C* smectic leads also to the formation of a helicoid structure, so that the azimuthal angle φ of rotation of the director in the smectic layer varies along the **Z** axis, $\varphi = qz + \varphi_0$. The existence of such a spontaneous orientational twisting deformation leads to an additional contribution to the spontaneous polarization as a result of the flexoelectrical effect. As a result the total spontaneous polarization is $P = \theta(\mu_p + \mu_f \partial\varphi/\partial z)$. Thus, the ferroelectric ordering in the C* smectic is not intrinsic and arises as a consequence of the tilting of chiral molecules in the layer. The transition itself from the smectic A phase into the C phase is in this case described by the two-component order parameter[1]

$$\xi_1 = n_z n_x, \qquad \xi_2 = n_z n_y, \tag{1}$$

where we have $\mathbf{z}\|\mathbf{e}$. Then the free energy of the ferroelectric LC can be written in the form

$$
\begin{aligned}
F = {} & a\,(\xi_1^2 + \xi_2^2) + b\,(\xi_1^2 + \xi_2^2)^2 + \lambda\left(\xi_1\frac{\partial\xi_2}{\partial z} - \xi_2\frac{\partial\xi_1}{\partial z}\right) \\
& - \mu_p\,(-\xi_1 P_y + \xi_2 P_x) - \mu_f\left(P_x\frac{\partial\xi_1}{\partial z} + P_y\frac{\partial\xi_2}{\partial z}\right) \\
& - \tilde{\mu}_f\left(\xi_1\frac{\partial\xi_2}{\partial z} - \xi_2\frac{\partial\xi_1}{\partial z}\right)(\xi_1 P_y - \xi_2 P_x) + \text{elastic terms.} \tag{2}
\end{aligned}
$$

Here the third term is the Lifshitz invariant which leads to the appearance of helicoidal structure, the fourth term describes the linear coupling between the spontaneous polarization and the order parameter, the fifth term is the flexoelectrical effect, and the sixth term is its anisotropy in the
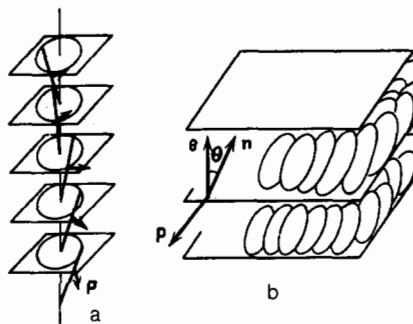

FIG. 1. Structure of a ferroelectric C* smectic. (a) Inclination of molecules in a smectic layer. (b) Helicoidal structure.

plane of the layer. For $\theta \neq 0$ a spontaneous polarization arises in the layer

$$\mathbf{P} = \mu_p \chi \, [\mathbf{ne}] \, (\mathbf{ne}) - \chi\mu_f \frac{\hat{\partial}}{\partial z} \mathbf{n} \, (\mathbf{ne}). \tag{3}$$

The helicoidal structure exerts a significant influence on the properties of the ferroelectric LC and this is particularly noticeable on the example of the permittivity $\chi = \chi_0 + \delta\chi_c$;

$$\delta\chi_C = \frac{1}{2}\chi_0^2 \left[\frac{\mu_p^2}{Kq_0^2} + \frac{(\mu_p - \widetilde{\mu}_f q\theta^2)^2}{K_0 q_0^2 - 4\alpha \, (T - T_c)} \right]. \tag{4}$$

The first term in (4) represents the contribution from the Goldstone mode associated with the untwisting of the helicoid, and the second term is determined by the "soft" mode corresponding to the simultaneous change in the polarization and the angle of inclination θ. In such a case the anisotropy of the flexoeffect leads to a strong temperature dependence of the permittivity in the C* phase due to the relation $\theta^2 \sim (T - T_c)^{2\beta}$. Experimental data show[2] that the permittivity of a helicoidal ferroelectric LC differs significantly from the permittivity of the CLC with an untwisted helix. Such a connection between the polarization and the helical structure represents one of the interesting properties of liquid crystal ferroelectrics.

The specific features of ferroelectric ordering in LC is manifested most clearly on the microscopic level. Indeed, the dipole-dipole interaction which is the basis of ferroelectric ordering in crystals cannot lead to the appearance of spontaneous polarization in C* smectics, since they are not sensitive to the chirality of the molecules, while ferroelectricity is observed only in chiral LC. Molecular theory[3] shows that spontaneous polarization in the C* phase arises due to the polar component of the energy of chiral interaction between molecules. For a more detailed description it is necessary to examine models of chiral molecules of a C* smectic, shown in Fig. 2. The chirality of the molecule shown in Fig. 2 is determined by the side chain forming a chiral center. Taking into account the fact that the maximum polarization is observed in C* smectics with a large dipole in the chiral fragment, it can be shown that the principal role is played by the induction interaction of this dipole with the anisotropic polarizability of the neighboring molecule taking into account the asymmetry of the shape of the molecules. Molecular theory enables one to relate the phenomenological constant μ_p, which determines the spontaneous polarization, with the model parameters of the molecules
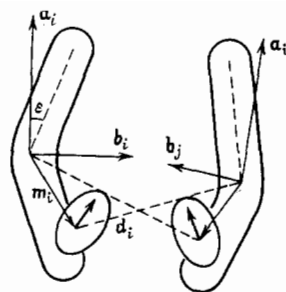

FIG. 2. Model of the interaction of chiral molecules in a ferroelectric LC.

$$\mu_p = \frac{1}{2} \frac{\rho^2}{kT} \frac{D}{L} D^{-5}\sigma \, (s_\perp d_\perp) \, \Delta \left(\chi_\perp + \frac{1}{2}\Delta\chi_\perp + \frac{15}{2}\Delta\chi \right), \tag{5}$$

where $s_\perp$ is the steric and $d_\perp$ is the electric dipole, D is the diameter, and L is the length of the molecule, χ is the polarizability of the molecule, σ is the number of nearest neighbors and $\Delta = (\mathbf{d}_i\mathbf{a}_i) ([\mathbf{d}_i\mathbf{a}_i]_i\mathbf{m}_i)$ is the measure of the chirality of the molecule the vectors $\mathbf{a}_i$ and $\mathbf{m}_i$ are shown in Fig. 2). We note that the polarization grows rapidly as the dipole at the chiral center is increased, $p \sim d_\perp^3$, and this corresponds to experiment.

It is interesting to note that the ferroelectric ordering can be induced in a nonchiral smectic by means of adding a small admixture of chiral molecules. This effect is connected with the fact that the chiral forces discussed above appear under the condition that at least one of the attracting molecules is a chiral one. In such a case the possibilities of producing new ferroelectric LC with optimal properties are significantly broadened, since the molecular parameters entering expression (5) are distributed among different components (for example, chirality and a large dipole moment).

In conclusion it should be noted that in recent years the practical importance of ferroelectric LC is rapidly increasing in connection with attractive prospects for their utilization in different electro-optical devices, which are characterized by considerably lower response times and controlling voltages than analogous devices in which nematic LC are used.

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