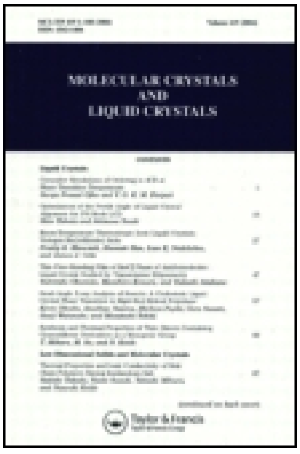

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Novel Features in Blue Phase Kossel Diagrams

Richard J. Miller [a], Helen F. Gleeson [a] & John E. Lydon [b]

[a] Department of Physics and Astronomy, University of Manchester, Manchester, MI3 9PL, United Kingdom

[b] Department of Biochemistry and Molecular Biology, University of Leeds, Leeds, LS2 9JT, United Kingdom

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NOVEL FEATURES IN BLUE PHASE KOSSEL DIAGRAMS

RICHARD J. MILLER, HELEN F. GLEESON†
Department of Physics and Astronomy, University of Manchester, Manchester M13 9PL, United Kingdom.

JOHN E. LYDON
Department of Biochemistry and Molecular Biology, University of Leeds, Leeds LS2 9JT, United Kingdom.

† Author for correspondence. e-mail: Helen.Gleeson@man.ac.uk

Abstract High resolution Kossel diagram images of the blue phases have been found to reveal previously unobserved features, some theoretically predicted by Belyakov, *et al.*. These features consist of gaps in the Kossel line intensity at the crossing point of two or more Kossel lines and interference fringes in regions of many-wave diffraction. A simple theory, side-stepping the need to solve Maxwell's equations, based on the interference of light diffracted from multiple sets of Bragg planes is shown to qualitatively explain the results. Also, these many-wave diffraction features are shown to allow a solution to the phase problem in the blue phases. The modelled results are found to be in contradiction with the double twist model of BPII.

INTRODUCTION

The blue phases[1] of liquid crystals are thermodynamically distinct phases which exist in materials with high chirality. The most commonly observed blue phases are blue phases I and II (denoted BPI and BPII respectively) which occur on increasing temperature above the chiral nematic phase and are known to have cubic structures. Theoretical and experimental investigations aimed at determining the blue phase space groups have relied primarily on the calculated and observed reflection intensities[1] and have associated the space groups $I4_132$ and $P4_232$ with BPI and BPII respectively[2]. However, the calculated reflection intensities, which are different for Landau and disclination theories[3], and the low number of orders observed suggest that these space group assignations are by no means conclusive.

Most of the blue phases have structures with three-dimensional periodicities of the order of visible wavelengths, allowing Bragg diffraction of visible light. The complete determination of any periodic structure using Bragg diffraction involves the measurement of three things[4]: the repeat distances (from the Bragg diffraction angles); the amplitudes of the Fourier components of the structure (from the diffraction intensities); and finally the relative phases of these Fourier components. Clearly, these three types of information about the structure become progressively harder to obtain. The final piece of the puzzle, the so called 'phase problem'[5], is the hardest to solve since it requires some form of interferometry to determine the relative phases of the various Bragg reflections. This paper provides new experimental data relevant to the phase problem in blue phases.

THEORETICAL

The Kossel diagram technique[6] has been used for some time in the determination of the blue phase symmetries. This technique exploits highly convergent or divergent light to create a diffraction pattern of circles, ellipses and straight lines, called Kossel lines. Many-wave diffraction conditions, where two or more Kossel lines cross, are common and the observed intensities at the region of intersection indicate the relative phases of the two reflections and hence of the corresponding Fourier components of the dielectric tensor. Here, experimental results are presented showing interference features at the crossing points of the Kossel lines. The data are modelled allowing phase information relating to the blue phase structures to be deduced.

In principle the optics of the blue phases may be determined analytically by considering the form of the periodic dielectric tensor and solving Maxwell's equations accordingly. However, in many-wave diffraction conditions coupled differential equations are obtained which have no analytic solution[7] and numerical analysis must be employed. In this paper a different approach to the study of many wave-diffraction conditions is considered, based on the interference of light scattered from two sets of Bragg planes. This model, to be explained in greater detail in a future paper, relies on the following assumptions:

(1) The incident light consists of concentric spherical wave fronts with no angular intensity variation - approximately true over small angle ranges.
(2) The polarization state of the diffracted light is assumed to be circular - hence only the amplitude and phase of the light need be considered in the theory.
(3) The chiral nature of the blue phase structures implies a phase shift in the structural Fourier harmonics on azimuthal rotation of the plane of incidence and diffraction around a reciprocal lattice vector. For example, the spacing of the (001) planes in the classic BPII structure is equivalent to a π rotation of the blue phase helix. Hence, an azimuthal π rotation about (001) is equivalent to a 2π phase shift in the (001) structural Fourier harmonic.
(4) Multiple diffraction is neglected - only thin sample approximation is considered.

Normally in Bragg diffraction an infinite set of Bragg planes is considered which gives diffraction in one direction defined by Bragg's law, $\lambda = 2nd\sin\theta_B$, where θ_B is the Bragg diffraction angle, λ the wavelength of the incident light, n the refractive index of the medium and d the layer spacing of the Bragg planes. In blue phases, where the layer spacing is relatively large compared to the sample thickness, the approximation to infinite number of planes is not valid. Hence, the amplitude, A, of the diffracted light is then given by the sum of contributions from the N layers

$$A = f^{1/2}\sum_{m=0}^{N-1}(1-f)^{m/2}e^{m\psi i} = f^{1/2}\frac{1-(1-f)^{N/2}e^{N\psi i}}{1-(1-f)^{1/2}e^{\psi i}},$$

where A contains information on the amplitude and phase of the resultant electric field of the diffracted light, f is the fractional intensity of the light scattered from each Bragg plane, and $\psi = 2\pi\sin\alpha/\sin\theta_B$ is the relative phase shift between light scattered at an angle α from adjacent Bragg planes.

Light diffracted from a second set of Bragg planes may experience a different path length due to a difference in the position of the second set of planes relative to the unit cell. Hence, this light acquires a relative phase shift of $\Delta = \delta\sin\beta/\sin\theta_B$, where β is the scattering angle and δ is the relative phase shift in the structural Fourier harmonic

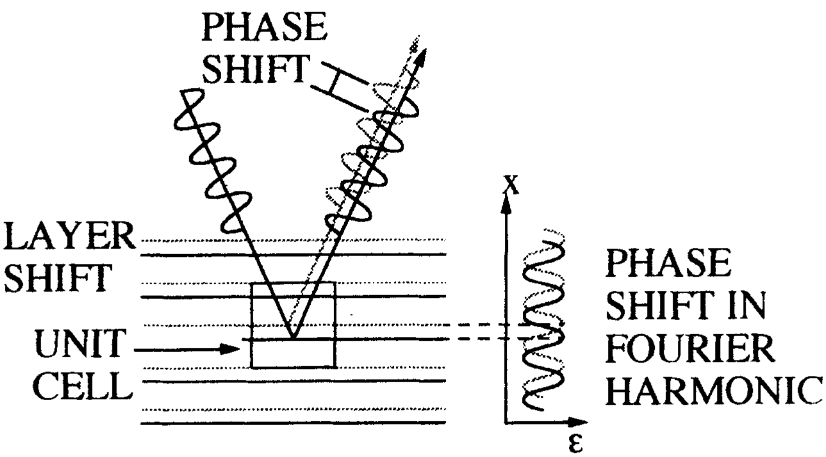


FIGURE 1 Schematic diagram illustrating how a relative shift in the Fourier harmonics associated with a set of Bragg planes results in a phase shift in the diffracted light.

associated with the second set of layers (fig. 1). As mentioned δ will include a phase shift due to rotation of the plane of incidence about the reciprocal lattice vector. As before, the amplitude B of the light diffracted from the second set of Bragg planes is then given by

$$B = f^{1/2} e^{\Delta i} \frac{1-(1-f)^{N/2} e^{N\phi i}}{1-(1-f)^{1/2} e^{\phi i}},$$

where $\phi = 2\pi \sin\beta / \sin\theta_B$ is the relative phase shift between light scattered from adjacent layers in the second set of Bragg planes. The resultant intensity of the light due to contributions from both sets of Bragg planes is then given by $I = (A+B)^*(A+B)$, where the asterisk denotes the complex conjugate.

Theoretical diffracted intensities were calculated using the above method. Two cases are reported: Kossel lines crossing at right angles (fig. 2a) and 'passing points' where two parallel Kossel lines pass close to each other (fig. 2b). The calculations assumed 50 layers in each set of Bragg planes giving a modelled sample thickness of $\sim 10\mu$m.

The theoretical results display four main features:

(1) The Kossel lines change intensity either side of the crossing point (except when $\delta = 0, \pi$) and display interference peaks along their ridges (fig. 2a).
(2) The position of the central interference peak, at a crossing point, depends on the relative phase, δ, of the structural Fourier harmonics (fig. 2a).
(3) Low intensity concentric interference fringes are predicted, centred on the passing point of two Kossel lines (fig. 2b).
(4) The diffracted intensity at the centre of the passing point of two Kossel lines (fig. 2b) depends strongly on the relative phase, reaching a maximum at $\delta = 0$.

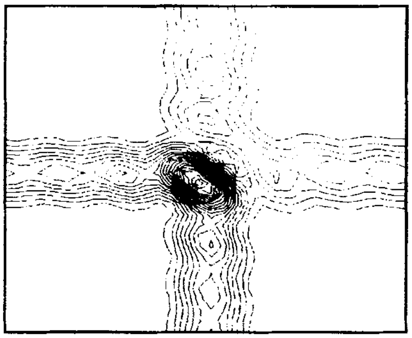
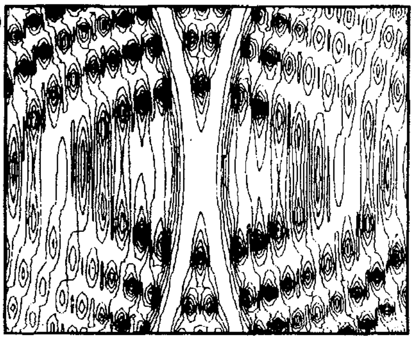
(a)  (b) 

FIGURE 2 Theoretical diffracted light intensity for Kossel lines meeting at (a) a crossing point and (b) a passing point (logarithmic contours). The phase shift δ has been chosen such that the features match the experimental results (figure 3). Parameters used: (a) $\lambda = 488nm$, $n = 1.6$, $d = 250nm$, $N = 50$, $f = 0.001$ and $\delta = 3\pi/2$; (b) $\lambda = 488nm$, $n = 1.6$, $d = 213nm$, $N = 50$, $f = 0.001$ and $\delta = 0$. Axes indicate angle from the Bragg condition.

EXPERIMENTAL

Experimental Kossel diagram images were produced from the BPI and BPII of a mixture of 20.1 ± 0.2 mol% of 4"-(2-methyl) butylphenyl-4'-(2-methyl) butyl-4-biphenyl carboxylate (CE2) in 4-cyano-4'-n-butylbiphenyl (4CB)[8]. The material was observed between two thin glass slides coated with rubbed polyvinyl alcohol to provide planar alignment and spaced by about 10μm. The apparatus used to generate the Kossel diagrams has been discussed in detail elsewhere[9,10]. Typical Kossel diagrams are presented here. Briefly, the highly convergent monochromatic light needed to generate Kossel diagrams was provided by a high numerical aperture oil immersion microscope objective (N.A. ≈ 1.3) and argon ion laser. The Kossel diagram image, which then appears in the back focal plane of the objective, was captured using a video camera and image digitisation system, giving a resolution of about 300×300 pixels per image. The temperature of the sample was controlled to better than ±0.01°C using a high stability temperature controller[11].

Fig. 3 shows small regions of Kossel diagram images, taken from BPI along the [011] crystal direction and BPII along the [111] crystal direction, in the vicinity of Kossel line crossing and passing points. These Kossel diagram regions are presented in the form of contour plots to illustrate details of the light intensity profiles. Fig. 3a shows the crossing point of the (110) and (101) lines in BPI while fig. 3b shows the passing point of the (100) and (010) lines in BPII. The diagram in fig. 3b is again a logarithmic plot of the intensity highlighting the low intensity interference fringes. The Kossel line crossing point in fig. 3a displays the main features predicted by the theory presented above. Interference peaks are seen along the ridges of the Kossel lines in the region of the crossing point. Also the lines show significantly different intensities either side of the crossing point. At the crossing point shown, the darker arm of the Kossel lines appear at larger scattering angles (i.e. on the inside of the curve of the other Kossel lines) suggesting that the relative phase of the Fourier harmonics is ~$3\pi/2$ for this crossing point. This behaviour at the Kossel line crossing point has been qualitatively predicted by Belyakov and co-workers[7,12] by considering the solution of Maxwell's equations. The

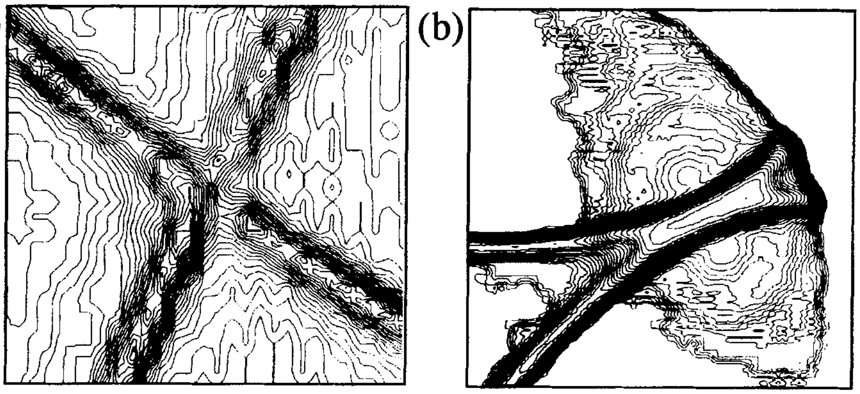


FIGURE 3 Contour plots of the measured light intensity at a Kossel line crossing point (a) and passing point (b). The scale in (b) is logarithmic. The sample thickness was ~10μm allowing multiple diffraction effects to be neglected.

phase difference, quoted here, includes the azimuthal phase shift of the light around the Kossel cones. Hence, information on the phase of the Fourier harmonics in the sample will depend on more complex analysis of the theory and data. At the alternative crossing point of these two Kossel lines (not shown here) the darker arms of the lines occur on the side of smaller scattering angle, confirming the predicted change in the apparent phase shift of the Fourier components due to the rotation of the plane of incidence of the light.

The passing point of the (100) and (010) lines in BPII, illustrated in fig. 3b, clearly shows the predicted concentric interference fringes. At the central passing point, the intensity of the Kossel lines reaches a maximum suggesting that there is no relative phase shift between the diffractions from the two sets of Bragg planes in the sample. This situation is somewhat easier to consider than the situation in figure 3a since the incident rays, diffracted rays and the helices in the structure are coplanar. This result, illustrated in figure 3b, is apparently in contradiction with the commonly illustrated double twist tube model of BPII presented in the literature (fig. 4)[3]. The proposed structure in fig. 4 shows that along the (100) direction the horizontal double twist tubes are encountered by the incident light before the vertical tubes. In the (010) direction, however, the vertical tubes are encountered first. Hence, it would be expected that there is a relative phase shift of π between the (100) and (010) reflections. It is found that the variation in the phase of the structural Fourier harmonic with azimuthal angle around the reciprocal lattice vectors will not account for this difference.

Multiple diffraction effects have been neglected in this treatment since: only 50 Bragg layers were considered in the model (corresponding to experimental sample thickness ~10μm); and circular dichroism spectra of monodomain blue phase samples[13] suggest the diffracted light intensity per layer $f \sim 0.001$. These parameters imply, at the Bragg condition, the diffracted intensity is ~5%, with correspondingly lower intensity secondary diffractions. Hence, secondary diffraction, or multiple diffraction, is unlikely to make a significant difference to the conclusions of the theoretical or experimental results.

The details of Kossel diagram images presented here display previously unobserved features which are found to be predicted by a relatively simple theory, based on the interference of diffracted light. Similar interference features have been observed at all the Kossel line crossing and passing points in blue phases one and two examined using our apparatus. The theory suggests that no other effect, such as multiple

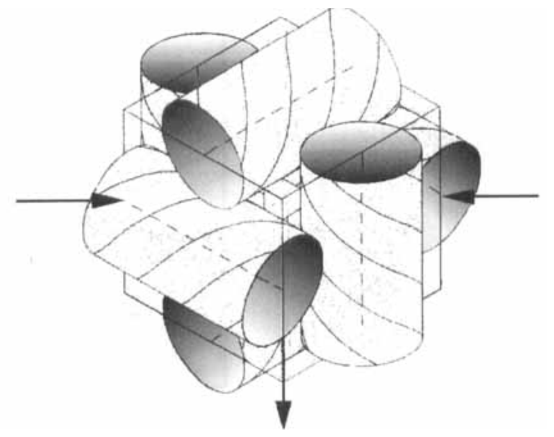


FIGURE 4 Schematic diagram illustrating the double twist tube structure commonly presented in the literature. Light incident on two faces may be diffracted in the same direction. However, the light incident from the two directions experiences significantly different structures in this model (half layer phase shift).

diffraction, need be considered to explain the essential features of the results. This theory also predicts interference peaks along Kossel lines in the region of a crossing point which have been observed but not previously predicted. The observed features depend strongly on the relative phase of the Fourier harmonics in the periodic structure and hence provide a solution to the phase problem in the blue phases.

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