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Optical activity in CE6 A new metastable blue phase?

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The optical rotation of a mixture of 60 per cent of chiral and 40 per cent of racemic CE6 as an 18 μm thick sample placed between glass plates treated with PI has been measured. This mixture exhibits one blue phase (BP1) on heating over a temperature range of about 0.1°C. On cooling the sample on the other hand, the BP region is expanded to 0.6°C and is divided into two regions. One region (BP1) (of range about 0.38°C below the isotropic-blue phase transition) shows two Bragg wavelengths which increase with decreasing temperature. For the second region (BPS) (of range about 0.22°C above the cholesteric-blue phase transition), one Bragg wavelength decreases with decreasing temperature, and a third Bragg wavelength appears. At constant temperature both phases remained stable for a period of several days.

1. Introduction

The rotation of the plane of polarization in oriented cholesterics may be very large and exhibits important spatial dispersion effects [1]. The essential features of this behaviour are described already in the theoretical approach by de Vries [2]: the optical rotation (φ) increases sharply together with the reflection coefficient when the optical wavelength in the sample (λ_s) approaches a narrow band centred around a characteristic length l and a sign inversion of φ occurs when $\lambda_s = l$. The length l is typically the pitch and the corresponding incident λ is the Bragg wavelength λ_B . We have carried out optical rotation measurements using an oriented layer of a 60 per cent chiral mixture of CE6 in order to determine, as a function of phase and temperature, the λ values where the optical rotation changes sign: all these wavelengths are called Bragg wavelengths λ_B .

2. Experimental

The sample is contained between two glass plates coated with polyimide and rubbed in the same direction. The thickness is 18 μm . Reflection spectra of the sample show strong modulation in the sidebands indicating good alignment [3]. The cell was placed in a triple shield oven which allowed temperature stabilization within 0.002°C. In this paper we will only present data for the blue phases. The optical rotation was measured using an Optical Activity AA-10 polarimeter, adapted for measurements as a function of wavelength. We measured the optical rotation values and transmitted intensities for wavelengths from 325 nm up to 800 nm.

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3. Theory

Belyakov *et al.* [1] calculated the optical rotation of single crystal BP structures. Their calculations are based upon the model of the BP structure consisting of a cubic lattice with well defined spiral axial directions τ . If $\tau^4 - 4(\mathbf{k} \cdot \tau)^2 \neq 0$ (\mathbf{k} being the wave vector of the light in the crystal), this results in [1]

$$\frac{\varphi}{L} = \sum_{\tau \neq 0} \frac{|\varepsilon(\tau, 2)|^2 [k^2 \tau^2 + (\mathbf{k} \cdot \tau)^2] (\mathbf{k} \cdot \tau)^2}{4\varepsilon_0^2 \tau^3 [\tau^4 - 4(\mathbf{k} \cdot \tau)^2]} \quad (1)$$

With the assumption that BP1 possesses the O^8 structure and that only the (110), (200) and (211) directions make important contributions to the spatial dispersion effects, the optical rotation for a wave incident along the (110) direction is

$$\begin{aligned} \frac{\varphi}{L} = \frac{k}{8\varepsilon_0^2 \lambda'} & \left[\frac{|\varepsilon(110, 2)|^2}{(\lambda'^2 - 1)} + \frac{5|\varepsilon(110, 2)|^2}{2(4\lambda'^2 - 1)} + \frac{3|\varepsilon(200, 2)|^2}{2\sqrt{2}(4\lambda'^2 - 1)} \right. \\ & \left. + \frac{7|\varepsilon(211, 2)|^2}{2\sqrt{3}(4\lambda'^2 - 1)} + \frac{4|\varepsilon(211, 2)|^2}{3\sqrt{3}(9\lambda'^2 - 1)} + \frac{13|\varepsilon(211, 2)|^2}{6\sqrt{3}(36\lambda'^2 - 1)} \right] \quad (2) \end{aligned}$$

The Bragg wavelengths belonging to (110) and (200) are in the proportion 2 to 1. On the other hand, two different beams are incident along the (110) and the other along the (200) direction. The ratio between the Bragg wavelengths would be $\sqrt{2}$ to 1.

4. Results

Typical optical rotation spectra are given in figures 1 and 2: figure 1 gives data for a cooling run with curves for the cholesteric phase, the supercooled BP and BP1. Figure 2 shows data for the BP1 phase generated by heating up from the cholesteric structure. A few remarks can be made:

- (i) on cooling from the isotropic phase:

the cholesteric spectrum behaves in the way predicted by theory [2]: the Bragg wavelength is about 460 nm, in the BP phase a strong enhancement of the optical rotation occurs around 300 nm, but it is preceded by one or two inversions in the optical rotation at longer wavelengths.

- (ii) on heating from the cholesteric phase into the BP, a spectrum is found that conserves the main properties characteristic of the cholesteric phase ($\lambda_B \simeq 430$ nm). Close inspection (see figure 2) of the spectrum shows a small inversion wiggle at 580 nm.

It is already clear from this description that hysteresis and metastability effects are present. This feature is made evident in figure 3 where two sets of experimental Bragg wavelengths are shown: part (a) relates to the sample cooled down from the isotropic phase, and part (b) to the same sample heated up from the equilibrium state in the cholesteric phase.

5. Supercooling the BP1

On heating, the BP1 temperature range is about 0.1°C and it can persist in a metastable state of overheating in the isotropic temperature range. While cooling

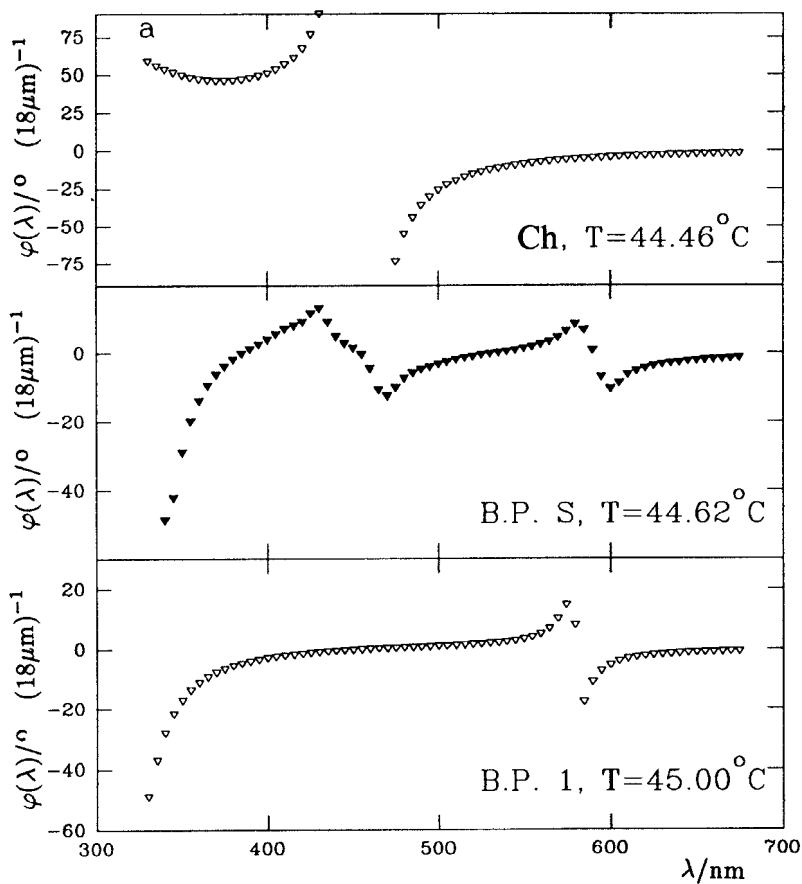


Figure 1. $\varphi(\lambda)$ in the BP region; on cooling.

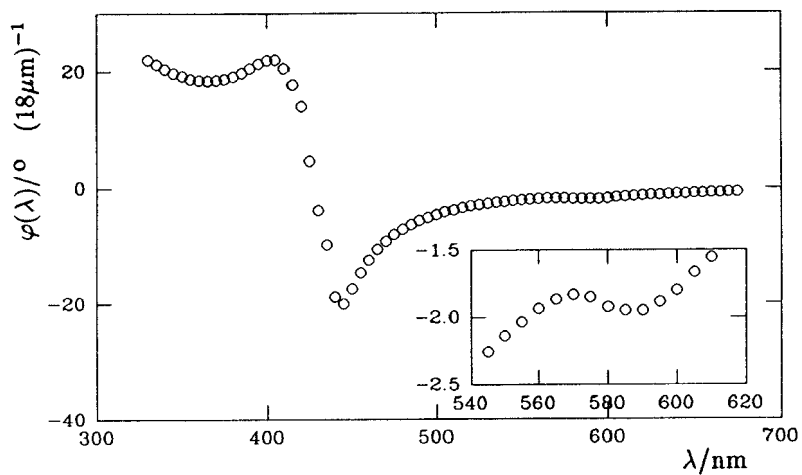


Figure 2. $\varphi(\lambda)$ in the BP region; on heating.

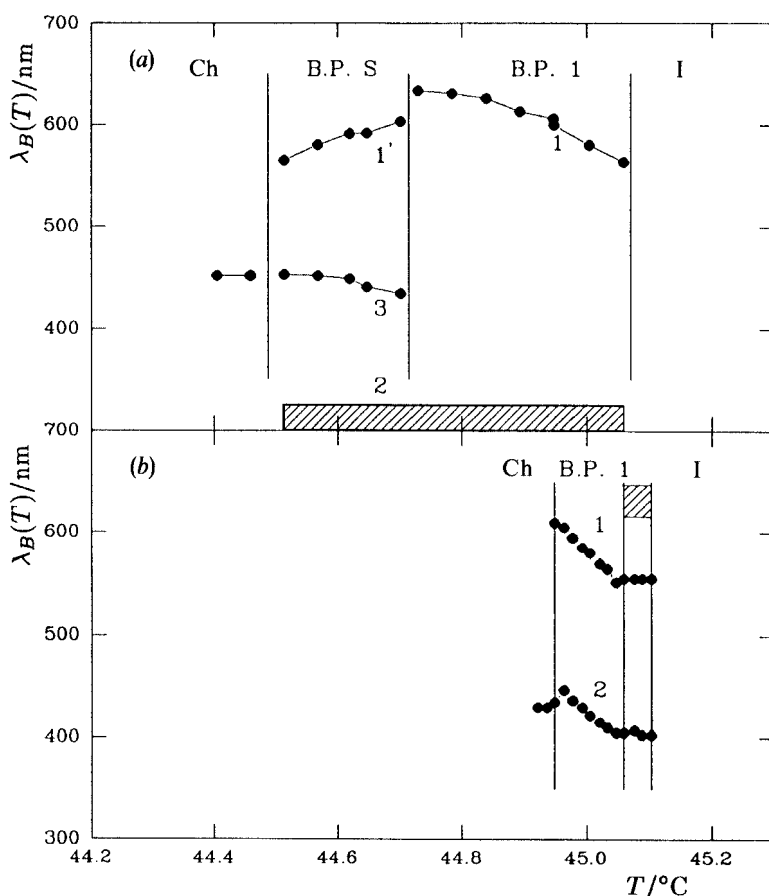


Figure 3. $\lambda_B(T)$; on cooling (a) and on heating (b). The shaded areas indicate that the experimental enhancement of the optical rotation suggests a Bragg wavelength in that region, but that it could not be determined with sufficient accuracy, as it is situated at or beyond the border of the experimentally accessible λ range.

down, there may be a temperature interval as large as 0.6°C between the isotropic and the cholesteric phases. Its width may depend on the cooling rate, but the metastable states may last for very long periods. The results in figure 3(a) were obtained by waiting for as long as 24 h after changing to the next temperature: the mean cooling rate was about 0.05°C per day.

It should be emphasized that in figure 3(a) two different regions are present in the supercooled BP1 phase: the first one extends from 44.9 to 44.7°C and is just an extrapolated BP1 phase. The range from 44.7 to 44.5°C however is qualitatively different: the Bragg wavelength—(1) in figure 3(a)—makes a jump and its temperature derivative has changed sign, while another λ_B appears—(3) in figure 3(a)—which has about the same value as the cholesteric Bragg wavelength.

Similar observations have already been made by Demikhov and Stegemeyer [4]: by studying the reflection properties of a $12\ \mu\text{m}$ thin layer of CE8, they observed on continuous cooling the appearance of a new BP phase thermodynamically stable with respect to the BP1 and metastable to the cholesteric phase. They named it the BPS phase.

6. Conclusions

- (i) Evidence is given of a supercooled blue phase (BPS) in a 60/40 chiral-racemic CE6 mixture: it is stable with respect to the BP1 and metastable with respect to the cholesteric phase.
- (ii) When the BP1 phase is formed from the isotropic phase two Bragg wavelengths are detected that are in the proportion of 2 to 1. This is compatible with the O^8 symmetry ascribed to this phase and an orientation of the $\{110\}$ axis perpendicular to the glass plates.
- (iii) When the BP1 phase is formed from the cholesteric phase where the helical axis is perpendicular to the glass plates, a trace of the cholesteric λ_B —(2) in figure 3(b)—persists, together with the main BP1 Bragg wavelength—(1) in figure 3(b)—whose value seems to be independent of the preceding phase. The proportion between both λ_B values is close to $\sqrt{2}$. This could mean that the sample does not have a perfect monodomain structure.
- (iv) In the BPS phase the ratio between the λ_B values is temperature dependent. This may be an indication of reorientation effects.

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