

High-resolution volumetric study of the smectic-*A*—smectic-*C* transition in 4-(*n*-pentyl)phenylthio-4'-(*n*-octyl)oxybenzoate ($\bar{8}S5$)

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High-resolution volumetric measurements have been made on pure $\bar{8}S5$. The molar-volume variations show a classical second-order smectic-*A*—smectic-*C* transition. These data are very well described by a mean-field Landau model and are inconsistent with the critical behavior of the three-dimensional *XY* model. The thermal-expansion coefficient α_p has been calculated and $\Delta\alpha_p = (0.50 \pm 0.02) \times 10^{-4} \text{ K}^{-1}$ at the phase transition estimated.

I. INTRODUCTION

All experimental studies of the smectic-*A* (*SmA*) to smectic-*C* (*SmC*) phase transition in liquid crystals show the transition to be second order. Huang,¹ however, suggests a possibility of a first order. Huang and Viner² have analyzed the heat capacity (C_p) data near this transition and give an explanation why nonmean-field critical exponents were obtained in some measurements. Birgeneau *et al.*³ have collected experimental data from which the critical exponents can be determined and concluded that the mean-field equations fit the data best although the evidence is not as unequivocal as one might wish. Recently, Meichle and Garland⁴ have made an extensive study of C_p in the neighborhood of the *SmA*—*SmC* transition. As has been shown previously,^{5,6} the volumetric measurements allow for high precision and we studied earlier binary mixtures of $\bar{8}S5$ - $\bar{7}S5$ [where $\bar{7}S5$ is 4-(*n*-pentyl)phenylthio-4'-(*n*-heptyl)oxybenzoate].⁶ We have repeated these measurements for pure $\bar{8}S5$. The pure compound $\bar{8}S5$ was investigated by many authors using different experimental techniques.⁷⁻¹⁰ We complement these data with precise molar volume and thermal expansion coefficient data in the vicinity of the *SmA*—*SmC* transition. The critical behavior three-dimensional (3D) *XY* model and mean-field Landau model were applied to describe our data. In Sec. II we report the experimental results which are analyzed and discussed in Sec. III. The conclusions are given in Sec. IV.

II. EXPERIMENTAL RESULTS

Accurate measurements of volume versus temperature were carried out according to procedures described by us previously.^{5,6} The new version of dilatometer used in this work consists of a 12 cm³ volume, connected at the bottom with a capillary 0.3 mm in diameter, 37 cm long, and at the top with a Teflon needle valve. At the bottom of the vessel and of the capillary about 2 cm³ mercury is placed; the presence of mercury allows making measurements with both increasing and decreasing temperature. Each run covered about 3.5 K. When using the dilatometer with such a long capillary containing mercury, one must take special care to keep the sample at constant pres-

sure. This was assured by compensating the pressure with an external manometer connected to the end of the capillary. The small differences in pressure (within a few Torr) were corrected in calculations by using the compressibility of the sample, determined three to four times during the run. The calibration run was made with deionized and degassed water; the results of volume vs height of mercury in the capillary were correlated by a second-order polynomial with a standard deviation $\sigma = 3 \times 10^{-6} \text{ cm}^3$. However, the absolute volume of the dilatometer could differ in individual runs by less than 0.001 cm³, i.e., 0.01%, owing to the use of a Teflon needle valve.

We carried out two sets of measurements of volume versus temperature in the vicinity of *SmA*—*SmC* transition temperature for two samples of 4-(*n*-pentyl)phenylthio-4'-(*n*-octyl)oxybenzoate ($\bar{8}S5$). The first run was done for sample I, synthesized and purified by recrystallization from heptane by "ZD Chemipan" (Warsaw). The results of the first run are shown in Fig. 1 ("lower curve," crosses) and represent the deviations of molar volumes V , with a linear background subtracted, versus temperature. One can see the rounding of intersection of the two $V(T)$ curves for *SmA* and *SmC* phases. This rounding in the immediate neighborhood of the transition may be due, or partly due, to impurities. This conclusion was confirmed by examining the nematic to isotropic transition, which indicated a wide two-phase region (see Table I, sample I). Sample I was further purified by us by a very slow crystallization from methanol. We obtained 5–6-cm long needles; the new transition temperatures are also listed in Table I (sample II). We carried out a second run of measurements of volumes vs temperature for sample II in steps 0.02 K in the immediate vicinity of transition. The results are shown in Fig. 1 (the "upper curve," circles), here the rounding disappeared and the intersection of the two $V(T)$ curves at the *SmA*—*SmC* transition is quite sharp. We did not attempt to purify sample II any further. Only results for sample II were analyzed.

III. DATA ANALYSIS AND DISCUSSION

The experimental results of molar volume variation with temperature were analyzed as follows. In recent pa-

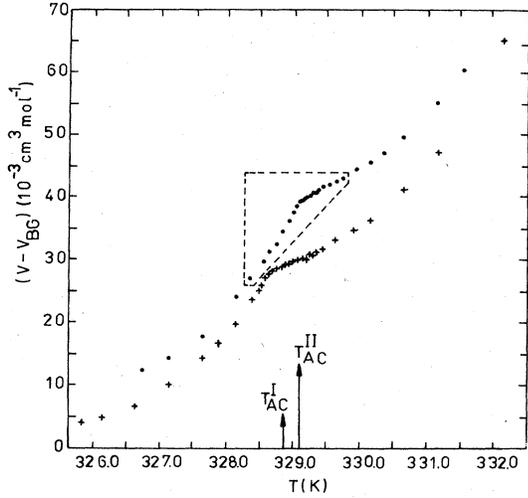


FIG. 1. Molar volume near the SmA—SmC transition in $\bar{8}S5$, with a linear background $V_{BG} = a + bT$ subtracted, plotted against temperature: (+) sample I, $T_{AC} = 328.88$ K, $a = 301.7183$ cm³ mol⁻¹, $b = 0.3177$ cm³ mol⁻¹ K⁻¹; (●) sample II, $T_{AC} = 329.10$ K, $a = 301.8509$ cm³ mol⁻¹, $b = 0.3177$ cm³ mol⁻¹ K⁻¹. Detail enclosed with dashed line is drawn on enlarged scale in the lower part of Fig. 2.

pers²⁻⁴ the critical behavior model and the Landau mean-field model were used to describe the specific heat (C_p) near and at the SmA—SmC transition.

The thermal expansion is related to C_p by

$$\left(\frac{dV}{dT} \right)_p = \frac{(\partial S / \partial T)_p}{(\partial p / \partial T)_s} = \frac{C_p}{T(\partial p / \partial T)_s}. \quad (1)$$

If $(\partial p / \partial T)_s$ is nonsingular at T_{AC} , we may take for the singular part of $(dV/dT)_p$ a similar functional form as that used for the singular part of C_p . As $T_{AC} = 329.10$ K and since the temperature range of our data is about 2 K on each side of the transition, it is immaterial that we replace either $(\partial p / \partial T)_s$ or $T(\partial p / \partial T)_s$ by a constant. In the case of the critical behavior²⁻⁴

$$C_p^{\text{sing}} = A_0 t^{-\alpha} (1 + D_0 t^{1/2}) + B. \quad (2)$$

We take this form for dV/dT and integrate to obtain

$$V = \begin{cases} At^{1-\alpha}(1 + Dt^{1/2}) + Bt + C, & T > T_{AC} \\ A't^{1-\alpha'}(1 + D't^{1/2}) + B't + C', & T < T_{AC} \end{cases} \quad (3a)$$

$$(3b)$$

TABLE II. Results of fitting the molar-volume data for $\bar{8}S5$ below the smectic-A—smectic-C transition to Eq. (3b) with $T_{AC} = 329.10$ K fixed in all fits; σ , standard deviation; the thermal-expansion coefficient at the transition temperature $\alpha_p(T_{AC}^-)$ calculated from Eq. (8). Values in parentheses were held fixed during the fit. Parameter D' in Eq. (3b) was set equal to zero.

Fit	T_{\min}^a (K)	$10^3 t_{\max}$	α'	A' (cm ³ mol ⁻¹)	B' (cm ³ mol ⁻¹)	C' (cm ³ mol ⁻¹)	$10^4 \sigma$ (cm ³ mol ⁻¹)	$10^4 \alpha_p(T_{AC}^-)$ (K ⁻¹)
1	327.6501	4.406	(-0.026)	55.37	-157.54	406.4454	1.01	11.78
2	327.6501	4.406	-0.134	20.08	-119.15	406.4456	0.96	8.91
3	326.7594	7.112	-0.724	116.50	-111.63	406.4454	1.57	8.34
4	326.7594	7.112	(-1)	369.14	-110.98	406.4452	1.85	8.30

^a $T_{\max} = 329.0916$ K, $t_{\min} = |T_{\max}/T_{AC} - 1| = 2.552 \times 10^{-5}$.

TABLE I. Transition temperatures (K) for two investigated samples of $\bar{8}S5$.

	T_{AC}	T_{AN}	T_{NI}
Sample I	328.88 ± 0.03	336.53 ± 0.03	358.66 – 358.90
Sample II	329.10 ± 0.01	336.74 ± 0.01	359.05 – 359.19

where $t \equiv |T/T_{AC} - 1|$.

In a mean-field theory, the singular part of the free energy is written as

$$F^{\text{sing}} = at\psi^2 + b\psi^4 + c\psi^6, \quad (4)$$

where a , b , and c are constants and ψ is the order parameter. Birgeneau *et al.*³ have quoted the equation for the specific heat anomaly in the neighborhood of a SmA—SmC transition, derived from Eq. (4), and used in the form

$$C_p^{\text{sing}} = \begin{cases} 0, & T > T_{AC} \\ a^2 T / 2bT_{AC}^2 (1 - 3t/t_0)^{-1/2}, & T < T_{AC} \end{cases} \quad (5)$$

where $t \equiv T/T_{AC} - 1$. Integrating Eq. (5) we obtain

$$\Delta S = \int_T^{T_{AC}} \frac{C_p^{\text{sing}}}{T} dT = \begin{cases} \text{const}, & T > T_{AC} \\ \frac{ab}{3cT_{AC}} [1 - (1 - 3t/t_0)^{1/2}], & T < T_{AC} \end{cases} \quad (6a)$$

$$(6b)$$

Here $t_0 \equiv b^2/ac$ is a crossover temperature as defined by Huang and Viner.² The right-hand side of Eqs. (6a) and (6b) with an added background term was used to fit our data. For $T < T_{AC}$ we took only a linear background term, whereas for $T > T_{AC}$ and for a larger temperature range, a quadratic background term was necessary. Hence,

$$V = \begin{cases} Bt + C \text{ or } Et^2 + Bt + C, & T > T_{AC} \\ A'(1 - 3t/t_0)^{1/2} + B't + C', & T < T_{AC} \end{cases} \quad (7a)$$

$$(7b)$$

The critical behavior model was tested for $T < T_{AC}$ only, since $V(T)$ for $T > T_{AC}$ was linear over the range of 0.8 K (see Fig. 1). The parameters of Eq. (3b) obtained in different fits along with the standard deviation are given in Table II. The phase-transition temperature T_{AC} was established during the preliminary fits; the value obtained

$T_{AC}=329.10$ K was then fixed in all calculations. In all fits reported $D'=0$ since an inclusion of this scaling term did not make any significant improvement in the fit. The heliumlike behavior—three-dimensional XY model—was tested with a critical exponent $\alpha'=-0.026$ (fit 1, Table II) held constant in the fitting procedure, and a fairly good description was obtained for $t < 4.41 \times 10^{-3}$. However, one should not rely on the least-squares fit of $V(T)$ alone; in this case the limiting value of thermal-expansion coefficient $\alpha_p(T_{AC}^-)=11.78 \times 10^{-4} \text{ K}^{-1}$ (see Table II) calculated from relation

$$\alpha_p(T_{AC}) = \frac{1}{V(T_{AC})} \left[\frac{dV}{dT} \right]_p = - \frac{B'}{T_{AC}C'} \quad (8)$$

appears to be unreasonably large [the whole range of the upper part of Fig. 2 is $(7.8-8.6) \times 10^{-4} \text{ K}^{-1}$]. On allowing the adjustable parameters A' , B' , C' , and α' to vary freely and using the nonlinear least-squares fitting procedure,¹¹ several sets of parameters were obtained. For the range $2.55 \times 10^{-5} < t < 4.41 \times 10^{-3}$ the best fit was obtained with $\alpha'=-0.134$ (fit 2); the calculated value of $\alpha_p(T_{AC})$ is too high. For the range $2.55 \times 10^{-5} < t < 7.11 \times 10^{-3}$, the critical exponent $\alpha'=-0.724$ (fit 3) was obtained; this value is close to $\alpha'=-1$, for which Eq. (3b) becomes second-order polynomial representing molar-volume changes of the smectic- C phase far away from the transition (fit 4). The sets of parameters with $\alpha' > 0$ were also obtained but are not quoted here; this case gives

$$\lim_{T \rightarrow T_{AC}^-} \left[\frac{dV}{dT} \right]_p = \infty$$

and we have not found, so far, the slightest evidence of such an infinite value of α_p .

We cannot conclude that our results are consistent with critical behavior. This model can provide a good representation (see column 8, Table II) for data below T_{AC} only, but not if, data above T_{AC} are included.

The Landau mean-field description, Eqs. (7), predicts a square-root singularity only at the low-temperature side and displaced by t_0 . It gives a good representation to all $V(T)$ data on both sides of T_{AC} . In Table III the param-

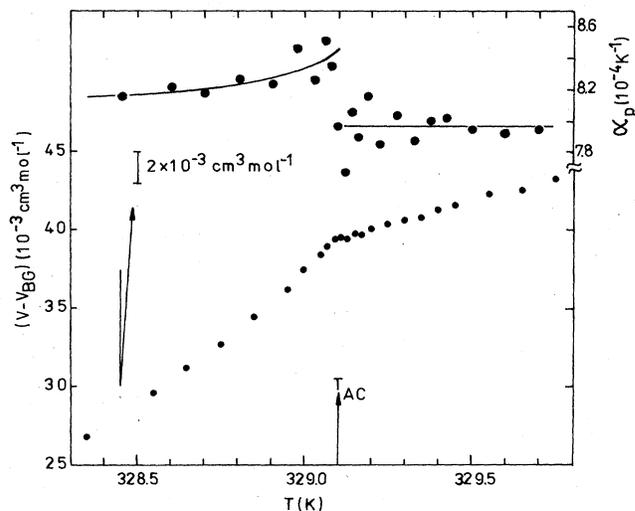


FIG. 2. Detailed view of the molar-volume changes (lower part) in a vicinity of the SmA-SmC transition in 8S5 (sample II). Upper part shows the thermal expansion coefficient α_p calculated for all pairs of neighboring unsmoothed data points (solid circles) and α_p calculated from Eq. (9) (solid line).

eters of Eqs. (7), calculated values $\alpha_p(T_{AC})$, $V(T_{AC})$, and standard deviation σ for different fits are given. The best description was obtained for the temperature range $328.35 < T < 329.75$ (fits 1 and 4) with the standard deviation 1.1×10^{-4} and $0.96 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ for $T > T_{AC}$ and $T < T_{AC}$, respectively. $V(T)$ in this temperature range is shown in the lower part of Fig. 2. In a wider temperature range (fits 2 and 5) the description is still satisfactory, although above T_{AC} for $t < 4.71 \times 10^{-3}$ the standard deviation increases to $2.23 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$. For fitting data in the whole temperature range between 326.76 K and 331.55 K (fits 3 and 6) the quadratic term, Eq. (7a), must be introduced to description $V(T)$ above $T_{AC}=329.10$ K. This strong residual dependence may be due to the close neighborhood of the smectic- A to nematic transition.¹² The coefficients of Eqs. (7) are almost independent of the temperature range (see Table III), although the crossover temperature t_0 changes slightly

TABLE III. Parameter values obtained from the fitting of molar-volume data for 8S5 above and below the smectic- A to smectic- C transition with the Landau model, Eqs. (7). Transition temperature $T_{AC}=329.10$ K was held fixed in all fits; σ , the standard deviation; $\alpha_p(T_{AC})$ calculated from Eq. (9); $V(T_{AC}^+)=C$ for $T > T_{AC}$ and $V(T_{AC}^-)=A'+C'$ for $T < T_{AC}$.

Fit	T_{\max}^a (K)	$10^3 t_{\max}$	E ($\text{cm}^3 \text{ mol}^{-1}$)	B ($\text{cm}^3 \text{ mol}^{-1}$)	C ($\text{cm}^3 \text{ mol}^{-1}$)	$10^4 \sigma$ ($\text{cm}^3 \text{ mol}^{-1}$)	$10^4 \alpha_p(T_{AC}^+)$ (K^{-1})	$V(T_{AC}^+)$ ($\text{cm}^3 \text{ mol}^{-1}$)	
$T > T_{AC}$									
1	329.7510	1.978		106.48	406.4453	1.12	7.96	406.4453	
2	330.6496	4.709		106.63	406.4452	2.23	7.97	406.4452	
3	331.5516	7.449	200.90	105.81	406.4456	2.49	7.91	406.4456	
$T < T_{AC}$	T_{\min}^b	$10^3 t_{\min}$	A'	B'	C'	$10^3 t_0$	$10^4 \sigma$	$10^4 \alpha_p(T_{AC}^-)$	$V(T_{AC}^-)$
4	328.3505	-2.277	-0.0063	106.16	406.4519	1.3	0.96	8.46	406.4456
5	327.6501	-4.406	-0.0093	105.67	406.4549	1.9	1.00	8.44	406.4456
6	326.7594	-7.112	-0.0130	104.20	406.4588	2.1	4.09	8.46	406.4458

^a $T_{\min}=329.1125$ K, $t_{\min}=T_{\min}/T_{AC}-1=3.798 \times 10^{-5}$.

^b $T_{\max}=329.0916$ K, $t_{\max}=T_{\max}/T_{AC}-1=-2.552 \times 10^{-5}$.

from 1.3×10^{-3} to 2.1×10^{-3} . The values of molar volume extrapolated to the transition temperature $V_{\text{Sm}A}(T_{AC}^+) = C$ and $V_{\text{Sm}C}(T_{AC}^-) = A' + C'$ are given in Table III. It is clearly seen that $V_{\text{Sm}A}(T_{AC}^+) = V_{\text{Sm}C}(T_{AC}^-)$ within the experimental uncertainty; this confirms that the transition is second order.

The upper part of Fig. 2 exhibits the thermal expansion coefficient calculated as the numerical derivative $\bar{\alpha}_p = \bar{V}^{-1} \Delta V / \Delta T$ for pairs of neighboring data points (\bar{V} is the average molar volume for each two points). The dependence of thermal-expansion coefficient α_p on temperature was also calculated from equation

$$\alpha_p(T) = \begin{cases} \frac{B}{V(T)T_{AC}}, & T > T_{AC} \\ \frac{1}{V(T)T_{AC}} \left[-\frac{3A'}{2t_0} \left(1 - \frac{3t}{t_0} \right)^{-1/2} + B' \right], & T < T_{AC} \end{cases} \quad (9a)$$

$$T < T_{AC} \quad (9b)$$

The curve obtained (solid line in the upper part of Fig. 2) reproduces very well the experimental $\bar{\alpha}_p$ from numerical differentiation. The values of α_p at the transition, $\alpha_p(T_{AC})$, are also given in Table III.

In this way we estimate $\Delta\alpha_p$ at the SmA – SmC transition as $\Delta\alpha_p = (0.50 \pm 0.02) \times 10^{-4} \text{ K}^{-1}$. Using the value of $\Delta C_p = 5R$ estimated^{2,3} for $\bar{8}S5$ from C_p data of Schantz and Johnson,⁷ we have been able to calculate the value of dT/dp from the relation

$$\frac{dT}{dp} = T_{AC} V(T_{AC}) \frac{\Delta\alpha_p}{\Delta C_p} \quad (10)$$

known as Ehrenfest's equation for second-order transition and being in analogy to the Clausius-Clapeyron equation.

We find $dT/dp = (16.1 \pm 0.6) \text{ K kbar}^{-1}$ in very good agreement with $dT/dp = 16.10 \text{ K kbar}^{-1}$ found by Cladis *et al.*⁸ in direct pressure investigations.

IV. CONCLUSIONS

In conclusion we have found that the molar-volume variations near the SmA – SmC transition for $\bar{8}S5$ are well described by the mean-field model with an unusually large sixth-order term, Eq. (4), and are not consistent with XY critical behavior like that observed in superfluid helium, although, the data for smectic-C only ($T < T_{AC}$) are described by the Landau model and by critical behavior equally well.

For the Landau mean-field model we have found the characteristic crossover temperature t_0 in the range from 1.3×10^{-3} to 2.1×10^{-3} , consistent with values of t_0 obtained by Huang and Viner,² by Birgeneau *et al.*,³ and by Meichle and Garland⁴ for other compounds, but in disagreement with $t_0 = 6.5 \times 10^{-3}$ cited in Refs. 2–4 and estimated from measurements of Schantz and Johnson.⁷

From our measurements of molar volumes versus temperature we have estimated the jump of the thermal-expansion coefficient at phase transition $\Delta\alpha_p(T_{AC}) = 0.50 \times 10^{-4} \text{ K}^{-1}$ and by using this value in conjunction with ΔC_p from Ref. 7 we calculated $dT/dp = (16.1 \pm 0.6) \text{ K kbar}^{-1}$ by Ehrenfest's equation; this value is in excellent agreement with that found by Cladis *et al.*⁸ from direct measurements.

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