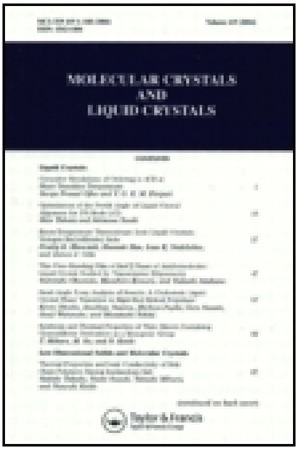

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AC Calorimetric Investigations of Heat Anomaly in Frustoelectric Liquid Crystals

Kenji Ema [a], Haruhiko Yao [a], Takahiro Matsumoto [b] [c] & Atsuo Fukuda [b]

[a] Department of Physics, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Meguro, Oh-okayama, Tokyo, 152-8550, Japan

[b] Department of Textile and Technology, Shinshu University, Ueda, Nagano, 386-8567, Japan

[c] Corporate Research Laboratory, Mitsubishi Gas Chemical Company, Inc., Tsukuba, Ibaraki, 300-4247, Japan

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AC Calorimetric Investigations of Heat Anomaly in Frustoelectric Liquid Crystals

KENJI EMA[a], HARUHIKO YAO[a], TAKAHIRO MATSUMOTO[bc] and ATSUO FUKUDA[b]

[a]*Department of Physics, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2–12–1 Oh-okayama, Meguro, Tokyo 152–8550, Japan,* [b]*Department of Textile and Technology, Shinshu University, Ueda, Nagano 386–8567, Japan and* [c]*Corporate Research Laboratory, Mitsubishi Gas Chemical Company, Inc., Tsukuba, Ibaraki, 300–4247 Japan*

High-resolution ac calorimetric investigations have been made on liquid crystals which exhibit a frustoelectric phase. In each case, a significant heat anomaly which showed a non-Landau critical behavior was observed. The transition was found to be weakly first-order. The data have been analyzed with a preasymptotic powerlaw equation which includes correction-to-scaling terms. The critical amplitude has been discussed with the two-scale-factor universality.

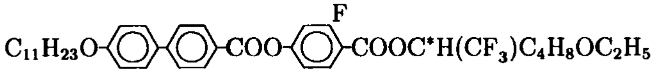
Keywords: heat capacity; ac calorimetery; frustoelectricity; critical phenomana

INTRODUCTION

Intensive studies [1, 2, 3, 4] have been devoted to a group of liquid crystals which show a so-called V-shaped switching instead of the tristable switching observed for usual antiferroelectricity. In a view that this type of dielectric behavior originates the frustration of ferro- and antiferroelectric interactions, it has been proposed to be called as "frustoelectricity". In spite of experiments and theoretical models developed so far, it seems that only a little is known at present for this "frustoelectric" phase. With such background, we have been carrying out a series of high-resolution heat capacity measurements on liquid crystals which exhibit a frustoelectric phase. It is believed that the heat capacity measurement is one of quite powerful tools in understanding phase transitions. In fact, recent ac calorimetric measurements could successfully reveal a significant 3D *XY* critical behavior which crosses over to a Gaussian tricritical behavior in an antiferroelectric liquid crystal MHPOBC and its related substances [5].

The liquid crystals which have been studied so far have the following molecular structures:

1.



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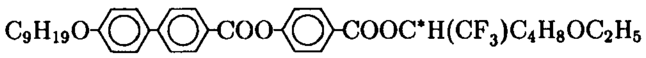

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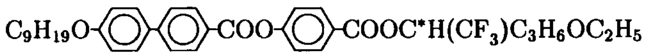

These substances equally show a phase sequence ferri–smectic-*A*(Sm-*A*)-isotropic(*I*) in free standing films [6]. Our measurements have revealed that the temperature width of the Sm-*A* phase is too narrow in case of liquid crystal **1** to obtain enough data for a quantitative analyses of the critical nature of the transition. Because of this, we will confine ourselves here to the results on liquid crystals **2** and **3**. The results will be analyzed with a renormalization-group expression which contains corrections-to-scaling terms. The critical amplitude will be discussed in connection with the two-scale-factor universality.

EXPERIMENTALS

The heat capacity was measured with a high-resolution ac calorimeter described elsewhere [7, 8]. Hermetically sealed gold cells which contained typically 30 mg liquid crystal sample were used. The sample cell was loosely linked to a thermal bath. The bath temperature was scanned about 1 mK/min in the transition region. The sample cell was heated periodically with a frequency of 0.03125 Hz, and the heat capacity was determined from the amplitude of the ac temperature oscillation of the cell. For every liquid crystal studied here, the transition temperature remained almost unchanged, showing a very slow drift rate of typically within 0.5 mK/day. This indicates the stability and high quality of the sample.

The values of the heat capacity C_p were determined as

$$C_p = \left(C_p^{\mathrm{obs}} - C_p^{\mathrm{empty}}\right)/m, \tag{1}$$

where C_p^{obs} and C_p^{empty} are the heat capacity of the filled cell and the empty cell, respectively, and m is the mass of liquid crystal sample.

RESULTS

Figure 1 shows the temperature dependence of the heat capacity C_p of liquid crystal **3** obtained on cooling. A distinct anomaly is seen accompanying the Sm-A to ferri phase transition located at T_c = 381.5 K. In Figure 1, thin solid line shows the normal part of the heat capacity determined as a quadratic function of the temperature which joins the observed heat capacity data smoothly at temperatures away from the transition on both sides. It is clearly seen that the excess heat capacity has a tail over several degrees above the transition. The existence of such a tail indicates the critical nature of the transition, and is incompatible with the extended Landau theory. The overall temperature dependence of the C_p data were quite similar for liquid crystal **2**, which have been preliminarily reported in Ref. [9].

Figures 2 and 3 show the detailed temperature dependences of the excess heat capacity ΔC_p, which have been obtained by subtracting the normal heat capacity from the C_p data, for liquid crystals **2** and **3**, respectively. In the ac calorimetry, the two-phase coexistence at a first-order transition is often detected as an anomalous increase in the phase delay ϕ of the sample temperature response with respect to the ac heating (see Figure 5 of Ref. [10]). In our present measurements also, it was observed that ϕ shows a distinct anomaly at the transition in all liquid crystals studied. The width of the coexistence region in the present data is about 70 mK for liquid crystal **2**, and about 100 mK for liquid crystal **3**. Such relatively narrow conexistence ranges imply that the first-order nature of the

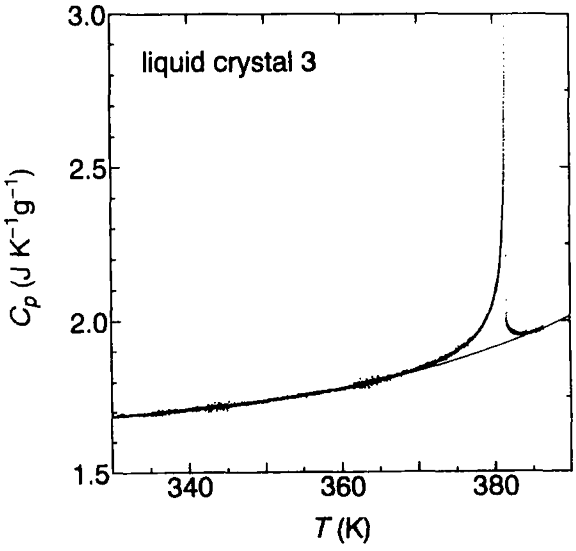

FIGURE 1. Tempereture dependence of heat capacity of liquid crystal **3** obtained on cooling. Thin solid line shows the normal part of the heat capacity.

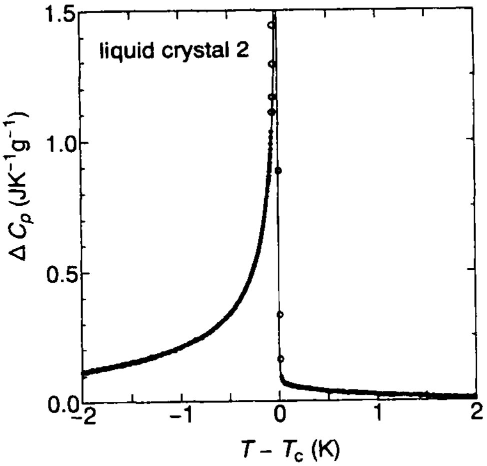

FIGURE 2. Temperature dependence of the excess heat capacity ΔC_p near the transition of liquid crystal **2**. The data in the two-phase coexistence region are shown as open circles. Solid line is a fit to the data with Eq. (3).

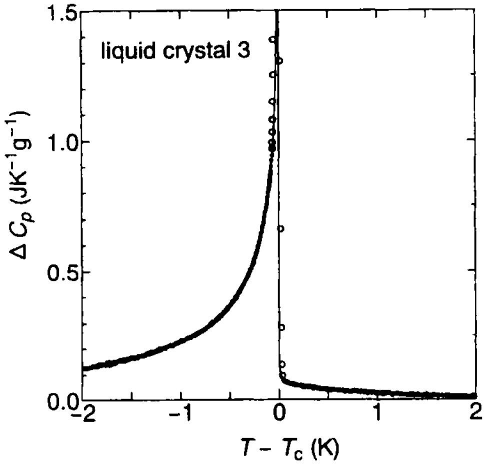

FIGURE 3. Temperature dependence of the excess heat capacity ΔC_p near the transition of liquid crystal **3**. The data in the two-phase coexistence region are shown as open circles. Solid line is a fit to the data with Eq. (3).

transition is rather weak for the present cases. Inside the two-phase coexistence region, shown as open circles in Figures 2 and 3, the ac response of the sample temperature is affected not only by the heat capacity of the sample but also by the latent heat absorbed/generated accompanying the first-order transition. Because of this, the C_p values does not necessarily correspond to the correct heat capacity within the coexistence region.

ANALYSIS AND DISCUSSION

The excess heat capacity ΔC_p has been analyzed with the following renormalization-group expression including the corrections-to-scaling terms [11].

$$\Delta C_p = \frac{A^{\pm}}{\alpha}|t|^{-\alpha}\left(1 + D_1^{\pm}|t|^{\theta} + D_2^{\pm}|t|\right) + B_c \quad , \tag{2}$$

where $t \equiv (T - T_c)/T_c$ is the reduced temperature, and the superscripts ± denote above and below the critical temperature T_c. Although the present data show first-order transitions, the use of above expression can be justified as a starting trial function, because the first-order nature is weak as pointed out already.

The fits have been made for three data ranges $|t|_{\max} = 0.001$, 0.003, and 0.01, where $|t|_{\max}$ is the maximum value of $|t|$ used in the fits. Unless stated otherwise, the critical exponent α was adjusted freely. The correction-to-scaling exponent θ was set at 0.5 in these fits, because it is only slightly dependent on the universality class and has a theoretically predicted value close to 0.5 [11]. In the fits with $|t|_{\max} = 0.003$ and 0.01, T_c was fixed to the value determined in the fit with $|t|_{\max} = 0.001$. This is because we do not know T_c a priori while it is inconsistent to use different T_c's for different data ranges. The data inside the two-phase coexisting region were excluded in the fitting.

The parameter values obtained in the fits are summarized in

Table 1. The first half shows the results for liquid crystal **2**, and the latter half for liquid crystal **3**. As easily noticed, the results are quite similar for both systems except some of the details. The results of the fits with Eq. (2) are labelled by "2" in the first column. The fits are good in the χ^2 sense, although those with $|t|_{\rm max} = 0.003$ and 0.01 are clearly unphysical because of negative A^-/A^+. It is also noticed that D_1^+ values are anomalously large and stable. These unphysical and unstable nature of the fits can be understood as follows. Since $\alpha \sim \theta$ in the present fits, the terms $(A^\pm D_1^\pm/\alpha)|t|^{\theta-\alpha}$ and B_c in Eq. (2) behave very similarly, which causes a strong correlation between D_1 and B_c values resulting in a large ambiguity in them. It is quite probable that this is also related to the first-order nature of the transition. Because the transition is first-order in the present case, the scaling constraint to have a common B_c is not required, and can have independent values for above and below T_c, say, B^+ and B^-. Thus the data want to make up the "gap" $\Delta B \equiv B^+ - B^-$, and settle in an unphysical but apparently adequate answer $[(D_1^+A^+ - D_1^-A^-)/\alpha]|t|^{\theta-\alpha}$, which is nearly constant.

From these considerations, we next tried fits with

$$\Delta C_p = \frac{A^\pm}{\alpha}|t|^{-\alpha}\left(1 + D_2^\pm|t|\right) + B^\pm \quad , \tag{3}$$

where the D_1 term has been absorbed into the constant term and now $\Delta B = B^+ - B^-$ is generally nonzero.

Results of the fits with Eq. (3) are labelled by "3" in Table 1. The results with $D_2^\pm = 0$ are adequate in the χ^2 sense for $|t|_{\rm max} =$ 0.001 and 0.003. The fit becomes fairly good also for $|t|_{\rm max} = 0.01$ when the $D_2^\pm$ term is included. If we exclude the relatively poor fits with $D_2^\pm = 0$ and $|t|_{\rm max} = 0.01$, the fits with Eq. (3) are stable against data-range shrinking, and are therefore expected to give a reliable set of parameter values. For liquid crystal **2**, we obtain $\alpha \sim$ 0.3–0.4, $A^-/A^+ \sim$ 10–12, and $\Delta B \sim$ 0.3–0.5. For liquid crystal **3**, we obtain $\alpha \sim$ 0.1–0.2, $A^-/A^+ \sim$ 17–22, and $\Delta B \sim$ 0.6–2.0. A rather large uncertainty for ΔB for liquid crystal **3** is probably due

TABLE 1. Least-squares values of the adjustable parameters for fitting ΔC_p with Eqs. (2) and Quantities in brackets were held fixed at the given values. In the fits with Eq. (2), B_c is shown in plac B^+. The units for A^+, B^+ and ΔB are $\mathrm{JK^{-1}g^{-1}}$.

System	Eq.	$\lvert t\rvert_{\max}$	$T_c(K)$	α	$10^4 A^+$	A^-/A^+	D_1^+	D_1^-	D_2^+	D_2^-	B^+	ΔB	χ
2	2	0.001	368.888	0.429	0.773	158	−1369	−18.9	[0]	[0]	0.192	[0]	1.2
2	2	0.003	[368.888]	0.481	−0.726	−118	7202	−68.8	[0]	[0]	0.999	[0]	1.2
2	2	0.010	[368.888]	0.527	−0.655	−98	−4786	43.0	[0]	[0]	−0.671	[0]	1.8
2	3	0.001	368.878	0.305	11.71	26.6	[0]	[0]	[0]	[0]	0.015	0.445	1.2
2	3	0.003	[368.878]	0.357	10.66	19.4	[0]	[0]	[0]	[0]	0.004	0.277	3.3
2	3	0.010	[368.878]	0.408	9.67	14.6	[0]	[0]	[0]	[0]	−0.005	0.180	8.8
2	3	0.010	[368.878]	0.331	9.74	26.6	[0]	[0]	−279	22.9	0.021	0.401	1.5
3	2	0.001	381.534	0.323	0.550	420	−1436	−16.1	[0]	[0]	0.117	[0]	0.9
3	2	0.003	[381.534]	0.391	−2.077	−71	723	−19.7	[0]	[0]	0.234	[0]	1.5
3	2	0.010	[381.534]	0.460	−1.586	−60	1991	−40.2	[0]	[0]	0.573	[0]	3.8
3	3	0.001	381.514	0.104	58.52	21.9	[0]	[0]	[0]	[0]	−0.068	2.033	0.9
3	3	0.003	[381.514]	0.224	30.73	16.6	[0]	[0]	[0]	[0]	−0.021	0.617	2.7
3	3	0.010	[381.514]	0.325	19.48	12.6	[0]	[0]	[0]	[0]	−0.018	0.269	8.0
3	3	0.010	[381.514]	0.183	35.56	20.5	[0]	[0]	−63.5	15.2	−0.020	0.979	1.6

to a somewhat wider two-phase coexistence region in comparison with liquid crystal **2**. In Figures 2 and 3, solid line show fits to the data with Eq. (3) for $|t|_{\max} = 0.01$ and $D_2^{\pm} \neq 0$. It is seen that the fits are adequate in both cases. All other plots for fits with $\chi^2 < 2$ look practically identical.

At first-order transitions, the temperatures where ΔC_p becomes singular will be different when the transition is approached from higher or lower temperature side. Therefore we should use different T_c's in analyzing the data above and below the transition. This can be accomplished by replacing the reduced temperature by $t^{\pm} \equiv (T - T_c^{\pm})/T_c^{\pm}$, where $\Delta T_c \equiv T_c^{-} - T_c^{+}$ is nonzero and positive. However, it was found that allowing ΔT_c to be nonzero yielded fits of the same quality, and parameter values were almost unchanged. Therefore their results are not shown here for simplicity.

The α values obtained here lies between the 3D $XY(-0.0066)$ and the tricritical(0.5) values. In the view that the Sm-A–Sm-C(or C^*) transition theoretically belongs to 3D XY universality class [12], we have also tried fits by fixing the exponents at 3D XY values ($\alpha = -0.0066$, $\theta = 0.524$) [11]. However, such fits were found to be very poor, $\chi^2 = 16.5$ for $|t|_{\max} = 0.001$ in case of liquid crystal **2**, for example. In a typical antiferroelectric liquid crystal MHPOBC and related substances, it was found that α depended markedly on the data-range, which was ascribed to a crossover from 3D XY to a Gaussian tricritical behavior [5]. In the present results for liquid crystal **2**, the α value seems insensitive to the data-range. In liquid crystal **3**, on the other hand, it could be possibly said that there exists an increase in α as $|t|_{\max}$ becomes larger, if we look at the results with Eq. (3) for $D_2^{\pm} = 0$. We should also bear in mind that the results of the fits could be affected by the first-order nature of the transition. In particular, the exclusion of the data in the coexistence region inevitably increases the uncertainty of the parameter values. In this sense we have to look for frustoelectric liquid crystal systems which exhibit transitions of the second order.

It is known that the singular free energy and the correlation volume are related to each other by the two-scale-factor universality [13], and thus

$$Y = F_{\rm sing}\xi^3/k_{\rm B}T \tag{4}$$

is a universal constant whose value is independent of the system studied in a given universality class. Here $F_{\rm sing}$ is the singular free energy per unit volume and ξ is the correlation length. In a generalized form for an anisotropic system as in the present case, it is expected that

$$(R_\xi^+)^3 = (\rho A^+/k_{\rm B})(\xi_{\|}\xi_{\perp}^2)_0 \tag{5}$$

is a universal quantity [14]. Here ρ is the density, A^+ is as defined in our Eq. (2) or (3), while $(\xi_{\|}\xi_{\perp}^2)_0$ is the amplitude of the correlation volume, with $\xi_{\|}$ and $\xi_{\perp}$ being correlation lengths parallel and perpendicular to the layer normal, respectively. Assuming $\rho = 1$, and using 3D *XY* value $R_\xi^+ = 0.36$, the critical amplitude A^+ obtained here, being 1–6 $\times 10^{-3}$ J/gK, yield the amplitude of the "effective" correlation length $\xi_{\rm eff0} = [(\xi_{\|}\xi_{\perp}^2)_0]^{1/3} = 5$–$9$ Å. This value is definitely smaller than $\xi_{\rm eff0} \sim 70$ Å, which is typical for usual Sm-*A* materials [15]. Therefore it can be said that the frustoelectric liquid crystals studied here have anomalously short correlation lengths compared with the other Sm-*A* systems and exhibits a "random" charater in that sense. However, it should be also noted the A^+ values obtained here are comparable with those for MHPOBC and related substances [5]. Because of this, we should say that such short correlation lengths are characteristic of not only frustoelectric liquid crystals but also other typical antiferroelectric liquid crystals. This seems reasonable because the competition between the ferro- and antiferroelectric interactions are significant in both groups. Of particular interest in this direction is to know $\xi_{\|0}$ and $\xi_{\perp 0}$ separately. For that purpose, measurements of the correlation length are especially desirable.

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