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WALL ORIENTATION OF SMECTIC C LIQUID-SINGLE CRYSTALS

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ABSTRACT : Using optical and X-ray techniques, we observe the texture of a thin smectic C liquid crystal (heptyloxybenzoic acid) obtained by slow cooling from a wall oriented nematic texture. Two orientations are obtained with the same molecular orientation and the smectic layers normal to the plates.

Smectic C liquid crystals (S_C) are layered systems. In the layers, the molecules form a two-dimensional liquid, with an average tilt angle ϕ compared to the layer normal. To make a S_C single crystal is in general difficult, because one has to control independently the orientation of the layers and of the molecules. Sometimes, the S_C phase is obtained by cooling down the isotropic liquid and it appears very difficult to fix both the layer and molecules orientations. The problem is simpler when one starts from an already oriented texture in a phase of higher symmetry. For instance, the S_C phase can be obtained by cooling down a S_A phase, which presents the same layer structure, but with $\phi = 0$; in that case, the orientation of the smectic layers is already imposed by the S_A texture, with a more or less continuous molecular tilt $\phi \neq 0$ developing inside the layers.

In other cases, the S_C phase is obtained from an oriented texture of the nematic phase. This situation, which corresponds always to a first order transition, gives in general complex textures for the S_C phase. The reason is that from the well ordered molecular direction $\vec{X}$, the only constraint on the layers is to make a cone of angle $(\frac{\pi}{2} - \phi)$ around $\vec{X}$. Hopefully the existence of boundary plates will favor in general some special orientation of the layers, decreasing the conical degeneracy. An additional difficulty is the twofold technique used to observe the orientation : the S_C is optically biaxial, but one can define the "molecular" orientation as the direction of the largest polarisability eigen direction of the optical tensor. The layers are in principle non visible. On the other hand, X-rays give a very good determination of the layer orientation but are less accurate for indicating the "molecular" orientation, because of the large orientational fluctuations. In addition, the X-ray observed samples are very often different from the one which would be of practical interest for applications, because of the constraint of reasonably large volume, and of X-ray transparent boundaries. In this paper, we present the first combined optical and X-ray observation of a smectic C texture obtained by cooling down from a nematic phase. As we are interest by practical applications, we specialize to the case of nematic texture orientated from the walls.

The sample we use is the seventh homolog of p-n alkyloxybenzoic acid (HOBA). This compound was the first where electrohydrodynamical instabilities were observed [1, 2, 3]. The molecule is a linear dimer. It is a solid crystal under 92°C, smectic C between 92°C and 98°C, nematic between 98°C and 146°C and isotropic above. ϕ is constant in the C phase of the order of 45° [4]. To prepare the cell, we used cleaved muscovite mica plates, of thickness around 35 μm. To induce a planar orientation in the nematic phase, these mica plates are treated with an oblique gold evaporation, analogous to the well-known S_iO technique. The $\vec{X}$ resulting orientation is parallel for the two plates. The choice of mica plates is convenient for X-ray transparency, but optically it prevents a simple interpretation of the polarized light observation, since it is also an optically biaxial material. The sample thickness is fixed to 45 μm by using mylar spacers, and placed inside a temperature regulated Mettler hot stage.

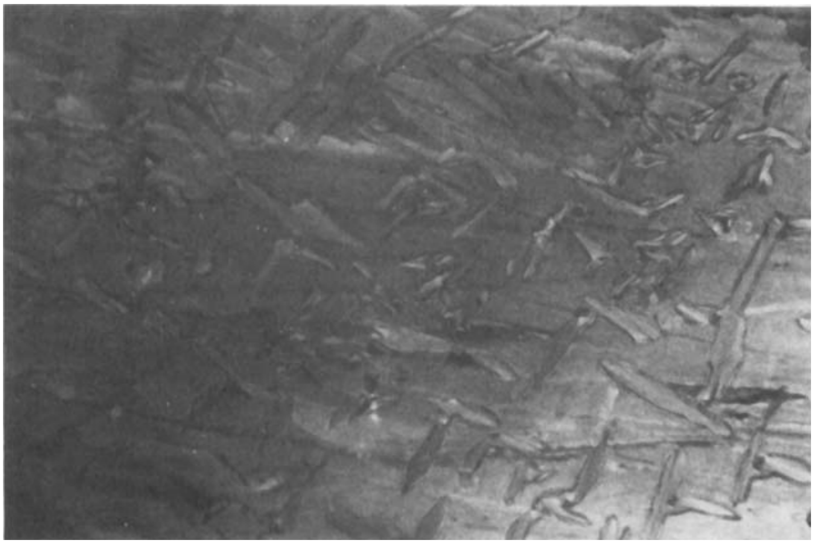

FIGURE 1 : Bicrystals (typical size 100 μm) of S_C phase growing slowly in the nematic phase. The X rubbing direction is horizontal. The Λ shape is associated with the two possible easy growth layer directions for one given molecular orientation.

We first cool slowly the sample from the $\vec{X}$ oriented planar nematic texture, under a polarizing microscope. At the S_C transition temperature (98°C), we observe the appearance of small needles of growing S_C phase. These needles are often associated to form Λ(or V) shaped objects, as shown on picture 1. Cooling down further, the needles coalesce to form a typical polydomain smectic C texture, as shown on Fig.2 corresponding to 95.5 °C. The molecular orientation inside the needles seen from the contrast in polarized light,appears to be uniform. We note also along the axis of the needles

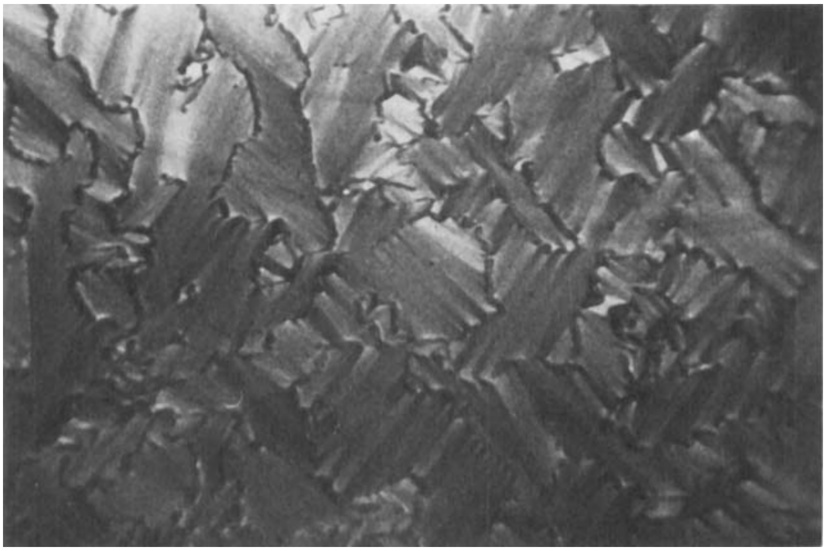

FIGURE 2 : Fully developed S_C texture. Each region (typical size 300 μm) of uniform orientation corresponds to one of the two possible smectic C crystals with molecules oriented along the horizontal $\vec{X}$, and the smectic layers perpendicular to the plate (and also to the picture).

thin bright lines, which we tentatively identify with smectic layers dislocations seen from the edge. In the cooling down process, when two parallel needles coalesce, they give rise to a single S_C domain, of uniform orientation. In this single domain, we keep observing the thin bright parallel layer dislocation edges, very visible close to the domain boundaries. On the other hand, when two non-parallel needles get into contact,a wall is formed between two different domains, with different edge dislocation orientations. The simplest interpretation is that the needles are S_C bicrystals growing preferentially along an easy direction, i.e. along the smectic layers. Note that the two branches of the Λ shaped bicrystals make an angle of 110°C. On the average, the $\vec{X}$ molecular orientation is about the bissector of the supplementary 70° angle. As the growth of the S_C crystals starts from the slightly cooler upper plate, our interpretation is that in the S_C the molecules remain aligned along $\vec{X}$ as in the nematic phase, and just two layer orientations perpendicular to the plates are selected on the $(\pi/2 - \phi)$ cone, giving rise to two kinds of crystals. From these observations, the molecular tilt ϕ would be $110/2 = 55°$.

We now put the sample in the X-ray diffraction set-up. The X-ray incident beam comes from a double bent graphite monochromator (CuKα). A 300 μm brass diaphragm was put close to sample and allows to select an area containing only two or three crystals; with a lower size of diaphragm,the contrast of the X-ray picture would be too bad. The sample temperature is regulated by a silicon oil circulation, the temperature was maintained within at 95.5 ± 0.5°C. A flat photographic film is put at 40 mm from the sample in the focussing plane of the monochromator. The mica plates are almost perpendicular to the horizontal X-ray beam and we can turn the sample holder around a vertical axis of ± 10°. The $\vec{X}$ molecular axis is oriented at about 45° from the vertical axis, so that the smectic layers are close to horizontal or vertical positions(Fig. 3).

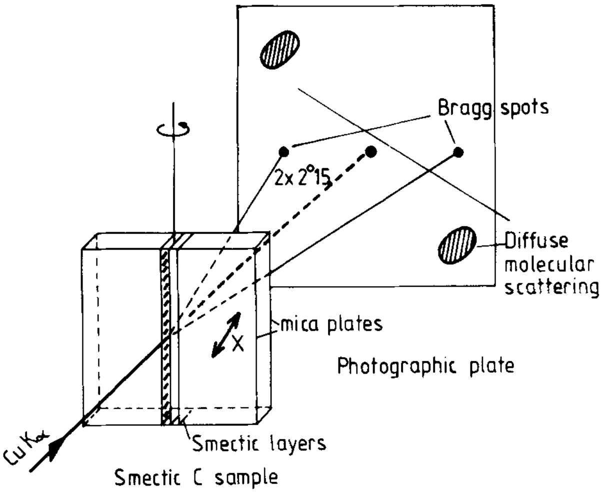

FIGURE 3 : Diffraction set up geometry.
The CuKα X-ray beam is horizontal
The mica plates and the film are vertical
The sample can be oriented around a vertical axis.
The $\vec{X}$ direction is the direction of the molecular axis.

A typical diffraction picture is shown on Fig. 4 : four Bragg reflections are seen at the center of the picture . They all correspond to a Bragg angle of 2.15°; the corresponding reticular distance of 20.6 Å is equal to the one

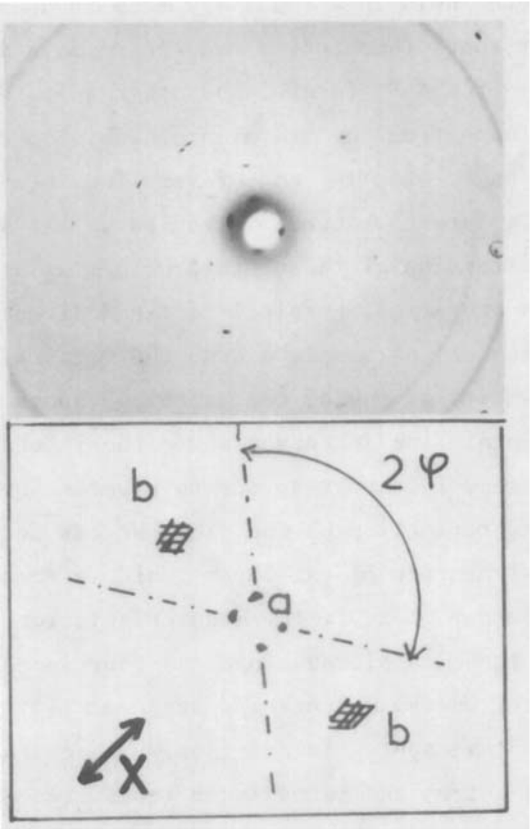

FIGURE 4 : X-ray diffraction pattern :
Four reflections(a) on the layer planes are seen, they come two by two from two kind of single crystal. The layers of the two crystals make an angle 2ϕ .

The two large angle diffuse spots (b) come from the in-layer interferences. The molecular axis is along the $\vec{X}$ direction imposed by the mica plates. Other small Bragg spots are seen and correspond to the diffraction by the mica plates.

measured in an other experiment made with a bulk sample of the same compound held in a capillary tube in a magnetic field. These four spots thus correspond to two main different orientations of the S_C layers. The other spots visible at larger angles come from the two mica plates. Two diffuse spots at a Bragg angle of ≃ 10° and of very low intensity come from the interference between molecules of the same layer. From the extension of these spots we can assert that all the molecules are almost parallel to the $\vec{X}$ direction.

By a rotation of the sample around the vertical axis by ± 4°, the intensity of one of the two Bragg spots lying on a quasi horizontal line increases whule the intensity of the second decreases. This corresponds to a better orientation for the Bragg reflection on one side. We can deduce the angular disorientation of the layer inside a domain : it can be of the order of ± 5°, the mean orientation being perpendicular to the mica plates. When the four spots show an equal intensity, we can measure the angle of 110° between the two pairs of Bragg spots. In addition we check that the diffuse spot coming from the intra layer interferences are aligned along the bissector of the supplementary angle of 70° (180°-110°). All these informations lead to the conclusion of the existence of two kinds of S_C crystals with the smectic layers normal to the mica plates and with the molecules parallel to the $\vec{X}$ direction.

In conclusion, we have made optical and X-ray observations on a S_C texture. The SmC crystals were obtained by slowly cooling a wall oriented nematic phase in a planar texture. Both observations confirm that the plates force the smectic layer to be normal to the plates and that the molecular orientation of the nematic phase is conserved. Further observations are necessary to check more refined points : for instance, a possible difference between the rubbing direction, the optical dielectric tensor axis and the X-ray observed molecular axis. The technique here described is a first step towards a single crystal growth which necessitates an other external field in order to favour one of the two possible orientations.

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