Measurement of the Mueller matrices of blue-phase structures

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Using polarized light scattered at 45° from mixtures of chiral CB15 and nonchiral E9 liquid crystals, we have measured the Mueller matrices characterizing the Bragg reflections of blue-phase structures BPI, BPIIA, and BPIIB. Surprisingly, all of these structures possess essentially the same Mueller matrix, namely, that of an elliptical polarizer with axial ratio ≈ 0.7. The implications of the results on the allowed space groups of the blue phases is discussed in the context of the theory of Hornreich and Shtrikman.

Recently, crystals with very large lattice parameters have been intensively studied.[1,2] Lattices of polystyrene spheres[1] are good examples of Wigner solids; their extreme "softness" has led to demonstrations of the effect of mechanical perturbations on a crystal structure and on its phase transitions. The blue phase,[2] a newly discovered phase which appears between the cholesteric and isotropic phases of a cholesteric liquid crystal, is thought to be a large lattice of defects.[3] Its structure is cubic, while at the same time possessing a chirality related to that of the cholesteric phase.[4–6]

Bragg scattering using visible light instead of x rays can be used to study the structure of these large lattices.[5] Since, however, *polarized* light is easy to produce and detect, detailed information is accessible which unpolarized x rays have been unable to provide. In general, this information is provided by the 4×4 Mueller matrix $\tilde{M}$ of the scattering structure.[7] $\tilde{M}$ relates the polarization state of a scattered beam, denoted by Stokes vector $\tilde{S}_2$, to that of the incident beam $\tilde{S}_1$ by the relation $\tilde{S}_2=\tilde{M}\,\tilde{S}_1$. $\tilde{M}$ contains a complete description of the optical response of the structure and can be related to structural symmetries through appropriate theories.

In this Communication we report the first measurement of the normalized Mueller matrices for the Bragg reflections of the blue phase. Actually, there are two thermodynamically stable blue phases—BPI and the higher temperature BPII.[2] BPI is body-centered cubic (bcc); BPII is either simple cubic (sc) or bcc.[5,6] (A possible third "fog" phase with no Bragg reflections lies between BPII and the isotropic phase.[8]) Mixtures of chiral and nematic materials have allowed these various blue phases to be examined as the lattice parameter is varied.[5,6,9] In mixtures of chiral CB15 and nonchiral E9 (Ref. 10) there are two BPII manifestations[5,6]: BPIIA, which appears in cholesterics with selective reflection wavelength $\lambda_c < 540$ nm, is separated from BPI by a gap in the Bragg wavelengths. BPIIB, which appears when $\lambda_c > 540$ nm, is not separated from BPI by a gap. BPI and BPIIB have been shown to be bcc; BPIIA is either sc or bcc.[6]

Hornreich and Shtrikman[11] (HS) have recently derived the Bragg scattering selection rules for the enantiomorphic sc and bcc space groups which pertain to the blue phase—T^{1-5} [for point group $T(23)$] and O^{1-8} [for point group $O(432)$]. They have also derived the Mueller matrix elements for Bragg reflection at any angle.[11] These elements depend on the strengths of five order-parameter coefficients: $\epsilon_0(hkl)$, $\epsilon_{\pm1}(hkl)$, and $\epsilon_{\pm2}(hkl)$ for each Bragg line. The presence or absence of any particular coefficient is in turn related to the space group of the scattering structure.

Our experiments, which were performed on CB15-E9 mixtures, show the temperature evolution of the Mueller matrices through the BPI-BPIIA and the BPI-BPIIB phases. The conclusions we have drawn are the following:

(1) There is marked variation of the Bragg wavelengths with temperature, both within the BPI phase and at the BPI-BPII phase transitions. Surprisingly, this behavior is not accompanied by any detectable structural change.

(2) The Mueller matrices of the BPI, BPIIA, and PBIIB phases are those of a homogeneous left elliptical polarizer, that is, of a material which reflects a specific elliptical polarization.[7]

(3) The data can be fitted to the theory of Hornreich and Shtrikman providing certain assumptions are made. Only ϵ_{-2} turns out to be nonzero, which implies that the bcc structure $O^8(I432)$ is favored for BPI and BPIIB, and either sc $O^2(P4_232)$ or bcc $O^8(I432)$ are favored for BPIIA.

Our experimental setup is shown in Fig. 1. Mixtures of CB15 and E9, having cholesteric selective reflection wavelengths of 530 and 605 nm, were prepared. Sample material was placed between the hypotenuse of a 45°-45°-90° prism and a nonreflecting cover slip, both of which were treated with poly-

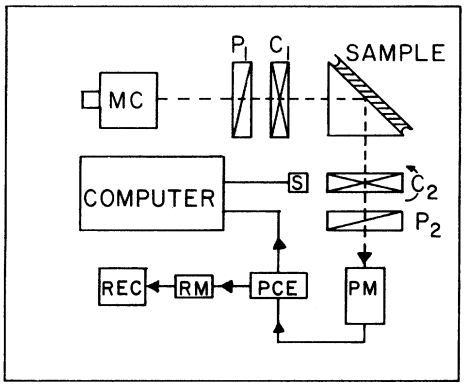

FIG. 1. Mueller matrix apparatus. Symbols are photomultiplier (PM), photon-counting electronics (PCE), rate meter (RM), recorder (REC), angular position sensor (S), monochromator (MC), polarizer (P), and compensator (C).

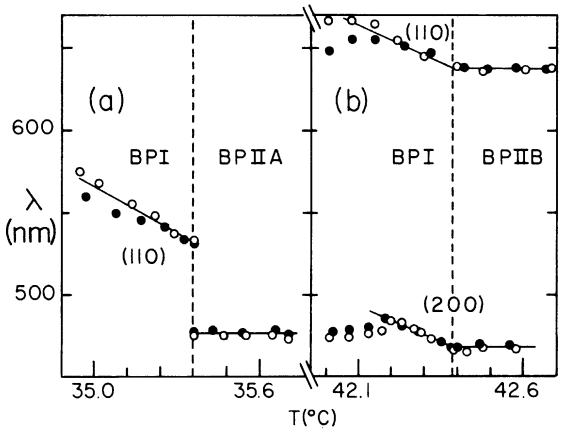

FIG. 2. Temperature dependence of the Bragg wavelengths at 45° scattering angle. Open (closed) circles are for boundaries rubbed perpendicular (parallel) to the scattering plane. The backscattered selective reflection wavelengths are (a) 605 and (b) 530 nm.

vinyl alcohol and rubbed for alignment. Alignment directions were parallel and perpendicular to the scattering plane; the sample thickness was $\simeq 25$ μm. The prism was then mounted in a temperature controlled chamber (stability $< \pm 0.02\,^{\circ}\mathrm{C}$) as shown in Fig. 1. The sample was brought to a particular temperature, a scan of its Bragg peaks made using monochromator (MC), and the optical wavelength fixed to the peak of the particular Bragg line studied.

Mueller matrices are obtained by the rotating compensator technique of Hauge,[12] the details of which will be described elsewhere. In essence, monochromatic incident beams of specified Stokes vectors $\tilde{S}_1$ are produced by fixed polarizer P_1 and adjustable compensator C_1. The scattered Stokes vectors $\tilde{S}_2$ are calculated by the computer from a measurement of the light intensity passing through analyzer P_2 and rotating compensator C_2 as a function of the angular position of C_2.

The wavelengths of the three Bragg lines measured are plotted as a function of temperature in Fig. 2. Since the Bragg scattering angle is 45°, the wavelengths are all blue shifted by $1/\sqrt{2}$ from their values in backscattering.[13] In the long-pitch samples [Fig. 2(a)] both the (110) and (200) lines (using bcc notation for convenience) are accessible; in the shorter-pitch sample [Fig. 2(b)] only the (110) line is accessible.

Figure 3(a) shows the normalized Mueller matrix versus temperature for both alignment directions of the BPI-BPIIA (110) line. Here each element is divided by M_{11}, so that the matrix only contains information on the polarization properties of the blue-phase structure. Despite the temperature variation of the Bragg wavelength in BPI and a wavelength jump at the BPI-BPIIA transition, no evidence for a structural change appears in the Mueller matrix. The matrix for the BPI-BPIIB (110) line, not shown, shows similar behavior.

Figure 3(b) shows the normalized Mueller matrix for the BPI-BPIIB (200) line. Over the blue-phase region ($42.20 < T < 42.60\,^{\circ}\mathrm{C}$) the behavior is again constant. Below 42.20 °C BPI becomes supercooled and the cholesteric peak, which grows in time and overlaps the BPI peak, causes the effective polarization to change. This effect also causes the wavelength dependence below 42.20 °C of Fig. 2(b).

The Mueller matrices for all the lines observed, regardless of the direction of surface alignment, fit to good approximation the Mueller matrix for a polarizer which reflects left elliptically polarized light of axial ratio $\simeq 0.7$.[7] The major axis of the ellipse is, however, tipped at an angle to the scattering plane which depends on the direction of sample alignment. Our interpretation of this result is that all the blue phases exhibit the same Bragg reflection properties, but that a rotatory effect, not unlike rotatory power, is imposed on the reflected ellipse by the alignment.

The fact that the observed Mueller matrices behave like left elliptical polarizers is consistent with the theory of Hornreich and Shtrikman. The part of the HS Mueller matrix associated with ϵ_{-2} represents, in fact, a left elliptical polarizer with axial ratio 0.707 and major axis perpendicular to the scattering plane. There are, however, problems with such a comparison. First, the HS matrices assume weak scattering whereas it is well known that the Bragg scattering from the blue phase is strong. This objection can only be overcome by solving the complete electromagnetic reflection problem with a detailed knowledge of the (at present unknown) structure. Second, the HS matrices neglect rotatory power, lacking the off-diagonal elements M_{i3} and M_{3i} ($i = 1, 2, 4$) seen in our data. We corrected for this effect by rotating the experimental Mueller matrices

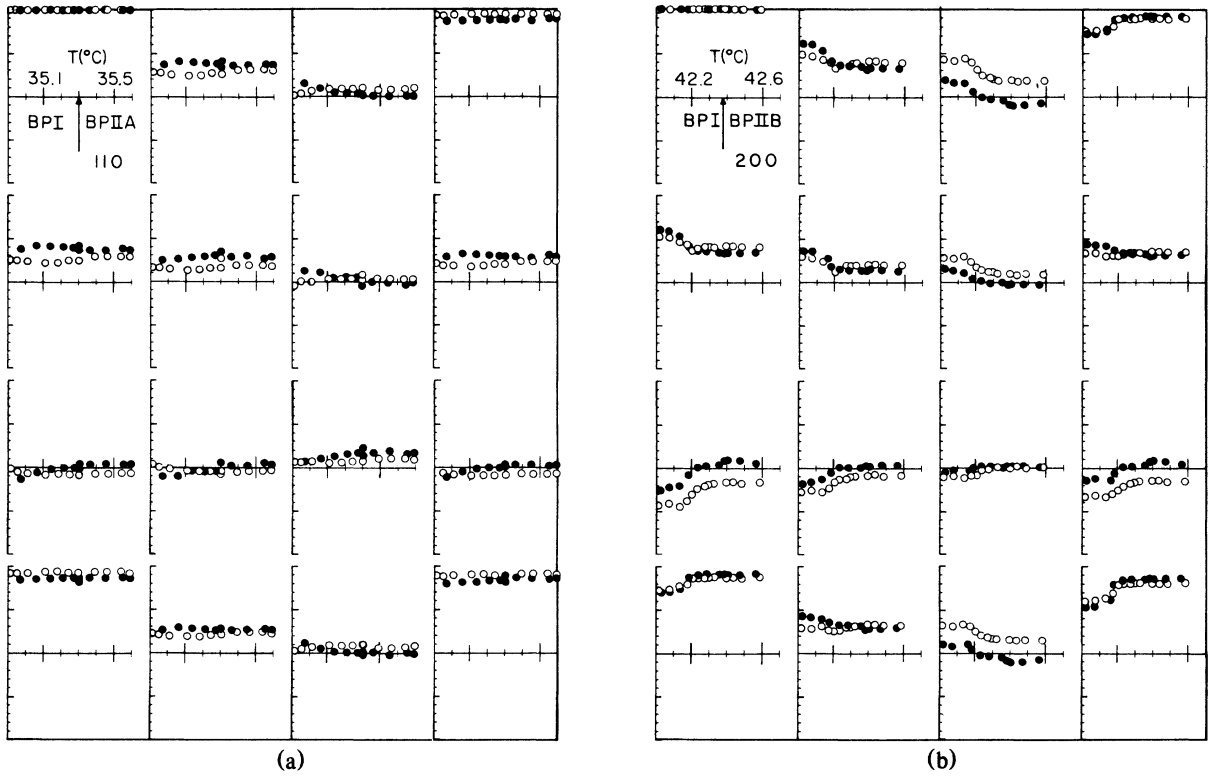

FIG. 3. Normalized Mueller matrices vs temperature for (a) BPI-BPIIA (110) line and (b) BPI-BPIIB (200) line. Open (closed) circles are for boundaries rubbed perpendicular (parallel) to the scattering plane. The notation is the same as Ref. 7 with x (y) lying $\perp$ ($\parallel$) to the scattering plane.

by a similarity transformation which minimized the M_{i3} and M_{3i} elements; this procedure removes the rotation of the major axis of the polarization ellipse. The resulting rotated data matrix was then least-squares fitted to the HS Mueller matrix using the four coefficients ϵ_0^2, $\epsilon_1^2+\epsilon_{-1}^2$, ϵ_2^2, and ϵ_{-2}^2 as fitting parameters. Summarizing the results for six fits (three lines with two surface orientations per line), the ϵ_0^2, $\epsilon_1^2+\epsilon_{-1}^2$, and ϵ_2^2 coefficients were never more than 4% of ϵ_{-2}^2. The typical rms difference between the elements of the rotated data matrix and the fitted matrix was 0.05.

The observation of only the ϵ_{-2} order-parameter coefficient allows us to draw tentative conclusions concerning the symmetry of the blue phases. BPI and BPIIB have already been shown[6,11] to belong to bcc space groups $T^3(I23)$, $T^5(I2_13)$, or $O^8(I4_132)$. $\epsilon_{\pm1}$ and ϵ_0 are forbidden in the $O^8(200)$ line, while only $\epsilon_{\pm1}$ is forbidden in the $O^8(100)$ line. Neither ϵ_0 nor $\epsilon_{\pm1}$ is forbidden in the T^3 and $T^5(110)$ lines while only $\epsilon_{\pm1}$ is forbidden in the T^3 and $T^5(200)$ line. The data therefore favor O^8 but do not completely rule out T^3 and T^5. For BPIIA, the data favor sc $O^2(P4_232)$ or bcc O^8 since these structures forbid ϵ_0 and $\epsilon_{\pm1}$ most strongly. However, sc $T^1(P23)$ and bcc T^3 and T^5 are still allowed if, in these symmetries, ϵ_0 and $\epsilon_{\pm1}$ are sufficiently weak.

In summary, we have shown that the Mueller matrix technique is a powerful tool for investigating large lattices and phase transitions in liquid crystals. Anticipated structural changes between the BPI and BPII phases are shown not to be present, and the nature of the polarization impressed on incident light by the lattice has been established. Connection with the theory of Hornreich and Shtrikman has limited the possible symmetries available to the blue phases.

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