Selective reflection in the cholesteric and blue phases of a chiral-racemic mixture of CE6

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Selective reflection in the cholesteric and blue phases of a chiral–racemic mixture of CE6

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The reflection spectrum for visible light is examined for the cholesteric and blue phases of chiral CE6. Pronounced side band oscillations are observed. The Bragg wavelength for total reflection diverges towards the smectic phase with an exponent $v = 0.71 \pm 0.05$. Going from the cholesteric phase to BPI, the lattice parameter increases by $(2)^{1/2}$. Evidence is given for the existence of a long-lived supercooled blue phase (BPS).

1. Introduction

In the 60 per cent chiral mixture of CE6 there exists only one blue phase, which is identified as BPI [1]. This phase can be supercooled with respect to the cholesteric phase. Reflection and transmission spectra of circularly polarized, normal incident light have been measured for a monodomain sample ($18\,\mu m$ thick) held between polyimide treated and rubbed surfaces.

The experimental set-up consists of a monochromator with a resolution of 1 nm, a halogen light source, two lock-in detectors and two photomultipliers. The light is circularly polarized by a Glan–Thompson prism and a $\lambda/4$ plate. The reflected light is detected via the $\lambda/4$ plate and the polarizer, by a photomultiplier. The transmitted light is detected by the second photomultiplier. The temperature is regulated and stabilized within $0.01°C$.

2. Reflection spectra

Figure 1 shows an experimental reflection spectrum for the cholesteric phase at $42.10°C$. It contains a band of total reflection and side arms with strong interferometric modulation effects. For comparison, a theoretical reflection spectrum is included in figure 1 (in order to avoid mixing up of the graphs, the experimental R is increased with a constant value of 0.2). The calculated curve was obtained from [2]

$$R_\sigma = \frac{\alpha^2 \sin^2(k^- L)}{4(k^-/K)^2 + \alpha^2 \sin^2(k^- L)}, \tag{1}$$

with

$\alpha = $ dielectric anisotropy,

$$K = \frac{2\pi\bar{n}}{\lambda}, \qquad \bar{n} = \text{mean refractive index},$$

$L = $ thickness of the sample,

$k^- = K[1 + \bar{\lambda}^2 - (4\bar{\lambda}^2 + \alpha^2)^{1/2}]^{1/2},$
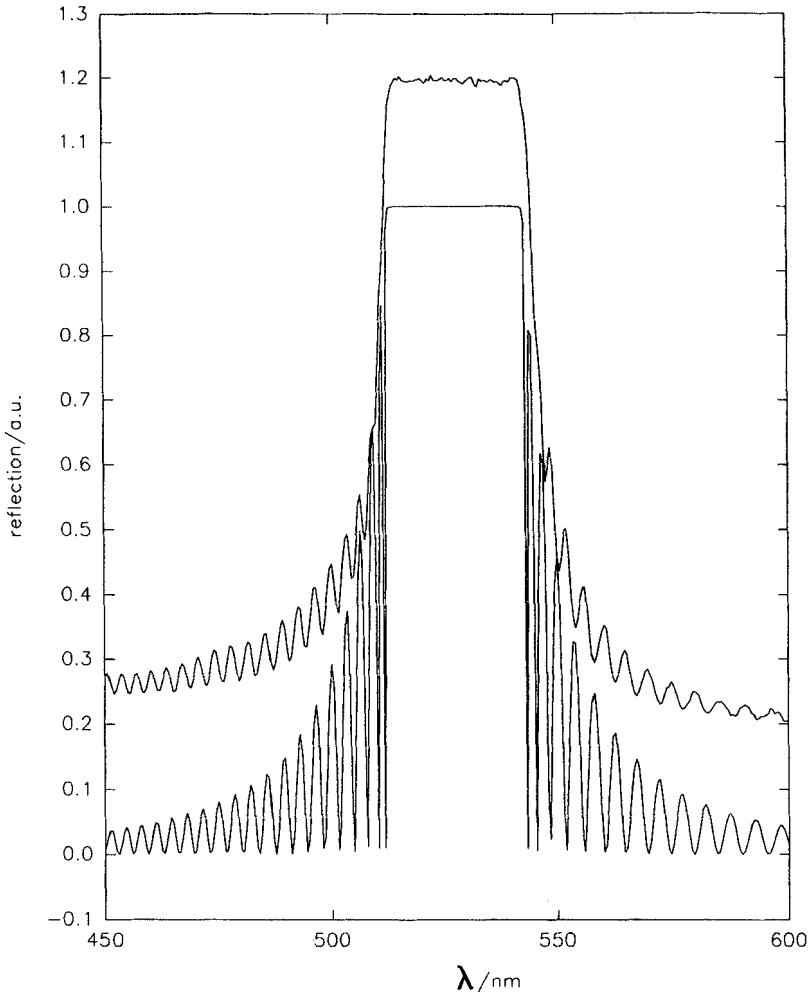
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Figure 1.   Reflection spectrum for the cholesteric phase. Experimental spectrum is shifted over
0·2 units. $\bar{n}L = 31\,\mu m$, $\lambda_p = 528\,nm$, $\alpha = 0·05$, $T = 42·10°C$.

and

$$\tilde{\lambda} = \frac{\lambda}{\lambda_B}.$$

The dielectric boundary reflection is neglected and the dielectric anisotropy α is assumed to be small. The width of the reflection band is given by

$$\omega_B(1 + \alpha)^{-1/2} < \omega < \omega_B(1 - \alpha)^{-1/2}.$$

The parameter values for the calculated curve in figure 1 are $\lambda_B = 528\,nm$, $\alpha = 0·05$ and $\bar{n}L = 31\,\mu m$. The minima in the Pendellösung beats do not match over the entire wavelength region. It is possible that the influence of the dielectric boundaries will have to be taken into account.
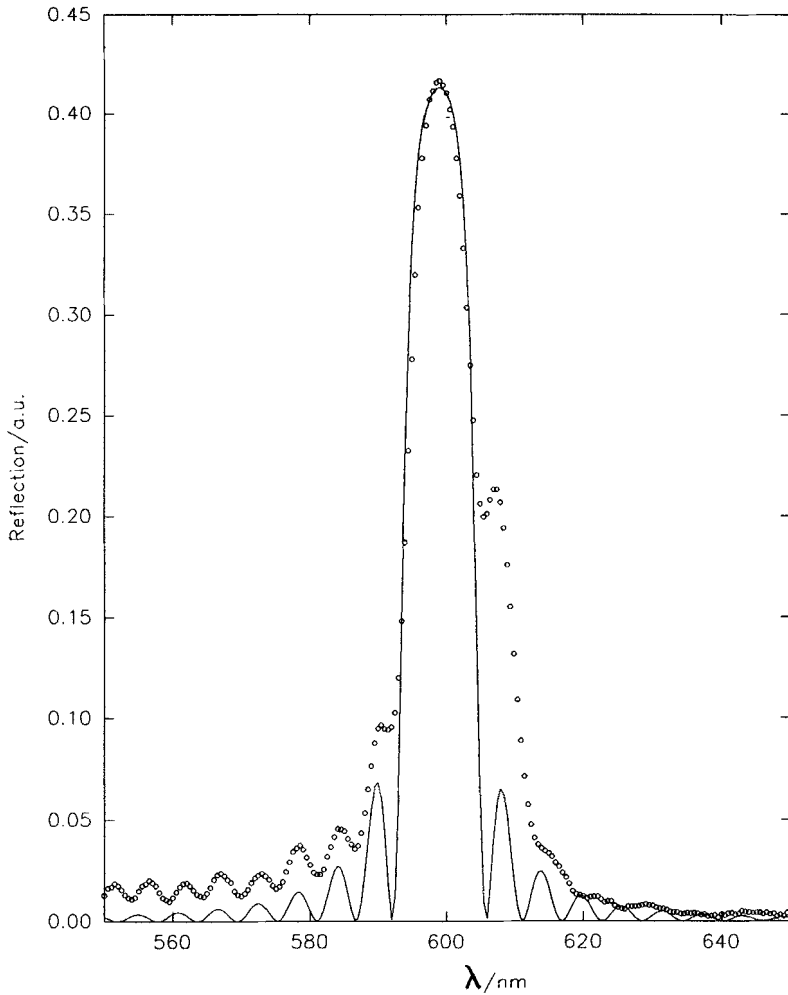
Figure 2. Reflection spectrum for BPI. (Full line) calculated spectrum (○) experimental spectrum. $\bar{n}L = 31 \, \mu\text{m}$, $\lambda_p = 599 \, \text{nm}$, $F_\sigma = 0.012$, $T = 45.12°\text{C}$.

An experimental reflection spectrum for the blue phase at $45.12°\text{C}$ is shown in figure 2. The theoretical curve is calculated according to [2, 3]

$$R_\sigma = \frac{\cos\left[KL(\delta^2 - |F_\sigma|^2)^{1/2}\right] - 1}{\cos\left[KL(\delta^2 - |F_\sigma|^2)^{1/2}\right] + 1 - (2\delta^2/|F_\sigma|^2)}, \tag{2}$$

with

$$\delta = \frac{2(\lambda_B - \lambda)}{\lambda_B},$$

$|F_\sigma|^2 = $ polarization structural factor.

For $\delta < 2|F_\sigma|$, the cos function has to be replaced by cosh. The same parameter values were used as for figure 1, with $F_\sigma = 0.012$.

It may be emphasized that in most experiments, the oscillations in the reflection spectra are smoothed out: our figures 1 and 2 give evidence of a well-structured sample.
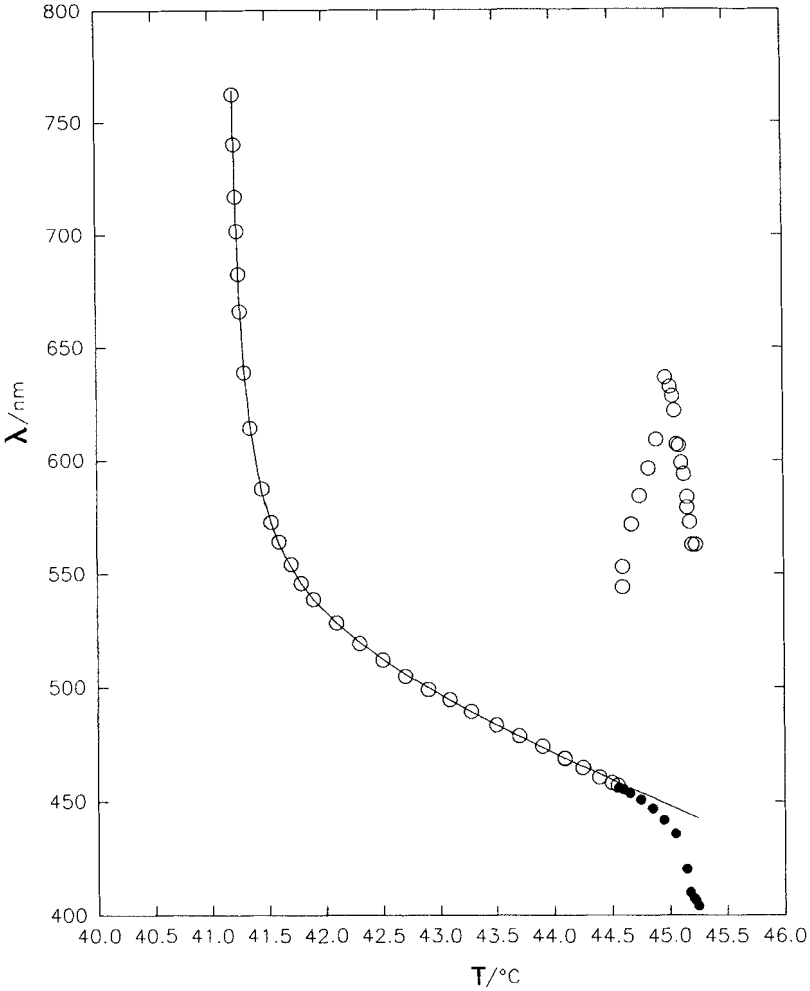
Figure 3.   Temperature dependence of the Bragg peak. (O) Cooling, (●) heating.

A detailed analysis of the oscillating behaviour will be given elsewhere. In this paper we will further concentrate on the temperature and phase dependence of the Bragg wavelength, which is essentially the cholesteric pitch.

3.   Temperature dependence of λ_B: the Bragg wavelength

Figure 3 shows the temperature dependence of the Bragg wavelength. The temperature effect on λ_B has already been studied in light scattering experiments by Pindak *et al.* [4]: they proposed as a fitting formula

$$\lambda_B = \lambda_{00}[1 + a(T - T_c)] + c'(T - T_c)^{-\nu}, \tag{3}$$

being a superposition of a regular temperature effect on p and $\bar{n}$ and a critical part due to pretransitional smectic fluctuations that form cybotactic groups whose dimensions diverge, like the correlation length, with exponent ν.
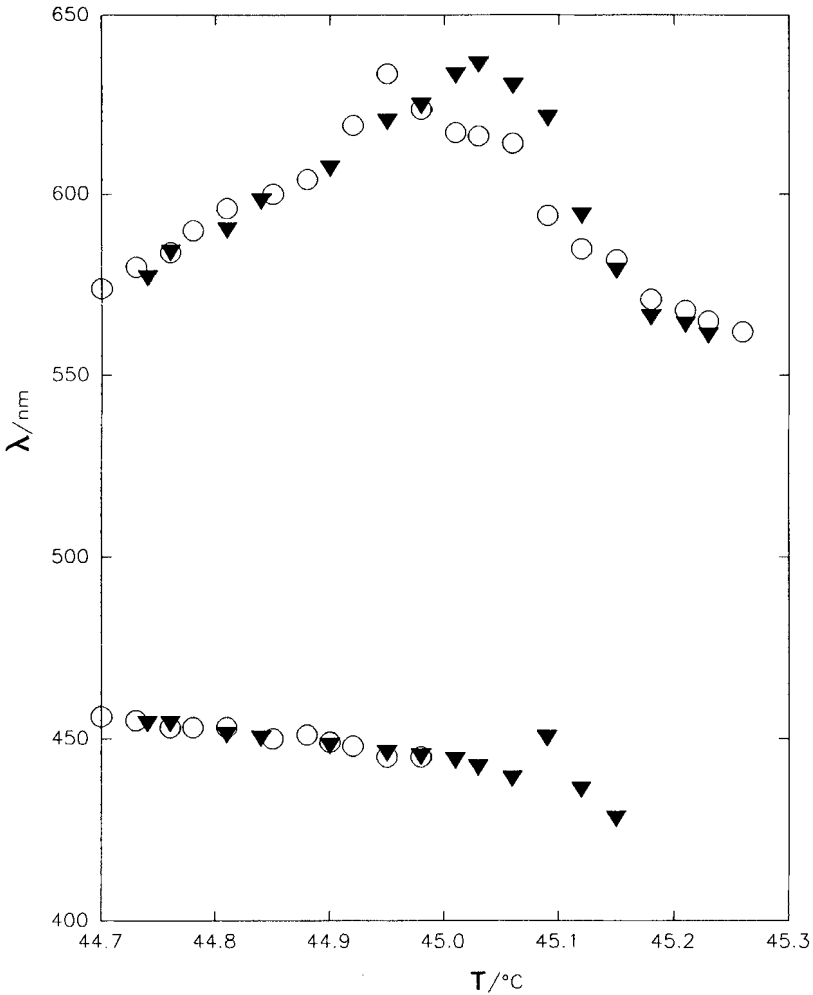
Figure 4. Temperature dependence of the Bragg peak on cooling to BPS and subsequent heating; (○) cooling, (▼) heating.

Fitting the data gives parameter values $v = 0\cdot71 \pm 0\cdot05$, $a = -0\cdot04/°C$, $T_c = 41\cdot15°C$, $\lambda_{00} = 511\,nm$, $c' = 31\cdot49 \pm 0\cdot025$. This compares well with $v = 0\cdot675$ for CN [4] and $v = 0\cdot67 \pm 0\cdot05$ [5]: it is consistent with the exponent values of the Ising universality class.

At the high temperature side of figure 3, including the BPI, other reflection bands appear and the data give evidence of metastable states.

On cooling from the isotropic phase, a reflection peak appears at 560 nm: it may be identified with the BPI lattice constant and it increases sharply with decreasing temperature. At a temperature, depending on the cooling rate, a sudden decrease occurs in λ_B and a second reflection peak λ_B' appears around 445 nm.

As shown in figure 5 there is coincidence of this λ_B' and the λ_B obtained while heating up the cholesteric phase: the remarkable point, however, is that this BPI-like value persists while cooling further over a quite large temperature range of 0·5°C. This may be
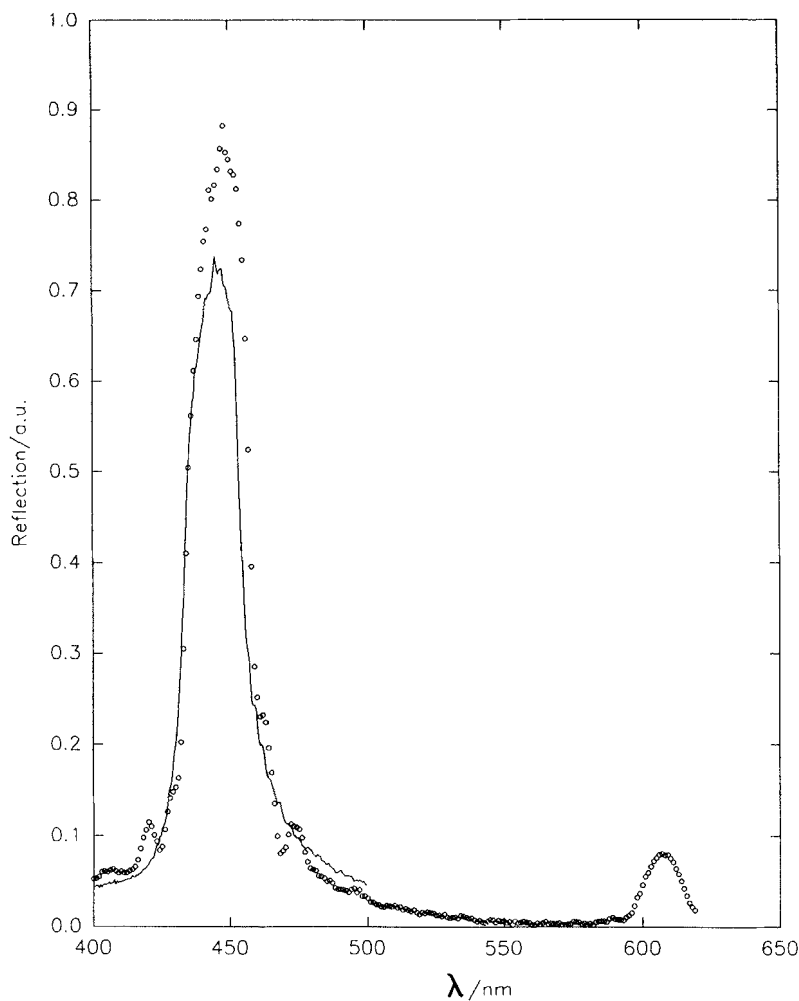
Figure 5. (○) Spectrum of BPS at 44·90°C; (—) spectrum of cholesteric phase at 44·96°C.

considered as evidence of a new phase similar to that observed by Demikhov and Stegemeyer in CE8 and called the supercooled blue phase BPS [6].

Contrary to the observations of [6], we could keep CE6 in the BPS phase for several days. It is at this moment not clear whether this difference is due to experimental circumstances (for example, fluctuations in T) or that it has to do with the temperature separation from the smectic transition point (the cholesteric range is 4 K in CE6 and 5·7 K in CE8).

The temperature dependence of the lattice constant on cooling of BPI (○) and on subsequent heating of BPS (▼) is shown in figure 4. The measurements were carried out at a rate of two points/day. The following observations were made:

On cooling below 45·18°C, BPI phase becomes supercooled and the lower the temperature it takes more and more time to stabilize the lattice constant.

The second peak appears before the value of $(d\lambda_B/dT)$ for the first peak changes sign. Figure 5 shows a spectrum of the BPS phase at 44·90°C (○) and a spectrum

of the cholesteric phase at 44·96°C (solid line). Once in the BPS phase, stabilization is reached immediately.

On heating from the BPS phase, between 44·98°C and 45·18°C (figure 4), the stabilization time becomes again very long.

If heating starts in the cholesteric phase, the lower reflection peak continues to exist into BPI. This is probably a different orientation of the BPI lattice with respect to the orientation on cooling, because the ratio of the lattice constants is

$(2)^{1/2}$. This was not the case on heating from the BPS phase.

The transmission spectra give minima at the same wavelength as the reflection maxima, except for the narrow temperature interval in which the stabilization time is long. In this interval the difference can be as much as 6 nm.

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