Smectic-A Phase with Two Collinear Incommensurate Density Modulations

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The first observation of a smectic-A phase with two collinear incommensurate density modulations is reported. X-ray diffraction studies of this incommensurate phase reveal reflections corresponding to both partially bilayer (A_d) and bilayer (A_2) periodicities, the relative intensities of the two reflections being strongly temperature dependent.

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A smectic-A liquid crystal may be described as an orientationally ordered fluid with a one-dimensional mass-density wave along the optic axis.[1] When the constituent molecules possess a strongly polar end group several types of smectic-A phases exist, which can be characterized unambiguously by x-ray diffraction.[2] The monolayer A_1 phase exhibits a peak at a wave vector $2q_0 = 2\pi/l$, where l is approximately equal to the molecular length; in addition there may be diffuse scattering centered at a wave vector intermediate between q_0 and $2q_0$. The bilayer phase (A_2) is characterized by two reflections, the fundamental at q_0 and its second harmonic at $2q_0$. In the case of the partially bilayer A_d phase, there is a reflection at $q_0' = 2\pi/l'$, where $l < l' < 2l$, and, generally, a diffuse maximum centered at $2q_0$. There is also the fluid antiphase $\tilde{A}$ whose characteristic x-ray pattern consists of a spot at $2q_0$ and two spots displaced from the Z axis (optic axis) in a perpendicular direction situated symmetrically about the q_0 position.[3] Recent high-resolution x-ray studies[4] have shown the existence of two types of $\tilde{A}$ phases with rectangular lattices of different symmetries.

Although theoretically predicted,[5,6] a smectic-A phase with two incommensurate collinear periodicities has never been observed so far. The only case reported to date of a smectic with two coexistent incommensurate density modulations is the three dimensionally ordered smectic-E phase of 4-octyl-4′-cyanoterphenyl.[7] We present here the results of our x-ray studies on binary mixtures of 4-octyloxy-4′-cyanobiphenyl (8OCB) and 4-n-heptyloxyphenyl-4′-cyanobenzoyloxybenzoate (DB7OCN). The studies have revealed a new type of A phase (referred to here as A_{ic}) which intervenes between the A_d and A_2 phases and which has *two collinear incommensurate density modulations*, one of wavelength $2\pi/q_0'$ and the other of wavelength $2\pi/q_0$. The amplitude of the former modulation decreases with decreasing temperature while that of the latter increases, leading finally to a lockin transition to the A_2 phase.

The phase diagram of the binary system (obtained by a combination of optical and x-ray diffraction techniques) in the region of existence of the A_{ic} phase is shown in Fig. 1. For 8OCB molar concentrations (X) < 24%, there is only the A_d-A_2 transition which is clearly seen as an abrupt change in the slope of the curve of layer spacing (d) versus temperature (Fig. 2). We have taken x-ray diffraction photographs[8] for several concentrations as a function of temperature in the A_d, A_{ic}, and A_2 phases. The sample had to be cooled extremely slowly (less than 1 °C per hour) in order to obtain a monodomain of the A_{ic} phase. Microdensitometer traces of a series of representative photographs scanned along the Z axis (parallel to the director) for the $X = 34.8\%$ mixture are given in Figs. 3(a)–3(f). Starting from the A_d phase at 119 °C [Fig. 3(a)], we see a sharp peak at q_0'. On cooling, a second sharp peak is seen at q_0, in addition to that q_0' [Fig. 3(b)]. This signifies the onset of the incommensurate phase. On further decrease of temperature the intensity of the reflection at q_0' decreases while that at q_0 increases with an accompanying increase in the intensity of the second harmonic at $2q_0$. The switchover of the relative strengths of the q_0' and q_0 reflections is clearly seen in Figs. 3(c) and 3(d). Finally at 108 °C the peak at q_0' has disappeared altogether [Fig. 3(f)] leaving a

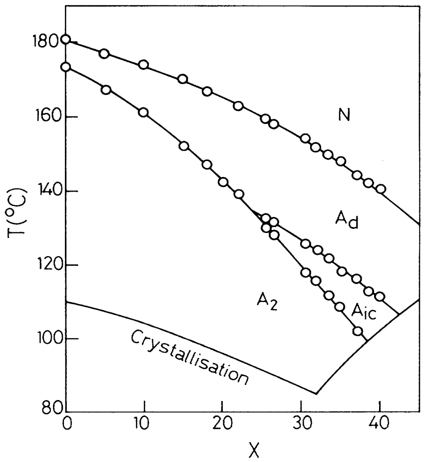

FIG. 1. Partial temperature-concentration (T-X) diagram for mixtures of 8OCB and DB7OCN. X is the mole percent of 8OCB in the mixture. The incommensurate A_{ic} phase intervenes between the partially bilayer (A_d) and bilayer (A_2) phases.

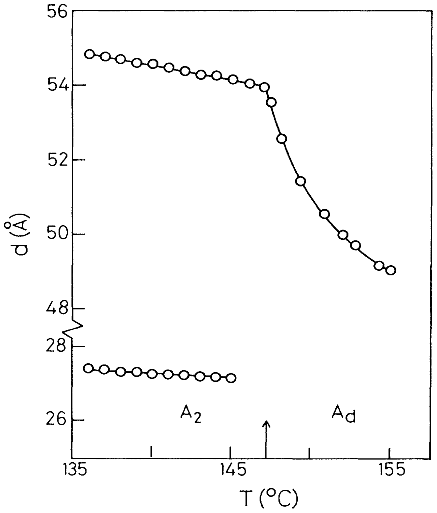

FIG. 2. Temperature variation of the layer spacing (d) in the A_d and A_2 phases of the $X=18\%$ mixture. The arrow represents the A_d-A_2 transition temperature.

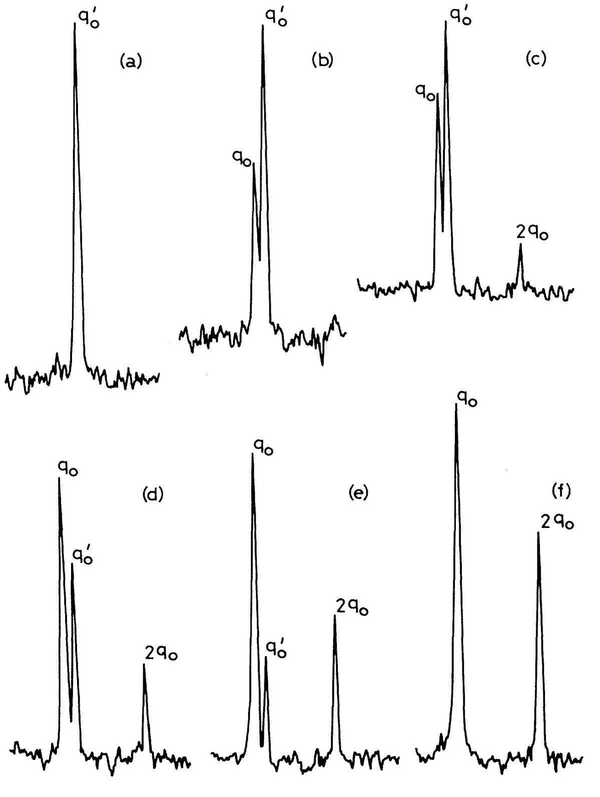

FIG. 3. Raw microdensitometer scans of the x-ray diffraction photographs taken for the $X=34.8\%$ mixture at different temperatures: (a) A_d phase, 119 °C; (b)-(e) A_{ic} phase, 117, 116, 114.5, and 112 °C, respectively; (f) A_2 phase, 108 °C. The wave vector corresponding to each reflection is marked. The direction of the scan is along the Z axis (optic axis) for all the photographs.

clear signature of the A_2 phase—strong reflections at q_0 and $2q_0$. It must be emphasized that regardless of their amplitudes, the sharpness of these reflections remains the same throughout at all temperatures. No reflections corresponding to combinations of q_0 and q_0' were recorded even with long exposures. [The setup did not allow very-low-angle reflections ($\theta < 0.5°$) to be recorded.] We have also verified from the high-angle diffraction maximum that the in-plane order is liquidlike in all the three phases.

Figure 4 gives the intensity contour diagram (obtained with an X-Y microdensitometer—Joyce-Loebl Scandig 3—in conjunction with an on-line computer) of the photograph taken for the $X=34.8\%$ mixture at 115.5 °C. Typical widths of the spots are 0.8×10^{-2} Å^{-1} in the Z direction and 1.7×10^{-2} Å^{-1} in the X direction. The larger width in the X direction arises from the geometry of the x-ray monochromator setup. However, it is evident that any displacement of the reflections along the X axis arising from a lateral periodicity of several hundred angstroms would at once be revealed in the contours. We therefore conclude that the three wave vectors are collinear along the Z axis.

The thermal evolution of the layer spacing corresponding to the different modulations in the A phases of the same mixture is shown in Fig. 5. The variations in the A_d and A_2 phases are similar to those seen for the 18% mixture (Fig. 2). In the A_{ic} phase, $2\pi/q_0'$ shows a marked decrease with decrease of temperature. Measurements of the layer spacing for a number of concentrations in the region of existence of the A_{ic}

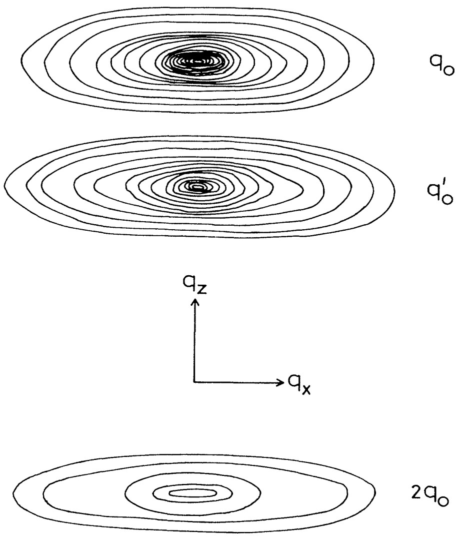

FIG. 4. Intensity contour diagram of a photograph taken for the $X=34.8\%$ mixture at 115.5 °C. Typical widths of the spots are $q_z=0.8\times10^{-2}$ Å^{-1} and $q_x=1.7\times10^{-2}$ Å^{-1}. The spot at $2q_0$ has been displaced (along Z) closer to the other spots for convenience of representation.

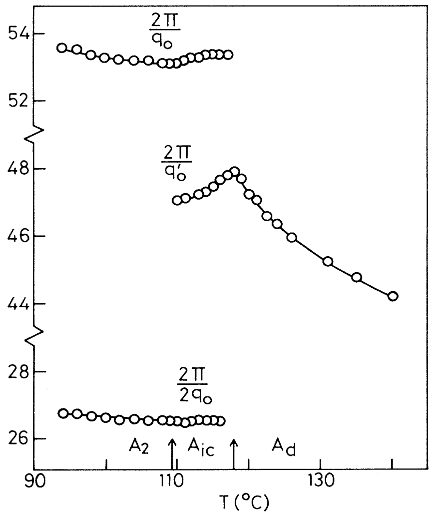

FIG. 5. Temperature variation of the layer spacing (d) in the A_d, A_{ic}, and A_2 phases of the $X = 34.8\%$ mixture. The wave vectors corresponding to the different periodicities are discussed in the text. The arrows indicate the temperatures of transition between the A phases.

phase have confirmed this behavior. This decreasing trend is exactly opposite to what one gets from a simple calculation of the layer spacing variation in the A_{ic} phase assuming it to be a two-phase region. Also, differential scanning calorimetry runs (taken with a Perkin-Elmer DSC-4 in conjunction with the Thermal Analysis Data Station) of the A_d-A_2 transition show a rapid decrease in the strength of the signal with increasing 8OCB concentration, and no signal is observable for $X \sim 20\%$ which is a few percent away from the concentration at which the A_{ic} phase makes its appearance. Even in the region where the A_{ic} phase exists, no signals were observed corresponding to the A_d-A_{ic} and A_{ic}-A_2 transitions. Thus the possibility of the A_{ic} phase being a two-phase region is ruled out.

Cladis and Brand[9] have recently observed an inverted cholesteric phase which appears as an island surrounded by different types of smectic-A phases in the temperature-concentration plane. These authors argued that their results imply that the coexistence of two percolating collinear density waves with different periodicities in a smectic-A phase is incompatible with the fluidity and order-parameter rigidity of the A phase. The present study shows that the A phase can support two incommensurate collinear periodicities over a range of temperature. Prost and Barois[5] have suggested two molecular models for the incommensurate A phase: Depending on the relative strengths of the elastic and lockin terms in the free-energy expansion, the incommensurate density modulations can coexist either by percolating through each other or as a multisoliton regime. Which of the two molecular models represents the A_{ic} phase remains to be settled. Clearly, further studies are needed for a complete understanding of this new phase.

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