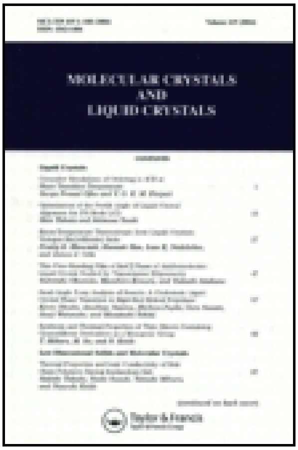

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Experimental Study on Higher Order Reflection by Monodomain Cholesteric Liquid Crystals

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Experimental Study on Higher Order Reflection by Monodomain Cholesteric Liquid Crystals

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Reflection spectra have been measured in the spectral region of the second and the third order selective reflections for monodomain cholesterics of various cell thicknesses at various angles of incidence. Thicker cells give rise to higher reflectance at larger angles of incidence. The second order reflection region consists of three bands which show characteristic polarization correlation: The central band is a total reflection band, where incident light of any polarization is reflected. The reflected light is σ polarized when π polarized light is incident and vice versa. Contrary to the central band, two side bands are selectively reflected; $\sigma(\pi)$ polarized light is reflected in the longer (shorter) wavelength band retaining its polarization. The third order reflection bands observed for the first time have been found to give the same polarization characteristics as that of the second order reflection bands.

1. INTRODUCTION

Helical structure of cholesteric liquid crystals gives rise to unique optical properties. Selective reflection is one of those which has most extensively been studied both experimentally and theoretically. Reflection takes place when right (left) circularly-polarized light is incident on a right- (left-) handed cholesteric monodomain cell along the

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helical axis in the spectral range of the first order Bragg reflection as observed by Dreher *et al.*[1] For such a normal incidence case, the light propagation can be dealt with rigorously on the basis of the spiralling dielectric ellipsoid model of Oseen.[2] On the contrary, theoretical treatment for the oblique incidence case is complicated and is possible only with proper approximations or with numerical approach. The experimental and theoretical studies for oblique incidence have been performed by Berreman and Scheffer[3] to certify that a cholesteric fluid is not locally biaxial but is uniaxial. Besides such points of view, study for oblique incidence provides us with characteristic phenomena which cannot be observed for normal incidence as follows:

1) Higher order reflection: It is due to the higher order Bragg reflection and is well known to appear in finite angles of incidence.

2) Total reflection: The existence of such a spectral region was theoretically predicted by Belyakov and Dmitrienko[4] and was experimentally observed by us recently.[5] In the region, obliquely incident light of any polarization is totally reflected. According to the numerical calculation for the optical eigenmode in various propagation direction,[6] all of the wavevectors of the optical eigenmodes are purely imaginary or are complex in the total reflection region, while two real and two purely imaginary in the selective reflection region.

3) Beat and swell: It is well known that reflection spectra exhibit subsidiary oscillation if a perfect monodomain cell is used. It was found just recently[7] that obliquely incident light of left (right) circular polarization to a left- (right-) handed helix gives rise to a beat structure in the subsidiary oscillation, while right (left) circular polarization causes a swell to be superimposed on the subsidiary oscillation. The beat structure was ascribed to the excitation of two sets of optical eigenmodes of slightly different wavelength, but the complete understanding has not been attained.

Among three phenomena mentioned above, we focus on the higher order reflection in this paper. So far experimental observation of the second order reflection bands has been made by Berreman and Scheffer.[3] But the reflection was measured only for the parallel component relative to the incident linear polarization, though the numerical calculation[8] includes the perpendicular component as well as the parallel component. Dmitrienko and Belyakov studied the higher order reflection on the basis of dynamic diffraction theory and pointed out the unique polarization characteristics in addition to information about the positions and the widths of the reflection bands. The purpose of this paper is to confirm the polarization characteristics of the second order reflection bands using a homogeneously aligned monodomain cell of high quality. Third order reflection bands are also observed for the first time. These will be presented in the following.

2. EXPERIMENTAL PROCEDURE

Preparation of sample cells has been described in our previous paper.[7] Only the difference in samples used is the mixing ratio of active and racemic *N*-(*p*-ethoxybenzylidene)-*p*-2-methylbutylaniline (EBMBA).[9] To find the second order reflection bands in a suitable wavelength region for optical measurements at various angles of incidence, the mixing ratio was chosen as 20 wt% of active and 80 wt% of racemic forms. Then the helical pitch is 1.0 μm. The most important point for this kind of measurement is to have monodomain cells of high quality, which were realized between two rectangular prisms treated by aqueous solution of poly(vinylalcohol) and rubbed back and forth along a certain axis.

The details for reflection spectra measurements have been described in our previous paper.[7] We only comment here about the absolute value of the reflectance. Because of refraction due to the rectangular prisms, the position of the sample cell is generally slightly deviated from the center of a goniometer, where a pinhole, an analyzer and a photomultiplier tube are mounted. Therefore, in order to find the optimum position, we cannot but iterate slight shifting and rotation of the cell while monitoring the intensity of the reflected light. Because of such a delicacy in optical alignment, the absolute value should be read with about $\pm 10\%$ error.

Measurements of refractive indices were carried out by observing beam diffraction of an Ar^+ laser (457.9 nm, 488.0 nm and 514.5 nm) and a He–Ne laser (632.8 nm) by a wedge shaped cell where racemic EBMBA is aligned along the groove.

3. EXPERIMENTAL RESULTS

Six sets of reflection spectra will be shown for various angles of incidence, various cell thicknesses and various combinations of polarizers. The first set of data shown in Figure 1 is a dependence of the reflection spectra on the angle of incidence, which are taken for left- and right-circularly-polarized light without an analyzer. The cell thickness is 38 μm. Three characteristic reflection bands are observed. These are second order reflection bands as proved to be by the first

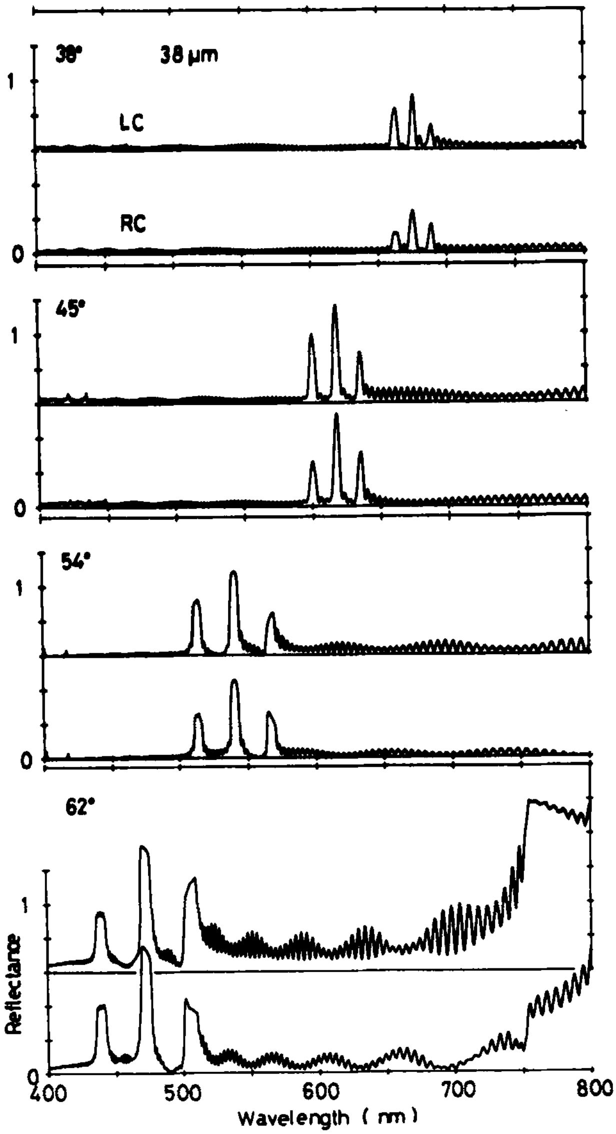

FIGURE 1 Reflection spectra in a monodomain cholesteric liquid crystal cell of 38 μm thickness at various angles of incidence. The incident polarizations used are left and right circular polarizations. An analyzer is not used.

order reflection band near 800 nm in the spectrum at 62° for left circular polarization. These bands become wide and large, and shift toward shorter wavelength side with increasing the angle of incidence.

The propagation of light is characterized by wavevectors of optical eigenmodes: It is well known that the wavevectors of the propagation modes are real, while that of the reflection modes are purely imaginary for the first order reflection band in case of normal incidence. According to the calculation for the second order reflection,[6,10] there exists triplet bands. All of the wavevectors of the optical eigenmodes in the central band are complex as that in the total reflection band in the first order reflection region, while the two side bands are selective reflection bands where both propagation and reflection modes exist. With increasing the angle of incidence, the band width becomes wide and the imaginary part of wavevectors increases, resulting in faster damping of the reflection modes, consequently in higher reflectance as observed experimentally. Generally all of the eigenmodes are excited by incident light of any polarization. The reflectance necessarily depends on the relative amplitude of four eigenmodes excited as well as the magnitude of the imaginary part of their eigenmodes, which in turn brings about the selective reflection.

It should also be noticed that a beat and a swell structures are clearly observed for left- and right-circularly polarizations, respectively, especially at 62°. Discussions about these structures were presented in our previous paper[7] and will not be made more in this paper.

To see the cell thickness dependence, reflection spectra at 45° in 6 μm^t, 18 μm^t and 38 μm^t cells are displayed in Figure 2. Incident polarizations used are left- and right-circularly polarized light without an analyzer. The reason why the reflection bands locate at different wavelengths for three cells of different thickness is as follows. In a homogeneously aligned cell of slightly wedge shape, there appear Grandjean-Cano lines due to discontinuous change in the number of helical turns. Thus the apparent helical pitch in an actual cell p_{app} is generally different from the intrinsic pitch p:

$$\left|\frac{p_{app} - p}{p}\right| < \frac{1}{2n},$$

where n is the number of full turn. It is very hard to have a cell whose surfaces are perfectly parallel. Most of our cells, actually, have one or two Grandjean-Cano lines. Therefore in thin cells such as 6 μm thickness, where only six full turns exist, the difference $p_{app} - p$ is serious and amounts to almost 10%. This explains the mutual dif-

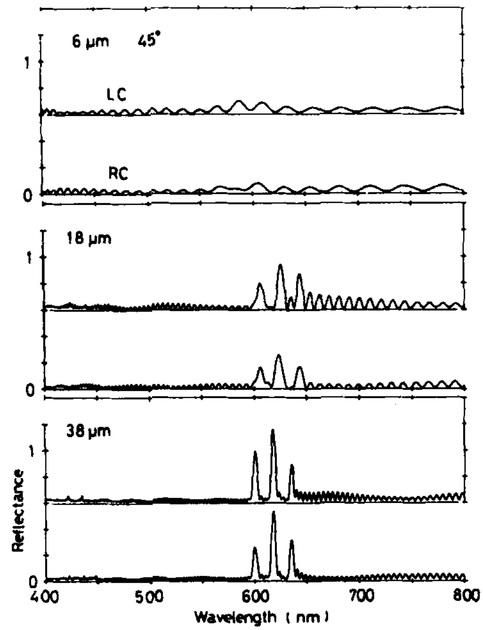

FIGURE 2 Reflection spectra at 45° in 6 μm^t, 18 μm^t and 38 μm^t cells.

ference in the wavelength of reflection bands among three cells of different thickness.

Reflectance is also governed by the cell thickness. In a thin cell, light passes through without suffering enough attenuation, resulting in low reflectivity as shown in the case of the 6 μm^t cell. The cell thickness dependence of the subsidiary oscillation is also remarkably seen in Figure 2, which was discussed in detail in our previous paper.[7]

The polarization correlation of the reflection bands may provide us with important information on optical eigenmodes, since there are no means for the direct observation of the eigenmodes.[7,12] The following three sets of data are reflection spectra measured at 45° using an analyzer. Figure 3 is for circularly-polarized light. In the central band region, a circular polarization does not change its polarization by reflection, while two side bands have components of counter circular polarization.

Characteristics selective reflection takes place for linear polarizations in the second order reflection bands as shown in Figure 4, while circular polarizations are characteristic in the first order reflection band by normally incident light. The linear polarizations used are π and σ which have the electric fields of radiation in the incident plane

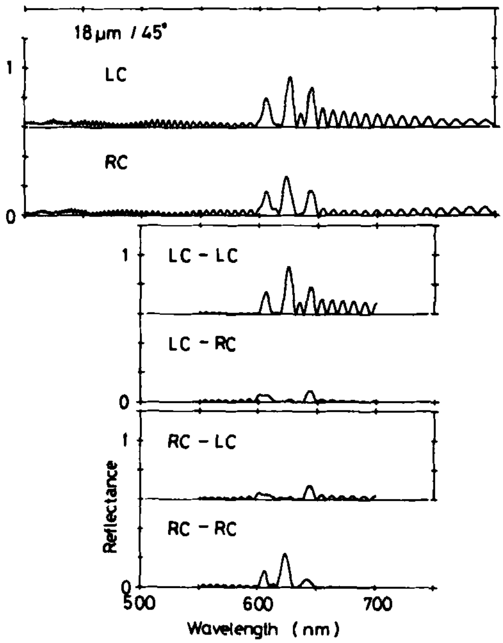

FIGURE 3 Reflection spectra by circularly-polarized light at 45° in a 18 μm' cell. The top is the spectra without an analyzer and the other are results for four combinations of a polarizer and an analyzer, which are denoted in the figure.

and perpendicular to the incident plane, respectively. Among three reflection bands, the central band is the total reflection band where incident light of any polarization is totally reflected. Actually both σ and π polarized light are reflected as shown in Figure 4, though the reflectance does not amount to 100% because of the thin cell. It should be noted that the reflected light is σ polarized when π polarized light is incident and vice versa. This characteristic polarization correlation is predicted by Dmitrienko and Belyakov.[10] Careful observation of Berreman's calculated spectra[8] also leads to the same characteristics. Contrary to the central band, the two side bands are selectively reflected; σ polarized light is reflected in the longer wavelength band and the reflected light is σ polarized, and π polarized light is reflected in the shorter wavelength band retaining its polarization. The characteristic polarization correlation is independent of cell thickness as shown in Figure 5 for a 38 μm' cell.

The last set of reflection spectra is for the third order reflection bands observed for the first time. As seen in some of the spectra shown above, there exist small bands ascribed to the third order

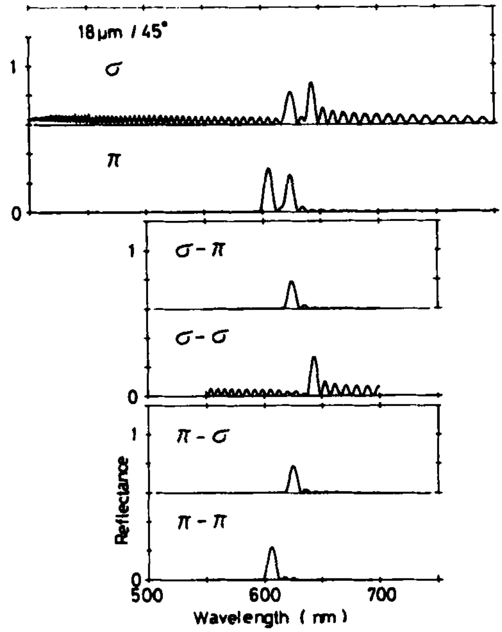

FIGURE 4 Reflection spectra by linearly-polarized light at 45° in a 18 $\mu m'$ cell.

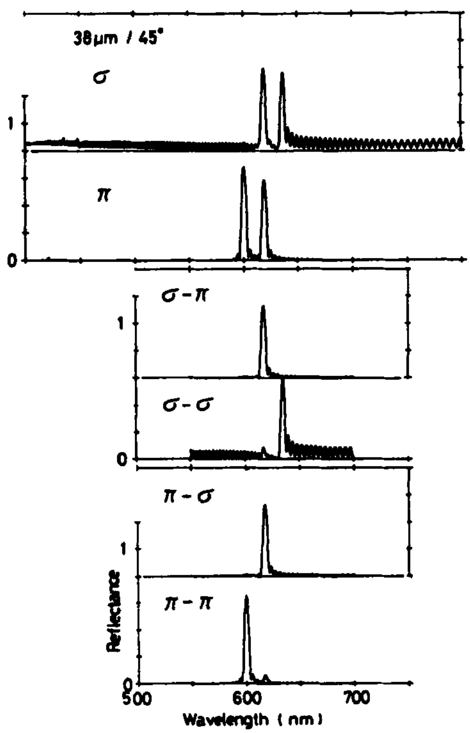

FIGURE 5 Reflection spectra by linearly-polarized light at 45° in a 38 $\mu m'$ cell.

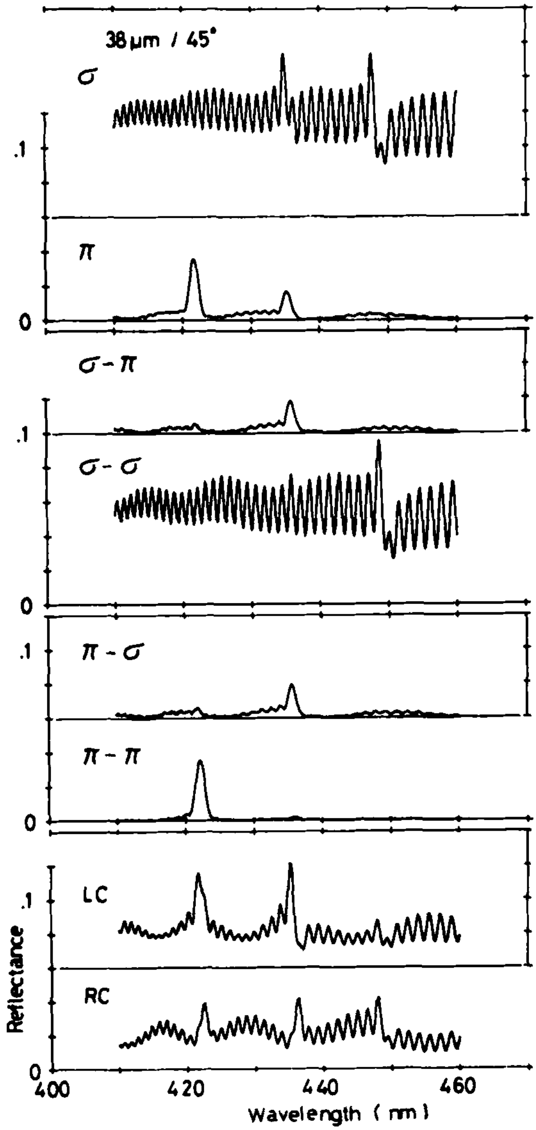

FIGURE 6 Reflection spectra in the third order reflection region. Note that both an ordinate and an abscissa are in an expanded scale.

reflection bands on shorter wavelength side than the second order reflection bands. The spectral region of the third order reflection is shown in Figure 6 in an expanded scale. The polarization correlation shows the same behavior as that of the second order reflection bands.

It is worthwhile to point out the similarity between the polarization correlation of the higher order reflection bands and that of the first order reflection band. As shown in our previous paper,[7] the first order reflection band splits into three. The central band is the total reflection band, where the perpendicular component relative to the incident linear polarization is much dominant compared with the parallel component.[7,13] It is also interesting that $\sigma(\pi)$ polarized light is reflected by $\sigma(\pi)$ polarized light incidence in the longer (shorter) wavelength region than the total reflection band in the first order reflection region as in the higher order reflection bands.

4. COMPARISON BETWEEN EXPERIMENTAL RESULTS AND CALCULATIONS

We now try to compare the experimental results with calculation based on dynamic diffraction theory,[10] since the theory has given analytic form for the position and the width of the higher order reflection bands. To perform the comparison, the refractive indices of EBMBA has to be measured including their dispersion. Figure 7 is a temperature dependence of refractive indices. The refractive indices

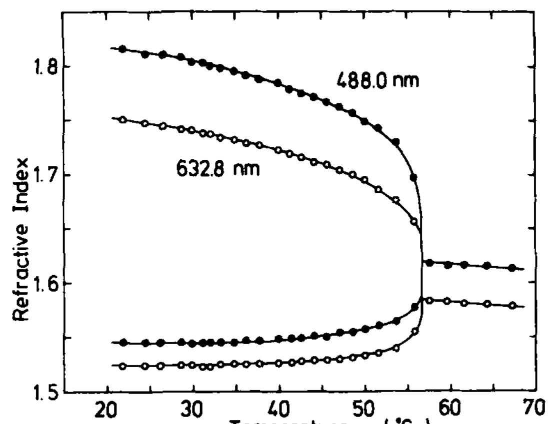

FIGURE 7 Temperature dependence of refractive indices of racemic EBMBA at two wavelengths, 488.0 nm and 632.8 nm.

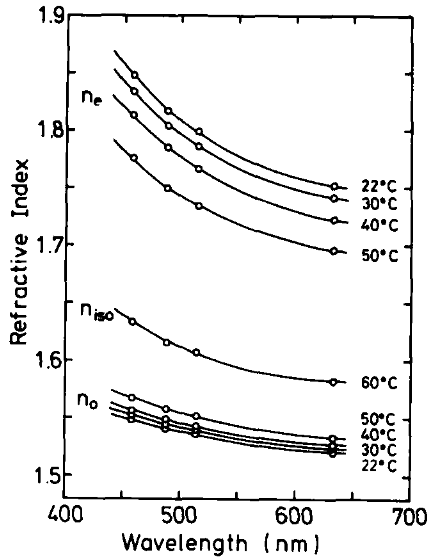

FIGURE 8 Dispersion of refractive indices of racemic EBMBA at several temperatures.

vary with wavelength as shown in Figure 8. Using the equations in ref. 10 and the refractive indices at room temperature, the relative position of three peaks $(\lambda_\sigma - \lambda_\pi)/\lambda_T$ and the reflection band width such as $\Delta\lambda_T/\lambda_T$ are obtained as listed in Table I, where, for instance, λ_σ is the wavelength of the band where σ polarized light is reflected and $\Delta\lambda_T$ is the band width of the total reflection band. The fairly good agreement with the experimental results is obtained, though the insufficient cell thickness does not bring about reflection bands of saturated structure, preventing the accurate determination of the band width.

TABLE I

Comparison between experimental and theoretical results on relative positions of three peaks and reflection band widths

			Theory	Experiment
position	2nd	$(\lambda_\sigma - \lambda_\pi/\lambda_T)$	0.053	0.057
	3rd	$(\lambda_\sigma - \lambda_\pi/\lambda_T)$	0.059	0.060
width	2nd	$\Delta\lambda_\sigma/\lambda_\sigma$	0.031	0.020
	2nd	$\Delta\lambda_T/\lambda_T$	0.020	0.015
	2nd	$\Delta\lambda_\pi/\lambda_\pi$	0.013	0.012
	3rd	$\Delta\lambda_T/\lambda_T$	0.0013	0.002

Comment should be made on the amplitude of the subsidiary oscillation. As seen in Figs. 4–6, ($\sigma - \sigma$) spectra has large amplitude in the subsidiary oscillation, while the others small. Especially the reflection bands in the ($\pi - \pi$) spectra are scarcely accompanied with the subsidiary oscillation as clearly seen in Figure 6. The qualitative agreement with the dynamic diffraction theory can be obtained in terms of eq. (26) in ref. 4; in the wavelength region which is far from the reflection region, reflected intensity ratio $I_{\sigma\sigma} : I_{\sigma\pi} : I_{\pi\sigma} : I_{\pi\pi}$ is given by $1 : \cos^2\theta : \cos^2\theta : \cos^4\theta$, where θ is the angle of incidence. In the longer wavelength region than the first order reflection band, however, this relation is not obtained experimentally even qualitatively as shown in our previous paper.[7] Some intuitive physical explanation must be considered.

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