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Positional order in the smectic-G, -F, and -C layers of HBHA (*)

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Résumé. — La longueur de corrélation de l'ordre de position « 03BE ~ » parallèle aux couches smectiques (Sm) dans les phases G, F et C du HBHA (70.6) a été mesurée par diffraction des rayons X. Dans la phase Sm-G, sa valeur est limitée par la taille des cristallites et se situe entre 1200 et 1500 Å. Lors de la transition Sm-G, Sm-F, 03BE ~ varie de 300 Å à 180 Å avec une dépendance en température correspondant à celle prédite par un modèle de fusion par l'intermédiaire des dislocations pour un réseau bidimensionnel. 03BE ~ varie de façon discontinue à la transition Sm-F, Sm-C. On trouve que la phase Sm-C a une longueur de corrélation inhabituellement grande (~ 50 Å), presque le double de celle de la phase Sm-A.

Abstract. — The positional order correlation length « 03BE ~ » parallel to the smectic (Sm) layers in the G, F and C phases of HBHA (70.6) has been measured by X-ray diffraction. In the Sm-G phase its value is limited by crystallite size and lies between 1200-1500 Å. At the Sm-G to -F transition 03BE ~ changes from 300 to 180 Å with a temperature dependence predicted by a dislocation mediated melting model of 2D lattice. At the Sm-F to -C transition 03BE ~ changes discontinuously. The Sm-C phase is found to have an unusually large correlation length (~ 50 Å), almost double of that in the Sm-A phase.

In the phase diagrams of some thermotropic liquid crystals the smectic phases [1] G, F, and C occur in that order with increasing temperature, with one possible exception [2]. In these phases molecules have a temperature dependent tilt with respect to the smectic layer normal. The smectic-G (Sm-G) phase is characterized by long-range translational and bond-orientational order in the smectic layer while the smectic-C (Sm-C) is believed to have 2D liquid-like layers. The smectic-F (Sm-F) phase was discovered rather recently and is exhibited by only a handful of compounds. A limited number of structural studies [3-5] of this phase indicates that it has some ordering of molecules in the smectic layers.

According to Halperin and Nelson [6], melting of a two dimensional solid occurs in two steps. As the temperature is increased, a transition to an intermediate phase called « hexatic » takes place due to the unbinding of dislocation pairs. The hexatic phase transforms at a higher temperature into a 2D liquid by the unbinding of disclination pairs. On the basis of this theory Birgeneau and Litster [7] suggested a consistent picture of smectic phases. According to them a system of stacked hexatic layers with infinitesimal interaction between layers would have long-range bond-orientational and positional order as found in the Sm-B and -G phases. However, if the interaction between layers was sufficiently weak, the system would still have 3D long-range bond-orientational order but exponential decay of the inplane positional order. Recently the Sm-B phase of 650BC has been shown [8] to be such a phase. It seems that the Sm-F phase may also be a system of this type. The Sm-C and -A phases correspond to stacked layers with short-range bond-orientational and positional order in the smectic layers. It is, therefore, important to study the inplane structure of the Sm-C, -F, and -G phases and the differences between them. In this paper the results of such a study of N-(4-heptyloxybenzyliden)-4-n-hexylaniline (HBHA) are presented. HBHA was selected due to its relatively high chemical stability and continuous miscibility with TB5A [9], a homolog of TBBA, that has been a subject of some other investi-
gations. The Sm-C to -F transition for this compound is first order with a discontinuity in smectic layer thickness [10]. During the present and previous high-resolution X-ray work [10, 11] on the smectic phases, coexistence of the Sm-F and -C phases was observed. However, there was no indication of the coexistence of the Sm-F and -G phases. The smectic layer thickness exhibited no discontinuity at the Sm-F to -G transition. The entropy of transition [10] was 0.01 R, which is comparable to the second order Sm-C to -A transitions [11] and about two orders of magnitude smaller than typical first order liquid crystalline transitions. From all available data on the Sm-F to -G transition it is clear that this is a nearly (if not purely) second order transition.

We utilized powder X-ray diffraction in parafocussing geometry, as shown in figure 1. The X-ray beam is focussed by a bent graphite monochromator onto a limiting slit $S_2$ (0.05 mm). A divergent beam falls on the sample surface at the centre of the diffractometer table. The reflected beam is focussed upon the analysing slit (0.1 mm) in front of the scintillation counter, 12 cm away from the sample. Thus, while achieving better resolution, intensity is also gained. The base of the resolution triangle of the experimental setup used is 0.005 Å$^{-1}$. The sample holder is shown as an inset in figure 1. The sample is held between two 6 μ thick mylar sheets and is embedded in a copper block. Temperature is measured near the sample surface with a relative precision of better than 0.1 °C. To increase the intensity of scattered radiation, the sample was aligned by cooling it from the isotropic to the Sm-C phase in a magnetic field of 4.5 kG. The magnetic field was turned off after aligning the sample.

The profile of reflections was recorded at different temperatures while sweeping both up and down in temperature. Representative profiles of reflections are shown in figure 2 for the Sm-G, -F and -C phases. The intensity of the Sm-C reflection on the right side appears higher than on the left due to the presence of a mylar peak at 2θ $\approx$ 25°. In order to do a detailed line shape analysis, effects of molecular form factor, mosaicity of the sample and experimental resolution function need to be taken into account. Without significantly better resolution and temperature control, and a more intense X-ray source, such an analysis is not warranted. From the measured half-widths at half-maximum (HWHM) $\epsilon$ of 2θ peaks one can calculate the correlation length $\xi_\parallel$ using the relation $\xi_\parallel = 2 \lambda / (\epsilon \cos \theta)$. This method, though not rigorous, gives an internally consistent measure of $\xi_\parallel$ and relative changes in its value. The numerical value of $\xi_\parallel$ obtained in this way is only an approximation to the actual value and should not be taken too seriously. The instrumental resolution enables measurement of $\xi_\parallel$ up to a maximum size of 2500 Å. The calculated values of $\xi_\parallel$ are plotted as a function of temperature in figure 3.

Fig. 1. — Experimental setup for powder X-ray diffraction in the parafocussing geometry. M, H and C are the graphite monochromator, the hot stage, and the scintillation counter respectively. The slits $S_1$, $S_2$ and $S_3$ are 0.4, 0.05 and 0.1 mm wide and 1 cm high. The inset shows the sample holder.

Fig. 2. — Outer reflections from the Sm-C, -F and -G phases. The points are from digitization of the experimental curves. The Sm-C peak has higher intensity on the right hand side than on the left due to the presence of a mylar peak at $\approx$ 25°.

Fig. 3. — Correlation length $\xi_\parallel$ of positional order parallel to the smectic plane in the Sm-G, -F and -C phases as a function of temperature. The solid line in the Sm-F region represents a fit to the function predicted by 2D melting model.
Scattering from the Sm-G phase shows two peaks which are not resolved. Since for a hexagonal structure the multiplicity of 110 spots is twice as large as that of 020 or 002 spots, we identify the peaks as 020 and 110 reflections. The reticular spacings suggest that the molecular tilt in the smectic layers is along a side (or towards an apex) of the hexagon. The hexagonal structure in the Sm-G phase is not distorted drastically, as is evident from the small splitting ($<0.5\%$) in the 110 and 020 peaks. Assuming an undistorted (regular) hexagonal structure and taking the values of layer thickness from an earlier high resolution work [9], the cell parameters can be determined as

\[ a = 5.01 \pm 0.02 \text{ Å} \]
\[ b = 8.69 \pm 0.03 \text{ Å} \]
\[ c = 28.16 \pm 0.02 \text{ Å} \]
\[ \gamma = 110.9^\circ \]

The direction of molecular tilt in the Sm-G phase of TB5A is perpendicular [2] to a side of the hexagon. It is interesting to note that in spite of a difference in the direction of molecular tilt, the Sm-G phases of these two compounds are found to be continuously miscible [9]. A transition in the direction of molecular tilt in the Sm-G phase should occur as the composition of TB5A and HBHA mixture is varied. Such a change may not be observed in a textural study. It should be possible to observe it with careful X-ray work.

The positional-order correlation length in the Sm-G phase should be infinitely large because it is known to have 3-dimensional structure. We obtain a value between 1200-1500 Å. The reason for this finite value (less than the resolution limit 2500 Å) is that it is limited by the crystallite size in the powder sample. The correlation length drops abruptly to 280 Å within 25 mdeg. at the Sm-G to -F transition. This is accompanied by a 50 % drop in the scattered intensity.

The correlation length $\xi_{||}$ in the Sm-F phase shows a pretransitional rise above the Sm-G to -F transition. A power law fit of the type

\[ \xi_{||}(T) = \xi_{||}^0 \exp\left[B(T - T_c)^v\right] \]

with $\nu$ lying between 0.37 and 0.40 for a triangular lattice. Such a temperature dependence of $\xi_{||}$ has been observed for the freezing transition of physisorbed xenon on graphite [12]. A reasonable fit of this form to our data, with $\nu$ fixed at 0.40, is obtained with $\xi_{||}^0 = 166.7$ Å, $B = 0.387$ and is shown by the solid line in the Sm-F region in figure 3. The Sm-F to -G transition, therefore, seems to be a dislocation mediated melting transition, and the Sm-F phase a stacked hexatic phase.

The correlation length attains a value of about 180 Å just before a jump to $\sim 53$ Å in the Sm-C phase. The value of $\xi_{||}$ in the Sm-C phase corresponds to more than 12 molecular thicknesses and is rather large for a phase that is believed to have liquid-like structure within the layers. No measurements on the Sm-A phase were made during this investigation.

It is important to note that the value of $\theta$, for the width of the outer ring of the Sm-C reflections reported by Benattar et al. [4] for TB5A agrees well with our measurements ($\sim 3.5^\circ$). For comparison, a value of $6.2^\circ$ for the Sm-A phase of 70.5 can be estimated from reference [13]. Also, for a mixture of 60CB and 80CB, the outer ring of the Sm-A phase has a width of about $6.7^\circ$ as measured by Kortan et al. [14]. These values give $\xi_{||} \sim 25$ Å or 5-6 molecules. A comparable value ($\sim 20$ Å) of $\xi_{||}$ is obtained by X-ray diffraction [15] from free standing Sm-A films of 40.8. Evidently the Sm-C layers are more structured than the Sm-A layers.

To summarize, in the Sm-G phase the value of $\xi_{||}$, limited by crystallite size, lies between 1200-1500 Å. It changes rather abruptly at the Sm-G to -F transition. The correlation length near the Sm-F to -G transition agrees with the prediction of the dislocation mediated melting model of a 2D triangular lattice. This indicates that the Sm-F phase may be a stacked hexatic phase. In the Sm-C phase $\xi_{||}$ has an unusually large value, more than double of that in the Sm-A phase. The Sm-C phase, therefore, has more order than the Sm-A, contrary to popular belief. Measurements of $\xi_{||}$ and the bond-orientational order in monodomain samples and free standing thin films of different smectic materials with higher resolution are essential to further clarify differences between the various smectic phases.

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References

[1] This nomenclature was suggested by GRAY and SACKMANN. For example, see:


