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Temperature and field dependence of the optical activity in the ferroelectric, antiferroelectric and subphases of AS661

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The effect of applied a.c. electric fields on the optical activity of an antiferroelectric liquid crystal which forms ferroelectric, antiferroelectric and subphases was investigated. Applied fields greater than $\sim 10\,\mathrm{kV\,m^{-1}}$ induced an additional phase in the region between the SmC* and SmC_A^* phases. Also, applied fields stabilize the SmC_{F2}^* phase at the expense of the SmC* phase.

1. Introduction

Chiral smectic liquid crystals have recently attracted much attention. The extraordinary optical and electro-optical properties of these novel phases offer great potential in display applications [1–3]. Moreover, the rich polymorphism that has been observed in these new smectic materials, make them very interesting from the point of view of basic research.

Antiferroelectric liquid crystals show complex and intriguing phase behaviour and may form the following phases in order of increasing temperature [4]: SmC_A^*–FI_L–SmC_γ^*(SmC_{FI}^*)–FI_H–AF(SmC_{F2}^*)–SmC*–SmC_α^*–SmA. The ferroelectric SmC* phase and the antiferroelectric SmC_A^* phase are the fundamental phases; the others are considered as subphases of the fundamental phases. The SmC_α^* phase is a tilted phase (presumably incommensurate) with nearly zero optical rotation [5]. The AF(SmC_{F2}^*) phase is antiferroelectric while the SmC_γ^* (SmC_{F1}^*), FI_H and FI_L phases are ferrielectric [6, 7].

In the ferroelectric, antiferroelectric and subphases of chiral smectic liquid crystals, chiral molecules are spontaneously tilted at a temperature-dependent angle (θ) with respect to the layer normal. In the ferroelectric phase, all layers tilt in the same direction and the spontaneous polarization appears perpendicular to the tilt plane. Owing to the chirality of the molecules, the direction of the tilt, and hence the spontaneous polarization, slowly precesses around the layer normal as one moves along the direction perpendicular to the smectic planes. The period of this helical structure is typically hundreds of smectic layers and therefore represents a small chiral pertubation to the system. The antiferroelectric phase is also helicoidal and is characterized by alternating layers that tilt in opposite directions. The spontaneous polarization also reverses in direction from one layer to the next. The neighbouring dipoles are nearly antiparallel and this results in very small value ($\approx$0) of the equilibrium electric polarization.

The structure of the subphases has been the subject of considerable debate in recent years, with Ising and Clock models used to describe the interlayer ordering. Resonant X-ray scattering [8] was used to establish that the unit cell in the SmC_{F1}^* and SmC_{F2}^* phases consists of three and four smectic layers respectively. However, perfect three- and four-layer structures cannot account for the large optical activity observed in the SmC_{F2}^* and SmC_{F1}^* phases [9–12]. A deformed clock model [11, 13] has been proposed to explain these rather large optical activities and such a model is supported by ellipsometric studies [14] on freely suspended ferrielectric films and by high resolution X-ray experiments [13].

Optical activity is a very sensitive tool for investigating phase transitions in chiral phases especially when such transitions are characterized by extremely small values of latent heat. This technique was instrumental in identifying the isotropic–BPIII critical point in chiral nematic liquid crystals [15]. There are only four reports on optical activity measurements in the various phases of antiferroelectric liquid crystals [9–12]. However, as far as we are aware, there is no account of how electric fields affect the optical activity of such phases. Optical activity could also be useful in identifying the structure of the intermediate phases since it is a sensitive function of the unit cell.

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2. Theory

For the case of light propagating along the helical axis of a chiral nematic phase, De Vries [16] developed an expression for the optical activity. When applied to chiral smectics [9, 12, 17, 18], the De Vries theory leads to the expression:

$$\phi = -\pi\lambda_0^3(\Delta n)^2 \sin^4 \theta \Big/ \left[4\langle n\rangle\lambda^2\left(\lambda_0^2-\lambda^2\right)\right] \qquad (1)$$

where ϕ is the optical activity, λ is the wavelength, $\langle n\rangle$ is the average refractive index, Δn is the optical anisotropy, θ the tilt and $\lambda_0=\langle n\rangle P$, where P is the pitch. Equation (1) is valid as long as Δn is small and λ is not too close to λ_0.

3. Experimental

We used a rotating analyser technique for measuring the temperature dependence of the optical activity. This technique has been described elsewhere [19] and will only be outlined here. The samples were homeotropically aligned with CETAB thus ensuring that the helical axis was normal to the glass substrates. Light from a He-Ne laser ($\lambda=543$ nm) was split into two beams, one of which passed through the sample (along the direction of the helical axis) and then through a rotating polarizer. The second beam emerging from the beam splitter served as the reference beam and was modulated by a two-blade chopper. The beams were then focused onto two photo diodes. The phase difference between the signals from the photodiodes was measured with a lock-in amplifier (EG&G Model 5104). The optical activity is half that recorded by the lock-in amplifier. All data were collected in the cooling mode. We also monitored the intensity of the light transmitted by the sample. For field-effect studies, a 23 Hz a.c. field was applied perpendicular to the helical axis.

4. Results and discussion

The temperature dependence of the optical activity in AS661 (chemical structure is given in reference [20]) is shown in figure 1. We observed discontinuities in both the optical activity and transmitted intensities for all transitions except the SmA–SmC* transition. The resolution of our equipment is 0.1 ° and no optical activity was detected in the SmA phase within this range. Hence, the detection of an optical activity signals the arrival of the SmC* phase. In addition, the reversal of the helix during the phase transition from the SmC^*_{F2} to the SmC^*_{F1} phase allows these two phases to be distinguished.

There is an anomaly in the optical actvity data in the SmC* phase (at ~88.5°C) which is due to the vicinity of the Bragg peak. When λ is close to λ_0, strong

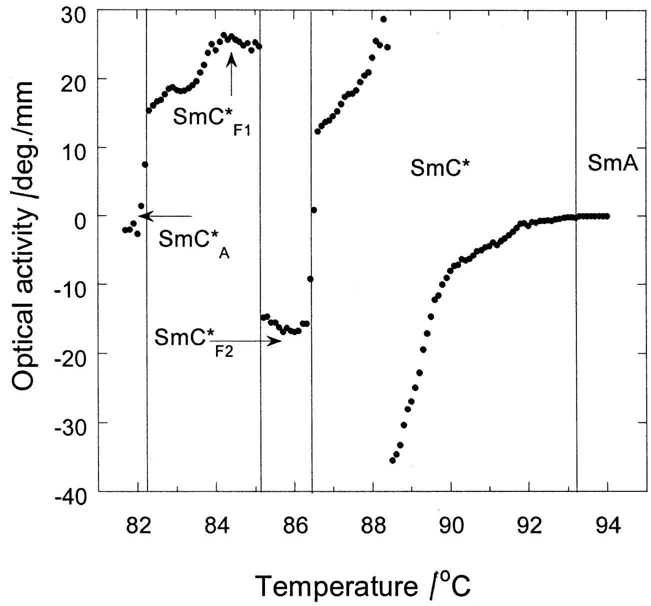

Figure 1. Temperature dependence of the optical activity in AS661 ($\lambda=543$ nm). Selective reflection occurs in the SmC* phase.

reflection bands occur and the optical activity changes sign. Hence, equation (1) is not valid in this region of the SmC* phase and a comparison between experimental and theoretical data is not possible. The optical activity in the SmC^*_A phase shows little variation with temperature (see figure 2). If the Bragg condition does not exist in either the SmC* or the SmC^*_A phases, then

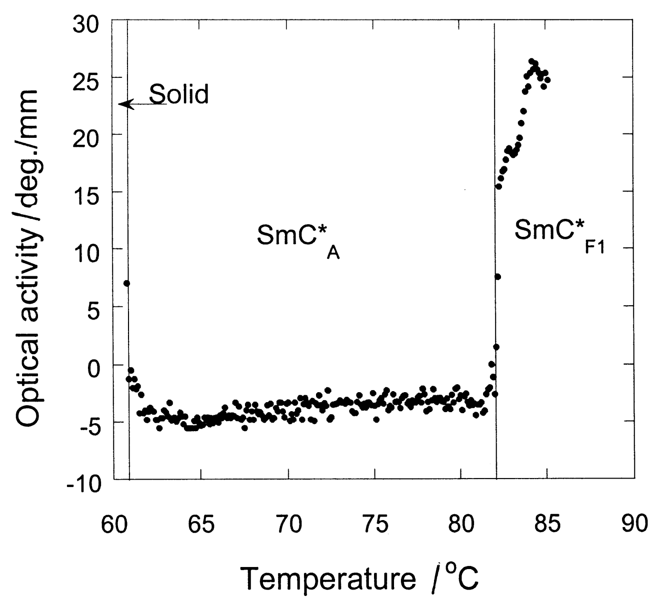

Figure 2. Temperature dependence of the optical activity in the SmC^*_A phase of AS661. The wavelength of the light used is 543 nm.

the optical activities in these phases are of opposite sign.

The effect of applied electric fields on the optical activity in the various phases is shown in the voltage–temperature diagram (see figure 3). What is immediately obvious is that field-induced phases appear in the region between the SmC* and SmC_A^* phases if the applied field exceeds 9.5 kV m^{-1} (50 V applied). The spontaneous polarization decreases in the order, SmC*→SmC_{F1}^*→SmC_{F2}^*→SmC_A^* and coupling between the polarization and the applied field would decrease likewise. Hence, the critical field required to unwind the helix completely would be least for the SmC* and increase in the above order. The extrapolated value at which the helix in the SmC* phase is completely unwound is ~50 kV m^{-1}. Thus, it is not surprising that the SmC_{F2}^* phase is stabilized at the expense of the SmC* phase as the strength of the applied field is increased. The range over which the SmC_A^* phase is stable is essentially unaffected by the fields that were applied in this study. We are unable, at this time, to identify the nature or structure of the field-induced phases.

For field-effect studies, we applied voltages (23 Hz a.c.) that varied from 25 to 150 V (4.75 to 28.50 kV m^{-1}). The SmA–SmC* transition is now accompanied by a discontinuity in the optical activity and is thus much easier to identify than for the zero field case. The field dependence of the optical activity for the weakest applied field (4.75 kV m^{-1}) is shown in figure 4. When the weak field of 4.75 kV m^{-1} is applied, the optical activity changes sign in both the SmC_A^* and SmC* phases. It is likely that the field increases the helicoidal pitch in these phases by different extents, such that selective reflection is possible in both phases. However, the topology of the curves in both phase is somewhat distorted from what is normally observed for selective reflection.

The effect of an applied field (19 kV m^{-1}, 23 Hz) on the optical activity is shown in figure 5. There are still three distinct phases in the subphase region, but the SmC_{F2}^* phase appears to be stabilized at the expense of the SmC* phase. There is also a stepwise change in the optical activity of the SmC* which may be attributed to a step-wise unwinding of the helix [21]. The SmC* phase is now stable over ~4.1 K and the SmC_{F2}^* over ~2 K. However, the combined range of the SmC* and subphases remains unchanged. The jump in the optical activity at the SmA–SmC* transition is greater at this higher field.

Owing to the unavailability of a high output a.c. source we were unable to apply fields higher that 28.5 kV m^{-1}. The optical activities at this higher field are shown in figure 6. The main difference here is that there is a divergence in optical activity in the SmC_{F2}^* phase. This might mean the transition between the SmC_{F2}^* phase and the unidentified phase is approaching a second-order transition. There is further stabilization of the SmC_{F2}^* phase at the expense of the SmC* phase.

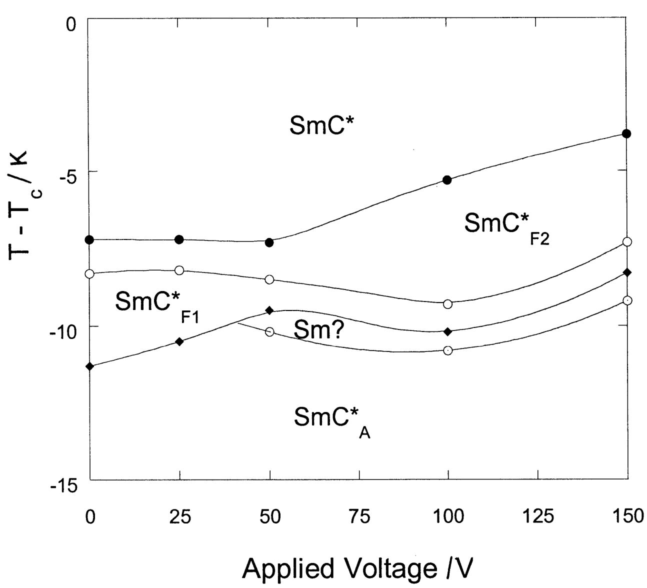

Figure 3. The voltage–temperature phase diagram for AS661. The distance between the electrodes of the electro-optic cell is 5.25 mm. T_C is the SmA–SmC* transition temperature.

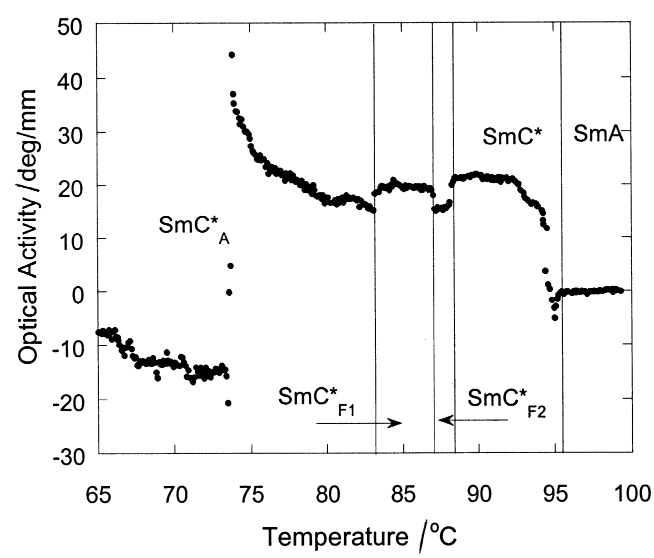

Figure 4. The effect of an applied a.c. electric field (4.75 kV m^{-1}, 23 Hz) on the temperature dependence of the optical activity in AS661. The entire SmC_A^* is not shown.

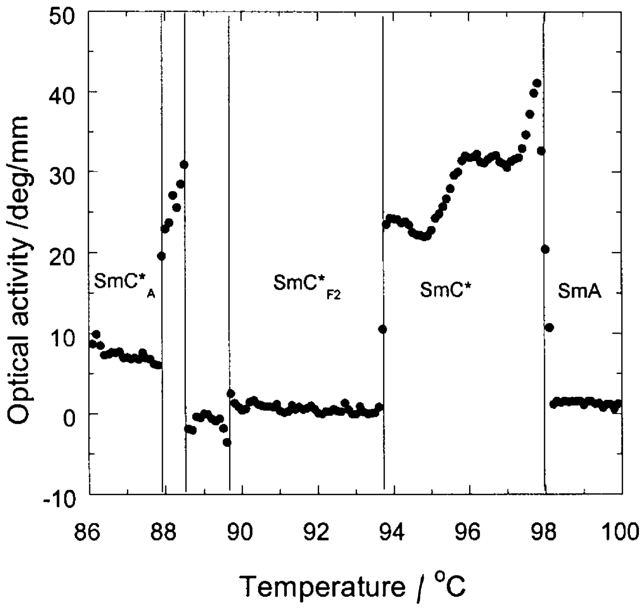

Figure 5. The effect of an applied a.c. electric field ($19\,kV\,m^{-1}$, 23 Hz) on the temperature dependence of the optical activity in AS661. The entire SmC_A^* range is not plotted.

Also, the optical activity of all phases present have the same sign (there is no reversal in the sign of the helix). Thus, field-effects dominate the temperature induced helical reversals.

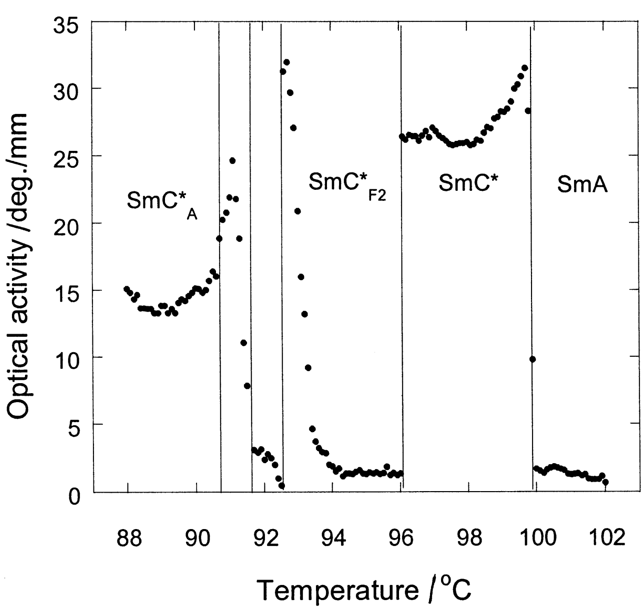

Figure 6. The effect of an applied a.c. electric field ($28.5\,kV\,m^{-1}$, 23 Hz) on the temperature dependence of the optical activity in AS661. The entire SmC_A^* range is not plotted.

5. Conclusion

We have demonstrated that optical activity is a sensitive probe for studying phase transitions in chiral smectic liquid crystals which form ferroelectric, anti-ferroelectric and subphases (intermediate phases). The pitch and the hence the optical activity are quite sensitive to external fields, which are applied to increase the pitch of the various chiral phases. Owing to differences in polarization, different phases couple to different degrees to the external fields.

When the applied field exceeded $\sim 10\,kV\,m^{-1}$, an additional phase was observed in the region between the SmC* and SmC_A^* phases when compared with the zero-field case. We have observed what appears to be a field-induced second order transition within the intermediate region at the highest applied field (this can be verified by using slightly larger fields). Also, the applied fields stabilize the SmC_{F2}^* phase at the expense of the SmC* phase.

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