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Nature of a Nematic–Smectic-*A* –Smectic-*C* Multicritical Point

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Recent x-ray data on the angles and 2-theta shifts in the smectic-*C* phase of a binary liquid-crystal mixture were analyzed via a mean-field theory. We demonstrated that the smectic-*A* –smectic-*C* transitions (*AC*) are mean-field–like. This conclusion is consistent with recent heat-capacity data along the *AC* transition line. Furthermore, the nematic–smectic-*A*–smectic-*C* point in this binary mixture is found to be in the vicinity of the *tricritical point* along the *AC* and nematic–smectic-*C* transition line.

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The smectic-*A* (*A*) and the smectic-*C* (*C*) phases in liquid crystals can be characterized by a one-dimensional density wave whose wave vector is along (*A*) or at an angle (*C*) to the nematic (*N*) director. Recently it has been shown that in appropriate binary liquid-crystal mixtures it is possible to have lines of second-order *NA* and *AC* transitions crossing over to a line of first-order *NC* transitions.[1] The triple point where these three transition lines intersect in the temperature-composition phase diagram is the *NAC* multicritical point (see Fig. 1). Many theoretical models[2-4] have been proposed to describe this system. Among these theories, the most appealing model, proposed by Chen and Lubensky, predicts that the *NAC* point is a Lifshitz point.[2] However, we will demonstrate that a simple theory based on a free-energy expansion of coupled order parameters by Benguigui[4] is consistent with recent x-ray and heat-capacity measurements[5-7] on the *AC* transition of mixtures of octyloxy- and heptyloxy-*p*-pentyl-phenyl thiolbenzoate ($\bar{8}$S5-$\bar{7}$S5). This theory predicts a correct *NAC* phase diagram obtained by thermodynamic studies.[8] In addition, a tricritical point on the *AC* line near the *NAC* point was predicted by the theory but the existing data analysis failed to prove it.[5-7]

Both the tilt angles and the 2-theta shifts in the smectic-*C* phase were measured by an x-ray scattering study in mixtures of $\bar{8}$S5 and $\bar{7}$S5.[5,6] In contrast to the usual fitting procedure with a simple power law for the order parameter (Ψ, the tilt angle in the *C* phase) of each mixture, the data were analyzed by employing an analytic expression obtained from a mean-field free energy including a Ψ^6 term. In doing so we were able to fit all of the experimental data points. Moreover, the salient features of this fitting result are the following: *(i) The AC transitions are mean-field like; (ii) the tricritical region increases as the concentration of $\bar{7}$S5 increases*

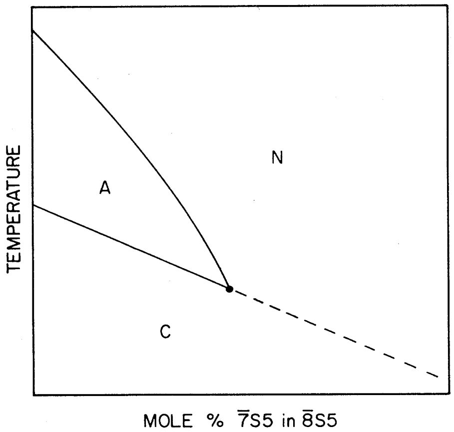

FIG. 1. Phase diagram near the *NAC* point. Two solid lines indicate continuous *NA* and *AC* transitions. The dotted line is the first-order *NC* transition line.

in the mixture; (iii) the NAC point is near the tricritical point of the AC and NC lines. Although Benguigui[4] gave a prediction on feature (iii), the physical origin of the tricritical point near this *NAC* point differs from the one suggested by Benguigui. On the basis of the free energy with coupled order parameters, we will give a plausible argument which leads to the occurrence of the tricritical point near the *NAC* point.

Recently our heat-capacity measurements[9] on racemic 4-(2′-methylbutyl) phenyl 4′-*n*-nonyloxy biphenyl-4-carboxylate (2M4P9OBC) have shown that the *AC* transition is mean-field-like with a small full width at half height of the mean-field heat-capacity jump. A simple Landau free energy including a Ψ^6 term, i.e.,

$$F = at\Psi^2 + b\Psi^4 + c\Psi^6,$$

was proposed by Huang and Viner[9] to explain the observed heat-capacity anomaly. Here $t=(T-T_c)/T_c$, and $(a, b, c) > 0$ for a second-order transition; T is the temperature and T_c is the transition temperature. Without any loss of generality, the constant a will be set equal to 1. After minimizing of the free energy with respect to Ψ, Ψ and the anomalous part of the heat capacity ΔC_v are zeros for $T > T_c$. In the case of $T < T_c$, one obtains

$$\Psi^2 = (b/3c)[(1+3t'/t_0)^{1/2} - 1] \tag{1}$$

and

$$\Delta C_v = \frac{T}{2(3c)^{1/2}T_c^{\,3/2}}(T_m - T)^{-1/2}, \tag{2}$$

where $t' = -t$, $t_0 = b^2/c$, and $T_m = T_c(1+t_0/3)$. Actually the full width at half height of the $(\Delta C_v/T)$ vs T curve is t_0 in the reduced-temperature scale. The fact that our heat-capacity data could be fitted over a wide temperature range by the mean-field expression [Eq. (2)][9] suggests that order-parameter data should be analyzed by use of Eq. (1) instead of a simple power law. Furthermore, from Eq. (1), if $t' \ll t_0$ then Ψ is proportional to $(t')^{1/2}$ which represents the critical behavior for a second-order mean-field transition. But if $t' \gg t_0$ then Ψ is proportional to $(t')^{1/4}$ which is characteristic of a tricritical point. Therefore the locus of t_0's will separate the second-order transition region from the tricritical region in the phase diagram.

Instead of a simple power-law fitting ($\Psi \sim |t|^\beta$) to the tilt angles,[5,6] we calculated the ratios of the measured tilt angle to $[(1+3t'/t_0)^{1/2} - 1]^{1/2}$ for each datum point. By varying of both T_c and t_0, the optimum values of T_c and t_0 were obtained by minimizing the relative deviation $\sigma = D/M$. Here D is the root mean square deviation of the data from the calculated average ratio (M) for a given set of data. This was done with the experimental weighting factor for each datum.[6] The same procedure was used to obtain the T_c and t_0 for the 2-theta shift data which are proportional to Ψ^2.[10] The calculated ratio for each datum point with the optimum T_c's and t_0's are shown in Figs. 2(a) and 2(b) for $\bar{8}$S5 and 42 mole % $\bar{7}$S5 in $\bar{8}$S5, respectively. It is clear that such a fit is excellent for all the measured experimental points. In the same figures, the original data and the best power-law fits are also shown. The data start to deviate from the simple power-law fittings (solid lines) in the regions to the right of the vertical arrows. In comparison, our fitting holds in a wider temperature range. The optimum values of T_c and t_0 for $\bar{8}$S5 and the 42 mole % mixture are listed in Table I with other relevant physical parameters. The T_c's obtained by this method are consistent with the reported T_c's from a power-law fitting. Also the value of t_0 for pure $\bar{8}$S5 is in good agreement with the full width at half height of the heat-capacity anomaly,[11] provided that a temperature-dependent background term is taken into account.

The fact[7] that the heat-capacity data show abrupt jumps at the T_{AC}'s and no fluctuation being discernible above the T_{AC}'s also suggest mean-field-like AC transitions. Moreover, from the full widths at half height of the heat-capacity anomalies, one can obtain t_0's which are shown in Fig. 3 as open circles[12] along with the solid

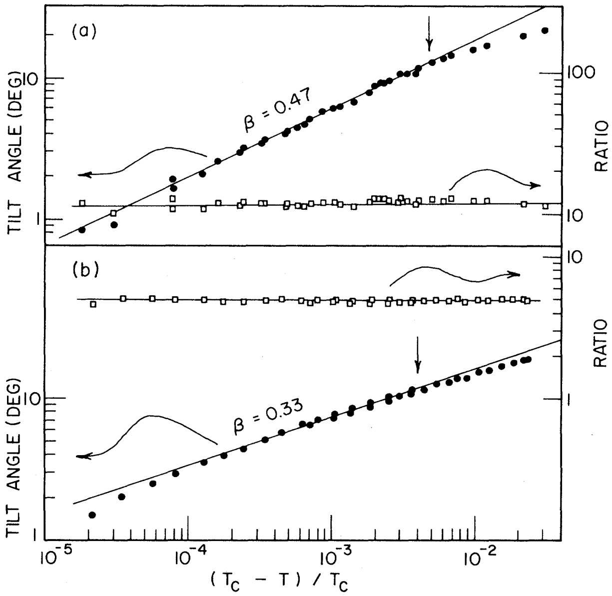

FIG. 2. The fitted results for the tilt angles of (a) pure $\overline{8}$S5 and (b) 42 mole % $\overline{7}$S5 in $\overline{8}$S5. The solid dots are the measured data on tilt angles (Ψ). To the right of the vertical arrows the data start to deviate from the best simple power-law fittings ($\Psi \sim |T_c - T/T_c|^{\beta}$) which are indicated by the straight lines through the solid dots. The ratio of Ψ to $[(1+3t'/t_0)^{1/2}-1]^{1/2}$ is shown by the square for each experimental datum. The solid lines through the squares are the mean values of the ratios. See the text for the fitting procedure and the discussions.

dots obtained from the reanalysis of x-ray data. These results clearly demonstrated that as T_{AC}/T_{NA} increases toward 1, t_0 montonically decreases toward zero and the tricritical region (the region with $t' \gg t_0$) montonically increases. Furthermore, the NAC multicritical point ($T_{AC}/T_{NA} = 1$) is in the vicinity of the tricritical point of the continuous AC transition line because $t_0 = 0$ means $b = 0$ in the Landau free energy. This conclusion is further supported by the fact that the AC and NC transition lines are joined continuously at NAC point with the NC transition line being first order.[7,8]

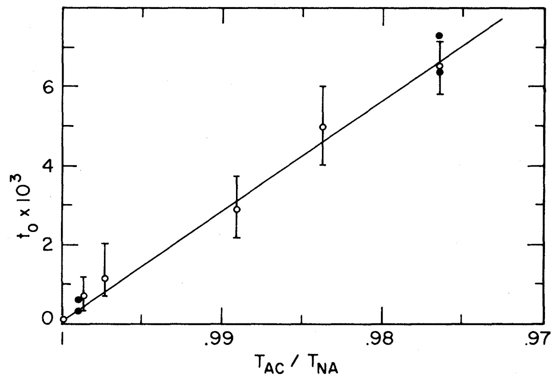

FIG. 3. t_0 vs (T_{AC}/T_{NA}). The solid line is a straight line through the data.

To explain our observation, a Landau free energy with coupled order parameters[13] can be written as

$$F_c = \alpha\varphi^2 + \beta\varphi^4 + t\Psi^2 + b'\Psi^4 + c\Psi^6 - d\varphi^2\Psi^2 .$$

Here φ is the smectic-A order parameter, β and b' are taken to be positive for the continuous NA and AC transitions, respectively, and d is positive, in order that the solution ($\varphi \neq 0$, $\Psi \neq 0$ corresponding to the smectic-C phase) will be possible. If we minimize G with respect to φ, then G can be expressed in terms of Ψ. We have

$$F_c = -\frac{\alpha^2}{4\beta} + \left(t + \frac{\alpha d}{2\beta}\right)\Psi^2 + \left(b' - \frac{d^2}{4\beta}\right)\Psi^4 + c\Psi^6 .$$

Hence the nature of the AC transition will be determined by $b = b' - d^2/4\beta$. As the system approaches the NAC point, with a narrowing of

TABLE I. The parameters related to the NA and AC transition lines.

Mole % of $\overline{7}$S5 in $\overline{8}$S5	Type of measurements[a]	T_{NA}[b] (K)	T_{AC}(± 5 mK)[b,c]	T_{AC}[d]	t_0[d]	T_{AC}/T_{NA}	σ[e]
0	A	336.085	328.170	328.171	0.0064	0.9765	0.044
	B			328.183	0.0073		0.105
42	A	323.030	322.726	322.727	0.0003	0.9991	0.020
	B			322.737	0.0006		0.069

[a] A, tilt angle; B, 2-theta shift.
[b] T_{NA}: nematic to smectic-A transition temperature; T_{AC}: smectic-A to smectic-C transition temperature.
[c] These values obtained from the power-law fitting (Ref. 6).
[d] Optimum values from our fitting.
[e] The minimum σ for the given set of data.

the smectic-*A* range, tilt-angle fluctuations will be induced more easily simply because the smectic-*A* order parameter will not have saturated at T_{AC}. This will enhance the coupling constant *d*. Also the nature of *NA* transitions undergoes significant change while the system approaches the *NAC* point.[5] This should change β such that *b* is zero near the *NAC* point. This observation will definitely stimulate microscopic studies as to the nature of the *NAC* multicritical point.

In conclusion, in mixtures of $\bar{8}$S5 and $\bar{7}$S5 we have demonstrated that the *AC* transitions are mean-field-like with the *NAC* point being near a tricritical point. Because of the presence of the continuous *NA* transition line, topologically this tricritical point differs from the ones found in metamagnets or ^{3}He-^{4}He mixtures.[14] Furthermore, x-ray scattering near the *NA* transition of the 42 mole % mixture ($T_{AC}/T_{NA} = 0.991$) shows a heliumlike behavior. In order to account for this helium behavior, one might have to treat the tilt-angle and the mass-density fluctuations simultaneously. However, light scattering or x-ray scattering studies of the mixture right at the *NAC* point should cast new light on the role played by the continuous *NA* transition line in the vicinity of the *NAC* multicritical point. Finally, a microscopic explanation of the smallness in t_0's even in the pure $\bar{8}$S5 should be important.

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