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Specific Heat Due to Smectic-C to Smectic-I Bond Orientational Ordering

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Specific Heat Due to Smectic-C to Smectic-I Bond Orientational Ordering

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A high-resolution calorimetric study of methylbutylphenyloctyloxybiphenyl carboxylate (8OSI) has been carried out near the smectic-C to hexatic smectic-I transition. The excess heat capacity peak ΔC_P is large but clearly rounded over a 300 mK range. The ΔC_P data and previously published C_6 order parameter data can be fit simultaneously using a phenomenological equation of state with a temperature independent tilt field H. Interpretation of the underlying effective critical exponents $\alpha = 0.47$ and $\beta = 0.077$ is not clear, but one possibility is that the SmC–SmI transition in the limit $H \rightarrow 0$ would be weakly first-order.

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In some liquid crystal phases, translational order is only short range but six-fold order in the direction of local crystalline axes (bond orientational, or BO, order) is long range. According to the theories of two-dimensional (2D) melting,[1] there may exist a hexatic phase with algebraically decaying BO order between the 2D solid and 2D liquid phases. This idea was applied to smectic liquid crystals by Birgeneau and Litster,[2] who proposed that a three-dimensional liquid crystal phase formed of 2D stacked hexatic layers would exhibit long range BO order due to the infinite susceptibility of the 2D BO order parameter. The 3D hexatic phases that can occur in smectic liquid crystals are (1) SmB_H where SmA-like order is supplemented by six-fold bond orientational order, (2) SmI, in which the molecules are tilted (with respect to the layer normal) towards a nearest neighbor, and (3) SmF, where the tilt direction lies between two nearest-neighbor molecules. Both SmI and SmF represent SmC-like order supplemented by bond orientational order. A 3D hexatic phase was first observed by Pindak and coworkers[3] in x-ray studies of the SmB_H phase of the liquid crystal 65OBC.

The symmetry of the hexatic order parameter places the SmA–SmB_H transition in the 3D XY universality class. However, heat capacity data[4] for numerous compounds yield large values of the critical exponent α (0.48 to 0.67), which are inconsistent with the 3D XY value $\alpha = -0.007$. In the case of the tilted hexatic phases, theory[5] predicts that a field H due to the tilt induces finite BO order in

the SmC phase which then grows rapidly in the transformation from SmC to SmI (or SmF). Thus the SmC and SmI (or SmF) phases are not thermodynamically distinct and this transition is considered to occur continuously in the presence of a field coupled to the order parameter.

It is important to emphasize that analysis of the variation of thermodynamic properties which depend on T and H requires knowledge of an equation of state for the system. The situation is analogous to that of the paramagnetic to ferromagnetic transition in an external field. A high-resolution x-ray study of the SmC–SmI transformation in aligned single domain 3D films of 8OSI has been carried out by Brock, et al.[6] They observed a continuous evolution of the hexatic order parameter C_6 and its higher harmonics C_{6n}. In addition, they discovered a novel scaling relation $C_{6n} = C_6^{\sigma_n}$ with $\sigma_n = n + 0.3n\,(n - 1)$ for the bulk films. Aharony et al.[7] developed a theory accounting for this interesting scaling of the harmonics and also suggested a general phase diagram for hexatic smectic systems. For SmA materials, the hexatic SmB_H to CrB (a 3D plastic crystal) transition is required by symmetry to be first order. Near the SmB_H/SmA/CrB triple-point coupling between the hexatic and crystal order parameters should drive the SmB_H to SmA transition first order. However, away from the triple point, this transition could become second-order at a tricritical point along the SmA–SmB_H transition line. The tilted analog of this phase diagram would have, if the tilt field were small enough, a SmI–SmC–CrJ triple point and a SmC–SmI tricritical point. Thus, depending upon the particular compound or mixture of compounds one might expect the smectic–hexatic transition to be either first- or second-order. For completeness, we should also remind the reader that the tilted hexatic smectic phases do not have perfect six-fold symmetry in the plane of the smectic layers; in view of the success of calculations[7] which ignore this fact, we think it not of great importance.

In this article, we report high-resolution ac-calorimetric C_P data for the SmC–SmI transformation in racemic methylbutylphenyloctyloxybiphenyl carboxylate (8OSI). The experimental technique has been described previously.[8] A simultaneous analysis of these C_P data and the published C_6 order parameter data[6] is carried out using a phenomenological parametric equation of state.

The temperature dependence of C_P in the vicinity of the SmC–SmI transformation is presented in Figure 1. The small feature observed below the large SmC–SmI peak is the first-order transition between the SmI and CrJ phases. CrJ, also called smectic J, is a plastic crystal with 3D translational long-range order.

The excess heat capacity ΔC_P associated with the SmC–SmI transformation was obtained by subtracting the background heat capacity C_{PB} shown as the dashed line in Figure 1. A detailed view of the ΔC_P variation near the SmC–SmI transformation is given in Figure 2. Any attempt to fit ΔC_P with a singular power law form would require deletion of the data over at least the range from 352.66 K to 352.96 K since the curve has points of inflection at these temperatures. This rounding is the result of the tilt-field acting upon the hexatic order parameter. In our analysis, we explicitly include the finite field aspect of the transition under the assumption that the magnitude of the tilt field acting on the hexatic order parameter is constant across the temperature range of interest. This enables us to fit the entire

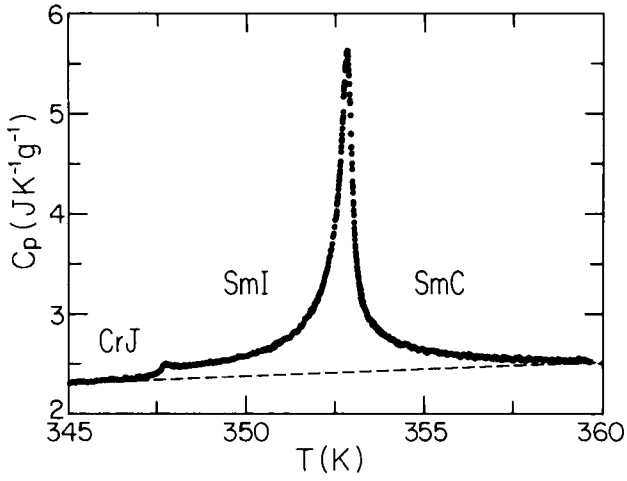


FIGURE 1 Specific heat of 8OSI associated with the SmC–SmI transformation and the freezing/melting transition into the plastic crystal CrJ phase. Hysteresis was observed near the first-order SmI–CrJ transition, but not near the SmC–SmI peak. Data are shown for a cooling run carried out at a scanning rate of 50 mK h^{-1}. The dashed line represents C_{PB}, the noncritical regular contribution to the heat capacity.

ΔC_P variation without omitting data in the rounded region and also to fit simultaneously the entire C_6 order parameter variation.

The parametric equation approach[9] is based on the idea that in the temperature and field space near a single critical point any thermodynamic quantity $X(T,H)$ with critical exponent x can be transformed to $X(r,\theta) = f_x(\theta)\, r^{-x}$, where r is the distance to the critical point and θ defines the path of approach: $\theta = 0$ on the

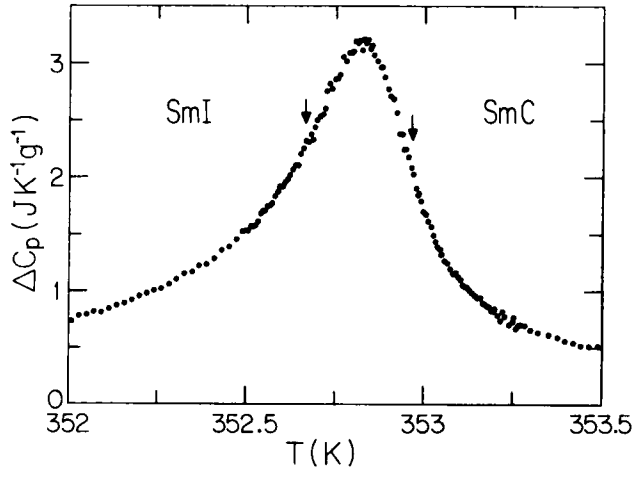


FIGURE 2 Detailed view of the SmC–SmI heat capacity peak in 8OSI. Note the smooth rounding of this peak. The points of inflection (marked by small arrows) are quite symmetrically disposed and are separated by 300 mK.

critical isochore, $\theta = \pm b^{-1}$ on the critical isotherm, and $\theta = \pm 1$ on the coexistence curve. The functions $f_x(\theta)$ are analytic and well behaved. Although the true field space of the SmC–SmI transformation is definitely more complex than a simple critical point, the transformation should be dominated ultimately by the proximity of a single fixed point with a given set of exponents for the hypothetical $H = 0$ transition. Experience with the parametric equation of state[9] shows that also it can describe data in a crossover region; in that case interpretation of the critical exponents is more complex. To justify fitting only the primary order parameter C_6 and ΔC_P to the equation of state, we remark that the contributions of fluctuations in C_{6n} to ΔC_P should be proportional to $\langle C_{6n}^2 \rangle$; near T_c where ΔC_P is large we expect the dominant contributions to ΔC_P come from C_6.

The parametric forms for the singular part of the free energy, the order parameter, and the singular part of the heat capacity are, respectively,

$$\begin{aligned} F(r,\theta) &= f(\theta) r^{2-\alpha} \\ C_6(r,\theta) &= m(\theta) r^{\beta} \\ \Delta C_{PH}(r,\theta) &= Ac(\theta) r^{-\alpha} + B_c \end{aligned} \tag{1}$$

and the transformation from (T,H) to (r,θ) variables is accomplished via $T(r,\theta) = t(\theta)r$ and $H(r,\theta) = h(\theta)r^{2-\alpha-\beta}$, using the forms $h(\theta) = \theta(1 - \theta^2)$ and $t(\theta) = (1 - b^2\theta^2)$. The functions $f(\theta)$ and $c(\theta)$ and the (T,H) to (r,θ) transformation all depend on α and β. In the present application, H is the tilt field, C_6 is the hexatic order parameter, and ΔC_{PH} is the excess heat capacity at constant H and constant pressure. In the above expression for ΔC_{PH}, B_c is a small critical contribution to the nonsingular part of the heat capacity. In our analysis, we have utilized a simple model with

$$m(\theta) = K\theta \text{ and } b^2 = (2 - \alpha - 4\beta)(2 - \alpha - 2\beta)^{-1}(1 - 2\beta)^{-1} \tag{2}$$

With this equation of state the parameters have a relatively simple physical interpretation, lines of constant r corresponding to paths of constant heat capacity at constant order parameter;[9] and the equation of state is called the linear parametric model.

In Table I, we present the results of an analysis using the linear parametric model. In fits to the data with Equations (1) and (2), the transition temperature T_c was allowed to have different values for the ΔC_P data and the C_6 data. The 8OSI samples were from different sources and were subject to different handling procedures; the resulting T_C values differ by ~2 K. In fit 1, we required the field to be equal for the heat capacity and order parameter in a simultaneous fit of both sets of data. In fit 2, we allowed the field values to be different for ΔC_P and for C_6 in a simultaneous fit, but the same values of α and β were still required for both sets of data. This yielded a significantly better fit (at a 99% confidence level) in which the tilt field value for the C_6 data is larger than that for the ΔC_P data. We believe this higher field value and the lower T_c value for the x-ray data can be

TABLE I

Parameter values for fits with the linear parametric equation of state

Fit	$A \times 10^4$	K	α	β	T_c	$H \times 10^5$	B_c	χ^2_ν
1	1.25	0.978	0.62	0.074	352.575[a]	10.405	−0.072	2.85
					350.484[b]			
2	2.45	1.023	0.47	0.077	352.671[a]	2.278	−0.318	1.31
					350.405[b]	5.593		
3	2.38		0.48	0.077	352.686[a]	2.419	−0.303	1.50
4		1.031	0.38	0.075	350.388[a]	3.304		0.91

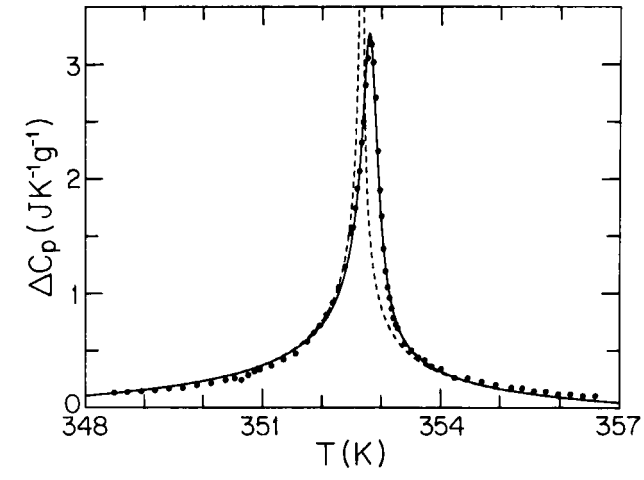
[a]Denotes values for ΔC_P. Units for A and B_C are $J\ K^{-1}\ g^{-1}$.
[b]Denotes values for C_6.

explained by impurities generated by thermal degradation of the sample during the film preparation and alignment in the high temperature SmA phase (T_{AC} = 405 K for 8OSI) and the long period of irradiation in the x-ray experiment.[10] Fit 3 represents a fit to the ΔC_P data alone, and fit 4 gives the results of fitting the C_6 data alone. We feel that the intrinsic field is more reliably obtained from the ΔC_P measurements, where the sample is of higher purity. On fitting the C_6 data alone, one obtains an artificially low α, and even then H is larger than for the ΔC_P data. We conclude the C_6 transition appears smeared out for two reasons: an intrinsic tilt field $H = 2.4 \times 10^{-5}$ and impurity broadening that can be mimicked with a larger effective field. The expected behavior for C_6 in a very pure sample is indicated by the dotted curve in Figure 3(b). Figure 3(a) and (b) show both data sets and the parametric curves for fit 2, with the dashed lines indicating the variation given by our parameters under the hypothetical case when H is set equal to zero. In all our fits, we have used an edited ΔC_P data set constructed by choosing every fifth point in the full set of Figure 1. The ΔC_P data cannot be fit with β fixed at 1/4 or with $\gamma = 2 - \alpha - 2\beta$ fixed close to 1; acceptable fits to ΔC_P require $\gamma \approx 1.2$–1.5. Using the result[11]

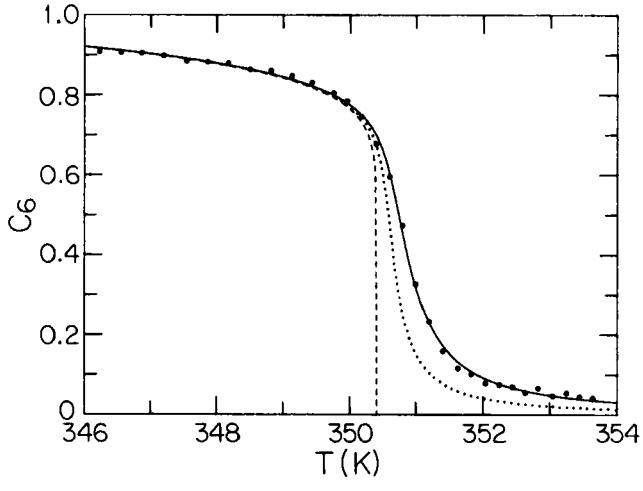
$$\frac{A^-}{A^+} = 4\left(\frac{\beta}{\gamma}\right)^2 \left(\frac{(1-2\beta)\gamma}{2\beta(\gamma-1)}\right)^{\gamma+2\beta} \tag{3}$$

we can predict the amplitude ratio for the power law form that is valid when $H = 0$, viz. $\Delta C_P^{\pm} = A^{\pm}|t|^{-\alpha} + B_c$, where $t \equiv (T - T_c)/T_c$. Using the exponents from fit 2, one finds $A^-/A^+ = 1.24$.

In addition to the fits with the linear parametric model we have tried fitting ΔC_P with a pure power law, excluding data for $|t| < 5 \times 10^{-4}$ where ΔC_P is obviously rounded off. This fit gave $\alpha = 0.80$ and $A^-/A^+ = 1.62$ with $\chi^2_\nu = 0.93$, but we consider it to be unsatisfactory since it does not account for the field-induced rounding of ΔC_P and is inconsistent with the C_6 data. We have also attempted to fit our data to an extended Landau model including all even terms up to C_6^{10} and bilinear coupling to an external field. This procedure gave statistically acceptable fits to the C_6 or ΔC_P data individually, but with physically implausible coefficients.



(a)



(b)

FIGURE 3 (a) Edited data set for ΔC_P near the SmC–SmI transition. The solid curve is the parametric equation fit 2 in Table I. The dashed line represents the equation's prediction for underlying critical behavior in the absence of a field. (b) C_6 order parameter variation near the SmC–SmI transformation. The solid and dashed lines have the same meaning as in part (a). The dotted line is the equation's prediction for the C_6 variation using the field from fit 3, and is a prediction for the C_6 variation in a very pure sample.

It failed completely to fit both sets of data simultaneously; thus it is clear that both the C_6 and ΔC_P data cannot be described well by the same extended Landau free energy.

The correct theoretical interpretation of the experimental results for the SmC–SmI transformation, as well as those for the untilted SmA–SmB_H transitions in other materials is still unclear. While we have found an empirical equation of state

which fits our data with a small number of parameters, the resulting critical exponents, especially the small value of β, are unexpected. It is well known[12] that small values of β are obtained when order parameter data for a weakly first-order transition are fit to a power law $|T - T_c|^{\beta}$. The α value close to 0.5 obtained from our equation of state suggests that the hypothetical zero field transition may be near a tricritical point but on the first-order side in 8OSI. There is then the question of consistency with the theory[7] of the harmonic scaling observed for the C_{6n} which implies 3D XY behavior away from the transition; however, the C_6 data near T_c could permit crossover to mean-field behavior. The C_6 data emphasize the region rather well below T_c, while ΔC_P results are dominated by the region close to T_c. One possible scenario for 8OSI is that the thermodynamic path followed, when projected onto the $H = 0$ plane, traverses a 3D XY region for $T \ll T_c$, then crosses over to a tricritical region, and intersects the first-order phase boundary near the tricritical point. Hypothetically, this crossover could be caused by the effects of dangerous irrelevant variables, in the renormalization group sense, or fluctuations; it would be desirable to test this with an explicit calculation. This scenario requires a particularly fortuitous set of material parameters for 8OSI, hence it would be desirable to examine the behavior of simultaneous C_6 and ΔC_P measurements in other liquid crystals. We note that available data on hexatic compounds show no sign of a trend in the exponent α towards the 3D XY value of -0.007. The existing ac calorimetric heat capacity data for SmA–SmB_H transitions,[13] where there is no tilt field, also show rounded maxima with points of inflection separated by 70 mK or more. Such rounding can be observed in the ac method when there is a narrow two-phase coexistence region. Also, effective exponents α larger than 0.5 have been found; we have observed[14] that a weakly first-order SmA–nematic transition near a tricritical point produces similar results. These seem to be strong reasons for studies using high-resolution adiabatic calorimetry.

Another attractive approach to understanding the behavior of the smectic–hexatic transition in 8OSI is the model used to explain the magnetic susceptibility of La_2CuO_4. This material consists of weakly coupled 2D layers of antiferromagnetically-interacting copper spins. A model which couples 2D antiferromagnetic layers in the mean field approximation works very well for this system.[15] When the same approach is applied to stacked 2D hexatic layers[16] it does not represent the temperature dependence of C_6 as well as the parametric equation of state does, and represents ΔC_P very poorly. However, one might expect the model to be improved if the layer interaction calculation were carried beyond mean field theory.

Thus, while we have found an empirical equation of state to represent the properties of 8OSI well with only five parameters, we do not yet understand the physical significance of all the parameters. The best hope for a theoretical explanation of the exponents given by the parametric equation fit currently lies in a more sophisticated model analogous to the one developed for La_2CuO_4.[15] In addition to this theoretical effort, we believe the questions raised by this work require the combination of x-ray structural measurements and high-resolution adiabatic calorimetry studies on several liquid crystals and their mixtures to be resolved. One

could then see if the behavior observed for 8OSI is typical of SmI or SmF materials and explore how much of the phase diagram proposed by Aharony et al.[7] can be observed.

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