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## Liquid Crystals

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### The effect of electric fields on blue phase III with negative dielectric anisotropy

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## The effect of electric fields on blue phase III with negative dielectric anisotropy

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In order to further understand the structure of the blue phase III (BPIII) phase of chiral liquid crystals, we have observed the effect of electric fields on the reflectivity of BPIII phases in which the liquid crystal has *negative* dielectric anisotropy. The reflectivity increases dramatically with increasing field, in contrast to the behaviour for materials of *positive* dielectric anisotropy. We compare the data with cubic domain and double-twist models for BPIII structure and we find that the data best agree with the double-twist model and possibly with an  $O^3$  cubic domain model.

### 1. Introduction

It has been known for some time that highly chiral liquid crystals have thermodynamic phases not present in liquid crystals of low or zero chirality [1, 2]. These new phases, collectively called blue phases, appear in a small ( $\sim 1^\circ\text{C}$ ) temperature interval between the cholesteric and isotropic phases. Two of them—blue phase I (BPI) and blue phase II (BP II)—appear to be well understood. In white light, both BPI and BP II exhibit sharply peaked circular polarized Bragg reflections. The polarizations and wavelengths of the peaks indicate the structure is both chiral and periodic, with a periodic length of the order of the wavelength of visible light in the material. The sharpness of the peaks, on the other hand, is the signature of long-range order—that is, of a periodic structure which preserves its phase over many period lengths. From both the Bragg reflection data and morphological observations, it has been determined that BPI and BP II possess body-centred cubic and simple cubic structure, respectively.

The third blue phase, BPIII, is not yet understood. In white light it exhibits only one broad, weak reflection peak [3], which indicates that the structure lacks long-range order. Visually, it appears cloudy and amorphous and it shows optical activity [4]. It is distinguished from the lower temperature BPI or BP II phases by a weak first order phase transition (transition enthalpy  $\Delta H \approx 2 \text{ J mole}^{-1}$ ) and from the higher temperature isotropic phase by a much stronger first order transition ( $\Delta H \approx 170 \text{ J mole}^{-1}$ ), which indicates that its intrinsic order is probably closer to the cubic blue phases than to the isotropic phase, despite its amorphous visual appearance [5, 6]. On the other hand, the shear modulus and viscosity of BPIII decrease gradually from BP II-like to isotropic-like through the BPIII temperature range [6], which may indicate that a significant decrease in the BPIII order parameter takes place within the BPIII temperature range.

Several models of BPIII, not all of which have been worked out quantitatively, have been proposed to explain the experimental results [1]. The *quasicrystal model* [7–10] proposes that BPIII has a quasiperiodic structure, with reciprocal lattice

vectors derived from the twelve vertex and thirty edge vectors of a regular icosahedron. A second model is the *double-twist model* [11], in which BPIII consists of a spaghetti-like tangle of 'double twist' cylinders. Each of these cylinders has a locally uniaxial order parameter whose principal axis (i.e. the director) rotates about any diameter of the cylinder and whose strength decreases in approximately gaussian fashion with increasing distance from the cylinder axis. A third model is the *cubic domain model*, in which BPIII consists of small domains or correlated regions having either simple cubic [4] or body-centred cubic  $O^5$  structure [12]. Finally, the fourth model is the *emulsion model* [13] which proposes an emulsion of droplets, each one having a complicated chiral structure, immersed in an isotropic background.

Several attempts have been made to test these models. Yang, Crooker and Tanimoto [14] have been able to produce a surface-aligned BPIII phase which has allowed them to test for the presence of higher-order off-angle Bragg reflections predicted by the quasicrystal model. These quasicrystal reflections were not, however, observed. In addition, they were able to search in unaligned films for higher-order reflections predicted for BPII-like cubic domains. These too were not observed.

Electric field response has also been used to elucidate BPIII structure [15]. If the cubic domain model is correct and the structure of the cubic regions is like BPII, one expects similarities between the electric field dependence of the BPII and BPIII reflectivities. Measurements in chiral mixtures having positive dielectric anisotropy ( $\delta\epsilon > 0$ ) have not, however, revealed any similarities.

Electric fields can also affect a double-twist structure by changing its alignment. Hornreich *et al.* [22] have shown that for  $\delta\epsilon > 0$ , the tube axis tends to orient parallel to the field, while for  $\delta\epsilon < 0$  the orientation is perpendicular. Consider, then, an experiment with randomly oriented double-twist cylinders between two conducting microscope slides and white light incident perpendicular to the slides. Since the intrinsic reflectivity of the structure is nonzero only when a tube *diameter* is aligned parallel to the light, an applied field should cause the tubes to become *less* reflecting when  $\delta\epsilon > 0$  and *more* reflecting when  $\delta\epsilon < 0$ .

Experiments for chiral mixtures with  $\delta\epsilon > 0$  have been carried out by Yang and Crooker [15]. At high fields, a new field-induced phase appears, but in the BPIII region, with increasing field, the wavelength of the reflection peak increases slightly, the intensity decreases slightly, and the lineshapes themselves remain essentially unchanged.

In the present study we apply fields to a BPIII phase with  $\delta\epsilon < 0$ . We first present a temperature-electric field phase diagram showing how the various blue phase boundaries are affected by the field. We then present the electric field dependence of the intensity and wavelength of the cholesteric (Ch), BPI, BPII, and BPIII reflection peaks at various points in the phase diagram, and we show the BPIII reflection spectrum at three applied fields. Our primary result for the BPIII reflection peak is that the electric field causes the peak height to increase dramatically, the linewidth to decrease, and the wavelength to remain constant. This behaviour is quite different from that found in  $\delta\epsilon > 0$  material. Taking the present and previously reported results together, we conclude that the most viable model for BPIII is the double-twist model or possibly the  $O^5$  cubic domain model.

## 2. Experiment

Our material is a mixture containing 21 CE2, 25 CE3, and 54 per cent CCN55 by weight [16]. CE2 is a chiral nematic with very short pitch, CCN55 is a nematic,

and CE3 is a chiral nematic with a wide temperature range Ch phase. Since both CE2 and CE3 lack strongly polar groups while CCN55, which has an axial CN group, has a dielectric constant  $\delta\epsilon = -8.2$ , one expects the overall mixture to have negative dielectric anisotropy. In fact, an applied electric field did stabilize the planar texture in the cholesteric phase, which experimentally demonstrates that  $\delta\epsilon < 0$ . Without an electric field, this mixture exhibits Ch, BPI, BPII and BPIII phases, with BPIII being fairly wide ( $0.36^\circ\text{C}$  at  $95.6^\circ\text{C}$ ). The observed selective reflection peaks are (with Miller indices where appropriate): Ch, 474 nm; BPI, 660 nm (110) and 465 nm (200); BPII, 549 nm (100); and BPIII, a broad peak at 490 nm. Samples were placed between conducting slides untreated for surface alignment and separated by  $12\ \mu\text{m}$  spacers. Phases were determined by examining textures in reflection using a Zeiss Universal Microscope with crossed linear polarizers and a modified Mettler hot stage (temperature stability  $< 3\ \text{mK}$ ) [17]. Spectra were obtained using a spectrometer connected to the camera port of the microscope. Applied voltages are AC at 1 kHz. Despite our use of spacers, some thickness nonuniformity was observed in our samples, hence we report rms voltages rather than electric fields.

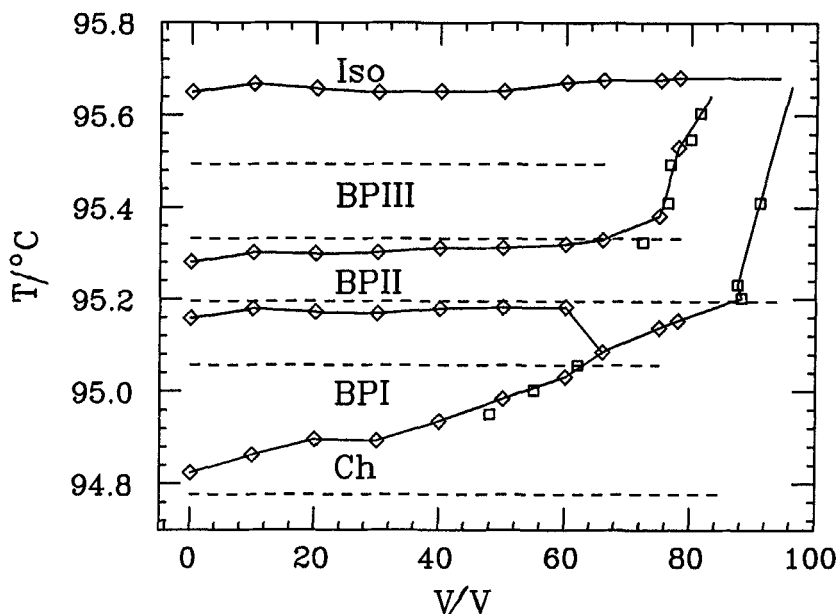


Figure 1. Temperature-applied voltage phase diagram. Solid lines are phase boundaries; dashed lines are regions of phase diagram for which spectra were measured. Data were taken at fixed voltage (diamonds) and fixed temperature (squares).

Figure 1 shows the temperature-electric field phase diagram for our mixture. The solid lines are the blue phase boundaries, found either by changing the temperature at fixed voltage (diamonds) or by changing the voltage at fixed temperature (squares). For this mixture no new high-field phase was detected, unlike the case of  $\delta\epsilon > 0$  [15] and the  $\delta\epsilon < 0$  material of Heppke *et al.* [23]. At zero field ( $V = 0$ ), the Ch, BPI, and BPII phases all show sharp reflection peaks which shift continuously to shorter wavelength through any one phase and shift discontinuously as the phase boundaries are traversed. In the BPIII phase the selective reflection is much weaker and broader

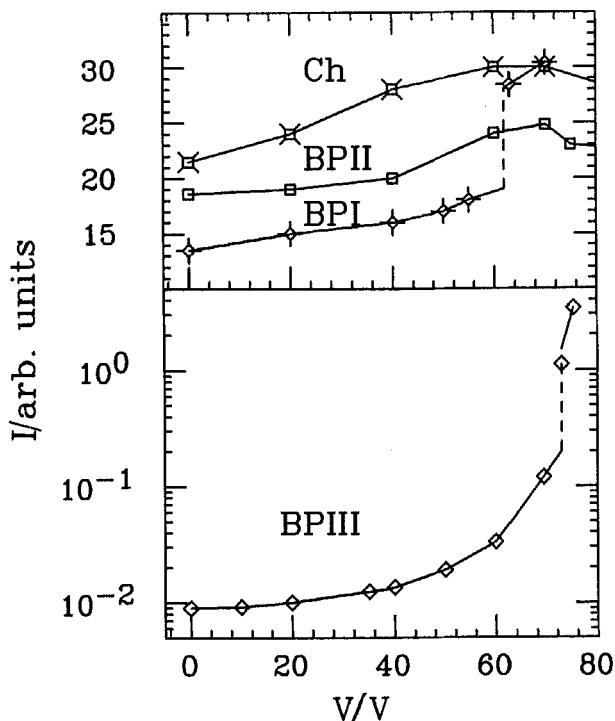


Figure 2. Reflected intensity (corrected for lamp spectrum) versus applied voltage along the dashed lines of figure 1. Although absolute intensity is uncalibrated, relative intensities in this figure and in figure 4 can be compared.

than in BPII and the wavelength of the peak is shifted downward from BPII. Since both BPIII and BPI supercool with decreasing temperature, all phase transition temperatures were determined by increasing the temperature.

The dashed lines in figure 1 are regions in the phase diagram where we have measured the spectra of the reflection lines. At  $T = 94.78^\circ\text{C}$ , where Ch is stable, the electric field aligns the twist axis perpendicular to the surface and in the direction of the incident light. This alignment is then retained even after the field is turned off. In this aligned state, an increasing field causes the intensity to increase slightly (figure 2) and the wavelength to remain essentially constant (figure 3).

At  $T = 95.06^\circ\text{C}$ , where BPI is stable, both the red (110) and blue (200) peaks are initially observed. Application of a field causes the (200) platelets to grow at the expense of the (110) platelets, unlike the case of  $\delta\varepsilon > 0$  material where the field stabilizes the (110) orientation [15]. Once in the (200) orientation, both the reflected intensity and the peak wavelength increase slightly with increasing field (figures 2 and 3) until the BPI-Ch boundary is reached, at which point there are discontinuous changes in both the intensity and the wavelength. The behaviour of BPII is similar. At  $95.20^\circ\text{C}$ , the texture consists of green (100) platelets and black regions, the latter presumably consisting of platelets having reflections either forbidden or in the ultra-violet. The electric field here stabilizes the (100) orientation as is the case with  $\delta\varepsilon > 0$  material. While the intensity again changes little with increasing field, the decrease in wavelength is much more pronounced than in the Ch and BPI cases. At 88.2 V, where

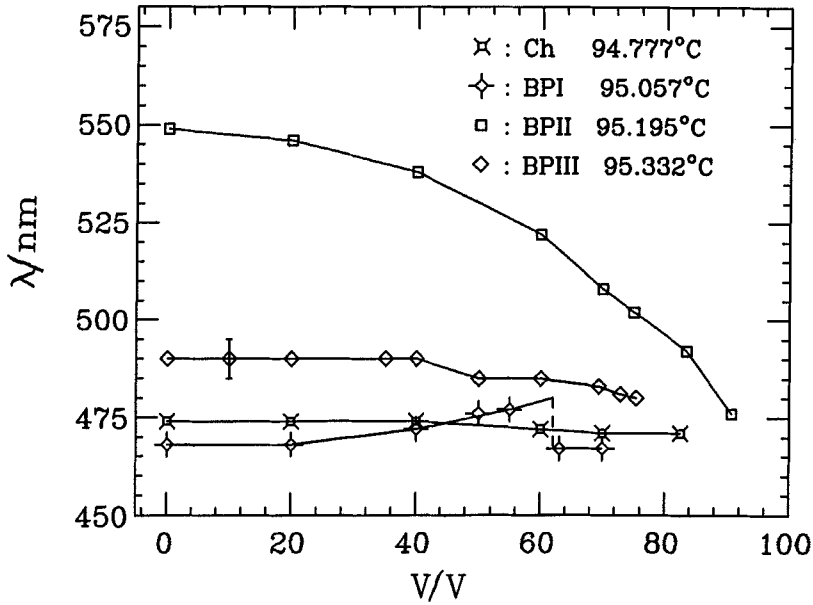


Figure 3. Peak wavelength versus sample voltage along dashed lines of figure 1.

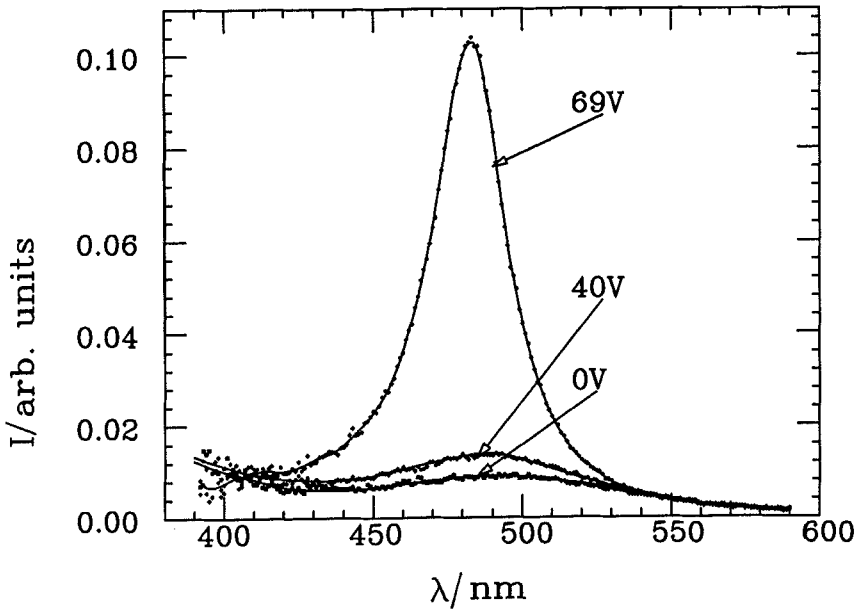


Figure 4. BPIII spectrum at several sample voltages.

there is a BPII-Ch transition, turbulence in the sample makes the transition difficult to study.

In BPIII, at 95.33°C, the peak intensity increases by over a factor of ten until the high-field BPII region is encountered. Figure 4 shows the evolution of the reflection spectra of BPIII at several voltages. This behavior is opposite to that of  $\delta\epsilon > 0$  material where the intensity *decreases* by 30 per cent before the higher field phase is

reached [15]. The wavelength of the peak, on the other hand, decreases only slightly over the same interval [15]. At the high-field transition to BPII, the intensity jumps discontinuously by approximately an order of magnitude, but the wavelength remains unchanged because the BPII and BPIII wavelengths are the same at this temperature and field. Finally we present the linewidth of the BPIII peak in figure 5. Notice that it narrows considerably in addition to growing.

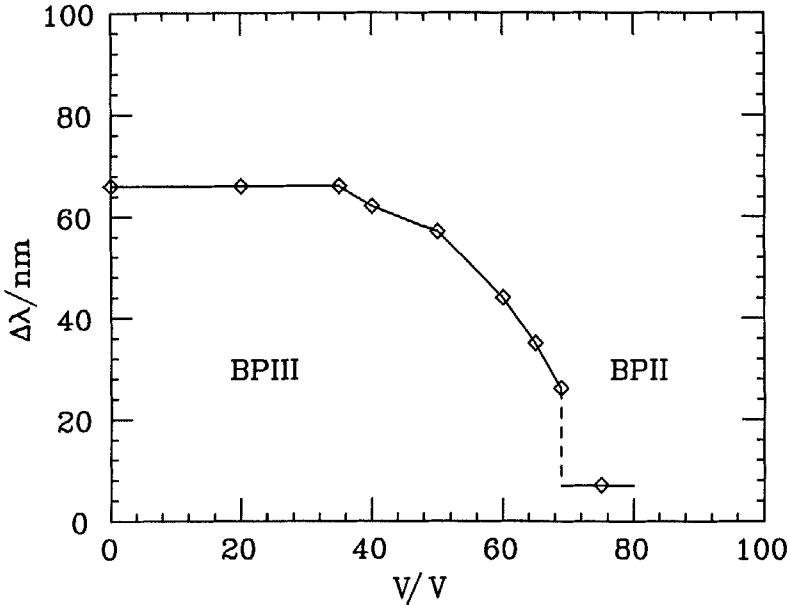


Figure 5. Linewidth (FWHM) of the BPIII peak versus voltage.

### 3. Discussion

The essential experimental features of BPIII with  $\delta\varepsilon < 0$  in an increasing electric field are: (1) The reflected intensity peak increases by more than tenfold (figure 2); (2) The wavelength of the peak remains constant (Figure 3); and (3) the linewidth of the peak decreases significantly (figures 4 and 5). We now review the implications of these features.

We assume that BPIII consists of small correlated regions or domains whose spatial structure is chiral and periodic. For convenience we imagine the order within these domains to be roughly gaussian—that is, to vary as  $\exp(-r^2/2L^2)$  in any one direction, although in only one of our models, the double-twist model, has such a behaviour actually been proposed [11]. Without an applied field, these domains are randomly oriented and the scattering from them is a broad, weak peak. The application of a field in the direction of the light beam then orders the domains and causes the reflected peak to be altered in a fashion which depends on the intrinsic domain structure.

One can measure the domain length  $L_z$  along the direction of the light beam by measuring the spectral linewidth  $\Delta\lambda$  (approximately FWHM) of the backscattered reflection peak. Letting  $D_z = 2L_z$  be the effective length of the domain, one obtains  $D_z = \lambda^2/\pi n \Delta\lambda$ , where  $n$  is the refractive index. One can also measure the domain width  $D_x = 2L_x$  in a direction perpendicular to the light beam by tilting the sample and measuring the angular linewidth  $\Delta\theta$  (FWHM) of the backscattered reflection peak; the result here is  $D_x = \lambda/\pi n \Delta\theta$ .

From the reflected intensity one can deduce the amount of aligned material in the sample. Actually, initially unoriented BPI and BPII with large positive or negative  $\delta\epsilon$  and Ch textures with  $\delta\epsilon < 0$  respond to an applied field with dramatic increase in reflected intensity. In these phases, the effect is caused by regrowth of the crystallites and is *irreversible*: when the field is removed, the crystallite orientation remains unchanged and the reflected intensity remains large. These phases have long-range order. In BPIII, however, the intensity is *reversible*—after the field is removed, BPIII reverts to its original amorphous state and the reflected intensity becomes small again. Long-range order is never established in BPIII, even in large electric fields.

The mechanism by which BPIII returns to the amorphous state after removal of the field is not clear. One possibility is thermal fluctuations, but then one would observe fluctuating dynamic effects. Another is the effect of order-inhibiting boundary conditions, but the sample texture in the bulk has been found to be insensitive to surface preparation [14]. The most likely possibility is that the intrinsic disclinations which themselves order in BPI and BPII are unable to do so in BPIII.

A feature of BPIII common to the other blue phases in our material is that the wavelength is relatively insensitive to the electric field. We therefore conclude that the electric field changes the orientation of the periodic direction and the dimensions of the domains but not the local order of the domains themselves. How these effects occur is model-dependent, so we next relate our data to several BPIII models.

We start with the cubic domain model, for which there are several possibilities. If the domains are BPII-like, the wavelength and intensity can be compared with that for BPII itself. Regardless of the sign of  $\delta\epsilon$ , it has been shown both experimentally ([15] and figure 2) and theoretically [18] that an electric field aligns BPII along the (100) direction and causes the reflected intensity to increase. In BPIII, however, experiment shows that the intensity *decreases* when  $\delta\epsilon > 0$  [15] and *increases* when  $\delta\epsilon < 0$  (figure 2), a result which argues against BPII-like domains. The wavelength dependences of the BPII and BPIII peaks are also different for  $\delta\epsilon < 0$ : the BPII wavelength decreases with increasing electric field while that of BPIII remains the same. A third piece of evidence against BPII-like domains is that BPII shows higher order Bragg peaks while BPIII does not [14]. Support for the BPII-domain model has mainly come from work by Collings [4] who was able to explain the measured rotatory power spectrum of BPIII by averaging the contributions from a random collection of BPII-like domains. The same argument applies to other chiral domains, however, and since the rotatory power spectra of Ch, BPI, and BPII phases are all similar, the BPII-like nature of the domains may not be an essential feature of the explanation.

Turning to other cubic forms, it is worth considering the  $O^5$  bcc structure originally proposed for BPI [19]. Originally this theory included only the (110) planes; subsequent calculations including higher harmonics [20] showed that the contribution of the next higher harmonic (200) is identically zero and that the effect on the light scattering of the following two higher harmonics [(211) and (220)] is  $< 3$  per cent. The lack of a (200) harmonic would explain the experimental failure to observe it in a BPIII composed of  $O^5$  domains [14]. Calculated phase diagrams [20] indicate that this phase is stable between the isotropic and simple cubic  $O^2$  phase, as is observed experimentally when the BPIII phase appears. For  $\delta\epsilon > 0$  material in an electric field, calculations [18] show that the  $O^5$  phase is stable in the (111) orientation; this reorientation will reduce the reflected intensity in the (110) direction, consistent with experiment [15]. No such calculations have yet been performed for  $\delta\epsilon < 0$  and experimentally no BPI with  $O^5$  structure has been observed, but if the BPIII peak corresponds to a (110) orientation and a field stabilizes that direction, one would



qualitatively expect the intensity to increase as observed (figure 2). Of course, a remaining question for the  $O^5$  cubic domain model is why it doesn't form large platelets.

Turning to the quasicrystal model, we are unable to draw any conclusions since there is as yet no theory giving the behavior in an electric field. Previous experiments on surface-aligned blue phases [14] have not detected harmonics which should be present, however, which argues against the quasicrystal model.

We finally consider the double-twist model. Application of an electric field to  $\delta\epsilon < 0$  material should cause the double-twist tubes to align perpendicular to the field direction and increase the reflected intensity. Experimentally this is what we observe (figure 2). For  $\delta\epsilon > 0$  the field should align the tubes parallel to the field and decrease the reflected intensity which is also in qualitative agreement with experiment [15].

Further information is available from the linewidth behaviour. In  $\delta\epsilon > 0$  material [15], the spectral linewidth  $\Delta\lambda$  is independent of the field, by which we conclude that the length  $D_z$  of the domains is unchanged. For the samples of [15],  $D_z$  turns out to be 816 nm which corresponds to 2.7 pitch lengths. For  $\delta\epsilon < 0$  samples, the spectral linewidths (figure 5) decrease as the field is increased. We conclude that the effective domain length increases with electric field—from 740 nm at 0 V ( $D_z = 2.3$  P) to  $1.88 \mu\text{m}$  at 69 V ( $D_z = 5.9$  P). In the double-twist model, this increased domain length could be caused by partial coherent stacking of the double twist tubes in the  $z$ -direction.

We can also re-evaluate previous results on surface-aligned BPIII [14]. The spectral linewidth data ( $\Delta\lambda = 80$  nm at  $\lambda = 450$  nm) indicates a thickness of the aligned BPIII layer of 537 nm ( $D_z = 1.8$  P), while the angular linewidth data ( $\Delta\theta = 2.7^\circ$  at  $\lambda = 450$  nm) yields a domain width of  $2.03 \mu\text{m}$  ( $D_x = 6.8$  P). In this case we conclude that the surface-induced alignment has produced considerable lateral alignment near the surface. In the double-twist model, if the directors at the surface of the double-twist tubes are parallel to the alignment direction, the tube axes themselves will be parallel to each other, evidently over large distances.

Other evidence in favour of the double-twist model is that the model contains no higher harmonics; none have been detected [14]. Finally, scanning electron microscope pictures of BPIII have shown a filamentary structure not inconsistent with a tangle of tubes [21]. The observed tube diameter is much less than a pitch, however, which is still a puzzle.

#### 4. Conclusion

We have measured the behaviour of the selective reflection peaks of the Ch, BPI, BPII and BPIII phases of a cholesteric liquid crystal with  $\delta\epsilon < 0$  in and electric field. For BPIII, the intensity increases dramatically, the linewidth decreases and the peak wavelength remains essentially constant with increasing field. From these and previous measurements we conclude that the double-twist model and possibly the  $O^5$  cubic domain model best explain the data.

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## References

- [1] CROOKER, P. P., 1989, *Liq. Crystals*, **5**, 751.
- [2] WRIGHT, D. C., and MERMIN, N. D., 1989, *Rev. mod. Phys.*, **61**, 385.
- [3] DEMIKHOV, E. I., DOLGANOV, V. K., and KRYLOVA, S. P., 1985, *Pisma Zh. éksp. Teor. Fiz.*, **42**, 15, [1985, *JETP Lett.* **42**, 15].
- [4] COLLINGS, P. J., 1984, *Phys. Rev. A*, **30**, 1990.
- [5] THOEN, J., 1987, *Phys. Rev. A*, **37**, 1754.
- [6] KLEIMAN, R. N., BISHOP, D. J., PINDAK, R., and TABOREK, P., 1984, *Phys. Rev. Lett.*, **53**, 2137.
- [7] HORNREICH, R. M., and SHTRIKMAN, S., 1986, *Phys. Rev. Lett.*, **56**, 1723.
- [8] HORNREICH, R. M., and SHTRIKMAN, S., 1986, *Physics Lett. A*, **115**, 451.
- [9] ROKSHAR, D. S., and SETHNA, J. P., 1986, *Phys. Rev. Lett.*, **56**, 1727.
- [10] FILEV, V. M., 1986, *Pisma Zh. éksp. teor. Fiz.*, **43**, 523 [1986, *JETP Lett.* **43**, 667].
- [11] HORNREICH, R. M., KUGLER, M., and SHTRIKMAN, S., 1982, *Phys. Rev. Lett.*, **48**, 1404.
- [12] BELYAKOV, V. A., DEMIKHOV, E. I., DMITRIENKO, V. E., and DOLGANOV, V. K., 1985, *Zh. éksp. teor. Fiz.*, **89**, 2035 [1986, *Sov. Phys. JETP*, **62**, 1173].
- [13] FINN, P. L., and CLADIS, P. E., 1982, *Molec. Crystals liq. Crystals*, **84**, 159.
- [14] YANG, D. K., CROOKER, P. P., and TANIMOTO, K., 1988, *Phys. Rev. Lett.*, **37**, 4001.
- [15] YANG, D. K., CROOKER, P. P., 1988, *Phys. Rev. A*, **61**, 2685.
- [16] The chemical structures are CE2: MB-Ph-Ph-COO-Ph-MB; CE3: MB-Ph-Ph-COO-Ph-O-C<sub>6</sub>H<sub>13</sub>; CCN: C<sub>5</sub>H<sub>11</sub>-Ch-Ch-(CN)-C<sub>5</sub>H<sub>11</sub>. Here MB = 2-methylbutyl, Ph = phenyl ring, Ch = cyclohexane ring, and (CN) = axial cyano group. All materials were obtained from BDH.
- [17] YANG, D. K., and CROOKER, P. P., 1987, *Phys. Rev. A*, **35**, 4419.
- [18] LUBIN, D., and HORNREICH, R. M., 1987, *Phys. Rev. A*, **36**, 849.
- [19] HORNREICH, R. M., and SHTRIKMAN, S., 1980, *J. Phys., Paris*, **41**, 335.
- [20] GREBEL, H., HORNREICH, R. M., and SHTRIKMAN, S., 1984, *Phys. Rev. A*, **30**, 3264.
- [21] ZASADZINSKI, J. A. N., MEIBOOM, S., SAMMON, M. J., and BERREMAN, D. W., *Phys. Rev. Lett.*, **57**, 364.
- [22] HORNREICH, R. M., KUGLER, M., and SHTRIKMAN, S., *J. Phys., Paris, Coll. C3, C-47*.
- [23] HEPPKE, G., JEROME, B., KITZEROW, H. S., and PIERANSKI, P., 1989, *Liq. Crystals*, **5**, 813.