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[1] L. D. Landau, Phys. Z. Sowjetunion 8, 113 (1935).

[2] E. K. Riedel and F. J. Wegner, Phys. Rev. Lett. 29, 349 (1972).

[3] F. J. Wegner and E. K. Riedel, Phys. Rev. B 7, 248 (1973).

[4] M. J. Stephen, E. Abrahams, and J. P. Straley, Phys. Rev. B 12, 256 (1975).

[5] E. K. Riedel, H. Meyer, and R. P. Behringer, J. Low Temp. Phys. 22, 369 (1976).

[6] H. -T. Shang and M. B. Salamon, in Proceedings of the International Conference on Magnetism, Munich, 1979 (to be published). For a review of tricritical behavior in metamagnets, see E. Stryjewski and N. Giordano, Adv. Phys. 26, 487 (1977).

[7] A. L. M. Bongaarts and W. J. M. de Jonge, Physica (Utrecht) 86–88B, 595 (1977).

[8] J. F. Nicoll and T. S. Chang, Phys. Lett. 64A, 477 (1978).

[9] H. -T. Shang, Ph.D. thesis, University of Illinois, 1979 (unpublished).

[10] H. -T. Shang and M. B. Salamon, to be published.

[11] T. S. Chang, A. Hankey, and H. E. Stanley, Phys. Rev. B 8, 346 (1973).

[12] G. Ahlers, A. Kornblit, and H. J. Guggenheim, Phys. Rev. Lett. 34, 1227 (1975).

# Structure of the Blue Phase of a Cholesteric Liquid Crystal

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Bragg diffraction of visible and near-ultraviolet light in the blue phase of a cholesteric liquid crystal have been observed. It is found that there are two distinct blue phases: One is stable from about 0.5°C below the clearing point to about 0.2°C below it and has either a body-centered-cubic or simple-cubic structure. A second, clearly distinct phase appears in the 0.2°C range immediately below the clearing point. The nature of this phase is unclear at this time.

Reports of the existence of a "blue phase" in cholesteric liquid crystals in a narrow temperature range just below the transition to the isotropic liquid (clearing point), date back at least to 1906 (Lehmann[1]). Coates and Gray[2] describe microscopic observations of the blue phase in a large number of cholesteric liquid crystals. The phase is best observed in reflected light, and typically is characterized by a blue overall scattering, on which in many cases appear brightly colored "platelets." Differential scanning calorimetry (DSC) traces by Armitage and Price,[3] and Bergmann and Stegemeyer[4] of cholesteryl nonanoate and cholesteryl myristate show a weak, but distinct, peak about half a degree below the much larger peak at the clearing point. Moreover the second authors[4] interpret a small shoulder about 0.1° below the clearing point as a transition to a second thermodynamically stable blue phase. Changes in color of light back-reflected from the blue phase, observed by Bergmann, Pollmann, Scherer, and Stegemeyer[5] also point to this conclusion.

Saupe[6] has speculated that the blue phase has a cubic structure, based on the observation that it is optically isotropic. Recently, Brazovskii and co-workers[7] have developed a Landau theory for the isotropic-cholesteric transition. They conclude that three phases can exist below the clearing point: one of hexagonal symmetry, one the regular one-dimensional spiral, and a biaxial phase. Alexander[8] has concluded that a body-centered-cubic (bcc) structure is consistent with a Landau theory. His treatment is along the lines of that given by Alexander and McTague[9] for crystal melting, with the density replaced by a tensorial order parameter. A similar treatment has been given by Hornreich and Shtrikman.[10]

In the present paper we report the observation of Bragg reflections in the blue phase of cholesteryl nonanoate and in a mixture of that compound and cholesteryl chloride. We confirm that, in addition to the regular helical (or focal conic) structure, there exist indeed two stable blue phases. One of these we identify as having a cubic structure. That of the other has not been def-

initely determined, but the observations are consistent with a simple helix. The latter phase is stable in a range of a few tenths of a degree immediately below the clearing point, while the cubic phase is stable for about 0.5 °C below this, but is easily supercooled by a few degrees.

As the unit-cell dimensions are expected to be of the order of magnitude of the cholesteric pitch, the experiment is done with visible and near-ultraviolet light. We measure, with a spectropho-

tometer, the transmission of a nearly parallel light beam through a thin sample, as function of wavelength over a range of 300 to 640 nm. The sample is contained between fused silica slides and has a thickness variously between 0.1 and 1 mm. Typical spectra are shown in Figs. 1 and 2. The traces in the figures give the ratio of the transmitted light intensity in the cholesteric phase and the transmitted intensity for the same sample in the isotropic phase (measured at a temperature just above the clearing point). The spectra shown were made with unpolarized light.[11] We interpret these spectra as follows: In the wavelength range used, the cholesteryl esters have negligible absorption; thus any drop in the relative intensity of the transmitted light below the 1.0 value is due to scattering out of the nearly parallel light beam by the sample. For a powder sample the $(hkl)$ Bragg reflection becomes possible when

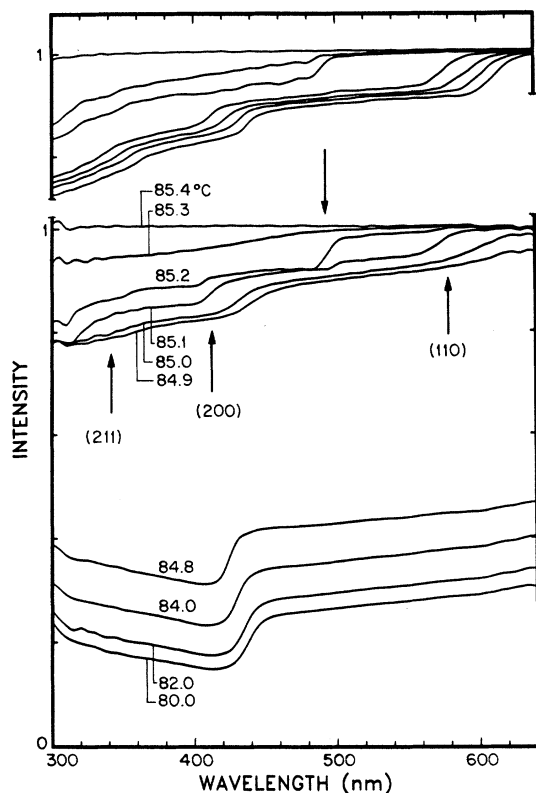$$\lambda_{hkl} \leq 2n(\lambda)d_{hkl} , \tag{1}$$



FIG. 1. Transmission spectra for a sample of 85% by weight of cholesteryl nonanoate and 15% cholesteryl chloride. The traces give the ratio of the transmission at the temperature indicated, and the transmission in the isotropic phase just above the clearing point; i.e. the spectrum of the isotropic phase is a horizontal line at 1.0 ordinate. The traces in the lower part of the figure (with temperatures indicated) give the results of a run with increasing temperature starting in the focal conic state and ending in the isotropic. The traces in the upper part of the figure are of a run starting in the supercooled blue phase at 84.8°C, with traces made at 0.1°C increments to 85.4°C for the top trace. The up arrows indicate Bragg reflections for a bcc lattice, and apply to the 85.1°C traces. Their correspondence to the observed steps is clearest in the upper part of the figure.
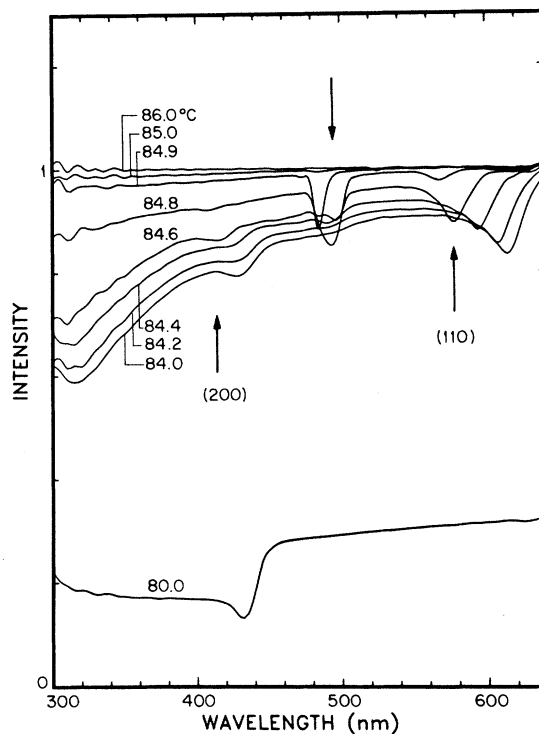


FIG. 2. Details as for Fig. 1, except that (1) the fused silica slides were covered with a thin layer of poly(vinyl alcohol) surfactant, and that (2) measurements were made at successively decreasing temperatures. The temperatures in this figure are about 0.4°C lower than those of the corresponding traces in Fig. 1, because of a small difference in sample composition.

where $\lambda_{hkl}$ is the vacuum wavelength, $n(\lambda)$ the index of refraction of the sample, and $d_{hkl}$ the spacing of the $(hkl)$ planes.

Thus the transmission spectrum of a powder sample is expected to exhibit a number of steps, the intensity dropping to a lower value at those wavelengths where Eq. (1) becomes satisfied. The steps are clearly evident in the traces of Fig. 1 and can be interpreted in a way similar to the rings in an x-ray powder photograph: We try to fit them to a specific crystal structure. An adjustment must be made for the wavelength dependence of the index of refraction $n(\lambda)$. For this purpose we have used the data of Boettcher and Graber,[12] extrapolated to shorter wavelengths using a simple dispersion formula.[13] The correction is small, amounting to 3.7% increase of the index at 300 nm relative to 600-nm wavelength.

Figure 1 shows spectra of a sample consisting of 85% by weight of cholesteryl nonanoate and 15% cholesteryl chloride. Before use the slides were cleaned in hot Chromerge (chromium trioxide dissolved in sulfuric acid). As is well known, the addition of cholesteryl chloride increases the cholesteric pitch, and it was used here to bring the spectra in a suitable wavelength range. In the mixture the spectra are shifted to longer wavelengths by about 20% relative to pure cholesteryl nonanoate. We checked that the behavior of the latter is quite similar to that of the mixture; specifically, spectra of pure nonanoate show the lowest-order steps in the same wavelength ratio as the 15% mixture, though the higher-order steps are outside the wavelength range.

Figure 1 represents the results of two actual runs. For the traces in the lower part of the figure the sample was originally at 80.0 °C, and had the focal conic texture. As expected, the spectrum shows a single step at 430 nm,[14] corresponding to the onset of Bragg scattering by the helical structure. As the temperature is increased from 80.0 °C, the transition to the blue phase takes place between 84.8 and 84.9 °C. In this phase the traces show a number of steps, most clearly seen in the upper part of the figure, which was made by cooling from the isotropic into the supercooled blue phase, and then raising the temperature in 0.1 °C steps, thus avoiding the focal conic structure. In the following discussion we identify these steps as the first three reflections for a bcc lattice: (110), (200), and (211). It should be noted, however, that the (100), (110), and (111) reflections of a simple-cubic lattice also fit our observations. We discuss the bcc case

here; the changes for simple cubic are straightforward, and will be summarized in the next-to-last paragraph. The up arrows give the calculated positions for these reflections, if one assumes the position of the (110) reflection and with the well-known relations of the bcc lattice $[d_{hkl} = a(h^2 + k^2 + l^2)^{-1/2}$ and the lattice form factors are nonzero only if $h + k + l$ is even[15]]. We assume here that the form factors derived for x-ray diffraction apply also to the present case of light propagating in a strongly optically active medium. Using standard relations,[15] one can easily show that face-centered-cubic or hexagonal-closed-packing structures will not produce the observed diffraction wavelengths.

The cubic structure is stable over a narrow range of temperatures, but a few tenths of a degree below the clearing point it changes into still another structure, as indicated by the trace of 85.2 °C. This trace is characterized by a single pronounced step near 500 nm, indicated by the down arrow. The structure of this phase is an open question at this time.

Corroborating results are shown in Fig. 2, which shows another run with the same material, but differing from that of Fig. 1 in two respects: (1) The fused silica slides containing the sample were covered with a thin layer of poly(vinyl alcohol) (PVA) as a surfactant; and (2) the spectra were recorded at successively lower temperatures, starting in the isotropic phase. An obvious feature of the traces in Fig. 2 are the pronounced intensity minima. They find their natural interpretation as Bragg reflections from oriented crystallites. Apparently, the PVA surfactant produces a preferred alignment on the surface. The oriented crystallites can no doubt be identified with the brightly colored "platelets" often observed in the microscope in reflected light.[2] As the positions of the minima in Fig. 2 coincide with the steps of the powder pattern in Fig. 1, it follows that, for the bcc structure, some crystallites are oriented with the (110) planes parallel to the surface (giving the minimum near 600 nm), and some with the (200) planes parallel to the surface (giving the minimum near 420 nm). If this interpretation is right, then we should expect additional minima, produced by Bragg scattering from other planes in these crystallites. The wavelength of the expected minima is given by

$$\lambda = p\lambda_{hkl}\sin\theta_{hkl}, \qquad (2)$$

where $\lambda_{hkl}$ is the wavelength for scattering from

the $(hkl)$ planes at normal incidence; $\theta_{hkl}$, the angle between these planes and the incident beam; and $p \approx 1$, the correction factor for the variation in the index of refraction.

With use of Eq. (2), it is found that in the (110)-oriented crystallites the (101), (10$\bar{1}$), (011), (01$\bar{1}$), (200), and (020) planes all scatter at a wavelength of 310 nm. Figure 2 shows indeed a pronounced minimum at this wavelength. It can be expected to be broader than the minimum near 600 nm, because a distribution in crystallite orientations affects it to first order, as compared with second order for the $\theta = 90°$ minima. The (200)-oriented crystallites should scatter from the (110), (1$\bar{1}$0), (101), and (10$\bar{1}$) planes at a wavelength coinciding with that for the (200) planes, and no separate minimum is therefore expected.

As mentioned, the (100), (110), and (111) reflections of a simple-cubic structure would give peaks at the same wavelength ratios as the first three bcc reflections. Higher-order reflections would be necessary to differentiate between the two structures. Neither can the results of Fig. 2 decide the issue: (100)-oriented crystallites would give (110) and (200) reflections at the positions observed in Fig. 2.

In conclusion, there seems to be good evidence for a cubic structure of the blue phase, in agreement with the predictions of a bcc phase of present theory.[7-10] However, there is a major discrepancy between experiment and theory in its present form: The latter predicts that the (110) bcc reflection should appear at the same wavelength as that for the helical (focal conic) phase. In fact, they appear at 610 and 440 nm, respectively. Neither does the theory account for the high-temperature phase.

[1]O. Lehman, Z. Phys. Chem. 56, 750 (1906).

[2]D. Coates and G. W. Gray, Phys. Lett. 45A, 115 (1973), and 51A, 335 (1975).

[3]D. Armitage and F. P. Price, J. Phys. (Paris), Colloq. 36, C1-139 (1975).

[4]K. Bergmann and H. Stegemeyer, Z. Naturforsch. 34a, 251 (1979).

[5]K. Bergmann, P. Pollmann, G. Scherer, and H. Stegemeyer, Z. Naturforsch. 34a, 253, 255, 1031 (1979).

[6]A. Saupe, Mol. Cryst. Liq. Cryst. 7, 59 (1969).

[7]S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. 69, 979 (1975) [Sov. Phys. JETP 42, 497 (1976)]; S. A. Brazovskii and V. M. Filev, Zh. Eksp. Teor. Fiz. 75, 1140 (1978) [Sov. Phys. JETP 48, 573 (1978)].

[8]S. Alexander, private communication.

[9]S. Alexander and J. McTague, Phys. Rev. Lett. 41, 702 (1978).

[10]R. M. Hornreich and S. Shtrikman, to be published.

[11]We did make one run with circularly polarized light, which showed that most of the scattering is by one circularly polarized component, the scattering of the other component being an order of magnitude weaker. This result must be considered as qualitative, because a high degree of polarization could not be maintained over the wavelength scan.

[12]B. Boettcher and G. Graber, Mol. Cryst. Liq. Cryst. 14, 1 (1971).

[13]We have fitted the data of Ref. 12 with the equation $n(\lambda) = [A + B/(\lambda_0^{-2} - \lambda^{-2})]^{1/2}$, with $\lambda_0 = 192$ nm, $A = 1.889\,48$, and $B = 7.883\,57 \times 10^{-6}$ nm$^{-2}$.

[14]As a check that this is indeed the first-order reflection, we have determined the pitch of the liquid crystal from grandjean rings. We find a pitch of 280 nm (for a $2\pi$ rotation), which, with an index of refraction of about 1.5, accounts for the 430-nm reflection.

[15]See, for instance, B. E. Warren, X-ray Diffraction (Addison-Wesley, Reading, Mass., 1969).