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A Body-Centered Cubic Structure for the Cholesteric Blue Phase

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Résumé. — Quelques structures possibles des cristaux liquides chiraux, lorsque la phase isotrope est thermodynamiquement instable, sont analysées à l'aide de la théorie de Landau. On montre que, quand le terme cubique de l'énergie libre est suffisamment faible, comparé au terme chiral, la transition peut avoir lieu vers un cristal liquide à structure cubique centrée plutôt que vers la phase cholestérique (hélicoïdale) habituelle. Nous avançons une conjecture suivant laquelle cette structure cubique centrée (I432) serait caractéristique de la phase cholestérique bleue. Nous présentons certains arguments en faveur de cette suggestion, ainsi que les difficultés qu'elle soulève.

Abstract. — Using Landau theory, possible structures that can occur in chiral liquid crystals when the isotropic phase becomes thermodynamically unstable are analyzed. It is shown that the transition may be to a liquid crystal phase having a body-centered cubic (I432) structure rather than to the usual cholesteric (helical) phase when the coefficient of the cubic term in the free energy is sufficiently small with respect to that of the chiral term. It is conjectured that this bcc structure characterizes the cholesteric blue phase. Arguments supporting this suggestion as well as the difficulties it presents are discussed.

1. Introduction. — Certain liquid crystals derived from cholesterol (e.g., cholesteryl oleyl carbonate (COC) and cholesteryl oleate (CO)) exhibit a so-called *blue phase* in a narrow temperature range between the isotropic and normal cholesteric (helical) phases. Although this intermediate phase was first reported [1] in 1906 and, as its name indicates, it is visually quite distinct from the helical phase, its structure is still unknown. However, the following experimental facts have been established: (a) the blue phase, like the isotropic one, is optically isotropic [2], (b) the isotropic to blue phase transition is thermodynamically similar to the isotropic-helical one [3, 4] (e.g., the anomalies in the specific heat are of approximately the same magnitude [3]), (c) the cholesteric to blue transition (i.e., with increasing temperature) is accompanied by a small thermal anomaly [3, 4], (d) the NMR spectrum of the blue phase indicates that this phase is a stable one with long-range orientational order; also, the blue and isotropic phases have similar spectra, which are distinct from that of the normal cholesteric phase [5], (e) there is a significant difference in the critical dynamics (in the isotropic phase) between cholesterics undergoing an isotropic to blue transition and those exhibiting an isotropic to helical transition [6, 7].

A possible structure for the blue phase has been suggested by Saupe [2]. His structure is essentially a bcc lattice of point defects and, except in their immediate vicinity, the local director configuration is

similar to that of the normal cholesteric phase. However, as pointed out by Saupe himself, he had no theoretical basis for his structural ansatz. Such a basis is provided by this work.

We shall here analyse some possible structures for chiral liquid crystals by studying the transition from the isotropic phase within the framework of Landau theory [8]. In addition to the classical cholesteric (helical) phase (phase I) two other simple phases are possible, characterized by body-centered cubic (bcc-phase II) and hexagonal (phase III) symmetry, respectively. In the next section, we shall show that phase II is expected to occur when the coefficient of the cubic invariant in the Landau free energy is sufficiently small compared with that of the chiral term [9]. In the concluding section, we discuss the possibility that the phase II bcc structure characterizes the blue phase [10] and compare calculated properties of the isotropic to bcc phase transition with those observed experimentally for the isotropic to blue transition. Arguments supporting this identification as well as the difficulties it presents are discussed.

2. Landau theory of cholesterics. — We begin by considering the isotropic to nematic phase transition. Let us expand the order-parameter characterizing this transition in spherical harmonics Y_l^m , where l, m ($|m| \leq l$) are integers. Since Y_0^0 belongs to the

unit representation, it does not appear. Neither do the functions Y_1^m , due to the requirement that the system be invariant under a rotation by π about the nematic axis. Thus, to lowest order, the isotropic to nematic transition can be described using as an order-parameter any real linear combination of the five functions Y_2^m , all of which are degenerate at $k = 0$ (see Fig. 1a).

As shown schematically in figure 1b this five-fold degeneracy, which is characteristic of the isotropic to nematic transition, is lifted when the isotropic liquid phase no longer possesses inversion symmetry. In this case the transition from the isotropic phase is expected to be to one of the three phases defined in Sec. 1, each of which is characterized by a set of equilibrium wave vectors $\{\mathbf{k}_i\}$, with $|\mathbf{k}_i| = k_0 \neq 0$, and a structure which is invariant under a π rotation about the axes $\hat{i} \equiv \mathbf{k}_i/k_0$. Since the functions $Y_2^{\pm 1}(\theta_i, \varphi_i)$ are not invariant under such a π rotation while the function Y_2^0 cannot, by itself, describe $k_0 \neq 0$ ordering, it follows that the (real) order-parameter appropriate to a description of the possible phase transitions of the chiral system will be basically a linear combination of basis functions

$$\Phi_i = Y_2^m(\theta_i, \varphi_i) \exp(i\mathbf{k}_i \cdot \mathbf{r}_i)$$

and their complex conjugates (cc)

$$\Phi_i^* = Y_2^{-m}(\theta_i, \varphi_i) \exp(-i\mathbf{k}_i \cdot \mathbf{r}_i),$$

with amplitudes μ_i and μ_i^* , respectively. These function-pairs each form a real irreducible representation of the group of the wave vector \mathbf{k}_1 . (Note that each function-pair Φ_i, Φ_i^* has been defined with respect to a distinct polar coordinate system, having \hat{i} as its polar axes. The zeros of the azimuthal angles φ_i are defined in an identical manner for all i).

Since, for isotropic to cholesteric phase transitions, the order-parameter Φ can also include a term proportional to Y_2^0 , we have finally

$$\begin{aligned} \Phi &= \Phi_0 + \sum_{i=1}^n (\Phi_i + \text{cc}) \\ &= \mu_0 Y_2^0(\theta_0, \varphi_0) + \sum_{i=1}^n (\mu_i Y_2^m(\theta_i, \varphi_i) \exp(i\mathbf{k}_i \cdot \mathbf{r}_i) + \text{cc}), \end{aligned} \quad (1)$$

for the Landau order-parameter. The coefficients μ_0, μ_i are position independent. To describe the isotropic

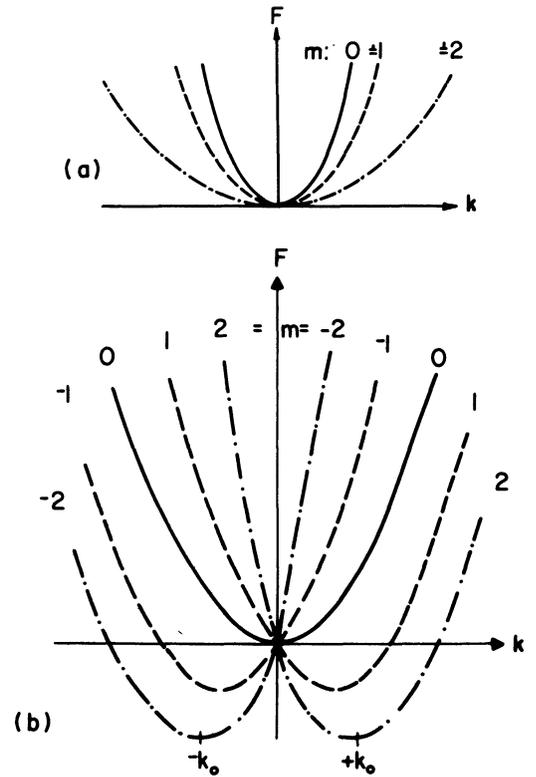


Fig. 1. — Schematic representation of the free energy associated with the order-parameter basis functions Y_2^m ($|m| \leq 2$), for the case of (a) an isotropic to nematic phase transition and (b) an isotropic to cholesteric phase transition.

to phase I (usual helicoidal) transition, we set $n = 1$ and $\theta_0 = \theta_1, \varphi_0 = \varphi_1$. For isotropic to phase II (bcc), we take $n = 6$, with the six vectors \mathbf{k}_i forming a regular tetrahedron and all $\mu = |\mu_i|$ equal. For this structure, we shall set $\mu_0 = 0$ as no mixed third-order invariant can exist. We thus neglect contributions of $O(\mu_0^4)$ in our treatment of this phase transition. Finally, for the isotropic to phase III (hexagonal) transition, $n = 3$, the three \mathbf{k} -vectors form an equilateral triangle, and again all $\mu \equiv |\mu_i|$ are equal. The polar angle θ_0 of Y_2^0 is defined relative to the axis \hat{z}_0 lying normal to the plane of the triangle.

We now expand the Landau free energy per unit volume F in powers of the order-parameter and its lowest-order spatial derivatives. Up to fourth-order in μ and μ_0 we have

$$F = F_2 + F_3 + F_4, \quad (2)$$

where

$$\begin{aligned} F_2 &= V^{-1} \int d^3r d\theta d\varphi \left[\alpha_0 \Phi^2 + id \sum_{i=1}^n (\Phi_i \nabla \Phi_i^* - \Phi_i^* \nabla \Phi_i) + 2c \sum_{i=1}^n (\nabla \Phi_i) (\nabla \Phi_i^*) \right] \\ &= \alpha_0 \mu_0^2 + 2n(\alpha_0 + dk + ck^2) \mu^2. \end{aligned} \quad (3a)$$

$$F_3 = \beta_0 V^{-1} \int d^3r d\theta d\varphi \Phi^3. \quad (3b)$$

$$F_4 = \gamma_0 V^{-1} \int d^3r d\theta d\varphi \Phi^4. \quad (3c)$$

Note that we have a simple form for the third- and fourth-order contributions to the free energy with only a single coefficient for each term. This is physically reasonable as the cholesteric phases are, on a microscope level, basically the same as the nematic phase. The explicit expressions for the third- and fourth-order contributions F_3 , F_4 depend upon which of the three phase transitions is being considered. For F_3 we obtain

$$F_{3I} = \beta(\mu_0^3 - 6\mu_0\mu^2), \quad (4a)$$

$$F_{3II} = -\beta(27/8)\sqrt{6}\mu^3 \quad (4b)$$

$$F_{3III} = \beta(\mu_0^3 + 3\mu_0\mu^2/8 - 27\sqrt{6}\mu^3/32), \quad (4c)$$

with

$$\beta = (5/\pi)^{1/2} \beta_0/7, \quad (4d)$$

for transitions to phases I, II, and III, respectively. Note that F_{3II} and F_{3III} are the *maximum* magnitudes for the third-order contributions, and were obtained by taking all the μ_i to have the same phase. (This is expected to correspond to the configuration with lowest free energy.)

The fourth-order contributions F_4 are as follows

$$F_{4I} = \gamma(\mu_0^2 + 2\mu^2)^2, \quad (5a)$$

$$F_{4II} = \gamma(1665/8)\mu^4, \quad (5b)$$

$$F_{4III} = \gamma(\mu_0^4 - 9\sqrt{6}\mu_0\mu^3/32 + 12\mu_0^2\mu^2 + (699/16)\mu^4), \quad (5c)$$

with

$$\gamma = (15/28\pi)\gamma_0. \quad (5d)$$

We stress that c and γ are assumed to be always positive.

Setting $(\partial F/\partial k)_{k=k_0} = 0$ yields $k_0 = -d/2c$ and

$$F_2(k = k_0) = \alpha_0\mu_0^2 + 2n(\alpha_0 - d^2/4c)\mu^2. \quad (6)$$

We now wish to determine, as we lower the temperature T of an isotropic phase cholesteric liquid crystal transition in the phase transition region, which of the above three possible ordered phases will first appear. In Landau theory, this is equivalent to varying α_0 , which can be written as [8]

$$\alpha_0 = \alpha(T/T_0 - 1) = \alpha t, \quad (7)$$

where T_0 is an idealized isotropic to ordered phase transition temperature for the case $d = \beta = 0$. The parameters $(d^2/4c)$, α , β and γ are, as usual, regarded as temperature-independent in the phase transition region.

We first consider the isotropic to helicoidal (phase I) transition. The total free energy density F_I is obtained by summing F_2 (with $n = 1$), F_3 , and F_4 , as given by (6), (4a), and (5a), respectively. For $\beta = 0$, it follows from (6) (with $n = 1$) that the transition will be a continuous one, occurring at $t = t_1 = d^2/4\alpha c$. The primary order-parameter is μ , with μ_0 being second-

dary. The crucial point, however, as noted by Brazovskii and Dmitriev [9], is that this situation remains *unchanged*, even when $\beta \neq 0$, as long as

$$\beta^2 \leq \beta_c^2 = (4/9)(d^2/4c)\gamma. \quad (8)$$

The reason for this is that, unlike the usual Landau expansion [8], the free energy term F_{3I} does *not* contain a contribution proportional to μ^3 , the cube of the primary order-parameter. Rather, we have, to leading order, a $\mu_0\mu^2$ term, which will result, since $\mu_0 \sim \mu^2$, in a *negative* (for minimum free energy) contribution proportional to μ^4 . *Only* when this negative contribution is greater in magnitude than the positive one proportional to γ will the transition temperature shift and the transition become of first order. This is analogous to the well-known Rodbell-Bean effect in magnetic phase transitions, where μ_0 would correspond to an elastic degree-of-freedom [11].

When $\beta^2 > \beta_c^2$, we should, for consistency, also consider the contributions to F_I of $O(\mu^6)$. Since this would require the introduction of yet another phenomenological coefficient, we shall restrict ourselves to the terms introduced previously. As we shall see, the region of interest will in any case be that in which $\beta^2 \lesssim \beta_c^2$.

For $\beta^2 > \beta_c^2$, the (first-order) thermodynamic transition to phase I occurs when

$$F_I = \partial F_I/\partial \mu = \partial F_I/\partial \mu_0 = 0.$$

Defining $t = t_1^*$ at this point, we obtain

$$(t_1^* - t_1)/t_1 = 4(f - 1)/9 + \Delta(2f + 1)/18, \quad (9a)$$

$$\Delta = (\beta^2 - \beta_c^2)/\beta_c^2, \quad f = \left[\frac{1 + \Delta/4}{1 + \Delta} \right]^{1/2}, \quad \Delta > 0. \quad (9b)$$

Thus, the isotropic to usual helicoidal phase transition would be of second-order at $t = t_1$ when $\beta^2 \leq \beta_c^2$ and of first-order, at $t = t_1^*$ for $\beta^2 > \beta_c^2$.

Let us now consider the isotropic to bcc (phase II) transition. We obtain the relevant free energy density F_{II} by summing F_2 (with $\mu_0 = 0$ and $n = 6$), F_{3II} , and F_{4II} , as given respectively by (6), (4b), and (5b). Here the transition is always first-order and the thermodynamic phase boundary is reached when $F_{II} = \partial F_{II}/\partial \mu = 0$. Defining $t = t_{II}^*$ at this point, we obtain

$$(t_{II}^* - t_1)/t_1 = (9/2960)(1 + \Delta), \quad (\Delta \geq -1). \quad (10)$$

Setting aside for the moment the possibility of a transition from the isotropic to the hexagonal phase (phase III), we find, by setting $t_1^* = t_{II}^*$ that the transition from the isotropic phase will be to the bcc rather than to the helicoidal phase whenever $\Delta \lesssim 0.15$ or

$$\beta^2 \lesssim 1.15\beta_c^2, \quad (11a)$$

$$|\beta| \lesssim 0.36(\gamma/c)^{1/2} |d|. \quad (11b)$$

In other words, whenever the transition from the isotropic to the helicoidal phase would be continuous or nearly so, the cholesteric liquid crystal system can lower its free energy by ordering instead in phase II with an I432 bcc structure. This is, of course, what one would expect to occur due to the cubic term in the phase II free energy expression.

We must still consider the possibility of a transition to hexagonal (phase III) ordering. The appropriate free energy density F_{III} is obtained by summing F_2 (with $n = 3$), $F_{3\text{III}}$, and $F_{4\text{III}}$, from (6), (4c), and (5c), respectively. Since only the parameter region $|\beta| \lesssim |\beta_c|$ is expected to be relevant, the *jump* in μ_0 at the phase transition will, to lowest order, just be proportional to μ^2 . It is therefore consistent with our treatment of F_{I} and F_{II} to consider the approximation

$$F_{\text{III}} \simeq \alpha_0 \mu_0^2 + 6(\alpha_0 - d^2/4c) \mu^2 + \beta(3\mu_0 \mu^2/8 - 27\sqrt{6}\mu^3/32) + \gamma(699/16)\mu^4. \quad (12)$$

Setting $F_{\text{III}}/\partial\mu_0 = 0$ yields

$$\mu_0 = - (3\beta/2\alpha_0) \mu^2 \quad (13)$$

and, upon substituting (13) into (12), we obtain

$$F_{\text{III}} \simeq 6(\alpha_0 - d^2/4c) \mu^2 - (27\sqrt{6}/32) \beta \mu^3 + (699\gamma/16 - 9\beta^2/4\alpha_0) \mu^4. \quad (14)$$

The first-order isotropic to phase III transition would occur at the thermodynamic phase boundary given by $F_{\text{III}} = F_{\text{III}}/\partial\mu = 0$. (We assume that the coefficient of the μ^4 term in (14) is positive.) Defining $t = t_{\text{III}}^*$ at the point, we obtain

$$\frac{(t_{\text{III}}^* - t_1)}{t_1} = \frac{27(1 + \Delta)}{32^2[(233/16) - (1 + \Delta)(1/3)t_1/t_{\text{III}}^*]}; \quad \Delta \geq -1. \quad (15a)$$

Clearly, $t_1/t_{\text{III}}^* \simeq 1$, so (15a) may be simplified to

$$\frac{(t_{\text{III}}^* - t_1)}{t_1} \simeq \frac{27(1 + \Delta)}{32^2[(233/16) - (1 + \Delta)/3]}; \quad \Delta \geq -1. \quad (15b)$$

Setting $t_{\text{III}}^* = t_1^*$ we find that, in order for an isotropic to phase III transition to occur, we must have $\Delta \lesssim 0.117$. Thus it is only necessary to examine the ratio $R = (t_{\text{III}}^* - t_1)/(t_{\text{III}}^* - t_1)$ for $-1 < \Delta < 0.117$ in order to determine, when the transition from isotropic to phase I would become continuous or nearly so, whether the actual transition will be to phase II ($R > 1$) or to phase III ($R < 1$). From (10) and (15b) we obtain for the minimum value of R

$$R_{\text{min}} = (t_{\text{III}}^* - t_1)/(t_{\text{III}}^* - t_1) |_{\Delta=0.117} = 1.63. \quad (16)$$

Thus the prediction, based on Landau theory, is that whenever (11) is satisfied, an ordered phase with bcc structure will occur at the thermodynamic instability of the isotropic phase. This prediction differs from that of Brazovskii and co-workers [10], who suggested that the hexagonal phase would be the relevant one.

3. Discussion. — In the previous section we have argued, using Landau theory, that under specified conditions cholesteric liquid crystal should order with an I432 body-centered cubic structure rather than the usual helicoidal one when the isotropic phase becomes thermodynamically unstable. It is tempting to identify this bcc structure as that of the experimentally observed blue phase which exists in this thermodynamic region [10]. Such an identification immediately satisfies two of the basic experimental require-

ments listed in Sec. 1; namely, the optical isotropy of the blue phase and the requirement that it be thermodynamically stable with long-range orientational order. The bcc phase also satisfies another property associated with the blue phase, namely, that it should be the thermodynamically stable phase only within a limited temperature range below T_{II}^* . The reason for this is that, in the bcc phase, the magnitude of the order parameter is *not* constant in space. As the temperature is lowered below T_{II} , the usual helicoidal phase, in which this magnitude is constant, will, eventually, have the lower free energy of the two when the contribution of the quartic term in F_{II} dominates that of the cubic one. This is shown qualitatively in figure 2.

A particularly interesting quantity in our model is the value of $|d|/c$ at which the *crossover* to the bcc phase is predicted to occur. If we make the strong assumption that the parameters β and γ are the same in nematic and cholesteric materials, we can estimate, from the Maier-Saupe theory of nematics, the value of $\lambda_c = 2\pi c/|d|$, the optical wavelength in the cholesteric phase (which is one-half the actual pitch) at which this crossover should occur. Using these molecular field (Maier-Saupe) results for β , γ and c in nematics [12], we obtain

$$\lambda_c \simeq 3(T^*/\Delta T^*)^{1/2} \xi_0. \quad (17)$$

Here T^* (~ 400 K) is the actual temperature of the

isotropic to nematic transition, the temperature difference $\Delta T^* = T^* - T_0$ (see (7)), and ξ_0 ($\sim 2\zeta$ Å) is the microscopic length appearing in the expression for the coherence length $\xi = \xi_0 |(T/T_0) - 1|^{-1/2}$. Clearly, λ_c , as given by (17), is very sensitive to the value chosen for ΔT^* . A completely self-consistent calculation, based on Maier-Saupe theory, gives [12] $\Delta T^*/T^* = 0.15$ or $\Delta T^* \simeq 46$ K, which is more than an order-of-magnitude larger than the experimental values of approximately 1 K [13]. If, on the other hand, we substitute experimental values of ΔT^* in (17), we obtain values for λ_c of the order of 10^3 Å, which is in agreement with the values usually found in cholesteric esters [12, 14]. It is thus at least possible that the cholesteric bcc structure can occur with a lattice constant in the blue region of the spectrum for reasonable values of the parameters appearing in the Landau free energy. On the other hand, it is by no means clear that the characteristic color of the blue phase is in fact due to Bragg scattering [15]. Preliminary measurements by us suggest that incoherent scattering processes may in fact play a dominant role. This point requires further study.

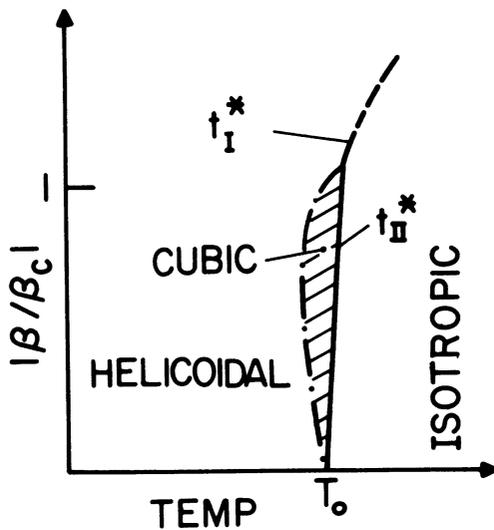


Fig. 2. — Possible phase diagram for cholesteric liquid crystals, showing schematically the region in which the isotropic, body-centered cubic, and helicoidal phases are each thermodynamically stable.

In order to further analyze the thermodynamic properties of the bcc phase, it is possible to compare the isotropic to bcc phase transition with the isotropic

to nematic one. Remembering that the order-parameter for the nematic case can be written as [14]

$$\Phi = \eta Y_2^0, \tag{18a}$$

we obtain for the Landau free energy

$$F_N = \alpha_0 \eta^2 + \beta \eta^3 + \gamma \eta^4. \tag{18b}$$

We can now compare, using (18b) and our previous results for F_{II} , the values of the two order-parameters just below their respective thermodynamic phase-transitions. We obtain

$$\bar{\eta} = -0.5 \beta/\gamma, \tag{19a}$$

$$\bar{\mu}_{II} = (8 \sqrt{6}/370) \beta/\gamma = 0.02 \beta/\gamma. \tag{19b}$$

If the ratio β/γ is the same for the two phase transitions, (19) indicates that the *jump* in the blue phase order-parameter is much smaller than that of the nematic one. The same conclusion would follow for the latent heats of the two transitions although, experimentally, both seem to be of the same order-of-magnitude [3, 4, 11]. This could be due to, e.g., different values of β/γ in nematics and cholesterics exhibiting a blue phase, or a need to include higher order terms in the Landau free energy in order to quantitatively describe first order transitions in liquid crystals.

To summarize, we have shown using Landau theory that, in addition to the usual helicoidal phase, cholesteric liquid crystals can, under specified conditions, order in an additional phase characterized by a body-centered cubic structure. We have considered identifying this structure as that of the cholesteric blue phase which has been observed experimentally. Many, but not all of these properties of the bcc phase are in agreement with those found experimentally for the blue phase. Clearly, additional data are needed and several investigations of the structural properties of the blue phase are now in progress [7, 15, 16].

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Note added in proof: Meiboom and Sammon have recently identified a body-centered cubic blue phase structure [17].

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