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## Absence of the Incommensurate Smectic- $A$ Phase in DB<sub>7</sub>OCN + 8OCB Mixtures

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The results of a high-resolution x-ray-diffraction study of the smectic phases in mixtures of DB<sub>7</sub>OCN and 8OCB show that the incommensurate smectic- $A_{i2}$  phase, previously reported in this mixture, is in fact a coexistence of the partially bilayer smectic- $A_d$  and the bilayer smectic- $A_2$  phases at a first-order phase transition between them.

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Liquid-crystal molecules with strong longitudinal dipoles have, for some time, been known to exhibit rich smectic- $A$  (Sm- $A$ ) polymorphism and multiple reentrance of nematic and smectic phases. Since the experimental discovery of the Sm- $A$ -to-Sm- $A$  transition [1], a large number of subsequent studies [2] have improved our developing theoretical understanding [3] of these systems. The phases exhibited by such polar systems can be understood in the framework of Prost's [3] phenomenological theory which introduces the order parameter  $\Psi_1(\mathbf{r})$  associated with smecticlike antiparallel dipolar ordering of molecules and includes  $\Psi_2(\mathbf{r})$ , the usual smectic mass density wave. The order parameters  $\Psi_1$  and  $\Psi_2$  naturally prefer to condense at two wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , where  $k_1 = 2\pi/2l$  and  $2\pi/2l < k_2 < 2\pi/l$ ;  $l$  being the molecular length. These wave vectors are, in general, not collinear or commensurate. The extent of coupling between the order parameters and the elastic terms in the free energy determine which modification of the Sm- $A$  phase is formed. In the Sm- $A_2$  phase  $|\Psi_1| \cong |\Psi_2|$  and  $\mathbf{k}_1 \parallel \mathbf{k}_2$ . Two quasi-Bragg reflections at commensurate wave vectors  $q_0 = 2\pi/2l$  and  $2q_0$  are observed in x-ray diffraction from this phase. For the Sm- $A_d$  phase,  $\Psi_1 > \Psi_2$  and two quasi-Bragg reflections at  $q' = k_2$  and  $2q'$  and a diffuse peak at  $2q_0$  are present. The Sm- $A_2$  and Sm- $A_d$  phases have the same symmetry and a first-order phase transition between them has previously been shown [4] to terminate at a critical point.

Theory [5] also predicted the existence of phases in which two incommensurate collinear density modulations coexist. In the strong order-parameter coupling limit, soliton regions with interpenetrating modulations corresponding to  $k_1$  and  $k_2$  separate Sm- $A_2$ -type lock-in regions, forming the *soliton* or Sm- $A_{i2}$  phase. On the other hand, if the order-parameter coupling is weak, two independent incommensurate modulations interpenetrate on a microscopic scale. The Sm- $A_{i1}$  phase should form when the order parameters  $\Psi_1$  and  $\Psi_2$  condense at incommensurate  $q'$  and  $q_0$ , respectively. Alternatively, the Sm- $A_{i2}$  phase with quasi-Bragg reflections at  $q_0$ ,  $2q_0$ , and  $q'$  is obtained if  $\Psi_1$  condenses at  $q_0$  and  $\Psi_2$  at  $q'$ . The first observation [6] of the Sm- $A_{i2}$  [7] phase was reported in binary mixtures of 4-*n*-heptyloxyphenyl-4'-cyanobenzoyloxybenzoate (DB<sub>7</sub>OCN) and 4-octyloxy-4'-cyanobiphenyl (8OCB). The discovery stimulated interest in this

system resulting in studies performed by several other techniques [8,9]. We conducted a high-resolution x-ray-diffraction study of the smectic order in mixtures of DB<sub>7</sub>OCN+8OCB to better understand this new phase. Our results show that the phase identified as Sm- $A_{i2}$  is, in fact, a region of coexistence of the Sm- $A_d$  and Sm- $A_2$  phases.

The experiments were performed on a 18-kW rotating anode source and a four-circle goniometer with a pair of Ge(111) crystals used as monochromator and analyzer. The instrumental resolution was  $4 \times 10^{-4} \text{ \AA}^{-1}$  in the longitudinal direction,  $2 \times 10^{-5} \text{ \AA}^{-1}$  in the transverse in-plane direction, and  $4 \times 10^{-2} \text{ \AA}^{-1}$  in the transverse out-of-plane direction. The sample temperature stability was  $\pm 10$  mK. The sample was aligned by cooling it slowly from the nematic phase in the presence of a  $\sim 2.5$ -kG field. The compound DB<sub>7</sub>OCN was synthesized using a standard procedure and purified by recrystallization. 8OCB was purchased from BDH Chemicals and used without further purification. Two mixtures with (A) 35.1 and (B) 28.0 mol% 8OCB were prepared by vigorous stirring in the nematic phase. Some samples were degassed by repeated freeze-melt cycles in vacuum. The degassed samples gave essentially the same results as nondegassed samples.

Mixture (A) exhibited a Sm- $A_d$  phase above 120°C and a Sm- $A_2$  phase below 108°C. The region between 108 and 120°C corresponds to what was previously identified to be the incommensurate Sm- $A_{i2}$  phase. In the Sm- $A_d$  phase at 121.35°C, we observed two quasi-Bragg peaks at  $q' = 0.1328$  and  $2q' = 0.2656 \text{ \AA}^{-1}$ , and a diffuse peak at  $2q_0 \sim 0.2389 \text{ \AA}^{-1}$  as shown in Fig. 1(a). An  $\omega$  scan,  $\omega = \theta - (2 - \theta/2)$ , at this temperature revealed a well-aligned sample with a mosaic half-width of  $\sim 2.3^\circ$ . The  $\omega$  scans through the two peaks (see Fig. 2) were identical, confirming that both reflections originated from the same scattering volume (domains) of the sample and that the corresponding mass-density modulations were collinear. The sample mosaic was found to gradually broaden at lower temperatures as the weak external field of 2.5 kG became ineffective in maintaining the molecular alignment in the Sm- $A_d$  phase.

At temperatures lower than 120°C, two additional resolution-limited peaks corresponding to the underlying Sm- $A_2$  phase appeared at  $q_0 = 0.1211$  and  $2q_0 = 0.2422$

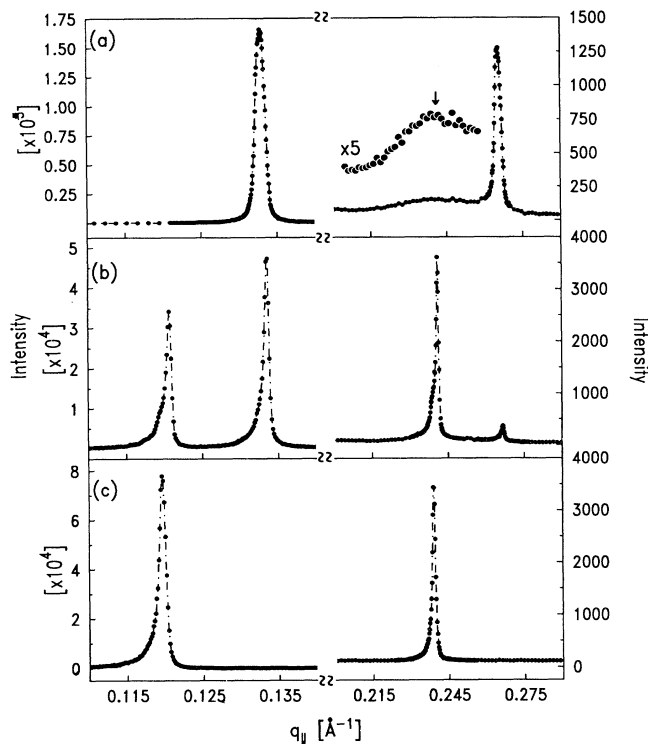


FIG. 1. X-ray scattering intensity obtained for the same counting time in longitudinal scans taken at different temperatures for 35.1 mol% 8OCB+DB<sub>7</sub>OCN mixture. (a) In the Sm- $A_d$  phase at 121.35°C, there are two quasi-Bragg peaks at  $q' = 0.1328$  and  $2q' = 0.2656 \text{ \AA}^{-1}$ , and a diffuse peak (also shown on  $5 \times$  scale) at  $\sim 0.2389 \text{ \AA}^{-1}$ . (b) In the coexistence region at 115.69°C, two  $A_d$  peaks at  $q' = 0.1335$  and  $2q' = 0.2667 \text{ \AA}^{-1}$  and two  $A_2$  peaks at  $q_0 = 0.1206$  and  $2q_0 = 0.2409 \text{ \AA}^{-1}$  are simultaneously present. (c) At 105.22°C, only the two Sm- $A_2$  peaks at  $q_0 = 0.1196 \text{ \AA}^{-1}$  and  $2q_0 = 0.2390 \text{ \AA}^{-1}$  remain. The origin of asymmetry in peaks (b) and (c) appears to be the concentration change accompanying phase separation in the coexistence region.

$\text{\AA}^{-1}$ . These peaks gradually became stronger and at 119.35°C their intensities became comparable to the peaks at  $q'$  and  $2q'$ . The four peaks were present at all temperatures above 108°C although their relative intensities changed with temperature. Figure 1(b) shows the four peaks at 115.69°C. It was not possible to observe the diffuse peak at  $2q_0$  in the presence of a sharp peak at the same position, with our high-resolution setup. Since the Sm- $A_{i2}$  phase is expected to have three reflections at  $q'$ ,  $q_0$ , and  $2q_0$ , the simultaneous presence of four peaks suggested a coexistence of the Sm- $A_d$  and Sm- $A_2$  phases rather than the formation of the Sm- $A_{i2}$  phase.

The shapes of  $\omega$  scan taken through the two Sm- $A_d$  peaks at 119.35°C were similar to each other as shown in Fig. 3. The  $\omega$  scans of the two Sm- $A_2$  reflections (Fig. 4) were also identical but quite different from those of Sm- $A_d$  peaks. We used longer counting times for peaks at  $2q_0$  and  $2q'$  because of their low intensity which resulted

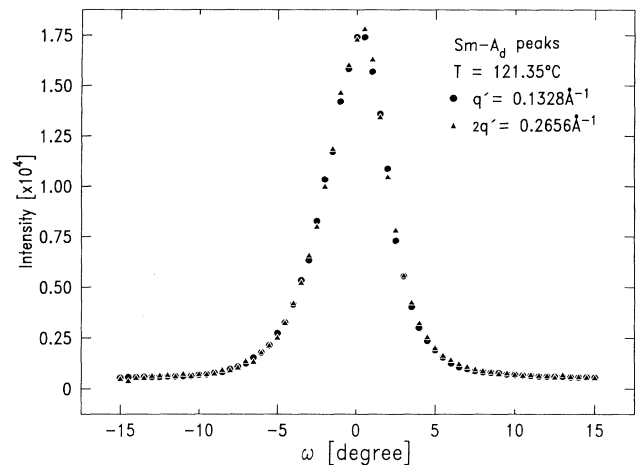


FIG. 2. The  $\omega$  scans through the two Sm- $A_d$  peaks at  $q' = 0.1328$  and  $2q' = 0.2656 \text{ \AA}^{-1}$  taken at 121.35°C possess half-widths of  $\sim 2.3^\circ$ . The  $2q'$  peak has been scaled and shifted.

in background counts different from that for the  $q_0$  and  $q'$  peaks. Also, the scans were taken at different times while the sample mosaic, as will be discussed later, was changing with time. These two factors were responsible for minor differences in the curves shown in Figs. 3 and 4. The half-width of the  $\omega$  scans of Sm- $A_d$  reflections was approximately  $4.7^\circ$  while that of Sm- $A_2$  peaks nearly  $7.2^\circ$ . The  $\omega$  scans for all Bragg reflections from a Sm- $A_{i2}$  phase should have been identical. Our observations show that smectic density wave vectors corresponding to the Sm- $A_d$  and Sm- $A_2$  phases not only are not collinear but also originate from different parts (domains) of the sample. The  $\omega$ -scan profiles obtained at the same temperature but during different runs were different and depended on sample history.

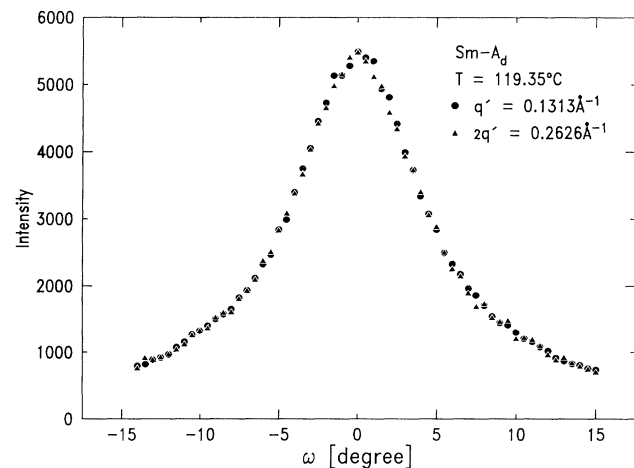


FIG. 3. The  $\omega$  scans through the two Sm- $A_d$  peaks in the coexistence region, at 119.35°C with half-widths of  $\sim 4.7^\circ$ . The  $2q'$  peak has been scaled and shifted for comparison.

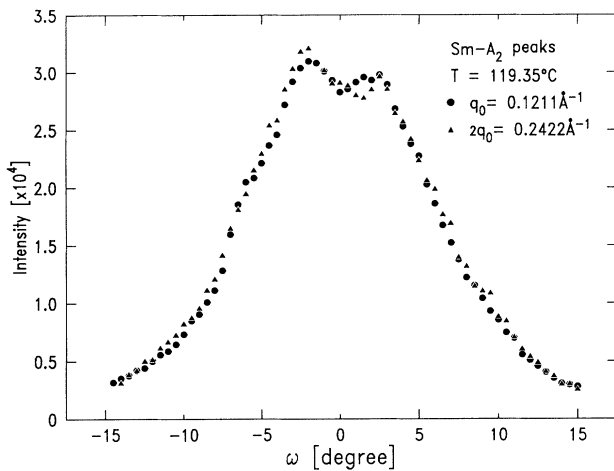


FIG. 4. The  $\omega$  scans through the Sm- $A_2$  peaks at 119.35°C in the coexistence region are similar and both have a half-width of  $\sim 7.2^\circ$ . The  $2q_0$  peak has been scaled and shifted for comparison.

The  $\omega$  scans taken at a fixed temperature in this coexistence region evolved very slowly with time. At 119.35°C, the intensity of  $q' = 0.1313 \text{ \AA}^{-1}$  peak diminished while that of  $q_0 = 0.1211 \text{ \AA}^{-1}$  peak grew with time. The Sm- $A_d$  peak, as shown in Fig. 5, became nearly 50% of the original height in approximately 13 h. The shape of the  $q_{\parallel}$  scans through each peak remained almost unchanged over this period. The time dependence of the intensities of Sm- $A_d$  and Sm- $A_2$  peaks, measured at another temperature (116.30°C) and shown in Fig. 6, reflect the rate at which Sm- $A_d$ -type order transformed into Sm- $A_2$ -type order. The solid lines represent exponential dependences with a time constant of approximately 12 h for both peaks. Growth of the Sm- $A_2$  peak and a simu-

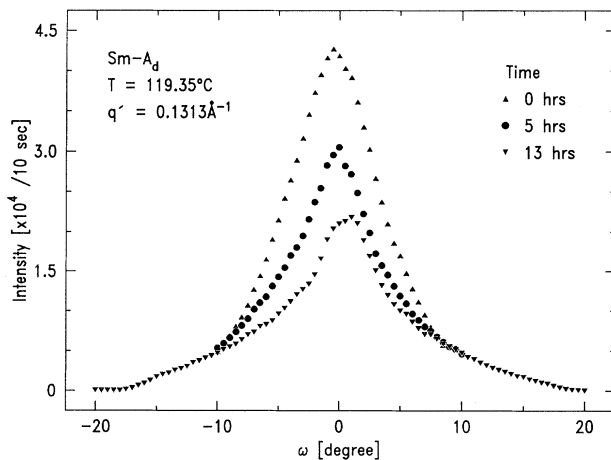


FIG. 5. Time evolution of the  $\omega$  scans through the peaks at  $q' = 0.1313 \text{ \AA}^{-1}$  at 119.35°C showing the slow disappearance of the Sm- $A_d$  order.

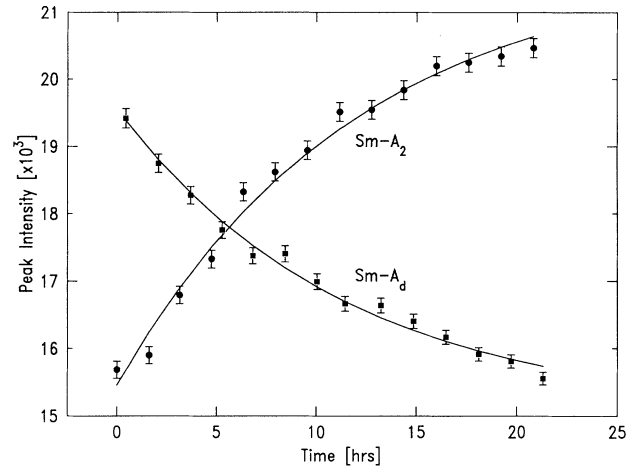


FIG. 6. Time dependence of the intensities corresponding to the Sm- $A_d$  (■) and Sm- $A_2$  peaks (●), with different vertical scales, measured at 116.30°C in the coexistence region at  $q' = 0.1336 \text{ \AA}^{-1}$  and  $q_0 = 0.1206 \text{ \AA}^{-1}$ , respectively. The solid-line fits give a time constant of 12 h.

aneous decrease in intensity of the Sm- $A_d$  peak provided further proof of the coexistence of the Sm- $A_d$  and Sm- $A_2$  phases. We observed similar qualitative behavior when the sample was cooled from the Sm- $A_d$  phase to a

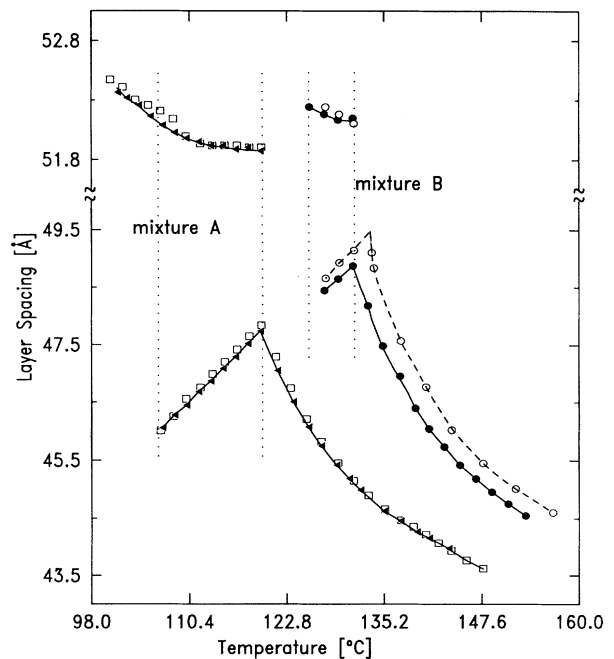


FIG. 7 Smectic layer spacing as a function of temperature in various phases for the (A) 35.1 and (B) 28.0 mol% 8OCB+DB<sub>7</sub>OCN mixtures. The  $\blacktriangle$  represent data taken after 30 min and  $\square$  after 4 h of equilibration time at each point. The differences arise as the sample is cycled through the coexistence region. The lines are drawn as a guide to the eye.

different temperature in the coexistence region.

The peaks at  $q_0$  and  $2q_0$  became more intense while those at  $q'$  and  $2q'$  grew weaker at lower temperatures and eventually disappeared at approximately 108°C. The two Sm- $A_2$  peaks at 105.22°C are shown in Fig. 1(c). The  $\omega$  scans through these reflections were, again, identical, suggesting that they originated from two colinear density modulations. Similar measurements were performed on mixture (B) and the results were completely analogous to those for mixture (A).

Smectic layer spacing,  $d$ , as a function of temperature is shown in Fig. 7 for both mixtures. The behavior of  $d$  in the two smectic regions and in the coexistence region is in qualitative agreement with the results of Refs. [6] and [8]. The measurements on mixture (A) were also repeated with different waiting time at every temperature to ensure thermal equilibration. The points represented by open squares in Fig. 7 were taken after waiting for 4 h and solid triangles after waiting for 30 min at every temperature. There is an observable difference in the two scans. The value of  $d$  obtained in a particular run depended on sample history and, specifically, on the time spent in the coexistence phase. The different  $d$  vs  $T$  curves shown in Fig. 7 for mixture (B) clearly show significant changes in the concentration of the sample volume that lies in the x-ray beam each time the coexistence region was traversed. The changes in  $d$  from one run to another did not show a trend, ruling out sample decomposition as a probable cause. At times we detected the presence of domains of several different concentrations. Our observation established that phase separation was occurring in the coexistence region.

Since the Sm- $A_2$  and Sm- $A_d$  phases have the same symmetry, there should be either no phase transition or a first-order transition between them. In the case of first-order transitions the two phases can coexist over a finite-temperature range. In the coexistence region, a phase separation normally results in domains of concentrations corresponding to the phase boundaries. The concentrations of these domains are expected to change with temperature and follow the boundary lines defining the coexistence region. One can argue [9] that in our measurements the temperature dependence of  $d$ , which depends linearly on concentration, should reflect this behavior and that the segments of  $d$  vs  $T$  curves in the coexistence re-

gion for different concentrations should fall on the same line. Our results shown in Fig. 7 do not completely fulfill this expectation because the system did not reach equilibrium during our experiments. The equilibration time constants appear to be long and one may have to wait for several days at every temperature in order to observe this behavior.

In summary, we have shown that the Sm- $A_d$  phase of 28.0 and 35.1 mol% 8OCB+DB<sub>7</sub>OCN mixtures undergoes a first-order transition to the Sm- $A_2$  phase and that the two phases coexist for nearly 5 and 10 K, respectively. In the coexistence region the equilibration is very slow and is accompanied by phase separation.

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