Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Critical Heat Anomaly in Frustoelectric Liquid Crystals

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

[a] Department of Physics, Faculty of Science, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro, Tokyo, 152-8551, 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

Version of record first published: 24 Sep 2006

To cite this article: Kenji Ema, Haruhiko Yao, Takahiro Matsumoto & Atsuo Fukuda (2000): Critical Heat Anomaly in Frustoelectric Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 346:1, 97-106

To link to this article: http://dx.doi.org/10.1080/10587250008023869

Mol. Cryst. Liq. Cryst., 2000, Vol. 346, pp. 97-106
Reprints available directly from the publisher
Photocopying permitted by license only

Critical Heat Anomaly in Frustoelectric Liquid Crystals

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

[a]*Department of Physics, Faculty of Science, Tokyo Institute of Technology, 2–12–1 Oh-okayama, Meguro, Tokyo 152–8551, 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*

Heat capacity of a liquid crystal which exhibits a frustoelectric phase has been measured by a high-resolution ac calorimeter. A significant heat capacity peak was observed at the transition. The excess heat capacity for this transition showed a non-Landau critical behavior. The transition was found to be weakly first-order. The data have been analyzed with a preasymptotic power-law equation which includes correction-to-scaling terms.

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

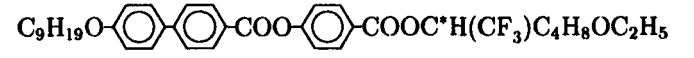
INTRODUCTION

A special attention has been paid to a group of antiferroelectric liquid crystals which show a V-shaped switching [1] instead of the tristable switching observed for usual antiferroelectricity [2]. Re-

cently it was claimed that the V-shaped switching is due to the orientational Goldstone (collective) mode of a ferroelectric smectic C^*(Sm-C^*) structure [3, 4]. In our view, however, it is essential that the system becomes extremely soft with respect to tilting direction and that a kind of randomization in the switching process results from frustration of ferro- and antiferroelectric interactions. It is therefore appropriate to name this type of dielectric behavior as "frustoelectricity".

Apart from terminology, it is doubtless that only a little is known at present for this "frustoelectric" phase. The heat capacity measurement is believed to be one of quite powerful tools in understanding phase transitions. In fact, recent ac calorimetric measurements have revealed 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]. Motivated by such background, we have carried out a high-resolution heat capacity measurement on liquid crystals which exhibit a frustoelectric phase.

The liquid crystal studied here has the following molecular structure:



The phase sequence of this liquid crystal in a homogeneous cell is as follows:

$$\text{ferri} \overset{368\text{K}}{\longleftrightarrow} \text{Sm}-A \overset{376\text{K}}{\longleftrightarrow} I,$$

where I stands for the isotropic phase.

EXPERIMENTALS

The heat capacity was measured with an ac calorimeter described elsewhere [6]. Hermetically sealed gold cells which contained typically 30 mg liquid crystal sample were used. The temperature of the

thermal bath surrounding the cell was scanned about 1 mK/min in the transition region. An ac heat input with a frequency of 0.03125 Hz was supplied to the sample cell, and the heat capacity was determined from the amplitude of the ac component of the sample temperature caused by the ac heating. The transition temperature remained unchanged within ± 0.01 K during the measurement period of about 3 weeks, which corresponds to a very slow drift rate of less than 0.5 mK/day. This indicates the stability and high quality of the sample.

The C_p values were determined as

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

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 obtained on cooling. A distinct anomaly is seen around the Sm-A to ferri phase transition located at 368.9 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.

Figure 2 shows the temperature dependence of the phase delay ϕ of the sample temperature response with respect to the ac heating. It is seen that ϕ shows a distinct anomaly at the transition. Such a phenomenon is usually believed to represent the existence of a two-phase coexistence region, and therefore indicates that the transiton

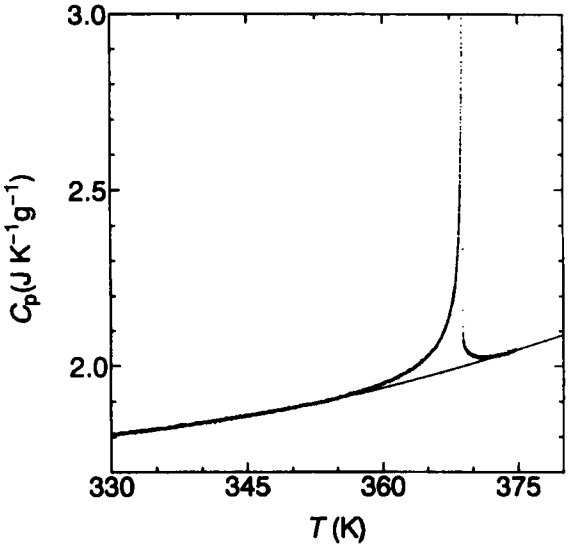


FIGURE 1. Tempereture dependence of heat capacity obtained on cooling. Thin solid line shows the normal part of the heat capacity.

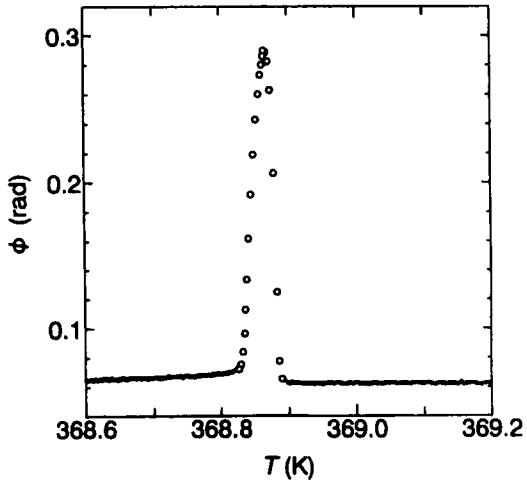


FIGURE 2. Temperature dependence of the phase delay ϕ.

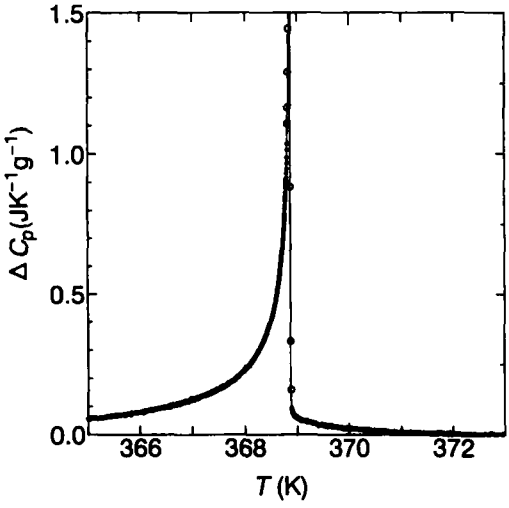


FIGURE 3. Temperature dependence of the excess heat capacity ΔC_p near the transition. The data in the two-phase coexistence region are shown as open circles. Solid line is a fit to the data with Equation (4) (see text).

is first-order (see Figure 5 of Ref. [7]). The width of the coexistence region in the present data, shown as open circles in Figure 2, is about 70 mK. Such a relatively narrow conexistence range implies that the first-order nature of the transition is rather weak. Inside the two-phase coexistence region, 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. Figure 3 shows the temperature dependence of the excess heat capacity ΔC_p near the transition.

ANALYSIS AND DISCUSSION

The excess heat capacity ΔC_p has been analyzed with the following renormalization-group expression including the corrections-to-scaling terms [8].

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

where $t \equiv (T - T_c)/T_c$ is the reduced temperature, and the superscripts $\pm$ denote above and below the critical temperature T_c. Although the present data shows a first-order transition, 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 data inside the two-phase coexisting region were excluded in the fitting.

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. Except the cases 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 [8]. 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 in the coexistence region are plotted by open circles.

The parameter values obtained in the fits are summarized in the first three lines in Table I. Quantities in brackets were held fixed at given values. The fits are good in the χ^2 sense, although those with $|t|_{\max} = 0.003$ and 0.01 are unphysical because of negative A^-/A^+. In the view that the Sm-A Sm-C(or C^*) transition belongs to 3D XY universality class [9], we have also tried fits by fixing the exponents at 3D XY values ($\alpha = -0.0066$, $\theta = 0.524$) [8]. However, such fits were found to be very poor, $\chi^2 = 16.5$ for $|t|_{\max} = 0.001$, for example.

We tried two modifications of Equation (2). The first one is

TABLE I. Least-squares values of the adjustable parameters for fitting ΔC_p with Equations (2)–(4). The first row shows the Equation number used in the fit. Quantities in brackets were held fixed at the given values. $\Delta B = B^+ - B^-$. In the fits with Equation (2), B_c is shown in place of B^+. The units for A^+, B^+, and ΔB are $JK^{-1}g^{-1}$.

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]	1.20
2	0.003	[368.888]	0.481	−0.726	−118	7202	−68.8	[0]	[0]	0.999	[0]	1.20
2	0.010	[368.888]	0.527	−0.655	−98	−4786	43.0	[0]	[0]	−0.671	[0]	1.86
3	0.001	368.888	0.452	0.773	185	−2717	−54.3	[0]	[0]	0.270	−0.495	1.20
3	0.003	[368.888]	0.337	0.178	1680	−5856	10.6	[0]	[0]	0.142	0.939	1.03
3	0.010	[368.888]	0.354	0.435	592	−2402	10.7	[0]	[0]	0.148	0.854	1.02
4	0.001	368.878	0.305	11.71	26.6	[0]	[0]	[0]	[0]	0.015	0.445	1.29
4	0.003	[368.878]	0.357	10.66	19.4	[0]	[0]	[0]	[0]	0.004	0.277	3.37
4	0.010	[368.878]	0.408	9.67	14.6	[0]	[0]	[0]	[0]	−0.005	0.180	8.86
4	0.003	[368.878]	0.274	11.90	34.7	[0]	[0]	−397	36.6	0.026	0.654	1.02
4	0.010	[368.878]	0.331	9.74	26.6	[0]	[0]	−279	22.9	0.021	0.401	1.50

due to the first-order nature of the transition. Because of this, the scaling constraint of having the same critical constant term B_c for above and below T_c is not required, and allows us to use independent constant terms. Thus we have,

$$\Delta C_p = \frac{A^{\pm}}{\alpha}|t|^{-\alpha}\left(1 + D_1^{\pm}|t|^{\theta} + D_2^{\pm}|t|\right) + B^{\pm} \quad , \tag{3}$$

where $\Delta B \equiv B^{+} - B^{-}$ is generally nonzero.

The second modification is based on the fact that the fits with Eq. (2) yielded α values close to 0.5. In such cases the first-order correction term, being expressed as $A^{\pm}D_1^{\pm}|t|^{\theta-\alpha}$, behaves almost as a tempereture independent constant term, and can be approximately absorbed into the critical constant term B_c. Thus the "renormalized" constant term becomes $B^{\pm} = B_c + A^{\pm}D_1^{\pm}$ and does not fulfill the scaling constraint $B^{+} = B^{-}$. This leads to the following expression:

$$\Delta C_p = \frac{A^{\pm}}{\alpha}|t|^{-\alpha}\left(1 + D_2^{\pm}|t|\right) + B^{\pm}. \tag{4}$$

Results of the fits with Equations (3) and (4) are also shown in Table I. The first row in the table shows the equation number used in the fits. In Figure 3, solid line shows a fit to the data with Equation (4) for $|t|_{\max} = 0.01$ and $D_2^{\pm} \neq 0$. It is seen that the fit is adequate in this case. All other fits with $\chi^2 < 2$ are also adequately good, and their plots look similar.

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 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, the obtained ΔT_c was rather small, being several mK, and other parameter values were not so different from those for $\Delta T_c = 0$. Therefore their results are not shown here for simplicity.

It is seen from Table I that Equations (2)-(4) yield equally good fits for narrow data ranges. However, fits with Equations (2)

and (3) seem less significant because the parameter values are unstable against data-range shrinking, D_1^+ is too large, and also negative A^-/A^+ for the case of Equation (2). On the other hand, fits with Equation (4) seem reliable not only because of the stability against data-range but also the reasonable value of the parameters. Rather large χ^2 in the fits with Equation (4) for $|t|_{\max} \geq 0.003$ with $D_2^{\pm} = 0$ is propbably because this Equation contains less adjustable parameters. As shown in the last two lines of the table, fits with Equation (4) for $D_2^{\pm} \neq 0$ are acceptably good. After all, most reliable fits seem to be those with Equation (4) with $D_2^{\pm} = 0$ for $|t|_{\max} = 0.001$, and with $D_2^{\pm} \neq 0$ for $|t|_{\max} = 0.003$ and 0.01. These three fits equally give $\alpha \sim 0.3$–0.4, insensitive to the data-range. The significance of the present α value is not clear. It lies between the 3D $XY(-0.0066)$ and the tricritical(0.5) values. However, the insensitiveness to the data-range of the present result is in a contrast with the results observed in MHPOBC and related substances, where α depended markedly on the data-range, and shows a crossover from 3D XY to a Gaussian tricritical behavior [5]. On the other hand, in some cases the crossover occurs quite slowly and is difficult to be observed as a function of temperature [10]. We should also bear in mind the possibility that the critical behavior could be affected by the first-order nature of the transition.

Another feature of the present result is the existence of a gap in ΔC_p at T_c, $\Delta B \sim 0.4$-0.7 J/gK. We note that the tendency of α being close to 0.5 in all fits with Equation (2), and the fit with Equation (3) for $|t|_{\max}$ =0.001, can be an artifact to make up this large ΔB. Although nonzero ΔB is allowed in first-order transitions, it is not clear if such a large ΔB is in agreement with the fact that the first-order nature is rather weak, as pointed out already.

Lastly we remark on the amplitude of the critical anomaly. It is known that the magnitude of the heat anomaly is related to the correlation length with the two-scale-factor universality [11], and the larger heat anomaly implies the shorter correlation length. The crit-

ical amplitude A^+ obtained here, being $\sim 10^{-3}$ J/gK, is of the same order or slightly smaller than the value for MHPOBC [5]. This seem to suggest that the correlation length in the present frustoelectric liquid crystal is not so much different from those in typical antiferroelectric liquid crystals like MHPOBC.

In conclusion, we should admit that some part of the discussion has been limited due to the first-order nature of the transition. Because of this, it is hoped to carry out similar measurements on frustoelectric liquid crystals with second-order transitions or at least much weaker first-order transitions.

References

[1] S. Inui *et al, J. Mater. Chem.* **6,** 671 (1996).
[2] A. Fukuda *et al, J. Mater. Chem.* **4,** 997 (1994).
[3] H. Takezoe *et al, Proceedings, Asia Display 1998 (Seoul).*
[4] P. Rudquist *et al,* preprint.
[5] K. Ema and H. Yao, *Phys. Rev. E* **57,** 6677 (1998), and refs. therein.
[6] K. Ema and H. Yao, Thermochim. *Acta* **304/305,** 157 (1997), and refs. therein.
[7] K. Ema, G. Nounesis, C. W. Garland, and R. Shashidhar, *Phys. Rev. A* **39,** 2599 (1989).
[8] C. Bagnuls and C. Bervillier, *Phys. Rev. B* **32,** 7209 (1985); C. Bervillier, *Phys. Rev. B* **34,** 8141 (1986); C. Bagnuls, C. Bervillier, D. I. Meiron and B. G. Nickel, *Phys. Rev. B* **35,** 3585 (1987).
[9] P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **21,** 49 (1973).
[10] C. W. Garland and G. Nounesis, *Phy. Rev. E* **49,** 2964 (1994), and refs. threin.
[11] P. C. Hohenberg, A. Aharony, B. I. Halperin, and E. D. Siggia, *Phys. Rev. B* **13,** 2986 (1976). Also see C. W. Garland, G. Nounesis, M. J. Young, and R. J. Birgeneau, *Phys. Rev. E* **47,** 1918 (1993).