Two-dimensional order in the smectic F phase
J.J. Benattar, F. Moussa, M. Lambert

To cite this version:

HAL Id: jpa-00208964
https://hal.archives-ouvertes.fr/jpa-00208964
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Two-dimensional order in the smectic F phase

J. J. Benattar, F. Moussa and M. Lambert (*)

Laboratoire Léon Brillouin, B.P. 2, 91190 Gif-sur-Yvette, France

(Reçu le 23 avril 1980, révisé le 10 juillet, accepté le 10 juillet 1980)

Résumé. — La phase smectique F de TBPA est caractérisée par un empilement de couches pseudo-hexagonales faiblement couplées. L’analyse du profil des anneaux de poudre obtenus par diffraction de rayons X permet la confrontation aux résultats théoriques concernant la structure des systèmes 2d : on en déduit une longueur de corrélation dans la couche voisine de 250 Å dans l’hypothèse où n’existe aucun couplage intercouches.

Abstract. — The smectic F phase of TBPA is characterized by a stacking of weakly coupled pseudo-hexagonal layers. A careful analysis of the shape of the Debye-Scherrer lines enables a comparison to the theoretical predictions concerning the structure of 2d systems: a correlation length of about 250 Å has been found within the layers under the assumption of completely uncoupled layers.

Introduction. — The SmF modification appears in the phase diagram of several mesomorphic compounds [1] between the SmBn and the SmC phases. The structure of oriented samples has been studied using either a strong magnetic field [1] or the melting of a single crystal of the solid phase [2]. In the case of TBPA both experiments show the existence of a rather long range orientational order: within the layers there is a pseudo-hexagonal packing similar to that of the SmBn phase. A first attempt to determine the nature of the positional order within the layers has been made using the oriented sample X-ray pattern [2]. The analysis of the Bragg spot profile led us to the conclusion that the three-dimensional positional order was effectively lost in the SmF phase but no conclusions could be given on the extent of correlations within the layers due to the large and unknown mosaic of the sample; in the case of a two-dimensional order (uncorrelated layers) the sample mosaic combined with the two-dimensional features of the scattering, which consists of rods perpendicular to the layer plane (Fig. 1), leads to a large additional broadening of the scattering which cannot be taken into account quantitatively since the mosaic (distribution of the layer normal around a mean position) is unknown [3]. In order to eliminate this effect and get a quantitative analysis of the Bragg reflection intensity profiles we decided to use Debye-Scherrer diagrams, assuming a statistical distribution of the crystal orientations. The analysis of the large angle ring intensity profile can then be used to measure the correlation length within the layers.

1. Experimental results. — The powder patterns were recorded with a Guinier camera equipped with an electric heating stage using a focused monochromatic beam ($\lambda\text{CoK}_\alpha = 1.7889$ Å). The polydomain sample is placed on a grating which oscillates...
in its plane; therefore, all the orientations are statistically represented.

The TBPA (Terephtalidene-bis-4-n-pentylaniline) previously used, has the advantage to be stable on some degrees in the SmF state; we indicate below its polymorphism (1) :

$$\text{Cr} \rightarrow 26.5^\circ \text{C} \rightarrow \text{SmB}_e \rightarrow 144^\circ \text{C} \rightarrow \text{SmF} \rightarrow 53.5^\circ \text{C} \times \text{SmE}_e \rightarrow 57^\circ \text{C} \times \text{SmC} \rightarrow 183.5^\circ \text{C} \rightarrow \text{SmA} \rightarrow 233.5^\circ \text{C} \rightarrow N \rightarrow 233^\circ \text{C} \rightarrow I. $$

The studies by means of Differential Thermal Analysis yield a large enthalpy variation at the SmF $\leftrightarrow$ SmC transition whereas the $5mBc \leftrightarrow$ SmF transition is weakly of the first order kind [4, 5].

Before discussing the results concerning the SmF phase, it is necessary to compare the powder patterns of the $5mBc$ and SmF phases.

In the first case, $5mBc$, the structure is three-dimensional with a monoclinic lattice. Inside each layer the 2d lattice is pseudo-hexagonal ($\sim 1$ % distortion from an hexagonal lattice), the 3d monoclinic symmetry being related to the tilt angle of the molecules with respect to the layer normal. The positions of the molecules in two adjacent layers are deduced by a translation parallel to the molecular axis ($c$). The powder diagram consists of :

- the very sharp 00l rings characteristic of a layered structure,
- the large angle $hkl$ rings among which the most intense are the 110 and 200 lines. These two lines would be superposed for a true hexagonal symmetry; in fact they appear close together since the difference between lengths of the corresponding reciprocal vectors is very small.

The parameters of the monoclinic C centred unit cell, measured at 132 °C, are the following :

$$a = 9.62 \pm 0.02 \ \AA, \quad b = 5.14 \pm 0.01 \ \AA, \quad c = 31.2 \pm 0.2 \ \AA, \quad \beta = 113.6 \pm 0.5^\circ. $$

The $c$ parameter is chosen along the molecular axis, $a$ and $b$ are in the smectic layer plane.

In the SmF phase, the $hkl$ type spots vanish; the diagrams exhibit only the 00l reflections and a rather broad diffuse ring at large angles almost at the same place as the previous 110 and 200 rings observed in the $5mBc$ phase. The mean structure within the layers being pseudo-hexagonal, the diffuse ring is therefore composed by the broadened 110 and 200 reflections; in order to analyse the experimental results, the parameters $a$ and $b$ are assumed to be the same as in the smectic $Bc$ phase.

If we suppose that the molecular length $l$ does not change anymore from the $5mBc$ phase to the SmF phase, the tilt angle $\alpha$ is given by $d_{001} = l \cos \alpha$; the interlayer spacing $d_{001}$ is measured on the diagrams and we find $\alpha = 20 \pm 1^\circ$ at 150 °C as compared to $\alpha = 23.6^\circ \pm 0.5^\circ$ in the $SmBc$ phase.

2. Analysis of the diffuse ring (SmF phase). — X-ray patterns of a single domain sample have shown that the smectic layers are weakly or not at all coupled [2]. In our calculations we assume that the layers are completely uncorrelated, the intensity scattered by all the layers is then proportional to the intensity scattered by one layer and in consequence the intensity of each $hk0$ reflection spreads, in the reciprocal space, along bars parallel to $c^*$ ($c^*$ is parallel to the layer normal) [3].

We choose to approximate the electronic density $\rho$ along the layer normal (Fig. 2) by :

$$\rho(y) \propto 5.4$$

with

$$\frac{c \cos \alpha}{4} \leq |y| \leq \frac{c \cos \alpha}{2}$$

for the aliphatic chains

$$\rho(y) \propto 9.2$$

with

$$|y| \leq \frac{c \cos \alpha}{4}$$

for the core of the molecules.

![Fig. 2. — Schematic drawing of one smectic layer and the corresponding electronic density along the layer normal.](image)

The intensity along bars is therefore given by the square of the Fourier transform of the electronic density, we obtain :

$$g(q_x) \propto (5.4 \sin (q_x c \cos \alpha/2)) + 3.8 \sin (q_x c \cos \alpha/4)) \cdot q_x^{-2}$$

where the $q_x$ axis is centred, at the 200 point of the reciprocal lattice and parallel to $c^*$ (Fig. 3).

In a first step [2], we have calculated the lineshape assuming that the layers are completely uncorrelated and the order is perfect within the layers; the width

(1) $SmBc$ and $SmEe$ are also called respectively $SmG$ and $SmH$. 

N° 11
Fig. 3. — Schematic drawing of the 
(a*, c*) reciprocal plane showing the intersection of a sphere of radius Q with the reciprocal space near the 200 point.

of such an intensity profile is too much narrow if compared with the experimental one, which implies that the 2d-order does not extend to large distances.

Therefore, we have to define a scattering function \( f_G \) in the 
(a*, b*) plane different from a \( \delta \)-function which takes the loss of order within one layer into account.

The intensity distribution \( I_G(Q) \) (Q is the scattering vector of the powder ring) is for this 2-dimensional system, obtained by summing the intensity located around a \( h0k \) point of the reciprocal lattice (G), over a sphere centred at the origin of the reciprocal space and whose radius is Q (Fig. 3). We obtain:

\[
I_G(Q) = \int_{-G}^{G} dq_x \int_{-G}^{G} dq_y \int_{-G}^{G} dq_z \times
\]

\[
\times \int_{-G}^{G} dq_z \int_{-G}^{G} dq_y \int_{-G}^{G} dq_x \delta(Q^2 - h(q_y)q_y) (1)
\]

where:

\[
\beta(q_y) = (Q^2 - (q_y + G)^2)^{1/2}
\]

\[
h(q_y) = (q_x + G)^3 + q_y^2 + q_z^2 + 2(q_x + G) q_y \sin \alpha
\]

\[
h(q_y) = Q^2 being the sphere equation
\]

\( f_G(q_x, q_y) \) is the expression of the scattering function corresponding to a vector \( G \) of the reciprocal plane \( (a*, b*) \) (\( G = 2a* \) or \( G = a* + b* \)) in the trihedral \( (q_x, q_y, q_z) \) centred at the 200 point.

3. Discussion of the results. — a) The theory of 2-dimensional melting built by Halperin and Nelson [6, 7] upon ideas of Kosterlitz and Thouless [8], predicts that melting could occur in two steps and they point out that one must consider the loss of successively positional and orientational order.

In a 2-dimensional lattice it is well known that true translational order cannot occur at a temperature different from zero and consequently the positional correlation function is approximated by a power law decay such that:

\[
\left< \exp(\omega r - \omega(0)) \right> \sim r^{-\eta_\omega(T)}
\]

where \( \eta_\omega(T) \) is related to the Lamé elastic constants. The Bragg \( \delta \)-function of a 3d solid is then replaced by \(|Q - G|^2 + \eta_\omega(T)\) at a set of reciprocal lattice vectors G but this 2d solid possesses a long range orientational order of the conventional sort. With increasing temperatures, the first step of melting is characterized by an unbinding of dislocation pairs; in this new phase called hexatic, there is an exponential decay of the translational order \( e^{-\eta_\omega \xi_\parallel} \), where \( \xi_\parallel \) is the correlation length in the layer plane, which leads to a Lorentzian structure factor:

\[
S(Q) \simeq (\xi_\parallel^2 |Q - G|^2 + 1)^{-1}
\]

In this phase, the authors show that the bond orientational correlations decay algebraically.

At higher temperatures, the dissociation of disclination pairs drives a transition into an isotropic phase in which both, the translational and orientational order decay exponentially.

b) Some experiments, such as inelastic neutron scattering [9] and X-ray diffraction [10], [11], have clearly shown that the bulk SmB phase has a conventional 3-dimensional structure with both the long range orientational and positional order (which is proved, by the existence of \( hkl \) reflections). The inelastic part of the scattering function can be written as:

\[
S(Q) \propto |Q - G|^2
\]

A description of the SmF phase, with both short range positional and orientational order, is not appropriate since the diffuse ring exhibited by the X-ray patterns of a single domain sample is too sharp and moreover, it is modulated by six maxima in the \( (a*, b*) \) plane [2]. The question is to determine if a description in terms of a 2d solid or an hexatic phase could be applied to the SmF phase. We have tried to analyse the lineshape of the powder ring by choosing the scattering function of the formula (1), in the \( (a*, b*) \) plane, such as:

\[
f_G(q_x, q_y) \propto |q_x^2 + q_y^2|^{-\eta/2}
\]

which corresponds to an algebraic decay of the positional order. We point out that the exponent \( \eta_\omega \) is theoretically proportional to \(|G|^2 \) [12], but, due to the very weak anisotropy of the pseudo-hexagonal lattice, we have kept the same value of \( \eta_\omega \) for both reflections 200 and 110 in our calculations. One can see on figure 4 that such a power law does not give an agreement with the experimental lineshape since the reflections remain well defined even for a value of \( \eta_\omega \) larger than the maximum value 1/3 predicted by the theory [12]. Then, an algebraic decay of the positional order is inadequate to characterize the smectic F phase.
Our best fit is obtained by using a Lorentzian structure factor for $f_0$ which leads us to introduce a correlation length $\xi_\parallel$ of the order of 250 Å $\pm$ 30 Å; the theoretical lineshape computed in this case is compared with the experimental one in figure 5. This value of the correlation length, although very large, is significant since it is much smaller than the limit of the experimental resolution ($\approx 1$ 000 Å). We have made the same calculation in the case where two layers are coupled and we have obtained $\xi_\parallel \approx 120$ Å, but such an analysis of the experimental lineshape is no longer possible for a larger number of layers ($n > 2$). It may be noticed that there is no particular reasons to suggest a pairing of the layers since the molecular ends consist of aliphatic chains.

It is also interesting to point out that the calculation made for a great number of correlated layers ($n \sim 40$) and with a scattering function

$$f_0(q_x, q_z) = |q_x^2 + q_z^2|^{-1}$$

allows to find again the intensity distribution of the SmB$_e$ phase.

4. Conclusion. — We have shown from our experimental observations and the above described analysis that in the bulk SmF phase the layers appear uncorrelated, meanwhile we cannot exclude interlayer correlations extending on two neighbouring layers. A power law decay of the positional order does not allow to explain the experimental lineshape while an exponential law is quite appropriate; it leads to a correlation length inside one layer to be limited to about 250 Å. Such a description of the SmF phase might correspond to the tilted hexatic phase predicted by Halperin and Nelson.

However we did not discuss the possibility of a contribution of inelastic processes to the broadening of the diffuse ring. Only neutron experiments will be able to answer this question : they are planned for the next future.

Since the beginning of our investigation of the bulk SmF phase, new phases J [13] and I [14] have been discovered which appear, from their powder patterns, similar to the SmF phase : we need to analyse more deeply the structure of these phases in order to understand the differences with the SmF structure.

Acknowledgments. — We are very grateful to C. Germain for synthesizing the compounds and A. M. Levelut for fruitful discussions. One of us is indebted to Prof. R. J. Birgeneau for a discussion on the influence of mosaic effects on the experimental lineshape. It is a pleasure to thank Prof. S. Doniach for stimulating discussions on 2d systems.

References
