

## Novel Liquid-Crystal Phase Diagram: An Inverted Cholesteric Phase Surrounded by Different Types of Smectic-*A* Phases

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We report the first observation of a cholesteric phase which appears as an island surrounded by smectic-*A* phases in a temperature-concentration phase diagram. The island of cholesteric form results from large fluctuations of two, collinear, incommensurate density waves whose coexistence violates smectic-*A* ordering. It provides novel evidence that smectic-*A* fluidity cannot support two incommensurate lengths.

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Here we describe a novel and unexpected phase diagram where a closed loop of a phase with higher symmetry (cholesteric) is found in the vicinity of the critical point between phases of the same symmetry (smectic *A*). We argue that the cholesteric island results because the coexistence of two collinear density waves with very different periodicities (an incommensurate smectic-*A* phase) is incompatible with the fluidity and order-parameter rigidity of a smectic-*A* phase.

When a molecular liquid is in the isotropic phase it has neither translational nor orientational ordering. In the nematic (and cholesteric)<sup>1</sup> phase, the system selects a special direction,  $\vec{n}$ . Nematic liquid crystals are anisotropic. A one-dimensional density wave parallel to  $\vec{n}$  breaks the nematic symmetry and defines the smectic-*A* phase. One-dimensional translational order does not exist in an infinite system,<sup>2</sup> but in finite systems, the smectic-*A* layer spacing is well defined. Smectic-*A* layers may bend but the distance between layers must remain constant. This has been referred to as order-parameter rigidity.<sup>3</sup> Symmetry-breaking transitions, such as the nematic-smectic-*A* transition, may be of first or second order. Their transition line can never end because symmetry cannot change continuously.<sup>2,3</sup>

Even though a fundamental understanding of the nematic-smectic-*A* transition still eludes us,<sup>4</sup> it is a common transition in liquid crystals. As it turns out, there are many varieties of smectic-*A* phases<sup>5</sup> differing only in the magnitude of the layer spacing,  $d$ , relative to the molecular length,  $l$ . In one smectic *A*, called  $A_D$ ,  $d/l$  is less than 2 but greater than 1. In another one,  $d/l \leq 1$  and this we call  $A_I$ . There is the same symmetry in the two *A* phases as, for example, at the liquid-gas or Mott metal-insulator transition. A line of first-order transitions between two phases of the same symmetry can, and frequently does, end at a critical point where "the transition simply disappears."<sup>2,3</sup> By observing the

passage of the  $A_D$ - $A_I$  transition line towards its critical point where large fluctuations of collinear but incommensurate lengths compete for control of the smectic-*A* layering, we found the surprising result that the smectic-*A* phase was destroyed (see Fig. 1).

Figure 1 shows a line of first-order phase transitions between the  $A_D$  and  $A_I$  phases ending at a higher-order critical point. Surprisingly, extending above this critical point is a cholesteric island. Indeed, being of broken symmetry, the cho-

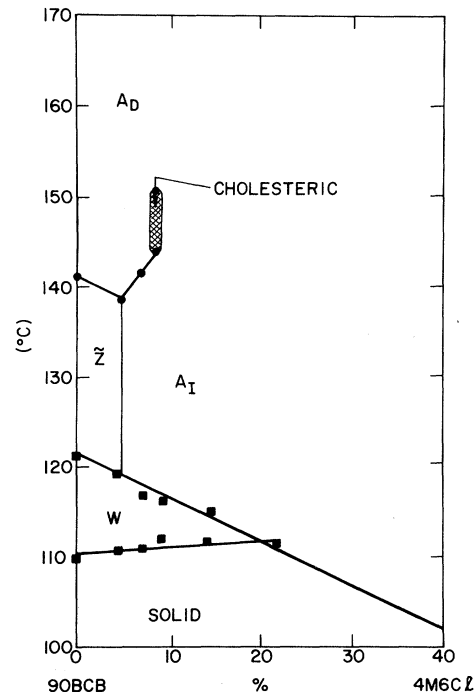


FIG. 1. Partial phase diagram for mixtures of 9OBCB and 4M6Cl showing the cholesteric island which emerges in the vicinity of the smectic- $A_D$ -smectic- $A_I$  critical point. The transition from the solid to the liquid-crystal phase called *W* is the melting transition.  $\tilde{Z}$  is a biaxial liquid-crystal phase. The abscissa is weight percent of 4M6Cl.

lesteric-smectic- $A$  transition line has no end! We call the island an inverted, rather than reentrant,<sup>6</sup> cholesteric phase because it is topologically disconnected from a higher-temperature cholesteric phase.

Figure 1 also shows a biaxial phase we call  $\tilde{Z}$  which is characterized by a two-dimensional (2D) periodic structure with two incommensurate lengths,  $d_1$  and  $d_2$ ;  $d_1 \leq l$  and  $d_2 > l$ .  $d_1$  is about the same length as the smectic- $A_I$  layer spacing and  $d_2$  is similar to the smectic- $A_D$  layer spacing. A 2D analog of  $\tilde{Z}$  has recently been found by modulating a periodic array of electrohydrodynamic rolls with a spatially periodic perturbation having a different length scale.<sup>7</sup> Phases similar to  $\tilde{Z}$  have been observed in other compounds<sup>8</sup> and have been proposed to result from the competition between two incommensurate lengths.<sup>9</sup> The coexistence of two, noncollinear lengths is at the expense of additional symmetry breaking:  $\tilde{Z}$  is periodic in 2D and fluid in 1D<sup>10,11</sup>; smectic  $A$  is periodic in 1D and fluid in 2D. Another kind of structure has been proposed where two, collinear lengths coexist without a change in smectic- $A$  symmetry, an incommensurate smectic- $A$  phase.<sup>9</sup> Figure 1 does not support this idea but suggests that the competition between two length scales in a phase as fluid as smectic  $A$  always engenders a change in symmetry: the cholesteric/nematic phase when collinear and  $\tilde{Z}$  when noncollinear.

The materials we chose are 9OBCB (nonyloxybiphenyl cyanobenzoate) and its mixtures with 4M6Cl [1-4 di(4-methylhexyloxybenzoate) 2-chlorophenyl]. Using differential scanning calorimetry (DSC) we determined the first-order transition lines ( $A_D$ - $A_I$ ,  $A_I$ -inverted-cholesteric) and verified the high purity of the materials under investigation. The actual traces will be presented in a more detailed account of the present work.<sup>12</sup> From optical microscopy, we evaluated the nearly second-order  $A_D$ -inverted-cholesteric and the first-order  $A_I$ -inverted-cholesteric transition lines. X-ray diffraction enabled us to distinguish  $A_D$  ( $d/l > 1$ ),  $A_I$  ( $d/l \leq 1$ ), and the inverted-cholesteric phase.

Perhaps the most dramatic way of observing the overall topology of this phase diagram is in a "contact preparation" where a planar interface is prepared between a drop of 9OBCB and 4M6Cl (see Fig. 2). We observe this preparation in the polarizing microscope while cooling slowly from the isotropic phase (above 240 °C) through a high-temperature cholesteric phase (above  $\sim 190$  °C) to the smectic- $A_D$  phase which looks black between crossed polarizers because its optic axis is parallel to

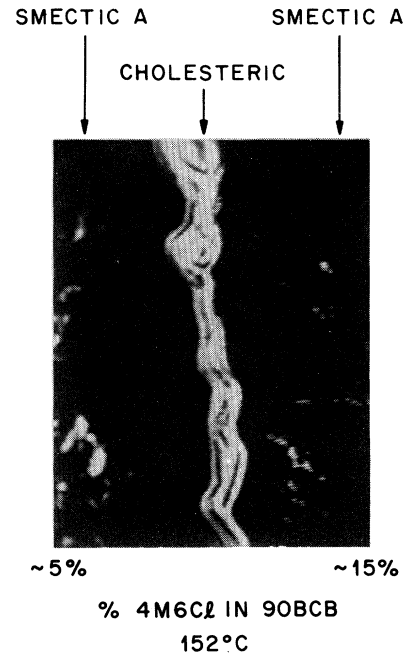


FIG. 2. Photomicrograph of a drop of 9OBCB in contact with 4M6Cl at a linear interface of 152 °C. This method of sample preparation produces a concentration gradient parallel to the horizontal axis of the photograph which can be estimated so that specific mixtures can be made for x-ray diffraction, DSC, and other studies. The black regions are smectic  $A$  and the bright ribbon is a large-pitch ( $\approx 20 \mu\text{m}$ ) cholesteric phase. Magnification is  $65\times$ .

the microscope axis. The transition  $A_D$ - $A_I$  cannot be detected by optical microscopy because the density waves of both phases are collinear with each other and with the optic axis. At 152.2 °C, a bright, thin ribbon of cholesteric running parallel to the contact line suddenly emerges in the middle of the black field of smectic  $A$  (see Fig. 2). The cholesteric phase is identified both by its characteristic texture in the optical microscope and by the absence of sharp peaks, which indicate layering, in x-ray diffraction. Upon further cooling, the ribbon first broadens and then narrows and disappears at 140 °C. A detail to be noted is that the inverted phase is nematic if we use the racemate rather than the chiral species of 4M6Cl. The advantage of a chiral dopant is the greater optical contrast between cholesteric and smectic- $A$  phases compared to nematic and smectic- $A$  phases. In the latter case, the inverted phase appears black in the optical microscope and it is quite difficult to distinguish it from the smectic- $A$  phases. The selected concentrations we made for DSC, x-ray, and optical microscopy are shown as points in Fig. 1.

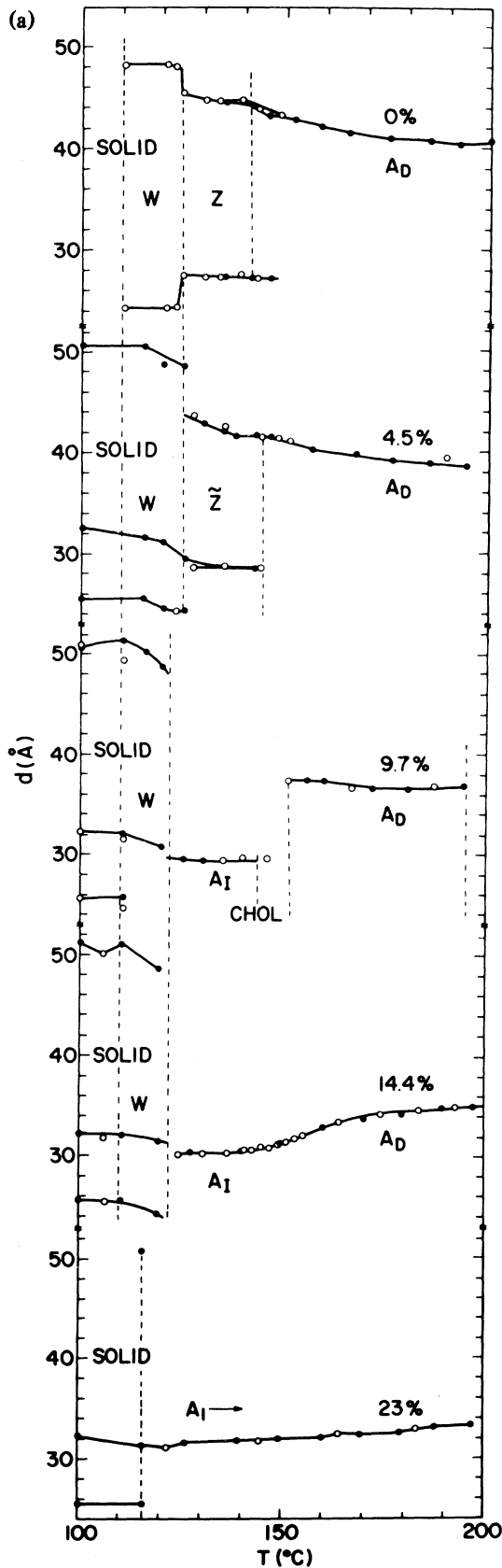


Figure 3(a) shows that the measured layer spacing in the smectic- $A$  phase at 0% and 4.5% 4M6Cl in 9OBCB is greater than the mean molecular length of the appropriate mixture of 9OBCB (31 Å) plus 4M6Cl (34 Å). This observation identifies the  $A_D$  phase. At 7% 4M6Cl [Fig. 3(b)], the  $\tilde{Z}$  phase is gone and smectic  $A_D$  transforms discontinuously to smectic  $A_I$ . At this transition the layer spacing jumps discontinuously from a value greater than the mean molecular length to a value less than the mean molecular length, identifying the lower-temperature phase as  $A_I$ . The  $A_D$ - $A_I$  transitions are not readily observed in the optical microscope as mentioned above because both density waves are collinear with each other and with the optic axis. In the 9.7% sample, the  $A_D$  and  $A_I$  phases are separated by the cholesteric island and at 14.4% there is no longer an  $A_I$ - $A_D$  transition: The layer spacing varies continuously with increasing temperature from very slightly below to very slightly above the mean molecular length.

In pure 9OBCB, the smectic- $A$  phase chooses a length  $d_2$  ( $> 40$  Å) larger than the molecular length ( $l = 31$  Å). Adding 4M6Cl ( $l = 34$  Å) alters the microscopic interactions such that a smectic- $A$  phase with periodicity  $d_1$  ( $\approx 29$  Å) smaller than the molecular length is more stable at lower temperatures and the system transforms from the higher-temperature  $A_D$  to the lower-temperature  $A_I$  phase via a line of first-order phase transitions. Approaching the higher-order critical point, competition between the two density waves becomes

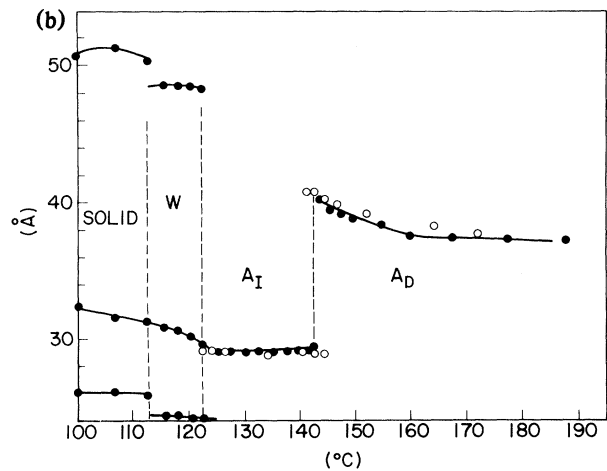


FIG. 3. (a) Layer spacing vs temperature of the selected mixtures shown in Fig. 1. (b) Layer spacing vs temperature of 7% 4M6Cl in 9OBCB showing discontinuity at the  $A_D$ - $A_I$  transition.

stronger leading to large fluctuations. The smectic- $A$  phase can only choose a single length since the simultaneous enforcement of two largely different periodicities is incompatible with the 2D fluidity of smectic  $A$ . Essentially, the out-of-layer microscopic displacements necessary to follow first one, then a second, density wave compromises order-parameter rigidity. The broken symmetry is restored and a phase without a density wave emerges.

Forcing smectic  $A$  to choose between two very different lengths has resulted in additional symmetry changes: either the  $\tilde{Z}$  phase or cholesteric/nematic phase, indicating that smectic- $A$  order is too fragile to survive frustration. We found no evidence to support the notion of Prost and Barois<sup>9</sup> that two incommensurate, collinear 1D lattices can coexist by percolating through each other without additional symmetry changes. This is expected since such a notion violates order-parameter rigidity. When driven to choose between two very different lengths, Fig. 1 shows that layering is destroyed and the inverted cholesteric/nematic phase occurs.

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<sup>1</sup>Nematics and cholesterics are thermodynamically the same phase. In general, in a cholesteric liquid crystal,  $\vec{n}$  twists with a constant pitch much greater than a molecular length  $\approx 25 \text{ \AA}$ . A nematic is the special case where the pitch is infinite. The smectic- $A$  layering is typically on a scale of a molecular length. The pitch of the cholesteric phase in this paper is  $\geq 20 \mu\text{m}$ .

<sup>2</sup>L. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980), Vol. 5, p. 258.

<sup>3</sup>For a recent summary of Landau's symmetry arguments, see P. W. Anderson, in *Symmetries and Broken Symmetries in Condensed Matter Physics*, edited by N. Boccaro (IDSET, Paris, 1981).

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<sup>7</sup>M. Lowe, J. C. Gollub, and T. C. Lubensky, *Phys. Rev. Lett.* **51**, 786 (1983).

<sup>8</sup>F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, *J. Chim. Phys.* **80**, 53 (1983).

<sup>9</sup>J. Prost and P. Barois, *J. Chim. Phys.* **80**, 65 (1983).

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<sup>11</sup>F. B. Rosevear, *J. Am. Oil. Chem. Soc.* **31**, 628 (1954).

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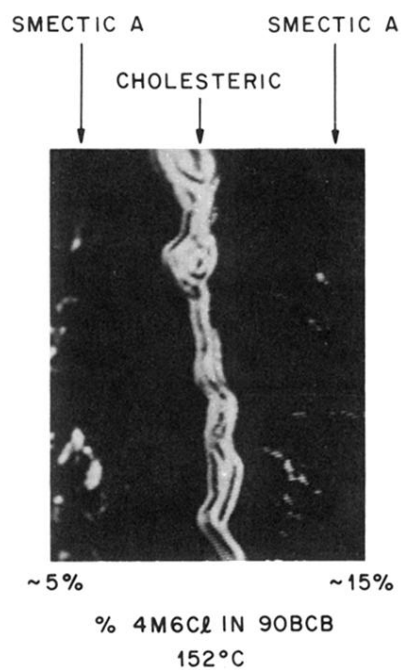


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