

Line Shapes of Field-Induced Blue-Phase-III Selective Reflections

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We have measured the electric-field dependence of the reflectivity of the blue phase III (BP III) of cholesteric liquid crystals when the dielectric anisotropy $\epsilon_a < 0$. We propose a model which assumes that the boundary aligns the sample to a depth L and in which L is increased by the applied field. The free energy is proportional to E^n , where n depends on the structure of BP III. The data are fitted well by a Lorentzian line shape, and the peak intensity and linewidth agree well with the theory for $n=2.1$. This value is consistent with the double-twist model of BP III, but not with cubic and quasicrystal models, since the energies of these latter structures depend on higher powers of E .

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Of the three blue phases found in chiral liquid crystals—BP I, BP II, and BP III—which have been observed in the absence of electric or magnetic fields, only BP I and BP II are well understood [1,2]. Both BP I and BP II are cubic; the bright selective reflection colors they exhibit are caused by Bragg scattering from regular crystal planes. These are examples of condensed-matter phases where *frustration* plays an important role: It modifies but does not disrupt the long-range order by creating a network of disclinations or regions in which the order parameter vanishes [3].

BP III, on the other hand, appears amorphous and reflects only a weak, broad band in the visible region, indicating that its scattering structures are small and long-range order is only poorly established. An elucidation of the still-unknown BP III structure remains one of the outstanding problems in liquid-crystal physics. Here frustration may actually prevent long-range order by creating a tangle of disclinations, while still allowing considerable order on scales up to that of the chiral pitch [3]. Based on a variety of data—rotatory power [4], heat capacity [5], and reflection spectra [6]—three “models” of the BP III phase have been suggested [1(a)]. These are as follows: (A) the *double-twist* model [7], which consists of a spaghettilike tangle of double-twist cylinders; (B) *cubic-domain* models [4,8], in which small cubic domains or correlation regions predominate; and (C) the *quasicrystal* model [9], in which the structure is characterized by reciprocal-lattice vectors derived from the edges and vertices of an icosahedron. (There is also a fourth model [10] in which BP III is not considered to be a true thermodynamic phase.) Only the quasicrystal model has been analyzed in any detail.

To date, the testing of these models by experiment has not been conclusive. In particular, higher spatial harmonics expected for the cubic and quasicrystal models have not been found [11]. Recent data showing the effect of electric fields on the BP III reflectivity peak have, however, been intriguing, especially the observation that for

BP III with negative dielectric anisotropy the application of an electric field causes the selective reflection peak to increase by several orders of magnitude and narrow dramatically [12,13]. Since, for reasons of symmetry, the electric field affects different model structures in different ways, it should be possible to obtain information on BP III structure from such data.

We first present precise measurements of the spectrum of the reflectivity in BP III samples to which electric fields have been applied and show explicitly how the linewidth and peak reflectivity depend on the field. We then briefly discuss a calculation by Hornreich [14] of surface- and field-induced ordering in the isotropic phase of a cholesteric liquid crystal and use that calculation to motivate a similar model for surface ordering in BP III. In our model, the electric field appears as E^n , where n depends on BP III structure. Data fits yield $n=2.1 \pm 0.1$. This result is inconsistent with both the cubic and quasicrystal models, for which $n \geq 4$. For the double-twist model, however, the observed value of n is quite acceptable.

Our measurements were performed on a mixture of 30.0 wt.% of the chiral compound S811 (Merck) and 70.0 wt.% of the nematic mixture EN18 (Chisso Corp.), which exhibits negative dielectric anisotropy. This mixture has been discussed previously [14,15]. The liquid crystal was confined between two electrically conducting glass slides, the thickness of which was fixed by 12.7- μm Mylar spacers. The sample temperature was controlled to 3 mK by a modified Mettler hot stage. Observations were made in reflection using crossed polarizers and a Zeiss Universal microscope. To record the reflection spectra, light from the camera tube was directed to a Jarrel-Ash spectrometer (1-nm spectral resolution) and then to a photomultiplier with photon-counting electronics for high sensitivity.

Close to the clearing temperature, the sample shows the phase sequence N^* -BP I-BP II-BP III-BP III/Iso-Iso. The transition temperatures were found to be

about 0.2 K higher than those previously reported [14,15], indicating a very small difference in the mixing concentrations. The measurements were carried out at 44.29 °C, which is above the BP-II-BP-III transition but below the BP III/Iso two-phase region. ac voltages at 1 kHz were applied to the sample; all reported voltages are rms. Reflection spectra were recorded in steps of about 5 V from 0 to 64.8 V, and then in steps of 1–2 V to 90.4 V. Raw spectra were corrected by first subtracting the background reflectivity $I_{\text{iso}}(\lambda)$ obtained from the isotropic sample at 52.20 °C, and then dividing by the lamp spectrum $I_{\text{lamp}}(\lambda)$ obtained by measuring the geometrically attenuated reflectivity of a mirror using parallel polarizers.

As found earlier [12,13], the peak intensity of the reflected light increases and the linewidth decreases as the field is increased. Between ≈ 74 and 76 V, BP III coexists with the field-induced phase BPE, the structure of which we have not identified, but which can be recognized visually by a wavelength shift and higher peak intensity. Above 76 V, BPE becomes absolutely stable with respect to BP III.

The data are displayed in Fig. 1, which shows typical reflected intensity spectra for applied voltages of 0, 60, and 80 V. At 0 V, an important feature of the reflected light is that it only appears when the sample surface is perpendicular to the incident and reflected light beams. If the sample is tilted, the reflection disappears, which indicates that the sample is aligned by the surface such that the reflecting planes are parallel to the surface. This effect has been reported earlier [11]. At higher voltages, the same situation obtains; here, however, the alignment can be attributed to the field. Figure 2 shows the peak

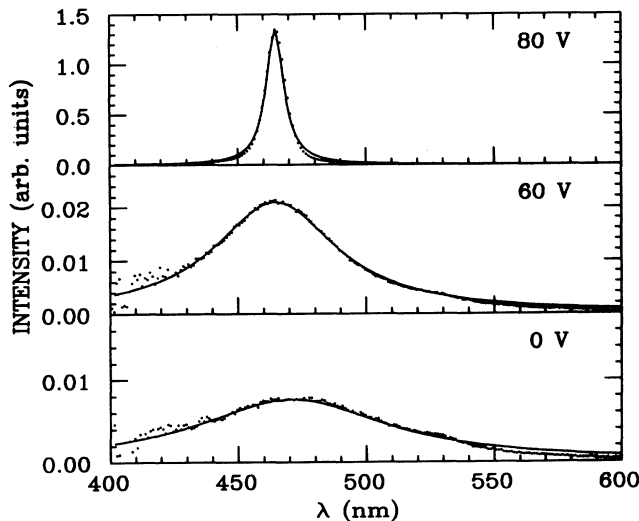


FIG. 1. Reflected intensity vs wavelength for three electric fields. Solid lines are best fits with Lorentzian line shapes. For 0 and 60 V the sample is in the BP III phase; at 80 V it is in the BPE phase.

height I and the linewidth $\Delta\lambda$ (full width at half maximum) derived from the spectra for the full range of voltages. From visual observation of the sample, examination of these figures, and the dependence of the peak wavelength versus voltage (not shown), it is clear that BP III behavior is represented by voltages below ≈ 76 V. Above this voltage the sample is in the BPE phase and has entirely different behavior.

Recently, Dmitrienko [16] has suggested that the sample walls may order the sample to a penetration depth L_0 , as has been observed previously by Yang, Crooker, and Tanimoto [11], and that an electric field may enhance the ordering and increase the penetration depth to $L > L_0$, thereby giving rise to the backscattering intensities and linewidths we observe. Hornreich [14] has, in fact, theoretically considered an analogous situation: the isotropic phase of a cholesteric liquid crystal with positive dielectric anisotropy confined to $z > 0$, an aligning boundary at $z = 0$, and a field perpendicular to z . In his theory the order parameter has two terms [1(c),17,18]—first, a term with coefficient $\mu_0(z)$ and a tensor corresponding to the spherical harmonic $Y_{20}(\theta, \phi)$; and second, a term with coefficient $\mu_2(z)$ and the tensor $Y_{22}(\theta, \phi)$, which rotates in screwlike fashion about the z axis. The relevant part of the free-energy density has the form

$$f = A_0\mu_0^2 + A_2\mu_2^2 + B_0(d\mu_0/dz)^2 + B_2(d\mu_2/dz)^2 - 3\mu_0\mu_2^2 - \mu_0e^2 - \nu(\mu_0 + \sqrt{3}\mu_2)\delta(z), \quad (1)$$

where the A_i and B_i have temperature and chirality dependences, e is a reduced electric field, and ν is the strength of an aligning torque which occurs only at $z = 0$. From this free energy, it can be shown that $\mu_0(z)$ has a spatially constant term proportional to e^2 which, when reinserted in (1), gives the $\mu_0\mu_2^2$ cross term the form $\mu_2^2e^2$. The solution is then $\mu_2(z) \propto \nu L \exp(-z/L)$, where the penetration depth $L = L_0[1 - (V/V_0)^2]^{1/2}$ and where

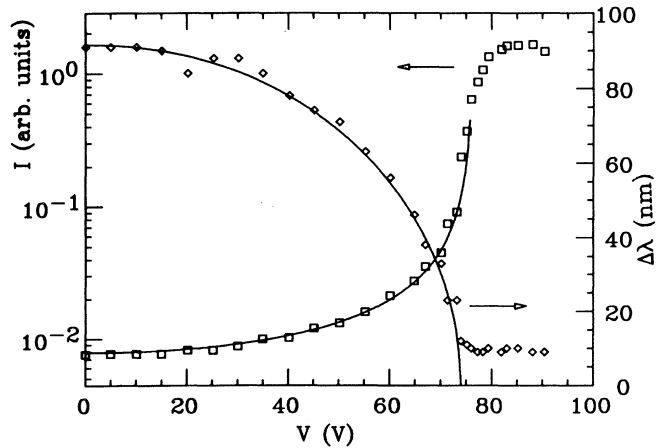


FIG. 2. Peak reflected intensity and linewidth (FWHM) vs sample voltage. Solid lines are fits by Eqs. (5) and (6) in the BP III region.

L_0 depends on temperature and chirality. Hornreich [14] notes that this result is also valid for negative dielectric material with an electric field along the z axis, and then discusses the case where an electric field is applied to a cubic structure [18]; there the field coupling term will have the form $\mu_2^2 e^n$ with $n=4$. The icosahedral structure has not been worked out in detail but, from symmetry [19], $n \geq 4$.

Although the Hornreich theory is not a model for BP III structure, which is unknown, it provides the motivation for a simple model of BP III which explains our data. In analogy to $\mu_2(z)$ in the isotropic phase, let $Q(z)$ be the scalar amplitude of that Fourier component of BP III order to which the light in our backscattering experiment responds. Q does not describe the complete BP III order, for which an *a priori* knowledge of BP III structure is required, but for helicoidal or cubic models Q is proportional to μ_2 of the Hornreich theory. In the spirit of the Hornreich theory, we then propose a free-energy density of the form

$$f = \frac{1}{2} [AQ^2 + B(dQ/dz)^2 - \chi Q^2 E^n]. \quad (2)$$

This free energy contains the μ_2 -dependent terms of (1) after minimization with respect to μ_0 , except that A , B , and χ are now assumed to be constant and the exponent of E is allowed to be a free parameter which will be determined by fitting the data. Rather than the boundary condition used by Hornreich, we take $Q=Q_0$ fixed at the boundary; this choice, in fact, gives a better fit to the peak intensity data.

Minimizing (2), we find that the sample is indeed ordered near the surface, with

$$Q(z) = Q_0 \exp(-z/L). \quad (3)$$

Defining $L_0 = \sqrt{B/A}$ and letting E be produced by a voltage $V \propto E$ across the sample, the penetration depth L is

$$L = L_0 [1 - (V/V_0)^n]^{1/2}, \quad (4)$$

where $V/V_0 = (\chi/A)^{1/n} E$. At $V=0$ the penetration depth is L_0 ; as V is increased the penetration depth increases to $L(V)$ and finally becomes infinite at V_0 .

Light incident on the sample along the z axis will now be backscattered from the periodic modulation near the surface. The scattered electric field $E(\mathbf{q})$ is proportional to the Fourier transform of this modulation, and the scattered intensity is $I(\mathbf{q}) \propto E(\mathbf{q})E^*(\mathbf{q})$. In the limit of narrow linewidth the resulting intensity has a Lorentzian line shape in the wavelength λ ; actually, we have fitted our data both with and without the Lorentzian approximation and we find that within our experimental precision, the difference is not significant. The peak intensity I is proportional to L^{-2} ; from (4) we have

$$I = \frac{I_0}{1 - (V/V_0)^n}. \quad (5)$$

The linewidth (FWHM) is $\Delta\lambda = \lambda_0^2/\pi L$. Again from (4)

we have

$$\Delta\lambda = \Delta\lambda_0 [1 - (V/V_0)^n]^{1/2}. \quad (6)$$

The theory has therefore yielded three expressions which can be experimentally tested. (A) The reflectivity has a Lorentzian line shape. This is a result of omitting higher-order terms in Q and is also a feature of Hornreich's weak-field analysis. (B) The peak intensities vary with applied voltage according to (5). This form depends on a fixed value of Q at the boundary; with the boundary condition of Hornreich the denominator would be squared. (C) The linewidth varies with applied voltage according to (6). This expression is also obtained by Hornreich.

In order to test the model, the intensity data of Fig. 2 was fitted by Eq. (5), with I_0 , V_0 , and n as adjustable parameters. The result is the solid line superimposed on the intensity data in Fig. 2, with $I_0 = (7.9 \pm 0.1) \times 10^3$, $V_0 = 76.4 \pm 0.1$ V, and $n = 2.10 \pm 0.03$. The linewidth data of Fig. 2 were fitted by (6), where $\Delta\lambda_0$, V_0 , and n were adjustable. The solid line on the linewidth data was obtained with $\Delta\lambda_0 = 92 \pm 1$ nm, $V_0 = 75.1 \pm 0.5$ V, and $n = 2.1 \pm 0.1$. Both fits are in good agreement with the data as well as with each other.

The fits of the reflection spectra by Lorentzian line shapes, the agreement of the peak intensity and linewidth with Eqs. (5) and (6), and the agreement of the parameters V and n with each other for both fits appear to justify the model given by Eq. (2). The zero-field penetration depth $L_0 = \lambda_0^2/\pi n \Delta\lambda_0 \approx 512$ nm. Taking the pitch to be $P = \lambda_0/n \approx 313$ nm (here $n \approx 1.5$ is the refractive index and $\lambda_0 \approx 470$ nm), we find that $L/P = 1.6$ at 0 V and diverges at 75 V. Note also that sample thickness is not an important factor in the fit. Using the above numbers and Eq. (4), L remains less than half the sample thickness of 12.7 μm until $V > 0.997V_0$.

Finally, our most important result is that $n \approx 2$, which rules out icosahedral or cubic structure for BP III. It thus appears that BP III is macroscopically amorphous while retaining considerable order over a correlated region with a length scale of the order of a pitch. These correlated regions clearly couple to electric fields as E^2 , at least near the surface; hence they must possess simple helicoidal or double-twist structure.

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