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# High-resolution volumetric study of the smectic-$A$ –to–nematic transition in 4-($n$-pentyl)phenylthiol-4′-($n$-octyloxy)benzoate ($\overline{8}$S5) and octyloxycyanobiphenyl (8OCB)

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High-resolution volumetric measurements have been made on pure $\overline{8}$S5 and 8OCB in the vicinity of the smectic-$A$–to–nematic ($A$-$N$) transition. The molar-volume variations show in both compounds a continuous second-order $A$-$N$ transition. For $\overline{8}$S5 the $A$-$N$ transition is well described by a critical three-dimensional $XY$ exponent $\alpha=\alpha'=-0.026$, but for 8OCB by the exponent $\alpha=\alpha'=0.19\pm0.07$. For 8OCB the anisotropic hyperscaling relation $2-\alpha=\nu_{\parallel}+2\nu_{\perp}$ is satisfied to within experimental error. The thermal-expansion coefficient $\alpha_p$ has been determined as a function of temperature.

## I. INTRODUCTION

In spite of numerous works on the nematic ($N$) –to–smectic-$A$ (Sm$A$) transition, there is not yet experimental or theoretical consensus on the universality class for critical behavior. The majority of measurements of the heat capacity $C_p$ in the vicinity of the phase transition have been done with differential scanning calorimetry (DSC) and ac calorimetry. Unfortunately, these measurements are not able to give a clear answer about the order of the transition, particularly if one deals with very weak first-order transitions. The continuity or discontinuity of the transition can be confirmed by precise measurements of enthalpy or volume as a function of temperature. Such measurements of enthalpy for liquid crystals were carried out by Thoen *et al.*[1] and Anisimov *et al.*[2] with an adiabatic-scanning calorimeter.

In previous papers[3,4] we reported a dilatometric method for precise measurements of volume as a function of temperature also in the vicinity of phase transitions. In these measurements we were able to detect relative changes in volume with high precision, $\sim3\times10^{-7}$.

In recent experimental investigations of the Sm$A$-$N$ transition the influence of structure, monolayer or bilayer smectic-$A$ phase, and of the width of the nematic range represented by the ratio $T_{AN}/T_{NI}$ on critical behavior was studied by different methods.

High-resolution calorimetric,[5–14] x-ray scattering,[13–15] and light-scattering[14,16] measurements have been carried out. In our recent work[4] the volumetric study of the smectic-$A$–to–smectic-$C$ ($A$-$C$) transition for 4-($n$-pentyl)phenylthiol-4′-($n$-octyloxy)benzoate ($\overline{8}$S5) was reported. Presently, we undertake the volumetric investigation of the Sm$A$-$N$ transition for $\overline{8}$S5 for which $T_{AN}/T_{NI}=0.937$ and also for bilayer (octyloxy)cyanobiphenyl (8OCB) for which $T_{AN}/T_{NI}=0.963$. $\overline{8}$S5 shows a continuous Sm$A$-$N$ transition[5,10] apparently with a small negative (close to zero) critical exponent $\alpha$. In the case of 8OCB, conflicting results about the order of the Sm$A$-$N$ transition and the critical exponent $\alpha$ have been reported.[6–12] It is supposed[4] that the thermal-expansion coefficient $\alpha_p$ could have the same singularity at the transition as the heat capacity $C_p$ and we have tried to extract the critical exponent from our $V(T)$ data. A power law with background terms was applied to describe the data. In Sec. II the experiment is described and the reported results 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 previously by us.[3,4] The dilatometer with a capillary 0.3 mm in diameter containing about 10 $\text{cm}^3$ carefully degassed sample of liquid crystal and about 2 $\text{cm}^3$ of mercury was placed in a 70-l water thermostat assuring vigorous stirring and a stability of local temperature better than ±0.2 mK. During the measurements the temperature of the bath was continuously monitored with a Hewlett-Packard quartz thermometer. Temperature was measured by means of a Tinsley 5187 SA platinum-resistance thermometer calibrated on International Practical Temperature Scale (IPTS)-68 at National Physical Laboratory (NPL), Teddington, United Kingdom, the resistance being measured with a Tinsley bridge, type 5840. The sensitivity of the dilatometer was so high that we were able to observe 1-mK temperature increments as an increase of a mercury column in the capillary by about 0.1 mm, what is equivalent to a volume change of $7.4\times10^{-6}$ $\text{cm}^3$. Total experimental error of the molar volume is estimated to be less than $1\times10^{-4}$ $\text{cm}^3\,\text{mol}^{-1}$. The measurements were done under a constant pressure[4] equal to 101.325 kPa.

The compounds used were synthesized and purified by "ZD Chemipan" (Warsaw). The sample of $\overline{8}$S5 was then purified by us,[4] whereas the 8OCB was used without any further purification. The transition temperatures $T_{AN}$ and $T_{NI}$ for both investigated compounds are given in Table I. The molar-volume variations with temperature for $\overline{8}$S5 and 8OCB near and at the Sm$A$-$N$ transition are presented in Figs. 1–4. The presence of a very small singularity of molar volume near the Sm$A$-$N$ transition temperature

TABLE I. Transition temperatures (K) for samples studied. For first-order transition, the coexistence range is reported.

| | $T_{AC}$ | $T_{AN}$ | $T_{NI}$ |
|---|---|---|---|
| $\bar{8}$S5 | 329.10 | 336.75 | 359.27–359.30 |
| 8OCB | | 339.99 | 353.05–353.10 |

superimposed on a large thermal expansion, requires that a linear background term must be subtracted. The thermal-expansion coefficients $\bar{\alpha}_p$ simply calculated as numerical derivatives from neighboring data points are also shown in Figs. 1 and 3 for $\bar{8}$S5 and 8OCB, respectively. The results shown in Figs. 1–4 were obtained during heating and cooling runs. Within the experimental resolution there is no hysteresis, as can be seen in Figs. 2 and 4 on an expanded temperature scale. The Sm$A$-$N$ transitions for these two compounds appear continuous.

## III. DATA ANALYSIS AND DISCUSSION

In our previous paper[4] we explained why the same power-law equation may be used to describe critical be-

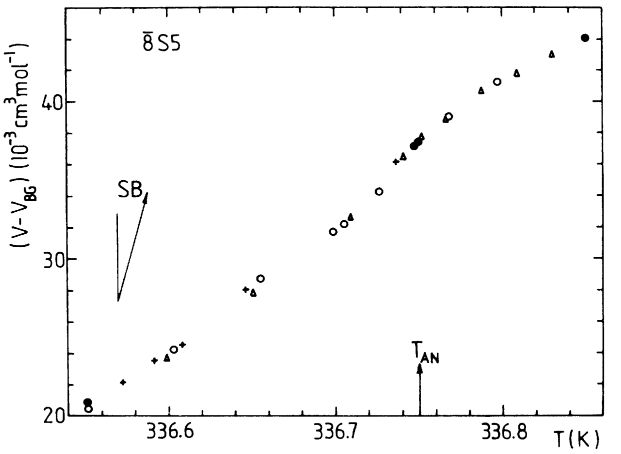

FIG. 2. Details of the molar-volume changes in the vicinity of the Sm$A$-$N$ transition in $\bar{8}$S5: one heating (△) and two cooling (○, +) runs. Solid circles refer to overlapping points of different runs.

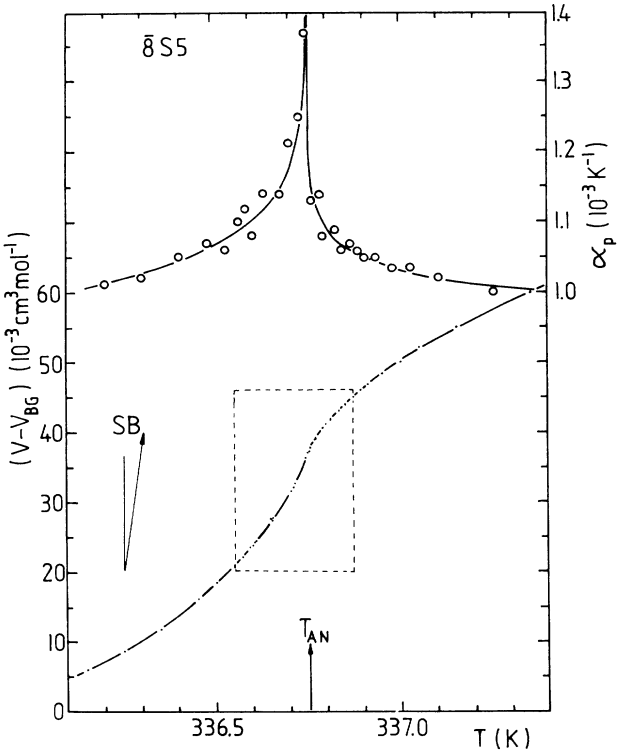

FIG. 1. Molar volume near the smectic-$A$–nematic transition in $\bar{8}$S5, with a linear background $V_{BG}=a+bT$ subtracted, plotted against temperature; $a=278.9612$ cm$^3$ mol$^{-1}$, $b=0.3866$ cm$^3$ mol$^{-1}$ K$^{-1}$. The upper part shows the thermal-expansion coefficient $\bar{\alpha}_p$ calculated from pairs of neighboring data points (circles) and $\alpha_p$ calculated from Eqs. (3) (solid line). The arrow *SB* shows the slope of the subtracted background.

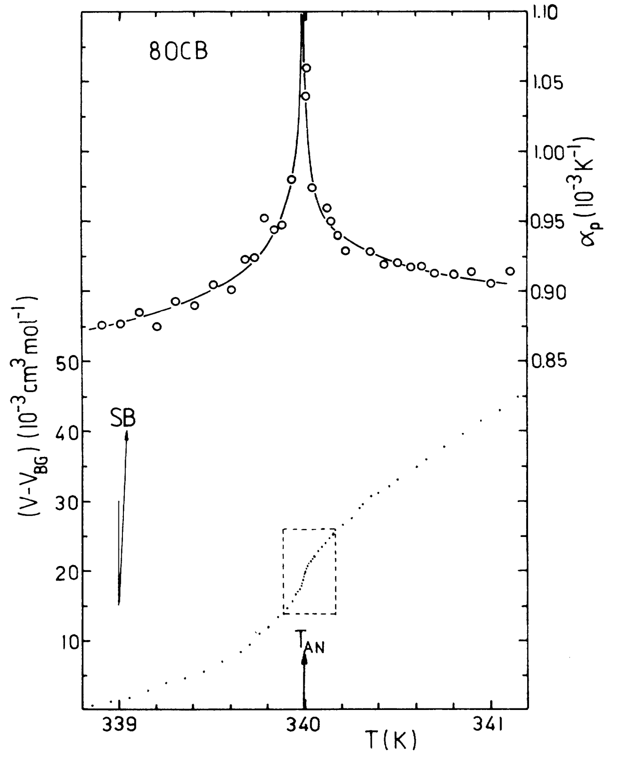

FIG. 3. Molar volume near the smectic-$A$–nematic transition in 8OCB, with a linear background $V_{BG}=a+bT$ subtracted, plotted against temperature; $a=217.8706$ cm$^3$ mol$^{-1}$, $b=0.2630$ cm$^3$ mol$^{-1}$ K$^{-1}$. The upper part shows the thermal-expansion coefficient $\bar{\alpha}_p$ calculated from pairs of neighboring data points (circles) and $\alpha_p$ calculated from Eqs. (3) (solid line). The arrow *SB* shows the slope of the subtracted background.

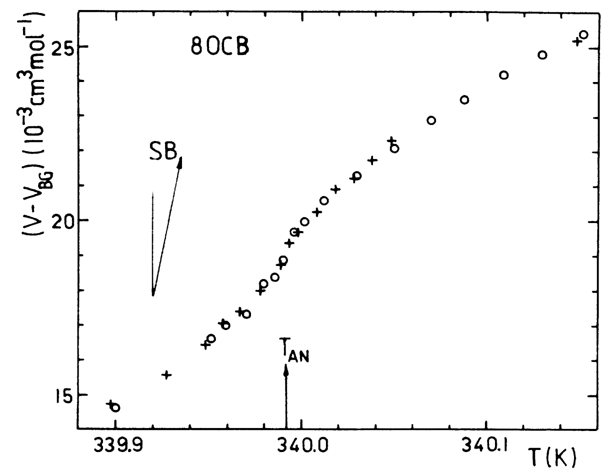

FIG. 4. Details of the molar-volume changes in the vicinity of the Sm$A$-$N$ transition in 8OCB: ○, heating; +, cooling.

havior of the heat capacity and of thermal expansion $(dV/dT)_p$ near and at the phase transition. To describe our present results the following equations were applied:

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

where $t\equiv|T/T_{AN}-1|$. Equations (1a) and (1b) were fitted to the experimental $V(T)$ data by a nonlinear least-squares procedure.[17] In principle, the transition temperature $T_{AN}$ should be treated as an adjustable parameter and it was varied during the fits presented in Tables II and IV for $\bar{8}$S5 and 8OCB, respectively. The quality of the fits is represented by chi square $\chi^2$ (Eq. 2) and standard deviation $\sigma$ values

$$\chi^2=\frac{1}{n-p}\sum_{i=1}^{n}W_i(V_i^{\text{expt}}-V_i^{\text{calc}})^2 , \qquad (2)$$

where $W_i$ is a weight of each point, $n$—number of experimental points, and $p$—number of adjustable parameters. The calculations were carried out twice for $W_i=1$ (then chi square is the square of the standard deviation of the fit, $\chi^2=\sigma^2$) and for $W_i=\sigma_i^2$ where $\sigma_i^2=\sigma_V^2+\sigma_T^2(dV/dT)^2$ with $\sigma_V=0.0001$ cm$^3$ mol$^{-1}$ and $\sigma_T=0.0002$ K. The second version of the calculation which yields a weighted chi square $\chi_\nu^2$ close to unity also gives us the uncertainty of the parameters; these values are presented in Tables III and V.

## A. $\bar{8}$S5

The $V(T)$ data for $\bar{8}$S5 (Figs. 2 and 3) show an inflection point at the transition temperature $T_{AN}$, which is very close to the value 336.75 K. The best transition temperature was established in separate fits of the data above and below $T_{AN}$ while the value of $T_{AN}$ was varied in steps of 5 mK. The results show a rather broad minimum of $\overline{\chi_\nu^2}$ value (see Table II); the transition temperature $T_{AN}=336.750\pm0.005$ K was chosen with the following criteria. For this value of $T_{AN}$ the critical exponents are equal, $\alpha=\alpha'$, in agreement with the scaling requirement and also $C=V(T_{AN}^+)$ comes out closest to $C'=V(T_{AN}^-)$ as expected for a second-order transition. The temperature of the transition thus established was fixed in further fits presented in Table III. With a rather narrow range of reduced temperature $t<2.7\times10^{-3}$ used in the fits 1–8 (three different ranges of $t$ were fitted), we simplified Eqs. (1a) and (1b) by the constraint $D=D'=0$ thus obtaining fits stable to range shrinking within the limits of parameter errors. The critical exponents are close to those of the three-dimensional (3D) $XY$ model proposed by de Gennes[18] and are roughly consistent with the scaling requirement $\alpha=\alpha'$. A fairly good description was obtained with

TABLE II. Results of the fits of molar-volume data for $\bar{8}$S5 near the nematic–to–smectic-$A$ transition for different transition temperatures $T_{AN}$. Data from temperature range 335.90–337.65 K were fitted with Eqs. (1a) and (1b) with $D=D'=0$. $\sigma$ is the standard deviation and $\overline{\chi_\nu^2}$ is the mean weighted value of square deviations calculated for each pair of fits above and below $T_{AN}$.

| $T_{AN}$ (K) | $\alpha,\alpha'$ | $A,A'$ (cm$^3$ mol$^{-1}$) | $B,B'$ (cm$^3$ mol$^{-1}$) | $C,C'$ (cm$^3$ mol$^{-1}$) | $10^4\sigma$ (cm$^3$ mol$^{-1}$) | $\overline{\chi_\nu^2}$ [a] |
|---|---|---|---|---|---|---|
| 336.745 | −0.031 | −223.104 | 326.999 | 409.1839 | 1.52 | 0.89 |
| | −0.027 | 410.443 | −494.256 | 409.1840 | 1.30 | |
| 336.750 | −0.028 | −221.155 | 327.914 | 409.1864 | 0.89 | 0.62 |
| | −0.028 | 406.816 | −489.338 | 409.1865 | 1.40 | |
| 336.755 | −0.027 | −221.018 | 328.563 | 409.1887 | 0.80 | 0.55 |
| | −0.029 | 417.060 | −496.412 | 409.1892 | 1.29 | |
| 336.760 | −0.025 | −229.255 | 337.765 | 409.1910 | 0.71 | 0.59 |
| | −0.030 | 418.076 | −494.496 | 409.1919 | 1.40 | |
| 336.765 | −0.026 | −216.986 | 326.488 | 409.1933 | 0.73 | 0.80 |
| | −0.031 | 420.782 | −494.566 | 409.1945 | 1.66 | |

[a] $\overline{\chi_\nu^2}=\frac{1}{N+N'}\sum_{i=1}^{N+N'}\sigma_i^{-2}(V_i^{\text{expt}}-V_i^{\text{calc}})^2$, where $N$ and $N'$ are the number of data points above and below $T_{AN}$, respectively. Here $N+N'=43$.

TABLE III. Parameter values for $\bar{8}$S5 obtained from separate fits of molar-volume data above and below the nematic–to–smectic-$A$ transition with Eqs. (1a) and (1b); constraint $D=D'=0$ was made in fits 1–8; transition temperature $T_{AN}=336.750$ K was chosen from the fits shown in Table II and was held fixed in all fits; $\sigma$ is the standard deviation; the thermal-expansion coefficient at the transition temperature $\alpha_p(T_{AN})$ is calculated from Eqs. (4). Values in parentheses were held fixed during the fit. $t_{\min}=|T/T_{AN}-1|=4.157\times10^{-6}$ for $T>T_{AN}$ and for $T<T_{AN}$.

| Fit | Phase | $\alpha,\alpha'$ | $A,A'$ (cm$^3$ mol$^{-1}$) | $B,B'$ (cm$^3$ mol$^{-1}$) | $C,C'$ (cm$^3$ mol$^{-1}$) | $D,D'$ | $10^3t_{\max}$ | $10^4\sigma$ (cm$^3$ mol$^{-1}$) | $10^3\alpha_p(T_{AN})$ (K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $N$ | $-0.030$<br>$\pm0.004$ | $-218.059$<br>$\pm26.1$ | 322.674<br>$\pm29.7$ | 409.1863<br>$\pm0.0001$ | | 0.475 | 0.91 | 2.34 |
| 2 | Sm$A$ | $-0.025$<br>$\pm0.003$ | 405.011<br>$\pm33.4$ | $-495.804$<br>$\pm33.9$ | 409.1864<br>$\pm0.0001$ | | 0.473 | 1.31 | 3.60 |
| 3 | $N$ | $-0.029$<br>$\pm0.004$ | $-218.447$<br>$\pm26.6$ | 324.676<br>$\pm27.0$ | 409.1863<br>$\pm0.0001$ | | 0.901 | 0.94 | 2.36 |
| 4 | Sm$A$ | $-0.028$<br>$\pm0.003$ | 409.134<br>$\pm28.3$ | $-489.544$<br>$\pm29.1$ | 409.1865<br>$\pm0.0001$ | | 0.886 | 1.38 | 3.55 |
| 5 | $N$ | $-0.028$<br>$\pm0.003$ | $-221.155$<br>$\pm25.6$ | 327.914<br>$\pm25.3$ | 409.1864<br>$\pm0.0001$ | | 2.668 | 0.89 | 2.38 |
| 6 | Sm$A$ | $-0.028$<br>$\pm0.003$ | 406.816<br>$\pm30.5$ | $-489.338$<br>$\pm31.2$ | 409.1865<br>$\pm0.0001$ | | 2.528 | 1.40 | 3.55 |
| 7 | $N$ | $(-0.026)$ | $-236.346$ | 343.291 | 409.1864 | | 2.668 | 0.90 | 2.49 |
| 8 | Sm$A$ | $(-0.026)$ | 426.266 | $-509.687$ | 409.1865 | | 2.528 | 1.55 | 3.72 |
| 9 | $N$ | $-0.028$<br>$\pm0.004$ | $-241.439$<br>$\pm27.0$ | 344.652<br>$\pm27.9$ | 409.1863<br>$\pm0.0001$ | $-0.093$<br>$\pm0.050$ | 2.668 | 0.87 | 2.50 |
| 10 | Sm$A$ | $-0.023$<br>$\pm0.002$ | 395.865<br>$\pm30.1$ | $-494.124$<br>$\pm30.8$ | 409.1864<br>$\pm0.0001$ | 0.272<br>$\pm0.026$ | 6.499 | 1.34 | 3.59 |
| 11 | $N$ | $(-0.026)$ | $-252.002$ | 355.874 | 409.1863 | $-0.078$ | 2.668 | 0.89 | 2.58 |
| 12 | Sm$A$ | $(-0.026)$ | 358.330 | $-455.762$ | 409.1864 | 0.299 | 6.499 | 1.40 | 3.31 |

fixed $\alpha=\alpha'=-0.026$ (fits 7 and 8), but the amplitude ratio $-A(1-\alpha)/A'(1-\alpha')$ equal to 0.55 is significantly lower than the ratio 1.1 expected for helium.

The correction-to-scaling terms were included in fits 9 and 10 with $\alpha$ and $\alpha'$ allowed to vary freely and in fits 11 and 12 with $\alpha=\alpha'=-0.026$ fixed. The inclusion of these correction terms did not make any significant improvement to the fits. Fits 11 and 12 with (3D) $XY$ exponents gave the amplitude ratio $-A/A'=0.70$ still smaller than that expected for $XY$ model and an unacceptably small value of $-D/D'=0.26$. A discontinuity at $T_{AN}$ in the thermal-expansion coefficient resulting from $B=-B'$ in Eqs. (3a) and (3b) is not expected in any simple theory. Therefore, strictly speaking, the $D$ coefficients obtained here for $\bar{8}$S5 cannot be interpreted as amplitudes of the correction-to-scaling terms. For 8OCB (see below) we find $B\cong-B'$.

The resulting values of molar volume extrapolated to the transition temperature $V(T_{AN}^{+})=C$ and $V(T_{AN}^{-})=C'$ are equal within the experimental uncertainty; this confirms that the transition is continuous.

The temperature dependence of thermal-expansion coefficient $\alpha_p=V^{-1}(dV/dT)_p$ was also calculated from the equations

$$\alpha_p(T)=\begin{cases}\dfrac{1}{V(T)T_{AN}}\left[(1-\alpha)At^{-\alpha}\left[1+\dfrac{1.5-\alpha}{1-\alpha}Dt^{1/2}\right]+B\right], & T>T_{AN} \quad (3a)\\[2ex] \dfrac{-1}{V(T)T_{AN}}\left[(1-\alpha')A't^{-\alpha'}\left[1+\dfrac{1.5-\alpha'}{1-\alpha'}D't^{1/2}\right]+B'\right], & T<T_{AN}\ . \quad (3b)\end{cases}$$

The curve obtained (solid line in the upper part of Fig. 1) reproduces very well the numerical values of $\bar{\alpha}_p$. The values of $\alpha_p$ at the transition temperature $T_{AN}$ were calculated as the limits of Eqs. (3a) and (3b) for $\alpha<0$ and $\alpha'<0$,

$$\alpha_p(T_{AN}^{\pm}) = \begin{cases} \dfrac{B}{T_{AN}C}, & T \to T_{AN}^{+} \\ \dfrac{-B'}{T_{AN}C'}, & T \to T_{AN}^{-} \end{cases} \tag{4}$$

and are also given in Table III.

### B. 8OCB

For this compound all data were fitted essentially in the same manner as for $\overline{8}$S5. The choice of the transition temperature $T_{AN}$ for 8OCB was easier than for $\overline{8}$S5. Here the quality of the fits strongly depends on $T_{AN}$ which was varied in smaller steps, of 2 mK (Table IV). For the transition temperature $T_{AN} = 339.992 \pm 0.002$ K, a clear minimum $\overline{\chi_\nu^2}$ occurs and simultaneously the scaling requirement $\alpha = \alpha'$ is obeyed. Further results of nonlinear least-squares analysis with fixed $T_{AN} = 339.992$ K are shown in Table V.

The $V(T)$ data from three different ranges of reduced temperature, $t < 0.5\times10^{-3}$, $t < 1\times10^{-3}$, and $t < 3\times10^{-3}$, were fitted separately to Eqs. (1a) and (1b) (fits 1–6). Again the constraint $D = D' = 0$ was made because of a rather narrow temperature range. There is no effect of range shrinking on $\alpha$ values in the nematic phase, however, in the smectic-*A* phase the values of $\alpha'$ from different fits differ slightly but within limits of parameter errors. In fits 3 and 4 ($t < 1\times10^{-3}$) the values $\alpha \cong \alpha' \cong 0.19$ were obtained with fairly good standard deviations. The molar volumes extrapolated to $T_{AN}$ temperature $V(T_{AN}^{+}) = C$ and $V(T_{AN}^{-}) = C'$ show a very small volume jump $\Delta V = C - C' = 3.3\times10^{-4}$ cm$^3$ mol$^{-1}$ at the Sm*A*-*N* transition, which could be indicative of a very weak first-order transition. However, this volume jump corresponds to $\Delta V/V = 1.1\times10^{-6}$ which seems very small and does not exceed by much our estimated total uncertainty of $3\times10^{-7}$.

The 3D *XY* critical exponent was also tested; for the smectic-*A* phase (fit 8) the best fit was then obtained, but for the nematic phase (fit 7) a description is clearly worse. Also, for these fits the parameters $C$ and $C'$ produce an apparent volume jump at the transition $\Delta V = 9\times10^{-4}$ cm$^3$ mol$^{-1}$ which, although exceeding the experimental error, remains in contradiction with the 3D *XY* model for which the transition is of second order.

The correction-to-scaling terms were included in fits 9–12 for a wider temperature range ($t < 3.5\times10^{-3}$ for $N$ and $t < 5.7\times10^{-3}$ for Sm*A*). On allowing all five parameters to vary freely, the critical exponents $\alpha = 0.19$ and $\alpha' = 0.18$ were obtained with a slight improvement of the fits. Fixed values $\alpha = \alpha' = 0.19$ were then tested over the same temperature range and with nonzero $D$ and $D'$ values (fits 11 and 12). These fits yield the amplitude ratios $-A/A' = 1.49$ and $-D/D' = 0.75$. The volume jump at the Sm*A*-*N* transition obtained from these fits $\Delta V = 2.1\times10^{-4}$ cm$^3$ mol$^{-1}$ is even smaller than that from fits with $D = D' = 0$. This volume change $\Delta V$ can be related to the corresponding latent heat by the Clausius-Clapeyron equation

$$\Delta H = T \Delta V \frac{dp}{dT_{AN}} \; . \tag{5}$$

Using this $\Delta V$ value and $dp/dT_{AN} = 57.7$ bar K$^{-1}$ estimated from the data of Cladis *et al.*,[19] we obtain a latent heat $\Delta H = 0.4$ J mol$^{-1}$. Such is also the case for the upper limit of latent heat obtained by Thoen *et al.*[1] for the Sm*A*-*N* transition in 8CB, considered by these authors as continuous. We therefore conclude that the Sm*A*-*N* transition in 8OCB is also continuous.

From the $V(T)$ data the thermal-expansion coefficients $\alpha_p(T)$ were also calculated according to Eqs. (3a) and (3b)

TABLE IV. Results of the fits of molar-volume data for 8OCB near the nematic–to–smectic-*A* transition for different temperatures $T_{AN}$. Data from temperature range 339.65–340.31 K were fitted with Eqs. (1a) and (1b) with $D = D' = 0$; $\sigma$ is the standard deviation and $\overline{\chi_\nu^2}$ is the mean weighted value of square deviations calculated for each pair of fits above and below $T_{AN}$.

| $T_{AN}$ (K) | $\alpha,\alpha'$ | $A,A'$ (cm$^3$ mol$^{-1}$) | $B,B'$ (cm$^3$ mol$^{-1}$) | $C,C'$ (cm$^3$ mol$^{-1}$) | $10^4\sigma$ (cm$^3$ mol$^{-1}$) | $\overline{\chi_\nu^2}$[a] |
|---|---|---|---|---|---|---|
| 339.988 | 0.216 | 4.116 | 81.975 | 307.3061 | 1.31 | 1.16 |
| | 0.124 | −10.540 | −74.898 | 307.3059 | 1.62 | |
| 339.990 | 0.190 | 5.234 | 80.691 | 307.3069 | 1.13 | 1.04 |
| | 0.160 | −6.524 | −80.150 | 307.3066 | 1.57 | |
| 339.992 | 0.189 | 4.746 | 82.469 | 307.3077 | 0.93 | 0.90 |
| | 0.192 | −4.656 | −82.418 | 307.3073 | 1.55 | |
| 339.994 | 0.156 | 6.940 | 79.388 | 307.3084 | 0.97 | 1.19 |
| | 0.192 | −5.287 | −80.216 | 307.3081 | 1.88 | |
| 339.996 | 0.145 | 7.641 | 78.869 | 307.3090 | 0.99 | 1.30 |
| | 0.186 | −6.008 | −78.498 | 307.3088 | 1.97 | |

[a] $\overline{\chi_\nu^2} = \dfrac{1}{N+N'}\sum_{i=1}^{N+N'} \sigma_i^{-2}(V_i^{\text{expt}} - V_i^{\text{calc}})^2$, where $N$ and $N'$ are the number of data points above and below $T_{AN}$, respectively. Here $N + N' = 41$.

TABLE V. Parameter values for 8OCB obtained from separate fits of molar-volume data above and below the nematic–to–smectic-$A$ transition with Eqs. (1a) and (1b); constraint $D=D'=0$ was made in fits 1–8; transition temperature $T_{AN}=339.992$ K was chosen from the fits shown in Table IV and was held fixed in all fits; $\sigma$ is the standard deviation; values in parentheses were held fixed during the fit. $t_{\min}=|T/T_{AN}-1|=1.235\times10^{-5}$ for $T>T_{AN}$ and $t_{\min}=|T/T_{AN}-1|=1.029\times10^{-5}$ for $T<T_{AN}$.

| Fit | Phase | $\alpha,\alpha'$ | $A,A'$ ($\text{cm}^3\,\text{mol}^{-1}$) | $B,B'$ ($\text{cm}^3\,\text{mol}^{-1}$) | $C,C'$ ($\text{cm}^3\,\text{mol}^{-1}$) | $D,D'$ | $10^3 t_{\max}$ | $10^4\sigma$ ($\text{cm}^3\,\text{mol}^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | $N$ | 0.193<br>±0.021 | 4.613<br>±1.6 | 82.326<br>±5.2 | 307.3076<br>±0.0001 | | 0.470 | 0.91 |
| 2 | Sm$A$ | 0.171<br>±0.025 | −6.306<br>±2.1 | −79.212<br>±3.9 | 307.3073<br>±0.0001 | | 0.414 | 1.73 |
| 3 | $N$ | 0.189<br>±0.071 | 4.746<br>±4.2 | 82.469<br>±7.0 | 307.3077<br>±0.0001 | | 0.919 | 0.93 |
| 4 | Sm$A$ | 0.192<br>±0.065 | −4.656<br>±3.9 | −82.418<br>±6.5 | 307.3073<br>±0.0001 | | 0.999 | 1.55 |
| 5 | $N$ | 0.194<br>±0.076 | 3.726<br>±3.5 | 85.502<br>±8.1 | 307.3078<br>±0.0001 | | 2.824 | 1.51 |
| 6 | Sm$A$ | 0.167<br>±0.063 | −8.446<br>±3.7 | −73.071<br>±6.5 | 307.3075<br>±0.0001 | | 3.057 | 1.91 |
| 7 | $N$ | (−0.026) | −108.689 | 190.332 | 307.3081 | | 2.824 | 2.17 |
| 8 | Sm$A$ | (−0.026) | 181.970 | −251.666 | 307.3072 | | 3.057 | 1.58 |
| 9 | $N$ | 0.192<br>±0.016 | 6.092<br>±0.9 | 73.008<br>±3.2 | 307.3076<br>±0.0001 | 5.490<br>±1.5 | 3.414 | 1.13 |
| 10 | Sm$A$ | 0.180<br>±0.015 | −4.875<br>±1.0 | −86.117<br>±2.2 | 307.3074<br>±0.0001 | −6.204<br>±1.5 | 5.651 | 1.54 |
| 11 | $N$ | (0.19) | 6.287 | 72.560 | 307.3076 | 5.462 | 3.414 | 1.13 |
| 12 | Sm$A$ | (0.19) | −4.227 | −87.651 | 307.3074 | −7.331 | 5.651 | 1.54 |

with parameters taken from fits 11 and 12. The curve obtained describes very well the numerical values of $\bar{\alpha}_p$ and is shown in Fig. 3 (solid line in the upper part).

Overall, $V(T)$ data in the vicinity and at the Sm$A$-$N$ transition for 8OCB are described very well by $\alpha=\alpha'=0.19\pm0.07$ which on the whole appear better than the negative values of $\alpha$ and $\alpha'$. This value corresponds very well to values obtained in the calorimetric measurements of the heat capacity.[11,12] On the other hand, conflicting results for $\alpha$ have been reported in literature. The logarithmic singularity in $C_p$ has been reported by Johnson *et al.*[6] as well as by LeGrange and Mochel[9,10] which for one sample ("earlier batch") obtained $\alpha=\alpha'=0.025\pm0.04$. However, the latter authors[9,10] reported $\alpha=\alpha'=0.25\pm0.02$ for the other sample which agrees with the values 0.27±0.04 as well as 0.24±0.03 obtained by Garland *et al.*[7,8] and by Viner and Huang,[11] respectively. These values of $\alpha$ are larger than 0.16±0.03 found by Hatta and Nakayama.[12]

The x-ray and light scattering measurements provide values of correlation length exponents $\nu_\parallel$ and $\nu_\perp$, parallel and perpendicular to the nematic director, respectively, which are connected with critical exponent $\alpha$ by the anisotropic hyperscaling relation proposed by Lubensky and Chen[20] $2-\alpha=\nu_\parallel+2\nu_\perp$. For 8OCB, the x-ray scattering[15] measurements give $\nu_\perp=0.58\pm0.04$ and $\nu_\parallel=0.71\pm0.04$ and light scattering[16] studies yield $\nu_\parallel=0.68\pm0.02$. These values yield $\nu_\parallel+2\nu_\perp=1.87\pm0.09$. Our critical exponent $\alpha=0.19\pm0.07$ obtained in volumetric measurements gives $2-\alpha=1.81\pm0.07$. These two values agree within the experimental error.

For $\overline{8}$S5 the experimental[21] correlation length exponents $\nu_\perp$ and $\nu_\parallel$ are 0.68 and 0.83, respectively. These values yield $\nu_\parallel+2\nu_\perp=2.19$. It is obvious that our critical exponent which is close to −0.026 does not obey the hyperscaling relation and deviation exceeds the combined experimental errors.

## IV. CONCLUSIONS

We have presented new experimental results for the temperature dependence of the molar volume near the Sm$A$-$N$ transition of the two liquid crystals $\overline{8}$S5 and 8OCB with different widths of the nematic range ($T_{AN}/T_{NI}=0.937$ and 0.963, respectively).

We have found that molar-volume variations near Sm$A$-$N$ transition for $\overline{8}$S5 are consistent with $XY$ critical behavior like that observed in superfluid helium with $\alpha=\alpha'=-0.026$, whereas for 8OCB from power-law analysis we obtained the critical exponent

$\alpha=\alpha'=0.19\pm0.07$. In both cases the critical exponents are insensitive to range shrinking.

Our $\alpha$ value for 8OCB is consistent with $\nu_{\parallel}$ and $\nu_{\perp}$ for the anisotropic correlation length and satisfies the anisotropic hyperscaling relation of Lubensky and Chen[20] within the experimental error.

The Sm$A$-$N$ transition in both investigated compounds is continuous second order, although for bilayer 8OCB the fitting analysis apparently yields a very small volume jump at $T_{AN}$, $\Delta V=2.1\times10^{-4}$ cm$^3$ mol$^{-1}$ (or $\Delta V/V=6.8\times10^{-7}$) which, however, hardly exceeds the limits of experimental uncertainty.

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