Generalized mean-field model for the smectic-A—chiral-smectic-C phase transition

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In light of our high-resolution and almost simultaneous measurements of the tilt angle and polarization in the chiral-smectic-C phase of p-(n-decyloxybenzylidene)-p-amino-(2-methylbutyl)-cinnamate (DOBAMBC), we have proposed a generalized mean-field model to describe the important features related to the smectic-A—chiral-smectic-C transition. This mean-field model is similar to the one proposed by Zeks. After carrying out least-squares fittings to the generalized mean-field model, we demonstrated that the temperature dependences of the tilt angle, polarization, and their ratio are well described by the model. The fitting to the temperature variation of the helical pitch is less satisfactory but the qualitative feature of the helical pitch anomaly is obtained. Furthermore, all the mean-field expansion coefficients can be calculated. Among the eleven coefficients, seven are in good agreement with the existing reported results, the four remaining will be reported here for the first time. The shortcoming of the prevailing phenomenological mean-field theory by Pikin and Indenbom will be discussed in detail.

I. INTRODUCTION

Since Huang and Viner[1] proposed an extended mean-field model to describe the behavior of the smectic-A (SmA) —smectic-C (SmC) phase transition, it has been experimentally demonstrated that this model provides excellent accounts for the temperature variations of the heat-capacity anomaly and tilt angle in both the SmA-SmC and SmA—chiral-smectic-C (SmC^*) phase transitions.[2,3] While the molecule tilt in the SmC phase has a constant azimuthal angle throughout the sample, the molecule tilt in the SmC^* phase precesses around the normal to smectic layers as one goes from one layer to another because of the chiral property of the constituent molecules. The existence of molecular chirality means lack of the center of inversion and results in possible spontaneous polarization perpendicular to both the molecule tilt and the smectic layer normal. Consequently, in the SmA-SmC^* phase transition, although the tilt angle has been demonstrated to be the primary order parameter,[4] various coupling terms involving polarization (P) and/or wave vector (q) for the helicoidal structure have to be included to describe some unique features of the SmC^* phase. Here we will demonstrate that those higher-order terms consisting of P and/or q are sufficiently small such that the extended mean-field model is still an excellent approximation for describing the heat-capacity and tilt-angle data in the vicinity of the SmA-SmC^* transition.

Based on the symmetry of the group representation for the SmC^* phase, Indenbom *et al.*[5] have proposed a phenomenological Landau free energy including leading chiral coupling terms involving P and/or q. This free-energy expansion simply serves as a starting point to describe the SmA-SmC^* transition but fails to explain most of the pertinent experimental results which are unique to the SmC^* phase. Assuming that all the coupling coefficients are constant, firstly, the theory predicts that the wave vector q associated with the helicoidal modulation is temperature independent. Many experimental results show that q drops very fast just below T_c, reaching a minimum in the region $T_c - T \lesssim 1$ K and then increases slowly as the temperature decreases.[6–8] Here T_c is the SmA-SmC^* transition temperature. In view of these experimental results, at least three modifications[9–11] have been given to remedy the shortcoming of the original theory. Secondly, the theory predicts that the polarization is proportional to the tilt angle. Our high resolution and almost simultaneous measurements[12,13] on the polarization (P) as well as the tilt angle (θ) of p-(n-decyloxybenzylidene)-p-amino-(2-methylbutyl)cinnamate (DOBAMBC) show that the ratio P/θ decreases slowly with temperature for $T_c - T \gtrsim 2$ K and drops precipitously near the T_c. The theory fails to explain our results again. Earlier experimental results by Ostrovskii and co-workers[14] with much less resolution indicated that temperature dependence of the tilt angle and polarization could be fitted to a simple power law but with different critical exponents.

In light of our almost simultaneous measurements on the polarization and the tile angle, we have found that a generalized mean-field model,[12] similar to the one proposed by Zeks,[11] can give us a fairly good fitting for the temperature variations of the tilt angle, polarization, and their ratio P/θ, and a qualitative explanation for the anomalous behavior of the helical wave vector q. In Sec. II the model suggested by Pikin and Indenbom[15] will be discussed in detail. A generalized mean-field model for the SmA-SmC^* and our fitting results will be presented in Sec. III. In Sec. IV we drawn our conclusions.

II. PHENOMENOLOGICAL MEAN-FIELD THEORY FOR THE SmA-SmC^* PHASE TRANSITION

Employing the theory of group representations, Indenbom and co-workers[5] have argued that ferroelectric polarization arises as a result of the deformation of the molecular arrangements and the manifestation of piezoelectric properties, which give rise to the phenomenon of "pseudointrinsic" ferroelectricity in the SmC^* phase. In general, these ferroelectrics exhibit a helicoidal structure. Including the contribution from flexoelectric property, Pikin and Indenbom[15] have suggested the following mean-field free-energy expression for the SmA-SmC^* transition:[16]

$$G_1 = G_0 + \tfrac{1}{2}a'\tilde{t}\theta^2 + \tfrac{1}{4}b'\theta^4 - \Lambda\theta^2 q + \tfrac{1}{2}K\theta^2 q^2 + \frac{1}{2\chi}P^2 - fP\theta q - zP\theta \ . \quad (1)$$

Here q is the wave vector of the SmC^* helix, K the elastic modulus, Λ the coefficient of the Lifshitz invariant term responsible for the helicoidal structure, χ the dielectric susceptibility, and f and z are coefficients of the flexoelectric and piezoelectric coupling between the tilt angle (θ) and the polarization (P). These linear coupling terms f and z are of chiral character, break the axial symmetry around the long axis of the molecular and induce a transverse polar ordering $(P \neq 0)$. The coefficients a' and b' are positive constants and the temperature difference $\tilde{t} = T - T_0$. Here T_0 is the "unrenormalized" transition temperature. G_0 is the nonsingular part of free energy and will be set to be zero for the rest of our discussions. Minimizing this free energy with respect to P, q, and θ, respectively, and rearranging the variables, we get

$$P = \chi(fq + z)\theta \ , \quad (2)$$

$$q = (\Lambda + fz\chi)/(K - f^2\chi) \quad (3)$$

and

$$[a'\tilde{t} + (f^2\chi - K)q^2 - z^2\chi]\theta + b'\theta^3 = 0 \ . \quad (4)$$

One can rewrite the coefficient of θ term in Eq. (4) as $a'(T - T_c)$. Then

$$T_c = T_0 + \frac{1}{a'}[(K - f^2\chi)q^2 + \chi z^2] \ . \quad (5)$$

Two major predictions result from this free energy expansion. First, assuming that all the expansion coefficients are temperature independent, Eq. (3) indicates that the helix pitch L $(=2\pi/q)$ is constant throughout the SmC^* phase. This prediction is at variance with experimental results[6-8] which show that q decreases slowly with temperature, reaching a minimum at $T \lesssim T_c - 1$ K and then sharply increases as the temperature approaches T_c. Secondly, Eq. (2) suggests that the spontaneous polarization is proportional to the tilt angle. This theoretical prediction fails again to explain our experimental results that the ratio P/θ increases abruptly for $T_c - T \lesssim 1$ K and then fairly slowly for $T_c - T \gtrsim 2$ K as the temperature decreases.

To our knowledge, there exist at least three different modifications[9-11] of the free energy that have been proposed to explain the anomalous temperature dependence of the helical pitch in the vicinity of T_c. We will discuss the approach taken by Zeks[11] later. Although the other two, namely, the critical fluctuations argument by Yamashita and Kimura[10] and the anomalous flexoelectric coefficient approach by Osipov and Pikin,[9] gave a reasonable account for the temperature behavior of q, in light of our recent experimental results on P and θ, it is not sufficient to simply propose a theoretical model to fix up the anomaly in q. From Eq. (2), the fast rise in q near the T_c will result in a fast drop in P/θ provided that f is a negative quantity and $(z + fq)$ a positive one. However, away from T_c, the slow decrease in q will lead to a slow increase in P/θ as the temperature increases. This is inconsistent with our experimental result.[12]

Before we go into the details of a generalized mean-field model, let us reexamine the free energy [Eq. (1)] and its outcome more carefully. First, assuming that the anomalous behavior in q can be fixed up some way and Eq. (2) still holds approximately in order to reconcile both anomalies in q and P/θ, especially just below the transition temperature, it requires that f be negative and z be greater $|fq|$. In general it is believed that f is negative, but the relative magnitude of piezoelectric term (z) to the flexoelectric term (fq) from other experimental measurements is inconclusive.[17,18] Our high-resolution P/θ measurement indicates that the piezoelectric term definitely has to be larger than the flexoelectric term for DOBAMBC. Secondly, let us calculate the magnitude of each individual term in the free energy [Eq. (1)] at $T_c - T = 5$ K where both P/θ and q are reasonably constant. Here is the list of the available data in mks units at about $T_c - T = 5$ K (Ref. 19): $a'\tilde{t} = 1.1\times10^5$ J/m^3, $b' = 2.6\times10^5$ J/m^3, $c' = 4.5\times10^6$ J/m^3, $P = 42$ μC/m^2, $\theta = 0.37$ rad, $q = 3\times10^6$ m^{-1}, $K = 10^{-11}$ N, $\chi = 2.6\times10^{-11}$ F/m, $z = 3.4\times10^6$ V/m, and $|f| \simeq \frac{1}{10}(z/q)$. Again, instead of c being the coefficient of the θ^6 term in the free-energy expansion as we did in the preceding paper,[13] here we choose $c'/6$ (Ref. 16) to be consistent with the conventional choice of the coefficients in Eq. (1). Using this information, the contribution of each individual term in Eq. (1), except $\Lambda\theta^2 q$, toward the total free energy has been calculated and listed in Table I. As one can see that the leading three terms, including $c'\theta^6/6$, are about several hundred times larger than the rest of the terms related to P and/or q for the SmC^* phase. Consequently, it is not surprising that the first three terms as in the extended mean-field model are sufficient to describe the behavior of the heat capacity and tilt angle.[20] This conclusion still holds in the generalized mean-field model with additional three expansion terms.

TABLE I. The magnitude of each individual term except $\Lambda\theta^2 q$ and G_0 in Eq. (1) at $T_c - T = 5$ K in units of J/m^3.

$\frac{1}{2}a'\tilde{t}\theta^2$	$\frac{1}{4}b'\theta^4$	$\frac{1}{6}c'\theta^6$	$\frac{1}{2}K\theta^2 q^2$	$\frac{P^2}{2\chi}$	$fP\theta q$	$zP\theta$
8.0×10^3	1.2×10^3	1.9×10^3	6	36	5	54

III. A GENERALIZED MEAN-FIELD MODEL FOR THE Sm A-Sm C^* PHASE TRANSITION

As we have demonstrated in Table I, all chiral terms in Eq. (1) are small in comparison with the three leading terms. Quantitatively, this manifests itself in three experimental observations. First, the spontaneous polarization is very small, which is about one hundred times smaller than the molecular dipole moment. Secondly, the weakness of the helicoidal force. The pitch is about one thousand times larger than the molecular length. Finally, the relative increase in T_c for the SmA-SmC^* with respect to the T_0 for the SmA-SmC transition of the racemic mixture is only about 0.2%, namely, $(T_c-T_0)/T_c \sim 0.2\%$.[3,4,21] Because the bilinear $P\theta$ coupling terms are small, the biquadratic coupling terms could becomes important in the SmC^* phase. The NMR measurements by Blinc *et al.*[22] of the ordering of molecules in a direction transverse to the molecular long axis do not show any significant difference between a chiral and a corresponding nonchiral compound. As the spontaneous polarization is directly related to the transverse order, this means that the biquadratic coupling term, $P^2\theta^2$, which is of a nonchiral character and therefore in both compounds become relevant for the transverse ordering of molecules as well as the bilinear coupling term $(P\theta)$, which characterizes the chiral properties are small. This quadratic coupling term is nonchiral and induces a transverse quadrupolar ordering $(P^2 \neq 0)$. To stabilize the system for far away T_c, we have to include one P^4 term. Finally, in order to explain the slow increase in q as the temperature decreases, one needs $dq\theta^4$ term which is equivalent to replacing the Lifshitz coefficient Λ by $\Lambda+d\theta^2$. These three terms have been considered by Zeks[11] in his mean-field model to explain the anomaly in the temperature dependence of pitch. From our work on the SmA-SmC (or SmC^*) transition we have demonstrated that the $c'\theta^6$ term is essential to describe the transition. The importance of the $c'\theta^6$ term is also clearly shown in Table I. Thus we propose that the total free energy $G=G_1+G_2$, where G_1 is given by Eq. (1), and G_2 has the following four terms:

$$G_2=-\tfrac{1}{2}eP^2\theta^2+\tfrac{1}{4}gP^4-dq\theta^4+\tfrac{1}{6}c'\theta^6 . \tag{6}$$

Now minimizing the total free energy with respect to q, one has

$$q=\frac{1}{K}(\Lambda+d\theta^2+fP/\theta) . \tag{7}$$

Substituting this expression for q into G, one obtains

$$G=G_A(\theta)+G_B(\theta,P) . \tag{8}$$

Here

$$\begin{aligned}G_A(\theta)&=\tfrac{1}{2}(a'T-\Lambda^2/K)\theta^2+\tfrac{1}{4}(b'-4\Lambda d/K)\theta^4\\&\quad+\tfrac{1}{6}(c'-3d^2/K)\theta^6\\&\equiv\tfrac{1}{2}a_2(T-T_c')\theta^2+\tfrac{1}{4}a_4\theta^4+\tfrac{1}{6}a_6\theta^6\end{aligned} \tag{9}$$

and

$$\begin{aligned}G_B(\theta,P)&=\tfrac{1}{2}(1/\chi-e\theta^2-f^2/K)P^2\\&\quad+\tfrac{1}{4}gP^4-[(z+\Lambda f/K)\theta+(df/K)\theta^3]P\\&\equiv gP_0^4(\tfrac{1}{4}\tilde{P}^4+\tfrac{1}{2}\alpha\tilde{P}^2-\beta\tilde{P}) .\end{aligned} \tag{10}$$

Again minimizing G with respect to $\tilde{P}=(P/P_0)$, one gets

$$\tilde{P}^3+\alpha\tilde{P}-\beta=0 . \tag{11}$$

Here $a_2=a'$, $T_c'=T_0+\Lambda^2/Ka'$, $a_4=b'-4\Lambda d/K$, $a_6=c'-3d^2/K$, $\alpha=\tfrac{3}{4}(1-y^2)$ with $y=\theta/\theta_1$ and $\theta_1^2=(1/\chi-f^2/K)/e$, $\beta=\tfrac{3}{4}(3h_4y+h_5y^3)$ with $h_4=\sqrt{g}(z+\Lambda f/K)/(2\sqrt{3}\theta_1^2e^{3/2})$, $h_5=\sqrt{3g}fd/(2Ke^{3/2})$, and $P_0=2\theta_1(e/3g)^{1/2}$. The solution for Eq. (11) can be written as[23]

$$\tilde{P}=\frac{\beta}{|\beta|}\frac{2}{\sqrt{3}}|\alpha|^{1/2}Y(x) ,$$

where

$$x=3^{3/2}|\beta|/(2|\alpha|^{3/2}) \tag{12}$$

and

$$Y(x)=\begin{cases}\sinh(\tfrac{1}{3}\sinh^{-1}x) & \text{for } \theta^2<\theta_1^2 ,\\ \cosh(\tfrac{1}{3}\cosh^{-1}x) & \text{for } \theta^2>\theta_1^2 \text{ and } x>1 ,\\ \cos(\tfrac{1}{3}\cos^{-1}x) & \text{for } \theta^2>\theta_1^2 \text{ and } x<1 .\end{cases}$$

The equation for θ can be obtained by minimizing G with respect to θ:

$$\begin{aligned}&a_2(T-T_c')\theta+a_4\theta^3+a_6\theta^6\\&\quad-[(\beta/\theta)+(2fd/K)\theta^2]P-e\theta P^2=0 .\end{aligned}$$

Choosing $y=\theta/\theta_1$ and $\tilde{P}=P/P_0$ as the dimensionless variables, we can rewrite the above equation as

$$h_1(T-T_c')y+h_2y^3+h_3y^5-y\tilde{P}^2/3-(h_4+h_5y^2)\tilde{P}=0 \tag{13}$$

and the equation for helical wave vector q as

$$q=h_6+h_7y^2+h_8(\tilde{P}/y) . \tag{14}$$

Here $h_1=ga_2/(4e^2\theta_1^2)$, $h_2=ga_4/(4e^2)$, $h_3=ga_6\theta_1^2/(4e^2)$, $h_6=\Lambda/K$, $h_7=d\theta_1^2/K$, and $h_8=2fe^{1/2}/[K(3g)^{1/2}]$. Recently we have demonstrated that our high-resolution heat-capacity and tilt-angle data near the SmA-SmC^* transition of DOBAMBC (Ref. 20) are well characterized by the expressions derived from the extended mean-field theory which includes a_2, a_4, and a_6 terms only. The relations among three sets of leading mean-field expansion coefficients used in this and the preceding paper[13] are $a/T_c=a_2/2\simeq a'/2$, $b=a_4/4\simeq b'/4$, and $c=a_6/6\simeq c'/6$. Thus a_2, a_4, and a_6 can be obtained from Table IV of the preceding paper.[13] The results in Table I suggest that the terms involving P and/or q in the total free energy G are higher-order correction terms. This observation still holds with three additional terms in the total free energy. Thus to reduce the number of free parameters in our least-squares-fitting process, we fixed the values of a_2 ($=4.52\times10^4$ J/m^3 K), a_4 ($=5.25\times10^5$ J/m^3), and a_6 ($=8.83\times10^6$ J/m^3) which are determined from our heat-capacity and tilt-angle measurements.[13] Then we need θ_1, P_0, h_4, and h_5 as adjustable parameters to get the best fit to temperature dependence of the polarization as well as the ratio of the polarization to the tilt angle. The fifth adjustable parameter in performing this fitting is $g/(4e^2)$. Because of relatively large contributions from three leading expansion terms toward the total free energy, our fitting results are fairly insensitive to the choice of this common factor [i.e., $g/(4e^2)$] in calculating h_1, h_2, and h_3 from a_2, a_4, a_6, and θ_1^2. For example, the standard deviations of our polarization data from the fitted curve are 2.32, 2.34, and 2.41 for $g/(4e^2)$ (in m^3/J) being set equal to 1×10^{-3}, 3×10^{-5}, and 1×10^{-5}, respectively. With such a small change in the standard deviation under a wide range of $g/(4e^2)$, we started our fitting with $g/(4e^2)=7\times10^{-4}$ m^3/J. This second step of fitting gave $P_0=2.33\times10^{-5}$ C/m^2, $\theta_1=0.164$ rad, $h_4=0.110$, and $h_5=-0.028$. Then the optimum choice of the rest of the three parameters (i.e., h_6, h_7, and h_8) can be obtained easily to get the best fit to the measured helicoidal wave vector q, i.e., Eq. (14). Under this circumstance, the experimental data and the fitted curve for the temperature variations of the tilt angle, polarization, the ratio P/θ, and the helical pitch ($=2\pi/q$) are shown in Figs. 1, 2, 3, and 4, respectively. Here we have tried to fit the helical pitch data by Ostrovskii *et al.*[6] [see Fig. 4(a)] and Musevic *et al.*[8] [see Fig. 4(b)]. It is clearly demonstrated that the fitting to our results of the tilt angle, polarization, and their ratio are very good, and a qualitative feature is obtained for both sets of the helical pitch data. The fact that there are five adjustable parameters (with one [$g/(4e^2)$] being fairly insensitive) in our fitting to the polarization data and we cannot achieve an excellent fitting, leads us to conclude that further improvement in the experimental measurements and/or the theoretical model are necessary. The results in Fig. 4(a) seem to be better than that in Fig. 4(b). Here we will discuss our fitting results based on the parameters being obtained from both cases. The relevant parameters resulting from the last step of the fitting, i.e., the one to the helicoidal pitch data are $h_6=9.5\times10^6$ m^{-1}, $h_7=2.7\times10^5$ m^{-1}, and $h_8=-1.3\times10^7$ m^{-1} for the data by Ostrovskii *et al.*, and $h_6=1.1\times10^7$ m^{-1}, $h_7=1.0\times10^6$ m^{-1}, and $h_8=-1.5\times10^7$ m^{-1} for the data by Musevic *et al.* Both h_5 and h_8 are proportional to f and are negative. This implies that the coefficient f is negative which agrees with our general argument based on the anomalous temperature dependence of P/θ and q. Furthermore, all the expansion coefficients involving q and/or P terms can be related to these fitting parameters and the elastic constant K as follows:

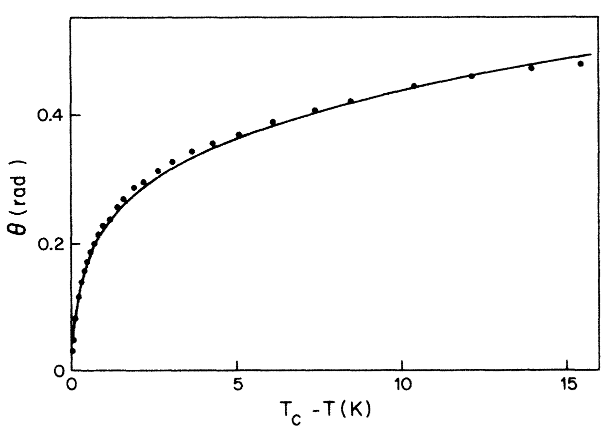

FIG. 1. The temperature dependence of the tilt angle for DOBAMBC. Solid circles, experimental data; solid line, fitted line.

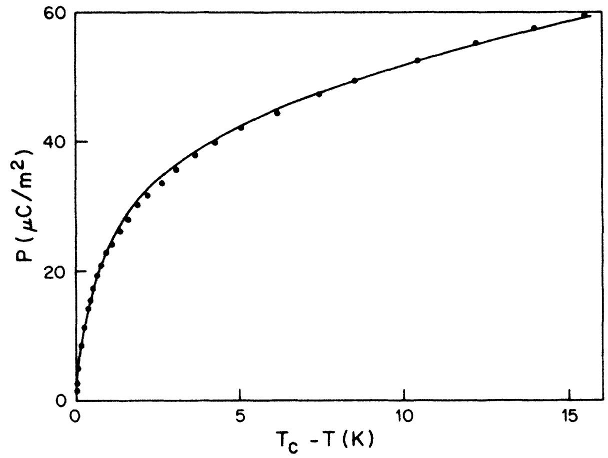

FIG. 2. The temperature dependence of the spontaneous polarization for DOBAMBC. Solid circles, experimental data; solid line, fitted result.

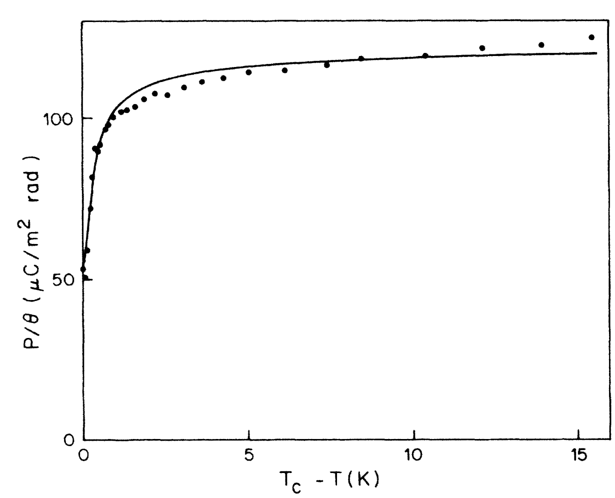

FIG. 3. The temperature dependence of the ratio P/θ for DOBAMBC. Solid circles, experimental data; solid line, fitted result.

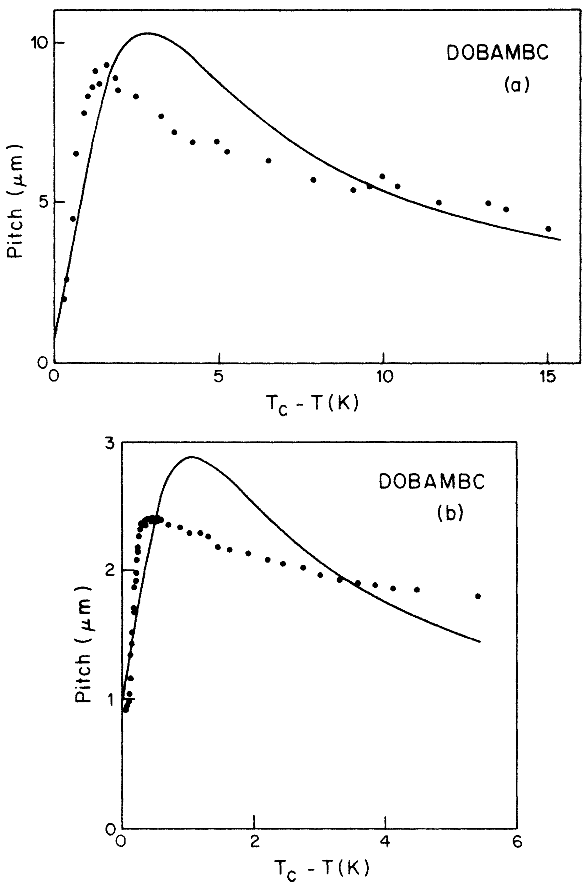

FIG. 4. The temperature dependence of the helical pitch for DOBAMBC. Solid circles, experimental data; solid line, fitted result. Experimental results obtained by Ostrovskii *et al.* (Ref. 6) and by Musevic *et al.* (Ref. 8) are displayed in (a) and (b), respectively.

$$\Lambda = h_6 K,\quad d = h_7 K/\theta_1^2,\quad f = h_8 K \theta_1 / P_0 ,$$
$$e = h_7 h_8 K/(h_5 P_0^2),\quad g = (2\theta_1)^2 h_7 h_8 K/(3 h_5 P_0^4) ,$$
$$z = 2\sqrt{3}\theta_1^2 e^{3/2} h_4 / g^{1/2} - \Lambda f/K ,$$

and $1/\chi = h_8 K \theta_1^2 (h_7/h_5 + h_8)/P_0^2$. Note that all these coefficients are proportional to the elastic constant. In principle, we can determine (g/e^4) from our fitting and obtain all the expansion coefficients. Practically, it is impossible as we discussed before. Thus in order to determine all the parameters, we have to choose the most reliable experimental result to determine K. Among the experimental measured results on χ, K, f, and z, we decided that $\chi = 2.6\times 10^{-11}$ F/m is the best one.[24] Then the rest of the constants can be calculated and are listed in Table II with all the available experimental results. As being argued and expected, the coefficient f is a negative quantity. Juding from the quality of our fitting to the helical pitch, the agreements with the existing data for the coefficients K, f, and z are fairly satisfactory. Moreover, the constants Λ, d, e, and g are determined for the first time. Now let us check the self-consistency of our choice of the common factor $g/(4e^2)$ for the three leading expansion terms in carrying out the fitting to the polarization. Here $g/(4e^2)$ is equal to 2.9×10^{-5} m^3/J and 1.7×10^{-5} (m^3/J) for cases A and B, respectively. We have repeated our fitting again with those values for $g/(4e^2)$ and obtained the change in fitting results being less than 0.5% which is within the resolution of our measurements.

In order to make comparisons of the relative importance of each individual term in the generalized mean-field model, again the contribution of each term to the total free energy G is calculated at $T_c - T = 5$ K with $P = 42$ $\mu C/m^2$ and $\theta = 0.37$ rad as well as at $T_c - T = 0.48$ K with $P = 15.6$ $\mu C/m^2$ and $\theta = 0.174$ rad. The results are displayed in Table III. Evidently, the leading three terms involving a', b', and c' are still the dominant ones in the free energy expansion. This is consistent with our experimental observation, i.e., the heat capacity and the tilt angle can be well characterized by the extended mean-field model. In both cases Table III shows clearly the relative importance of biquadratic term $P^2\theta^2$ and P^4 terms in comparison with terms involving $\theta^2 q^2$, $\theta^2 q$, P^2, $P\theta q$, and $P\theta$. Consequently, in the temperature range in which relatively reliable data can be obtained easily, the biquadratic term $P^2\theta^2$ and P^4 are not negligible. In the Sm*A*-Sm*C* transition, we require θ^6 term to describe the transition and in the Sm*A*-Sm*C** transition, the terms involving θ^6, $\theta^2 P^2$, $q\theta^4$, and P^4 are necessary to explain the major

TABLE II. The constant coefficients in the generalized mean-field model for describing the Sm*A*-Sm*C** transition of DOBAMBC. Cases A and B correspond to employ the helicoidal pitch data by Ostrovskii *et al.* (Ref. 6) and by Musevic *et al.* (Ref. 8), respectively, in our data fitting from which the mean-field expansion coefficients can be calculated.

Constant	Our fitted result		Other experimental		Units
	Case A	Case B	Result	Reference	
χ	2.6[a]		2.6	24	10^{-11} F/m
K	2.5	1.0	3	25	10^{-12} N
Λ	2.3	1.1			10^{-5} J/m^2
d	2.5	3.9			10^{-5} J/m^2
f	−0.22	−0.11	−0.4	17	V
e	5.7	10			10^{11} $J\,m/C^2$
g	3.8	6.7			10^{19} $J\,m^5/C^4$
z	2.8	2.4	3.4	17	10^6 V/m

[a]χ was chosen to be the same as the experimental result in order to determine the rest of the constants.

TABLE III. The magnitude of each individual term in the generalized mean-field free energy at $T_c - T = 5$ K (case A) and 0.48 K (case B) in units of J/m^3.

	$\frac{1}{2}a'\tilde{t}\theta^2$	$\frac{1}{4}b'\theta^4$	$\frac{1}{6}c'\theta^6$	$\frac{1}{2}K\theta^2q^2$	$\Lambda\theta^2 q$	$P^2/2\chi$
Case A	8.0×10^2	1.2×10^3	1.9×10^3	0.15	3.1	36
Case B	170	60	20	7.4×10^{-2}	0.47	4.7
	$fP\theta q$	$zP\theta$	$\frac{1}{2}eP^2\theta^2$	$\frac{1}{4}gP^4$	$dq\theta^4$	
Case A	3.4	45	71	32	0.45	
Case B	0.84	7.6	2.1	0.56	3.2×10^{-2}	

features of the transition. Theoretically one should address why all those higher-order terms are so important in both the SmA-SmC and the SmA-SmC^* transition.

Finally, here we have 11 expansion coefficients for the free energy. In this 11-dimension parameter space, there may exist several subspaces in which temperature dependences of polarization and/or tilt angle have unique features. For example, in the original work by Zeks,[11] he identified an S-shaped temperature variation of the tilt angle and polarization. Our data do not show this S-shaped feature. Recently Filipic *et al.*[26] have claimed that such an S-shaped temperature dependence has been observed in spontaneous polarization of DOBAMBC. Since their transition temperature $T_c = 82.7\,^\circ$C is more than 10 K below our T_c's or the most reported T_c's for DOBAMBC, it is not clear how relevant this result is to the physical properties of DOBAMBC near its SmA-SmC^* transition.

IV. CONCLUSIONS

After about ten years extensive research activity in both experimental and theoretical aspects of the SmA-SmC^* transition, here we provide one of the crucial experimental results and propose a more realistic theoretical model to obtain better understanding of the nature of this both technologically and academically important phase transition. Although the fitting to the well-known helical pitch anomaly is not too good, the tilt angle, polarization, and their ratio are well-described by the model. Detailed and high-resolution measurements on the helical pitch of DOBAMBC are in progress. Even with this less satisfactory result in describing the helical pitch anomaly, our determination of the Landau free-energy expansion coefficients either is brand new information or is in reasonable agreement with the existing data. We plan to study other chemically much more stable compounds near their SmA-SmC^* phase transition.

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