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On the origin of Grandjean–Cano lines in liquid-crystalline blue phases

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A model is proposed to explain the Grandjean–Cano lines occurring in wedge-shaped samples of liquid-crystalline blue phases I and II. Between stretched and compressed areas of the cubic BP lattice edge dislocations occur which give rise to the observed Cano lines. The results for the BP I are in agreement with a b.c.c. lattice in (110) orientation parallel to the surface whereas for the BP II a s.c. lattice in (100) orientation was derived.

1. Introduction

In wedge-shaped samples of cholesteric liquid crystals so-called Grandjean–Cano lines can be observed by means of polarizing microscopy [1, 2]. These lines are optical discontinuities caused by singular lines in a helically structured director field alternately compressed and expanded by surface action in the wedge. In cholesterics with their optically uniaxial properties the origin of these lines is well understood [3]. Some years ago we observed Cano lines also in liquid-crystalline blue phases (BP) [4]. For these BPs which occur in several cholesterogenic systems within a tiny temperature range just below the clearing point [5, 6] a helically structured molecular distribution with a cubic symmetry has been accepted for experimental [6] as well as for theoretical reasons [7]. Some problems, however, seemed to arise when attempting to explain the Cano steps of BPs in terms of the cubic BP structure [4]. These steps must be qualitatively different from those in cholesterics but no model has been proposed hitherto [8]. In this paper we shall demonstrate that Cano steps can be interpreted in terms of edge dislocations in a cubic BP lattice built up by defects.

2. Experimental

2.1. *Cano preparation*

The samples were prepared between a glass plate and a plano-convex lens after rubbing the surfaces with diamond paste and cellulose tissue. We used plano-convex lenses of reduced thickness in order to control the temperature by a Mettler heating state, model FP 52/5. Wedges with extremely small angles were realized between two microscopic slides separated at one end by a 125 μm teflon spacer. The Cano lines were observed with a polarizing microscope, Leitz Ortholux II-Pol BK, and their distances measured by a digital ocular micrometer, Leitz ILT 2–5, from which the helical pitch was calculated by standard methods [2, 3, 9].

2.2. *Selective reflection measurements*

The selective reflection of circularly polarized light which is observed for cholesterics as well as for the BPs [5] has been measured with a Cary 17 spectrophotometer. To obtain the selective reflection of wedge-shaped samples we used a self-made microscope spectrometer; a detailed description of this is given in [10, pages 11 and 12]. From the selective reflection wavelength λ_R the lattice constant a of the cubic BP structures can be calculated by means of the Bragg equation, provided normal light incidence,

$$\lambda_R = \frac{2\bar{n}a}{(h^2 + k^2 + l^2)^{1/2}}, \tag{1}$$

with the mean refractive index $\bar{n}$ and Miller indices h, k, l.

2.3. *Mesogenic compounds*

The following cholesteryl esters (Merck, Darmstadt), were used: chloride (CC), nonanoate (CN), and benzoate (CB). As a nematogen we used 4-*n*-octyloxphenyl-4′-*n*-octyloxybenzoate (8OBE), which was prepared by a standard procedure [10]. All substances were purified by repeated recrystallization.

3. Results and discussion

3.1. *Cano lines in a monomorphic BP system*

In some cholesteric systems of appropriate helical pitches only one BP occurs which has been found generally to be of the type BP I [6, 11]. In the mixed system 8OBE/CB only the BP I occurs in the mole fraction range $0{\cdot}24 \leqslant x_{CB} \leqslant 0{\cdot}37$ [10]. We studied the Cano lines in a monomorphic system 8OBE/CB with 31·9 mol % CB. The result is shown as the microphotograph in figure 1. For smaller sample thicknesses the Cano lines appear as double lines with alternately strong and weak contrast. The double lines vanish on annealing and run together to form single lines. The orange colour of the rings is caused by the longest wavelength Bragg reflection. The maximum selective reflection has been measured in the microspectrometer at $\lambda_R = 615$ nm. For larger sample thicknesses blue platelets occur with a reflection at 435 nm but in this part Cano rings never developed. Sometimes we observed orange hexagonal-shaped liquid crystals in the wedge with a selective reflection, also at 615 nm. As described elsewhere [6, 12] these hexagonal crystals are oriented with their (110) faces parallel to the substrate. Because of their selective reflection wavelength it follows from equation (1) that the blue platelets are (200) oriented. By means of equation (1) a cubic lattice parameter $a_I = 290$ nm results from the selective reflection of the (110) and (200) oriented platelets. Using the standard calculation method for cholesterics [3, 9] the vertical spacing d between two Cano lines b_n and b_{n+1}, as shown in figure 2, can be determined from the line distance. We obtained a value $d_I = 208$ nm which corresponds neither with the optically determined lattice parameter a_I nor with the cholesteric helical pitch $p = 300$ nm of this mixture.

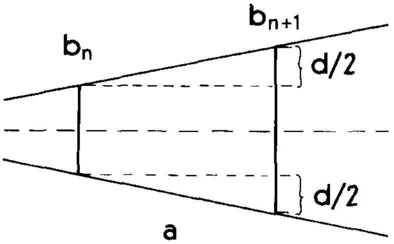

Figure 2. Wedge sample (schematic) with two Cano lines b_n and b_{n+1} demonstrating their vertical spacing d (a position of the undisturbed structure).

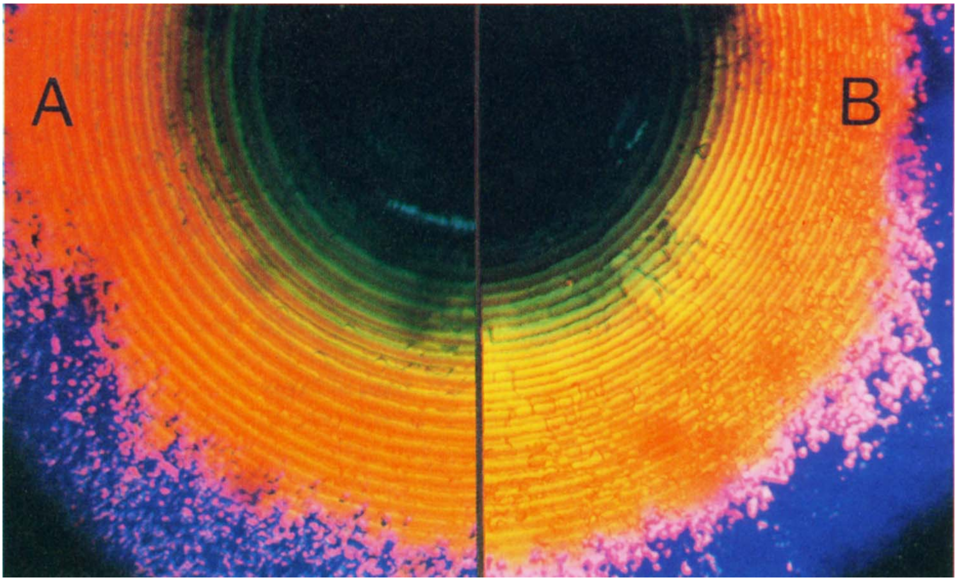

Figure 1. Microphotograph of the Cano lines in the monomorphic BP I of a 8OBE/CB mixture with 31·9 mol % CB. Wedge sample between convex lens and plane plate. Temperature 91·2° C. A, immediately after growing from the isotropic phase exhibiting double lines; B, after annealing, the double lines condensed to single lines.

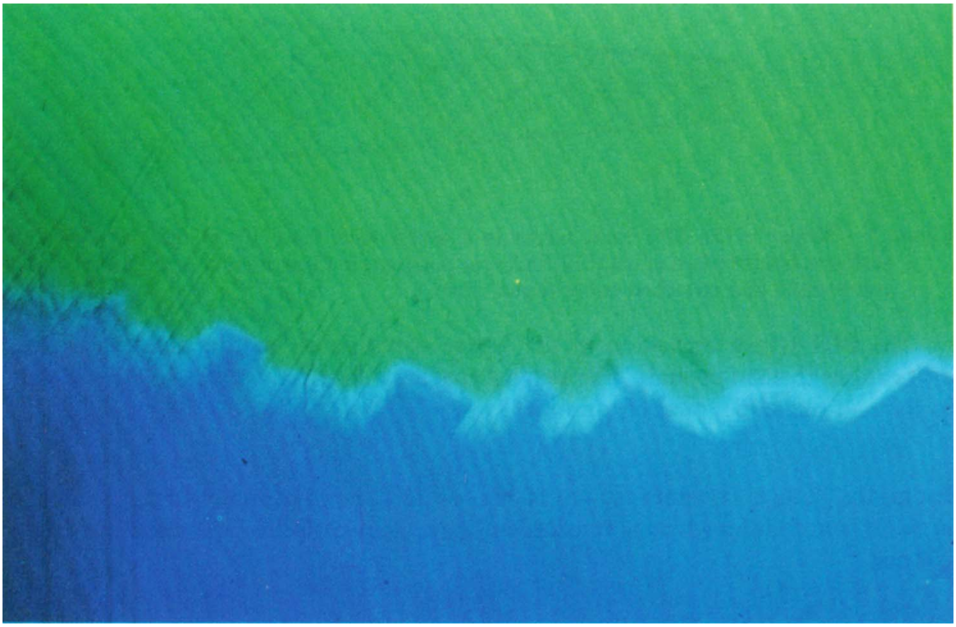

Figure 4. Microphotograph of the Cano lines in the dimorphic BP system CN/CC with 10 mol % CC at the phase boundary BP I (green)/BP II (blue), temperature 83·65°C. Sample geometry as in figure 1.

We now present a model of the BP I in the wedge which explains the origin of the Cano lines and gives a relation between the parameters $a_{\rm I}$ and $d_{\rm I}$. In our model we consider that the BP I forms a body-centred cubic lattice of singular points built up by defects [6, 7] and that the molecules adjacent to the substrates orient parallel to the rubbing direction. As shown in figure 3 the b.c.c. lattice of the BP I is arranged in the wedge with its (110) planes parallel to the glass surfaces, according to our experimental results. Because of the surface effects we find undisturbed cubes only at those positions of the wedge where the sample thickness s is an integer of the half cube diameter ($s = na_{\rm I}/\sqrt{2}$; positions *a* in figure 3). If $s \lessgtr na_{\rm I}/\sqrt{2}$ the cubes are compressed or stretched, respectively. This model is rather similar to the well-known arrangement of cholesteric helices in a Cano wedge [3]. Between the relaxed positions *a* the stretched structure switches into a compressed one because of the elastic BP behaviour [13] which results in a discontinuous spatial change of the polarizability tensor components. These discontinuities (position *b* in figure 3) can be detected in the polarizing microscope analogously to the Cano lines of cholesterics (cf. figure 1). As we can see from figure 1 the selective reflection colour between two Cano lines varies from yellow to red with a colour discontinuity just at the line. According to equation (1) this variation of Bragg scattered light can be interpreted in terms of a lattice constant variation as sketched in figure 3. This effect, which is analogous to the observation in wedge-shaped cholesterics [14], is striking evidence for the lattice compression and stretch implied in our model. Pieranski *et al.* [15] observed an analogous effect in the vicinity of a dislocation in BP I single crystals.

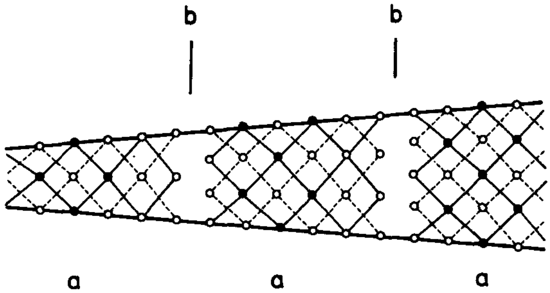

Figure 3. Model of the BP I b.c.c. lattice in a wedge with the (110) planes parallel to the surfaces. Undisturbed cubes (full circles) at positions *a*; Cano lines at positions *b* between compressed and stretched cubes (open circles).

The BP I lattice distortion in the wedge corresponds to the well-known edge dislocations in solid crystals. The vertical spacing *d* between two Cano lines is equal to the half plane diagonal of a unit cell

$$d_{\rm I} = a_{\rm I}/\sqrt{2}. \tag{2}$$

From the lattice constant $a_{\rm I} = 290\,\mathrm{nm}$ of the monomorphic BP I a value of $d_{\rm I} = 205\,\mathrm{nm}$ follows which is in excellent agreement with the experimental result of 208 nm.

3.2. *Cano lines in a dimorphic BP I/BP II system*

Mixtures of the cholesteryl esters CN and CC exhibit both BP I and BP II if the cholesteric pitch is small enough [16, 17]. Cano lines were observed in both BPs of this system, as demonstrated by figure 4. The Cano lines of the BP II (blue) run into the

BP I area (green) across the phase boundary; the ring distance, however, increases in the BP I. In the BP I we found double lines, as described for the monomorphic BP I in the preceding section, which vanish on annealing. In the BP II, however, such double rings never occur.

Adjacent to the phase boundary, BP II/BP I, straight lines at right angles occur in those parts of the BP I which have just been transformed from the BP II. These lines intersect the Cano lines at angles of about 30° and 60°. They are identical with the typical cross-hatching observed in all BP I samples just after the phase transition from the BP II [18]. This cross-hatching can be understood in terms of birefringent domains caused by a BP I paramorphosis [6]. In the wedge sample the cross-hatching anneals at a small distance of the phase boundary. The green colour of the BP I rings is due to the longest wavelength Bragg reflection. Consequently, the BP I lattice of this system is also oriented with its (110) planes parallel to the substrate as described in the previous section (cf. figure 3). In the BP II area of the wedged sample a blue colour appears which is caused by the longest wavelength Bragg reflection. This indicates that the observation direction is normal to the (100) lattice planes which are oriented parallel to the glass surface.

In a CN/CC mixture with 20 mol % CC the following data have been obtained. The BP I exhibits a long wavelength selective reflection at $\lambda_R = 604$ nm from which we derive a lattice parameter $a_I = 285$ nm by means of equation (1). From the Cano lines of the BP I we determine a vertical spacing $d_I = 214$ nm. Because of the lattice orientation given in figure 3 a lattice parameter $a_I = 302$ nm results (cf. equation (2)) which is of the order of magnitude of the value obtained by selective reflection. From the longest wavelength reflection of the BP II at $\lambda_R = 529$ nm we obtain a lattice parameter $a_{II} = 179$ nm, cf. equation (1) with (100). The vertical spacing of the Cano lines is $d_{II} = 188$ nm.

The data for the BP II cannot be interpreted in terms of the model used for the BP I (cf. figure 3). For the BP II we consider a simple cubic lattice in the wedge with (100) lattice planes parallel to the substrates; the model is shown in figure 5. Because of the surface effects the s.c. lattice can be arranged in the wedge without stress only at those positions (*a* in figure 5) where the sample thickness s is an integer of the lattice constant a_{II}. If $s \lessgtr na_{II}$ the cubes will be compressed or stretched. At certain positions (*b* in figure 5) the structure switches from compressed into stretched cubes because of the elastic forces [13]. The result is a discontinuous change of the polarizability, observable as a Cano line. Comparable to the model given for BP I (cf. figure 3) the lattice distortion in the wedged BP II can again be understood in terms of edge dislocations.

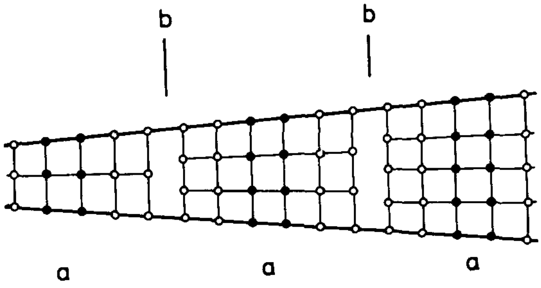

Figure 5. Model of the BP II s.c. lattice in a wedge with the (100) planes parallel to the surfaces. Designations as in figure 3.

However, our data of the BP II are in agreement only with a simple cubic lattice oriented with its (100) planes parallel to the wedge surfaces. In this case the vertical spacing d_{II} must be equal to the lattice parameter a_{II} of the s.c. unit cell. The experimental values are nearly equal within the limit of experimental error and support the proposed s.c. cubic model.

3.3. *Phase transition BP I/BP II in a wedge*

The phase transition between the BP I and the BP II is shown in figure 4. Comparing the models of the two BPs in a wedge given in figures 3 and 5 we can derive the following structure change. A unit cell of the b.c.c. BP I lattice in (110) orientation with a lattice parameter a_{I} transforms into a unit cell of the s.c. BP II lattice in (100) orientation with a lattice parameter $a_{\mathrm{II}} = a_{\mathrm{I}}/\sqrt{2}$. During this transition additional singular points must be created; a b.c.c. structure with the lattice parameter a_{I} contains two lattice points in the unit cell with volume a_{I}^3 whereas in a s.c. lattice with a parameter a_{II} only one lattice point is given in a unit cell with volume a_{II}^3. Since, in our case, we have $a_{\mathrm{II}} = a_{\mathrm{I}}/\sqrt{2}$ it follows that after the BP I → BP II transition there are $2^{3/2}$ s.c. unit cells in the initial volume a_{I}^3. Thus, the number of lattice points increase by a factor of $\sqrt{2}$ accompanied by a contraction of the Cano lines as observed experimentally. Since the texture does not change drastically across the phase boundary BP I/BP II (cf. figure 4) reorientation on a molecular scale is not expected to be too dramatic which also follows from the extremely small enthalpy of this transition [5]. The lattice transformation during the phase transition, however, causes a mechanical strain which leads to birefringence domains along the [110] direction, observable as the cross-hatching in figure 4 [6, 18].

3.4. *Cano double lines*

Sometimes pairs of Cano lines (double lines) have been observed in wedge-shaped BP samples. Three facts must be summarized:

(i) double lines only occur in the BP I (cf. figure 1 A) but have never been observed in the BP II (cf. figure 4);
(ii) they appear if the BP I grows from the isotropic liquid (figure 1 A) as well as from the BP II (cf. figure 4);
(iii) the double lines anneal in time (cf. figure 1 B).

In cholesteric wedges double lines have been observed and explained by the dissociation of a χ disclination line into a $\lambda^+\lambda^-$ pair (cf. [3], figure 6.25). As there are some different possibilities of the director field topology in the BP I lattice structure with I $4_1 32$ symmetry [19, 20] it cannot be decided if the BP I double lines are of the same origin as in cholesterics. In this context the observation of pairs of steps on (100) faces of BPI crystals as described by Pieranski *et al.* [15] should be considered. They explained the existence of double steps by a double periodicity of the potential V_{110} governing the surface energy in the [110] direction. Additional to the periodicity a_{110} they discuss the possibility of secondary minimum of slightly increased height in the surface energy along [110]. As we have found Cano double lines only in the (110) oriented BP I the two different values in surface energy may cause two different anchorings of the (110) planes which lead to the observed double lines in the transition region between the compressed and stretched lattice. As the orientation with lower surface energy is favoured annealing of the double lines is plausible.

4. Conclusions

A model has been proposed to explain the Cano lines which occur in wedge-shaped samples of the BP I and BP II. The BP Cano lines are quite similar to those observed in cholesteric samples though the director configuration are basically different for these phases. The BP Cano lines can be interpreted in terms of edge dislocations between different areas of the BP lattice which are either compressed or stretched by means of surface action in the wedge. Our results for selective reflection and ring distance for the BP I are consistent with a b.c.c. lattice in (110) orientation with respect to the wedge surfaces. In the BP II, however, our results are in agreement with a s.c. lattice in (100) orientation and provide additional evidence that the BP II must be simple cubic, which is still a controversial problem.

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