

Phenomenological theory of the polarized helicoidal smectic C phase*

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We present a Landau theory of the smectic *A* to helicoidal smectic *C* phase transition which has recently been discovered. We analyze qualitatively the molecular interactions between chiral molecules in order to explain the appearance of a twisted smectic *C* phase. Using an expansion of the free energy, we show how a second-order transition takes place. We also study the properties of the system near the phase change: (i) the behavior of the dielectric susceptibility and piezoelectric coefficient; (ii) the transition to a regular smectic *C* phase by means of an electric field. Comparison is made with the available experimental results.

I. INTRODUCTION

It is well known¹ that by adding chiral molecules as a solute in a nematic phase, one obtains a so-called *N** phase in which the nematic director precesses around a direction perpendicular to the director itself. This is a cholesteric phase,¹ which is also the usual liquid crystal phase if the molecules in the sample are all chiral. A strikingly similar effect is obtained in the smectic *C* phase of liquid crystals. A small amount of chiral molecules in a smectic *C* induces a precession of the director around the direction perpendicular to the smectic layers (the *z* axis).¹ Such a "helicoidal smectic *C*" is often called *C** and can be obtained also, similarly to cholesterics, if the sample is composed only of chiral molecules.

Microscopic and elastic theories and a large amount of experiments on the cholesteric phase exist (see, for example, Refs. 1 and 2), but the situation with regard to the *C** phase is still in its early development. Only very recently have new chiral materials been synthesized,³⁻⁷ which are shown to exhibit a *C** phase with peculiar behavior. One of these materials is *p*-decyloxybenzylidene *p*'-amino 2-methyl butyl cinnamate^{5,6} (DOBAMBC). Its molecule has a permanent dipole moment, besides being chiral.

The following effects involving both molecular and dipole ordering^{3-5,7} in the smectic phases have been observed. Shear of the smectic layers over one another produces a distortion in the plane of the shear and a bulk polarization perpendicular to this plane. Conversely, an electric field in the plane of the layer induces a polarization parallel to the field and a distortion normal to the field. The above effects suggest that there is a linear

coupling³ between the polarization and the tilt angle of the *C** phase similar to piezoelectricity (for small angles). This leads to the hypothesis that each layer of the *C** phase is spontaneously polarized. The layer polarization precesses around the *z* axis exactly like the director and is perpendicular to the tilt plane in each layer. There is no bulk polarization in the absence of an external field or a shear, even though some authors agree on the name "ferroelectric" for this phase.

The electric susceptibility⁷ and piezoelectric coefficient⁵ have been measured as functions of temperature in both *A* and *C** phases. Both functions seem to exhibit a cusp at the *A*-*C** phase transition point T_c . If the external electric field is applied in the smectic *C** phase, then the induced uniform polarization and tilt distort the helicoidal structure. The helix disappears completely⁴ at some critical field E_c and one obtains an ordinary (uniform) smectic *C* phase. The pitch of the helix and the tilt angle have also been measured⁴ as functions of temperature, in DOBAMBC and other materials. The results are not clearcut and more experiments are needed. What seems to be suggested so far is that the *A*-*C** phase transition is nearly second order, with a smoothly varying tilt angle and a layer polarization appearing at T_c . Theoretically, there seem to be many questions open in this very interesting field, and we would like to formulate some of them here, and to try to give them a plausible answer: (i) What is the nature of the interaction responsible for the distortion and the polarization in the shear flow experiment and for the close relation between the layer polarization and the molecular alignment? (ii) What is the distortion itself in the presence of the electric field? (iii) In analogy with usual

ferroelectrics, should one expect singularities in the dielectric constant at the $A-C^*$ transition temperature, and of what kind? (iv) What is the electric field dependence of the transition temperature from the A (or C , see below) to the C^* phase?

In Sec. II we propose a possible form of the interaction between the molecules in terms of first- and second-rank tensors, and give arguments as to how they could be responsible for the helicoidal arrangements in the C^* phase. In Sec. III we apply the Landau theory of second-order phase transitions to the $A-C^*$ transition of DOBAMBC and related materials. With all the drawbacks of this point of view, it seems to us that we can obtain from it a correct qualitative picture and some quantitative predictions which can stimulate more experimental work. The relations of the physically observable quantities among themselves and with the parameters of the theory are found in Sec. IV; more precise experiments are needed to check our results, but the qualitative features seem to be in agreement with the available experimental results.

II. INTERMOLECULAR INTERACTION

The problem of the intermolecular interaction between chiral molecules in liquid crystals has been studied recently in the literature.^{2,8} To our knowledge all work of the sort has been aimed at explaining the existence of the cholesteric phase^{2,8} N^* , but as for the C^* phase little or no effort has been made.

Similarly to Ref. 2, let us consider each molecule as being rigid and characterized by first- and second-rank tensors as follows: let us define three unit vectors $\hat{v}^1, \hat{v}^2, \hat{v}^3$ in the directions of the axes 1, 2, 3 fixed with the molecule. The components of the vectors \hat{v}^i with respect to the laboratory axes x, y, z , will be written

$$v_{\alpha}^i \quad (\alpha = x, y, z; \quad i = 1, 2, 3).$$

A permanent dipole moment \vec{p} in the molecule is a first-rank quantity and can be written $\vec{p} = \sum_i p^i \hat{v}^i$. Second-rank tensors like the susceptibilities of the molecule can be written as direct products of v_{α}^i (Refs. 1 and 2):

$$S_{\alpha\beta} = \tau (c^{ij} v_{\alpha}^i v_{\beta}^j).$$

The quantities c^{ij} are constants and depend on the molecule. The symbol τ stands for symmetrization and subtraction of the trace. We can express the interaction between two molecules located at positions \vec{r} and \vec{r}' as a sum of contributions of the form first-rank–first-rank, first-rank–second-rank, and second-rank–second-rank type. In our case, only the terms which are pseudoscalar are

interesting, since we want to examine the effect of chirality on the possible molecular orderings. The lowest order terms of this sort are as follows: one of the first-rank–first-rank type,

$$H_{11} = \sum_{ij} h_{11}^{(ij)} (|\vec{r} - \vec{r}'|) (r_{\alpha} - r'_{\alpha}) \epsilon_{\alpha\beta\gamma} v_{\beta}^i(\vec{r}) v_{\gamma}^j(\vec{r}'), \quad (2.1)$$

where $\epsilon_{\alpha\beta\gamma}$ is the totally antisymmetric tensor in three dimensions; the second is of the first-rank–second-rank type

$$H_{12} = \sum_{ijk} h_{12}^{(i,j,k)} (|\vec{r} - \vec{r}'|) (r_{\alpha} - r'_{\alpha}) v_{\beta}^i(\vec{r}) S_{\beta\alpha}^{jk}(\vec{r}'). \quad (2.2)$$

(Repeated indices of the type α, β , or γ are summed over.) A term of the type (2.2) has been used in a theory of a biaxial cholesteric.² Similar terms of higher orders have been used to explain usual cholesterics.⁸ For the purpose of the discussion in this section, we will consider only terms of the type (2.2). It will be easy to see the effect of terms (2.1) and higher-order terms. All terms up to second-rank–second-rank will be implicitly included in the free-energy expansion of Sec. III.

Usually it is not possible to solve a model with all the interactions exactly, and a number of approximations must be made. For example, when a fast rotation of the molecules around their long axis is present, one could approximate the real molecule with an axially symmetric object. This means to replace the true variables \hat{v}^i describing each molecule, with their time average; therefore in this case terms in (2.1), (2.2) and higher-order terms with $i, j, k = 1, 2$ would not contribute, because the time average of \hat{v}^1, \hat{v}^2 is zero. This is the case considered in Ref. 8. As a further example, the term in (2.2) with $i = j = k = 3$ is of the form

$$c^{33} h_{12}^{(3,3,3)} (|\vec{r} - \vec{r}'|) [(\vec{r} - \vec{r}') \cdot \hat{v}^3(\vec{r}')] [\hat{v}^3(\vec{r}) \cdot \hat{v}^3(\vec{r}')]. \quad (2.3)$$

If $h_{12}^{(3,3,3)}$ is negative, it favors an arrangement in which the long axes of the two molecules are parallel to each other and to the line joining them.

In biaxial cholesterics,² the rotational degree of freedom is frozen and a term in (2.2) with $i = 2, j = 3, k = 1$ favors the biaxial arrangement of the cholesteric twist.

In the case of DOBAMBC the dipole is perpendicular to the 3 axis: the point of view^{3,5} that the smectic layers are polarized leads us to the assumption that the rotation around the 3 axis is frozen. A term in (2.2) with $i = k = 2, j = 1$ favors a precession of layer polarization and a tilting of the director. (Given the geometry of the mole-

cule, we define $\vec{p} = p^1 \vec{v}^1$.) This, together with a simple free-energy stability argument⁹ (which shows how a finite-layer polarization is brought about by the dipole-dipole interaction) can give a rough idea of the types of interactions responsible for the C* phase observed.³⁻⁶

At this point we will not solve the complete model Hamiltonian, expressed as a sum of contributions due to terms of types (2.1) and (2.2) and other similar terms which are appropriate for usual nonchiral molecules. Instead, we will write down a phenomenological free-energy expansion in the spirit of the Landau theory of second-order phase transitions, including implicitly dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole terms.

III. A-C* PHASE TRANSITION

Since it is suggested by experiment³ that the A-C* phase transition is very nearly second order and that the properties of the system vary continuously at T_c , we will assume that it is indeed second-order. We can now apply the Landau theory,¹⁰ to find the dipole and molecular ordering in the C* phase, starting from the symmetry of the A phase. According to the Landau theory,¹⁰ the ordering arising in the lower-symmetry (smectic C*) phase is characterized by a set of functions which transform according to a certain irreducible representation of the space group of the higher-symmetry (smectic A) phase. Further, these functions must represent a field of a certain physical tensor¹¹; the latter must obviously be involved in the phase transition in question. In the case of a smectic A to C* phase transition one is, first of all, concerned with the field of a tensor describing the deviation of the long molecular axis (the director \hat{n}) from the z axis. For such a tensor one can choose the two-component quantity (Q_{xz}, Q_{yz}) , where Q_{xz}, Q_{yz} are related to the Cartesian components n_x, n_y, n_z of the director and to its polar

angles θ and ϕ by the formulas

$$\begin{aligned} Q_{xz} &= n_x n_z = \frac{1}{2} \sin 2\theta \cos \phi, \\ Q_{yz} &= n_y n_z = \frac{1}{2} \sin 2\theta \sin \phi. \end{aligned} \quad (3.1)$$

Such a choice reflects the equivalence of \hat{n} and $-\hat{n}$. Further, the quantity (Q_{xz}, Q_{yz}) is an irreducible tensor, i.e., it transforms under the elements of the point group D_∞ of the smectic A phase of DOBAMBC according to an irreducible representation of this group. Instead of Q_{xz}, Q_{yz} , it is convenient to use the complex components

$$Q_{\xi z} = Q_{xz} + iQ_{yz}, \quad Q_{\eta z} = Q_{\xi z}^*. \quad (3.2)$$

Note that for small θ the parameter $Q_{\xi z}$ coincides with de Gennes'¹ order parameter $\theta e^{i\phi}$ of the C phase. However, for our purposes it is more convenient to use the quantities (3.2).

Another physical tensor involved in the phase transition under consideration is the polarization vector \vec{P} . Thus we have to consider the five-component field $\{Q_{\xi z}(x, y, n), Q_{\eta z}(x, y, n), \vec{P}(x, y, n)\}$, where n enumerates the successive molecular layers in the z direction. This field is obviously reducible with respect to the space group of the smectic A phase (the latter is a semidirect product of the subgroup of pure translations and the point group D_∞). One has to find the irreducible part of this field which is associated with the A to C* phase transition. For this purpose one has to expand the free energy F up to second order¹⁰ in the field components. Since the field of the z component of \vec{P} cannot be coupled to the field of $Q_{\xi z}, Q_{\eta z}$ in the second-order term in the expansion of F (because of the axial symmetry of the A phase), only the components

$$P_\xi = P_x + iP_y, \quad P_\eta = P_\xi^* \quad (3.3)$$

of \vec{P} need to be considered. Then, the second-order term in the expansion of F can be written in the form

$$\begin{aligned} F_2 = \sum_{n, n'} \iiint \iiint [& A_{11}(\rho^2, n - n'; T) Q_{\xi z}(x, y, n) Q_{\eta z}(x', y', n') \\ & + A_{12}(\rho^2, n - n'; T) Q_{\xi z}(x, y, n) P_\eta(x', y', n') \\ & + A_{21}(\rho^2, n - n'; T) P_\xi(x, y, n) Q_{\eta z}(x', y', n') \\ & + A_{22}(\rho^2, n - n'; T) P_\xi(x, y, n) P_\eta(x', y', n')] dx dy dx' dy', \end{aligned} \quad (3.4)$$

where T is the temperature, and

$$\rho^2 = (x - x')^2 + (y - y')^2. \quad (3.5)$$

Note that the second and third terms in square brackets in (3.4) are of the type (2.2), or dipole-quadrupole interaction. The presence of such in-

teraction, as will be clear later, makes it possible to explain, first of all, the appearance of the tilt *together* with the layer polarization at T_c , and secondly, the definite relationship between the direction of the layer polarization and the tilt plane, as mentioned in Sec. I. (Another way to

obtain these effects is discussed in Ref. 12.) A further remark should be made here: each term in (3.4) takes automatically into account the fact that the molecules are chiral, through certain symmetry requirements on the coefficients A_{ij} . In fact, the symmetry of these coefficients reflects, as usual in Landau theory, the symmetry of the higher-symmetry phase. Thus the dependence of A_{ij} ($i, j = 1, 2$) on x, y, n, x', y', n' in the combination defined by (3.5) and only on the difference $n - n'$, reflects the isotropy of the A phase in the xy plane and the periodicity in the z direction. Further properties of the coefficients A_{ij} are as follows. Since F_2 is real, we have

$$A_{ij}^*(\rho^2, n - n'; T) = A_{ji}(\rho^2, n' - n; T). \quad (3.6)$$

F_2 must be invariant under the rotation by π about the x axis, which transforms $P_\xi(x, y, n)$ into $P_\eta(x, -y, -n)$ and $Q_{\xi z}(x, y, n)$ into $-Q_{\eta z}(x, -y, -n)$. It follows that

$$A_{12}(\rho^2, n - n'; T) = -A_{21}(\rho^2, n' - n; T). \quad (3.7)$$

Let us now introduce the Fourier components of $Q_{\xi z}$, $Q_{\eta z}$, P_ξ , P_η , and A_{ij} according to

$$Q_{\xi z}(x, y, n) = \sum_{\vec{k}} q_{\xi z}(\vec{k}) e^{i(k_x x + k_y y)} e^{i k_z n b}, \quad (3.8a)$$

$$P_\xi(x, y, n) = \sum_{\vec{k}} p_\xi(\vec{k}) e^{i(k_x x + k_y y)} e^{i k_z n b}, \quad (3.8b)$$

(and similarly for $Q_{\eta z}$ and P_η), and

$$A_{ij}(\rho^2, n - n'; T) = \sum_{\vec{k}} a_{ij}(\kappa^2, k_z; T) \times \exp\{i[k_x(x - x') + k_y(y - y') + k_z(n - n')b]\}, \quad (3.9)$$

where $\kappa^2 = k_x^2 + k_y^2$ (the dependence of a_{ij} on κ^2 is due to the axial symmetry), and b is the distance between layers. k_z varies only in the interval $(-\pi/b, \pi/b)$. Substituting (3.8) and (3.9) into (3.4), we obtain

$$F_2 = V \sum_{\vec{k}} [a_{11}(\kappa^2, k_z; T) |q_{\xi z}(\vec{k})|^2 + a_{12}(\kappa^2, k_z; T) q_{\xi z}(\vec{k}) p_\xi^*(\vec{k}) + a_{21}(\kappa^2, k_z; T) p_\xi(\vec{k}) q_{\xi z}^*(\vec{k}) + a_{22}(\kappa^2, k_z; T) |p_\xi(\vec{k})|^2] \quad (3.10)$$

(V is the volume of the system); here we have used the obvious relations

$$q_{\xi z}^*(\vec{k}) = q_{\eta z}(-\vec{k}), \quad p_\xi^*(\vec{k}) = p_\eta(-\vec{k}). \quad (3.11)$$

In view of (3.6), the coefficients $a_{ij}(\kappa^2, k_z; T)$ obey the Hermiticity relations

$$a_{ij}^*(\kappa^2, k_z; T) = a_{ji}(\kappa^2, k_z; T); \quad (3.12)$$

hence the expression (3.10) can be diagonalized by an appropriate unitary transformation from the variables $q_{\xi z}(\vec{k}), p_\xi(\vec{k})$ to the new variables $X_\xi(\vec{k}), Y_\xi(\vec{k})$:

$$q_{\xi z}(\vec{k}) = \alpha_{11}(\kappa^2, k_z; T) X_\xi(\vec{k}) + \alpha_{12}(\kappa^2, k_z; T) Y_\xi(\vec{k}), \quad (3.13)$$

$$p_\xi(\vec{k}) = \alpha_{21}(\kappa^2, k_z; T) X_\xi(\vec{k}) + \alpha_{22}(\kappa^2, k_z; T) Y_\xi(\vec{k}),$$

so that

$$F_2 = V \sum_{\vec{k}} [a_1(\kappa^2, k_z; T) |X_\xi(\vec{k})|^2 + a_2(\kappa^2, k_z; T) |Y_\xi(\vec{k})|^2]. \quad (3.14)$$

The new coefficients, $a_1(\kappa^2, k_z; T)$ and $a_2(\kappa^2, k_z; T)$ are the eigenvalues of the matrices $a_{ij}(\kappa^2, k_z; T)$, and they are obviously real. When $T > T_c$, the system is smectic A and the minimum of F (at fixed T) is achieved for $X_\xi(\vec{k}) = Y_\xi(\vec{k}) = 0$ for all \vec{k} . It follows that for $T > T_c$ we must have $a_1(\kappa^2, k_z; T) > 0$ and $a_2(\kappa^2, k_z; T) > 0$ for all κ, k_z . As the temperature is lowered, either $a_1(\kappa^2, k_z; T)$ or $a_2(\kappa^2, k_z; T)$ (say a_1 , without loss of generality) may vanish for certain values of κ and of k_z , (for which a_1 is obviously a minimum) and of the temperature T . This is the transition temperature T_c .^{10,13,14} Therefore T_c is determined by the equation

$$\text{Min}_{\kappa, k_z} \{a_1(\kappa^2, k_z; T_c), a_2(\kappa^2, k_z; T_c)\} = 0. \quad (3.15)$$

The values of k_x, k_y, k_z corresponding to this minimum satisfy the equations

$$\frac{\partial a_1}{\partial k_x} = 0, \quad \frac{\partial a_1}{\partial k_y} = 0, \quad \frac{\partial a_1}{\partial k_z} = 0. \quad (3.16)$$

Since k_x and k_y enter only in the combination $\kappa^2 = k_x^2 + k_y^2$, the first two equations in (3.16) are identically satisfied for

$$k_x = k_y = 0. \quad (3.17)$$

In principle there may be other solutions for k_x, k_y , but only the solution (3.17) is imposed by symmetry, and is the only physical one. In fact a solution with $k_x \neq 0$ or $k_y \neq 0$ would represent a phase in which the molecular orientations vary within the same smectic layer, and it has never been observed in liquid crystals. On the contrary, there is no similar restriction due to symmetry for k_z . Therefore, the minimum of the free energy is achieved for some general $k_z = k_0$, which is in principle a function of temperature. To find $k_0(T)$ one should substitute (3.17) in the third equation of (3.16) and solve with respect to k_z . Within the framework of our phenomenological theory we cannot determine the T dependence of a_1 , therefore also $k_0(T)$ remains undetermined. Below T_c , $a_1(0, k_0, T) < 0$, and therefore the minimum of the free energy F is achieved for a finite value¹⁰ of $X_\xi(k_0, \hat{z})$.

Whenever $k_0(T) \neq 0$ (which is the case in general), the system is a helicoidal C phase¹⁵ (or C^*), with a pitch $\bar{l} = 2\pi\hat{z}/k_0(T)$. Below T_c , but in its vicinity, the minimum of $a_2(\kappa^2, k_z; T)$ is positive, so that the equilibrium values of $Y_\xi(\vec{k})$ are zero. It is possible, in principle, that when T decreases further, this minimum also becomes negative, bringing about an additional phase transition. We shall not investigate this case. We will assume that $Y_\xi(\vec{k})$ is always zero, i.e., we will be concerned with a small enough temperature interval near T_c .

The molecular and dipole ordering in the C^* phase are described by the helicoidal fields

$$Q_{xz}(x, y, n) = \alpha_{11}(0, k_0; T) X_\xi(k_0, \hat{z}) e^{ik_0 nb}, \quad (3.18a)$$

$$P_\xi(x, y, n) = \alpha_{21}(0, k_0; T) X_\xi(k_0, \hat{z}) e^{ik_0 nb}. \quad (3.18b)$$

The fields (3.18a) and (3.18b) [with $X_\xi(k_0\hat{z})$ as a variable] together with their complex conjugates, constitute that irreducible part of the general field $\{Q_{xz}(x, y, n), Q_{yz}(x, y, n), \vec{P}(x, y, n)\}$ which is associated with the $A-C^*$ phase transition. It is easy to express the local biaxiality and the layer polarization in terms of the quantities defined above. One can write

$$Q_{xz}(x, y, n) = |Q| \cos(\phi - \phi_0), \quad (3.19)$$

$$Q_{yz}(x, y, n) = |Q| \sin(\phi - \phi_0), \quad (3.20)$$

$$P_x(x, y, n) = |P| \cos(\phi - \phi_0 + \phi_1), \quad (3.21)$$

$$P_y(x, y, n) = |P| \sin(\phi - \phi_0 + \phi_1), \quad (3.22)$$

where $\phi = k_0 nb$, and the quantities $|P|$, $|Q|$, ϕ_0 , ϕ_1 , are given by

$$|Q| \cos \phi_0 = \text{Re} \alpha_{11} \text{Re} X_\xi(k_0\hat{z}) - \text{Im} \alpha_{11} \text{Im} X_\xi(k_0\hat{z}), \quad (3.23)$$

$$|Q| \sin \phi_0 = \text{Re} \alpha_{11} \text{Im} X_\xi(k_0\hat{z}) + \text{Im} \alpha_{11} \text{Re} X_\xi(k_0\hat{z}), \quad (3.24)$$

$$|P| = |Q| \left| \frac{\alpha_{21}}{\alpha_{11}} \right|, \quad (3.25)$$

$$\phi_1 = \arg(\alpha_{21}/\alpha_{11}). \quad (3.26)$$

It is clear that ϕ_1 is also the angle between the layer polarization $\vec{P} = P_x \hat{x} + P_y \hat{y}$ and the tilt plane (the plane parallel to z and the long molecular axis). It can be easily shown that

$$\alpha_{21}/\alpha_{11} = a_{21}/(a_1 - a_{22}). \quad (3.27)$$

(a_{21} , a_{22} , and a_1 are defined above.) From (3.7) it follows that

$$a_{12}(\kappa^2, k_z; T) = -a_{21}(\kappa^2, k_z; T). \quad (3.28)$$

This, together with (3.12), means that $a_{21}(\kappa^2, k_z; T)$ is purely imaginary. Since a_1 and a_{22} are real, (3.27) is also imaginary and the angle ϕ_1 is equal

to $\frac{1}{2}\pi$. The physical meaning of this result is clear: the polarization in each smectic layer is perpendicular to the tilt plane of the layer. This result was suggested by Meyer *et al.*³ from general symmetry arguments, assuming that the local symmetry of the C^* phase is monoclinic. However, theoretically, one cannot exclude the possibility of triclinic local symmetry, in which case there is no restriction on the direction of the polarization in the layer. Thus, our result above shows that, if the $A-C^*$ transition is second order, the triclinic case is ruled out.

To find the temperature dependence of $X_\xi(k_0\hat{z})$ we have to continue the expansion of F , now in terms of $X_\xi(k_0\hat{z})$ alone, to fourth order

$$F = a_1(0, k_0; T) |X_\xi(k_0\hat{z})|^2 + B |X_\xi(k_0\hat{z})|^4 + \dots \quad (3.29)$$

B is assumed to be positive and practically independent of T . As usual, we assume that $a_1(0, k_0(T); T) \simeq a(T - T_c)$ near T_c . Thus we have

$$|X_\xi(k_0\hat{z})| = (a/2B)^{1/2} (T_c - T)^{1/2}, \quad (3.30)$$

and accordingly $|Q| \propto |P| \propto (T_c - T)^{1/2}$ near T_c . Since k_0 and a_{ij} are in general temperature dependent, the variation of $|Q|$ and $|P|$ with T will be no longer proportional to $(T_c - T)^{1/2}$ when T is well below T_c .

The tilt angle θ of the C^* phase vanishes at T_c also as $(T_c - T)^{1/2}$, since it is proportional to $|Q|$ in the limit $|Q| \rightarrow 0$.

IV. ELECTRIC SUSCEPTIBILITY, AND PHASE TRANSITION IN THE PRESENCE OF AN ELECTRIC FIELD

It is well known¹ that if one applies an electric field to a cholesteric phase in a direction perpendicular to the axis of the helix, then in certain cases there is a critical field E_c above which the helix disappears. In our phase C^* one could expect the same effect, and this has been observed in an electric field. We have to bear in mind, though, that the effect occurring in cholesterics comes from a contribution to the energy quadratic in the field, in the absence of any net magnetic or electric dipole moments in the molecule. In our case, where polarization effects are important, the interaction between the electric dipoles and the electric field has a linear contribution, which should be the greatest one. Therefore, we will introduce a term linear in the field in the expansion of F and study its effects at small fields.

We shall consider only a uniform field and write, instead of (3.29)

$$F = a(T - T_c) |X_\xi(k_0 \hat{z})|^2 + B |X_\xi(k_0 \hat{z})|^4 + a_{11} |q_{\xi z}(0)|^2 + a_{12} q_{\xi z}(0) p_\eta(0) + a_{21} p_\xi(0) q_{\eta z}(0) + a_{22} |p_\xi(0)|^2 + |X_\xi(k_0 \hat{z})|^2 \times [c_{11} |q_{\xi z}(0)|^2 + c_{12} q_{\xi z}(0) p_\eta(0) + c_{21} p_\xi(0) q_{\eta z}(0) + c_{22} |p_\xi(0)|^2] - \frac{1}{2} [p_\xi(0) E_\eta + p_\eta(0) E_\xi], \quad (4.1)$$

where we have designated $a_{ij} \equiv a_{ij}(0, 0; T)$, $E_\xi = E_x + iE_y$, $E_\eta = E_z^*$. In (4.1) $p_\xi(0)$, $p_\eta(0)$ describe the uniform component of the polarization and $q_{\xi z}(0)$ is the uniform component of the field $Q_{\xi z}(x, y, z)$. We have neglected terms of fourth order in $p_\xi(0)$, $p_\eta(0)$, $q_{\xi z}(0)$, $q_{\eta z}(0)$, since we shall suppose the field to be small. Further, we consider only temperatures near T_c (above and below). Thus the coefficients a_{ij} and c_{ij} are practically temperature independent. In the same manner as (3.12) and (3.28), it can be shown that

$$c_{ij} = c_{ji}^*, \quad c_{12} = -c_{21}, \quad (4.2)$$

so that c_{12} and c_{21} are purely imaginary, like a_{12} , a_{21} .

In thermodynamic equilibrium we have the following stationarity conditions: $\partial F / \partial X_\xi(k_0 \hat{z}) = 0$, $\partial F / \partial q_{\eta z}(0) = 0$, and $\partial F / \partial p_\eta(0) = 0$, which yield the three equations

$$X_\xi(k_0 \hat{z}) [a(T - T_c) + c_{11} |q_{\xi z}(0)|^2 + c_{12} q_{\xi z}(0) p_\eta(0) + c_{21} p_\xi(0) q_{\eta z}(0) + c_{22} |p_\xi(0)|^2 + 2B |X_\xi(k_0 \hat{z})|^2] = 0; \quad (4.3)$$

$$[a_{11} + c_{11} |X_\xi(k_0 \hat{z})|^2] q_{\xi z}(0) + [a_{21} + c_{21} |X_\xi(k_0 \hat{z})|^2] p_\xi(0) = 0; \quad (4.4)$$

$$[a_{12} + c_{12} |X_\xi(k_0 \hat{z})|^2] q_{\xi z}(0) + [a_{22} + c_{22} |X_\xi(k_0 \hat{z})|^2] p_\xi(0) = 0. \quad (4.5)$$

One of the solutions of (4.3) is $X_\xi(k_0 \hat{z}) = 0$, and we get, by substituting it into (4.4), (4.5) and then solving

$$q_{\xi z}(0) = -a_{12} E_\xi / 2 \text{deta}_{ij}, \quad (4.6)$$

$$p_\xi(0) = a_{11} E_\xi / 2 \text{deta}_{ij}. \quad (4.7)$$

From (4.7) we find the electric susceptibility

$$\chi = a_{11} / 2 \text{deta}_{ij}, \quad (4.8)$$

which is also the zero-field susceptibility of the smectic A phase. Equation (4.6) indicates that the presence of a uniform electric field gives rise to a uniform tilt and therefore it distorts the A phase into an ordinary C phase. The plane of the uniform tilt is normal to the field, because $q_{\xi z}(0) / E_\xi$ is imaginary. This is a remarkable result, and it is due to the interaction of the first-rank-second-rank type and the symmetry requirements on the free energy. Equations (4.3)–(4.5) have also a solution with $X_\xi(k_0 \hat{z}) \neq 0$. If $|T - T_c|$ and $|E_\xi|$ are sufficiently small, we can neglect

$|X_\xi(k_0 \hat{z})|^2$ in Eqs. (4.4) and (4.5). Then substituting (4.6) and (4.7) in (4.3), we get

$$|X_\xi(k_0 \hat{z})|^2 = -[a(T - T_c) + bE^2] (2B)^{-1} \quad (4.9)$$

[with $E = |E_\xi| = (E_x^2 + E_y^2)^{1/2}$], where

$$b = \frac{c_{22} a_{11}^2 + c_{11} |a_{12}|^2 + 2a_{11} c_{12} a_{12}}{4(\text{deta}_{ij})^2}. \quad (4.10)$$

Solution (4.9) exists only if $a(T - T_c) + bE^2 < 0$. This condition defines the new phase-transition temperature

$$T_c(E) = T_c - (b/a)E^2. \quad (4.11)$$

Experimentally, if we turn on the field at $T < T_c$, we reach a critical E_c at which the twist disappears. Therefore, $T_c(E)$ should be smaller than T_c , or $b > 0$ since $a > 0$. The sign of b cannot be obtained from our theory, but we can relate it to the behavior of the dielectric zero-field susceptibility near T_c , as will be shown below. Equation (4.11) can also be used to find this critical field

$$E_c(T < T_c) = (a/b)^{1/2} (T_c - T)^{1/2}. \quad (4.12)$$

If $E \neq 0$, the C-C* transition is of second order; if we define

$$\Delta T = T_c(E) - T, \quad (4.13)$$

we find

$$|X_\xi(k_0 \hat{z})| = (a/2B)^{1/2} (\Delta T)^{1/2}, \quad (4.14)$$

similarly to (3.30). The line $T_c(E)$ is shown in Fig. 1.

In the next order of approximation, using (4.9) in (4.4) and (4.5), the values of $q_{\xi z}(0)$ and $p_\xi(0)$ are

$$q_{\xi z}(0) = \frac{a_{12} E_\xi}{2 \text{deta}_{ij}} + \frac{b'}{B} E_\xi [a(T - T_c) + bE^2], \quad (4.15)$$

$$p_\xi(0) = \frac{a_{11} E_\xi}{2 \text{deta}_{ij}} + \frac{b}{B} E_\xi [a(T - T_c) + bE^2], \quad (4.16)$$

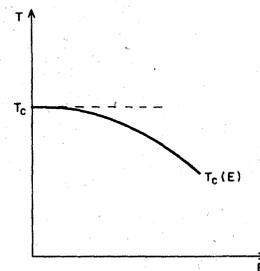


FIG. 1. Schematic phase diagram in the E - T plane. The smectic A and undistorted C* phases exist only at $E = 0$. If $E \neq 0$, above the line $T_c(E)$ we have a smectic C, and below it we have a distorted C*.

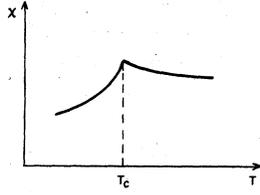


FIG. 2. Qualitative temperature dependence of the dielectric susceptibility (the field is parallel to the smectic layers) at $E \rightarrow 0$.

where

$$b' = \frac{a_{12}(a_{22}c_{11} + a_{11}c_{22} + a_{12}c_{12}) - c_{12}a_{11}a_{22}}{4(\det a_{ij})^2}. \quad (4.17)$$

The physical significance of (4.9), (4.15) and (4.16) can be understood if we translate them to the language of "tilt" and "polarization." A non-zero $X_\xi(k_0\hat{z})$ means precessing polarization and tilt, which disappear at $T \geq T_c(E)$. $q_{iz}(0)$ and $p_\xi(0)$ mean, respectively, a uniform biaxiality and a uniform polarization, independent of coordinates; they are proportional to the electric field and appear as soon as the field is turned on. Their effect can be described also as a tilting of the axis around which the molecules precess, with respect to the z axis. As the electric field increases, the aperture of the cone described by the molecules around this new axis decreases. Therefore the C^* phase is distorted in the electric field. When T is raised at constant E , or E is raised at constant T , this distorted C^* undergoes a transition to an ordinary C phase.

Within the approximations used here for small E , this transition is not accompanied by an "unwinding effect," as is the case in the cholesteric-nematic transition in the presence of an external field.¹ The helix of the C^* phase disappears only because $|X_\xi(k_0\hat{z})| \rightarrow 0$ at the transition.

From (4.16) one can calculate the zero-field susceptibility, which is shown schematically in Fig. 2:

$$\chi = \frac{a_{11}}{2\det a_{ij}} + \frac{ba}{B}(T - T_c). \quad (4.18)$$

χ is continuous through T_c [see (4.8) and (4.18)], but

$$\left. \frac{d\chi}{dT} \right|_{T > T_c} = \frac{d}{dT} \left(\frac{a_{11}}{2\det a_{ij}} \right) \quad (4.19)$$

and

$$\left. \frac{d\chi}{dT} \right|_{T < T_c} = \left. \frac{d\chi}{dT} \right|_{T > T_c} + \frac{ba}{B} \quad (4.20)$$

(assuming ba/B nearly T independent). The discontinuity in $d\chi/dT$ gives a cusp if $ba/B > 0$ and a dip if $ba/B < 0$. Since a and B are positive, a cusp corre-

sponds to $b > 0$ and to a decrease of $T_c(E)$ as a function of E . Although Meyer *et al.*³ suggested that χ should diverge at T_c , experimental work⁷ shows the existence of a cusp, which supports our prediction.

From (4.16) we can see that a discontinuity in χ itself is predicted at $T_c(E)$ if $E \neq 0$.

Shear-flow measurements⁵ have been interpreted as showing a divergent response to the applied distortion at T_c . If we define

$$q(0) = |q_{iz}(0)| = [q_{xz}^2(0) + q_{yz}^2(0)]^{1/2}, \quad (4.21)$$

we can calculate (above and below T_c)

$$\frac{\partial q(0)}{\partial E} = \frac{a_{12}}{2\det a_{ij}}, \quad T > T_c; \quad (4.22)$$

$$\frac{\partial q(0)}{\partial E} = \frac{a_{12}}{2\det a_{ij}} + \frac{b'}{B}[a(T - T_c) + bE^2], \quad T < T_c. \quad (4.23)$$

The quantity $\partial q(0)/\partial E$ is proportional to the piezoelectric coefficient. From (4.22) and (4.23) we can see that it exhibits a cusp or a dip, according to the sign of b' ; this behavior is analogous to that of χ . The experimental curve⁵ does not seem to be in contradiction with our prediction.

V. CONCLUSION

In the present work we have proposed a theoretical approach to the smectic C^* phase. We have presented a molecular interaction which can give an explanation for the appearance of the twisted smectic C^* phase. Using the Landau theory of second-order phase transitions, we were able to predict the basic properties of the $A-C^*$ transition. Using the fact that the point group of the smectic A phase is D_∞ we have shown that the polarization inside the layer must be perpendicular to the tilt plane. When the transition takes place, the pitch has in general a finite value but its temperature variation cannot be predicted by our theory. At the transition, the electric susceptibility and the piezoelectric coefficient are both continuous but have a discontinuous derivative with respect to the temperature. A uniform electric field applied to the C^* phase produces a second-order transition to a regular smectic C , i.e., the helix disappears. On physical grounds, one can think that the transition temperature decreases with the field, and we have shown that this corresponds to a cusp rather than a dip in the electric susceptibility. We have to emphasize that the transition to the uniform smectic C is not analogous to the behavior of a cholesteric in the presence of a mag-

netic field. In the case of the smectic C^* , the pitch is not necessarily influenced by the external field, at small fields. Qualitatively, our results are in agreement with the experimental data on this type

of materials.³⁻⁷ However, it seems that further experiments are necessary to check all our conclusions, in particular the exact picture of the transition in the presence of an electric field.

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