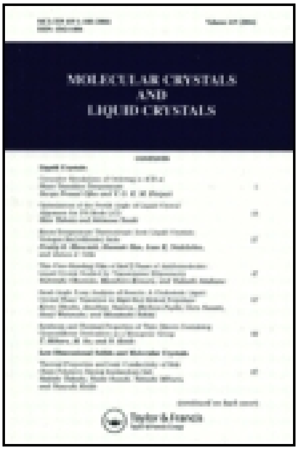

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Chirality and Phase Transitions in Smectic Liquid Crystals

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CHIRALITY AND PHASE TRANSITIONS IN SMECTIC LIQUID CRYSTALS

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Abstract A variety of new critical phenomena and phase behavior becomes accessible in chiral liquid crystals. Reported here are heat-capacity results for isotropic–blue phase III and smectic-C–hexatic smectic–I critical points and calorimetric data for systems exhibiting twist-grain-boundary TGB_A and TGB_C phases.

INTRODUCTION

The phase transitions among the many phases exhibited by thermotropic liquid crystals have been widely studied and extensively reviewed.[1] The present paper gives a brief summary of several recent calorimetric studies of chiral compounds. The essential features are stressed and a variety of details are omitted since they are available in the cited references.

ISOTROPIC–BLUE PHASE III CRITICAL POINT

Chiral compounds often exhibit complex blue phase structures. Two of these (BP_I and BP_{II}) possess cubic lattices of defects, but BP_{III} (the blue fog) appears to consist of an amorphous array of defects.[2] Early work on cholesteryl nonanoate (CN) established that transitions involving blue phases were first order although the I–BP_{III} transition has substantial pretransitional C_p wings as well as a first-order latent heat of 323 ± 50 mJ g^{-1}.[3] In addition, there were various indications that increasing the chirality of a system decreased the first-order character of the I–BP_{III} transition and drove this toward a continuous evolution.[4,5]

A study of the highly chiral compound S,S–(+)–4″–(methylbutylphenyl)–4′–(methylbutyl)–4–biphenylcarboxylate (S,S–MBBPC) with high-resolution calorimetry and both static and dynamic light scattering revealed a supercritical evolution of BP_{III} into I with no thermodynamic transition separating these two phases.[6] The logical consequence of this is the fact that the BP_{III} and I phases possess the same macroscopic symmetry.

The existence of a first-order BP_{III}–I coexistence line that terminates at an isolated critical point is consistent with the theoretical model of Lubensky and Stark,[7] which predicts that the BP_{III}–I transition should be in the same Ising universality class as the liquid-gas transition. A recent investigation of mixtures of S,S–MBBPC and its racemate confirm the existence of a BP_{III}–I critical point.[8] Both calorimetric and optical activity data indicate that this BP_{III}–I critical point occurs for a mixture with chiral mole fraction $X_c \simeq 0.45$, and the critical heat capacity obtained with a high-resolution ac technique is shown in Fig. 1. The latent heat L at the first-order BP_I–BP_{III} transition is 9.7 mJ g^{-1} while the integrated enthalpy $\delta H = \int \Delta C_p \, dT$ associated with the BP_{III}–I critical point has the substantial value 1120 mJ g^{-1}.[8] The BP_{III}–I heat capacity data were analyzed with the usual renormalization power-law form,

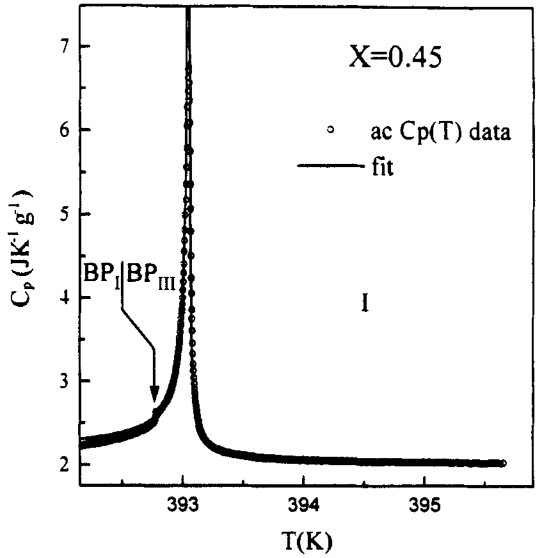

FIGURE 1 Heat capacity of a critical mixture of S,S–MBBPC and its racemate (chiral mole fraction $X_c = 0.45$). The smooth curve represents the best fit with Eq. (2).

$$C_p = A^{\pm}|t|^{-x}\,(1 + D_1^{\pm}|t|^{\Delta_1} + D_2^{\pm}|t|^{2\Delta_1}) + B + E(T - T_c) \ , \qquad (1)$$

where $\Delta_1 \simeq 0.5$ and the exponent x is dependent on the path of approach to the critical point. A detailed discussion is given in Ref. 8, but analysis of C_p and optical activity data indicate mean-field behavior with $x = \gamma = 1$ rather than Ising fluctuation behavior. In this case, Eq. (1) can be rewritten as

$$C_p = A^{\pm}|t|^{-x} + A_2^{\pm}|t|^{-y} + B^{\pm} + E(T - T_c) \ , \qquad (2)$$

where $y = x - \Delta_1$, $A_2^{\pm} = A^{\pm}D_1^{\pm}$, and $B^{\pm} = B + A^{\pm}D_2^{\pm}$. The fit shown in Fig. 1 is based on Eq. (2) with $x = 1$, $y = 0.5$. It is speculated that mean-field behavior can be explained by the Ginzburg criterion in that the fluctuation critical regime is too small for experimental observation.

SMECTIC–C – SMECTIC-I CRITICAL BEHAVIOR

The smectic–C (SmC) phase is a simple tilted smectic, but the smectic–I (SmI) phase is a hexatic phase that exhibits bond-orientational (BO) order in addition to a smectic tilt. However, this BO order in SmI does not change the point group symmetry from that of SmC. Thus the situation is qualitatively analogous to that for a liquid-gas transition in a simple fluid (or the BP_{III}–I transition discussed above): a first-order SmC–SmI transition can terminate in a critical point, beyond which there is a supercritical evolution of both BO order and tilt. Theory[9] predicts that this SmC–SmI critical point should belong to the same universality class as SmA–SmA and chiral SmC*–SmC* critical points, although mean-field behavior cannot be ruled out if the Ginzburg critical regime is very narrow.

A detailed experimental study has been carried out for the static and dynamic thermal behavior at a SmC–SmI critical point.[10] Chirality is not an essential ingredient for BO ordering, and this study was made on racemic methylbutyl phenyl octylbiphenyl-carboxylate (8SI) and the racemic octyloxybiphenyl analog (8OSI). It has been known for some time that 8OSI exhibits a supercritical SmC–SmI evolution,[11] and 8SI undergoes a strongly first-order SmC–SmI transition.[10]

A study of binary 8SI + 8OSI mixtures determined that the critical composition X_c is 75 weight percent 8OSI, and the critical SmC–SmI heat capacity behavior is shown in Fig. 2. The data shown in this figure were obtained with the ac calorimetric technique at sufficiently low frequencies (3.5 mHz near T_c) that they correspond to static heat capacity values except very close to T_c. A fit of these C_p data with Eq. (2) yields $x = 1.06 \pm 0.08$ and $y = 0.5$, which are mean-field values since the critical exponent x corresponds to the exponent γ due to the path of approach; see Ref. 10 for a detailed discussion.

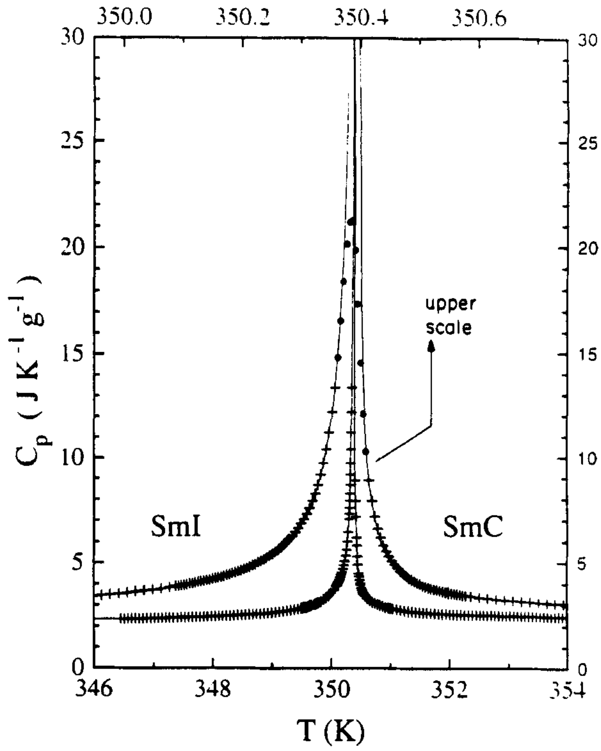

FIGURE 2 Static heat capacity of the critical 8SI + 8OSI mixture containing 75 wt% 8OSI (Ref. 10). Data points close to T_c denoted by filled circles were excluded from the fit. The smooth curves represent a fit with Eq. (2).

For the critical mixture and several supercritical samples, frequency-dependent complex heat capacities were observed near the maximum in the SmC–SmI heat capacity peak. In the case of the 75% critical mixture, a frequency dependence for Re $C_p(\omega)$ and nonzero values for Im $C_p(\omega)$ were observed over the range $-0.4K < T - T_c < +0.3K$.[10] Thus the heat capacity corresponds to a dynamical response function, and the relaxation time τ for critical slowing down can be extracted from the data. The available dynamical data are well described by a single Debye relaxation process, and the resulting τ values are shown in Fig. 3. Analysis of these τ data show that τ diverges like $|T - T_c|^{-z\nu}$ with the dynamical critical exponent given by $z\nu = 0.95 \pm 0.07$.[10] This value is in excellent agreement with the van Hove value $z\nu = 1$ for classical slowing down at a critical point.

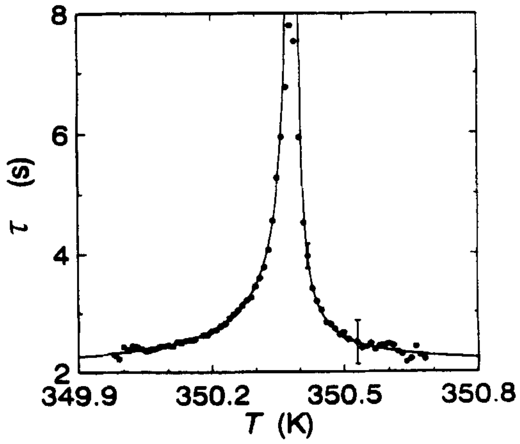

FIGURE 3 Relaxation time τ associated with the SmC–SmI critical point in a 8SI + 8OSI mixture with X_C = 75 (Ref. 10).

TWIST-GRAIN BOUNDARY SYSTEMS

The twist-grain-boundary (TGB) phase of a chiral liquid crystal exhibits long range order that combines a helical twist and smectic layering.[12] This phase, which is an intermediate structure between SmA and the cholesteric N*, is the liquid-crystal analog of the Abrikosov flux vortex lattice in type-II superconductors whereas the SmA phase is analogous to the Meissner phase. Indeed, Kamien and Lubensky[13] have predicted significant short-range TGB structure in the cholesteric phase at low temperatures, corresponding to a liquid of screw dislocations to be called a chiral line liquid and denoted here by N_L^*. It should be stressed that N_L^* and N* are not thermodynamically distinct phases but they differ significantly in the extent of short-range smectic layer formation. The N_L^* region would correspond to an Abrikosov vortex liquid in high-T_C superconductors.

Studies of TGB systems with a new calorimeter capable of both high-resolution ac operation and a nonadiabatic scanning mode that detects latent heats have made possible detailed thermal data about the many phase transitions that occur in such systems. Several members of two closely related homologous series have been investigated.[14,15] The first system is 3–fluoro–4[1–methylheptyloxy]4′–(4″–alkoxy–3″ fluorobenzoyloxy) tolane [$nFBTFO_1M_7$], which exhibits the phase sequence I–BPs–N*–TGB_A–SmA. The second system is the homologous series $nF_2BTFO_1M_7$, which is the 2″,3″–difluorobenzoyloxy analog of $nFBTFO_1M_7$. The higher homologs of this series (n = 11 and 12) exhibit tilted TGB_C phases instead of TGB_A.

The most interesting feature of these TGB studies is the significant thermal evidence for the evolution of short-range chiral line liquid structures (N_L^*) on cooling the cholesteric phase. This is illustrated by the heat capacity data for $9FBTFO_1M_7$ shown in Fig. 4. It should be stressed that the large rounded heat capacity peak (T_5) in the N* phase does not represent a thermodynamic phase transition but is consistent with the evolution of short-range chiral line liquid (N_L^*) character. The ac technique does not detect the small latent heats at the TGB_A–N_L^* and SmA–TGB_A transitions, but these were determined from the nonadiabatic scanning technique to be 8.1 mJ g^{-1} and 40 mJ g^{-1}, respectively, in $9FBTFO_1M_7$.[14] These values can be compared with the large excess enthalpy (1800 mJ g^{-1}) associated with the T_5 peak in $9FBTFO_1M_7$. References 14 and 15 show that all the observed transitions involving TGB phases are first order with small latent heats and no pretransitional fluctuation effects. Very slow scans (20-30 mK/h) for $11F_2BTFO_1M_7$ and $12F_2BTFO_1M_7$ show that there are two closely spaced transitions in the region where a single TGB_C–N* transition was expected. This strongly suggests the existence of two distinct TGB_C phases.

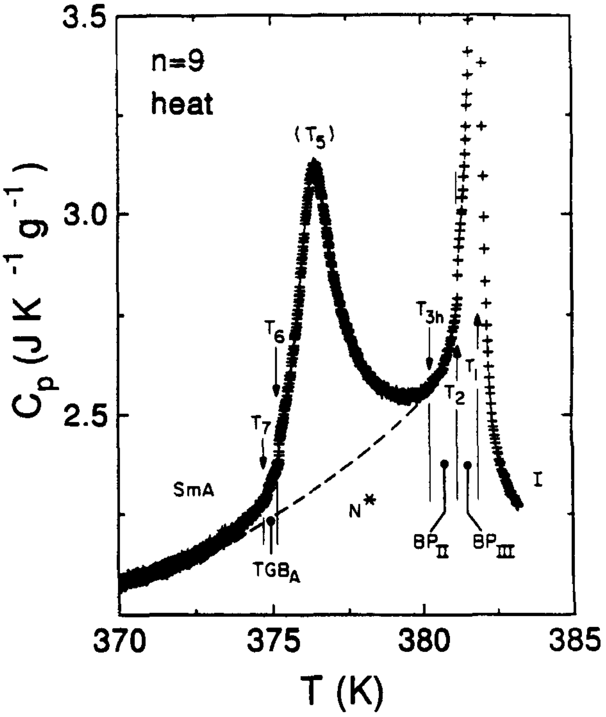

FIGURE 4 Heat capacity of $9FBTFO_1M_7$ obtained with an ac calorimeter (Ref. 14)

ACKNOWLEDGMENTS

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