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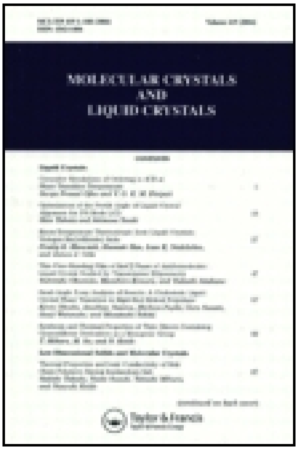

Molecular Crystals and Liquid Crystals

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A Molecular Theory of Chiral Smectic C iquid Crystals I

Masahiro Nakagawa [a]

[a] Department of Electrical Engineering, Faculty of engineering, The Technological University of Nagaoka, Kamitomioka 1603, Nagaoka, Niigata, 949-54, Japan

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A Molecular Theory of Chiral Smectic C Liquid Crystals I

MASAHIRO NAKAGAWA

Department of Electrical Engineering, Faculty of Engineering, The Technological University of Nagaoka, Kamitomioka 1603, Nagaoka, Niigata 949-54, Japan

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A molecular theory of chiral smectic C liquid crystals is formulated. On the basis of molecular field theories of smectic A and cholesteric liquid crystals, Landau free energy associated with tilt and twist deformations of director is obtained from a microscopic point of view. Then the temperature dependences of the tilt angle and the helical pitch in chiral smectic C and cholesteric phases are numerically calculated. One finds the qualitative agreement between the present theoretical result and the experimental findings for the critical exponent of the tilt angle but not for that of the helical pitch. In addition it is also pointed out that the temperature dependence of orientational order is significant to drive chiral smectic C-smectic A phase transitions, rather than that of translational order.

1. INTRODUCTION

As is well known, chiral smectic C (SmC*) liquid crystals possess the layer and helical structures like as smectic A (SmA) and cholesteric (N*) ones, respectively. In addition, the long molecular axes in SmC* phase incline with a certain angle with respect to the layer normal as seen in smectic C (SmC) phase. SmC* molecule has a permanent dipole along the short molecular axis. Therefore, as an unique property of SmC* phase, it possesses spontaneous polarization parallel to $\mathbf{n} \times \mathbf{k}$, where $\mathbf{n}$ is the local director with unit length and $\mathbf{k}$ is the wave vector of the one-dimensional density wave. (See Figure 1) The existence of such a ferroelectric mesophase was first predicted by Meyer[1] and it was realized by him and coworkers.[2] Michelson *et al.*[3] pointed out, in a phenomenological theory, that the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions are sufficient to explain the ferroelectric ordering, which results from the

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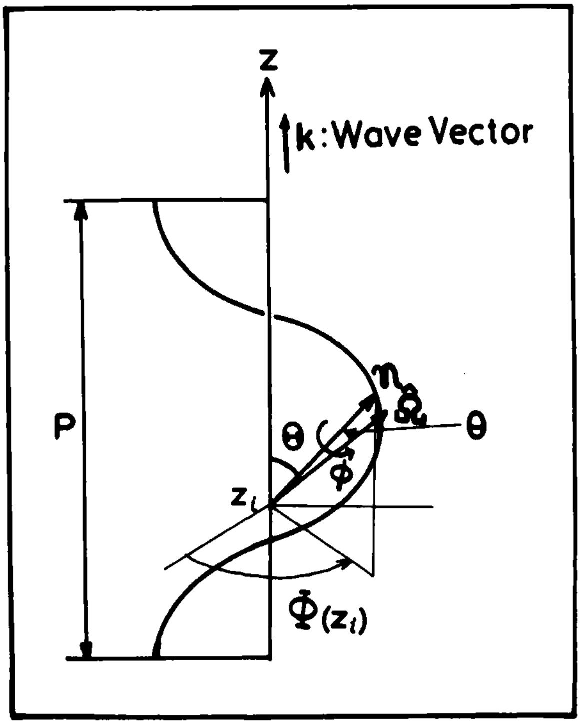

FIGURE 1 The SmC* structure. Here *n* and *k* are the local director and the wave vector normal to the smectic layers, *P* and Θ are the helical pitch and the tilt angle, respectively.

piezo- and *flexoelectric* effects.[1] *The former* is closely related to the coupling effects between the tilted director alignment and the ordering of permanent dipoles. On the other hand, *the latter* appears as a result of the uniform bend deformation of director which results from the tilted and twisted molecular alignment. On account of the direct interaction between the spontaneous polarization and an electric field, SmC* molecules respond rapidly to the applied electric field, compared with the case of the nematic liquid crystals which have usually no spontaneous polarization. From the view-point of application, a high-speed electric switching may be achieved by utilizing such ferroelectric behavior of SmC* liquid crystals.[4]

To investigate the elastic and thermal properties of SmC* liquid crystals, Pikin and Indenbom[5] formulated a phenomenological Landau-de Gennes theory on the basis of symmetry considerations. This theory was successfully applied to a variety of problems, *e.g.* elastic

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deformation under electric fields,[6,7] temperature dependence of the helical pitch,[8] SmC*-SmA (or SmC) phase transitions.[9,10] However, as is accepted nowadays,[11] Landau-de Gennes theory has several shortcomings as well as advantages in comparison with mean field treatment. That is, within the framework of phenomenological approach, there is no favorable way to relate directly the coefficients of the Landau expansion of the free energy to the intermolecular interactions between SmC* molecules in a molecular statistical manner. In addition the temperature dependences of them are to be appropriately assumed with an ambiguity. Therefore, from the theoretical point of view, it is of interest and worthwhile to derive the Landau-theory constants, which depend on the intermolecular interactions and vary with temperature, from a microscopic theory.

In the present work, we shall focus our interest on the thermally induced phase transitions of SmC* liquid crystals at a constant volume and formulate a molecular theory of them on the basis of the molecular field theories of SmA liquid crystals, developed by Senbetu and Woo,[12] and of N* liquid crystals, formulated by Lin-Liu *et al.*[13] Our approach is as follows. Firstly the free energy associated with the SmA structure is derived and minimized to determine the translational and orientational order parameters of molecules for a given temperature. Subsequently, making use of these order parameters, Landau expansion of the free energy produced by the spatial variation of director in SmC* or N* phase is obtained as a perturbation. Here the expansion coefficients are derived at a molecular level and directly related to the intermolecular interactions between SmC* molecules. Finally minimizing the Landau free energy, we can determine the tilt angle and the helical pitch at the temperature. In the present framework, as was pointed out by Meyer *et al.*,[1,2] it is assumed that the effects of the permanent dipoles of SmC* molecules may be neglected because SmC*-SmA phase transition is driven by the intermolecular forces producing the molecular tilt, and but not by the ferroelectric coupling related with the permanent dipoles. Therefore, as a first approximation, the ordering of SmC* molecules about their long axes is assumed to be uniaxial in the present approach. In addition, within the mean field approximation, we shall completely neglect the steric effects arising from the intermolecular repulsions and all of the correlations between molecules. The general theory and the Landau expansion of the free energy are presented in Section 2. The numerically calculated results are given together with several discussions on them in Section 3. Finally, Section 4 is devoted to provide several conclusions and discussions on the present approach.

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2. THEORY

2.1 Intermolecular potential

We shall put the intermolecular potential $\Phi_{\text{int}}(Q_1,Q_2)$ between the molecule 1 and 2 as follows,

$$\Phi_{\text{int}}(Q_1,Q_2) = \Phi^{\text{S}}_{\text{int}}(Q_1,Q_2) + \Phi^{\text{SB}}_{\text{int}}(Q_1,Q_2) + \Phi^{\text{C}}_{\text{int}}(Q_1,Q_2), \tag{1}$$

where $Q_i = (r_i,\Omega_i)$, r_i and $\Omega_i = (\theta_i,\phi_i)$ are the position and the orientation of ith molecule, respectively; here θ_i and ϕ_i are the polar and azimuthal angles of the molecular orientation with respect to the laboratory frame, respectively. The three components of the intermolecular interaction in the rhs of Eq. (1) are given by

$$\Phi^{\text{S}}_{\text{int}}(Q_1,Q_2) = A_{00}(r_{12}) + A_{22}(r_{12})\,P_2(\hat{\boldsymbol{\Omega}}_1\cdot\hat{\boldsymbol{\Omega}}_2) + A_{44}(r_{12})\,P_4(\hat{\boldsymbol{\Omega}}_1\cdot\hat{\boldsymbol{\Omega}}_2), \tag{2}$$

$$\Phi^{\text{SB}}_{\text{int}}(Q_1,Q_2) = A_{20}(r_{12})\cdot P_2(\hat{\mathbf{r}}_{12}\cdot\hat{\boldsymbol{\Omega}}_1) + A_{02}(r_{12})P_2(\hat{\mathbf{r}}_{12}\cdot\hat{\boldsymbol{\Omega}}_2) + A_{40}(r_{12})\cdot P_4(\hat{\mathbf{r}}_{12}\cdot\hat{\boldsymbol{\Omega}}_1) + A_{04}(r_{12})P_4(\hat{\mathbf{r}}_{12}\cdot\hat{\boldsymbol{\Omega}}_2), \tag{3}$$

$$\Phi^{\text{C}}_{\text{int}}(Q_1,Q_2) = B(\mathrm{r}_{12})\,(\hat{\boldsymbol{\Omega}}_1\times\hat{\boldsymbol{\Omega}}_2)\cdot\hat{\mathbf{r}}_{12}\,(\hat{\boldsymbol{\Omega}}_1\cdot\hat{\boldsymbol{\Omega}}_2), \tag{4}$$

where $r_{12} = r_2 - r_1$, $r_{12} = |r_{12}|$, $\hat{r}_{12} = r_{12}/r_{12}$, $\hat{\boldsymbol{\Omega}}_i$ is the unit vector pointing the direction Ω_i, $P_\ell(x)$ is the Legendre polynomial of ℓth order, and we assumed that the molecules are non-polar and uniaxial about their long axes. Here $\Phi^{\text{S}}_{\text{int}}(Q_1,Q_2)$ is the spherical part with respect to $\hat{r}_{12}$ of the intermolecular potential and contributes to the parallel alignment of molecules along the local director and also to the stability of layer structure in SmC* or SmA phase.[14] Next $\Phi^{\text{SB}}_{\text{int}}(Q_1,Q_2)$ is the symmetry-breaking component which reflects the anisotropy of the molecular shape and was first employed by Senbetu and Woo.[12] Recently, it was studied in more detail in the previous work on SmA liquid crystals.[14] It should be noted here that the effect of the symmetry-breaking component appears only in the layer structure and completely vanishes in the spatially disordered phases.[12,14]

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As will be shown later, this type of interaction is significant to produce the tilted alignment of molecules, as appearing in SmC* or SmC phase, and to drive SmC*-SmA phase transition. Finally, $\Phi^{C}_{\text{int}}(Q_1,Q_2)$ gives rise to the helical structure. This type of potential has been employed to study the temperature dependence of the helical pitch in N* phase.[13,15,16] If $B < 0$, then the helix is right-handed. On the other hand, if $B > 0$, the helix is left-handed. Apparently, the model potential expressed by Eq. (1) has the following symmetry,

$$\begin{aligned}\Phi_{\text{int}}(Q_1,Q_2) &\equiv \Phi_{\text{int}}(\mathbf{r}_{12},\hat{\boldsymbol{\Omega}}_1,\hat{\boldsymbol{\Omega}}_2)\\ &= \Phi_{\text{int}}(\mathbf{r}_{12},-\hat{\boldsymbol{\Omega}}_1,\hat{\boldsymbol{\Omega}}_2)\\ &= \Phi_{\text{int}}(\mathbf{r}_{12},\hat{\boldsymbol{\Omega}}_1,-\hat{\boldsymbol{\Omega}}_2)\\ &= \Phi_{\text{int}}(\mathbf{r}_{12},-\hat{\boldsymbol{\Omega}}_1,-\hat{\boldsymbol{\Omega}}_2)\\ &= \Phi_{\text{int}}(\mathbf{r}_{21},\hat{\boldsymbol{\Omega}}_2,\hat{\boldsymbol{\Omega}}_1). \end{aligned} \tag{5}$$

2.2 Helmholtz free energy

Let us consider the N body system in thermal equilibrium with temperature T and volume V. Here we shall consider thermally induced phase transitions at constant volume but not at constant pressure. Neglecting the excluded-volume effects, within mean field approximation, the Helmholtz free energy F_N is given by[12,14]

$$\begin{aligned}F_N = {}& \frac{\rho^2}{2}\int dQ_1 dQ_2\, f(Q_1)\, f(Q_2)\, \Phi_{\text{int}}(Q_1,Q_2)\\ &+ \rho\kappa T\int dQ_1 f(Q_1)\log f(Q_1),\end{aligned} \tag{6}$$

where $\rho = N/V$ is the average number density, κ is the Boltzmann constant, $f(Q_i)$ is the one-body distribution function of ith molecule and must satisfy the following condition,

$$\int dQ f(Q) = V. \tag{7}$$

Under the above constraint, minimizing the free energy F_N with re-

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spect to $f(Q)$, one may obtain the following integral equation for $f(Q)$,

$$\kappa T \log\{Z_1 f(Q_1)\} + \rho \int dQ_2 f(Q_2)\, \Phi_{\rm int}(Q_1, Q_2) = 0, \tag{8}$$

where Z_1 is a Lagrange multiplier which must be determined by Eq. (7). Here, in Eq. (8), putting $f(Q_1)$ into the following Boltzmann's form,

$$f(Q_1) = \exp(-\Phi_1(Q_1)/\kappa T)/Z_1, \tag{9}$$

one obtains the following expressions,

$$\Phi_1(Q_1) = \rho \int dQ_2 f(Q_2)\, \Phi_{\rm int}(Q_1, Q_2), \tag{10}$$

$$Z_1 = \frac{1}{V} \int dQ_1 \exp(-\Phi_1(Q_1)/\kappa T). \tag{11}$$

Here Φ_1 is the one-body pseudo-potential and Z_1 corresponds to the one-body partition function. Now the minimized Helmholtz free energy can be written as

$$F_N = -\frac{\rho^2}{2} \int dQ_1 dQ_2 f(Q_1) f(Q_2)\, \Phi_{\rm int}(Q_1, Q_2) - N\kappa T \log Z_1. \tag{12}$$

To study the phase transitions of SmC* liquid crystals, we shall introduce the order parameters specifying the microscopic state of the system as well as two macroscopic variables, tilt angle and helical pitch into Eqs. (9)–(12), in next subsection.

2.3 Internal energy

In this subsection, we shall introduce the order parameters of SmC* molecules and calculate the internal energy for the intermolecular potential given by Eq. (1). The total internal energy U_N consists of the three parts corresponding to those of Eq. (1). That is,

$$U_N = U_N^{\rm S} + U_N^{\rm SB} + U_N^{\rm C}, \tag{13}$$

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where

$$U_N^{\mathrm{S}} = \frac{\rho^2}{2}\int \mathrm{d}Q_1\,\mathrm{d}Q_2\, f(Q_1)\, f(Q_2)\, \Phi_{\mathrm{int}}^{\mathrm{S}}\,(Q_1,Q_2), \tag{14}$$

$$U_N^{\mathrm{SB}} = \frac{\rho^2}{2}\int \mathrm{d}Q_1,\,\mathrm{d}Q_2\, f(Q_1)\, f(Q_2)\, \Phi_{\mathrm{int}}^{\mathrm{SB}}\,(Q_1,Q_2), \tag{15}$$

$$U_N^{\mathrm{C}} = \frac{\rho^2}{2}\int \mathrm{d}Q_1\mathrm{d}Q_2\, f(Q_1)\, f(Q_2)\, \Phi_{\mathrm{int}}^{\mathrm{C}}\,(Q_1,Q_2). \tag{16}$$

To introduce the order parameters specifying the molecular alignment, we shall expand the one-body distribution function as follows, taking the layer normal as z axis,

$$f(Q_i) = \sum_{k\ell} \frac{2}{1+\delta_{k0}}\,\frac{2\ell+1}{4\,\pi}\,\langle \cos kz P_\ell\rangle \times \cos kz_i\, P_\ell\,(\hat{\boldsymbol{\Omega}}_i\cdot \boldsymbol{\eta}\,(z_i)), \tag{17}$$

where the expansion coefficients,

$$\langle \cos kz P_\ell\rangle = \frac{1}{V}\int \mathrm{d}Qf(Q)\,\cos kz P_\ell\,(\hat{\boldsymbol{\Omega}}_i\cdot \boldsymbol{\eta}\,(z_i)), \tag{18}$$

are the order parameters. Here k is the wave number and takes the values, $2\pi/d$ × (0 or integer), where d is the layer spacing. We assumed here that the helical axis coincides with z axis. Moreover, as was previously noted, we assumed the uniaxial ordering of SmC* molecules about the local director **n**, which can be now represented in terms of Cartesian components for the reference system,

$$\boldsymbol{\eta}(\eta_i) = (\eta\cos\Phi\,(z_i),\ \eta\sin\Phi\,(z_i),\ \xi), \tag{19}$$

and

$$\eta = \sin\Theta,\ \xi = \cos\Theta,\ \Phi\,(z_i) = q\,z_i,\ q = 2\pi/P. \tag{20}$$

Here Θ and P are the tilt angle of director and the helical pitch in

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SmC* structure. (See Figure 1) Thus the macroscopic variables η (or Θ) and q (or P) in SmC* structure have been related to the microscopic order parameters $\langle \cos kzP_\ell\rangle$ in similar to the case of the molecular theories of N* liquid crystals,[13,15,16] in which $\eta = 1$. Now let us set down U_N^S, U_N^{SB}, and U_N^C below. Substituting Eq. (17) into Eqs. (14), (15), and (16), with the aid of the addition theorem of spherical harmonics, one obtains, after some straightforward calculations, the following results,

$$U_N^S = \frac{N}{2}\sum_{k\ell} \tilde{A}_{\ell\ell}\,(k;\,\eta,q)\,\langle \cos kzP_\ell\rangle^2, \tag{21}$$

$$\tilde{A}_{\ell\ell}(k;\eta,q) = \frac{2}{1+\delta_{ko}}\rho\int d\mathbf{r}_{12}\cos kz_{12}P_\ell(1+\eta^2(\cos qz_{12}-1)) \times A_{\ell\ell}(r_{12}), \tag{22}$$

$$U_N^{SB} = \frac{N}{2}\sum_{k\ell}\{\tilde{A}_{\ell o}\,(k;\eta) + \tilde{A}_{o\ell}\,(k;\eta)\}\,\langle \cos kz\rangle \times \langle \cos kz\;P_\ell\rangle, \tag{23}$$

$$\tilde{A}_{\ell o}(k;\eta) = \frac{2}{1+\delta_{ko}}\,\rho\int d\mathbf{r}_{12}\,\cos kz_{12}\,P_\ell\,(\cos\beta)\,A_{\ell o}\,(r_{12}) \times P_\ell\,(\xi), \tag{24}$$

$$\tilde{A}_{o\ell}(k;\eta) = \frac{2}{1+\delta_{ko}}\,\rho\int d\mathbf{r}_{12}\,\cos kz_{12}\,P_\ell\,(\cos\beta)\,A_{o\ell}(r_{12}) \times P_\ell\,(\xi), \tag{25}$$

$$U_N^C = \frac{N}{2}\sum_{k}\tilde{B}\,(k;\eta\;q)\,\langle \cos kzP_2\rangle^2, \tag{26}$$

$$\tilde{B}(k;\eta,q) = \frac{2}{1+\delta_{ko}}\,\rho\int d\mathbf{r}_{12}\,\cos kz_{12}\,\cos\beta\,\sin qz_{12} \times B\,(r_{12})\,\eta^2\,\{1+\eta^2\,(\cos qz_{12}-1)\}; \tag{27}$$

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here $\delta_{l_1 l_2}$ is the Kronecker's δ-function, $\cos\beta = \hat{r}_{12}\cdot\hat{z}$, where $\hat{z}$ is the unit vector along z axis. It should be noted here that $\tilde{A}_{0\ell}(0;\eta) = \tilde{A}_{\ell 0}(0;\eta) = 0$. That is, as was previously mentioned, the symmetry-breaking components are efficient only in SmC* or SmA phase with positional order. Now the total internal energy U_N can be written as follows,

$$U_N = \frac{N}{2}\sum_{k\ell_1\ell_2}\{\tilde{A}_{\ell_1\ell_2}(k;\eta,q) + \tilde{B}(k;\eta,q)\,\delta_{\ell_1 2}\,\delta_{\ell_2 2}\}$$
$$\times\ \langle\cos kzP_{\ell_1}\rangle\cdot\langle\cos kzP_{\ell_2}\rangle. \tag{28}$$

Then the Helmholtz free energy F_N may be written, instead of Eq. (12), as follows,

$$F_N = -\frac{N}{2}\sum_{k\ell_1\ell_2}\{\tilde{A}_{\ell_1\ell_2}(k;\eta,q) + \tilde{B}(k;\eta,q)\,\delta_{\ell_1 2}\delta_{\ell_2 2}\}$$
$$\times\ \langle\cos kzP_{\ell_1}\rangle\cdot\langle\cos kzP_{\ell_2}\rangle \tag{29}$$
$$-\ N\kappa T\log z_1,$$

and

$$Z_1 = \frac{2\pi}{d}\int_o^d dz\int_{-1}^{+1} d(\cos\theta)\exp(-\Phi_1(z,\theta)/\kappa T), \tag{30}$$

$$\Phi_1(z,\theta) = \sum_{k\ell_1\ell_2}\{\tilde{A}_{\ell_1\ell_2}(k;\eta,q) + \tilde{B}(k;\eta,q)\delta_{\ell_1 2}\delta_{\ell_2 2}\}$$
$$\times\langle\cos kzP_{\ell_2}\rangle\cos kz\,P_{\ell_1}(\cos\theta), \tag{31}$$
$$\cos\theta = \hat{\boldsymbol{\Omega}}\cdot\boldsymbol{\eta}(z).$$

In principle, minimizing F_N expressed by Eq. (29) with respect to $\langle\cos kzP_\ell\rangle$, η, and q, one could determine them as functions of temperature. However, it is too difficult and troublesome to determine simultaneously these variables at a given temperature. Therefore, in similar to the case of N* liquid crystals,[13] in the present work we shall introduce a perturbation method as shown in next subsection.

2.4. Perturbation method

To introduce a perturbation method, we shall firstly separate the free energy F_N into two parts as follows.

$$F_N(\eta,q,\langle\cos kzP_\ell\rangle) = F_N^0(\langle\cos kz\rangle) + F_N^1(\eta,q,\langle\cos kzP_\ell\rangle), \qquad (32)$$

where

$$F_N^0(\langle\cos kzP_\ell\rangle) = F_N(0,0,\langle\cos kzP_\ell\rangle), \qquad (33)$$

$$F_N^1(\eta,q,\langle\cos kzP_\ell\rangle) = F_N(\eta,q,\langle\cos kzP_\ell\rangle) - F_N(0,0,\langle\cos kzP_\ell\rangle). \qquad (34)$$

Next, the internal energy may be also separated into two parts,

$$U_N = U_N^0 + U_N^1, \qquad (35)$$

and

$$U_N^0 = \frac{N}{2}\sum_{k\ell_1\ell_2} \tilde{A}^0_{\ell_1\ell_2}(k)\,\langle\cos kzP_{\ell_1}\rangle\,\langle\cos kzP_{\ell_2}\rangle, \qquad (36)$$

$$U_2^1 = \frac{N}{2}\sum_{k\ell_1\ell_2}\{\tilde{A}^1_{\ell_1\ell_2}(k;\eta,q) + \tilde{B}(k;\eta,q)\,\delta_{\ell_1 2}\,\delta_{\ell_2 2}\} \times \langle\cos kzP_{\ell_1}\rangle\,\langle\cos kzP_{\ell_2}\rangle, \qquad (37)$$

where, in similar to Eqs. (33) and (34), $\tilde{A}^0_{\ell_1\ell_2}$ and $\tilde{A}^1_{\ell_1\ell_2}$ are defined by

$$\tilde{A}_{\ell_1\ell_2}(k;\eta,q) = \tilde{A}^0_{\ell_1\ell_2}(k) + \tilde{A}^1_{\ell_1\ell_2}(k;\eta,q), \qquad (38)$$

$$\tilde{A}^0_{\ell_1\ell_2}(k) = \tilde{A}_{\ell_1\ell_2}(k;0,0), \qquad (39)$$

$$\tilde{A}^1_{\ell_1\ell_2}(k;\eta,q) = \tilde{A}_{\ell_1\ell_2}(k;\eta,q) - \tilde{A}_{\ell_1\ell_2}(k;0,0). \qquad (40)$$

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Making use of Eqs. (22), (24), and (25), $\tilde{A}^0_{\ell\ell}$, $\tilde{A}^1_{\ell\ell}$, $\tilde{A}^0_{\ell 0} = \tilde{A}^0_{0\ell}$, and $\tilde{A}^1_{\ell 0} = \tilde{A}^1_{0\ell}$ may be derived as

$$\tilde{A}^0_{\ell\ell}(k) = \frac{2}{1+\delta_{k0}}\,\rho \int d\mathbf{r}_{12} \cos kz_{12}\, A_{\ell\ell}(r_{12}), \tag{41}$$

$$\tilde{A}^1_{\ell\ell}(k;\eta,q) = \frac{2}{1+\delta_{k0}}\,\rho \int d\mathbf{r}_{12} \cos kz_{12}\, A_{\ell\ell}(r_{12}) \times (P_\ell(1+\eta^2(\cos q\, z_{12}-1)) - 1), \tag{42}$$

$$\tilde{A}^0_{\ell 0}(k) = \frac{2}{1+\delta_{k0}}\,\rho \int d\mathbf{r}_{12} \cos kz_{12}\, A_{\ell 0}(r_{12})\, P_\ell(\cos\beta) = \tilde{A}^0_{0\ell}(k), \tag{43}$$

$$\tilde{A}^1_{\ell 0}(k;\eta,q) = \frac{2}{1+\delta_{k0}}\,\rho \int d\mathbf{r}_{12} \cos kz_{12}\, A_{\ell 0}(r_{12}) \times P_\ell(\cos\beta)\,(P_\ell(\xi) - 1) = \tilde{A}^1_{0\ell}(k;\eta,q). \tag{44}$$

From Eq. (42), we must note that $\tilde{A}^1_{00}(k;\eta,q) = 0$ because of $P_0(x) = 1$. Similarly, the one-body pseudo-potential may be separated as

$$\Phi_1(z,\theta) = \Phi_1^0(z,\theta) + \Phi_1^1(z,\theta), \tag{45}$$

$$\Phi_1^0(z,\theta) = \sum_{k\ell_1\ell_2} \tilde{A}^0_{\ell_1\ell_2}(k)\,\langle \cos kz P_{\ell_2}\rangle \cos kz P_{\ell_1}(\cos\theta), \tag{46}$$

$$\Phi_1^1(z,\theta) = \sum_{k\ell_1\ell_2} \{\tilde{A}^1_{\ell_1\ell_2}(k;\eta,q) + \tilde{B}(k;\eta,q)\,\delta_{\ell_1 2}\,\delta_{\ell_2 2}\} \times \langle \cos kz P_{\ell_2}\rangle \cos kz P_{\ell_1}(\cos\theta). \tag{47}$$

Now F_N may be given by

$$F_N = -(U_N^0 + U_N^1) - N\kappa T \log Z_1, \tag{48}$$

$$Z_1 = \frac{2\pi}{d}\int_0^d dz \int_{-1}^{+1} d\,(\cos\theta)\,\exp\{-(\Phi_1^0 + \Phi_1^1)/\kappa T\}. \tag{49}$$

Here comparing Eqs. (32) and (48), one finds

$$F_N^0 = -U_N^0 - N\kappa T\log Z_1^0, \tag{50}$$

$$F_N^1 = -U_N^1 - N\kappa T\log(Z_1 / Z_1^0), \tag{51}$$

where

$$Z_1^0 = \frac{2\pi}{d}\int_0^d dz \int_{-1}^{+1} d(\cos\theta)\,\exp(-\Phi_1^0(z,\theta)/\kappa T). \tag{52}$$

Provided that we regard the free energy F_N^1 associated with the tilted and twisted structure as a perturbation in comparison with F_N^0, from Eq. (51) F_N^1 reduces to U_N^1 as follows,

$$F_N^1 \approx U_N^1. \tag{53}$$

Now we can determine the microscopic order parameters $\langle\cos kzP_\ell\rangle$ and the macroscopic variables, η and q, in terms of the following relations,

$$\left(\frac{\partial F_N^0}{\partial\langle\cos kzP_\ell\rangle}\right)_{\rho,T} = 0, \tag{54}$$

i.e.

$$\langle\cos kzP_\ell\rangle = \frac{2\pi}{d}\int_0^d dz \int_{-1}^{+1} d(\cos\theta)\,\exp(-\Phi_1^0/\kappa T) \times \cos kzP_\ell(\cos\theta)/Z_1^0, \tag{55}$$

and

$$\left(\frac{\partial F_N^1}{\partial\eta}\right)_{q,\,\langle\cos kzP_\ell\rangle} = \left(\frac{\partial F_N^1}{\partial q}\right)_{\eta,\,\langle\cos kzP_\ell\rangle} = 0, \tag{56}$$

respectively. Since F_N^0 does not involve the macroscopic variables, η and q, our approach may be separated into the following two steps.

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Firstly we determine the translational and orientational order parameters at a given temperature from Eqs. (50) and (55). Next, making use of these order parameters, we can determine the corresponding values of η and q from Eq. (56). In next subsection, we shall expand the free energy F_N^1 as a power series of η and q, i.e. obtain the Landau expansion of the free energy and compare it with that formulated by Pikin and Indenbom.[5]

2.5. Landau expansion of the free energy

To calculate the coefficients, $\tilde{A}^0_{\ell_1\ell_2}$, $\tilde{A}^1_{\ell_1\ell_2}$, and $\tilde{B}$ defined by Eqs. (41) – (44), and (27), in practice, we take simply Gaussian[12,17] and put

$$A_{\ell_1\ell_2}(r_{12}) = -a_{\ell_1\ell_2} \exp(-r_{12}^2 / r_0^2),$$

$$(\ell_1, \ell_2 = 0,2,4), \tag{57}$$

$$B(r_{12}) = -b \exp(-r_{12}^2 / r_0^2), \tag{58}$$

where r_0 is the effective range of the attractive interactions which is the order of the molecular length. Substituting Eq. (57) into Eqs. (41) and (43), the coefficients $\tilde{A}^0_{\ell\ell}$ and $\tilde{A}^0_{\ell 0} = \tilde{A}^0_{0\ell}$ can be immediately calculated. Here we must note that in real systems $0 \leqq \eta = \sin\Theta \leqq 1$ and $P \gg r_0$. Therefore we may expand F_N^1 as a series of the macroscopic variables, η and $Q = q \cdot r_0 \ll 1$. After some straightforward algebra, one finds the Landau free energy f_1,

$$\begin{aligned} f_1 \equiv \frac{F_N^1}{V} = \frac{\rho}{2}\{&\alpha_{22}\eta^2Q^2 + \alpha_{24}\eta^2Q^4 + \alpha_{44}\eta^4Q^4 \\ &+ 2\alpha_{20}\eta^2 + 2\alpha_{40}\eta^4 + \beta_{21}\eta^2Q \\ &+ \beta_{23}\eta^2Q^3 + \beta_{43}\eta^4Q^3 + \beta_{25}\eta^2Q^5\}, \end{aligned} \tag{59}$$

where we retained the terms η^mQ^n such that $m + n \leqq 8$, and the coefficients, $\alpha_{\ell_1\ell_2}$ and $\beta_{\ell_1\ell_2}$, were defined as

$$\alpha_{22} = \sum_k \sum_{\ell=0}^{4} a_{\ell\ell}^{22}(k) \langle \cos kzP_\ell \rangle^2, \tag{60}$$

$$\alpha_{24} = \sum_k \sum_{\ell=0}^{4} a_{\ell\ell}^{24}(k) \langle \cos kzP_\ell \rangle^2, \tag{61}$$

$$\alpha_{44} = \sum_{k} \sum_{\ell=0}^{4} a^{44}_{\ell\ell}(k)\, \langle \cos kz P_\ell \rangle^2, \tag{62}$$

$$\alpha_{20} = \frac{1}{2} \sum_{k} \sum_{\ell=2}^{4} (a^{20}_{\ell 0}(k) + a^{20}_{0\ell}(k))\, \langle \cos kz \rangle \times \langle \cos kz P_\ell \rangle, \tag{63}$$

$$\alpha_{40} = \frac{1}{2} \sum_{k} (a^{40}_{40}(k) + a^{40}_{04}(k))\, \langle \cos kz \rangle \times \langle \cos kz P_4 \rangle, \tag{64}$$

$$\beta_{21} = \sum_{k} b^{21}(k)\, \langle \cos kz P_2 \rangle^2, \tag{65}$$

$$\beta_{23} = \sum_{k} b^{23}(k)\, \langle \cos kz P_2 \rangle^2, \tag{66}$$

$$\beta_{43} = \sum_{k} b^{43}(k)\, \langle \cos kz P_2 \rangle^2, \tag{67}$$

$$\beta_{25} = \sum_{k} b^{25}(k)\, \langle \cos kz P_2 \rangle^2. \tag{68}$$

Here the coefficients $a^{mn}_{\ell_1\ell_2}$ and b^{mn} are formulated in Appendix. Now we shall consider symmetry of the free energy density f_1 expressed by Eq. (59). One can easily see

$$f_1(\eta, Q) = f_1(-\eta, Q), \tag{69}$$

$$f_1(\eta, Q) \neq f_1(\eta, -Q). \tag{70}$$

That is, SmC* liquid crystals show the bistability with respect to the molecular tilt and have not mirror plane in similar to N* ones but the inherent chirality.

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At this stage, we shall compare the above obtained free energy density with that formulated by Pikin and Indenbom,[5] which may be simply written as follows,

$$\begin{aligned} f = \alpha\Theta^2 + \beta\Theta^4 + \frac{K}{2}\,\Theta^2 q^2 \\ + \lambda\Theta^2 q, \end{aligned} \tag{71}$$

and

$$\alpha = a^0\,(T/T_1 - 1), \qquad \beta > 0, \tag{72}$$

where a^0 is a positive constant, T_1 is the Curie temperature, and we completely neglected the terms related to the ferroelectric coupling. Comparing Eqs. (59) and (71), and putting $\eta = \sin\Theta \sim \Theta$, one finds the following correspondences.

$$\rho\,\alpha_{20} \longleftrightarrow \alpha, \tag{73}$$

$$\rho\,\alpha_{40} \longleftrightarrow \beta, \tag{74}$$

$$\rho\,\alpha_{22} \longleftrightarrow K/r_o^2, \tag{75}$$

$$\rho\,\beta_{21} \longleftrightarrow 2\,\lambda/r_o. \tag{76}$$

From the above correspondences, the following must be noted. Firstly, it should be born in mind that the tilted molecular alignment is supported by the symmetry-breaking components α_{20} and α_{40}, or A_{20} $(=A_{02})$ and A_{40} $(=A_{04})$ in Eq. (3), as was previously noted. Next one finds that the SmC*-SmA phase transitions may be driven by the temperature dependence of α_{20} corresponding to α in Eq. (71). The temperature dependence of α_{20} will be shown in Section 4. In addition, as can be easily seen from Eqs. (63) and (64), the thermal fluctuation of the orientations of molecules is essential to give rise to SmC*-SmA phase transitions rather than that of the translational order. In fact, in a perfectly aligned system without thermal fluctuation of the orientations of molecules, SmC*-SmA phase transition will not occur because of the similar temperature dependences of α_{20} and α_{40} as can be readily seen from Eqs. (63) and (64) together with $a_{20}^{mn}(0) = a_{40}^{mn}(0) = 0$. In other words, the difference between the

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temperature dependences of $\langle \cos kzP_2\rangle$ and $\langle \cos kzP_4\rangle$ is significant to drive SmC*-SmA phase transitions. The coefficient α_{22} corresponds to the elastic constant of the twist and bend deformations, K. Finally, α_{21} corresponds to the constant λ, which is the modulus of the Lifschitz invariant.[5] Thus we have derived the Landau-theory constants at a molecular level. In next section, we shall investigate the effects of each intermolecular interaction on SmC*-SmA-N*-I phase transitions and show the temperature dependences of the microscopic order parameters $\langle \cos kzP_\ell\rangle$, and the macroscopic variables, η and Q.

3. RESULTS

We shall provide the numerically calculated results in this section. For mathematical tractability, we shall retain only the order parameters corresponding to $(k, \ell) = (0, 2)$, $(0, 4)$, $(\bar{k}, 0)$, $(\bar{k}, 2)$, and $(\bar{k}, 4)$, where $\bar{k} = 2\pi / d$ is the fundamental wave number of the one-dimensional density wave. Therefore there are five order parameters, $\langle \cos\bar{k}z\rangle$, $\langle \cos\bar{k}zP_2\rangle$, $\langle \cos\bar{k}zP_4\rangle$, $\langle P_2\rangle$, and $\langle P_4\rangle$, specifying the translational and orientational orders of the molecules. These values must be self-consistently determined in terms of Eq. (55) for a given temperature, comparing the free energies computed by Eq. (50) for the following three cases,

(I) $\langle \cos\bar{k}z\rangle \neq 0$, $\langle \cos\bar{k}zP_2\rangle \neq 0$, $\langle \cos\bar{k}zP_4\rangle \neq 0$,
$\langle P_2\rangle \neq 0$, $\langle P_4\rangle \neq 0$. (Smectic State)

(II) $\langle \cos\bar{k}z\rangle = 0$, $\langle \cos\bar{k}zP_2\rangle = 0$, $\langle \cos\bar{k}zP_4\rangle = 0$,
$\langle P_2\rangle \neq 0$, $\langle P_4\rangle \neq 0$. (Nematic State)

(III) $\langle \cos\bar{k}z\rangle = 0$, $\langle \cos\bar{k}zP_2\rangle = 0$, $\langle \cos\bar{k}zP_4\rangle = 0$,
$\langle P_2\rangle = 0$, $\langle P_4\rangle = 0$. (Isotropic State)

These order parameters are substituted into Eqs. (60)–(68) to determine the corresponding values of η and Q from Eqs. (56) and (59).

Before showing the effects of the potential coefficients, $a_{\ell_1\ell_2}$ and b, on the molecular ordering of the system, let us consider the role of them. The coefficient a_{00} represents the spherical component of the intermolecular interactions and contributes to the thermal stability of the layer structure in smectic phase.[14,17,18] The coefficient a_{22} which supports parallel alignment of molecules must be the most dominant one of the interactions because such nematic order exists over wide mesomorphic temperature range, i.e. in SmC*, SmA, and N* phases.

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The coefficient a_{44} becomes large with increasing octapole-octapole interaction as the molecular length increases. The symmetry-breaking components, a_{20} ($=a_{02}$) and a_{40} ($=a_{04}$), must be negative in the case of the rod-like molecules.[12,14,20] As was previously noted, $b > 0$ for the right-handed helix and $b < 0$ for the left-handed one. For the sake of convenience, we shall introduce the normalized quantities as follows,

$$\alpha^*_{mn} = \alpha_{mn}/(\rho^* a_{22}), \beta^*_{mn} = \beta_{mn}/(\rho^* a_{22}),$$

$$a^*_{00} = a_{00}/a_{22}, a^*_{44} = a_{44}/a_{22},$$

$$a^*_{02} = a_{02}/a_{22}, a^*_{20} = a_{20}/a_{22},$$

$$a^*_{04} = a_{04}/a_{22}, a^*_{40} = a_{40}/a_{22},$$

$$b^* = b/a_{22}, \rho^* = \rho \cdot r_0^3, T^* = \kappa T/(\rho^* a_{22}),$$

$$C_V^* = \left(\frac{dU_N^{*0}}{dT^*}\right)_{\rho^*}, U_N^{*0} = U_N^0/(N\rho^* a_{22}),$$

$$d^* = d/r_0,$$

$$K^* = \alpha_{22}/(\rho^* a_{22}), (a_{22} > 0) \tag{77}$$

where C_V^* and K^* are the normalized specific heat at constant volume and the normalized elastic constant, respectively.

Now we shall show the numerically calculated results for the microscopic order parameters $\langle \cos kzP_l \rangle$ and the macroscopic variables, η and Q, and the effects of each coefficient of the intermolecular potential on the phase transitions.

First of all we shall show the effects of the symmetry-breaking component, a^*_{04} ($=a^*_{40}$). The results for Nos. 1–6 in Table I are given in Figures 2 (a)–(f). With increasing $|a^*_{04}|$, one finds that the smectic-nematic transition temperature tends to be decreased, whereas the nematic-isotropic transition one remains to be constant because $\bar{A}^0_{04}$ ($=\bar{A}^0_{40}$) vanishes in nematic state. In addition the increase of $|a^*_{04}|$ diminishes not only the translational order but also the orientational one along layer normal. Consequently, the temperature range of the nematic state increases with increasing $|a^*_{04}|$. For Nos. 1, 2, and 5, SmA phase appears and the SmC*-SmA phase transitions seem to

TABLE I

The model parameters.

No.	d^*	a^*_{00}	a^*_{02}	a^*_{04}	a^*_{44}	b^*
1	3.0	0.1	−0.1	−0.23	0.1	0.1
2	3.0	0.1	−0.1	−0.25	0.1	0.1
3	3.0	0.1	−0.1	−0.3	0.1	0.1
4	3.0	0.1	−0.1	−0.5	0.1	0.1
5	5.0	0.1	−0.1	−0.65	0.1	0.1
6	5.0	0.1	−0.1	−1.0	0.1	0.1
7	3.0	0.1	−0.09	−0.25	0.1	0.1
8	3.0	0.1	−0.11	−0.25	0.1	0.1
9	3.0	0.09	−0.1	−0.25	0.1	0.1
10	3.0	0.11	−0.1	−0.25	0.1	0.1
11	2.8	0.1	−0.1	−0.25	0.2	0.1
12	3.0	0.1	−0.1	−0.25	0.2	0.1
13	2.95	0.1	−0.1	−0.1	0.1	0.1
14	3.05	0.1	−0.1	−0.1	0.1	0.1
15	3.0	0.1	−0.1	−0.1	0.1	0.08
16	3.0	0.1	−0.1	−0.1	0.1	0.12

be almost second-order ones with η going continuously to 0. On the other hand, for Nos. 3, 4, and 6, SmA phase disappears and the first-order SmC*-N* (or I) transitions occur. With increasing temperature, Q slightly decreases and increases in SmC* and N* phases, respectively.

Next we shall show the effects of another symmetry-breaking component a^*_{02}, which contributes to the parallel alignment of molecules

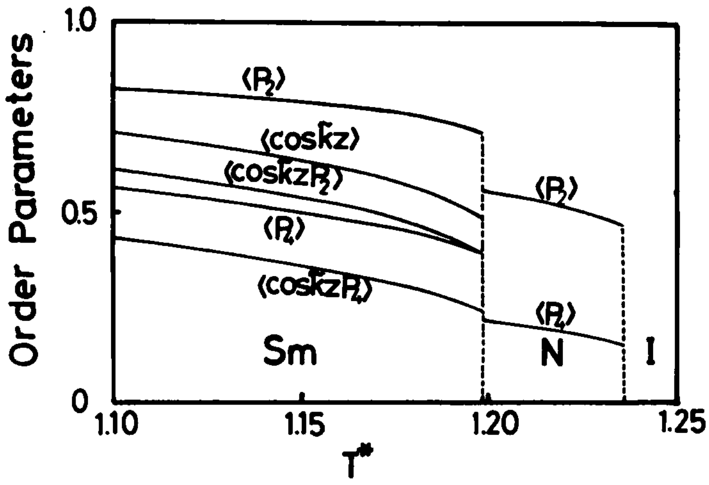

FIGURE 2(a)1 The order parameters for No. 1.

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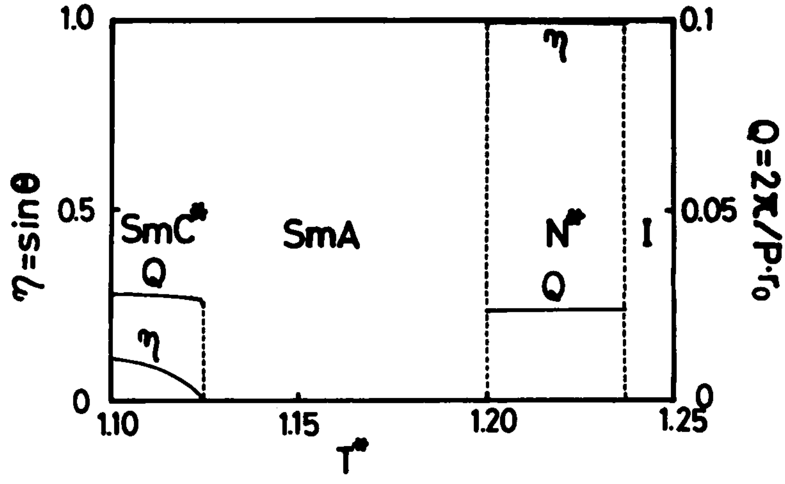

FIGURE 2(a)2 The macroscopic variables for No. 1.

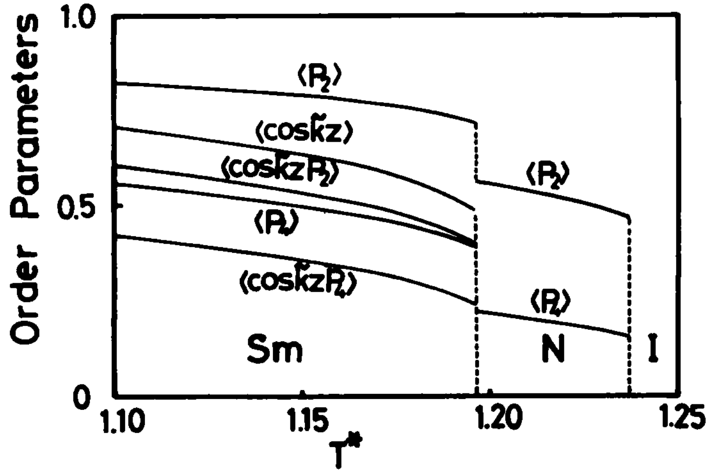

FIGURE 2(b)1 The order parameters for No. 2.

along the layer normal, in Figures 2 (g) and (h). These results are for Nos. 7 and 8 in Table I. With the increase of $|a_{02}^*|$, the smectic phase becomes to be stabilized.[12,14] At the same time, the molecular tilt angle tends to be decreased with the increase of $|a_{02}^*|$. Therefore the symmetry-breaking components a_{02}^* and a_{04}^* result in the opposite effects for the thermal stability of smectic phase and the molecular ordering along the layer normal, and support the tilted alignment.

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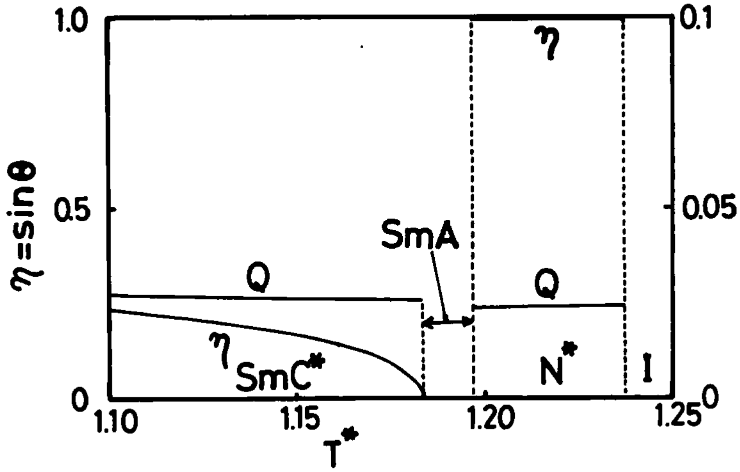

FIGURE 2(b)2 The macroscopic variables for No. 2.

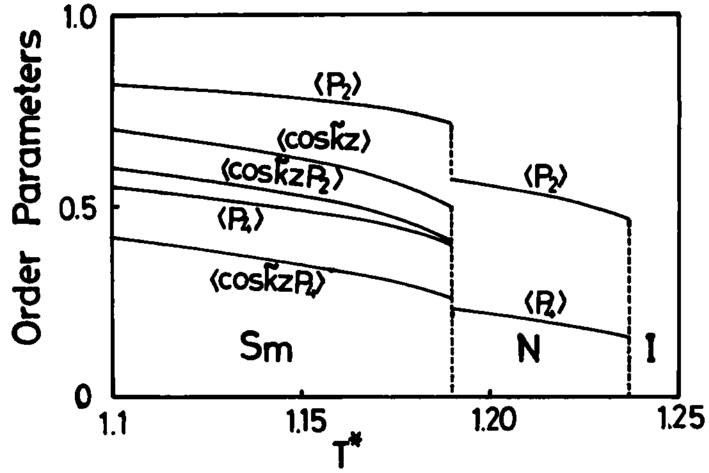

FIGURE 2(c)1 The order parameters for No. 3.

Next we shall show the effect of the coefficient a_{00}^*, for Nos. 9 and 10 in Table I, in Figures 2(i) and (j). With increasing a_{00}^*, the smectic phase tends to be stabilized,[14,17,18] and both the SmC*-SmA and SmA-N* phase transition temperatures are increased. Since, of course, $\langle \cos\tilde{k}z \rangle$ vanishes in N* phase, the N*-I phase transition temperature is not affected by a_{00}^*.

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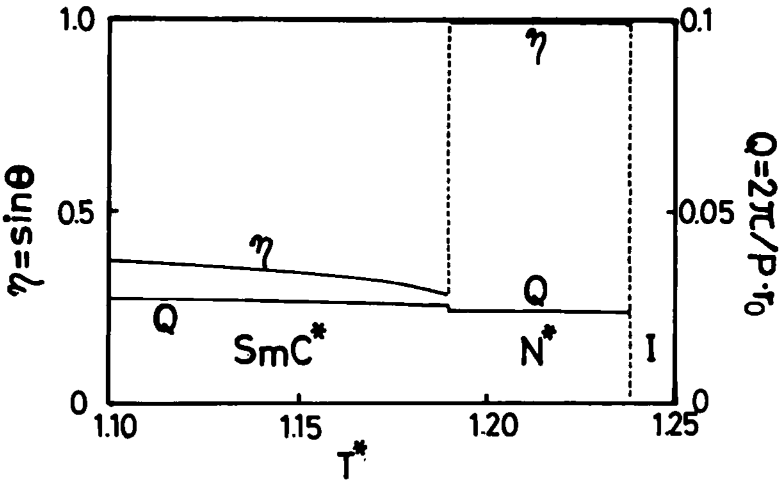

FIGURE 2(c)2 The macroscopic variables for No. 3.

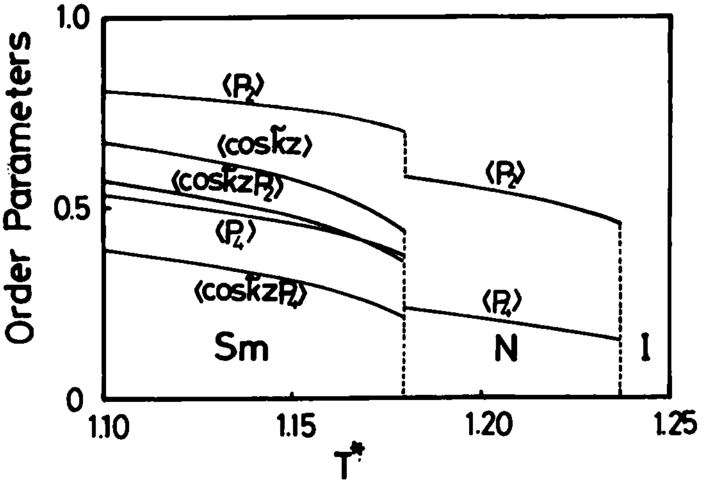

FIGURE 2(d)1 The order parameters for No. 4.

Let us now present the effect of the layer spacing in Figures 2(k)–(n). According to McMillan,[17] the increase of the layer spacing d^* corresponds to the increase of the molecular length. With the increase of d^*, N* phase disappears because of the stabilization of smectic phase as shown in Figure 2 (l), whereas it still appears in Figure 2(n). In addition, comparing Figures 2(b) and (l), one finds that with in-

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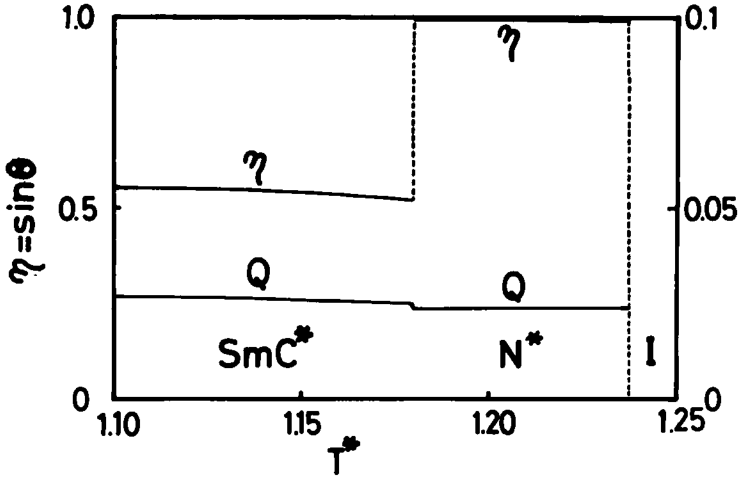

FIGURE 2(d)2 The macroscopic variables for No. 4.

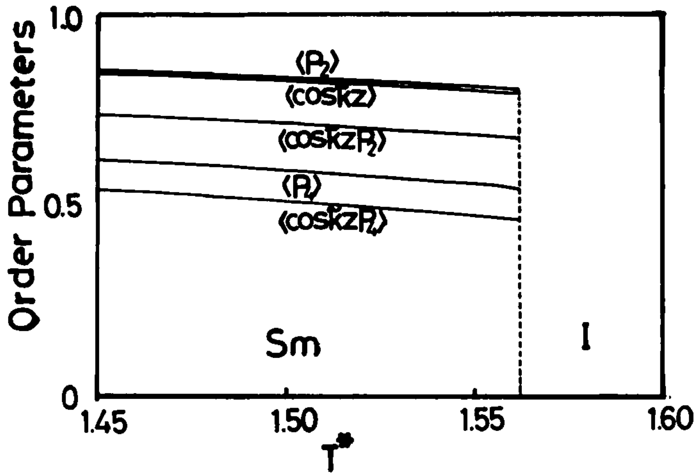

FIGURE 2(e)1 The order parameters for No. 5.

creasing a_{44}^* the smectic phase tends to be more stabilized than nematic phase.

Finally we shall show the effects of the chiral coefficient b^* in Figures 2 (o) and (p). From this result, as can be expected in terms of Eq. (59), one finds the relation $Q \propto b^*$ in SmC* and N* phases.

In the above obtained results, as a whole, with increasing temperature Q slightly decreases and increases in SmC* and N* phases,

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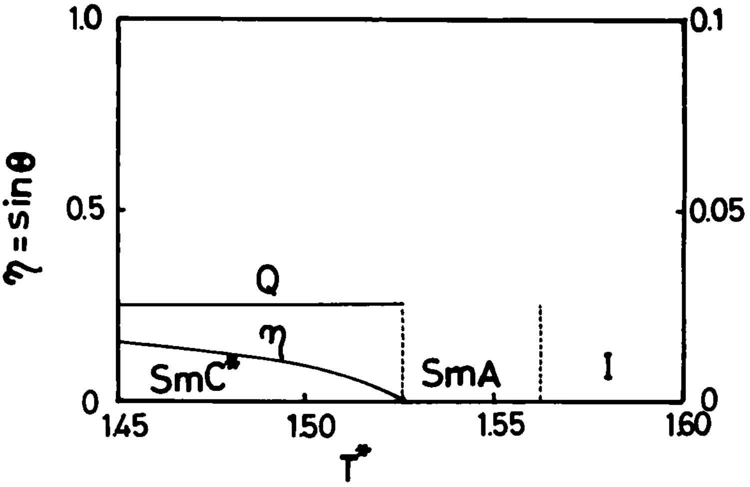

FIGURE 2(e)2 The macroscopic variables for No. 5.

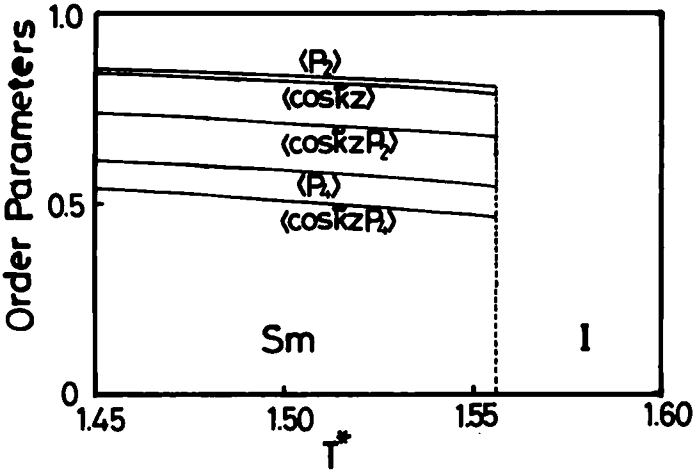

FIGURE 2(f)1 The order parameters for No. 6.

respectively. In addition, SmC*-SmA phase transitions seem to be almost second-order, whereas SmC* (or SmA)-N* (or I) phase transitions are apparently first-order. Through the above computations, it was numerically found that F_N^0 is always larger than F_N^1 by about order of 2. Therefore the perturbation method presently used may be justified. To investigate further the effects of these interaction parameters on the phase transitions, we must study the correspond-

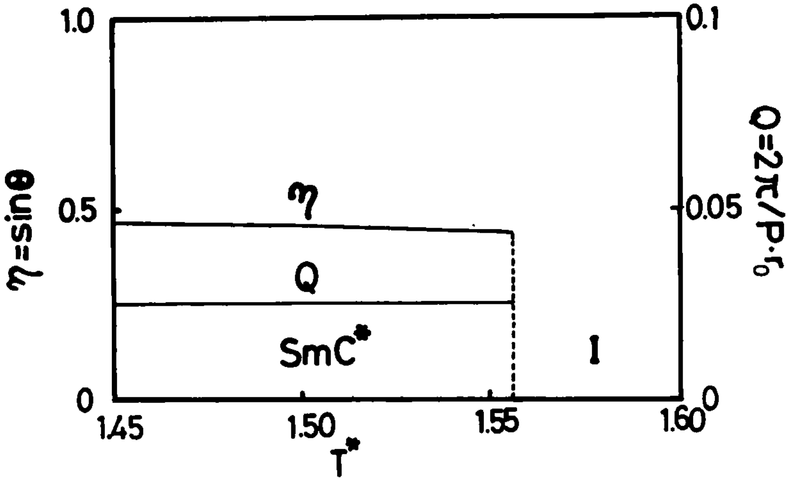

FIGURE 2(f)2 The macroscopic variables for No. 6.

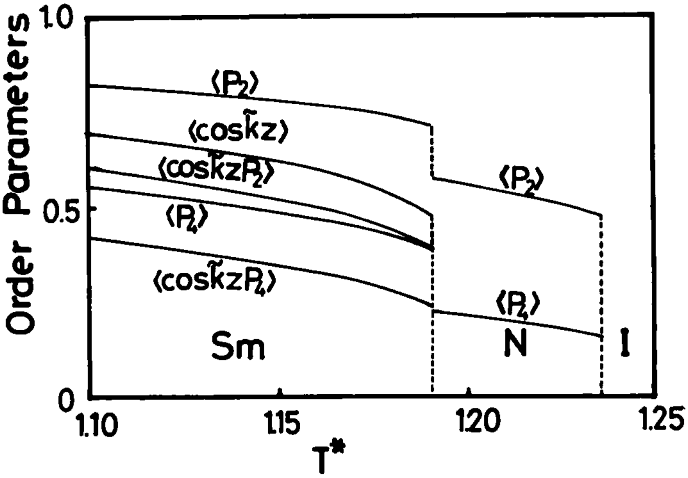

FIGURE 2(g)1 The order parameters for No. 7.

ence between the molecular shapes or the molecular structures and the potential coefficients in detail. However, this problem is beyond the scope of the present work and will not be mentioned any more in this paper.

Finally we shall show the temperature dependences of the elastic constant and the specific heat for Nos. 2,5, and 11 in Figures 3(a)–

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(c). The elastic constant K^* decreases with increasing temperature, showing discontinuities at Sm-N, N-I, and Sm-I transition points. It should be noted that the apparent value of the elastic constant η^2K^* must more rapidly change by the factor η^2 in SmC* phase than that in N* phase where $\eta = 1$.

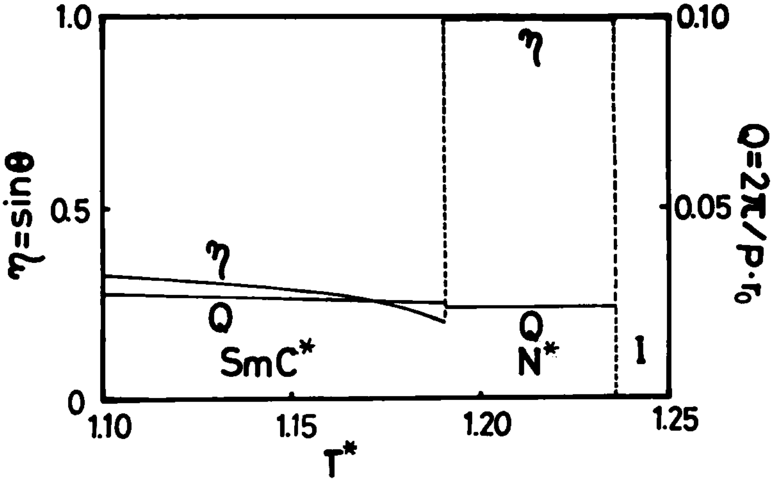

FIGURE 2(g)2 The macroscopic variables for No. 7.

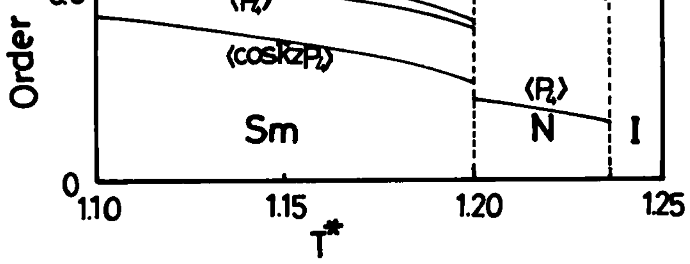

FIGURE 2(h)1 The order parameters for No. 8.

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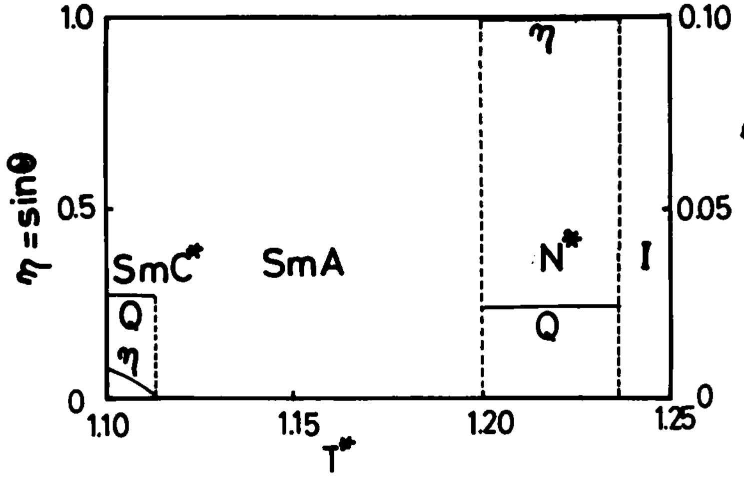

FIGURE 2(h)2 The macroscopic variables for No. 8.

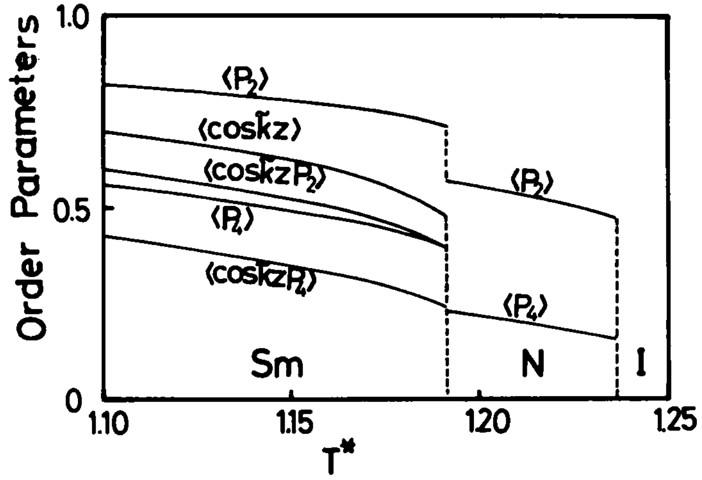

FIGURE 2(i)1 The order parameters for No. 9.

4. DISCUSSIONS AND CONCLUSIONS

We have shown a molecular theory of SmC* liquid crystals and investigated the effects of the potential coefficients on the phase transitions of them. From the numerically calculated results, one finds that SmC*-SmA phase transitions are almost second-order, where the tilt angle Θ vanishes continuously to 0 as temperature increases,

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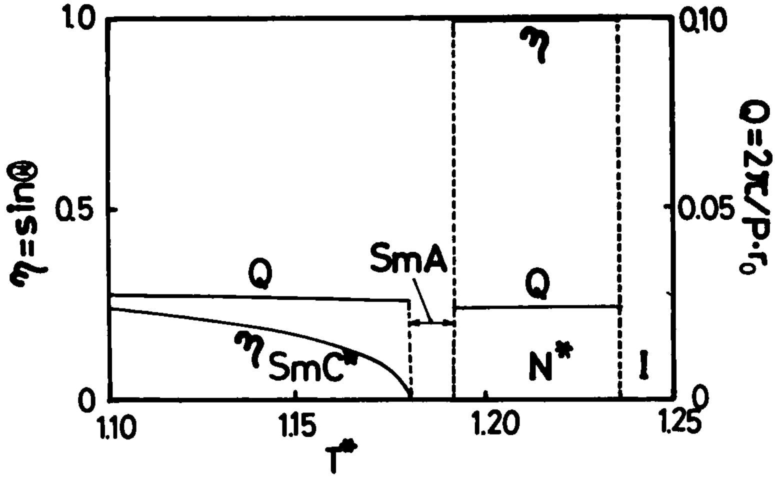

FIGURE 2(i)2 The macroscopic variables for No. 9.

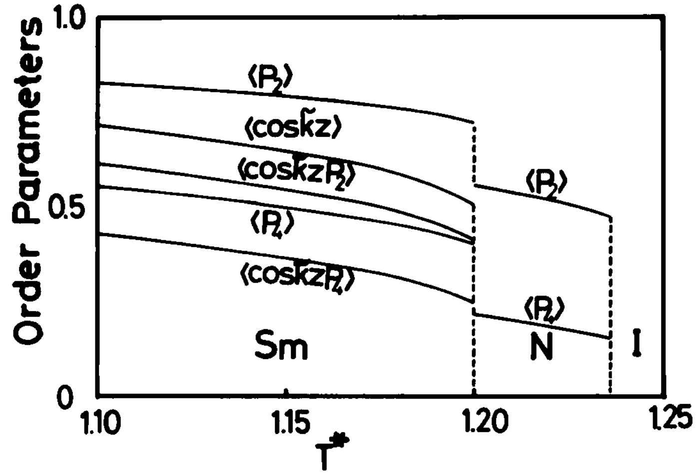

FIGURE 2(j)1 The order parameters for No. 10.

whereas SmC* (or SmA)-N* (or I) phase transitions are apparently first-order. In addition it is also found that the helical pitch slightly increases and decreases in SmC* and N* phases, respectively, in qualitative agreement with the experimental findings.[21-25]

Now we shall compare the critical exponents of η and Q obtained in the present approach with those in experiments. Let us denote SmC*-SmA transition temperature as T_c. In Figure 4 we shall show the experimental result for DOBAMBC by Ostrovskii *et al.*[24] From

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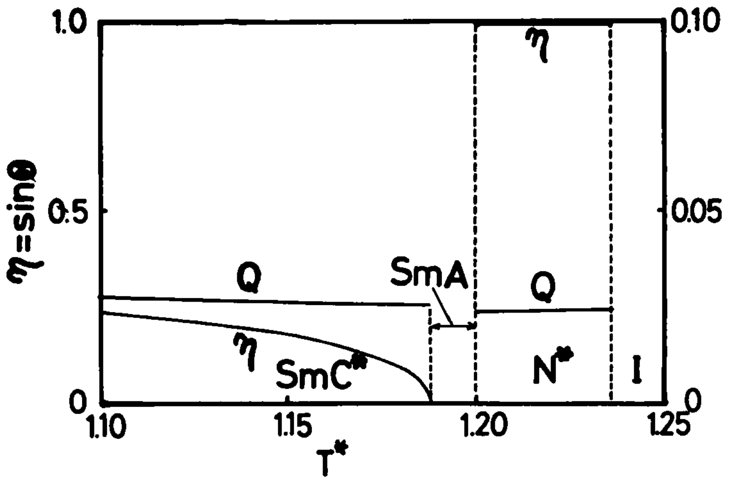

FIGURE 2(j)2 The macroscopic variables for No. 10.

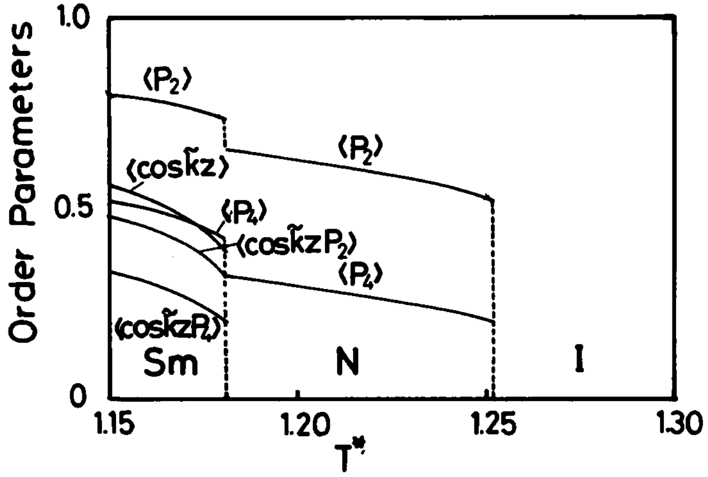

FIGURE 2(k)1 The order parameters for No. 11.

this, one finds that η and Q do not simply change according to $\eta_0(1 - T/T_c)^\alpha$ and $Q_0(1 - T/T_c)^\beta$ over SmC* temperature range, respectively. Here α and β are critical exponents, and η_0 and Q_0 are constants. For reference the values of α and β may be estimated as 0.32 and 0.28 at $T/T_c = 0.99$, respectively. On the other hand, for Nos. 2 and 5 in Table I, we shall show the corresponding temperature dependences in Figures 5(a) and (b). The critical exponents α and β are

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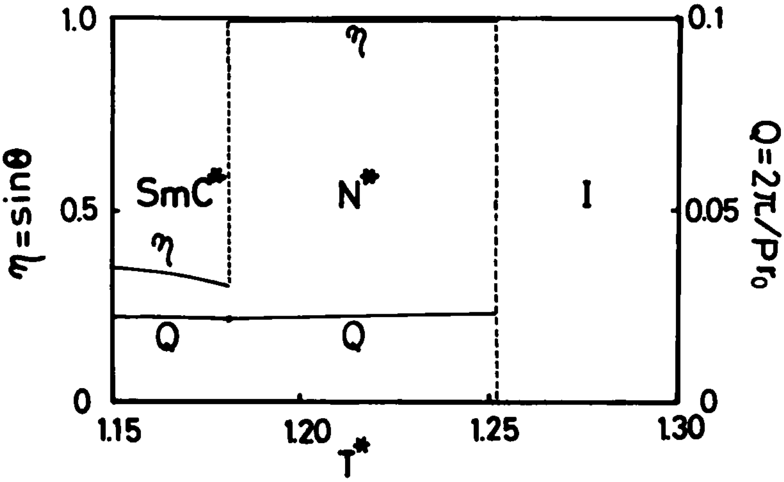

FIGURE 2(k)2 The macroscopic variables for No. 11.

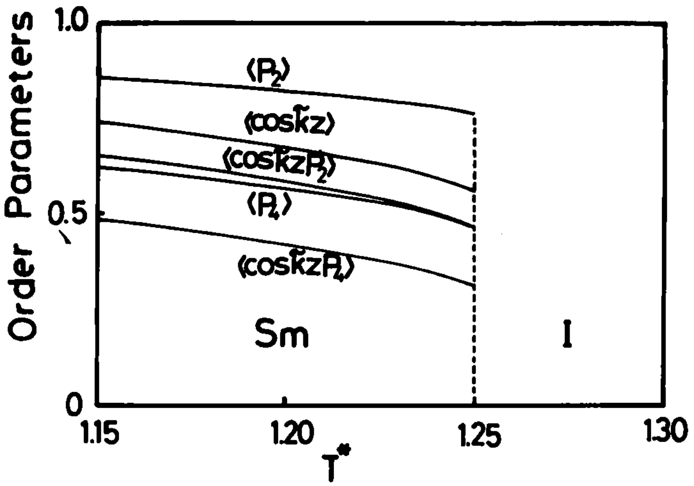

FIGURE 2(l)1 The order parameters for No. 12.

equal to 0.40 and 0.024 for No. 2 and to 0.57 and 0.004 for No. 5, respectively. The qualitative agreement could be found for α but not for β. This discrepancy for β is considered as a result of disregard of the higher order interaction which must be involved in Eq. (3). In fact, Lin-Liu *et al.*[13] pointed out theoretically the significance of the higher order component to explain the abrupt change with temperature of helical pitch in N* phase.

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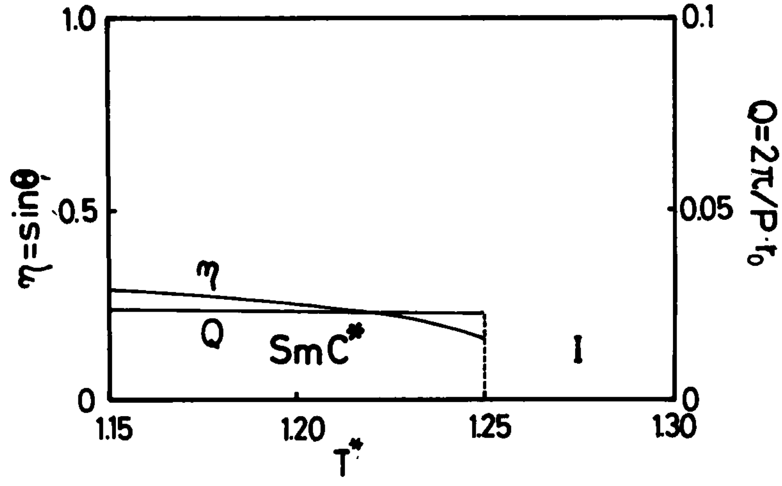

FIGURE 2(l)2 The macroscopic variables for No. 12.

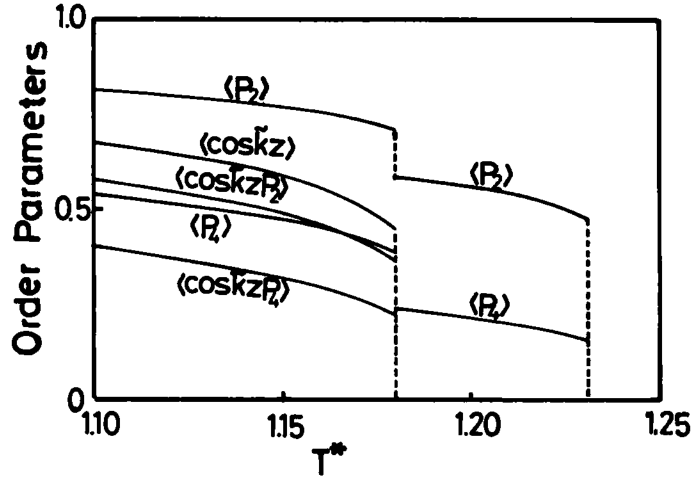

FIGURE 2(m)1 The order parameters for No. 13.

Finally we shall present the temperature dependences of the coefficients α_{20}^*, α_{40}^*, and β_{21}^* in Figures 6(a)–(c) for Nos. 2, 5, and 11. From these results one finds that α_{40}^* and β_{21}^* also critically depend on temperature as well as α_{20}^*. Therefore the temperature dependences of α_{40}^* and β_{21}^*, which are neglected in the phenomenological theory by Pikin and Indenbom,[5] seem to be important to study the phase transitions of SmC* liquid crystals. Here, in similar to α in

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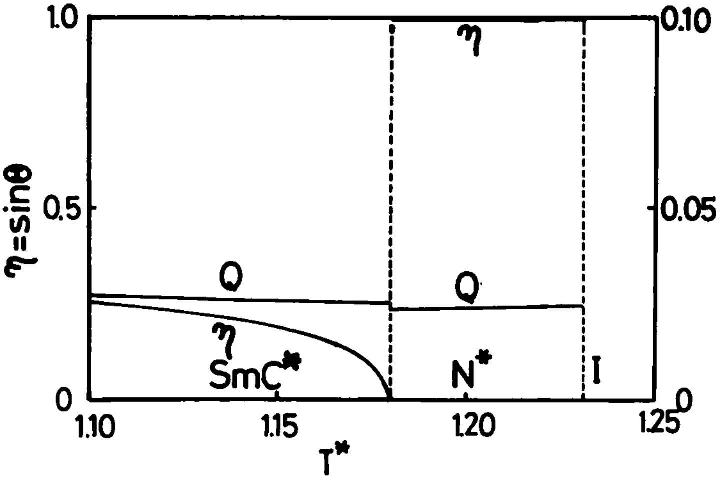

FIGURE 2(m)2 The macroscopic variables for No. 13.

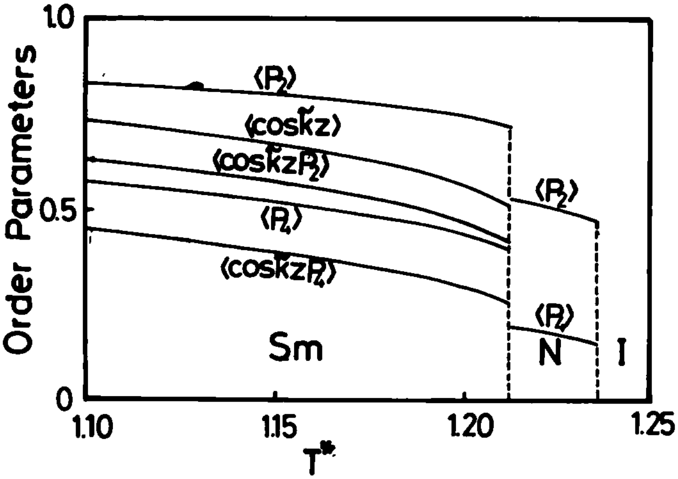

FIGURE 2(n)1 The order parameters for No. 14.

Eq. (71), α_{20}^* approximately varies with temperature according to $a^0(T/T_1 - 1)$ near the SmC*-SmA transition points.

In the present treatment we assumed $Q \ll 1$, so that we can not study the abrupt decrease of the helical pitch in SmC* phase prior to SmC*-SmA phase transition as was experimentally observed by Kondo *et al.*[21] and explained by Yamashita and Kimura[8] making use of the phenomenological theory. To treat this problem, we must

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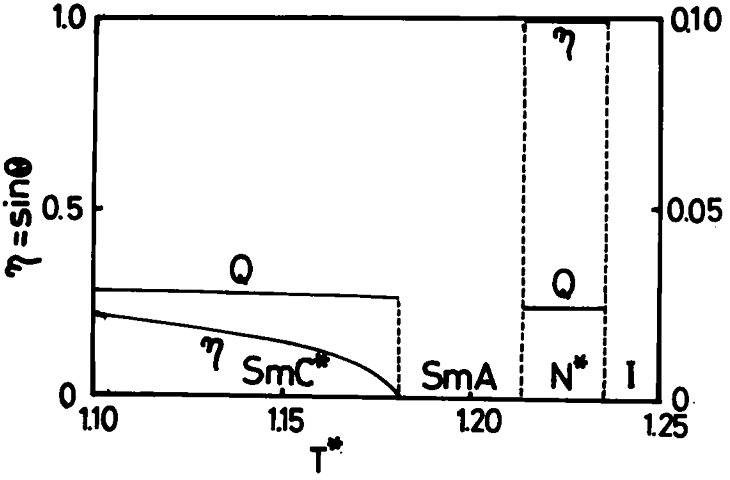

FIGURE 2(n)2 The macroscopic variables for No. 14.

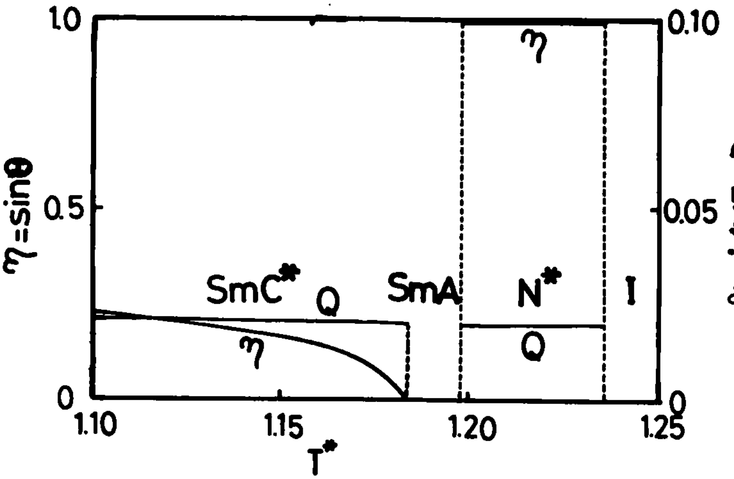

FIGURE 2(o) The macroscopic variables for No. 15.

minimize the free energy by Eq. (29) with respect to $<\cos kzP_l>$, η, and Q without making use of the Landau expansion of the free energy, whose validity is ensured only in the case $Q \ll 1$. These problems will be studied and reported in the future, together with the effects of the ferroelectric coupling.

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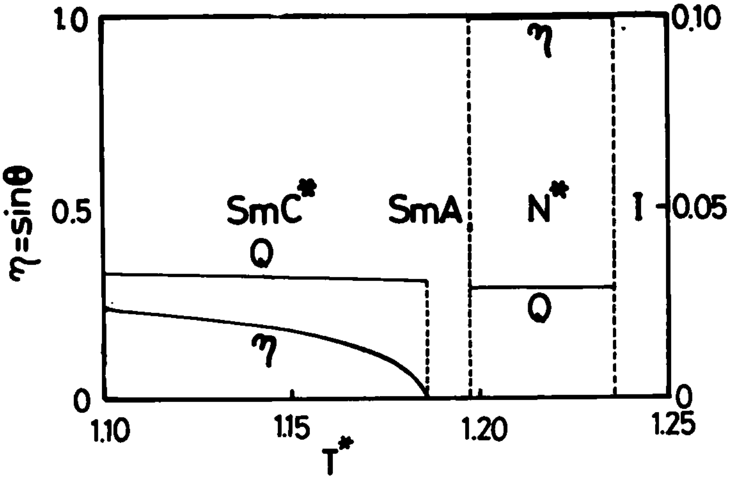

FIGURE 2(p) The macroscopic variables for No. 16.

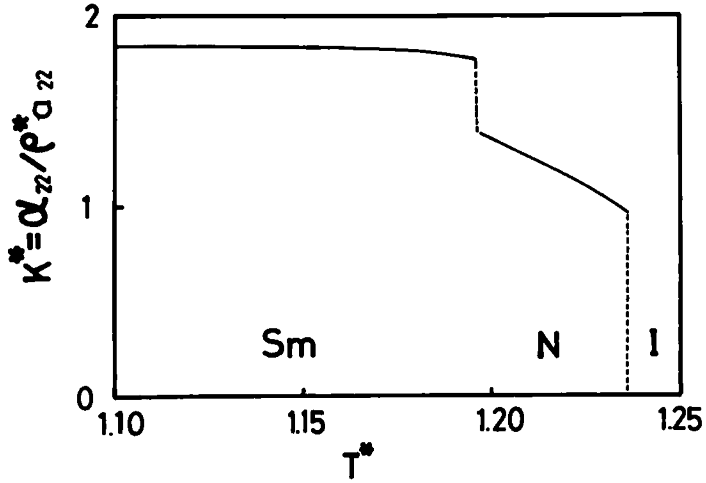

FIGURE 3(a)1 The elastic constant for No. 2.

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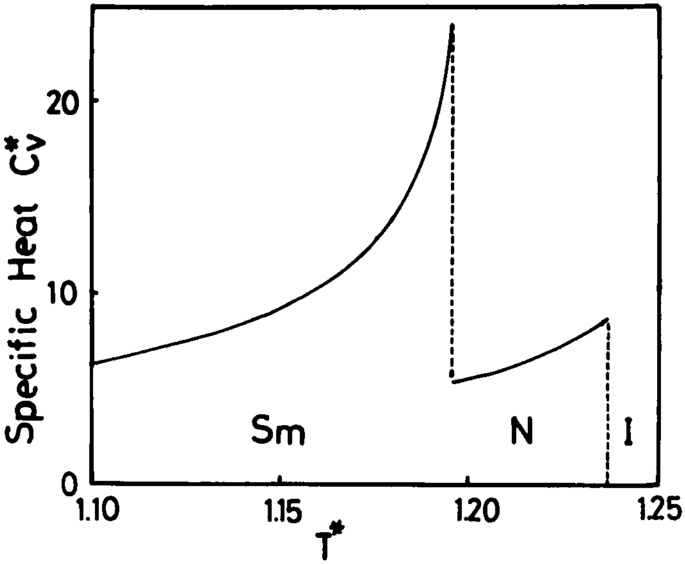

FIGURE 3(a)2 The specific heat for No. 2.

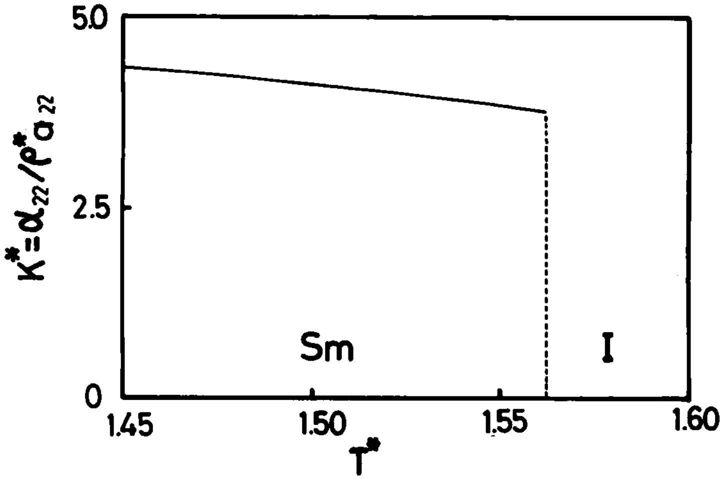

FIGURE 3(b)1 The elastic constant for No. 5.

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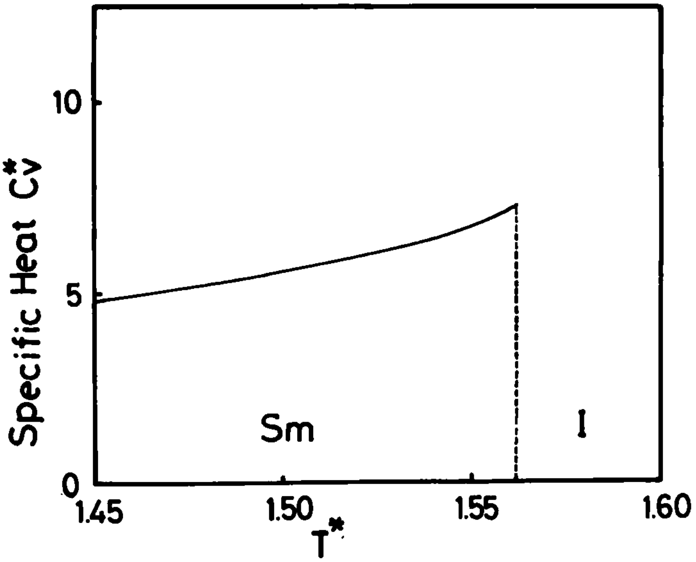

FIGURE 3(b)2 The specific heat for No. 5.

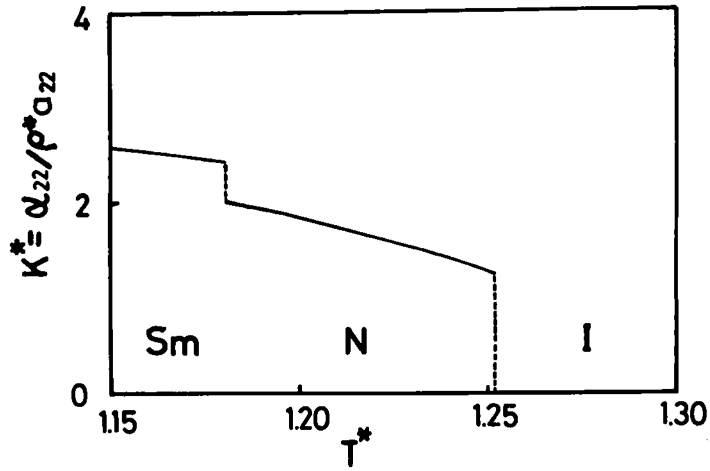

FIGURE 3(c)1 The elastic constant for No. 11.

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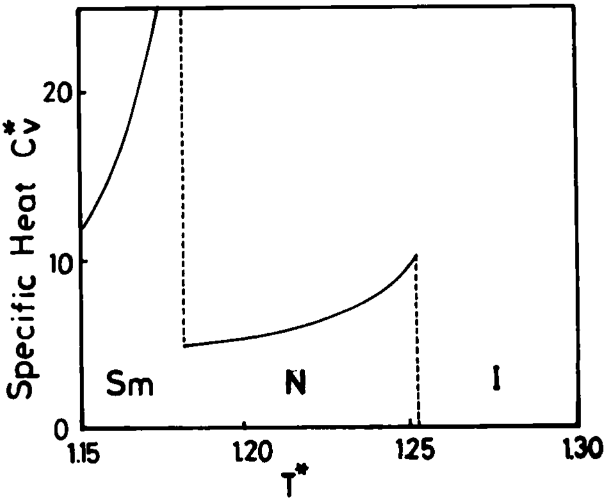

FIGURE 3(c)2 The specific heat for No. 11.

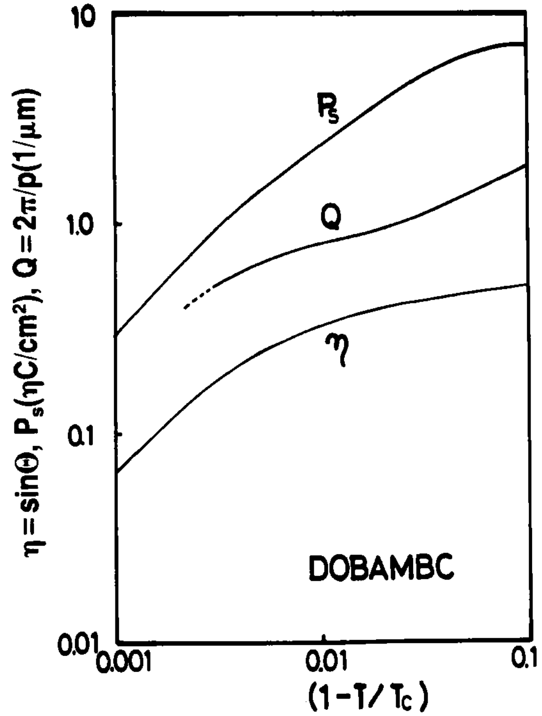

FIGURE 4 The experimental results for molecular tilt η, $Q=2\pi/P$, and spontaneous polarization P_s.[24]

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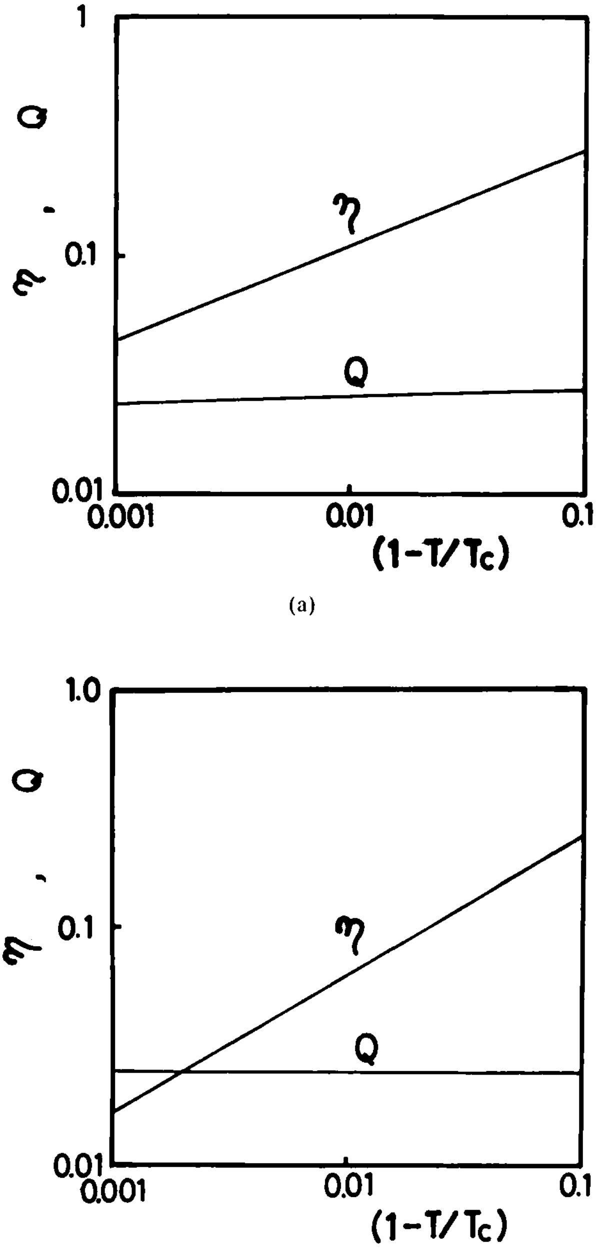

(a)

(b)

FIGURE 5 (a) The theoretical results, η and Q, for No. 2. (b) The theoretical results, η and Q, for No. 5.

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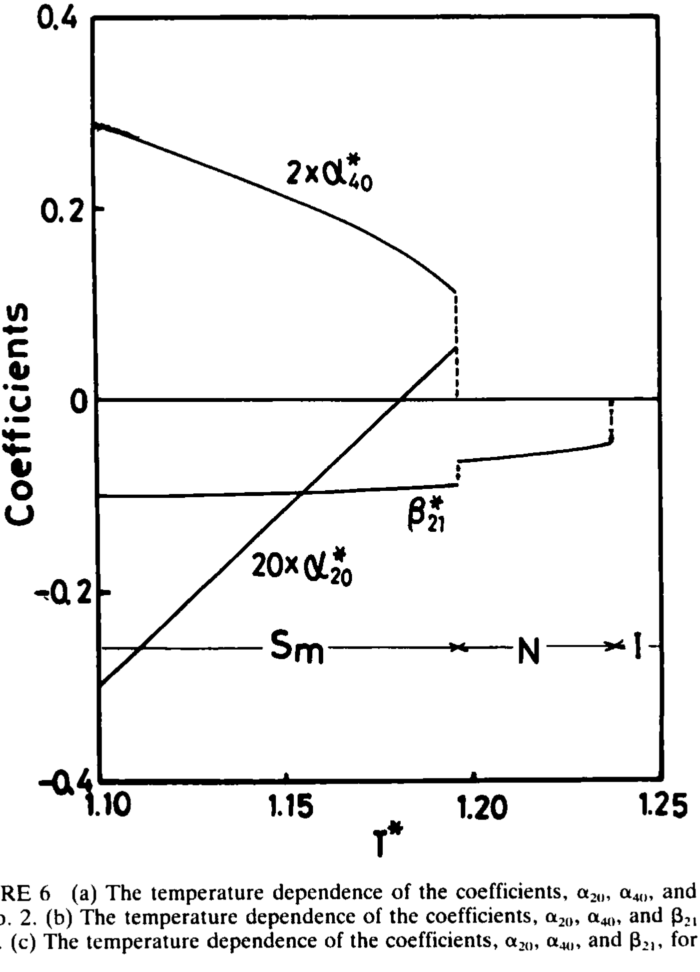

FIGURE 6 (a) The temperature dependence of the coefficients, α_{20}, α_{40}, and β_{21}, for No. 2. (b) The temperature dependence of the coefficients, α_{20}, α_{40}, and β_{21}, for No. 5. (c) The temperature dependence of the coefficients, α_{20}, α_{40}, and β_{21}, for No. 11.

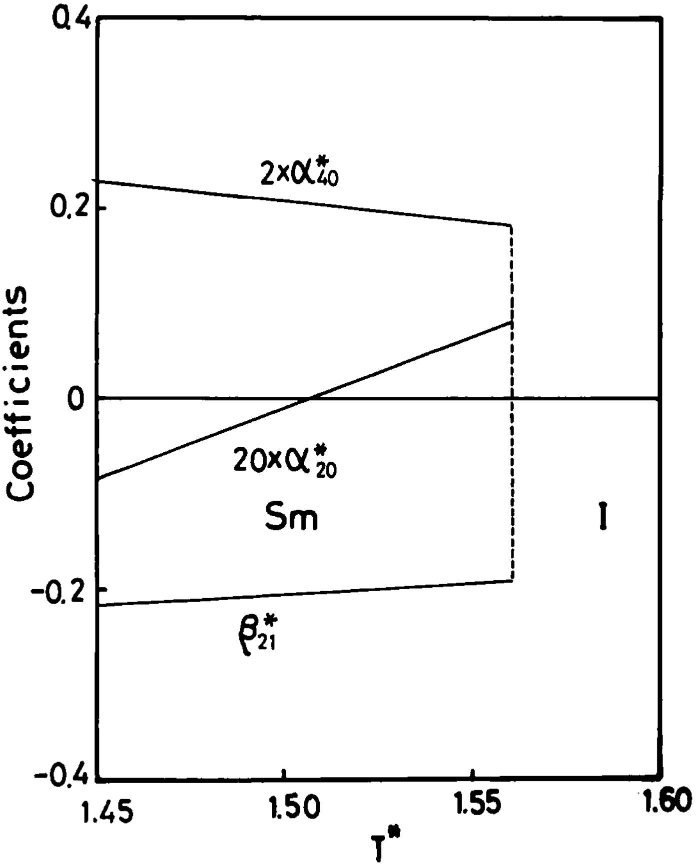

FIGURE 6(b)

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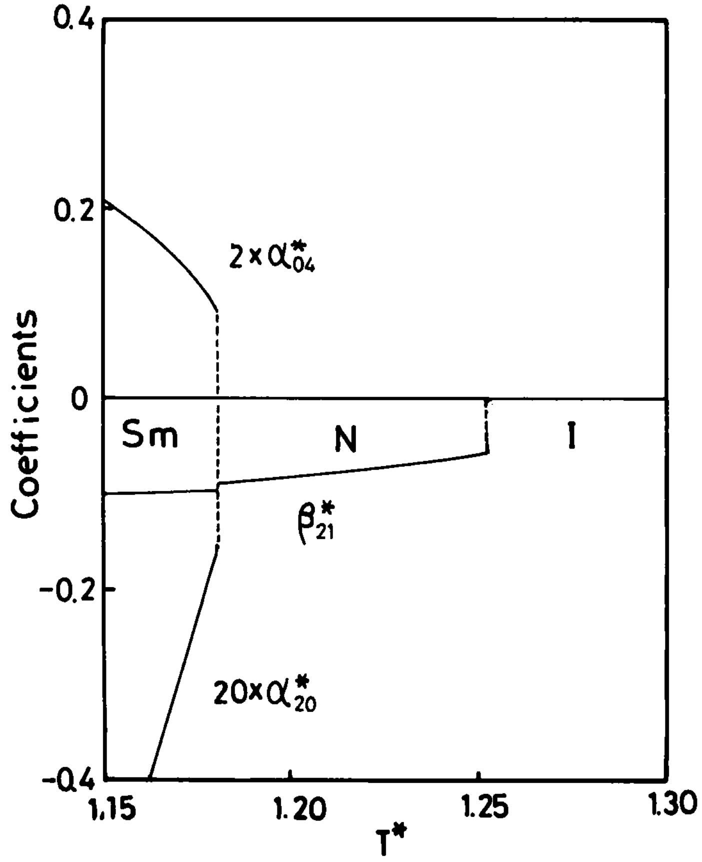

FIGURE 6(c)

Acknowledgment

The author would like to thank Professor T. Akahane for his invaluable discussions and critical reading of the manuscript.

APPENDIX

For convenience we shall define the following functional of $h\ (z_{12},\beta)$, which is a function of z_{12} and β.

$$I\{h\} \equiv \frac{2}{1+\delta_{k0}} 4\pi\rho \int_0^\infty r_{12}^2 \, dr_{12} \int_0^1 d(\cos\beta) \cos kz_{12} e^{-(r_{12}/r_0)^2} \times h(z_{12},\beta). \qquad (A.1)$$

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Making use of this functional, we may set down the coefficients, $a^{mn}_{\ell_1\ell_2}$ and b^{mn}, below.

$$a^{22}_{22}(k) = \frac{3}{2} I \left\{ \left(\frac{z_{12}}{r_0} \right)^2 \right\} a_{22}, \tag{A.2}$$

$$a^{24}_{22}(k) = -\frac{1}{8} I \left\{ \left(\frac{z_{12}}{r_0} \right)^4 \right\} a_{22}, \tag{A.3}$$

$$a^{44}_{22}(k) = -\frac{3}{8} I \left\{ \left(\frac{z_{12}}{r_0} \right)^4 \right\} a_{22}, \tag{A.4}$$

$$a^{22}_{44}(k) = 5\, I \left\{ \left(\frac{z_{12}}{r_0} \right)^2 \right\} a_{44}, \tag{A.5}$$

$$a^{24}_{44}(k) = -\frac{5}{12} I \left\{ \left(\frac{z_{12}}{r_0} \right)^4 \right\} a_{44}, \tag{A.6}$$

$$a^{44}_{44}(k) = -\frac{45}{8} I \left\{ \left(\frac{z_{12}}{r_0} \right)^4 \right\} a_{44}, \tag{A.7}$$

$$\begin{aligned} a^{20}_{20}(k) &= \frac{3}{2} I \{P_2(\cos\beta)\}\, a_{20}, \\ &= a^{20}_{02}(k) \end{aligned} \tag{A.8}$$

$$\begin{aligned} a^{20}_{40}(k) &= 5\, I \{P_4(\cos\beta)\}\, a_{40}, \\ &= a^{20}_{04}(k) \end{aligned} \tag{A.9}$$

$$\begin{aligned} a^{40}_{40}(k) &= -\frac{35}{8} I \{P_4(\cos\beta)\}\, a_{40}, \\ &= a^{40}_{04}(k) \end{aligned} \tag{A.10}$$

$$b^{21}(k) = -I\left\{\cos\beta \times \frac{z_{12}}{r_0}\right\} b, \tag{A.11}$$

$$b^{23}(k) = \frac{1}{6} I\left\{\cos\beta \times \left(\frac{z_{12}}{r_0}\right)^3\right\} b, \tag{A.12}$$

$$b^{43}(k) = \frac{1}{2} I\left\{\cos\beta \times \left(\frac{z_{12}}{r_0}\right)^3\right\} b, \tag{A.13}$$

$$b^{25} = -\frac{1}{120} I\left\{\cos\beta \times \left(\frac{z_{12}}{r_0}\right)^5\right\} b. \tag{A.14}$$

References

1. R. B. Meyer, Mol. *Cryst. Liq. Cryst.*, **40**, 33 (1977).
2. R. B. Meyer, L. Liébert, L. Strzelecki and P. Keller, *J. de Phys. Lett.*, **36**, 69 (1975).
3. A. Michelson, L. Benguigui and D. Cabib, *Phys. Rev.* **A16**, 394 (1977).
4. M. A. Handschy and N. A. Clark, *Appl. Phys. Lett.*, **41**, 39 (1982).
5. S. A. Pikin and V. L. Indenbom, *Sov. Phys. Usp.* **21**, 487 (1978).
6. V. E. Dmitrienko and V. A. Belyakov, *Sov. Phys. JETP* **51**, 787 (1980).
7. B. I. Ostrovskii, S. A. Pikin and V. G. Chigrinov, *Soc. Phys. JETP* **50**, 811 (1979).
8. M. Yamashita and H. Kimura, *J. Phys. Soc. Jpn.*, **51**, 2419 (1982).
9. S. A. Pikin and K. Yoshino, *Jpn. J. Appl. Phys. Lett.* **20**, 557 (1981).
10. M. Yamashita and H. Kimura, *J. Phys. Soc. Jpn.*, **52**, 1509 (1983).
11. For ex. E. B. Priestley, P. J. Wojtowicz and P. Sheng, *Introduction to Liquid Crystals*, Plenum Press (1974).
12. L. Senbetu and C.-W. Woo, *Phys. Rev.* **A17**, 1529 (1978).
13. Y. R. Lin-Liu, Y. M. Shih and C.-W. Woo, *Phys. Rev.*, **A14**, 2550 (1976).
14. M. Nakagawa and T. Akahane, *J. Phys. Soc. Jpn.*, **53**, 1951 (1984).
15. H. Kimura, M. Hosino and H. Nakano, *J. de Phys.*, **C3**, 174 (1979).
16. H. Kimura, M. Hosino and H. Nakano, *J. Phys. Soc. Jpn.*, **51**, 1584 (1982).
17. W. L. McMillan, Phys. Rev. **A4**, 1238 (1971); *ibid* **A6**, 936 (1972).
18. K. K. Kobayashi, J. Phys. *Soc. Jpn.*, **29**, 101 (1970).
19. J. A. Pople, Proc. *Roy. Soc.* **A221**, 498 (1954).
20. M. Nakagawa and T. Akahane, *Mol. Cryst. Liq. Cryst.*, **90**, 53 (1982).
21. K. Kondo, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.*, **21**, 224 (1982).
22. H. Takezoe, K. Kondo, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys. Lett.*, **21**, 627 (1982).
23. S. Skarp, K. Flatischler, K. Kondo, Y. Sato, K. Miyasato, H. Takezoe, A. Fukuda and E. Kuze, Jpn. *J. Appl. Phys.* **22**, 566 (1983).
24. B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin and B. A. Strukov, *Sov. Phys. JETP*, **47**, 912 (1978).
25. B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, E. L. Sorkin, B. A. Strukov and S. A. Taraskin, *Ferroelectrics* **24**, 309 (1980).

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