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OPTICAL ROTATORY DISPERSION IN SINGLE CRYSTALS OF THE CHOLESTERIC BLUE PHASES

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Abstract Large quadratic single crystals (0.5 mm on a side) of Blue Phase I and Blue Phase II were grown using both pure cholesteryl esters and mixtures of cholesteryl esters. The optical rotatory dispersion of these single crystals was studied in the wavelength region 220-600 nm. All spectra show a single first order anomalous region, indicating that the orientation of the single crystals is nearly perfect in both Blue Phases. Sometimes the second order anomalous region can also be observed at very short wavelengths. A slight asymmetry in the first order peaks provides a quantitative estimation of the small lack of perfect orientation present. All single crystals were grown from the "Fog Phase", which also possesses a characteristic optical rotatory dispersion spectrum.

INTRODUCTION

The Blue Phases of cholesteric liquid crystals are distinct thermodynamically stable phases which occur in a narrow temperature region just below the transition to the isotropic liquid. These phases possess optical rotatory power and selective reflection of circularly polarized light, but show no birefringence. Both theoretical and experimental evidence seems to indicate that these phases have a cubic symmetry.[1-3]

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Experimental investigations have for the most part been performed on polycrystalline samples (platelet texture), with different regions of the sample having different orientations of the crystalline axes. For this reason experiments have been quite successful in determining wavelength infomation, but less successful in obtaining quantitative data of other properties of the phases.

Onusseit and Stegemeyer have shown that well-oriented single crystals of these Blue Phases can be grown if the cooling rate is extremely slow.[4] Measurements in these single crystals would probe a well-determined direction within these phases, producing quantitative information about their optical properties in addition to the normal wavelength dependence.

In this paper, the results of optical rotatory dispersion (ORD) experiments in single crystal Blue Phase samples are reported. The ORD confirms that the orientation of these single crystals is indeed nearly perfect, even allowing a quantitative estimation of the deviation from perfect order. In addition, these investigations were carried out at short enough wavelengths to obtain quantitative ORD data on the little-understood "Fog Phase", thus supplying important new information concerning the properties of this phase.

EXPERIMENTAL METHOD

All compounds were recrystallized several times until transition temperatures were constant. The sample was placed between two quartz plates (15mm in diameter, 1 mm thick), separated by a 12 μm mylar spacer. Single crystals were grown by extremely slow cooling from the isotropic (40 mK/min) in

a Mettler FP52 Hot Stage with a FP5 Controller. A modification of the Controller allowed accurate and reproducable 10 mK temperature changes.[5] The Blue Phase transitions possessed a width of 30 mK, indicating that the temperature gradient in the sample was less than this value.

This extremely slow cooling rate allowed the single crystals to grow together, with no disordered region between them. In samples where the Blue Phase II (BP II) was visible, one saw the same color throughout, with only the intersection of the single crystals visible as faint lines. In the Blue Phase I (BP I), the entire field of view was again filled with large single crystals, but now possessing cross-hatching as described previously.[4]

All ORD spectra were obtained in a Jasco J-20 Spectropolarimeter, which has an accuracy of 1 nm and a range from 185 to 740 nm. The rotation angle could be measured to an accuracy of 0.02°. Absorption within the quartz plates and sample made measurements at wavelengths less than 220 nm impossible.

ORD spectra were obtained for various esters of cholesterol (myristate, nonanoate, valerate, and chloride) as well as mixtures of cholesteryl nonanoate and cholesteryl chloride. Spectra were usually taken with decreasing temperature in the "Fog", BP II, and BP I Phase, but experiments upon heating yielded similar results.

EXPERIMENTAL RESULTS

Figs. 1 and 2 show typical ORD spectra in the BP II and BP I phases respectively. The value of the rotation angle in the anomalous region is greater than any previously reported,[6-9] indicating that the degree of orientation is much better in these samples. The existence of only one anomalous region (with possibly a second order anomalous region at half the wavelength) confirms that the entire sample has the same orientation. The anomalous effect in BP I is not as large

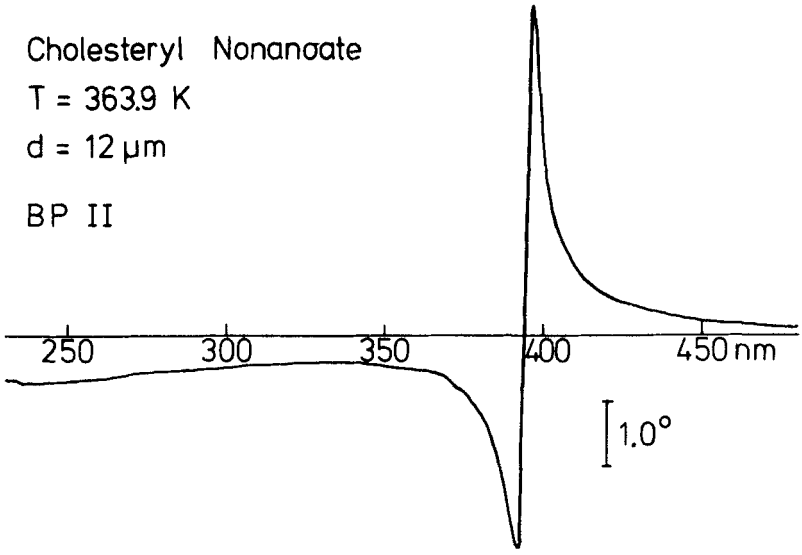

FIGURE 1. ORD spectrum of single crystals in BP II.

as in BP II, and usually is slightly broader. When the anomalous region occurs at large enough wavelength, a second order anomalous region is always present at half the wave-

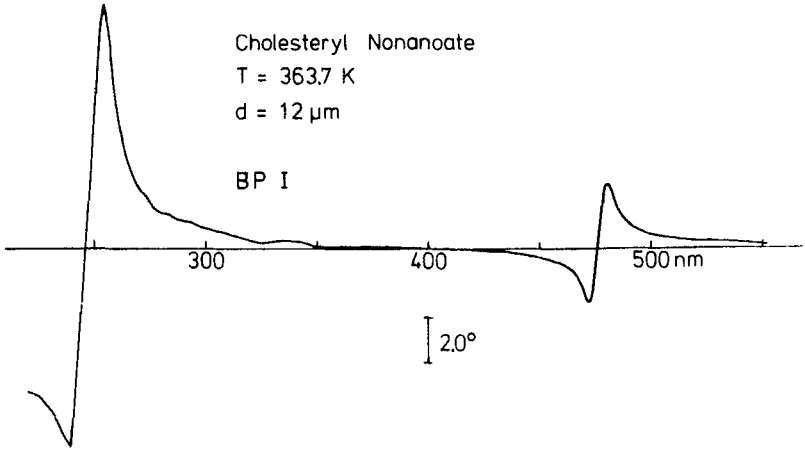

FIGURE 2. ORD spectrum of single crystals in BP I.

length in both the BP I and BP II phases. An example of this can be seen in Fig. 2. For comparison, a typical ORD spectrum from cholesteryl valerate, which forms a platelet texture rather than single crystals, is included as Fig. 3. Note that the rotation angles are much smaller and that anomalous regions are present at $\sqrt{1/2}$ and $\sqrt{1/3}$ of the largest wavelength.

The sharpness of the ORD anomalous regions allows precise determination of the wavelength of this effect. The results of such an experiment are shown in Fig. 4, where one can see that the center of the anomalous region shifts to shorter wavelength in both the BP I and BP II phases as the temperature is increased. Previous investigations with cholesteryl esters have not been this successful in determining the temperature dependence of the selective reflection maximum in BP II.[9]

Finally, the wavelength at which the anomalous region occurs is strongly dependent on the pitch of the cholesteric

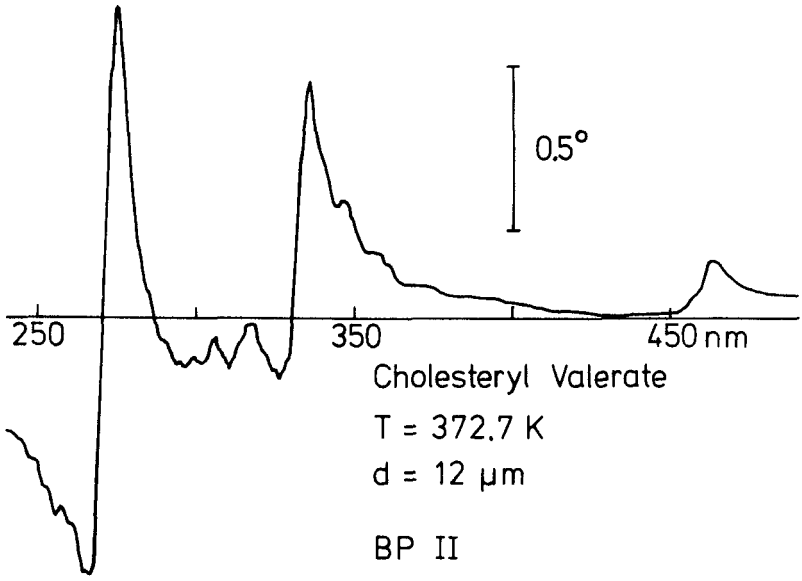

FIGURE 3. ORD spectrum of platelet texture in BP II.

phase at the transition to the BP I. Fig. 5 shows that a linear dependence is present for both pure compounds and mixtures, being different only when very different esters of cholesterol are examined.

When cooling from the isotropic phase, the BP II ORD spectrum is not the first one observed. Upon both heating and cooling, a phase with a broad ORD spectrum is always present for a temperature interval of approximately 50 mK. This is undoubtably the "Fog Phase" noted by other experimentalists.[9-10] An example of such a spectrum is presented as Fig. 6.

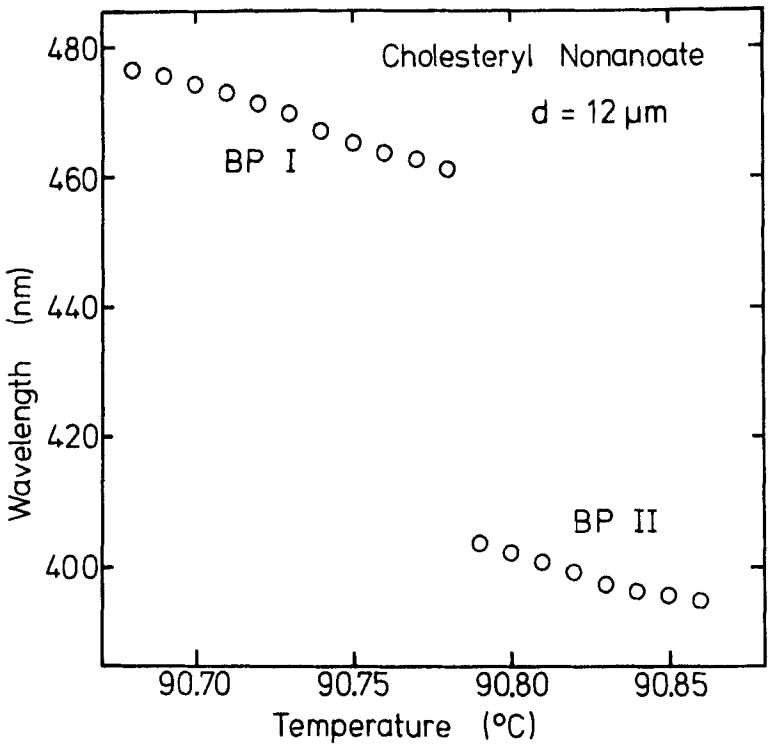

FIGURE 4. Temperature dependence of the ORD.

DISCUSSION

It should be pointed out that although the large single crystals appear uniform in transmitted light, this is not the case in reflected light. Parts of a single crystal can appear dark in reflected light, as can entire single crystals. These regions cannot be ones with another orientation, as that would cause the color in transmitted light to be very different. Perhaps the reflected light probes only

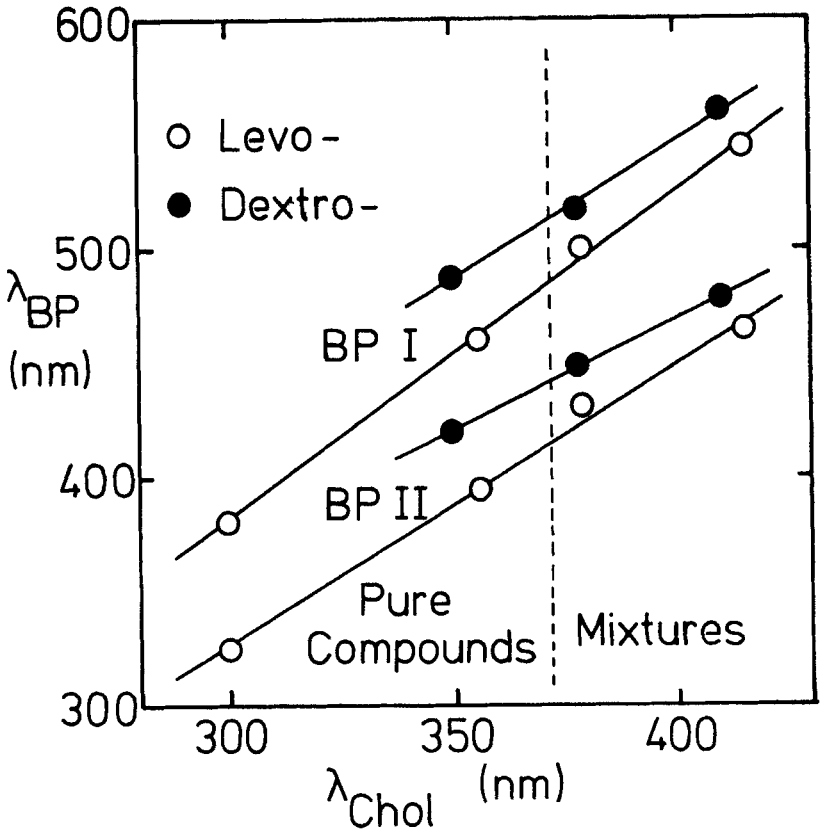

FIGURE 5. ORD for various pure and mixed samples.

a small portion of the sample next to the top plate, and here the orientation or structure is different. Perhaps these regions contain crystals at a slight angle, thus reflecting light out of the viewing field. At any rate, neither of these possibilities would have a large effect on the ORD spectra.

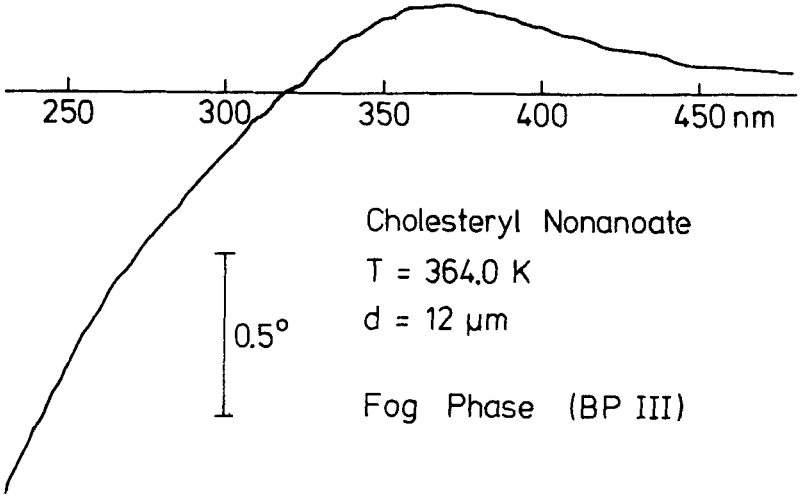

FIGURE 6. ORD spectrum of the "Fog Phase".

In all cases, a slight asymmetry is observed in the anomalous ORD peaks. The short wavelength side is always smaller in magnitude than the long wavelength side. This effect can be linked to the lack of perfect order in these samples by a simple calculation. If one assumes that as the angle between the direction of light propagation and the crystal axis, θ, is varied, the anomalous region shifts to shorter wavelength according to the Bragg condition, $\lambda = \lambda_o \cos\theta$, one can then take into account that some of the sample possesses an orientation where $\theta \neq 0$. The calculation starts with an hypothetical $\theta = 0$ symmetric ORD spectrum with a width typical for these BP II samples, but assumes that many regions of different orientation are present with a distribution given by $\exp(-\theta/\theta_R)$, where θ_R is an input parameter. The contributions from all of these regions are

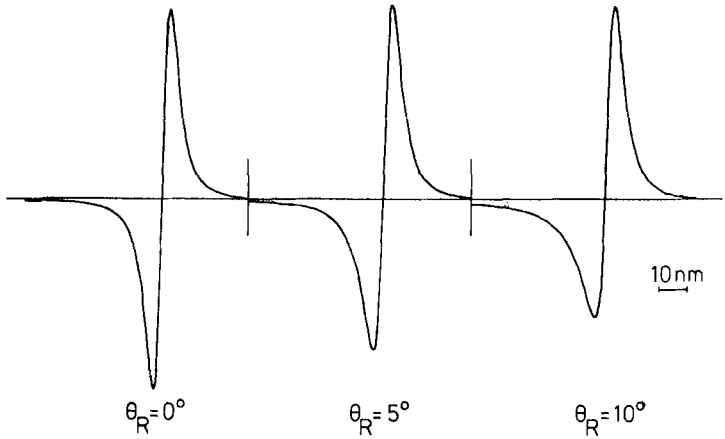

FIGURE 7. Calculated effect of a distribution in the orientation of the single crystals on the ORD.

added together to give a spectrum for a slightly unoriented sample. θ_R is a quantitative measure of the amount of disorientation. Fig. 7 shows the results of such a calculation, where it is clear that this lack of perfect orientation has the effect of lowering the shorter wavelength peak relative to the longer wavelength peak. Comparison of these results to actual BP II spectra indicates that a θ_R value of about 8° best describes the lack of perfect orientation present. This quantitative estimation of how well the sample is oriented is not surprising if one keeps in mind that these crystals are in fact fluids, with only singular points occupying lattice sites.

In cases where the wavelength is long enough, a second order anomalous region occurs at approximately half the wavelength of the first order region. This is usually the case with BP I samples, because the anomalous region occurs

at longer wavelength. Second order regions can also be observed in BP II phases when the wavelength is long enough. The second order peak comes at a wavelength 5% higher than expected, due to a slight dispersion in the index of refraction in these cholesteryl esters.[11] In many cases the second order anomalous region shows significantly greater optical rotation angles, probably due to the intrinsic increase in optical rotatory power as the wavelength is decreased.

The presence of a single ORD anomalous region in BP I indicates that the different parts of the cross-hatched "single" crystal do not possess different orientations relative to the direction of light propagation. Perhaps the polycrystalline aspect of these "single" crystals represents different azimuthal angles and is the reason the ORD effect is smaller in magnitude and slightly broader. In any case, a large difference in orientation is certainly not present. One must ask, therefore, why the cross-hatching seems to possess more than one color when viewed through a microscope.

The ORD spectrum from a platelet texture in cholesteryl valerate (Fig. 3) is interesting due to the presence of the third anomalous region at $\sqrt{1/3}$ the wavelength of the longest anomalous region. Theoretically it has been shown that simple cubic BP structures should not possess a strong chiral reflection at this wavelength.[1] Recent reflection experiments have also observed a chiral reflection at this wavelength in the BP II phase of quite a different liquid crystal, leading the authors to conclude that BP II must be body-centered cubic.[12] The strong ORD anomalous region in the BP II of cholesteryl valerate would seem to indicate that BP II is body-centered cubic in this liquid crystal also.

The "Fog Phase" ORD spectrum is quite an interesting result. Its broad anomalous quality is suggestive of a disordered phase, as has been proposed by others.[9, 10] This "Fog Phase" certainly behaves as a stable thermodynamic phase, in that it appears over the same temperature range (approximately 50 mK) upon both heating and cooling. Interestingly enough, such a "Fog Phase" could not definitely be found in cholesteryl valerate, and this compound also did not form single crystals. One must wonder if the presence of the "Fog Phase" is required for these quadratic single crystals of BP II to form. Extensive measurements on the "Fog Phase" are in progress and will be the subject of a future article.

CONCLUSION

The growth of large single crystals definitely provides a method to probe properties of the Blue Phases along a specified direction within the crystal. The ORD measurements presented here confirm that a unique direction is being examined, and even indicate the degree of disorientation present. There is no reason why other directions in these single crystals could not be investigated through angular optical measurements, although such experiments would require modification of the commercial equipment used in theses studies.

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