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Preliminary communication
A possible structural model of the SmC$_\beta^*$ phase

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The so-called chiral smectic C-beta (SmC$_\beta^*$) phase has been reported as distinct from the SmC* phase in several materials that exhibit antiferroelectric liquid crystal mesophases and subphases. The SmC$_\beta^*$ phase is known to be chiral, tilted and to exhibit ferrielectric switching, but no structure had been suggested which explains these effects. This paper presents a possible structure for the SmC$_\beta^*$ phase which can explain the ferrielectric properties. The model is proposed on the basis of complementary optical, electric and X-ray diffraction studies of a chiral liquid crystal. The layer spacing, optical and steric tilt and spontaneous polarization over the temperature range of the SmC$_\beta^*$ phase are described. The complementary experimental techniques used reveal the occurrence of inversion phenomena, on which this model is based.

The sequences of frustrated phases that occur in highly chiral systems are both complex and interesting. The ferroelectric SmC* phase and antiferroelectric SmC$_A^*$ phase are the fundamental phases. Others, including at least two ferrielectric phases with different q_t values, one other antiferroelectric phase and the SmC$_\alpha^*$ phase are considered as subphases of the SmC* and SmC$_A^*$ phases. In addition to these subphases, the SmC$_\beta^*$ phase is reported in several systems, including the first report of antiferroelectric liquid crystals that identifies four tilted smectic C phases [1].

The SmC$_\beta^*$ phase has to some extent been considered to be the same as the ferroelectric SmC* phase on the basis of differential scanning calorimetry measurements performed as a function of the optical purity of the substance MHPOBC [2–4]. However, recent work suggests that the nature of this phase may not be as straightforward as was first thought. The SmC$_\beta^*$ phase is thought to be ferrielectric, is characterized by large electroclinic coefficients in the higher temperature SmA phase, and exhibits field dependent dielectric constants [5]. Its occurrence also appears to depend on the chirality of the sample, decreasing optical purity causing the disappearance of the SmC$_\beta^*$ phase in favour of the SmC* phase. Recently Uehara *et al.* [6] found that the dielectric behaviour of the SmC$_\beta^*$ phase is quite different from that of the SmC* phase, the complex dielectric constant exhibiting a two step decrease with increasing bias field compared with a one step decrease for the SmC* phase. The nature of the SmC$_\beta^*$ phase is still not fully understood and to date no model for the structure of this phase has been put forward. By using several different techniques in conjunction, it is however possible to probe different aspects of the phase and develop a picture of the structure. This paper discusses recent results of a complementary study of the material AS573 (figure 1), which exhibits a SmC$_\beta^*$ phase. These investigations, in conjunction with the earlier observations discussed above, allow a proposed structure of the SmC$_\beta^*$ phase of AS573 to be inferred. Many of the phenomena that are reported were also observed in several other materials [7].

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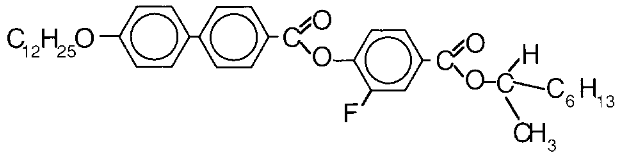

(a) Cr $\xrightarrow{53.3}$ SmC*$_A$ $\xrightarrow{78.3}$ SmC*$_\gamma$ $\xrightarrow{82.0}$ SmC* $\xrightarrow{90.7}$ SmA $\xrightarrow{105.7}$ I

(b) SmC*$_A$ $\xrightarrow{78.3}$ SmC*$_\gamma$ $\xrightarrow{83.5}$ AFE $\xrightarrow{85}$ FiLC $\xrightarrow{90}$ SmC* $\xrightarrow{93}$ SmA $\xrightarrow{105.7}$ I

Figure 1. The structure of AS573 and its phase sequences according to: (*a*) Goodby [8] and Robinson [7, 9]; (*b*) Panarin [10].

The structure of AS573 is shown in figure 1 together with two of the phase sequences that have been reported for this material. Discrepancies between phase transition temperatures reported for the same frustrated system are not unusual and can be due to the stable nature of the AF and SmC$^*_A$ phases, the influence of substrate interfaces, and optical purity [11]. A further complication arises from the fact that although the relative accuracy of transition temperature measurement is frequently as good as ±0.1°C, the differences in absolute temperature measurements between different experiments and sample environments could easily lead to uncertainties of up to ±1.5°C between data sets. The remainder of this paper concentrates on the high temperature mesophase region of AS573 only, and the complete phase behaviour is discussed in detail elsewhere [12]. In particular the high temperature tilted phase regime, denoted both SmC* and FiLC in figure 1, is discussed here as the SmC$^*_\beta$ phase.

For measurements of the optical tilt angle and the spontaneous polarization (current pulse method), the material was held in antiparallel rubbed devices of nominal thickness 5 μm. The uncertainties of the measurements were ±0.5° and ±2 nC cm^{-2}, respectively. X-ray measurements were performed at the SRS, Daresbury on unaligned samples approximately 1 mm thick [13]. Layer spacing measurements were used to deduce the steric tilt angle of the system with an accuracy of ±0.2°. The steric tilt angle, δ, is deduced from the layer spacing measurements, d, using the equation $\cos\delta = d/l$. The value of molecular length, l, used in the calculation was 39.3 Å, confirmed by both molecular modelling and the value of d in the SmA phase.

The layer spacing measurements for AS573 confirm a non-tilted phase that persists over 15°C below the isotropic phase transition. This differs from the phase assignations of Panarin *et al.* [10] who, on the basis of dielectric relaxation spectroscopy reported a SmA phase of only 12.7°C range. The smectic to isotropic phase transition temperature was confirmed *in situ* during the layer spacing measurements by the obvious disappearance of diffraction peaks. The Bragg peaks due to diffraction from the smectic layers exhibited no unusual behaviour and showed that the layers were well defined across the smectic phase range. Both the optical tilt angle and $\mathbf{P}_S$ of AS573 are field dependent, with double current pulse behaviour observed in the low field regime for 15°C below the SmA phase transition. The areas under the current peaks were unequal, with the ratio of the first peak to the second approximately 3:1, as shown in figure 2 [7]. Although this asymmetric double pulse behaviour is characteristic of a ferrielectric system, the values of the spontaneous polarization in each part of the switching cycle imply a q_t value > 1/2 [10], which is unusual in ferrielectric systems.

Figure 3 shows the temperature dependence of the steric tilt of AS573 together with the optical tilt angle and spontaneous polarization, measured on application of sufficiently high fields to ensure saturation to the ferroelectric value. $\mathbf{P}_S$ and θ have similar temperature dependencies (fitting [14] gives exponents of ~0.5 and ~0.6 ± 0.05, respectively), while the steric tilt exhibits a different temperature dependence, with an exponent of ~0.25, indicating behaviour quite different from a SmC*

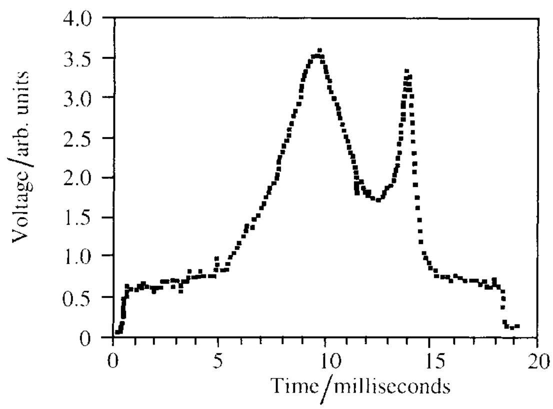

Figure 2. Current pulse data 8°C below the SmA transition in AS573. The applied is voltage 1.5 V_{rms}.

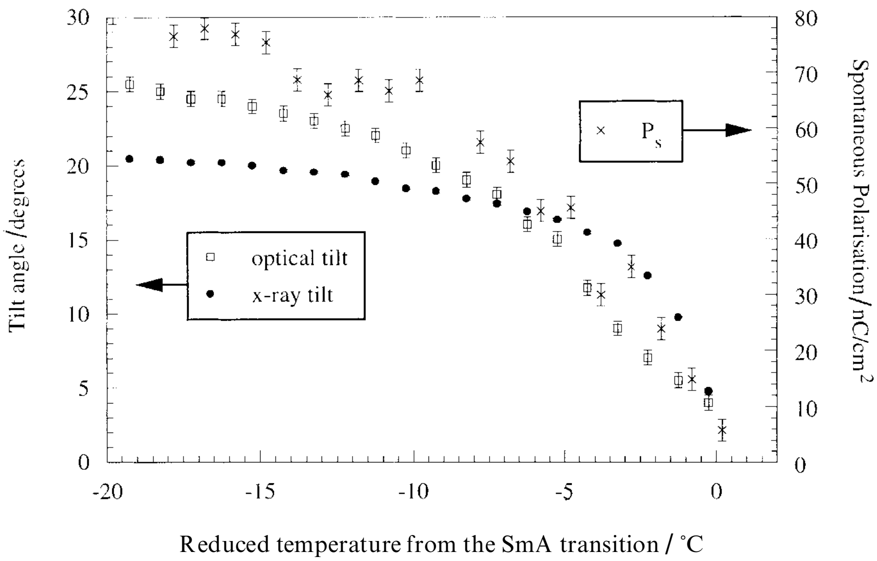

Figure 3. The optical (θ) and steric (δ) tilt angles and $\mathbf{P}_S$ of AS573.

phase. Figure 3 also shows evidence of an inversion phenomenon occurring at $T - T_{SmA} = -8$°C. Above this temperature, the steric tilt angle, δ, is higher than the optical value, θ, indicating that the molecular chains are more tilted than the cores.

The values cross at approximately -8°C, resulting in $\delta < \theta$, as is more common. The conformation change associated with such inversion phenomena has been reported in several other systems [15–17] and is depicted schematically in figure 4. The mass and polarizability axes are illustrated for the two conformational types by full and dashed lines, respectively. The simple model depicted in figure 4 takes no account of the molecular bend that is known to occur in frustrated materials such as AS573 [18]. Further, it should be emphasized that although figure 4 illustrates how inversion phenomena are implied by data such as those in figure 3, the situation illustrated is for equal layer spacing. In general the molecular tilt and hence layer spacing change with temperature, independently of the population of different conformers.

We now consider the proposed model of the SmC$^*_\beta$ phase. The significant evidence of conformational changes within this phase gives insight into its structure, allowing a model of the SmC$^*_\beta$ phase to emerge. The model of the SmC$^*_\beta$ phase suggested here assumes that in this phase different layers are occupied by different populations of the conformers, producing a high temperature phase that exhibits ferrielectric-like switching. The model is depicted in figure 5 and differs from inversion phenomena previously reported since a significant separation of the conformers in different layers is proposed, while normally a statistical distribution would be expected. The figure indicates only one conformation occupying each layer, though it is more likely entropically that there is an excess of specific conformations in each layer. The layers have the same spacing, irrespective of the direction of tilt of the molecules within them. As the temperature reduces, both molecular conformers will tilt further, in

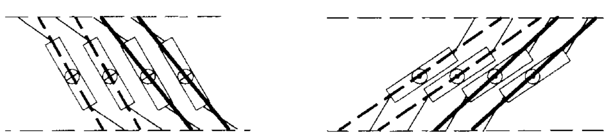

Figure 4. A schematic of conformational-driven inversion phenomena in ferroelectric systems. The bold dashed lines indicate the optical axis of the molecules, while the full lines show the mass axis.

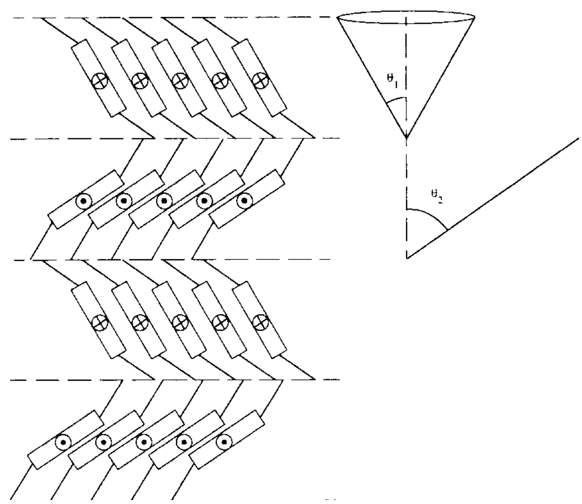

Figure 5. A schematic of the proposed model of the SmC$^*_\beta$ phase showing different conformers populating different layers. Each layer probably contains an excess of specific conformers, and complete phase separation does not necessarily occur as shown.

common with all the tilted phases. Thus, the layer spacing will reduce as the temperature decreases, as is observed. Since the steric tilt angle is deduced from the average orientation of the molecular axes, the temperature dependence is hard to predict. However, the optical tilt angle and $\mathbf{P}_S$ in figure 3 are measured in the field-driven ferroelectric regime, so it might be expected that their temperature dependences will behave approximately as expected for ferroelectric systems. The model accounts for the ferrielectric-like nature of the high temperature regime of the tilted phase and would explain why the apparent value of q_t is $>1/2$. However, the phase is not *truly* ferrielectric. As the different populations of conformations vary with temperature, the ferrielectric nature of the phase will vary and a Devil's staircase (as defined in terms of q_t) would probably not occur.

The idea of ferrielectric structures forming from layers of different tilt is not new. A model was proposed in 1990 [19] in which molecules in neighbouring layers tilt by different amounts in opposite directions. Such a model explains the lower $\mathbf{P}_S$ and tilt observed in the ferrielectric phase, but was discounted as unphysical since the X-ray scattering data did not show the two different layer spacings. However, such a model would be more practicable if the layer spacings for the two different tilt directions were the same. Since we do not suggest complete phase separation of species in each layer, the layer spacings will be appropriately weighted averages of those expected from each conformer, which are in any case likely to be very similar (seen schematically in figure 5), making such a model feasible.

If the left hand population dominates at high temperatures, and reduces as the temperature is lowered, then the optical tilt will grow faster than the steric tilt, as is observed for AS573. Further the spontaneous polarization will, for first order, change in the same way as the optical tilt, again as is observed. It should be emphasized that while figure 5 shows equal numbers of oppositely tilting layers, and that they alternate, there is no reason why this should be the case. Indeed different numbers of layers tilting in a specific direction would be expected as the temperature-dependent conformer population varies.

In conclusion, this paper has discussed the unusual physical properties of the SmC^*_β phase. Previous work has identified this phase as exhibiting ferrielectric-like switching and possessing a high value of the parameter q_t. Complementary X-ray and optical measurements have shown that conformational changes come into play within the SmC^*_β phase of AS573, giving insight into the structure of this phase. From this evidence a model has been proposed for the SmC^*_β phase explaining many of the physical properties of the high temperature regime of the material AS573 reported both here and elsewhere.

It is clear from the X-ray and optical data that different populations of conformers occur in the high temperature regime of the tilted phases, so the inclusion of such a feature in the model is reasonable. The evidence from low field $\mathbf{P}_S$ measurements and dielectric data published by other authors that the high temperature regime is ferrielectric in nature is not in dispute, nor is the fact that some of the properties of the phase are 'unusual' (including $q_t > 1/2$). The model suggested here explains how such a large apparent q_t value may seem to occur. Indeed, the model is consistent with the measurement of double current pulses of unequal heights, as was mentioned. Further, large electroclinic coefficients and unusual electroclinic behaviour have been observed [20]. If the SmC^*_β phase is as suggested, the pretransitional regime in the SmA phase would not be expected to exhibit the usual temperature dependences.

The model suggested appears to explain many of the features of the SmC^*_β phase. While it seems likely that refinements to the model will occur, it at least provides a start in explaining the properties of one of the least understood smectic subphases.

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