

Thermodynamic states and symmetry of liquid crystals

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All the diverse types of liquid-crystalline states can be described in a unified manner by analogy with the group-theoretical description of the symmetry and properties of crystals. The symmetry properties of liquid crystals with respect to the orientation of the molecules, and the conditions for the appearance of a modulated orientational structure, are considered. The phase diagrams in liquid crystals are described, and a general scheme of the phase transitions between liquid-crystalline phases is given. The problem of the ferroelectric state in liquids is considered, and the classes of anisotropic liquids that possess ferroelectric and piezoelectric properties are demonstrated. A thermodynamic description is given of the ferroelectric phenomena observed experimentally in smectic liquid crystals. The question of the physical nature of the low-symmetry smectic phases is discussed and the character of the phase transitions in liquid crystals is considered.

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1. INTRODUCTION

Liquid crystals are one of the forms of existence of living and inanimate matter, discovered less than a hundred years ago.¹ Regarded originally as a curiosity of Nature, in the last ten years these surprising substances have become the subject of thorough scientific investigations and a component of numerous practical developments. A component part of the most diverse systems, from electro-optical displays to biological membranes, liquid crystals exhibit a wealth of structure and properties. The so-called thermotropic liquid-crystalline modifications can be extremely sensitive to electromagnetic fields and mechanical stresses, with distinct phases existing in temperature intervals from fractions of a degree to hundreds of degrees. Multi-component lyotropic liquid crystals, which perform important biological functions (e.g., bile), can undergo a series of structural changes as the concentrations of

the different components are varied. In practical applications it is usually the lability of the physical properties of the liquid crystals that is used, but there are opposite examples, e.g., the liquid-crystalline structure of solutions of polymers predetermines the ultrahigh strength of certain artificial fibers.

A. The traditional classification

Experimental observations have shown that liquid crystals are anisotropic liquids, consisting of molecules of elongated shape. At present it is customary²⁻⁴ to classify the thermodynamic states of such mesophases, i.e., phases intermediate between solid-crystalline and isotropic-liquid states, by the form of the functions for the density $\rho(\mathbf{r})$ and local orientation $\mathbf{n}(\mathbf{r})$ of the molecules. The unit vector $\mathbf{n}(\mathbf{r})$, called the director, indicates the direction along which the long molecular axes point, on the average, at the given point \mathbf{r} . A phase

with $\rho = \text{const}$ and $\mathbf{n} = \text{const}$ is called a *nematic* liquid crystal (NLC). The mesophases in which the function $\rho(\mathbf{r})$ is periodic along a distinct axis z and constant in the xy planes are called *smectic* liquid crystals (SLC) and are characterized by a layer structure. In their flow properties, NLC are most similar to an ordinary isotropic liquid with $\rho = \text{const}$. SLC possess fluidity within the layers and behave almost as solids under uniaxial stress perpendicular to the layers. Media with $\rho = \text{const}$ and a macroscopically modulated structure $\mathbf{n}(\mathbf{r})$, called *cholesteric* liquid crystals (CLC), form a special category. The molecules of a CLC possess unique properties: they are chiral¹⁾, i.e., they do not contain any symmetry planes and are found in one of two possible enantiomorphic forms.

B. Correlation functions in liquid crystals

The traditional classification is not adequate for the description of the above-mentioned multiplicity of liquid-crystalline structures and the possible structural transformations.⁵ A more complete analysis of the symmetry properties of LC is possible on the basis of the study of the mutual correlations between the positions of the different atoms.⁶ Here one frequently encounters situations in which it is sufficient to investigate only the point symmetry of the correlation functions, just as in the case of crystals it is found to be sufficient to consider the corresponding crystallographic classes.⁷ The possibility of investigating the modulated structures in systems with chiral molecules is assured by taking into account the Lifshitz invariants,⁸ which play the same role here as in ordinary crystals.⁸

The description of the structure and symmetry of liquid crystals requires, generally speaking, an analysis of many-particle correlations in the disposition of the atoms.²⁾ Sometimes it is recommended⁶ to use the pair correlation function $\rho_{12}(\mathbf{r}_{12})$, where \mathbf{r}_{12} is the distance between atoms 1 and 2, and $\rho_{12}dV_2$ is the probability of finding atom 2 in the volume dV_2 when atom 1 has a given position. However, structures not having a center of symmetry cannot be described by means of the function $\rho_{12}(\mathbf{r}_{12})$, since this function possesses even parity.⁹ Therefore, to describe chiral structures, more-complicated correlation functions, e.g., four-particle correlations between the positions of the atoms, are necessary. The presence or absence of a center of symmetry in a system of molecules can be characterized by the pair correlation function $\rho_{12}^m(\mathbf{r}_{12}, \mathbf{l}_1, \mathbf{l}_2)$, which depends on the distance \mathbf{r}_{12} between the centers of gravity of the molecules and on the orientations \mathbf{l}_1 , and \mathbf{l}_2 of the long axes of the molecules 1 and 2. From the three vectors \mathbf{r}_{12} , \mathbf{l}_1 , and \mathbf{l}_2 we can form the pseudoscalar $[\mathbf{l}_1 \times \mathbf{l}_2] \cdot \mathbf{r}_{12}$; however, we should expect that the pseudoscalar

$$([\mathbf{l}_1 \times \mathbf{l}_2] \cdot \mathbf{r}_{12})(\mathbf{l}_1 \cdot \mathbf{l}_2) \quad (1)$$

will appear in the function ρ_{12}^m , inasmuch as the axes \mathbf{l}_1 and \mathbf{l}_2 are not polar and the function ρ_{12}^m should be invariant under the replacement of \mathbf{l}_1 by $-\mathbf{l}_1$ and \mathbf{l}_2 by $-\mathbf{l}_2$. Liquid crystals whose molecules possess well defined short axes require a still more complicated description. In the group-theoretical approach, which will be considered below, the structure of a liquid crystal can be described in a unified manner in the language of the representations of the corresponding symmetry groups, and this makes it possible, in principle, to take into account all the possible changes in the degrees of freedom in phase transformations.

2. SYMMETRY WITH RESPECT TO THE ORIENTATION OF THE MOLECULES

A. The order parameter

The most symmetric phase of a LC is the isotropic liquid. Its symmetry group does not contain translational-symmetry elements and is a well defined point group. The point symmetry of the LC is most clearly exhibited at short distances, where it can be interpreted as the point symmetry of the molecular groups (subunits) forming the LC. The symmetry group of an isotropic liquid, as is well known, can be either the full orthogonal group (the group K_h) or simply, in the case of chiral molecules, the full group of rotations about a point (the group K), which differs from the group K_h by the absence of a center of symmetry. The lowering of the symmetry of the isotropic liquid as a result of phase transitions usually leads to the appearance of a nematic or centrosymmetric smectic-*A* phase (the transition $K_h \rightarrow D_{\infty h}$), a smectic-*A* phase without a center of symmetry (the transition $K \rightarrow D_{\infty}$), or a cholesteric phase. All the known uniaxial LC of the above types correspond to the symmetry groups $D_{\infty h}$ and D_{∞} . In such LC, the two directions along the axis of full axial symmetry (i.e., along the director \mathbf{n}) are equivalent.³⁾

For the order parameter in these cases we can use the tensor with components

$$Q_{ik}(\mathbf{r}) = \langle l_i l_k \rangle - \frac{1}{3} \langle l_j l_j \rangle \delta_{ik} = Q(\mathbf{r}) \left[n_i(\mathbf{r}) n_k(\mathbf{r}) - \frac{1}{3} \delta_{ik} \right], \quad (2)$$

which are local averages of bilinear combinations formed by projections of the unit vector \mathbf{l} of the long molecular axis. The quantity $Q(\mathbf{r})$ defines the fraction of molecular axes pointing along \mathbf{n} at the given point.¹⁰ In the isotropic phase $Q = 0$.

B. Modulated orientational structure

We emphasize that in a liquid ($\rho = \text{const}$) a phase transition from a state with symmetry K to a state with a spatially uniform order parameter Q_{ik} is impossible, since this uniform state is unstable against spatial modulations of $\mathbf{n}(\mathbf{r})$. The presence in CLC of macroscopic nonuniformity of $\mathbf{n}(\mathbf{r})$ over distances large compared

¹⁾The term "chiral" (from the Greek word for "hand") is used to describe the symmetry of right-handed and left-handed helical structures.

²⁾We note that in ordinary crystals it is sufficient to consider only the density function $\rho(x, y, z)$; however, the axes are assumed to be fixed, which is equivalent, in effect, to taking many-particle correlations into account.

³⁾Uniaxial LC with the axial-symmetry groups C_{∞} , $C_{\infty v}$, and $C_{\infty h}$, which would correspond to the presence of an electric polar axis (the groups C_{∞} and $C_{\infty v}$) or an axis of magnetization (the group $C_{\infty h}$), have not been observed experimentally.

with the molecular sizes is connected with the existence in the expression for the free-energy density F of an invariant of the form

$$\frac{1}{2} K_2 (q + \mathbf{n} \operatorname{rot} \mathbf{n})^2; \quad (3)$$

here $K_2 \sim Q^2$ is an elastic constant, dependent on the temperature, and the quantity q has the dimensions of the wave number of the nonuniform structure. In (3) the Lifshitz invariant $\mathbf{n} \cdot \operatorname{rot} \mathbf{n}$ is present, and corresponds, as is well known,⁸ to the formation of a modulated (in the present case, helical³) structure. A cholesteric helical structure with director components

$$n_z = 0, \quad n_x = \cos qz, \quad n_y = \sin qz \quad (4)$$

minimizes the expression (3). It arises at the limiting phase-transition temperature below which $Q=0$.

In a CLC the quantity $\mathbf{n}(\mathbf{r})$ is a slowly varying function of the coordinates: $ql \ll 1$, where l is the molecular length. The distribution of the molecular axes about the local orientation of the director (4) is described by the symmetry group D_∞ . Such a uniaxial distribution is reminiscent of the situation in NCL; however, the corresponding correlation function ρ_{12}^m should have in the CLC a pseudoscalar contribution $\delta\rho_{12}^m$ of the form (1). The interaction potential v_{12}^m of the molecules also contains an analogous correction δv_{12}^m . Assuming that, as in the NCL, the function ρ_{12}^m has a sharp maximum for collinear $\mathbf{l}(\mathbf{r})$ and $\mathbf{n}(\mathbf{r})$, while the potential v_{12}^m falls off rapidly over distances of the order of l , it is not difficult to obtain the Lifshitz invariant from microscopic considerations. Since, with the assumptions made, we can put $\mathbf{l}_1 = \mathbf{n}(\mathbf{r})$, $\mathbf{l}_2 = \mathbf{n}(\mathbf{r}) + (\mathbf{r}_{12} \cdot \nabla)\mathbf{n}(\mathbf{r})$, the extra terms $\delta\rho_{12}^m$ and δv_{12}^m change the free-energy density by an amount

$$\delta F^{(4)} = \frac{N}{V} \int (v_{12}^m \delta\rho_{12}^m + \rho_{12}^m \delta v_{12}^m) dV_2 d\mathbf{l}_1 d\mathbf{l}_2 = \text{const} \cdot \mathbf{n} \operatorname{rot} \mathbf{n}.$$

Oriental symmetry gives rise to the most fundamental properties of LC, but does not exhaust all the symmetry properties. There exist various layered LC, to describe which we need to take translational symmetry into account.

3. SMECTIC-A LIQUID CRYSTALS

A. The free-energy density

The formation of a smectic-A phases with the symmetry groups $D_{\infty h}$ and D_∞ corresponds to the appearance of a density wave¹¹

$$\rho(z) = \rho_0 + |\psi| \cos(kz + \omega)$$

($|\psi|$ and ω are the amplitude and phase of the wave, and $k = 2\pi/l$), and of orientational order (2), the director \mathbf{n} being parallel to the z axis. Generally speaking, to describe the phase transitions in SLC it is necessary to consider the space symmetry groups. Nevertheless, in a number of cases, as for ordinary crystals, it is sufficient to confine oneself to considering the point symmetry: 1) if the space group is symmorphic, i.e., does not contain screw axes or glide planes and is a product of a point group with a group of translations, and 2) if the phase transitions in the SLC occur with preservation of the smectic layers (analogously to phase transitions

in crystals with no change in the number of atoms in the unit cell⁷).

The free-energy density F in the case under consideration includes invariants formed from the order parameters $|\psi|$ and Q_{ik} , and can be written in the form

$$F = F_N(Q_{ij}) + F_A(|\psi|) + F_{NA}(Q_{ij}, |\psi|). \quad (5)$$

The quantity $F_N\{Q_{ij}\}$ is the free-energy density of the uniaxial nematic phase. Since from the tensor components Q_{ij} it is possible to form the combination $Q_{ij}Q_{jp}Q_{pi}$, which is invariant under the transformations of the group K_N , the expansion of F_N in powers of Q contains a term of third order in Q :

$$F_N = a_1 Q^2 + b_1 Q^3 + c_1 Q^4 + \dots \quad (6)$$

We shall put $a_1 = a_1'(T - T_1)$, $b_1 < 0$, $c_1 > 0$. In this case the expression (5) describes a first-order phase transition from the isotropic phase (I) to the nematic phase (N) at a temperature T_{IN} :

$$a_1(T_{IN}) = \tilde{a} \equiv \frac{b_1^2}{4c_1},$$

with a corresponding discontinuity in the parameter Q :

$$Q(T_{IN}) = \tilde{Q} \equiv -\frac{b_1}{2c_1}.$$

The quantity $F_A\{|\psi|\}$ describes a one-dimensional crystal—a system with the two-component order parameter $|\psi| \exp[i(kz + \omega)]$ —and contains only even powers of $|\psi|$:

$$F_A(|\psi|) = a_2 |\psi|^2 + c_2 |\psi|^4 + \dots \quad (7)$$

The mixed term F_{NA} can be written in the form

$$F_{NA} = -|\psi|^2 f(Q), \quad f(Q) > 0, \quad (8)$$

where $f(Q)$ includes invariant combinations of the type $k_i k_j Q_{ij} \sim Q(|\mathbf{k}| = k)$, $Q_{ij}^2 \sim Q^2$, etc. The fact that the quantity $f(Q)$ is positive means physically that additional orientational order induced by the appearance of the density wave corresponds to an increase in the forces of attraction between the molecules, i.e., it decreases the energy of the system.

Using (5)–(8) it is not difficult to investigate the LC phase diagram, which is determined by the relative sizes of the coefficients in the expansions (6)–(8). These coefficients are parameters of the substance and depend on the structure of the molecules, e.g., on the molecular length l .

We shall suppose that $a_2 > 0$ and $c_2 < 0$, since, experimentally, SLC of all types possess orientational order ($Q \neq 0$), and SLC with $Q = 0$ are unknown. Minimizing F , as given by (5)–(8), with respect to the amplitude $|\psi|$, we obtain

$$|\psi|^2 = \begin{cases} \frac{f(Q) - a_2}{2c_2}, & f(Q) > a_2, \\ 0, & f(Q) < a_2. \end{cases} \quad (9)$$

Thus, phase transitions to a smectic-A phase are possible only under the condition that these transformations are accompanied by sufficiently high orientational order Q . In this case transitions to the A phases are possible from both the nematic and the isotropic phase.

$N \rightarrow A$ phase transitions, at temperature T_{NA} , can, generally speaking, be both second-order and first-

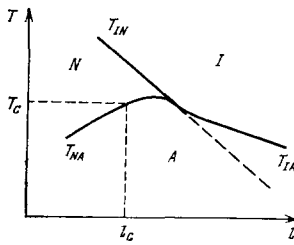


FIG. 1. Phase diagram describing the phase transformations between the isotropic (*I*), nematic (*N*), and smectic (*A*) modifications of an LC. The dependence of the phase-transition temperatures T_{IN} , T_{NA} , and T_{IA} on the length l of the molecules (from Ref. 12) is typical for a homologous series of substances.

order. Putting $Q(T_{NA}) \gg \bar{Q}$ or $|a_1(T_{NA})| \gg \bar{a}$, one can show that the phase transition, at a temperature T_{NA} determined from the equation

$$f(Q(T_{NA})) = a_2(T_{NA}), \quad (10)$$

is a second-order transition if the inequality

$$\left(\frac{df}{dQ}\right)_{T=T_{NA}}^2 \geq 8c_2 |a_1(T_{NA})|. \quad (11)$$

is fulfilled. The equality in (11) determines a critical point T_c on the phase-transition line T_{NA} . At the point T_c the character of the $N \rightarrow A$ phase transition changes (Fig. 1): the second-order transition becomes a first-order transition when the inequality (11) is reversed.

If the discontinuity in the orientational order parameter \bar{Q} is sufficiently large, the lines of $I \rightarrow N$ and $N \rightarrow A$ phase transitions come together and, when the condition $f(\bar{Q}) = a_2$ is fulfilled, the lines T_{IN} and T_{NA} intersect (see Fig. 1). With further increase of the parameter \bar{Q} , $f(\bar{Q}) \geq a_2$, the smectic-*A* phase is formed directly from the isotropic phase as a result of a first-order $I \rightarrow A$ phase transition, the transition temperature T_{IA} being determined from the equation

$$a_1(T_{IA}) = \bar{a} + \frac{f(\bar{Q}) - a_2}{c_2 \bar{Q}^2}. \quad (12)$$

The general pattern of the phase transitions between the *I*, *N*, and *A* phases is depicted in Fig. 1.

The exhibited results generalize phenomenologically the conclusions reached by McMillan¹²⁻¹⁴ in an analysis of a microscopic model, and supplement the investigations of de Gennes^{3,11} on second-order phase transitions describable by a two-component order parameter $|\psi| \exp[i(kz + \omega)]$. Relations analogous to (9)–(12) are also valid for phase transitions from the isotropic liquid to the cholesteric and smectic-*A* phases. It can be seen from (9)–(12) how the phase diagram of a substance changes as a function of the microscopic properties of the system. In particular, the coefficients in the expansions (6)–(8) should depend strongly on the length l of the molecule, or, in other words, on the position of the substance in its homologous series.¹² All the situations enumerated have been observed experimentally, as also have the dependences of the temperature and heat of the phase transitions on the length of the molecules (see Fig. 1).¹²⁻¹⁷

B. Stability of the smectic phase

The question of the stability of smectic-*A* LC against violation of the macroscopic uniformity of such liquid-crystalline modifications and against the “smearing-out” of the periodic function $\rho(z)$ by thermal fluctuations is of interest. Smectic-*A* LC with the symmetry group $D_{\infty h}$, like NLC, are stable against the formation of a modulated structure, since here Lifshitz invariants are absent. Smectic-*A* LC with the symmetry group D_{∞} , like CLC, permit the existence of a Lifshitz invariant of the type [cf. (3), (4)]

$$n_x \frac{\partial n_y}{\partial x} - n_y \frac{\partial n_x}{\partial x},$$

if the director \mathbf{n} deviates from the z axis of the one-dimensional crystal. However, such deviations of the director are possible in the case when the coefficient of the invariant

$$n_x^2 + n_y^2,$$

which is also present in the expansion of the free energy, is negative. In practice this situation corresponds to a phase transition as a result of which the symmetry of the smectic layer is lowered (see the Table I below, and Fig. 3). Such phase transitions with a two-component transition parameter $\sim(n_x, n_y)$ will be described below.

We consider the role in SLC of thermal fluctuations, which, theoretically, forbid the existence of unbounded three-dimensional substances with a density function that is periodic in one dimension only.⁵ We shall show that in layers of sufficiently small (but macroscopic) thickness L the elastic interactions that exist in smectic-*A* LC oppose the “smearing-out” of the function $\rho(z)$ by thermodynamic fluctuations. Admitting the possibility of a displacement u_z of the smectic layers and assuming that, for small deformations, the director \mathbf{n} remains normal to the smectic layer, it is easy to obtain the following relations:

$$n_z = 1, \quad n_x = \frac{\partial u_z}{\partial x}, \quad n_y = \frac{\partial u_z}{\partial y}, \quad \text{div } \mathbf{n} = \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2}. \quad (11')$$

Taking into account the relations (11') and the invariance of the free energy under a change of sign of \mathbf{n} , in the expansion of the quantity ΔF in terms of the displacements u_z we must keep the following terms¹⁸:

$$\Delta F = \frac{1}{2} B \left[\frac{\partial u_z}{\partial x} - \frac{1}{2} \left(\frac{\partial u_z}{\partial x} \right)^2 - \frac{1}{2} \left(\frac{\partial u_z}{\partial y} \right)^2 \right]^2 + \frac{1}{2} K_1 \left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} \right)^2, \quad (12')$$

where $K_1 \sim Q^2$ is the Frank constant, and $B \sim |\psi|^2$ is the elastic modulus of the SLC for a uniaxial deformation. The presence in the expression (12') of the derivatives $\partial u_z / \partial x$ and $\partial u_z / \partial y$ (in the terms of third and higher order in u_z) is connected with the fact that bending of the layers, without changing the number and sizes of the layers along the z -axis, gives an additional dilatation (Fig. 2)

$$-(n_x^2 + n_y^2)/2. \quad (13)$$

The expressions (12') and (13') correspond to invariance of the quantity F under rotations of the SLC as a whole about the x and y axes.

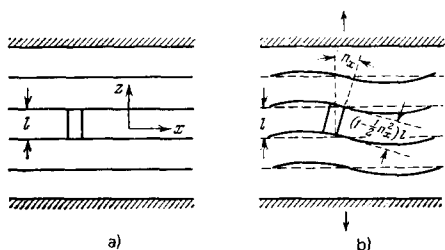


FIG. 2. Mechanical instability of smectic layers under conditions of uniform stretching along the crystal axis. a) No stress; b) bending of the layers under stress (the arrows). The dilatation of a selected element of volume, induced by the director deviation n_x , is shown.

Using (12), we obtain for the mean square displacement vector

$$\langle u_z^2 \rangle = \frac{T}{8\pi^2} \int \frac{dk_x dk_y}{Bk_x^2 + K_1 k_y^2} \sim \frac{T}{8\pi^2} \frac{1}{\sqrt{BK_1}} \ln \frac{L}{l}, \quad (14)$$

where L is the layer thickness of the SLC. Since $K_1 \sim 10^{-6}$ dyne, $T \sim 300$ K $\sim 4 \times 10^{-14}$ erg, and $\sqrt{K_1/B} \sim 1 \sim 10^{-7}$ cm, the root mean square displacement $\sqrt{\langle u_z^2 \rangle}$ can amount to a quantity of order $1 \sim 10^{-7}$ cm only when $L \sim e^{50} l$!

Weak external perturbations, e.g., mechanical, lead to the appearance of instability of smectic-A LC with respect to violation of their macroscopic uniformity, as attested by experiment.¹⁹⁻²¹ We emphasize that this type of mechanical instability is not connected with the existence of Lifshitz invariants. The modulated structure in this case consists of periodically curved smectic layers (Fig. 2b), with preservation of the local symmetry of the SLC (the director is perpendicular to the plane of the smectic layer).

Starting from (12'), one can show¹⁸ that there exists a critical value u'_c of the constant deformation $u' = \partial u_x / \partial z$ above which perturbations of the type

$$\delta u_x \sim u_1 \sin \frac{\pi x}{L} \sin \pi z, \quad \delta u_z = 0 \quad \text{at } z=0, L \quad (15)$$

begin to grow without limit. In fact, when (13) is taken into account the change in the free energy (per unit area) associated with the fluctuation (15) is

$$\delta F = \int_0^L \Delta F dz - \frac{(u')^2}{2} BL = \frac{L}{4} \left\{ B \left[\left(\frac{\pi}{L} \right)^2 - p^2 u' \right] + K_1 p^4 \right\} u_1^2 \sin^2 \pi x. \quad (16)$$

The quantity $\delta F \leq 0$, if

$$u' \geq u'_c = \frac{2\pi}{L} \sqrt{\frac{K_1}{B}} \sim \frac{2\pi l}{L}, \quad p_c = \left(\frac{\pi}{L} \right)^{1/2} \left(\frac{B}{K_1} \right)^{1/4} \sim \left(\frac{1}{Ll} \right)^{1/2} \ll \frac{1}{l}. \quad (17)$$

Thus, a small but finite uniform stretching of SLC layers along the z axis leads to instability of the macroscopically uniform state.

In the absence of external perturbations the layer structure of the smectic-A phase is relatively stable. Similar stability is also displayed by SLC with lower orientational symmetry.

4. THE PROBLEM OF THE FERROELECTRIC STATE IN LIQUIDS

The study of ferroelectric phase transitions in liquid crystals has a special aspect. Until recently, liquid

ferroelectrics were unknown. Evidently, the interaction of the constant electric dipole moments rigidly attached to the molecules is weaker than the van der Waals forces of attraction between molecules with a high molecular weight. Therefore, as the temperature is lowered the liquid phase can be transformed to the solid before the transition to the ferroelectric state becomes possible. There can be an insignificant dipole moment per molecule if in the liquid the polar molecules form groupings or clusters in which the constant dipole moments are compensated.

The hypothetical ferroelectric phase transitions from the isotropic liquid are enumerated in the monograph of Ref. 22 and in Ref. 5. In particular, phase transformations with the symmetry change $K \rightarrow C_\infty$ and $K_h \rightarrow C_{\infty v}$ (the so-called proper ferroelectrics, in which the spontaneous polarization \mathbf{P} is the true transition parameter) are discussed. Since a liquid in which a center of symmetry is absent admits the existence in F of the invariant (cf. Ref. 8)

$$\mathbf{P} \text{ rot } \mathbf{P},$$

a $K \rightarrow C_\infty$ phase transition should be accompanied by the appearance of a helical ferroelectric structure, resembling a CLC [cf. (4)]. As a result of a $K_h \rightarrow C_{\infty v}$ phase transformation a uniform polar phase could be formed. However, it has been shown by Khachatryan²³ that an unshorted sample of such a liquid ferroelectric should break up into domains with broad intermediate zones similar to smeared-out Bloch walls, forming, as a whole, a structure similar to a helical ferroelectric. Neither of these two types of ferroelectric liquid crystals has yet been observed experimentally.

Meyer predicted²⁴ the possibility of the onset of spontaneous polarization in special smectic phases—the so-called chiral SLC of the smectic-C and smectic-H types, and this has been confirmed experimentally.²⁴⁻²⁸ It should be noted that measurement of the spontaneous polarization indicates a small effective dipole moment P_0 per molecule: $P_0 \sim 10^{-3} - 10^{-2}$ debye. This means that the dipole-dipole interactions certainly cannot be determining the observed phase-transition temperature $T_c \sim 350^\circ\text{K}$. In Ref. 24 this phenomenon is associated with a phase transformation, observed in SLC, that is accompanied by a lowering of the maximum symmetry D_∞ (the A phase) to the symmetry of the crystallographic class C_2 (the polar C phase). Rather than the polarization, another physical quantity, describing the orientation of the director in space, can serve as the transition parameter in this case. Owing to the linear relationship between this transition parameter and the polarization, there arises, as a secondary phenomenon, a macroscopic distribution of the electric dipole moment.

The effects enumerated become comprehensible if the structure and properties of the liquid-crystalline phases are analyzed on the basis of constructing representations of the corresponding symmetry groups,⁵ in accordance with the well developed techniques of the theory of polymorphous phase transformations.^{6,7} We note that for LC with correlations whose point symmetry is described by one of the 32 crystallographic classes,

the phase transitions are analyzed entirely in analogy with the treatment in Ref. 7. The various representations of the initial group correspond to different degrees of freedom in the transition to a phase with lower symmetry. The greatest interest lies in the analysis of the phase transitions from the high-symmetry smectic phases (the symmetry groups D_∞ and $D_{\infty h}$).⁵

Since the theory predicts the existence of a whole series of new phases, we shall need to introduce some notation for them. We shall retain the usual notation A, B, C , etc. for the centrosymmetric SLC, and we shall distinguish the new modifications that appear by means of extra symbols: an asterisk for noncentrosymmetric phases, a tilde for modulated structures, a prime in the case of ordering of the transverse axes of the molecules, and a bar for polar phases.

5. AN EXAMPLE. PHASE TRANSITIONS FROM A SMECTIC LIQUID CRYSTAL WITH D_∞ SYMMETRY

As the initial phase, we shall consider first a smectic liquid crystal of the type A^* , formed by nonpolar molecular groupings that exist in one of two possible enantiomorphic forms and possess an axis of infinite order, oriented at right angles to the layers (Fig. 3a). The point symmetry of the binary correlator ρ_{12}^m (and the point symmetry of each layer) corresponds to the group D_∞ . This group contains the following generating symmetry elements: rotations $C(\varphi)$ through an arbitrary angle φ about the longitudinal infinite-order axis C_∞ , and rotations U_2 through an angle π about the transverse second-order axes. The representations of the group D_∞ are given in Table I, which shows the characters of the representations, the components of the polarization vector \mathbf{P} , director \mathbf{n} and unit vector \mathbf{n}' perpendicular to the director that serve as the transition parameters, and also the groups that arise in the corresponding phase transformations which are subgroups of the initial group D_∞ .

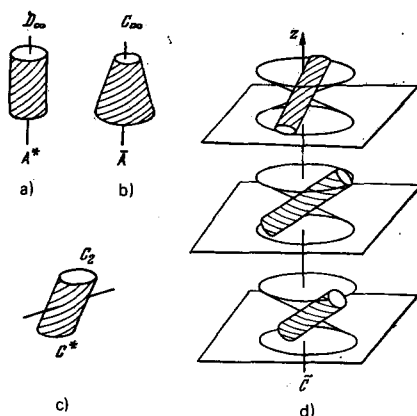


FIG. 3. Phase transitions in smectics with chiral molecules. The symmetry of the subunits in one layer is shown schematically for the initial phase (a) and the phases induced by the representations A_2 (b) and E_1 (c), together with the further change in the space symmetry group on the formation of a modulated structure (d). The point symmetry of the subunits and the proposed notation for the phases are indicated.

TABLE I.

Representation	Transition parameters	Characters of the representation		Subgroup
		$C(\varphi)$	U_2	
A_1		1	1	
A_2	P_z	1	-1	C_∞
E_1	(P_x, P_y) $(n_z n_y, -n_z n_x)$	$2 \cos \varphi$	0	C_2
E_2	$(n_x^2 - n_y^2, 2n_x n_y)$	$2 \cos 2\varphi$	0	D_2
E_m	$(\cos m\varphi, \sin m\varphi)$	$2 \cos m\varphi$	0	D_m

Using Table I in accordance with the usual rules we can analyze the invariant combinations of the transition parameters, confirm the possibility of a second-order transition (for this, third-order invariants should be absent), and ascertain whether the transition occurs to a uniform or to a spatially modulated phase (in the latter case, Lifshitz invariants exist). A calculation shows that second-order transitions are not forbidden anywhere here, and Lifshitz invariants arise for all the two-dimensional representations.

The one-dimensional representation A_1 is the identity representation and corresponds to the symmetry of the initial phase. The one-dimensional representation A_2 is a vector representation and induces a ferroelectric phase transition with the appearance of polarization along the z axis. This hypothetical transition is possible if the molecular groupings are polar and possess dipole moments along the long axes of the molecules. Ordering of the orientation of such subunits would lead to the appearance of a smectic polar phase with lowering of the point symmetry of the binary correlations (and the symmetry of the layers) to C_∞ (Fig. 3b), such that the sequence of polar layers would correspond to the "head-to-tail" rule.²² The two-dimensional representations E_m for $m \geq 2$ describe a lowering of the symmetry of the subunits in which the latter, while losing the C_∞ axis, i.e., acquiring a certain azimuthal asymmetry, retain a finite-order axis C_m and transverse second-order axes. The symmetry of the layers is lowered to D_m . In this case, in the subunits we can distinguish transverse axes \mathbf{n}' whose orientation becomes ordered (Fig. 4a and 4b). Since, here, invariants of third order in the transition parameter are absent and Lifshitz invariants exist, the possible second-order phase transitions should be accompanied by a helical twisting of the transverse axes of the molecule, of the type in Fig. 4c. In the case $m=2$ the structure of the smectic- \bar{A} phase that arises should be analogous to that of a cholesteric phase in the sense of the spatial distribution of the orientations of the unit vector \mathbf{n}' .

The two-dimensional representation E_1 is a vector representation and corresponds to the appearance of polarization in the plane of the layers. This ferroelectric transition is possible if the subunits have dipole moments perpendicular to the long axes of the molecules. However, there exist other, more realistic possibilities of appearance of electric polarization in the case of loss of stability with respect to the representation E_1 . These variants are analyzed below.

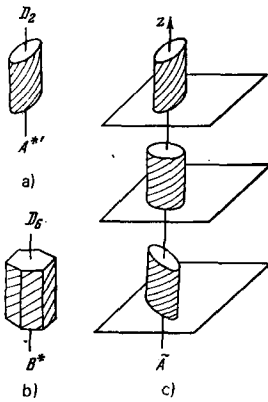


FIG. 4. Symmetry of the chiral subunits in the phases induced by the representations E_2 (a) and E_6 (b), and the helical twisting of the short axes \mathbf{n}^r (c).

6. PSEUDO-PROPER FERROELECTRICS

Since, according to Table I, the components P_x and P_y of the polarization vector transform according to the representation E_1 , these components can serve formally as the parameters of the phase transition induced by the representation E_1 . Physically, however, the transition parameters may turn out to be entirely different quantities.

In particular, it is not difficult to see that the bilinear combinations $n_x n_x$ and $n_y n_y$ of the director components n_i also transform according to the representation E_1 . Here the phase transformation is associated with a tilt of the molecular axes through a certain polar angle θ , lowering the symmetry of the layers to C_2 (see Fig. 3c). Since the molecular groupings in smectic liquid crystals have not been observed to have appreciable transverse dipole moments, the tilt effect is the determining factor and for the transition parameters we should choose not P_x and P_y , but

$$\xi_1 = n_x n_x, \quad \xi_2 = n_y n_y. \quad (18)$$

We note that, under rotations $C(\varphi)$ and U_2 the components P_x and P_y transform like ξ_2 and $-\xi_1$, respectively. Therefore, there exist an invariant

$$P_x \xi_2 - P_y \xi_1 \quad (19)$$

and an analogous invariant with the components of the polarization vector replaced by components of the electric-field intensity, and, consequently, the symmetry of the liquid crystal permits a piezo-effect of the type

$$P_x = D n_x n_x, \quad P_y = -D n_y n_y. \quad (20)$$

Owing to the piezo-effect (20), electric polarization can be induced by the spontaneous tilt of the molecules in the layers.

As is well known,⁸ in the crystallographic classes D_2 , D_4 , and D_6 there exist Lifshitz invariants

$$P_x \frac{\partial P_y}{\partial z} - P_y \frac{\partial P_x}{\partial z}, \quad (21)$$

which, as was pointed out in Refs. 7 and 8, could give rise to stratification (helicity) of the ferroelectric structure. Subsequently, in analogy with the investiga-

tions of modulated magnetic substances,²⁹ theoretical³⁰ and experimental^{31,32} investigations of modulated ferroelectrics have been carried out over a number of years, but until recently no reliably established examples of helical ferroelectric crystals have been found.

In our case, the maximal symmetry group D_∞ , corresponding to the point symmetry of the initial liquid-crystalline phase A^* , also permits the existence of the variant (21) and the analogous invariant

$$\xi_1 \frac{\partial \xi_2}{\partial z} - \xi_2 \frac{\partial \xi_1}{\partial z} \quad (22)$$

owing to the relation $\{E_1^2\} = A_2$, which states that the anti-symmetric square of the two-dimensional vector representation E_1 contains the one-dimensional vector representation A_2 . The presence of the invariant (22) induces a helical twisting of the molecular axes, of the type in Fig. 3d, i.e., the phase transition from the smectic phase A^* occurs not, in fact, to the C^* phase but to the so-called chiral phase \bar{C} , which possesses a helical ferroelectric structure.

According to (20), the ferroelectric and orientational analyses of the $A^* - \bar{C}$ transition are formally equivalent; however, the above-mentioned absence of an appreciable dipole moment on the subunits and the corresponding small value of the coefficient D make the orientational treatment of the transition preferable. Since polarization is not the true transition parameter, the ferroelectric that arises cannot be regarded as normal. It could be compared with the new classification, predicted in Ref. 8, of ferroelectrics in which polarization cannot be the transition parameter. At present these ferroelectrics are called improper,³³ and the electric polarization in them is proportional to the true order parameter raised to a power greater than unity. Since, in the given case, the polarization is proportional to the transition parameter, the ferroelectric might be called "pseudo-proper" (see, e.g., Ref. 34).

We note also that the symmetric cube of the representation E_1 does not contain the identity representation ($\{E_1^3\} = E_3 + 3E_1$), so that the given phase transformation can be a second-order transition. By constructing the invariants associated with the representation E_1 one can investigate the thermodynamics of the phase transformation $A^* - \bar{C}$.

7. FERROELECTRIC PHENOMENA IN SMECTIC LIQUID CRYSTALS

A. The free-energy density of chiral smectic liquid crystals

Besides the piezo-effect of the type (20), an important piezo-effect of another kind can be found in SLC; polarization appears as a result of bending and twisting of the director in space, because of the relationship

$$P_x = \mathcal{D} \frac{\partial \xi_1}{\partial z}, \quad P_y = \mathcal{D} \frac{\partial \xi_2}{\partial z}, \quad (23)$$

which, simultaneously with the invariant

$$P_x \frac{\partial \xi_1}{\partial z} + P_y \frac{\partial \xi_2}{\partial z} \quad (24)$$

is permitted in the group D_∞ because of the relation $A_2 \times E_1 = E_1$. The existence of an analogous piezo-effect

(the so-called flexo-electric effect) in the nematic phase was predicted by Meyer³⁵ and has been observed experimentally.^{36,37} It is not difficult to convince oneself that in an $A^* \rightarrow \bar{C}$ phase transformation the piezo-effect (23) gives rise to the phenomenon of pseudo-proper ferroelectricity.

Assuming the degree of order Q of the long axes of the molecules to be constant, we can write the free-energy density of the smectic phase with allowance for the invariants (19), (22), and (24) in the form

$$F = a(\xi_1^2 + \xi_2^2) + b(\xi_1^2 + \xi_2^2)^2 + \lambda \left(\xi_1 \frac{\partial \xi_2}{\partial x} - \xi_2 \frac{\partial \xi_1}{\partial x} \right) + \frac{1}{2} K_3 \left[\left(\frac{\partial \xi_1}{\partial x} \right)^2 + \left(\frac{\partial \xi_2}{\partial x} \right)^2 \right] + \frac{1}{2\chi} (P_x^2 + P_y^2) - \mu_1 (P_x \xi_2 - P_y \xi_1) - \mu_2 \left(P_x \frac{\partial \xi_1}{\partial x} + P_y \frac{\partial \xi_2}{\partial x} \right) + \dots, \quad (25)$$

where ξ_1 and ξ_2 are defined by (18), $a = a'(T - T_0)$, $b > 0$, K_3 is an elastic constant, μ_1 and μ_2 are the piezo-constants, and χ is the dielectric susceptibility. The ferroelectric phase is characterized in the given case by a tilt of the director through an angle θ from the z -axis and by a helical twist of the director about this axis. Minimizing the expression (25) with respect to the polarization \mathbf{P} and substituting the values

$$\xi_1 = \frac{1}{2} \sin(2\theta) \cos(qz), \quad \xi_2 = \frac{1}{2} \sin(2\theta) \sin(qz),$$

we obtain for $|\theta| \ll 1$

$$P_x = \bar{D} \theta \sin(qz), \quad P_y = -\bar{D} \theta \cos(qz), \quad \bar{D} = \chi(\mu_1 - \mu_2 q), \\ F = \left[a - \frac{1}{2} \chi \mu_1^2 - \frac{(\lambda + \chi \mu_1 \mu_2)^2}{2(K_3 - \chi \mu_1^2)} \right] \theta^2 + b \theta^4 + \frac{1}{2} (K_3 - \chi \mu_1^2) \theta^2 (q - q_c)^2, \quad (26) \\ \frac{\partial F}{\partial q} \Big|_{q=q_c} = 0, \quad q_c = \frac{\lambda + \chi \mu_1 \mu_2}{\chi \mu_1^2 - K_3}.$$

The expression (26) has meaning only for sufficiently small values of the piezo-constant μ_2 : $\chi \mu_2^2 \ll K_3$. For $\chi \mu_2^2 \gg K_3$ the last term in (26) becomes negative and the minimum of the quantity F should correspond to large values of $q \sim 1^{-1}$. But in this case ($ql \sim 1$) the expansion (26) is incorrect, since it is necessary to take gradient terms of higher order in q into account. Typical estimates ($K_3 \sim 10^{-6}$, $\chi \sim 1$, $\mu_2 \sim 10^{-4}$ in cgs units³) show that $\chi \mu_2^2 \ll K_3$.

From (26) it can be seen that below the transition point T_c , determined by the relation

$$T_c = T_0 + \frac{\chi \mu_1^2}{2a'} + \frac{1}{2a'} (K_3 - \chi \mu_1^2) q_c^2,$$

the appearance of a finite angle of tilt of the molecular axes leads to the development in the \bar{C} phase of a pseudo-proper polarization with amplitude

$$|\mathbf{P}| \sim \chi |\mu_1 - \mu_2 q| \theta. \quad (27)$$

According to (26), the direction of the polarization is perpendicular to the z axis and rotates about this axis with pitch $2\pi/q$.

If $|\mu_1| \ll |\mu_2 q|$,⁴⁾ the effective dipole moment per mole-

⁴⁾ Apparently, this situation is observed in experiment: cf. B. I. Ostrovskiy, A. Z. Rabinovich, S. A. Sonin, B. A. Strukov, and S. A. Taraskin, in the book of the Fourth International Conference on Ferroelectricity, Leningrad, 1977, Report 4F-5; see also Zh. Eksp. Teor. Fiz. 74, 1748 (1978) [Sov. Phys. JETP 47, 912 (1978)].

cule in the liquid helical ferroelectric is proportional to the wave vector q and should amount to a small fraction, of order ql , of the magnitude of the constant dipole moment (of the order of a debye) rigidly attached to an individual molecule. The measure electric polarization per molecule amounts to hundredths of a debye, which agrees with the typical value $ql \sim 10^{-2}$ in such an SLC.

We note that, generally speaking, a modulated structure arises because of the presence in the expression (25) of two Lifshitz invariants, which correspond to different physical effects. If the piezo-effects (20) and (23) play the dominant role, we can neglect the contribution of the invariant (22) and put $\lambda = 0$. In this case, from (26) we find

$$q \sim -\frac{\chi \mu_1 \mu_2}{K_3}, \quad \bar{D} \sim \chi \mu_1, \quad |\lambda| \ll \chi |\mu_1 \mu_2|. \quad (28)$$

In the opposite case, when the flexo-electric effect (23) is small, we can put $\mu_2 = 0$. Now the helical twisting is determined by a cholesteric effect, characterized by the quantity λ , and from (26) it follows that

$$q \sim -\frac{\lambda}{K_3}, \quad \bar{D} \sim \chi \mu_1, \quad \chi |\mu_1| \mu_2^2 \ll |\lambda \mu_2| \ll |\mu_1| K_3. \quad (29)$$

Under the condition

$$\lambda + \chi \mu_1 \mu_2 = 0 \quad (30)$$

the contributions of the two Lifshitz invariants cancel, and the existence of a macroscopically uniform ferroelectric state is possible:

$$q = 0, \quad \xi_1 = \theta, \quad \xi_2 = 0, \quad P_x = 0, \quad P_y = -\chi \mu_1 \theta. \quad (31)$$

Apparently, this effect can be realized experimentally by forming LC mixtures whose components are characterized by different relative sizes of the cholesteric and flexo-electric effects.

It should be noted that in the cholesteric phase and in smectic phases of the \bar{A} type, for which the expressions (19), (20), (23), and (24) are valid, the phenomenon of pseudo-proper ferroelectricity is impossible, since the equality $n_x = 0$ or $n'_x = 0$, respectively, forbids the existence of polarization.

B. Change of the pitch of the helical structure

In the approximation considered, the pitch of the helix is a constant quantity, independent of temperature. This result can change when thermal fluctuations are taken into account. Using (25) we can calculate the mean square fluctuation of the pitch of the helix:

$$\langle (q - q_c)^2 \rangle = \frac{T_c}{V(K_3 - \chi \mu_1^2) \theta^2(T)}. \quad (32)$$

From (32) it can be seen that the variance of q increases like θ^{-2} as $T \rightarrow T_c$.

It is not difficult to see that allowance for long-wavelength fluctuations near the phase-transition point T_c does not give rise to a singularity in the temperature dependence that appears in the average $\bar{q}(T)$ when an anharmonic term of the form

$$b' q \theta^4, \quad (33)$$

where the sign of the coefficient b' is arbitrary, is included in the expression (26). From (26) and (33) it can

be seen that the inclusion of invariants depending on the wave vector q leads, in fact, to a corresponding renormalization of the coefficients a and b in the effective Hamiltonian:

$$\left. \begin{aligned} \delta F &= \int \left\{ \left[a'(T_i - T_c) + \frac{1}{2} K_3 (q - q_c)^2 \right] \theta^2(\mathbf{r}) \right. \\ &\quad \left. + (b + b'q) \theta^4(\mathbf{r}) + q_{\parallel} \left(\frac{\partial \theta}{\partial x} \right)^2 + q_{\perp} \left[\left(\frac{\partial \theta}{\partial x} \right)^2 + \left(\frac{\partial \theta}{\partial y} \right)^2 \right] \right\} dV, \\ \theta(\mathbf{r}) &= \theta + \delta \theta(\mathbf{r}), \quad \delta \theta(\mathbf{r}) = \sum_{\mathbf{k}} \theta_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad \theta_{\mathbf{k}} = \theta_{\mathbf{k}} + i\theta_{\mathbf{k}}, \\ F &= -T \ln \int e^{-\delta F} \prod_{\mathbf{k}} d\theta_{\mathbf{k}} d\theta_{\mathbf{k}}^*, \quad \frac{\partial F}{\partial q} \Big|_{q=q_c} = 0. \end{aligned} \right\} \quad (34)$$

As is well known,⁶ such a renormalization does not change the critical indices pertaining to the singular temperature dependence of the quantity F .

Thus, the singular part of the free energy can be written in the form

$$\delta F = -(R + R'b'q) \left[\frac{T_c - T}{T_c} - \frac{K_3}{2T_c a'} (q - q_c)^2 \right]^{2-\alpha}, \quad T < T_c. \quad (35)$$

From the extremal condition for the quantity δF , we find

$$\bar{q} - q_c \sim \frac{a'b'R'(T_c - T)}{(2-\alpha)RK_3} \xrightarrow{T \rightarrow T_c} 0. \quad (36)$$

We note that, according to (35) and (36), the average $\bar{q} = q_c$ if $b' = 0$. As the temperature is lowered the deviation $\bar{q} - q_c$ can become of the order of magnitude of q_c when

$$T_c - T \sim \frac{RK_3 q_c}{a'b'R'},$$

i.e., in the immediate vicinity of the point T_c , if $q_c l \ll 1$. The experimentally observed²⁵ temperature behavior of the pitch of the helical structure agrees qualitatively with the estimates obtained above: the pitch of the helix changes in a narrow temperature interval (of roughly a few degrees), q varies linearly near T_c , and there is no singularity. Since the pitch of the helix can change substantially near the transition point, according to (27) the temperature dependences of the polarization and angle of tilt of the molecules do not, generally speaking, coincide. As regards the dependence $\theta \sim (T_c - T)^\beta$, according to (18) the phase \bar{C} , like the phase C can be modeled in practice by a system of planar rotators (the Vaks-Larkin³⁸ model), which has been analyzed numerically³⁹ and is characterized by the critical indices $\alpha = 0.02$ and $\beta = 0.33$. The latest experimental data²⁸ state that $\beta \approx 0.31$, and that the temperature dependences of the quantities $\theta = |\mathbf{P}|$ are different.

C. Piezo-effect in the A^* phase

Above the temperature T_c , in the smectic- A^* phase, the piezo-effect of the type (20) leads to a corresponding tilt of the director \mathbf{n} away from the z axis under the action of an electric field \mathbf{E} parallel to the smectic planes:

$$n_z n_y = d^* E_x, \quad n_z n_x = -d^* E_y. \quad (37)$$

A uniform external field \mathbf{E} gives rise to a uniform tilt of the director \mathbf{n} . In this case the free-energy density can be written in the form

$$F = \left(a - \frac{1}{2} \chi \mu_1^2 \right) \theta^2 + b\theta^4 - \chi \mu_1 \theta E, \quad (38)$$

where $E_x = E$, $E_y = 0$, $n_y = 0$, and $n_z = \theta$. Minimizing the expression (38) with respect to the order parameter θ , we obtain

$$\theta \sim \begin{cases} -\frac{\chi \mu_1 E}{2a'(T - T_c) + K_3 q_c^2}, & E \ll \frac{a^3}{\chi \mu_1 \sqrt{b}}, \\ \sqrt[3]{\frac{\chi \mu_1 E}{4b}}, & E \gg \frac{a^3}{\chi \mu_1 \sqrt{b}}. \end{cases} \quad (39)$$

We emphasize that, according to (37) and (39), by virtue of the inequality $lq_c \ll 1$ the temperature dependence of the coefficient d^* is close to the Curie law. However, near the transition point T_c the quantity d^* remains finite:

$$d^* = \frac{\chi \mu_1}{K_3 q_c^2}, \quad T \gg T_c. \quad (40)$$

The equality (40) is valid if the correlation length r_c , which is proportional to $(T - T_c)^{-1/2}$ in the approximation under consideration, is greater than the pitch of the helix: $r_c \gg q_c^{-1}$. At temperatures corresponding to the inequality $r_c < q_c^{-1}$ the response of the system to an external perturbation is similar to the response of a spatially uniform medium (the Curie law). The linear effect (39) has been observed experimentally.⁴⁰

D. Behavior of the helical structure in an external field

An experimental proof of the existence of spontaneous polarization in the \bar{C} phase is the unwinding of the helix in an external field \mathbf{E} as a result of the interaction of the dipole moments with the electric field.^{24,28} Putting $E_x = 0$, $E_y = E$, and $q = d\varphi/dz$, we write the free-energy density of the system in the external field in the form [cf. (26)]

$$F = F_0 + \frac{1}{2} K_3 \theta^2 \left(\frac{d\varphi}{dz} - q_c \right)^2 + \chi \mu_1 E \theta \cos \varphi. \quad (41)$$

Varying the expression (41) with respect to φ , we obtain an equation describing the distribution of the angle $\varphi(z)$ in the external field:

$$K_3 \theta \frac{d^2 \varphi}{dz^2} + \chi \mu_1 E \sin \varphi = 0. \quad (42)$$

In a weak field $E \ll K_3 q_c^2 \theta / \chi \mu_1$, the solution of Eq. (42) has the form

$$\varphi = q_c z + \frac{\chi \mu_1 E}{K_3 q_c^2 \theta} \sin(q_c z), \quad (43)$$

which corresponds to the appearance of a spatially uniform electric-polarization component

$$\delta P_y = \frac{1}{2} \frac{\tilde{D} \mu_1}{K_3 q_c^2} \chi E = \begin{cases} \frac{K_3}{2\chi \mu_1^2} \chi E, & |\mu_2 \lambda| \ll \chi |\mu_1| \mu_2^2 \ll |\mu_1| K_3, \\ \frac{1}{2} \frac{\chi \mu_1 \mu_2}{\lambda} \frac{\mu_1 K_3}{\mu_2 \lambda} \chi E, & \chi |\mu_1| \mu_2^2 \ll |\mu_2 \lambda| \ll |\mu_1| K_3, \\ \frac{1}{2} \frac{\chi \mu_1 \mu_2}{\lambda} \chi E, & \chi |\mu_1| \mu_2^2 \ll |\mu_1| K_3 \ll |\mu_2 \lambda|. \end{cases} \quad (44)$$

At a certain threshold value $E = E_c$ of the electric field, complete unwinding of the helix occurs: $\varphi = \pi$. From (41) we find that

$$E_c = \frac{K_3 q_c^2 \theta}{2\chi \mu_1} = \begin{cases} \frac{\lambda^2 \theta}{2K_3 \chi |\mu_1|}, & |\lambda| \gg \chi |\mu_1 \mu_2|, \\ \frac{\chi |\mu_1| \mu_2^2 \theta}{2K_3}, & |\lambda| \ll \chi |\mu_1 \mu_2|. \end{cases} \quad (45)$$

We note that from the experimental data on the pitch $2\pi/q$ of the helix, on the threshold field $E_c \sim \theta$, and on the uniform polarization component $|\delta P| \sim E$ and spontaneous polarization $|\mathbf{P}| \sim \theta$ in the \bar{C} -phase, and also from the data on the piezo-effect $\theta \sim E$ in the A^* -phase, the material constants λ , μ_1 , μ_2 , χ , and K_3 that appear in the expressions (26), (27), (39), (44), and (45) can, in principle, be determined.

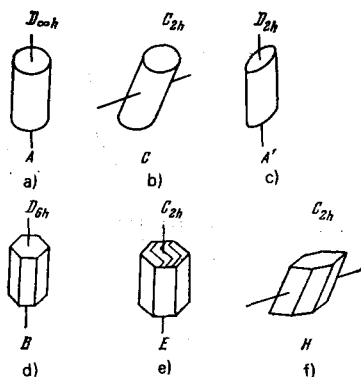


FIG. 5. Phase transitions from a centrosymmetric A phase. The symmetry of the subunits in one layer is shown schematically for the initial phase (a) and the phases induced by the representations E_{1g} (b), E_{2g} (c), and E_{2g} (d), together with the further symmetry change $D_{6h} \rightarrow C_{2h}$ induced by the representations E_{2g} (e) and E_{1g} (f).

8. GENERAL SCHEME OF THE PHASE TRANSITIONS BETWEEN LIQUID-CRYSTALLINE PHASES

By analogy with the case considered above, in which the initial (high-symmetry) phase had D_{∞} symmetry, phase transitions from liquid-crystalline phases with a different initial symmetry can be investigated. If the initial phase is a centrosymmetric smectic- A crystal (Fig. 5a), the point symmetry of the correlations corresponds to the group $D_{\infty h}$. The irreducible representations of this group are found from the irreducible representations of the group D_{∞} and are divided into two classes: the symmetric representations, which possess the same characters for operations of the first and second kinds, differing by an inversion, and the antisymmetric representations, in which the characters for operations differing by an inversion have opposite signs. Modulated structures do not arise in this case, since Lifshitz invariants do not exist. Therefore, the phenomenon of pseudo-proper ferroelectricity is absent. Amongst the representations of the group $D_{\infty h}$ we note the following:

The one-dimensional antisymmetric representation A_{2u} , which induces a transition to the noncentrosymmetric phase A^* considered in Sec. 3;

the two-dimensional symmetric representation E_{1g} , describing the experimentally observed second-order phase transition to a C phase, with lowering of the symmetry of the layers to C_{2h} (Fig. 5b);

the two-dimensional symmetric representation E_{2g} , describing a hypothetical second-order transition to an A' phase (Fig. 5c), with lowering of the symmetry of the layers to D_{2h} ;

the two-dimensional symmetric representations E_m with $m \geq 3$, which induce phase transitions analogous to the observed phase transformation of an A -phase to a B -phase,³ if this is interpreted as the corresponding lowering of the point symmetry of the subunits (Fig. 5d).

Further lowering of the symmetry of the smectic phases, e.g., for a B -phase with the symmetry group

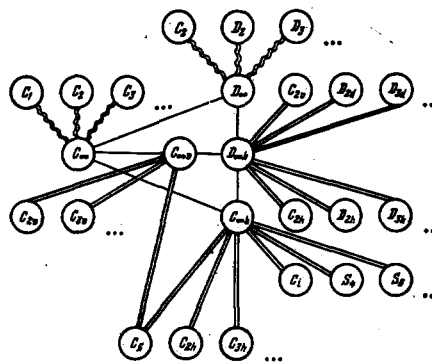


FIG. 6. General scheme of the possible phase transitions from a uniaxial smectic- A phase (point symmetry group $D_{\infty h}$). The symmetry changes induced by one-dimensional representations (the straight lines) and two-dimensional representations (the double lines), including the formation of helical structures (the wavy lines), are indicated.

D_{6h} , is treated in analogy with Ref. 7 and gives a wealth of possible transformations. For example, $D_{6h} \rightarrow C_{2h}$ transitions of two types are possible: a first-order transition, induced by the representation E_{2g} , to a phase of the type of the observed smectic E^{41} (Fig. 5e), and a second-order transition, induced by the representation E_{1g} , to a phase of the type of the observed smectic H^{42} (Fig. 5f). The general scheme of the possible types of lowering of the symmetry of the initial phase with the maximal symmetry group $D_{\infty h}$ is shown in Fig. 6. It follows from this scheme that the possibilities for experimental discovery of liquid-crystalline structures of different types are still far from exhausted.

9. PHASE DIAGRAMS IN LIQUID CRYSTALS

One type of phase diagram has been described above (see Fig. 1). We shall discuss another example of the phase diagrams recently observed experimentally.⁴³ Figure 7a depicts schematically $N \leftrightarrow A$, $A \leftrightarrow C$, and $N \leftrightarrow C$ phase-transition lines that intersect at one point T^* , corresponding to a certain intermediate concentration M^* in a liquid-crystalline mixture. To describe this pattern of phase transitions, it is necessary to include in the expansion of the free-energy density F

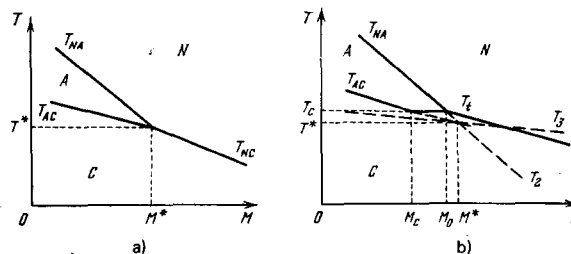


FIG. 7. Phase diagram describing the transformations between the nematic (N) and smectic (A and C) modifications of mixtures of LC with different concentrations M . a) T_{NA} , T_{AC} , and T_{NC} are lines of second-order phase transitions; b) T_4 is a line of first-order $A \leftrightarrow C$ (for $M_c < M < M_0$) and $N \leftrightarrow C$ (for $M > M_0$) phase transitions. T_2 and T_3 are lines of $N \leftrightarrow A$ and $A \leftrightarrow C$ phase transitions, with an intersection point T^* , M^* in the absence of interaction between the corresponding order parameters.

the invariants that can be formed from the order parameters characterizing the *A* and *C* phases. The one-dimensional crystalline order is described by a function ψ (and its conjugate function ψ^*): $\psi = |\psi| \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega)]$, $\mathbf{k} \cdot \mathbf{r} = kz$. Assuming the degree of orientational order Q to be constant in the *N*, *A*, and *C* phases, we shall distinguish the smectic modifications *A* and *C* by the value of the angle θ formed by the wave vector \mathbf{k} and the director \mathbf{n} . In the *A* phase, the angle $\theta = 0$; in the *C* phase, $\theta \neq 0$. Thus, the *A* and *C* phases can be characterized by the following order parameters:

- a) ψ —phase *A*
 b) $(\mathbf{n} \cdot \mathbf{k})[\mathbf{n} \times \mathbf{k}] \psi$ —phase *C* (46)

We note that the order parameters (18) and (46b) coincide to within an unimportant constant factor in the case when the crystal structure $(\mathbf{k}, |\psi|, \omega)$ is fixed and only the orientation of the director varies.

Putting $|\theta| \ll 1$, $|\mathbf{n} \times \mathbf{k}| = k|\theta|$, and $\mathbf{k} = \text{const}$, and using (46) we write an invariant expression for the free-energy density F in the following form

$$\left. \begin{aligned} F &= F_A + F_C + F_{AC}, \\ F_A &= a_2 |\psi|^2 + c_2 |\psi|^4 + e_2 |\psi|^6 + \dots, \\ F_C &= a_3 \theta^2 |\psi|^2 + c_3 \theta^4 |\psi|^4 + a_4 \theta^4 |\psi|^2 + \dots, \\ F_{AC} &= -\nu \theta^2 |\psi|^4; \end{aligned} \right\} \quad (47)$$

here the coefficients c_2 , c_3 , a_4 , e_2 , and ν are positive quantities, depending weakly on the temperature. The last term in (47) describes the interaction of the order parameters a) and b) from (46). Physically, the fact that the coefficient ν is positive means that a uniform tilt of the molecules in the *C* phase corresponds, on the average, to an increase of the attraction between the molecules in the layers and, correspondingly, to an increase of the amplitude $|\psi|$ of the density wave.

The coefficients a_2 and a_3 depend strongly on the temperature:

$$a_2(T) = a'_2(T - T_2), \quad a_3(T) = a'_3(T - T_3), \quad a'_2 > 0, \quad a'_3 > 0,$$

where the quantities T_2 and T_3 are functions of the concentration M of the mixture and, at a certain value $M = M^*$, are equal: $T_2(M^*) = T_3(M^*) = T^*$. We shall assume that $T_2 > T_3$ for $M < M^*$.

Minimizing the expression (47) with respect to the parameters $|\psi|$ and θ , it is not difficult to analyze the possible phase transitions in the given system. If $M < M^*$, the second-order phase transitions from the nematic phase to the smectic-*A* phase and then to the smectic-*C* phase occur, as depicted in Fig. 7a, at temperatures T_{NA} and T_{AC} determined from the equations

$$\left. \begin{aligned} a_2(T_{NA}) &= 0, \\ \nu a_2(T_{AC}) + 2c_2 a_3(T_{AC}) &= 0. \end{aligned} \right\} \quad (48)$$

When $M = M^*$ the points T_{NA} and T_{AC} coincide with T^* .

If $M > M^*$ the *N* → *A* phase transition does not occur, since in this case the appearance of the density wave is accompanied by a spontaneous tilt of the director through an angle θ at the temperature T_{NC} :

$$\left. \begin{aligned} a'_3(T_{NC}) - 4a_2(T_{NC}) a_4 &= 0, \\ |\psi|^2 \sim T_{NC} - T, \quad \theta^2(T_{NC}) &= -\frac{a_3(T_{NC})}{2a_4}. \end{aligned} \right\} \quad (49)$$

Thus, the given second-order phase transition is characterized by a continuous variation of the amplitude $|\psi|$ of the density wave that arises along the *z* axis, which makes a finite angle with the orientation of the director \mathbf{n} . We note that the quantity $\theta(T_{NC})$ grows with increase of the concentration M , and $\theta(T^*) = 0$.

The expressions (49) have meaning only for sufficiently large values of the parameters $a_4 > |a_3|$ and $c_2 > \nu^2/4c_3$. The role of the mixed invariant F_{AC} in (47) becomes extremely important if the parameter $\bar{c} = c_2 - (\nu^2/4c_3) < 0$. We note that the quantity \bar{c} is the renormalized coefficient c_2 in F_A , which arises after minimization of the free energy (47) with respect to the angle θ under the condition $|\bar{c}|c_3 \gg a_4 e_2$. For negative values of the coefficient \bar{c} , which depends on the concentration M , the character of the *N* → *C* and *A* → *C* phase transformations changes: they become first-order transitions.

If the quantity \bar{c} changes sign when $M > M^*$, then, on the line $T_{NC}(M)$ determined by (49), there exists a critical point $T_{NC}(M_c)$, where the value $M = M_c$ satisfies, in order of magnitude, the relation $c_3 |\bar{c}(M_c)| \sim a_4 e_2$. A different situation arises if $\bar{c} < 0$ when $M < M^*$. We shall discuss this case in more detail.

We shall assume that $\bar{c}(M) \leq 0$ for $M \geq M_c$, and that

$$|\bar{c}| \ll c_3, \quad |\bar{c}(M^*)| c_3 \gg a_4 e_2, \quad \bar{c}(M_c) = 0, \quad M_c < M^*. \quad (50)$$

In this case a critical point T_c arises on the line of *A* → *C* phase transitions; for $M < M_c$ the line of second-order phase transitions is determined by Eq. (48), while for $M > M_c$ the *A* → *C* phase transformation occurs, as a first-order transition, at the temperature

$$\left. \begin{aligned} T_t &= T^* + \frac{T_c - T^*}{M_c - M^*} (M - M^*) + \frac{1}{4} \frac{\bar{c}^2}{e_2 (a'_2 + a'_3 \sqrt{c_2/c_3})}, \\ \left| \frac{M - M^*}{M^*} \right| &\ll \frac{|\bar{c}|^{3/2} \sqrt{c_3}}{e_2 |a_3(0)|}. \end{aligned} \right\} \quad (51)$$

According to (48) and (51), the phase-transition lines $T_{NA}(M)$ and $T_t(M)$ intersect at a point (M_0, T_0) : $M^* - M_0 \sim \bar{c}^2$. For $M > M_0$, in the approximation under consideration, the formula (51) defines a line of first-order *N* → *C* phase transitions. The phase diagram described is depicted in Fig. 7b.

The discontinuities in the density $|\psi|$ and tilt angle θ on the first-order phase-transition line $T_t(M)$ are given, according to (47), (50), and (51), by the expressions

$$\left. \begin{aligned} |\psi|^2 &= \left\{ \begin{aligned} 0, & \quad M > M_0, \quad T > T_t, \\ -\frac{a_2}{2c_2}, & \quad M < M_0, \quad T > T_t, \\ \frac{1}{3e_2} \left[|\bar{c}| + \sqrt{\bar{c}^2 - 3e_2 \left(a_2 + \sqrt{\frac{c_2}{c_3}} a_3 \right)} \right], & \quad T \leq T_t, \end{aligned} \right\} \end{aligned} \right\} \quad (52)$$

$$\theta^2 = \frac{\nu |\psi|^2 - a_3}{2c_3 |\psi|^2} \quad \text{for} \quad T \leq T_t.$$

Since $|a_3(T_t)| \ll \nu |\psi|^2$ for $M > M_0$, on the line of *N* → *C* phase transitions, according to (52), the quantity θ^2 is approximately equal to $\theta^2 = \nu/2c_3$, and with increase of M grows linearly with $\nu(M)$.

We note that the experimental data of Ref. 43 evidently correspond to a situation with $M_c < M^*$. A detailed study of the thermodynamics of the phase transitions in the vicinity of the points (M_c, T_c) and (M_0, T_0) would be of

great interest. In particular, the existence of first-order $A \rightarrow C$ phase transitions in the concentration range $M_c < M < M_0$, together with the possibility of second-order $N \rightarrow C$ transitions for $M^* < M < M_c$, has fundamental significance.

10. SMECTIC-B AND SMECTIC-H PHASES

A. The $A \leftrightarrow B$ phase transition

We mentioned above that the observed phase transitions from a smectic- A phase to a smectic- B phase can be regarded as transformations induced by symmetric representations E_m (with $m \geq 3$) of the group $D_{\infty h}$. In such phase transformations the point symmetry of the subunits undergoes a lowering associated with a well defined ordering of the orientation of the short axes of the molecules, corresponding to the acquisition by the molecular groupings of a certain azimuthal asymmetry (see Fig. 5d). The correlation function $\rho_{12}(r_{12})$, which can be determined from x-ray data, should acquire the corresponding asymmetry at short distances. Treating the function $\psi_A \equiv \psi$ as the order parameter in the A phase, on the basis of the table of irreducible representations of the group $D_{\infty h}$ (see Table I) we choose as the order parameter in the B phase the functions

$$\psi_B^+ = |\psi| S \exp[i(kz + 6\varphi)], \quad \psi_B^- = |\psi| S \exp[i(kz - 6\varphi)], \quad (53)$$

where the quantity S is a measure of the orientational order in a B phase with point symmetry group D_{6h} .

Using the functions (53) it is not difficult to write for the free-energy density F an invariant expression analogous to the formula (47) with $a_4 = 0$, in which we must substitute the quantity S for θ .

It follows from experiment that $A \rightarrow B$ phase transformations are first-order transitions, but in a number of substances these transitions are accompanied by comparatively small entropy and volume discontinuities: the latter have the same order of magnitude as in phase transitions from the isotropic to the nematic phase.⁴⁴ With the assumption that $\nu^2 > 4c_2c_3$, i.e., for sufficiently strong coupling of the positional and orientational order parameters, such behavior of a system in the vicinity of a line of $A \rightarrow B$ phase transitions is described by formulas analogous to (51) and (52).

It is necessary to note that there exist hypotheses⁴⁵⁻⁴⁸ according to which a smectic- B phase can be represented in the form of a set of independent or weakly correlated hard planes, i.e., the $A \rightarrow B$ phase transition is treated as a two-dimensional solidification with the development of long-range positional order, or as a transformation to a plastic crystal. X-ray structural analysis⁴⁹⁻⁵² and other experimental data⁵³⁻⁵⁷ do not give any clear indication of the existence of long-range order in the smectic planes, while at the same time, they do indicate the presence of short-range order in the disposition of the molecules. The size of the discontinuities in the first thermodynamic derivatives can correspond both to the idea of a two-dimensional solidification and to that of an orientational phase transition. There are also experimental data⁵⁸ indicating the presence in the B phase of a special shear vibrational mode (hyper-

sound), which admits an interpretation on the basis of the concept of subunits whose angle φ of orientation oscillates as in an amorphous solid, if the period of the action of the external forces is small compared with the corresponding Maxwell relaxation time.⁵⁹

B. Smectic phases with low point symmetry

McMillian^{47,48} has made an attempt to interpret the structure of low-symmetry smectic phases when the presence of ferroelectric or antiferroelectric ordering of the constant dipole moments in the smectic layers is assumed. These conclusions do not yet have experimental confirmation^{57,60} and come up against the above-mentioned problem of the existence of proper ferroelectricity and antiferroelectricity in a liquid. We emphasize that, in the framework of the phenomenological theory described in Sec. 8, the structure of the smectic phases possessing the same physical properties as the observed mesophases by no means requires the existence of spontaneous polarization with long-range order in the arrangement of the dipole moments of the molecules.

At the same time, phase transitions accompanied by the appearance of electric quadrupole moments in the subunits or molecular clusters are permissible in SLC. The phase transitions with lowering of the symmetry of the subunits that were discussed in Sec. 8 can be interpreted as the result of the appearance of the corresponding quadrupoles and multipoles. In this case the smectic- B phases should possess a well defined electric structure in which the point symmetry of the layer corresponds to the appropriate spontaneous quadrupole moment. For example, by assigning to the figure in Fig. 5d a structure of the type depicted in Fig. 8a we see that such a B phase has the lower symmetry D_{3h} and is induced by the irreducible representation E_{3u} of the group $D_{\infty h}$.

The phase transition from the smectic- C phase to the so-called B phase with tilted molecules^{49,61} can serve as another example. From the point of view of the change in the point symmetry, such a phase transformation can be interpreted as a $C_{2h} \rightarrow C_i$ transition induced by the one-dimensional representation B_g with the formation of an electric structure of the type depicted in Fig. 8b. We note that the above-mentioned smectic phase of the H type (see Fig. 5d) can also possess the lower symmetry C_i , and coincides essentially with the above variant of the B phase.

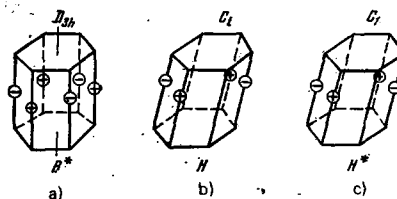


FIG. 8. Symmetry of the subunits in one layer for the low-symmetry smectic phases induced by the representations E_{3u} of the group $D_{\infty h}$ (a), B_g of the group C_{2h} (b), and B of the group C_2 (c). As above, we use the notation adopted in Ref. 72 for the irreducible representations.

Finally, there recently appeared a report⁶² of the discovery of a chiral smectic- \bar{B} phase with tilted molecules, which might also be called the chiral \bar{H} phase. This phase arises experimentally from a chiral \bar{C} phase, and this can be interpreted as a phase transition with a change in the point symmetry of the smectic layer from C_2 to C_1 . The spatial structure of this phase should consist of shapes of the type depicted in Fig. 8b, twisted helically about the normal to the layers. Unfortunately, at the present time there are practically no x-ray structure data that would permit us to establish the symmetry groups of the smectic- B and smectic- H phases and the more complicated modifications.

11. CHARACTER OF THE PHASE TRANSITIONS IN LIQUID CRYSTALS

Depending on the type of irreducible representation of the point or space symmetry group and on the relative sizes of the invariants, the corresponding phase transformation can be either a second order or a first order transition. First-order phase transitions can also occur in the absence of third-order invariants if a fourth-order invariant is negative. When the system is described by several parameters interacting with each other, in practice the coefficient of an invariant of fourth order in the corresponding parameter is renormalized, and this coefficient becomes negative if the interaction is sufficiently large.

On the other hand, the presence of third-order invariants does not always give rise to a first-order transition, if the phase transformation is described by a multi-component order parameter. In this case a second-order phase transition is possible provided that the principal components, responsible for the transformation, appear only to an even power in the corresponding invariants while the remaining components, regarded as a perturbation, form invariants of odd order. Such a situation is possible, e.g., in CLC when the appearance of nonuniaxiality is taken into account.⁶³ At sufficiently large values of the phenomenological parameter proportional to the wave vector q of the helix, the principal components, describing the phase transition from the isotropic liquid to the cholesteric phase, become the quantities

$$S \sin [2\varphi(z)], S \cos [2\varphi(z)],$$

where the transition parameter S is the degree of orientation of the transverse molecular axes along the direction $n'(z)$ (see Sec. 5 and Table I). The tensor Q_{ij} does not now have the simple form (2). The presence of the invariant $Q_{ij}Q_{jp}Q_{pi}$ does not rule out the existence of a second-order transition, since the components indicated can appear in invariant expressions as even powers only, while the orientational order of type (2) appears only as a perturbation.

There exist, however, physical reasons why phase transformations classified as second-order transitions in the framework of a given phenomenological theory turn out, in reality, to be first-order (although close to second-order) transitions. In all such cases the essential factor turns out to be the presence of additional interaction between the generalized coordinates of the

system undergoing the phase transition⁶⁴ (the thermodynamic average value of these coordinates is the transition parameter in the system). Such degrees of freedom include uniform and nonuniform elastic deformations in SLC, and also perturbations of the orientation of the molecules in LC.

A. The role of orientational fluctuations

The possibility of a first-order $N \rightarrow A$ phase transition as a consequence of thermal fluctuations of the director orientation $\delta n(\mathbf{r})$ was pointed out by Halperin, Lubensky, and Ma.⁶⁵ Allowance for small deviations of the director \mathbf{n} from the z axis is equivalent to changing the phase of the basis functions $\psi = |\psi| \exp(\pm ikz)$ by an amount $\pm k(\delta n_x \cdot x + \delta n_y \cdot y)$. Since the quantity F should not change under a rotation of the system as a whole, the expansion of F with gradient terms taken into account has the form

$$F = a_2 |\psi|^2 + c_2 |\psi|^4 + g_{11} \left| \frac{\partial}{\partial z} \psi \right|^2 + g_{\perp} \left[\left| \left(\frac{\partial}{\partial x} - ik \delta n_x \right) \psi \right|^2 + \left| \left(\frac{\partial}{\partial y} - ik \delta n_y \right) \psi \right|^2 \right] + \frac{1}{2} K_1 \left(\frac{\partial}{\partial x} \delta n_x + \frac{\partial}{\partial y} \delta n_y \right)^2 + \frac{1}{2} K_2 \left(\frac{\partial}{\partial x} \delta n_y - \frac{\partial}{\partial y} \delta n_x \right)^2 + \frac{1}{2} K_3 \left[\left(\frac{\partial}{\partial x} \delta n_x \right)^2 + \left(\frac{\partial}{\partial x} \delta n_y \right)^2 \right]. \quad (54)$$

Expanding the fluctuating quantity $\delta n(\mathbf{r})$ in a Fourier series in a volume V ,

$$\delta n = \sum_{\mathbf{p}} \delta n_{\mathbf{p}} e^{i\mathbf{p}\mathbf{r}}, \quad \delta n_{-\mathbf{p}} = \delta n_{\mathbf{p}}^*,$$

we obtain using (54)

$$\left. \begin{aligned} \langle |\delta n_{\mathbf{p}}|^2 \rangle &= \frac{T}{V} \left[\frac{1}{2g_{\perp} k^2 |\psi|^2 + K_1 p_x^2 + K_2 p_y^2 + K_3 p_z^2} + \frac{1}{2g_{\perp} k^2 |\psi|^2 + K_1 p_y^2 + K_2 p_x^2 + K_3 p_z^2} \right], \\ \langle (\delta n)^2 \rangle_V &= \int \langle |\delta n_{\mathbf{p}}|^2 \rangle e^{i\mathbf{p}\mathbf{r}} \frac{d\mathbf{p}}{(2\pi)^3}. \end{aligned} \right\} \quad (55)$$

From (55) there follows an important qualitative result: for $K_1 = K_2 = K_3 = \bar{K}$ we obtain

$$\langle (\delta n)^2 \rangle_V = \text{const} - \frac{T}{2\pi^3 V \bar{K}} \sqrt{\frac{2g_{\perp} k^2 |\psi|^2}{\bar{K}}}. \quad (56)$$

Thus, according to (54) and (56), because of orientational fluctuations, in the expansion of F in powers of $|\psi|$ there appears a term of third order in $|\psi|$ with a negative coefficient:

$$F = a_2 |\psi|^2 + b_2 |\psi|^3 + c_2 |\psi|^4, \quad a_2 = a_2'(T - T_2), \quad b_2 = -\frac{T}{4\pi^3 V} \left(\frac{2g_{\perp} k^2}{\bar{K}} \right)^{3/2}, \quad c_2 > 0. \quad (57)$$

The expression (57) corresponds, as is well known, to a first-order phase transition at the point

$$T_{NA} = T_2 + \frac{b_2^2}{4a_2'c_2}$$

with temperature hysteresis of order $\delta T \sim b_2^2/4a_2'c_2$.

B. The role of compressibility and impurities

The compressibility of the lattice in the smectic phases can also give rise to a weak first-order phase transition. Since the shear modulus in a one-dimensional lattice is equal to zero, the isotropic model⁶⁴ does not lead to the effect under consideration in such a lattice. However, allowance for the small anisotropy of the elastic properties should change the sign of the effective interaction between the fluctuational oscilla-

tions, as a result of which a first-order transition will occur.⁶⁶

The experimental data⁶⁷ show that the temperature hysteresis, if it exists, is extremely small: $\delta T \leq 10^{-3}$ K, i.e., the effects mentioned are relatively weak. At the same time, a sharp difference is observed between the temperature dependence of the order parameter $|\psi|$ and the behavior of the thermodynamic characteristics near the point T_M as predicted by de Gennes¹¹ on the basis of the analogy between the $N \rightarrow A$ phase transformation and the phase transition to the superfluid state in ^4He . The experimental dependence $|\psi(T)|$ is found to be appreciably weaker.⁶⁷ We note that this weakening of the temperature dependences could be due to the presence in the LC of various impurities; it is well known⁶⁴ that, at a sufficient concentration, these change the character of a transition from first to second order and damp the large-scale fluctuations in the system, thereby weakening the singularities of the thermodynamic quantities. Analogous experimental results⁶⁸ and theoretical conclusions⁶⁹⁻⁷¹ also exist in the case of phase transitions from a cholesteric phase to a smectic- A^* phase. It may be thought that the role of compressibility and defects is especially important in the phase transitions between the different smectic phases, e.g., $A \rightarrow B$, $C \rightarrow H$, $B \rightarrow H$, and $\bar{C} \rightarrow \bar{H}$.

12. CONCLUSION

The attempt undertaken in this review to give a unified description of the thermodynamic states of liquid crystals not only demonstrates the possibility of a group-theoretical analysis of the structure and symmetry of LC, but also shows at the same time the difficulties that arise. In place of the density function, which is sufficient for the description of ordinary crystals, in the case of LC we must use many-particle correlators, and this complicates the identification of the physically independent parameters of the phase transformations. The actual set of symmetry groups necessary for the description of LC remains unclear up to now, since the structures of a number of smectic modifications are not experimentally established. The question of the existence of two-dimensional crystalline layers remains open.

In the review, examples have been given of the formation of spatially nonuniform structures in phase transformations and as the result of the application of an external stress. In both cases the modulations of the structure directly determined the most important physical properties of the LC. These examples are far from encompassing all the types of spatial nonuniformities in LC. Experimentally one observes diverse textures, specific structural defects, and complicated domain structures, which by no means always admit a unique interpretation.

Amongst the phase transformations considered in the review, transformations controllable by external fields are of special interest. Interesting prospects arise in connection with the discovery of liquid ferroelectrics. It follows from the estimates given in the review that it is theoretically possible to obtain not only helical, but

also macroscopically uniform ferroelectric LC. It may be hoped that the group-theoretical approach to the description of the structure, symmetry, and properties of LC will turn out to be just as fruitful as in the case of ordinary crystals.

Notes added in proof. To Sec. 7b. Phenomenologically, the temperature dependence of the pitch of the helix in the \bar{C} phase is described by the expression $\bar{q} = q_c + q'\theta^2 + q''\theta^4$, where $q' < 0$ and $q'' > 0$, which follows from (26) when anharmonic corrections are taken into account.

To Sec. 10b. The possibility of first-order phase transitions from a C phase with preservation of the point symmetry C_{2h} , as a result of which molecular clusters of a different type are formed, is also permitted. In $C \rightarrow H$ transitions the corresponding clusters order orientationally, while in $C \rightarrow F$ transitions such ordering is absent. Further lowering of the symmetry from C_{2h} to C_i corresponds to the formation of a G phase⁵⁰: $F \rightarrow G$, $H \rightarrow G$, and also $E \rightarrow G$; in this case the subunits depicted in Figs. 8b and 8c correspond to the phases G (b) and G^* (c).

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