ANTIFERROELECTRIC LIQUID CRYSTALS WITH 45° TILT - A NEW CLASS OF PROMISING ELECTRO-OPTIC MATERIALS

K. D'HAVÉ[a]*, A. DAHLGREN[a], P. RUDQUIST[a],
J.P.F. LAGERWALL[a], G. ANDERSSON[a], M. MATUSZCZYK[a],
S.T. LAGERWALL[a], R. DABROWSKI[b], W. DRZEWINSKI[b]

[a] School of Physics and Engineering Physics,
Chalmers University of Technology, S-412 96 Göteborg, Sweden;
[b] Institute of Chemistry,
Military University of Technology, PL-00-908 Warszawa, Poland

Antiferroelectric liquid crystals with a tilt angle of 45 degrees have very interesting optical properties, which seem to have been overlooked so far - perhaps because such materials have hardly been available. We have prepared a four-component mixture of partially fluorinated compounds with a SmC_a^* phase in the interval between 27.4°C and 121.6°C, in which the tilt angle θ saturates at 45 degrees for T≤80°C, and we investigate the optical properties, theoretically and experimentally. One of the surprising features of 45 degree materials is that they permit a remarkably high contrast by virtue of an excellent dark-state, in spite of the fact that AFLC materials are notoriously difficult to align. This is because a 45° AFLC turns out to be (negatively) uniaxial instead of biaxial. We describe these properties and propose a number of potentially interesting new applications, including a polarizer-free display mode and a three-level "phase-only" modulator.

Keywords uniaxial antiferroelectric liquid crystal; 45° tilt; Sm C_a^*; AFLC dielectric tensor; new electro-optic modes.

* Permanent address: Ghent University, Department of Electronics and Information Systems, Sint-Pietersnieuwstraat 41, B-9000 Gent, Belgium

INTRODUCTION

Antiferroelectric liquid crystals show a tri-state electro-optic switching behavior which is appealing for display applications because of its inherent DC compensation, fast response, easy gray scale and wide viewing angle. However, the initial linear response and problems with high quality alignment have so far resulted in low contrast which has prohibited widespread application of AFLC's. With two exceptions AFLC materials with a tilt angle near 45° do not seem to have been reported earlier. The first similar material is MHTAC, synthesized in 1976 by Keller et al.[1] with a tilt angle approximating 45 degrees ($\theta \approx 48°$), for which the electro-optic properties have been investigated by Cladis and Brand[2]. A more recent example was found by W. K. Robinson et al.[3][4] who have reported bi-mesogenic organosiloxane liquid crystals with an antiferroelectric phase. These materials show a temperature-independent tilt angle built into the molecule which reaches up to 43.5°. For these liquid crystals the antiferroelectricity is a consequence of the molecular conformation. The mixture presented here obtains its antiferroelectricity from the anticlinic order between neighboring layers.

THE ANTIFERROELECTRIC MATERIAL

It is practically excluded to make 45° AFLC materials with a second order SmA*-SmC* transition, because the tilt typically saturates around 25° in the C* phase and does not increase very much further in the underlying C_a* phase. In this mixture, called W107, the A*-C* transition is strongly first order, with an immediate jump in θ to 32°. The sharpness of the transition is clearly exhibited in Figure 1, showing the tilt angle as a function of the temperature, and in Figure 2, showing the spontaneous polarization as a function of temperature. It is also clearly born out in the dielectric spectroscopy measurements and well observed in polarizing microscopy.

The polarization of W107 was measured by the reversal method using a capacitance bridge. It reaches values as high as 300 nC/cm^2 at the low end temperature range of the antiferroelectric phase. The tilt angle was measured using the turntable of a polarizing microscope and a switching sample.

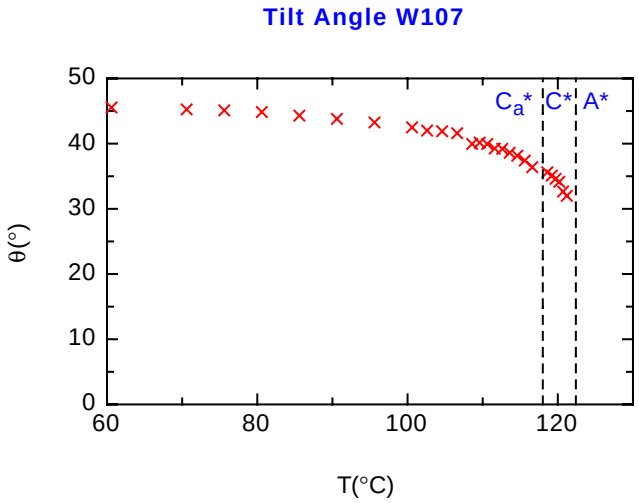


FIGURE 1 The measured tilt angle of the mixture W107, saturating at about 45° in the antiferroelectric phase.

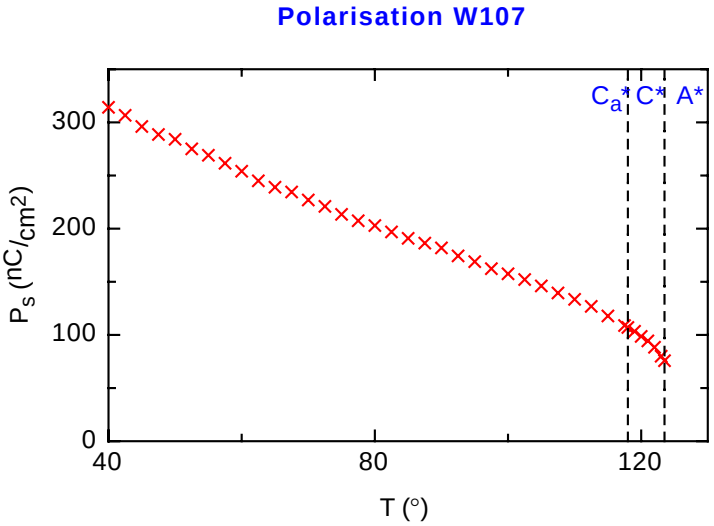
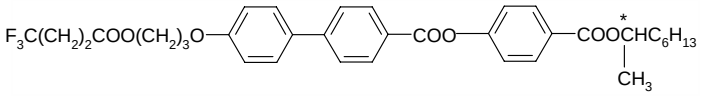
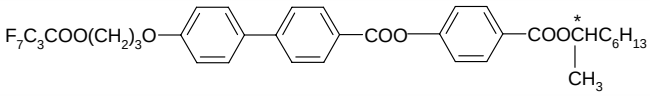
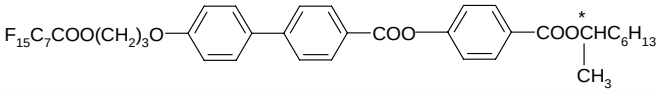
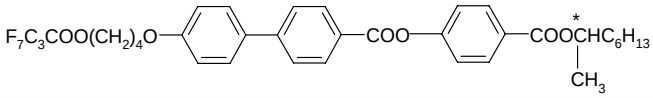


FIGURE 2 The measured polarization of the mixture W107.

The structure of the liquid crystal compounds contained in the mixture W107 can be found in Table 1. A complete description of this series of partially fluorinated compounds is given in the paper by W. Drzewinski et al.[5]. The phase transition temperatures of this mixture were measured with Pyris 1 DSC equipment. The phases were checked by polarizing microscopy. The transitions, upon heating, can

TABLE 1 Composition of the mixture W107.

%wt	molecule
6.31	
20.77	
32.45	
40.47	

be summarized as following (temperatures in degrees Celsius)

K - 27.4 - SmC_a^* - 119.5- SmC* - 121.6 - SmA* - 132.3 - I

which are also displayed in the DSC traces. It is an interesting and intuitively surprising fact that, whereas the A*-C* transition, i.e. the onset of the tilt, is strongly first order, in contrast, the C*-C_a* transition takes place practically with no enthalpy change (see inset of Figure 3). The transition from synclinic to anticlinic order at θ=36° seems to involve only a minimal disturbance of the system. This is also underlined by the perfectly continuous functions θ(T) and P_s(T) in Figure 1 and Figure 2. Thus from these curves no phase transitions could have been noticed. On this point dielectric spectroscopy is invaluable, in disclosing (Figure 4) that in reality there is a very sharp transition between synclinic and anticlinic order.

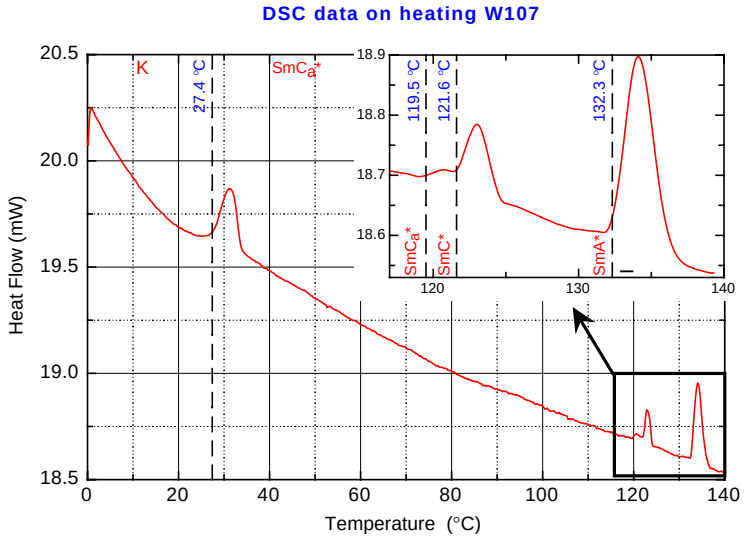


FIGURE 3 DSC curve for the mixture W107, taken on heating.

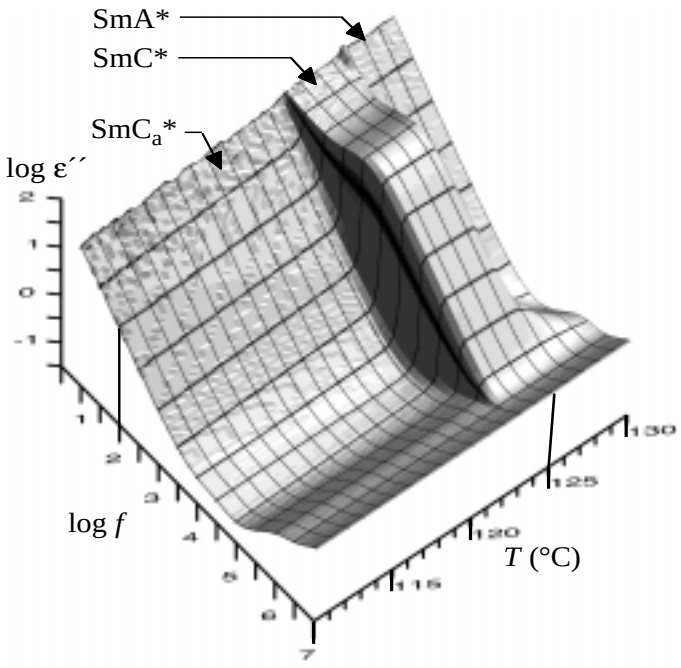


FIGURE 4 A 3D overview of the dielectric behavior of W107. Note the sharp transition, from A* to C*, but in particular also from C* to C_a*. Data were taken on a 36 µm sample.

OPTICAL PROPERTIES

The optical properties of a surface-stabilized AFLC (unwound helix as equilibrium condition) can be analyzed starting from the herring-bone structure of Figure 5(a). The xz plane is parallel to the plane of the cell and contains the alternating tilt director in the assumed bookshelf geometry. If we consider light incident perpendicular to the cell, (thus in the y direction) vibrations along z will be essentially along the molecules, thus encountering a high polarizability and a high refractive index n_γ, whereas vibrations along x will be along the molecular axis to a lesser degree and feel a lower value of n_β. The difference between these refractive indices depends on the tilt angle θ: for small values of θ it will be large, but in contrast vanish for $\theta=45°$, as we will further elaborate on below. For light incident along x, vibrations along z will feel the same high index n_γ, while vibrations along y will always be perpendicular to the long molecular axis and therefore encounter the lowest refractive index n_α, furthermore independent of the tilt angle θ. This means that the optic axial plane of the biaxial indicatrix will be the yz plane as illustrated in Figure 5(b). In the particular case of $\theta=45°$ this means that $n_\gamma=n_\beta$, so that the medium becomes *uniaxial*, with the optic axis along y. The AFLC is then, in fact, negative uniaxial and in

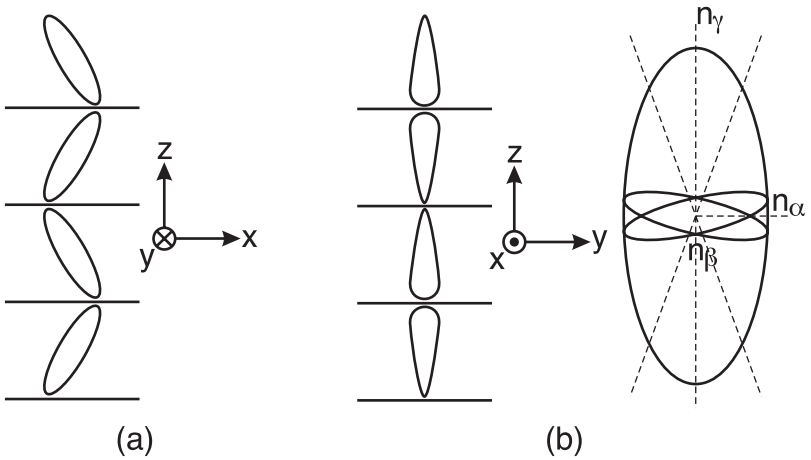


FIGURE 5 Herringbone order of the antiferroelectric seen in the tilt plane (a) and perpendicular to it (b). The axial plane of the indicatrix (containing the maximum and minimum index values) is perpendicular to the tilt plane.

bookshelf geometry it is isotropic in the cell plane, i.e. behaves as a *homeotropically* aligned medium. This means that, regardless how the layer normal points, we have an extinction state between crossed polarizers.

THE DIELECTRIC TENSOR

The above reasoning is corroborated by simple calculations. Let us first consider the dielectric tensor for a general AFLC material with tilt angle θ in its imagined synclinic state, as to the right in Figure 6(a). (This would correspond to the field-induced ferroelectric state if dielectric effects are neglected.) In the molecular frame x'y'z' in which z' is along the director and y' along the C_2 axis the tensor is diagonalized with its principal values ε_1, ε_2 and ε_3, cf. Figure 6(b),

$$\varepsilon' = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}. \qquad (1)$$

This tensor is transformed to our lab reference system, where z is along the smectic layer normal, by a similarity transformation, giving[6]

$$\varepsilon = U\varepsilon' U^{-1} = \begin{pmatrix} \varepsilon_1\cos^2\theta + \varepsilon_3\sin^2\theta & 0 & (\varepsilon_3 - \varepsilon_1)\sin\theta\cos\theta \\ 0 & \varepsilon_2 & 0 \\ (\varepsilon_3 - \varepsilon_1)\sin\theta\cos\theta & 0 & \varepsilon_1\sin^2\theta + \varepsilon_3\cos^2\theta \end{pmatrix}. \qquad (2)$$

If we now go to the anticlinic state, to the left in Figure 6(a), every second layer is described by a tensor which is obtained from (2) by replacing θ with -θ. For propagation of visible light, the relevant tensor will be the average tensor, hence

$$\varepsilon_{AF} = \frac{1}{2}\varepsilon_{+\theta} + \frac{1}{2}\varepsilon_{-\theta} = \begin{pmatrix} \varepsilon_1\cos^2\theta + \varepsilon_3\sin^2\theta & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_1\sin^2\theta + \varepsilon_3\cos^2\theta \end{pmatrix}. \qquad (3)$$

This is the general expression for the dielectric tensor in an antiferroelectric liquid crystal, describing its biaxial properties. As the

elements ε_{13} and ε_{31} in the molecular forms canceled out on averaging we see that this tensor is diagonal in the lab frame corresponding to z along the smectic layer normal. In the limit of small θ the principle values in this frame approach the values (1) valid for the molecular frame. We now also see that the material will become uniaxial for θ=45°. In this case

$$\varepsilon(45°)= \begin{pmatrix} \bar{\varepsilon} & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \bar{\varepsilon} \end{pmatrix} \tag{4}$$

where $\bar{\varepsilon}$ is the average of ε_1 and ε_3. At optical frequencies ε_2 is smaller than $\bar{\varepsilon}$. Hence a 45° AFLC is a negative uniaxial material with the optic axis *perpendicular* to the plane of tilt. From Figure 5(b) the ordinary and extraordinary indices are given by $n_e=\sqrt{\varepsilon_2}$ and $n_o=\sqrt{\bar{\varepsilon}}$ .A thorough analysis of the direction of the optical axis in the general AFLC case can be found in the article by A. De Meyere et al.[7].

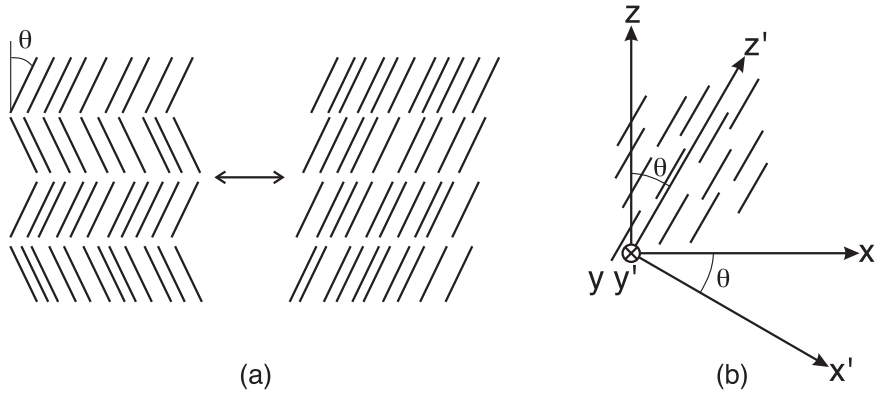


FIGURE 6 (a) Anticlinic and synclinic smectic state with the same tilt angle θ; (b) molecular (x'y'z') and lab frame (xyz) in the synclinic state.

OPTICAL AND ELECTRO-OPTICAL CONSEQUENCES

A smectic A* phase is positively uniaxial, with the optic axis along the smectic layer normal z. A conventional smectic C_a* phase has a certain biaxiality but behaves in a similar way, shows extinction if

homeotropically aligned between crossed polarizers. A SmC_a^* phase with 45° tilt, however, behaves in the same way as a homeotropic SmA*, when the Sm C_a^* is in *planar* alignment, i.e. in bookshelf geometry. It will keep the extinction even when the sample is rotated under crossed polarizers. This has the attractive consequence that the field-free extinction will be good even if, due to slight misalignment, the smectic layer normal varies across the sample. As the SmC_a^* materials are hard to align and as the insufficient zero-field extinction normally is a problem for AFLC displays, 45° materials offer an interesting option, quite in addition to the obvious fact that when switching to the 45° ferroelectric state, the polarization plane of the incident light is rotated by 90°, thus allowing maximum transmission in the bright state. It is also likely that the light leakage due to the pretransitional behavior at small applied fields will be smaller for 45° materials, because the indicatrix has to undergo a much more drastic change (from oblate to prolate) in order to give a visible shift in the apparent optic axis.

INVESTIGATING THE OPTICAL PROPERTIES

We assume a surface-stabilized bookshelf structure, i.e. with the helix permanently unwound by the surface torques. It is further assumed that the tilt plane is parallel to the plane of the cell. With the sample aligned such that the smectic layer normal is along one of the crossed polarizer-analyzer directions we will have extinction in the field-free state (E=0). The transmission (normalized to 1 for passage through parallel polarizers) in the fully switched state will then be given by

$$T_{on} = \sin^2 2\theta \ \ \sin^2\left(\pi \Delta n_{syn} \frac{d}{\lambda}\right) \qquad (5)$$

where θ is the molecular tilt, d is the cell thickness, λ is the wavelength of light in vacuum and Δn_{syn} is the birefringence at the field-induced synclinic state (the "ferroelectric state"). This implies that the liquid crystal must have a tilt angle of 45° if we want to achieve the maximum contrast, in addition to the requirement that the optical thickness should be adjusted to the half wave condition ($\Delta n_{syn}\, d=\lambda/2$).

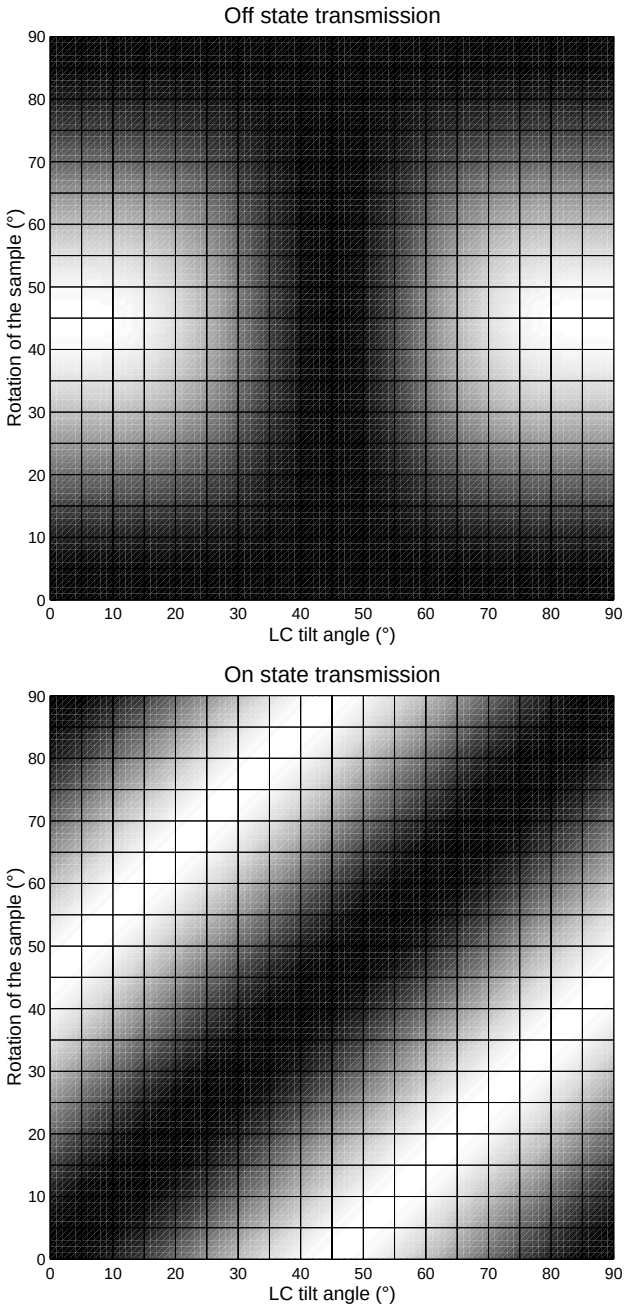


FIGURE 7 Calculated transmission of an AFLC bookshelf sample between crossed polarizers. For θ=45° the field-off transmission is zero and independent of the angular position of the sample. Under the same conditions an AFLC with θ=30° will show a bright state when turning the sample.

On the other hand, if we rotate the antiferroelectric structure by the angle α out of the extinction position, under zero applied field, the off-state transmission varies according to

$$T_{off} = \sin^2 2\alpha \quad \sin^2\left(\pi \Delta n_{anti} \frac{d}{\lambda}\right) \qquad (6)$$

where α is the angle between the smectic layer normal and the polarizer axis and Δn_{anti} is the birefringence for the anticlinic order. In Figure 7 we have visualized T_{off} and T_{on} as functions of the molecular tilt and rotation of the sample between crossed polarizers (equations 5 and 6).

In order to verify the predictions, sandwich type cells were constructed from glass substrates with patterned ITO giving a pixel dimension of 4 x 4 mm. Both substrates were coated with Pyraline, which gives planar alignment, but only one side was buffed. Polymer spacer balls with a diameter of 1.5μm were mixed in UV curable glue.

(a) (b) (c)

FIGURE 8 A sequence of micrographs showing (a) the non switched dark state (E=0), (b) switching with propagating fingers ($0<E<E_{syn}$) and (c) the switched bright state ($E \geq E_{syn}$).

As can be seen from the micrographs in Figure 8, we obtained an excellent alignment. Because the dark state is insensitive to small fluctuations in the smectic layer direction, the quality of the alignment can actually only be judged from observing the partially switched state, as shown in Figure 8(b). A further striking example of the optical properties of a 45° AFLC is observed by rotating the sample between crossed polarizers by an angle of 45°. The sample should now switch between three dark states. The finger-like domains of antiferroelectric state that appear in the ferroelectric state upon switching should then be indistinguishable from each other. This has been confirmed experimentally, showing only dark states during the entire switching process.

APPLICATIONS

In addition to increasing the contrast in the conventional AFLC display mode, a 45° material offers some new unique applications. One of the most attractive is a three-level "phase-only" modulator. Non-mechanical beam steering and dynamic holography devices utilizing liquid crystal spatial light phase-only modulators have great potential within for instance the fast expanding field of fiber telecommunication. The requirements for microsecond switching of such devices has directed the interest towards ferroelectric liquid crystals and today binary phase modulation devices such as optical interconnects based on surface stabilized ferroelectric liquid crystals have successfully been demonstrated. However, the binary feature of SSFLC's (providing a relative phase shift of for instance 0 or 180°) limits their efficiency as half of the diffracted light is "lost" in negative diffracted orders. Therefore multilevel phase modulation, making possible approximated blazed gratings, would be desirable. Scalar diffraction theory gives that using three levels of phase modulation instead of only two in a 1D multi-pixel array the maximum intensity of the first order diffraction increases from 40.5% to about 68%. By using a 45° tilt AFLC material we can achieve this in the following way, illustrated in Figure 9. Consider linearly polarized light at normal incidence with its plane of polarization at 45° with respect to the smectic layer normal in the case of a surface stabilized 45 degree AFLC. In the two synclinic field-induced ferroelectric states (corresponding to applied positive and negative fields $+E_F$ and $-E_F$) the light wave will vibrate along and perpendicular to the director, respectively. Thus, it will experience the pure n_e or n_o depending on the sign of the applied voltage. On the other hand, at zero field the light will experience an isotropic medium with an effective refractive index n_{eff} being an average of n_e and n_o, i.e. $n_{eff} \approx (n_e+n_o)/2$. By adjusting the cell thickness d such that $d\Delta n = 2\lambda/3$, where $\Delta n = n_e - n_o$, a relative retardation of 0° (E=$-E_F$), 120° (E=0), or 240° (E=$+E_F$) is achieved. Note that *none of these three retardation states will influence the polarization of the light*, i.e. the incident light remains linear and no rotation of the plane of polarization occurs.These principles are presently being tested in a device and the results will be presented in a forthcoming paper[8] .

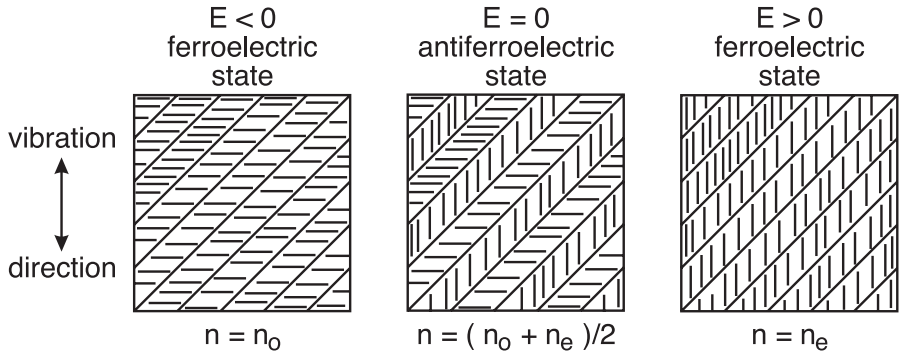


FIGURE 9 The states of a phase only modulator with a 45° tilt antiferroelectric liquid crystal, showing a different effective birefringence and hence three level modulation.

Finally we propose a new electro-optic mode for AFLC's. Consider a randomly oriented sample of a 45 degree AFLC where the texture is built up of surface-stabilized micron sized bookshelf domains. Each micro domain has a well defined orientation of the smectic layer normal in the plane of the cell but there is no correlation in this orientation between the domains. Provided that the "grain boundaries" between the domains do not significantly scatter light the sample will be essentially transparent, since all domains will appear isotropic with the identical refractive index at normal incidence. However, if an electric field is applied and the AFLC is driven into one of the ferroelectric states the domains will appear strongly birefringent and there will be a mismatch of the refractive indices between adjacent domains due to the different orientation of the domain optic axes. This will cause scattering of light and, hence, we have a field-controlled scattering device. Attractive features of such a device would be that it would work without any polarizers and may be actively driven between transparent and scattering states by means of suitable waveforms. The creation of a conveniently randomized AFLC bookshelf structure is now under study.

Acknowledgments

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