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Joseph T. Mang  
*Kent State University - Kent Campus*

Brian Cull  
*Kent State University - Kent Campus*

Yushan Shi  
*Kent State University - Kent Campus*

Prem Patel  
*Kent State University - Kent Campus*

Satyendra Kumar  
*Kent State University - Kent Campus, skumar@kent.edu*

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True Incommensurate Phase in Mixtures of Two Polar Liquid Crystalline Materials

Joseph T. Mang, Brian Cull, Yushan Shi, Prem Patel, and Satyendra Kumar

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
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High-resolution x-ray scattering measurements of 23.0 and 28.4 mole % mixtures of TBBA in DB6 have led to the observation of a true incommensurate phase in a liquid crystal system. The phase is characterized by two primary quasi-Bragg reflections at incommensurate wave vectors. X-ray scattering measurements of a freely suspended film in the new phase have revealed that it possesses sixfold in-plane symmetry, suggesting it to be an incommensurate crystal-B or -E phase.

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Since the discovery by Sigaud, Hardouin, and Achard [1] of a phase transition between two smectic-A phases in a system of liquid crystal molecules possessing strong longitudinal dipole moments, considerable theoretical [2–4] and experimental [5–10] work has been carried out to study these polar compounds which are known as frustrated smectics. The mean-field theory of Barois, Prost, and Lubensky [2] was able to explain the phases formed by these systems and also predicted the existence of new phases including incommensurate phases. Subsequent x-ray studies of like systems led to the apparent discovery of the incommensurate A12 phase [8] in mixtures of DB7OCN + 80CB and the A1, A2, and soliton A1s phases [9] in mixtures of 80BCAB + DB8OCN. However, high-resolution x-ray studies [11–13] of these same systems have shown that these reported incommensurate phases are actually a coexistence of two or more phases. Recently, an incommensurate liquid crystal phase has also been reported [14] in a single component liquid crystal system. We have conducted a high-resolution x-ray diffraction study of mixtures of TBBA and DB6. We report here the discovery of a true incommensurate liquid crystalline phase, below the A2 phase, in mixtures of 23.0–28.4 mole % TBBA in DB6. The phase is primarily characterized by two incommensurate density waves, and it is found to possess sixfold in-plane positional order.

The mean-field theory [2] which describes frustrated smectic systems involves two order parameters, \( \Psi_i(r) = |\Psi_i(r)| e^{i\mathbf{q}_i \cdot \mathbf{r}} \) (\( i = 1, 2 \)). One of the density waves, \( \Psi_1(r) \), is associated with the long-range head-to-tail arrangement of polar molecules and the other, \( \Psi_2(r) \), is associated with the usual mass density modulation of a smectic-A (A) phase. In general, the wave vectors \( \mathbf{q}_1 \) and \( \mathbf{q}_2 \) are not collinear or commensurate. In the absence of coupling between them, the order parameters would condense at their natural wave vectors \( k_1 = 2\pi/l' \) and \( k_2 = 2\pi/l \), where \( l' \) is the length associated with an antiferroelectrically ordered pair of molecules and \( l \) is the length of a molecule. The importance of the coupling terms in the free-energy expansion depends upon the relative size of \( l' \) and \( l \). The coupling terms, \( \Psi_1 \Psi_1^* \) and \( \Psi_2 \Psi_2^* \), favor lock-in of the two wave vectors at \( q_1 = q_2 \) and \( q_1 = q_2/2 \), respectively. The extent of this coupling and the elastic energy of the system account for the observed polymorphism in compounds with molecular constituents of different lengths.

Within this theoretical framework, several phases are expected to form. With \( |\Psi_1| = |\Psi_2| = 0 \), no smectic order exists and the nematic phase is found. The monolayer smectic-A1 (A1) phase is formed when the mass density modulation develops, \( |\Psi_1| = 0, |\Psi_2| \neq 0 \) with \( q_2 = k_2 \). If both a mass density and a polarization wave develop (i.e., \( |\Psi_1| \neq 0, |\Psi_2| \neq 0 \)), either of the two following cases can occur: If \( l' = l \), the cubic coupling term requires \( q_2 = 2q_1 = 2\pi/2l \) and the bilayer smectic-A2 (A2) phase is formed, but if \( l' < l \), then the partial bilayer smectic-A3 (A3) phase is obtained. The frustration in the system caused by the competition of the two order parameters can be relieved by the formation of other phases (e.g., \( \tilde{A}, \tilde{C} \), etc.) in which the two density modulations do not remain collinear. Alternatively, if the two wave vectors are collinear but the ratio of the two wave vectors \( k_2/k_1 \) cannot be expressed as a ratio of two integers, then an incommensurate phase forms. Several incommensurate phases are predicted. The strength of the coupling between the two order parameters determines which one will form. When the coupling is weak, two interpenetrating density waves can coexist throughout the system, forming either the smectic-A11 or smectic-A22 phase. On the other hand, if the coupling is strong, the soliton smectic-A1s phase is formed. In this phase, soliton-like regions of two interpenetrating modulations separate A2 type lock-in regions.

Several concentrations of the TBBA-DB6 system, above and below the expected A1-A2 tricritical point, have been extensively studied using the x-ray scattering technique [10]. We have performed high-resolution x-ray scattering experiments on concentrations ranging from 0.0 to 28.4 mole % TBBA in DB6. In this Letter, we focus on the 23.0 and 28.4% mixtures which have led to the discovery of a new phase which is a true incommensurate phase, but not one of the phases predicted by the theory.

The experiments were performed using a Rigaku 18 kW rotating anode x-ray generator with a copper
target which is described in detail elsewhere [11]. A pair of Ge(111) single crystals were used to obtain high resolution; $\Delta q_0 = 4 \times 10^{-4}$ Å$^{-1}$, $\Delta_{q_4} = 2 \times 10^{-5}$ Å$^{-1}$, and $\Delta_{q_5} = 4 \times 10^{-2}$ Å$^{-1}$. Mixtures of TBBA and DB6 were prepared by vigorous stirring and then degassing by a repeated freeze-melt cycle under vacuum. The samples were then sealed between two 8 µm thick Mylar sheets and a 1.5 mm thick and 6 mm inner diam Teflon O ring. The samples were aligned, in the presence of a 2.5 kG magnetic field, by slow cooling from the nematic phase. The sample temperature was kept stable to better than 10 mK. Longitudinal ($q_0$) and $\omega$ scans were performed to determine the structure and sample mosaicity at different temperatures. Mosaic scans are important in determining if the given reflections arise from the same scattering volume and not due to a coexistence of phases.

A plot of scattering vectors, corresponding to various quasi-Bragg peaks, as a function of temperature is shown in Fig. 1(a) for the 23.0% sample. In the figure, the solid points indicate the most (condensed) intense peaks. The graph shows the appearance of a single quasi-Bragg peak, at $2q_0 = 0.2318$ Å$^{-1}$, and its faint second harmonic in the A$_1$ phase. At 119.79 °C, the system undergoes an abrupt change to the A$_2$ phase as witnessed by the appearance of quasi-Bragg peaks at two commensurate wave vectors, $q_0 = 0.1160$ Å$^{-1}$ and $2q_0 = 0.2320$ Å$^{-1}$. The faint higher-order harmonic at 0.4640 Å$^{-1}$ is still present. At 104.71 °C, an unexpected, discontinuous phase transition was observed to a new phase which is characterized by condensed peaks at two incommensurate wave vectors, $q_1 = 0.1211$ Å$^{-1}$ and $q_2 = 0.2257$ Å$^{-1}$. Also visible are five other peaks at $q$ values corresponding to $q_2 - q_1$, $q_2 + q_1$, $2q_1$, $3q_1$, and $2q_2$. The system continues in this new phase until 91.20 °C, where it undergoes a transition to a crystalline phase. High-resolution $q_\parallel$ and $\omega$ scans were performed for all seven reflections in the new phase. The results of these scans as well as a comparison of peak intensities can be seen in Figs. 2 and 3 and Table I. A shoulder is visible in the longitudinal scan of the $q_2$ peak shown in Fig. 2. The origin of this shoulder is the splitting of the Kα line. A similar shoulder is apparent in the $2q_0$ peak of the A$_1$ and A$_2$ phases. At small values of $q$, the splitting is unresolved, as evidenced by the scan of $q_1$ (Fig. 2), while the splitting is more apparent for higher-order reflections, as expected. The mosaic scans of the two (incommensurate) primary peaks and the three harmonics are similar, indicating that they arise from the same scattering volume (mosaic scans performed for the $q_0$ and $2q_0$ peaks and the higher-order harmonic in the A$_2$ phase were identical). However, the mosaics of the $q_2 + q_1$ and $q_2 - q_1$ reflections are very different from those of the other reflections. The intensity levels of these reflections are three orders of magnitude smaller (Table I) than the primary reflections, making it evident that they contain a large multiple-scattered component.

Evidence of the transition from the A$_2$ to this new phase is also apparent in differential scanning calorimetry.

![Figure 1](image1.png)

**FIG. 1.** Temperature dependence of the scattering vectors in the different phases of the (a) 23.0 and (b) 28.4 mole% mixtures of TBBA in DB6. Both concentrations exhibit the incommensurate phase. The primary (intense) reflections are denoted by solid symbols.

![Figure 2](image2.png)

**FIG. 2.** $q_1$ and mosaic scans for the primary reflections (23.0%) of the incommensurate phase at $T = 100.32$ °C. The mosaic scans are identical proving that the Bragg reflections are arising from the same domains. The $q_\parallel$ scan of $q_2$ shows a shoulder due to $K\alpha_2$. 
(DSC) measurements, and polarizing microscopy reveals a change in the texture at the appropriate temperature. High-resolution x-ray studies have revealed significant in-plane order in this phase suggesting that it is not a smectic-A phase, but a more ordered smectic. In order to make a more complete identification of this phase, a freely suspended film of the 23.0% sample was prepared and low-resolution powder x-ray scattering measurements performed which revealed seven easily detectable reflections, ruling out the presence of the hexatic-B phase. Figure 4 shows the result of a \( \chi \) scan at the brightest reflection \( q = 1.36 \text{ Å}^{-1} \) 92.80°C in the new phase. Six equally spaced peaks are clearly visible, indicating that the system possesses sixfold in-plane symmetry (albeit with multidomain structure) and confirming that the new phase is likely to be the crystal-B or -E phase.

Figure 1(b) shows a plot of scattering vector versus temperature for a 28.4 mole% sample which appears similar to that of the 23.0% mixture, except for the obvious shifts in transition temperatures. Indeed, this concentration shows the same phase sequence as the 23.0% mixture, undergoing the \( A_1-A_2 \) transition at \( T = 112.67°C \) and then entering the incommensurate phase at 97.89°C with a temperature range of \( \sim 12 \) K. The phase behavior, however, was somewhat different. In the present mixture, the \( A_2 \) phase appeared to be influenced by the proximity of the incommensurate phase. While \( A_2 \) fluctuations first appeared in the form of a broad peak centered around \( q_0 = 0.1174 \text{ Å}^{-1} \) at 112.67°C, the \( q_0 \) peak did not condense as is typical. Instead, the reflection remained weak, showing a modest increase in intensity.

### TABLE I

Comparison of peak positions and intensity for the seven peaks found in the incommensurate phase of both the 23.0 and 28.4 mole% samples. The strongest and weakest peaks differ in intensity by three orders of magnitude.

<table>
<thead>
<tr>
<th>Peak Position (Å(^{-1}))</th>
<th>(q_2 - q_1)</th>
<th>(q_1)</th>
<th>(q_1)</th>
<th>(2q_1)</th>
<th>(q_1 + q_2)</th>
<th>(3q_1)</th>
<th>(2q_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity (10(^5) m counts/s)</td>
<td>0.1044</td>
<td>0.1212</td>
<td>0.2256</td>
<td>0.2422</td>
<td>0.3463</td>
<td>0.3633</td>
<td>0.4510</td>
</tr>
<tr>
<td>Intensity (10(^5) m counts/s)</td>
<td>23.0%</td>
<td>280</td>
<td>132 000</td>
<td>88 400</td>
<td>1400</td>
<td>140</td>
<td>240</td>
</tr>
<tr>
<td>Intensity (10(^5) m counts/s)</td>
<td>28.4%</td>
<td>360</td>
<td>99 300</td>
<td>118 500</td>
<td>1150</td>
<td>210</td>
<td>205</td>
</tr>
</tbody>
</table>
over almost 15 K before condensing at \( q_1 = 0.1212 \text{ Å}^{-1} \) in the new incommensurate phase. Figure 5 shows a longitudinal scan at 94.82°C in the new phase which exhibits the same seven scattering peaks as the 23.0% sample, indicating that it is in fact the same phase. The peak intensities are summarized in Table I. Mosaic scans of these quasi-Bragg peaks were performed and again found to be identical, with slight differences (possibly due to multiple scattering and the splitting of \( K_1 \) and \( K_2 \)) for the five primary peaks.

In summary, we have found an incommensurate phase below the \( A_2 \) phase in 23.0 and 28.4 mole% mixtures of TBBA in DB6 which exists over a wide concentration range (at least \(-23.0 \text{ to } 28.4 \text{ mole%})\). Mosaic scans of the Bragg peaks have confirmed that the observed reflections are arising from the same phase and are truly incommensurate. Evidence for this new phase is also found in DSC and polarizing microscopy measurements. X-ray scattering measurements on a freely suspended film show that the new phase possesses sixfold in-plane symmetry and is most probably a crystal-\( B \) or -\( E \) phase. Further studies are planned in order to determine the complete and high-precision phase diagram of this system.

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