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Electric Field Effects on the Pretransitional Optical Activity of CB15

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Abstract. — The influence of applied electric fields on the pretransitional optical activity ($\phi$) in the chiral nematic 4-cyano-4-(2-methyl)butylphenyl (CB15) was investigated. A rotating analyzer system was used to measure the optical activity and fields up to 800 kV/m were applied. The zero-field results are consistent with theoretical predictions and contributions from the $m = 2$ mode to $\phi$ are evident in the data. Large electric fields destroyed the contributions from the $m = 2$ mode.

Introduction

Significant progress towards the understanding of phase transitions in highly chiral nematics stemmed from the realization that the order in such systems can be represented by a linear combination of five basic structural modes [1, 2]. These modes labelled $m = \pm 2$, $\pm 1$ and 0 represent the planar spiral, conical spiral and the nonchiral modes respectively (for schematic representations of these structural modes [3, 4]). Each mode has its own correlation radius and a characteristic temperature, $T_m^*$, at which this correlation radius diverges. All the $T_m^*$ are lower than the transition temperature, $T_c$, and $T_1^* < T_2^*$.

Chiral nematics of sufficiently short pitch [5, 6] are intriguing because they form the blue phase in a narrow temperature interval between the isotropic and cholesteric phases. If the isotropic-blue phase transition is approached by cooling, thermodynamic fluctuations in the isotropic phase become more correlated and this results in a sharp increase of many properties (e.g., intensity of light scattered and the electric or magnetic-induced birefringence). Another property which behaves similarly is the pretransitional optical activity. Although this effect was not anticipated [7], it has proven to be a sensitive probe into the nature of such fluctuations. The first evidence for this enhanced optical activity ($\phi$) was presented by Cheng and Meyer [8]. They calculated and verified the $(T - T^*)^{-0.5}$ dependence of $\phi$. Dolganov, Krylova and Filev [9] using the same framework as Cheng and Meyer confirmed this divergent behavior in a mixture of N-(p-methoxybenzylidene)-p-butylaniline (MBBA) and 5% cholesteryl capriate. Bensimon, Domany and Shtrikman [10] extended the theory to include the blue phase.

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In these earlier versions of the theory [8–11], only the contributions from the \( m = \pm 1 \) modes were considered. Filev [12] in his theoretical approach, proposed a mode coupling hypothesis whereby the \( m = \pm 2 \) modes could become activated, but unfortunately, did not provide all the details of the calculations. He predicted that close to \( T_c \), in highly chiral systems, \( \phi \) would reach a maximum and then decrease (since the planar spiral and conical spiral modes make opposite contributions to the optical activity). This maximum in \( \phi \) was first observed by Demikov and Dolganov [13] in the isotropic phase of cholesteryl nonanoate.

However, the \( m = \pm 2 \) modes contribute directly to \( \phi \) in the isotropic phase without coupling between the \( m = \pm 1 \) modes and \( m = \pm 2 \) modes. The dominant contribution to \( \phi \) is from the \( m = \pm 1 \) modes. However, at temperatures very close to \( T_c \), contributions from the \( m = \pm 2 \) modes and the \( m = \pm 1 \) may become comparable; also, contributions from the \( m = \pm 2 \) modes are expected to increase with increasing chirality. Demikov and Dolganov [14] have reported that in the highly chiral nematic 4-cyano-4-(2-methyl)butylphenyl (CB15) the contributions made by fluctuations of the \( m = \pm 2 \) modes in the temperature range \( 1 \text{ K} < T - T_c < 8 \text{ K} \) is 10 to 1% of the total optical activity.

The pretransitional optical activity in CB15 followed a nonmonotonic curve with a nonmonotonic region \( (T - T_c \approx 0.2 \text{ K}) \). This effect is due to direct contributions from the \( m = \pm 2 \) modes [3,14] and not mode coupling as has been suggested in many cases [4,12,15–18]. In addition, Demikov and Dolganov [14] claimed that contributions from the \( m = \pm 2 \) modes [14] should vary as \( (T - T^{+}_c)^{-1.5} \) while those of the \( m = \pm 1 \) modes should vary as \( (T - T^{-}_c)^{-0.5} \). Collings [3] has confirmed that the fit using an exponent of \(-1.5\) for the \( m = \pm 2 \) modes is significantly better than using an exponent of \(-0.5\). Further evidence for contributions from the \( m = \pm 2 \) modes to \( \phi \) has been reported in a number of cases [15–18].

We investigated the influence of D.C. electric fields on the pretransitional optical activity of CB15. According to the literature [19], CB15 possesses the shortest cholesteric pitch as well as a high positive dielectric anisotropy. Hence, it is expected to show a large pretransitional Kerr effect. An increase in field-induced ordering would enhance \( \phi \). The applied field could also affect the magnitude and temperature dependence of \( \phi \) depending on how it interacts with the planar and conical modes.

There are only four reports [4,20–22] of attempts to measure field induced optical activity. The first such experiment [20] in which cholesteryl oleate was used, did not show any evidence of electric-field-induced optical activity. The second experiment on the pretransitional region of a smectic A material [21] showed only a small effect. Much larger effects were observed by Kang and Dunmur [4] on mixtures of the chiral nematic (S)-4’(2-methylbutylphenyl)-4-n-decyloxybenzoate (CE6) and the nematic n-pentylanobiphenyl (CB5). In some of these mixtures, the applied fields increased the pretransitional optical activity. In other mixtures, the pretransitional optical activity changed sign on the application of large electric fields. The most recent study on highly chiral propionate ester liquid crystals revealed a pretransitional behaviour which did not follow a simple Landau-de Gennes temperature dependence. The pretransitional optical activity in these esters, which form chiral smectic phases, are five to eight times greater than in CE6 and at least twice that of CB15. In the laterally fluorinated propionate ester, the pre-transitional optical activity decreased slightly with applied fields.

1. Theory

1. Theory

The theoretical fundamentals of optical activity in chiral nematics have been treated in detail in several places [8–13]. We will therefore, only present the results established by these studies. Plane polarized light travelling through an optically active medium of thickness \( z \) will be rotated
through an angle $\phi$:

$$\phi = \phi_0 + \phi_{m=\pm 1} + \phi_{m=\pm 2}$$  \hspace{2cm} (1)

$\phi_0$ the molecular optical activity (which has no orientational order) is given by:

$$\phi_0 = \frac{16\pi^3 N \lambda \beta}{\lambda^2 c}$$  \hspace{2cm} (2)

where $\beta$ is the optical rotatory parameter, $N$ the number density, $\lambda$ the wavelength of light and $c$ the vacuum velocity of light.

The structural optical activity which is much greater than the molecular contribution appears as soon as orientational correlations exist. The contribution to $\phi$ from the $m = \pm 1$ modes is given by:

$$\phi_{m=\pm 1} = \frac{k_B T k_0^2 q_0}{48\pi (\varepsilon)} \frac{c}{2b} \left[ 1 + \frac{c}{2b} \right]^{-3/2} \frac{1}{(T - T^*)^{1/2}}$$  \hspace{2cm} (3)

where $k_B$ is the Boltzmann's constant, $k_0$ the wave vector of the light, $(\varepsilon)$ the average dielectric constant and $q_0$ represents the chirality of the system ($q_0 = 4\pi / \text{Pitch}$).

The contribution to $\phi$ due only to the $m = \pm 2$ modes is given by:

$$\phi_{m=\pm 2} = -\frac{k_B T k_0^2 q_0}{48\pi (\varepsilon)} \frac{c}{2b} \left[ 1 + \frac{c}{2b} \right]^{-3/2} \frac{1}{(T - T^*)^{3/2}}$$  \hspace{2cm} (4)

Wyse, Ennis and Collings [23] measured both the temperature and wavelength dependence of $\phi$ and fitted the data to a function expressed as even powers of $(k/q_0)$. This function included a coupling term in the fourth order coefficient and contained the same exponent (-0.5) for the temperature dependence of the second and fourth-order coefficients. However, more recent theoretical work [3, 14] predicts that the $m = \pm 1$ modes contribute in the second order term of the wavelength expansion, but both the $m = \pm 1$ and $m = \pm 2$ modes contribute directly in the fourth order term. The exponents for the second and fourth order terms are also different. The temperature dependence of $\phi$ (at fixed wavelengths) is given by:

$$\phi(T) = \frac{A}{(T - T^*)^{0.5}} + \frac{B}{(T - T^*)^{1.5}} + \frac{C}{(T - T^*)^{1.5}} + \phi_0$$  \hspace{2cm} (5)

The first term in equation (5) represents the dominant $m = 1$ contribution. For different wavelengths, $A$ varies as the second power of $(k/q_0)$ while $B$ and $C$ vary as the fourth power of $(k/q_0)$.

2. Experimental Details

The optical activity was measured using a rotating analyzer system similar to that described elsewhere [8, 17] (see Fig. 1). Light from a He-Ne laser was split into two beams, one of which passed through the sample and then through a rotating polaroid. For field-effect studies, this beam propagated perpendicular to the direction of the applied field. The second beam emerging from the beam splitter served as the reference beam and was modulated by a two blade chopper attached to the rotating polaroid. The beams were then focused onto two photodiodes. The phase difference between the signals from the photodiodes was measured with a lock-in amplifier (EG&G Model 5104). The optical rotation is half that recorded by the lock-in amplifier. A precision of $\pm 0.01^\circ$ is possible with our apparatus. The molecular component of $\phi$ was determined by measuring the optical activity at a temperature at least
Fig. 1. — The rotating analyser system for measuring optical activity. LS (laser), P (polarizer), BS (beam-splitter), M (mirror), S/C (sample surrounded by coolers), CH (chopper), L (focusing lens), PD (photo-diode), LA (Lock-in amplifier), MC (microcomputer).

Fig. 2. — Top view with cover glass missing and longitudinal cross-section of the electro-optic cell. The dimension of the cell are as follows: gap between electrodes = 3.75 mm; sample thickness = 1.12 mm.
40 K above $T_c$ [23] (room temperature for CB15) were pretransitional effects are very small. The structural optical activity is the difference between the measured values and $\phi_0$.

The cell used is shown in Figure 2. The cell consisted of two thoroughly cleaned microscope slides bonded with epoxy to two T-shaped aluminum plates which acted both as electrodes and spacers for setting the optical path length. The gap between the electrodes was filled with CB15 (by capillary action) and sealed with quick drying epoxy. A microscope with a ruled eyepiece was then used to measure the spacing between the electrodes and check the uniformity of the gap. The laser light passed through the central portion of the cell where the field is most homogeneous and edge effects are negligible. The fields used were large enough to induce measurable effects but not large enough to produce field-induced phases and electrohydrodynamic effects [24].

The cell was sandwiched between cascaded annular-shaped (to allow for the passage of the laser beam) thermoelectric coolers. These coolers (Melcor RH annular series) allowed us to control the sample temperature electrically. The coolers and cell were attached to two large metal plates which were cooled with dry ice. It was possible to control the temperature to within at least ±0.01 K with the dry ice/coolers combination. The sample was kept at a constant temperature for at least 15 min before temperatures, transmitted intensities and phase angles were recorded, since at low temperatures structural relaxation times are long. We assumed that the liquid crystal was in thermodynamic equilibrium when these three quantities were constant. The temperatures were recorded with a 5 k $\Omega$ thermistor from Fenwal Electronics which is accurate to at least ±0.005 K.

3. Results and Discussion

The temperature dependence of $\phi$ for CB15 shows a pretransitional maximum at 0.53 K above $T_c$ (Fig. 3). This extremum in $\phi$ is consistent with theoretical predictions that close to $T_c$ contributions from the $m = 2$ modes are comparable with those of the $m = 1$ modes but of opposite sign. The data were fitted to equation (5) and the following six fitting parameters were found:

$$A = 75 \pm 7 \text{ (deg} \times \text{K}^{-1/2}/\text{cm}) \quad B = 70 \pm 14 \text{ (deg} \times \text{K}^{1.5}/\text{cm})$$

$$\phi_0 = -18 \pm 3 \text{ (deg/cm)} \quad C = -55 \pm 21 \text{ (deg} \times \text{K}^{1.5}/\text{cm})$$

$$T_2^* = 238.7 \pm 0.8 \text{ (K)} \quad T_1^* = 238.3 \pm 2.7 \text{ (K)}$$

The least-squares fit is quite good except in the immediate vicinity of the pretransitional extremum where there is a 7% difference between experiment and theory. The magnitudes of the parameters $B$ and $C$ are close, which might suggest that the contributions from the planar and conical modes are comparable in the fourth order term. The six fitting parameters can be varied considerably while still maintaining a good fit, therefore, this is not the best method to measure $T_1^*$ and $T_2^*$; it would be much better to measure each temperature directly using the back-scattering of circularly polarized light [25].

The isotropic-BPI transition in CB15 is quite difficult to detect from any momentary decrease in the transmitted intensity. However, the transition temperature, $T_c = 239.30 \text{ K}$, is taken at the point where the optical activity changes sign [14]. There are just two published values [14, 26] (248 K and 243.9 K) for the transition temperature of CB15. The actual sample temperature is likely to be different from the measured value owing to close proximity of the coolers and temperature gradients between the glass and the sample. However, if the positions of the components are not altered during the experiment, only systematic errors will result which should not affect the determination of temperature differences necessary for the analysis of the critical phenomena associated with the phase transition.
Fig. 3. — Theoretical fit (solid line) to the optical activity in the isotropic phase of CB15. The circles represent the experimental data. The wavelength of light is 633 nm.

The pretransitional optical activity for several voltages are shown in Figure 4. The most obvious trend is the decrease in magnitude of the pretransitional maximum with increasing applied fields. This decrease may be attributed to the field unwinding of the local helix. The optical activity data for applied fields contain three regions (I, II and III) with different pretransitional optical activity dependence. Consequently, the fit to equation (5) is poor, especially for large fields.

For example, at an applied voltage of 500 V, region I corresponds to the temperature interval \( \sim 260 \text{ K} \) to 251 K, region II to the interval \( \sim 251 \text{ K} \) to 247.5 K and the rest of the data is considered to be region III. The data for other voltages can be similarly grouped. Region III which contains the peak of the data is destabilized by the field and is virtually gone at 3 kV. Large fields therefore, destroy the contributions of the \( m = 2 \) mode towards \( \phi \). Contributions from the \( m = 1 \) mode which are expected to be the dominant contribution in regions I and II appear to be almost field independent.

Similar studies [22] on the (S) enantiomer of a laterally fluorinated propiolate esters have revealed that \( \phi \) decreased slightly on application of a field of 3 V/ \( \mu \text{m} \) without any significant enhancement or appearance of new features. Binary mixtures of the R and S enantiomers behaved similarly. The dielectric anisotropies of these materials are small and negative and as such, will show poor field alignment. However, when the (R) enantiomer was mixed with CB5 which has a large positive dielectric anisotropy a large enhancement in \( \phi \) was seen. It is surprising that both CB15 and the propiolate esters both show a decrease in \( \phi \) with applied fields since the phases below the isotropic phase in these materials are different and CB15 has a positive dielectric anisotropy.
Fig. 4. — Field dependence of the pretransitional optical activity in CB15 for applied voltages varying from zero to 3 kV. The wavelength of light is 633 nm.
The voltage dependence of the peak optical activity is shown in Figure 5. The peak optical activity decreases rapidly for applied voltages \( \leq 1 \) kV. For higher voltages, the peak optical activity depends only weakly on the applied fields which is probably due to complete molecular alignment of the sample. The extremum of \( \phi \) in the negative dielectric anisotropic fluorinated propiolate esters of reference [22] is insensitive to the large applied field.

Also, when fields are present, the optical activity changes sign at temperatures about 8 K above the temperature corresponding to the peak optical activity. Kang and Dunmar [4] have reported a change in sign of the optical activity in mixtures of CE6/CE6R/CB5 on the application of large electric fields (1 kV/mm). In CB15 which has a greater positive dielectric anisotropy than the above mixtures, this change in sign of optical rotation appears in fields as low as 0.125 kV/mm. Contributions from the planar spiral mode could result in a change in the sign of the optical activity but this effect only occurs close to \( T_c \) [14]. There are no permanent dipoles in CB15 which point at an angle to the long molecular axis and hence the possibility of a field induced sign change in the dielectric anisotropy is not expected. It is thus not possible to offer an explanation for this change in sign of the optical activity.

The shift in transition temperature (\( \Delta T \)) with applied fields (\( E \)) is given by the Kirkwood-Helfrich [27] relation:

\[
\Delta T = \frac{1}{2} \frac{T_c M}{\rho \Delta H} (\varepsilon_2 - \varepsilon_1) \varepsilon_0 E^2
\]

where \( T_c \) is the transition temperature at zero field, \( M \) the molar mass, \( \rho \) the density, \( \Delta H \) the molar transition enthalpy and \( \varepsilon_1 \) and \( \varepsilon_2 \) are the permittivities of the two phases under discussion. For the isotropic-BPI transition, this shift is expected to be small if not zero since
$\Delta \epsilon \approx 0$ in this case. The electric field has little effect on the transition temperature for the low fields (500 V and 750 V). However, for the higher fields the transition shifts to slightly higher temperatures. Unfortunately, we cannot (owing to the unavailability of a microscopic cold stage) determine optically if this shift is a new effect or an experimental artifact due to the field strength. In order to determine $T_c$ accurately, the thermistor should be in contact with the sample itself and not the glass cell. Unfortunately, this is very difficult to achieve experimentally.

The maximum optical activity, on the other hand, is more sensitive to applied fields shifting to higher temperatures with increasing fields. On the other hand, the peak value of $\phi$ in the propiolate esters appears to be both field and temperature independent. The phase transitions when 2000 and 3000 V were applied were detected by the first decrease in intensity measured at the output of the first photo diode. These reductions in intensities were not detected for the smaller voltages.

The coefficient of the dominant term in the expression for $\phi$ has been found by Battle, Miller and Collings [17] to increase with increasing chirality and by Kang and Dunmur [4] to decrease linearly with increasing field. The magnitude of $A$ decreased (though not linearly), with increasing field strengths. This is evident from the best fits of the data to equation (5).

Recent experimental results has confirmed that the isotropic-BPIII transition in S,S-$(+)-4 \,|\,-(methylbutylphenyl)-4\/-\,(methylbutyl)-4biphenylcarboxylate$ (CE2), is continuous [28]. Since CB15 is highly chiral (very short pitch) and forms just one blue phase (BPI) [14,19], our results (no decrease in transmitted intensities at the transition) raise the question whether the isotropic-BPI transition is continuous in this material.

Conclusion

We have reported the results of field-induced optical activity in the pretransitional isotropic region of the highly chiral nematic CB15. Field effects can be a useful probe for studying local molecular interactions in chiral systems. Electric field-chirality interactions appear to be quite complex and outside the scope of the present form of the theory.

The results indicate that the $m = 2$ contributions to $\phi$ is destroyed by large electric fields. Also, close to the transition, the magnitude of the optical activity decreases considerably with increasing fields. The zero field results are consistent with the theoretical model.

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