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Correct Phase Diagrams of Liquid Crystals Reported to Exhibit the (Nonexistent) Incommensurate Smectic-A Phases.

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PACS. 81.30D – Phase diagrams of other materials.

Abstract. – Three different incommensurate phases predicted by the phenomenological theory of frustrated smectics were reportedly found in mixtures of DB₈OCN and 8OBCAB and DB₇OCN and 8OCB. The results of our high-resolution X-ray diffraction study of these materials show that these *phases* are, indeed, coexistences of two or more smectic-A phases. The correct phase diagrams of the two systems are found to be in excellent agreement with the phenomenological models. At this time, there remain no known materials that exhibit an incommensurate smectic-A phase.

Materials with a large electric-dipole moment along the long molecular axis have been known [1,2] to exhibit rich smectic-A polymorphism. Phenomenological theories [3-6] have been remarkably successful in understanding the formation of nearly ten frustrated smectic liquid-crystal phases. These theories invoke two order parameters to account for the two density modulations that exist in these phases. One of the density modulations results from the layered structure of the smectic phases, while the second one arises from the dipole pairing of the molecules. A large number of smectic-A phases are naturally predicted on the basis of relative amplitudes and periodicities of the two modulations and the directions of corresponding wave vectors relative to each other. In the simplest monolayer smectic- A_1 (A_1) phase, there is no significant dipole pairing and the layer spacing, d , is equal to the molecular length l . The bilayer smectic- A_2 (A_2) phase, with two modulations of periodicities l and $2l$, is formed when antiparallel molecules form pairs of length $2l$. However, if the molecules form pairs with a significant length-wise overlap, the partial bilayer smectic- A_d (A_d) phase with layer spacings of l' and $2l'$ ($l < 2l' < 2l$) is formed.

Three *incommensurate* smectic-A phases were also predicted [3-6]. The wave vectors of the two density modulations in these phases are collinear but incommensurate, *i.e.* the ratio of their wave numbers is not a rational fraction. The incommensurate smectic- A_{11} (A_{11}) and smectic- A_{12} (A_{12}) phases form when the order parameter coupling is weak. In the A_{11} and A_{12} phases, molecular orderings similar to the A_1 and A_d and the A_2 and A_d phases, respectively,

interpenetrate on the microscopic scale. In the strong-coupling limit, lock-in regions similar to the A_2 phase are separated by *soliton* regions in which the two modulations are out of phase with each other. This is known as the incommensurate soliton or A_{1s} phase.

The binary mixtures of (A) 4-*n*-octyloxyphenyl-4'-cyanoazobenzoyloxybenzoate (DB₈OCN) and 4-*n*-octyloxybenzoate-4'-cyanoazobenzene (8OBCAB) were reported [7] to exhibit all three incommensurate phases. Dotted lines in fig. 1a) represent the phase diagram reported in ref. [7]. The positions of X-ray diffraction peaks and their temperature dependence in these incommensurate phases were, apparently, in accordance with the theory. The A_{1s} phase gave rise to diffraction peaks at $2q_0$, q'' , and $q_s (= 2q_0 - q'')$, in excellent agreement with the theory. A second system (B), mixtures of 4-*n*-heptyloxyphenyl-4'-cyanoazobenzoyloxybenzoate (DB₇OCN) and 4-octyloxy-4'-cyanobiphenyl (8OCB), had also been reported [8,9] to exhibit the A_{12} phase. The phase diagram calculated for this system from an extension [10] of the original phenomenological model [5] was strikingly similar to that obtained experimentally [8].

Very recently, we have applied high-resolution X-ray diffraction to further investigate the structure of these phases. Our results have revealed [11] that the A_{11} and A_{1s} phases of system A are coexistences of the A_d and A_1 and the A_d , A_1 , and A_2 phases, respectively. The A_{12} phase of system B was found [12] to be a coexistence of the A_d and A_2 phases. Here, we present evidence that the A_{12} phase of system A is also a coexistence of the A_d and A_2 phases.

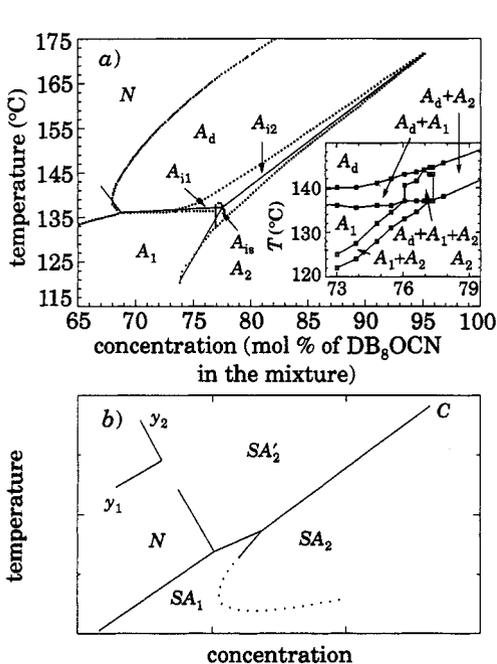


Fig. 1.

Fig. 1. - a) Experimental phase diagram (dotted lines) of DB₈OCN + 8OBCAB system from ref. [7]. Solid lines represent the approximate first-order transition lines. The inset shows the partial phase diagram based on results of the present study. b) Theoretical phase diagram, from ref. [5], replotted after a rotation by $\sim 122^\circ$ to generate the temperature-concentration phase diagram.

Fig. 2. - a) Longitudinal scan at 147.97°C , and b) ω -scans taken at 145.77°C for 80.1 mole% DB₈OCN mixture. The ω -scans of the two A_2 peaks are identical but different from that of the A_d peak, confirming their coexistence.

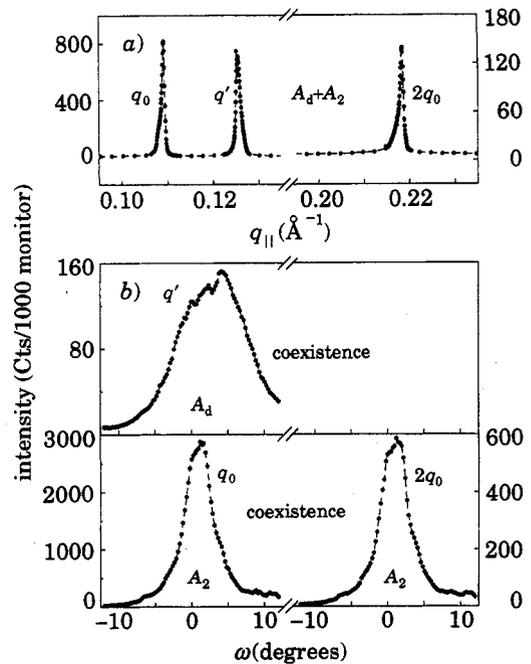


Fig. 2.

We report the correct phase diagrams of these systems obtained from the present study, which are in excellent agreement with a theoretical [5] phase diagram obtained nearly ten years ago.

The experimental set-up used in our study is described elsewhere [11,12]. The temperature stability during these measurements is better than ± 10 mK. Longitudinal scans are conducted on magnetically aligned samples to determine the layer spacings and their temperature dependence in various smectic phases. ω -scans are performed to obtain the mosaicity or the distribution of layers of a fixed d . Two reflections from one phase, for example, at q_0 and $2q_0$ from the A_2 phase, must originate from the same scattering volume (domains) in the sample and must have identical ω -scans. Conversely, if the ω -scans of two reflections are different, they must originate from physically different parts of the sample. ω -scans are, thus, a powerful tool to determine the coexistence of two or more phases and to study the time evolution of the volume fractions of sample in different phases.

The partial phase diagram, inset in fig. 1a), obtained from our X-ray study of system A is qualitatively similar to that of ref. [7]. We identify three single-phase and four coexistence regions. The transition temperatures are $(2 \div 3)$ K higher than previously reported, suggesting high purity of our samples. A theoretical phase diagram [5] is reproduced in fig. 1b) and will be discussed later.

Two quasi-Bragg reflections are present in the A_d phase of 80.1 mole% $\text{DB}_8\text{OCN} + 80\text{BCAB}$ mixture. The positions of these peaks are strongly temperature dependent and the intensity of the second peak is nearly three orders of magnitude weaker than the first. Due to its low intensity and the tendency of these materials to decompose at high temperatures, we did not scan the second A_d peak at all temperatures. At 147.97°C , in the « A_{12} phase» region, the A_d peak at q' and the two A_2 peaks at q_0 and $2q_0$ are simultaneously present (as shown in fig. 2a)), suggesting a coexistence. The ω -scans of the three reflections at 145.77°C are shown in fig. 2b). Obviously, mosaics of the two A_2 reflections (lower panel) are identical as expected. But they are quite different from the mosaic of the A_d peak, proving beyond the shadow of a doubt that the sample is constituted of domains of A_d and A_2 phases.

At a fixed temperature in this region the A_2 peaks grow, while the A_d peaks diminish with a time constant of $(7 \div 8)$ h. Their slow time evolution suggests that the measurements of the previous reports [7-9] were, perhaps, not equilibrium measurements. This inequilibrium appears to be responsible for the observed coexistence of the two phases at this concentration and the three phases at other concentrations in this two-component system.

We infer from similar measurements that the A_1 and A_2 phases also coexist (fig. 3) from 133.0 to 137.0°C in a mixture with 76.1 mole% DB_8OCN . Two diffuse peaks, one on either side of q_0 , appear in the A_1 phase [13]. These seem to be the two A_{18} reflections reported previously at 77.2% concentration. Low resolution of the powder diffraction technique used in the previous study [7] may have misled the researchers into believing that these were quasi-Bragg peaks due to the A_{18} phase. We find that, once a sample has been cycled through a coexistence region, it undergoes severe phase separation, making it impossible to reproduce the results. However, no difficulty was encountered in reproducing the results with a second virgin sample. During a repeat cycle on 76.1% mixture, we monitored the time evolution of the diffuse peaks at 141.0°C . We find that they continuously move towards q_0 with diminishing intensities (open circles in fig. 3). After approximately 7 hours, both of these peaks collapse on to the q_0 peak which belongs to the underlying A_2 phase, again confirming that the frustrated smectics equilibrate very slowly across first-order transitions.

With the realization that all of the incommensurate phases previously reported are in fact coexistences of two or more smectic phases, the solid lines (fig. 1a)) can be drawn through the middle of these regions to represent the approximate phase boundaries. Figure 1b) shows the

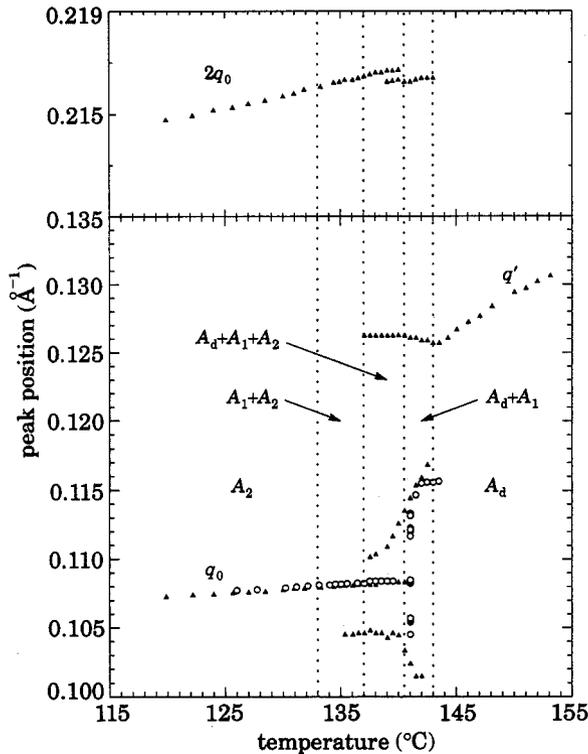


Fig. 3. - Temperature dependence of peak positions in various phases of 76.1 mole% DB₈OCN + 80BCAB mixture. Points represented by (○) were obtained during a repeat cycle. The points at 141 °C represent the time evolution of the two diffuse peaks around q_0 , showing low equilibration in these materials.

theoretical phase diagram taken from ref. [5]. This phase diagram was originally plotted in terms of parameters y_1 and y_2 , which are linear functions of temperature and concentration. We have replotted it after a simple rotation of nearly 122° to generate, to a first approximation, the temperature-concentration phase diagram. It appears remarkably topologically similar to the experimental phase diagram (solid lines in fig. 1a)). Evidently, the original theory [5] is in excellent agreement with experimental results.

Similar measurements are carried out on system *B* at several 80CB concentrations. As was previously reported, four peaks are observed in the « A_{i2} » region. The q_0 and q' peaks are resolvable only up to a concentration of 15%. At lower concentrations, we rely on the lineshape of the q' peak to determine the coexistence range, as discussed below.

The reflections from the A_d and A_2 phases have typical half-widths of $1.2 \cdot 10^{-3} \text{ \AA}^{-1}$ due to sample mosaic and are not resolution limited. Consequently, we cannot resolve the A_d and A_2 peaks when they are closer than their half-widths in dilute mixtures. However, we observe a significant broadening of the A_d peak near the transition, followed by a sharpening after entering the A_2 phase (fig. 4). This is accompanied by a decrease in peak intensity in the proximity of the transition. In the supercritical region, continuous evolution of the peak position is expected without the observed peak broadening. We attribute the peak broadening to the simultaneous presence of A_d and A_2 peaks due to their coexistence. The coexistence range can be estimated from the width-*vs.*-temperature or intensity-*vs.*-

temperature curves shown in fig. 4 for 13.8 and 0.0 mole% mixtures. The points believed to be in the coexistence region on these curves are shown as filled circles and triangles for the two concentrations.

The temperature dependence of the scattering vectors for various 8OCB concentrations is shown in fig. 5a). The solid points on the continuous curves belonging to 13.8, 12.5, 10.0 and 0.0 mole% 8OCB are in the coexistence region. Coexistence of the two phases in pure DB₇OCN suggests non-equilibrium measurements and that the critical point lies at negative 8OCB concentrations. The dotted lines are drawn as an approximate outline of the observed coexistence of the A_d and A₂ phases. Note that the exact coexistence range cannot be determined due to its dependence on rate of cooling, long relaxation times, etc. Theoretically,

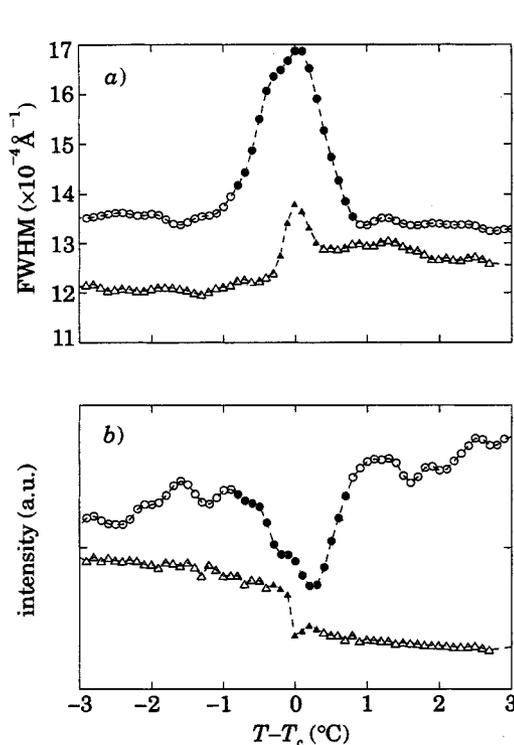


Fig. 4.

Fig. 4. – Temperature dependence of the a) peak width (FWHM) and b) peak intensity of the q' peak, which evolves into the q_0 peak, for 13.8 (circles) and 0.0 (triangles) mole% 8OCB in 8OCB + DB₇OCN mixtures. The FWHM for the 0.0% 8OCB sample has been shifted down for clarity by $1 \cdot 10^{-4} \text{ \AA}^{-1}$. The increase in peak width and the accompanying decrease in peak intensity near the A_d-to-A₂ transition are due to a coexistence of the two phases when the q' and q_0 peaks are not resolved. The temperature range (solid points, $T_c = 150.61 \text{ }^\circ\text{C}$ (circles), $T_c = 166.61 \text{ }^\circ\text{C}$ (triangles)) of this increase/decrease is used to estimate the coexistence region.

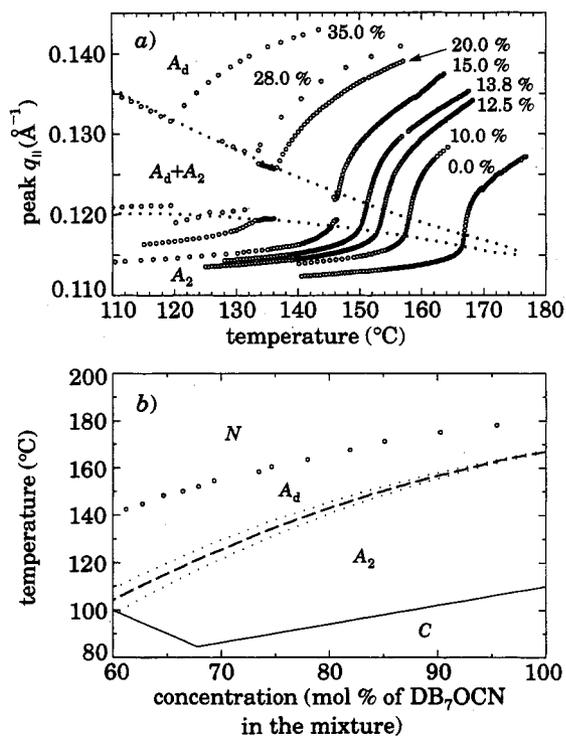


Fig. 5.

Fig. 5. – a) Wave vector q' and q_0 as a function of temperature for several 8OCB concentrations of system B. The coexistence of the A_d and A₂ phases is inferred from the simultaneous presence of the A₂ and A_d peaks with different mosaic and from increased width (●) of the peak. b) Phase diagram of system B replotted in terms of DB₇OCN concentration. The dotted curves define the boundaries of the A_d and A₂ coexistence and the dashed line in this region represents the first-order A_d-to-A₂ transition. Its resemblance with the upper halves of the phase diagram of system A and the theoretical phase diagram, fig. 1a) and b), respectively, is striking.

the coexistence of the A_2 and A_d phases should terminate at a critical point in much the same way as in a liquid-vapor phase diagram. Figure 5a) bears remarkable resemblance to the theoretical [5] wave vector-*vs.*-temperature graph. Similar coexistence of A_d and A_2 phases has previously been observed [14] in several other systems.

The phase diagram of system B has been redrawn in fig. 5b) with DB_7OCN concentration along the abscissa. The first-order A_d -to- A_2 phase transition, represented by a dashed line, now extends to 100% concentration. Topological similarity of this phase diagram with that of system A and the theoretical phase diagram, upper parts of fig. 1a) and b), is obvious.

In summary, we have shown that the incommensurate phases previously reported in $80BCAB + DB_8OCN$ and $DB_7OCN + 80CB$ mixtures are merely coexistences of two or more smectic phases. Since these were the only two systems reported to form the incommensurate smectic- A phases, there remain no such known phases. In the light of the results presented here, renewed theoretical and experimental efforts are necessary to predict and to search for them in more suitable materials.

* * *

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