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Structure and Properties of the Cholesteric Blue Phases

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A study of Bragg reflections in both blue phases (BPI, BPII) of two mixtures of chiral and nonchiral biphenyls indicates both phases probably have the same translational symmetry and are either body-centered or simple cubic. The temperature dependence of several Bragg reflections indicates that the BPI-BPII transition may be either continuous or discontinuous and that, given the bcc lattice, the lattice parameter is commensurate with the pitch. These results are discussed relative to existing theories.

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The cholesteric "blue phase" is an optically isotropic phase of matter[1] that is stable over a very narrow range of temperatures (~0.5 °C) between the cholesteric and the normal isotropic liquid phases. Its existence has long been known[2] but its structure has been a mystery. A clue to the solution is that the blue phase exhibits brightly colored platelets in reflected light under crossed polarizers.[3] As the temperature is changed, these platelets exhibit a sharp color change in roughly the middle of the blue-phase range implying that in fact there are *two* blue phases,[4,5] called BPI and BPII, with BPII being the higher-temperature phase.

Recently, Meiboom and Sammon[6] (MS) have studied BPI spectrophotometrically. From steps in their transmitted intensity versus wavelength data, they inferred that BPI is either simple cubic or body-centered cubic (bcc). This agrees with a suggestion by Saupe[1] that the blue phase is cubic, and with a more complete theory of the phase by Hornreich and Shtrikman.[7] The BPII data of MS exhibited only one step, thus leaving the structure of BPII open. From a theoretical point of view, the blue phase is of current interest for two reasons. First, the recent work of Brazovskii *et al.*[8] suggests that the isotropic–blue-phase transition may be an example of a new class of phase transitions in which the fluctuations are degenerate on a surface or line in reciprocal space. The orientational degeneracy of the cholesteric twist fluctuations is the determining feature here. Second, a recent Landau theory of the blue phase by Hornreich and Shtrikman[7] predicts a bcc lattice of point defects in the order-parameter field, which suggests an analogy with the problem of melting in three dimensions.[9]

In this Letter we report the first direct measurements of Bragg reflections from surface oriented platelets in *both* blue phases of two mixtures of biphenyl materials having different cholesteric pitches. Most of our measurements were made while the platelets are simultaneously observed under the polarizing microscope in reflection mode. We summarize the conclusions we have drawn from our data and observations.

(1) Reflections from both blue phases of *both* mixtures are consistent with body-centered– and simple–cubic structure. The reflections have Bragg-like angular dependence.

(2) In BPI of both mixtures the lattice contracts until the lattice parameter (given the bcc struc-

ture) becomes equal to the cholesteric pitch where the transition to BPII occurs. The lattice parameter remains nearly constant throughout BPII of both mixtures.

(3) For the shorter-pitch system, the BPI to BPII transition appears to be a discontinuous lattice contraction. For the longer-pitch system, the transition is continuous and the contracting lattice of BPI stabilizes at the value of the cholesteric pitch.

(4) Not all "blue phases" are blue. The color is determined by Bragg scattering.

(5) The Bragg peaks of the blue phases are much sharper and do not exhibit[10] the characteristic flat top or thin-film fringes of the cholesteric Bragg peaks.

Our measurements were primarily of Bragg back reflections from samples consisting of thin (25-μm) films on microscopic slides coated with polyvinyl alcohol and rubbed for alignment. This allowed us to readily produce large bright surface platelets. For the longer-pitch sample, the (110) back reflections were in the infrared; consequently these measurements were made at a Bragg angle of 45°, leading to the latter half of conclusion (1) above. The temperature was controlled by a Mettler heating stage and observations were made with a polarizing microscope in reflection mode. The eyepiece was replaced by an optical tee diverting half the light to an eyepiece for observation while sending the rest to a Jarrel-Ash spectrophotometer by way of a light pipe.

The inset to Fig. 1 shows typical spectrophotometer peaks for the cholesteric and blue phases. The cholesteric peaks exhibited the characteristic broad (300–350 Å) flat top and fringes expected of thin well-aligned planar cholesterics.[10] The blue-phase peaks, on the other hand, were much narrower (100–150 Å), more sharply peaked, and without fringes. The data in Figs. 1 and 2 show the behavior of the selective-reflection wavelength versus temperature in the cholesteric and both blue phases of, respectively, 50-50 vol% and 42-58 vol% mixtures of chiral (CB15) and nonchiral (mixture E9) biphenyl.[11] The scatter is due to hysteresis effects, possibly associated with surface pinning of the blue-phase lattice.

We have labeled the observed selective-reflection peaks on the basis of Bragg scattering from a bcc lattice,[12] i.e., $\lambda(h,k,l) = 2nd\sin\theta/(h^2+k^2+l^2)^{1/2}$, where n is the wavelength-dependent index of refraction, θ is the Bragg angle, d is the lattice parameter, and (h,k,l) are the Miller

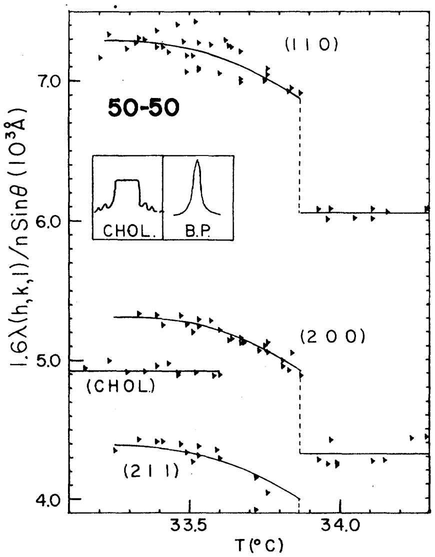

FIG. 1. Selective-reflection wavelength vs temperature in the cholesteric, BPI, and BPII phases of the 50-50 vol% mixture of CB15 and E9. All data were taken on back reflection ($\theta = \pi/2$) and were normalized by the factor $1.6/n$ (see Ref. 11). Note that BPI supercools substantially into the cholesteric below 33.6°C. The inset illustrates the striking difference between the cholesteric and blue-phase line shapes.

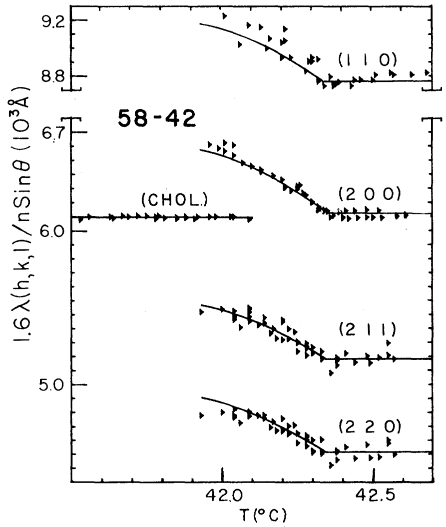

FIG. 2. Selective-reflection wavelength vs temperature in the cholesteric, BPI, and BPII phases of the 58-42 vol% mixture of E9 and CB15, respectively. All data except that labeled (110) were taken on back reflection ($\theta = \pi/2$). The (110) data were taken at $\theta = \pi/4$. All data were normalized by the factor $1.6/n$ (see Ref. 11). Note that BPI supercools substantially below the cholesteric to BPI transition at 42.1°C.

indices. The data in Figs. 1 and 2 have been normalized to $n(5350\ \text{Å}) = 1.6$ with use of n vs λ data[13] taken by us on the 42% CB15 sample. The dispersion of the refractive index for 4000 to 7500 Å, relative to $n(5350\ \text{Å}) = 1.6$, was approximately +3% and −1.5%. For the bcc lattice, Miller indicates for Bragg scattering are constrained to $h+k+l$ even while for the fcc lattice h, k, l must be all odd or all even. In the simple cubic (sc) all h, k, l are allowed. With the above constraints, the first four bcc reflections come from the (110), (200), (211), and (220) planes.

The agreement of these bcc Miller-index assignments with our data is best illustrated by plotting $[n \sin\theta/\langle\lambda(h,k,l)\rangle]^2$ vs $h^2+k^2+l^2$ which should *give a straight line through the origin* if our assignments are consistent with the Bragg law for a bcc crystal. We have done this in Fig. 3. Since the BPI data are temperature dependent, we have taken average values, $\langle\lambda(h,k,l)\rangle$, by fitting the data with a straight line over the narrow (~0.25 °C) temperature region in which BPI is stable, and choosing fitted values from the low-temperature end of the fit range to avoid confusion with BPII points. The error bars on the plotted points in Fig. 3 are sufficiently large to include the uncertainty in $\langle\lambda(h,k,l)\rangle$ due to scatter in the data. For BPII the angular brackets represent a simple algebraic average of the data since these data are nearly temperature independent. It is clear from Fig. 3 that data for both blue phases of both mixtures studied are consistent with our bcc Miller-index assignments. They are also consistent with the sc assignments[14] (100), (110), (111), and (200), but they are inconsistent with any simple fcc assignments. We also ruled out possible hcp assignments by an examination of selective-reflection wavelength ratios. It is very important to note that the platelets observed visually to produce the (110), (200), etc., lines in BPI are the same platelets that produce the data so labeled in BPII, strongly suggesting that BPI and BPII have the same symmetry.

In spite of the fact that BPI and BPII have here shown to be structurally similar (probably identical) and that both appear either to be bcc or sc, we believe that neither is described by the theory of Hornreich and Shtrikman[7] (HS) in its present form. Our judgment is based on the fact that the HS theory predicts a pitch commensurate with the (110) plane spacings but we find it to be commensurate with the (200) spacing. Both mixtures have $\lambda(2,0,0) \geqslant \lambda(\text{Chol})$ in BPI with the equality holding at the BPI-to-BPII transition and $\lambda(2,0,0) = \lambda(\text{Chol})$ throughout BPII of the longer-pitch mixture. If this is a universal result, it would appear that $\lambda(2,0,0) = \lambda(\text{Chol})$ just below all BPI-to-BPII transitions, and that a continuous BPI-to-BPII transition, in which the lattice parameter is stabilized at the pitch of the cholesteric, occurs for sufficiently long-pitch cholesterics.

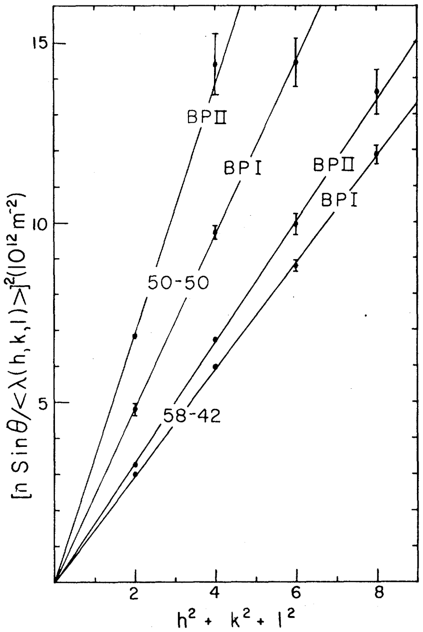

FIG. 3. $[n/\langle\lambda(h,k,l)\rangle]^2$ vs $h^2+k^2+l^2$ for both blue phases of both mixtures. See the text for meaning of the angular brackets. This graph illustrates the consistency of our Miller-index assignments (see Figs. 1 and 2) with the predictions of the Bragg law for a bcc crystal.

We now speculate on the three-dimensional melting analogy. According to theoretical ideas,[1,7,8] the BP lattice is a lattice of defects in the order-parameter field. Given that the formation of defects adds entropy to the ordered cholesteric, the *formation of the defect lattice* on heating the cholesteric into the BP is analogous to the *destruction of the atomic lattice* on heating a solid to the isotropic liquid in that both processes increase the entropy. Furthermore, lattice *contraction of the BP*, which we have shown occurs on heating, increases the defect density and hence the entropy. This is analogous to lattice *expansion in a solid* which also normally occurs on heating and also increases the entropy. Thus for identical entropy reasons, heating creates and contracts a lattice of defects but expands and annihilates a lattice of atoms. This raises the question as to why the BP lattice should be bcc if the universal factor favoring the relatively open, bcc structure near the melting point of solids is an entropy factor as suggested by Alexander and McTague.[9] One might guess, based on that argument, that a more closely packed arrangement of defects (fcc or hcp) would be preferred near the BP-isotropic transition and a more open structure (bcc or sc) near the BP-cholesteric transition. Its closeness in entropy to the cholesteric would then determine the BP structure, a reasonable result since the cholesteric-BP transition indeed exhibits less latent heat than the BP-isotropic transition.

Finally we discuss conclusion (4) above that not all blue phases are blue. Short-pitch blue phases are transparent and blue on reflection, while our long-pitch blue phase is opaque and snow white on reflection. Both observations are consistent with optical properties dominated by Bragg scattering where one expects all wavelengths $\lambda(h,k,l) \leqslant 2nd(h,k,l)$ to be scattered from bulk material. For our longer-pitch blue phase where $\lambda(1,1,0) \sim 9000$ Å, strong scattering occurs throughout the visible wavelength range, which explains its opaque white color. Note that the bulk focal conic cholesteric phase of our longer-pitch mixture is visually opaque and blue on reflection, again a result of Bragg scattering at wavelengths $\lambda' \leqslant \lambda(\mathrm{Chol})$ where $\lambda(\mathrm{Chol})$ is orange (6100 Å). In shorter-pitch blue phases, only blue and violet light is scattered at visible wavelengths, thus their blue color, their name, and their transparency. The existence of white "blue phases" raises the question of whether we can have blue phases in cholesterics having pitches in the red or even infrared. This is an important point since present theories[7,8] suggest that the BP is restricted to short-pitch cholesterics.

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[13] These data are represented to within ± 0.001 by the relationship $n = a\lambda^{1/2} + b\lambda^{-1/2}$ where $a = 9.2177\times10^{-3}$ and $b = 67.695$; they were taken in the isotropic phase. Although the absolute values of n were very weakly temperature dependent, the dispersion was independent of temperature to within the accuracy of the data.

[14] In principle, one could distinguish bcc from sc by the existence of the (321) reflection which has no counterpart in sc. However, we find a sharp uv absorption edge at 3700 Å in the 58-42-vol% sample.