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Investigation of the helix unwinding process in thick freely suspended smectic films

A. DAHLGREN*, M. BUIVYDAS, F. GOUDA†, L. KOMITOV, M. MATUSZCZYK and S. T. LAGERWALL

Chalmers University of Technology, S-412 96, Sweden

†Umm Al-Qura University, Makkah, P. O. Box 715, Saudi Arabia

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Optical and electro-optical measurements have been performed on free-standing chiral smectic films sufficiently thick ($\sim$10 000 layers) to preserve the natural smectic helix. The Goldstone mode appears at about 200 Hz, showing that these films are a much better approximation of the 'ideal' smectic bulk state than a thick planar sample between glass plates (where the Goldstone mode is found at about 3 kHz). In these films the unwinding of the helix is studied, as a function of applied electric field, by monitoring Bragg reflections and their Fourier components. When the helix deforms, a reflection appears which at first sight might be taken for a subharmonic, but must be interpreted as the main 'full pitch mode' reflection relative to the 'half pitch' reflection from the undeformed helix. Our measurements further confirm that in anticlinic materials no helix unwinding takes place prior to the antiferroelectric–ferroelectric transition.

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1. Introduction

The geometry of freely suspended films provides new experimental possibilities for observations of thermodynamically stable structures which are suppressed in common cells due to boundary constraints of the azimuthal angle (and sometimes for the polar angle) on solid substrates [1, 2]. For instance, one- and two-dimensional modulated patterns along the film surface have been observed in thin freely suspended films of the SmC phase [3, 4]. Most research activity has been concentrated on these thin and ultrathin films, which have a thickness from two to tens of layers. Freely suspended films that are thousands of layers thick, on the other hand, would permit the study of translational periodic structures characteristic of the bulk, in particular the undisturbed properties of the helix. The differences in the temperature dependence of the helical pitch in a freely suspended film relative to that in a homeotropic glass cell have already been reported [5]. In this paper we report measurements of the electro-optic response in a free-standing film and compare it with the dielectric relaxation spectrum of a planar cell. Our measurements show that the characteristic frequency of the Goldstone mode is appreciably lower in a freely suspended film than in a thick planar cell.

*Author for correspondence.

The main topic of our study is, however, the free film characteristics of the helix unwinding in an electric field. We monitor this unwinding by optical methods (Bragg reflection) and interpret the Fourier components that appear in the spectrum due to deformation of the helix during the unwinding process.

2. Experimental

The sample holder used to suspend the films is shown in figure 1. It was made from an epoxy glass laminate covered by a thin copper foil. The copper foil was appropriately etched in order to form the electrode pattern. The holder was furnished with a precise hole of dimensions $2 \times 5\,mm^2$, and this hole was used as the frame. The film was prepared by drawing the liquid crystal across the frame and then permitting it to relax to uniform thickness. Special measures were taken to obtain a relatively thick film (30–60 μm, containing about 10 000 layers) in order to incorporate at least ten helical periods.

The film holder was inserted in a specially designed hot-stage mounted inside a Shimadzu 3101PC spectrophotometer capable of recording a wide range of wavelengths (from 300 to 3200 nm). The incident beam of the spectrophotometer is almost non-polarized. When non-polarized light propagating in the direction of the helix axis and with wavelength equal to the pitch hits the

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(*a*)

(*b*)

Figure 1. (*a*) The schematic picture of the sample holder. (*b*) Picture explaining the principle of the spectrophotometric measurement.

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sample, it is split into two orthogonal circular forms, of which the one with the same handedness as the helix is Bragg-reflected, while the other is transmitted. If p is the periodic pitch, we will thus find a dip in the transmission spectrum when the wavelength λ' in the medium equals the pitch,

$$\lambda' = \lambda/n = p$$

corresponding to a spectrometer reading

$$\lambda = np$$

with n being an effective index of refraction for light vibrating perpendicular to the helix axis. The value of n can be extracted from relations given by Parodi [6]. This conditions is valid only in a stop band of width proportional to the effective birefringence Δn, so the presence of a helix shows up experimentally as a dip in the transmission spectrum.

The copper electrodes enable the application of the voltage across the film, in the direction along the layers. The construction of our sample holder allows application of a maximum of 3 kV d.c.; at higher voltages there is a growing risk of electric break-down.

Microscope observations were carried out by inserting the sample holder into a Mettler hot stage mounted on the turntable of the polarization microscope. Texture observations normally require crossed polarizers, but sometimes, especially when taking pictures, the polarizers were uncrossed by 3–5 degrees to ensure satisfactory brightness.

For electric fields much lower than the unwinding field the electro-optic response of the helix shows up as a small tilt of the average optic axis. We have used a spatial filtering technique [7] in order to sense this tilt. For light with longer wavelength that the pitch, the undisturbed helical SmC* sample is effectively uniaxial, thus it corresponds to the centred conoscopic image in figure 2. A small disturbance of the SmC* helix by an electric field forces the average optic axis to tilt; this corresponds to a movement of the conoscopic cross and gives the appearance of a small biaxiality. (For reasons of clarity we neglect the contribution of biaxiality in figure 2.)

The movement of the conoscopic cross cannot be sensed by the photodiode attached to the ocular of the microscope, unless the centre of the conoscopic cross leaves the viewing area. Such a large tilt of the effective optic axis is observed only at relatively large voltages. Instead, by inserting an extra aperture in the microscope, we can select one part of the focal plane as shown in figure 2. This technique helps us to observe small variations of tilt of the effective optic axis at low applied voltage.

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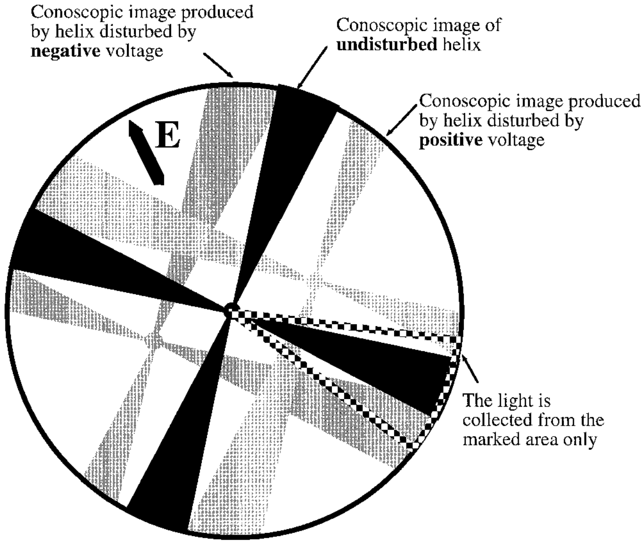


Figure 2. Principle of the spatial filtering. In the long wavelength limit, the SmC* sample with undisturbed helix at zero voltage is identical to a uniaxial crystal with the optic axis perpendicular to the smectic layers. Application of the voltage disturbs the helix and forces the average optic axis to tilt. In order to increase the change in the light intensity produced by the tilt of the optic axis, we collect light only from the marked area. The filtering is performed by a special diaphragm inserted in the back focal plane of the condenser.

3. Results

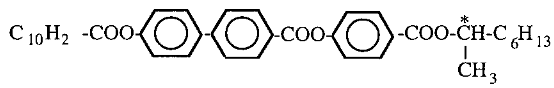
3.1. *Materials*

Measurements have been performed on three different smectic materials designated LC1, LC2 and LC3.

LC1 is an antiferroelectric mixture commercially available from Chisso, CS-4000, with the phase sequence

$$[\mathrm{I}\ 100°\ \mathrm{SmA^*}\ 82.9°\ \mathrm{SmC}^*_{\alpha}\ 81.8°\ \mathrm{SmC}^*_{x}$$
$$79.1°\ \mathrm{SmC}^*_{A}\ -10°\ \mathrm{Cr}]$$

LC2 is the antiferroelectric single substance,



$$[\mathrm{I}\ 140.1°\ \mathrm{SmA^*}\ 115.1°\ \mathrm{SmC^*}\ 108.1°\ \mathrm{SmC}^*_{\gamma}$$
$$103.5°\ \mathrm{SmC}^*_{A}\ (57.8°\ \mathrm{SmI}^*_{A})\ 62.7°\ \mathrm{Cr}]$$

LC3 is a ferroelectric mixture commercially available from NIOPIK, Moscow, ZKS 2508,

$$[\mathrm{I}\ 70°\ \mathrm{SmA^*}\ 54°\ \mathrm{SmC^*}\ -1°\ \mathrm{Cr}]$$

3.2. *Spectra*

A typical transmission spectrum taken on LC3 is shown in figure 3. It exhibits relatively strong dip and characteristic periodic maxima and minima. The dip

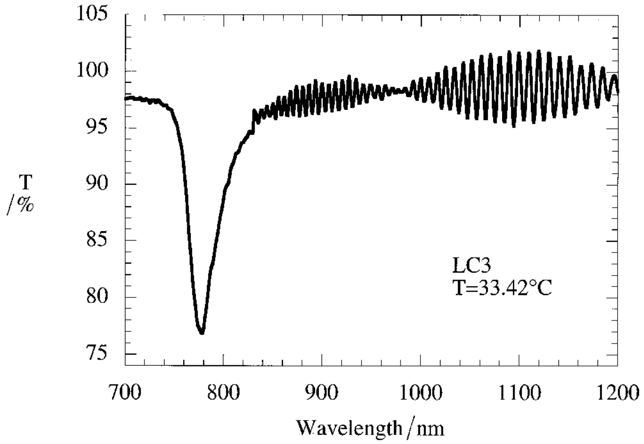


Figure 3. The experimentally obtained spectrum for a 61.7 μm thick freely suspended film of the smectic C* liquid crystal LC3 at 33.42°C.

is due to selective reflection of light with left-handed circular polarization by the left-handed smectic helix of the substance. The periodic maxima and minima are due to the interference of light reflected from the two free surfaces of the film, that is thickness fringes. They have a characteristic 'modulated' shape which seems, in our opinion, to be due to the calibration of the instrument in the SmA* phase. The base line of the spectrophotometer was recorded with the film inside the instrument, because the insertion of the film limits the aperture of the instrument and results in a large loss of light intensity. Thus, 100% transmittance corresponds to the transmittance of the freely suspended film in the smectic A* phase. In other words, the baseline contains the thickness fringes in the smectic A phase, so that the thickness fringes in the smectic C* phase and the thickness fringes in A* phase, memorized in the baseline, produce the observed beats.

3.3. *Texture investigations*

The freely suspended films investigated here exhibit two main types of texture. The first one is a stripe texture figure 4 (*a*), which normally appears in tilted phases with a tight pitch, like the anticlinic smectic C* phase (SmC_A^*) and the synclinic smectic C* phase (SmC*)†. This texture corresponds to an in-plane rotation of the two dimensional **c**-director. According to Demikhov and Dolganov [8] the stripe pattern appears because of the contribution of the flexoelectricity in the freely suspended film in the gravity field. The stripe texture is normally seen in materials with short pitch. If the pitch is equal to the wavelength of the visible light, then the texture has a colour (e.g. green) which is complementary to the colour of the reflected light. Tilted phases with a long pitch, for instance SmC_γ^*, SmC_α^* and in some cases the SmC* phase, normally exhibit a kind of schlieren texture, figure 4 (*b*). The schlieren texture corresponds to a smooth variation of the two dimensional **c**-director and it is similar to the schlieren texture observed in planar nematic cells. This texture often exhibits large low frequency fluctuations. The SmA* phase, being untilted, appears black between crossed polarizers.

When applying the d.c. field to the films one can observe material flow, which slowly develops into an in-layer rotation. (The in-layer character of the rotation can be confirmed by the fact that the helical pitch is preserved in the anticlinic samples.) The threshold for the appearance of material flow is about 100 V mm^{-1}. It does not depend on the phase, but is slightly dependent on the temperature of the film.

† We think, that the terms 'synclinic' and 'anticlinic' materials describe the volume properties of SmC* and SmC_A^* phases better than the commonly used terms 'ferroelectric' and 'antiferroelectric' materials. Thick cells of SmC* are not ferroelectric (they are helielectric), and only in very thin cells do SmC* materials become truly ferroelectric.

3.4. *Electro-optic response of a thick freely suspended film*

An investigation of the collective dynamics in the freely suspended film by dielectric relaxation spectroscopy is virtually impossible because the strongly disordered boundary regions on the film holder give a much larger contribution to the dielectric effects than the film itself. However, there is a simple way to observe the collective motion by monitoring the electro-optic response optically under an applied electric field. Such a method would also work in the quasi-homeotropic cell, if the field is applied along the smectic layers. The response to an applied a.c. field is a harmonic variation of the direction of the average optic axis, see figure 5 (*a*). In order to minimize the disturbance of the helix, we use a low electric field. Since a decrease of the applied field decreases the amplitude of the tilt of the average optic axis, we used the spatial filtering technique described above. The signal measured using the spatial filtering technique is shown in figure 5 (*a*). On plotting the frequency dependence of such a response and comparing it with the frequency dependence of the real part of the dielectric constant in a 'thick cell', one sees, figure 5 (*b*), that the Goldstone mode frequency in a cell which is normally assumed to be 'thick' and without disturbance of the SmC* helix, is about 15 times higher than the corresponding relaxation frequency in a helical freely suspended film: the electro-optic response in the film shows a cut-off as low as about 200 Hz. Thus, the thick freely suspended film seems to approximate better the behaviour of an 'ideal' smectic system for which the 'true'

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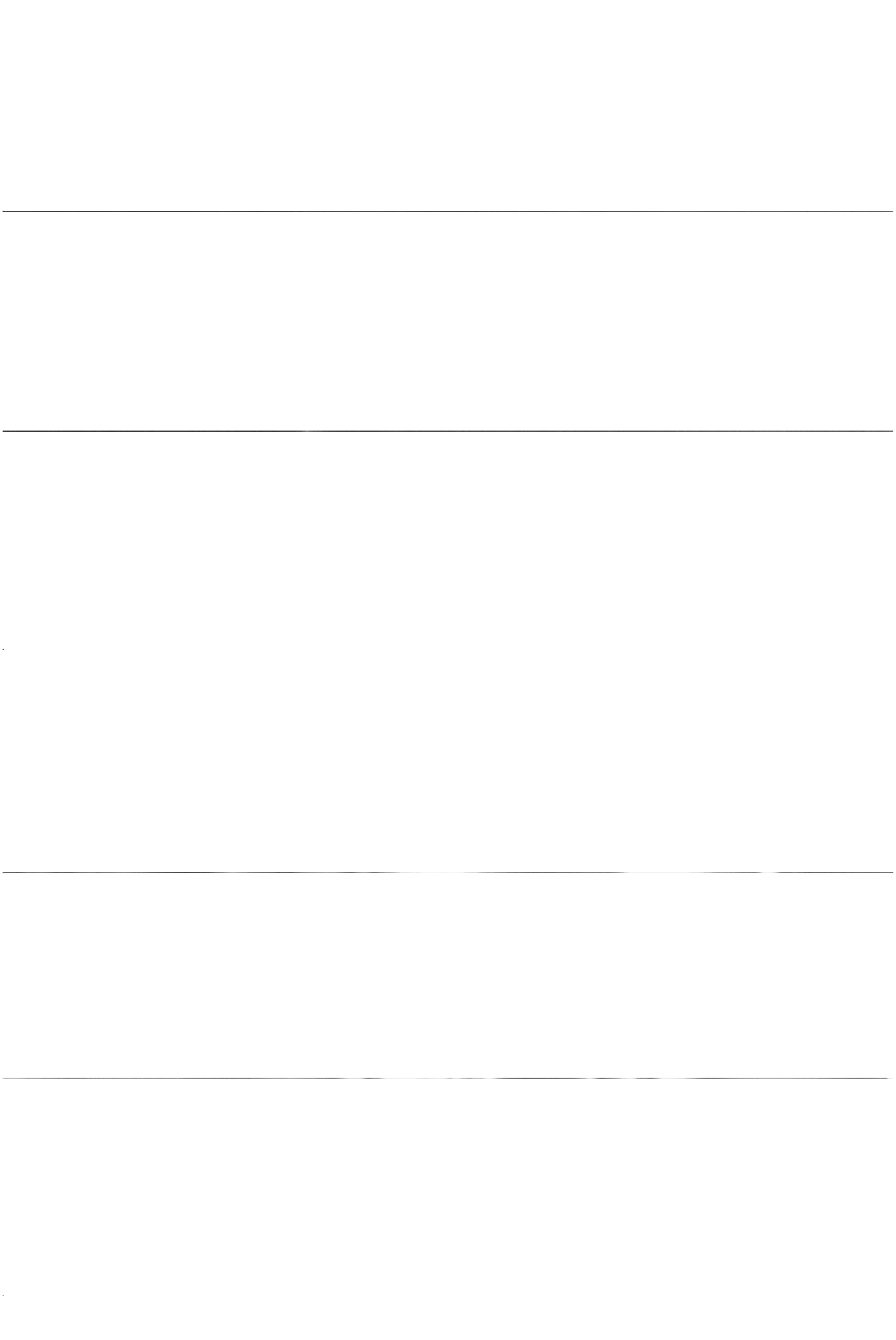
(a)



(b)

Figure 4. (a) Stripe texture in the SmC_A^* phase. (b) Schlieren texture in the SmC_γ^* phase. The material is LC1.

Goldstone mode lies at zero frequency. Consequently the frequency of the Goldstone mode is increased by the solid surfaces of the cell, and thus the helix in the cell may be regarded as having an elasticity created by pinning effects even if the cell thickness is appreciably larger than the helix pitch.

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Figure 5. (*a*) The spatially filtered electro-optic response of the helical freely suspended film of LC3. (*b*) The dielectric spectrum of a 10 μm thick cell (open circles) and the electro-optic response of a 6 μm thick film of the same substance.

3.5. *Observation of unwinding of the* SmC_A^* *and SmC* helix*

As for the electric field unwinding of the SmC* helix in a thick freely suspended film, it is not in its character appreciably different from the corresponding process in a homeotropic cell [9].

This is an indication that the surface anchoring effects which we observe may still be considered as relatively weak. When increasing the applied d.c. voltage, the length of the pitch becomes larger, while the width, measured at 50% of the selective reflection depth, is almost constant. The width of the dip increases very steeply only in the vicinity of the critical (unwinding) field (see figure 6). When we have a film of a substance with anticlinic order, the pitch is practically constant as in LC1, see figure 7 (*a*), or it marginally increases as in LC2, see figure 7 (*b*).

Only when the anticlinic order is finally broken does the ferroelectric-like unwinding process take over and the pitch length begin to increase. On the other hand, we observe a widening of the reflection dip in the anticlinic state, accompanied by a small change of the depth of the minimum, as well as a change of the total transmittance. The widening is preserved when the anticlinic state is broken and a synclinic state is induced. It can be related to an increase of the effective birefringence Δn, due to the breaking of the anticlinic order. There is a strong memory effect involved in the widening of the reflection dip. If the d.c. field is switched off and the sample is short circuited, the wide dip relaxes very slowly

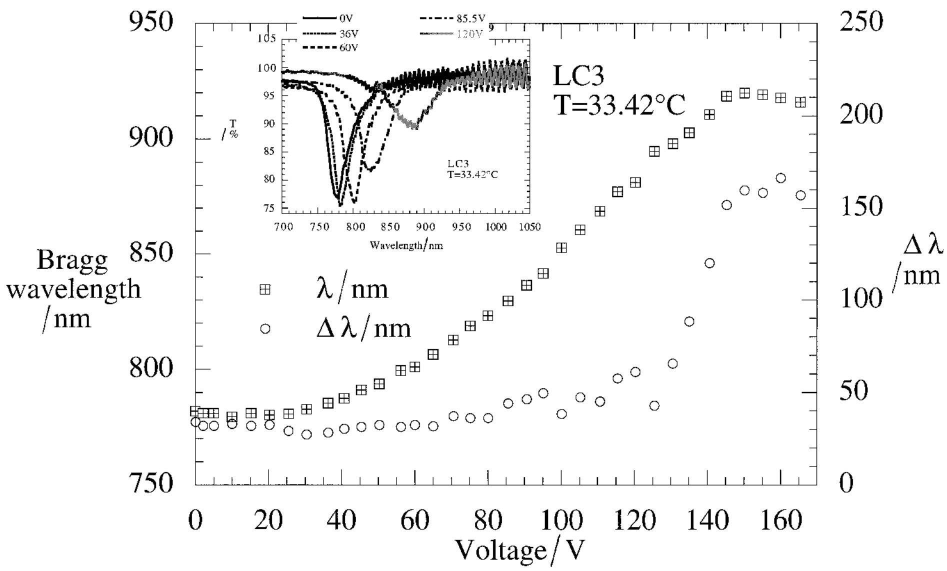

Figure 6. Bragg reflection wavelength and width of the transmission minimum, measured at 50% of the depth, as a function of the applied voltage in the synclinic (FLC) material LC3. The inset curves are transmission spectra of the synclinic material at different applied fields.

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Figure 7. Bragg reflection wavelength and width of the transmission minimum, measured at 50% of the depth, as a function of applied voltage in two anticlinic materials, (*a*) LC1, (*b*) LC2. The inset curves in (*a*) are the transmission spectra of the material at different applied voltages.

back to the narrow shape. This process takes several days at room temperature and a couple of hours in the vicinity of the phase transition.

3.6. *Deformation of the SmC* helix*

By observing the spectrum in a broad range of wavelengths we can observe the effect of deformation of the smectic helix. If the undeformed smectic helix exhibits a single Bragg reflection, which appears as a dip in the spectrum at λ_{min}, then the field-deformed helix ($15\ \mathrm{V\,mm^{-1}}$) exhibits an additional reflection at about 2/3 of the wavelength of the original reflection, $2/3\lambda_{min}$, (see figure 8). Application of a higher field ($30\ \mathrm{V\,mm^{-1}}$) deforms the helix in such a way that one can observe a couple of additional reflections corresponding to

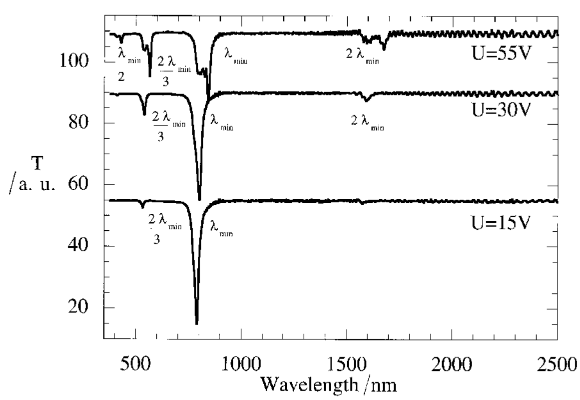

Figure 8. Transmission spectra of the FLC films at different applied voltages. The material is LC3.

periodicities of $\lambda_{min}/2$ and $2\lambda_{min}$. The electric field deforms the smectic helix continuously, such that the intensity of the main reflection decreases continuously and the intensity of the sub-reflections increases continuously with increase of the applied field. The ratios between the wavelengths of the reflections deviate slightly from the exact values 1/2, 2/3 and 2, but this deviation has the same order of magnitude (a few per cent) as the measured dispersion of the refractive indices.

At 55 V mm^{-1} a clear splitting of the single dips into double dips takes place. This splitting is almost absent in the maiden sample and becomes more pronounced in films which are repeatedly treated by a d.c. voltage. Since the microscopic observations confirm the building up of defects under a d.c. field, the reason for the splitting might be the pinning of the helix to these defects. We also observe that the 'pinned helix' becomes stiffer and is more difficult to unwind by applying an electric field.

4. Conclusions

The unwinding of the SmC* helix appears in the spectrum as multiple reflections, both at shorter and longer wavelengths ($\lambda_{min}/2$, $2\lambda_{min}/3$, $2\lambda_{min}$). The appearance of the reflection at the double wavelength can be explained as follows. For light travelling along the undeformed helix, the periodicity that is seen equals half the pitch, because $+\theta$ and $-\theta$ give identical values of the effective refractive index. The dip that we actually see in the transmission spectrum at zero field is due to Bragg reflection from this periodicity. Sometimes in the literature this is called the 'half pitch mode', despite the fact that the wavelength of the reflected light corresponds to a full helical pitch length multiplied by the effective refractive index.

The application of an electric field perpendicular to the helical axis deforms the helix. In the deformed helix a new periodicity equal to the full pitch appears, because there is no longer any glide-rotation correspondence between the director states at $+\theta$ and $-\theta$. Despite the fact that this is sometimes called the 'full pitch mode', the Bragg-reflected wavelength corresponds to the double helical pitch length multiplied by the effective refractive index. The deformation of the helix furthermore leads to the appearance of higher Fourier components. Thus the reflection at 1/2 of the original wavelength is the second Fourier component of the original ('half pitch') reflection, whereas the reflection at 2/3 of the original wavelengh is the third Fourier component of the 'full pitch' ($2\lambda_{min}$) mode. The second component of the latter also gives a contribution to λ_{min} and the perturbation due to the pinning of the full pitch is also transferred to the splitting of all overtones.

The helix in the anticlinic material is unwound in two steps as predicted earlier [10] from dielectric data. This phenomenon is very clear in LC2. The first step is the breaking of the anticlinic order. During this process the helix is undeformed and has the same length as in the field free state. When the anticlinic state is completely broken, then the unwinding of the helix takes on its usual character. The helix becomes longer and it deforms in the same way as the SmC* helix. The deformation of the helix is less pronounced in LC1.

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References

[1] Rosenblatt, Ch., Pindak, R., Clark, N., and Meyer, R. B., 1979, *Phys. Rev. Lett.*, **42,** 1220.
[2] Amador, S. M., and Pershan, P. S., 1990, *Phys. Rev. A*, **41,** 4326.
[3] Maclennan, J., and Seul, M., 1992, *Phys. Rev. Lett.*, **69,** 2082.
[4] Maclennan, J., Sohling, U., Clark, N. A., and Seul, M., 1994, *Phys. Rev. E*, **49,** 3207.
[5] Gouda, F., Dahlgren, A., Lagerwall, S. T., and Stebler, B., 1996, *Ferroelectrics*, **178,** 187.
[6] Parodi, O., 1975, *J. de Phys.*, **36,** C1–325.
[7] Lagerwall, S. T., and Stebler, B., 1979, in Proceedings of Liquid Crystal Conference, Bangalore, p. 223.
[8] Demikhov, E. I., and Dolganov, V. K., 1996, *Ferroelectrics*, **181,** 175.
[9] Rozanski, S. A., and Kuczynski, W., 1984, *Chem. Phys. Lett.*, **105,** 104.
[10] Buivydas, M., Gouda, F., Lagerwall, S. T., and Stebler, B., 1994, *Liq. Cryst.*, **18,** 879.

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