Is Blue Phase II fcc?

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It is commonly thought that blue phase II (BP II) is a simple-cubic structure. It is demonstrated that BP II in (+)-2-methylbutyl-*p*-[(*p*-methoxybenzylidene)amino] cinnamate is fcc and it is argued that this is possibly true for all other BP II's as well.

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In recent years it has been established that cholesteric liquid crystals of sufficiently short pitch may form up to three complex structures in a narrow temperature interval preceding the transition to the isotropic phase.[1] Named in order of increasing temperature they are blue phase I (BP I), which is thought to be bcc with O^8 ($I4_132$) symmetry; blue phase II (BP II), believed to be simple-cubic (sc) O^2 ($P4_232$); and blue phase III (BP III), a seemingly amorphous phase whose structure is still unknown. The determinations of the two cubic structures and their symmetries have been made through a variety of techniques including morphological studies[2-6] and Bragg-scattering measurements[7-12] analyzed with the use of selection rules developed by Hornreich and Shtrikman for cubic cholesteric structures.[1b,13-15]

Although the evidence in support of an O^8 structure for BP I seems substantial, the amount of data supporting an O^2 assignment for BP II is quite meager. Also, many investigators have not even considered the possibility that BP II might be an fcc structure. The purpose of this Letter is to demonstrate that BP II in one material is fcc of O^3 or O^4 symmetry and to argue that the existing data for the BP II's of other materials are also consistent with an O^4 structure. In addition, it will be shown that the reflection selection rules are violated, thus possibly calling into question the identification of BP I as an O^8 structure.

The subject of this investigation is (+)-2-methylbutyl-*p*-[(*p*-methoxybenzylidene)amino] cinnamate (MBMBAC), which has been studied recently by Kuczyński.[16,17] The most useful feature of this compound is that it exhibits all three types of blue phase in spite of the rather large cholesteric pitch; there are, therefore, many more Bragg reflections in the visible and near-visible spectrum for both BP I and BP II than are seen in any other material. In powder pattern, BP II of MBMBAC yields back reflection at 946, 813, 595, 502, and 443 nm, and these lines have been indexed to a sc lattice by Kuczyński.[16]

Single-crystal diffraction results have also been presented by Kuczyński[17] for platelets which appear blue (502 nm) in BP II. That study showed that the blue reflection is from a threefold axis and Kuczyński concluded that the selection rules do not hold. As possible explanations of this violation it has been suggested that BP II in MBMBAC is a distorted cubic lattice[18] or an icosahedral quasicrystal.[19] The present study, which includes single-crystal diffraction results from gold (595 nm) and violet (443 nm) platelets as well as blue, shows that the structure is cubic with little or no distortion and that the selection rules are indeed violated as postulated by Kuczyński.

My apparatus is similar to that used by Kuczyński.[17] The polarizing-microscope hot stage is placed on a goniometer which allows tilting of and rotation about the normal to the sample plane. A glass hemisphere of $\frac{1}{2}$ in. radius sits on top of the sample which is illuminated with white light and viewed in the reflected mode. Wavelengths are measured by the diversion of light from the eyepiece to a 1-nm bandpass monochromator. Samples purchased from Eastman Kodak and others synthesized and purified by T. B. Tripp of the University of Maine at Preque Isle gave similar results.

Platelets of the different colors are grown in various ways. On cooling from BP III into BP II a preponderance of blue platelets is usually produced. If one lets the samples sit in BP II for several hours many of these platelets will meld and, with luck, a large blue platelet will result. Large gold and violet platelets are much easier to produce. To do this the sample is sheared by displacement of one of the glass surfaces relative to the other. If this is done very slowly by, say, a gentle pushing on the microscope slide, a large violet platelet will be obtained. If, however, the shearing action is made more rapid by the tapping on the slide at the rate of a few times a second, then a large gold platelet will result. Uniform platelets with areas of about 1 cm^2 have been produced by these methods. Smaller platelets, or large platelets with defects, often exhibit bogus reflections which are never seen in the large, uniform platelets. The origin of these spurious lines is unclear but it has been observed that they invariably occur in pairs on either side of a defect line or of a boundary between two small platelets.

Single-crystal diffraction results for the three types of large platelets are given in the polar plots of Fig. 1. Figure 1(a) duplicates the result of Kuczyński[17] showing that the blue platelets are being viewed along a threefold

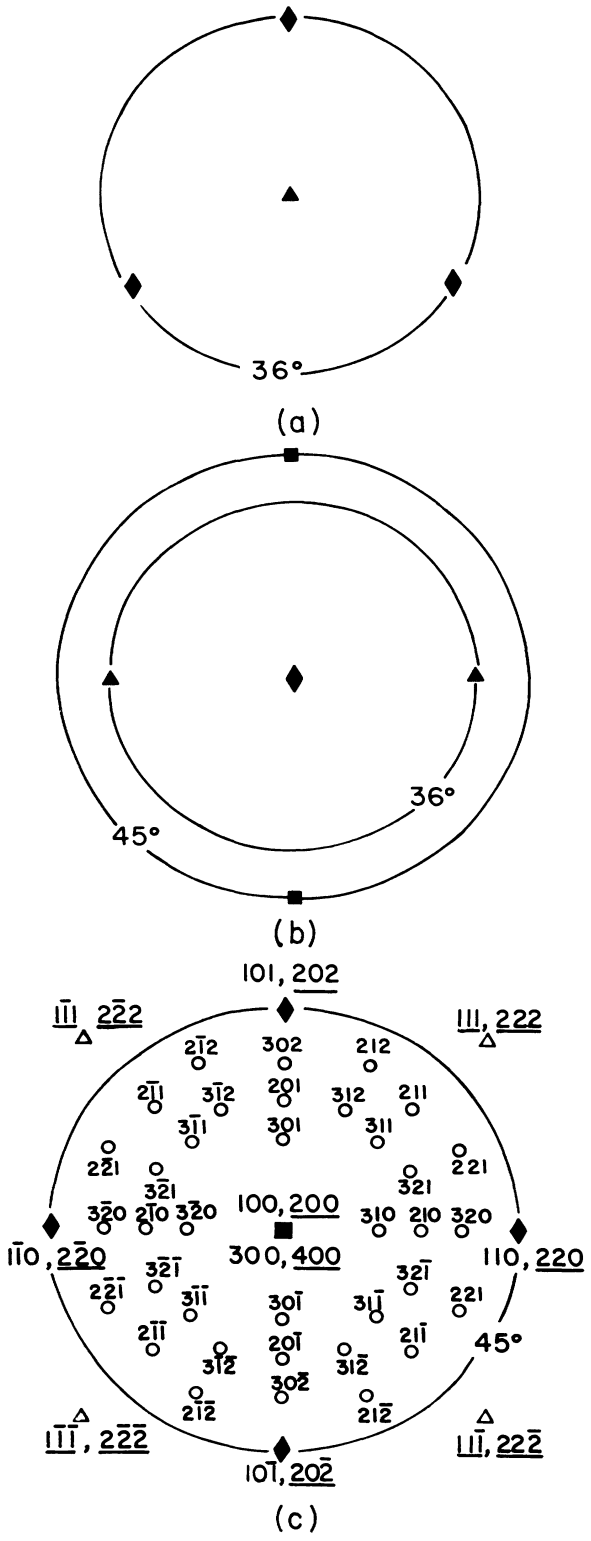

FIG. 1. Polar plots of the selective reflections for platelets of three different initial orientations. The wavelengths of the reflections are 502 nm, triangles; 595 nm, lozenges; and 443 nm, squares.

axis. New results are in Figs. 1(b) and 1(c), which demonstrate that the gold and violet platelets correspond to twofold and fourfold axes, respectively. Note that the angles between the three types of reflections are, to within a degree, identical to those expected for the symmetry axes of a cube.

The wavelength ratios also fit fairly well to a cubic indexing. As already mentioned by Kuczyński,[17] the lowest-order index compatible with the blue line is (222), which then means that the gold line should be a (220) reflection. Because of the fourfold axis, the violet line should be indexed (400) rather than any of the possibilities proposed by Kuczyński.[16] The two lines in the infrared at 916 and 813 nm are thus most likely due to (111) and (200) reflections, respectively. The dispersion of this particular material is not known, but if the refractive index should drop by about 6% on going from 450 to 900 nm, which is not unreasonable, then the wavelength ratios would be just as expected for a cubic lattice.

By now it should be apparent that the Miller indices for this structure are those of an fcc lattice (all even or all odd). This point is made in Fig. 1(c) where all possible cubic indices out to order (400) are given, and the ones which have actually been identified by experiment are underlined. [Note that for completeness the (*hhh*) reflections are shown in this plot even though they lie past the maximum of 50° by which the goniometer may be tilted.] The data are inconsistent with a bcc structure because of the presence of the (111) line. Also, one would expect to find (110), (211), (310), and (321) lines for bcc structure. If the structure is sc, even more lines are missing making this possibility remote. The only fcc line which is not seen is the (311) reflection; it is not clear why this line should be missing since it is allowed by the selection rules.

On the other hand, it is clear that three or four reflections which are forbidden by the selection rules are seen. These include the (111) and (222) lines which are predicted to be absent for all cubic cholesteric blue phases.[1b,13,15] There are three possible types of fcc blue phases. One of these, the T^2 ($F23$), is incompatible with the observed fourfold axis. Of the remaining two possibilities, the O^4 ($F4_132$) should not give a (400) reflection and the O^3 ($F432$) should be missing the (200) line as well,[14,15] but both lines are seen in the experiments.

It is important to understand why and under what conditions the selection rules are violated. Consider, for example, what would happen if we had an O^4 fcc structure and the selection rules were not violated. The lowest-order back reflections would be from the (200), (220), and (311) planes[14,15] and platelets corresponding to the longest wavelength would be square shaped. This situation would be compatible with all other measurements which have been made on BP II to date, including the wavelength ratios[11,12] as well as the shape of the

platelets.[2,5,12] The T^2 and O^3 fcc structures would not fit these observations since the lowest-order reflection is from a twofold axis in both cases.

It is possible, therefore, that BP II is fcc in these other materials but has been mistakenly identified as sc.[20] If this is not true, then the structure of BP II must be material dependent, which is also a new development.

Preliminary studies indicate that BP I in MBMBAC is bcc as it is in other materials, but this work is not yet completed and will be reported on later. It is appropriate to note at this point, however, that it does not seen to be possible to distinguish between the O^5 and O^8 structures by morphological evidence, since both have fourfold, threefold, and twofold axes, nor by Bragg-scattering results if the selection rules are violated. It is the presence of the (200) reflection, which is forbidden for O^5, that has been used as the primary basis for the identification of BP I as O^8 in other materials.[2-4,7-10] But if the selection rules should prove to be violated in these other systems as well, then the structure of BP I might be in doubt.[21] Clearly more work is needed to understand the processes that lead to these disallowed reflections and to elucidate the structures of the blue phases with greater certainty.

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[20]This possibility was first pointed out to me by P. E. Cladis.

[21]Note, however, that according to Ref. 6 the smallness (Ref. 3) or absence (Ref.6) of (100) facets probably favors O^8 over O^5.