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Anomalous heat capacity above the isotropic–chiral-smectic-*C* phase transition

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A phenomenological model is developed to describe the isotropic–chiral-smectic-*C* phase transition. The anomalous part of the heat capacity of the chiral-smectic-*C* liquid crystals above the isotropic–chiral-smectic-*C* phase transition is calculated using Landau's fluctuation theory. The temperature dependence of the heat capacity above the transition point is calculated first for the Gaussian model and then taking the cubic and the quartic terms as a perturbation. The theoretical results are found to be in good agreement with experiment.

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I. INTRODUCTION

The pretransitional behavior in the isotropic phase of the smectogenic mesophases is still an active and an unknown area in the field of liquid crystals research. In recent years the transitions from a smectic phase to an isotropic phase have attracted much attention. This includes experimental [1–5] and theoretical [6–10] studies. The isotropic to chiral-smectic-*C*(I-Sm*C**) is one such phase transition which has a considerable current interest. The chiral-smectic-*C*(Sm*C**) phase represents a spatially modulated structure [11]. The ferroelectric ordering in the Sm*C** phase is usually discussed in terms of hindrances of rotation of the molecules around their long axis. However, the microscopic origin of this ordering remained obscure. A number of experiments [12–17] have been carried out on the I-Sm*C** phase transition. All the materials studied the I-Sm*C** phase transition appears to be first order. Ema *et al.* [5] measured the temperature dependence of the heat capacity for 2-{4-[(R)-2-fluro-hexyloxy]phenyl}-5-{4-[(S)-2-fluro-2-methyldecanoyloxy]phenyl}pyrimidine (RSFPPY) both above and below the phases of the I-Sm*C** phase transition. The analysis of the temperature dependence of the heat capacity reveals an appreciable anomalous component, i.e., in the heat capacity above and below the transition. This anomalous component showed quite different behavior depending on whether the measurement was made on heating or cooling. They observed the complicated structure of the heat anomaly accompanying the I-Sm*C** phase transition on cooling. However, they did not succeed to reproduce the detailed behavior of the heat anomaly near the I-Sm*C** phase transition.

On the theoretical side there is only one attempt [18] to study the I-Sm*C** phase transition. In this recent work Mukherjee *et al.* [18] developed a Landau model to describe the direct I-Sm*C** phase transition. In this work they explained the key features of the I-Sm*C** phase transition. The purpose of the present paper is to explain the anomalous heat capacity in the isotropic region within the framework of Landau's fluctuation theory. We calculate directly the temperature dependence of the heat capacity in the isotropic phase of the I-Sm*C** phase transition.

II. THEORY

A. Free energy

The construction of the Landau free energy for the I-Sm*C** phase transition is rather complex. We start by describing the order parameters involved in the I-Sm*C** phase transition. The layering in the Sm*C** phase is described by the order parameter $\psi(\mathbf{r})=\psi_0\exp(-i\Phi)$, whose modulus ψ_0 is defined as the amplitude of a one dimensional density wave characterized by the phase Φ. The wave vector $\boldsymbol{\nabla}_i\Phi$ is parallel to the director n_i in the smectic-*A* phase. The layer spacing is given by $d=2\pi/q_0$ with $q_0=|\boldsymbol{\nabla}\Phi|$. The tilt angle in the Sm*C** phase is described by the tensor order parameter

$$Q_{ij}(\mathbf{r}) = \frac{S(\mathbf{r})}{2}[3n_i(\mathbf{r})n_j(\mathbf{r}) - 1]. \tag{1}$$

The quantity $S(\mathbf{r})$ denotes the fraction of molecules at $\mathbf{r}$ aligned parallel to $\mathbf{n}$. The director $n_i(\mathbf{r})$ in terms of the tilt angle $\theta(\mathbf{r})$ and azimuthal angle ϕ can be expressed as

$$n_i(\mathbf{r}) = e_x\sin\theta(\mathbf{r})\cos\phi(z) + e_y\sin\theta(\mathbf{r})\sin\phi(z) + e_z\cos\theta(\mathbf{r}), \tag{2}$$

where $\theta(\mathbf{r})$ is the angle between the layer normal and the director $n_i(\mathbf{r})$. While the tilt is varying from layer to layer, the layer normal (z axis) is fixed. The azimuthal angle ϕ describing the average position of the molecules on the cone which changes with the coordinate z as $\phi=qz$, q being the wave vector of the helix. This selection of the tensor order parameter is not unique, and different definitions of the order parameter will result in different coefficients in the free energy expansion, but the thermodynamic quantities calculated will not be affected by the definition of the order parameter.

The in-plane spontaneous polarization is defined as

$$\mathbf{P}=P_0(-\sin\phi(z),\cos\phi(z),0). \tag{3}$$

Here P_0 is the magnitude of the spontaneous polarization in the unwound ferroelectric state.

Considering the above described order parameters, the total free energy near the I-Sm*C** transition can be written as [18]

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$$F(\mathbf{r}) = F_0 + \frac{1}{3}aQ_{ij}(\mathbf{r})Q_{ij}(\mathbf{r}) - \frac{4}{9}bQ_{ij}(\mathbf{r})Q_{jk}(\mathbf{r})Q_{ki}(\mathbf{r}) + \frac{1}{9}c[Q_{ij}(\mathbf{r})Q_{ij}(\mathbf{r})]^2 + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\gamma|\psi|^4 + \frac{1}{2\chi_0}\mathbf{P}^2 + \frac{1}{3}\delta Q_{ij}(\mathbf{r})Q_{ij}(\mathbf{r})|\psi|^2$$
$$+ \eta Q_{ij}(\mathbf{r})P_iP_j + \frac{1}{2}d_1|\nabla_i\psi|^2 + \frac{1}{2}d_2|\Delta\psi|^2 + \frac{1}{2}L_1\nabla_iQ_{jk}(\mathbf{r})\nabla_iQ_{jk}(\mathbf{r}) + L_3\varepsilon_{ijk}Q_{il}(\mathbf{r})\nabla_kQ_{jl}(\mathbf{r}) + \frac{1}{2}eQ_{ij}(\mathbf{r})(\nabla_i\psi)(\nabla_j\psi^*)$$
$$+ \frac{1}{2}fQ_{il}(\mathbf{r})Q_{jl}(\mathbf{r})(\nabla_i\psi)(\nabla_j\psi^*) + \frac{1}{2}hQ_{ij}(\mathbf{r})Q_{kl}(\mathbf{r})(\nabla_i\nabla_j\psi)(\nabla_k\nabla_l\psi^*) + \frac{1}{2}g_{ijkl}P_l\nabla_kQ_{ij}(\mathbf{r}), \quad (4)$$

where F_0 is the free energy of the isotropic phase. Here $a = a_0(T-T_1^*)$, and $\alpha = \alpha_0(T-T_2^*)$. T_1^* and T_2^* are the critical temperature for a hypothetical second order transition. a_0, α_0, b, c, γ, η, d_1, and d_2 are positive constants. δ is a coupling constant. A negative value of δ increases the smectic ordering and favors the SmC^* phase over the isotropic phase. χ_0 is the dielectric susceptibility. L_1 is the elastic constant. Another elastic term $\sim L_2\nabla_iQ_{ik}(\mathbf{r})\nabla_jQ_{jk}(\mathbf{r})$ is neglected for simplicity. Here ε_{ijk} is the antisymmetric third rank tensor. The chiral character of the SmC^* phase results in the pseudoscalar first order spatial derivative term in the free energy. Thus the coefficient L_3 is analogous to the coefficient of the Lifshitz-invariant term and induces the helical modulation of the SmC^* phase. The gradient terms $\sim e$, $\sim f$ and $\sim h$ involving $Q_{ij}(\mathbf{r})$ governs the relative direction of the layering with respect to the director and lead to the tilt angle of the SmC^* phase. In general a negative value of e favors the stability of the SmC^* phase. There is no direct linear coupling term $\sim|\psi|^2Q_{ij}(\mathbf{r})$ in the free energy (4), since such a term cannot exist in the isotropic phase [6]. Here g_{ijkl} takes the form $g_{ijkl} = g(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$. The coefficient g is analogous to the flexoelectric coefficient. This coupling term is of chiral character and induces a transverse polar ordering. A coupling term $\sim\mathbf{P}^2|\psi|^2$ can also be added in the free energy (4). An important feature of the model free energy (4) is that θ is not a separate order parameter but arises from the competition between $Q_{ij}(\mathbf{r})$ and ψ. The above free energy describes the direct first order I-SmC^* phase transition.

Now we consider the phase in which the translational order parameter is spatially homogeneous, i.e., $\psi_0 = \text{const.}$ for the simplicity of the calculation. The substitution of Q_{ij}, and ψ in Eq. (4), and eliminating the equilibrium values of ψ_0, θ, P_0, q_0, and q from Eq. (4), leads to the free energy density as a function of $S(\mathbf{r})$ alone can be written as

$$H(\mathbf{r}) = F(\mathbf{r}) - F_0^* = \left(1 - \frac{3m}{4n}\right)\frac{e^*\alpha^*}{2\gamma}S(\mathbf{r}) + \frac{1}{2}a^*S^2(\mathbf{r}) - \frac{1}{3}b^*S^3(\mathbf{r}) + \frac{1}{4}c^*S^4(\mathbf{r}) + \frac{1}{2}L_1^*[\nabla S(\mathbf{r})]^2. \quad (5)$$

Equation (5) considers both the spatial fluctuations of $S(\mathbf{r})$ and $\theta(\mathbf{r})$. The tilt angle fluctuations in Eq. (5) appear as $\sim[\nabla S(\mathbf{r})]^2$, $\sim S[\nabla S(\mathbf{r})]^2 \sim S^2[\nabla S(\mathbf{r})]^2$, etc. However, we have considered only the $\sim[\nabla S(\mathbf{r})]^2$ term and neglect the terms like $\sim S[\nabla S(\mathbf{r})]^2 \sim S^2[\nabla S(\mathbf{r})]^2$, etc. for simplicity of the calculation. The dependence of the Ginzburg-Landau parameters and the elastic constant L_1 becomes more complicated, when such terms are considered.

The tilt angle θ in the SmC^* phase can be expressed as

$$\sin^2\theta = \frac{(3e^*\alpha^*/4\gamma) + mS}{2nS}. \quad (6)$$

The behavior of the tilt angle θ in the SmC^* phase is completely determined by the behavior of the orientational order parameter S. In this connection we point out that the modulus of the orientational order parameter in the SmC^* phase was measured experimentally by Dollase and Fung [21] and described the smectic-A–SmC^* transition by the jump of the modulus of the orientational order parameter.

While deriving Eqs. (5) and (6) we have done the series expansion of $[1+(g^2\chi_0/2L_1)]^{-1}$ and consider the terms up to $(g^2\chi_0/2L_1)^2$.

The renormalized coefficients are

$$F_0^* = F_0 - \frac{\alpha^{*2}}{4\gamma} - \frac{9}{64n}\left(\frac{e^*\alpha^*}{\gamma}\right)^2,$$

$$a^* = a_0^*(T - T^*),$$

$$b^* = b_0(T - T_3^*),$$

$$c^* = c_0(T - T_4^*),$$

$$L_1^* = \frac{3}{8}L_1,$$

$$e^* = ed_1/2d_2,$$

$$f^* = fd_1/2d_2,$$

$$h^* = hd_1/d_2$$

$$h^{**} = hd_1^2/d_2^2$$

$$h_0 = h^{**} - (e^2/d_2)$$

$$\delta^* = \delta - \frac{e^2}{4d_2} - f^* + (h^{**}/4)$$

$$a_0^* = a_0 - \frac{\delta^* \alpha_0}{\gamma} - b_2,$$

$$b_0 = [-3e(f - h^*)\alpha_0/4\gamma d_2],$$

$$c_0 = (\alpha_0/2\gamma d_2^2)[d_2(f - h^*)^2 - he^2],$$

$$b_1 = \frac{x^2}{2Z}\left(1 - \frac{yd_1^2}{4d_2}\right),$$

$$b_2 = \left[y + \left(1 - \frac{yd_1^2}{4d_2}\right)w\right]\frac{x^2\alpha_0}{2Z},$$

$$x = \left(\frac{9L_3^2u}{16L_1} - \frac{3e^{*2}}{4\gamma}\right),$$

$$y = \frac{3(f^* - h_0)}{4\gamma x},$$

$$Z = \frac{9L_3^2uv}{16L_1} - \frac{9e^{*2}}{16\gamma},$$

$$w = \frac{9(h_0 + e^{*2})}{32\gamma Z},$$

$$T^* = \left[a_0T_1^* - \left(b_2 + \frac{\delta^*\alpha_0}{\gamma}\right)T_2^* + b_1 + \frac{e^{*2}}{2\gamma} - \frac{\delta^* d_1^2}{4\gamma d_2}\right] \Big/ a_0^*,$$

$$T_3^* = T_2^* - \left[b - \frac{3\delta^* e^*}{2^\gamma} + \frac{3ed_1^2(f - h^*)}{16\gamma d_2^2}\right] \Big/ b_0,$$

$$T_4^* = T_2^* + \frac{d_1^2}{4d_2\alpha_0} - \left[c - \frac{\delta^{*2}}{\gamma} - \frac{ee^*(f - 2h^*)}{2\gamma d_2}\right] \Big/ c_0,$$

$$m = -\frac{3e^{*2}}{4\gamma} + \frac{3\alpha^*(f^* - h_0)}{8\gamma} + \frac{9L_3^2u}{16L_1},$$

$$n = -\frac{9e^{*2}}{16\gamma} - \frac{9\alpha(h_0 + e^{*2})}{32\gamma} + \frac{9L_3^2uv}{16L_1},$$

$$u = 1 + (g^2\chi_0/2L_1) + (g^2\chi_0/2L_1)^2,$$

$$v = (g^2\chi_0/2L_1)u.$$

The above described renormalized coefficients are utmost complicated although the calculations are straightforward. We have done the series expansion of $m^2/2n$ in order to obtain the renormalized coefficient a^* .

Equation (6) shows that the tilt angle is influenced by the chirality of the system. Although in the Landau expansion of free energy (4) no change of the values of b and c are allowed as one approaches the transition temperature. The renormalized coefficients b^* and c^* are now temperature dependent. This is justified since the renormalization group analysis and the Monte Carlo simulation results indicates the renormalization of the Landau coefficients as one approaches the transition temperature. We assume $T^* \approx T_3^* \approx T_4^*$. The renormalized temperature T^* shows that the chirality slightly changes the I-SmC^* transition temperature but does not influence the nature of the I-SmC^* transition (since b and c are not influenced by the chirality). Thus the I-SmC^* phase transition temperature has been slightly shifted for the SmC^* liquid crystal in comparison with the SmC compound. Since the quartic coefficient c^* changes with temperature and can be negative, then stabilizing fifth and sixth order terms $\sim DS^5(\mathbf{r})$ and $\sim ES^6(\mathbf{r})$ with $E > 0$ should be added in the free energy (5).

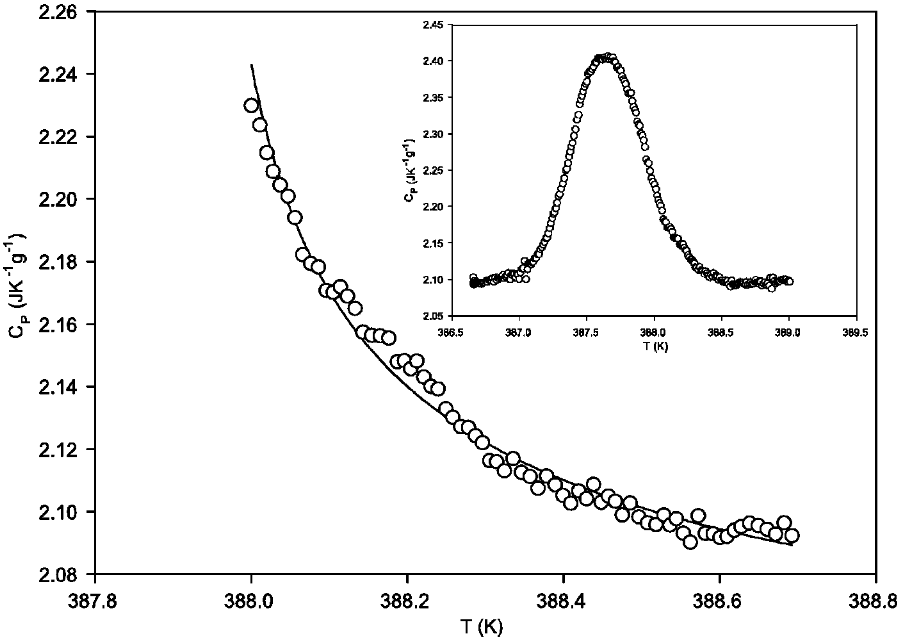

FIG. 1. The anomalous part of the measured heat capacity $C_P(T)$ of the liquid crystal RSFPPY in the isotropic phase above the isotropic to smectic-C^* transition. The measured data (circle) are from Ref. [5], and the line is the best fit of Eq. (13). The upper inset shows the measured heat capacity over the full temperature range.

The partition function, averages, and correlation function are calculated with the weight

$$W[S] = \exp\left(-\beta \int H(\mathbf{r})d\mathbf{r}\right), \tag{7}$$

with $\beta = 1/k_B T$ and k_B is the Boltzmann constant. We now proceed to calculate the anomalous heat capacity. To calculate the heat capacity we have followed the methods adopted by Imura *et al.* [19] and Fixman [20].

B. Gaussian model

Setting $b^* = 0$ and $c^* = 0$ in Eq. (5), the free energy of the system of volume V can be written as

$$g_0 = \int_V H(\mathbf{r})d\mathbf{r}. \tag{8}$$

The entropy density associated with the fluctuation is obtained by differentiating Eq. (5) with respect to the temperature,

$$\Delta s'(T,S) = -\frac{1}{2}\left(\frac{\partial a^*}{\partial T}\right)S^2(\mathbf{r}). \tag{9}$$

The ensemble average of Eq. (9) gives the entropy change due to the fluctuations,

$$\langle \Delta s'(T)\rangle = -\frac{1}{2}\sum_k \left(\frac{\partial a^*}{\partial T}\right)\langle |S(\mathbf{k})|^2\rangle, \tag{10}$$

where

$$\langle |S(\mathbf{k})|^2\rangle \approx \frac{k_B T}{a^* + L_1^* k^2} \equiv G(\mathbf{k}) \tag{11}$$

is the k-dependent order parameter fluctuation and $G(\mathbf{k})$ is the reciprocal-space correlation function. The wave vector k is summed over all the modes of the system. Here $\langle S(\mathbf{k})\rangle = 0$ in the isotropic phase in the absence of external field. Now $\Sigma_k \rightarrow (1/8\pi^3)\int_0^{q_{\max}} d\mathbf{k}$, where $q_{\max}$ is the cutoff wave vector.

Hence the excess entropy in terms of the correlation function G can be expressed as

$$\langle \Delta s'(T)\rangle = -\frac{a_0^*}{16\pi^3}\int_0^{q_{\max}} G(\mathbf{k})d\mathbf{k}. \tag{12}$$

The corresponding heat capacity at constant pressure per unit volume due to the fluctuations is then given, taking $q_{\max} \rightarrow \infty$, as

$$\Delta C_P(T) = \frac{\partial}{\partial T}(T\langle \Delta s'\rangle) = C_1 T^2 (T - T^*)^{-1/2}, \tag{13}$$

where $C_1 = (k_B/16\pi)(a_0^*/L_1^*)^{3/2}$.

C. Contributions of the cubic and the quartic terms

The contributions of the cubic and the quartic terms in the free energy can be obtained using perturbation theory, with the Gaussian model taken as the zeroth-order perturbation. We divide the total free energy into two parts: $g = g_0 + g_1$. Here g_0 is the free energy in the Gaussian model and g_1 is given by

$$g_1 = \int_V \left[-\frac{1}{3}b^* S^3(\mathbf{r}) + \frac{1}{4}c^* S^4(\mathbf{r})\right]d\mathbf{r}. \tag{14}$$

Using the method of Feynman graphs [22], the correlation function can be written in the $q_{\max} \rightarrow \infty$ limit, to the second order in b^* and the first order in c^*, as

$$G'(\mathbf{k}) = \frac{k_B T}{a^* + k^2\left[L_1^* + \frac{k_B T}{32\pi}\xi_0^3 (b^*/L_1^*)^2\right] - \frac{3k_B T}{4\pi}\xi_0^{-1}(c^*/L_1^*) - \frac{k_B T}{8\pi}\xi_0 (b^*/L_1^*)^2} \tag{15}$$

with $\xi_0 = (L_1^*/a_0^*)^{1/2}(T - T^*)^{-1/2}$. Utilizing the same procedures employed above, the excess heat capacity at constant pressure per unit volume due to the fluctuation is obtained as

$$\begin{aligned}\Delta C_P(T) = C_1 T^2 \Bigg\{ & [1 + C_2 T(T - T_3^*)^2 (T - T^*)^{-3/2}]^{-3/2} [(T - T^*) - 4C_2 T(T - T_3^*)^2 (T - T^*)^{-1/2} - C_3 T(T - T_4^*)(T - T^*)^{1/2}]^{-1/2} \\ & \times \left[1 - 2C_2 T[4(T - T_3^*)(T - T^*)^{-1/2} - (T - T_3^*)^2 (T - T^*)^{-3/2}] - C_3 T\left((T - T^*)^{1/2} + \frac{1}{2}(T - T_4^*)(T - T^*)^{-1/2}\right)\right] - 3(C_2/2)T \\ & \times [1 + C_2 T(T - T_3^*)^2 (T - T^*)^{-3/2}]^{-5/2} [4(T - T_3^*)(T - T^*)^{-3/2} - 3(T - T_3^*)^2 (T - T^*)^{-5/2}][(T - T^*) - 4C_2 T \\ & \times (T - T_3^*)^2 (T - T^*)^{-1/2} - C_3 T(T - T_4^*)(T - T^*)^{1/2}]^{1/2} \Bigg\},\end{aligned} \tag{16}$$

where $C_2 = 2C_1 b_0^2/a_0^{*3}$ and $C_3 = 12 C_1 c_0/a_0^{*2}$.

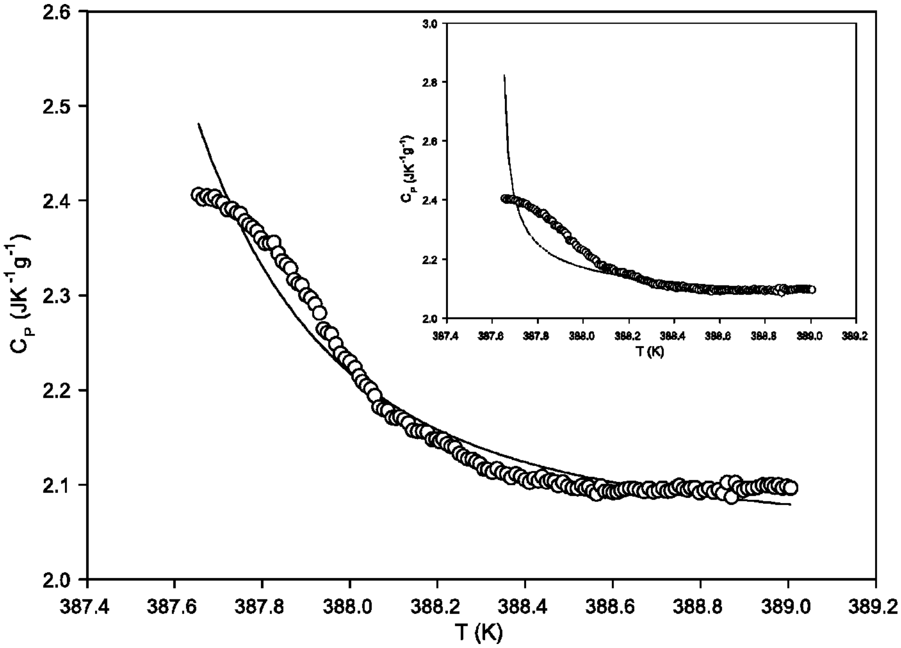

FIG. 2. The heat capacity $C_P(T)$ over the entire temperature range of the liquid crystal RSF-PPY in the isotropic phase above the isotropic to smectic-C^* transition. The measured data are from Ref. [5]. The line is the best fit of Eq. (16). The upper inset shows the fit of Eq. (13) of the same data over the same temperature range.

III. COMPARISON WITH EXPERIMENT

The temperature dependence of the heat capacity of RS-FPPY was reported by Ema *et al.* [5]. The heat capacity $C_P(T)$ in the I-SmC^* transition on heating measured by Ema *et al.* [5] is shown in the upper inset of Fig. 1. As can be observed, the normal heat capacity is much higher than the anomalous contribution. The strong large magnitude of the normal component relative to the anomalous contribution renders it progressively more difficult to separate out the anomalous part as one gets further away from the transition temperature. We have therefore fitted Eq. (13), plus a normal component C_0 representing the normal component, to the measured data, over a restricted temperature range above the I-SmC^* transition, using C_1, T^*, and C_0 as a fit parameters. $C_0=2.01$ J K^{-1} g^{-1} was selected for the good fit. The fit (line) and the measured data (circle) are shown in Fig. 1. As can be observed, the agreement of the measured data with functional form predicted by theory is reasonably good. The fit yields $C_1=4.64\times10^{-7}$ J K$^{-5/2}$ g^{-1}. We also fitted the same data by using Eq. (16), which includes the contribution of the cubic and quartic terms in the free energy. The line obtained in the fit overlaps the line that shown in Fig. 1 on the scale of the figure with different fit parameters. What transpires from Fig. 1 is that only the first order theory is sufficient to explain anomalous behavior of heat capacity above the I-SmC^* transition. We further fitted the full heat capacity data above the I-SmC^* transition by Eq. (13) where the fit (line) is shown in the upper inset of Fig. 2. The fit yields $C_1=6.43\times10^{-7}$ J K$^{-5/2}$ g^{-1}. As can be seen from the upper inset of Fig. 2, the agreement is not reasonably good. We have therefore fitted the same data by Eq. (16) with C_2 and C_3 as a fit parameters and taking the same value of $C_1=6.43\times10^{-7}$ J K$^{-5/2}$ g^{-1} obtained for the upper inset of Fig. 2. The fit (line) and the measured data (circle) are shown in Fig. 2. The fit shows that the contributions to the cubic and the quartic terms are indeed important and a perturbation theory is justified in this case. The fit yields $C_2=4.13\times10^{-3}$ K$^{-3/2}$ and $C_3=-1.06\times10^{-2}$ K$^{-3/2}$. Equation (16) is very sensitive to the values of T^*, T_3^*, and T_4^*. From the fit we observe that $T^*\approx T_3^*\approx T_4^*$ which justifies our assumption.

Finally we also observe that the amplitude of the order parameter (tilt angle or orientational ordering) fluctuation increases abnormally near the I-SmC^* transition temperature (T_{C^*I}) and brings about the anomalous increment in heat capacity. This may be caused by a macroscopically inhomogeneous distribution of bulk impurities. From Eq. (13) it is clear that the heat capacity has a square root divergence in the isotropic phase. Thus the critical exponent $\alpha'=0.5$ which is same as in the case of isotropic-nematic and isotropic–smectic-*A* transition and indicate the fluidlike analogy in the isotropic phase of the I-SmC^* transition.

IV. CONCLUSION

We have presented here a Landau fluctuation theory analysis to describe the anomalous behavior of the heat capacity in the isotropic phase of the I-SmC^* transition. The analysis presents theoretical support with the experimental observation. Although the agreement between experiment and theory is reasonable, Eqs. (13) and (16) are sensitive to the values of C_1, C_2, and C_3 which depends on a_0^* and L_1. The value of L_1 can be obtained in principle from the light scattering measurements. A reliable estimation of the phenomenological coefficients and the elastic constant L_1 is not possible due to the lack of experimental data, e.g., order parameters, light scattering, etc. The accurate measurements of the thermodynamic quantities near the I-SmC^* transition will speak for reasonableness of the values of C_1, C_2, and C_3 obtained from the fit. The present theory shows that a first order theory is sufficient to explain only the anomalous behavior of the heat capacity above the I-SmC^* transition point. However, the cubic and the quartic contributions are found to be important to explain the nature of the heat capacity over the entire temperature range above the I-SmC^* transition point. Accurate heat capacity and elastic constant measurements near the I-SmC^* transition are called for to determine the validity range of the present theory.

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