RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 53, NUMBER 4 APRIL 1996

Gaussian tricritical behavior of heat capacity at the smectic-A–smectic-C liquid crystal transition

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(Received 12 December 1995)

High resolution ac calorimetric measurements have been carried out near the smectic-A–smectic-C phase transition in a racemic mixture of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC). The heat capacity data show a distinct pretransitional excess above the transition temperature as well as below it. Analysis of the data reveals Gaussian tricritical behavior of this transition. It is also found that the anomaly is described well with the renormalization-group expression with corrections-to-scaling terms.

PACS number(s): 64.70.Md, 61.30.−v, 64.60.Fr, 65.20.+w

The liquid crystalline smectic-A (Sm-A)–smectic-C (Sm-C) transition and the smectic-A–chiral-smectic-C (Sm-C*) transition are theoretically classified into the three-dimensional (3D) XY universality class [1]. On the other hand, almost all experimental data reported earlier on the Sm-A–Sm-C(or C*) transitions show classic mean-field behavior and are well described by the extended Landau theory which includes up to sixth-order term in the tilt order parameter (see Refs. [2–5], and also references cited therein). A few examples have been found for which the heat capacity shows Landau behavior while the ultrasonic velocity shows non-Landau behavior [6,7]. Benguigui and Martinoty [6] claim that the critical region for the Sm-A–Sm-C transition is dependent on the observable property studied, and they assert that the heat capacity is less sensitive to fluctuation effects than ultrasonic velocities.

However, we recently found that the heat capacity anomaly of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) at the Sm-A–Sm-C_α^* transition shows a clear deviation from the Landau behavior and is described well with the 3D XY renormalization expression [8]. Here the Sm-C_α^* phase in an antiferroelectric version of the Sm-C* phase. Very recently, Reed *et al.* [9] reported that the heat capacity near the Sm-A–Sm-C transition of 5-n-decyl-2-[4-n-(perfluoropentyl-metheleneoxy) phenyl] pyrimidine (H10F5MOPP) shows a non-Landau, almost tricritical behavior. These examples show that the Sm-A–Sm-C(or C*) transition can really exhibit theoretically expected non-Landau critical behavior, and therefore it is of special interest to search for further similar examples.

In this Rapid Communication we report the results of ac calorimetric measurements on a racemic mixture of MHPOBC which exhibits the following phase sequence [10]:

$$\text{Sm-}C_A \overset{386\ \text{K}}{\leftrightarrow} \text{Sm-}C \overset{394\ \text{K}}{\leftrightarrow} \text{Sm-}A \overset{420\ \text{K}}{\leftrightarrow} I.$$

The results described below reveal that the heat capacity shows significant critical behavior at the Sm-A–Sm-C transition. Moreover, the present system is a clear example of a Sm-A–Sm-C transition which exhibits Gaussian tricritical behavior.

The heat capacity was measured using an ac calorimeter with basically the same setup as described elsewhere [8,11]. About 37 mg of sample was hermetically sealed in a gold cup. Temperature scan rate was about 0.03 K/h in the transition region. The sample showed an excellent stability, with the drift rate in the transition temperature being about −0.004 K/day.

Figure 1 shows the overall temperature dependence of the heat capacity C_p. A large anomaly is seen at the Sm-A–Sm-C transition located at 394.3 K. No indication of first-order character was found at this transition. The heating and cooling data agreed perfectly, and the phase shift of the ac temperature response remained unchanged within 0.005 rad near the transition. The dashed line in Fig. 1 shows the normal background part of the heat capacity determined as a linear function of the temperature which smoothly joins the observed data at temperatures far away from the transition on the both sides. After subtracting the normal part, the excess heat capacity ΔC_p has been plotted in the vicinity of the Sm-A–Sm-C transition in Fig. 2. It is seen that the heat capacity shows significant divergent character on *both* sides of the transition temperature. In particular, the existence of such divergent excess above the transition temperature clearly indicates that this transition is not of the mean-field type.

Firstly, the ΔC_p data have been analyzed with the following renormalization-group expression including the corrections-to-scaling terms [12]:

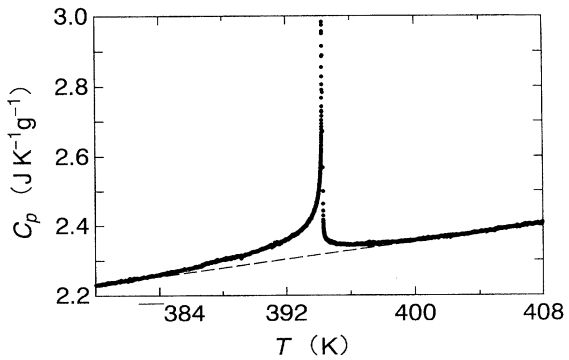

FIG. 1. Overall temperature dependence of the heat capacity C_p for a racemic mixture of MHPOBC. The dashed line shows the background heat capacity (see text).

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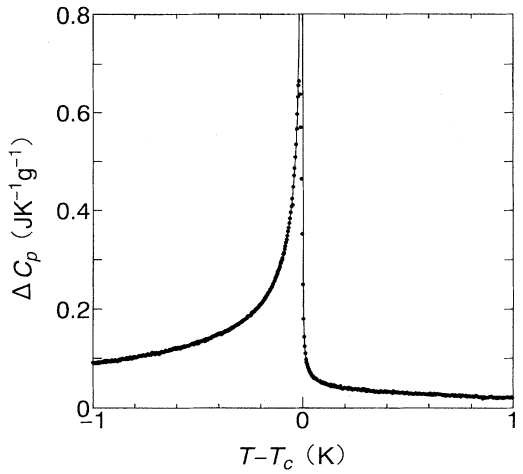

FIG. 2. Detailed view of the excess heat capacity ΔC_p near the Sm-A–Sm-C phase transition for a racemic mixture of MHPOBC. Solid line shows the theoretical tricritical fit with Eq. (3) (see text).

$$\Delta C_p = A^{\pm}|t|^{-\alpha}(1+D_1^{\pm}|t|^{\Delta_1})+B_c, \tag{1}$$

where $t \equiv (T-T_c)/T_c$ is the reduced temperature, and the superscripts $\pm$ denote above and below T_c [13]. The exponent α was adjusted freely in the least-squares fitting procedure. The correction-to-scaling exponent Δ_1 is actually dependent on the universality class, but has a theoretically predicted value quite close to 0.5 (0.524 for 3D XY, and 0.496 for the 3D Ising model [12]). Therefore, we fixed its value at 0.5 in this fitting procedure. There is usually a narrow region very close to T_c where data are artificially rounded due to impurities or instrumental effects. The extent of this region was carefully determined in the way described elsewhere [14], and data inside this region were excluded in the fitting. Typically, the rounding region thus determined is $-4\times10^{-5}<t<+1\times10^{-5}$. Fits were made for the data over three ranges, $|t|_{\max}=0.001$, 0.003, and 0.01, where $|t|_{\max}$ is the maximum value of $|t|$ used in the fit. The first three lines in Table I show the values of the critical exponent α, the critical amplitude ratio A^-/A^+, and other adjustable parameters thus obtained. It is seen that the fits yield α values very close to the tricritical value 0.5. Thus we see that the present data show nonclassical (Gaussian) tricritical behavior in contrast with the Landau tricritical behavior reported so far on some Sm-A–Sm-C transitions [4,15].

We next fitted the data fixing α at 0.5. If we still choose to assume $\Delta_1=0.5$, the corrections-to-scaling term in Eq. (1) merges precisely with the constant term B_c. As a result, we can rewrite Eq. (1) as

$$\Delta C_p = A^{\pm}|t|^{-1/2}+B^{\pm}, \tag{2}$$

where $B^{\pm}=B_c+A^{\pm}D_1^{\pm}$ and $\Delta B \equiv B^+-B^-\neq 0$. The last three lines in Table I show the results of fits with Eq. (2). The fit is quite good for $|t|_{\max}=0.001$ but becomes worse for $|t|_{\max}=0.003$ and 0.01, indicating that higher-order corrections are needed. We also note here that the parameter values obtained in the fits with Eq. (2) are all stable against the data-range shrinking. Rather large variation of $D_1^{\pm}$ with $|t|_{\max}$ seen in Table I for the fits with Eq. (1) can be understood as caused by strong coupling between B_c and $D_1^{\pm}$.

Finally, the data were fitted with an equation including both first- and second-order correction terms [12,16]. For $\alpha=0.5$ and $\Delta_1=0.5$,

$$\Delta C_p = A^{\pm}|t|^{-1/2}(1+D_2^{\pm}|t|)+B^{\pm}. \tag{3}$$

Table II shows the results of fitting with Eq. (3). In Figs. 2 and 3, the solid curve shows the theoretical fit with Eq. (3) to the data with $|t|_{\max}=0.01$. The agreement between the observed data and the theoretically calculated smooth curve is satisfactory. We also note here that the slight bend at large $|t|$ and the hump around $t\sim10^{-3}$ seen in Fig. 3 are due to the contribution from the corrections-to-scaling terms. The slope of the curve tends to the asymptotic value -0.5 in the small $|t|$ limit. The present $D_2^{\pm}$ values are in a qualitative agreement with those obtained for tricritical nematic–Sm-A_1 transition [16,17] in the sense that $D_2^{\pm}<0$. However, $D_2^-/D_2^+\cong$ 0.03–0.16 for the present results is further away from the theoretical expectation $D_2^+=D_2^-$ and in the opposite direction in comparison with the nematic–Sm-A_1 transition, where $D_2^-/D_2^+\cong$ 2.6–5.0.

Logarithmic corrections are theoretically expected at tricritical points since the upper marginal dimension d_u is 3. As a preliminary test of this, we have tried fits with the following asymptotic heat capacity variation as predicted by Lawrie and Sarbach [16,18]:

$$\Delta C_p = A^{\pm}|t|^{-1/2}(1+L^{\pm}\ln|t|)^q+B_c, \tag{4}$$

where $q=-6(n+4)/(3n+22)=-9/7$ for an XY model ($n=2$). A fit with $|t|_{\max}=0.001$ yielded $L^+=-2.6$,

TABLE I. Least-squares values of the adjustable parameters for fitting ΔC_p with Eqs. (1) and (2). Here $\Delta B=B^+-B^-$, and $\nu=N-p$, where N is the number of data points and p is the number of free parameters. Quantities in brackets were held fixed at the given values. $D_1^{\pm}$ are not shown for the fits with Eq. (2), since the first-order correction term merges with B_c in these cases (see text). The units for A^+, B^+, and ΔB are J K^{-1} g^{-1}.

Eq.	ν	$\lvert t\rvert_{\max}$	T_c (K)	α	10^4A^+	A^-/A^+	D_1^+	D_1^-	B^+	ΔB	χ_ν^2
1	202	0.001	394.232	0.494	5.52	9.16	−221.0	−28.5	0.134	[0]	0.98
1	543	0.003	394.233	0.528	2.45	14.20	837.5	57.2	−0.226	[0]	1.14
1	1474	0.010	394.233	0.516	2.91	13.46	1337	96.9	−0.413	[0]	0.97
2	204	0.001	394.232	[0.5]	5.29	9.03			0.018	0.019	1.06
2	545	0.003	394.232	[0.5]	5.86	8.16	-		0.013	0.016	2.88
2	1476	0.010	394.232	[0.5]	6.46	7.60			0.007	0.016	5.65

TABLE II. Least-squares values of the adjustable parameters for fitting ΔC_p with Eq. (3). $\nu=N-p$, where N is the number of data points and p is the number of free parameters. The units for A^+ and $B^\pm$ are $J\,K^{-1}\,g^{-1}$.

ν	$\lvert t\rvert_{max}$	T_c (K)	10^4A^+	A^-/A^+	B^+	B^-	D_2^+	D_2^-	χ_ν^2
202	0.001	394.232	5.18	9.16	0.020	0.003	−167.3	−27.6	0.99
543	0.003	394.232	4.72	10.15	0.027	0.001	−603.4	−21.2	0.96
1474	0.010	394.232	5.27	8.96	0.021	0.004	−338.3	−30.8	1.02

$L^-=0.010$, $A^-/A^+=0.10$, and $\chi_\nu^2=1.05$. It was found, however, that the value of L^+ is quite sensitive to $|t|_{max}$. With $|t|_{max}=0.0005$, we obtained $L^+=-1.4$. With $|t|_{max}=0.002$, the quality of the fit was almost the same for all values of $L^+<-10$. Such a behavior suggests that the logarithmic corrections are still not important within the present fitting range, and therefore higher-order corrections contained in Eq. (3) are mainly responsible for the explanation of the ΔC_p data for $|t|_{max}\geqslant 0.003$.

It is known that the tricritical amplitude ratio A^-/A^+ is not universal over experimentally accessible $|t|$ ranges. Fisher and Sarbach [19] showed that the tricritical amplitude ratios in an exactly solvable spherical ($n=\infty$) model are functions of the single variable $z=(a/R_0)^3$, where a is the lattice spacing and R_0 is the range of interaction. Their results yield $A^-/A^+=(1-z^2)^{1/2}/z$, so that as the interaction range becomes infinitely large, z goes to zero and therefore A^-/A^+ goes to infinity, recovering the Landau behavior. The value of A^-/A^+ obtained in the present work shown in Table II yields $z=0.11$. This is smaller than the values found for tricritical nematic–Sm-A transitions (0.530 in nonpolar mixtures, and 0.707 in polar cyanobiphenyls) [16] and is rather close to the value 0.12 for ^{3}He-^{4}He [19].

It is unusual for the heat capacity at the Sm-A–Sm-C transition to show Gaussian rather than mean-field tricritical behavior as described above. Therefore, the origin of fluctuation effects for the present system is of special interest. Because enantiomorphic MHPOBC also shows non-Landau critical behavior [8], being a racemate cannot explain this critical behavior. It is quite probable that coexistence of antiferroelectric and ferroelectric interactions is the main cause of the criticality. Enantiomorphic MHPOBC exhibits successive transitions including antiferro-, ferro-, and ferrielectric phases [20–22]. Further, the Sm-C_α* phase disappears in racemic MHPOBC and the system undergoes a transition from Sm-A to ferrodistortive Sm-C phase [10,23]. These facts indicate that the ferro- and antiferrodistortive arrangements have almost the same energy, and each phase appears as a result of delicate competition. This allows various fluctuation modes to be excited relatively easily, and therefore enhances the critical behavior. We also note that the considerably asymmetric and flexible molecular shape of MHPOBC [21] has possibly some relation with the above situation.

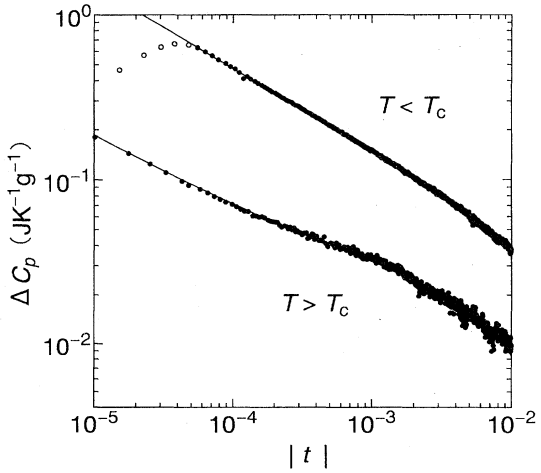

FIG. 3. Log-log plot of the excess heat capacity ΔC_p near the Sm-A–Sm-C phase transition for a racemic mixture of MHPOBC. Data points omitted in the fitting procedure are shown as open circles. Solid line is the theoretical tricritical fit with Eq. (3).

Comparison of the heat anomalies of MHPOBC, MHPBC (the octylbiphenyl analog of MHPOBC [24]), and MHPOCBC (the octyloxycarbonylbiphenyl analog of MHPOBC [25]) is also of interest. These substances have quite similar molecules, and their phase sequences are also quite alike. However, their heat capacity anomalies show a marked contrast. In MHPBC, the critical behavior is discernible but less significant than in MHPOBC [26]. In MHPOCBC, the critical behavior is hardly noticeable and Landau behavior is observed [27]. Probably such a difference in the magnitude of fluctuation effect is caused by the difference in the width of the Sm-A phase, which is about 26 K for chiral and racemic MHPOBC, 33 K for MHPBC, and 41 K for MHPOCBC. It is conceivable that the Sm-A phase is so wide in MHPOCBC that the smectic order-parameter is well saturated before the tilt transition occurs, and therefore the fluctuation is suppressed. This explains that the criticality diminishes in the order of MHPOBC, MHPBC, and MHPOCBC. Since MHPOCBC does not have a ferroelectric phase, it is also possible that the competition between the ferro- and antiferroelectric order is relatively weak so that the enhancement of the flucutation as described above is less effective. Such ideas will be most directly verified by the measurement of correlation length, since we know from the Ginzburg criterion [28] that larger critical heat capacity implies shorter correlation length.

We have recognized three types of tricritical behaviors at the Sm-A–Sm-C(or C*) transitions. The first one is the Landau tricritical behavior reported in earlier works [4,15]. The recent study by Reed *et al.* [9] on H10F5MOPP gives the second type. In that case, a deviation from the Landau behavior is seen, but the anomaly is not explained adequately with a renormalization expression because of the persistent mean-field nature of the anomaly. The third one is a purely

Gaussian tricritical behavior observed for a racemic mixture of MHPOBC in the present study. Since the critical anomaly is most significant and is compatible with the preasymptotic scaling behavior in this case, this system should help to enhance our understanding of tricritical phenomena as well as the Sm-A–Sm-C transition. The results of more detailed tricritical analyses of the heat capacity data will be reported in the near future. Measurements on other physical quantities for this material near its Sm-A–Sm-C transition would be of significant interest.

We wish to thank Professor H. Takezoe for supplying us high-quality MHPOBC samples. We are also grateful to Professor C. W. Garland for helpful discussions.

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