

# X-ray scattering in the smectic *A* phase of the liquid crystal octylcyanobiphenyl (8CB)

A. N. Zisman, D. V. Nikiforov, B. I. Ostrovskii, and E. M. Terent'ev  
*Institute of Crystallography, Academy of Sciences of the USSR*

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An x-ray study has been made of the structure of the smectic *A* phase of octylcyanobiphenyl with a high-resolution spectrometer. There is a block structure with a size scale  $\sim 5 \mu\text{m}$  in the oriented smectic *A*. The results are interpreted on the basis of the assumption of a condensation of point defects in the smectic *A* phase.

The phase transition from the nematic phase (*N*) to the smectic *A* phase (*A*) results from the onset of a one-dimensional translational order in a three-dimensional liquid. A characteristic feature of such one-dimensionally ordered systems is the absence of a true long-range order, because of an instability with respect to long-wave fluctuations in the phase of the order parameter.<sup>1</sup> As a result, the structure factor  $S(\mathbf{Q})$ , which characterizes the scattering of x radiation with wave vector  $\mathbf{Q}$ , and which is given by  $S(\mathbf{q}) \sim \delta(\mathbf{q})$  for a system with a long-range positional order, can be written as follows in the harmonic approximation (for the case  $\mathbf{q} \parallel \mathbf{Q}$ ):

$$S(q) \sim |q|^{-2+\eta}; \quad \mathbf{q} = \mathbf{Q} - \mathbf{Q}_0, \quad (1)$$

where  $\mathbf{Q}_0 = 2\pi/d$  is the wave vector corresponding to the period ( $d$ ) of the layered structure, and the exponent  $\eta$  is determined by how close  $\tau$  ( $\tau \equiv 1 - T/T_c$ ) is to the

temperature of the phase transition,  $T_c$  (Refs. 2 and 3). Incorporating anharmonic effects, we find a slightly different expression for this structure factor<sup>4,5</sup>:

$$S(q) \sim q^{-2} [1 - \gamma \ln(aq)]^{4/5}, \quad (\mathbf{q} \parallel \mathbf{Q}_0). \quad (2)$$

In the sole experimental study which has been carried out to test these assertions<sup>6</sup> it was found that the intensity of the x-ray scattering near  $\mathbf{Q}_0$  in the  $A$  phase of the liquid crystal 8OCB can be described by expression (1), even in the immediate vicinity of the phase transition to the nematic liquid crystal (at  $\tau \approx 10^{-6}$ ). This agreement is somewhat surprising, since expressions (1) and (2) were derived without consideration of fluctuations in the amplitude of the order parameter,  $|\psi|$ , which should contribute strongly to the scattering near the transition. We might also note that Als-Nielsen *et al.*<sup>6</sup> did not consider a possible change in the line profile because of the bounded nature of the regions of homogeneity of the  $A$  phase (the block nature), which is determined by defects of various types.

In this letter we report the results of a similar study of x-ray in the smectic  $A$  phase of the liquid crystal 8CB. In the course of this study we found that the scattering profile found in the  $A$  phase has a width which exceeds the instrumental function of the x-ray diffractometer. It also has an asymmetric shape, so that it was not possible to confirm the applicability of expressions (1) and (2). We did establish, however, that the dimensions ( $L$ ) of the homogeneous regions in the  $A$  phase are small, although still macroscopic:  $\approx 4.8 \mu\text{m}$  ( $\approx 1500$  layers). At the point of the  $A$ - $N$  transition, the value of  $L$  does not depend on the boundary conditions or the history of the sample.

The experimental layout is shown in Fig. 1. An x-ray beam from a Mo anode undergoes triple (220) Bragg reflection at the slit crystal of a monochromator (1) made of silicon and then passes through a slit (2), where the  $K_{\alpha 1}$  line is singled out. The radiation scattered by the sample (3) undergoes a triple reflection at the slit analyzer crystal (4) and is then detected by a scintillation detector (5). The use of a dispersion-free arrangement of the crystals and slit monochromators<sup>7</sup> makes it possible to study the cross section of a reciprocal-lattice site in the direction parallel to  $\mathbf{Q}_0$  with an angular resolution  $\approx 2.9''$ . Figure 2 shows a typical curve of the scattering in the

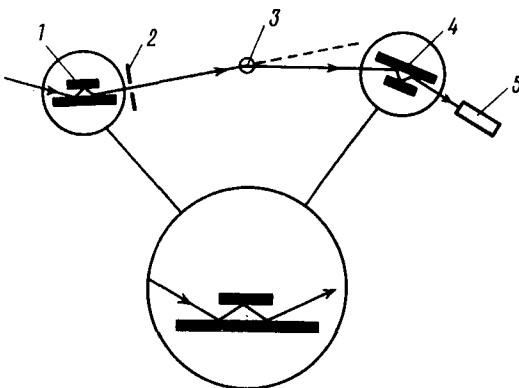


FIG. 1. The experimental geometry. 1—Monochromator; 2—collimator; 3—sample; 4—analyzer crystal; 5—detector.

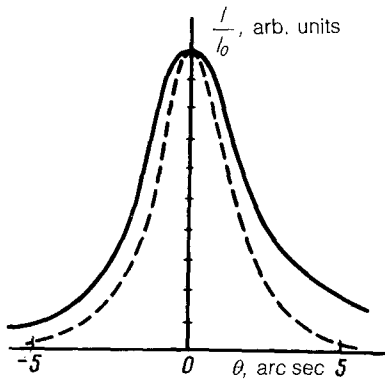


FIG. 2. Profile of the x-ray line near reciprocal-lattice vector  $Q_0$ . The dashed line is the instrumental function of the spectrometer.

smectic  $A$  phase near  $Q_0 = 0.1985 \text{ \AA}^{-1}$  (the Bragg angle is  $\theta = 0.642^\circ$ ). The dashed line is the instrumental function of the spectrometer in these experiments.

The samples are held in a constant-temperature chamber; the temperature is regulated and measured within 0.01 K. The director is oriented in a magnetic field  $H \approx 0.2 \text{ T}$  with the help of miniature permanent magnets made of a Sc-Co alloy.

A sample of the liquid crystal octylcyanobiphenyl, 8CB (made by BDH Chemicals) in one version is a freely suspended  $\sim 1\text{-mm}$  drop, which is held in the working zone of the constant-temperature chamber by surface-tension forces. In another version, the sample is placed in a thin-walled quartz capillary. The wall thickness is  $\sim 0.01 \text{ mm}$ , and the diameter of the capillary is 1 mm. The height of the sample is 2–3 mm. In most cases, the sample is brought slowly through the  $I$ - $N$  transition ( $\approx 41^\circ \text{ C}$ ) and the  $N$ - $A$  transition ( $\approx 33^\circ \text{ C}$ ) and cooled to  $\approx 25^\circ \text{ C}$ . The disorientation of the director is  $\approx 3^\circ$ ; it does not change as the  $A$ - $N$  transition is approached.

Comparison of the profile of the scattering line with the instrumental function of the apparatus (Fig. 2) shows that over the entire temperature interval in which the  $A$  phase exists the width of the diffraction peaks is 4–6" and greater than the width of the instrumental function of the diffractometer. We feel that the most natural explanation for this circumstance is (by analogy with an ordinary crystal) the bounded nature of the homogeneous regions (the block nature) of the smectic  $A$  phase. It follows from Refs. 3 and 8 that when a sample of a liquid crystal has finite dimensions, the scattering intensity will be determined by two terms, one of which is an expression like (1) or (2), while the other is a rudimentary Bragg reflection  $\delta(\mathbf{q})$ . If the dimensions of the blocks are small, however, one will observe, instead of a  $\delta$ -function, a profile of finite width,  $I(q)$ , described by an expression of the type

$$I(q) \sim (\sin^2 qL)/q^2, \quad (3)$$

where  $L$  is the block size.<sup>9</sup> It should also be kept in mind that when the blocks have small dimensions, it is also necessary to alter singular expressions (1) and (2). The intensity of the scattered signal does not exceed 20 counts/s, so that it was not possible to reliably distinguish the contributions from the rudimentary Bragg reflection, the

fluctuations in the amplitude of the order parameter, and the fluctuations in its phase—especially since all three contributions have an approximately  $1/q^2$  decay law.

In this situation the only reliable information is the characteristic size of a block, which is found from the linewidth. We studied the behavior of this quantity as a function of the temperature. It turns out that in the case of the freely suspended drop, the linewidth and thus the characteristic block size  $L$  are essentially independent of the temperature; the latter has a value  $\approx 4.8 \mu\text{m}$ . When the sample is placed in a quartz capillary, the linewidth in the deep  $A$  phase ( $\tau \gtrsim 0.01$ ) is about 1.5 times that for a free drop; correspondingly, we find  $L \approx 3 \mu\text{m}$ . As the temperature of the  $A-N$  transition is approached, the linewidth initially decreases, in accordance with an increase in the size of the homogeneous blocks; at the transition point it is equal to the width found in the case of a free drop (Fig. 3).

We will attempt to give at least a qualitative explanation for these results.

The difference in the behavior  $L$  in the free drop and in the capillary can be explained quite naturally on the basis that in the latter case the special boundary conditions (the director is directed perpendicular to the axis of the cylindrical capillary) there is an increase in the density of dislocations in the interior of the sample. As the transition is approached ( $\tau \rightarrow 0$ ), according to Ref. 10, a coalescence of individual dislocations, a decrease in their concentration, and an increase in the effective size of the blocks are favored from the energy standpoint. A question that remains unclear, however, is why the size of the blocks is limited to  $\sim 5 \mu\text{m}$  in the immediate vicinity of the transition, regardless of the boundary conditions.

One possibility is that the size of the blocks near the transition is determined primarily by impurities, whose concentration in the liquid crystal is 0.01–0.001. Ac-

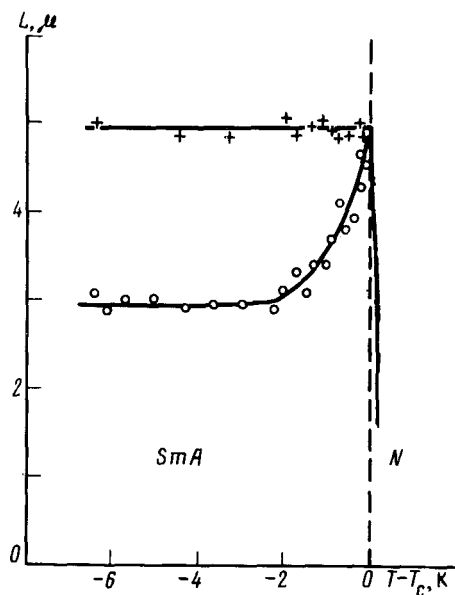


FIG. 3. The block size  $L$  versus the temperature.  $\circ$ —In a quartz capillary;  $+$ —in a free drop.

According to the reciprocity theorem,<sup>11</sup> the interaction of the point defects, which produce a deformation field  $U_D \sim d^2 \exp(-\rho^2/4\lambda|z|)/z$  in the *A* phase, is described by an attractive potential of the type  $\Phi \sim Kd^4 \exp(-\rho^2/4\lambda|z|)/\lambda z^2$ , where  $\lambda = \sqrt{K/B}$ , *B* and *K* are elastic constants, and  $\rho$  and *z* are the coordinates in the plane and along the normal to the layers. Consequently, upon the formation of the *A* phase (*B* > 0) point defects begin to coalesce. This process is analogous to the precipitation of a new phase from a solid solution.<sup>12</sup> The limited volume prevents us from analyzing the equilibrium shape of the impurity condensate and its formation kinetics in this case (this will be done in a separate study). At this point, we would simply like to state that the condensate should precipitate in a time  $\sim 0.1$  s and should consist of thin layers (of thickness  $\sim d$ ) oriented parallel to the main smectic layers.

In summary, the correlation properties of smectic order should differ from those in an ideal structure. The presence of randomly positioned foreign layers in a system should lead to a disruption of the phase of the smectic order parameter, so that the sample will become polycrystalline along the direction normal to the layers. The characteristic dimension *L* along the *z* axis of single-domain regions can be estimated easily by working from the impurity concentration (*X*) in the material:  $L \sim 2d/X \leq 6 \mu\text{m}$ , for  $X \geq 0.001$ . This estimate agrees well with the results of our experiments.

We repeat that the phenomenon described here can be explained on the basis of the existence of other extended defects (e.g., dislocations) in the *A* phase, but in that case it would not be clear why the concentration of these defects at the transition point does not depend on the boundary conditions or the history of the sample.

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