PHYSICAL REVIEW A VOLUME 25, NUMBER 4 APRIL 1982

Crystallography of "blue" phases I and II

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(Received 16 July 1981)

Morphological evidence is presented showing that the high-temperature cholesteric "blue" phase (BP II) has a simple-cubic point group, while the low-temperature phase (BP I) is probably body-centered cubic. This evidence was gathered through optical microscopy on platelets oriented with their shortest reflecting wave vector along the direction of observation. The "crosshatch" markings commonly observed during the BP I-II transition are explained in terms of the relationship between the unit cell of the BP II product and that of the BP I from which it arose.

I. INTRODUCTION

Recent experiments have shown that the cholesteric "blue" phases (BP) possess three-dimensional translational periodicity just as a crystal does.[1–6] Most investigators report both BP's (not counting the "blue fog"[1]) to have cubic symmetry.[2–5]

Most of the structural information about the BP has been obtained through study of the Bragg diffraction of visible and near-uv light from the "crystals".[2,3] Unfortunately, the powder patterns from simple-cubic (sc) and bcc lattices match up to the seventh reflection. So far, no one has observed the seven reflections thus needed to distinguish sc from bcc.

This problem can be solved by determining the symmetry of the lattice with respect to an axis parallel to the shortest wave-vector. In other words, when looking down the axis normal to the Bragg planes of greatest spacing, does the crystal show a fourfold { 100 } symmetry? We shall see that the age-old method of looking at the external crystal form can provide this answer.

II. EXPERIMENTAL

Two samples were used in this study: Sample no. 1, which consisted of a mixture of 36.9-wt. % cholesteryl *p*-nonylphenyl carbonate in BDH "*E*7" nematic mixture, and sample no. 2, which was made of 65-wt. % cholesteryl oleate in *E*7. Both samples were made by placing a drop of the appropriate mixture between a microscope slide and coverslip. The glass for no. 1 was detergent cleaned but otherwise untreated, while that for no. 2 was cleaned, treated with ACM-72 surfactant, and rubbed to procure parallel alignment. This alignment procedure and choice of composition allowed the growth of a large BP I platelet (crystal) with its direction of longest *d* spacing normal to the glass, and thus along the observation direction.

The samples were inserted in a Mettler FP5/52 hot stage and examined by transmission and reflection microscopy with crossed polarizers. The samples were cooled slowly through the isotropic point and then left at a constant temperature for several hours in order to produce large, defect- and strain-free platelets.

It is important to be sure that the BP's used in these experiments are indeed cubic. There are several pieces of evidence for this notion. First, there is the fourfold symmetry discussed below. Also, I have looked for birefringence and anisotropic reflection and did not find any such effect. Thus, the BP's must be cubic, tetragonal, or orthorhombic. If the structure were either of the latter two, there should be a splitting of the major diffraction peaks. None is seen. In particular, sample no. 1 shows platelets which tumble freely, thus indicating a lack of surface interaction. Therefore, [001], [010], and [100] faces should appear with equal frequency. However, there is only one wavelength appearing for all platelets displaying the shape discussed below. The platelet is therefore cubic. A similar argument applies if the observed reflection is, say [110].

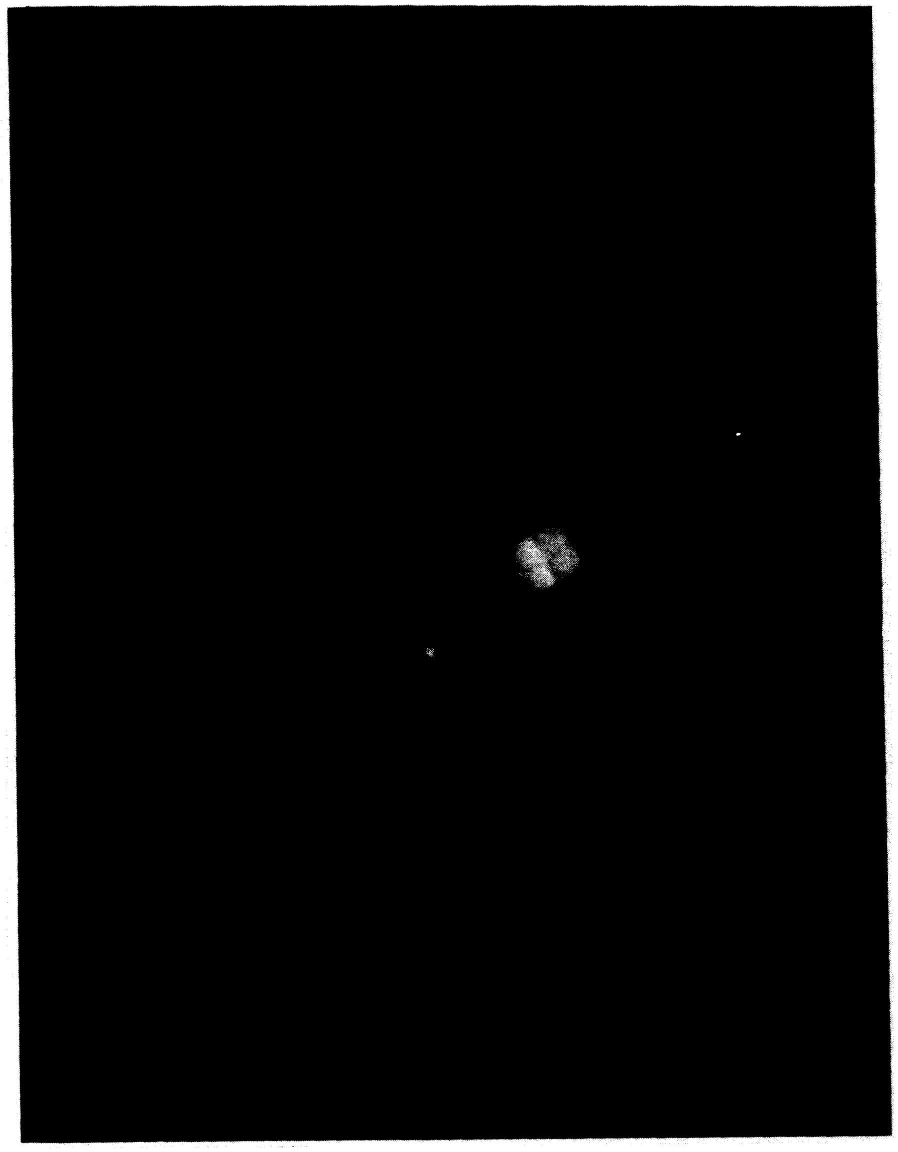


FIG. 1. Isolated BP II platelet in sample no. 1, seen in reflection at the longest wavelength observed for this sample. Note fourfold symmetry.

III. RESULTS

A photograph of an isolated BP II platelet in sample no. 1 is shown in Fig. 1. This picture was taken in reflection mode, after the sample had been at a constant temperature for a day. The two platelets visible in this picture (one as a small dot) are both greenish yellow in color, the longest-wavelength color visible in this sample in BP II. This color is also the longest-wavelength color visible in a polycrystal in transmission. If there were a reflection in the infrared, the accompanying optical rotatory dispersion in the visible would cause a reddish appearance which is not seen. I have seen this red color in many mixtures in which ir reflections are seen. Examples include cholesteryl nonanoate-cholesteryl chloride, CB15-*E*9, and a chiral-racemic mixture.[7] The symmetry here is obviously fourfold. The cross visible in the picture appeared on many of the larger square platelets,

FIG. 2. BP I-II transition in sample no. 2. The light areas are BP II growing into the BP I.

and always reached from side to side, no matter what the orientation of the polarizers. That the $(h00)$ reflection is allowed (I have seen it in the microscope), and is the longest-wavelength reflection, shows that $h=1$, and that the translation group of BP II in this compound is simple cubic.

In Fig. 2 (sample no. 2), we see BP II (light areas, actually yellow) growing in a matrix of BP I (dark, actually dark red). This picture was taken in transmission. Because this sample's surfaces have undergone an alignment treatment, the BP I shows up as a single large platelet (after annealing for a few hours), with its longest-wavelength-reflecting direction parallel to the observation direction. The yellow color of the BP II product of the BP II transition was the longest-wavelength color visible in a "polycrystalline" BP II sample of the same material as sample no. 2. Therefore, the statement made above about the orientation of the BP I also holds for BP II. I have observed square platelets in reflection in the BP II of the cholesteryl oleate-$E7$ mixture just like the ones discussed for sample no. 1. Thus, I deduce that the BP II's in both samples are the same.

It is clear that the BP II "lines" did not grow in a random direction relative to the BP I. Rather,

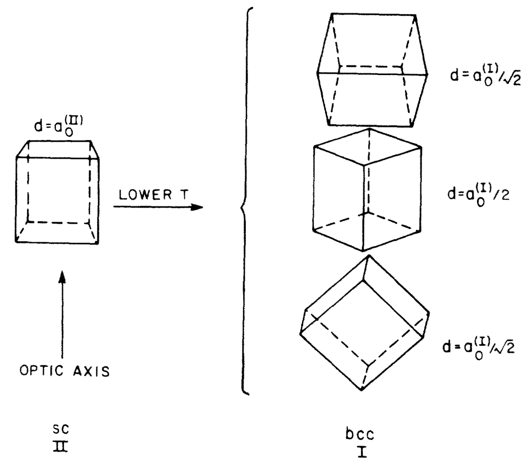


FIG. 3. Possible orientation relations in the BP I-II transition, showing how one orientation of the initial phase can result in three orientations of the product.

there were preferred directions, giving rise to an "oblique grid" appearance. I measured the angle of the grid intersections as $68\pm4°$. Since the angle is neither 60 or 90°, the "straight-up" direction in the BP I cannot be [100] or [111]. The [111] direction is further ruled out by the diffraction measurements, which allow a "longest-wavelength" direction of [100] or [110]. I will now show that the geometry found can be reproduced with [110] straight up.

Suppose that the straight-up direction is [110]. Then, directions in the picture plane must be expressible as $[h\bar{h}k]$, since such directions must be perpendicular to [110]. We want the two directions of the BP II "laths" to be "equivalent" in the sense of being related by the cubic symmetry of the BP I. Two such directions are $[\bar{1}12]$ and $[1\bar{1}2]$, which would put the BP I-II interfaces on $(\bar{1}1\bar{1})$ and $(11\bar{1})$ planes of the BP II lattice. An alternative arrangement interchanges the indices of lath and interface-normal directions. In either case, the angle between laths is 70.5°. These assignments are the only ones involving low-index planes which predict an interlath angle consistent with experimental results. The first-mentioned alternative has the advantage of putting the BP I-II growth direction into a low-index direction, thus allowing a simple relation between the two unit cells. With this hypothesis, I can explain the "crosshatching" often observed at the BP I-II transition,[4] as well as the fact that the direction of longest-wavelength reflection can remain unchanged during the phase transition.

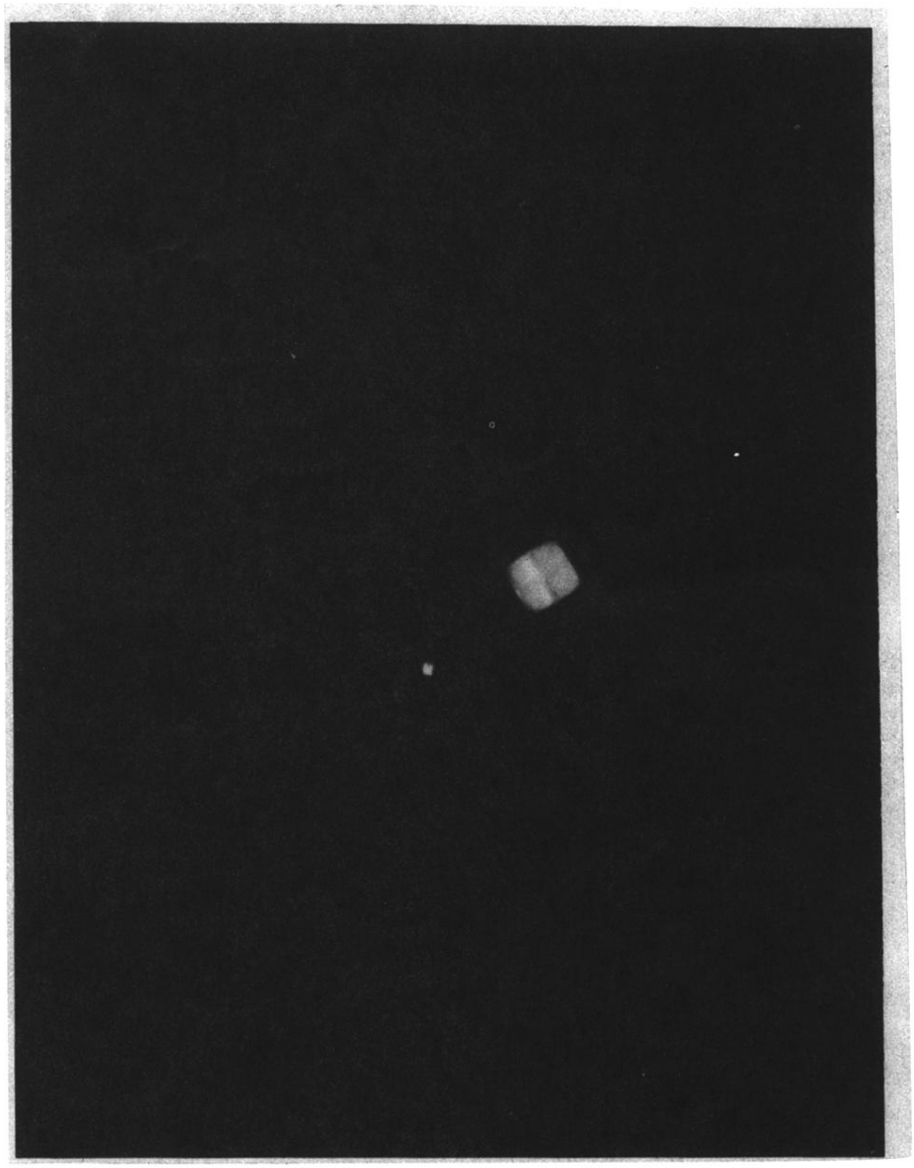
The top-left shape in Fig. 3 shows the BP II unit cell oriented with [100] along the observation direction. Suppose the transition involves a 45° rotation about a [100] direction. Since the three directions [100], [010], and [001] are symmetry equivalent, the rotation can occur about any of these axes, leading to the three outcomes pictures on the top right of Fig. 3. Of these three orientations, two have [110] or equivalent planes normal to the observation direction, while the third does not. Therefore, one might expect to see bands of alternating color, with one of these colors being the longest allowed wavelength. Similarly, the I-II transformation yields three choices, of which one allows reflection at the longest wavelength in the product. It is this orientational ambiguity which causes the banding or crosshatching visible when crossing the I-II phase boundary in either direction.

Similar arguments show that there should be a right-angled crosshatching on going from BP II to BP I when the transforming phase has its lowest-order Bragg planes along the viewing axis. Sample no. 2 just after the BP II-I transition looks much like a piece of tweed cloth, with a definite fourfold symmetry.

IV. CONCLUSIONS

I have shown that the translation groups of BP I and BP II are most probably body centered and simple cubic, respectively, for at least one case. A possible geometry for the BP II-I transition is given, which explains the crosshatching commonly observed.

[1]M. Marcus, J. Phys. (Paris) 42, 61 (1981).
[2]S. Meiboom and M. Sammon, Phys. Rev. Lett. 44, 882 (1980).
[3]D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. 45, 641 (1981).
[4]S. Meiboom, and M. Sammon, Phys. Rev. A 24, 468 (1981).
[5]H. Onusseit and H. Stegemeyer, Z. Naturforsch. 36a, 1083 (1981).
[6]A. J. Nicastro and P. H. Keyes (unpublished).
[7]M. Marcus and J. Goodby, Mol. Cryst. Liq. Cryst. (in press).



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