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Plenary Lecture. The blue phases. A review of experiments

P. P. Crooker[a]

[a] Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii, U.S.A.

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Plenary Lecture

The blue phases

A review of experiments

by P. P. CROOKER

Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

We present a review of the experimental aspects of research on the blue phases of chiral liquid crystals. First a general description of blue phases is given and their relation to other important condensed matter problems is mentioned. Experimental proof for the existence of blue phases is followed by a description of experiments relating to the structure of BP I and BP II and of the electric field-induced phases BPH and BPX. The remainder of the review is then devoted to the structure of BP III, which is still one of the outstanding problems of liquid crystal physics. A brief discussion of outstanding questions and new directions completes the review.

1. Introduction

Although liquid crystal blue phases were first detected exactly 100 years ago [1], they have only recently begun to be fully understood. This understanding has come about as part of a general interest in liquid crystals which began around 1970, when it was realized, first, that liquid crystals had important technological applications and, second, that new ideas in condensed matter physics could be applied successfully to liquid crystal phenomena [2–4]. Blue phase research started about 10 years later when, almost simultaneously, theoretical studies showed that blue phases *should* exist, while experiment showed that they *did* exist and, indeed, have many of the features predicted by theory. A close interplay between experiment and theory has been the hallmark of blue phase research; this article is designed to review essentially the experimental aspects of that research.

To come quickly to the point of the review, figure 1 shows in a very schematic way the phases of *non-chiral* nematic liquid crystals and *chiral nematic* liquid crystals. (Historically, chiral nematic liquid crystals have been called cholesteric because they were originally made from cholesteryl derivatives. Nowadays that need not be true, so we use the more modern term chiral nematic instead. Furthermore, we reserve the term 'helical phase' for what used to be termed the cholesteric phase.) For non-chiral molecules there are just two phases (see figure 1 (*a*)): nematic and isotropic. Chirality in the molecule, however, induces a macroscopic chirality in the liquid crystal structure, and, if the macroscopic chirality is sufficiently large, new phases appear (see figure 1 (*b*)). These new phases are BP I, which is generally thought to have a body centred cubic (b.c.c.) symmetry, BP II, which is simple cubic (s.c.), and BP III, the structure of which is not known at present. The BP I and BP II structures have been

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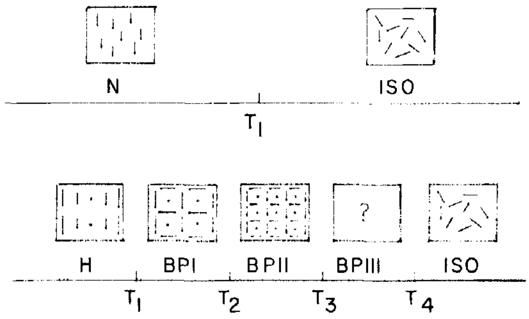


Figure 1. Schematic representation of liquid crystal phases for non-chiral and chiral molecules. (*a*) Non-chiral molecules have only a nematic and isotropic phase. (*b*) Chiral molecules possess a helical phase, up to three blue phases, and the isotropic phase.

studied intensively and the crystal symmetries are considered to be understood. However, BP III has received much less attention, and an elucidation of its structure is one of the outstanding problems of liquid crystal physics.

That a liquid crystal, which is ostensibly a liquid, can have a cubic structure is truly remarkable, and there are a number of implications which impact on general ideas of condensed matter physics. For a long time it was thought that chiral nematics were merely twisted forms of non-chiral nematics and no thermodynamic implications resulted. Now we know that chirality alone can cause new phases to appear, and not only one phase, but three. This is now explained by the necessity, demanded by the lack of mirror symmetry, of adding a chiral term to the Landau free energy of the nematic phase [5–7]. The chiral term complicates the minimization of the free energy enormously and is ultimately the cause of the new phases. This difficulty, incidentally, only exists in three dimensions. In four dimensions the free energy is quite tractable [8, 9], which is of little consolation to experimenters.

The chiral term has another profound effect, described by Brazovskii [10] and Crooker [11]. The nematic–isotropic transition is an example of a transition between two spatially uniform phases, which means the transition takes place at a point at the origin of wavevector space. Fluctuations of the system away from this point, which would add spatially periodic components to the structure, are energetically unfavourable and hence do not play a significant role in the transition. However, the helical–isotropic (or blue phase) transition is an example of a transition between a uniform upper phase and spatially periodic lower phase. Now the transition takes place on a spherical shell of radius $q_0 = 2\pi/\text{pitch}$ in wavevector space. Fluctuations of the system along the surface of the shell, which merely alter the direction of the periodic axis but do not change the magnitude of the free energy, are now allowed, with the result that these fluctuations can affect significantly the nature of the transition. So the chiral term makes the helical/blue phase–isotropic transition fundamentally different from the nematic–isotropic transition, essentially by changing the topology of the minimal free energy surface in phase space. Other transitions which are affected by the Brazovskii mechanism are the smectic C–nematic transition and the Rayleigh–Benard instability in fluids.

Another important feature of the blue phases is that of *frustration* [12]. In frustrated systems different terms in the free energy dictate different molecular arrangements, and the competition between these two terms may result in a more complex structure. The blue phases are such systems: the lowest energy director configuration is the *double-twist* structure in which the director rotates spatially about any radius of a cylinder. (It is parallel to the cylinder axis at the centre of the cylinder.) Fitting these double-twist cylinders into a three dimensional structure so that the directors match everywhere is topologically impossible, however, and so *disinclinations*, defects in the orientational arrangement of the molecules, are necessary to relieve the elastic strain energy [13]. The cubic blue phases can therefore be described as lattices of double twist tubes or, equivalently, lattices of defects [14]. Indeed, a qualitative model for the melting of the helical phase into the blue phases can be made based on defect mediated melting ideas [11]. In essence, the helical phase, which has no disclinations, melts into the blue phase, which has a regular array of disclinations, and then into the isotropic phase, which can be thought of as a lattice saturated with disclinations. The interesting feature of this model is the disclination array; the same model applied to the ordinary solid–liquid transition has this phase missing.

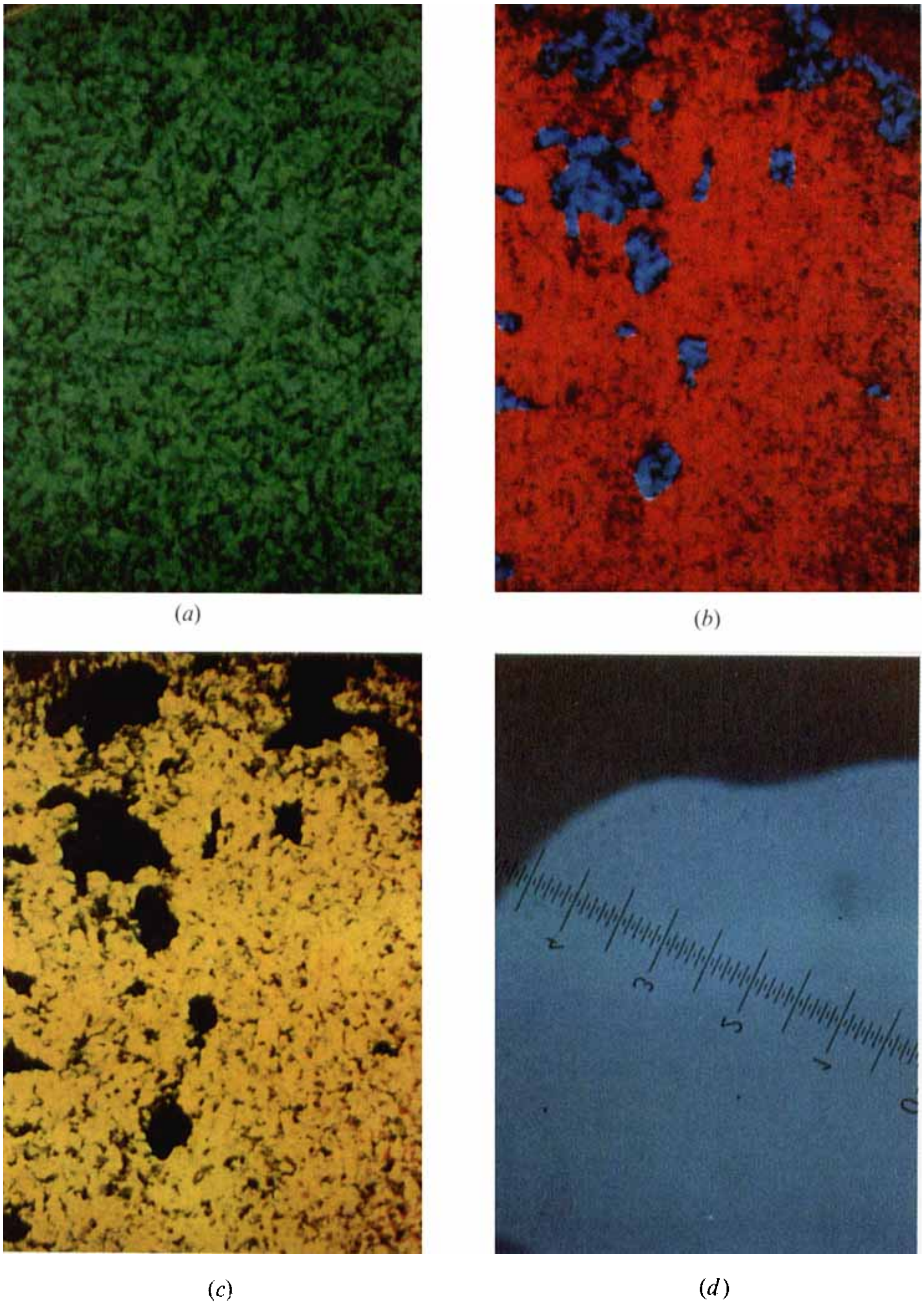
The blue phase has been reviewed previously. We call attention to the articles by Stegemeyer and co-workers [15, 16], Belyakov and Dmitrienko [17], Crooker [11] and Cladis [18]; see also Hornreich and Shtrikman [19]. In particular, BP I and BP II have been discussed extensively and need not be reviewed again here. We therefore pass over these phases rather quickly in favour of the more recent data on field-induced blue phases and, in particular, BP III. Continuing our disclaimers, this review does not attempt to provide a systematic history of the subject, nor does it cover any theoretical details except to mention models when appropriate. The main thrust of the review is to follow that work which elucidates blue phase structures; consequently all aspects of blue phase research are not covered. Finally, it is not attempted to produce every reference in the field, but instead papers are referenced from which the reader should be able to obtain the original work.

2. The existence of blue phases

Blue phases are difficult to detect unless it is known *a priori* that they exist. They were originally encountered in cholesteryl esters such as cholesteryl nonanoate, where they reflect light weakly at deep violet or ultraviolet wavelengths. Using transmitted light, which is the way in which most liquid crystals are observed, blue phases are seen rather poorly, and they occupy a temperature span of less than 1°C at a temperature where they are easily confused with transient phenomena associated with the helical–isotropic transition. Consequently it is not surprising that there was a lingering suspicion for a while that they did not even exist. Figure 2 shows the visual appearance of the blue phases when cyanobiphenyl liquid crystals, in this case a mixture of CB15 and E9, or of CE2 and M18 [20], are used. Both BP I and BP II are now seen to reflect colours other than blue, while BP III still appears faint and rather foggy-looking.

That the blue phases really are thermodynamically distinct was first indicated by discontinuities in density measurements [21–23] and by the initial experiments of Stegemeyer and co-workers [24–29]. However, the most convincing evidence for the existence of all the blue phases has come from the heat capacity measurements of Kleiman *et al.* [30] and most recently by Thoen [31]. We show Thoen's data for cholesteryl nonanoate in figure 3; from the shapes of the peaks, Thoen concluded that all of these phases are separated by first order transitions. The sizes of the latent heats are important here; they are (in J mol^{-1}):

H – 18 – BP I – 5·8 – BP II – 1·9 – BP III – 170 – I



(*a*) (*b*) (*c*) (*d*)

Figure 2. Appearance of textures for: (*a*) helical phase, (*b*) BP I, (*c*) BP II, (*d*) BP III and isotropic phase. Note that the single green colour of the helical phase is replaced by two discrete colours (red and blue) in BP I which then change to two new discrete colours (yellow and purple) in PB II. Other textures showing platelets may be observed by varying the growth technique (cf. [15]). (*a*)–(*c*) are CB15–E9; (*d*) is a mixture of CE2 and M18.

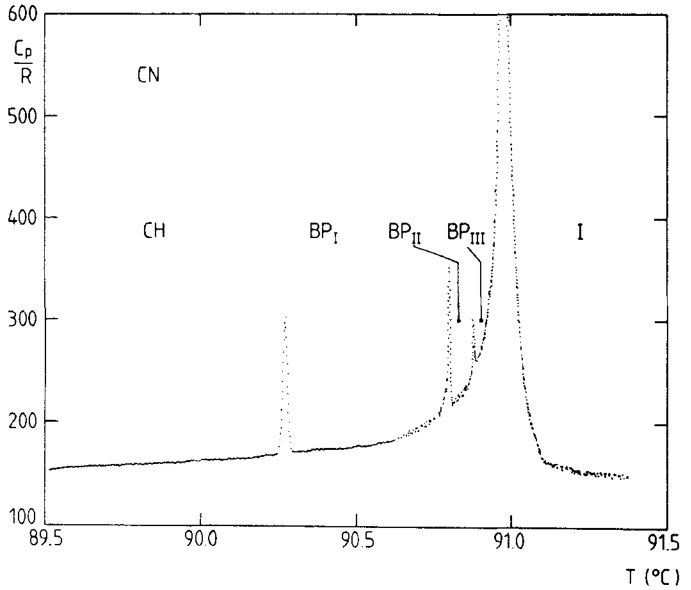


Figure 3. Heat capacity, C_p/R, versus temperature, T, through the blue phases of cholesteryl nonanoate (CN). CH = helical phase; BP I, BP II, BP III = blue phases; I = isotropic phase. (From Thoen, [31].)

The value of $170\,\mathrm{J\,mol^{-1}}$ is typical for the nematic–isotropic transition, whereas the others are significantly smaller. From the relative sizes of the latent heats, it can be seen qualitatively that the amount of order in the blue phases is closest to that of the helical phase, and that this order is essentially retained through all the blue phases up to the isotropic transition.

As this experimental description of the blue phases was accumulating, Hornreich and Shtrikman were developing a theory of blue phases based on Landau theory [32]. In the theory, temperature and chirality (the chirality is just 1/pitch) are the parameters causing the blue phases, and theoretical phase diagrams showing transition temperatures for various possible blue phases as a function of chirality were proposed [33, 34]. To test these theoretical phase diagrams, the experimenter would like to change only the chirality in his or her samples in a similar manner. However, making such an independent variation of chirality is not easily achieved in most condensed matter systems. Experiments with two different materials of different chirality can change the chirality [35–37], but at the expense of also changing the non-chiral coefficients of the free energy. Nevertheless, to a good approximation, chirality *can* be varied independently by mixing a chiral liquid crystal with its racemate: except for their chirality the left and right handed molecules are chemically identical. Chiral–racemic phase diagrams of various materials have been presented by Marcus and Goodby [38], Crooker and co-workers [37, 39, 40] and Collings [41]. Figure 4 shows the chiral–racemic phase diagram of CE2, which is one of the most chiral liquid crystals available [40, 42]. If the pitch of a mixture is P, the chirality $1/P$ is linearly related to the amount X of purely chiral material (i.e. the enantiomer) in the chiral–racemic mixture by the equation $P_0/P = X$ (P_0 is the pitch of the enantiomer), as shown on the top and bottom horizontal axes. The most significant feature of this data is that BP II only exists over a finite chirality range, whereas BP I and BP III

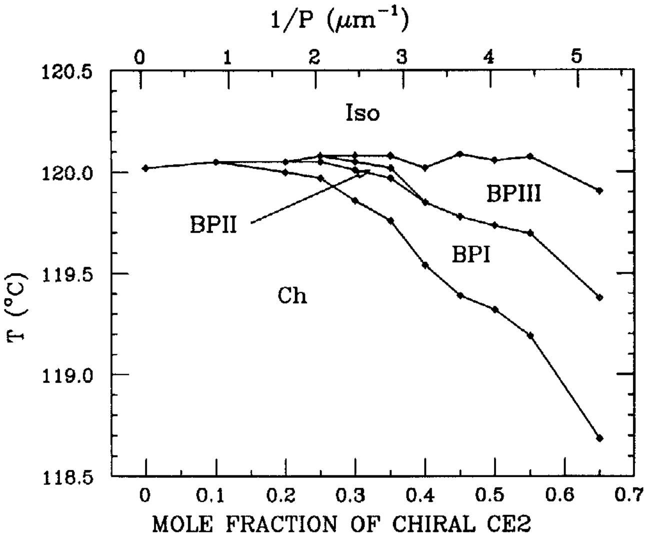


Figure 4. Transition temperatures, T, versus mole fraction chiral CE2 in a chiral–racemic mixture. Note the limited chirality range of BP II. (From Yang and Crooker, [40].)

become more stable as the chirality increases. The high chirality termination of BP II is also seen in other chiral–racemic phase diagrams, and we have argued that it may be a universal feature of blue phase systems [40]. Interestingly, the theoretical diagrams [33, 34] do not show the termination of BP II with increasing chirality, nor do they show BP III.

3. BP I and BP II

Interest in the blue phases centred initially on elucidating the structures of BP I and BP II. Theoretical predictions, working either from a Landau theory [32–34, 43–45] or from a presumed lattice of disclinations [8, 9, 14, 46, 47], have indicated that these phases are cubic, with both simple cubic (s.c.) and body-centred cubic (b.c.c.) structures being proposed. The lattice parameter of the unit cell is of the order of a half-pitch of the helical phase, and since this distance is just that required to Bragg scatter light in the visible wavelength region, optical methods have been of great utility. Experimental techniques which have been most useful have involved Bragg reflection of light in various ways, and the observation of crystal growth morphology under a microscope. Rotatory power, elastic measurements and some other techniques have also been used, but with less-definite results. To summarize the current state of BP I and BP II, there is now common agreement that: (*a*) both phases are chiral and non-birefringent; (*b*) they both grow crystallites (platelets) which Bragg reflect visible and U.V. light; (*c*) the Bragg reflections are accompanied by rotatory power anomalies, as is seen in the helical phase; (*d*) BP I is b.c.c. with a space group symmetry of O^8, whereas BP II is s.c. with space group symmetry O^2.

3.1. *Bragg scattering experiments*

Various types of Bragg reflection experiments provided the initial evidence that BP I and BP II were cubic. After the observation of Bragg peaks and anomalous rotatory power in blue phases [24, 26, 27, 48], Meiboom and co-workers measured the transmitted intensity spectrum for white light in polycrystalline samples [49–51]. Bragg scattered light missing from this intensity gives rise to steps which mark the Bragg wavelengths for each crystal plane. However, the Bragg peaks may easily be observed directly in reflection, using a microscope–spectrometer system [52–57]. Such a spectrum is shown in figure 5 for a mixture of chiral CB15 and nematic E9 [52]. Note that the helical phase has only one reflection at wavelength $\lambda = nP$, ($n(\lambda)$ is the refractive index) whereas the reflections from each blue phase have wavelength ratios of λ_0, $\lambda_0/2^{1/2}$, $\lambda_0/3^{1/2}$, . . . , λ_0 being the reflection of longest wavelength. These ratios are the signature of both b.c.c. and s.c. lattices; discriminating between the two becomes the next task.

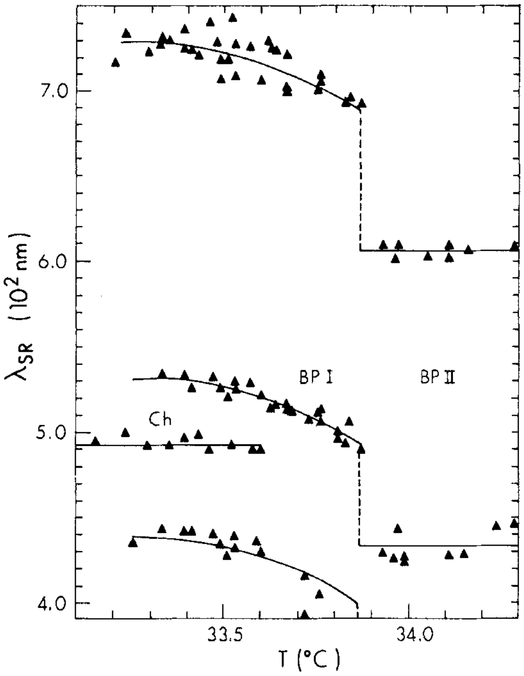


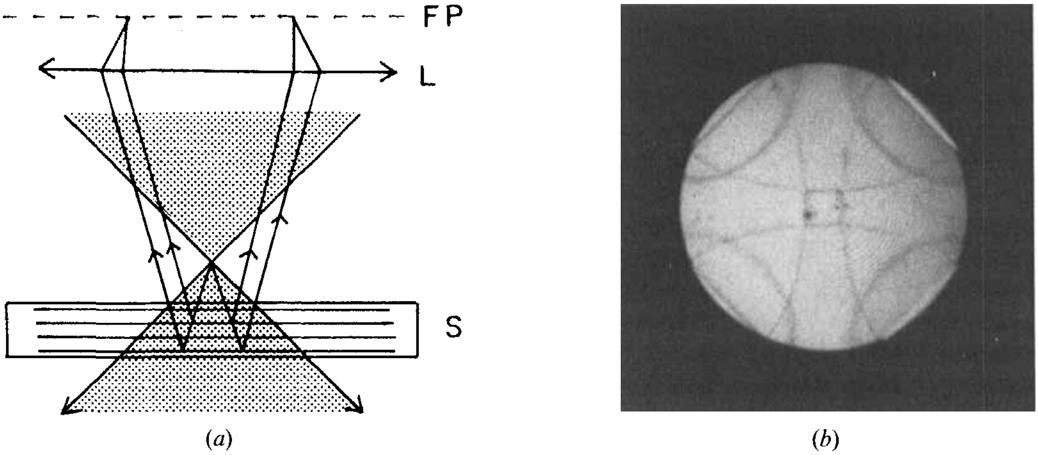
Figure 5. Selective reflection wavelengths λ_{SR} versus temperature for a mixture of CB15 and E9. Note that BP I supercools whereas the BP II transition is reversible. The ratios of the wavelengths are those for simple cubic or body centred cubic lattice symmetry. (From Johnson *et al.*, [52].)

As these measurements were being made, Hornreich and Shtrikman [58, 59] and Belyakov *et al.* [60] were working out the polarization selection rules for each possible chiral b.c.c. or s.c. space group symmetry. The theory contains five order parameter coefficients, ε_0, $\varepsilon_{\pm 1}$ and $\varepsilon_{\pm 2}$, for each set of Bragg planes. Each $\varepsilon_m(h\,k\,l)$ represents the Fourier amplitude of a particular dielectric tensor symmetry, which in turn controls the polarization of light in a particular way. Clearly, additional measurements with various kinds of polarized light would help further describe the blue phase symmetry.

At the lowest level, the presence or absence of a particular coefficient can be used as a selection rule for particular lattices. For example, the third line of the s.c. lattice (s.c. $\langle 1\,1\,1 \rangle$) should reflect light as an ordinary mirror, whereas the third b.c.c. line (b.c.c. $\langle 211 \rangle$) should only reflect light of one circular polarization. However, when such measurements were made [61–65], lines were observed which were forbidden by the selection rules and which contradicted the platelet growth morphology data emerging simultaneously. Thus, the observation that the third line of BP II is circularly polarized indicates that BP II is b.c.c., yet platelet growth morphology and Kossel diagram data clearly show BP II to be s.c. It now appears that the polarized Bragg scattering mechanism is more complicated than expected [60–66] and a simple interpretation of the data is probably incorrect. At present the situation is still not clear and other methods of identification have proven more useful.

There have been various attempts to determine the magnitude of the order parameter coefficients. Ideally, we should like to utilize the strength of the scattered light; however, this is difficult unless perfect crystals are used. It has been possible to deduce order parameters from lineshapes of blue phase spectral lines [67, 68], and scattering intensities and rotatory power from polycrystalline blue phases is another possibility [69, 70]. Measurements in which polarized light is Bragg scattered at an angle to the platelet orientations have also been used to determine the magnitude of the five possible order parameters [71, 72]. For this experiment the blue phase was produced on the hypotenuse of a 45°–45°–90° prism and light was scattered at 45° from it through the other prism faces. The polarizations of the incident and scattered light beams are each described by four-component Stokes vectors while the 4×4 matrix which transforms one to the other (and describes the blue phase) is the Mueller matrix. From a measurement of the total Mueller matrix it was determined that that ε_{-2} completely dominates the other order parameters, which then rules out certain space groups.

The final Bragg scattering technique which should be mentioned is the Kossel diagram technique of Pieranski and co-workers [73–75]. Figure 6 (*a*) illustrates the basic principle. The diagram shows one of the sets of crystal planes for a sample S illuminated by highly convergent monochromatic light from a microscope objective L. Of the many incident rays, a particular cone of rays satisfies the Bragg scattering condition and is backscattered, re-focussed and brought to an image in the back focal plane, FP, of the objective. Examination of this plane reveals the Kossel diagram (see figure 6 (*b*)),



(*a*) (*b*)

Figure 6. Principle of the Kossel diagram technique. (*a*) From the cone of incident monochromatic light, sets of crystal planes in sample S Bragg scatter light back through objective lens L to make a Kossel diagram at focal plane FP. (*b*) Each set of planes is represented by an arc in the Kossel diagram. (Kossel diagram by B. Jerome.)

in which each set of crystallographic planes presented by the sample is represented by a piece of a circle. Without further analysis it is clear that the symmetry of the resulting diagram is just the symmetry of the crystal, so we can distinguish between, say, the b.c.c. ⟨110⟩ direction and the s.c. ⟨100⟩ direction by the presence of fourfold rotation symmetry. However, quantitative measurement can also reveal the angles and spacings of the planes. This method has proven to be of great utility in characterizing the electric field-induced BPX phase and in determining that BP II has O^2 symmetry.

3.2. *Crystallite morphology*

Much of the original information on blue phases was deduced from microscopic examination of the textures [76, 77]. In particular, observation of the shapes of single crystal platelets grown at a phase boundary has proven most useful. The macroscopic symmetry of a carefully grown crystallite has the microscopic symmetry of the crystal itself. Growing the crystallites in a two phase region of a multicomponent mixture and/or in a temperature gradient has resulted in quite impressive crystallites. This work is primarily due to Stegemeyer and co-workers [78–82] and Pieranski and co-workers [83–86], who have published beautiful pictures of both two and three dimensional single crystals and have provided the most convincing evidence that the structure of BP I is O^8 and that of BP II is O^2. The review of Stegemeyer *et al.* [16] discusses this work extensively.

Electron microscopy of freeze-fractured blue phase structures has also been performed, but the results are much more difficult to interpret [87–89].

3.3. *Rotatory power measurements*

The experimental signature of a chiral structure is rotatory power. The earliest rotatory power measurements [24, 26, 90] established the chiral nature of the blue phase peaks. Later measurements [70, 91, 92] have followed and have even been able to provide values of the order parameters [70]. Theory for the behaviour has been provided by Bensimon *et al.* [93] and Belyakov *et al.* [70].

3.4. *Nuclear magnetic resonance*

Although there exists a theory for the N.M.R. behaviour of the cubic blue phases [94], the experiments have not so far been able to provide detailed evidence on the structure of BP I and BP II [95, 96]. The method may be more useful for BP III, however (see § 5).

3.5. *Viscoelastic measurements*

An important question to ask of the cubic blue phases is whether they are liquid or solid. The cubic structure is not one of atomic positions as in a conventional crystal; the liquid crystal molecules are, presumably, free to diffuse randomly throughout the blue phase lattice, changing their orientation *en route* so as to preserve the blue phase's order parameter specification. Solids are characterized by a non-zero static shear elastic constant, whereas a liquid will not support static shear. Conventional viscometric techniques through the blue phase temperature range, which now seem rather crude considering the fragile nature of the blue phase lattice, initially showed a large viscosity peak at the cholesteric–isotropic transition [97–99]. Viscosities and other transport coefficients associated with the pretransitional region of the isotropic phase were addressed by light scattering [100–103]. Once the cubic nature of the blue phase was established, attempts to measure the elastic constants appeared shortly thereafter [30, 104, 105], with those of Kleiman *et al.* [30] being the most extensive. The experiments are very delicate, since the blue phase lattice is both soft and weak; torsional oscillators configured as cup viscometers were used and the shear distortion was kept to less than 0·02 per cent. The results of Kleiman *et al.* for both the shear elasticity, G, and the viscosity, η, is shown in figure 7. These data are taken at various frequencies and must be extrapolated to 0 Hz to obtain the static properties. In the helical phase the extrapolation is somewhat dependent on the model; however, the authors argue that G becomes *nearly* zero in the cholesteric phase and about 710 dyn cm^{-2} in BP I. However, BP I also possesses viscosity, in short, BP I behaves like a viscoelastic solid.

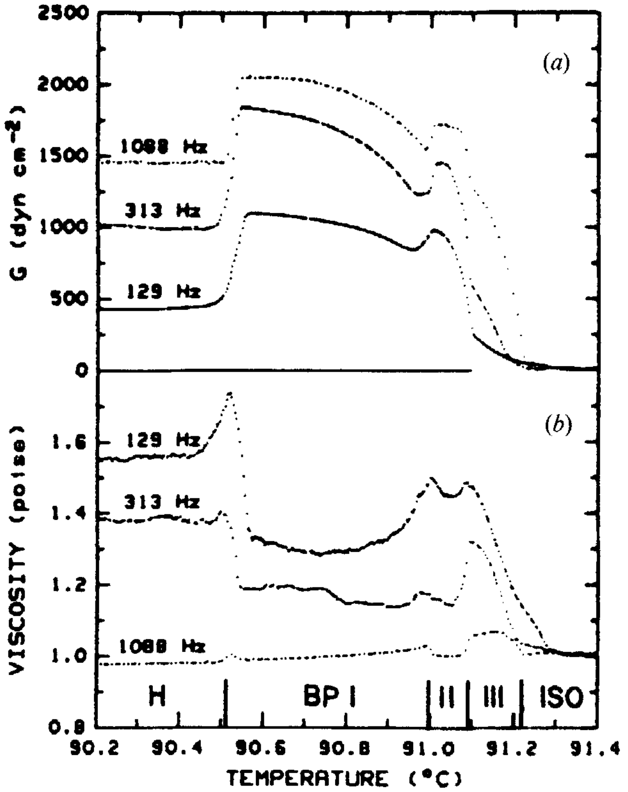


Figure 7. The shear elasticity (*a*) and viscosity (*b*) for cholesteryl nonanoate for different frequencies. (From Kleiman *et al.*, [30].)

Another way to assess the elastic constants in the blue phases is to observe their behaviour in the Cano wedge configuration, which tends to strain the blue phase lattice parameter. This strain raises the free energy and alters the blue phase transition temperatures, as has been shown by Feldman *et al.* [106]. For more discussion of blue phases in the Cano wedge configuration, see also [107, 108].

4. Field-induced blue phases

So far, the experimental parameters giving rise to the blue phases have been temperature and the chirality. Electric and magnetic fields are also legitimate thermodynamic variables, however, and a number of experiments have shown that electric fields, at least, can produce blue phases not otherwise seen.

The first experiments with electric fields started by showing that that an increasing field initially lengthens the blue phase lattice parameter and causes birefringence. A theory for weak fields was given by Lubin and Hornreich [109]. With larger fields the blue phases may transform between themselves, to the helical phase, and ultimately to the nematic phase [110–116]. Fields also affect the orientation and facetting of blue phase crystallites [85, 86, 117].

At the same time a theoretical prediction [118, 119] that a two dimensional hexagonal blue phase, BPH(2D), should be stabilized by an electric field spurred interest in looking for other crystal structures. Subsequent temperature–electric field phase diagrams [120, 122] showed that other phases did in fact occur, but identification of the new structures was much more difficult. Figure 8, by Porsch and Stegemeyer [120], shows a mixture of CB15 and E9 in which a new phase, BPE, is detected. Figure 9, due to Pieranski *et al.* [123] shows the same material and identifies platelet shapes seen in the BP II–isotropic two phase region which were not seen by the previous authors. The lack of agreement between phase diagrams is, incidentally, not unique to these authors.

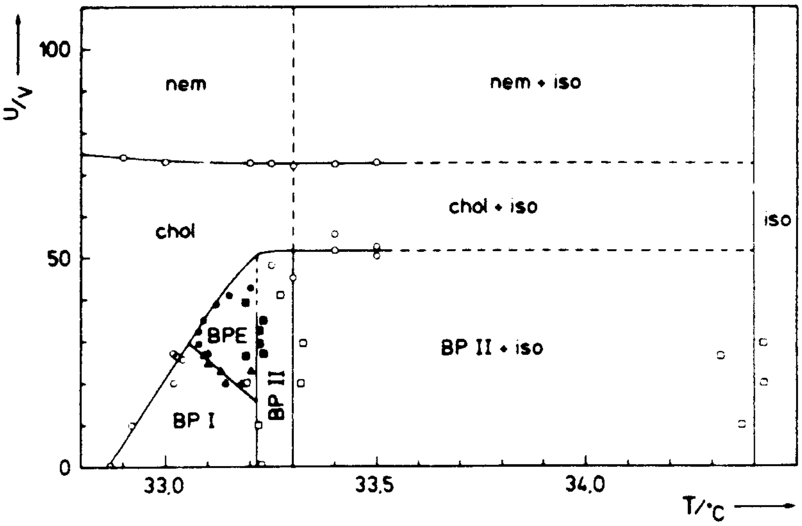


Figure 8. Voltage–temperature phase diagram for a 49·6 per cent mixture of CB15 in E9. Chol = helical phase; the structure of BPE is not determined. (From Porsch and Stegemeyer, [120].)

Observation of an identifiable hexagonal phase was first reported by Pieranski *et al.* [123], who observed the hexagonally shaped crystallites indicated in figure 9. This hex phase was not the predicted BPH(2D) phase, however; the hex crystallites exhibited strong circularly polarized Bragg reflections along the hexagonal axis, leading to the conclusion that they are a *three* dimensional BPH(3D) phase. Later work [124] has shown that increasing the electric field causes the reflected intensity to weaken and finally, at a threshold field, to disappear altogether. The platelets remain, however; they are in the BPH(2D) phase and are detectable in transmission. Reversing the process cuases the coloured hex platelets to return.

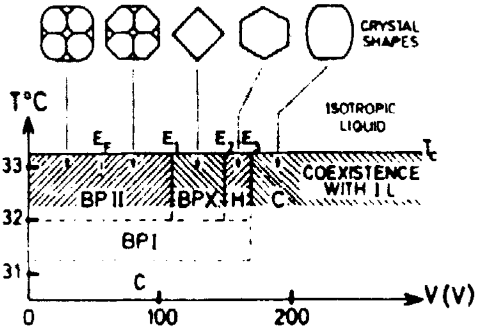
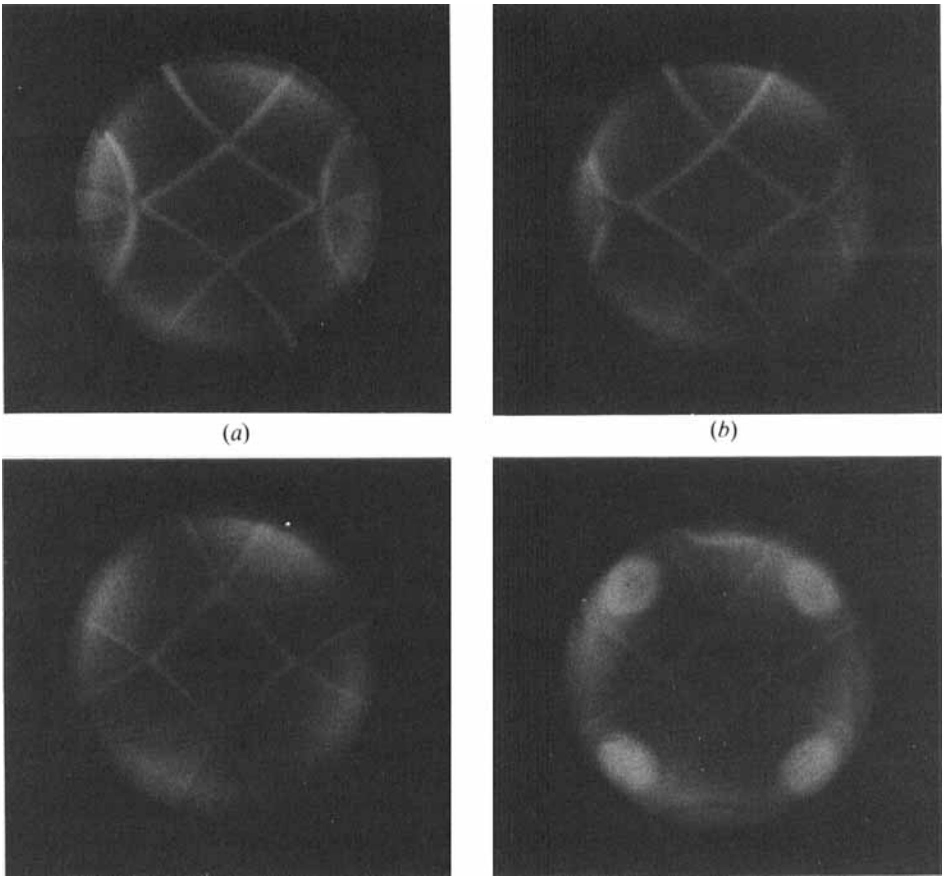


Figure 9. Schematic temperature–voltage phase diagram for 49·8 per cent mixture of CB15 in E9. Shaded region is the coexistence region in which crystals of different shapes appear. H is the hexagonal BPH(3D) phase; C is the helical phase. (From Pieranski *et al.*, [123].)


(*a*) (*b*)

(*c*) (*d*)

Figure 10. Kossel diagrams of the [110] direction of BP I, showing the transformation to BPX with increasing field. (*a*) $V = 0$, (*b*) $V = 70$ V, (*c*) $V = 90$ V, (*d*) $V = 100$ V. Wavelength is 529 nm in (*a*)–(*c*) and 496 nm in (*d*). (From Cladis *et al.*, [74].)

Further investigation on the same system [74, 75] has revealed a second field-stabilized phase, called BPX, which has a tetragonal unit cell. The elucidation of this structure was accomplished with the Kossel diagram technique, which we reproduce in figure 10 to show the power of the method. In figure 10 (*a*) the Kossel diagram of the BP I b.c.c. ⟨110⟩ direction is shown at $\lambda = 529\,\mathrm{nm}$. Upon application of an electric field (see figure 10 (*b*)) the distorted b.c.c. unit cell becomes orthorhombic, and above a critical field (see figure 10 (*c*)) the tetragonal symmetry locks in. Figure 10 (*d*) shows the Kossel diagram for light of shorter wavelength ($\lambda = 496\,\mathrm{nm}$), so that more lines can be seen. Note that the Kossel diagrams show the evolution of the symmetry clearly, whereas measurements from the diagrams reveals details of the transition and of the resulting lattices.

The present situation, then, is that electric fields not only distort the blue phase structure and alter the phase transition temperatures, they also cause new phases to appear. Three phases, BPH(2D), BPH(3D) and BPX, have been positively identified, but only one, BPH(2D), was predicted before the experiment. Happily, theoretical work on the remaining phases is currently underway [125].

5. BP III

We now turn to BP III, at present the most enigmatic of the blue phases. This phase has been variously called the grey phase by Stegemeyer and Bergmann [15] the fog by Marcus [76], BP III by Meiboom and Sammon [50], the blue fog by Finn and Cladis [111], and the foggy phase in the English translation of the 1983 paper of Demikhov and Dolganov [126]. Recent writings appear to favour BP III, and it is our hope that BP III will remain BP III forevermore.

5.1. *Initial experiments*

The first mention of BP III is probably in the 1975 paper by Coates and Gray [127] who describe seeing the blue apparition (i.e. the blue phase) without the usual platelets. Stegemeyer and Bergmann clearly identify BP III in their 1980 review article [15]; their colour pictures show a gray amorphous-appearing phase which is definitely distinct from the adjacent BP II and isotropic phases. Marcus [76] mentions obtaining BP III upon cooling cholesteryl esters from the isotropic phase. The phase persisted overnight, showed optical rotation and, since it showed no conoscopic figure, was not birefringent. In a temperature gradient the BP II–BP III and BP III–isotropic boundaries were sharp, thereby precluding the possibility that BP III was really a manifestation of pretransitional fluctuations at the BP II phase–isotropic transition. Marcus went on to speculate that BP III is a quasi-liquid; it has blue phase structure, but in a disordered state. Such a quasi-liquid would be expected to be less stable than the crystalline blue phase and hence appear at a higher temperature. Furthermore, it should have a diffuse Bragg like peak associated with the local order.

The first quantitative measurements on BP III were by Meiboom and Sammon [49, 50] who measured a marked decrease in transmitted light intensity in the BP III temperature region (between 91·84 and 91·96°C for cholesteryl nonanoate) at wavelength below about 400 nm. Since the transmitted light is just the incident light minus the Bragg reflected light, the upper cut-off wavelength was just the peak mentioned by Marcus [76]. Furthermore, since the transmission dip only occurred for light circularly polarized in one sense and not in the other, the scattering structure of BP III is definitely chiral. The circularly polarized transmission studies have since been repeated (here they are called circular dichroism spectra) by Kizel' and Prokhorov [63] with similar results.

Subsequent measurements capitalized on the chiral aspects of BP III by measuring the rotatory power as a function of temperature at one wavelength [126] and as a function of both wavelength and temperature [128]. Figure 11 shows the rotatory power obtained by Collings [128] in both BP III and the isotropic phase of cholesteryl nonanoate. The results of this experiment were twofold. First, the distinct breaks in the rotatory power between different blue phases lent credence to the fact that BP III was a thermodynamically distinct phase (this issue was considered still unresolved by many). Secondly, when Collings modelled BP III as a distribution of small, randomly oriented, BP II-like domains, the calculated rotatory power spectrum was found to look very similar to that of figure 11.

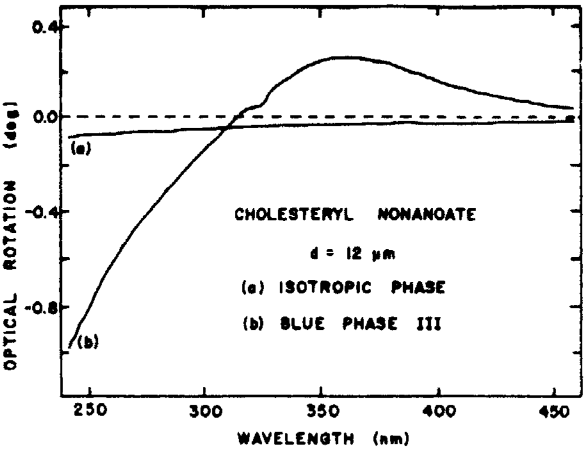


Figure 11. Rotatory power spectrum of cholesteryl nonanoate. (From Collings, [128].)

While these optical measurements were under way, the question of the stability of BP III was finally laid to rest by Kleiman *et al.* [30], who performed careful specific heat measurements across the whole blue phase region and observed distinct peaks at the temperature boundaries of all of the blue phases, including BP III. However, they could not conclude that the BP III–isotropic transition was first order. The refinement of this data by Thoen [31] has already been shown in figure 3. From a detailed analysis of his data, Thoen has concluded that all the transitions, including the BP III–isotropic transition, are first order. Recalling that the BP II–BP III latent heat is 1·9 J mol^{-1} and the BP III–isotropic latent heat is 170 J mol^{-1}, or approximately 100 times larger, we must conclude that *the order of BP III is much closer to that of BP II than to the isotropic phase*. How we can have a structure that appears so featureless visually and yet has almost the same order as BP II is the central issue in understanding BP III.

The position of BP III in the overall scheme of blue phases has been shown in the phase diagrams of Marcus and Goodby [38] and Yang and Crooker [40] (see figure 4). Of all the blue phases, BP III requires the higest chirality but, unlike BP II, it appears to be increasingly stable as the chirality increases further. For doubly chiral molecules (i.e. having two chiral end chains of the same handedness) the longest reported actual pitch at the onset of BP III is about 500 nm [38, 40], whereas for singly chiral molecules (having one chiral end chain) the longest pitch appears to be about 250 nm [40]. CE2 (figure 4) is remarkable for its high chirality; in its pure enantiomeric form it has an actual pitch of 100 nm and a BP III range we estimate to be 1·1°C.

Returning to the optical properties of BP III, the first measurement of the selective reflection wavelength of BP III was made by Demikhov *et al.* [129] in a mixture of cholesteryl nonanoate and cholesteryl chloride. Figure 12 shows their data, as well as the peaks from the other blue phases. Note that the BP III peak is much wider and weaker than that of BP I or BP II; this is the signature of scattering from small, randomly ordered regions containing only a few Bragg planes. From the broad width of the peak we can estimate the size of the ordered region and the authors obtain a correlation length of about 1·1 μm or about four to five pitch lengths. Interestingly, the relative size of the correlation length to the pitch is similar to that found from X-ray measurements in amorphous substances (here the lattice parameter must be substituted for the pitch length), but is much less than that found in polydomain samples [129].

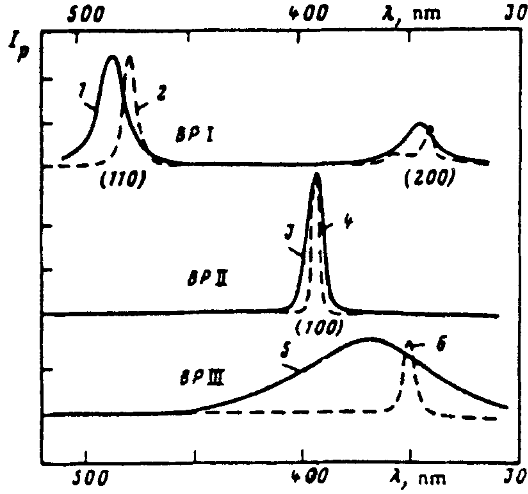


Figure 12. Reflection peaks in cholesteryl nonanoate. 1, 2, BP I at two temperatures; 3, 4, BP II; BP III; 6, helical phase. The height of the BP III peak is actually six times smaller. (From Demikhov *et al.*, [129].)

Zasadzinski *et al.* [88] have attempted to observe directly the ordered regions of BP III using transmission electron microscopy on freeze-fractured samples of CE4. Although BP III in this material occupies a temperature range of only 0·6°C at 37°C, the authors nevertheless claim to be able to freeze it in place by dropping it into liquid propane. The frozen sample is then fractured, replicated, and examined in an electron microscope. The resulting image, different from similar images for the helical phase, BP I, and the isotropic phase, is shown in figure 13. From the local filamentary structure of this figure, the authors argue that the BP III structure is a tangled, spaghetti-like network of cylinders of various diameters and lengths that are locally parallel. If BP I and BP II are ordered networks of double twist cylinders, as mentioned earlier, it is tempting to say that the same cylinders are represented here, but without any long range ordering. Unfortunately, the BP I/BP II cylinders are supposed to have a diameter of the order of the pitch, about 0·16 μm for CE4 [40], whereas the sizes of those in figure 13 are ten times smaller.

Additional information on the structure of BP III has come from the elastic measurements of Kleiman *et al.* [30] shown in figure 7. Since the mechanical properties

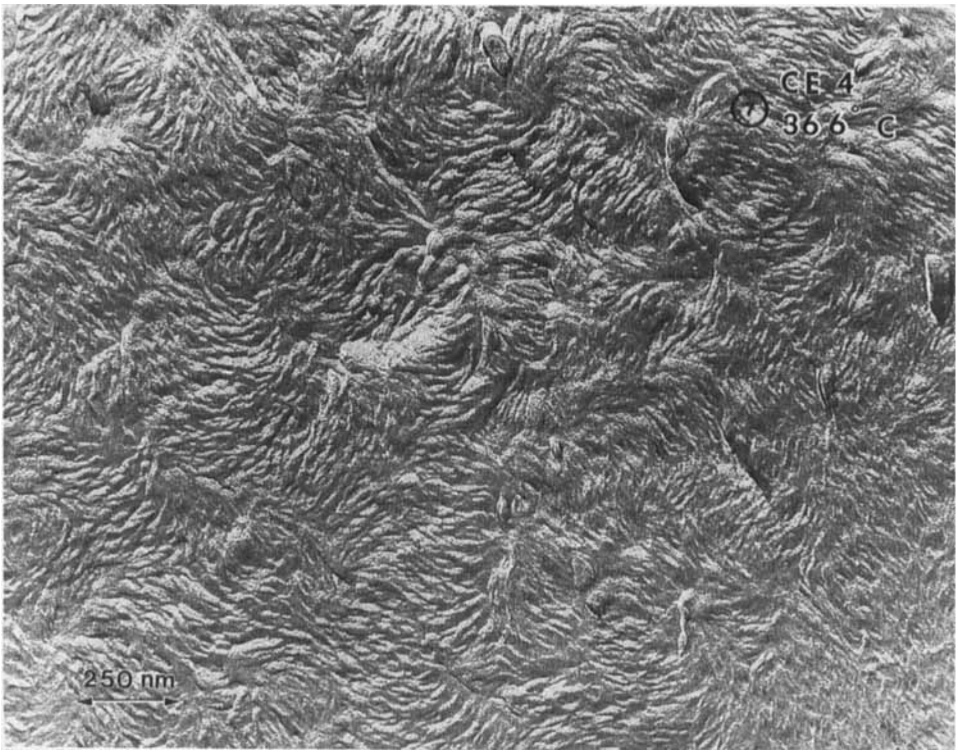


Figure 13. Electron micrograph of freeze-fractured BP III phase in CE4. (From Zasadzinski *et al.*, [88].)

of BP III change progressively from BP II-like to isotropic-like as the temperature is raised through the BP III phase, Kleiman *et al.* argued that BP III consists of a network of double twist lines which continuously loses its long range order as the temperature is increased. Such a dramatic change in the long range order would manifest itself in by an increase of the linewidth of the selective reflection line with temperature, which, as we shall see, has not been observed in other materials [122]. Therefore, the implications of this data are still unresolved.

5.2. *Models of BP III*

The experimental evidence for the properties of BP III that has so far emerged is: (*a*) BP III is a thermodynamically distinct phase which becomes more stable with increasing chirality; (*b*) its order is probably much closer to that of BP II than to the isotropic phase; (*c*) optically it is chiral, non-birefringent, and it exhibits rotatory power with a value between BP I/BP II and the isotropic phases; (*d*) it has a broad, circularly polarized reflection peak; (*e*) its mechanical properties are more like the isotropic phase than like BP I/BP II, at least near the high temperature end of BP III; and (*f*) electron micrographs reveal a disordered filamentary structure. The question now becomes: what microscopic structures will exhibit this behaviour?

There are now, in fact, a number of models for blue phase structure. One of the earliest speculations was that BP III was simply a manifestation of pretransitional fluctuations in the isotropic phase at the blue phase–isotropic phase transition [6, 7].

Hornreich and Shtrikman [59] have argued that the observed BP III scattering [50] is several orders of magnitude larger than would be expected for pretransitional fluctuations but, in any case, the specific heat data [30, 31] conclusively rule out the pretransitional fluctuation model.

Looking at the situation from an experimenter's point of view, we recognize four models for BP III structure. (Not all of these models are theoretically satisfactory, in that there are details which still need to be worked out, but we shall not let that deter us here.) Figure 14 gives, in a highly schematic fashion, the essential features of each model.

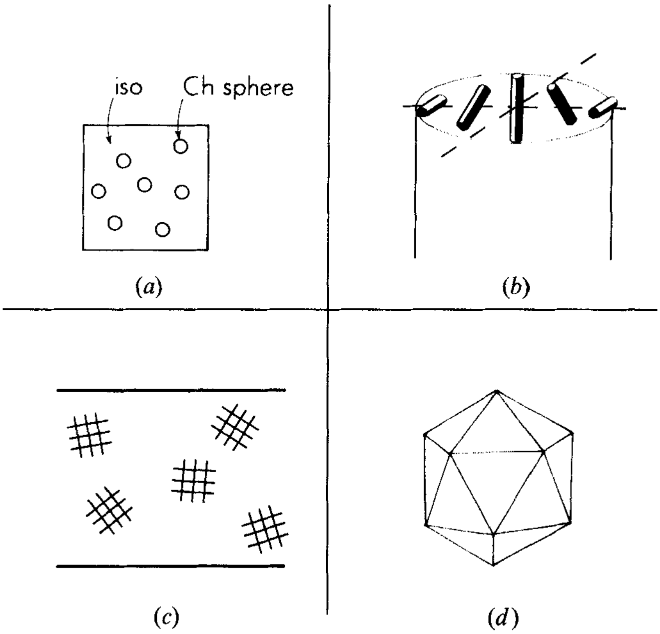


Figure 14. Models of BP III. (*a*) Emulsion model. Helical droplets are suspended in an isotropic background. (*b*) Double twist model. Director orientation for a double twist tube. Any diameter of the tube will have a similar twist. (*c*) Cubic-domain model. Randomly oriented correlated regions have cubic symmetry and area a few pitch lengths in size. (*d*) Icosahedral model. The reciprocal lattice vectors are from centre to vertex and from vertex to vertex of a regular icosahedron.

In the emulsion model, suggested by Finn and Cladis [111], BP III consists of an emulsion of droplets in the helical phase in an isotropic background (see figure 14 (*a*)). The droplets have random position and orientation in BP III; in BP II they order into a lattice. This model requires a mixture of liquid crystals, two coexisting phases over a range of temperatures is impossible in a single component material. Although BP III is commonly seen in ostensibly single component materials, it might be argued whether the purity is ever sufficiently high to preclude the emulsion possibility.

A second model, the double twist model of Hornreich *et al.* [130], suggests that BP III consists of a spaghetti-like tangle of double twist cylinders (see figure 14 (*b*)). Each cylinder has a uniaxial order parameter whose principal axis (i.e. the director) rotates spatially around any diameter of the cylinder, and whose strength dies away in gaussian-like fashion with increasing distance from the cylinder axis. Calculations show that the diameter of these cylinders is about a half-pitch but, ignoring that detail, a picture of these cylinders might look like figure 13.

A third model, the cubic domain model (see figure 14 (*c*)), includes the possibility that BP III consists of small cubic domains or correlated regions. For these regions, Collings [128] has suggested a BP II s.c. structure, whereas Belyakov *et al.* have proposed a BP I b.c.c. O^5 structure [70].

The last model, the quasi-crystal model [131–134], is especially intriguing from a theoretical point of view. Starting from the Landau theory of Hornreich and Shtrikman [32], a structure with reciprocal lattice vectors derived from a regular icosahedron is postulated (see figure 14 (*d*)). Using the 12 vertex vectors (from the centre to the vertices) and the 30 edge vectors (from vertex to vertex), an unstable structure with free energy considerably higher than that of, say, the O^5 cubic phase is found. If, however, the symmetry is broken by shifting the phases of the edge vectors, the free energy can be lowered until the structure is *almost*, but still not quite, stable. One then hopes that with the inclusion of contributions from neglected higher order terms in the order parameter and its spatial derivatives, the quasi-crystal structure would be made credible [131].

Although all of these models explain the principal features of BP III, they also contain the ingredients for further experimentation. Some of these possibilities are addressed in the next section.

5.3. *Further experiments*

One way to test the validity of the quasi-crystalline model for BP III is by examining its N.M.R. spectrum. Both Hornreich and Shtrikman [135] and Filev [136] have calculated the N.M.R. spectrum for the quasi-crystal model and found that it consists of a single rounded peak, while that of BP I or BP II is double peaked. Filev [136] has also calculated the N.M.R. spectrum for a tangle of double twist cylinders and find that it, too, is double peaked. The experiment has not yet been performed, but the observation of a BP III single peak would be strong evidence in favour of quasi-crystalline BP III.

In our own laboratory we have concentrated on optical experiments, which are notoriously difficult to perform. The BP III optical reflection spectrum is usually in the U.V. region, making it difficult to identify visually textures in the microscope and rendering conventional visible light spectroscopy impossible. Attempts to utilize U.V. techniques are also frustrating, since commercially available stable chiral materials have benzene rings which, in turn, have a high U.V. absorption. Furthermore, accessable polar chiral molecules (for electric field studies) have transition temperatures inconveniently high, making precise temperature control over the small BP III temperature range difficult.

We have taken two approaches to testing the various models. The first is to apply an electric field to a BP III consisting of polar molecules and to attempt to reorient either the BP III domains or the molecules within the domains. If the domains are not strongly coupled to each other the reorientation effects, which could be monitored by the reflected intensity, might be dramatic. For this experiment the sample consisted of a mixture of CE1, CE2 and K18, which has a polar BP III 0·6°C wide and a visibly observable reflection peak at 438 nm [122]. The effect of an electric field on this material is shown in figure 15. In this temperature–electric field phase diagram BP III has a limited range of stability, becoming an unknown new phase at high fields,

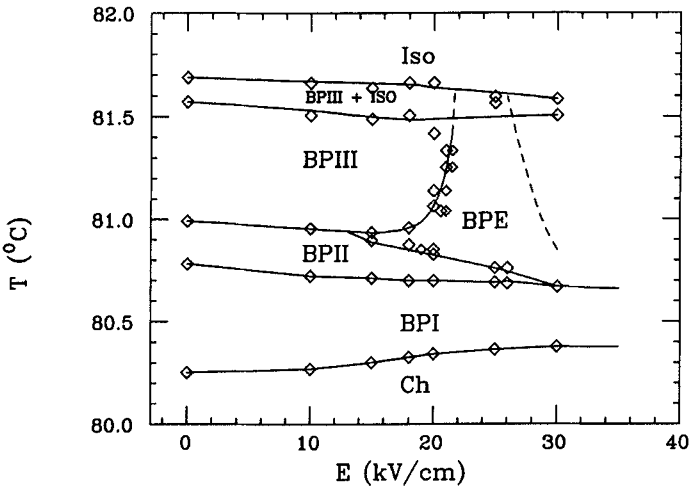


Figure 15. Temperature–electric field phase diagram in a CE1–CE2–K18 mixture showing BP III behaviour. BPE is a distinct but unidentified phase; the broken lines indicate where the reflected intensity of BPE decreases rapidly. (From Yang and Crooker, [122].)

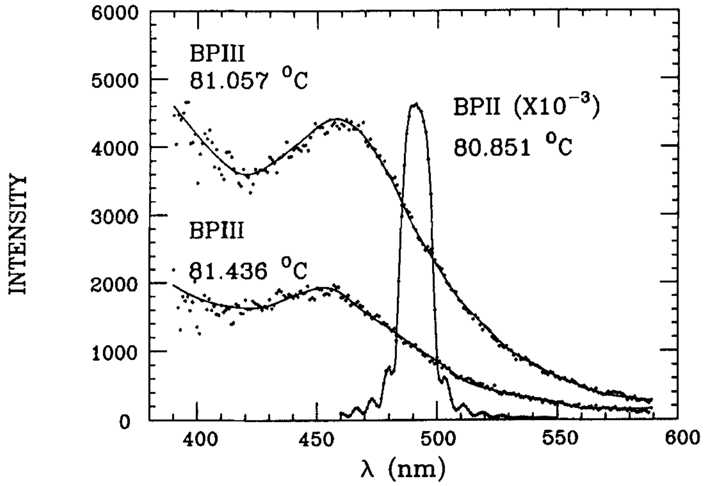


Figure 16. Reflected intensity versus selective reflection wavelength along the $E = 0$ line of figure 15. (From Yang and Crooker, [122].)

reminiscent of the BP I/BP II phase diagrams [120, 121] described previously. Exploration of the intensity and spectrum of the reflected light over the BP III region of figure 15 can be summarized as follows. (*a*) The spectrum of BP III, shown in figure 16, consists of a broad peak and a sloping background, unlike the corresponding spectrum in cholesteryl esters [129]. If the amount of long range order changed rapidly with temperature, as suggested by Kleiman *et al.* [30], the linewidth of this peak would change. In fact, the form of this spectrum changed little over the whole BP III region. (*b*) The wavelength of the BP III peaks shows < 1 per cent change with either increasing temperature or electric field, whereas the wavelength of the BP II peak increased by about 4 per cent with electric field. That the lattice parameter of BP III is even more resistant to electric fields than that of BP II is surprising. (*c*) Starting from the lower left hand corner of the BP II region in figure 15, the amplitude of the peak decreased by about half as the temperature increased vertically to 81·5°C or the field increased horizontally to 18 kV cm^{-1}. Thus, the BP III order is seen to be fairly rigid with respect to both temperature and field.

In the course of these measurements we discovered that the intensity of BP III could be significantly enhanced by a factor of 20 by rubbing the sample substrate, and that this enhancement was destroyed if the sample was tilted [137]. Subsequent investigations showed that BP III was aligned to a depth of several pitches at the surface, allowing us to measure the Bragg reflections at various angles and providing for a direct test of BP III models. In particular, aligned quasi-crystal domains should show vertex–vector and edge–vector peaks which have a wavelength ratio of 1·05 and an angular separation of 37°. The inset to figure 16 shows our scattering experiment; its main feature is a temperature controlled universal stage (used previously by others [65, 66]) which allows observation of the sample at large angles of incidence. Figure 17 (*a*) shows results on BP I, which is known to be cubic: the b.c.c. ⟨110⟩ at $\theta = 0°$ and $\lambda = 618$ nm becomes the b.c.c ⟨200⟩ line at $\theta = 45°$ and $\lambda = 442$ nm. However, when the $\lambda = 460$ nm, $\theta = 0°$ line of BP III is examined (see figure 17 (*b*)), no indication of a quasi-crystal line at $\theta = 37°$ is observed. In fact, *visual observation of the sample over the whole θ–ψ parameter space reveals no higher order reflections of any kind.* How this result can be reconciled with the quasi-crystal model is not clear.

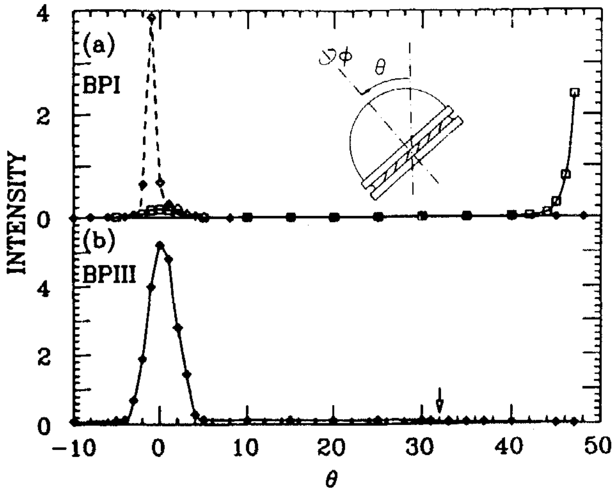


Figure 17. Reflected intensity versus angle in the BP I and BP III phases. (*a*) BP I phase: ⟨110⟩ line at 618 nm (diamonds) and ⟨200⟩ line at 442 nm (squares). (*b*) BP III phase $\lambda = 460$ nm. The arrow shows the expected location of a quasi-crystal peak. Inset: geometry of the angular reflection apparatus. (From Yang and Crooker, [137])

We have also looked for cubic domains using U.V. reflection spectroscopy from amorphous BP III. If the longest wavelength reflection of a cubic domain in λ_0, then a second peak should be observable at $\lambda_0/2^{1/2}$, as is seen in BP I and BP II. We have constructed a mixture of CE1, CE2 and M18 in which the BP III wavelength is 555 nm and for which the second cubic peak should occur at 380 nm, well within the range of our experiment (see figure 18). This peak is not observed, however, which is difficult to understand if BP III domains are cubic.

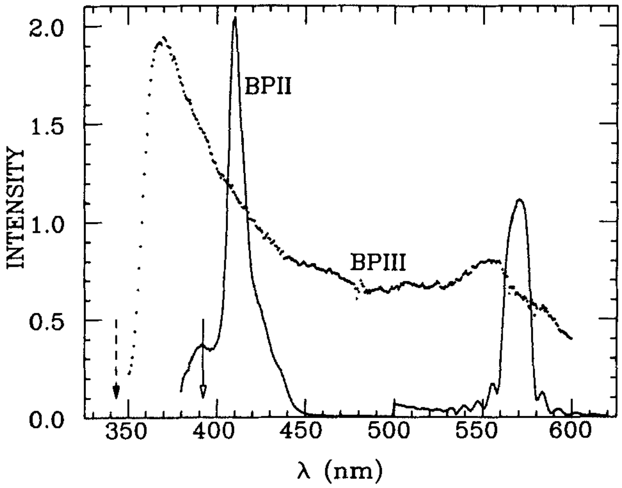


Figure 18. Reflected intensity versus wavelength for unaligned BP III and for BP II peaks. Solid (broken) arrow shows the expected location of higher order reflection in the cubic (quasi-crystal) model. (From Yang and Crooker, [137].)

To summarize, we see no evidence of lines which are allowed for quasi-crystal and cubic BP III structures. The BP III models which seem to be most compatible with our experiments are those with only a single scattering vector. The double twist model is such a candidate, as is the emulsion model. However, since the emulsion model seems to be ruled out by the freeze-fracture results, we currently favour the double twist model.

6. Future experiments

Although we have come a long way in our understanding of blue phases since 1979, there are many problems remaining, some of which have been pointed out previously [17, 19]. First on the list of problems to solve is the question of the structure of BP III. Many models exist, as we have seen, so it is up to experimenters to distinguish among them or perhaps eliminate all of them in favour of an entirely new model. Optical experiments (reflectivity and rotatory power) have already indicated problems with models that yield more than one Bragg harmonic; N.M.R. experiments should give further insight on the problem. We are somewhat materials limited; new materials with blue phases of longer pitch, lower transition temperatures and, for electric field experiments, strong polarity would be of great utility.

There is still more to do on BP I and BP II. They appear to be soft cubic crystals containing regular arrays of defects, and we believe we know their space groups, not to mention those of the BPH(2D), BPH(3D) and BPX phases. However, a complete understanding really requires a knowledge of how the molecules are oriented, and that has not yet been achieved.

Another aspect of BP I and BP II that is not understood is the observation of spectral lines which are forbidden by symmetry. Section 3 discusses this problem; probably a new theoretical understanding of the scattering processes is necessary here.

It is not yet known whether the experimental temperature–chirality phase diagrams have universal features. More diagrams on generically different systems will help. However, the experimental phase diagrams have several features which do not appear in the theoretical phase diagrams. One is the presence of BP III. Another is that the s.c. structure becomes unstable at high chiralities, and a third is that experimentally the high chirality, high temperature phase is not b.c.c., as is the case theoretically. Universality in temperature–electric field diagrams is also interesting. Clearly more theoretical and experimental work is still required.

Experiments on the viscoelastic properties have only begun. The cubic blue phases are unique; we can, in principle, compress the lattice, by using constraining boundary conditions, for example, without actually compressing the molecules. The elastic constant is of the order $K_2q_0^2$, and Dmitrienko [138] has already provided preliminary calculations of how light scattering can provide the actual numbers. The anomalous viscosity observed in the blue phase region is almost certainly due to yielding of the crystal lattice, but the actual yield strength is still unknown.

Finally, the nature of the pretransitional behaviour at the BP–isotropic transition is highly interesting. Experiments in the pretransitional region have included light scattering [100–102, 139] and rotatory power measurements [92, 140–143]. Are pretransitional regions near the BP III–I BP II–I BP I–I and H–I transitions all similar, or is the size of the first order transition sufficiently small that the low temperature order is manifested, as it is in nematics? Light scattering should be able to solve these problems; however, meaningful scattering geometries and polarizations are complicated.

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