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Classification

Physics Abstracts

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## Heat capacity measurements near the nematic-smectic- $A_1$ and smectic- $A_1$ -smectic- $\tilde{C}$ transitions in octyloxyphenyl cyanobenzoyloxy benzoate

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**Résumé.** — La chaleur spécifique ( $C_p$ ) du benzoate octyloxyphenyl-cyanobenzoyloxy (8OPCBOB) a été mesurée au voisinage des transitions nématique(N)-smectique- $A_1$ ( $SmA_1$ ) et smectique- $A_1$ ( $SmA_1$ )-smectique- $\tilde{C}$ ( $Sm\tilde{C}$ ) par une technique calorimétrique ac de haute résolution. La transition  $SmA_1$ - $Sm\tilde{C}$  est faiblement du premier ordre avec une chaleur spécifique excédentaire de type Landau (pas de  $C_p$  excédentaire dans la phase haute température). Nous présentons une analyse détaillée des variations de  $C_p$  du 8OPCBOB, associées à la transition de deuxième ordre N- $SmA_1$ , et aussi de données préalablement publiées sur un mélange de benzoate pentylphenyl-cyanobenzoyloxy ( $DB_5CN$ ) et de stilbène cyanobenzoyloxy pentyl ( $C_5$  stilbène). Les deux systèmes présentent le même comportement critique pour  $C_p$ , conformément au modèle XY. En particulier le rapport des amplitudes critiques  $A^-/A^+$  est 0,990, ce qui est en bon accord avec la valeur théorique pour le modèle XY mais qui est qualitativement en désaccord avec le modèle XY inverse. 8OPCBOB ainsi que quelques autres systèmes présentent des déviations systématiques juste au-dessous de  $T_c$ , qui sont probablement intrinsèques à toutes les transitions N- $SmA$  de type XY.

**Abstract.** — The heat capacity  $C_p$  of octyloxyphenyl cyanobenzoyloxy benzoate (8OPCBOB) has been measured with a high-resolution ac calorimetric technique near the nematic (N)-smectic- $A_1$  ( $SmA_1$ ) and smectic- $A_1$  ( $SmA_1$ )-smectic- $\tilde{C}$  ( $Sm\tilde{C}$ ) transitions. The  $SmA_1$ - $Sm\tilde{C}$  transition is weakly first order with a Landau-like excess heat capacity (i.e., no excess  $C_p$  in the high-temperature  $SmA_1$  phase). A detailed analysis of the  $C_p$  variation associated with the second-order N- $SmA_1$  transition is presented for 8OPCBOB and for previously published data on a mixture of pentylphenyl-cyanobenzoyloxy benzoate ( $DB_5CN$ ) and cyanobenzoyloxy pentyl stilbene ( $C_5$  stilbene). Both systems exhibit the same critical  $C_p$  behavior, which agrees well with the XY model. In particular, the critical amplitude ratio  $A^-/A^+$  is 0.990, which agrees quite well with the theoretical ratio for the XY model but is qualitatively inconsistent with the expected inverted-XY value. 8OPCBOB and several other systems exhibit a pattern of systematic deviations just below  $T_c$  that may be intrinsic to all XY-like N- $SmA$  transitions.

## 1. Introduction.

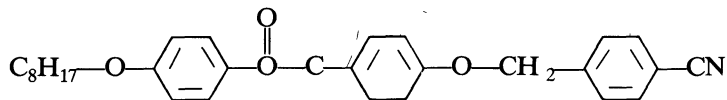
The nematic (N)-smectic-A(SmA) transition has been extensively studied in nonpolar liquid crystals and in polar compounds having only two benzene rings in the aromatic core. The former compounds form monomeric smectic phases ( $\text{SmA}_m$ ) and the latter partial-bilayer smectic phases ( $\text{SmA}_d$ ). High-resolution X-ray and calorimetric studies of N- $\text{SmA}_m$  and N- $\text{SmA}_d$  transitions [1, 2] yield effective critical exponents that exhibit a systematic trend with the width of the nematic range ( $T_{\text{NI}} - T_{\text{NA}}$ ) and do not agree with those of the expected XY universality class [3].

Recently, high-resolution work has begun on polar liquid crystals with long (three-ring) aromatic cores. These compounds exhibit a wide range of smectic polymorphism, including the monolayer smectic-A( $\text{SmA}_1$ ) and bilayer smectic-A( $\text{SmA}_2$ ) as well as  $\text{SmA}_d$  and others [4]. X-ray and heat capacity measurements on T7 and T8 (alkoxybenzyloxy-cyanostilbenes) yield N- $\text{SmA}_1$  critical exponents  $\gamma$ ,  $\nu_{\parallel}$ ,  $\nu_{\perp}$ , and  $\alpha$  that are close, but not identical, to those expected for an ideal XY transition [5]. X-ray measurements on  $\text{DB}_6\text{CN} + \text{TBBA}$  (hexylphenyl cyanobenzoyloxy benzoate + terephthal-bis-butylaniline) mixtures with N- $\text{SmA}_1$  transitions that are not close to the N- $\text{SmA}_1$ - $\text{SmA}_2$  point yield exponents  $\gamma$  and  $\nu_{\parallel}$  compatible with XY values but  $\nu_{\perp} < \nu_{\text{XY}}$  [6]. In both of these systems, the results are complicated by thermal instabilities at high temperatures which cause  $T_c$  to drift and limit the resolution near  $T_c$ . Recent heat capacity measurements on the N- $\text{SmA}_1$  transitions in  $\text{DB}_n\text{CN} + \text{C}_5$  stilbene (alkylphenyl cyanobenzoyloxy benzoate + cyanobenzoyloxy pentyl stilbene) mixtures yield values of the critical exponent  $\alpha$  that are very close to  $\alpha_{\text{XY}}$  [7]. Thus the available studies of the N- $\text{SmA}_1$  transition suggest that it is much closer to XY universality than are the extensively studied N- $\text{SmA}_m$  and N- $\text{SmA}_d$  transitions. Perhaps this is related to the saturation of the orientational order parameter  $S$  in the nematic phase just above most N- $\text{SmA}_1$  transitions but not above most N- $\text{SmA}_d$  or N- $\text{SmA}_m$  transitions.

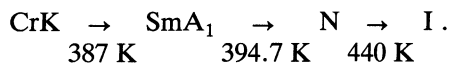
The present work involves ac calorimetric measurements on 8OPCBOB (octyl-oxyphenyl cyanobenzoyloxy benzoate), a compound that is attractively stable at high temperatures. Critical exponents  $\gamma \approx 1.06$  and  $\nu_{\parallel} \approx 0.52$  have been reported [8] for this compound on the basis of a preliminary x-ray study in the N phase covering a single decade in reduced temperatures ( $3 \times 10^{-4} < t < 3 \times 10^{-3}$ ). This surprising indication of possible tricritical behavior (for which  $\gamma = 1$ ,  $\nu = 0.5$ ,  $\alpha = 0.5$ ) for a compound with a 45 K nematic range is not confirmed by our heat capacity results. Indeed, as discussed in section 3, the XY model provides a very good description of the  $C_p(\text{N-SmA}_1)$  data for 8OPCBOB. A brief presentation of this conclusion has been made elsewhere [9].

## 2. Results.

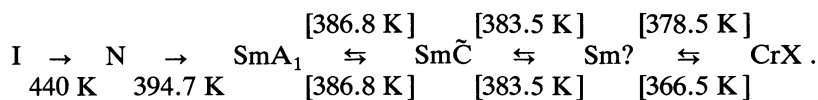
The sample of 8OPCBOB was synthesized and purified at the Technical University of Berlin, and the heat capacity measurements were made at MIT using a high-resolution ac calorimeter [10]. The structure of this compound is



and the molecular mass is 457.5 g. On heating from room temperature, the phase sequence was



On cooling, two monotropic liquid crystal phases and one metastable crystal phase are observed in the sequence



The phase sequence on heating from room temperature agrees with that reported previously [11], but there are several new features observed on cooling (and on immediate reheating). A small but well-defined excess  $C_p$  peak associated with the  $\text{SmA}_1$ - $\text{Sm}\tilde{\text{C}}$  transition was observed at 386.78 K on cooling and on prompt reheating. There is also a broad excess heat capacity anomaly centered at 383.5 K on both cooling and prompt reheating. This feature, which is larger than the  $\text{SmA}_1$ - $\text{Sm}\tilde{\text{C}}$  peak, has been observed from DSC measurements [11]. On cooling runs, the compound freezes at 366.5 K, where  $C_p$  undergoes a discontinuous decrease of  $0.08 \text{ J K}^{-1} \text{ g}^{-1}$ . On a subsequent heating run that started at 365 K, a large melting transition peak was observed at 378.5 K, which shows that the sample froze into a metastable crystal form CrX not the stable crystal CrK. The structures of CrX and the smectic phase that occurs between  $\text{Sm}\tilde{\text{C}}$  and CrX are unknown.

The small  $C_p$  peak associated with the  $\text{SmA}_1$ - $\text{Sm}\tilde{\text{C}}$  transition is shown in figure 1. This transition is weakly first order with a 100 mK-wide coexistence region between 386.70 K and 386.80 K. Over this 100 mK region, the apparent  $C_p$  and the phase shift  $\phi$  of the ac temperature oscillations are anomalously high, features correlated with two-phase coexistence. This  $\text{SmA}_1$ - $\text{Sm}\tilde{\text{C}}$  heat capacity variation in 8OPCBOB is qualitatively similar to that observed in  $\text{DB}_8\text{ONO}_2 + \text{DB}_{10}\text{ONO}_2$  mixtures (octyl and decyl homologs of alkoxyphenyl-nitrobenzoyloxy benzoate) [12]. The asymmetry of the  $C_p$  peak resembles the mean-field behavior observed at second-order  $\text{SmA}_m$ - $\text{SmC}_m$  transitions [13] and at the very weakly first-order N- $\text{SmC}$  transition near the N- $\text{SmA}$ - $\text{SmC}$  multicritical point [14].

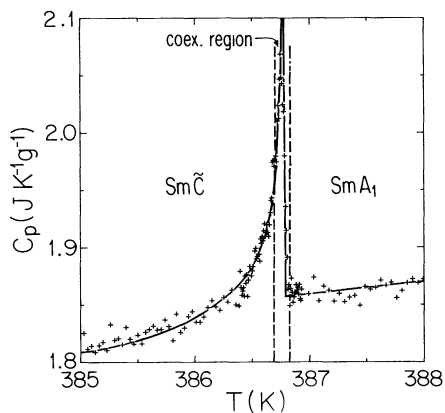


Fig. 1.

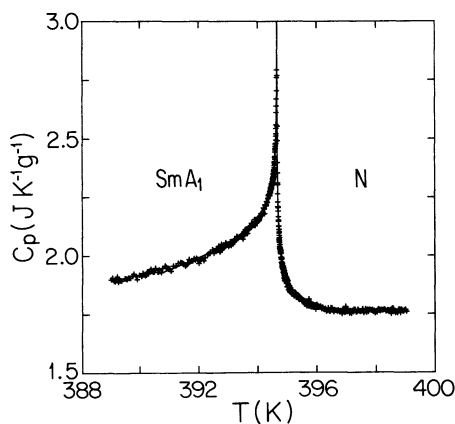


Fig. 2.

Fig. 1. — Specific heat capacity of 8OPCBOB in the vicinity of the  $\text{SmA}_1$ - $\text{Sm}\tilde{\text{C}}$  transition. Two-phase coexistence occurs over the 100 mK temperature range between the two dashed lines. The solid curve represents a least-squares fit with equation (1).

Fig. 2. — Specific heat capacity of 8OPCBOB associated with the N- $\text{SmA}_1$  transition. The smooth curve represents equation (2) with the fit-4 parameter values listed in table I.

The  $C_p$  data obtained in the vicinity of the N-SmA<sub>1</sub> transition are presented in figure 2. These data were obtained on a slow heating run (+ 30 mK/h for  $|\Delta T| < 0.3$  K). A heat capacity peak of the same size and shape was obtained on a subsequent cooling run. There was, however, a very small shift in the position of the peak due to a drift in  $T_c$  of  $-0.9$  mK/h. This drift rate is much lower than those encountered at other N-SmA<sub>1</sub> transitions ( $-2$  to  $-10$  mK/h) [5-7], and corrections for the drift had negligible effect on the parameter values obtained from the least-squares fits described below.

### 3. Analysis.

Unlike the usual SmA-SmC transitions, the SmA<sub>1</sub>-Sm $\tilde{C}$  transition is first order in the mean-field approximation [15]. The present SmA<sub>1</sub>-Sm $\tilde{C}$  data cannot be well represented by the standard Landau form unless one allows a discontinuity in the background heat capacity, which is physically plausible since the transition is first order. In this case, the SmA<sub>1</sub>-Sm $\tilde{C}$  heat capacity can be fit with

$$C_p^- = A^*(T_k - T)^{-1/2} + B^- + E(T - T_1) \quad T < T_1 \quad (1a)$$

$$C_p^+ = B^+ + E(T - T_1) \quad T > T_1 \quad (1b)$$

where  $T_1$  is the first-order transition temperature and  $T_k > T_1$  represents the metastability limit for the ordered phase [14]. The best least-squares fit to the data outside the coexistence region is shown in figure 1, and the parameter values are  $A^* = 0.057 \text{ J K}^{-1/2} \text{ g}^{-1}$ ,  $B^- = 1.784 \text{ J K}^{-1} \text{ g}^{-1}$ ,  $B^+ = 1.858 \text{ J K}^{-1} \text{ g}^{-1}$ ,  $E = 0.001 \text{ J K}^{-1} \text{ g}^{-1}$ , and  $T_k = 386.802$  K. The value of  $T_1$  is taken to be the mid-point of the abrupt change in  $C_p$  (386.778 K), but any value in the range 386.75-386.80 K could be chosen since data in the coexistence region are not reliable and are not used in the fitting procedure.

The N-SmA<sub>1</sub> heat capacity data have been analyzed [9] in terms of the expression

$$C_p^\pm = A^\pm |t|^{-\alpha} (1 + D_1^\pm |t|^{0.5} + D_2^\pm |t|) + B + E \Delta T \quad (2)$$

where  $t \equiv (T - T_c)/T_c$  is the reduced temperature and  $\pm$  superscripts denote above and below  $T_c$ . The coefficients  $D_1^\pm$  and  $D_2^\pm$  are the amplitudes of the first and second correction terms. The term  $D_1 |t|^{0.5}$  corresponds to the first « corrections-to-scaling » term with exponent  $\Delta_1 = 1/2$ . The term  $D_2 |t|$  is a combination of the second corrections-to-scaling term  $D_{2c} |t|^{2\Delta_1}$  and the analytic correction term  $D_a t$  [16]. The temperature-independent quantity  $B$  contains a regular background contribution  $B_{\text{reg}}$  and a critical contribution  $B_c$ . The term  $E \Delta T = E(T - T_c)$  represents the small linear background variation in  $C_p$  seen in noncritical fluids.

The stability of least-squares fits with equation (2) was tested by range shrinking, and three ranges of data were used :

$$\begin{aligned} \text{range I: } |t|_{\text{max}} &= 10^{-3} \\ \text{II: } &= 3 \times 10^{-3} \\ \text{III: } &= 10^{-2}. \end{aligned} \quad (3)$$

Ten data points close to  $T_c$  exhibited systematic deviations and were omitted from the fit. As a result, there is a gap of 40 mK and  $t_{\text{min}} = +1 \times 10^{-5}$  and  $-9 \times 10^{-5}$ . Fits in which the critical exponent is a freely adjustable parameter yield  $\alpha$  values in the range  $-0.0054$  to  $-0.0093$  for all three fitting ranges [9]. Thus, we have fixed  $\alpha$  at  $-0.007$ , which corresponds

to a well-known theoretical  $\alpha_{XY}$  value [17] that has been widely used for the detailed analysis of  $XY$  critical behavior [18, 19]. Furthermore,  $E$  was fixed at zero for all fits since the maximum range is only  $T_c \pm 4$  K and data obtained far from  $T_c$  suggest no appreciable temperature difference [20].

The least-squares parameter values and the  $\chi^2_\nu$  values for several fits are given in table I. Fits 1-3 were made with  $D_2^\pm$  fixed at zero, as is usual with most  $C_p$  fits reported in the literature. These fits show that there are small but systematic trends in all the parameters as the range is varied. Also fit 3 for range III is not of very good quality. This situation is usually caused by neglect of a higher-order term that becomes more important as the range is broadened. Allowing  $E \neq 0$  does not improve the situation [20] but allowing  $D_2^\pm \neq 0$  provides a dramatic improvement as shown by fit 4. It should be noted that the magnitude of the first-correction coefficients  $D_1^\pm$  is very much larger for this N-SmA<sub>1</sub> transition in a polar liquid crystal than for the normal-superfluid transition in helium ( $D_1^+ = -0.020$ ) [21] or the N-SmA<sub>m</sub> transition in nonpolar 40.7, butyloxybenzylidene heptylaniline ( $D_1^+ = -0.045$ ) [9]. Thus it is reasonable that the second-correction terms play a significant role over the largest reduced temperature range.

Table I. — *Fits of  $C_p$ (N-SmA<sub>1</sub>) for 8OPCBOB: least-squares values of the parameters occurring in equation (2).  $E = 0$  for all fits, and  $D_2^\pm = 0$  for all except fit 4. Values in parentheses were held fixed at the specified value. The fitting ranges are defined in equations (3); the number of data points is 214 for range I, 352 for range II, and 534 for range III. The units are  $J K^{-1} g^{-1}$  for  $A^+$  and  $B$ .*

| Fit            | Range | $\alpha$ | $A^+$  | $A^-/A^+$ | $D_1^+$ | $D_1^-/D_1^+$ | $B$   | $T_c(K)$ | $\chi^2_\nu$ |
|----------------|-------|----------|--------|-----------|---------|---------------|-------|----------|--------------|
| 1              | I     | (-0.007) | -30.64 | 0.988     | -0.243  | 1.071         | 30.83 | 394.660  | 1.19         |
| 2              | II    | (-0.007) | -27.46 | 0.986     | -0.201  | 0.789         | 27.86 | 394.662  | 1.42         |
| 3              | III   | (-0.007) | -23.13 | 0.982     | -0.161  | 0.422         | 23.80 | 394.664  | 2.25         |
| 4 <sup>a</sup> | III   | (-0.007) | -28.54 | 0.987     | -0.241  | 1.034         | 28.87 | 394.662  | 1.21         |

<sup>a</sup>For this fit,  $D_2^+ = 0.496$ ,  $D_2^-/D_2^+ = 2.55$ .

The parameters for fit 4 not only provide a much better fit over range III but also an excellent fit over range II ( $\chi^2_\nu = 1.39$ ) and an acceptable fit over range I ( $\chi^2_\nu = 1.60$ , which means the fit is as good as fit 1 within 99 % confidence limits). All of this is accomplished with no further adjustment of the parameters as the range is narrowed.

Figure 2 shows the fit-4 theoretical curve over range III (approx.  $\pm 4$  K), and figure 3 shows the fit over range I (approx.  $\pm 0.4$  K) and the even narrower range  $|t| \leq 3 \times 10^{-4}$  (approx.  $\pm 0.12$  K). On the scale of figure 3, differences between fits 1 and 4 cannot be seen over range I and are quite small even over the  $\pm 3 \times 10^{-4}$  range. Figure 3 shows seven of the ten points omitted from the fitting procedure. Inclusion of four more points below  $T_c$  narrows the gap around  $T_c$  to 27 mK and changes  $t_{\min}$  from  $-9 \times 10^{-5}$  to  $-6 \times 10^{-5}$ . Although the  $\chi^2_\nu$  values increase by a factor of  $\sim 1.4$ , the overall conclusions are unaffected.

The role of the  $D_2^\pm |t|$  terms is clearly shown by the deviation plots presented in figure 4. Introduction of  $D_2^\pm |t|$  correction terms eliminates the large systematic deviations occurring for  $|t| > 2 \times 10^{-3}$  in fits with  $D_2^\pm = 0$ . Note also, as shown in table I, that  $D_2^\pm |t|$  terms play a significant role only at large reduced  $|t|$  values. The other parameters in fit 4 are very close to

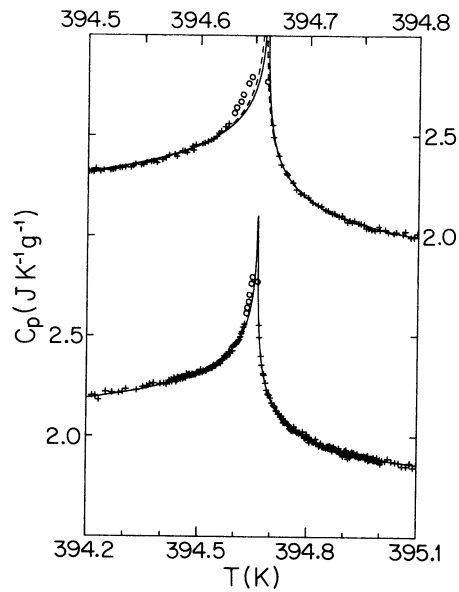


Fig. 3. — Detailed view of  $C_p(\text{N-SmA}_1)$  data for 8OPCBOB and theoretical curves obtained with fit 1 (dashed curve) and fit 4 (solid curve) over  $\pm 10^{-3}$  range, lower temperature scale, and  $\pm 3 \times 10^{-4}$  range, upper scale.

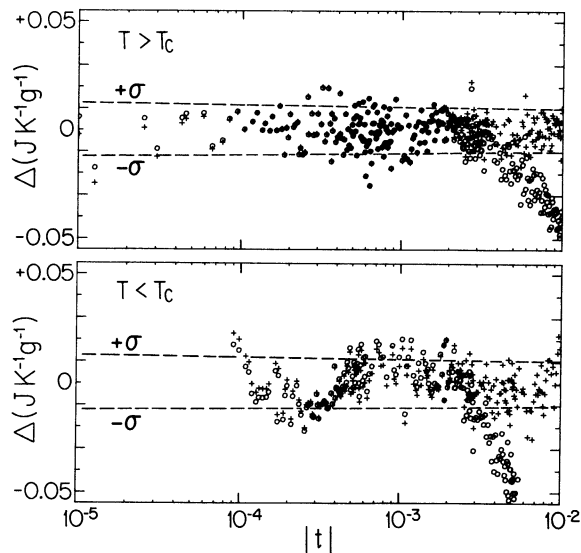


Fig. 4. — Deviations  $\Delta = C_p(\text{data}) - C_p(\text{fit})$  for 8OPCBOB over the reduced temperature range  $|t| \leq 10^{-2}$ . The open circles are deviations obtained on using the parameters from fit 2, for which  $D_2^* = 0$ , and the crosses are deviations from fit 4. The dashed lines represent estimated values of  $\pm \sigma$ , where  $\sigma$  is the standard deviation.

their values in fits 1 and 2. For range III, fit 4 not only yields a significant improvement in  $\chi^2_\nu$  but also gives a  $D_1^-/D_1^+$  ratio close to 1, as expected theoretically and observed in helium [21].

The success of fitting 8OPCBOB heat capacity data with a form including second corrections-to-scaling terms led us to reanalyze recent  $C_p(N-SmA_1)$  data on  $DB_nCN + C_5$  stilbene mixtures (Ref. [7]) in a parallel manner [9]. The least-squares fitting parameters for a  $DB_5CN + C_5$  stilbene mixture with a  $C_5$  stilbene mole fraction of 0.492 are given in table II. Fits 1'-4' are directly analogous to fits 1-4 for 8OPCBOB. The quality of these fits is excellent as indicated by the  $\chi^2_\nu$  values and as shown in figures 5-7. Indeed, the fits are slightly better

Table II. — *Fits of  $C_p(N-SmA_1)$  for a  $DB_5CN + C_5$  stilbene mixture : least-squares values of the parameters occurring in equation (2). There are 234 data points in range I, 437 in range II, and 571 in range III. See the caption of table I for further information.*

| Fit             | Range | $\alpha$ | $A^+$  | $A^-/A^+$ | $D_1^+$ | $D_1^-/D_1^+$ | $B$   | $T_c(K)$ | $\chi^2_\nu$ |
|-----------------|-------|----------|--------|-----------|---------|---------------|-------|----------|--------------|
| 1'              | I     | (-0.007) | -18.69 | 0.994     | -0.232  | 1.272         | 19.78 | 424.422  | 0.99         |
| 2'              | II    | (-0.007) | -15.36 | 0.991     | -0.156  | 1.128         | 16.66 | 424.426  | 1.14         |
| 3'              | III   | (-0.007) | -13.15 | 0.987     | -0.117  | 0.804         | 14.58 | 424.429  | 1.85         |
| 4' <sup>a</sup> | III   | (-0.007) | -17.26 | 0.992     | -0.236  | 1.311         | 18.43 | 424.425  | 1.04         |

<sup>a</sup>For this fit,  $D_2^+ = 0.716$ ,  $D_2^-/D_2^+ = 2.11$ .

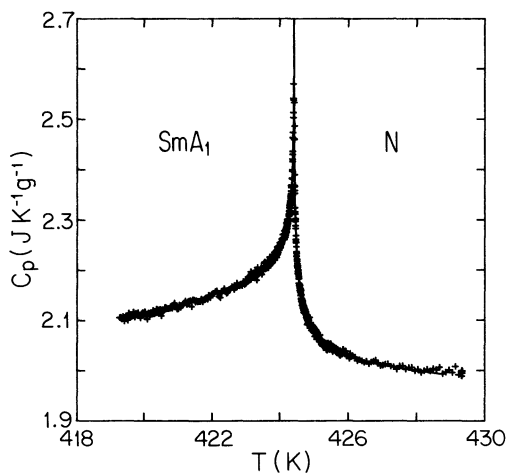


Fig. 5.

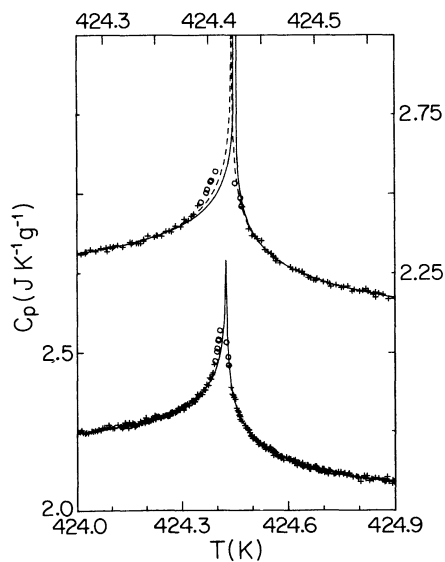


Fig. 6.

Fig. 5. — Specific heat capacity of a  $DB_5CN + C_5$  stilbene mixture near the  $N-SmA_1$  transition (data taken from Ref. [7]). The smooth curve represents fit 4'.

Fig 6. — Detailed view of  $C_p(N-SmA_1)$  data for  $DB_5CN+C_5$  stilbene and theoretical curves obtained with fit 1' (dashed curve) and fit 4' (solid curve) over  $\pm 10^{-3}$  range, lower temperature scale, and  $\pm 3 \times 10^{-4}$  range, upper scale.



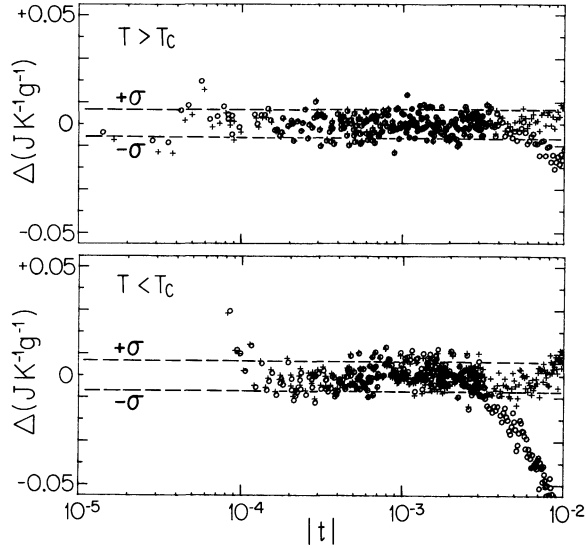


Fig. 7. — Deviations  $\Delta = C_p(\text{data}) - C_p(\text{fit})$  for  $\text{DB}_5\text{CN} + \text{C}_5\text{stilbene}$  over the reduced temperature range  $|t| \leq 10^{-2}$ . The open circles are deviations obtained on using the parameters from fit 2', for which  $D_2^\pm = 0$ , and the crosses are deviations from fit 4'. The dashed lines represent estimated values of  $\pm \sigma$ , where  $\sigma$  is the standard deviation.

than those for 8OPCBOB with the random scatter and systematic deviations both being smaller. Every feature of the fitting procedure is directly parallel to the case of 8OPCBOB. As with 8OPCBOB, excellent fits can be obtained with  $\alpha = \alpha_{XY}$  and  $D_2^\pm = 0$  for ranges I and II but not for range III (see fits 1'-3' in Tab. II). Allowing  $D_2^\pm \neq 0$  provides a very good fit over range III, and fit 4' without any further adjustment of parameters also yields  $\chi_\nu^2 = 1.02$  for range II and  $\chi_\nu^2 = 1.09$  for range I. Figure 6 shows nine of the thirteen points close to  $T_c$  omitted from the fitting procedure; the resulting gap is 42 mK wide and  $t_{\min} = +2.0 \times 10^{-5}$  and  $-8.2 \times 10^{-5}$  for the fits in table II. Inclusion of eight more points, narrowing the gap to 22 mK, increases the  $\chi_\nu^2$  values by a factor of  $\sim 1.2$  but does not change the overall conclusion that fit 4' provides an excellent fit.

#### 4. Discussion.

The results of fitting  $C_p(\text{N-SmA}_1)$  data for the pure compound 8OPCBOB and the binary mixture  $\text{DB}_5\text{CN} + \text{C}_5\text{stilbene}$  are remarkably similar [22]. In both cases, excellent fits can be achieved with equation (2) out to  $|t|_{\max} = 10^{-2}$  when first and second correction terms are included. The critical exponent  $\alpha$  is consistent with the theoretical 3D-XY value [9, 17]. The critical amplitude ratio  $A^-/A^+$  lies in the range 0.987-0.992, the ratio  $D_1^-/D_1^+$  lies in the range 1.0-1.3, and the ratio  $D_2^-/D_2^+$  lies in the range 2.1-2.6 [16]. Note that the experimental ratio  $A^-/A^+$  is not sensitive to the inclusion of  $D_2^\pm$  terms, as shown by tables I and II. The most recent calculation [23] of the 3D-XY amplitude ratio gives  $A^-/A^+ = 0.9714 \pm 0.0126$  for  $\alpha_{XY} = -0.007$ , and our experimental ratio agrees fairly well with this 3D-XY value. However, it is expected theoretically that nematic-smectic-A transitions should be described by the inverted-XY model, for which the critical exponents are the same as those in the XY model but the heat capacity amplitude ratio is the inverse of that for the XY model [3]. Thus the inverted-XY ratio is  $A^-/A^+ = 1.0294 \pm 0.0134$ . Since the asymmetry of the  $C_p$  peak is

determined by whether  $A^-/A^+ < 1$  or  $A^-/A^+ > 1$ , the present data are qualitatively inconsistent with inverted- $XY$  behavior; see reference [9] for further discussion of this conclusion.

Unfortunately, the detailed analysis presented here cannot be carried out on the  $C_p(\text{N-SmA}_1)$  data available for T7 and T8 [5]. For both these compounds there are two serious limitations on the analysis of  $C_p$ : the drift in transition temperature due to poor thermal stability limited the resolution close to  $T_c$ , and even more important is the small size of the heat capacity peaks. For T7 and T8 the maximum  $C_p$  value observed at the transition is only 6 percent above the noncritical background  $C_p$  value, whereas the critical  $C_p$  contribution is 10 times larger than this for 8OPCBOB and 5 times larger for  $\text{DB}_5\text{CN} + \text{C}_5$  stilbene. However, the asymmetry of the  $C_p$  peak for T7 and T8 is qualitatively the same as that shown in figures 2 and 5. Thus if these T7 and T8 data were fit using the  $XY$  exponent value, the resulting  $A^-/A^+$  would also be inconsistent with inverted- $XY$  behavior.

Next, we wish to point out a curious systematic trend in the deviations  $\Delta \equiv C_p(\text{data}) - C_p(\text{fit})$  for N-SmA transitions that are  $XY$ -like. The deviations arising from fits with equation

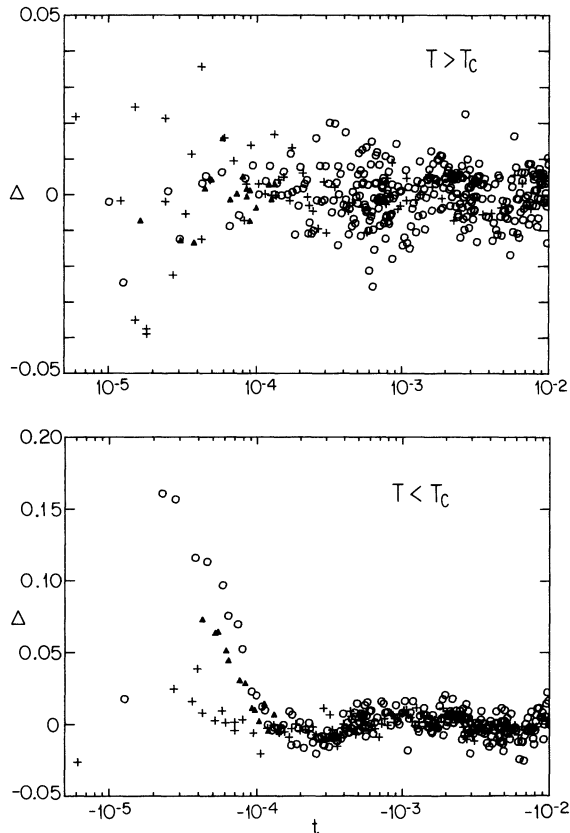


Fig. 8. — Deviations  $\Delta = C_p(\text{data}) - C_p(\text{fit})$  above and below  $T_c$  for nonpolar 40.7 (+, N-SmA<sub>m</sub> transition) and polar 8OPCBOB (O, N-SmA<sub>1</sub> transition). Deviations for  $\text{DB}_5\text{CN} + \text{C}_5\text{stilbene}$  (▲) are also shown for  $|t| < 1.5 \times 10^{-4}$ ; in other regions these deviations agreed with those shown for 40.7 and 8OPCBOB. Note the different vertical scales used above and below  $T_c$ . Data points for 8OPCBOB and  $\text{DB}_5\text{CN} + \text{C}_5\text{stilbene}$  between  $-10^{-5}$  and  $-8.5 \times 10^{-5}$  were excluded from the fits reported here. In the case of 40.7, the four points between  $-6 \times 10^{-6}$  and  $-4 \times 10^{-5}$  were excluded from the fit reported in reference [9].

(2) including both first and second correction terms are random over the entire  $t$  range above  $T_c$ , but there is a small systematic pattern to these deviations below  $T_c$ . Figure 8 shows such deviations for nonpolar 40.7 [9], where the systematic effect is small but visible, and for 8OPCBOB, where the systematic trend is quite pronounced. Note the oscillation in  $\Delta$  for  $t$  values between  $-10^{-2}$  and  $-1.4 \times 10^{-4}$ . In addition, there is an obvious increase in  $\Delta$  for 8OPCBOB as  $t$  varies from  $-1.5 \times 10^{-4}$  to  $-2 \times 10^{-5}$ ; data points inside  $-9 \times 10^{-5}$  were excluded from the fits. Exactly the same systematic pattern of deviations below  $T_c$  is observed for the  $\text{DB}_5\text{CN} + \text{C}_5$  stilbene mixture, but the magnitudes are slightly smaller. Since the various samples were synthesized at different laboratories and investigated by different research workers using slightly different experimental arrangements, we feel that these systematic deviations below  $T_c$  could be an intrinsic aspect of all  $XY$ -like N-SmA transitions. Such deviations are not observed for N-SmA transitions with positive effective  $\alpha$  values in the range 0.15-0.3 [2, 24, 25]. Note that the deviations close to  $T_c$  are *not* compatible with the idea that  $A^-/A^+$  crosses over to the inverted  $XY$  value as  $T_c$  is approached more closely.

It is clear that the N-SmA<sub>1</sub> heat capacity of 8OPCBOB does not show the tricritical behavior suggested by the critical exponents  $\gamma = 1.06$  and  $\nu_{\perp} = 0.52$  [8]. It is likely that these exponent values, which are based on X-ray data over only one decade in reduced temperature, have a substantial uncertainty [8, 26]. Indeed, anisotropic hyperscaling requires that  $\alpha + \nu_{\parallel} + 2\nu_{\perp} = 2$ . Even if one assumed that  $\nu_{\parallel} - \nu_{\perp} = 0.2$ , which is a large anisotropy compared to known values for other N-SmA transitions [1, 2, 5, 6], the quantity  $\alpha + \nu_{\parallel} + 2\nu_{\perp}$  would equal only 1.75. A high-resolution X-ray determination of  $\gamma$ ,  $\nu_{\parallel}$  and  $\nu_{\perp}$  for 8OPCBOB is in progress [26], and it would be desirable to carry out such a study for a  $\text{DB}_n\text{CN} + \text{C}_5$  stilbene mixture. In particular, it is important to determine whether or not critical anisotropy in the divergence of the correlation lengths  $\xi_{\parallel}$  and  $\xi_{\perp}$  is present for these N-SmA<sub>1</sub> transitions, as it is for N-SmA<sub>m</sub> and N-SmA<sub>d</sub> transitions. An X-ray study of T7 and T8 yielded  $\nu_{\parallel} - \nu_{\perp} = 0.69 - 0.63 = 0.06 \pm 0.06$  [5], but the result  $\nu_{\parallel} - \nu_{\perp} = 0.20 \pm 0.06$  was reported for  $\text{DB}_6\text{CN} + \text{TBBA}$  (Ref. [6]). Thus the experimental situation for X-ray studies of N-SmA<sub>1</sub> transitions is still unclear.

## 5. Summary.

High-resolution  $C_p$  data associated with the N-SmA<sub>1</sub> transition in 8OPCBOB and in a mixture of  $\text{DB}_5\text{CN} + \text{C}_5$  stilbene have been analyzed over the reduced temperature range  $|t| < 10^{-2}$ . Very good fits are achieved with a power-law form including both first and second correction terms. The critical exponent  $\alpha$  is consistent with the  $XY$  value  $-0.007$ . The ratio of critical amplitudes  $A^-/A^+$  ( $= 0.990$ ) is definitely less than 1, which is inconsistent with predicted inverted- $XY$  model. Small but systematic deviations from the best fit curve occur below  $T_c$  but not above. The pattern of these deviations is the same in both polar and nonpolar systems, and the deviations grow as  $T$  approaches  $T_c$  but not in a manner suggestive of crossover to inverted- $XY$  behavior.

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+0.007 J K<sup>-2</sup> g<sup>-1</sup>. Inclusion of a variable  $E \Delta T$  term has little effect on the quality of the fit  
or the values of the important adjustable parameters  $\alpha$  and  $A^-/A^+$  even when unphysical  $E$   
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