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Microscopic Observations of the Cholesteric Blue Phase in Mixtures of Varying Pitch

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Theories for the blue phase proposed recently by Brazovskii and Dmitriev and by Hornreich and Shtrikman predict that this phase can exist only for cholesterics of sufficiently short pitch. In this article we demonstrate this dependence upon pitch through microscopic observations of three sets of binary mixtures, one set consisting of mixtures of cholesterics of opposite chirality and the other two consisting of cholesteric-nematic mixtures.

In the course of these studies we have developed techniques for growing particularly large platelets of the blue phase. We present photographs of these platelets demonstrating, for the first time, the optical anisotropy of the blue phase, which is evident when the platelets are sufficiently large. Characteristic twinning patterns are also evident in the photographs.

A few years ago Brazovskii and Dmetriev[1] demonstrated that cholesterics having symmetries different from the usual helicoidal ordering are to be expected in materials with sufficiently strong chirality. This observation is largely responsible for the recent renewed interest in the long neglected cholesteric blue phase. Hornreich and Shtrikman[2] have proposed as a model for the blue phase a structure with body-centered-cubic symmetry and have established that this bcc phase has a lower free energy than either

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the isotropic or helicoidal phase in a narrow temperature interval between these two phases. Experimental evidence has been forthcoming supporting the existence of bcc phases in certain cholesterics but indicating at the same time the need for refinements to the Hornreich–Shtrikman theory.[3,4]

In this paper we present, first of all, measurements on mixtures demonstrating quantitatively the dependence of the blue phase temperature range upon pitch. Secondly, we give evidence from polarizing microscopy studies which supports the notion of a lattice-like ordering within the blue phase but indicates that in many cases the lattice cannot be cubic.

Kozawaguchi and Wada[5] have measured the cholesteric pitch for several different binary mixtures. Their results for two of these binary systems, EBBA/Cholesteryl Nonanoate and EBBA/Cholesteryl Chloride are displayed in Figure 1. Note that the composition range over which the pitch is short is large for one system and small for the other; this factor motivated the selection of these two systems for our blue phase studies.

Figures 2 and 3 give the observed phase transitions for these systems. The difference in the effects of the nematic EBBA upon the two cholesterics is

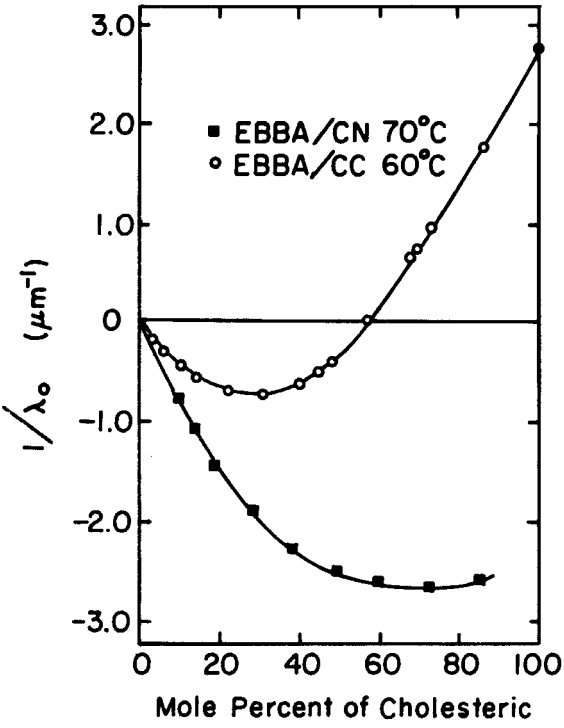

FIGURE 1 Selective reflection data for two binary mixtures (after Kazawaguchi and Wada[5]).

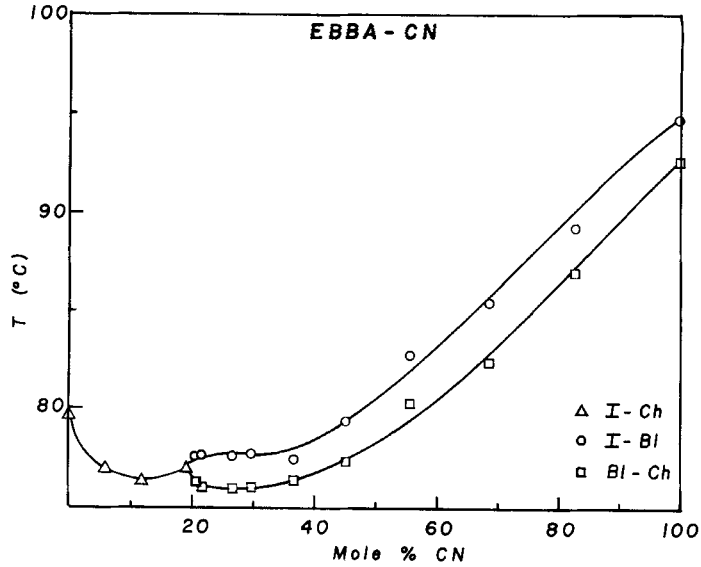

FIGURE 2 Transition temperatures vs. composition for EBBA/CN mixtures.

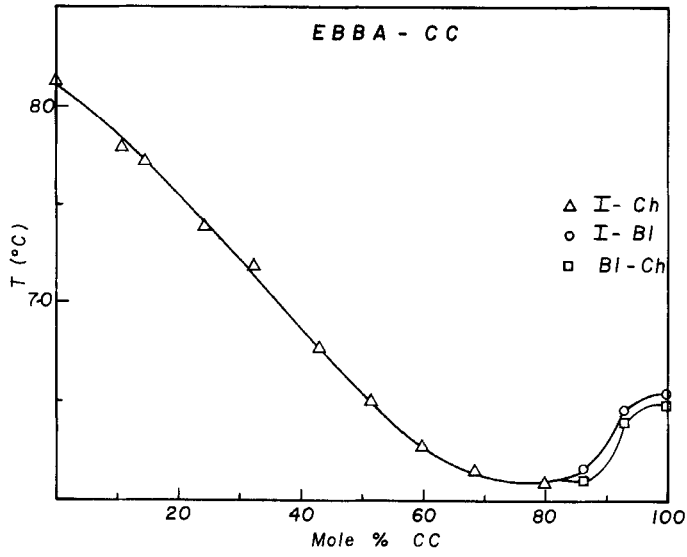

FIGURE 3 Transition temperatures vs. composition for EBBA/CC mixtures.

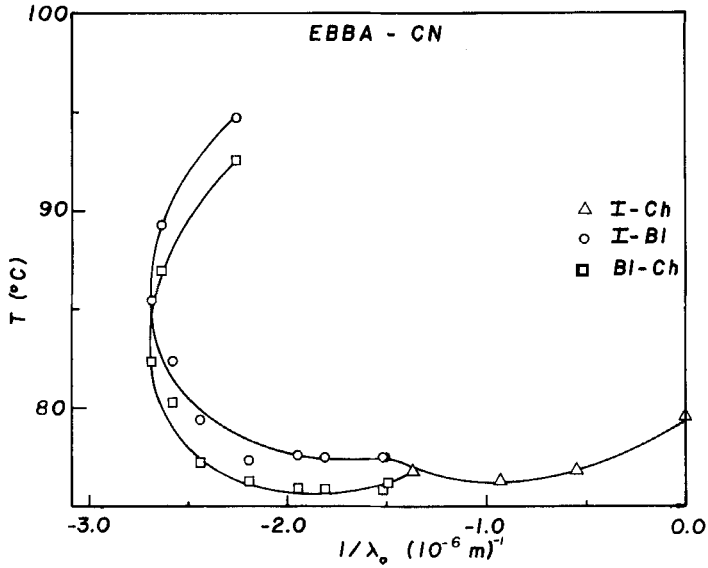

FIGURE 4 Transition temperatures vs. pitch parameter λ_0^{-1} for EBBA/CN mixtures.

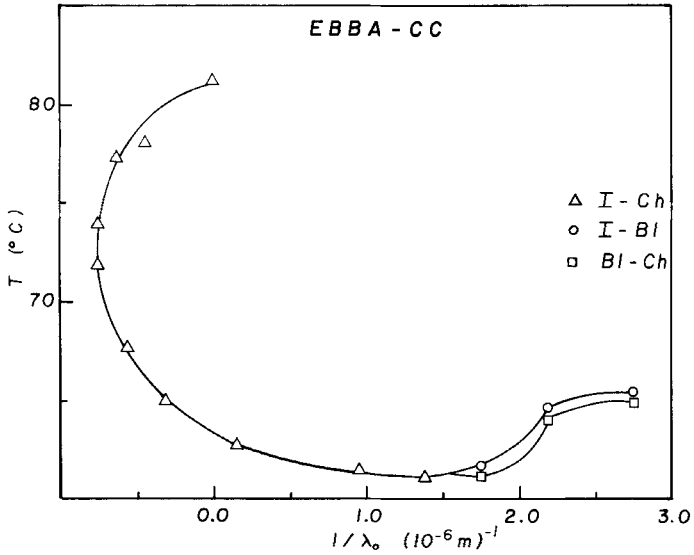

FIGURE 5 Transition temperatures vs. pitch parameter λ_0^{-1} for EBBA/CC mixtures.

striking; more than 80% nematic is needed to remove the blue phase from CN, whereas less than 20% nematic is sufficient to do the same for CC. This asymmetry is removed, however, when the results, as shown in Figures 4 and 5, are presented as functions of the pitch parameter $1/\lambda_0$ obtained from the data of Figure 1. In order to have a blue phase one must have in both cases $|1/\lambda_0| > 1.4\ \mu^{-1}$ or $\lambda \lesssim 7000$ Å. Note that the wavelength within the liquid crystal is down by a factor of n ($\simeq 1.5$) and that the periodicity L of the helix is one-half the wavelength so that one has $L \sim 2300$ Å.

In Figure 6 are shown the results of a similar experiment performed on a mixture of cholesteryl oleyl carbonate and cholesteryl chloride, which have chiralities of opposite signs. For intermediate compositions, where the pitch is large, we find that the blue phase is not formed. Pitch vs. composition data for this system are not available; we can, however, make a crude estimate of this dependence by assuming a linear interpolation between the pitches of the pure components. The results of such an estimate are that the blue phase disappears in the COC-rich materials at $\lambda_0^{-1} \simeq 0.7\ \mu^{-1}$ and in the CC-rich materials at $\lambda_0^{-1} \simeq 1.1\ \mu^{-1}$, values which are not too different from those found in the other two sets of mixtures.

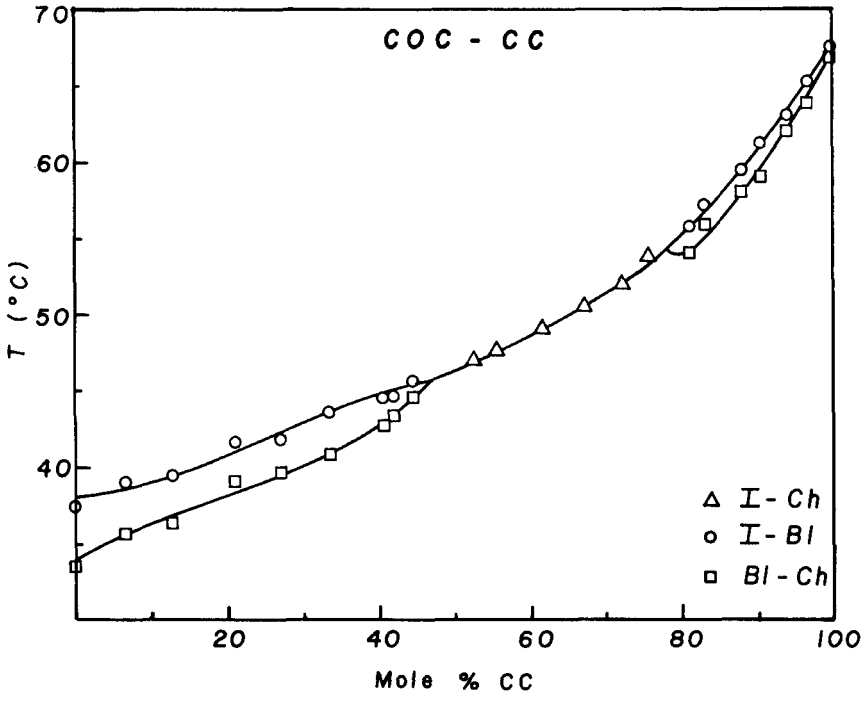

FIGURE 6 Transition temperatures vs. composition for COC/CC mixtures.

In summary, in these mixtures we find that a value of λ_0 less than roughly 1 μ is needed in order to form blue phase. It is conceivable that in other systems this value could be quite different. In both the Brazovskii–Dmetriev and Hornreich–Shtrikman theories it is not just λ_0 but a combination of parameters including λ_0 which determine when new phase will occur. Thus, for example, even if λ_0 is large a blue phase can be formed if B, the coefficient of the cubic term in the Landau–deGennes free energy expansion is small enough.

Our observations of the phase transitions in these mixtures have been carried out using a microscope with reflected light and crossed polarizers. Under these conditions the blue phase usually appears to consist of small platelets of different colors. Often, however, the sudden appearance of a haze within the field of view accompanied by a bluish band around the edge of the cover slip signatures the arrival of the blue phase. In some of these cases higher magnification of the haze reveals that it is made up of very small platelets.

An exceedingly fine-grained sample will of course appear to be optically isotropic. In order to perform meaningful optical crystallographic studies it is necessary to have resolvable platelets; ideally one should have large platelets so as to minimize grain boundary effects. One method of producing large platelets is to cycle back-and-forth between the isotropic and blue phases in the presence of a small temperature gradient. Figure 7 illustrates the effect of one such cycle. The region consisting of large platelets had once contained smaller platelets which were melted; upon cooling regrowth into the isotropic region, the dark area, produced the larger platelets. With patience we have succeeded in growing "single crystal" columnar platelets 1 mm in length.

Often, particularly when the cooling rate and the temperature gradient are small, the platelets will develop growth faults as shown in Figure 8. This twinning pattern strongly supports the hypothesis of a lattice-like ordering with the blue phase.

We have performed a systematic study of the blue phases formed in twelve of the aliphatic esters of cholesterol. In most of these compounds we find that the blue phase platelets are optically anisotropic, that is, they change intensity (but not color) when the microscope stage is rotated. This phenomenon is illustrated in Figure 7 for cholesteryl hexanoate. Such materials cannot have a local cubic ordering. Some of the compounds do exhibit isotropic platelets as in cholesteryl valerate, for example. In cholesteryl valerate, however, the ratio of wavelengths of reflected light, i.e., the colors of the platelets are consistent with an fcc structure rather than the bcc proposed by Hornreich and Shtrikman. In fact, only two compounds, cholesteryl propionate and cholesteryl butyrate, display both isotropic platelets and

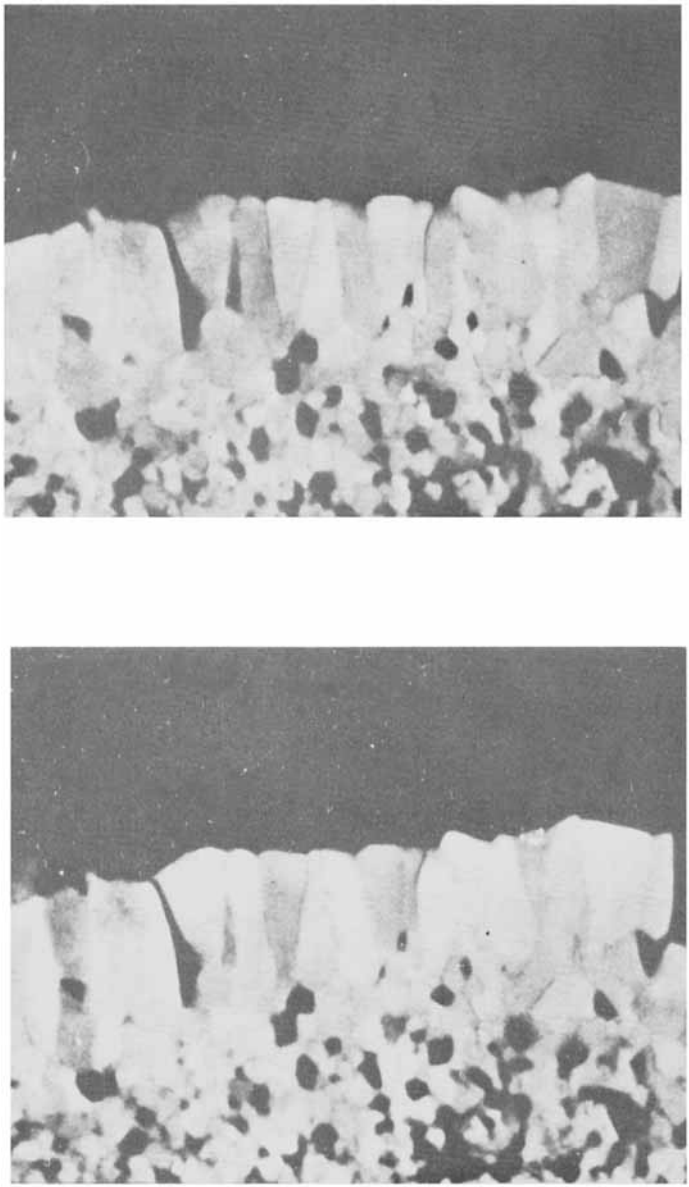

FIGURE 7 Platelets observed in reflected light with crossed polarizers in the blue phase of cholesteryl hexanoate. The orientation of the microscope stage differs by 45° between the upper and lower photos.

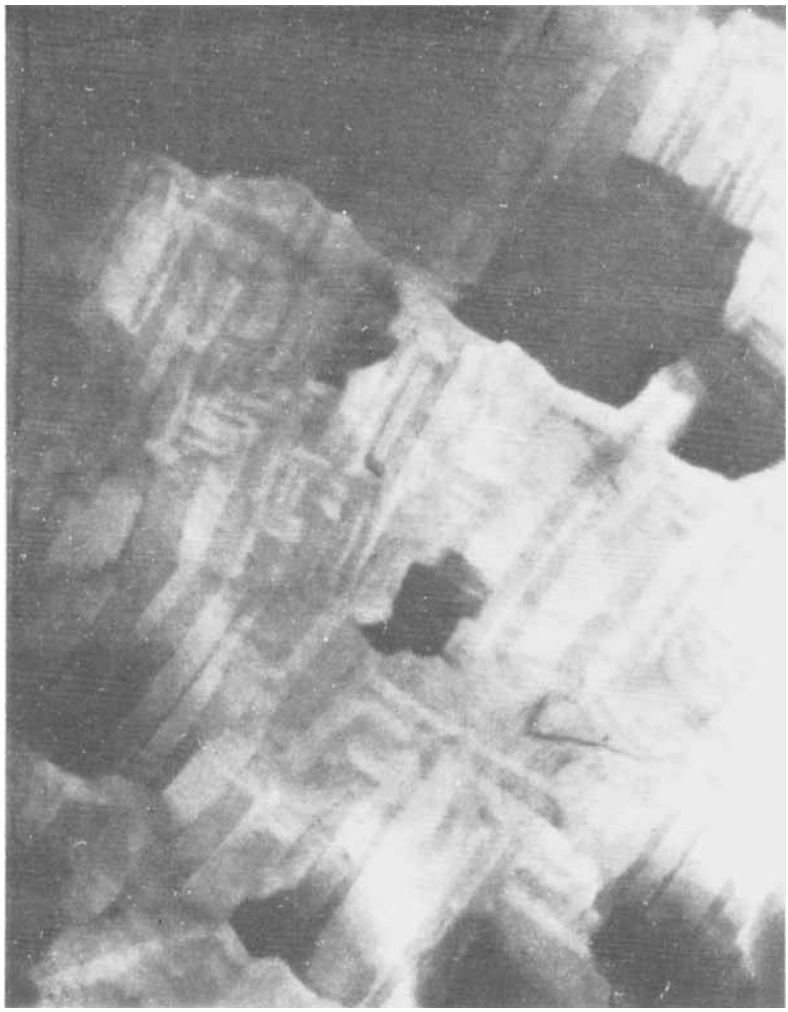

FIGURE 8 Platelets of cholesteryl hexanoate exhibiting twinning patterns. The extinction angles of neighboring twins differ by approximately 45°. The dark areas are platelets which are extinct in this particular configuration.

wavelength ratios consistent with a bcc structure. The details of these "Bragg reflection" experiments will be presented elsewhere.[6]

In conclusion it appears that our understanding of the blue phase is far from complete. The current theories have indicated why and under what conditions this phase will form and they have suggested a structure which

seems to apply in some cases, but they have not yet begun to describe the diversity of behavior which is displayed in the experiments.

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References

1. S. A. Brazovskii and S. G. Dmitriev, *Zh. Eksp. Teor. Fiz.*, **69**, 179 (1975) [*Sov. Phys. JETP*, **42**, 497 (1976)].
2. R. M. Hornreich and S. Shtrikman, *J. Physique (Paris)*, **41**, 335 (1980); and in *Liquid Crystals of One- and Two-Dimensional Order* (W. Helfrich, G. Heppke, eds.) Springer Series in Chemical Physics (1980)–in press.
3. S. Meiboom and M. Sammon, *Phys. Rev. Letters*, **44**, 882 (1980).
4. D. L. Johnson, J. H. Flack, and P. P. Crooker, *Phys. Rev. Letters*, **45**, 664 (1980).
5. H. Kozawaguchi and M. Wada, *Mol. Cryst. Liq. Cryst.*, **45**, 55 (1978).
6. A. J. Nicastro and P. H. Keyes, to be published.