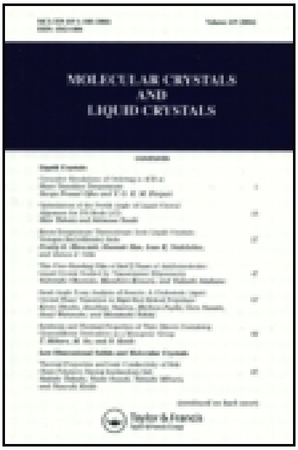


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# Angular Dependence of Blue Phase Selective Reflection in the Electric Field

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# Angular Dependence of Blue Phase Selective Reflection in the Electric Field†

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The angular dependence of the selective reflection peaks has been investigated for BP1 and BP2 as well as for non-cubic BP-structures occurring in the electric field. Although at normal light incidence the ratios of the wavelengths of reflection bands are known to fit in a Bragg condition, we found that the angular dependence behaves non-Bragg-like, i.e. certain reflection peaks are shifted to longer wavelengths with increasing angle of reflection. The angular dependence can be used to distinguish between the effects of deformation, reorientation and phase transitions occurring under the influence of the electric field.

*Keywords: Blue Phase, field-effects on cubic structures, field-induced phase transitions*

## INTRODUCTION

Due to the cubic structure of the molecular arrangement, two of the Blue Phases (BP1 and BP2) exhibit sharp selective reflection bands of circularly polarized light.[1] Several peaks can be observed in the visible wavelength region showing ratios of the wavelength of maximum intensity which are characteristic for either body centered cubic (BP1) or simple cubic structures (BP2). By applying an electric field, the wavelengths of the reflection peaks are shifted. To study whether this effect is due to changes of symmetry and periodicities or re-

†Part of a poster presented at the 11th International Liquid Crystal Conference, Berkeley 1986.

orientation of the BP unit cells, the angular dependence of the selective reflection at different voltages was investigated.

The influence of an uniaxial field on a structure exhibiting a cubic symmetry can be described theoretically by regarding the symmetry elements. Due to the chirality and the optical activity of the cubic Blue Phases, the crystal classes 23 (T) and 432 (O) have to be considered. The uniaxial (electric) field is supposed to be parallel to one of the three main directions ([1,0,0], [1,1,1] and [1,1,0]). According to the principle that the deformed structure may exhibit only those symmetry elements which are common to the applied field and the undeformed structure, the resulting crystal classes with maximal remaining symmetry are listed in Table I. The resulting space groups for the most probable Blue Phase structures are also mentioned. They belong to the tetragonal, trigonal and orthorhombic crystal systems.

## EXPERIMENTAL

The experimental set-up is shown in Figure 1. The incident light exhibiting the spectral distribution shown in the inset of Figure 1 illuminates the sample at an adjustable angle θ to the surface normal. The reflection spectra are recorded at the same angle θ to the surface normal using a multi-element spectroradiometer (Photo Research Spectrascan PR-710) and a circular analyzer of the same handedness in order to exclude the reflections at the glass surface. The spectral range is limited by the spectroradiometer from 390 to 730 nm. The sample is a 9 μm TN-type cell (Videlec) containing one of the systems listed in Table II. The surfaces of these cells are coated and rubbed

TABLE I

Resulting crystal classes and space groups under the influence of the electric field on initially cubic structures:

| Cubic structures | Resulting structures for field-direction along [100] | [111] | [110] |
|---|---|---|---|
| Crystal classes | | | |
| 432 (O) | 422 ($D_4$, tetragonal) | 32 ($D_3$, trigonal) | 222 ($D_2$, orthorhombic) |
| 23 (T) | 222 ($D_2$, orthorhombic) | 3 ($C_3$, trigonal) | 2 ($C_2$, monoclinic) |
| Space groups | | | |
| $I4_132$ ($O^8$) | $I4_122$ ($D_4^{10}$) | R32 ($D_3^7$) | F222 ($D_2^7$) |
| $P4_232$ ($O^2$) | $P4_222$ ($D_4^5$) | R32 ($D_3^7$) | C222 ($D_2^6$) |

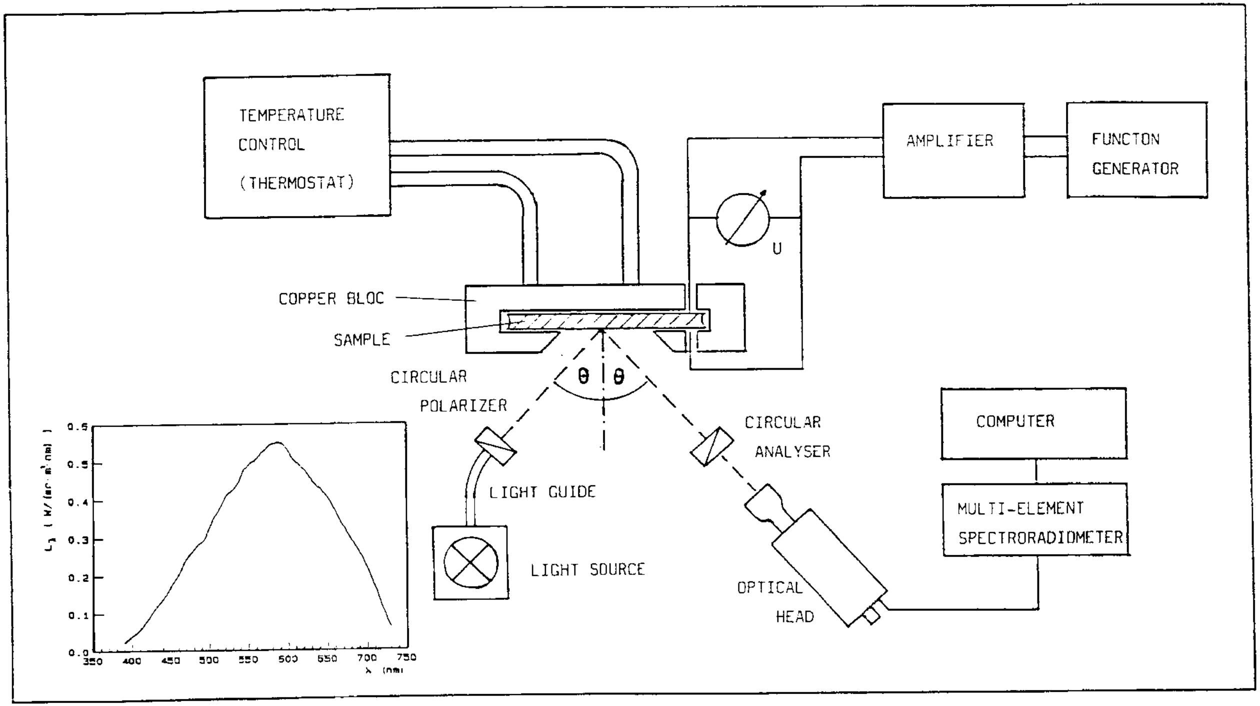
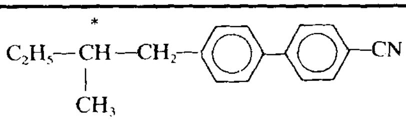


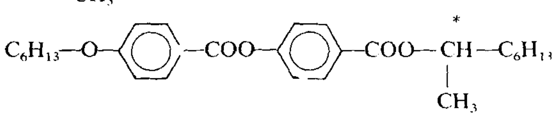

FIGURE 1 Experimental set-up. The spectral distribution of the incident light is shown in the inset.

TABLE II

Investigated systems

| System No. | Weight-% of chiral component | Chiral compound | Nematic component | Δε | Field-induced phase transitions |
|---|---|---|---|---|---|
| I | 48.7 | CB 15 (BDH) | E 9 (BDH) | + | two |
| II | 53.8 | CB 15 | E 9 | + | two |
| III | 62.2 | CB 15 | RO-TN 404 (Roche) | + | not found |
| IV | 57.4 | CB 15 | RO-TN 404 | + | two |
| V | 59.9 | CB 15 | ZLI 1612 (Merck) | + | one |
| VI | 25.5 | S 811 (Merck) | EN 18 (Chisso) | − | not found |
| VII | 27.2 | S 811 | ZLI 2585 (Merck) | − | not found |

CB 15 

S 811 

Δε means the dielectric anisotropy of the nematic phase of the respective racemic mixture.

for parallel alignment of the molecules. The cell is placed in a copper block connected to a Haake-F3/S thermostat. Voltages up to 30 V at a frequency of 1 kHz (sine) have been applied, corresponding to field strengths up to $3 \cdot 10^6$ V/m.

## RESULTS AND DISCUSSION

### 1. Field-free state

The BP1, when obtained on cooling from the BP2, gives two reflection peaks at normal incidence for the systems I–V. They correspond to platelets of different orientations with respect to the surface normal, which is established by the wavelength ratio of about 1.4. Because the (1,0,0)-maximum is not allowed for body centered structures, the peak at longer wavelength must be the (1,1,0)-maximum of the [1,1,0]-

orientated unit cells, while the other peak originates from reflections at the (2,0,0)-planes in the [1,0,0]-orientated unit cells.

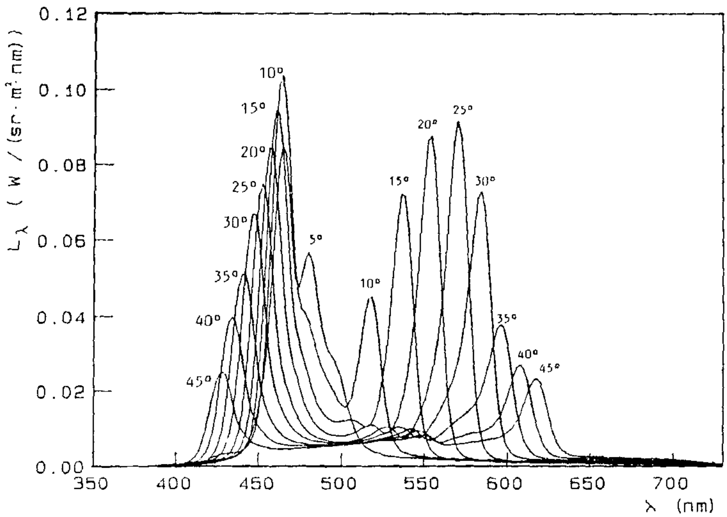
On heating from the cholesteric Grandjean-texture, the BP1 appears only in the [1,0,0]-orientation. Corresponding angular dependences as for the spectra in Figure 2 have been found in the systems I–IV (Table II). While one of the peaks shows Bragg-like behaviour other peaks are shifted to longer wavelength side with increasing angle to the surface normal. A similar behaviour has been observed by Kizel' and Prokhorov[2] while investigating the circular dichroism of Blue Phases. In order to explain their experimental data obtained in the transmission mode, the authors assume that the peaks showing Bragg-like behaviour are due to reflections at planes parallel to the surface. Peaks shifting to longer wavelength, when the angle of light incidence is increased, are assumed to originate from planes oblique to the surface. To fit their data, certain azimuthal angles $\varphi$ (0°, 35°, 55°, 90°) between the edges of the unit cell and the plane determined by the surface normal and the direction of light incidence were considered.

For comparison with our data, first of all the angle $\theta$ in our experiment has to be corrected due to the refraction at the surface, leading to

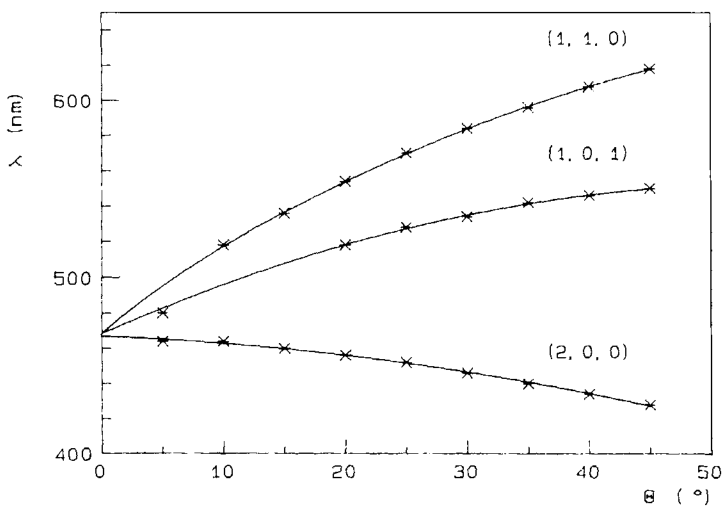
$$\theta' = \arcsin(\sin\theta/\bar{n}),$$

where $\theta'$ is the corrected angle in the sample and $\bar{n}$ is the mean refractive index which was assumed to be 1.6. Although our results are in good agreement with the formula given in Reference 2 assuming an angle $\varphi$ of 35° (see Figure 3), an additional mechanism has to be considered for our geometry because, for scattering planes being oblique to the surface, the direction of the scattered beam does not coincide with the direction of observation. This can be corrected by assuming either diffuse scattering of the reflected beam or a second reflection occurring at the glass surface behind the liquid crystal: If the incident beam is not perpendicular to the reflection planes a fraction of the light may be transmitted, exhibiting the reversed handedness. This beam can be reflected at the second interface, which reverses the handedness again. Thus the beam has the same wavelength and handedness as the originally reflected light, but its direction is only determined by the reflection at the second interface, allowing an observation.

Two discrepancies remain using this interpretation of $\varphi$ as an azimuthal angle: the very different intensities of the (0,1,1) and (1,0,1)




(a)




(b)

FIGURE 2 Results for the BP1 obtained on heating ([1,0,0]-direction parallel to the surface normal, system II, $t$ = 28.6°C): (a) Reflection spectra for different angles θ. The spectral radiance is plotted versus wavelength; (b) The wavelengths of maximum intensity are plotted versus angle θ. The lines are guide to the eyes.

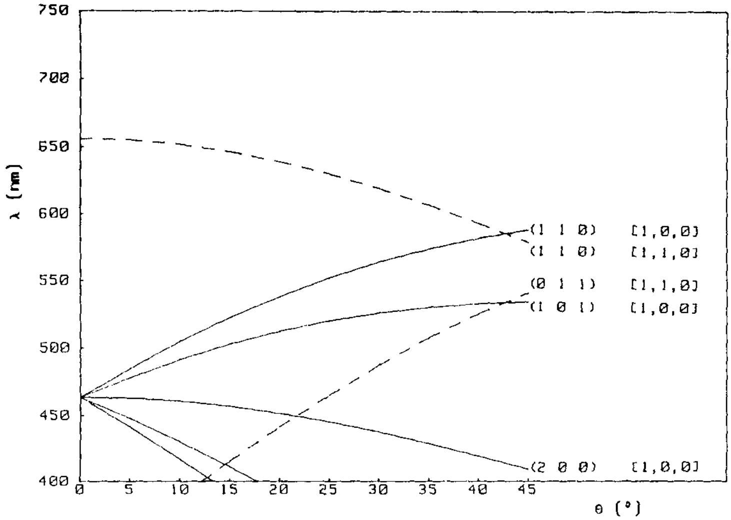
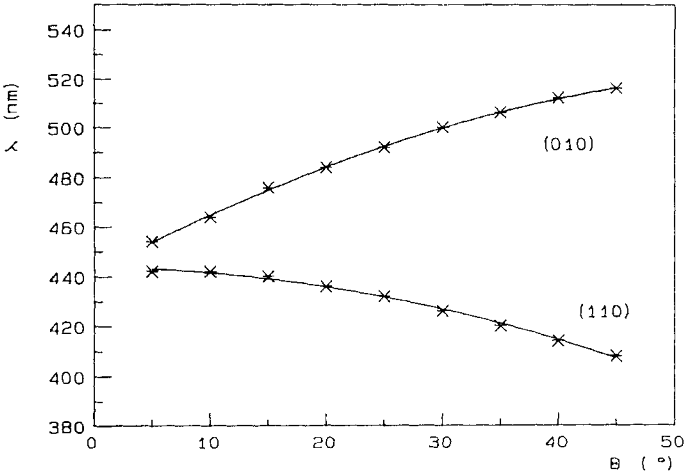


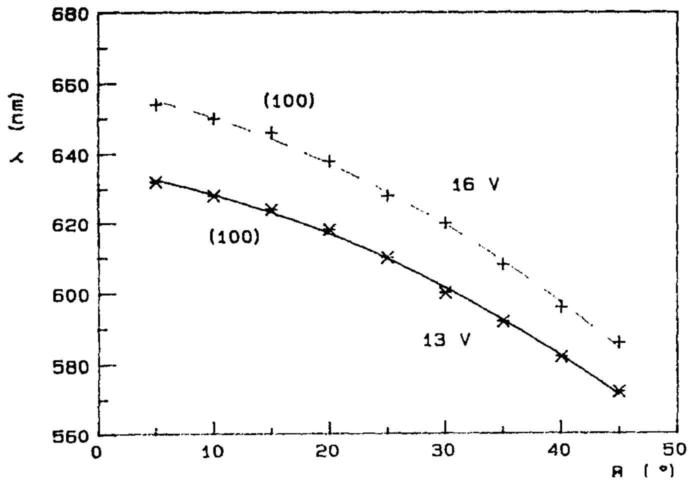

FIGURE 3 The angular dependences calculated using the formula given in Reference 2 assuming a refractive index of 1.6 and an azimuthal angle of $\varphi = 35°$. The Miller indices [H,K,L] designate the direction in the lattice being parallel to the surface normal, the indices (h,k,l) characterize the scattering planes. For comparison with experimental data see Figure 2b and Figure 6 respectively.

reflections and the fact that we did not observe any variation of the reflection spectra when the azimuthal angle was changed by rotating the sample around the surface normal.

For BP2, usually only one peak can be observed in the visible wavelength range because of the low critical pitch for the occurrence of this phase. For mixture I containing a suitable low concentration of CB 15 a second peak is observed. Thus this system is chosen to report the effects observed in the electric field below. On cooling from the isotropic phase, the BP2, assumed to be simple cubic, appears in the [1,1,0]-orientation. This orientation is characterized by the angular dependence shown in Figure 4a. One of the maxima (corresponding to the (1,1,0)-planes) shows the Bragg-like behaviour, the other is shifted to longer wavelength, when the angle of light incidence is increased. While both maxima coincide at normal incidence, the wavelength gap between the maxima is 108 nm at $\theta = 45°$. If the BP2 of this system is obtained on heating from BP1, a reflection at higher wavelength appears. The peak is shifted to shorter wavelength, when the angle is increased, and thus the reflecting planes are concluded to be parallel to the sample surface. Hence, this peak can be identified as the (1,0,0)-reflection, which is not forbidden in simple cubic structures, indicating the [1,0,0]-orientation of the unit cells.

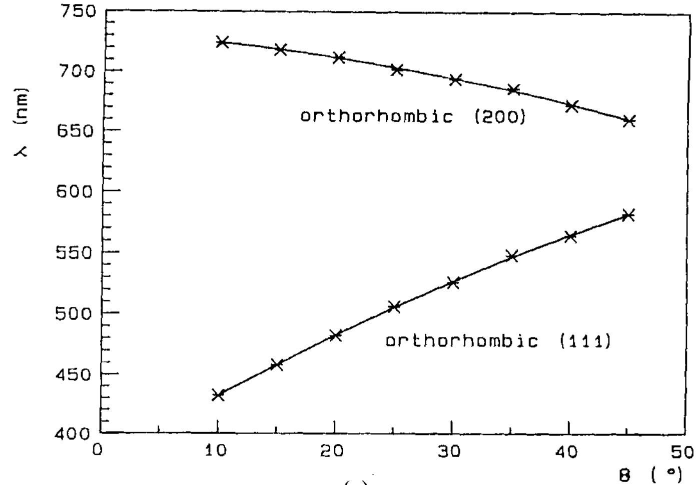



(a)




(b)

FIGURE 4 Characteristic angular dependence (system I, $t = 33.1°C$) for the different phases or orientations occurring in the electric field (cell-thickness: 9 μm). For designation of the maxima see text. (a) Field-off state: Simple cubic BP2 in the [1,1,0]-orientation with respect to the surface normal; (b) U = 13 V and 16 V respectively: tetragonal BP2′ in the [1,0,0]-orientation; (c) U = 17 V: A field-induced phase transition has lead to a probably orthorhombic BP1′. Scattering planes are designated with respect to the face centered orthorhombic unit cell, which is [1,0,0]-orientated, because its edges are not parallel to those of the cubic unit cell.




(c)

FIGURE 4 *(continued)*

## 2. Influence of an electric field

All possible effects occurring in electric field can be demonstrated in system I starting from the BP2 in [1,1,0]-orientation, which is obtained on cooling from the isotropic phase. The Figures 4a, b, c show characteristic angular dependence for the structures occurring at different voltages. In Figure 5 the wavelengths of selective reflection at maximum intensity are plotted against the applied voltage for a fixed angle ($\theta = 45°$). The wavelength gap at this angle in the field-free state (Figure 4a) reappears at the left side in Figure 5.

On increasing the voltage, the gap becomes smaller indicating a deformation of the unit cell. The deformation is correlated with a change of the molecular arrangement leading to a slight dielectric anisotropy of the unit cell.[3] Therefore, it can be reoriented by the electric field. In all investigated systems with positive dielectric anisotropy, the preferred orientation for the BP1 in the electric field seems to be that with the twofold axis [1,1,0] being parallel to the field direction, while for the BP2, the fourfold axis [1,0,0] is favoured. The stability of these orientations in the electric field has also been observed recently by Porsch and Stegemeyer[4] for samples between untreated glass slides. However, for the BP1 the results differ from the preferred orientation found by Pieranski et al.[5] for free rotating single crystals surrounded by the isotropic liquid.

In system I the reorientation takes place at 13 V, which is characterized by the appearance of the reflections at the (1,0,0)-planes

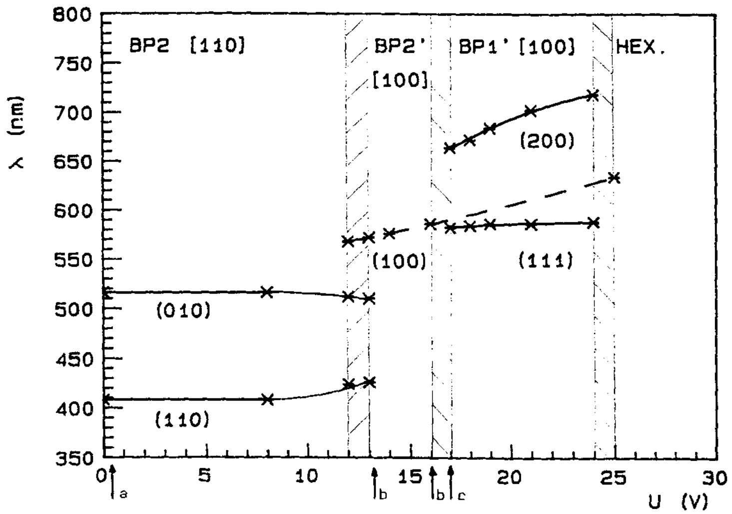



FIGURE 5 The wavelength of the peaks of selectively reflected light at θ = 45° are plotted versus applied voltage (system I, $t$ = 33.1°C). The characteristic angular dependences at four different voltages marked by arrows are presented in Figure 4. In the hatched voltage regions, reorientation (at 12 V) and phase transitions (at 17 and 25 V) occur. The orientations are explained in Figure 4.

being parallel to the sample surface (Figure 4b). The deformation resulting in tetragonal symmetry (BP2') becomes stronger on increasing field-strength and the peak is continuously shifted to longer wavelength.

The discontinuity in the wavelength-shift observed at 17 V is related to a field-induced phase transition. In contrast to the reorientation, this effect is reversible and the ratio of the wavelengths of the appearing maxima to that of the former existing maxima is neither $1:\sqrt{2}$ nor $1:\sqrt{3}$. In the reflection mode at normal incidence, the sample looks black because both maxima are out of the visible wavelength range (Figure 4c). One of the peaks is very sensitive to angular variations. For the induced phase not only the SR-wavelength at normal incidence,[6] but also the angular dependence corresponds to the continuously deformed BP1 of the system (Figure 6). Thus we designate this non-cubic phase as BP1'. As mentioned above, the [1,1,0]-orientation is preferred for the BP1 in the electric field. So the field direction is parallel to the twofold axis leading to an optically biaxial structure (space group F222, see Table I). This would be in agreement with the observed birefringence for the BP1 in the electric field.[7]

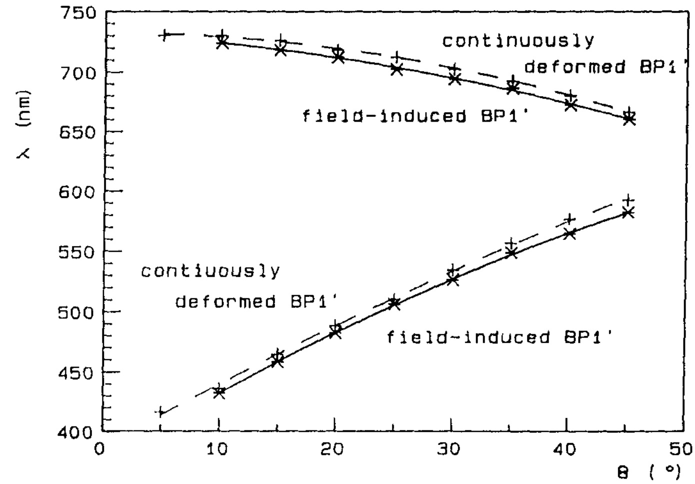



FIGURE 6 By comparing the angular dependence of the phase which is induced by the field when starting from BP2 (system I, $t = 33.1°C$) and the continuously deformed BP1 ($t = 31.5°C$), the phases are found to be identical. This structure, designated by us as BP1′, is assumed to be orthorhombic (see Table I).

At higher voltages, a second phase transition occurs (see Figure 5, 24 V). The reflection peak exhibits a Bragg-like behaviour. Taking into account the theoretical predictions of Hornreich et al.[8] and the observations of Pieranski et al.,[9] a hexagonal structure can be anticipated for this phase. It has to be mentioned that field induced phase transitions could not be observed in all systems, e.g. we have not seen phase transitions in the systems with negative dielectric anisotropy investigated so far.

## Acknowledgments

We thank R. Didier for helpful discussions concerning the space group considerations. The referee's suggestion to consider reflections at the second interface is gratefully acknowledged. This work has been supported by the Deutsche Forschungsgemeinschaft.

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Recently, a field-induced phase transition from the orthorhombic BP 1′ to a tetragonal structure (BP X) has been detected using Kossel diagrams.[10] At this phase transition only the lattice constants perpendicular to the field direction are changed discontinuously. From the data given in reference 10, the angular dependences of the reflection bands can be calculated for both phases and they are found to be indistinguishable in our experimental set-up.