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M. Marcus

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Quasicrystalline behaviour and phase transition in cholesteric « blue » phase

M. Marcus

Bell Laboratories, 600 Mountain avenue, Murray Hill, New Jersey 07974, U.S.A.

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Résumé. — L'hypothèse dite « quasi-cristalline » (QC) énonce que la phase bleue (BP) d'un cholestérique est ordonnée comme un réseau périodique tridimensionnel. Les propriétés physiques et la morphologie de la phase bleue sont discutées en fonction de cette hypothèse (QC). Puisque la longueur d'onde associée à la période du réseau cristallin de cette phase est dans le domaine du visible, il est possible de voir au microscope les effets de la diffraction de Bragg soit par transmission, soit par réflexion.
L'expérience qui permet de vérifier cette hypothèse est décrite.
L'existence d'une phase qui peut être interprétée comme un état « liquide » de la BP cristalline est signalée pour la première fois. Lorsque cette phase est présente, on la trouve dans une gamme de température très étroite entre la BP cristalline et l'état isotrope liquide du cholestérique. Elle a l'aspect d'un brouillard uniforme dont le pouvoir rotatoire tourne dans la même direction que celui de la BP cristalline.
On montre que les défauts de la BP peuvent être interprétés comme des dislocations. Ceci est un argument supplémentaire en faveur de l'hypothèse QC. Lorsque ces défauts sont disposés linéairement, ils ont les mêmes propriétés que les joints de grains à petits angles.
Finalement, on discute dans le contexte de l'hypothèse QC, la transition de phase trouvée par Bergmann *et al.* en mettant l'accent sur les observations de la morphologie de croissance.

Abstract. — The properties and morphology of the cholesteric « blue » phase (BP) are discussed in terms of the « quasicrystalline » (QC) hypothesis, which states that the BP is ordered with three-dimensional translational periodicity. The lattice parameter of the « crystalline » BP is comparable to optical wavelengths, giving rise to Bragg diffraction effects. These effects provide the means by which the BP is made visible in reflection and transmission microscopy. Experimental evidence is presented which backs up this claim.
A phase which may be the « liquid » version of the « crystalline » BP is reported for the first time. This phase looks like a uniform fog, with optical rotation in the same direction as the BP, and exists for some compounds in a narrow temperature range between the BP and isotropic state.
Defects in the BP are shown, and found to be explainable as dislocations, further supporting the QC hypothesis. Linear arrays of such defects are found to occur, and to have the properties expected of low-angle grain boundaries. The phase transition seen by Bergmann *et al.* is discussed, with emphasis on the growth morphologies observed, and how it fits into the QC hypothesis.

1. **Introduction.** — The cholesteric « blue » phase (called BP hereafter) is a modification of the cholesteric state, occurring in a narrow range of temperatures between the cholesteric and isotropic phases. This phase is characterized by a distinctive « platelet » texture, selective reflection of a single wavelength and sence of circular polarization, and optical isotropy [1]. There is some theoretical [2] and experimental [3] evidence suggesting that the order parameter in the BP is a three-dimensionally periodic function of position, with a cubic space group. In other words, the BP is ordered with crystalline symmetry. The lattice parameter is generally comparable to the wavelength of visible light, accounting for the observed effects. The coloured « platelets » observed under the microscope are thus analogous to the grains in polycrystalline solids.

In this paper, it will be shown that many of the features the BP shows in reflection and transmission microscopy are explained by the « quasicrystalline » (QC) hypothesis (the idea that the BP has crystalline symmetry, and thus crystal-like behaviour in some respects), including some phenomena reported here for the first time. These « new » phenomena include the appearance of defects resembling dislocations and grain boundaries (low- and high-angle), anisotropy of growth of the BP from isotropic liquid, and oriented growth in the « solid-solid » phase transition [10].

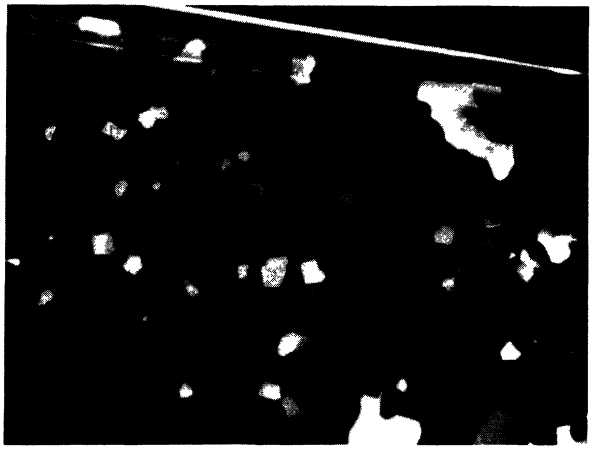
2. **Experimental.** — Several compositions were used in this study : CNCCl, consisting of 15 w/o cholesteryl chloride in cholesteryl nonanoate (CN), CPCBOOA, made of 20-40 w/o cholesteryl proprionate in CBOOA, and CN6OCB, which is 25 w/o 6OCB in CN.

Pure compounds were also examined, and with the exception of the phase transition discussed below, they showed the same phenomena that were exhibited by the mixtures. The mixtures were used for most of the work reported here because the addition of a nematogen to the cholesterogen makes the BP appear with a longer lattice parameter (wide range of colours visible), and brighter platelets than is the case for pure cholesterol derivatives. The nematogen addition lengthens the pitch of the cholesteric, thus bringing the selective-reflection wavelengths farther into the visible band. Also, the dielectric anisotropy of the nematogen is usually greater than that of the cholesterogen, thus improving the brightness of the BP.

All compounds were used as-received, with no further purification. If the components were recrystallized from hot hexane, the transition temperatures would be raised by about two degrees, but the purification did not induce any qualitative changes, so was not used. All compounds except cholesteryl nonanoate and 6OCB were purchased from Eastman Organics. The CN was obtained from Van Schuppen, and the 6OCB from BDH. The components were weighed into a vial and stirred. The vial was placed in a vacuum oven in which it was heated overnight to temperatures above the isotropic point. Samples were vacuum-loaded into flat capillaries. The capillaries were 0.1-0.2 mm thick, and were sealed off after loading. This procedure produced stable samples which did not degrade after repeated cycling to the clearing point.

The samples were observed in a Mettler FP5/52 hotstage, using a polarizing microscope with reflection objectives. The light source was heavily filtered to cut down on the heat reaching the sample. This precaution was needed in order to avoid temperature gradients caused by the light. Also, if the filters were omitted, a switch from transmission to reflection mode caused structural changes in the BP, due to the temperature change produced by the shifting illumination. Crossed polarizers were used both in transmission and reflection. No contrast was visible without polarizers in transmission. In reflection mode, the contrast was vastly improved by the use of polarizers, since the light reflected from the BP was circularly polarized, and the background light reflected from the capillary had the same polarization as the incident light.

3. **Results.** — 3.1 « POLYCRYSTAL » STRUCTURE AND OPTICAL PROPERTIES. — First, let us review the well-known features of the platelet texture to see how they fit into the QC theory. In reflection, the sample looks like a collection of bits of coloured, metallic foil, floating at different heights within the thickness of the specimen as shown in figure 1*a*. The reflected light one sees is circularly polarized, as mentioned above. However metallic the platelets look, they are also transparent, in the sense that other platelets are visible below a given platelet. There are usually areas which appear to be devoid of platelets. When examined in transmission, between crossed polarizers, these areas turn out to be occupied by platelets that are invisible in reflection. Figures 1*a* and 1*b* show the same area in both viewing modes. In the QC theory, the reflected light comes from Bragg diffraction. Thus, for a platelet (i.e. crystal) to be visible, it must be oriented with a reflecting plane forming equal angles to the incident and observed ray. Platelets for which no such plane exists are therefore invisible in reflection.



a) Reflection.

b) Transmission.

Fig. 1. — *a*) BP of CN-40 w/o CBOOA in reflection. *b*) Same area as in figure 1*a*, but in transmission.

This point was checked by reducing the range of directions of the incident beam (originally a cone, centred about the microscope's optic axis), and noting that many of the platelets disappeared, while the brightness of some was unchanged. This test verified that each visible platelet reflected only the rays

coming from a small set of directions. It was noted that the platelets are all slightly different in colour. This effect is a consequence of the fact that the angle between the incident and observed rays was not perfectly well-defined. Thus, by Bragg's law, the platelets which reflect light through the largest angles would reflect the longest wavelengths. This was verified by noting that the sample appeared bluer when viewed from the side ($\theta = 45^{\circ}$) than when seen in back-reflection. The selectivity in angle and wavelength gives rise to the impression of transparency mentioned above. Consider two platelets, A and B, of slightly different orientations, with the light coming from above. Assume that A is above B. Since A and B are of different orientations, any light that will reflect from A will not bounce off B, and *vice-versa*. Thus, A reflects some light and is visible, and it transmits unaffected all other light, included in which is all the light of the correct direction and wavelength to be reflected by B. Thus, the apparent brightness of B is unaffected by the presence of A. The « metallic » appearance of the platelets is probably due to the specular nature of Bragg diffraction. One of the obvious questions is why the platelets appear so two-dimensional. Although the BP looks like a collection of thin flakes in an isotropic matrix, I know of no theory which states that this appearance is the true state of the BP. However, the QC model offers an explanation for the discrepancy between theory and observation. It is known that diffraction from a uniform cholesteric texture can be dynamical, i.e. the diffraction is so strong that the incident beam does not propagate very many layers into the bulk before being scattered. The superficial appearance of the platelets may be explained by assuming a Darwin width of a few percent, a figure consistent with preliminary results of a diffraction experiment now being performed, and with well-known results for cholesterics. If the Darwin width is 2 %, and the lattice parameter is 2 000 Å, then the extinction depth is ten microns. Since typical platelet dimensions are an order of magnitude larger than this length, only the top layer contributes to the observed scattering. These dynamical effects would also explain why platelets which are heavily loaded with defects are often brighter than perfect ones, just as the X-ray diffraction intensity from a crystal can be increased by surface damage.

Now, let us consider what the BP looks like in transmission mode. For concreteness, pick a platelet which would back-reflect left-circularly-polarized (lcp) light at a wavelength of 5 000 Å. Now, suppose that this platelet is oriented with the normal to the reflecting planes 37° away from the incident ray direction. Then, lcp light of wavelength 4 000 Å is reflected by the platelet and does not reach the objective lens. Right-circularly-polarized (rcp) light, and lcp light of wavelengths other than 4 000 Å passes through the platelet unaffected. Since transmission observation is done with crossed polarizers, the linearly-polarized light with $\lambda \neq 4\,000$ Å will not pass through the analyser. The situation with respect to light of $\lambda = 4\,000$ Å is different. There, the linearly-polarized light from the polarizer becomes right-elliptically-polarized, since some or all of the lcp light is scattered away. Some of this light thus passes through the analyser. Thus, the platelet shows up as violet (4 000 Å) in transmission, and may not be visible at all in reflection, depending on the geometry of illumination. If we assume that the reflection observation is done in back-reflection (nearly true for this investigation), we find that the colour seen in transmission must be blueshifted from that seen in reflection, the amount depending on the orientation of the platelet. We thus predict a multi-coloured appearance in transmission, especially if there are more than one possible reflecting plane, which Meiboom and Sammon's [3] work indicates is generally true.

Figure 2 shows a sample of CP-40 w/o CBOOA photographed in transmission in sodium-vapour light in three ways : crossed polarizers (*a*), lcp light (*b*), and rcp light (*c*). In figure 2*a*, the platelets are light on a dark backround, for reasons explained above. In figure 2*b*, the platelets appear dark on a light ground, with those that were lightest in figure 2*a* appearing darkest in figure 2*b*. In figure 2*c*, the platelets don't appear at all. The platelets appear dark in figure 2*b* because they scatter away some of the light. Some platelets look almost black, indicating that their diffraction efficiency can be very high. These are the platelets one would expect to show up the most brightly with crossed polarizers, as is seen. No platelets appear in figure 2*c* because rcp light is not reflected at all by any platelet.

The chirality of the reflection has another effect. Consider light of the polarization which is diffracted (rcp in the above example). The sharp resonance in the reflection as a function of wavelength should, by Kramers-Kronig arguments, be accompanied by a dispersion-like shift in the refractive index for this polarization as shown in figure 3. De Vries' theory [4] for cholesterics predicts a similar result. Since this effect occurs for one polarization and not the other, one would expect a wavelength-dependent rotation of the plane of polarized light. This rotation was in fact observed by Bergmann *et al.*, and by Brog and Collings [5], who found that the rotation got larger as the incident wavelength got closer to a « reflecting » wavelength. For a sample of thickness 0.2 mm, such as was used in this study, the maximum rotation would amount to about 2°. The rotation is thus a small effect compared to the reflection of all the rcp light of certain wavelengths, and shows up principally when the polarizers are not exactly crossed.

In figure 1*b*, we see the bright platelets with dark lines as borders. In reflection, the border between two highly-visible platelets appears dark, while that between two barely-visible ones shows up as a bright line (Fig. 4). In the QC theory, since the platelets are

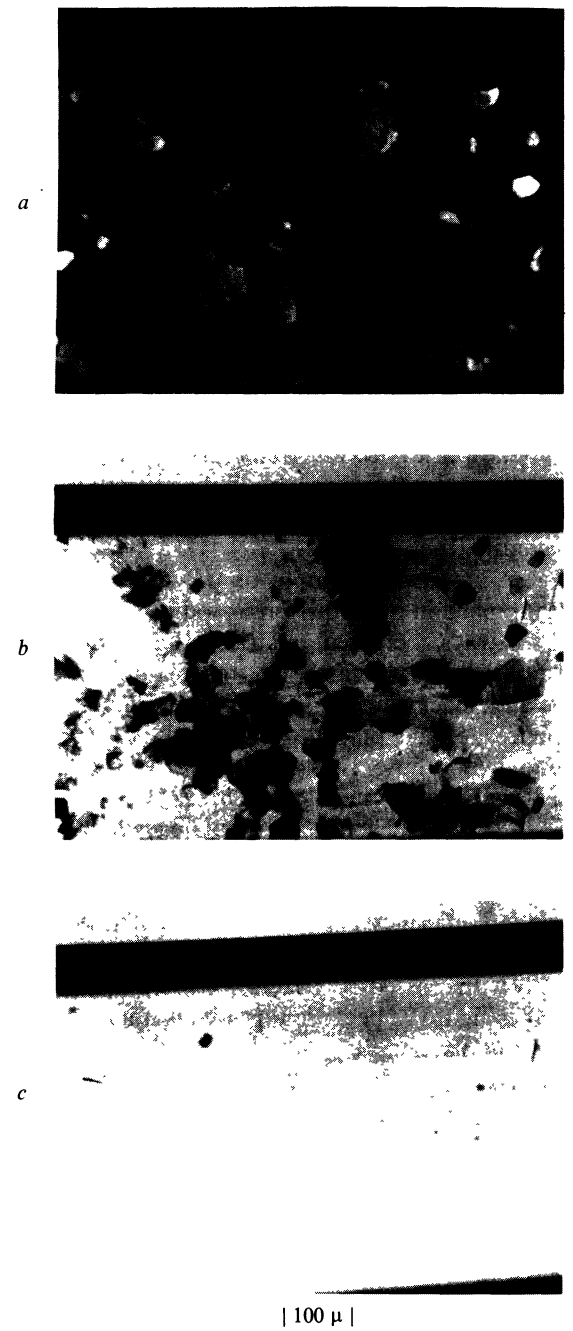


Fig. 2. — *a*) 40 w/o CBOOA in CP, 102.99°, seen in transmission with Na-vapour light, with crossed polarizers. *b*) The same area as figure 2*a*, but seen in lcp light. *c*) The same area as figure 2*a*, but seen in rcp light.

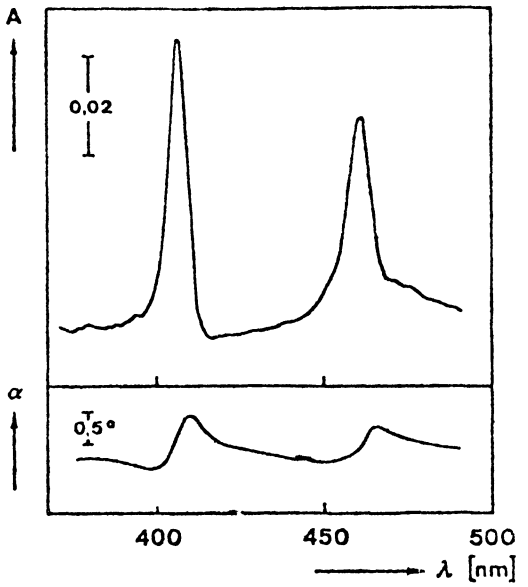
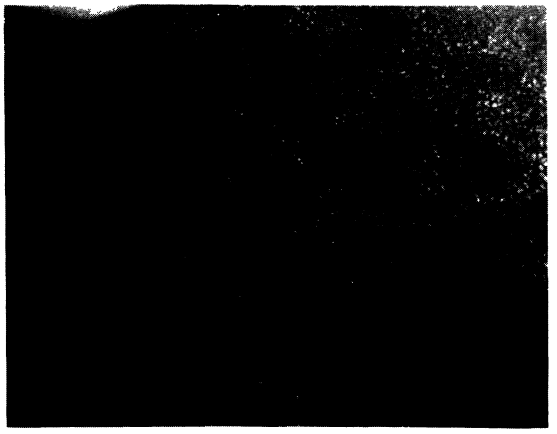


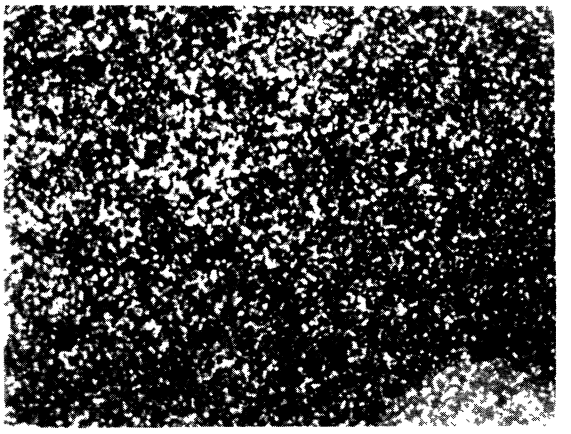
Fig. 3. — Selective light reflection $A(\lambda)$ and optical rotatory dispersion $\alpha(\lambda)$ of CN at the BPI ↔ BPII transition, from reference [10].

Fig. 4. — Reflection photograph of high-temp. BP in CP-40 w/o CBOOA showing dislocations and high- and low-angle grain boundaries.

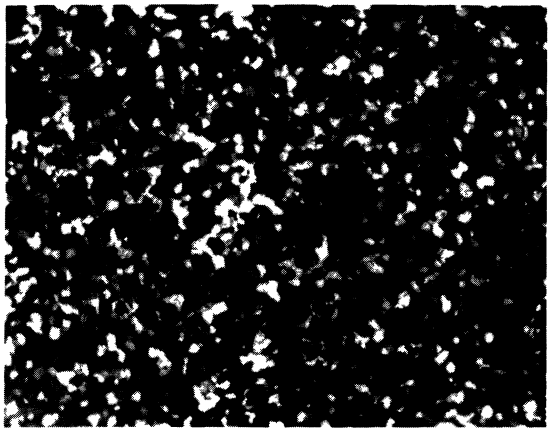
« crystals », the borders must be « grain boundaries ». In a solid polycrystal, a grain boundary is a region of strain, and shows up dark in bright-field TEM and X-ray topographic photographs. Similarly, a strained area between two platelets is not likely to diffract light in the same way as either platelet. Thus, a boundary between two bright platelets is itself dark. Similarly, if the platelet reflects weakly, the scattering may be enhanced near the boundary, if the local orientation in the strained region satisfies the Bragg condition better than that in the unstrained areas. Thus, between two dark platelets, one can get either a dark line (strain in wrong direction for reflection), or, more rarely, a bright boundary, as mentioned above. The shapes of the platelets greatly resemble those found in equiaxed, annealed polycrystals [6]. Five, six, and seven-sided platelets are common, and boundaries always intersect in threes and curve gently if at all. In polycrystals, these features result from the movement of grain boundaries so as to reduce the total boundary area, and thus the energy. Such motions were observed in this investigation. Small grains were seen to disappear, while larger ones grew, so that the average grain size increased with time. Figures 5*a-d* show this process at times of 0.083, 0.5, 4.2, and 135 min. after the sample was quenched from the isotropic to the blue phase.



a) 1/12 min.



b) 0.5 min.



c) 4.2 min.

d) 135.5 min.

Fig. 5. — *a-d*) Coarsening of platelets in CP-20 w/o CBOOA, seen in transmission. Times since cooling to the BP are 1/12, 1/2, 4.2, and 135.5 min.

Grains were seen to change from their initial forms (squares, blobs, or needles — see below) into the convex, 5, 6, or 7-sided polygons typical of the later stages of the coarsening process.

3.2 INITIAL GROWTH. — There are two situations in which the BP may appear totally featureless, like a fog. In certain mixtures, as the sample is cooled from the isotropic phase, the first texture to appear is a faint blue or gray fog, which persists over a temperature range of less than 0.1° before being replaced by platelets. This behaviour is seen in mixtures of cholesterol nonanoate with cholesterol chloride, and 6OCB, as well as in pure cholesterol nonanoate. An example is shown in figure 6, which shows a capillary filled with CN-6OCB (37.5 w/o) along which is a temperature gradient. To the right, the mixture is isotropic, to the left it is BP, and in the middle is the fog. The fog persisted overnight, leading to the conclusion that it is a stable phase. Observation in transmission and reflection at magnifications of several hundred fail to show any structure in the fog. The fog shows optical rotation and no conoscopic figure, like the BP. Note that the fog has sharp boundaries with the isotropic and « blue » phases. This observation precludes identification of the fog with opalescence due to pre-transition fluctuations or segregation, both of which would gradually tail off into the isotropic phase.

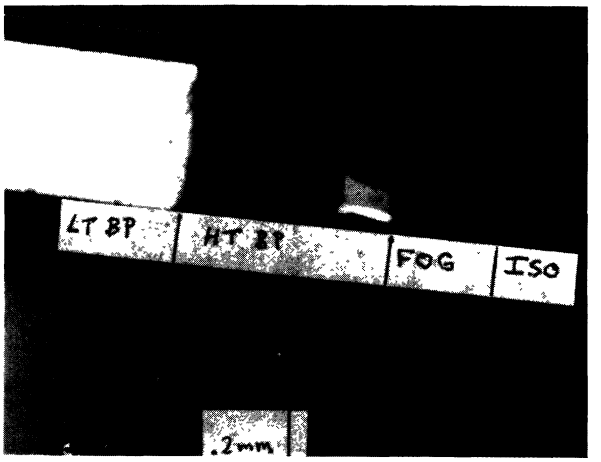


Fig. 6. — Blue fog, isotropic, and both « blue » phases in CN-25 w/o 6OCB.

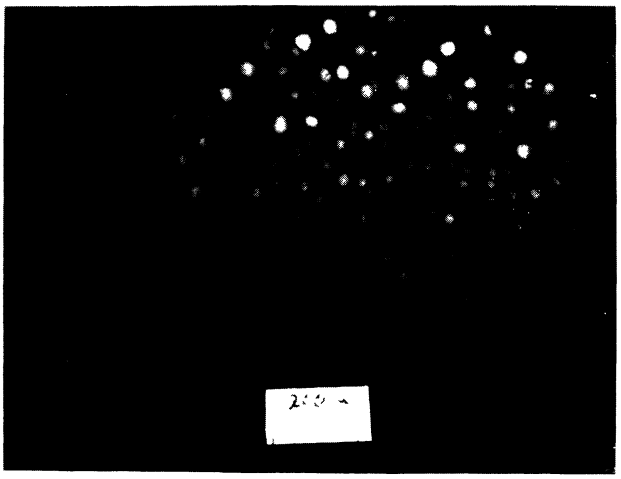
It may be speculated that if the BP is a « quasi-solid » then the fog is a « quasi-liquid », bearing the same relation to the BP as a liquid does to a solid. Such a « liquid » would show all the properties outlined above. It is reasonable to expect the « quasi-liquid » to be stable at higher temperatures than the BP. Carrying the analogy further, one arrives at the conclusion that the fog should show a diffuse Bragg reflection roughly corresponding to the most intense « crystal » reflection. Meiboom and Sammon have observed such a reflection at temperatures just below the isotropic point [7], in mixtures for which I have seen the fog. However, since Meiboom's apparatus does not allow microscopic observations, the identification of the diffuse scattering with the fog remains speculative.

The second circumstance under which the BP looks foggy occurs when the sample is rapidly quenched from the isotropic state. A green fog (CN-CCl mixtures) forms, in which tiny platelets are seen after a few seconds. The platelets grow as described above into a typical platelet texture. The green fog is optically rotatory as is the blue fog described above, and shows no features. It may be speculated that if the blue fog is a « liquid », then the green one is a supercooled « liquid » which « crystallizes » into platelets. The colour difference between the fogs is similar and probably related to that between the platelets at low and high temperatures. In other words, the temperature dependence of the lattice parameter could explain the colour difference between green and blue fogs.

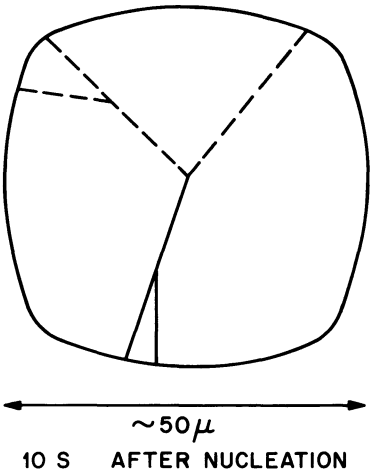
In most cases, the fog is not seen, so the first appearance of the BP on cooling from the isotropic is in the form of platelets. In all cases, the platelets start from isolated nuclei and grow outward until they impinge on each other. This behaviour is typical of first-order transitions, such as the freezing of a liquid. Depending on the sample's composition, the platelets may emerge as circles, squares (including rounded squares and four-pointed stars), « dendrites », or irregular shapes. Sigaud [8] has observed hexagonal platelets in CN-2-(4'-n-heptyloxy benzylideneamino) fluorenone. The circles are seen in CN-CBOOA with > 40 w/o CBOOA, and in CP with < 20 w/o CBOOA. An example is shown in figure 7*a*. The platelets start out as monochromatic circles, but soon develop grain boundaries as shown in the figure. The circular shape may be a result of interfacial tension between the blue and isotropic phases. When two of these « droplets » come together, they coalesce, forming a larger droplet.

Rounded squares are seen in CN-6OCB (25 w/o). A drawing of such a platelet is shown in figure 7*b*. Platelets of this type often show low-angle grain boundaries radiating out from the centre.

In figure 7*c*, we see the « star » and « dendritic » modes. The platelet starts as a tiny square or four-pointed star. As it grows larger, it develops « arms » growing out of the sides of the square. Later, the



a)



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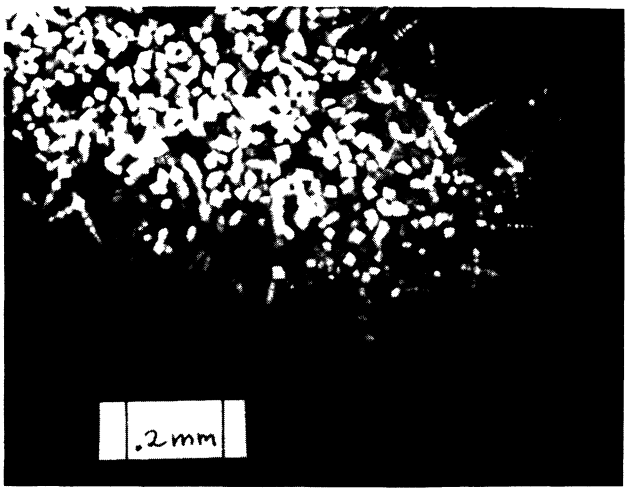


c)

Fig. 7. — *a)* Round platelets growing from isotropic in CP-5 w/o CBOOA. This compound seems to have only the low-temp. BP. (Photograph courtesy P. Finn.) *b)* Drawing of « rounded-square » morphology in CN-6OCB. *c)* « Star » nucleation and dendritic growth in CP-40 w/o CBOOA.

edges of the « arms » become wavy, with the waves becoming deeper. These waves then grow into new arms at right angles to the original. This process demonstrates the dendritic [6] instability which is well-known in, but not restricted to crystalline solids. The growth of the waviness shows that the BP-isotropic interface was unstable against sinusoidal perturbations — the essence of the dendritic instability.

The square shape of the initial platelets in some mixtures is most naturally interpreted in terms of crystalline growth anisotropy. This picture would require that the slowest-growing planes would be perpendicular to each other. Since the structure of the higher-temperature BP is not yet clear, it is impossible to identify the slow-growing planes.

The growth process provides some evidence concerning structural anisotropy in the BP. This point will come up again in the discussion of the BP-BP transitions. The occurrence of dendritic growth is another bit of testimony to the analogy between the BP and solid states.

3.3 DEFECTS AND STRAINS. — Elastic strains in solids can be detected by their effect on the Bragg diffraction. In figure 8, we see what may be a similar effect in the BP. One of the larger platelets reflects light only from some areas, and not from others. In transmission, the colour of this platelet was found to vary smoothly from one end to the other. This behaviour is what would be expected from an elastically-bent platelet. A very rough estimate of the strain, based on assumed values of thickness and the angle through which the platelet is bent, is about 0.5 %.

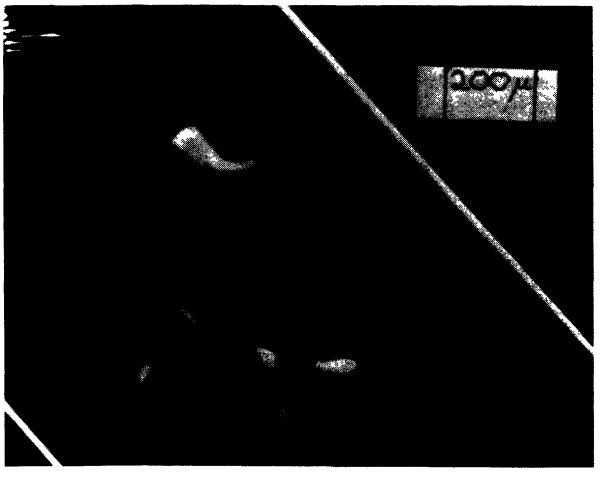


Fig. 8. — Elastically strained platelet in reflection (CP-40 w/o CBOOA).

In figure 4, we see platelets with what appear to be black dots on their surfaces. If these dots are examined in detail, one finds a « halo » around each dot. The « halo » is black on one side, and light on the other, indicating the presence of a dipole-like strain field. In some cases, the platelet is dark, and the dots are bright, in analogy with the grain-boundaries mentioned above. In transmission, the dots appear as black dots or lines, as shown in figure 9. The dots often appear in linear arrays, as seen in figures 4 and 9. An orientation difference is often visible between areas on either side of such a line.

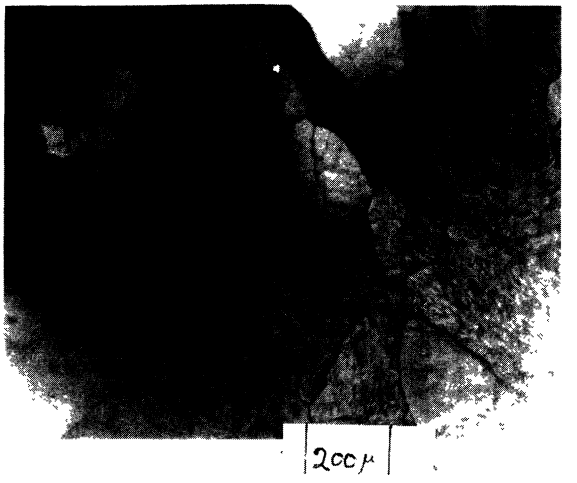


Fig. 9. — Dislocations seen in transmission in low-temp. BP in CN-15 w/o CCl.

The only defect I can think of which would have all the properties just listed is a dislocation with an edge component. Such a defect would have a dipole-like strain [9]. In thin films (a BP sample with $d_0 = 2\,000$ Å and a thickness of 50 μ has 250 lattice planes, as would a solid sample only 800 Å thick), dislocations tend to end at the film surfaces. Therefore, since only the top 10 μ of a platelet is visible in reflection, one would see a dot or a short line, surrounded by its strain field, just as observed. In transmission on thick samples, one would see dark lines, while thin samples (say 20 μ or less) would show dots, since dislocations would tend to shorten themselves by orienting perpendicular to the sample plane. This behaviour is also observed.

Some dislocations show a « strain-halo » that is small and circular, which could be explained if the dislocation had no edge component. Such dislocations have strain fields of circular symmetry.

A low-angle tilt boundary can be analysed as a string of identical dislocations [6]. Figure 4 shows a number of such strings. In one (in the upper left), an orientation difference across the boundary is visible. Close inspection of figure 9 will reveal some planes covered with a regular « hatching » of dislocations. Such areas are probably grain boundaries seen from an angle. In all cases, the dislocations forming an array show strain fields whose dipole axes point in the same direction, indicating that the Burger's vectors are identical, as would be required for the array to be a grain boundary. The spacing between dislocations in an array have been seen to vary from nearly-

imperceptible to $> 10\,\mu$. As a general rule, colour shifts across the array were greater for arrays with the smallest spacings, as expected, since the orientation difference across a boundary is inversely proportional to the spacing [6]. The arrays with very small spacings looked much like high-angle grain boundaries. We thus go continuously from isolated dislocations to a high-angle grain boundary.

The identification of defect arrays with low-angle grain boundaries makes it necessary for the defects to be dislocations, since the units making up the boundary must have the sort of long-range strain field characteristic of a dislocation. Any other type of strain would not result in an orientation change without other long-range strain.

By watching an area for a few minutes, it is possible to see dislocation motion. Dislocations usually move towards a high-angle grain boundary, not necessarily the nearest, at which point they are swallowed up by the boundary and lost. This is the eventual fate of isolated dislocations. In low-angle boundaries, the dislocations can move outward toward the high-angle boundaries at each end of the low-angle boundary. The net effect is then a decrease in the dislocation density along the low-angle boundary. In other words, the grains on either side rotate to decrease the mismatch between them until the boundary disappears. If the dislocations don't move outward, then the whole boundary can move in a direction perpendicular to itself. The elastic forces between dislocations keep them in line while the whole array moves, and eventually collides with high-angle boundaries. Dislocation annihilation has also been seen. Two dislocations approach each other and merge into a black dot (seen in transmission), which then shrinks and disappears.

So far, I have not mentioned how dislocations are created. No dislocation-creation has been observed while the sample is in a single phase, possibly because there is little mechanical stress on the sample. However, when a phase transition occurs, the resulting platelets are full of dislocations. Figures 4 and 9 show samples which were taken from the low-temperature BP (see below) to the high-temperature BP. The change in « crystal » structure produces many residual defects.

3.4 PHASE TRANSITION IN THE BP. — In figure 10 is shown a sample of CN-6OCB above (10*a*) and below (10*b*) its BP-BP phase transition [10]. The overall colour of the sample, seen in transmission, changes from green (above) to red (below). Also, the low-temperature phase shows parallel streaks rather like those seen in solids with crystal-crystal phase transitions. The obvious question at this point is whether both phases are really « blue » phases. I have observed all the phenomena described above (growth from the isotropic excepted, of course) in both phases. The optical properties and defect structure of both phases are as described above. Therefore,

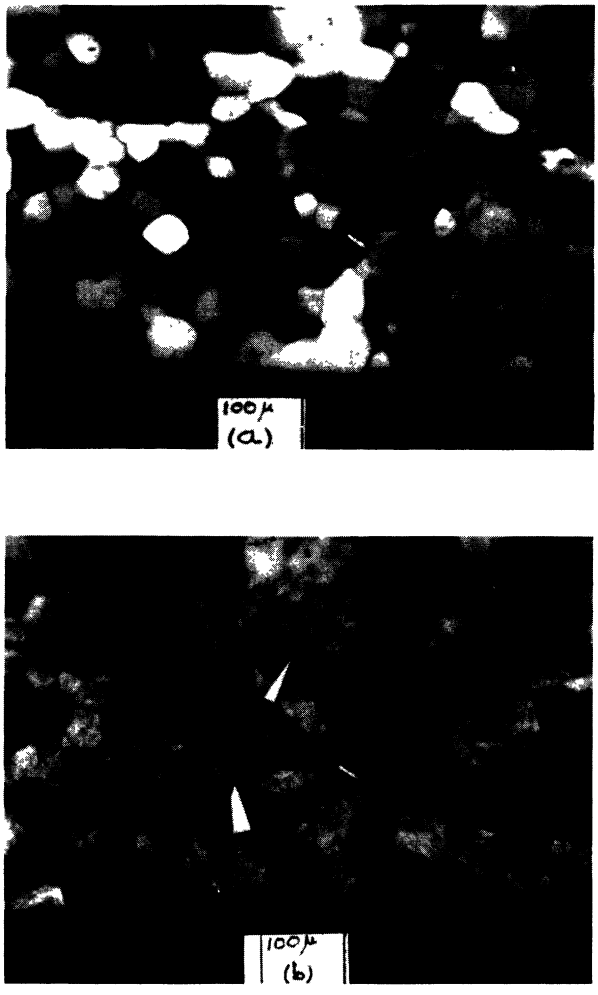
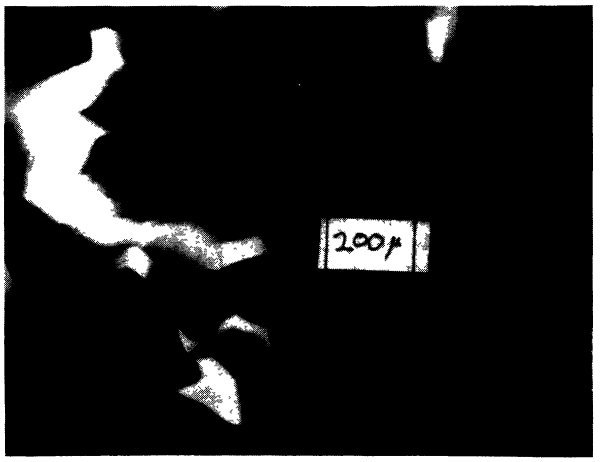


Fig. 10. — *a*) Transmission picture of high-temp. BP in CN-37 w/o 6OCB (80.32°). *b*) Same area, but low-temp. BP (80.30°).

I feel justified in calling them both « blue » phases. In figure 11, we see a sample of CN-CCl above (*a*) and below (*b*) its phase transition, both observed in reflection. With the exception of the crosshatching on the low-temperature phase, and the differing colours (blue above the transition, green below), the two phases present similar appearances.

The crosshatching stems from the way one phase grows into the other. For instance, consider the growth of the green (low-temperature) phase of CN-CCl into the blue as the temperature drops (see Fig. 12). First, small green patches appear, which are longer than they are wide. Some have their long axes all aligned in a particular direction, and the others are all aligned in a perpendicular direction. These platelets then grow as shown in figure 12, until they meet. The crosshatching is thus seen as the residuum of the growth process. On going back up through the transition (green → blue), the same process occurs, with blue platelets growing and replacing the green. The direction of the platelet long axes is the same in the blue → green and green → blue transitions. Once the blue phase is reached, the crosshatching anneals



a) HT BP 86.04°.

b) LT BP 85.96°

Fig. 11. — *a*) CN-15 w/o CCl in reflection, high-temp. BP (86.04°). *b*) Same area, but low-temp. BP at 85.96°.

out very rapidly, and thus is not visible in the photographs. However, the green phase is much slower to anneal and exhibits much slower dislocation motion than does the blue, so the remnant structure lasts for hours instead of seconds.

In all the mixtures and pure compounds I have studied (CN with 6OCB, CCl, 8OBC, and cholesterol proprionate with CBOOA and 4,4'-diheptyloxyazoxybenzene) there is a phase transition, and the low-temperature phase has a longer lattice parameter and much slower annealing and dislocation motion than does the high-temperature phase. In most mixtures the phase transition does not proceed by the dispersed-nucleation mechanism just described. Instead, the growing phase starts out from one or a few points, and sweeps over the sample in a front. If the temperature is changing very slowly, so the front

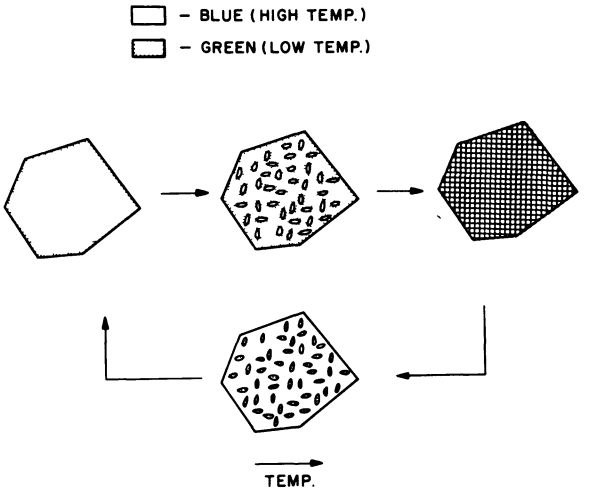


Fig. 12. — Schematic of « solid-solid » phase transition in CN-15 w/o CCl.

moves slowly, the outlines of the original grains will be retained in the new phase. Otherwise, the grain structure of the new phase need have no relation to that of the old. The process shown in figure 12 is one that occurs for low growth rates. Often, one can see a « crinkling » of the shrinking phase just ahead of the front, indicating the presence of strain.

4. **Discussion.** — We have seen that the BP (both of them) can be analysed as if it were a solid crystal but with a large lattice parameter. The selective reflection indicates that the unit cell contents are completely chiral in that the order parameter could be analysed as a sum of cholesteric spirals, all twisting in the same direction. The quasicrystal hypothesis provides a framework for explaining all of the observed optical properties and appearances of the BP, including its defects.

There are a number of theories in existence which embody the QC hypothesis by expressing the order parameter as a sum of the minimum number of cholesteric spirals needed to establish three-dimensional periodicity. However, such theories do not explain why the BP *d*-spacing is always longer than the cholesteric pitch, the presence of phase transitions, the existence of the blue fog, or the observation of higher-order diffraction lines right up to the BP-isotropic transition.

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