Extended Fisher renormalized tricritical behavior of the nematic–smectic-A transition in liquid-crystal mixtures

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We report a high-resolution x-ray scattering study of the nematic–smectic-A transition around the tricritical point in mixtures of heptyloxypentylphenylthiobenzoate and octyloxycyanobiphenyl. Unusually large susceptibility and correlation length critical exponents are observed; this is explained as a clear example of Fisher renormalization. The underlying exponents, over a large range of impurity concentrations, are in good agreement with those observed previously in homologous mixture tricritical studies.

The physics of the nematic (N) to smectic-A (Sm-A) liquid-crystal phase transition, most especially in the vicinity of the tricritical point, continues to be an active subject of research.[1] Tricritical behavior, in which the transition crosses over from being second to first order, has been studied extensively in a number of systems including most notably ^{3}He-^{4}He mixtures[2] and metamagnets such as $FeCl_2$ (Ref. 3) and $Dy_3Al_5O_{12}$ (Ref. 4). In general, the experimental tricritical results for such systems are in good agreement with the predictions of mean-field theory as expected on the basis of the Ginzburg criterion.[5] Studies of liquid-crystal homologous series which show a tricritical point as a function of chain length, however, have shown puzzling deviations[1] from mean-field exponents and this problem clearly warrants further study. As yet there exists no detailed information on the critical-tricritical crossover behavior in nonhomologous mixtures apart from recent heat capacity studies by Garland and co-workers.[6,7] Studies of such systems are extremely interesting both because of the information they yield on tricritical phenomena and also because they are expected to reveal pronounced Fisher renormalization[8] in which exponents are renormalized because the experimental path is singular in temperature, concentration space. Fisher renormalization has been observed for the Ising phase separation transition in ternary mixtures where full[9–11] or partial[12] exponent renormalization has been reported. However, in these cases the renormalization is quite subtle since the heat capacity exponent is small ($\alpha=0.11$). Much more dramatic behavior is expected at a tricritical point where full renormalization would imply a doubling of the critical exponents. To date, the only example of Fisher renormalization in liquid-crystal systems other than the above-mentioned work of Garland and co-workers is for the smectic-A_1–smectic-A_2 transition in mixtures of hexylphenyl cyanobenzoyloxy benzoate (DB_6) and terephtal-*bis*-butylaniline (TBBA) where the underlying transition is Ising-like.[13]

In this note we report a detailed x-ray scattering study of the N–Sm-A transition in mixtures of the nonhomologous materials octyloxycyanobiphenyl (8OCB) and heptyloxypentylphenylthiobenzoate ($\overline{7}$S5) for concentrations in the vicinity of the tricritical point. These results compliment the heat-capacity measurements[6] which show dramatic renormalization of the critical exponent α; specifically, near the tricritical point $\alpha \simeq -1$ rather than $+\frac{1}{2}$ as expected for a normal tricritical point. We begin with a brief discussion of the physics behind Fisher renormalization before describing the system under study and outlining the experimental apparatus. The results and a brief discussion conclude this paper.

For mixtures, the transition is, by necessity, observed along an experimental path of constant concentration so that the difference in the chemical potential of the two species fluctuates in equilibrium with the other degrees of freedom under this constraint. Fisher[8] showed that this path is singular,

$$\Delta T^* = a\Delta T^{1/(1-\alpha)}(1-b\Delta T^{\alpha/(1-\alpha)}) , \tag{1}$$

where ΔT^* is the distance to the transition along a path of constant chemical potential difference, and ΔT the measured distance. It is this singularity that gives rise to the exponent renormalization, so that asymptotically close to the transition the observed exponents are

$$2-\alpha_R = \frac{2-\alpha}{1-\alpha}, \quad \gamma_R = \frac{\gamma}{1-\alpha}, \quad \nu_R = \frac{\nu}{1-\alpha} , \tag{2}$$

where the exponents α, ν, and γ are the ideal heat capacity, correlation length, and susceptibility exponents, respectively, and the subscript R refers to the renormalized values. The crossover temperature ΔT_R, above which ideal behavior is seen, is controlled by the amplitude of the singularity, a in Eq. (1), which is proportional to the square of the transition temperature gradient times the impurity concentration.[8,14]

$\overline{7}$S5 is a nonpolar molecule with first-order isotropic-nematic and nematic–smectic-C transitions at $T_{I\text{-}N}=355$ K and $T_{N\text{-Sm-}C}=310$ K, respectively. Although $\overline{7}$S5 exhibits no Sm-A phase, it is unstable to that phase as illustrated by the fact that the nearby homolog $\overline{8}$S5 does ex-

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hibit Sm-A ordering.[1] It was discovered by Martinez-Miranda *et al.*[15] that small amounts of the liquid-crystal material 8OCB, a shorter, polar molecule, also stabilizes the Sm-A phase producing the well-studied[15] N–Sm-A–Sm-C multicritical point at $X_{8OCB}=0.0217$. As the 8OCB concentration increases the N–Sm-A transition temperature increases rapidly, while the I-N transition temperature is relatively insensitive to the composition. From both theory[16] and previous experiments[1] one expects that as the nematic range decreases there will be a crossover from second- to first-order behavior at a tricritical point. As shown by Huster, Stine, and Garland,[6] this is indeed the case for $\overline{7}S5+8OCB$ (see Fig. 1). Because of the very steep phase boundary, as well as the large heat-capacity exponent ($\alpha=\frac{1}{2}$) associated with the tricritical point, this system should represent an especially interesting case study for Fisher renormalization.

This high-resolution x-ray scattering experiment was carried out using Cu $K\alpha$ x rays from a rotating anode source. The experimental arrangement was very similar to that used in previous experiments done in this laboratory.[1,15,17,18] The spectrometer was used in a dispersive configuration with perfect Si(111) crystals for the monochromator and analyzer. The in-plane longitudinal resolution was 3×10^{-4} Å^{-1} full width at half maximum (FWHM), while the in-plane transverse resolution was essentially perfect. The out-of-plane resolution, which was determined simply by collimating slits, was 0.08 Å^{-1} FWHM. The samples were taken from the same batch of material used by Huster, Stine, and Garland.[6] A silicon thermistor-based temperature controller produced oven temperatures stable to ±0.005 K for the duration of a scan. A 5 kG magnetic field aligned the nematic director. The transition temperature drift was typically $\sim$20 mK per day; this effect is negligible over the duration of a scan, which is about 30 min, and could be readily corrected for in extended studies.

Transverse and longitudinal scans through the wave-vector position $(0,0,q_{\parallel}^{0})$ with $q_{\parallel}^{0}=0.235$ Å^{-1} were taken over the reduced temperature range $7\times10^{-5}<t=(T/T_{N\text{-Sm-}A}-1)<10^{-2}$ and fitted to the standard form of a Lorentzian with a fourth-order correction in the transverse direction[17]

$$S(\mathbf{q})=\frac{\sigma_0}{1+\xi_{\parallel}^{2}(q_{\parallel}-q_{\parallel}^{0})^2+\xi_{\perp}^{2}q_{\perp}^{2}(1+c_4\xi_{\perp}^{2}q_{\perp}^{2})}\ , \tag{3}$$

which was then convolved with the measured resolution function. The goodness of fit parameter χ^2 was typically between 1 and 3 for fits of the scattering to this form. Figure 2 shows some representative scans with the fitted cross section for the $X=0.0338$ sample. Critical exponents are extracted by fitting the parameters σ_0, $\xi_{\parallel}$, and $\xi_{\perp}$ obtained from these fits to simple power laws:

$$\xi_{\parallel,\perp}=\xi_{\parallel,\perp}^{0}t^{-\nu_{\parallel,\perp}},\quad \sigma_0=\sigma^0 t^{-\gamma}\ . \tag{4}$$

An example of such fits is shown for the $X=0.0561$ sam-

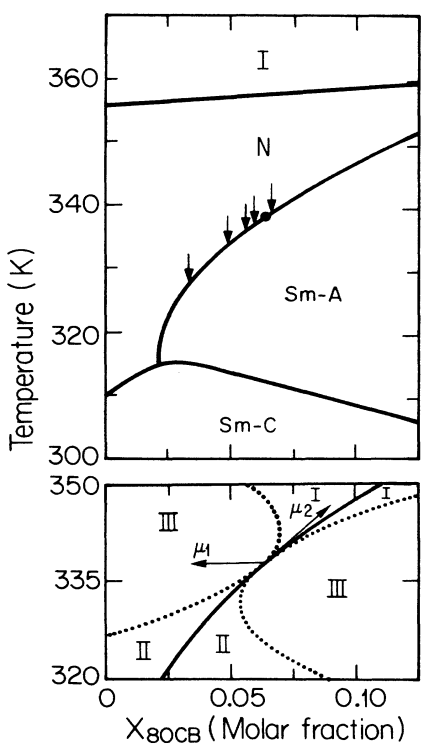

FIG. 1. (a) Phase diagram for the $8OCB_x\overline{7}S5_{1-x}$ system, as given in Ref. 6. The arrows mark the concentrations studied. (b) The dotted lines, purely for illustration purposes, show the shape of the crossover region, greatly exaggerated, as explained in the text. The observed extended tricritical behavior implies that the crossover lines border the phase boundary much more closely.

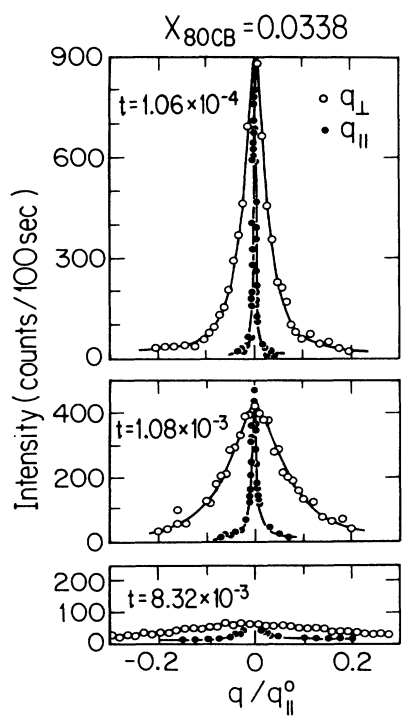

FIG. 2. Longitudinal and transverse scans taken through $(0,0,q_{\parallel}^{0})$ for the $X=0.0338$ sample at three reduced temperatures. The solid lines are the results of fits to Eq. (3).

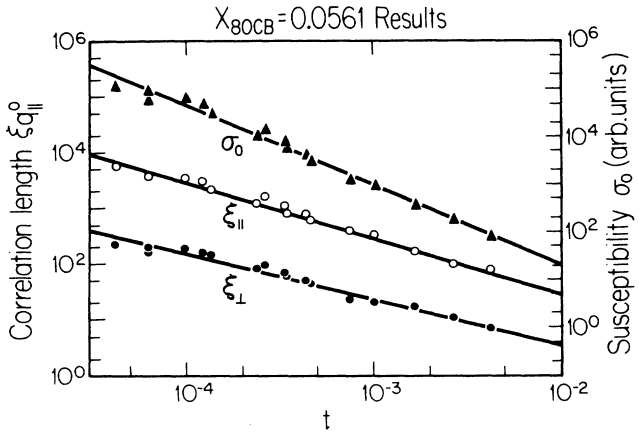

FIG. 3. Single power-law fits for the susceptibilities, transverse and longitudinal correlation lengths obtained from Eq. (3) for the $X=0.0561$ sample.

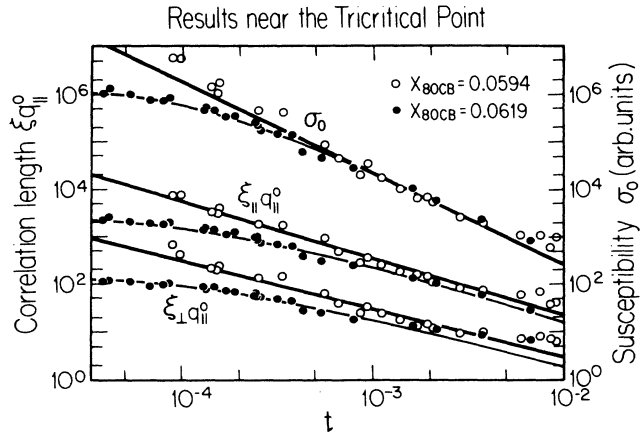

FIG. 4. Smectic susceptibility, longitudinal and transverse correlation length vs reduced temperature for the two samples nearest the tricritical point. Note the saturation in the $X=0.0619$ sample, which results from an overestimation of T_c as defined by the point at which the longitudinal peak becomes resolution limited.

ple in Fig. 3. The transition temperature could be accurately determined from anomalies in the transverse and longitudinal profiles as discussed by Ocko *et al.*[1]

The samples with 8OCB molar concentrations $X \leq 0.0594$ showed no systematic departure from the single power-law behavior down to reduced temperatures of $t \sim 7\times10^{-5}$. However, as may be seen in Fig. 4, the $X=0.0619$ sample clearly exhibits a saturation of the three critical quantities below $t \sim 1.2\times10^{-4}$, which implies that the transition is first order.[1,19] This is consistent with the measurements of Huster, Stine, and Garland,[6] which put the tricritical point for this series close to $X=0.0614$. The solid lines in Fig. 4 for $X=0.0619$ are the results of best fits to the form

$$\xi_{\parallel,\perp}=\xi^0_{\parallel,\perp}(t+t')^{-\nu_{\parallel,\perp}}, \quad \sigma_0=\sigma^0(t+t')^{-\gamma} . \tag{5}$$

This regards the first-order transition as preempting an underlying second-order transition; t' is just $(T_{c_1}-T_{c_2})/T_{c_2}$ where the subscripts 1 and 2 refer to the first- and second-order transitions, respectively. To estimate t' we first fixed the exponents at their $X=0.0594$ values and allowed t' to vary during fits of σ_0, $\xi_\parallel$, and $\xi_\perp$. We then held t' fixed at the average value to obtain the exponents in Table I. This average value, $t'=1.24\times10^{-4}$, corresponds to a putative second-order transition 42 mK below the observed first-order transition; this is well outside of our estimate of the transition temperature error of ±10 mK.

It is strikingly apparent when one looks at the observed, effective critical exponents (Table I) that they are exceptionally large as was anticipated by Huster, Stine, and Garland.[6] Following those authors, it is evident that these anomalously high exponents represent a clear example of Fisher renormalization. Table II shows the underlying exponents calculate using values for α from Ref. 6 and the assumption that the exponents are fully renormalized. The consequent underlying exponents are close to, but significantly different from, the mean-field tricritical values $\nu_\parallel=\nu_\perp=0.5$, $\gamma=1$, and $\alpha=0.5$. However, the intrinsic values for the $X=0.0594$ sample given in Table II agree quite well with those measured directly for decyloxypentylphenylthiobenzoate ($\overline{10}$S5), which has $T_{N\text{-Sm-}A}/T_{N\text{-}I}=0.98$ and is close to the tricritical concentration in the $\overline{n}$S5 homologous series.[1] The agreement is not quite so good for nonylcyanobiphenyl (9CB), which has $T_{N\text{-Sm-}A}/T_{N\text{-}I}=0.995$ although the exponents agree at the extrema of the error limits. Thus the susceptibility and correlation length exponents in the $\overline{7}$S5+8OCB system exhibit the same discrepancies from mean-field tricritical theory as were observed previously in homolo-

TABLE I. Exponents resulting from best fits to Eqs. (4) and (5). These are the observed, i.e., renormalized, values. Values of α_R are from Ref. 6. The errors are two standard deviations from the best least-squares fit and are therefore probably generous estimates. X denotes the mole fraction of 8OCB. The asterisk denotes exponents arising from fits that assume the observed first-order transition is preempting a second-order transition. The second-order transition temperature is fixed at an average value obtained by first allowing it to vary for each of the three sets of data.

	Observed critical exponents				
X	$(\nu_\parallel)_R$	$(\nu_\perp)_R$	γ_R	α_R	$(\nu_\parallel)_R+2(\nu_\perp)_R+\alpha_R$
0.0338	0.91±0.06	0.78±0.08	1.52±0.06	−0.55±0.30	1.92±0.52
0.0500	1.01±0.06	0.73±0.04	1.59±0.10	−0.64±0.26	183±0.40
0.0561	1.00±0.06	0.82±0.06	1.67±0.08	−0.78±0.23	1.86±0.41
0.0594	1.20±0.10	1.02±0.12	2.05±0.16	−0.86±0.20	2.38±0.54
0.0619	1.20±0.06*	0.92±0.10*	2.02±0.10*	−0.93±0.17	2.11±0.43

TABLE II. Unrenormalized exponents obtained by inverting Eq. (2). Mean-field tricritical predictions and the results for $\overline{10}$S5 and 9CB are included for comparison purposes. (The $\overline{10}$S5 and 9CB samples are close to their respective tricritical points.)

		Underlying critical exponents				
X	$T_{N\text{-Sm-}A}/T_{N\text{-}I}$	$\nu_{\parallel}$	$\nu_{\perp}$	γ	α	$\nu_{\parallel}+2\nu_{\perp}+\alpha$
0.0338	0.91	0.59±0.12	0.51±0.11	0.98±0.20	0.35±0.13	1.96±0.47
0.0500	0.93	0.62±0.11	0.45±0.08	0.97±0.17	0.39±0.10	1.91±0.37
0.0561	0.93	0.56±0.08	0.46±0.06	0.94±0.12	0.44±0.07	1.92±0.27
0.0594	0.94	0.62±0.09	0.55±0.09	1.10±0.15	0.46±0.06	2.18±0.34
0.0619	0.94	0.65±0.07	0.48±0.07	1.04±0.11	0.48±0.05	2.09±0.26
$\overline{10}$S5[a]	0.98	0.61±0.03	0.51±0.05	1.10±0.05	0.45±0.05	2.08±0.18
9CB[b]	0.99	0.57±0.03	0.37±0.07	1.09±0.05	0.53±0.03	1.84±0.20
Tricritical		0.5	0.5	1.0	0.5	2.0

[a]Reference 1, Brisbin *et al.*
[b]Reference 1, Thoen, Marynissen, and Van Dael.

gous mixtures. This conundrum has not yet been explained.

Hyperscaling in this intrinsically anisotropic system requires

$$\nu_{\parallel}+2\nu_{\perp}+\alpha=2 \ . \tag{6}$$

Further, following the arguments of Essam and Garelick,[20] one expects such scaling relationships to hold for both the intrinsic and Fisher renormalized exponents. The results of these experiments together with those of Huster, Stine, and Garland[6] are combined in Tables I and II to determine the left-hand side of Eq. (5), $\nu_{\parallel}+2\nu_{\perp}+\alpha$. It is evident that both the intrinsic and renormalized exponents do indeed obey hyperscaling, as expected. This is probably the most severe of such tests of hyperscaling which have been carried out to date.

Following the arguments of Huster, Stine, and Garland,[6] Fisher renormalization is readily seen in this system because of the extreme dissimilarity of the two molecules. The 8OCB impurity, which is polar and tends to form incommensurate pairs, is quite different from the nonpolar $\overline{7}$S5 molecule, and hence can be considered a true hidden variable in the sense of Fisher's theory.[8] The steep phase boundary, a direct consequence of the distinctiveness of the two molecules, together with the tricritical $\alpha=\frac{1}{2}$, makes $\Delta T_R[\sim(dT_{N\text{-Sm-}A}/dX)^{2/\alpha}]$ very large and Fisher renormalization becomes readily observable. Further, the large observed critical exponents directly reflect the large value of $\alpha=0.5$, that is, the renormalized exponents are doubled. The unobservability of Fisher renormalization in homologous series data may also be readily explained. The similarity of the molecules means that there is a very small transition temperature gradient; specifically,

$$\frac{1}{T_{N\text{-Sm-}A}}\frac{dT_{N\text{-Sm-}A}}{dX}=0.016 \ ,$$

in the $\overline{n}$S5 series, compared with 0.86 in $(\overline{7}\text{S5})_{1-x}(\text{8OCB})_x$. Thus at the tricritical point, ΔT_R is $\sim 3\times 10^3$ times smaller in $\overline{n}$S5 mixtures compared with $\overline{7}$S5+8OCB mixtures and the crossover to renormalized exponent behavior is not accessible experimentally.

An unexpected result of this study is that even for the $X=0.0338$ sample the underlying exponents γ, $\nu_{\parallel}$ and $\nu_{\perp}$ are still close to their tricritical values. In order to discuss this one must consider the appropriate scaling fields. Tricritical points are intrinsically more complex than critical points; one manifestation of this is that the singular part of the free energy is not just a homogeneous function of the experimental field but of more generalized scaling fields μ_1 and μ_2, which are determined by the geometry of the tricritical point. In general, one field variable traces a path tangential to the phase boundary, the other a path away from it. Appropriate linear scaling fields[21] are

$$\mu_1=C_{1,T}\frac{T-T_t}{T_t}+C_{1,x}\frac{X-X_t}{X_t}, \quad \mu_2=C_{2,T}\frac{T-T_t}{T_t} \ , \tag{7}$$

where $C_{1,x}/C_{1,T}$ is chosen so that μ_2 is tangential to the phase boundary at the tricritical point. The crossover lines from tricritical to critical behavior are defined by $z=|\mu_1/\mu_2^{\phi}|\sim$ constant, where $\phi=2$ for a mean-field tricritical point.[19] Lines with z chosen to be 30 (with $C_{1,T}=1$, $C_{1,x}=-0.0633$, $C_{2,T}=1$) are sketched in the lower panel of Fig. 1 for illustrative purposes. Even for this large value of z it is evident that the region in which the effective tricritical exponents would be measured may be quite extended. Our data imply that the crossover value of z is, in fact, closer to unity or less.

In conclusion, we have observed dramatic Fisher renormalization in a liquid-crystal system that has an extended tricritical region. This results from the unusually large transition temperature gradient caused by the nonhomologous nature of the molecules. The underlying correlation length and susceptibility exponents deviate significantly from mean-field values, but are in good agreement with previous results in homologous systems. The discrepancies are comparable to those seen for the same exponents at ordinary nematic–smectic-A transitions.[22] Thus we still lack a satisfacory theory for both the critical and tricritical N–Sm-A problems.

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