[3]R. B. Stephens, Phys. Rev. B **13**, 852 (1976).

[4]A. C. Anderson, in *Fast Ion Transport in Solids*, edited by P. Vashishta *et al*. (North-Holland, Amsterdam, 1979), p. 255, and references therein.

[5]S. Hunklinger and W. Arnold, *Physical Acoustics* (Academic, New York, 1976), Vol. XII, p. 155.

[6]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[7]W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[8]H. U. Beyeler, Phys. Rev. Lett. **37**, 1557 (1976); H. U. Beyeler, L. Pietronero, S. Strässler, and H. J.

Wiesmann, Phys. Rev. Lett. **38**, 1532 (1977).

[9]H. U. Beyeler, L. Pietronero, and S. Strässler, Phys. Rev. B **22**, 2988 (1980).

[10]J. Frenkel and T. Kontorova, J. Phys. (Moscow) **1**, 337 (1939).

[11]L. Pietronero and S. Strässler, Phys. Rev. Lett. **42**, 188 (1979).

[12]L. Pietronero, W. R. Schneider, and S. Strässler, to be published.

[13]J. Bernasconi, H. U. Beyeler, S. Strässler, and S. Alexander, Phys. Rev. Lett. **42**, 819 (1979).

Theory of the Blue Phase of Cholesteric Liquid Crystals

S. Meiboom

Bell Laboratories, Murray Hill, New Jersey 07974

and

James P. Sethna

Princeton University, Princeton, New Jersey 08540

and

P. W. Anderson

Princeton University, Princeton, New Jersey 08540, and Bell Laboratories, Murray Hill, New Jersey 07974

and

W. F. Brinkman

Bell Laboratories, Murray Hill, New Jersey 07974

We present a theory of the cholesteric blue phase, assuming a first-order cholesteric-isotropic transition. We show, on the basis of the Oseen-Frank elasticity equations, that the planar helix structure, generally associated with the cholesteric phase, becomes unstable at temperatures near the transition point. It transforms into a phase characterized by a network of disclination lines.

In many cholesteric liquid crystals the transition between the regular helical cholesteric phase and the isotropic phase occurs through one or more intermediate phases. These are the cholesteric "blue phases," which are thermodynamically stable over a narrow temperature range, often less than 1 °C. Recently, there has been a renewed interest in the study of the blue phases,[1-10] largely stimulated by a theoretical explanation for their existence by Brazovskii.[11-13] From the observation of Bragg reflections at visible wavelengths,[7,10] it is now well established that at least in some cases the blue phases have a structure of cubic symmetry, with unit-cell dimensions of the order of the cholesteric pitch.

Attempts at a theoretical treatment of the blue

phases[11-13] have been based on Landau theory. This theory predicts a phase in which the order parameter is locally biaxial in large regions of the unit cell of the cubic material. In addition, the theory appears to be difficult to use in predicting more than one blue phase whereas experimentally there are known to be up to three separate phases. Moreover, the important parameter of the theory for estimating when the predicted phase is stable is $Kq_0^2/l(\Delta T/T_1)$, where K is a typical elastic constant, q_0 is 2π divided by pitch, l is the latent heat of the first-order transition, and $\Delta T = (T_c - T_1)$, with T_c the extrapolated second-order transition temperature and T_1 the first-order transition temperature. This ratio is just the elastic energy associated with the twist di-

vided by the free energy difference of the two phases at T_c. Typically, this ratio is of order 0.2 whereas it needs to be ~1.0 in the Brazovskii theory.[14]

In the theory presented here we take the other extreme position: We consider a first-order transition of sufficient strength for the cholesteric phase to be adequately described by the conventional director and scalar order parameter, up to the isotropic transition. We can then base the theory on the well-known phenomenological elastic equations for nematics and cholesterics (the Oseen-Frank equations). We obtain the remarkable result that the ordinary helical cholesteric must become unstable at a temperature near the isotropic transition, and transforms into a structure characterized by a network of disclinations—presumably the blue phases. We estimate that this occurs a few degrees below the isotropic transition point, in accord with the typical temperature range of the blue phases of about one degree.

We consider a model in which the blue-phase structure is a lattice of disclinations. The core of the disclinations is assumed to be isotropic, while the material between them is in the cholesteric phase. Various structures suggest themselves. One example is a body-centered-cubic lattice with $S = -\frac{1}{2}$ disclinations along the body diagonals of the unit cell.[15] Another interesting structure consists of two interpenetrating diamond lattices of disclinations. We shall describe this in more detail at the end of this Letter. Other possibilities of course exist.

The crucial point we make here is that in a cholesteric the free energy of such a disclination structure will become lower than the energy of the ordinary helical cholesteric structure, provided the temperature is near enough to the cholesteric-isotropic transition. An alternative, and somewhat paradoxical, way of formulating this thesis is that, near enough the transition, the free energy of a disclination will become negative.

To substantiate this claim, we begin with the well-known expression of the elastic energy of a cholesteric:

$$F_1 = \int dV[\tfrac{1}{2}K_{11}(\operatorname{div}\vec{n})^2 + \tfrac{1}{2}K_{22}(q + \vec{n} \cdot \operatorname{curl}\vec{n})^2 + \tfrac{1}{2}K_{33}(\vec{n} \times \operatorname{curl}\vec{n})^2]. \tag{1}$$

Here the three terms represent the splay, twist, and bend, respectively. However, if one peruses the derivation of these equations, as, for instance, given by Nehring and Saupe,[16] one finds that there is an additional term[17]

$$F_2 = +\tfrac{1}{2}\int dV(K_{22} + K_{24})\nabla \cdot [(\vec{n}\cdot\nabla)\vec{n} - \vec{n}(\nabla\cdot\vec{n})]. \tag{2}$$

The standard argument for dropping this term is that it has the form of a divergence, and its integral over the sample can therefore be transformed into a surface integral and consequently neglected. For the proposed disclination model of the blue phase, however, the integral must be taken over the surface of the core of the disclinations as well, and since the latter area increases as the third power of the sample dimension the standard argument fails. The calculation of the contribution F_2 for an $S = -\frac{1}{2}$ disclination is straightforward: We integrate over the surface of a cylinder surrounding the disclination. The result is

$$F_2 = -\pi(K_{22} + K_{24}) \equiv -\pi K, \tag{3}$$

where F_2 is now the energy per unit length along the disclination. (For simplicity we take $K_{11} = K_{22} = K_{33} = K$. Nehring and Saupe[16] show, on rather general assumptions, that in this case $K_{24} = 0$, and so $K_{22} + K_{24} = K$.) Note that the result (3) is independent of the radius (so long as it is small compared to the pitch).

We now write the total energy of a cholesteric with an $S = -\frac{1}{2}$ disclination as made up of the following terms[18]:

$$F = F_{\text{core}} + F_{\text{interface}} + F_2 + F_1. \tag{4}$$

We take all these terms per unit length along the disclination.

The first term represents the excess free energy of the disclination core. For a first-order cholesteric-iostropic transition, the free energy is represented by two lines intersecting at the transition temperature T_1. Thus, for a temperature T near T_1 we write

$$F_{\text{core}} = a(T_1 - T)\pi R^2, \tag{5}$$

where R is the radius of the core.

The second term represents a surface energy at the interface between core and cholesteric. It is characterized by a surface tension, σ; thus

$$F_{\text{interface}} = 2\sigma\pi R. \tag{6}$$

In contrast to the F_2 term, this energy is also present in a nematic and its magnitude has been estimated by Kahlweit and Ostner.[19] The values given there show that it is probably of minor im-

portance.

For the third term we adopt the expression (3). There remains to estimate the F_1 term, which represents the elastic energy in the cholesteric phase. Its calculation for a specific cubic lattice can only be done numerically. However, as a rough estimate we use the expression for the elastic energy for a nematic surrounding an $S = -\frac{1}{2}$ disclination, given by de Gennes[20]:

$$F_1 = \tfrac{1}{4}\pi K \ln(R_{max}/R), \tag{7}$$

where R_{max} is a cutoff radius. Collecting all terms we get

$$F = a(T_1 - T)\pi R^2 + 2\sigma\pi R - \pi K$$

$$+ \tfrac{1}{4}\pi K \ln(R_{max}/R). \tag{8}$$

The blue phase will be stable with respect to the helical cholesteric when expression (8) becomes negative. If, for simplicity, we take $\sigma = 0$, the minimum of F occurs for

$$R = [K/8a(T_1 - T)]^{1/2}. \tag{9}$$

Introducing this into (8), we find that $F = 0$ for

$$\ln(R_{max}/R) = 3.5 \text{ or } R_{max}/R \approx 33.$$

For $R_{max} = 1000$ Å this gives $R = 30$ Å at the transition from cholesteric into blue phase. Note that the core region is a small fraction of the total volume $(R/R_{max})^2 \simeq 0.1\%$. The coefficient a can be estimated from the latent heat of the cholesteric-isotropic transition. We find[21] $a = 8 \times 10^4$ ergs deg^{-1} cm^{-3}. Introducing this in (9), and using $K = 3 \times 10^{-7}$ dyne (near the transition temperature), we find for the transition temperature $T_1 - T \approx 5°C$, quite reasonable in view of the crudeness of the theory.

The treatment presented depends on the presence of the negative term, Eq. (2). For the benefit of skeptics, it may be useful to make this term plausible by presenting a simple physical picture of its origin. It is well known that the helicity of a cholesteric liquid crystal is due to the presence of a screw sense in the individual molecules. This will cause the molecules to stack on the average at some finite angle, rather than parallel as in a nematic. In the ordinary cholesteric helix, the helical stacking is present in the direction of the twist axis, but in the direction perpendicular to this axis the molecules are constrained to parallel stacking. If helical stacking could be achieved in both directions, the energy would be reduced. This is indeed the significance of the F_2 term in Eq. (2). However, be-

cause of the global requirements of topology, a double twist cannot extend over a large volume without generating singularities in the director field. In the absence of singularities, F_2 must therefore vanish, and this is the essence of the traditional argument mentioned above. However, there is no *a priori* reason why the energy reduction achieved by local double twist cannot overcome the energy cost of disclinations. This indeed occurs near the clearing point, where the free-energy cost of disclinations tends to zero.

One means of constructing possible structures for the blue phases is to interlace space with sets of tubes, so constructed that the director points along the tube axis in the center, and rotates about the radial direction as one moves out, making an angle of 45° on the surface of the tubes. If, for example, sets of such tubes are placed with their axes along three orthogonal directions, so that mutually orthogonal tubes touch, but do not intersect, we obtain a simple cubic structure with a network of $-\frac{1}{2}$ disclinations that form two interpenetrating diamond-type lattices. Other possibilities of course exist. The lattice parameters and free energies of such structures can be estimated numerically, allowing comparison with experiment, but we do not attempt this here.

[1]D. Coates and G. W. Gray, Phys. Lett. 45A, 115–116 (1973), and 51A, 335–336 (1975).

[2]D. Armitage and F. P. Price, J. Phys. (Paris), Colloq. 36, C1-139–142 (1975).

[3]P. J. Collins and J. R. McColl, J. Chem. Phys. 69, 3371–3373 (1978).

[4]H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, Springer Series in Chemistry, Vol. 11, edited by W. Helfrich and G. Heppke (Springer, New York, 1980).

[5]K. Bergmann and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. 82, 1309–1311 (1978), and Z. Naturforsch. 34A, 251–252, 1031–1033 (1979).

[6]P. Pollmann and G. Scherer, Z. Naturforsch. 34A, 255–256 (1979), and High Temp.-High Pressures 12, 103–108 (1980).

[7]S. Meiboom and M. Sammon, Phys. Rev. Lett. 44, 882–885 (1980).

[8]E. T. Samulski and Z. Luz, J. Chem. Phys. 73, 142–147 (1980).

[9]M. Marcus, J. Phys. (Paris) 42, 61 (1981).

[10]D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. 45, 641–644 (1980).

[11]S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. 69, 979 (1975) [Sov. Phys. JETP 42, 497 (1976)]; S. A. Brazovskii and V. M. Filev, Zh. Eksp. Teor. Fiz. 75, 1140 (1978) [Sov. Phys. JETP 48, 573 (1978)].

[12]R. M. Hornreich and S. Shtrikman, J. Phys. (Paris) 41, 335–340 (1980), and in *Liquid Crystals of One- and Two-Dimensional Order*, Springer Series in Chemistry, Vol. 11, edited by W. Helfrich and G. Heppke (Springer, New York, 1980).

[13]S. Alexander, in Proceedings of the Colloque Pierre Curie, Paris, 1–5 September 1980 (to be published).

[14]The Brazovskii work (Ref. 11) actually defines $\alpha = (2/27)(Kq_0^2)/l\,(\Delta T/T_1)$ and he finds that the hexagonal state he calculates enters at $\alpha \simeq 0.1$; rough experimental values have $\alpha = 0.02$.

[15]A. Saupe, Mol. Cryst. Liq. Cryst. 7, 59 (1969), has suggested this model. Although this author sketches the director field on the faces of the cubic unit cell only, an extension to the remainder of the cell produces the above structure.

[16]J. Nehring and A. Saupe, J. Chem. Phys. 54, 337 (1971).

[17]There are two more terms in the equations derived by Nehring and Saupe. However, as argued there, one of these terms is zero for a nonpolar material which we assume to be the case. The other term involves second derivatives, and will be disregarded here.

[18]Equation (4) can be derived from the Landau expansion used by Brazovskii and an explicit expression for σ obtained within that theory. The term F_2 explicitly appears in such a calculation.

[19]M. Kahlweit and W. Ostner, Chem. Phys. Lett. 18, 589 (1973). These authors estimate $\sigma \geqslant 5 \times 10^{-4}$ erg cm^{-2} which would make the surface term comparable to the F_2 term for $R \approx 30\,000$ Å, and thus completely negligible. However, the number given is only a lower limit, and the actual value could well be orders of magnitude larger.

[20]P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, Oxford, 1975), p. 131.

[21]We use the relation $(\partial G/\partial T)_p = -S$, where G is the Gibbs free energy. Applying this equation to both the isotropic and cholesteric phases, and taking the difference, gives $(G_{iso} - G_{chol})/(T_1 - T) = \Delta S$, where T_1 is the transition temperature. Extensive tabulations of ΔS are given by E. M. Barrall and J. F. Johnson, in *Liquid Crystals and Plastic Crystals*, edited by G. W. Gray and P. W. Winsor (Wiley, New York, 1974), Vol. II, p. 254. The values range between 0.2 and 1.5 cal mole^{-1} °K^{-1}. We take the value 0.7, a molecular weight of 350, and a density of 1; then $\Delta S \approx 9 \times 10^4$ ergs cm^{-3} °K^{-1}, which can be identified with the coefficient a.