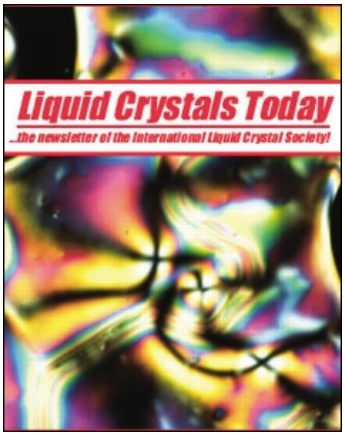


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# Rhapsody in Blue

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# Rhapsody in Blue

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**The blue phases are, to those liquid crystal scientists who have not studied them, a somewhat obscure and esoteric branch of the field. However to those who have had a chance to see them in a microscope glowing with an iridescent multitude of colours and to study them in depth, they represent some of the most beautiful and complex of the liquid crystal phases.**

As many reviews of the blue phases state, the blue phases were actually reported in the very early days of the study of liquid crystals. Our old friend Reinitzer [1], as long ago as 1888, reported an iridescent effect on cooling past the clearing point of a chiral nematic phase. Owing to the very narrow temperature range of the behaviour, for many years it was seen simply as a transitional effect associated with chiral nematic phases. Work on the blue phases really began during the flurry of interest in liquid crystals in general, following the commercial success of the cyanobiphenyls and liquid crystal displays. As more liquid crystal phases were added to the pantheon so more blue phases were discovered. Theoretical and experimental evidence quickly accumulated to back the proposition that these blue phases were indeed distinct thermodynamic entities. The clinching landmark study came in 1987, where Thoen [2], using adiabatic differential scanning calorimetry, managed to resolve first-order phase transition peaks for the blue phases from that of the clearing point transition. Finally the blue phases had come into their own as genuine thermodynamic phases.

The naming of these phases as blue is somewhat historic. In general they are found to strongly reflect circularly polarized light, and in the earliest cases this light was usually blue. These properties reflect the most important feature of the phases, that is their highly twisted, or chiral, periodic structure causing Bragg reflection. However, unlike their one dimensionally periodic chiral nematic phase cousins, the blue phases are periodic in all three dimensions. Hence one blue phase crystal structure can reflect light from many different lattice planes and at many different wavelengths simultaneously.

One of the greatest challenges of the blue phases was to pin down their structure more exactly and to explain how a three-dimensional structure could be constructed from chiral nematic style helices. Much work was done to determine the crystallographic space groups of the phases. A key technique in this process was an adaptation of a technique first presented by Kossel [3] in 1935 that had languished for some time following its initial application. The Kossel technique involves passing divergent radiation through a single crystal structure from a point source, onto a detector. Some of the radiation fulfils the Bragg condition within the crystal and is diffracted causing shadows at the detector, which take the form of conic sections. Since each line in the pattern relates to a specific reciprocal lattice vector then the complete pattern reflects the symmetry of the crystal. Historically the technique has been used with both X-rays and electrons to elucidate crystal structures, but for the blue phases visible light is used. In this way much valuable information about the structures of the blue phases was deduced [4].

Finally, it was determined that the most common periodic blue phases were cubic in nature. These are, in the great tradition of liquid crystal phase nomenclature, rather unromantically called blue phase one (BPI) and blue phase two (BPII). Blue phase one was determined to have a body centred cubic lattice, with an $I4_132$ space group symmetry, while blue phase two has a simple cubic structure, space group $P4_232$. Fitting a helical structure around these cubic structures is a problem that puzzled workers for some time. It is now generally accepted that the phase stability depends on a fine balance between an array of so-called 'double twist tubes' and coexisting defect lines. The 'double twist tube' structures, where helices twist in all directions perpendicular to a central axis, are locally energetically favourable compared to the one-dimensional twist of a chiral nematic phase but topologically impossible to fit into three-dimensional space without forming defect lines. Consequently, the phases only become stable in materials of high chirality and close to the clearing point, where the energy cost of defects is lower. Typically these phases are less than a degree wide.

A lot of the early studies using optical Kossel diagrams, as the patterns are called, focused on the symmetries of the different blue phases. However, other work [5] demonstrated that quantifiable measurements on the blue phases could be made using this technique. With this in mind, Dr Helen Gleeson, of the University of Manchester in the UK, and myself, as a graduate student,

embarked on a program of research in 1990. This was primarily centred around constructing an optical Kossel diagram apparatus to take high quality images showing unprecedented detail of the diagrams, to push back the limits of the optical technique and to investigate its possibilities. This collaboration was later to include Dr John Lydon of Leeds University.

## Equipment

Four essential features are required in order to generate Kossel diagrams in blue phases; short wavelength monochromatic light, highly convergent or divergent light, an optical system to image the diagrams and high stability temperature control to allow growth of large enough blue phase monodomain crystals. In the equipment we chose to use a 20 mW argon ion laser as the light source, an adapted Olympus reflection microscope, an oil immersion objective with a high numerical aperture and a temperature controller built in house with a long term stability of <10 mK [6]. We also added a high-resolution CCD camera and image digitizing equipment to allow a detailed analysis of the Kossel images.

The intensity of the laser, as an illumination source, aided observation while its monochromicity and coherence aided the resolution and interpretation of the images. The laser was coupled to the microscope via a fibre optic bundle. The speckle pattern due to the coherence of the laser was effectively removed from the Kossel images by mechanical vibration of the bundle. This fibre bundle also aided coupling of the laser to the microscope. Achieving uniform illumination of the sample is problematic. The high numerical aperture objective of the reflection microscope was considered a reasonable compromise.

## Geometry of optical Kossel diagrams

Most scientists are familiar with the concept of Bragg diffraction where incident light is reflected from a periodic structure at a specific incident angle, $\theta$, related to the wavelength, $\lambda$, of the incident light and the periodicity, $d$, of the structure by

$$\lambda = 2d \sin\theta.$$

Bragg's law may also be written in the form

$$\mathbf{k}_\tau = \mathbf{k}_0 + \tau,$$

where $\mathbf{k}_0$ and $\mathbf{k}_\tau$ are respectively the wavevectors of the incident and diffracted waves and $\tau$ is the reciprocal lattice vector. The reciprocal lattice vector points normal to a set of planes with magnitude equal to $2\pi/d$.

Clearly only those layers with $|\tau| < 2|\mathbf{k}_0|$ can cause diffraction and the possible directions for the diffraction form a cone with the axis along $\tau$. For a general crystal, with many reciprocal lattice vectors, illumination from all angles generates many cones of diffracted light emanating from the crystal. Light diffracted in any specific direction is parallel and may be focused to a point in the back focal plane of an optical system. Hence, the cones of light form a pattern in this back focal plane, which is called a Kossel diagram. The back focal plane may be made to coincide with a screen or camera. Then, provided that the focal length of the optical system is large compared to the Kossel diagram image size, the radial distance of a point on the Kossel diagram is proportional to the sine of the angle of light diffracted from the crystal. Hence, the diagram takes the appearance of the intersection lines between the cones and the sphere projected down onto a flat plane (figure 1). The edge of the Kossel diagram image is determined by the numerical aperture of the optical system and may be easily related to an angle within the crystal by Snell's law.

The Bragg condition is only exact for crystal samples of infinite thickness, whereas in the real world typical blue phase samples may only contain ten to twenty layers. Hence, the lines in the Kossel diagram have a finite width and the light changes phase across this width.

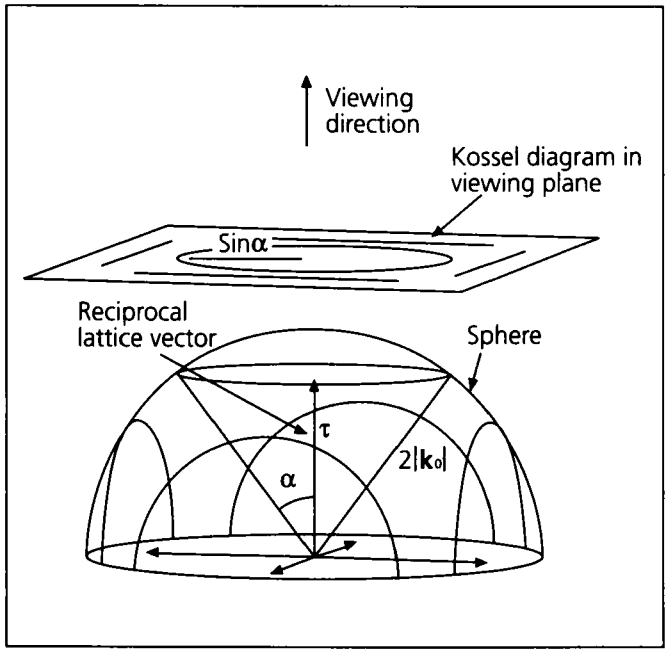


*Figure 1.* Geometrical technique used to construct Kossel diagrams. Each reciprocal lattice point within the sphere generates a Kossel line.

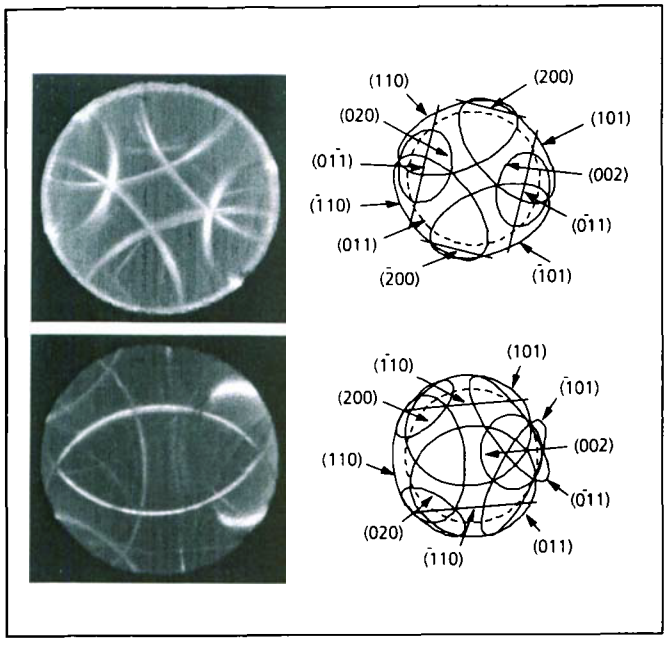


*Figure 2.* Two sample Kossel diagrams generated by blue phase one and their theoretical equivalents.



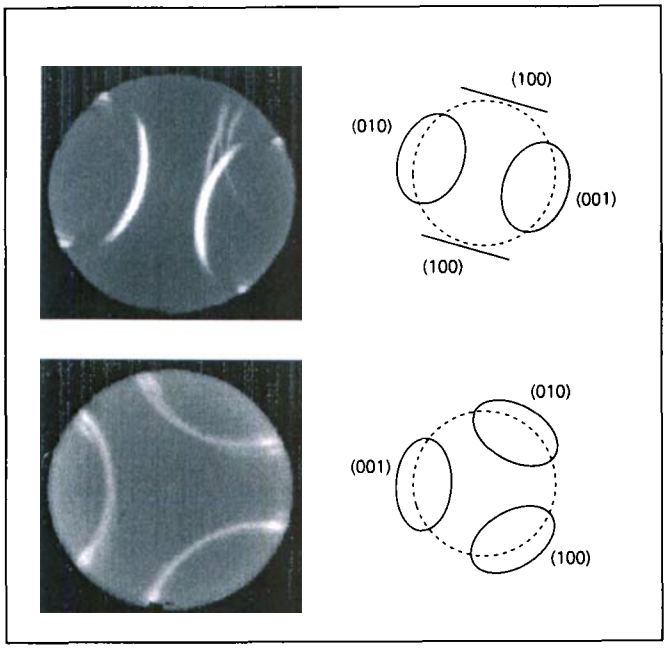


*Figure 3.* Two sample Kossel diagrams generated by blue phase one and their theoretical equivalents.

## Kossel diagram examples in the blue phases

The following figures show actual Kossel diagram images beside theoretical representations illustrating the Miller indices associated with each line. The blue phases were formed in a mixture of 20% w/w of CE2 in 4CB [7]. Figure 2 shows Kossel diagram images of blue phase, one viewed along the [011] crystal axis (figure 2(*a*)) and the [112] crystal axis (figure 2(*b*)). Figure 2(*a*), in particular, clearly shows the two-fold rotation symmetry of the blue phase one space group ($I4_132$). Figure 3 shows Kossel diagram images from the same mixture heated up into blue phase two, $P4_232$ space group. These show views along the [011] crystal axis (figure 3(*a*)), where there is two-fold rotation symmetry, and the [111] crystal axis (figure 3(*b*)), where the rotation symmetry is three-fold. These images clearly show patchy illumination of the Kossel lines, caused by uneven sample illumination, and faint evidence of multiple images, due to neighbouring crystal domains. The dotted lines in the line drawings show the edge of the Kossel diagram images dictated by the numerical aperture of the microscope objective.

In our first study of the blue phase Kossel diagrams [8] we simply carried out lattice parameter measurements. To our surprise we found that the diagram illustrated in figure 2(*a*) showed a crystal compression of about 5±1% along the viewing axis. This is not obvious from the diagram. This compression is slight and so extra care was taken to check possible sources of error. Imaging a diffraction grating checked for example the approximation of the Kossel diagram geometry, illustrated in figure 1. This gave twelve diffraction orders in the Kossel images and allowed calibration of the image. Further more this gave the total numerical aperture of the system as 1.23±0.01.

## Order parameters

The order parameter in the blue phases is more complex than in a nematic. There is some flexibility in the choice of an order parameter in any system. For the sake of convenience, in blue phases the anisotropic part of dielectric properties are chosen. This is similar in principle to the dielectric anisotropy but in blue phases it is described by a spatially periodic tensor. Hence, the tensor may be easily broken up into its Fourier components. Each of which relates exactly to a reciprocal lattice vector.

The application of the Landau theory [9] of phase transitions using this order parameter has been highly successful in predicting the existence of the blue phases. In particular this theory was developed by Brazovskii and co-workers [10] and Hornreich and Shtrikman [11] (see also reviews [12]). In work by Belyakov *et al.* [13] the order parameter in the blue phases was determined, to within a common scaling factor, from the blue phase transmission spectra. This momentous work also showed that the

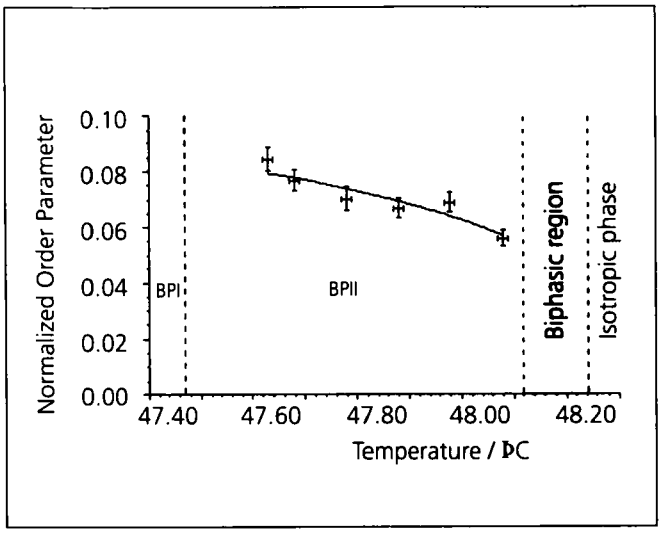


*Figure 4.* Normalized blue phase scalar order parameter in blue phase two.

complexity of the blue phase order parameter could be reduced. This is possible since the relative magnitudes of the Fourier components, numerically calculated by Landau theory, were shown to be approximately constant with temperature. Hence, a simple scalar order parameter may be factored out and was found to follow an equation of the form

$$\varepsilon_s = \alpha\left[1+\sqrt{1/9+\beta(T_c-T)}\right]$$

It can then be shown [14] using kinematic light scattering theory that the diffracted peak intensity of a Kossel line is proportional to the square of this scalar order parameter multiplied by a purely geometrical factor.

Using the blue phase two Kossel diagrams, which give a cleaner image, a whole series of diffracted intensity data points were taken at a range of temperatures across the phase. The order parameter equation was then fitted to this data and scaled to unity at zero Kelvin (figure 4). This shows an order parameter dropping rapidly by 25% over 0.5 K. The absolute values of 0.08 dropping to 0.06 are not unreasonable. However, direct comparisons with the order parameter in nematic phases are not strictly possible.

## Many wave scattering

One area in which Kossel diagrams are uniquely suited is their application to the phase problem of crystal structures. This suitability is simple due to the use of highly convergent light and the consequent frequent occurrence of many wave scattering conditions.

In the standard Bragg diffraction geometry a single parallel beam of light impinges on a periodic crystal, and only one beam is diffracted out of the incident beam path. This is one-wave scattering. More complex behaviour is possible in this experiment when the Bragg condition is met simultaneously for more than one set of planes in the sample. In this case more than one diffracted spot appears at the detector. This condition is where many-wave diffraction occurs.

Key information about the crystal is potentially available when many-wave diffraction conditions occur. This information relates directly to the relative positions of the diffracting layers within the unit cell of the crystal. However, this information is held in the relative phases of the diffracted light beams and such information is typically lost at the detector. Hence, classical X-ray diffraction can only reveal the orientation and periodicity of a set of crystal planes but not its exact position. This is the classic phase problem of X-ray crystallography, which is only recently becoming solvable with the advent of free electron lasers.

In Kossel diagrams, where a coherent light source is used, this problem is easily solved. Generally the intensity of light at one position on a Kossel line in a diagram is simply due to one wave scattering. However, where two or more Kossel lines cross many wave scattering comes into play. This is because the light is diffracted from two possible incident directions and the resulting diffracted light is combined into one output. Clearly, if coherent incident light is used, all the possible interference effects come into play and the light pattern in the region of the Kossel line crossing point reveals the relative phases of the diffraction. Hence, patterns at the Kossel line crossing points potentially reveal the final piece of the puzzle of the positions of the lattice planes in the crystal.

## Unexpected features

When we started our experiments we were aware of work by Belyakov and Dmitrienko [15] that relates to the many-wave light scattering in blue phases. In principle one simply has to solve Maxwell's wave equation. However, in the true many-wave condition analytical solutions are not possible. Belyakov and Dmitrienko approached the problem via a perturbation theory and showed that strange things do indeed happen at Kossel line crossing points.

We were surprised and delighted by the complexity of behaviour in regions where Kossel lines were close in the diagrams, but this was not all. Also we observed

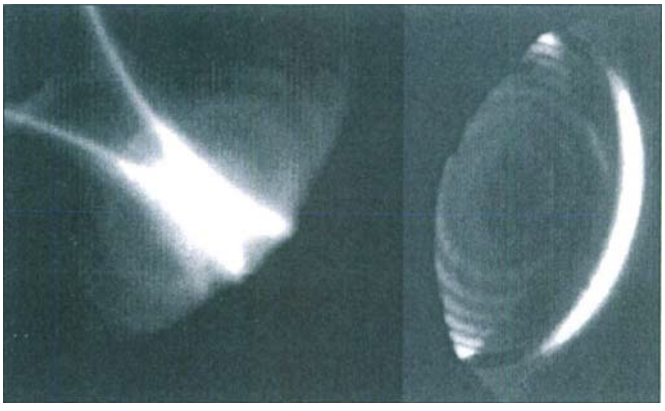

*Figure 5.* Example Kossel diagram images showing interference fringes.

interference fringes far from the isolated Kossel rings with which they were associated. To our knowledge neither of these effects had ever been observed before. Examples of these images are shown in figure 5.

A simplistic numerical model, based on summation of phasor contributions, was considered to try and reproduce the essential features of the observed many-wave effects [16]. The simplistic model successfully reproduced all of the essential interference features at the crossing point of the (110) and (101) lines in BPI and the passing point of the (100) and (010) lines in BPII. The modelled results for the crossing of the (110) and (101) lines in BPI even suggested relative phase of about $3\pi/2$ between the Fourier components. The estimated phase difference apparently contradicted the generally accepted structure of blue phase one. However, this may have been an artefact of the simplistic model and really one would need to treat the optics properly to be certain.

## Helical phases

Further surprises were in store when we used the Kossel technique to examine the properties of a twist grain boundary A phase in the material 14P1M7 [17]. This displayed a single broad annulus in the Kossel diagram, as would be expected, but also showed spiral structure within this annulus [18]. This led us to consider the better understood system of chiral nematic phases [19]. A thermochromic sample, TM533 [7], was prepared and a detailed study of the refractive index and pitch behaviour of this mixture was made using standard techniques. Finally a series of Kossel diagram images were taken on planar well-aligned samples of the chiral nematic helix. These images also showed the same spiral structure

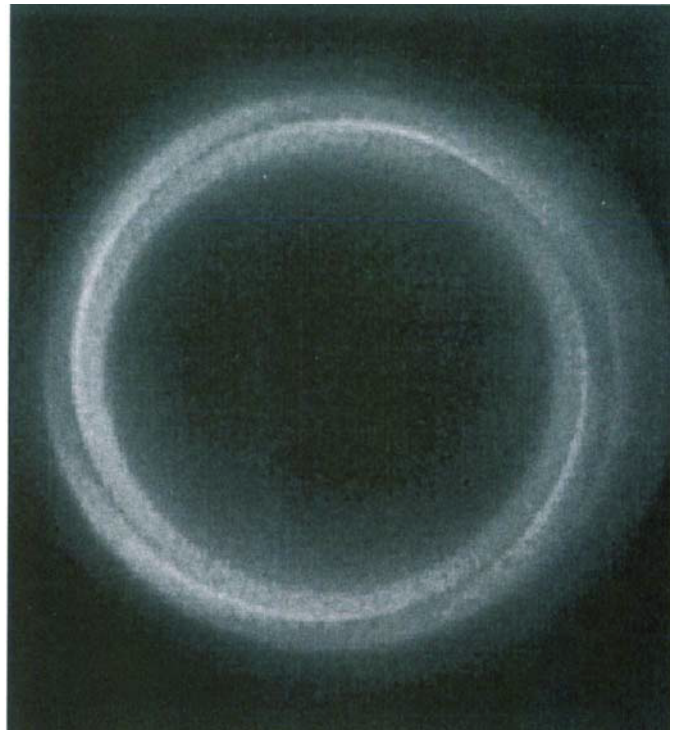

*Figure 6.* Kossel diagram of a well aligned right handed chiral nematic helix. The 'left-hand' spiral structure can be clearly seen.

(figure 6). Hence, empirically demonstrating that the optics of the TGBA phase are the same as the chiral nematic phase.

By reducing the pitch of the sample the annulus first appears as a bright circle. This circle expands and then breaks into an annulus. At this point there is no sign of any spirals. As the annulus is made to expand the spiral pattern appears within a narrow line at the centre of the bright band. Then as the annulus expands further the spiral starts to dominate the image.

Experimentally, these four spirals are found to bodily rotate with the polarizers, opposite arms being rotated by each polarizer. Also the handedness of the Kossel spiral is found to reflect the handedness of the chiral nematic helix with the 'left hand' spiral of figure 6 being caused by a right handed chiral nematic helix.

At first glance this appears to be a simple system. Several theoretical studies of oblique reflection from helical phases have been made, particularly Dreher and Meier [20], Sugita *et al.* [21], Takezoe *et al.* [22], Miraldi *et al.* [23] and Oldano *et al.* [24]. In virtually all cases the fit between numerical calculations and experimental results is near perfect. However, the lack of a true analytical solution makes understanding the spiral features complex.

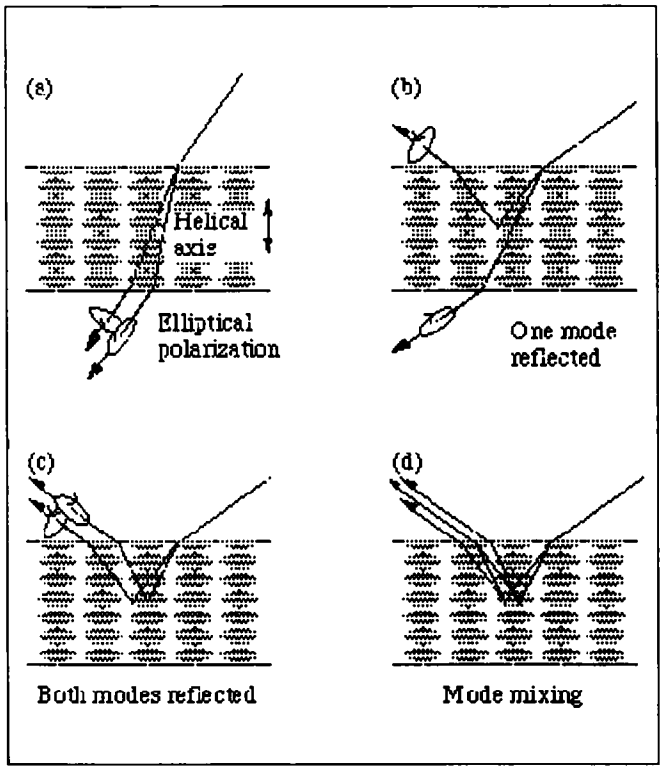


*Figure 7.* Schematic diagrams of the optical behaviour of light incident on a helix at oblique angles.

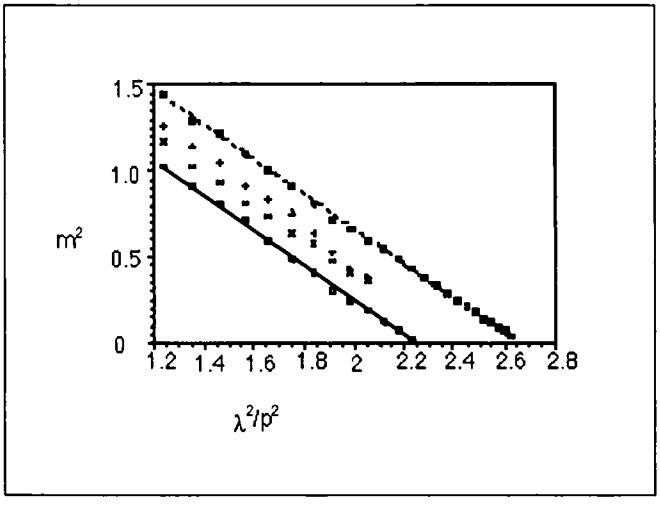


*Figure 8.* Positions of features on the Kossel diagrams of a well aligned helix. Lines are fitted to the points representing the annulus edge and are found to fit Bragg's law. Inner points represent edges of total reflection band (figure 7(c)).

Light hitting the sample, as in all birefringent crystals, splits into two components with conjugate polarization states. The polarization states vary from left and right circular polarization states at near normal incidence to linear s and p states at 90° to this. In general the polarizations are elliptical (figure 7). When the Bragg

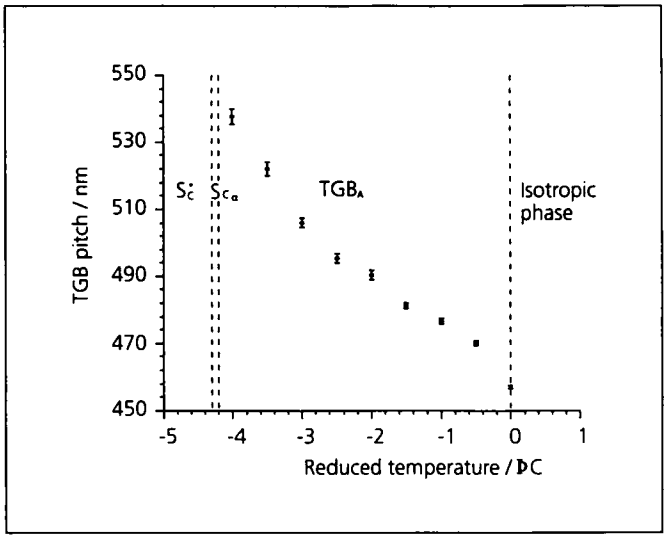


*Figure 9.* Pitch in TGBA phase measured from Kossel diagrams. Note the pretransitional pitch divergence.

condition is met then one or both of these polarized components may be reflected. Further, at very high incidence angles these two polarization states become coupled (figure 7(*d*)). We proposed that the major axis of the elliptically polarized light reflected from the sample rotates 90° from one side of the annulus to the other. This behaviour is not clear from theoretical studies, which have never considered Kossel diagrams, but this rotation is consistent with the spiral images.

## Selective reflection and Bragg's law

Bragg's law may be rewritten as

$$m^2=n^2-\lambda^2/p^2$$

where $m$ is the radial position on the Kossel diagram, $n$ is the refractive index of the medium, $\lambda$ the wavelength and $p$ the helical pitch. Taking data from the various annuli edges and plotting $m^2$ against $\lambda^2/p^2$ gives the graph in figure 8.

Clearly it can be seen that the edges of the annulus follow Bragg's law very well (figure 8). The gradients for the linear fits to the outer and inner edges are both found to be within about 2% of unity while the intercepts correspond exactly with the parallel and perpendicular components of the refrac-tive index. Having confirmed the validity of the Bragg equation measured from the edge of the annuli it was possible to derive pitch measurements from the Kossel diagrams of the TGBA phase. The final results gave the pitch variation within a 4 K wide phase to an extremely high accuracy and clearly illustrated pretransitional pitch divergence within the phase (figure 9).

## Summary

As can be seen above the Kossel diagram technique not only reveals the beautiful symmetry of periodic phases but deeper examination reveals a wealth of information about the phase structure. In the blue phases we can ascertain the orientation, periodicity and phase of all the Fourier components of the structure and the order parameter, i.e. almost a complete description of the phase. In the helical phases we can determine the pitch and handedness without even using circularly polarized light. Clearly a lot of this information is available via other techniques but rarely is so much available from the one relatively simple technique. For much of the work presented here it was not possible to do much more than a cursory study to test the potential of the technique. With more time and resources it would have been informative and fun to carry out a full study of all the blue phases and to model the results more accurately to determine completely the Fourier components. However, as is so often true in life, we were fortunate to have had the time to study such an esoteric area that we did.



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