Biaxial cholesterics: Temperature dependence of the order parameters and pitch of the helix

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A simple model is proposed which describes the orientational ordering of the molecules of a biaxial cholesteric liquid crystal in the mean field approximation. It is shown that, depending on the model parameters, the transition of a cholesteric from the anisotropic to the isotropic phase can be either a first-order or second-order transition. The temperature dependence of the components of the orientation tensor of the cholesteric and the temperature dependence of the pitch of the cholesteric helix are studied and the results are compared with experiment. The possibility of a phase transition between two cholesteric phases differing in the sign of the helix is discussed. It is shown that the proposed model can also be used to examine nonhelical cholesteric structures.

INTRODUCTION

According to the elementary models a cholesteric liquid crystal is a locally nematic liquid crystal in which the direction of the macroscopic ordering of the molecules (the director **n**) changes continuously from layer to layer, rotating about an axis **l** known as the axis of the cholesteric helix. Such a model implicitly assume a uniaxial symmetry of the cholesteric phase, as is typical of nematic liquid crystals: The dielectric-ellipsoid tensor is uniaxial (with a long axis **n**) and rotates about the medial axis **l**.

This simple model is in need of refinement, however, as it is intuitively clear that the presence of two distinguished directions, **n** and **l**, should lead to biaxiality of the cholesteric phase. In fact, as was shown in Ref. 1, the orientation tensor of a cholesteric is always biaxial (the corresponding dielectric ellipsoid is not an ellipsoid of rotation). The degree of biaxiality, defined as the square of the ratio of the length d of the molecule to the pitch p of the helix, is small (of the order of 10^{-3}–10^{-4}) for ordinary cholesterics (derivatives of optically active steroids). By now, however, a wide class of so-called chiral nematogens has been synthesized.[2,3] The pitch of the cholesteric helix of these nonsteroid compounds in the liquid-crystal state varies (depending on the material) from several microns to tens of angstroms. In the latter case the pitch of the helix is commensurate with the length of the molecules, so that the biaxiality of the cholesteric phase is by no means small and its structure cannot be described by a single director. Furthermore, the very nature of the phase transition of the cholesteric from the isotropic phase to the liquid-crystal phase changes as the pitch of the helix is changed, from a first-order phase transition for $p \gg d$ through a tricritical point to a second-order phase transition at $p \sim d$. This interesting result was obtained by Brazovskiĭ and Dmitriev[1] in the framework of the phenomenological theory of Landau and de Gennes.

The conclusions of Ref. 1 have not as yet been confirmed by concrete calculations based on the molecular-statistical models of cholesterics. The problem is that in the existing models the biaxiality of the helical phase has either been ignored completely[4–6] or assumed small.[7–9] A recent series of studies has considered a cholesteric consisting of biaxial molecules, and the equations of the oriented state of a biaxial cholesteric have been derived in the mean field approximation. The resulting complex system of self-consistency conditions was not solved in Refs. 7–9, however: The authors of those papers assume $d/p \ll 1$, whereupon the temperature dependence of the order parameters of the cholesteric becomes the same as in a nematic, in disagreement with the experiments of Carr *et al.*[10]

In a recent paper Schröder[11] proposed a molecular-statistical model which incorporates in a simple way the molecular and phase biaxiality of cholesterics without assuming it to be small. The orientational ordering is described by two scalar order parameters (in the models of Refs. 7 and 9 there are four). However, Schröder kept only the first nonvanishing terms in the expansion of the binary-interaction Hamiltonian for the molecules of the cholesteric in irreducible spherical tensors and was thus unable to get the temperature dependence of the pitch of the cholesteric helix. Furthermore, instead of numerically solving the system of self-consistency equations obtained for the order parameters in the mean field approximation, Schröder merely expanded the free energy in powers of these parameters (the Landau–de Gennes approximation). It is not surprising, therefore, that the results of Ref. 11, as Schröder himself points out, are precisely the same as the results of Ref. 1.

In what follows we propose a simple cholesteric model which is free of the shortcomings mentioned above. This model yields a description of the observed temperature dependence of the pitch of the helix and enables one to track the influence of biaxiality on the orientational ordering and on the phase transition between the cholesteric liquid crystal and the isotropic liquid.

ORIENTATIONAL EQUATIONS OF STATE FOR A BIAXIAL CHOLESTERIC

We shall characterize the orientation of the molecule at point $\mathbf{r}^\alpha$ by the tensor

$$s_{ik}^\alpha = \left(\frac{3}{2}\right)^{1/2} \left(\nu_i^\alpha \nu_k^\alpha - \frac{1}{3}\delta_{ik}\right), \tag{1}$$

where $\boldsymbol{\nu}^\alpha$ is a unit vector along the long axis of the molecule. Retaining only the first terms in the expansion of the binary-

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interaction energy of the molecules in powers of s_{ik}, we write the Hamiltonian of the cholesteric in the form

$$H=H_{n1}+H_{n2}+H_{c1}+H_{c2},$$

$$H_{n1}=-\frac{1}{2}\sum_{\alpha\neq\beta}A_1(r)\,s_{ik}{}^{\alpha}s_{ik}{}^{\beta},\qquad H_{c1}=-\sum_{\alpha\neq\beta}B_1(r)\,e_{ijk}r_is_{jl}{}^{\alpha}s_{kl}{}^{\beta},\tag{2}$$

$$H_{n2}=-\frac{1}{4}\sum_{\alpha\neq\beta}A_2(r)\,s_{ik}{}^{\alpha}s_{lm}{}^{\alpha}s_{ik}{}^{\beta}s_{lm}{}^{\beta},$$

$$H_{c2}=-\sum_{\alpha\neq\beta}B_2(r)\,e_{ikl}r_ls_{ij}{}^{\alpha}s_{mn}{}^{\alpha}s_{kj}{}^{\beta}s_{mn}{}^{\beta},$$

where $A(r)$ and $B(r)$ are interaction potentials which depend on the distance $r=|\mathbf{r}^{\beta}-\mathbf{r}^{\alpha}|$ between the molecules, e_{ijk} is the Levi-Civita tensor. The terms H_{n1} and H_{n2} in (2) are responsible for the parallel (nematic) ordering of the molecules, while H_{c1} and H_{c2} give rise to the spontaneous helicity of the cholesteric phase (the pseudoscalars B_1 and B_2 are nonzero only for chiral molecules). By virtue of the condition $(\mathbf{v}^{\alpha})^2=1$, Hamiltonian (2) does not contain scalar invariants which are odd in s_{ik}: For example, the third-degree invariant

$$\sum_{\alpha\neq\beta}C(r)\,[s_{il}{}^{\alpha}s_{ik}{}^{\alpha}s_{lk}{}^{\beta}+s_{il}{}^{\alpha}s_{ik}{}^{\beta}s_{lk}{}^{\beta}]$$

reduces to H_{n1}. If only the terms quadratic in s_{ik} are retained in (2), the resulting Hamiltonian $H_{n1}+H_{c1}$ satisfactorily describes the orientational ordering of a biaxial cholesteric,[12] but does not give the temperature dependence of the pitch of the helix. To obtain this temperature dependence one must keep the terms H_{n2} and H_{c2} in (2).

Let us now go over from the microscopic Hamiltonian (2) to a mean field Hamiltonian, using the procedure proposed in Ref. 13. To do this let us write s_{ik} as the sum of the statistical average $\langle s_{ik}\rangle=\eta_{ik}$ and a fluctuation $(s_{ik}-\eta_{ik})$, so that, for example,

$$s_{ik}{}^{\alpha}s_{ik}{}^{\beta}=s_{ik}{}^{\alpha}\eta_{ik}{}^{\beta}+s_{ik}{}^{\beta}\eta_{ik}{}^{\alpha}+(s_{ik}{}^{\alpha}-\eta_{ik}{}^{\alpha})\,(s_{ik}{}^{\beta}-\eta_{ik}{}^{\beta}).$$

Hereafter neglecting the fluctuations (the last terms in the above expression) and keeping only terms up to second order in the gradients in the expansion of the macroscopic tensor $\eta_{ik}(\mathbf{r}^{\beta})$ about the point $\mathbf{r}^{\alpha}$, we obtain the Hamiltonian of a cholesteric in the mean field approximation:

$$E=E_{n1}+E_{n2}+E_{c1}+E_{c2},$$

$$E_{n1}=\sum_{\alpha}\left(\frac{1}{2}\eta_{ik}-s_{ik}\right)\left(\lambda\eta_{ik}+\frac{L}{2n}\Delta\eta_{ik}\right),$$

$$E_{n2}=\sum_{\alpha}\left(\frac{3}{4}\eta_{ik}-s_{ik}\right)\left(\mu\eta_{ik}+\frac{M_1}{n}\Delta\eta_{ik}\right)\eta_{lm}{}^2,\tag{3}$$

$$E_{c1}=\sum_{\alpha}2\frac{Lq_0}{n}e_{ijl}\left(\frac{1}{2}\eta_{ik}-s_{ik}\right)\frac{\partial\eta_{jk}}{\partial r_l},$$

$$E_{c2}=\sum_{\alpha}2\frac{M_2q_0}{n}e_{mjl}\eta_{mn}\left(\frac{3}{2}\eta_{ik}-s_{ik}\right)\frac{\partial(\eta_{ik}\eta_{jn})}{\partial r_l}.$$

Here we have introduced the notation $\lambda=\Sigma A_1(r)$ and $\mu=\Sigma A_2(r)$ for the molecular-field parameters. The contribution to E from the energy of the inhomogeneities is determined by the elastic moduli

$$L=n\Sigma r^2A_1(r),\quad Lq_0=n\Sigma r^2B_1(r),$$
$$M_1=n\Sigma r^2A_2(r),\quad M_2q_0=n\Sigma r^2B_2(r),$$

where L, M_1, and M_2 all have the dimensions of force, n is the number density of the particles, and q_0^{-1}, which has dimensions of length, characterizes the scale of the helical structure. In the expression for E_{n2} we have dropped the terms proportional to the gradients of η_{ik}^2, as they go to zero for the helical cholesteric structure considered below. We note further that the systematic application of the mean field method to the microscopic Hamiltonian (2) does not give rise to terms in E of the form $(\partial\eta_{ik}/\partial r_i)^2$ as are found in the phenomenological theories. Besides, these divergence invariants do not contribute to the partition function for the helical structure.

The orientational ordering of the helical phase of a cholesteric can be described by the tensor

$$\eta_{ik}=\frac{Q}{\sqrt{2}}(n_in_k-k_ik_k)+\left(\frac{3}{2}\right)^{1/2}R\left(l_il_k-\frac{1}{3}\delta_{ik}\right),\tag{4}$$

which is expressed in terms of the unit vectors

$$\mathbf{n}=(\cos qz,\ \sin qz,\ 0),\quad \mathbf{l}=(0,0,1),\quad \mathbf{k}=[\mathbf{l}\times\mathbf{n}]\tag{5}$$

and scalar order parameters

$$R=\langle P_2(\mathbf{l}\cdot\mathbf{v})\rangle,\quad Q=\frac{1}{\sqrt{3}}\langle P_2(\mathbf{n}\cdot\mathbf{v})-P_2(\mathbf{k}\cdot\mathbf{v})\rangle\tag{6}$$

(P_2 is the second Legendre polynomial). The normalization in (4) is chosen such that $\eta_{ik}{}^2=Q^2+R^2$. The tensor η_{ik} admits three uniaxial structures with director $\mathbf{l}$, $\mathbf{n}$, or $\mathbf{k}$. In each of these cases, of course, only one independent order parameter remains in (4): For $Q=0$ we have a uniaxial nematic with director $\mathbf{l}$, while for $Q=\pm R\sqrt{3}$ we find, using the identity $n_in_k+k_ik_k+l_il_k=\delta_{ik}$, a uniaxial structure with director $\mathbf{k}$ or $\mathbf{n}$, respectively. This structure could in principle be cholesteric, but, as we shall show, such a uniaxial solution is thermodynamically unstable.

Writing the macroscopic orientation tensor in form (4) corresponds in fact to isolating the normal orientational modes[1]: a longitudinal mode (optic axis $\mathbf{l}$) corresponds to the order parameter R and the transverse mode to the order parameter Q; the simple model (5) of the helical structure does not support a longitudinal-transverse (conical) mode.

Hamiltonian (3) permits calculation of the free energy of the cholesteric

$$F=-T\ln\int\ldots\int\prod_{\alpha=1}^{N}d\mathbf{v}^{\alpha}\exp(-E/T).$$

Using the explicit form of the tensors s_{ik} and η_{ik}, we obtain after integration

$$\Delta F/\lambda N=aQ^2/2+R^2/2-R-\gamma R^3-cRQ^2+{}^3/_4\times(\gamma R^2+bQ^2)\,(R^2+Q^2)-\tau\ln\psi;\tag{7}$$

$$\psi=\int_0^1dx\exp[\eta(1-x^2)]I_0[\xi(1-x^2)],$$
$$\eta=-\frac{3R}{2\tau}(1+\gamma R^2+cQ^2),\quad \xi=\frac{Q\sqrt{3}}{2\tau}(a+bQ^2+cR^2).\tag{8}$$

Here $\Delta F = F - F_0$, where F_0 is the free energy of the isotropic phase, $\tau = T/\lambda$ is the dimensionless temperature, $x = \mathbf{l} \cdot \mathbf{v}$, I_0 is the modified Bessel function of the first kind,

$$a=1+2q_0q-q^2, \quad c=\gamma-\gamma_1q^2+2\gamma_2q_0q,$$
$$b=2c-\gamma, \quad \gamma=\mu/\lambda, \quad \gamma_1=M_1/L, \quad \gamma_2=M_2/L. \tag{9}$$

The quantities q and q_0 appearing in (9) are dimensionless: the length unit is taken to be $(2L/n\lambda)^{1/2}$.

The conditions of thermodynamic equilibrium, $\partial F/\partial Q = 0$ and $\partial F/\partial R = 0$ lead to the orientational equations of state:

$$Q=\frac{\sqrt{3}}{2}\frac{\partial \ln \psi}{\partial \xi}, \quad R=1-\frac{3}{2}\frac{\partial \ln \psi}{\partial \eta}, \tag{10}$$

which, of course, coincide with the self-consistency conditions $\eta_{ik} = \langle s_{ik} \rangle$. Finally, minimizing the free energy with respect to q gives the equation for the pitch $p = \pi/q$ of the cholesteric helix:

$$q=q_0\frac{1+\gamma_2(Q^2+R^2)}{1+\gamma_1(Q^2+R^2)}. \tag{11}$$

Equations (8)–(11) form a complete system for the temperature dependence of the order parameter and pitch of the helix. We note that this system admits an isotropic solution $Q = R = 0$ at all temperatures. One is readily convinced also that for $q_0 = 0$ equations (8)–(11) describe uniaxial nematic phases with $Q = 0$ and $Q = \pm R\sqrt{3}$. In the case $Q = 0$ one obtains for the nematic order parameter $S_0 = R(T)$ the familiar equation of the Maier-Saupe theory:

$$S_0=\frac{3}{2}\left(\frac{\partial \ln \Phi}{\partial \sigma}-\frac{1}{3}\right), \quad \Phi(\sigma)=\int_0^1 \exp(\sigma x^2)\,dx,$$
$$\sigma=\frac{3S_0}{2\tau}. \tag{12}$$

The same equation can also be obtained for $Q = \pm R\sqrt{3}$ by setting $S_0 = -2R$ and using the identity

$$\int_0^1 \exp\left[\frac{\sigma}{2}(1-x^2)\right] I_0\left[\frac{\sigma}{2}(1-x^2)\right]dx=\int_0^1 \exp(\sigma x^2)\,dx.$$

For $q_0 \neq 0$ equations (8)–(10) admit the existence of a uniaxial cholesteric with

$$q=2q_0(1+\gamma_2S_0^2)/(1+\gamma_1S_0^2), \tag{13}$$

where $S_0^2 = Q^2 + R^2$; this solution is not thermodynamically stable however [cf. (13) and (11)]. Equations (8)-(11), which describe a biaxial cholesteric, have a definite parity with respect to Q, so that the states with $Q > 0$ (long axis of the dielectric ellipsoid along **n**) and $Q < 0$ (long axis along **k**) depend in an identical manner on temperature and have the same stability [see (7)]; for this reason we shall henceforth discuss only positive Q.

Formula (11), in which γ_1 and γ_2 can have any sign, gives three types of temperature dependence for the pitch of the helix: falling, rising, and inverting (for which the pitch of the helix changes sign at a certain temperature τ_i). The first of these types is most often found in pure cholesterics (see, e.g., Ref. 14), the second is rather rare,[15] and the third is observed in mixtures of right-handed and left-handed cholesterics and has been detected only once, by Durand[16] in cholesteryl-2-(2-ethoxyazoxy) ethyl carbonate, but his results have not been confirmed by later experiments.[15] We see no fundamental reasons, however, why inversion of the pitch of the helix should be forbidden in pure cholesterics.

RESULTS OF CALCULATIONS AND COMPARISON WITH EXPERIMENT

The order parameters of a cholesteric change from zero in the isotropic phase to $Q = \sqrt{3}/2$ and $R = -\frac{1}{2}$ at $\tau = 0$. Near the Curie-Weiss temperature τ_*, where Q and R are small, one can construct a solution of the system of self-consistency conditions from a series in powers of $(\tau - \tau_*)^{1/2}$. In zeroth order of perturbation theory the Curie-Weiss temperature is $\tau_* = (1 + q_0^2)/5$. Subsequent approximations give the temperature dependence of the order parameter and the pitch of the helix near τ_* as

$$Q=[35q_0^2\varkappa(\tau-\tau_*)]^{1/2}, \quad R=-25\varkappa(1+q_0^2)(\tau-\tau_*),$$
$$q=q_0[1+35q_0^2\varkappa(\gamma_2-\gamma_1)(\tau-\tau_*)]. \tag{14}$$

Here we have introduced the notation

$$\varkappa^{-1}=5(1+q_0^2)({}^{10}/_7-q_0^2)+7q_0^2[\gamma+2q_0^2(2\gamma_2-\gamma_1)]. \tag{15}$$

As can be seen from (14), the character of the branching of Q at the Curie-Weiss point (and, hence, the order of the cholesteric-isotropic phase transition) is governed by the sign of $\varkappa$: for $\varkappa > 0$ there exist nonzero solutions for Q and R in a certain temperature region $\tau > \tau_*$, and the transition is of first order; the temperature τ_c of the equilibrium transition (the so-called clearing point) is determined in this case from the joint solution of the self-consistency equations and the equation $\Delta F = 0$. For $\varkappa < 0$ the parameter Q branches to the left (the Landau law), i.e., the phase transition is of second order, with $\tau_c = \tau_*$. Finally, the special case $\varkappa^{-1} = 0$ corresponds to a tricritical point, near which $Q \sim (\tau_* - \tau)^{1/4}$ and $R \sim (\tau_* - \tau)^{1/2}$.

If only the terms H_{n1} and H_{c1} are retained in (2) (the "simplified" cholesteric model),[12] then the coefficients, γ, γ_1, and γ_2 vanish; here it follows from (11) that $q = q_0$—the pitch of the helix does not depend on temperature, and only the first term remains in expression (15) for $\varkappa$. The tricritical value q_0 in this case is equal to $(10/7)^{1/2}$, corresponding to a helix pitch $p = \pi(7L/5n\lambda)^{1/2}$; for $n \sim 10^{21}$ cm^{-3}, $L \sim 10^{-6}$ dyn and $\lambda \sim 10^{-13}$ erg, this amounts to tens of angstroms. Thus the "simplified" model, in agreement with the phenomenological theory,[1] admits a second-order phase transition for cholesterics with a short pitch. The complete model lifts this restriction: as can be seen from (15), at suitable values of γ, γ_1, and γ_2 the parameter $\varkappa$ can turn out to be negative for $q_0 \ll 1$ also.

To determine the temperature dependence of the order parameters and helix pitch over the entire existence region of the mesophase, equations (8)–(11) were solved numerically for various values of q_0, γ, γ_1, and γ_2. For the purpose of comparing the calculated results with experiments it proved convenient to transform from the normal modes Q and R to their combinations:

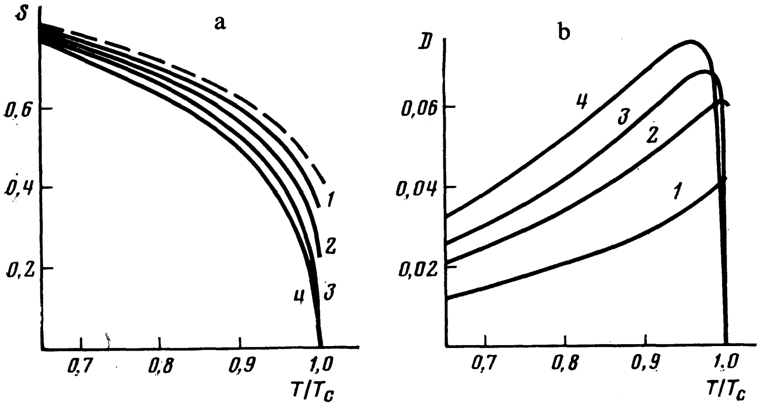

FIG. 1. Temperature dependence of the order parameter S (a) and the biaxiality parameter D (b) in the "simplified" model ($\gamma=\gamma_1=\gamma_2=0$) for various values of q_0^2: 1) 0.5, 2) 1, 3) 10/7 (the tricritical curve), 4) 2; the dashed curve corresponds to the Maier-Saupe model of a uniaxial nematic ($q_0=0$).

$$S=\frac{Q\sqrt{3}-R}{2}=\langle P_2(\mathbf{n}\cdot\boldsymbol{\nu})\rangle,$$
$$D=\frac{Q+R\sqrt{3}}{2}=\frac{1}{\sqrt{3}}\langle P_2(\mathbf{l}\cdot\boldsymbol{\nu})-P_2(\mathbf{k}\cdot\boldsymbol{\nu})\rangle. \qquad (16)$$

As is seen from the definition, S characterizes the degree of ordering of the molecules in a quasinematic layer, while D serves as a natural measure of the biaxiality: If the dielectric ellipsoid with long axis $\mathbf{n}$ were an ellipsoid of revolution, D would be identically zero. Unfortunately, experimenters have been captive to the orthodox point of view that a cholesteric is a helically twisted uniaxial nematic and have not attempted to measure D, and the experimental data on S are extremely scanty (the methods of measuring S in cholesterics are in the development stage).[10,17]

Figure 1 demonstrates the influence of q_0 on the degree of ordering and on the measure of biaxiality of a cholesteric in the "simplified" model. It is seen that as q_0 increases (i.e., as the pitch of the helix decreases), the jump in the parameter S at the point T_c decreases from a value of 0.429 at $q_0=0$ (the Maier-Saupe model) to zero (second-order phase transition) at $q_0^2\geqslant 10/7$. The biaxiality parameter D increases with increasing q_0 and T; at values of q_0 greater than the tricritical value, $D(T)$ goes through a maximum in a narrow pre-transition temperature interval and falls to zero at the point of the cholesteric-isotropic transition.

Figure 2 shows the function $S(T)$ for fixed values $q_0=0.5$ and $\gamma=0$ with various values of γ_1 and γ_2. With increasing γ_1 the jump in the order parameter at the transition point decreases: The first-order phase transition becomes progressively closer to second order. It follows from (15) that the chosen value $q_0=0.5$ is tricritical for $\gamma=\gamma_2=0$ and $\gamma_1^*\approx 8.42$; the second-order transition is realized for $\gamma\geqslant\gamma_1^*$. For positive values of γ_1 the pitch of the helix decreases with increasing temperature, while negative values correspond to an increase of the pitch with temperature; as we know, both types of $p(T)$ behavior occur in cholesterics. Values $\gamma_2>0$ affect the orientational state and the pitch of the helix of cholesterics in approximately the same way as do values $\gamma_1<0$, and vice versa. The lower curve in Fig. 2, corresponding to $\gamma_2=-0.5$, is in good agreement with the ESR-spectroscopy data[10] for cholesteryl benzoate.

As was mentioned in the Introduction, for esters of cholesterol in the liquid-crystal phase the period of the helical structure is large ($q_0^2\ll 1$), i.e., the biaxiality D is small (see Fig. 1). Therefore, for calculating the temperature dependence of the helix pitch $p(T)$ of steroid compounds, one can neglect the biaxiality, setting $q=0$ in Eqs. (8)–(11). In this approach the pitch of the helix is determined by formula (11), where now Q^2+R^2 must be replaced by S_0^2 from (12). The expression thus obtained gives a good description of both types of behavior observed for $p(T)$—the falling (Fig. 3) and the rising (Fig. 4).

The most interesting effect described by formula (11) is the inversion of the pitch of the helix: at a certain tempera-

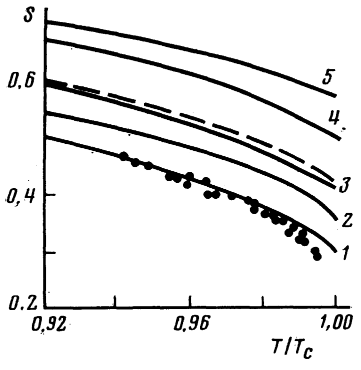

FIG. 2. $S(T)$ curves for $q_0=0.5$ and $\gamma=0$. Curve 1) $\gamma_1=0, \gamma_2=-0.5$; 2) $\gamma_1=0.5$, $\gamma_2=0$; 3) $\gamma_1=\gamma_2=0$; 4) $\gamma_1=-0.5$, $\gamma_2=0$; 5) $\gamma_1=0$, $\gamma_2=0.5$; the dashed curve is for $q_0=\gamma=\gamma_1=\gamma_2=0$. The experimental data for cholesteryl benzoate are taken from Ref. 10.

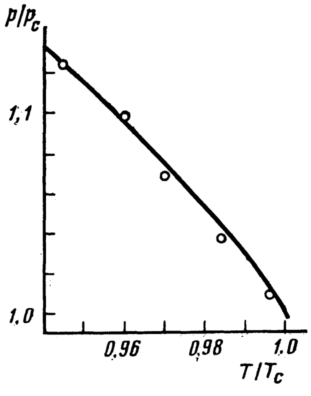

FIG. 3. Temperature dependence of the pitch of the helix in cholesteryl pelargonate (data of Ref. 14). The theoretical curve was constructed for $\gamma=\gamma_1=0$, $\gamma_2=-0.715$.

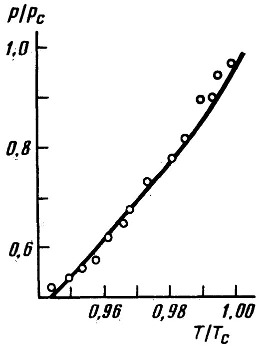

FIG. 4. Temperature dependence of the pitch of the helix in cholesteryl-2-(2-ethoxyazoxy) ethyl carbonate (data of Ref. 15). The theoretical curve was constructed for $\gamma = \gamma_2 = 0$. $\gamma_1 = -2.194$.

ture τ_i determined by the relation $Q^2 + R^2 = -\gamma_2^{-1}$ the wave vector q changes sign, passing through zero. This is possible for $\gamma_2 < -1$ (recall that $Q^2 + R^2 \leqslant 1$). Figure 5 shows the solution of system (8)–(11) for $q_0 = 0.5$, $\gamma_2 = -2.5$, and $\gamma = \gamma_1 = 0$. It is seen from the figure that at these values of the parameters that in addition to the cholesteric-isotropic phase transition at the point $\tau_c = 0.250$ there is another, first-order transition at $\tau_k = 0.202$ in the existence region of the mesophase; this transition is between two cholesteric phases differing in the magnitude and sign of $p = \pi/q$. The inversion point $q = 0$ corresponds to a temperature $\tau_i = 0.197$ and lies on the unstable (shown by dashed curves) sections of the S and D curves. Therefore, the cholesteric-nematic phase transition discussed in Refs. 5 and 6 cannot occur: The pitch of the helix does not go to infinity anywhere but undergoes only a finite jump and inversion of the sign at a temperature τ_k.

ALLOWANCE FOR MOLECULAR BIAXIALITY

We have heretofore considered only the phase biaxiality due to the anisotropy of the intermolecular interaction in the cholesteric; the molecules themselves have been assumed uniaxial. In actuality, of course, chiral molecules are nonaxisymmetric, and their biaxiality makes an additional contribution to the macroscopic (phase) biaxiality of cholesterics.

The orientation of a biaxial molecule can be described by the tensor

$$s_{ik} = \left[\frac{3}{2(1+3\rho^2)}\right]^{1/2} \left[\left(\nu_{1i}\nu_{1k} - \frac{1}{3}\delta_{ik}\right) + \rho(\nu_{2i}\nu_{2k} - \nu_{3i}\nu_{3k})\right]. \tag{17}$$

Here $\mathbf{v}_\beta$ is a unit vector along the β(th) principal axis of the molecule, and ρ is the form factor of the molecule ($\rho^2 \leqslant 1$). For $\rho = 0$ we recover a rod-shaped molecule with long axis $\mathbf{v}_1 \equiv \mathbf{v}$ [cf. (1)]; the values $\rho \equiv \mp 1$ correspond to disk-shaped molecules with normals to the plane of the disk along $\mathbf{v}_2$ or $\mathbf{v}_3$, respectively. The normalization in (17), as in (1), is chosen such that $s_{ik}^2 = 1$.

With allowance for the molecular biaxiality, the macroscopic orientation tensor $\eta_{ik} = \langle s_{ik} \rangle$ describes, as before, two scalar order parameters [see (4)], for which we obtain, using (17).

$$\begin{aligned} R &= \frac{1}{(1+3\rho^2)^{1/2}} \langle P_2(\mathbf{l}\mathbf{v}_1) + \rho[P_2(\mathbf{l}\mathbf{v}_2) - P_2(\mathbf{l}\mathbf{v}_3)]\rangle, \\ Q &= \frac{1}{3^{1/2}(1+3\rho^2)^{1/2}} \langle P_2(\mathbf{n}\mathbf{v}_1) - P_2(\mathbf{k}\mathbf{v}_1) \\ &\quad + \rho[P_2(\mathbf{n}\mathbf{v}_2) - P_2(\mathbf{k}\mathbf{v}_2) - P_2(\mathbf{n}\mathbf{v}_3) + P_2(\mathbf{k}\mathbf{v}_3)]\rangle. \end{aligned} \tag{18}$$

For $\rho = 0$ these formulas go over to (6).

By substituting expressions (4) and (17) into the mean field Hamiltonian (3), we can perform the averaging in (18); we obtain as a result a system of self-consistency equations in which the integration is over the three Euler angles specifying the orientation of the principal axes of the molecule with respect to the laboratory coordinate system. Let us merely give one result without writing out these equations. In the "simplified" model ($\gamma = \gamma_1 = \gamma_2 = 0$) the Curie temperature $\tau_* = (1 + q_0^2)/5$ does not depend on the molecular form factor ρ, and we find for the order parameters near τ_*

$$\begin{aligned} R &= -5\frac{\tau - \tau_*}{q_*^2 - q_0^2} \frac{1 - 9\rho^2}{(1+3\rho^2)^{3/2}} \\ Q &= \pm\left(\frac{7q_0^2}{1+q_0^2}\right)^{1/2} \left(\frac{\tau - \tau_*}{q_*^2 - q_0^2}\right)^{1/2}, \end{aligned} \tag{19}$$

where we have introduced the notation for the critical wave number

$$q_*^2 = \frac{10}{7} \frac{(1 - 9\rho^2)^2}{(1+3\rho^2)^3}. \tag{20}$$

In the case of uniaxial molecules [either rod-shaped ($\rho = 0$) or disk-shaped ($\rho^2 = 1$)] equation (20) gives the value $q_*^2 = 10/7$ indicated above, and formula (19) goes over to (14). Recall that the latter describes a biaxial cholesteric. The biaxiality of the molecules ($0 < \rho^2 < 1$) only enhances the phase biaxiality of the cholesteric. In fact, for biaxial molecules one has $q_*^2 < 10/7$, so that at the same temperatures the parameter Q turns out to be larger than for uniaxial molecules [see (19)]. The degree of biaxiality D (16) of the cholesteric phase near the Curie temperature is simply equal to $Q/2$.

The cholesteric-isotropic phase transition is of first order for materials with parameter $q_0 < q_*$ and of second order

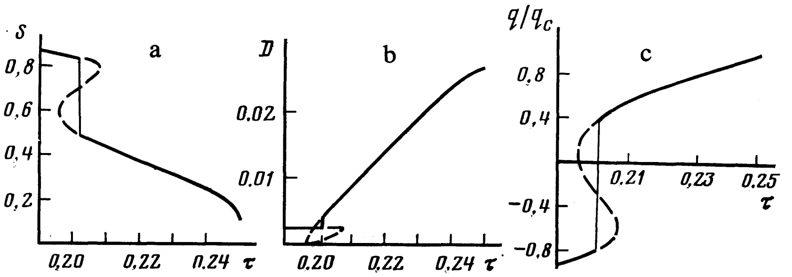

FIG. 5. Temperature dependence of S (a), D (b), and q (c) for $q_0 = 0.5$, $\gamma_2 = -2.5$, $\gamma = \gamma_1 = 0$. The vertical straight-line segments correspond to a first-order phase transition between right- handed and left-handed cholesterics.

for $q_0 > q_*$. As is seen from (20), the biaxiality of the molecules decreases the tricritical value q_*, which goes to zero at $\rho^2 = 1/9$. One can therefore expect that if the biaxiality of the molecules is sufficiently high, second-order phase transitions should also occur in cholesterics with a large helix pitch. This is perhaps the most important consequence. Generally, however, allowance for the biaxiality of the molecules does not lead to qualitative changes in the picture of the orientational ordering of cholesterics from that described in the previous sections of this paper. The situation is quite different in nematics ($q_0 = 0$), which are made up of nonaxisymmetric molecules. In nematic liquid crystals the uniaxial phases with ρ^2 close to zero and with ρ^2 close to unity are separated in the (T, ρ) plane by a biaxial phase.[18] Such a structure of the phase diagram of a nematic is, of course, due to the fact that the biaxiality of the molecules is the only factor capable of causing macroscopic biaxiality of the nematic. In a cholesteric, on the other hand, because of the specific anisotropy of the intermolecular interaction and the consequent appearance in Hamiltonian (2) of the pseudoscalar potentials $B_1(r)$ and $B_2(r)$ responsible for the spontaneous helicity, the wave number $q_0 \neq 0$, so that the phase biaxiality is nonzero even for uniaxial molecules and grows with increasing q_0 (see Fig. 1).

NONHELICAL STRUCTURES IN CHOLESTERICS

The proposed model can also be used to consider cholesteric phases of other (nonhelical) symmetry. For example, to describe the conical phase of a cholesteric[19] we must substitute the following unit vectors [rather than those of (5)] into formula (4)

$$\begin{gathered}\mathbf{n} = (\sin\beta\cos qz,\ \sin\beta\sin qz,\ \cos\beta),\\ \mathbf{l} = (-\cos\beta\cos qz,\ -\cos\beta\sin qz,\ \sin\beta),\ \mathbf{k} = [\mathbf{ln}]\end{gathered} \tag{21}$$

(here $\beta(T)$ is the "tilt" angle between the local director and the axis of the helix) and include in the mean field Hamiltonian the divergence invariants which were dropped in (3). In the expression for E_{n1}, for example, a term $(L'/n)\partial^2\eta_{lk}/\partial r_i \partial r_l$ will appear in the sum with $(L/n)\Delta\eta_{ik}$. The tensor η_{ik} obtained upon substitution of (21) in (4) will contain three independent orientational modes: longitudinal, transverse, and longitudinal-transverse; for $\beta = \pi/2$ (the helical case) the first two go over to R and Q, respectively, while the third vanishes. The solution of the self-consistency equations for the conical phase of the cholesteric can be found in Ref. 19.

There is currently a very active research interest[20] in the cholesteric blue phases, which are observed in a narrow temperature interval between the isotropic and helical phases. The blue phases can be studied in the framework of our model by assigning the corresponding symmetry to the tensor η_{ik}.

A possible blue-phase structure which has been discussed[21] is a uniaxial conical phase with a "magic" tilt angle between the director and the optic axis, viz. $\beta_* \approx 54.74°$, at which $P_2(\cos\beta_*) = 0$. In fact, for $\beta = \beta_*$ and $Q = \pm R\sqrt{3}$ the longitudinal orientational mode responsible for the birefringence vanishes, i.e., such a phase is optically isotropic; this is precisely typical of the blue phase. The self-consistency equation obtained for the "magic" phase is of the form of (12), but with $S_0 = -2R$ and

$$\sigma = \frac{3S_0}{2\tau}\zeta, \quad \zeta = 1 - \frac{12q_0^2 h}{(3-h)^2}, \tag{22}$$

where $h = L'/L$, and for the orientational part of the free energy we find

$$\frac{\Delta F}{\lambda N} = \zeta\left[\frac{S_0(S_0+1)}{2} - \frac{\tau}{\zeta}\ln\Phi(\sigma)\right]. \tag{23}$$

Expressions (12), (22), and (23) differ from the equations of the Maier-Saupe theory for nematics only in the scale of the temperature (τ is replaced by τ/ζ), so that one can immediately give the temperature of the first-order phase transition between the blue phase and the isotropic liquid as $\tau_1 = 0.220\zeta$. By comparing the free energies of the helical (7) and "magic" (23) phases, one can infer that if the temperature τ_c of the transition of the helical phase to the isotropic liquid lies below τ_1, then in a certain temperature interval $\Delta\tau = \tau_1 - \tau_2$, where $\tau_2 \lesssim \tau_c$, the "magic" blue phase is stable. At the point τ_2 there is a first-order phase transition from the blue phase to the helical cholesteric. The width $\Delta\tau$ of the existence region of the blue phase is nonzero for $-3 < h < -1$ and grows with increasing q_0, as has been confirmed experimentally[22]: the blue phase has only been observed in cholesterics with small pitches. Numerical calculations carried out by the present authors for $h = -1.5$ and for two values of q_0 gave $\tau_1 = 0.2298$, $\tau_2 = 0.2251$ for $q_0^2 = 0.05$ and $\tau_1 = 0.2395$, $\tau_2 = 0.2300$ for $q_0^2 = 0.1$. The interval $\Delta\tau$ is thus very narrow: for $\tau_1 \approx \tau_2 \sim 300$ K the existence region of the "magic" phase is of the order of 1 K. Qualitative agreement with experiment[22] is also found for the calculated jump in the order parameter corresponding to the transverse orientational mode: The blue phase turns out to be less ordered than the helical phase of the cholesteric.

Three blue phases are currently distinguished.[20] The "magic" phase considered here can evidently be identified with the low-temperature blue phase I (Ref. 23). The use of the mean field model to study blue phases having more complicated symmetry is made rather difficult by the need for self-consistency of a large number of equations.

Note added in proof (February 27, 1984): A recent paper by Z. Yaniv, G. Chidichimo, and J. W. Doane [Phys. Rev. A **28**, 3012 (1981)] reported measurements of the degree of biaxiality of a number of cholesteric mixtures. The experiments showed that the biaxiality of a cholesteric liquid crystal is larger for shorter helix pitches and grows with increasing temperature, in complete agreement with our calculated results shown in Fig. 1b.

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