# Crossover from *XY* critical to tricritical behavior of heat capacity at the smectic-*A*–chiral-smectic-*C* liquid-crystal transition

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High resolution ac calorimetric measurements have been carried out for two liquid-crystal systems: 4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC), and 2-fluoro-4-{[(1-trifluoromethyl) undecyloxy] carbonyl} phenyl 4′-(dodecyloxy) biphenyl-4-carboxylate (12BIMF10). The heat-capacity anomaly around the smectic-*A* to the chiral-smectic-*C* transition has been analyzed in detail. It is revealed that the heat anomaly for both systems shows a crossover from three-dimensional *XY* critical behavior to tricritical behavior. All the data are described well with a crossover function which has been obtained from a modification of the original Rudnick-Nelson-type expression. [S1063-651X(96)50107-8]

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Tricritical systems provide an attractive example with a marginal dimensionality $d_u=3$, and have been a focus of intensive studies in the field of critical phenomena [1]. Of particular interest is to describe the crossover from tricritical to ordinary critical behavior. When the tricritical point is located very close to, but not on the experimental path, tricritical behavior is observed far away from the transition, which changes into ordinary critical behavior in the vicinity of the transition. According to the scaling theory, the singular part of the free energy for example takes the form

$$F^{\text{sing}}(t,g)\cong|t|^{2-\alpha_t}\Phi(g/|t|^{\phi}), \quad (1)$$

where $\alpha_t$ is the tricritical exponent of the heat capacity, $\phi$ is the crossover exponent, $t[=(T-T_c)/T_c]$ is the reduced temperature, and $g$ is the scaling field. Far away from the transition region the crossover function approaches a constant value $\Phi(0)$ and therefore $F^{\text{sing}}$ behaves tricritically. Near the $\lambda$ line, the behavior of $F^{\text{sing}}$ is governed by the crossover function $\Phi$. Various theoretical attempts have been reported to describe the crossover behavior, including an explicit calculation of the crossover function by Nelson and Rudnick [2]. On the other hand, experimental verification of such theoretical predictions has been quite limited. As for the Ising systems, metamagnets $FeCl_2$ [3] and $Dy_3Al_5O_{12}$ [4] are such examples. The $^3$He-$^4$He mixture is the only *XY* system for which detailed analyses of the crossover behavior have been made [5]. The nematic (*N*) to smectic-*A* (Sm-*A*) liquid-crystal transition is another example of a three-dimensional (3D) *XY* system which also exhibits tricritical behavior, and the crossover has been studied for several cases [6–8]. It was found, however, that both heat-capacity and correlation length data are well described by a single effective exponent value over a wide temperature range, suggesting that the crossover is too broad.

In this paper we report the results of the crossover-scaling analyses of recent heat-capacity data on two liquid-crystal systems that exhibit a smectic-*A* (Sm-*A*) to chiral-smectic-*C* (Sm-*C**) phase transition. It is revealed that the heat-capacity anomaly at the Sm-*A*–Sm-*C** transition shows a universal crossover from 3D *XY* critical behavior to Gaussian tricritical behavior as a function of temperature.

One of the systems studied here is 4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC), which exhibits the following phase sequence [9]:

$$\text{Sm-}C_A^* \overset{391.6\text{ K}}{\leftrightarrow} \text{Sm-}C_\gamma^* \overset{392.4\text{ K}}{\leftrightarrow} \text{Sm-}C^* \overset{394.1\text{ K}}{\leftrightarrow} \text{Sm-}C_\alpha^* \overset{395.2\text{ K}}{\leftrightarrow} \text{Sm-}A \overset{421\text{ K}}{\leftrightarrow} I.$$

Here Sm-$C_A^*$ and Sm-$C_\alpha^*$ are antiferroelectric, Sm-$C^*$ are ferroelectric, and Sm-$C_\gamma^*$ are ferrielectric phases, respectively. The other system is 2-fluoro-4-{[(1-trifluoromethyl) undecyloxy] carbonyl} phenyl 4′-(dodecyloxy) biphenyl-4-carboxylate (12BIMF10), which exhibits the following phase sequence [10]:

$$\text{Sm-}C_A^* \overset{325.1\text{ K}}{\leftrightarrow} \text{FIL} \overset{325.4\text{ K}}{\leftrightarrow} \text{FIH} \overset{326.3\text{ K}}{\leftrightarrow} \text{Sm-}C_\alpha^* \overset{328.6\text{ K}}{\leftrightarrow} \text{Sm-}A \overset{342.8\text{ K}}{\leftrightarrow} I.$$

Here, FIL and FIH are ferrielectric phases.

The heat capacity was measured using an ac calorimeter as described elsewhere [11,12]. After subtracting the normal part, the excess heat capacity $\Delta C_p$ has been plotted in the vicinity of the Sm-*A*–Sm-$C_\alpha^*$ transition in Fig. 1 for MHPOBC [13], and in Fig. 2 for 12BIMF10. Small anomalies are seen at 394.8 K and 392.7 K in MHPOBC, and at 326.9 K in 12BIMF10, which are due to the restructuring

 

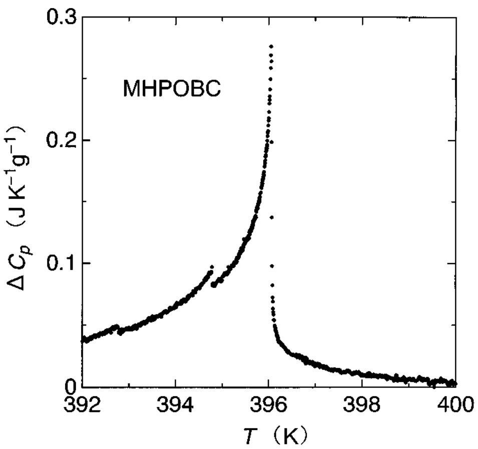


FIG. 1. Temperature dependence of the anomalous heat capacity $\Delta C_p$ of MHPOBC.

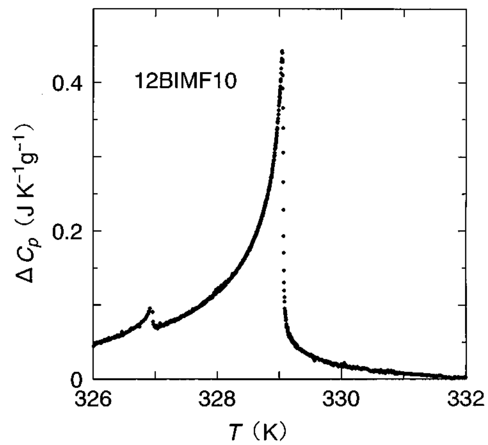


FIG. 2. Temperature dependence of the anomalous heat capacity $\Delta C_p$ of 12BIMF10.

transitions between the chiral smectic-$C$ phases. It was found that these anomalies have a slight effect on the analyses. To avoid this, the anomalies have been eliminated assuming normal cusplike behavior. The details of this procedure will be described in a future publication [14].

First, the $\Delta C_p$ data have been analyzed with the following renormalization-group expression including the corrections-to-scaling terms [15]:

$$\Delta C_p = A^{\pm}|t|^{-\alpha}(1 + D_1^{\pm}|t|^{\Delta_1}) + B_c, \tag{2}$$

where $t \equiv (T - T_c)/T_c$ is the reduced temperature, and the superscripts $\pm$ denote above and below $T_c$. The exponent $\alpha$ was adjusted freely in the least-squares fitting procedure. The correction-to-scaling exponent $\Delta_1$ 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 [15]). 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 a manner described elsewhere [16], and data inside this region were excluded from the fitting. The rounding region thus determined is $-4\times10^{-5} < t < +1\times10^{-5}$ for MHPOBC, and $-10\times10^{-5} < t < +1\times10^{-5}$ for 12BIMF10. Table I shows the values of the critical exponent $\alpha$, and other adjustable parameters thus obtained. Fits were made for the data over several ranges, and $|t|_{\max}$ shown in Table I is the maximum value of $|t|$ used in the fit. It is seen that the $\alpha$ value depends significantly on the fitting range, indicating that the anomaly shows a crossover behavior. In particular, $\alpha$ seems to approach the 3D $XY$ value $\alpha_{XY} = -0.0066$ [15] in the small $|t|_{\max}$ limit, while it moves to the direction of the tricritical value $\alpha_t = 0.5$ for larger $|t|_{\max}$.

Next we analyze the $\Delta C_p$ data with crossover scaling theory. Using an expression of Rudnick-Nelson type [2] as the crossover function and adding a constant term which is needed in describing the heat-capacity data, we obtain

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

We have assumed $\phi = 1/2$. This expression is approximated as

$$\Delta C_p \cong A^{\pm}|t|^{-\alpha_t} + B \tag{4}$$

for $|t| \gg 1$, and

$$\Delta C_p \cong A^{\pm}(a^{\pm})^{\omega}|t|^{-(\omega/2)-\alpha_t} + B \tag{5}$$

for $|t| \ll 1$. However, it is easily seen that this expression cannot be applied to the present case of the crossover from the 3D $XY$ value $\alpha_{XY} = -0.0066$ to the tricritical value $\alpha_t = 0.5$. The critical amplitude should be negative in the

TABLE I. Least-squares values of the adjustable parameters for fitting $\Delta C_p$ with Eq. (2). Here, $\nu = N - p$, with $N$ being the number of data points and $p$ the number of free parameters. The units for $A^+$ and $B_c$ are J K$^{-1}$ g$^{-1}$.

| System | $\|t\|_{\max}$ | $T_c$ (K) | $\alpha$ | $A^+$ | $A^-/A^+$ | $D_1^+$ | $D_1^-$ | $B_c$ | $\nu$ | $\chi_\nu^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| MHPOBC | 0.0003 | 396.086 | 0.01 | 1.8280 | 1.116 | 0.43 | -1.75 | -1.9519 | 33 | 0.93 |
| | 0.0005 | 396.085 | 0.07 | 0.1487 | 1.751 | 2.63 | -4.44 | -0.2326 | 64 | 0.97 |
| | 0.0010 | 396.085 | 0.09 | 0.0944 | 1.969 | 3.43 | -4.30 | -0.1654 | 136 | 0.96 |
| | 0.0025 | 396.086 | 0.14 | 0.0302 | 2.877 | 1.00 | -5.63 | -0.0532 | 367 | 1.37 |
| | 0.0100 | 396.087 | 0.18 | 0.0137 | 3.866 | -5.06 | -6.52 | -0.0109 | 874 | 1.39 |
| 12BIMF10 | 0.0005 | 329.071 | 0.03 | 0.9834 | 1.332 | 1.72 | -3.25 | -1.2334 | 94 | 2.24 |
| | 0.0010 | 329.072 | 0.10 | 0.1197 | 2.389 | 3.30 | -6.65 | -0.2260 | 199 | 1.87 |
| | 0.0030 | 329.073 | 0.17 | 0.0282 | 4.072 | -2.07 | -8.18 | -0.0488 | 533 | 2.16 |
| | 0.0100 | 329.073 | 0.23 | 0.0116 | 5.394 | -8.31 | -8.05 | -0.0056 | 1122 | 4.38 |

TABLE II. Least-squares values of the adjustable parameters for fitting $\Delta C_p$ with Eq. (10). Equation (11) or (12) has been used as $\Delta C_p^{\mathrm{Landau}}$. $T_c$ = 396.085 K in MHPOBC, and $T_c$ = 329.072 K in 12BIMF10. $|t|_{\max}$ = 0.01 in every case. The units for $A^{\pm}$, $L$, and $B$ are J $\mathrm{K}^{-1}\,\mathrm{g}^{-1}$.

| System | Eq. | $A^+$ | $A^-$ | $a^+$ | $a^-$ | $B$ | $b$ | $L$ | $r^{XY}$ | $\chi_\nu^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| MHPOBC | 11 | -2.3024 | -2.1161 | 0.136 | 0.209 | 2.2818 | 0.0225 | 0.00459 | 0.91 | 3.04 |
| | 12 | -2.3039 | -2.0568 | 0.132 | 0.209 | 2.2836 | 0.0316 | 0.00924 | 0.89 | 1.80 |
| 12BIMF10 | 11 | -4.0959 | -3.7230 | 0.077 | 0.120 | 4.0663 | 0.0210 | 0.00906 | 0.90 | 3.14 |
| | 12 | -4.2313 | -3.7012 | 0.068 | 0.110 | 4.2041 | 0.0255 | 0.01611 | 0.87 | 1.55 |

$XY$ regime, and positive in the tricritical regime. On the other hand, Eqs. (4) and (5) imply that the amplitudes for the two regimes have the same sign.

The above situation is not so surprising because Eq. (3) describes only the leading behavior, while nonsingular terms become important when $\alpha<0$. One way to remove this difficulty is as follows. If we start from the temperature derivative of $\Delta C_p$, the crossover occurs between the exponent values $\alpha_{XY}+1=0.9934$ and $\alpha_t+1=1.5$, the amplitudes being both positive. Therefore, we can use the following form:

$$\frac{d\Delta C_p}{dT}=\widetilde{A}^{\pm}|t|^{-1.5}(1+\widetilde{a}^{\pm}|t|^{-1/2})^{-1.0132}. \tag{6}$$

By integrating this expression, we obtain

$$\Delta C_p=A^{\pm}(1+a^{\pm}|t|^{-1/2})^{-0.0132}+B, \tag{7}$$

which is approximated as

$$\Delta C_p\cong-0.0132A^{\pm}a^{\pm}|t|^{-1/2}+(A^{\pm}+B) \tag{8}$$

for $|t|\gg 1$, and

$$\Delta C_p\cong A^{\pm}(a^{\pm})^{-0.0132}|t|^{0.0066}+B \tag{9}$$

for $|t|\ll 1$, thus yielding the correct exponents and the amplitude signs in both regimes (note that $a^{\pm}>0$).

It is seen, however, that Eq. (7) contains another difficulty concerning the amplitude ratio in the $XY$ and tricritical limit. Denoting the amplitude ratio in the $XY$ regime by $r^{XY}$, we see from Eq. (9) that $r^{XY}$ is given as $(A^-/A^+)(a^+/a^-)^{0.0132}$. Since $(a^+/a^-)^{0.0132}\cong 1$ because of the smallness of the exponent, the universality of $r^{XY}$ implies that $A^-/A^+$ is approximately universal. If we expect that $a^-/a^+$ is universal [17], the amplitude ratio in the tricritical regime, given by $A^-a^-/A^+a^+$, also becomes universal and contradicts the fact that the tricritical amplitude ratio is actually nonuniversal [18]. Note that this is also the case in the original Rudnick-Nelson-type crossover expression.

The nonuniversality of the amplitude ratio in the heat capacity of a tricritical system can be ascribed to the Landau part of the heat capacity that exists only below $T_c$. We therefore tried the following expression:

$$\Delta C_p=A^{\pm}(1+a^{\pm}|t|^{-1/2})^{-0.0132}+\Delta C_p^{\mathrm{Landau}}+B^{\pm}. \tag{10}$$

If the fluctuation effect is sufficiently weak, the first term in Eq. (10) can be viewed as a small correction to the Landau behavior. In this case, the Landau contribution $\Delta C_p^{\mathrm{Landau}}$ is simply given by the usual Landau theory [19]:

$$\Delta C_p^{\mathrm{Landau}}=L(|t|+b^2)^{-1/2}. \tag{11}$$

On the other hand, the situation is different in the presence of an appreciable fluctuation effect. While $\Delta C_p^{\mathrm{Landau}}$ behaves as $\sim|t|^{-1/2}$ for large $|t|$, the distinction between the Landau part and the critical part becomes unclear as $T_c$ is approached, and probably $\Delta C_p^{\mathrm{Landau}}$ merges into the constant background. One possible form which satisfies this requirement is

$$\Delta C_p^{\mathrm{Landau}}=\frac{L|t|^{-1/2}}{1+b|t|^{-1/2}}. \tag{12}$$

We tried both Eqs. (11) and (12), and the results are shown in Table II. To be consistent with the scaling requirement, we further assumed that the nonsingular part in $\Delta C_p$ has equal value just above and below $T_c$, and therefore $B\equiv B^-+L/b=B^+$. For all cases shown here $|t|_{\max}=0.01$. In these fits, it was often found that some parameters could not be determined precisely due to strong correlation between them. Because of this, a constraint was imposed so that the tricritical amplitude ratio which comes from the first term in Eq. (10) becomes equal to the 3D $XY$ Gaussian value, $\sqrt{2}$ [20]. It is seen that the value of the $XY$ amplitude ratio $r^{XY}$ is close to the theoretical value 0.971 [15] in every case. The fits with Eq. (12) are satisfactory in the $\chi_\nu^2$ sense, while those with Eq. (11) are clearly worse. This indicates that the fluctuation effect is so significant that $\Delta C_p$ cannot be written as

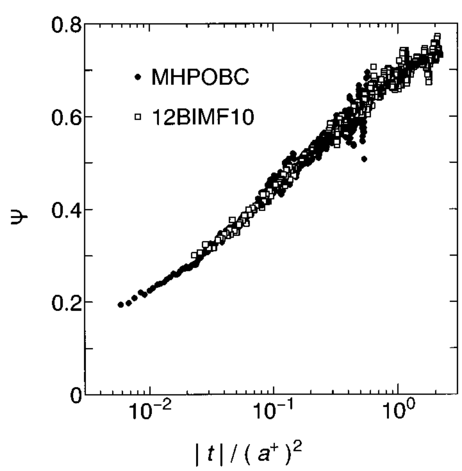


FIG. 3. Scaling plot of the anomalous heat capacity $\Delta C_p$ of MHPOBC and 12BIMF10 above $T_c$. Vertical axis shows $\Psi$ calculated with Eq. (13) from $\Delta C_p$ data and the parameter values shown in Table II, and horizontal axis shows $|t|/(a^+)^2$, which is the squared inverse of the scaling variable.

a simple sum of the critical part and the usual Landau behavior, as noted already. The parameter $a^{\pm}$ measures the crossover temperature, which is given by the condition $a^{\pm}|t|^{-1/2}\sim 1$. The fact that $a^{\pm}$ are smaller in 12BIMF10 than in MHPOBC shows that the transition is closer to the tricritical point in 12BIMF10.

It is to be noted, if we confine ourselves to the case above $T_c$, that Eq. (10) reduces to Eq. (7) and is therefore universal. Since the crossover function becomes a constant at large $|t|$ limit, we see from Eqs. (7) and (8) that we are assuming

$$\Psi(a^{+}/|t|^{1/2}) = -\frac{|t|^{1/2}}{0.0132a^{+}A^{+}}[\Delta C_p - (A^{+}+B^{+})] \qquad (13)$$

as the crossover function. We have normalized $\Psi$ so that it becomes unity for large $|t|$. Figure 3 shows the experimentally obtained crossover-scaling function. Here the vertical axis shows $\Psi$ calculated with Eq. (13) from $\Delta C_p$ data and the parameter values shown in Table II, and horizontal axis shows $|t|/(a^{+})^2$, which is the squared inverse of the scaling variable. The data for MHPOBC and 12BIMF10 fall on a single curve, indicating the universal behavior of the crossover. This coincidence is remarkable because, apart from the constant term $[=A^{+}+B^{+}$ in Eq. (13)] which determines the base line and the multiplying factor $(=-1/0.0132a^{+}A^{+})$ which determines the magnitude of the anomaly, there is only one adjustable parameter $a^{+}$ which decides the crossover temperature.

In summary, we have seen that the $\Delta C_p$ data of MHPOBC and 12BIMF10 show a universal crossover behavior from 3D $XY$ to a tricritical regime as described with a modified Rudnick-Nelson crossover function. The Landau contribution had to be taken into account to obtain the correct amplitude ratios. Because the present result is a 3D $XY$ system in which the heat capacity shows a clear crossover from critical to tricritical behavior as a function of temperature, it would be of great interest to carry out measurements on other physical quantities for these materials near the Sm-$A$–Sm-$C^*$ transition.

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