Heat-capacity study of tricritical behavior
at the smectic-A –chiral-smectic-C liquid-crystal transition

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The smectic-A (Sm-A) to chiral-smectic-C transition has been studied by high-resolution ac calorimetry in seven mixtures of two chiral esters of 2,5-diphenyl pyrimidine ($2f + 3f$) over the range $38.72 \leq X_{2f} \leq 65.30$, where X_{2f} is the mole percent of $2f$. The heat-capacity results have been fit below the transition temperature using an extended mean-field model and show that the transition is quite close to a tricritical point over the entire range of composition. In all seven mixtures, the excess heat capacity above the transition temperature is observed to scale in the same manner as the Landau contribution does below the transition. This behavior is consistent with the presence of thermal fluctuations in the Sm-A phase.
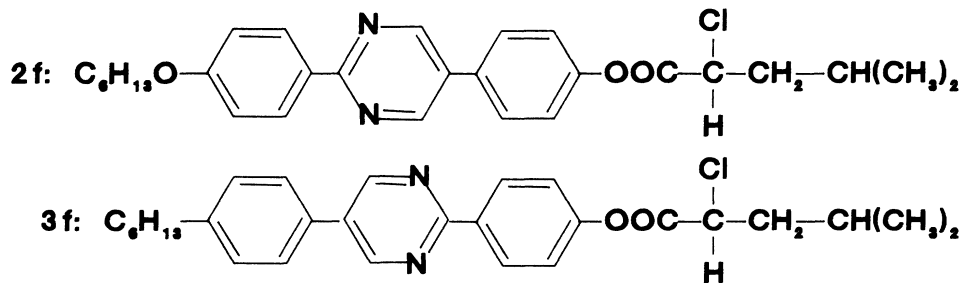
I. INTRODUCTION

The smectic-A (Sm-A) to smectic-C (Sm-C) or chiral-smectic-C (Sm-C^*) transition in liquid crystals can be described with a two-component order parameter $\psi = \theta e^{i\phi}$. The component θ is the angle of the molecular tilt relative to the normal to the smectic layer plane, and the other component is the azimuthal orientation ϕ of the director about the layer normal. In the Sm-A phase, where the long molecular axis is perpendicular to the layers, both components are zero. Upon cooling from the Sm-A phase, optically inactive molecules can form a Sm-C phase with the development of a nonzero θ and a ϕ value which is the same for all layers in a given domain. The Sm-C^* phase is formed from the Sm-A phase when a chiral center is coupled to a polar group perpendicular to the long molecular axis. This molecular configuration generates a component of the permanent molecular dipole parallel to the layer planes and leads to a spontaneous polarization within each layer. Chiral interactions cause the azimuthal angle of the molecular tilt direction to vary from layer to layer; this gives rise to a helicoidal arrangement of the spontaneous polarization, and therefore, a net bulk spontaneous polarization of zero in the Sm-C^* phase.[1]

An early prediction was made that the Sm-A –Sm-C (or Sm-C^*) transition should be in the three-dimensional XY universality class.[2] However, it has been well established that Sm-A –Sm-C (and Sm-C^*) transitions can be described within the framework of extended mean-field theory.[3,4] Prior to 1986, the known Sm-A –Sm-C (and Sm-C^*) transitions were found to be second-order transitions well described by a Landau free energy with anomalously large sixth-order terms.[3,4] Since then, several liquid crystals that possess large spontaneous polarization have been shown to exhibit first-order Sm-A –Sm-C^* transitions.[5-7]

The factors responsible for the first-order character of the Sm-A –Sm-C^* transition in these ferroelectric liquid crystals are of interest. In nonpolar liquid-crystal systems, the temperature width of the Sm-A phase has been found to correlate with the closeness of a system to a tricritical point. As the Sm-A temperature range is decreased, the system moves closer to the tricritical point.[3(b)] Because the chiral materials that exhibit a first-order Sm-A –Sm-C^* transition have similar or larger Sm-A ranges[6,7] than the nonchiral or weakly polar liquid crystals[3(b)] that show second-order behavior, it is apparent that the magnitude of the spontaneous polarization is also an important factor. Additional evidence for the importance of the spontaneous polarization is the observation of a second-order Sm-A –Sm-C^* transition in the racemic (nonpolar) mixture of a chiral molecule for which the pure enantiomers show weakly first-order behavior.[7]

Heppke, Lötzsch, and Shashidhar[8] reported the existence of a tricritical point in a binary liquid-crystal system in which both compounds possess a large spontaneous polarization in their Sm-C^* phases. The two components of this system, both chiral esters of 2,5-diphenyl pyrimidines, are 2-(p-n-hexyloxyphenyl)5-[p-(2-chloro-4-methylpentanoyloxy)-phenyl] pyrimidine (designated $2f$) and 5-(p-n-hexylphenyl)2-[p-(2-chloro-4-methylpentanoyloxy)-phenyl]pyramidine (designated $3f$). The chemical structures are

2f: $C_8H_{13}O$—[benzene ring]—[pyrimidine ring with N, N]—[benzene ring]—OOC—C(Cl)(H)—CH$_2$—CH(CH$_3$)$_2$

3f: C_8H_{13}—[benzene ring]—[pyrimidine ring with N, N]—[benzene ring]—OOC—C(Cl)(H)—CH$_2$—CH(CH$_3$)$_2$

The Sm-A–Sm-C^* transition in pure $3f$ is second order, while mixtures with compositions (mol % $2f$) $X_{2f} = 58.27$ and 60.2 are reported to show near-tricritical and strongly first-order behavior, respectively. Thus the result for pure $3f$ indicates that a large spontaneous polarization need not impose a first-order character on the Sm-A–Sm-C^* transition. This fact, coupled with the existence of the tricritical point in the mixed system, suggests that there may be a competition between the effects arising from polarization and Sm-A temperature range, since $3f$ has a large Sm-A temperature range (≈ 40 K) and $2f$ has no Sm-A phase.[8]

The goal of our research was to characterize by ac calorimetry the evolution of the tricritical point in mixtures of $2f + 3f$. This work represents the first systematic study of the progression toward a Sm-A–Sm-C^* tricritical point in a liquid-crystal system. Although unambiguous first-order behavior was not observed in the composition range studied, the calorimetric results do indicate a movement toward a tricritical point as the percentage of $2f$ in the mixture increases. Furthermore, a small excess heat capacity has been observed above the transition temperature that scales, in a fashion which suggests that Sm-C^* fluctuations persist into the Sm-A phase.

II. METHOD AND RESULTS

Seven mixtures of $2f$ and $3f$ with compositions $38.72 \leq X_{2f} \leq 65.30$ were investigated using an ac calorimetric technique, the details of which have been described previously.[4(a),9] Because of the reactivity of these mixtures to indium and tin, the sample cell design used in this study was modifed slightly from that described in Ref. 4(a). Instead of cold welding the lid onto the silver sample cup, the silver foil lid was cut with a diameter about 3 mm larger than that of the cup, and the foil was tightly folded over the lip of the cup. The total mass of the silver cell, liquid crystal, and addenda was approximately 0.5 g, of which 35–45 mg were $(2f + 3f)$ mixture.

A drift in the Sm-A–Sm-C^* transition temperature of ~ 30 to ~ 80 mK/h was observed from measurements of the heat capacity in successive heating and cooling runs. Although there was some reduction in the C_p peak height in sequential runs, the overall shape and size of the excess heat-capacity peak were not altered significantly. We report here only the data acquired during the first heating of the sample.

Our transition temperatures, corrected for the drift noted above, are plotted in Fig. 1. Also included in Fig. 1 are the results obtained from the optical microscopy and

x-ray scattering studies of Ref. 8; the agreement among the three sets of data is quite good.

In the extended Landau model, which has been used to describe SmA–Sm-C and Sm-A–Sm-C^* transitions, the free energy G is written as an expansion in powers of the order parameter ψ,

$$G = G_0 + at\psi^2 + b\psi^4 + c\psi^6 , \qquad (1)$$

where G_0 is the free energy of the disordered Sm-A phase. The reduced temperature t is defined as $(T - T_0)/T_0$. The Landau coefficients a and c are positive, while b can be positive, negative, or zero.

With the exception of a small region around the transition temperature, the asymmetric heat-capacity peaks which were obtained from all seven mixtures could be well fit below the transition temperature with the following equation derived from the extended Landau model:[4(c)]

$$C_p = C_p^0 + A^* \frac{T}{T_0}(T_k - T)^{-1/2}, \quad T < T_0 \text{ or } T_1 \qquad (2)$$

where C_p^0 is the "base-line" Sm-A heat capacity, $A^* = (a^3/12cT_0)^{1/2}$, and $T_k \equiv T_0 + (b^2T_0/3ac)$ is the metastability limit $(T_0 < T_k)$. The base-line heat capacity was represented by a linear expression $C_p^0 = B + E(T - T_0)$. According to Landau theory, a second-order transition occurs at T_0 when $b > 0$, a first-order transition occurs at $T_1 = T_0 + (b^2T_0/4ac)$ when $b < 0$, and a tricritical point occurs at $T_k = T_0$ when $b = 0$.
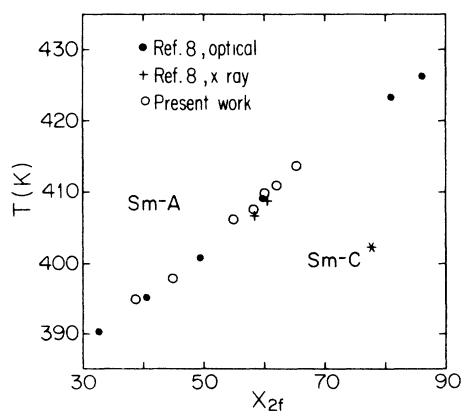

FIG. 1. Partial phase diagram for mixtures of $2f + 3f$. See Ref. 8 for the complete diagram. The Sm-A–Sm-C^* tricritical point is reported to lie near $X_{2f} = 58.3$.
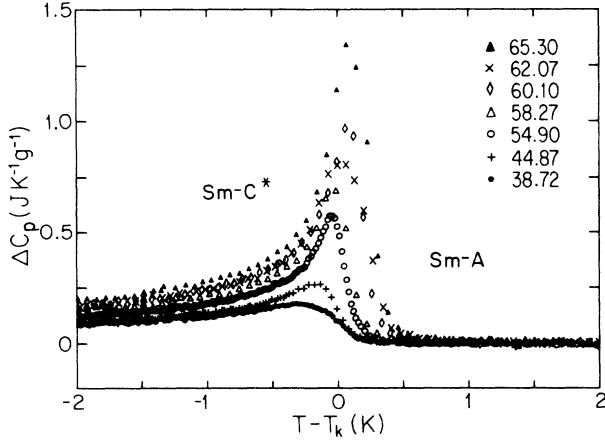
FIG. 2. Excess heat capacity $\Delta C_p \equiv C_p - C_p^0$ associated with the Sm-A –Sm-C^* transition for seven X_{2f} values.

Plots of the excess heat capacity, $\Delta C_p = C_p - C_p^0$ are given in Fig. 2 over a 4-K range near the transition. Fits of the C_p values were made over a much wider range, down to $T = T_k - 10$. During the fitting procedure, the C_p values were weighted with an uncertainty equal to $0.002C_p$. Numerical values of the fitting parameters and the χ_ν^2 values for the weighted fits are summarized in Table I.

Previous investigators have observed a narrow region of heat-capacity data near Sm-A –Sm-C (Sm-C^*) transitions where the Landau model does not fit the data.[3,4,10] The theoretical Landau heat capacity rises to a sharp maximum at T_0 (or T_1) and falls immediately to zero above T_0 (or T_1). However, the experimental heat-capacity curves exhibit rounded maxima and drop to zero over a finite-temperature range. The temperature interval over which the excess heat capacity drops from 90% to 10% of its maximum value has been used to characterize this region. The 90–10 % widths obtained in our experiments are given in Table I. Typically, 90–10 % widths of 20–200 mK have been reported for second-order Sm-A –Sm-C transitions[3,4,10] and T_0 has been taken as the temperature at the midpoint of the ramp. In such previous studies, the value of $T_k - T_0$ was fairly large, and this convention gave reasonable values for T_0. However, had we assigned T_0 in this manner, there would have been an internal inconsistency for samples

with $X_{2f} > 44.87$, since $T_k - T_0$ would be negative, which is impossible. For the fits of data for the higher $2f$ compositions, we set $T_0 = T_k$ in Eq. (2), but this has a trivial effect on the fitting procedure.

III. DISCUSSION

Within the framework of the extended Landau model, the parameters A^* and T_k determine the size and position of the heat-capacity peak, while T_0 determines only the temperature at which the excess heat capacity drops to zero. As a Landau system evolves from a second-order regime to a tricritical point, T_0 approaches T_k and the maximum height of the heat capacity peak should increase since the ΔC_p value at T_0 is given[4(c)] by $A^*(T_k - T_0)^{-1/2}$. Once in the first-order regime, the system undergoes a transition at T_1 ($T_0 < T_1 < T_k$). Excluding any latent heat contribution, the heat-capacity maximum should decrease as the transition becomes more strongly first order, since the ΔC_p value at T_1 is given by $A^*(T_k - T_1)^{-1/2}$. Figure 2 shows that, with the exception of a slight rounding of the $X_{2f} = 62.07$ data, our results display a systematic increase in the heat-capacity maximum with increasing X_{2f}. The heat-capacity maxima do not display the monotonic decrease expected above $X_{2f} = 58.27$, the tricritical composition reported by Heppke, Lötzsch, and Shoshidhar,[8] nor do the heat-capacity curves show any distortions that indicate anomalous temperature effects associated with a large latent heat.

A first-order phase coexistence can be detected in the ac calorimetric method by the appearance of an increase in the phase shift of the temperature oscillation of the sample with respect to the heat input signal and by hysteresis in the transition temperature determined from heating and cooling measurements.[9] However, the phase shifts obtained from all seven mixtures showed no indication of two-phase coexistence. The presence of drifts in transition temperatures with time prevented us from checking on possible hysteresis between heating and cooling behavior.

The data for the seven compositions have been fit over a temperature range of $0.975 < T/T_0 < 1.012$. Because $T/T_0 \approx 1$ over this range, ΔC_p from Eq. (2) can be well approximated as $A^*(T_k - T)^{-1/2}$. With the exception of a few experimental points close to the transition, all the

TABLE I. Least-squares values of the fitting parameters appearing in Eq. (2) for the Sm-A –Sm-C^* heat capacity.

| X_{2f} (mol %2f)	χ_ν^2	B (J K^{-1} g^{-1})	$E \times 10^3$ (J K^{-2} g^{-1})	A^* (J K$^{-1/2}$ g^{-1})	T_k (K)	T_{midpt} (K)	10–90 % width (mK)	$T^* - T_k$ (mK)
38.72	0.75	2.5458	4.54	0.1226	393.845	393.79	290	0
44.87	0.58	2.5411	4.92	0.1372	396.420	396.40	240	0
54.90	0.66	2.7536	2.47	0.1777	403.864	403.93	200	85
58.27	1.15	2.5359	7.14	0.2117	405.888	405.99	190	150
60.09	1.28	2.5735	9.65	0.2393	408.869	409.06	170	230
62.07	1.41	2.6405	6.47	0.2383	409.905	410.13	240	300
65.30	1.64	2.4475	12.23	0.2754	413.154	413.41	250	325
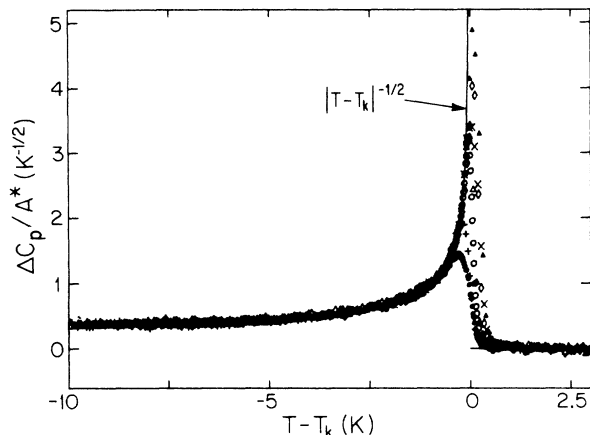
FIG. 3. Landau scaling plot of the excess heat capacity associated with the Sm-A–Sm-C^* transition. The values of A^* and T_k are given in Table I. The theoretical curve $|T - T_k|^{-1/2}$ extends down to $T = T_k - 10$ but is obscured by the data points. The symbols have the same meaning as in Fig. 2.

ΔC_p curves can be scaled by plotting $\Delta C_p / A^*$ versus $T - T_k$, as shown in Fig. 3. The solid line of Fig. 3 represents the theoretical ΔC_p dependence, $(T_k - T)^{-1/2}$ below the transition and zero above. Figure 4 shows the detailed behavior of ΔC_p in the region where deviations from Landau behavior are observed.

It is clear from Fig. 4 that there is a small but significant high-temperature wing for the ΔC_p data at all compositions. Since there are data available for seven mixtures of the same two compounds, it is possible to test whether this excess ΔC_p^+ *above* the transition evolves in a systematic way. Indeed, as shown in the inset of Fig. 4, $\Delta C_p^+ / A^*$ values do scale as a function of $T - T^*$, where T^* is an empirical characteristic temperature value that
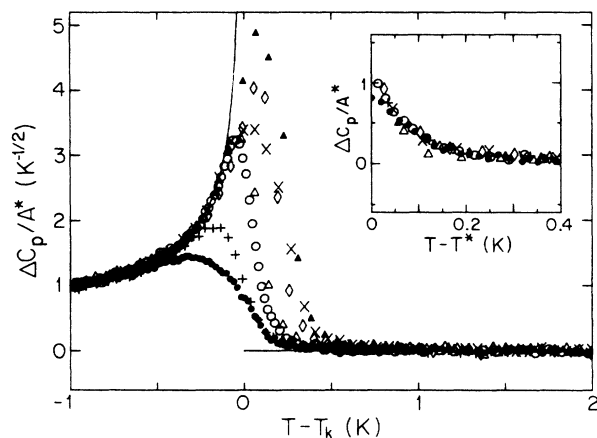

FIG. 4. Detailed view of the deviations from the Landau model both above and below the transition temperature. The inset shows that the excess heat capacity ΔC_p above the transition temperature scales with the same amplitude A^* as that below the transition. The values of the empirical parameter T^* are given in Table I; the symbols have the same meaning as in Fig. 2.

differs slightly from T_k when $X_{2f} > 50$ (see Table I). The significance of this shift in the temperature scale is not clear, but the fact that ΔC_p^+ values scale with the same amplitude factors obtained from the Landau fits to the ΔC_p data in the Sm-C^* phase suggests that ΔC_p^+ is directly related to pretransitional effects rather than to impurity or wall effects.

Recent studies of the dynamics of ferroelectric liquid crystals show evidence of a helical wave vector above the transition.[11,12] In particular, photon correlation spectroscopy on methylbutyl-phenyl-octylbiphenyl carboxylate (CE8) shows that there are pretransitional fluctuations with a helical structure in the Sm-A phase even 0.25 K above the Sm-A –Sm-C^* transition. The fluctuations are a bulk effect and not due to wall alignments.[12] Such helical fluctuations would be in accord with the idea that ΔC_p^+ is a true pretransitional thermal effect. We have at present no understanding of why fluctuation effects might cause the observed rounding of ΔC_p just below the transition of why there should be an anomalous region between T_k and T^*. The possibility that the rounding of the C_p peak and the excess heat capacity in the high-temperature wing are both caused by inhomogeneities in the sample is also being explored.[13]

We have analyzed the temperature dependence of the tilt angle in the Sm-C^* phase using the layer spacing data reported in Ref. 8 for a sample with $X_{2f} = 58.27$. The tilt angle θ was evaluated using the expression $\theta = \cos^{-1}(d_{C^*}/d_A)$, where the subscripts indicate the layer spacing in the Sm-C^* and Sm-A phases. Since the tilt angle has been demonstrated to be the primary order parameter ψ for the Sm-A –Sm-C^* transition,[1] it is appropriate to fit θ^2 with the equation for ψ^2 derived from Eq. (1):

$$\psi^2 = C + A(T_k - T)^{1/2}, \quad T < T_0 \text{ or } T_1 \qquad (3)$$

where $A = 2A^*/a$ and $C = -(b/3c)$. The θ^2 data are presented in Fig. 5, and the solid line represents the fit to $\psi^2 = \theta^2$ with $A = 0.045 \pm 0.001$ rad$^2 K^{-1/2}$, C
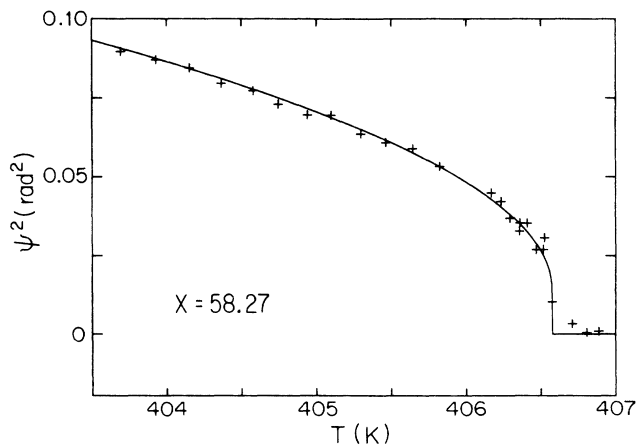

FIG. 5. Temperature dependence of the square of the tilt order parameter $\psi = \theta$. Tilt angles are calculated from data in Ref. 8. The parameters for the Landau fitting form are given in the text.

$=0.014\pm0.001$ rad^2, and $T_k=406.576\pm0.001$ K. The small positive value of C (hence a negative b) suggests that the transition is already weakly first order at this composition and not tricritical as proposed in Ref. 8. However, there are not sufficient high-resolution tilt angle data near the transition temperature to establish with certainty whether C is slightly negative or positive.

The lack of a clear first-order character to the Sm-A–Sm-C^* transition observed in our C_p measurements for $X_{2f}>58.27$ suggests that there are significant differences between our experiments and the x-ray experiments described in Ref. 8. It should be noted that during the x-ray experiments strong "pinning" effects were observed in the Sm-A phase close to the Sm-A–Sm-C^* transition.[14] As a result, there was an unusually wide temperature range (greater than 1 K) over which density modulations of both Sm-A and Sm-C^* phases were seen. Had the pinning effect, which was due to the influence of the wall of the capillary on the macroscopic sample orientation, not been identified, this temperature region might have been interpreted incorrectly as a coexistence region. However, pinning effects were minimized for the published x-ray results[8] by using wider-than-normal (0.7-mm-diam) capillaries. It is unclear how the sample configuration used in our experiments (for example, having a coil of gold wire immersed in the sample) affects the factors which lead to pinning. It seems likely that small discrepancies in the composition at which the system reaches a tricritical point could arise from differences in the effects of pinning on the nature of the transition.

Our high-resolution ac calorimetric results show that the excess heat capacity associated with the Sm-A–Sm-C^* transition is surprisingly close to tricritical over a wide concentration range from $X_{2f}=38.72$ to 65.30. As X_{2f} increases, the amplitude A^* of the ΔC_p curve increases monotonically but T_k-T_0 is essentially zero for all compositions. The major difference in the behavior of the scaled quantity $\Delta C_p/A^*$ is a distinct rounding of the peak for low X_{2f} (second order), a fairly sharp peak near T_k for $X_{2f}=54.90$ and 58.27 (possibly near tricritical), and a large excess above T_k for $X_{2f}\geq60.10$ (possibly first-order). In all seven mixtures, there is a small excess heat capacity ΔC_p^+ above the transition temperature that scales in the same way as the Landau contribution below the transition. This is consistent with thermal fluctuation effects in the Sm-A phase, but may be due to inhomogeneities caused by pinning.

The evolution toward the tricritical point observed in our investigation of the $(2f+3f)$ system is consistent with results[6,7] obtained from the study of other Sm-A–Sm-C and Sm-A–Sm-C^* transitions which show that a decrease in the Sm-A temperature range drives the transition toward a first-order character. However, the spontaneous polarization (P_s) in the mixtures would be expected to increase with increasing X_{2f}, since P_s is greater for $2f$ than for $3f$,[8] and therefore, the Sm-A temperature effect may only be partially responsible for the change in second-order character of the transition.

ACKNOWLEDGMENTS

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