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Birefringence in the smectic and hexatic chiral phases of CE-8

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The temperature dependence of the birefringence in the S_A, S_C^* and S_I^* phases of 4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8) has been measured. Whereas in the S_A phase the birefringence is nearly temperature independent, we observe a smooth decrease in the S_C^* and a small and discontinuous increase at the S_C^*–S_I^* phase transition. The observed temperature dependence of the birefringence is in quantitative agreement with a first order approximation to the wave equation in birefringent and spatially modulated media. The tilt angle, as determined from our measurements, shows a mean-field temperature dependence $\beta = 0{\cdot}48 \pm 0{\cdot}02$ close to T_{AC*} and a crossover to the value $\beta = 0{\cdot}33 \pm 0{\cdot}02$ for $T < T_{AC*} - 1$ K.

1. Introduction

The optical properties of helically modulated liquid crystalline phases have been the subject of considerable theoretical [1–5] and experimental [6–9] interest during the last decade. They are attractive and challenging not merely because of the complexity of the problem, but also because of the fact that many of the thermodynamical properties of these phases can be conveniently studied with different optical methods. For example, quasielastic light scattering spectroscopy can give us unique information on the thermally excited dynamics of liquid crystalline phases. In order to be able to analyse these data, one has to understand and quantitatively describe the optical properties of chiral phases.

It is well known that the problem of light propagation in helicoidally modulated, birefringent phases can be solved analytically only in the case of light propagation along the helical axis [10]. For a general direction, one has to use approximations and numerical methods. There are different approaches to this problem and they are based on different formalisms, like the well-known Berreman's 4×4 matrix [1] approach, etc.. Recently, there has been significant progress in the understanding of the optical properties of birefringent, spatially modulated phases that was initiated by the work of Oldano *et al.* [4]. Based on his work, we have recently formulated a simple perturbative approach [8] to the optics of chiral phases to explain the observed magnetic field induced birefringence. The approach correctly explains the structure of the reflection bands of the S_C^* phase and gives a quantitative agreement for the optics of the soliton-like distorted helical antiferroelectric structure.

The aim of the present work was to study the temperature dependence of the birefringence in ferroelectric phases. According to the perturbative approach, the birefringence of the helical S_C^* phase should decrease below T_{AC*} as a square of the magnitude of the order parameter, i.e. the tilt angle. By comparing the calculated tilt angle from the birefringence measurements to the values obtained by other methods we can thus test the validity of the perturbative approach to the optics of chiral birefringent media.

2. Theory

The perturbative approach to the optical properties of tilted and helicoidally modulated smectic phases is based on the fact that the periodic part of the dielectric tensor in these structures is typically 10^{-1} to 10^{-2} smaller than the principal values of the dielectric constant for optical frequencies. Furthermore, the numerical calculations by Oldano [4] have shown that the optical eigenmodes and their eigenvalues in chiral smectics can be very well approximated by the linearly polarized σ and π waves with the corresponding linear dispersion relations. The exceptions are here the points of degeneracy of the eigenvalues, where the simple approximation breaks down. This corresponds to (i) the propagation

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of light along the helix, (ii) propagation at the Bragg angle and (iii) a critical value of the tilt angle [4, 5].

Following the approach of Peterson [11], we define a tensor-weighted inner product of the two eigenfunctions $|\mathbf{k},p\rangle$ and $|\mathbf{k}',p'\rangle$ as

$$\langle \mathbf{k}',p'|\mathbf{k},p\rangle = \langle \mathbf{E}_{k',p'}|\mathbf{E}_{k,p}\rangle = \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{r}\,\mathbf{E}^*_{k',p'}\underline{\varepsilon}(\mathbf{r})\mathbf{E}_{k,p} \tag{1}$$

Here $\mathbf{E}_{k,p}$ denotes the electric field of the eigenwave with a wave-vector $\mathbf{k}$ and polarization p, propagating in a medium, characterized by the dielectric constant $\underline{\varepsilon}(\mathbf{r})$. In the helicoidally modulated phases, the dielectric tensor is

$$\underline{\varepsilon}(z) = \begin{bmatrix} \frac{1}{2}[(\varepsilon_1+\varepsilon_2)+(\varepsilon_3-\varepsilon_2)\sin^2\theta] & 0 & 0 \\ 0 & \frac{1}{2}[(\varepsilon_1+\varepsilon_2)+(\varepsilon_3-\varepsilon_2)\sin^2\theta] & 0 \\ 0 & 0 & \varepsilon_3-(\varepsilon_3-\varepsilon_2)\sin^2\theta \end{bmatrix}$$

$$+(\varepsilon_3-\varepsilon_2)\sin\theta\cos\theta \begin{bmatrix} 0 & 0 & \cos\Phi(z) \\ 0 & 0 & \sin\Phi(z) \\ \cos\Phi(z) & \sin\Phi(z) & 0 \end{bmatrix}$$

$$+\tfrac{1}{2}[(\varepsilon_2-\varepsilon_1)+(\varepsilon_3-\varepsilon_2)\sin^2\theta] \begin{bmatrix} \cos 2\Phi(z) & \sin 2\Phi(z) & 0 \\ \sin 2\Phi(z) & -\cos 2\Phi(z) & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{2}$$

Here ε_i, $i = 1\ldots 3$ are the principal values of the dielectric tensor of a liquid crystal, θ is the tilt angle and $\Phi(z)$ is the phase angle as indicated in the inset to figure 1. The inhomogeneous parts of the dielectric tensor are both temperature dependent through the tilt angle $\theta(T)$ and are typically 10^{-1} to 10^{-2} smaller than the principal, homogeneous part of the dielectric constant. The wave equation for the light propagation in the media can be written as

$$\underline{\varepsilon}_0^{-1}\nabla\times\nabla\times|\mathbf{k},p\rangle - \frac{\omega^2}{c_0^2}\underline{\varepsilon}_0^{-1}\delta\underline{\varepsilon}|\mathbf{k},p\rangle = \frac{\omega^2}{c_0^2}|\mathbf{k},p\rangle \tag{3}$$

where $\underline{\varepsilon}_0$ and $\delta\underline{\varepsilon}$ are the homogeneous and the inhomogeneous parts of the dielectric tensor, respectively, ω is the frequency and c_0 is the speed of light in a vacuum. In the limit of a small tilt angle, $\theta\to 0$, the second and the third terms in equation (2) represent a small periodic perturbation, which changes the nature of the wave-functions and the spectrum of the eigenfrequencies. In particular, in the presence of this periodic perturbation, one has to define a Brillouin zone which is determined by the periodicity of the medium. As a consequence of this periodic perturbation, the band gaps appear at the edges of the Brillouin zone, giving rise to the selective or total reflection, respectively.

It has been shown [8] that in the first order perturbative approach to equation (3) the optical properties are described by the space averaged dielectric constant, whereas the eigenwaves are just linearly polarized ordinary and extraordinary waves. Within this approximation, and in the absence of external fields that break the continuous helical symmetry of the modulated phases, the space-averaged dielectric tensor is uniaxial

$$\langle\varepsilon\rangle_{xx} = \tfrac{1}{2}[(\varepsilon_1+\varepsilon_2)+(\varepsilon_3-\varepsilon_2)\sin^2\theta] \tag{4 a}$$

$$\langle\varepsilon\rangle_{yy} = \tfrac{1}{2}[(\varepsilon_1+\varepsilon_2)+(\varepsilon_3-\varepsilon_2)\sin^2\theta] \tag{4 b}$$

$$\langle\varepsilon\rangle_{zz} = \varepsilon_3-(\varepsilon_3-\varepsilon_1)\sin^2\theta \tag{4 c}$$

The components of the dielectric tensor $\langle\varepsilon\rangle_{ii}$ are here temperature dependent because of the temperature dependence of the tilt angle $\theta(T)$. In particular, the 'average' ordinary index of refraction $\bar{n}_o = \langle\varepsilon\rangle_{xx}^{1/2}$ increases, whereas the 'average' extraordinary index $\bar{n}_e = \langle\varepsilon\rangle_{zz}^{1/2}$ decreases with increasing tilt angle. This means that the birefringence $\Delta\bar{n} = \bar{n}_e - \bar{n}_o$ should decrease with the onset of the tilt angle in the S_C^* phase.

The average refractive indices $\bar{n}_i$, as measured at an angle α with respect to the helical axis are

$$\bar{n}_o^2 = \tfrac{1}{2}(\varepsilon_1+\varepsilon_2)+\tfrac{1}{2}(\varepsilon_3-\varepsilon_2)\sin^2\theta \tag{5 a}$$

$$\frac{1}{\bar{n}_e^2} = \frac{\sin^2\alpha}{\varepsilon_3-(\varepsilon_3-\varepsilon_2)\sin^2\theta} + \frac{\cos^2\alpha}{\frac{1}{2}(\varepsilon_1+\varepsilon_2)+\frac{1}{2}(\varepsilon_3-\varepsilon_2)\sin^2\theta} \tag{5 b}$$

In the limit of small tilt angles, $\sin\theta \ll 1$, the temperature dependence of the average birefringence of the S_C^* phase is found to vary with the square of the amplitude of the order parameter

$$\bar{n}_e - \bar{n}_o \cong (n_e - n_o) - C\sin^2\theta \tag{6}$$

and decreases below T_{AC^*}. Here $(n_e - n_o)$ is the

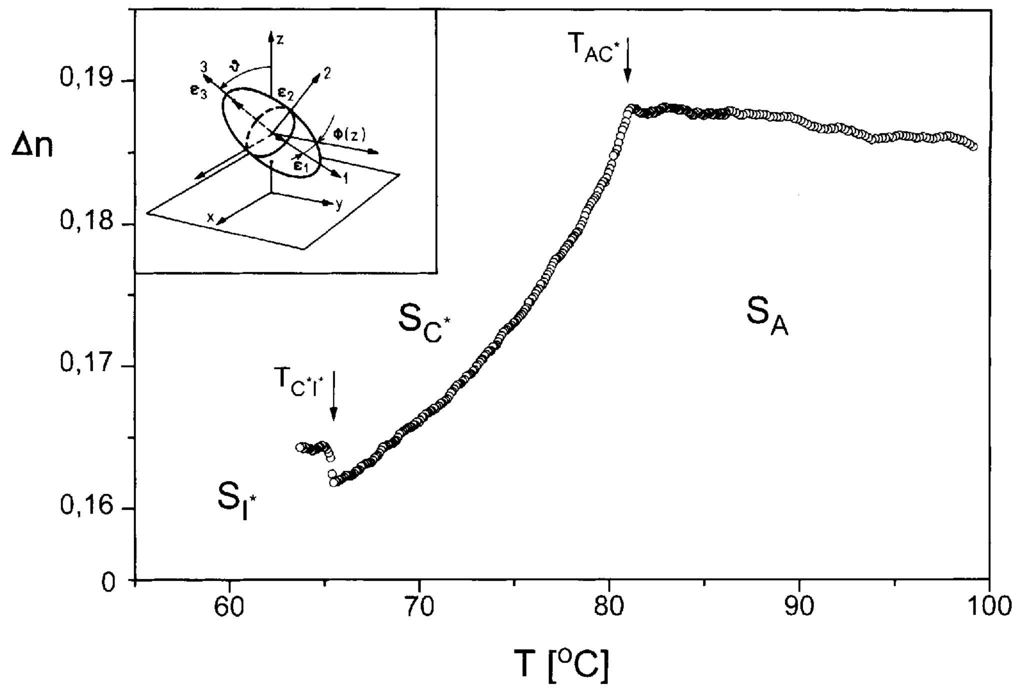

Figure 1. Temperature dependence of the birefringence in the S_A, S_C^* and S_I^* phases of 4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8). The inset shows the definition of the reference frame and corresponding angles. The accuracy of the birefringence measurements is ±0·001.

birefringence of the homogeneous S_A phase and C is a constant.

3. Experimental results and discussion

The temperature dependence of the birefringence in the chiral smectic phases of 4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8) was measured with an automatic system described elsewhere [12]. The birefringence measuring system is incorporated into a polarizing microscope and allows for a visual inspection of the quality of the sample. The system is based on the Senarmont compensating method and is capable of detecting very small birefringence changes of the order of $\Delta n \approx 10^{-6}$.

We used 50 μm thick, homeotropically aligned samples of CE-8. The sample was put in a sample holder, so that the normal to the glass was inclined at 15 degrees to the optical axis of the system. The temperature of the sample was controlled to better than 0·1 K and was automatically swept towards room temperature at a very slow scanning rate, starting from the S_A phase. The optical quality of the sample was checked through the microscope and the measurements were always performed in defect-free areas. A narrow band filter of 604 nm was used.

The temperature dependence of the birefringence in the S_A, S_C^* and S_I^* phases of CE-8 is shown in figure 1. One can see a slowly increasing birefringence in the S_A phase, followed by a clear and continuous decrease in the chiral S_C^* phase. At the phase transition into the S_I^* phase ($\approx$65°C), the birefringence shows a small and discontinuous increase. In the lower temperature G* phase, the birefringence could not be measured accurately because of defects.

The observed temperature dependence of the average birefringence of CE-8 is in agreement with theoretical considerations. The gradual increase of the birefringence in the S_A phase is here the result of a nearly saturated behaviour of the nematic order parameter *S*. As is known, cooling a liquid crystal results in a gradual increase of the component ε_3, and a consequent increase of the extraordinary index n_e. The observed continuous decrease of the birefringence below 81°C is a result of the onset of the S_C^* order parameter and is in clear agreement with the predictions of a simple perturbative approach (equation 6). At the phase transition to the S_I^* phase, a small increase in the birefringence is attributed to a small decrease of the S_C^* order parameter in the S_I^* phase as will be discussed below.

Using the equations (5 *a*) and (5 *b*) we have determined the value of the temperature dependence of the tilt angle in the S_C^* and S_I^* phases, which is shown in figure 2. Here, the background birefringence $n_e - n_o$, equation (6), of the S_A phase was fitted with a power law and extrapolated into the tilted smectic phases. The tilt angle, as obtained within the perturbative approximation is in

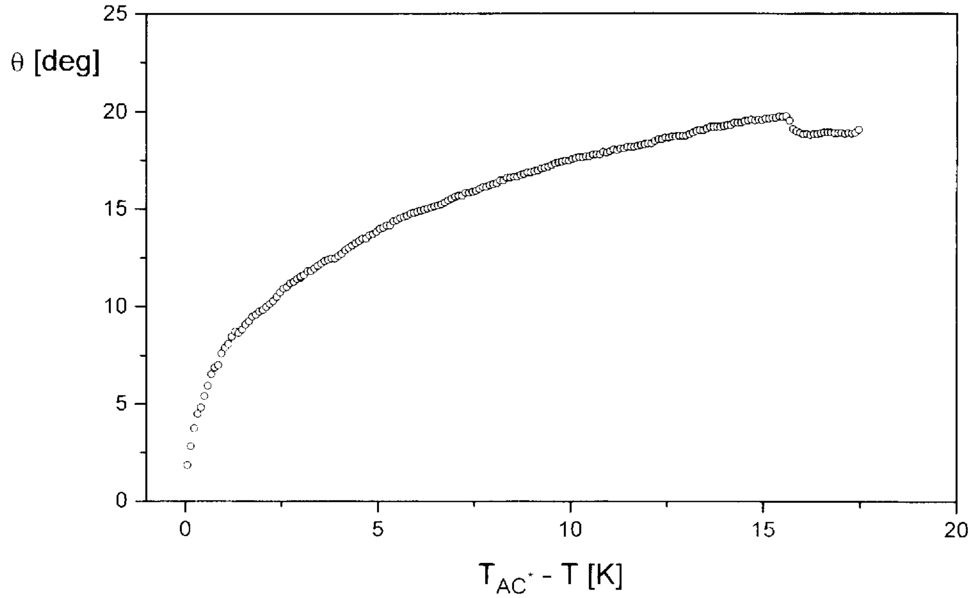

Figure 2. Tilt angle in the S_C^* and S_I^* phases of 4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8), as determined from the birefringence measurements. The error bar is of the size of the data points.

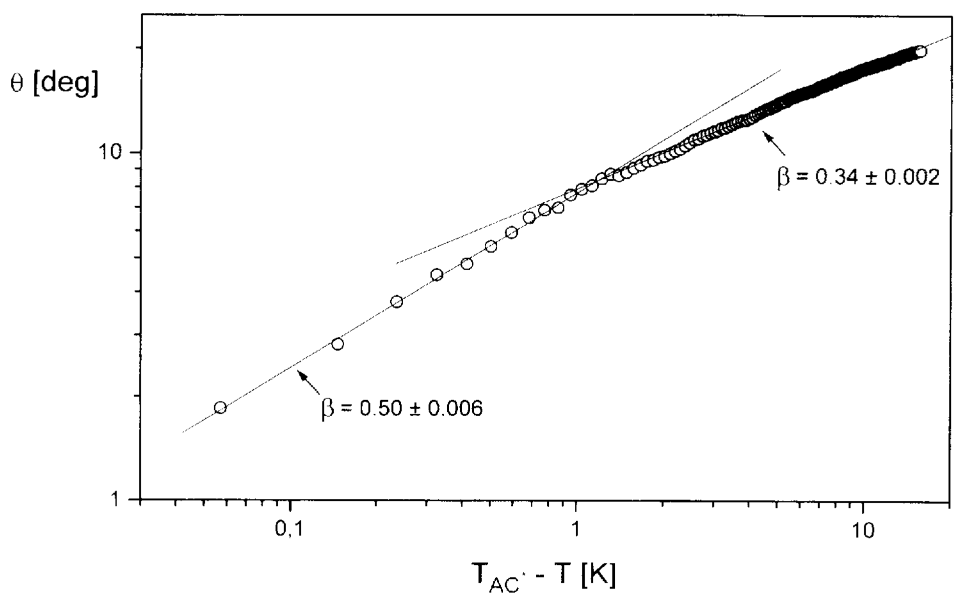

Figure 3. Power-law behaviour of the tilt angle in the chiral smectic C* phase of CE-8, as determined from the birefringence measurements.

very good quantitative agreement with other measurements. For example, Raya *et al.* [13] report a value of 19·4 degrees for the tilt angle close to the S_C^*–S_I^* phase transition, which is very close to our measurements. In their X-ray experiment they have also observed a slight decrease of the tilt in the S_I^* and G* phases, which is in agreement with our measurements and the X-ray measurements of Brand and Cladis [14].

The log–log plot of the temperature dependence of the tilt angle is shown in figure 3 and shows a clear power law behaviour for temperatures lower than 1 K below T_{AC^*}. In most of our measurements, there are indications of the crossover of the tilt angle exponent β from the value $\beta = 0{\cdot}48 \pm 0{\cdot}02$ very close to the transition, to the value $\beta = 0{\cdot}33 \pm 0{\cdot}02$ far from the transition. The above values for β are taken as an average of the observed values for a set of experiments on different samples. The exponent β varies slightly from sample to sample, but we have observed that the crossover point is always at $T_{AC*} - T \approx 1$ K. The above value of the critical exponent $\beta \approx 0{\cdot}5$ close to T_{AC*} is in qualitative agreement with the mean-field model, as discussed by de Gennes [15]. Helium-like deviations from the mean-field behaviour, if any, should be seen for $T_{AC*} - T < 0{\cdot}1$ K, which is below the resolution of the present experiment. On the other hand, far from T_{AC*} the experiment clearly shows the value of the exponent $\beta = 0{\cdot}33$, which is due to the higher order terms in the free-energy expansion as stated by Huang and Viner [16]. They have stressed the importance of the sixth order terms in the free-energy expansion, which drives the phase transition in the vicinity of the tricritical point (see also [15]). Consequently, one may observe in the experiment an apparent non-mean-field critical exponent, which is just due to the crossover from the classical value $\beta = 0{\cdot}5$ close to the transition to the tricritical value $\beta = 0{\cdot}25$ far from the transition. Similar crossover of the exponent β was indeed observed in optical experiments on chiral smectic phases of other materials [7, 17].

4. Conclusions

The measurements of the birefringence in the helically modulated tilted smectic phases confirm the validity of the first order approximation to the wave equation which describes the optical properties of these phases. Within this approximation, light is propagating through the birefringent and modulated medium in a form of ordinary and extraordinary linearly polarized waves with a linear dispersion relation. The exceptions are here the points of degeneracy, where the nature of the optical eigenwaves and eigenvalues changes dramatically and gives rise to the well-known phenomenon of Bragg reflection.

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