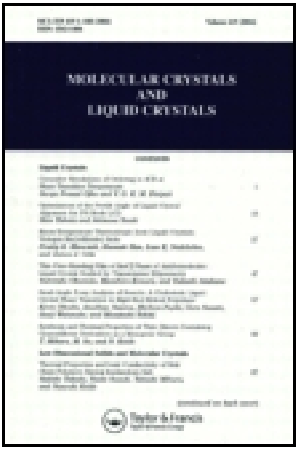

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Critical Behavior of Birefringence in Two Smectic-A Pentylbenzenethio-Alkoxybenzoates Near the Smectic-C Phase

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Critical Behavior of Birefringence in Two Smectic-A Pentylbenzenethio-Alkoxybenzoates Near the Smectic-C Phase

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The birefringence has been measured in detail in the smectic-A phase of 4-*n*-pentylbenzenethio-4′-*n*-octyloxyaniline and 4-*n*-pentylbenzenethio-4′-*n*-decyloxyaniline. The reduction of the birefringence near the smectic-C phase has been analyzed in terms of the effect of pretransitional short-range tilt-angle fluctuations. The results show that the two materials exhibit quantitatively similar critical suppression of the birefringence which can be characterized, within the temperature range of the fits, by a specific-heat critical exponent α of 0.15 ± 0.12 and 0.16 ± 0.08, respectively.

INTRODUCTION

The smectic-A to smectic-C (AC) phase transition has been a subject of intense interest following de Gennes' suggestion that it may be continuous and exhibit helium-like critical behavior.[1] The exprimental situation is not conclusive. Most measurements have been made on the pretransitional behavior of the order parameter and the susceptibility. The reported critical exponents vary from being mean-field[2–5] to helium-like[6,7] to having values in between.[8,9]

We have made high-resolution measurements of the optical birefringence Δn near the AC transition. An unusual suppression of Δn in the smectic-A phase due to the occurrence of short-range smectic-C order has been reported.[10] The critical behavior in Δn is potentially useful for extracting information about the singular part of the specific heat. This is particularly interesting in view of the unusually weak specific-heat anomaly that has been observed.[11] In our first measurement on 4-*n*-pentylbenzenethio-4′-*n*-octyloxybenzoate ($\bar{8}$S5), a preliminary data analysis yielded a specific-heat critical exponent α of 0.32 ± 0.12.[10] This value of α is unusually high and disagrees with the value $\alpha' = -0.54 \pm 0.07$ obtained from a specific-heat measurement.[11] The sample of $\bar{8}$S5 that was studied had a relatively low AC transition temperature T_{AC} of 328.125 K and was not tested for purity.

In order to study the effect of purity on the results, we have made additional measurements of Δn near the AC transition in samples of $\bar{8}$S5 of known purity. Since $\bar{8}$S5 has a smectic-A temperature range of only 7 K, it is suspected that pretransitional behavior near the nematic to smectic-A (NA) transition might interfere with the data near the AC transition. We have therefore also studied Δn near the AC transition in 4-*n*-pentylbenzenethio-4′-*n*-decyloxybenzoate ($\overline{10}$S5), which has a smectic-A temperature range of 17K. The results of these new measurements on $\bar{8}$S5 and $\overline{10}$S5 are reported in this paper.

EXPERIMENTAL

Samples of $\bar{8}$S5 and $\overline{10}$S5 were synthesized by esterification of the appropriate acid chloride with 4-*n*-pentylbenzenethiol.[12] Using a Perkin–Elmer DSC1B differential scanning calorimeter, the purity of the $\bar{8}$S5 sample was estimated to be $(99.87 \pm 0.03)\%$. Elemental analysis the $\overline{10}$S5 sample (calculated 76.13 % C, 9.15 % H, 7.28 % S; found 76.27 % C, 9.07 % H, 7.21 % S) suggested a purity of at least 99.9 %.

Planar samples between glass slides, with the director aligned in a direction parallel to the slides, were studied. By decreasing the temperature slowly from the nematic phase, sample alignment was maintained in the smectic-A phase. The sample temperature was maintained to a stability of 1 mK. The temperature gradient in the illuminated part of the sample was estimated to be less than 6 mK. The birefringence Δn was measured using a rotating-analyser technique with a sensitivity of 4×10^{-6}.[13] The intensity of light scattered by the sample was measured simultaneously to monitor T_{AC}.

RESULTS AND ANALYSIS

All the samples show qualitatively the same behavior of Δn in the smectic-A phase near the AC transition. It increases considerably less with decreasing temperature than in materials that do not have an AC transition. The value of Δn reaches a plateau at about 0.1 K above T_{AC} and decreases on further cooling to a local minimum at T_{AC}. On the smectic-C side, the apparent Δn rises sharply with decreasing temperature.

The data in the smectic-A phase have been analyzed in terms of the effect of short-range fluctuations of the tilt angle θ on Δn. If Δn_0 is the birefringence in the absence of the AC transition, we have[10]

$$\Delta n = \Delta n_0(1 - \langle \theta^2 \rangle). \tag{1}$$

Since $\langle \theta^2 \rangle$ is related to the singular part of the free energy, one expects

$$\langle \theta^2 \rangle \sim t^{1-\alpha}, \tag{2}$$

where $t = (T - T_{AC})/T_{AC}$. The background term Δn_0 is expected to have an essentially linear temperature dependence. The data were therefore fitted to the expression

$$\delta(\Delta n) \equiv \Delta n - \Delta n_c - Bt = At^{1-\alpha} \tag{3}$$

using a non-linear least-squares method with Δn_c, A, B and α as adjustable parameters. Since the transition is second order, the value of T_{AC} measured from the minimum in Δn was used.

The fitting is complicated by the cusp-like nature of the singular term and the large temperature-dependent background term. We have examined systematically the effect of the temperature range of the data used in the fit on the values of the parameters. Because the data are non-diverging, the fit is found to be insensitive to the minimum value of t used in the fit. We have therefore used all the data points closest to T_{AC}. The fit, however, is sensitive to the maximum value t_{max} of t. If t_{max} is too small, the data within the temperature range do not have sufficient variations to uniquely determine the parameters appearing in Eq. (3). If t_{max} is too large, the linear background correction is questionable. We have sought to determine the range of t_{max} which gives a "stable" fit. A stable fit is defined as one which is characterized by (a) a negative background coefficient B *and* (b) a value of the exponent α which remains constant for a considerable range of t_{max}. For the two samples of $\overline{8}$S5 and one sample of $\overline{10}$S5 studied, such a stable fit can be found. The results are summarized in Table I. The quality of the fit is shown in Figure 1 for one sample of $\overline{8}$S5 and in Figure 2 for $\overline{10}$S5. Outside of the range of t_{max} listed in Table I, the parameters are found to be unstable to the addition

TABLE I

Parameters obtained by fitting data on two samples of $\bar{8}$S5 and one of $\overline{10}$S5 to Eq. (3). The range of t_{max} is that for which a stable fit, as defined in the text, is obtained.

Sample	T_{AC}(K)	Range of t_{max}	A	B	$1 - \alpha$
$\bar{8}$S5(#1)	328.783	$2.3 \times 10^{-3} - 6.9 \times 10^{-3}$	0.129	−0.388	0.85 ± 0.10
$\bar{8}$S5(#2)	328.769	$2.3 \times 10^{-3} - 6.5 \times 10^{-3}$	0.115	−0.368	0.85 ± 0.12
$\overline{10}$S5	337.890	$4.4 \times 10^{-3} - 8.1 \times 10^{-3}$	0.089	−0.298	0.84 ± 0.08

or deletion of data points and often the sign of the coefficient B is positive, which is opposite to what is expected of the background term.

In an attempt to extend the temperature range of the fit, we have also fitted the data to an expression with a quadratic background correction.

$$\delta(\Delta n) \equiv \Delta n - \Delta n_c - Bt - Ct^2 = At^{1-\alpha}. \tag{4}$$

We find, however, that the addition of a fifth coefficient greatly increases the uncertainty in the parameters and the sensitivity of the fit to the temperature range.

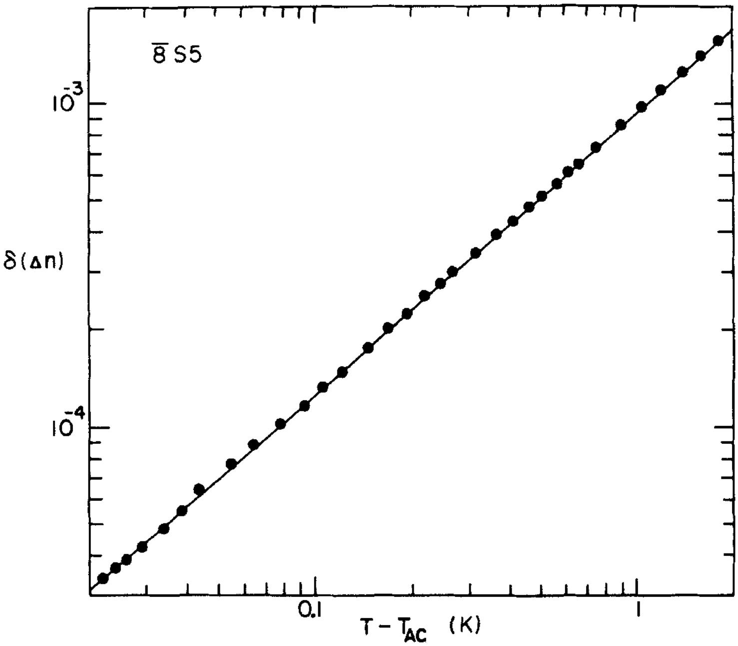

FIGURE 1 Fit of birefringence data on first $\bar{8}$S5 sample to Eq. (3) with parameters listed in Table I. The straight line has a slope of 0.85.

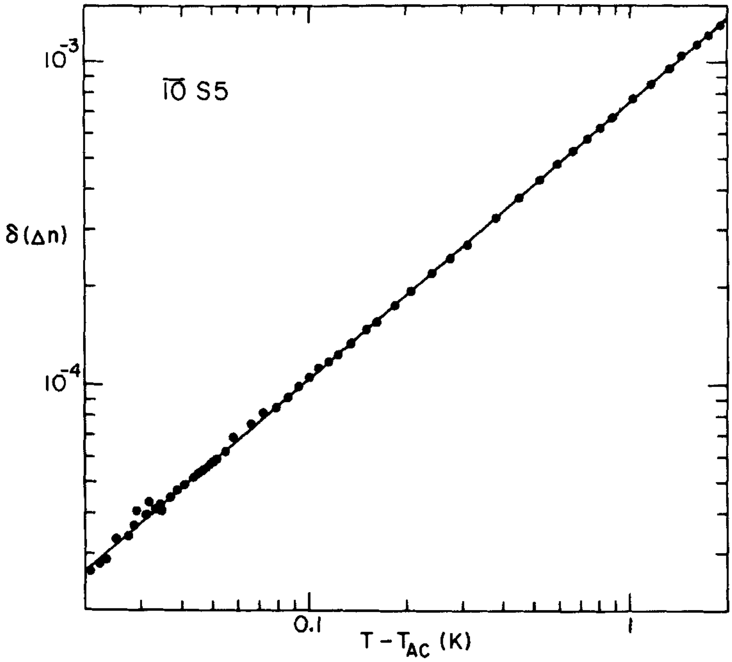

FIGURE 2 Fit of birefringence data on $\overline{10}$S5 to Eq. (3) with parameters listed in Table I. The straight line has a slope of 0.84.

It can be seen from Table I that the two samples of $\bar{8}$S5 with slightly different T_{AC} give a consistent result of $\alpha = 0.15 \pm 0.12$. An almost identical result of $\alpha = 0.16 \pm 0.08$ is obtained for $\overline{10}$S5. The difference between this result for $\bar{8}$S5 and that obtained earlier[10] with a sample with a considerably lower T_{AC} may be attributed to the difference in sample purity. We should note, however, that the lower density of data points in the earlier study did not permit a systematic analysis of the fit as a function of temperature range. The consistency of the current results for $\bar{8}$S5 and $\overline{10}$S5, which have quite different smectic-A temperature ranges, show that any interference from the NA pretransitional effects is not significant. While the fit has been obtained over a considerable range of t_{max}, the large number of parameters and the cusp-like data have prevented us from decreasing the value of t_{max} beyond 2.3×10^{-3}. We are thus unable to examine the possible existence of any crossover effect, such as that observed in a specific-heat measurement near the NA transition.[14] Subject to this reservation, our results that $\bar{8}$S5 and $\overline{10}$S5 exhibit quantitatively similar critical suppression of Δn near the AC transition and that, within the temperature range of the fits, the critical exponent α is neither mean-field nor helium-like in both materials.

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