

## Smectic- $A_d$ -Smectic- $A_2$ Critical Point

R. Shashidhar, B. R. Ratna, S. Krishna Prasad, and S. Somasekhara  
*Raman Research Institute, Bangalore 560080, India*

and

G. Heppke  
*Technical University of Berlin, D-1000 Berlin 12, Germany*  
 (Received 24 February 1987)

The first observation of the smectic- $A_d$ -smectic- $A_2$  critical point is reported. Detailed x-ray studies show that a first-order phase transition between the partially bilayer smectic- $A_d$  and the bilayer smectic- $A_2$  phases which have the same symmetry terminates in a critical point in the temperature-concentration plane.

PACS numbers: 64.70.Md, 64.70.Fx

The smectic- $A$  phase can be characterized as a one-dimensional density wave in an orientationally ordered fluid.<sup>1,2</sup> When the constituent molecules are symmetric only one type of smectic- $A$  phase occurs, viz., the monolayer  $A_1$  phase in which the periodicity of the density wave (or the layer spacing  $d$ ) is approximately equal to the molecular length ( $l$ ). When the molecules have a strongly polar end group, several types of  $A$  phases are seen.<sup>3</sup> In addition to the monolayer  $A_1$  phase, there are the partially bilayer  $A_d$  phase, the bilayer  $A_2$  phase, and the incommensurate  $A_{ic}$  phase.<sup>4</sup> They can be identified unambiguously on the basis of the x-ray diffraction patterns obtained from monodomain samples. The  $A_1$  phase gives a strong diffraction maximum (quasi-Bragg peak) at a wave vector  $2q_0 = 2\pi/l$ ; the  $A_2$  phase two maxima, the fundamental at  $q_0$  and the second harmonic at  $2q_0$ . The  $A_d$  phase also has two maxima, these being at  $q'_0 = 2\pi/l'$  (where  $l < l' < 2l$ ) and  $2q'_0$ . In addition, a diffuse maxima centered around  $2q_0$  is seen in the  $A_d$  phase.

The smectic- $A$  polymorphism exhibited by the terminally polar compounds has been successfully explained in terms of a phenomenological model.<sup>5-8</sup> More recently, the nature of the  $A_d$  phase and its relation to the  $A_1$  and  $A_2$  phases were examined theoretically by Barois, Prost, and Lubensky.<sup>9</sup> They used the phenomenological model within the framework of the mean-field theory to study phase diagrams as well as x-ray scattering intensities. It has been argued that, the symmetries of the  $A_d$  and  $A_2$  phases being identical, there cannot be a second-order phase transition between them. (These arguments should, in principle, be valid for the  $A_1$ - $A_d$  transition also. The  $A_1$ - $A_2$  transition can, however, be second order<sup>10</sup> because of the exact doubling of the layer periodicity.<sup>11</sup>) The theory of Barois, Prost, and Lubensky<sup>9</sup> also predicts that a first-order phase boundary along which the  $A_d$  and  $A_2$  phases coexist can terminate at a critical point similar to the gas-liquid critical point. There have been some experimental attempts<sup>12-14</sup> to observe the  $A_d$ - $A_2$  critical point, but they have so far remained un-

successful.

We present in this Letter the results of our miscibility and x-ray studies on binary mixtures of 4- $n$ -undecyloxyphenyl-4'-(4''-cyanobenzyloxy) benzoate (or 11OPCBOB) and 4- $n$ -nonyloxybiphenyl-4'-cyanobenzoate (or 9OBCB) which have led to the first observation of the  $A_d$ - $A_2$  critical point (CP). We show that the first-order  $A_d$ - $A_2$  transition characterized by a jump in the wave vectors terminates at a CP in the temperature-concentration plane. We also show that the width of the coexistence region associated with the  $A_d$ - $A_2$  transition, as well as the difference in the wave vectors at the transition, goes to zero at a CP.

The phase diagram of the 11OPCBOB-9OBCB binary system is shown in Fig. 1. This diagram has been obtained by observing under a polarizing microscope the optical textures exhibited by the different phases. It is seen that for the mole fractions of 11OPCBOB ( $X$ ) less than 0.52, the ribbon phase  $\tilde{C}$  intervenes between the  $A_d$  and  $A_2$  phases. However, with increasing  $X$  the  $\tilde{C}$  gets suppressed leading to a direct  $A_d$ - $A_2$  transition which is seen optically as a readjustment of the focal conic texture. We shall show in the following that the first-order  $A_d$ - $A_2$  transition terminates at a critical point (CP) in the temperature-concentration plane.

The results of x-ray studies for a number of concentrations on either side of CP are shown in Fig. 2. These high-precision data were obtained using a computer controlled Guinier diffractometer (Huber model 644). Cu  $K\alpha_1$  and  $K\alpha_2$  lines were separated by using a bend quartz monochromator in the Johansson geometry and only the  $K\alpha_1$  line was used for the experiment. The sample filled in a Lindemann glass capillary (0.5 mm in diameter) was oriented by slow cooling from the nematic to the  $A_d$  phase in the presence of a 2.4-T magnetic field. The oriented sample was then transferred along with the temperature controlled oven to the goniometer of the diffractometer. Temperatures were held constant to  $\pm 5$  mK or better during any measurement of the Bragg angle  $\theta$ . The precision in the determination of the wave

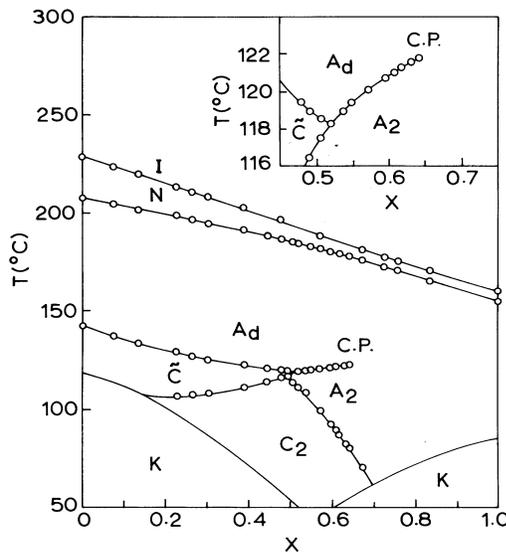


FIG. 1. Temperature-concentration ( $T$ - $X$ ) diagram for the binary mixtures of 11OPCBOB in 9OBCB.  $X$  is the mole fraction of 11OPCBOB in the mixture. The  $A_d$ - $A_2$  transition terminates at the critical point (CP). The phase diagram in the vicinity of CP is shown in the inset on an enlarged scale:  $K$ , crystalline;  $N$ , nematic;  $I$ , isotropic;  $\bar{C}$ , bidimensional ribbon (Ref. 15); and  $C_2$ , bilayer  $C$  phases (Ref. 15).

vectors characterizing the  $A_d$  and  $A_2$  phases was  $\pm 2 \times 10^{-4} \text{ \AA}^{-1}$ .

The x-ray diffraction pattern in the  $A_d$  phase was found to consist of quasi-Bragg peaks at wave vectors  $q'_0$  and  $2q'_0$ , while that in the  $A_2$  phase showed peaks at  $q_0$  and  $2q_0$  (Fig. 2). We also sometimes observed, depending on the mosaicity of the aligned sample, diffuse scattering centered around  $2q_0$  in the  $A_d$  phase. The signature of the  $A_d$ - $A_2$  transition was a two-phase region whose diffraction pattern consisted of both  $q_0$  and  $q'_0$ , as well as the wave vectors corresponding to the second harmonic [Fig. 2(b)]. This is exactly as is expected and indeed seen earlier<sup>16</sup> for a first-order transition between two smectic phases with different layer periodicities. Figure 3 gives the temperature variation of  $q_0$  and  $q'_0$  for binary mixtures with  $X=0.550, 0.571, 0.597, 0.619, 0.642, 0.715, 0.80,$  and  $1.0$  (or 11OPCBOB). For all  $X < 0.642$ , the  $A_d$ - $A_2$  transition is seen. Figure 3 also shows the data in the coexistence region. It is seen that the variations of  $q'_0$  and  $q_0$  in this region are nothing but continuations of the trends in the variation of the wave vectors in the  $A_d$  and  $A_2$  phases, so much so, we can associate a jump in the wave vector at the  $A_d$ - $A_2$  transition. (Exactly similar results have been obtained for the wave vector of the second harmonic also, but these will not be discussed here.)

It is clear from Fig. 3 that the magnitude of the wave vector jump which is about  $0.0037 \text{ \AA}^{-1}$  (this corresponds to a layer spacing change of  $2 \text{ \AA}$ ) for  $X=0.550$ ,

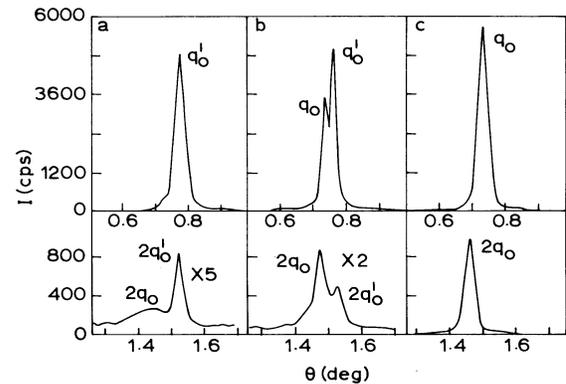


FIG. 2. Raw diffractometer scans taken along the equatorial direction ( $q_{\perp}=0$ ) for the  $X=0.608$  mixture showing the x-ray scattered intensity  $I$  (counts per second) as a function of the scattering angle ( $\theta$ ). (a)  $A_d$  phase,  $T=121.5^{\circ}\text{C}$ . The quasi-Bragg peaks are at  $q'_0$  and  $2q'_0$ ; the latter one is seen overriding on the diffuse scattering centered around  $2q_0$ . (b) Two-phase region ( $T=121.1^{\circ}\text{C}$ ) showing the coexistence of  $q_0$  and  $q'_0$  as well as of  $2q_0$  and  $2q'_0$ . (c)  $A_2$  phase ( $T=120.3^{\circ}\text{C}$ ) with the diffraction peaks at  $q_0$  and  $2q_0$ . The intensities of the second harmonics in (a) and (b) have been multiplied by a factor of 5 and 2, respectively.

decreases with increasing  $X$  with an accompanying decrease in the width of the two-phase region until at  $X=0.642$ , no jump is seen within the resolution of our experimental setup. Instead, a "vertical inflection point" is observed for this concentration. All these features—the shrinking of the two-phase coexistence region associated with the first-order  $A_d$ - $A_2$  transition and the accompanying decrease in the difference between  $q_0$  and  $q'_0$  at the transition, the vertical inflection point—are clearly indicative of the existence of a critical point at  $X=0.642$ . For higher  $X$  values, the inflection point becomes less pronounced as is expected on moving away from the critical point and  $A_2$  evolves continuously from the  $A_d$  phase without a phase transition. Thus, we have shown that two smectic- $A$  phases with different layer spacings can coexist along a line (of first-order transitions) terminating at a critical point beyond which the distinction between the two phases ceases to exist.

The mean-field theory of Barois, Prost, and Lubensky<sup>9</sup> had initially suggested that the  $A_d$ - $A_2$  critical point might be similar to a gas-liquid type of critical point. However, a recent theoretical approach<sup>17</sup> based on renormalization-group theory appears to indicate that because of layer fluctuations and coupling of the order parameter to elastic degrees of freedom this critical point may belong to a new universality class, with  $d_c=6$  and anisotropic correlation length exponents. Clearly, further high-resolution experiments are needed to classify the  $A_d$ - $A_2$  critical point.

The authors are highly indebted to Professor S. Chandrasekhar but for whose keen interest and support this

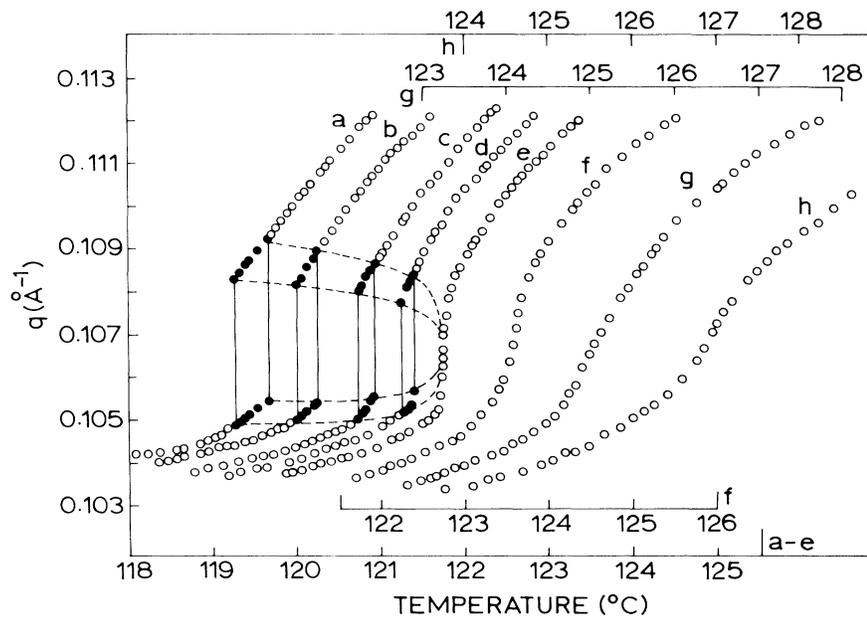


FIG. 3. Plots of wave vectors  $q_0$  and  $q'_0$  vs temperature ( $T$ ) for different mixtures of 11OPCBOB in 9OBCB. The mole fractions ( $X$ ) of 11OPCBOB in the mixture are (a) 0.55, (b) 0.571, (c) 0.597, (d) 0.619, (e) 0.642 (f) 0.715, (g) 0.80, and (h) 1.0 or 11OPCBOB. The corresponding temperature scales are identified. For  $X < 0.642$  (plots a-d), a first-order  $A_1$ - $A_2$  transition is seen which manifests as a jump in the wave vector. The data in the two-phase region are shown as circles, while the vertical lines represent the approximate width of this region. Dashed lines are envelopes of the ends of the two-phase regions and are only guides to the eye. The critical point (CP) is identified by the vertical inflection point seen for  $X = 0.642$  (plot e).

work would not have been possible. Many important discussions with him are thankfully acknowledged.

<sup>1</sup>R. Schaetzing and J. D. Litster, *Adv. Liq. Cryst.* **4**, 147 (1979).

<sup>2</sup>J. D. Litster, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 65.

<sup>3</sup>For a recent review on the polymorphic forms of the  $A$  phase, as well as for a discussion of phase diagrams involving these  $A$  phases, see J. Prost, *Adv. Phys.* **33**, 1 (1984), and references cited therein.

<sup>4</sup>B. R. Ratna, R. Shashidhar, and V. N. Raja, *Phys. Rev. Lett.* **55**, 1476 (1985).

<sup>5</sup>J. Prost, *J. Phys. (Paris)* **40**, 581 (1979).

<sup>6</sup>J. Prost, in Ref. 2, p. 125.

<sup>7</sup>J. Prost, in *Symmetries and Broken Symmetries in Condensed Matter Physics*, edited by N. Boccara (Institut pour le Développement de la Science, l'Éducation et le Technologie, Paris, 1981), p. 159.

<sup>8</sup>J. Prost and P. Barois, *J. Chim. Phys. Phys. Chim. Biol.* **80**, 65 (1983).

<sup>9</sup>P. Barois, J. Prost, and T. C. Lubensky, *J. Phys. (Paris)* **46**, 391 (1985).

<sup>10</sup>K. K. Chan, P. S. Pershan, L. B. Sorensen, and F. Hardouin, *Phys. Rev. Lett.* **54**, 1694 (1985), and *Phys. Rev. A* **34**, 1420 (1986).

<sup>11</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1982), Pt. 1, p. 468.

<sup>12</sup>F. Hardouin, M. F. Achard, C. Destrade, and Nguyen Huu Tinh, *J. Phys. (Paris)* **45**, 765 (1984).

<sup>13</sup>F. Hardouin, M. F. Achard, Nguyen Huu Tinh, and G. Sigaud, *J. Phys. (Paris), Lett.* **46**, 123 (1985).

<sup>14</sup>S. Krishna Prasad, R. Shashidhar, B. R. Ratna, B. K. Sadashiva, G. Heppke, and S. Pfeiffer, *Liq. Cryst.* **2**, 111 (1987).

<sup>15</sup>F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, *J. Chim. Phys. Phys. Chim. Biol.* **80**, 53 (1983).

<sup>16</sup>P. S. Pershan, G. Aeppli, J. D. Litster, and R. J. Birgeneau, *Mol. Cryst. Liq. Cryst.* **67**, 205 (1981).

<sup>17</sup>Y. Park, T. C. Lubensky, P. Barois, and J. Prost, presented at the American Physical Society Meeting, New York, March, 1987 (unpublished).