Fréedericksz structural transition in an orthorhombic nematic

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A model of the orientation effect is developed for an orthorhombic nematic subjected to crossed electric and magnetic fields. The conditions are found for the existence of a threshold transition and the limiting orientation of an orthorhombic nematic in high fields is determined. It is shown that two consecutive structural transitions can take place in different external fields and this may be used as a criterion of the biaxial nature of the phase when nematic liquid crystals are identified. A study is made of the feasibility of finding experimentally the elastic constants of an orthorhombic nematic from measurements of the critical field at the primary and secondary bifurcation points in the course of the Fréedericksz transitions.

INTRODUCTION

A class of nematic liquid crystals (NLC) which represents mesophases with a biaxial breakdown of the total rotational symmetry $O(3)$, typical of an isotropic liquid, has recently been identified and is being actively investigated. Phases of this kind, labeled NLC_2, had been observed first[1] in lyotropic liquid crystals and later[2] in thermotropic liquid crystals. These NLC_2 phases can have arbitrary point symmetry groups which are subgroups of $O(3)$, including the groups which are forbidden in the crystal lattice. The symmetry of the majority of the biaxial nematic phases encountered in practice has not yet been determined.

Investigations of the NLC_2 phases have included the development of a continuum theory of elasticity,[3-5] hydrodynamics,[3,4,6] a theory of phase transitions,[7] flexoelectricity,[8] and classification of disclinations.[9] The great variety of the forms of symmetry of biaxial nematic phases can give rise to familiar difficulties in their identification by calorimetric measurements in the vicinity of a phase transition from a uniaxial (NLC_1) to a biaxial (NLC_2) nematic in the absence of x-ray diffraction methods. It is therefore important to investigate the behavior of biaxial nematics in external electric **E** and magnetic **H** fields. This point is discussed in Ref. 10 from the point of view of changes in the thermodynamic state of an NLC_2 phase or, more exactly, changes in the temperature and nature of the NLC_1–NLC_2 phase transition.

The orientational instability of a biaxial nematic in an external electric field (known as the Fréedericksz structural transition) has been considered already for the cubic[11] and hexagonal[12] nematic phases: The investigation reported in Ref. 12 was limited to finding the critical values E_c of the fields, but did not extend to a study of the stability of inhomogeneous nematic structures that appeared in fields above E_c (or, using the language of bifurcation theory, it was limited to the task of finding the primary bifurcation points). It is known[13] that the high symmetry of a system permits a whole series of stable stationary states separated along the E axis by what are known as the secondary bifurcation points. Such points can be expected, for example, in the case of the Fréedericksz transition in a hexagonal NLC under special conditions imposed on the elastic moduli and the permittivity tensor of a liquid crystal.

The interest in the Fréedericksz transition in the NLC_2 phases is also due to the opportunity of obtaining the still missing information on the elastic constants of the biaxial phases[14] and determining the limiting orientation of an NLC_2 phase in high external fields, as well as the nontrivial, in contrast to NLC_1, behavior under such conditions.

We shall limit our treatment to a study of the Fréedericksz structural transitions in an orthorhombic nematic with the D_{2h} symmetry. We selected an NLC_2 phase with this symmetry because of the relatively small number (15) of the elastic constants[4,5] (in the case of a monoclinic nematic the number of such constants is 25, whereas for a triclinic NLC it is 45). On the other hand, the symmetry is fairly low, so that degeneracy of the interaction of the NLC_2 phase with the vector fields, which is quadratic in E, is avoided[13] in contrast to the degeneracy which occurs in cubic liquid crystals[11] and in NLC_2 phases of intermediate symmetries.[12]

Our task was to describe possible structures and types of transitions which may occur between these structures in a plane-parallel layer of a biaxial nematic with the point symmetry group D_{2h} subjected to external electric and magnetic fields when strong coupling obtains at the boundary of the liquid crystal.

FORMULATION OF THE PROBLEM

The orthorhombic symmetry makes it impossible to transfer the concepts of the "planar" (p) and "homeotropic" (h) orientations from a uniaxial to a biaxial nematic phase and, as a consequence, to separate the main types (splay, bend, and twist) of strains typical of the Fréedericksz transition in the NLC_1 phase.

We consider only the situation when one of the vectors of the unperturbed triplet of the unit vectors $\mathbf{n}_i^0$ has the h orientation at the boundaries of the NLC_2 layer. In the absence of external **E** and **H** fields, the vectors fields $\mathbf{n}_i^0(\mathbf{r})$ are homogeneous and throughout the layer and the boundary conditions at the upper and lower surfaces of the layer are symmetric. The orientations of the fields **E** and **H** can generally be arbitrary. It follows from the symmetry considerations that it is sufficient to investigate a structural transition in a phase with the h orientation for just one of the vectors of the triplet $\mathbf{n}_i^0$, for example $\mathbf{n}_2^0$, as is done below. Then, the Fréedericksz transitions in an orthorhombic nematic with the h orientation of the vectors $\mathbf{n}_1^0$ (or $\mathbf{n}_2^0$) can be described by a suitable substitution of the elastic constants, and of the components of the tensors describing the dielectric $\varepsilon_{ij}^{(a)}$ and diamagnetic $\chi_{ij}^{(a)}$ anisotropies in the final ex-

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pressions for the threshold fields E and H and in the dependence of the scalar order parameters of the deformed NLC_2 phase on the external **E** and **H** fields. We consider the initial orientation of the vector triplet $\mathbf{n}_i^0$ shown in Fig. 1 and assume that the orientations of the fields **E** and **H** are arbitrary.

The expression for the density of the free energy of an elastically deformed orthorhombic nematic is[5]

$$2F_v=\sum_{i=1}^{3}K_i\operatorname{div}^2\mathbf{n}_i+\sum_{i,j}^{3}K_{ij}\langle\mathbf{n}_i,\operatorname{curl}\mathbf{n}_j\rangle^2$$

$$+2\sum_{i=1}^{3}\varkappa_i\operatorname{div}(\langle\mathbf{n}_i,\operatorname{grad}\rangle\mathbf{n}_i-\mathbf{n}_i\operatorname{div}\mathbf{n}_i),\qquad(1)$$

where the three surface $\varkappa_i$ and twelve volume (bulk) K_i and K_{ij} constants of a biaxial nematic are related by sixteen inequalities of thermodynamic origin:

$$K_{ii}+\varkappa_j+\varkappa_k\geqslant\varkappa_i,\quad(K_i+K_{jk})(K_i+K_{kj})\geqslant(2\varkappa_i-K_i)^2,$$
$$K_i+K_{jk}\geqslant0,\quad(K_{jj}+\varkappa_i+\varkappa_k-\varkappa_j)(K_{kk}+\varkappa_i+\varkappa_j-\varkappa_k)\geqslant\varkappa_i^2,$$

$$(K_{11}+\varkappa_2+\varkappa_3-\varkappa_1)\varkappa_1^2$$
$$+(K_{22}+\varkappa_1+\varkappa_3-\varkappa_2)\varkappa_2^2+(K_{33}+\varkappa_1+\varkappa_2-\varkappa_3)\varkappa_3^2+2\varkappa_1\varkappa_2\varkappa_3$$
$$\leqslant(K_{11}+\varkappa_2+\varkappa_3-\varkappa_1)(K_{22}+\varkappa_1+\varkappa_3-\varkappa_2)(K_{33}+\varkappa_1+\varkappa_2-\varkappa_3).\qquad(2)$$

The expressions for the orientational part of the density W of the energy of the interaction between an orthorhombic nematic and the external E and H fields, considered in an approximation quadratic in the field, are

$$-2W=\sum_{i=1}^{2}\left(\frac{\varepsilon_i^{(a)}}{4\pi}\langle\mathbf{n}_i,\mathbf{E}\rangle^2+\chi_i^{(a)}\langle\mathbf{n}_i,\mathbf{H}\rangle^2\right),\qquad(3)$$

where $\varepsilon_i^{(a)}$ and $\chi_i^{(a)}$ are related to the diagonal values of the trace-free tensors $\varepsilon_{ij}^{(a)}$ and $\chi_{ij}^{(a)}$, respectively. The following orthogonality relationships are retained in the deformed NLC_2 phase:

$$\langle\mathbf{n}_i,\mathbf{n}_j\rangle=\delta_{ij}.\qquad(4)$$

The free energy of the deformed NLC_2 phase in the fields **E** and **H**, calculated per unit area of the surface of the plane-parallel liquid crystal layer, is described by the functional

$$J=\frac{1}{2L}\int_{-L}^{L}(F_v+W)\,dz,\qquad(5)$$

where F_v is the volume (bulk) part of the density of the free energy F and $2L$ is the thickness of the NLC_2 layer. The boundary conditions for stronger coupling to the liquid crystal are

$$\mathbf{n}_i(\pm L)=\mathbf{n}_i^0.\qquad(6)$$

Derivation of the appropriate Euler–Lagrange equations for the variational problem with the functional J and the holonomic relationship (4) leads to a system of nonseparable nonlinear differential equations for the functions $\mathbf{n}_i(z)$. An analysis of the system, makes it possible to identify the nature of the functions that minimize J and satisfy the conditions (4) and (6), which is equivalent to application of the direct Ritz variational method. This gives rise to a certain algebraic polynomial with several variables, which can be investigated by simple analytic methods. This approach is in full agreement with the view expressed by Guyon[16] on the Fréedericksz structural transition in a liquid crystal regarded as an analog of a phase transition.

FREE-ENERGY FUNCTIONAL

Going over to a spherical coordinate system (Fig. 2)

$$n_{ix}=\sin\theta_i\cos\varphi_i,\quad n_{iy}=\sin\theta_i\sin\varphi_i,\quad n_{iz}=\cos\theta_i,$$

introducing the angular coordinates θ_E, φ_E and θ_H, φ_H, for the vectors **E** and **H**, respectively, and using the orthogonality of the vectors of Eq. (4):

$$\langle\mathbf{n}_1,\mathbf{n}_2\rangle=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)=0,\qquad(7)$$

we find that Eqs. (1) and (3) can be reduced to a form (see Appendix A) which allows us to consider the angular tilts $\theta_i(z)$ and $\varphi_i(z)$ or the vectors $\mathbf{n}_i$, related by Eq. (7), as independent single-component order parameters interacting with one another. The order parameters introduced in this way are of nonthermodynamic nature, in contrast to the tensor parameters of the orientational order Q_{ij}, R_{ijkl}, ... for a liquid crystal.[17]

It is now convenient to go over from θ_i, φ_i to new variables τ_i, ψ_i (Fig. 2) using the relationships

$$\tau_i=\frac{\pi}{2}-\theta_i,\quad\psi_1=\varphi_1,\quad\psi_2=\frac{\pi}{2}-\varphi_2.\qquad(8)$$

If we regard the state of the NLC_2 phase with $\tau_i=\psi_i=0$ as unperturbed, we can find a power series ex-

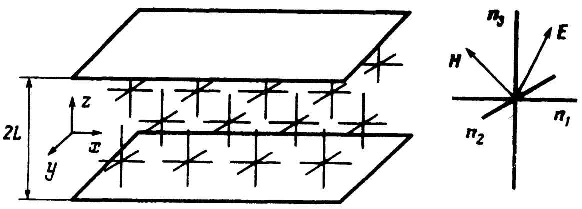

FIG. 1. Orthorhombic nematic in external electric and magnetic fields.

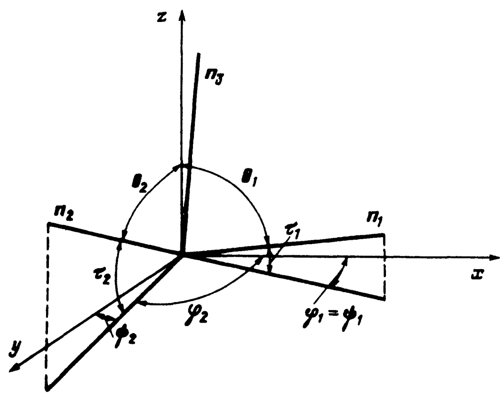

FIG. 2. Perturbed molecular "hedgehog" of an orthorhombic nematic.

pansion for F_v and W in terms of τ_i and ψ_i and their derivatives in the vicinity of this unperturbed value. The term in the power series at which the expansion can be terminated should be of even order in order to guarantee the stability of the stationary solution[6] and is determined by the nontrivial nature of the behavior of a biaxial nematic in external **E** and **H** fields. The leading term of the power-series expansion determines the number of the trial functions used to approximate the exact solution which minimizes the functional J. In investigations of the structural of the structural transitions in the NLC_2 phase we shall select the ν^4 model describing first-and second-order transitions.[18]

Expanding the orthogonality relationship (7) as a series in τ_i and ψ_i, we obtain

$$\psi_1+\psi_2+\tau_1\tau_2\left[1+\frac{1}{3}(\tau_1^2+\tau_2^2)+\sum_{k=2}^{\infty}P_{2k}(\tau_1,\tau_2)\right]=0, \tag{9}$$

where $P_{2k}(\tau_1,\tau_2)$ is a homogeneous polynomial of the $2k$ th degree in τ_1 and τ_2. Equation (9) is related to a familiar geometric fact: Small variations of the orthogonal triplet of the vectors $\mathbf{n}_i$ oriented along the axes of an octane in the coordinate space displace at least one vector of the triplet outside of the octane. If in Eq. (5) we ignore terms higher than of the fourth order in τ_i and ψ_i, we find that the power expansions for F_v and W suitable for our model are

$$\begin{aligned}2F_v=&(K_1+K_{23})\left(\frac{d\tau_1}{dz}\right)^2+(K_2+K_{13})\left(\frac{d\tau_2}{dz}\right)^2+K_{11}\left(\frac{d\psi_1}{dz}\right)^2\\&+K_{22}\left(\frac{d\psi_2}{dz}\right)^2-2K_{13}\tau_1\frac{d\tau_2}{dz}\frac{d\psi_2}{dz}-2K_{23}\tau_2\frac{d\tau_1}{dz}\frac{d\psi_1}{dz}\\&+(K_3+K_{21}-K_1-K_{23})\tau_1^2\left(\frac{d\tau_1}{dz}\right)^2+2(2K_{33}-K_{13})\tau_1^2\left(\frac{d\tau_2}{dz}\right)^2\\&+(K_3+K_{12}-K_2-K_{13})\tau_2^2\left(\frac{d\tau_2}{dz}\right)^2+2(2K_{33}-K_{23})\tau_2^2\left(\frac{d\tau_1}{dz}\right)^2\\&+2(K_3-4K_{33})\tau_1\tau_2\frac{d\tau_1}{dz}\frac{d\tau_2}{dz}+K_{13}\tau_1^2\left(\frac{d\psi_2}{dz}\right)^2+K_{23}\tau_2^2\left(\frac{d\psi_1}{dz}\right)^2\\&+(K_{31}-2K_{11})\tau_1^2\left(\frac{d\psi_1}{dz}\right)^2+(K_{32}-2K_{22})\tau_2^2\left(\frac{d\psi_2}{dz}\right)^2,\end{aligned} \tag{10}$$

$$\begin{aligned}-2W=\text{const}+\sum_{i=1}^{2}\Big\{&g_1^{(i)}\left(\tau_i-\frac{2}{3}\tau_i^3-\frac{1}{2}\tau_i\psi_i^2\right)\\&+g_2^{(i)}\left(\psi_i-\tau_i^2\psi_i-\frac{2}{3}\psi_i^3\right)+g_3^{(i)}\left(\tau_i^2-\frac{1}{3}\tau_i^4\right)\\&+g_4^{(i)}\left(\tau_i\psi_i-\frac{2}{3}\tau_i^3\psi_i-\frac{1}{6}\tau_i\psi_i^3\right)\\&+g_5^{(i)}\left(\psi_i^2-\tau_i^2\psi_i^2-\frac{1}{3}\psi_i^4\right)\Big\},\end{aligned} \tag{11}$$

where

$$\begin{pmatrix}g_1^{(1)}\\g_1^{(2)}\end{pmatrix}=\frac{E^2}{4\pi}\sin 2\theta_E\begin{pmatrix}\varepsilon_1^{(a)}\cos\varphi_E\\\varepsilon_2^{(a)}\sin\varphi_E\end{pmatrix}+H^2\sin 2\theta_H\begin{pmatrix}\chi_1^{(a)}\cos\varphi_H\\\chi_2^{(a)}\sin\varphi_H\end{pmatrix},$$

$$g_2^{(i)}=\frac{E^2}{4\pi}\varepsilon_i^{(a)}\sin^2\theta_E\sin 2\varphi_E+H^2\chi_i^{(a)}\sin^2\theta_H\sin 2\varphi_H,$$

$$\begin{pmatrix}g_3^{(1)}\\g_3^{(2)}\end{pmatrix}=\frac{E^2}{4\pi}\begin{pmatrix}\varepsilon_1^{(a)}[\cos^2\theta_E-\sin^2\theta_E\cos^2\varphi_E]\\\varepsilon_2^{(a)}[\cos^2\theta_E-\sin^2\theta_E\sin^2\varphi_E]\end{pmatrix}+H^2\begin{pmatrix}\chi_1^{(a)}[\cos^2\theta_H-\sin^2\theta_H\cos^2\varphi_H]\\\chi_2^{(a)}[\cos^2\theta_H-\sin^2\theta_H\sin^2\varphi_H]\end{pmatrix},$$

$$\begin{pmatrix}g_4^{(1)}\\g_4^{(2)}\end{pmatrix}=\frac{E^2}{4\pi}\sin 2\theta_E\begin{pmatrix}\varepsilon_1^{(a)}\sin\varphi_E\\\varepsilon_2^{(a)}\cos\varphi_E\end{pmatrix}+H^2\sin 2\theta_H\begin{pmatrix}\chi_1^{(a)}\sin\varphi_H\\\chi_2^{(a)}\cos\varphi_H\end{pmatrix},$$

$$g_5^{(i)}=(-1)^i\left[\frac{\varepsilon_i^{(a)}}{4\pi}E^2\sin^2\theta_E\cos 2\varphi_E+\chi_i^{(a)}H^2\sin^2\theta_H\cos 2\varphi_H\right]. \tag{12}$$

Going back to the Euler–Lagrange equations for the functional J of Eq. (5), we can show[19] that the conditions for the existence of nontrivial solutions of these equations are

$$g_1^{(i)}=g_2^{(i)}=g_4^{(i)}=0, \tag{13}$$

which eliminates from Eq. (11) the terms of low symmetry that destroy the threshold nature of the structural transition.

We consider in greater detail the conditions for orientation of the **E** and **H** fields which guarantee a nonzero threshold ($E_*\neq 0$, $H_*\neq 0$) for the Fréedericksz transition in an orthorhombic nematic. Nontrivial solutions (E_*,H_*) of the system of equations (13) obtained allowing for Eq. (12) are ensured by

$$\begin{aligned}&\sin 2\theta_E\sin 2\theta_H\\&\quad\times(\varepsilon_1^{(a)}\chi_2^{(a)}\sin\varphi_H\cos\varphi_E-\varepsilon_2^{(a)}\chi_1^{(a)}\sin\varphi_E\cos\varphi_H)=0,\\&\sin^2\theta_E\sin^2\theta_H\sin 2\varphi_E\sin 2\varphi_H(\varepsilon_1^{(a)}\chi_2^{(a)}-\varepsilon_2^{(a)}\chi_1^{(a)})=0,\\&\sin 2\theta_E\sin 2\theta_H\\&\quad\times(\varepsilon_1^{(a)}\chi_2^{(a)}\sin\varphi_E\cos\varphi_H-\varepsilon_2^{(a)}\chi_1^{(a)}\sin\varphi_H\cos\varphi_E)=0.\end{aligned} \tag{14}$$

The simultaneous solution of the system of equations (14) gives the conditions for orientation of the external fields: The fields **E** and **H** should be directed along the rotation axes C_2 of an orthorhombic nematic.

If these conditions are not satisfied, the Fréedericksz transition threshold disappears; more exactly, for any values (no matter how low) of the fields E and H, the NLC_2 phase may be in a state with a perturbed orientation. This phenomenon is analogous to the threshold-free Fréedericksz transition in a uniaxial nematic[20,21] and is usually characterized by a quadratic dependence of the structural order parameters on the applied fields. We confine ourselves to the Fréedericksz transition with a threshold.

We now turn to the problem of minimizing the free-energy functional. In constructing the trial functions $\tau_i(z)$ and $\psi_i(z)$ that minimize the functional J and satisfy the boundary conditions (6), we shall use a system of orthogonal (in the interval $[-2L, 2L]$) functions[1)] $\{\cos nqz\}$, where $q=\pi/2L$. It follows from the orthogonality condition (4) that the coefficients in the Fourier expansion are related. It should be noted that among them there are no more than three independent coefficients (one-dimensional order parameters) in accordance with the three rotational degrees of freedom of an orthorhombic molecular "hedgehog."

Using the structural periodic solutions of a system of nonlinear differential equations of sufficiently general nature with one small parameter, demonstrated in Ref. 23, and generalizing this system to a system of the Euler–Lagrange equations for the functional J with several small parameters, we can show[19] that the Fourier coefficient with index n is represented by a Maclaurin series of the following form:

$$\sum_{k=0}^{\infty} T_{n+2k}(\xi,\zeta,\eta),$$

where $T_n(\xi,\zeta,\eta)$ is a homogeneous polynomial of the nth degree, while ξ, ζ, η are one-dimensional order parameters.

In the ν^4 model it is sufficient to consider the first two harmonics in the Fourier expansion. An analysis of the Euler–Lagrange equations leads to the following forms of the functions $\tau_i(z)$ and $\psi_i(z)$:

$$\begin{pmatrix}\tau_1(z)\\ \tau_2(z)\\ \psi_1(z)\\ \psi_2(z)\end{pmatrix} = \begin{Bmatrix} \xi[1+\gamma_1(\xi,\zeta,\eta)]\\ \zeta[1+\gamma_2(\xi,\zeta,\eta)]\\ \eta[1+\gamma_3(\xi,\zeta,\eta)]\\ -\eta[1+\gamma_4(\xi,\zeta,\eta)]\end{Bmatrix}\cos qz + 2\begin{Bmatrix}\beta_1(\xi,\zeta,\eta)\\ \beta_2(\xi,\zeta,\eta)\\ \beta_3(\xi,\zeta,\eta)\\ \beta_4(\xi,\zeta,\eta)\end{Bmatrix}\cos^2 qz, \quad (15)$$

where the orthogonality relationships (6) impose the following constraints on β_i and γ_i:

$$\beta_3+\beta_4+{}^1/_2\xi\zeta=0,\quad \eta(\gamma_3-\gamma_4)+{}^3/_2(\beta_2\xi+\beta_1\zeta)=0,$$

$\beta_i(\xi,\zeta,\eta)$, $\gamma_i(\xi,\zeta,\eta)$, where $i=1, 2, 3$, and 4, are quadratic functions of the type

$$\beta_1=b_1\zeta\eta,\quad \beta_2=b_2\xi\eta,\quad \beta_3=b_3\xi\zeta,$$

$$\beta_4=b_4\xi\zeta,\quad (\gamma_1\gamma_2\gamma_3\gamma_4)=(\xi^2\zeta^2\eta^2)((c_{ij})), \quad (16)$$

and $((c_{ij}))$ is a 4×3 matrix. The coefficients b_i and c_{ij} can be found[19] by substituting the expressions from the system (15) into the Euler–Lagrange equations and using the relationships in Eq. (16). Next, integrating Eq. (5) subject to Eqs. (10) and (11), and using the trial functions given by the system (15), we obtain the following expression for the polynomial $J(\xi,\zeta,\eta)$:

$$J=A_1\xi^2+A_2\zeta^2+A_3\eta^2+2D\xi\zeta\eta+B_1\xi^2\zeta^2+B_2\xi^2\eta^2+B_3\zeta^2\eta^2 +{}^1/_2(C_1\xi^4+C_2\zeta^4+C_3\eta^4), \quad (17)$$

where the coefficients A_i, B_i, C_i, and D are found in Ref. 19 and are given in the Appendix B.

We note that Eq. (17) for J can be obtained bearing in mind that in the case of the orthorhombic point symmetry groups the minimum integral rational basis of the invariants, derived using the components of the axial vector (ξ,ζ,η), includes the following four invariants:[24]

$$J_1=\xi^2,\quad J_2=\zeta^2,\quad J_3=\eta^2,\quad J_4=\xi\zeta\eta. \quad (18)$$

Then, in the ν^4 model the functional J assumes the form given by Eq. (17):

$$J=a_1J_1+a_2J_2+a_3J_3+a_4J_4+d_1J_1J_2 +d_2J_1J_3+d_3J_2J_3+{}^1/_2(l_1J_1^2+l_2J_2^2+l_3J_3^2). \quad (19)$$

This approach relying on the integral rational basis of the invariants for the relevant point symmetry group is universal, but its shortcoming is the physical indeterminacy of the coefficients a_i, d_i, and l_i, in contrast to Eq. (17).

STATIONARY STATES AND STRUCTURAL TRANSITIONS

The stationary states of an orthorhombic nematic in fields **E** and **H** are determined by the set of critical points of the polynomial J, whereas the positive definite nature of the Hessian matrix $((\partial^2 J))$ defines the regions of parametric space $(q^2K_i, q^2K_{ij}, g_i^{(j)})$ where the stationary states are stable.

The critical points ξ_*, ζ_*, and η_* of the polynomial (17) are given by the following system of equations:

$$\begin{aligned}&\xi(A_1+C_1\xi^2+B_1\zeta^2+B_2\eta^2)+D\zeta\eta=0,\\ &\zeta(A_2+B_1\xi^2+C_2\zeta^2+B_3\eta^2)+D\xi\eta=0,\\ &\eta(A_3+B_2\xi^2+B_3\zeta^2+C_3\eta^2)+D\xi\zeta=0,\end{aligned} \quad (20)$$

which has the following solutions that are locally stable in the relevant parts of the parametric space:

(0) trivial

$$\xi_*=\zeta_*=\eta_*=0, \quad (21)$$

$$A_1>0,\quad A_2>0,\quad A_3>0; \quad (22)$$

1a) primary

$$\xi_*=\zeta_*=0,\qquad \eta_*^2=-\frac{A_3}{C_3}, \quad (23a)$$

$$A_3<0,\quad C_3>0,\quad A_1C_3>A_3B_2,\quad A_2C_3>A_3B_3, \quad (24a)$$

$$(A_1C_3-A_3B_2)(A_2C_3-A_3B_3)+D^2A_3C_3>0;$$

1b) primary

$$\xi_*=\eta_*=0,\qquad \zeta_*^2=-\frac{A_2}{C_2}, \quad (23b)$$

$$A_2<0,\quad C_2>0,\quad A_1C_2>A_2B_1,\quad A_3C_2>A_2B_3,$$
$$(A_1C_2-A_2B_1)(A_3C_2-A_2B_3)+D^2A_2C_2>0; \quad (24b)$$

1c) primary

$$\zeta_* = \eta_* = 0, \quad \xi_*^2 = -\frac{A_1}{C_1}, \tag{23c}$$

$$A_1<0, \quad C_1>0, \quad A_2C_1>A_1B_1, \quad A_3C_1>A_1B_2,$$
$$(A_2C_1-A_1B_1)(A_3C_1-A_1B_2)+D^2A_1C_1>0; \tag{24c}$$

2) secondary

$$\xi_* \neq 0, \quad \zeta_* \neq 0, \quad \eta_* \neq 0. \tag{25}$$

The nonzero solutions are the points of intersection of three second-order surfaces in the space (ξ^2, ζ^2, η^2). The analytic forms of such solutions are cumbersome. We can use the symmetry considerations to show quite readily that there may be eight such solutions [two series with four solutions in each corresponding to transpositions of the signs of ξ, ζ, η: a) $(+\,+\,+)$, $(+\,-\,-)$, $(-\,+\,-)$, $(-\,-\,+)$; b) $(-\,-\,-)$, $(-\,+\,+)$, $(+\,-\,+)$, $(+\,+\,-)$] or four solutions (one of these series). We can also have a situation when there are no solutions whatever. Furthermore, degenerate situations can occur when there are continuous sets of solutions lying on curves in the space (ξ, ζ, η). The stability of the structures is governed by the positive definite nature of the corresponding Hessian matrix.[19]

This pattern of alternation of critical points of the polynomial (17), which are locally stable in different regions of the parametric space, is typical of the bifurcation tree in a $(3+m)$-dimensional space[25] (m is the number of controlling parameters of the system) with a trivial core of Eq. (21), and with the primary (23) and secondary (25) bifurcation, governed by the conditions $A_i = 0$ accompanied by the appearance of locally stable states (23) as a result of a second-order structural transition. This corresponds to rotation of the molecular NLC_2 "hedgehog" round one of the nonpolar twofold axes (Fig. 3). At the points of a secondary bifurcation the states (23) become unstable and new states (25) appear as a result of a structural transition of the first or second order. This results in a new rotation of the molecular "hedgehog" around the second of the twofold axes.

The first fairly complete treatment of secondary bifurcations in a system with two interacting order parameters and one control parameter for the case of reflection symmetry was solved in Ref. 26. This symmetry of the functional J appears on transition from the orthorhombic D_{2h} to the tetragonal D_{4h} point symmetry group of a nematic when the **E** and **H** fields are directed along a fourfold rotation axis. The polynomial of Eq. (17) then implies[19] because of the constraints

$$g_5^{(1)}=0, \quad g_3^{(1)}=g_3^{(2)}=g_3, \quad A_1=A_2,$$
$$B_1=B_2, \quad C_1=C_2, \quad C_*=D=0.$$

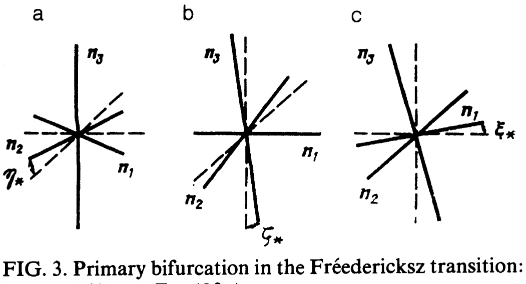

FIG. 3. Primary bifurcation in the Fréedericksz transition: a) Eq. (23a); b) Eq. (23b); c) Eq. (23c).

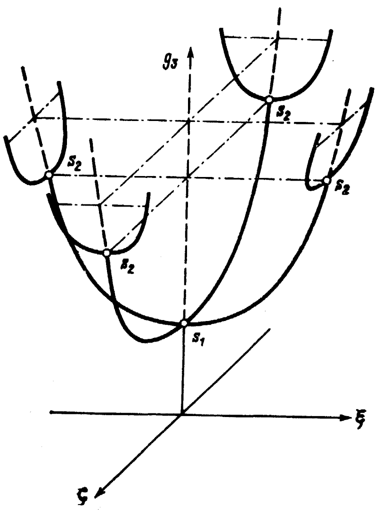

FIG. 4. Bifurcation tree of the Fréedericksz transition for a tetragonal nematic: s_1 and s_2 are the primary and secondary bifurcation points, respectively.

The primary and secondary branches of the bifurcation tree are shown for this case in Fig. 4. It should also be noted that there is a degenerate family of the critical points of the polynomial (17), which corresponds from the physical point of view to precession of the molecular "hedgehog" around the **E** and **H** fields coinciding in direction (the vector $\mathbf{n}_3$ forms a conical surface as a result of precission). In the vicinity of the degenerate critical state the polynomial of Eq. (17) considered in the quadratic approximation is degenerate in one variable, and the state itself is locally unstable.

LIMITING ORIENTATION OF AN ORTHORHOMBIC NEMATIC IN HIGH FIELDS

A direct variational method for minimization of the functional J used in the present study provides a fairly complete description of the behavior of the nematic phase of a liquid crystal in the vicinity of the bifurcation points of the Fréedericksz transition. However, this method does not work in high fields ($E \gg E_*$, $H \gg 5H_*$). The question of the limiting orientation of an orthorhombic nematic in such fields is not trivial, in contrast to the behavior of a uniaxial nematic under similar conditions.

Turning to the Euler–Lagrange equations and using the continuous dependence of the solutions on the parameters occurring in these equations,[19] we can find a system of trigonometric equations for the limiting angular tilts θ and φ by going to the limit $E, H \to \infty$ in the Euler–Lagrange equations. Introducing dimensionless ratios

$$\rho_i = \frac{\varepsilon_i^{(a)}}{4\pi\chi_i^{(a)}}\left(\frac{E}{H}\right)^2, \qquad \bar{\rho}_i = \lim_{E,H\to\infty} \rho_i,$$

we can reduce the system of equations for θ_i and φ_i to the form

$$[\bar{\rho}_i \sin 2\theta_E \cos(\varphi_i-\varphi_E)+\sin 2\theta_H \cos(\varphi_i-\varphi_H)]\cos 2\theta_i$$
$$+[\rho_i(\sin^2\theta_E \cos^2(\varphi_i-\varphi_E)-\cos^2\theta_E)+\sin^2\theta_H \cos^2(\varphi_i-\varphi_H)$$
$$-\cos^2\theta_H]\sin 2\theta_i+[\cos\theta_i \sin\theta_j \cos(\varphi_i-\varphi_j)$$
$$-\sin\theta_i \cos\theta_j]2\lambda_i=0, \tag{26a}$$

where $i \neq j = 1,2$;

$$[\cos\theta_i \cos\theta_E + \sin\theta_i \sin\theta_E \cos(\varphi_i - \varphi_E)]$$
$$\times \bar{\rho}_i \sin\theta_i \sin\theta_E \sin(\varphi_i - \varphi_E)$$
$$+ [\cos\theta_i \cos\theta_H + \sin\theta_i \sin\theta_H \cos(\varphi_i - \varphi_H)]$$
$$\times \sin\theta_i \sin\theta_H \sin(\varphi_i - \varphi_H)$$
$$+ (-1)^{i+1} \bar{\lambda}_i \sin\theta_1 \sin\theta_2 \sin(\varphi_1 - \varphi_2) = 0, \qquad (26b)$$

where $\bar{\lambda}_i \lim_{E,H\to\infty} (\lambda / \chi_i^{(a)} H^2)$, and $\lambda(E,H)$ is an undetermined Lagrange multiplier. The four equations in the system (26) should be supplemented by the orthogonality condition (4).

Consider now a simple orientation of external fields characterized by $\theta_E = \theta_H = 0$. The system of equations (26) then reduces to the two equations

$$\frac{\chi_1^{(a)}(1+\bar{\rho}_1)}{\chi_2^{(a)}(1+\bar{\rho}_2)} = \frac{\sin 2\theta_2 [\sin\theta_1 \cos\theta_2 - \sin\theta_2 \cos\theta_1 \cos(\varphi_1 - \varphi_2)]}{\sin 2\theta_1 [\sin\theta_2 \cos\theta_1 - \sin\theta_1 \cos\theta_2 \cos(\varphi_1 - \varphi_2)]}$$
$$\sin\theta_1 \sin\theta_2 \sin(\varphi_1 - \varphi_2) = 0,$$

which have the obvious solutions

1) $\theta_1 = 0$, $\theta_2 = \pi/2$; 2) $\theta_1 = \pi/2$. $\theta_2 = 0$

and also the degenerate solutions $\varphi_1 = \varphi_2$ and $|\theta_1 - \theta_2| = \pi/2$ when

$$\chi_1^{(a)}(1+\bar{\rho}_1) = \chi_2^{(a)}(1+\bar{\rho}_2). \qquad (27)$$

This last solution can be interpreted physically as the precission of the molecular "hedgehog" of an orthorhombic nematic around the directions of the external fields.

CONCLUSIONS

A phenomenological theory of the elasticity of a biaxial nematic has been used to develop a theory of the Fréedericksz structural transition in an orthorhombic nematic subjected to electric and magnetic fields simultaneously.

Such a structural transition has a threshold if the external fields are directed along the twofold rotation axes of an NLC in its unperturbed state. A specific feature of the Fréedericksz effect in an orthorhombic nematic, which distinguishes it from a uniaxial nematic, is the possible occurrence of two consecutive structural transitions induced by different external fields, which corresponds to a gradual reduction in the symmetry of the physical phenomena in a liquid crystal cell along the orthorhombic–monoclinic–triclinic series. This feature may be the decisive criterion of the biaxial nature of the phase used to identify nematic liquid crystals in polarized light.

In high fields, in addition to the obvious limiting orientations of the molecular "hedgehog" along two rotation axes there is a nontrivial limiting orientation which appears in the case of the special balance between the electric and magnetic fields [see Eq. (27)]. Such an orientation may be interpreted as the precission of the molecular "hedgehog" of an orthorhombic nematic around the directions of the external fields.

We now consider the possibility of finding the elastic constants of an orthorhombic nematic by measuring the critical fields E_* and H_* at the primary and secondary bifurcation points of the Fréedericksz structural transition. We can easily show that for the homeotropic orientation of the director $\mathbf{n}_3^0$ we can vary the directions and the values of the fields **E** and **H** to reduce our system to each of the three primary bifurcation points s_1, which gives the following three relationships:

$$K_1 + K_{23} = q^{-2} g_3^{(1)}, \quad K_2 + K_{13} = q^{-2} g_3^{(2)},$$
$$K_{11} + K_{22} = q^{-2} (g_5^{(1)} + g_5^{(2)}).$$

The fourth relationship, which links all the elastic constants, can be found by reducing this system to the secondary bifurcation points s_2. Next, selecting the experimental geometry with the homeotropic orientation of the directors n_1^0 and n_2^0, respectively, and applying the above procedure we obtain eight additional relationships. Therefore, we can derive nine linear and three nonlinear equations for twelve elastic constants of an orthorhombic nematic.

The author regards it as his pleasant duty to thank E. I. Kats and S. A. Pikin for their interest in this investigation and valuable comments.

APPENDIX A

In this appendix we give the expression for the density of the volume part F_v of the free energy of an elastically deformed orthorhombic nematic:

$$2F_v = K_1 \left(\frac{d\theta_1}{dz}\right)^2 \sin^2\theta_1 + K_2 \left(\frac{d\theta_2}{dz}\right)^2$$
$$\times \sin^2\theta_2 + K_{11} \left(\frac{d\varphi_1}{dz}\right)^2 \sin^4\theta_1$$
$$+ K_{22} \left(\frac{d\varphi_2}{dz}\right)^2 \sin^4\theta_2 + K_3 \Big[\Big(\frac{d\theta_2}{dz} \sin\theta_1 \cos\theta_2$$
$$+ \frac{d\theta_1}{dz} \sin\theta_2 \cos\theta_1\Big) \sin(\varphi_1 - \varphi_2)$$
$$- \left(\frac{d\varphi_1}{dz} - \frac{d\varphi_2}{dz}\right) \cos\theta_1 \cos\theta_2\Big]^2$$
$$+ K_{33} \Big[2\Big(\frac{d\theta_1}{dz} \sin\theta_2 \cos\theta_2 - \frac{d\theta_2}{dz} \sin\theta_1 \cos\theta_1\Big) \sin(\varphi_1 - \varphi_2)$$
$$- \Big(\frac{d\varphi_1}{dz} + \frac{d\varphi_2}{dz}\Big) \cos^2\theta_1 \cos^2\theta_2 - \Big(\frac{d\varphi_2}{dz} \cos^2\theta_1 \sin\theta_2$$
$$+ \frac{d\varphi_1}{dz} \cos^2\theta_2 \sin^2\theta_1\Big)\Big]^2 + K_{12} \Big[\frac{d\theta_2}{dz} \sin\theta_1 \sin(\varphi_1 - \varphi_2)$$
$$+ \frac{d\varphi_2}{dz} \cos\theta_1\Big]^2 \cos^2\theta_1 + K_{21} \Big[\frac{d\theta_1}{dz} \sin\theta_2 \sin(\varphi_2 - \varphi_1)$$
$$+ \frac{d\varphi_1}{dz} \cos\theta_2\Big]^2 \cos^2\theta_2 + K_{13} \Big[\frac{d\theta_2}{dz} \sin\theta_1 \sin(\varphi_1 - \varphi_2)$$
$$+ \frac{d\varphi_2}{dz} \cos\theta_1\Big]^2 \sin^2(\varphi_1 - \varphi_2) \sin^2\theta_1 \sin^2\theta_2$$
$$+ K_{23} \Big[\frac{d\theta_1}{dz} \sin\theta_2 \sin(\varphi_2 - \varphi_1) + \cos\theta_2 \frac{d\varphi_1}{dz}\Big]^2$$
$$\times \sin^2(\varphi_2 - \varphi_1) \sin^2\theta_1 \sin^2\theta_2$$

$$+K_{31}\left[\frac{d\varphi_1}{dz}\sin\theta_1\cos\theta_1\sin(\varphi_1-\varphi_2)-\frac{d\theta_1}{dz}\cos(\varphi_1-\varphi_2)\right]^2\sin^2\theta_2$$

$$+K_{32}\left[\frac{d\varphi_2}{dz}\sin\theta_2\cos\theta_2\sin(\varphi_2-\varphi_1)-\frac{d\theta_2}{dz}\cos(\varphi_2-\varphi_1)\right]^2\sin^2\theta_1.$$

APPENDIX B

In this appendix we give the expressions for the coefficients A_i, B_i, C_i, and D which occur in the polynomial describing the free energy J [Eq. (17)]:

$$4A_1=q^2(K_1+K_{23})-g_3^{(1)},\quad 4A_2=q^2(K_2+K_{13})-g_3^{(2)},$$
$$4A_3=q^2(K_{11}+K_{22})-(g_5^{(1)}+g_5^{(2)}),$$
$$2B_1=q^2[c_{12}(K_1+K_{23})+c_{21}(K_2+K_{13})+2(b_3^2K_{11}+b_4^2K_{22})-(b_4K_{13}+b_3K_{23})+{}^1/_4(K_3-K_{13}-K_{23})]$$
$$-[g_3^{(1)}c_{12}+g_3^{(2)}c_{21}+3g_5^{(1)}b_3^2+3g_5^{(2)}b_4^2],$$
$$2B_2=q^2[c_{13}(K_1+K_{23})+c_{31}K_{11}+c_{41}K_{22}+b_2(K_{13}-{}^1/_2K_{23})+{}^1/_8(K_{13}+K_{31}-2K_{11})]$$
$$-[g_3^{(1)}c_{13}+3g_3^{(2)}b_2^2+g_5^{(1)}c_{31}+g_5^{(2)}c_{41}-3g_5^{(1)}],$$
$$2B_3=q^2[c_{23}(K_2+K_{13})+c_{32}K_{11}+c_{42}K_{22}-b_1(K_{23}-{}^1/_2K_{13})+{}^1/_8(K_{23}+K_{32}-2K_{22})$$
$$-[3g_3^{(1)}b_1^2+g_3^{(2)}c_{23}+g_5^{(1)}c_{32}+g_5^{(2)}c_{42}-3g_5^{(2)}],$$
$$C_1=q^2[c_{11}(K_1+K_{23})+{}^1/_8(K_3+K_{21}-K_1-K_{23})]-(c_{11}g_3^{(1)}-{}^1/_8g_3^{(1)}),$$
$$C_2=q^2[c_{22}(K_2+K_{13})+{}^1/_8(K_3+K_{12}-K_2-K_{13})]-(c_{22}g_3^{(2)}-{}^1/_8g_3^{(2)}),$$
$$C_3=q^2(c_{33}K_{11}+c_{43}K_{22})-(c_{33}g_5^{(1)}+c_{43}g_5^{(2)}-g_5^{(1)}-g_5^{(2)}),$$
$${}^3/_4\pi D=q^2[b_1(K_1+K_{23})+b_2(K_2+K_{13})+b_3K_{11}-b_4K_{22}+{}^1/_4(K_{13}-K_{23})]$$
$$-(b_1g_3^{(1)}+b_2g_3^{(2)}+b_3g_5^{(1)}-b_4g_5^{(2)}).$$

[1)] Inclusion of the functions sin nqz in the Fourier expansion suppresses an extremum of the functions $\tau_i(z)$ and $\psi_i(z)$ in the middle of a liquid crystal layer ($z=0$). Such a solution usually does not correspond to a deformed state of a nematic with a minimum free energy.[22] It should be noted that a similar Fourier expansion for the Fréedericksz effect in a uniaxial nematic contains only the odd harmonics $\cos(2n+1)qz$.

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