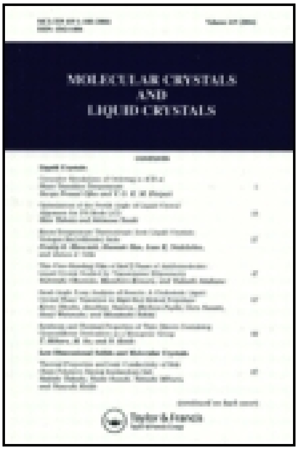

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Dependence of the Tilt Angle on External Forces for Smectic-C And Chiral Smectic-C Liquid Crystals—Measurement of the Heat Capacity of DOBAMBC

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Dependence of the Tilt Angle on External Forces for Smectic-C And Chiral Smectic-C Liquid Crystals—Measurement of the Heat Capacity of DOBAMBC

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A measurement of the specific heat of DOBAMBC is presented, and it is shown that a Landau expansion of the free-energy density with a sixth-order term is adequate to describe the measurement. The coefficients in the Landau expansion are estimated from this measurement.

The dependence of the tilt angle on applied electric and magnetic fields is discussed for both smectic-C and chiral (ferroelectric) smectic-C liquid crystals. Numerical estimates of the Landau coefficients are used to show that the effect of external forces on the tilt angle is negligible except when being less than approximately 0.2 K from the transition to the smectic-A phase. The effect on the smectic-C–smectic-A phase-transition temperature is also discussed.

Boundary effects can also affect the tilt angle, and an expression for the penetration depth of a boundary-induced disturbance is calculated. For thin, planar samples, a coupling between the two boundaries can induce a transition to the smectic-A phase. It is demonstrated that this transition is analogous to the ordinary Freederickz transition in nematic liquid crystals.

I. INTRODUCTION

Smectic-C (Sm C) and chiral smectic-C (Sm C*) liquid crystals are layered structures where two variables are needed to describe the order within each layer (see Figure 1). One variable is the tilt angle, θ, between the average molecular direction and the normal to the smectic planes. The other variable is the average angle between the projection of the molecules into the smectic plane and some reference direction in this plane, and it is here

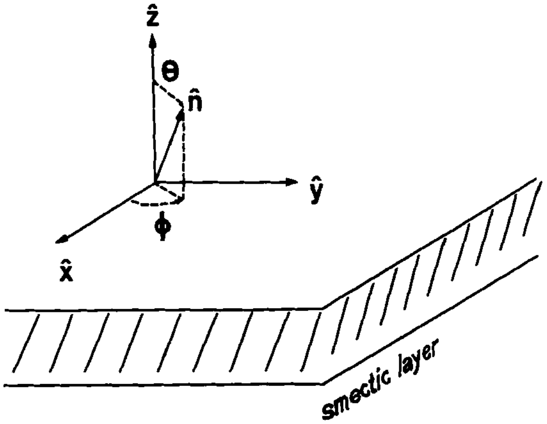

FIGURE 1 Definition of coordinates in the present work. The smectic layers are parallel to the *xy*-plane. The average molecular direction, the director, is given by a unit vector, $\hat{n}$, which is determined by the angles θ and ϕ.

denoted by ϕ. In a homogeneous, undisturbed sample of the Sm C phase, both θ and ϕ will be constant throughout space. In the Sm C* phase, on the other hand, there is a spontaneous twist between the layers where ϕ changes with a constant value from layer to layer but where θ remains constant. ϕ is easily disturbed by external fields and boundary conditions, but θ is usually assumed to be determined by temperature only.

Recently, however, some authors have discussed variations of θ as a result of the influence of external forces. Pikin and Yoshino[1] discuss a change in the Sm A–Sm C* phase-transition temperature which is due to the influence of boundary conditions and which causes θ to vary in the sample. Kondo *et al.*[2] interpret measurements of the electric response near the phase transition as an evidence of field influence on the tilt angle. It is well known that internal strain caused by dislocations can modify the tilt angle, thus making the dislocations visible near the Sm A–Sm C phase transition.[3] Recently Clark and Lagerwall[4] have pointed out the possibility of making fast-switching displays using Sm C* liquid crystals. An analysis of such a device will, of course, differ considerably depending on whether or not one can assume that θ is constant during the switching.

The aim of this paper is to analyze to what extent θ can be assumed to be constant under the influence of different external fields and disturbances. We will also discuss the changes in the Sm C (Sm C*)–Sm A phase-transition temperature that these fields will cause. To do so we will proceed as follows. In Section II we develop the Landau expansion of the free-energy density for the Sm C (Sm C*) phase, including electric and magnetic fields. We also discuss the different material parameters which are needed for a full description of our problem. In Section III a measurement of the specific heat of DOBAMBC is presented, and it is shown that a Landau expansion with a sixth-order term in θ is adequate to describe both measurements of the specific heat and of the tilt angle. The coefficients in the Landau expansion are estimated from the measurements. The values differ noticeably from some of those given in the literature. Using a full set of material parameters, we are able to make an estimate of the magnitude of the effects on the tilt angle caused by external forces. In Section IV we study the effects of an induced twist and an applied magnetic field (nonoblique). We have divided the discussion of the response to an applied electric field into two parts. The first part, which will also be discussed in Section IV, is due to the induced polarization of the molecules. When discussing the Sm C* phase, we know that these compounds are ferroelectric. We also have a response due to a fixed macroscopic dipole moment which couples linearly to an applied electric field, and which is stronger than the induced part. This is discussed in Section V along with oblique magnetic fields. In Section VI we discuss the effects of imposed boundary conditions. In Section VII we summarize our results.

If our values for the material constants are correct, even very strong external forces will cause only a very small change in the Sm C (Sm C*)–Sm A phase-transition temperature. We also conclude that, except in the very vicinity of the phase transition (of the order of one-tenth of a degree from it), the effects on the tilt angle are negligible.

II. FREE ENERGY DENSITY

In order to analyze the problem we must develop the expression for the free energy per unit volume. First we define our coordinates as shown in Figure 1: the z-direction is normal to the smectic planes, and ϕ is defined as the angle between the projection of the director into the smectic plane and the x-axis. We can give the following expression for the director:

$$\begin{aligned} n_x &= \sin\theta\cos\phi \\ n_y &= \sin\theta\sin\phi \\ n_z &= \cos\theta \end{aligned} \tag{II.1}$$

In order to concentrate on the question posed, we now limit our discussion to those problems where no undulation of the smectic planes occur, i.e. the smectic layers are assumed to be true planes. We also restrict θ to be small. In Section VII we show that this implies no loss of generality of application in our results. The following expresses the free-energy density as a sum of different terms:

$$g(\theta, \phi) = g_0 + g_L + g_\Lambda + g_T + g_M + g_E + g_\nabla \tag{II.2}$$

where g_0 is the background energy and is independent of θ and ϕ, and thus has no effect on the problem. Let us call g_L the Landau energy and g_Λ the chiral energy. g_T is the energy due to the twisting of the layers $(d\phi/dz \neq 0)$. There should be other elastic terms too, that couple deformations of ϕ inside the layers with the tilt angle. In this context, the effects of g_T should be representative for all of these terms. g_M and g_E are the magnetic and electric energies respectively, and g_∇ is the energy built into the system if θ is allowed to vary in space.

Landau energy

If we retain the two leading terms in the Landau expansion of the free energy for an undisturbed Sm C liquid crystal we get[5]

$$g_L = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 \tag{II.3}$$

For a small θ we are close to the Sm C–Sm A phase transition, and according to the Landau theory of second-order phase transitions we make the following assumptions for a and b:

$$\begin{aligned} a &= \alpha(T - T_0) \\ \alpha &> 0 \\ b &> 0 \end{aligned} \tag{II.4}$$

where α and b are constants and T_0 is the Sm C–Sm A phase-transition temperature. The magnitude of α and b are of utmost importance in our problem. The values given in the literature[6,7] are strongly at variance. In Section III we give the values of α in the above references and present our own measurements of α and b.

Twist and chiral energy

If the layers are twisted with respect to each other ($\phi = \phi(z)$; $(d\phi/dz) \neq 0$) and if the liquid crystal consists of chiral molecules we have a free-energy density[8] of

$$g_T + g_\Lambda = \frac{1}{2}K_{33}\left\{\left(\frac{d\xi_1}{dz}\right)^2 + \left(\frac{d\xi_2}{dz}\right)^2\right\} + \Lambda\left\{\xi_1\frac{d\xi_2}{dz} - \xi_2\frac{d\xi_1}{dz}\right\} \tag{II.5}$$

where ξ_1 and ξ_2 are defined by

$$\begin{aligned}\xi_1 &= n_x n_z = \sin\theta\cos\theta\cos\phi \\ \xi_2 &= n_y n_z = \sin\theta\cos\theta\sin\phi \qquad \text{(II.6)}\end{aligned}$$

Λ is the chirality parameter and K_{33} is an elastic constant. If θ is constant throughout the whole sample, we can rewrite Eq. (II.5) as

$$\begin{aligned} g_T + g_\Lambda &= \sin^2\theta\cos^2\theta\left\{\frac{1}{2}K_{33}\left(\frac{d\phi}{dz}\right)^2 + \Lambda\frac{d\phi}{dz}\right\} \\ &= \sin^2\theta\cos^2\theta\left\{\frac{1}{2}K_{33}\left(\frac{d\phi}{dz} + \frac{\Lambda}{K_{33}}\right)^2 - \frac{\Lambda^2}{2K_{33}}\right\} \qquad \text{(II.7)}\end{aligned}$$

In Eq. (II.7) we see that the presence of Λ in the free-energy density will cause ϕ to vary in an undisturbed medium as follows:

$$\frac{d\phi}{dz} = -\frac{\Lambda}{K_{33}} \qquad \text{(II.8)}$$

If we define the pitch, λ_0, of the medium through the equation

$$\frac{d\phi}{dz} = \frac{2\pi}{\lambda_0} \qquad \text{(II.9)}$$

we get

$$\Lambda = -\frac{2\pi K_{33}}{\lambda_0} \qquad \text{(II.10)}$$

Making an analogy with the elastic theory of nematic liquid crystals, the energy g_T is in fact of bend type. We however prefer to call g_T a twist energy as it is related to the energy associated with the twisting of the layers with respect to each other. There is no reason to assume that K_{33} should not be of the same order of magnitude as the elastic constants of the nematic liquid crystals. We therefore estimate K_{33} to be of the order $5 \cdot 10^{-12}$ N. The pitch varies from 1 to 10 μ; thus we can estimate Λ to be of the order of 10^{-5} N/m.

Magnetic energy

If we apply an oblique magnetic field across the sample, the free energy per unit volume is given as[9]

$$g_M = -\frac{\chi_a}{2\mu_0}(\mathbb{B}\cdot\hat{n})^2 \qquad \text{(II.11)}$$

With no loss of generality we can assume this field to be in the xz-plane.

$$\mathbb{B} = B_x\hat{x} + B_z\hat{z} \tag{II.12}$$

Eqs. (II.1), (II.11), and (II.12) now give

$$g_M = -\frac{\chi_a}{2\mu_0}\{B_x^2 \sin^2\theta \cos^2\phi + B_z^2 \cos^2\theta + B_xB_z \sin 2\theta \cos\phi\} \tag{II.13}$$

χ_a is the anisotropy of the magnetic susceptibility and μ_0 is the vacuum permeability. χ_a should be of the same order of magnitude in Sm C (Sm C*) materials as in nematics, and we set[10] χ_a at approximately 10^{-6}.

Electric energy

The energy in an electric field can be divided into two terms. First there is the effect of the induced polarization of the molecules, which can be written[9]

$$g_E' = -\frac{1}{2}\varepsilon_a\varepsilon_0(\mathbb{E}\cdot\hat{n})^2 \tag{II.14}$$

If we assume the electric field to be in the x-direction

$$\mathbb{E} = E\hat{x} \tag{II.15}$$

Eqs. (II.1, II.14 and II.15) give

$$g_E' = -\frac{1}{2}\varepsilon_a\varepsilon_0E^2 \sin^2\theta \cos^2\phi \tag{II.16}$$

where ε_a is the dielectric anisotropy and ε_0 is the vacuum permittivity. ε_a should be of the same order of magnitude as in nematics and we set[11] $|\varepsilon_a|$ at approximately 10.

Sm C* materials are ferroelectric and also respond to an electric field due to a fix macroscopic dipole moment, $\mathbb{P}$, which is proportional[12] to θ. $\mathbb{P}$ always lies in the smectic plane and is perpendicular to the projection of the director in this plane. With the definition of ϕ according to Eq. (II.1) we can write

$$\mathbb{P} = \mu\theta(-\sin\phi\,\hat{x} + \cos\phi\,\hat{y}) \tag{II.17}$$

where μ is the dipole moment per unit volume of the medium. The free-energy density thus becomes

$$g_E'' = -\mathbb{E}\cdot\mathbb{P} = \mu\theta E \sin\phi \tag{II.18}$$

A typical value of μ is[6,12] 30 esu/cm^2 = 10^{-4} Coulomb/m^2.

Energy as affected by spatial variations of θ

If θ varies in space we have to add another elastic-energy term, g_∇, to the expression of g. The usual way to write g_∇ is

$$g_\nabla = \frac{1}{2}K_0(\nabla\theta)^2 \tag{II.19}$$

In general, the elastic-energy term should also depend on the direction of the gradient of θ. Assuming strong anchoring conditions on the boundaries and further a way to control the direction of the smectic planes, we see in Figure 2 that there are two fundamentally different ways in which θ can vary. In Figure 2a the smectic planes are parallel to the walls and θ will vary from plane to plane, remaining constant within each plane. This case demands one separate elastic constant. In Figure 2b the smectic planes are assumed to be perpendicular to the walls, and here θ varies within each plane, but not when it goes from one plane to another. In this case two elastic constants are involved. We thus conclude that Eq. (II.19) is a one-constant approximation. The value of K_0 is not established in the literature. Ostrovski *et al.*[6] have suggested the value 10^{-10} N. We have used this value here.

Small-angle approximation of the free energy density and summary of the material constants

Neglecting the constant part of g, we now expand Eqs. (II.7), (II.13), and (II.16) to second order in θ and rewrite Eq. (II.2) as

$$g = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 - \lambda\theta + \frac{1}{2}\kappa\theta^2 + \frac{1}{2}K_0(\nabla\theta)^2 \tag{II.20}$$

where we have defined λ and κ as follows:

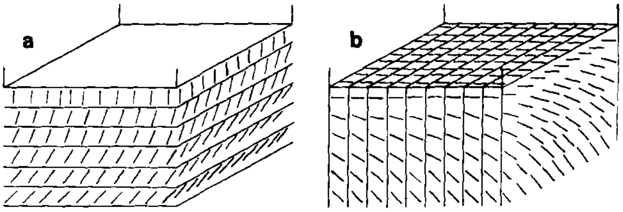

FIGURE 2 Two fundamental ways for the tilt angle to vary in space. (a) The tilt angle remains constant within each smectic plane but varies when going from one plane to another. (b) The tilt angle remains constant between planes but varies within each smectic plane.

$$\lambda = -\mu E \sin \phi + \frac{\chi_a}{\mu_0} B_x B_z \cos \phi$$

$$\kappa = K_{33}\left(\frac{d\phi}{dz} + \frac{\Lambda}{K_{33}}\right)^2 - \frac{\Lambda^2}{K_{33}} - \frac{\chi_a}{\mu_0} B_x^2 \cos^2 \phi + \frac{\chi_a}{\mu_0} B_z^2 - \varepsilon_a \varepsilon_0 E^2 \cos^2 \phi \tag{II.21}$$

In Table I we summarize the values of the material constants discussed so far. The magnitudes of α and b are discussed in Section III.

III. MEASUREMENTS OF SPECIFIC HEAT

The most direct way to study the coefficients in the Landau expansion of the free energy is to study the specific heat. Measurements of specific heat at the transition Sm C–Sm A have been done by Schantz and Johnson,[13] and the transition in DOBAMBC has been investigated by Ostrovski.[14,15] In this section we present another measurement of the specific heat of DOBAMBC. Our aim is to get a rough estimate of the magnitude of the coefficients in the Landau expansion. First we discuss the experimental procedure, then the evaluation problem and the experimental data.

Experimental

We have used the commercial system, Mettler TA3000, to measure specific heat using the DSC (Differential Scanning Calorimetry) method. In this instrument fairly small samples are used (about 30 mg). The change in specific heat at the Sm C–Sm A transition is smaller than it is in other phase transitions, and the noise-to-signal ratio is large. By averaging several successive runs, the noise is reduced to an acceptable level. The measurements were performed on 32.2 mg ferroelectric DOBAMBC (T_0 = 95.3°C) synthetised by Bengt Otterholm at the Organic Chemistry Department of the University of Gothenburg. We had a fairly pure sample: during the experiments the temperature of the transition between the Sm A

TABLE I

Values of the material parameters used in this work

K_{33}	Λ	χ_a	$\lvert\varepsilon_a\rvert$	μ	K_0
$5 \cdot 10^{-12}$ N	10^{-5} N/m	10^{-5} (SI)	10	10^{-4} C/m^2	10^{-10} N

and isotropic phases declined from 118.2°C to 117.2°C. All measurements were done by reducing temperature from the isotropic phase through the Sm A phase and into the Sm C phase. This procedure was chosen in order to prevent the formation of dislocations: a crystallization could cause dislocations having latent heat. The choice of cooling rate is critical: we must reach balance between noise in the c_p values and bad temperature resolution. At a cooling rate of 1 K/min the noise is fairly high and at 5 K/min the low temperature resolution smears out the transition peak, so we have worked mainly with 2 K/min and used the cooling rates of 1 K/min and 5 K/min to check both the temperature resolution and the curve shape obtained.

Curve shape obtained

We got the same kind of triangular shape as did Schantz and Johnson,[13] with a slow rise on the Sm C* side and a rapid fall-off on the Sm A side (see Figure 3). The slope on the Sm A side is strongly dependent on the cooling rate. The shape which Ostrowski[15] obtained is not similar to ours.

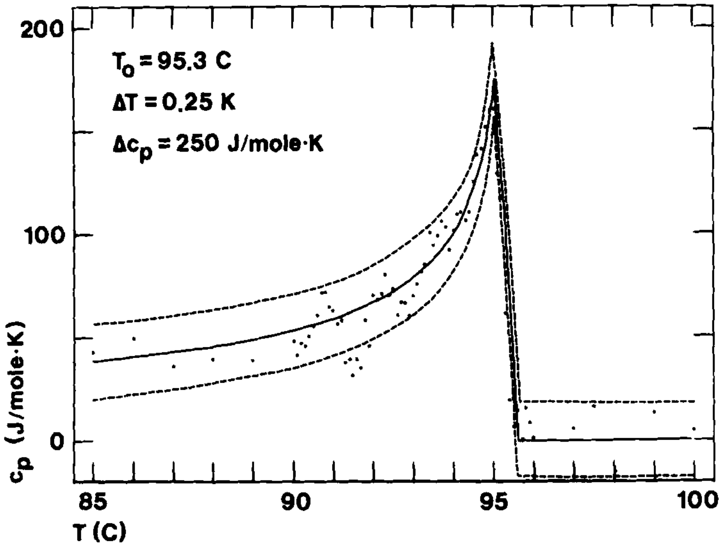

FIGURE 3 Specific heat for DOBAMBC: the dots represent measured values. The solid line represents theoretical curve as given by Eq. (III.7) averaged over a temperature interval T ±0.3 K. The broken lines represent the solid line plus/minus two standard deviations of the measured values.

Connection to the Landau expansion

The experimental data on Sm C liquid crystals have the common element of being too uncertain to facilitate the selection of any theory as the "right" theory. They can only divide possible theories into two groups: the ones that are compatible with experiments and the ones that are not. Nevertheless, it is very useful to have one theory that is compatible with experiments and which only contains measurable parameters. The simple Landau expansion

$$g = \frac{1}{2}\alpha(T - T_0)\theta^2 + \frac{b}{4}\theta^4 \qquad \text{(III.1)}$$

gives, by minimization with respect to θ,

$$\theta_0^2 = \frac{\alpha}{b}(T_0 - T) \qquad \text{for } T < T_0, \qquad \text{otherwise zero}. \qquad \text{(III.2)}$$

This value can be inserted in g, and gives

$$g = -\frac{1}{4}\frac{\alpha^2}{b}(T_0 - T)^2 \qquad \text{for } T < T_0, \qquad \text{otherwise zero}. \qquad \text{(III.3)}$$

By the relation

$$c_p = -T\left(\frac{d^2g}{dT^2}\right)_p \qquad \text{(III.4)}$$

one finds an almost constant contribution in the Sm C phase, with a step at the transition of

$$\Delta c_p = \frac{\alpha^2}{2b}T_0 \qquad \text{(III.5)}$$

This theory is evidently too simple. It does not give the temperature dependence observed for either θ or c_p. Adding the sixth-order term gives the free-energy density

$$g = \frac{1}{2}\alpha(T - T_0)\theta^2 + \frac{b}{4}\theta^4 + \frac{c}{6}\theta^6 \qquad \text{(III.6)}$$

The expression for the specific heat thus becomes

$$c_p = \Delta c_p \frac{T}{T_0}\sqrt{\frac{\Delta T}{T_0 + \Delta T - T}} \qquad \text{for } T < T_0, \qquad \text{otherwise zero} \qquad \text{(III.7)}$$

where Δc_p is defined by Eq. (III.5) and

$$\Delta T = \frac{b^2}{4\alpha c} \qquad \text{(III.8)}$$

At the transition temperature T_0 we still have the same step in c_p as given in Eq. (III.5). The behavior in the Sm C* phase according to Eq. (III.8) is however much more like the observed behavior. The tilt angle is also modified by the presence of the sixth-order term in the following way:

$$\theta^2 = \frac{b}{2c} \cdot \left\{-1 + \sqrt{1 + \frac{T_0 - T}{\Delta T}}\right\} \tag{III.9}$$

Using measurements of the temperature dependence of c_p and θ it should be possible to determine α, b and c in Eq. (III.6). Thus the measured curves are easily interpreted using this theory. The usual way of treating θ-measurements is to find an exponent β, such that

$$\theta \propto (T_0 - T)^\beta \tag{III.10}$$

If one tries to adjust the free-energy expression so that this temperature dependence is obtained, one usually gets a divergence in the expression for c_p. Since this divergence is not observed, it becomes difficult to extract any numerical parameters from the specific heat measurements. With the free energy in Eq. (III.6), the θ values cannot be fitted to Eq. (III.10) using a constant β value. We can redefine β as the slope in a log-log plot of θ vs $T_0 - T$. At temperature differences of $T_0 - T$ smaller than ΔT, β is about 0.5. At much greater temperature differences, β is about 0.25, but the

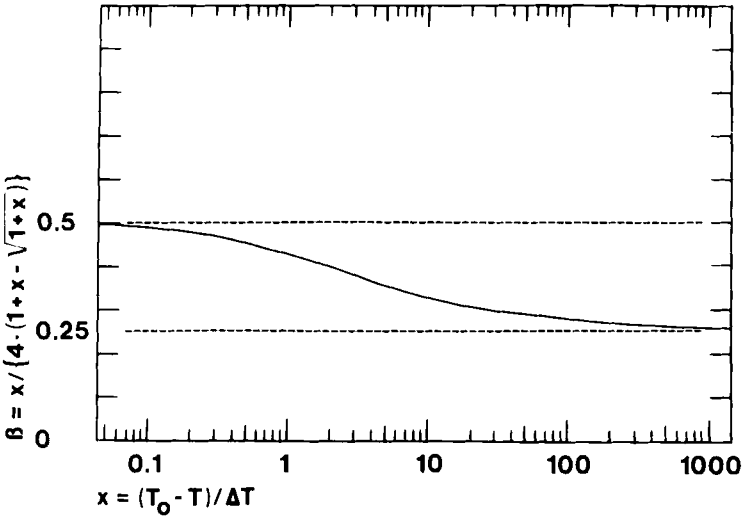

FIGURE 4 β is the slope in a log-log plot of θ vs $T_0 - T$ if a sixth-order Landau expansion of the free-energy density is used. Here β is shown as a function of temperature in logarithmically reduced temperature scale. The transition region from the "classical" value $\beta = 0.5$ to the value 0.25 is broader than the experimentally useable region.

transition region where β changes is fairly broad (see Figure 4; note the logarithmic scale for temperature).

Concerning only measurements of the tilt angle, the experimental data are still so dispersed, that it is practically impossible to say if β is constant or if it varies. We have studied Martinot-Lagarde's[16] measurements and compared his fitted functions (which are based on a constant β) with the expression (III.9) for θ. Calculations made using a minicomputer with graphic capabilities show easily that the difference between these theoretical curves is much smaller than the uncertainty in Martinot-Lagarde's measurements. Thus the Landau expansion is compatible with the experimental data. There are some experimental indications in the literature of a changing exponent β; see the article by Galerne[17] concerning measurements very near the transition.

The measurement of θ should give information about both α/b and α/c in the Landau expansion, and the c_p measurements should give Δc_p and ΔT. This gives an overdetermined set of constants for the determination of α, b, and c. The data on θ are rather insensitive to the choice of ΔT, so this value can be estimated from the c_p measurements, and we get still a good fit to the θ measurements.

Experimental data

In the Sm A phase outside the transition regions the c_p values fit rather well to a straight line, so this line (estimated from c_p values in the region of 96°C to 110°C) was used to estimate the background in the Sm C* region. The amplitude of the transition peak above the background was 130 J/mole K for a cooling rate of 5 K/min, 160 J/mole K for a cooling rate of 2 K/min, and 204 J/mole K for a cooling rate of 1 K/min. The effect of the nonzero cooling rate can be taken as an averaging of the c_p values over a temperature interval, where the length of the interval is proportional to the cooling rate. Under this assumption the measurements can be fitted to Eq. (III.7). The best fit is obtained for a step in specific heat Δc_p of 250 J/mole K (for zero cooling rate) with an estimated uncertainty of ±50 J/mole K. This value of Δc_p seems to be in accordance with the measurements of Ostrovski.[15] ΔT determines the slope on the Sm C* side of the transition, and a value of 0.25 K gives a slope of the right magnitude. These values of Δc_p and ΔT were used in the calculation of the continuous curve in Figure 3. The broken curves represent the continuous curve with two standard deviations of the experimental points added and subtracted respectively.

Martinot-Lagarde[16] has performed both optical measurements of θ in homeotropic and planar samples and X-ray measurements of layer thickness that can be used to calculate θ indirectly. We use his optical measurements on homeotropic samples to calculate b/α, since these measurements give data for small angles, where the sensitivity to errors in ΔT is smallest. These measurements do not depend on the theoretical model for the coupling between the layer thickness and the tilt angle. Martinot-Lagarde got $\beta = 0.44$ for a temperature interval of 2 degrees from T_0. Using our value of ΔT we get b/α equal to 17 K. Ostrovski's[18] measurements also seem to fit to these values of b/α and ΔT rather well. He got $\beta = 0.31 \pm 0.05$ for a temperature interval of 30 degrees. If, for instance, the planar measurements of Martinot-Lagarde had been used instead, b/α should have been higher.

We summarize our values as follows:

$$\Delta c_p = \frac{\alpha^2}{2b} T_0 = 250\ \text{J/mole K}, \qquad \Delta T = \frac{b^2}{4\alpha c} = 0.25\ \text{K},$$
$$b/\alpha = 17\ \text{K} \qquad \text{(III.11)}$$

which gives

$$\alpha = \frac{2\Delta c_p}{T_0}\frac{b}{\alpha} = 5 \cdot 10^4\ \text{J/m}^3\ \text{K}, \qquad b = 85 \cdot 10^4\ \text{J/m}^3,$$
$$c = 1.4 \cdot 10^7\ \text{J/m}^3 \qquad \text{(III.12)}$$

The density of DOBAMBC is assumed to be 10^3 kg/m^3. Since the value of b/α is rather uncertain, this estimate of α can be erroneous by a factor of 2.

Comparison with other measurements on α

Ostrovski *et al.*[6] have made an estimate of α ($2a'$ in their notation) below 10^3 cgs esu/degree = 10^2 J/m^3 K. Their value is based on a theoretical explanation of the temperature dependence of the dielectric constant. The evaluation is based on the assumption of the temperature independence of at least three constants, one of which is K_{33}. Four parameters are then varied to fit a rather smooth, extrapolated, experimental curve. Their expression for free energy does not give the right temperature dependence for the helical pitch where K_{33} is involved. It can be dangerous to rely too heavily on such a theory. They point out that Garoff and Meyer[7] have probably given an erroneous estimate of α, since Garoff and Meyer left out the term $\bar{K}q_c^2$ in Ostrovski's notation (equal to $4\pi^2K_{33}/\lambda_0^2$ in our notation). The magnitude of this term is $1.2 \cdot 10^2$ J/m^3 if the pitch 4 μm is used. This term relates to the difference in transition temperature between samples with and

TABLE II

Summary of the values of the Landau parameters given in the literature

	Ostrovski *et al.*[6]	Estimated from Musevic *et al.*[19]	Garoff and Meyer[7]	This work
α [N/m^2 · K]	$<10^2$	$>2 \cdot 10^3$	10^4	$5 \cdot 10^4$
b [N/m^2]				$85 \cdot 10^4$
c [N/m^2]				$1.4 \cdot 10^7$

without developed helix. Since the measurements of Garoff and Meyer were performed in the Sm A phase (without a helix), and the transition temperature was fitted to the data, Ostrovski's term should not really matter. The estimate of Garoff and Meyer is that α is of the order 10^5 cgs unit or 10^4 J/m^3 K, which agrees fairly well with our measurements.

Musevic *et al.*[19] have measured the change in the Sm A–Sm C* phase-transition temperature as function of a very strong, applied magnetic field. This change was less than 50 mK for a magnetic field of up to 14.5 T. If we use our Eqs. (IV.5) and (IV.11), we can make a lower estimate of α from their experiments: $\alpha > 2000$ J/m^3 K. In their article a more detailed calculation is made. A calculation of their type will give the same estimate. Both our own and others[2] estimations of α are summarized in Table II.[†]

IV. DEPENDENCE OF TILT ANGLE AND PHASE TRANSITION TEMPERATURE ON κ

We now are in a position to calculate how the tilt angle and the Sm C (Sm C*)–Sm A phase-transition temperature react to various external forces. Using the values for the material constants given in Tables I and II we now derive numerical estimates of the effects. In this section we investigate the effects of κ, which is defined in Eq. (II.21).

In Eq. (III.2) we have given the equilibrium tilt angle, θ_0, for the undisturbed Sm C phase. This is derived by minimizing the Landau energy, Eq. (II.3), with respect to θ. We now use the general expression for the

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[†] C. C. Huang and J. M. Viner (Phys. Rev. *A25*, 3385, (1982)) have also studied the Sm C (Sm C*)–Sm A phase transition using a sixth-order Landau expansion. From their yet unpublished but very careful heat capacity measurements of DOBAMBC (C. C. Huang, personal communication) we can extract $\Delta T \simeq 0.39$ K and $\Delta C_p \simeq 124$ J/mole · K. From this and from the tilt-angle measurements of P. Martinot-Lagarde[16] we can estimate the Landau parameter α to be: $\alpha \simeq 2.6 \cdot 10^4$ N/m^2 · K.

free-energy density, Eq. (II.20), including the Landau term and the term containing κ (for the transparency of the formulas derived we disregard the term $\frac{1}{6}c\theta^3$, discussed in section III, since it would make no significant change in the results).

$$g = \frac{1}{2}(a + \kappa)\theta^2 + \frac{1}{4}b\theta^4 \tag{IV.1}$$

where κ is defined by Eq. (II.21). Minimizing with respect to θ gives

$$\theta^2 = -\frac{a + \kappa}{b} = -\frac{a}{b}\left(1 + \frac{\kappa}{a}\right) \tag{IV.2}$$

Using Eqs. (II.4) and (III.2) we now write

$$\theta^2 = \theta_0^2\left(1 - \frac{\kappa}{\alpha(T_0 - T)}\right) \tag{IV.3}$$

The transition to the Sm A phase occurs when θ equals zero. If we denote this new phase-transition temperature as T_c we get

$$1 - \frac{\kappa}{\alpha(T_0 - T_c)} = 0 \tag{IV.4}$$

giving

$$T_c = T_0 - \frac{\kappa}{\alpha} \tag{IV.5}$$

Using Eqs. (III.2) and (IV.5), we can rewrite Eq. (IV.3) as

$$\theta^2 = \frac{\alpha}{b}(T_c - T) \tag{IV.6}$$

We see that θ has the same temperature dependence as before, the only difference being that it is shifted rigidly by the amount κ/α (Figure 5). We can thus conclude that it is the numerical value of κ/α which plays the most essential role in the variations of θ occurring as a function of external forces. Irrespective of how small κ/α is, the effects will always be large when the phase transition is reached.

Effect of chirality

Let us first discuss the difference between a chiral and a nonchiral compound. We imagine that we have two compounds with exactly the same material parameters, the only difference is that one is chiral and one is not. In the nonchiral compound, Λ is zero and ϕ is constant, so that κ is equal

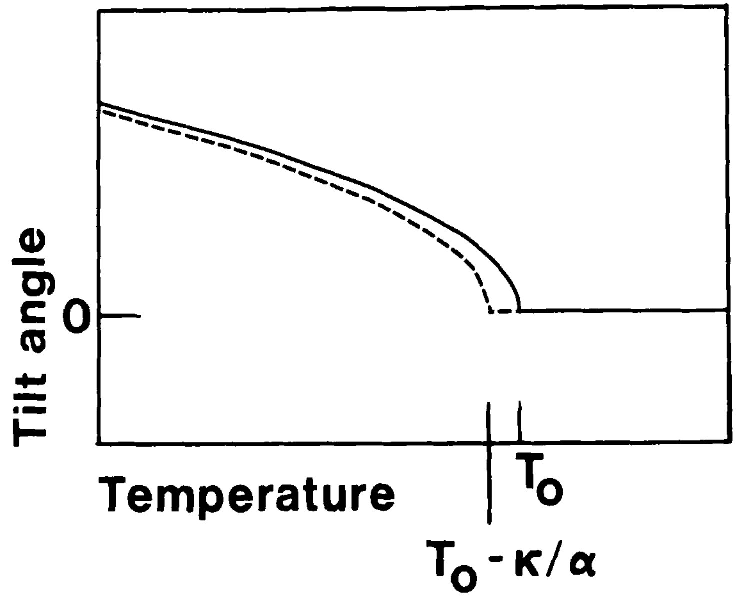

FIGURE 5 Tilt angle as a function of temperature for an undisturbed Sm C (Sm C*) liquid crystal (solid line). At T_0 the tilt angle continously drops to zero according to $\theta^2 = \alpha/b(T_0 - T)$. The effect of κ is shown in the broken line. The graph of θ has been shifted rigidly by the amount κ/α, giving $\theta^2 = \alpha/b(T_0 - \kappa/\alpha - T)$.

to zero. In the chiral compound, on the other hand, a spontaneous twist has developed, $(d\phi/dz) = \Lambda/K_{33}$. In this case we get:

$$\kappa_\Lambda = -\frac{\Lambda^2}{K_{33}} \simeq -0.5\ \mathrm{N/m^2} \qquad \left|\frac{\kappa_\Lambda}{\alpha}\right| \simeq 4 \cdot 10^{-4}\ \mathrm{K} \tag{IV.7}$$

Thus we see that the changes due to chirality in both tilt angle and phase-transition temperature are negligible. Chirality is, of course, not an external effect, but is built into the medium. In the following discussion of various effects, we will not have to consider whether the liquid crystal is chiral or not. As is seen in Eqs. (IV.4) and (IV.5), chirality only changes the phase-transition temperature, thus redefining a. The effect of chirality is then incorporated in the term $\frac{1}{2}a\theta^2$ in the Landau expansion.

Effect of twist $\left(\frac{d\phi}{dz} \neq \frac{2\pi}{\lambda_0}\right)$

If we disturb the twist in a Sm C liquid crystal in one way or another or if we induce one in the Sm C phase, we have, by Eq. (II.21)

$$\kappa_T = K_{33}\left(\frac{d\phi}{dz} + \frac{\Lambda}{K_{33}}\right)^2 \qquad \text{(IV.8)}$$

Typical values for κ_T are given by setting $(d\phi/dz) = 0$ in Eq. (IV.8) and we get

$$\kappa_T = \frac{\Lambda^2}{K_{33}} \simeq 0.5\ \text{N/m}^2 \qquad \frac{\kappa_T}{\alpha} \simeq 4 \cdot 10^{-4}\ \text{K} \qquad \text{(IV.9)}$$

Effect of magnetic fields

Concerning the effects of magnetic fields, we have, by Eq. (II.21)

$$\kappa_M = \frac{\chi_a}{\mu_0}(B_z^2 - B_x^2 \cos^2 \phi) \qquad \text{(IV.10)}$$

If we apply a very strong magnetic field of the order of 10 T, we get

$$\kappa_M \simeq 10^2\ \text{N/m}^2 \qquad \frac{\kappa_M}{\alpha} \simeq 2 \cdot 10^{-3}\ \text{K} \qquad \text{(IV.11)}$$

Effect of electric fields (the polarizability part)

We now study the response of an applied electric field taking into account only the induced polarization (the field is assumed to be in the smectic planes) and get, by Eq. (II.21)

$$\kappa_E = -\varepsilon_a\varepsilon_0 E^2 \cos^2 \phi \qquad \text{(IV.12)}$$

Let the electric field be of the order of 1 $\text{V}/\mu = 10^6$ V/m, which gives, by setting ϕ equal to zero

$$|\kappa_E| \simeq 10^2\ \text{N/m}^2 \qquad \frac{|\kappa_E|}{\alpha} \simeq 2 \cdot 10^{-3}\ \text{K} \qquad \text{(IV.13)}$$

This effect is negligible, but we see that increasing the field by a factor of 10 would give measurable effects near the phase transition. The question, however, is how strong the electric fields are that can be applied before the liquid crystal breaks down for other reasons.

Summary of the effects of κ

We see in Eqs. (IV.9), (IV.11) and (IV.13) that, at least for electric fields that are not too large, the value of κ/α is of the order of $2 \cdot 10^{-3}$ or less. Even very close to the phase-transition point ($T_0 - T \lesssim 0.2$ K), we see by

Eq. (IV.6) that the effect on θ is small. The only case in which we can expect to find some effect on θ is where there are very strong electric fields, but even here the effect will be very small except in a temperature region of about 1 K from the Sm C (Sm C*)–Sm A phase-transition point. The conclusion is thus that when studying phase transitions, the coupling of θ to the applied field should be taken into account but when studying the elastic properties away from the phase-transition point, we can regard θ as a constant.

V. DEPENDENCE OF TILT ANGLE AND PHASE TRANSITION TEMPERATURE ON λ

In this section we discuss the effects of λ on the tilt angle and the Sm A–Sm C (Sm C*) phase-transition temperature. λ contains two different terms. One is the influence of an oblique magnetic field, and the other is the influence of an electric field applied parallel to the smectic layers due to the fix macroscopic dipole moment which exists in the ferroelectric Sm C* phase. Looking at Eq. (II.20) we see that there is now an entirely new situation, since λ introduces a term which is linearly dependent on θ in the free-energy density. We thus get

$$g = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 - \lambda\theta \qquad \text{(V.1)}$$

where

$$\lambda = -\mu E \sin\phi + \frac{\chi_a B_x B_z \cos\phi}{\mu_0} \qquad \text{(V.2)}$$

Minimizing g with respect to θ gives

$$b\theta^3 + a\theta - \lambda = 0 \qquad \text{(V.3)}$$

Dividing Eq. (V.3) by b and introducing two new parameters r and p we get

$$\begin{aligned} &\theta^3 + r\theta - p = 0 \\ &r = \frac{a}{b} = \frac{\alpha}{b}(T - T_0) \\ &p = \frac{\lambda}{b} \end{aligned} \qquad \text{(V.4)}$$

We see that the effect of λ is to introduce the constant term, p, into Eq. (V.4), so that $\theta = 0$ is no longer a solution to the problem. In Figure 6a

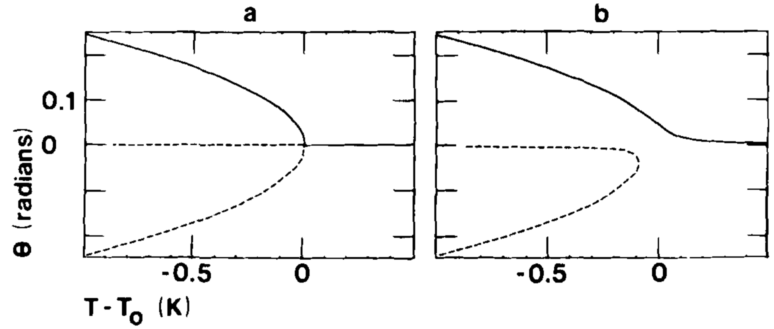

FIGURE 6 Tilt angle as a function of temperature for a ferroelectric liquid crystal, with an electric field applied parallel to the smectic planes (the solutions of Eq. (V.4)). The solution which minimizes the free-energy density is shown as a solid line. In (a) we have drawn the solution without the electric field (with p equal to zero in Eq. (V.4)). In (b) we have included the effects of the electric field due to the fix macroscopic dipole moment of the liquid crystal. The material parameters used are taken from Tables I and II and the applied electric field is of the magnitude 10^6 V/m.

we have plotted the solution of Eq. (V.4), letting p be equal to zero. Below T_0 we have three solutions

$$\begin{aligned} \theta_1 &= 0 \\ \theta_{2,3} &= \pm\theta_0 \end{aligned} \tag{V.5}$$

The stable solution, which is obtained by minimizing g, is either θ_2 or θ_3. The final choice is a matter of sign convention. Here we have chosen the positive solution as the stable one. Above T_0 there is only one solution to the equation: $\theta = 0$. The solid line in the figure represents the stable solution, and we see the usual behavior of the second-order phase transition. Introducing the effects of λ, the situation gets more complicated. The solution of Eq. (V.4) in this case is given by

$$\begin{aligned} \theta_1 &= A + B \qquad & A &= \sqrt[3]{\frac{p}{2} + \sqrt{\frac{p^2}{4} + \frac{r^3}{27}}} \\ \theta_{2,3} &= -\frac{A+B}{2} \pm \frac{A-B}{2}\sqrt{-3} \qquad & B &= \sqrt[3]{\frac{p}{2} - \sqrt{\frac{p^2}{4} + \frac{r^3}{27}}} \end{aligned} \tag{V.6}$$

This is plotted in Figure 6b, where the stable solution is again shown as a solid line. Both figures are drawn in the same scale, a and b are taken from Table II, and λ is 10^2 N/m^2. This value is obtained by taking the value of μ from Table I, letting $\sin\phi = -1$ and applying an electric field of 10^6 V/m to the liquid crystal. To get the same value of λ using an oblique magnetic field we will have to apply a field of 35 T or more. Since this is a strong magnetic field indeed, the largest effect of a magnetic field is less than that of a large electric field. We thus conclude that 10^2 N/m^2 is the largest value of λ which is realistic to consider. We can see some interesting features in Figure 6. First we see that the temperature T^* where two of the solutions disappear, is slightly changed. According to the theory for cubic equations this happens when

$$\frac{p^2}{4} + \frac{r^3}{27} = 0 \tag{V.7}$$

which, with the definition in Eq. (V.4) gives

$$T^* = T_0 - \sqrt[3]{\frac{27b\lambda^2}{4\alpha^3}} \simeq T_0 - 8 \cdot 10^{-2}\ \mathrm{K} \tag{V.8}$$

Above T^*, however, θ is not exactly zero, but adopts a small but finite value which decreases with temperature. At T^*, we denote θ by θ^* and get

$$\theta^* = \sqrt[3]{4\frac{\lambda}{b}} \simeq 8 \cdot 10^{-2}\ \mathrm{rad} \simeq 5° \tag{V.9}$$

We thus conclude that there is no longer a sharp transition to the Sm A phase. In the vicinity of T^* the tilt angle goes down to a few degrees but the Sm C* phase will remain.

To get a more transparent numerical expression for the change of the tilt angle due to λ, we expand Eq. (V.6) in the case $|p| \ll |r|$. This condition is the same as $|\lambda| \ll |a|$, which is always valid except in the vicinity of T_0. We then get

$$\begin{aligned} \theta_1 &\simeq -\frac{\lambda}{\alpha(T_0 - T)} \\ \theta_2 &\simeq \theta_0 + \frac{\lambda}{2\alpha(T_0 - T)} \\ \theta_3 &\simeq -\theta_0 + \frac{\lambda}{2\alpha(T_0 - T)} \end{aligned} \tag{V.10}$$

where θ_2 corresponds to the stable solution in Figure 6b. Thus we again see that it is the ratio between the coupling constant of the external field and α which determines the magnitude of the effect. Our numerical estimations give

$$\frac{\lambda}{2\alpha} \simeq 10^{-3}\ \mathrm{K} \tag{V.11}$$

with an electric field of 10^6 V/m. Thus the relative change of the tilt angle is negligible except in the very near vicinity of T_0.

VI. THE TILT ANGLE COHERENCE LENGTH

Let us assume that we have prepared a uniform sample of a Sm C (Sm C*) liquid crystal using strong anchoring conditions for the molecules and that we can control the direction of the smectic planes. This will impose a tilt angle at the boundary which will not be equal to the tilt angle in the bulk. We thus have a situation in which we have forced θ to vary in space. As shown in Figure 2, there are several different possible ways whereby this spatial variation of θ can occur. Concentrating on the situation represented in Figure 7, we can calculate what we will call the tilt-angle coherence length, and denote ξ_θ. This is the distance by which a disturbance in θ from its bulk value will relax. With the choice of coordinates given in Figure 7, we can write the free-energy density (Eq. (II.20)) as

$$g = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{2}K_0\left(\frac{d\theta}{dz}\right)^2 \qquad \text{(VI.1)}$$

g is minimized by the condition

$$\frac{\partial g}{\partial \theta} - \frac{d}{dz}\left(\frac{\partial g}{\partial \theta'}\right) = 0 \qquad \text{(VI.2)}$$

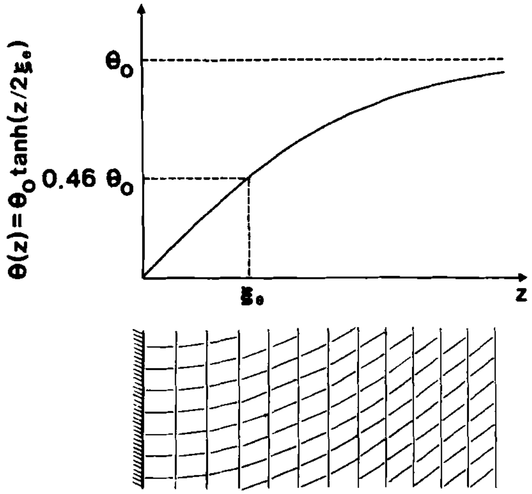

FIGURE 7 Definition of the tilt angle coherence length, ξ_θ. In this calculation the smectic planes are assumed to be parallel to the glass plate, and strong anchoring conditions assure that the tilt angle, θ, is zero at the surface. At a distance of ξ_θ from the glass plate, the tilt angle has reached about half its bulk value.

where θ' is defined as

$$\theta' = \frac{d\theta}{dz} \tag{VI.3}$$

Eqs. (VI.1), (VI.2) and (VI.3) give the differential equation

$$K_0 \frac{d^2\theta}{dz^2} - a\theta - b\theta^3 = 0 \tag{VI.4}$$

Far from the boundary, $d^2\theta/dz^2$ will equal zero and Eq. (VI.4) will give the usual equilibrium value for the tilt angle, θ_0, according to Eq. (III.2)

$$\theta_0^2 = -\frac{a}{b} = \frac{a_0}{b} \tag{VI.5}$$

In Eq. (VI.5) we have defined the positive quantity a_0 as

$$a_0 = -a = \alpha(T_0 - T) > 0 \tag{VI.6}$$

Before calculating $\theta(z)$ we have to establish the boundary conditions. These are given by

$$\begin{aligned} \theta(0) &= 0 \\ \theta(\infty) &= \theta_0 \\ \theta'(\infty) &= 0 \end{aligned} \tag{VI.7}$$

Making use of the equality

$$\frac{d^2\theta}{dz^2} = \theta' \frac{d\theta'}{d\theta} \tag{VI.8}$$

we can rewrite Eq. (VI.4) and integrate, making use of the boundary conditions

$$\int_{\theta'}^{0} \theta' \, d\theta' = \int_{\theta}^{\theta_0} \left(-\frac{a_0}{K_0}\theta + \frac{b}{K_0}\theta^3 \right) d\theta \tag{VI.9}$$

Performing the integrations in Eq. (VI.9) we get

$$\theta'^2 = -\frac{a_0}{K_0}\theta^2 + \frac{b}{2K_0}\theta^4 + \frac{a_0}{K_0}\theta_0^2 - \frac{b}{2K_0}\theta_0^4 \tag{VI.10}$$

Substituting Eq. (VI.5) for θ_0^2 in Eq. (VI.10) gives

$$\theta'^2 = \left(\sqrt{\frac{b}{2K_0}}\,\theta^2 - \frac{a_0}{\sqrt{2K_0 b}} \right)^2 \tag{VI.11}$$

Taking the square root of Eq. (VI.11) and choosing the minus sign give

$$\frac{d\theta}{dz} = \sqrt{\frac{b}{2K_0}}(\theta_0^2 - \theta^2) \qquad \text{(VI.12)}$$

which can be integrated as

$$\int_0^\theta \frac{d\theta}{\theta_0^2 - \theta^2} = \sqrt{\frac{b}{2K_0}}\int_0^z dz \qquad \text{(VI.13)}$$

This gives

$$\theta = \theta_0 \tanh\left(\frac{z}{2\xi_\theta}\right) \qquad \text{(VI.14)}$$

where ξ_θ is defined as

$$\xi_\theta = \sqrt{\frac{K_0}{2a_0}} \qquad \text{(VI.15)}$$

The graph $\theta(z)$ is plotted in Figure 7. Letting z be equal to ξ_θ in Eq. (VI.14) gives

$$\theta(\xi_\theta) = \theta_0 \tanh(0.5) \simeq 0.46\ \theta_0 \qquad \text{(VI.16)}$$

We thus see that ξ_θ is the distance in which a disturbance decays (exponentially) to about half its value. The temperature dependence of ξ_θ is given by the temperature dependence of the coefficient a (Eq. (II.4)):

$$\xi_\theta = \sqrt{\frac{K_0}{2\alpha(T_0 - T)}} \qquad \text{(VI.17)}$$

As expected, ξ_θ diverges at T_0. In order to get an idea of its magnitude we use the values of K_0 and α in Tables I and II, letting $T_0 - T$ be equal to 1 K.

$$T_0 - T = 1\ \text{K} \Rightarrow \xi_\theta \simeq 300\ \text{Å} = 3 \cdot 10^{-2}\ \mu \qquad \text{(VI.18)}$$

This should be compared with typical sample thicknesses which are of the order of 1 μ or more.

Boundary-induced Sm A–Sm C (Sm C*) phase transition in a thin planar sample

If we make a thin planar sample of a Sm C (Sm C*) liquid crystal with the same geometry as that in Figure 7 ($\theta = 0$ at both surfaces), we can get two entirely different situations. In one case we will have a Sm C (Sm C*) liquid crystal with two boundary layers of the order of ξ_θ, where θ varies from zero at the surfaces to θ_0 in the bulk. In the other case the two boundary layers couple to each other and induce a transition to the Sm A phase in the whole sample. A qualitative argument for the occurrence of this phase transition is that ξ_θ should exceed a certain fraction of the sample thickness d. We denote this fraction by γ and write the condition for the transition as

$$\xi_\theta = \gamma d \tag{VI.19}$$

Eqs. (VI.17) and (VI.19) give

$$T_c - T_0 = -\frac{1}{2\gamma^2}\frac{K_0}{\alpha d^2} \tag{VI.20}$$

where T_c is the new Sm A–Sm C (Sm C*) phase transition temperature. Pikin and Yoshino[1] have studied this problem in greater detail and shown that γ is equal to π^{-1}.

This transition is analogous to the Freedericksz transition in nematic liquid crystals. In this case we have a planar sample of a nematic liquid crystal having strong anchoring conditions and an applied electric or magnetic field which opposes these conditions. For a strong enough field a transition takes place where the sample aligns along the field except at the walls, where transition layers are formed. In the case described above the field is replaced by an intrinsic property of the medium, namely the spontaneous tilt which occurs in the bulk. Changing the temperature has the same effect in our case as changing the strength of the applied field has in the Freedericksz case. That is, the coherence length of the disturbance changes. We now apply the same condition to the Freedericksz transition as we have used in Eq. (VI.19), i.e. that the electric (or magnetic) coherence length should be a certain fraction of the sample thickness, and compare this with the exact solution. Denoting the magnetic coherence length by ξ_H and the Freedericksz field by H_F, we get[20]

$$\xi_H = \sqrt{\frac{K_{22}}{\chi_a}}\frac{1}{H}$$

$$H_F = \frac{\pi}{d}\sqrt{\frac{K_{22}}{\chi_a}} \tag{VI.21}$$

We can easily see that this gives the same value for γ as we got for the Sm A–Sm C (Sm C*) transition.

As is true for the ordinary Freederickz transition, we can imagine different geometrical arrangements for the Sm A–Sm C (Sm C*) transition described above. By varying the geometrical situations one can measure the different elastic constants which are involved in the spatial variations of θ.

A numerical estimation, however, shows that the change of the phase-transition temperature is small. Using the values of K_0 and α in Tables I and II, choosing a sample thickness of 1 μ, we get

$$T_c - T_0 = -\frac{\pi^2}{2}\frac{K_0}{\alpha d^2} \simeq -10^{-2}\,\mathrm{K} \qquad \text{(VI.22)}$$

VII. RESULTS AND DISCUSSION

In discussing the elastic properties of Sm C and Sm C* liquid crystals there are two different approaches to the problem. One is to consider the tilt angle as being fixed and as determined only by temperature, irrespective of what external fields or forces are acting on the liquid crystal. In this case we deal with θ as if it were a material constant and have reduced the determination of how the director varies in space to a problem involving only one coordinate, namely ϕ. A more general approach is to realize that θ is also a coordinate which should be treated in the same way as ϕ. The problem is thereby more complex since it involves two coordinates which couple and must be determined at the same time. In this study we have shown that the first and simpler way to handle the problem is correct except in the very vicinity of the transition to the Sm A phase. The relative change of the tilt angle from its equilibrium value, θ_0, is of the order of $\varepsilon/\alpha(T_0 - T)$ (Eqs. (IV.3) and (V.10)), where ε is the coupling parameter dependent on the various forces (ε is a common notation for what we have called κ and λ in the cases discussed here) which act on the sample. α is a Landau parameter as defined by Eqs. (II.3) and (II.4) and T_0 is the Sm A–Sm C (Sm C*) phase-transition temperature. The different cases we have considered are summarized in Table III. We now define τ in such a way that in a temperature regime between $T_0 - \tau$ and the new phase transition temperature T_c, the relative change of the tilt angle is larger than one percent. Inside the interval $[T_0 - \tau, T_c]$ the more general approach to the problem must be used.

$$\frac{\varepsilon}{\alpha\tau} = 0.01$$

$$\tau = 100\frac{\varepsilon}{\alpha} \qquad \text{(VII.1)}$$

To give a numerical value of τ we must estimate ε and α. As we have shown ε would not be expected to exceed 10^2 N/m^2. The value of α is at present an open question in the literature and is discussed in Section III. Our measurements of c_p for DOBAMBC give a value of α which is $5 \cdot 10^4$ N/m$^2 \cdot$ K,

TABLE III

Summary of the results derived in this work

	Contribution to κ	*Contribution to λ*
Chirality	$-\dfrac{\Lambda^2}{K_{33}}$	
Twist	$K_{33}\left(\dfrac{d\phi}{dz} + \dfrac{\Lambda}{K_{33}}\right)^2$	
Electric field	$-\varepsilon_a\varepsilon_0 E^2 \cos^2 \phi$	$-\mu E \sin \phi$
Magnetic field	$\dfrac{\chi_a}{\mu_0}(B_z^2 - B_x^2 \cos^2 \phi)$	$\dfrac{\chi_a B_x B_z \cos \phi}{\mu_0}$
	Effect of κ	*Effect of λ*
Tilt-angle dependence	$\theta^2 = \theta_0^2\left(1 - \dfrac{\kappa}{\alpha(T_0 - T)}\right)$	$\theta = \theta_0 + \dfrac{\lambda}{2\alpha(T_0 - T)}$ (Far from T_0) See Eq. (V.6) (Near T_0)
Shift in phase-transition temperature	$-\kappa/\alpha$	No sharp transition to the Sm A phase (See Eq. (V.8))
	Effect of boundary conditions	
Tilt-angle coherence length	$\sqrt{\dfrac{K_0}{2\alpha(T_0 - T)}}$	
Shift in phase-transition temperature for a sample of thickness d	$-\dfrac{\pi^2}{2}\dfrac{K_0}{\alpha d^2}$	

a result which agrees with both the value given by Garoff and Meyer[7] and the lower limit which can be calculated from the data of Mucevic *et al.*[19]

Choosing our value of α, $5 \cdot 10^4$ N/m$^2 \cdot$ K, gives τ the value 0.2 K. This means that, in studying the elastic properties of Sm C and Sm C* liquid crystals, one need not attend to corrections in θ when the temperature is more than 0.2 K away from the Sm A phase. (The exact limit will of course differ from case to case, depending both on what kind of disturbance is acting on the liquid crystal and on the strength of this disturbance. The limit will also differ from compound to compound.) In this case we treat θ as a "quasi-material parameter". On the other hand, in the very near vicinity of T_0, we have to consider variations of both ϕ and θ, making the analysis more complex. We should note, however, that if Ostrovski's value of α is correct, the effects are multiplied by a factor of about 500. In this case the variations of θ are important for all temperatures, at least for large disturbances. Not only the value of α but also the magnitudes of the different material constants given in Table I are of great importance. Some of these are established in the literature but others are given by "reasonable estimations". It should be of utmost importance for the analysis of the elastic behavior of Sm C and Sm C* liquid crystals to determine τ thoroughly. Therefore a systematic determination of all material constants for Sm C and Sm C* liquid crystals would be of great interest.

Finally, we shall comment on the small-angle approximation done in the free-energy density. Considering the discussion of phase-transition temperatures, this causes no restriction since the phase transition always takes place at small angles. In discussing the variations of θ, we have proven that they are negligible for temperatures further away from the Sm A phase than 0.2 K. By Eq. (III.2), putting $T_0 - T$ equal to 0.2 K, we get

$$\theta_0 = \sqrt{\frac{\alpha}{b}(T_0 - T)} \simeq 0.1 \text{ rad} \simeq 6° \qquad \text{(VII.2)}$$

This is indeed small enough to justify the approximations made. Going further away from the phase-transition point, we ultimately come to a temperature for which the small-angle approximation is no longer valid. We would then expect a quantitative but not a qualitative change in our results, but the statement that the relative change of θ is negligible is, of course, still valid.

Acknowledgment

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