

## Crystal habit of liquid-crystal blue phase I

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Large-faceted monocrystals of blue phase I are grown and observed in coexistence with the isotropic liquid. Observations of this three-dimensional polyhedral habit, combined with a conjecture that facets perpendicular to screw axes are absent, are compatible with the  $I(4_132)$  space group for blue phase I. The (200) planes Bragg reflect approximately the same wavelength as the cholesteric spiral indicating that the blue phase I lattice constant is the cholesteric pitch even very close to the isotropic phase.

There is a single screw axis in the cholesteric phase about which a director  $n$  twists with constant pitch  $P$ . On a scale small compared to  $P$ , the cholesteric is weakly biaxial<sup>1</sup> whereas on a scale large compared to  $P$ , it is uniaxial. Cholesteric blue phases (BP) refer to three mysterious phases which frequently (but not always) appear in a small temperature interval ( $\approx 0.5^\circ\text{C}$ ) between the cholesteric liquid crystal phase and the isotropic liquid when  $P \leq 3000 \text{ \AA}$ .<sup>2</sup> They are optically isotropic phases. When all three blue phases are present, they appear with increasing temperature in the sequence: BPI, BPII, and BPIII or the fog. BPI and BPII are believed to be cubic phases, whereas the fog has no ordering associated with it.

By including higher harmonics in the basic spatial frequency in the order parameter, Hornreich and Shtrikman<sup>3</sup> were the first to predict for blue phases with "intermediate chiralities," a bcc structure with  $O^8$  ( $I4_132$ ) symmetry. On the basis of their observations of the polarization of the Bragg reflected light from oriented samples of blue phases, Flack, Crooker, and Svoboda,<sup>4</sup> concluded that their data favored  $O^8$  ( $I4_132$ ) for BPI but they did not completely rule out  $T^3$  and  $T^5$ . More recently Meiboom, Sammon, and Berreman,<sup>5</sup> claimed agreement between their measurements of scattered light intensities from a powder sample in the blue phase with their calculation of the intensity expected for specific director models of the blue phases with  $O^8$  general symmetry for BPI. Both these groups worked with materials which possessed at least two blue phases so that BPI is sandwiched between the cholesteric phase and BPII. Some differences were observed which could be due to multiple scattering or differences in the materials used. For example, Flack *et al.*,<sup>4</sup> observe a reflection they index as (220) in BPI whereas Meiboom *et al.*,<sup>5</sup> do not see (nor expect) such a reflection.

In this paper we investigate the structure of blue phase I in large-faceted monocrystals grown directly from the isotropic liquid. The facetting enables us to associate, with a greater degree of certainty than a powder spectra, a crystallographic plane of index  $(hkl)$  with a particular spacing  $d_{hkl}$  using microspectroscopy (Fig. 1). We do not discuss here facetting in monocrystals of BPII grown under similar circumstances. BPII crystallites grown from the isotropic phase develop a "cross-hatched" pattern when cooled to BPI and are thus not useful for determining BPI symmetry.<sup>6,7</sup> Here, we describe the three-dimensional polyhedral habit of BPI monocrystals. We index its facets and determine its point symmetry. The Bravais lattice is deter-

mined from Bragg reflections from crystallites of known orientations. We conjecture that the absence of some facets is related to the existence of a screw axis perpendicular to them.

The essential details of the experimental setup are depicted in Fig. 1: the sample (BP) is sandwiched between a microscope glass slide (S) and a glass cylinder (GC). The temperatures of the aluminum piece (P1) and of the microscope objective (MO) are regulated by two independent systems. Due to the use of an oil immersion objective [which eliminates light reflection from the lower surface of the glass slide (S)] the maximum temperatures were below  $50^\circ\text{C}$ . The possibility of introducing thermal gradients by setting different temperatures  $T_1$  and  $T_2$  proved useful in the control of BPI nucleation.

We used the samples A and B (compositions given in Table I), prepared previously for the study of the elastic modulus,<sup>8</sup> and another sample C, prepared by mixing a nematic E9 (E9 is a commercially available four-component BDH mixture) with a cholesterogen CB15 [4-cyano-4'-(2-methyl)butylbiphenyl] (used also in Ref. 9). In all three

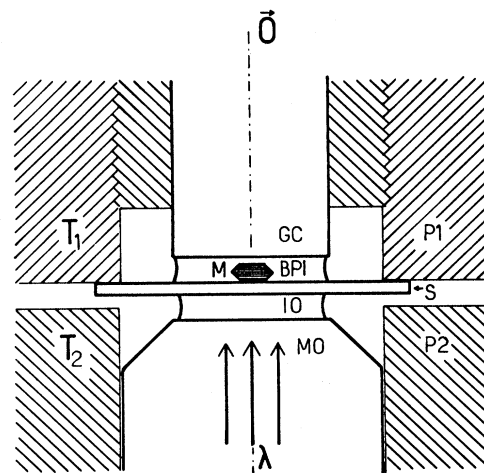


FIG. 1. Microspectroscopy: a sample of blue phase (BP) is sandwiched between a glass slide (S) and a glass cylinder (GC). A monocrystal (M) grown on the glass surface is illuminated by a monochromatic light (of a wavelength  $\lambda$ ) through an oil immersion (IO) objective (MO). For the wavelength  $\lambda$ , adjusted to the Bragg condition for crystal planes perpendicular to  $\bar{O}$ , the monocrystal appears as a brilliant polyhedron on a dark background in reflection.

TABLE I. Summary of microspectroscopic observations of BPI monocrystals grown in coexistence with the isotropic phase. In all cases,  $\lambda_{A,B,C}^{s,p} \approx \lambda_{(200)}^{BPI} \pm 10$  nm. The cholesteric bandwidth is about 50 nm. ZLI1840 is a commercially available eight-component Merck mixture.

Two-dimensional profile: $p$	(1)	(2)	(3)
View of a monocrystal shown in:	Fig. 3(a)	Fig. 3(b)	Fig. 3(c)
Sample A: 58.5% CB15 in ZLI1840	$\lambda_{110}^A = 558$ nm	$\lambda_{211}^A < \lambda_{\min}$	$\lambda_{200}^A = 400$ nm
Sample B: 55.5% CB15 in 60CB	$\lambda_{110}^B = 676$ nm	$\lambda_{211}^B = 414$ nm	$\lambda_{200}^B = 502$ nm
Sample C: 42.5% CB15 in E9	$\lambda_{110}^C = 832$ nm $\lambda_{220}^C = 436$ nm	$\lambda_{211}^C = 495$ nm	$\lambda_{200}^C = 582$ nm
Crystal planes parallel to S:	(110)	(211)	(200)
Occurrence	On a glass surface	On a glass surface	In bulk

samples, transitions from isotropic to BPI were of first order with a wide ( $\approx 3^\circ\text{C}$ ) region of two-phase coexistence.

The nucleation process of blue phase I in the isotropic phase was strongly dependent on cooling rates as well as on the existence of temperature gradients in the sample. Fast cooling rates ( $\approx 0.1^\circ\text{C}/\text{min}$ ) favored bulk nucleation of a large number of small crystallites with random orientations. Slow cooling rates favored nucleation of a small number of crystallites on the surface of the glass slide (S) when  $T_2 < T_1$ . By carefully controlling the cooling rate, we were able to grow defect-free monocrystals 100–200  $\mu\text{m}$  in size. These large monocrystals were observed with monochromatic illumination of various wavelengths  $\lambda$ . In all three samples the crystals grown on surfaces had only two common two-dimensional profiles: (1,1,0) and (2,1,1) referred to as  $p=1$  and 2, respectively, in Table I. These “surface” crystallites became brilliant at a particular wavelength  $\lambda^{s,p}$  (given in Table I) where  $s$  is the index of the sample ( $s=A,B,C$ ). On the other hand, crystallites with the square profile  $p=3$  in Table I) were rare on surfaces but, under bulk nucleation, they occurred frequently in all samples.

Further observations of crystallites of a given class ( $s,p$ ) were made under monochromatic illumination of wavelength  $\lambda = \lambda^{s,p} \pm \delta\lambda$ , where  $\delta\lambda \approx 5\text{--}30$  nm. With the aperture diaphragm almost completely closed (i.e., parallel illumination) we distinguished clearly individual facets such as those shown in Fig. 2.

The observations of crystals from all classes ( $s,p$ ) lead us to formulate the following working hypotheses: there exists one crystal habit common to all classes ( $s,p$ ), which is a manifestation of one crystal symmetry. The different profiles of Table I correspond to different orientations of the same crystal habit. For given profile  $p$  the different colors  $\lambda^{s,p}$  of Bragg reflections correspond to different lattice constants in different samples  $s$ .

The common crystal habit we propose is shown in Fig. 3. It is a superposition of two special forms: a {110} rhombic dodecahedron and a {211} icositetrahedron.<sup>10</sup> It has been independently proposed by Blümel and Stegemeyer<sup>11</sup> to account for the appearance of similar blue phase crystallites observed in different materials. These two special forms occur in three different classes  $O(432)$ ,  $T_h(2/m, \bar{3})$ , and

$O_h(4/m, \bar{3}, 2/m)$  of the cubic system so that the point symmetry of BPI could not, in principle, be uniquely determined. However, two of these possible groups have to be eliminated because they contain the inversion symmetry element—incompatible with the optical activity of blue phase I (the Bragg reflections indicated in Table I are all cir-

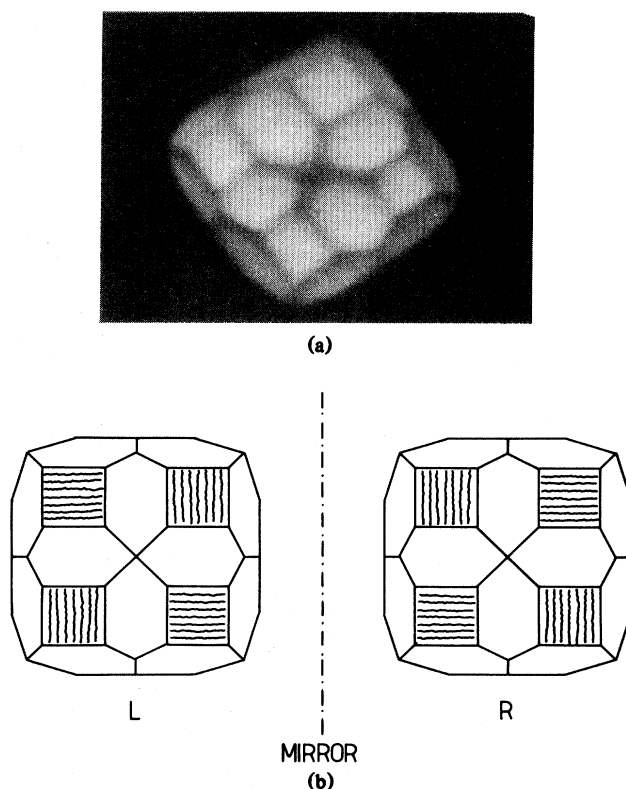


FIG. 2. (a) Photograph of a monocrystal of blue phase I oriented with its [100] axis parallel to the optical axis of the microscope ( $\bar{O}$  in Fig. 1). (b) Schematic of line structure observed on (110) faces of the two-dimensional profile  $p=3$  shown in (a). These lines reveal lack of inversion symmetry.

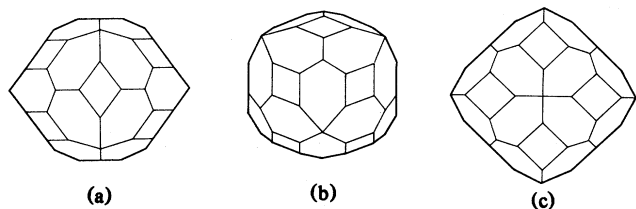


FIG. 3. (a)–(c) Views of the three-dimensional crystal of BPI observed, respectively, from [110], [211], and [100] directions. Two-dimensional profiles correspond to  $p = 1, 2,$  and  $3$  in Table I.

cularly polarized). We, therefore, concluded that the point symmetry group must be  $O(432)$ . Another way to arrive at this choice is to note that the (110) facets of monocrystals are not smooth but have a series of grooves or stripes parallel to edges of the facets [Fig. 2(b)]. Decorated by stripes, the apparent symmetry ( $O_h$ ) of Fig. 2(a) is broken so that its point symmetry group must be  $O(432)$ .

The three-dimensional habit, when observed from different directions presents different “two-dimensional” profiles. Figures 3(a)–3(c) show that the profiles 1–3 correspond to the observation direction [110], [211], and [100] (indicated in the last row of the table). Profiles 1 and 2, observed with crystallites grown on the glass surface (S in Fig. 1), correspond to the orientation of BPI crystals with planes (110) or (211) parallel to the glass surface which seems to indicate that the Wulff plots of the energy of interfaces BPI isotropic and BPI/glass must have cusps in the [110] and [211] directions.<sup>12</sup> The third profile (see Fig. 2) is observed in the bulk where the orientation of the [100] direction is random. In general, the (200) reflection is the same as the cholesteric pitch and, indeed, the color of the square crystallites is the same as the cholesteric. This indicates that the BPI lattice parameter is equal (or slightly larger) than the pitch  $P$  and not the half-pitch even when BPI is nucleated within  $0.1^\circ\text{C}$  of the isotropic phase.

A large monocrystal of sample C, oriented with its [110] direction parallel to  $\vec{O}$ , exhibited two Bragg peaks: a small one at  $\lambda'' = 436$  nm and a larger one at  $\lambda' = 835$  nm. As  $\lambda'' \approx \frac{1}{2}\lambda'$ , the larger peak corresponds to the (110) reflection from a cubic (bcc or sc) crystal while the smaller one could correspond to the (220) reflection in the absence of multiple scattering. These two peaks are situated at the limits of the range of visible wavelengths so that a sc structure (111), (200), (210), and (211) reflections should all occur in the visible range. Although we found strong reflections from crystals with orientations  $[100] \parallel \vec{O}$  and  $[211] \parallel \vec{O}$ , no reflection corresponding to (210) and (111) planes were observed.

A related observation was made on a monocrystal of sample A, with the orientation  $[110] \parallel \vec{O}$  and  $\lambda_{110} = 558$  nm. If the crystal structure is sc, the (100) reflection should be present in the spectrum of crystals with “square profile.”<sup>6,7</sup> Since this reflection is missing we conclude that the Bravais lattice of BPI is cubic of  $I$  type (bcc).

Once the crystal class [ $O(432)$ ] and its lattice type ( $I$ ) is known, a unique determination of the space group is still

impossible because this group can be nonsymmorphic. In fact, the lack of (100) facets in the crystal habit suggests that the space group is  $I4_132$ .<sup>3,13</sup> In ordinary crystals (with a small number of atoms in one unit cell) the density  $\rho(r)$  of atoms is modulated periodically in a given direction  $[hkl]$ . A screw axis in this direction reduces both the period and the amplitude of this modulation, and inhibits the occurrence of a facet  $(hkl)$  perpendicular to it. How can one transpose this argument to the case of blue phases, where one unit cell contains about  $10^7$  molecules?

In blue phases, the molecules do not occupy particular sites in the unit cell but only their orientations are correlated to their actual positions  $\vec{r}$ . Usually, this orientational order is described by a symmetric, traceless tensor  $\epsilon_{ij}$ , constructed using for example the dielectric constant tensor  $\epsilon_{ij}^d(\vec{r})$ . This tensorial order parameter is modulated [like  $\rho(\vec{r})$ ] in a given direction as is obvious in the expansion of  $\epsilon_{ij}(\vec{r})$  in a Fourier series proposed by Grebel, Hornreich, and Shtrikman.<sup>13</sup>

$$\epsilon_{ij}(\vec{r}) = \sum_{h,k,l,m} \epsilon_{ij}(h,k,l,m) \exp[iq(hx + ky + lz)]$$

The terms with  $m = \pm 2$  and  $m = \pm 1$  correspond to rotations of  $\epsilon_{ij}$  while the term with  $m = 0$  represents the modulation of the order parameter amplitude.

Due to the large magnitude of the BPI lattice constant, a free-energy density per unit surface,  $f_s(x)$  can be defined in thin ( $\Delta x \ll q^{-1}$ ) parallel slices whose normal is parallel to the  $[hkl]$  direction of the crystal. Like  $\rho(r)$ ,  $f_s(x)$  is modulated along  $[hkl]$  and should respect crystal symmetry. The occurrence of a facet perpendicular to  $[hkl]$  depends to a first approximation on both the depth of the minima of  $f_s(x)$  as well as the magnitude  $\Delta x$  in real space over which the minimum occurs. In the [100] direction, the presence of a fourfold screw axis implies  $f_s(x + \pi q^{-1}/2) = f_s(x)$ , i.e., a relatively rapid modulation so that  $f_s(x)\Delta x$  is too small to stabilize facets in this direction.

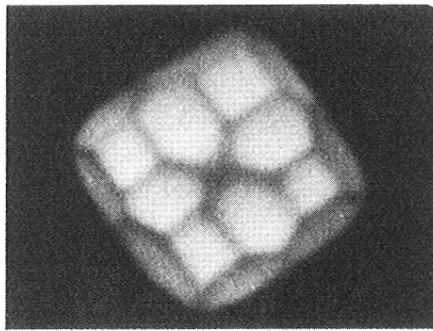
We use this same argument [that facets occur at minima of  $f_s(x)$ ] to account for the presence of two steps on the facet perpendicular to [110]. In this case, it is found<sup>14</sup> that  $f_s(x)$ , where  $x$  is now a linear dimension along [110], has two distinct minima between two (110) planes. We identify each step with one of the minima.

In conclusion, this investigation of blue phases by microspectroscopy consists in (1) the description of the polyhedral habit of BPI monocrystals, (2) the determination of their symmetry ( $O$ ), and (3) the measure of Bragg reflection spectra with crystals of *known* orientation. The space group compatible both with the crystal form and with the Bragg reflections was found to be  $I4_132$ , and the BPI lattice constant is the cholesteric pitch.

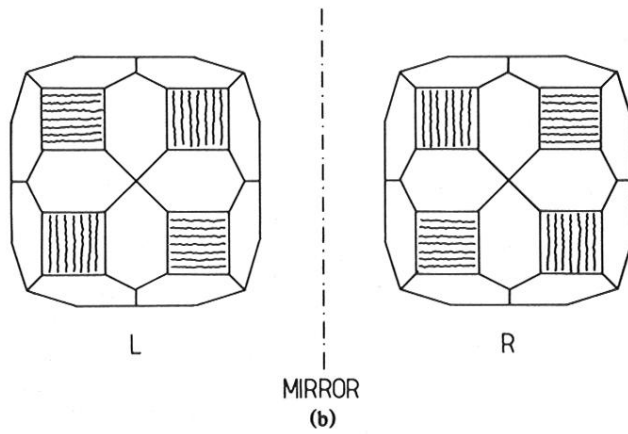
The investigation of crystal growth phenomenon and the systematics of crystal defects are two of many aspects of this study to be developed in the near future using the method of microspectroscopy.

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(a)



(b)

FIG. 2. (a) Photograph of a monocrystal of blue phase I oriented with its  $[100]$  axis parallel to the optical axis of the microscope ( $\vec{O}$  in Fig. 1). (b) Schematic of line structure observed on  $(110)$  faces of the two-dimensional profile  $p=3$  shown in (a). These lines reveal lack of inversion symmetry.