

Observation of the Smectic-*C*–Smectic-*I* Critical Point

S. Krishna Prasad and D. S. Shankar Rao

Raman Research Institute, Bangalore 560080, India

S. Chandrasekhar

Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore 560013, India

M. E. Neubert

Liquid Crystal Institute, Kent State University, Kent, Ohio 44240

J. W. Goodby

University of Hull, Hull HU6 7RX, United Kingdom

(Received 2 August 1994)

We report the first observation of the smectic-*C*–smectic-*I* (*C*-*I*) critical point by x-ray diffraction studies on a binary system. These results are in agreement with the theoretical idea of Nelson and Halperin that coupling to the molecular tilt should induce hexatic order even in the *C* phase, and as such both *C* and *I* (a tilted hexatic phase) should have the same symmetry. The results provide evidence in support of the recent theory of Defontaine and Prost proposing a new universality class for critical points in layered systems.

PACS numbers: 61.30.Eb, 64.60.Fr, 64.70.Md

Smectic *C* (*C*) and smectic *I* (*I*) are liquid crystalline phases in which the molecules are tilted with respect to the layer normal. In the *I* phase the tilt order is supplemented by a sixfold bond orientational (BO) order. Nelson and Halperin [1] predicted that coupling to molecular tilt should induce long-range BO order even in the *C* phase. This has been confirmed by synchrotron x-ray studies [2]. Since only the magnitude of BO order is different, both *C* and *I* phases have the same point group symmetry. An immediate consequence of this feature is that there can be either a first-order transition or no transition, but a continuous evolution from one phase to the other. The existence of a first-order transition for some systems [3–5], together with the continuous evolution situation for others [2,5], implies that there should exist a critical point (CP) in the phase diagram. However, the occurrence of such a point has not been experimentally observed so far. These studies have been made more significant by the recent predictions of Defontaine and Prost (DP) [6]. The DP theory, based on the concept of the existence of qualitatively different spatial directions in layered systems, expects the CP in smectic systems to belong to the same but new universality class.

Two of the critical points considered to be in the DP universality class have already been observed experimentally. They are the smectic-*A*₁–smectic-*A*₂ CP [7] and the electric field induced smectic-*C**–smectic-*C* CP [8]. The critical exponents obtained in these cases [8,9] suggest that the universal description of CP in layered systems is a definite possibility.

In this Letter we present the results of x-ray studies on binary mixtures of terephthal-bis-decylaniline [10] (TB10A for short) and 4-*n*-decyloxy biphenyl 4-(2'-methylbutyl)

benzoate [11] (C10 for short) which have led to the first observation of the *C*-*I* critical point. We demonstrate that the first-order transition characterized by a jump in the layer spacing and the two-phase coexistence region terminates at a CP in the temperature-composition plane. Further, we observe that the values of β and δ , the critical exponents associated with the order parameter, and the course of the critical isochore are in close agreement with the experimental results obtained in other layered smectics and also with the DP predictions for the new universality class. Both the pure compounds exhibit *C* and *I* phases. (Although the compound C10 is chiral, for the purposes of this paper, we shall ignore the differences between chiral and nonchiral materials.) The partial phase diagram for this binary system is shown in Fig. 1. This diagram has been obtained by observing the optical textures exhibited by the different phases under a polarizing microscope and also simultaneously monitoring the transmitted intensity and temperature on a computer. The latter method was particularly useful for identifying the *C*-*I* transition. The twist grain boundary (TGB) phase was identified by its characteristic vermic texture [12]. The *C* and *I* phases show the standard bubble texture. High precision layer spacing measurements were performed using an aligned sample obtained by cooling at a slow rate (~ 1 °C/h) from the cholesteric phase in the presence of a magnetic field (2.4 T). Once the sample was in the *C* phase, the temperature-controlled oven was shifted to the x-ray goniometer head. The x-ray setup used has been described in detail elsewhere [13]. Briefly recalling the essential details, a Ge monochromator positioned to allow only $K\alpha_1$ radiation and a linear position sensitive detector using a quartz wire enable the precision in

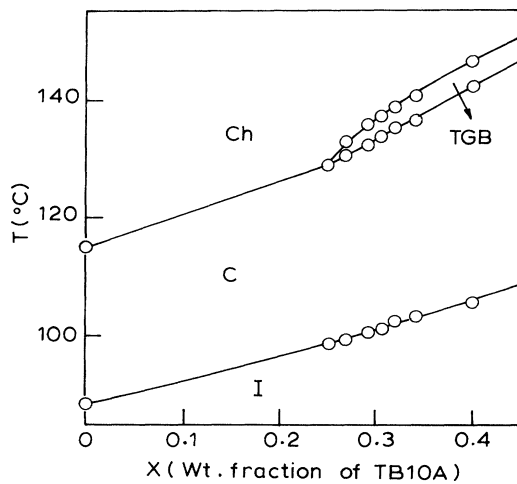


FIG. 1. Partial temperature-composition (T - X) phase diagram of the binary systems TB10A and C10. Here X indicates the weight fraction of TB10A in the mixture. The different phases seen are cholesteric (Ch), twist grain boundary phase (TGB), smectic C (C), and smectic I (I). The circles indicate the concentrations for which x-ray studies have been done. Lines are meant to be a guide to the eye.

the wave vector determination to be $2 \times 10^{-4} \text{ \AA}^{-1}$, while the resolution in the equatorial direction (also the scanning direction) is $1 \times 10^{-3} \text{ \AA}^{-1}$ HWHM. The precision in the determination of the temperature is reckoned to be ± 2 mK and during any scan the temperature of the sample was maintained to a constancy of ± 10 mK.

Figure 2(a) shows the layer spacing determined as a function of temperature for TB10A. The transformation from C to I is signalled by the coexistence of the peaks due to both the phases [see insets of Fig. 2(a)], exactly as is expected and seen earlier for first-order transitions between two smectic phases with different layer periodicities [7,13,14]. In contrast the d variation is smooth for C10 [Fig. 2(b)], which, together with the fact that the two phases have the same symmetry, indicates a continuous evolution. Now, it is quite natural to expect a CP to exist for a suitable composition of the two compounds. To locate the CP, x-ray studies have been performed on seven different mixtures, $X = 0.40, 0.34, 0.32, 0.305, 0.29, 0.27$, and 0.25 (where X indicates the weight fraction of TB10A in the mixture). The thermal variation of d for these mixtures is shown in Fig. 3. It is observed that for $X > 0.27$ the transition is first order accompanied by a jump in d , while for $X = 0.25$ and beyond there is only a continuous evolution; the composition $X = 0.27$ shows a vertical inflection. Both Δd , the jump in the layer spacing, and the width of the two-phase region are observed to decrease smoothly to zero as the concentration $X = 0.27$ is approached (see Fig. 4). All these features show unambiguously that there is a critical point at or in the immediate vicinity of $X_c = 0.27$.

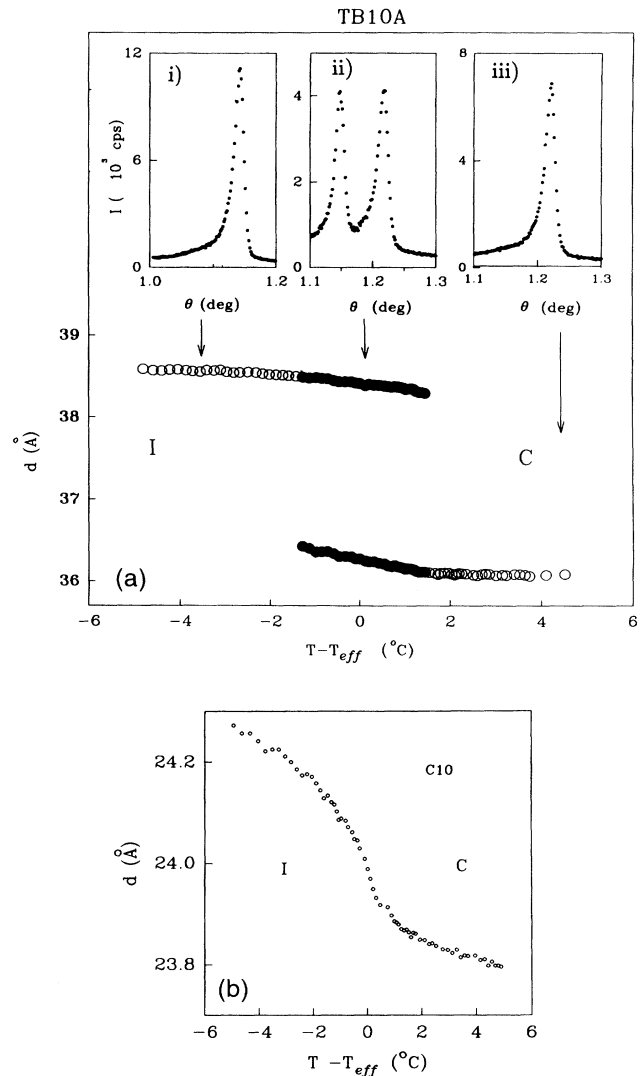


FIG. 2. (a) Temperature dependence of the layer spacing d for TB10A showing a two-phase coexistence in the transition region. The insets show raw x-ray line profiles in the (i) I phase, (ii) coexistence region, and (iii) C phase. T_{eff} is the transition temperature. (b) Layer spacing variation in C10 showing a continuous evolution from C to I phase. T_{eff} refers to the temperature of the inflection point.

Since Δd serves as the order parameter for the transition, on approaching CP it is expected to follow

$$\Delta d \propto |t|^\beta, \quad (1)$$

with $t = T_{\text{eff}} - T_c$. T_c is the critical temperature and T_{eff} is the transition temperature of the mixing being taken as the mean of the high- and low-temperature limits of the coexistence region. A plot of Δd as a function of t is also shown in Fig. 4 along with a least-squares fit by Eq. (1). The fit yields $\beta = 0.51 \pm 0.01$. For smectic-layered systems, the path of approach to CP along $X = X_c$ is analogous to the approach along the critical pressure

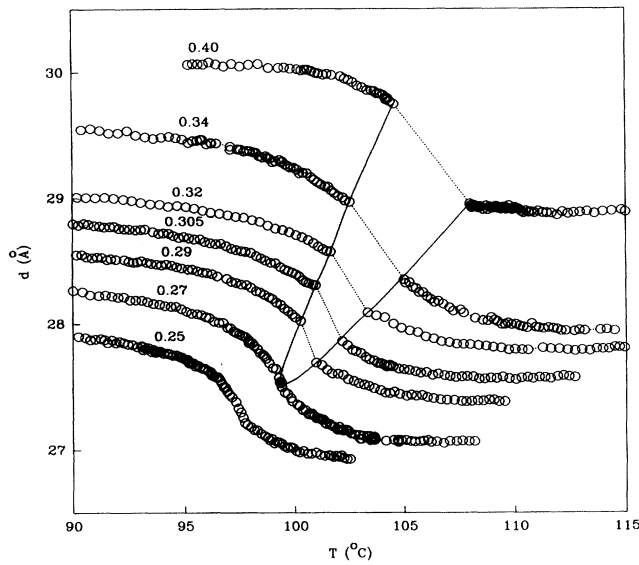


FIG. 3. d versus T plots for different concentrations near the CP. The concentrations are indicated above each plot. The dashed lines serve as a guide to the eye through the two-phase region. The solid line is a locus of the boundary of the two-phase region for different mixtures. The values of T_{eff} for different concentrations are $X = 0.4$, 105.94 °C; $X = 0.34$, 103.50 °C; $X = 0.32$, 102.70 °C; $X = 0.305$, 101.36 °C; $X = 0.29$, 100.76 °C; $X = 0.27$, 99.35 °C; and $X = 0.25$, 98.62 °C. $X = 0.27$ shows a vertical inflection due to the presence of the critical point (indicated by a solid circle).

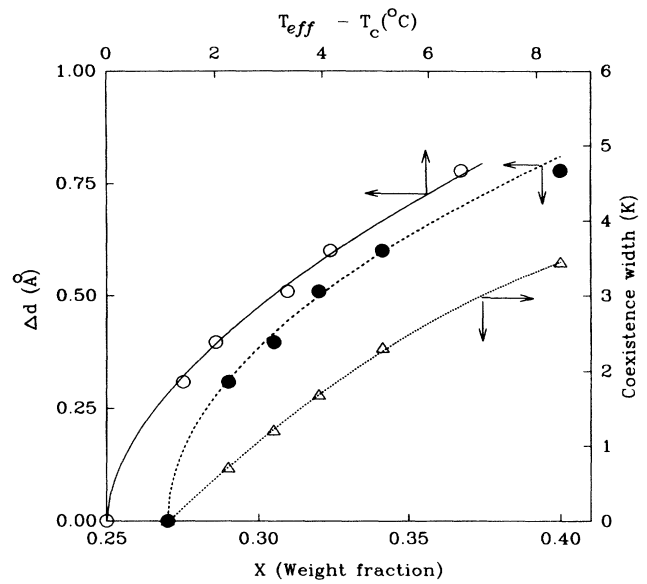


FIG. 4. Variation of the jump in the order parameter Δd (solid circles) and the width of the coexistence region (triangles) as the CP concentration $X_c = 0.27$ is approached. The lines are meant to be a guide to the eye. Open circles indicate the order parameter jump obtained for different concentrations as a function of $T_{eff} - T_c$. Notice that as T_{eff} approaches T_c , the jump decreases to zero. The solid line represents the “critical isochore” and is a fit by Eq. (1), yielding $\beta = 0.51 \pm 0.01$. The scales for the different data sets are indicated by arrows.

for the liquid-gas systems [9]. In such a situation for $X = X_c$, the temperature variation of the layer spacing can be written as

$$d = d_c + A^\pm |t|^{1/\delta} + B(T - T_c). \quad (2)$$

Here d_c is the d value at T_c , A^\pm denotes the amplitudes above and below T_c , and the linear term describes a background variation. A fit by Eq. (2) for the d variation at $X_c = 0.27$ is shown in Fig. 5 and gives a δ of 1.82 ± 0.2 . The ratio A^-/A^+ comes out to be -1.06 . Although the value of β ($= 0.51 \pm 0.01$) agrees with the mean field (MF) value of 0.5, the δ value (1.82 ± 0.2) is appreciably different from the MF value of 3. It may be recalled here that similar features were seen for the C^*-C critical point [8]. Also, the δ value agrees closely, within the experimental errors, with that obtained for the A_d-A_2 critical point [9]. The δ value is also comparable to the theoretical value of 2 ± 0.1 given by DP. However, the theory suggests that the order parameter variation is described by the ratio β/Δ rather than β . Since $\beta/\Delta = 1/\delta \sim 0.5$, the variation of Δd and the temperature dependence of d at $X = X_c$ yield the same exponent. However, it should be noted that the β/Δ value for the new universality class is not different from the MF β value. In view of this, we suggest that our results support the concept of universal behavior of critical points in layered systems. Specific heat measurements on the $C-I$

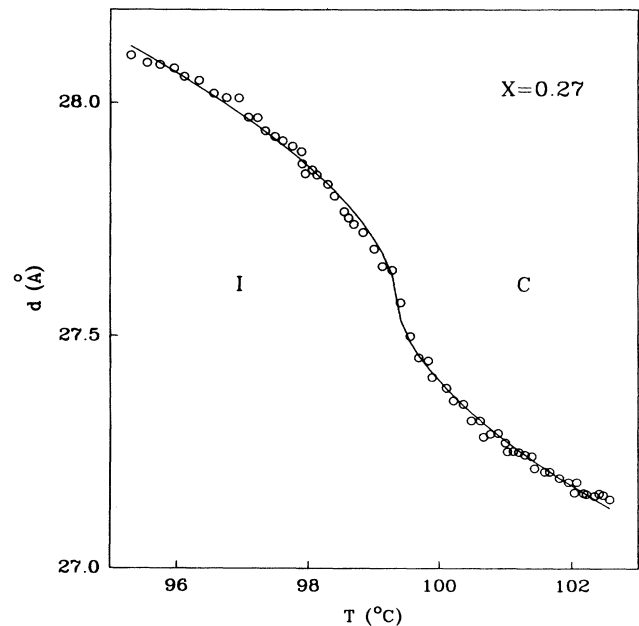


FIG. 5. Enlarged view of d versus temperature in the critical region for $X_c = 0.27$. The solid line is a fit by Eq. (2) giving $\delta = 1.82 \pm 0.2$.

critical point would be interesting and test the theoretical predictions further.

Thanks are due to K. Subramanya for technical assistance. We are grateful to Prof. J. Prost for his useful comments.

-
- [1] D.R. Nelson and B.I. Halperin, *Phys. Rev. B* **21**, 5312 (1980). See also J. Prost, in *Symmetries and Broken Symmetries*, edited by N. Boccara (IDSET, Paris, 1981), p. 159.
- [2] J.D. Brock, A. Aharony, R.J. Birgeneau, K.W. Ewans-Lutterodt, J.D. Litster, P.M. Horn, G.B. Stephenson, and A.R. Tajbakhsh, *Phys. Rev. Lett.* **57**, 98 (1986).
- [3] J.J. Benattar, F. Moussa, and M. Lambert, *J. Chem. Phys.* **80**, 99 (1983).
- [4] S.B. Dierker and R. Pindak, *Phys. Rev. Lett.* **59**, 1002 (1987).
- [5] V.N. Raja, S. Krishna Prasad, D.S. Shankar Rao, J.W. Goodby, and M.E. Neubert, *Ferroelectrics* **121**, 235 (1981).
- [6] A.D. Defontaines and J. Prost, *Phys. Rev. E* **47**, 1184 (1993). The ideas on which this theory has been formulated appeared in earlier works on the $A-A'$ critical points, e.g., P. Barois, J. Prost, and T.C. Lubensky, *J. Phys. (Paris)* **46**, 391 (1985); Y. Park, T.C. Lubensky, P. Barois, and J. Prost, *Phys. Rev. A* **37**, 2197 (1988).
- [7] R. Shashidhar, B.R. Ratna, S. Krishna Prasad, S. Somasekhara, and G. Heppke, *Phys. Rev. Lett.* **59**, 1209 (1987).
- [8] Ch. Bahr and G. Heppke, *Phys. Rev. A* **44**, 3669 (1991).
- [9] Y.H. Jeong, G. Nounesis, C.W. Garland, and R. Shashidhar, *Phys. Rev. A* **40**, 4022 (1989); X. Wen, C.W. Garland, R. Shashidhar, and P. Barois, *Phys. Rev. B* **45**, 5131 (1992).
- [10] M.E. Neubert and L.J. Maurer, *Mol. Cryst. Liq. Cryst.* **43**, 313 (1977). This compound was purified by repeated recrystallization from ethanol until its transition temperatures were constant. Its structure was confirmed by IR and NMR studies. Under these conditions, the purity of the compound was found to be better than 99%.
- [11] J.W. Goodby and T.M. Leslie, *Mol. Cryst. Liq. Cryst.* **110**, 175 (1984). The purity of this compound was determined by HPLC ($\lambda = 254$ nm) under normal and reverse phase conditions. Normal phase chromatography was carried out over silica gel (5 μ m pore size 25×0.46 cm) using dichloromethane as the eluent. The reverse phase was carried out over Octodecal Soloxane, ODS (5 μ m pore size 25×0.46 cm). In both cases the compound was found to be better than 99% pure. In addition, CHN analysis was found to be consistent with the proposed structure of the compound. The compound was further purified by repeated recrystallization from a mixture of ethanol and petroleum ether (40–60 °C) until the transition temperatures were constant.
- [12] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, and J.S. Patel, *Nature* **337**, 449 (1989).
- [13] S. Krishna Prasad, V.N. Raja, D.S. Shankar Rao, G.G. Nair, and M.E. Neubert, *Phys. Rev. A* **42**, 2479 (1990).
- [14] P.S. Pershan, G. Aeppli, J.D. Litster, and R.J. Birgeneau, *Mol. Cryst. Liq. Cryst.* **67**, 205 (1981).