

Theory of structure and properties of cholesteric blue phases

R. M. Hornreich and S. Shtrikman

Department of Electronics, Weizmann Institute of Science, Rehovot, Israel

(Received 5 February 1981)

Using Landau theory, we show that the red shift of the primary Bragg reflection in cholesteric blue phases and the appearance of more than one cubic structure can be understood by including harmonics of the basic spatial frequency in the order parameter. A new nonsymmorphic bcc structure, having $O^8(14_132)$ symmetry and no isotropic (defect) points, is found at intermediate chiralities.

Recently there has been a sharp surge of both experimental¹⁻⁸ and theoretical⁹⁻¹³ interest in the so-called blue phase (BP), which appears below the clearing point in certain cholesteric liquid crystals. Using Landau theory, we have shown⁹ that a symmorphic body-centered cubic (bcc) phase, with symmetry $O^5(1432)$, can exist in a narrow temperature region between the isotropic (*I*) and usual cholesteric (Ch) phases when the chirality is sufficiently strong. Experimentally, however, strong evidence^{1-3,8} has accumulated for the existence of at least two blue phases, BPI and BPII, between Ch and *I*. Recent optical Bragg scattering experiments have shed considerable light on the structural properties of these phases and lead to the following observations:

(a) BPI and BPII satisfy the same selection rules for unpolarized light scattering and have cubic structures^{2,3} [either bcc or simple cubic (sc)].

(b) In both BPI and BPII, all the observed Bragg reflections of Johnson *et al.*³ exhibit circular selective reflection; i.e., they appear in back-reflection only for circularly polarized incident light.¹⁴ Similar behavior was noted by Meiboom and Sammon.²

(c) BPII appears to consist of *two* distinct phases, implying the existence of at least *three* blue phases! Denoting these phases by BPII_a and BPII_b (at longer and shorter pitch, respectively), BPII_a → BPI (which occurs with decreasing temperature) is second order while BPII_b → BPI and BPII_a → BPII_b are first order.^{3,14}

(d) the BPII unit-cell size is essentially temperature independent for materials whose Ch-phase period is temperature independent. Also, the first BPII Bragg reflection is "red shifted" with respect to the Ch re-

flexion. In BPI there is an additional, approximately linear, red shift, or increase in the unit-cell parameter, with decreasing temperature, particularly below BPII_a → BPI.³

The above observations provide evidence that cholesteric blue phases exhibit a number of different structures. In this Communication we show, using an extended version of our previous model,⁹ how such structures arise naturally. In particular, we find that a *new*, nonsymmorphic bcc structure, with symmetry $O^8(14_132)$, can exist for intermediate chirality.

Since *I*-phase cholesterics lack inversion symmetry, all cubic [as required by (a)] blue phases must belong to the *T* and *O* crystal classes. Using Landau theory, we have shown⁹ that O^5 is the energetically preferred cubic structure in the high-chirality limit, where a *single spatial frequency only* appears in the structure factor. However, since additional Bragg reflections are observed, other frequencies (harmonics) are also present. We shall see that these harmonics have two important consequences: (1) The primary BP Bragg selection need not appear at the same wavelength as the Ch-phase reflection, and (2) other cubic structures can, under certain conditions, have a lower free energy than O^5 . We consider primarily bcc structures since the optical selection rules appropriate to BP scattering¹⁵ show that only such structures are consistent with (b). However, sc structures, which are also, in principle, possible,¹⁰ will be mentioned briefly.

In general, phase transitions in thermotropic liquid-crystal systems are described using the anisotropic part of the dielectric tensor $\epsilon_{ij}(\vec{r})$ with $\text{Tr}(\epsilon) = 0$ as an order parameter. For cholesteric systems, the free-energy density is then given by¹⁶

$$F = V^{-1} \int d\vec{r} \{ [a \epsilon_{ij}^2 + c_a (\partial_i \epsilon_{ij})^2 + c_b \partial_i \epsilon_{ij} \partial_i \epsilon_{ij}] - d_{0ij} \epsilon_{in} \partial_i \epsilon_{jn} + \beta_0 \epsilon_{ij} \epsilon_{jl} \epsilon_{li} + \gamma_0 (\epsilon_{ij}^2)^2 \} , \quad (1)$$

$$\epsilon_{ij}(\vec{r}) = \frac{1}{2} \sum_{hkl} \{ \bar{\epsilon}_{ij}(\sigma) \exp[iq(hx + ky + lz)] + \text{c.c.} \} , \quad (2a)$$

where c.c. denotes complex conjugation, $\sigma = q(h^2 + k^2 + l^2)^{1/2} / \sqrt{2} q_0$ (q_0 is defined below) and, for each $[hkl]$,

$$\bar{\epsilon}_{ij} = \frac{1}{2} \left[\epsilon_2 e^{i\psi_2} \begin{pmatrix} 1 & i & 0 \\ i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \epsilon_1 e^{i\psi_1} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & i \\ 1 & i & 0 \end{pmatrix} + \sqrt{2/3} \epsilon_0 e^{i\psi_0} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \epsilon_{-1} e^{i\psi_{-1}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & -i \\ 1 & -i & 0 \end{pmatrix} + \epsilon_{-2} e^{i\psi_{-2}} \begin{pmatrix} 1 & -i & 0 \\ -i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right], \quad (2b)$$

with $\epsilon_m \geq 0$. It is convenient to rewrite the order parameter in the equivalent form

$$\Phi(\bar{r}) = \frac{1}{2} \left(\frac{8}{15} \pi \right)^{1/2} \sum_{hkl;m} (\epsilon_m(\sigma) \{ Y_2^m(hkl) \exp[iq(hx + ky + lz) + i\psi_m(hkl)] + \text{c.c.} \}) , \quad (3)$$

where $Y_2^m(hkl)$ is the (jm) spherical harmonic in a suitably chosen local coordinate system whose polar axis is along $[hkl]$. The quadratic (in ϵ or Φ) part of F now becomes¹⁶

$$F_2 = \sum_{hkl;m} \{ \alpha - mdq(h^2 + k^2 + l^2)^{1/2} + [c_1 + c_2(4 - m^2)] q^2(h^2 + k^2 + l^2) \} \epsilon_m(\sigma)^2 , \quad (4)$$

where, for stability, $c_1 > 0$ and $c_1 + 4c_2 > 0$. Not all $\epsilon_m(\sigma) \neq 0$ (see below).

For nonchiral or racemic (R) systems, $d=0$, and the transition is to a state with $q=0$. When $d \neq 0$, we have a cholesteric system and, for example, the usual $I \rightarrow \text{Ch}$ transition is associated with the $m=2$ branch minimum (for $d > 0$), its c.c., and the state $m=q=0$. In general, the equilibrium wave vector is found by setting $\partial F/\partial q = 0$. In Landau theory, the explicit q dependence of higher than second order in Φ contributions to F is ignored, thus $\partial F/\partial q = \partial F_2/\partial q = 0$, and

$$r = \frac{q}{q_0} = \left(\frac{\sum [m(h^2 + k^2 + l^2)^{1/2} \epsilon_m^2]}{2^{1/2} \sum \left[1 + (4 - m^2) \frac{c_1}{c_2} \right] [(h^2 + k^2 + l^2) \epsilon_m^2]} \right)^{1/2} \quad (5)$$

with $q_0 = d/\sqrt{2}c_1$. Ch is characterized by the single wave vector, $Q_{\text{Ch}} \equiv q_{\text{Ch}}(h^2 + k^2 + l^2)^{1/2} = \sqrt{2}q_0$, and the wavelength (in the material) at which the Bragg back-reflection occurs is $\lambda_{\text{Ch}} = 4\pi/Q_{\text{Ch}} = 4\pi/\sqrt{2}q_0$.

The $I \rightarrow O^5$ transition has been described⁹ by including in Φ only the states $\langle 110; m=2 \rangle$. Of course, if $I \rightarrow \text{BP}$ were second order, this description would be adequate and only one spatial frequency would appear in the structure factor immediately below the phase transition. We would then observe a single Bragg reflection only, associated with the $\{110\}$ planes, which are separated by $d_{110} = 2\pi/\sqrt{2}q_0$. Thus, in this hypothetical case, the BP $\{110\}$ Bragg back-reflection would also occur at λ_{Ch} . However, since $I \rightarrow \text{BP}$ is in fact first order, other spatial frequencies and helicities m can appear in Φ , as indicated in Eq. (3). As a result, the lattice constant $2\pi/q$ is not equal to $2\pi/q_0$ and is dependent upon the relative intensities of the harmonics. For bcc structures $\epsilon_m(\sigma)$

can be nonzero only when $h+k+l=2n$ (n integer) and it is clear from Eq. (5) that $q < q_0$. We thus expect a "red shift" of the BP $\{110\}$ back-reflection with respect to λ_{Ch} , in agreement with (d). Note that this shift is a collective effect and that it provides a quantitative measure of the harmonic contribution to the BP order parameter.

The full selection rules for a given $\epsilon_m(\sigma)$ to be nonzero have been given elsewhere.¹⁵ Consider, for example, the lowest-lying $\langle 200; 2 \rangle$ harmonic. For O^5 , symmetry demands that $\epsilon_2(\sqrt{2}r) = 0$, and these states are therefore forbidden. For O^8 , on the other hand, $\langle 200; 2 \rangle$ states are allowed. Let us therefore examine the consequences of including these states in Φ . Rewriting $\epsilon_2(r) = \mu$, $\epsilon_2(\sqrt{2}r) = \nu$, and $\psi_2(110)$, $\psi_2(1\bar{1}0)$, $\psi_2(200)$ and their cyclic permutations as ξ_j , η_j , and ζ_j , respectively ($j=1, 2, 3$), the higher-order contributions to F for both O^5 and O^8 are

$$F_3 = \beta \left\{ -\frac{81}{16} \sqrt{6} \left[\cos(6\alpha_0 - \sum \eta_j) + \sum \cos(6\alpha_0 + \xi_j - \xi_{j+1} - \eta_{j+2}) \right] \mu^3 \right. \\ \left. - \frac{3}{4} (3\sqrt{6} + 4\sqrt{2}) \sum [\cos(\zeta_j - \xi_j - \eta_{j+1}) - \cos(\zeta_j - \xi_{j+2} - \eta_{j+2})] \mu^2 \nu \right\} , \quad (6a)$$

$$F_4 = \gamma \left[\left(\frac{711}{4} + \frac{25}{8} \sum \cos(\xi_j - \xi_{j+2} + \eta_j - \eta_{j+2}) \right) \mu^4 + 39\nu^4 \right. \\ \left. + \left(\frac{3}{2} (151 + 12\sqrt{2}) \sum [\cos(\zeta_j + \zeta_{j+1} - 2\xi_j) + \cos(\zeta_j - \xi_{j+1} - 2\eta_j)] \right) \mu^2 \nu^2 \right. \\ \left. - \frac{1}{4} (17 + 12\sqrt{2}) \sum [\sin(\zeta_j - \xi_j - \eta_j - \eta_{j+1}) + \sin(\zeta_j - \xi_j + \eta_{j+1} + \eta_{j+2}) \right. \\ \left. - \sin(\zeta_j - \xi_j + \xi_{j+1} - \xi_{j+2}) - \sin(\zeta_j - \xi_{j+1} - \eta_j + \eta_{j+2})] \mu^3 \nu \right] , \quad (6b)$$

where $\alpha_0 = \arcsin(\frac{2}{3})^{1/2}$, $\gamma > 0$, $\beta < 0$ for rodlike molecules, and all sums are on $j(\text{mod } 3)$.

For O^5 , we set $\xi_j = \eta_j = 0$, noting that, as expected, the $\mu^2\nu$, $\mu^3\nu$, and $\mu^3\nu$ terms now vanish for all ζ_j . The contribution proportional to ν^2 (from F_2 and F_4) is easily seen to be positive at the $I \rightarrow O^5$ transition, and O^5 is thus stable with respect to a transition to a new phase with $\mu, \nu \neq 0$. Noting that $\xi = \xi_R(T_{cR}) = (c_1/\alpha)^{1/2}$ is a correlation length at the $I \rightarrow R$ transition, we define $p = \xi/\lambda_{Ch}$.

Considering only I , Ch , and O^5 , we obtain the phase diagram shown in Fig. 1(a). As expected,⁹ O^5 appears for sufficiently high chirality p . The ordinate is in units of the difference between the actual and extrapolated-from-the-disordered-phase transition temperatures for the racemic mixtures. This is¹⁷ $0.5-1^\circ\text{C}$; thus cubic phases are thermodynamically stable only within a narrow temperature range. Note that we have assumed, for simplicity, that the Landau coefficients are additive as one changes p by, e.g., mixing left- and right-handed enantiomers.

Considering now the possibility of an O^8 phase, we obtain the new phase diagram shown in Fig. 1(b). We find that a *new cubic phase*, with O^8 structure, can appear for intermediate values of p . This structure, unlike O^5 , is nonsymmorphic and has *no* isotropic (defect) points. The inclusion of $\langle 200;2 \rangle$ states in Φ is a key element in obtaining this new phase. Experimentally, $n \approx 1.6$ (Ref. 3) and $\xi \approx 250 \text{ \AA}$ (Ref. 18); thus, for $p = 0.10-0.15$, we have $\lambda_{B}^{\text{AIR}} = 4000-6000 \text{ \AA}$, in agreement with experiment.¹⁻³

Of course, Fig. 1(b) is only suggestive; the inclusion of all allowed higher harmonics and helicities in Φ could, in principle, result in O^5 (or some other structure) being energetically preferred. However, at least as regards O^5 vs O^8 , the allowed additional states—except for $\langle 200;2 \rangle$ —are essentially the same for both structures.¹⁵ Thus their effect on the free-energy *difference* between the two structures is likely to be small. Further support for an O^8 phase comes from observation (b), since in O^8 (but not O^5) the $\langle 200 \rangle$ line will exhibit circular selection reflection.

In O^8 the calculated red shift is approximately $r \approx 0.9$ or 10%. This is less than the experimentally observed values of 20–30%, and indicates that other states, in addition to $\langle 110;2 \rangle$ and $\langle 200;2 \rangle$, have non-negligible amplitudes.

It is pertinent to ask how other cubic structures could be obtained since, as noted in (c), additional bcc structures appear to have been observed. Two candidates for such phases which immediately present themselves are $T^3(I23)$ and $T^5(I2_13)$. The former is a subgroup of O^5 and can be obtained to lowest order by including in $\Phi(\bar{r})$, in addition to $\langle 110;2 \rangle$, the states $\langle 200;2 \rangle$. The latter is a subgroup of O^8 and appears when $\langle 110;1 \rangle$ is added to $\Phi(\bar{r})$ of O^8 .

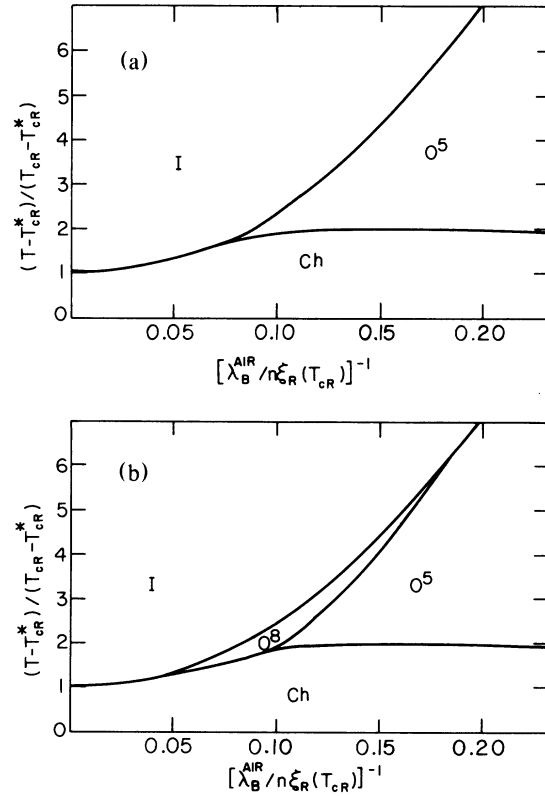


FIG. 1. Calculated phase diagrams when (a) only I , Ch , and O^5 phases are allowed, and (b) only I , Ch , O^5 , and O^8 phases are allowed. Here T_{cR} , T_{cR}^* are the actual and extrapolated $I \rightarrow R$ transition temperatures for racemic mixtures, λ_B^{AIR} is the Ch -phase Bragg back-reflection wavelength in air, n is the index of refraction, and $\xi_R(T_{cR})$ is a racemic-mixture correlation length at the phase transition. All transitions shown are first order.

Both $O^5 \rightarrow T^3$ and $O^8 \rightarrow T^5$ can, by the Landau rules, be second order and are described by $n = 1$ (Ising) order parameters. The $O^8 \rightarrow T^5$ transition is especially interesting since, if we assign O^8 and T^5 to $BPII_a$ and BPI , respectively, the additional linear red shift in the latter phase noted in (d) follows naturally from Eq. (5) when $\langle 110;1 \rangle$ states are introduced. Simple cubic structures can be obtained similarly; by adding $\langle 100;2 \rangle$ to $\langle 110;2 \rangle$ we produce an $O^2(P4_232)$ structure, while adding $\langle 100;2 \rangle$ and $\langle 110;1 \rangle$ gives $T^1(P23)$. In all cases, both bcc and sc, appropriate phases must be chosen. Details are planned to be given elsewhere.

We are grateful to Professor P. P. Crooker for informing us of his experimental results prior to publication and for very useful correspondence and discussions and to H. Grebel for programming assistance.

- ¹For a review, see H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 161.
- ²S. Meiboom and M. Sammon, *Phys. Rev. Lett.* **44**, 882 (1980).
- ³D. L. Johnson, J. H. Flack, and P. P. Crooker, *Phys. Rev. Lett.* **45**, 641 (1980).
- ⁴E. T. Samulski and Z. Luz, *J. Chem. Phys.* **73**, 142 (1980).
- ⁵P. H. Keyes, A. J. Nicastro, and E. M. McKinnon, *Mol. Cryst. Liquid Cryst.* (in press); A. J. Nicastro and P. H. Keyes (unpublished).
- ⁶D. Armitage and R. J. Cox (unpublished).
- ⁷J. H. Flack and P. P. Crooker, *Mol. Cryst. Liquid Cryst.* (in press).
- ⁸M. Marcus, *J. Phys. (Paris)* (in press).
- ⁹R. M. Hornreich and S. Shtrikman, (a) *Bull. Israel Phys. Soc.* **25**, 46 (1979); (b) *J. Phys. (Paris)* **41**, 335 (1980) and erratum (in press); (c) in Ref. 1, p. 185.
- ¹⁰S. Alexander, in *Proceedings of the Colloque Curie, Paris, September 1980* (unpublished).
- ¹¹H. Kleinert and K. Maki (unpublished).
- ¹²W. Kuczynski, K. Bergmann, and H. Stegemeyer, *Mol. Cryst. Liquid Cryst. Lett.* **56**, 283 (1980); H. Stegemeyer, *Phys. Lett.* **79A**, 425 (1980).
- ¹³H. Schröder, in Ref. 1, p. 196.
- ¹⁴P. P. Crooker (private communication); (unpublished).
- ¹⁵R. M. Hornreich and S. Shtrikman (unpublished).
- ¹⁶S. A. Brazovskij and S. G. Dmitriev, *Zh. Eksp. Teor. Fiz.* **69**, 979 (1975) [*Sov. Phys. JETP* **42**, 497 (1976)].
- ¹⁷Y. Poggi, P. Atten, and J. C. Filippini, *Mol. Cryst. Liquid Cryst.* **37**, 1 (1976).
- ¹⁸C. C. Yang, *Phys. Rev. Lett.* **28**, 955 (1972).