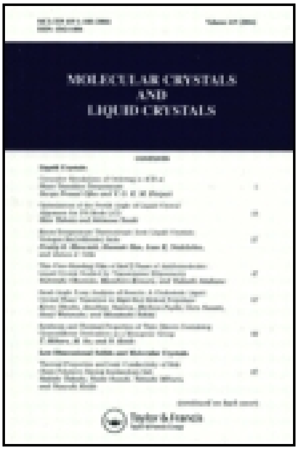

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Conoscopic Observations of Multiple Ferrielectricity in a Chiral Liquid Crystal

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The sequence of antiferroelectric, ferrielectric and ferroelectric phases in the material AS573 (Hull, UK) has been investigated via conoscopy and selective reflection. Evidence was found to support the division of the phase previously labelled SmC^*_γ into two ferrielectric sub-phases. A revised phase sequence for the material, based on this study, is presented.

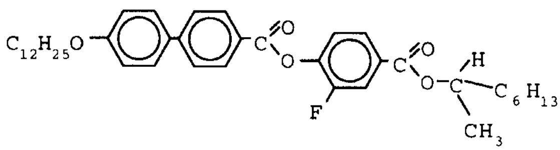
Keywords: Ferrielectric phases; Conoscopy; Liquid Crystals

INTRODUCTION

Ferrielectric phases have been observed in many chiral liquid crystal compounds, and it is predicted that ferrielectric subphases fill up the 'Devil's Staircase' of q_t values between the antiferroelectric SmC^*_A phase (q_t=0) and the ferroelectric SmC* phase (q_t=1). The material AS573 (figure 1) has a rich phase behaviour and has been studied by many authors[1,2]. In particular, it is one of the few materials thought to exhibit a ferrielectric subphase with a q_t parameter greater than 1/2[2]. There remains some uncertainty as to the exact phase sequence of this material; figure 1 shows two of those reported.

Recent experiments have revealed anomalous behaviour in some of the mesophases of this compound. Ellipsometry experiments[3] showed a divergence of ellipsometry data in the middle of the region denoted as the

SmC^*_γ phase, and a comparison of tilt angle data[4] gave a crossover point between the X-ray and optical tilt angles of the material at a reduced temperature of 8°C from the orthogonal to tilted phase transition. Conoscopic observations of such systems are known to provide structural information of the mesophases[5], and this paper reports the conoscopic observations of a homeotropically aligned sample of AS573 across the whole mesophase range, both with and without applied fields. The studies were augmented by observation of the pitch of the systems via selective reflection.



(a) $K \xrightarrow{53.3} SmC_A^* \xrightarrow{78.3} SmC_\gamma^* \xrightarrow{82.0} SmC^* \xrightarrow{90.7} SmA \xrightarrow{105.7} I$

(b) $SmC_A^* \xrightarrow{78.3} SmC_\gamma^* \xrightarrow{83.5} AF \xrightarrow{85} FiLC \xrightarrow{90} SmC^* \xrightarrow{93} SmA \xrightarrow{105.7} I$

FIGURE 1 The chemical structure of AS-573 (Hull, UK) and phase sequences as reported by (a) Robinson[1] and (b) Panarin et al[2]

EXPERIMENTAL DETAILS

Conoscopic figures were obtained using a Leica Leitz polarising microscope and captured using an IBM compatible PC equipped with a framegrabber card. The size of the figures was determined by the numerical aperture of the system, which was limited to 0.5 by the hot stage entry cone. White light was used to illuminate the sample. Temperature control was achieved with a Linkam hot stage, with a relative accuracy of ± 0.1°C and absolute accuracy of approximately ± 0.5°C. The sample was prepared in a cell of nominal thickness

23 μm which had been treated with chrome complex to ensure homeotropic alignment. 1mm separated in-plane ITO electrodes in the cells enabled electric fields to be applied in a direction perpendicular to the smectic layer normal, and a high voltage amplifier supplied voltages of up to 450 V. Triangular waveforms of frequency ~ 0.5Hz were applied to the cells in order to study closely the voltage dependence of the conoscopic figures.

The microscope was equipped with a secondary light source for the purpose of reflection studies. This made it possible to carry out qualitative selective reflection studies in the various phases of the sample via any reflection colours observed.

RESULTS AND ANALYSIS

In order to distinguish between different phases in the sample, the behaviour of the conoscopic figures under applied voltage was observed. Six different responses were observed on cooling across the mesophase range, the first five of which are presented in figure 2, along with their temperature boundaries and a qualitative voltage dependency. Any reflection colours present in the phases are also shown, as a function of temperature, along the right hand side of figure 2. These colours are samples compiled from the actual colours observed in the phase, which were captured and recorded in a similar way to the conoscopic figures. It was observed that the cell cleared at 106 ± 0.5 °C, and all temperatures in figure 2 are given as reduced temperatures from this transition.

In mesophase a), a uniaxial homeotropic conoscopic figure was produced which at higher temperatures did not vary with the field. At lower temperatures a continuous field-dependent tilting was observed from the movement of the

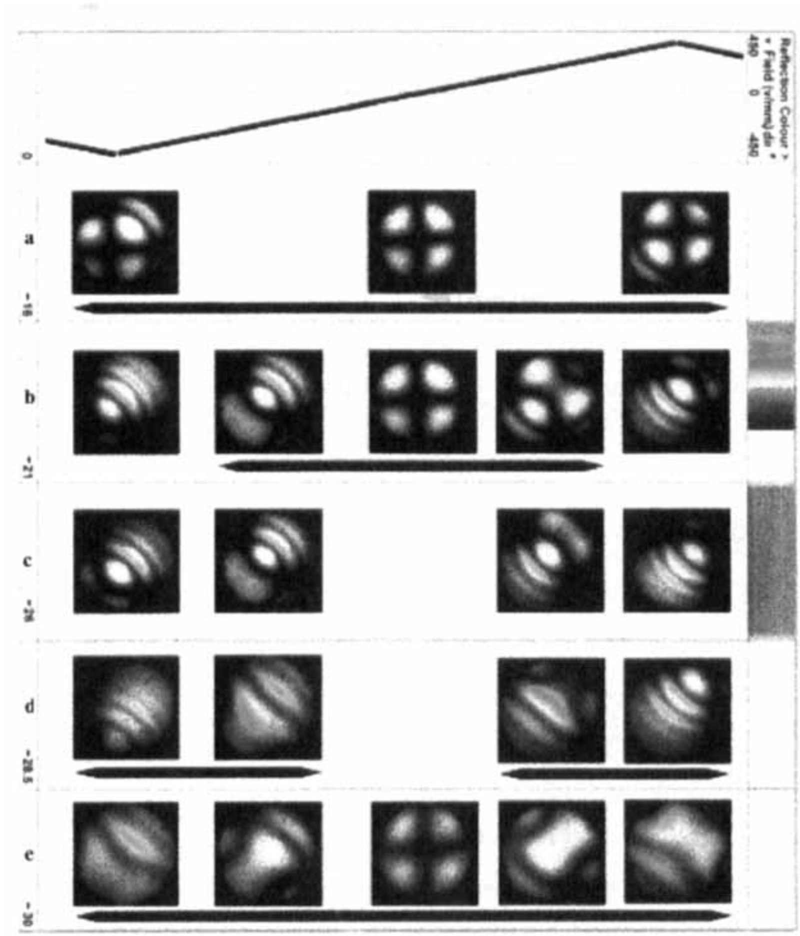


FIGURE 2 Qualitative schematic showing freeze-frame conoscopic figures between various reduced temperature ($T-T_{SA/I}$) boundaries (given left). A qualitative voltage dependency is given at the top of the figure and reflection colours are given along the right of the diagram. Conoscopic figure changes which are continuous with changes in field are linked by black arrows.
(See color plate I at the back of this issue)

centre of the conoscopic figure, consistent with electroclinic behaviour. Although such an observation is also consistent with helix unwinding, no helicoidal structure was observed within this temperature range.

In phase b), the conoscopic figures at zero field were uniaxial and untilted. As the field was increased, the conoscopic figures gradually became tilted and biaxial. These observations indicate the presence of a helix in a tilted biaxial system, with the system winding into a uniaxial one under low fields. Field-dependent unwinding in the conoscopic figures was observed to cease at a stable tilt angle, yet application of a greater field prompted a discontinuous jump to a conoscopic figure with higher tilt. The direction of the optic plane was deduced from the splitting of the isogyres due to the biaxiality of the system, and was parallel to the tilt direction in the conoscopic figures at both tilts. The observation of two different tilt angles is consistent with a ferrielectric phase[5], and the orientation of the optic plane in the low tilt conoscopic figures implies a high q_t parameter. The high tilt (saturated-field) figures were SmC*-like. Bright reflection colours were observed in the phase, from violet at T_R = -16°C to red at T_R= -19°C, which disappeared approaching -21°C.

In phase c), the switching mechanics of the system changed slightly in that the conoscopic figures no longer displayed the helical winding effect at low fields, instead the system made jumps which were discontinuous with voltage, between the low tilt angle figure at positive field and the low tilt angle conoscopic figure at negative field. The direction of the optic plane in the conoscopic figures shows that the system still has a high q_t parameter. Reducing the field frequency (or removing the field), resulted in the conoscopic figure at zero volts becoming that of a wound system. A slight purple haze was visible in reflection throughout the region.

Phase d), observed between T_R = -26 and -28.5°C, exhibits similar characteristics to phase c) - there was no helical winding as the driving voltage oscillated through the zero position, although, as in phase c), removing a field from the sample did result in a wound conoscopic figure forming. Unlike phase c), however, the direction of the optic plane was at right angles to the tilt direction in the lower tilt figures, evidence of a ferrielectric phase with a lower value of q_t. Conoscopic figures of this type have been seen in many systems with SmC^*_γ phases, where q_t takes the value of 1/3[5]. On increasing the field, the conoscopic figures undergo a continuous change to high tilt SmC* like (saturated-field) conoscopic figures. No refection colours were observed.

Ferrielectric behaviour was also observed in phase e), between T_R = --28.5 and -30°C. Again, optic plane observations show a low q_t parameter. A continuous change with voltage through a zero volt uniaxial (wound) conoscopic figure was observed, and the lower tilt angle conoscopic figures were stable to increases in field beyond that required to unwind the system. The voltages available were not sufficient to cause a transition to a SmC*-like conoscopic figure. No reflection colours were seen in the phase.

At T_R = -30°C, a red reflection colour was seen which changed through yellow and green to blue at T_R = -31°C. Between -30 and -31°C, it was possible to field-drive the system into phase e), but at low fields and T_R < -31°C, a uniaxial conoscopic figure was seen, which became slightly biaxial under the application of field, but remained untilted. As with phase e), it was not possible to apply a sufficiently high voltage to prompt the jump to a SmC* like conoscopic figure. The blue reflection colour eventually became violet as the temperature was reduced.

DISCUSSION AND CONCLUSIONS

The difficulty of assigning structures to ferrielectric subphases has been noted[6]. However, on the basis of the discussion given here, together with observations[1-4], the sequence given in figure 3 may be proposed.

$$SmC_A^* \xrightarrow{76°C} SmC_\gamma^* \xrightarrow{78°C} Fi_H \xrightarrow{80°C} Fi_1 \xrightarrow{85°C} Fi_2 \xrightarrow{90°C} SmA \xrightarrow{106.5°C} I$$

FIGURE 3 The revised phase sequence for the material AS573

Firstly, between $T_R = 0$ and -16°C, the conoscopic figures indicate a SmA phase with strong electroclinic behaviour[5]. The untilted nature of the phase in this region has been confirmed by x-ray scattering[4] and the electroclinic observations are consistent with those from ellipsometry experiments[3].

The phases between T_R = -16 and -30 °C all display two stable tilt angles conoscopically as the field is varied, consistent with ferrielectric-like behaviour. However, the orientation of the optic plane in the conoscopic figures between T_R = -16 and -26°C reveals that the q_t of the system in this region is higher than in commonly observed ferrielectric phases[5,6], placing the system in the Fi region of the q_t ladder[7]. Observations of the field dependent conoscopic figures make it difficult to decide whether there are two phases present in this temperature region - there is no textural evidence of a phase transition, and switching characters above and below -21°C are very similar. The differences in low field switching above and below -21°C could be pitch related. The reflection colours in this region show clear evidence of a temperature dependant pitch increase between T_R= -16 and -19°C. The return of a purple colour at -21°C indicates that the pitch has reduced, although the hazy nature of the colour indicates it is less well defined. It is possible that a ferrielectric state exists between -16 and -21°C, whilst there is an antiferroelectric state between -21 and -26°C (with half the pitch of the ferrielectric system), though the switching is not consistent with an AFE phase. On the basis of all the evidence, a tentative phase transition has been assigned at T_R = -21°C.

A clear phase transition is seen both texturally and via conoscopic figure observations at T_R = -26°C, to a ferrielectric system whose apparent tilt[1] and optic plane place it within the Fi_H region[7] of the q_t ladder. The apparently continuous field variation of the conoscopic figures on approaching the saturated ferroelectric state may be due to a field-induced devil's staircase. Ellipsometry experiments[3], indicate a phase transition at T_R = -28°C. Textural observations and conoscopic switching observations confirm the existence of this phase transition, conoscopic figures in the phase between -28 and -30°C being typically SmC*γ-like[5,6,7]. The apparent stability of the phase to voltage is consistent with the phase below. Finally, the conoscopic figures and reflection colours observed in the phase below T_R = -30°C are typical of a stable SmC^*_A phase appearing at the bottom of the q_t ladder, whose stability under the available fields is consistent with observations made elsewhere[1].

Acknowledgements
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