Quasi-two-dimensional Ising critical behavior of de Vries liquid crystals observed in the heat capacity and dielectric response

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Heat capacity and dielectric measurements have been made on a liquid crystal compound exhibiting de Vries type of smectic-A^* (Sm-A^*) phase. Heat capacity shows a significant anomaly which is almost symmetric for above and below the Sm-A^*-Sm-C^* transition temperature. The transition was found to be very weakly first order. The critical exponent γ determined from the dielectric data lies 1.8 ± 0.2. The present heat capacity data as well as former data for another compound of de Vries type have been analyzed in detail. It was found that the heat capacity data for both compounds are fitted well with a logarithmic divergence except in the immediate vicinity of the transition. These results agree with an expectation that de Vries Sm-A^*-Sm-C^* transition can exhibit quasi-two-dimensional Ising critical behavior.

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I. INTRODUCTION

Theoretically, liquid crystalline smectic-A(Sm-A)-smectic-C(Sm-C) phase transition belongs to the XY universality class [1]. Although many early experiments reported classical behaviors which can be described successfully with an extended Landau theory [2,3], later it was found that the critical behaviors around the Sm-A-Sm-C^* transition exhibited by several liquid crystals showing antiferroelectricity are explained well with the three-dimensional (3D) XY critical exponents [4].

Recently, a group of liquid crystals showing Sm-A-Sm-C (or C^*) transition has been recognized, characterized by almost no layer-shrinkage behavior through the transition, and also unusually large electroclinic effects if the compound is chiral [5–10]. A plausible explanation for these remarkable features is offered by a structure suggested by de Vries *et al.* [11,12], hence these compounds are often called as de Vries liquid crystals. Calorimetric measurements were carried out by the present authors on such compounds [13]. It was revealed that the results can be fitted with the 3D XY model. On the other hand, however, Selinger *et al.* [7] obtained critical exponent γ lying 1.51-1.75 for siloxane-containing de Vries liquid crystals from the measurement of birefringence. Here, γ is a critical exponent for the susceptibility χ, implying $\chi \propto |T-T_c|^{-\gamma}$ around the transition temperature T_c. These values of γ disagree with the 3D XY theoretical expectation $\gamma=1.316$ [14]. Similarly large γ values have been obtained for other de Vries compounds from electrooptical measurements of electroclinic response [15,16].

In this article we report results of high-resolution calorimetric and dielectric measurements carried out on TSiKN65, for which abovementioned large γ value was reported by Selinger *et al.* [7]. For comparison, our heat capacity data on 8422[2F3] reported earlier [13] have been reanalyzed. It has been found, for both compounds, that the observed anomalies some distance away from the Sm-A^*-Sm-C^* transition can be understood as a manifestation of a quasi-two-dimensional Ising behavior. We discuss how the Ising behavior becomes possible for de Vries phase transitions. Further expectations drawn from the scenario are also given.

II. EXPERIMENTALS

The molecular structure of TSiKN65 is shown in Fig. 1. The phase transition sequence was reported in Ref. [7] as

$$\text{Sm-}C^* \overset{298\ \text{K}}{\leftrightarrow} \text{Sm-}A^* \overset{329\text{K}}{\leftrightarrow} \text{Iso}.$$

Heat capacity C_p has been measured with an ultra-low-frequency ac calorimeter [18], which can also be operated in nonadiabatic scanning (NAS) mode [19]. A hermetically sealed gold cell that contained 6.4 mg of TSiKN65 sample was used. The temperature scan rate was about 0.03 K/h in the transition region. No noticeable drift in the transition temperature was observed, indicating the stability and high quality of the sample.

For dielectric measurement, a standard liquid crystal cell with a cell thickness of 12.5 μm was used. The complex dielectric constant was measured over a frequency range of 1 Hz to 100 kHz. The ac signal from an oscillator, with an amplitude of 100 mV, was applied to a series circuit of the sample cell and a standard resistor, and the voltage across the resistor was read with a lock-in amplifier (Stanford Research

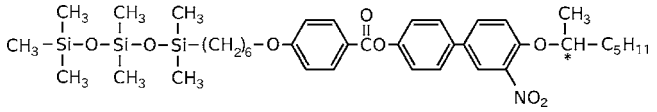

FIG. 1. Molecular structure of TSiKN65 [7,17].

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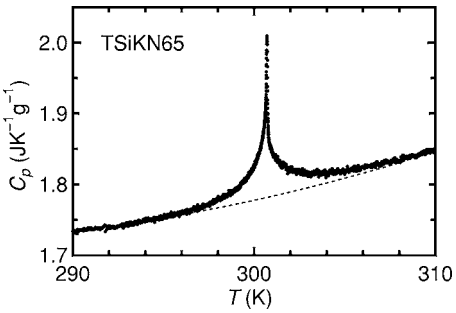

FIG. 2. Temperature dependence of heat capacity C_p of TSiKN65. The data are acquired in a cooling run.

Systems SR830). The temperature was scanned with a rate of 0.03 K/min.

III. RESULTS AND DATA ANALYSES

A. Calorimetric data

Typical temperature dependence of C_p data is shown in Fig. 2. The C_p data display a distinct λ-shape anomaly around the Sm-A^*-Sm-C^* transition temperature T_c located at 300.7 K. A striking feature is that the anomaly is almost symmetric for above and below T_c. The dashed line in the figure shows the background heat capacity C_p (background), determined as a quadratic function of temperature which joins the measured C_p data smoothly at temperatures away from T_c on both sides of the transition. Measurement was also carried out in the NAS mode, and a typical result near T_c is shown in Fig. 3 together with the AC-mode data. It is seen that the NAS data, shown by open circles, exhibit a much more pronounced peak near the transition in comparison with the anomaly exhibited by the AC data shown by closed circles, thus indicating the existence of latent heat. The value of the latent heat has been evaluated from the integration of this excess part, yielding 0.14±0.01 J/g. In accordance with this observation, in the AC-mode measurement, two-phase coexistence region of 130–140 mK in width was found where the phase shift of the AC response of the sample showed an anomalous increase. The present result that the transition is first-order is in agreement with the differential scanning calorimetry (DSC) measurement by Selinger *et al.*

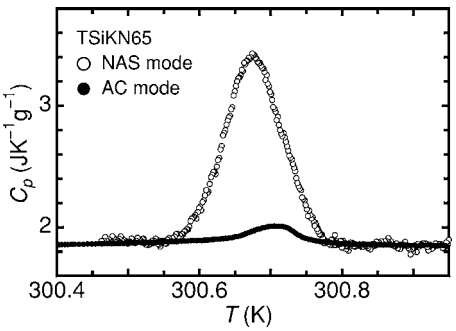

FIG. 3. Comparison of heat capacity data for TSiKN65 in the vicinity of T_c obtained in the NAS mode (open circles) and in the AC mode (closed circles).

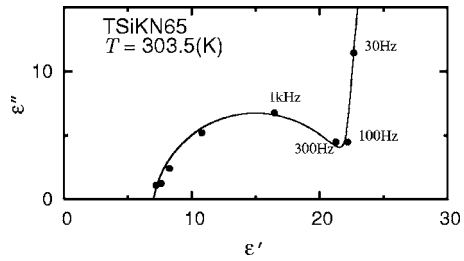

FIG. 4. Typical Cole-Cole plot obtained from the dielectric measurement for TSiKN65. The solid line is a fitting curve with Eq. (2).

[7] which revealed the existence of thermal hysteresis. The smallness of the latent heat as well as the significant pretransitional heat anomaly and also the relatively narrow two-phase coexistence region indicate that the first-order nature is weak.

In our previous work [13] it was found that the C_p anomaly for 8422[2F3] away from the transition can be fitted with the 3D *XY* model. Hence the present C_p data have been tentatively analyzed assuming the 3D *XY* behavior. The excess heat capacity accompanying the transition, denoted as ΔC_p, has been obtained by subtracting C_p (background) from the measured C_p data. Then the ΔC_p data have been fitted with the renormalization-group expression [14]

$$\Delta C_p = \frac{A_c^{\pm}}{\alpha}|t|^{-\alpha}[1 + D_1^{\pm}|t|^{\Delta_1}] + B_c, \tag{1}$$

where $t \equiv (T - T_c)/T_c$ is the reduced temperature and $\pm$ indicates above and below T_c. The $D_1^{\pm}$ term represents the first-order correction to the leading singularity, while B_c is a temperature-independent critical contribution [14]. The critical exponents were fixed at 3D *XY* theoretical values $\alpha = -0.0066$ and $\Delta_1 = 0.524$ [14]. The parameter values obtained from the fitting are summarized in Table I. Here, $|t|_{\max}$ and $|t|_{\min}$ are the maximum and minimum values of $|t|$ used in the fit, respectively. In the 3D *XY* fit for 8422[2F3], the ΔC_p data in a range $|t| < 0.003$ were excluded from the fit, because there the data showed tricritical behavior due to the first-order nature of the transition [13]. In the present fit, the width of such a region has been checked by changing $|t|_{\min}$ systematically, as shown as fits 1a-1d. The quality of the fitting in the statistical sense can be judged from values of χ_ν^2, the normalized mean squared residuals, shown in the

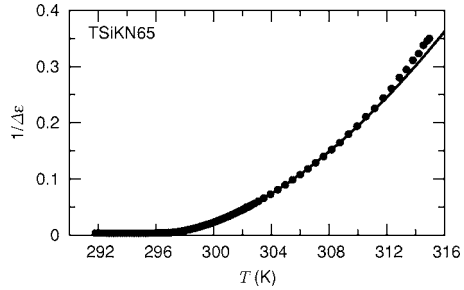

FIG. 5. Temperature dependence of reciprocal of the relaxation strength $\Delta\epsilon$ obtained for TSiKN65. The solid line is a fitting curve obtained using Eq. (4) with γ fixed at 1.75 (see text).

TABLE I. Fitting parameters and least-squares values obtained from fittings of the TSiKN65 ΔC_p data to Eq. (1). The exponents α and Δ_1 were fixed at the 3D *XY* values. The units are J K^{-1} g^{-1} for $A_c^{\pm}$ and B_c, and K for T_c. In fits 1a-1d and 2, $D_1^{\pm}$ have been fixed at zero. Data in a range $|t|_{\min}<|t|<|t|_{\max}$ have used in the fit.

Fit	$\|t\|_{\max}$	$\|t\|_{\min}$	T_c	α	$10^2A_c^+$	A_c^-/A_c^+	D_1^+	D_1^-/D_1^+	B_c	χ_ν^2
1a	0.01	0.0005	300.574	[−0.0066]	2.573	1.0020	[0]	[1]	3.797	1.24
			±0.005		±0.021	±0.0001			±0.030	
1b	0.01	0.001	300.561	[−0.0066]	2.543	1.0022	[0]	[1]	3.754	1.19
			±0.009		±0.025	±0.0001			±0.036	
1c	0.01	0.002	300.537	[−0.0066]	2.446	1.0026	[0]	[1]	3.612	1.15
			±0.019		±0.036	±0.0002			±0.052	
1d	0.01	0.003	300.534	[−0.0066]	2.319	1.0027	[0]	[1]	3.426	1.14
			±0.038		±0.055	±0.0003			±0.080	
2	0.02	0.001	300.565	[−0.0066]	2.267	1.0024	[0]	[1]	3.351	2.28
			±0.011		±0.022	±0.0002			±0.032	
3	0.01	0.001	300.537	[−0.0066]	3.487	1.0023	−0.058	1.12	5.116	1.01
			±0.014		±0.15	±0.0005	±0.008	±0.12	±0.22	
4	0.02	0.001	300.537	[−0.0066]	3.730	1.0021	−0.070	1.08	5.467	1.01
			±0.009		±0.075	±0.0003	±0.003	±0.04	±0.11	

table. The χ_ν^2 value increases slightly for $|t|_{\min}<0.001$, while parameter values remain almost unchanged. Hence only the results for $|t|_{\min}=0.001$ are shown in the table for other cases. As a whole, it is seen that the fits are adequate in the χ_ν^2 sense. A noticeable feature is, however, the critical amplitude ratio A_c^-/A_c^+ is very close to unity, instead of agreeing with the theoretical value 0.971 [20]. The disagreement is clearly beyond the statistical error shown in the table. This can be also checked by fits with a constraint $A_c^-/A_c^+=0.971$, yielding an unacceptably high value of $\chi_\nu^2=8.8$ in case of fit 4, for instance.

B. Dielectric data

Figure 4 shows a typical example of Cole-Cole plot. The lower-frequency dispersion which is almost temperature independent is ascribed to extrinsic origins such as dc conductivity and/or surface effects. Assuming a standard Debye expression for the higher-frequency dispersion, the data have been fitted with

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1+[i(f/f_r)]^\beta} + g(f), \tag{2}$$

where f is the measuring frequency, f_r is the relaxation frequency, and $g(f)$ represents the lower-frequency contribution. The data were fitted well with this equation in most cases, as shown by the solid line in the figure as an example.

The reciprocal of the relaxation strength $\Delta\epsilon$ has been plotted against temperature in Fig. 5. In the present dielectric measurement, no sign of first-order nature was observed. The results for heating and cooling processes did not show any noticeable hysteresis, and no jump of the data suggesting a first-order transition was found. This is not surprising in view of the fact that the first-order nature is quite weak as revealed in the calorimetric measurement. We also note that the transition temperature observed in the dielectric measurement, around 297 K, is slightly lower than that for the C_p measurement, while it agrees with the one reported in Ref. [7]. This is understood to be caused partly by the relatively thin thickness of the cell used in the dielectric and birefringence measurements.

The critical exponent γ has been determined from a fit to a power law

$$(\Delta\epsilon)^{-1} = A_D|t|^\gamma. \tag{3}$$

We have not succeeded in measuring dielectric dispersion with bias field. The available data are for zero field, and the soft-mode dispersion is hidden by the Goldstone-mode below T_c. Therefore, only data above T_c were used in the fit. The obtained parameter values are summarized in Table II as fits e1-e3. These results are for data ranges of $T=297.3-303.1$ K (range A), $T=297.3-306.0$ K (range B), and $T=297.3-310.0$ K (range C), roughly corresponding to $|t|_{\max}=0.02$, 0.03, and 0.05, respectively. Fits with narrower

TABLE II. Fitting parameters and least-squares values obtained from fittings of the $\Delta\epsilon$ data for TSiKN65 to Eqs. (3) and (4). The unit for T_c is K. The parameters in brackets were held fixed at the shown value in the fits. Data in a range $T=297.3-303.1$ K (range A), $T=297.3-306.0$ K (range B), and $T=297.3-310.0$ K (range C) have been used in the fit. In this table the mean squared residual χ_ν^2 has not been normalized.

Fit	Range	T_c	γ	A_D	B_D	χ_ν^2
e1	A	295.14	1.96	72.5	[0]	3.9
e2	B	295.47	1.83	48.6	[0]	6.1
e3	C	295.45	1.83	48.5	[0]	9.5
e4	A	296.61	1.66	32.7	0.0038	2.5
e5	B	296.67	1.65	31.4	0.0039	2.2
e6	C	295.77	1.79	44.8	0.0011	9.2

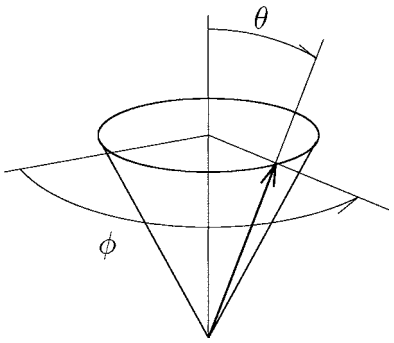

FIG. 6. Molecular orientation in smectic phases. Thick arrow represents the liquid crystal molecule.

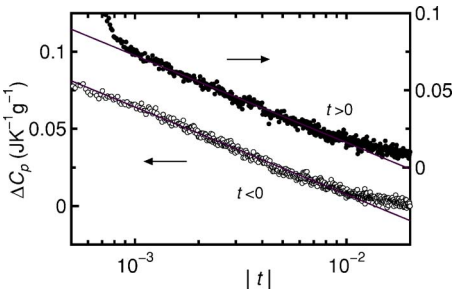

FIG. 7. (Color online) Semilogarithmic plot of ΔC_p data for TSiKN65. Straight lines show calculated values with Eq. (6).

data ranges yielded rather unstable results because of the one-sided fit as mentioned above, and also because the density of the data is much less than the C_p data, and are not included in the table. Although somewhat large uncertainty are seen in the parameter values, we see that the γ value which gives the best fit in the χ_ν^2 sense lies 1.8-2.0. Fits have been also tried by adding a constant term to the expression (3), thus having

$$(\Delta\epsilon)^{-1} = A_D|t|^{\gamma} + B_D. \tag{4}$$

This modification is justified in the existence of surface-layer with low, temperature-independent dielectric constant, for example. The result is shown as fits e4-e6 in Table II. In these cases the γ value lies 1.6-1.8. Altogether, it can be said that the present results reveal $\gamma=1.8\pm0.2$, in agreement with the value $\gamma=1.75\pm0.08$ obtained from the birefringence measurement reported in Ref. [7]. In fact, fixing γ to 1.75 in the present data also gives acceptably good fit, as shown by the solid line in Fig. 5 for the case of range C and nonzero B_D. The fact that the γ values obtained from different experimental methods coincide ensures their reliability and significance.

IV. DISCUSSION

The γ value obtained in the present work as well as former report by Selinger *et al.* [7] do not agree with the 3D *XY* value 1.316 [14]. In our present fit, fixing γ to 1.316 causes χ_ν^2 become worse by more than an order. On the other hand, the γ value does agree with the theoretical value for 2D Ising model $\gamma=1.75$ [21]. In our former analyses on 8422[2F3] in Ref. [13], we were not aware of the possibility that the transition belongs to the Ising universality class. We here claim, however, that this can be the case from the following consideration.

Let us start with a Hamiltonian of a spin system expressed as

$$\mathcal{H} = -\sum_{i,j} V_{ij}\boldsymbol{n}_i \cdot \boldsymbol{n}_j, \tag{5}$$

where $\boldsymbol{n}_i$ is a spin at lattice cite i. Depending on the dimensionality of freedom of the spin, the Hamiltonian describes Ising *XY* or Heisenberg model. In the present case for smectic liquid crystals, $\boldsymbol{n}_i$ is read as the direction of each molecule [22]. In ordinary Sm-*A*-Sm-*C* (or C^*) transitions, the orientation of molecules has two-dimensional freedom, characterized with θ and ϕ as shown in Fig. 6, leading to an expectation that the system belongs to the *XY* model. In de Vries liquid crystals, it is often conjectured that the fluctuation along the ϕ direction is much more pronounced in comparison with that along the θ direction. Even assuming θ to be constant in the transition region, the upper end of molecules moving along the surface of the cone drawn in the figure, results in a reasonable explanation of experimental results [7]. Under such a condition, effectively only one-dimensional freedom for $\boldsymbol{n}_i$ plays the essential role, and therefore the system is expected to behave almost similar to an Ising model. This situation seems to resemble with the case that the Heisenberg spin system with anisotropic interaction can exhibit Ising-like behavior. Finally, quasi-2D behavior is expected if the interaction between adjacent layers is sufficiently weak.

TABLE III. Fitting parameters and least-squares values obtained from fittings of the ΔC_p data for TSiKN65 to Eq. (6). The units are J K^{-1} g^{-1} for A_L and $B_L^{\pm}$, and K for T_c. Data in a range $|t|<0.001$ have not been used in the fit.

Fit	$\|t\|_{\max}$	T_c	10^2A_L	B_L^+	B_L^-/B_L^+	χ_ν^2
5	0.01	300.556	2.455	−0.097	1.087	1.18
		±0.009	±0.024	±0.001	±0.006	
6	0.02	300.565	2.193	−0.082	1.097	2.23
		±0.011	±0.021	±0.001	±0.006	

TABLE IV. Fitting parameters and least-squares values obtained from fittings of the ΔC_p data for 8422[2F3] to Eq. (6). The units are J K^{-1} g^{-1} for A_L and $B_L^{\pm}$ and K for T_c. Data in a range $|t|<0.003$ have not been used in the fit.

Fit	$\|t\|_{\max}$	T_c	10^2A_L	B_L^+	B_L^-/B_L^+	χ_ν^2
7	0.01	338.443	1.452	−0.045	1.211	1.22
		±0.052	±0.041	±0.002	±0.022	
8	0.02	338.443	1.424	−0.044	1.222	1.20
		±0.034	±0.020	±0.001	±0.012	

TABLE V. Fitting parameters and least-squares values obtained from the 3D *XY* fittings of the ΔC_p data for 8422[2F3] to Eq. (1). The exponents α and Δ_1 were fixed at the 3D *XY* values. The parameters in brackets were held fixed at the shown value in the fits. The units are J K^{-1} g^{-1} for A_c and $B_c^{\pm}$ and K for T_c. Data in a range $|t|<0.003$ have not been used in the fit.

Fit	$\|t\|_{\max}$	T_c	α	$10^2 A_c$	A_c^-/A_c^+	D_1^+	D_1^-/D_1^+	B_c	χ_ν^2
9	0.01	338.443	[−0.0066]	1.500	1.0043	[0]	[1]	2.227	1.22
		±0.052		±0.043	±0.0004			±0.062	
10	0.02	338.443	[−0.0066]	1.467	1.0045	[0]	[1]	2.179	1.20
		±0.034		±0.021	±0.0002			±0.031	
11	0.01	339.473	[−0.0066]	1.434	0.9840	−0.071	−1.7	2.113	1.12
		±0.23		±0.54	±0.007	±0.05	±2.7	±0.78	
12	0.02	338.290	[−0.0066]	1.585	1.0062	−0.004	4.7	2.351	1.19
		±0.09		±0.165	±0.0014	±0.016	±15	±0.24	

Based on the above consideration, the present ΔC_p data for TSiKN65 have been analyzed with the logarithmic expression

$$\Delta C_p = -A_L \ln|t| + B_L^{\pm}, \tag{6}$$

which is expected for the 2D Ising case [23]. It has been assumed that the critical amplitudes are the same for above and below T_c from the scaling expectation thus $A_L^+=A_L^-=A_L$, while the critical constant term B_L was allowed to be different for the both sides of T_c, being B_L^+ and B_L^-, taking the first-order nature of the transition into account. The obtained parameter values are shown in Table III. The fitting is adequate except the immediate vicinity of T_c, as seen from Fig. 7, showing the result for fit 5 as an example. In a statistical sense these 2D Ising fits are of equal quality to the 3D *XY* fits shown in Table I. Comparing χ_ν^2 for fits 1-2 and fits 5-6 since they have equal number of free parameters, we see they almost coincide. This is not surprising because the values of α for the two cases are very close to each other. From physical viewpoint, however, the 3D *XY* fits suffered from unreasonable value of amplitude ratio, as already noted. Note that the tendency of the amplitude ratio being very close to unity becomes natural if we consider this quasi-2D-Ising nature of the transition. Also, the appearance of quasi Ising critical behavior in turn justifies validity of applying the structure proposed by de Vries *et al.* [11,12] to this group of liquid crystals.

Because our former data of ΔC_p for 8422[2F3] reported in Ref. [13] look similar to the present data for TSiKN65, being almost symmetric above and below T_c, it is natural to expect the 2D Ising behavior also for that case. Hence we reanalyzed the ΔC_p data for 8422[2F3] using the logarithmic divergence form of Eq. (6). The results are summarized in Table IV. The fits are adequate. In this case, the data $|t|<0.003$ were excluded in the fits to be consistent with the 3D *XY* fits reported earlier [13]. For comparison, the results of the 3D *XY* fits for 8422[2F3] are also summarized here in Table V. From χ_ν^2 values for the fits 7-8 and 9-10, we find again that the 2D Ising fits are of equal quality in the statistical sense, while the 3D *XY* fits come out to be defective in the critical amplitude ratio values. After all we see that not only for TSiKN65 but also for 8422[2F3], the behavior of ΔC_p data can be more favorably and consistently described with the 2D Ising model, rather than the 3D *XY* model.

Several points deserve mentioning. The quasi-Ising behavior is expected to diminish in the immediate vicinity of the critical point, because relatively unimportant fluctuation along the θ direction eventually becomes equally significant there. However, in cases of TSiKN65 and 8422[2F3], such a region is perhaps invisible because of the first-order nature of the transition. It is noticed from Table V that the amplitude ratio obtained for the case $|t|=0.01$ and nonzero $D_1^{\pm}$ in 8422[2F3] is somewhat closer to the 3D *XY* value. We feel, though, that the fitting range is too narrow to draw out a decisive answer. Note also that the de Vries transition can be either two- or three-dimensional depending on the magnitude of anisotropy. This may be related with our former observation that ΔC_p data for 8O23[7F8-] exhibited clearly asymmetric anomaly [13]. Further point is that, for 8422[2F3], Krueger *et al.* [24] reported a considerably broad mean-field regime for the dielectric soft-mode susceptibility, which seems to contradict the present result. The reason is not clear at moment. As judged from Fig. 9(a) in Ref. [24], the mean-field behavior is observed in the data by Krueger *et al.* for $|T-T_c|>4$ K, corresponding to $|t|>0.012$. Hence it might be possible that a crossover occurs in that region. After all, understanding the de Vries Sm-A^*-Sm-C^* transitions is an ongoing experimental as well as theoretical challenge.

In conclusion, high-resolution calorimetric as well as dielectric measurements have been made on a de Vries liquid crystal TSiKN65. The critical exponent γ obtained from the dielectric data lies 1.8±0.2, in agreement with the former reported one from birefringence measurement. The heat capacity data for TSiKN65 as well as for 8422[2F3] are fitted well with a logarithmic divergence. These agree with an expectation that de Vries Sm-A^*–Sm-C^* transition can exhibit quasi-2D-Ising critical behavior, and supports the validity of applying the structure proposed by de Vries *et al.* to this group of liquid crystals.

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