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Thickness dependence of chiral smectic C liquid crystal phase transitions

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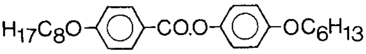
In this paper we consider the influence of solid boundaries on the transition temperatures of a chiral smectic C liquid crystal. Particular attention has been paid to the S_C^*–S_A transition. A simple model to explain the thickness dependence of the S_C^*–S_A transition is proposed. An experimental method to determine some elastic constants and the anchoring energy of ferroelectric liquid crystal molecules is demonstrated.

The growing interest in the study of chiral smectic C liquid crystals is due to the combination of ferroelectric and liquid crystal properties, which makes it possible to realize unique effects in these materials [1, 2]. The ferroelectric state of such liquid crystals exists within a definite temperature range which is why the study of the influence of different factors on different phase transitions is important. In this paper we investigate the influence of limiting solid walls on the transition temperatures of ferroelectric liquid crystals. We also consider, both the first order chiral smectic C–cholesteric (S_C^*–Ch) and the second order chiral smectic C–smectic A (S_C^*–S_A) transitions to the ferroelectric phase on the cooling.

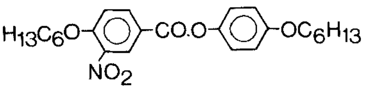
The mesogen studied is 4′-*n*-hexyloxyphenyl-4-*n*-octyloxy benzoate



In order to induce ferroelectricity this compound was doped with the polar chiral dopant *p*-Cl-benzylidene 1-menthon (C_m = 0·08). The mixture obtained has the phase

$$C \underset{36^\circ C}{\overset{42^\circ C}{\rightleftharpoons}} S_C^* \xleftrightarrow{48\cdot 5^\circ C} Ch \xleftrightarrow{81^\circ C} I$$

In order to obtain a S_C^*–S_A phase transition the same liquid crystal has been doped with the smectogen, 4′-*n*-hexyloxyphenyl-3-nitro-4-*n*-hexyloxybenzoate



and then doped with the same chiral dopant (C_m = 0·08). The transition temperatures of this mixture are

$$C \underset{12^\circ C}{\overset{24^\circ C}{\rightleftharpoons}} S_C^* \xleftrightarrow{36\cdot 5^\circ C} S_A \xleftrightarrow{48^\circ C} Ch \xleftrightarrow{55^\circ C} I$$

The cell thickness was varied in the range from 2 to 100 μm. In order to obtain a homogenious orientation of the director the surface was strongly rubbed with a tissue.

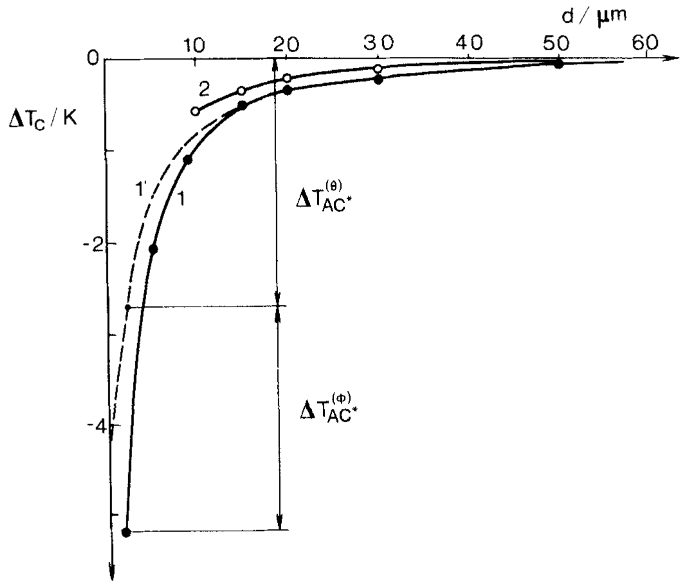


Figure 1. The dependence of the chiral smectic C–smectic A (curve 1) and chiral smectic C–cholesteric (curve 2) phase transition temperatures upon the electrooptic cell thickness.

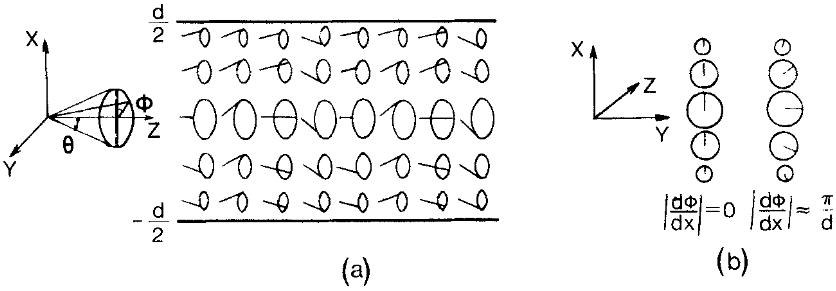


Figure 2. (*a*) The director arrangement in the chiral smectic C-phase (*b*) The c-director distribution in the x direction for the layers with $\phi = 0$ and $\pi/2$.

The thickness and temperature were characterized by the accuracy 0·5 μm and 0·025°C, respectively.

The results of the measurement are shown in the figure 1. Curve 1 corresponds to the S_C^*–S_A transition and shows, that the transition temperature decreases on increasing the cell thickness. The molecular arrangement within the chiral smectic C phase is shown in figure 2; the smectic layers are in the XY plane and the cell is in the YZ plane. As we show in the figure both the tilt angle, θ, and the azimuthal angle, ϕ, change in the direction perpendicular to the cell plane. These variations in θ and ϕ result from the planar anchoring of the liquid crystal director to the solid surface and the removal of free rotation of the director molecules at the surface, respectively. The first deformation increases the energy per unit layer by the value of $\frac{1}{2}G_\theta(d\theta/dx)^2$ and the second increases the energy by $\frac{1}{2}G_\phi(d\phi/dx)^2\theta^2$ (the later is true for small θ, which is satisfied near the S_C^*–S_A transition), where G_θ and G_ϕ are the elastic constants for the corresponding deformations. Thus, we can represent the bulk free energy per unit layer as

$$F = F_A + \tfrac{1}{2}a\theta^2 + \tfrac{1}{4}b\theta^4 + F_d, \tag{1}$$

where F_A is the free energy of the smectic A phase, $a = a'(T - T_{AC^*})$ and b are coefficients of the Landau expansion, while F_d is the distorsion free energy

$$F_d = \tfrac{1}{2}\, G_\theta \left(\frac{d\theta}{\mathrm{dx}}\right)^2 + \tfrac{1}{2} G_\phi \left(\frac{d\phi}{dx}\right)^2 \theta^2. \tag{2}$$

The true dependence of $\theta(x)$ and $\phi(x)$ do not essentially distinguishes from a linear law. To simplify the problem we shall suppose that the gradients $(d\theta/dx)$ and $(d\phi/dx)$ are independent of the x coordinate for the cell with a given thickness. In this case the free energy functional reduces to a free energy function and the general problem is to relate the gradients to the cell thickness, the liquid crystal elastic properties and the anchoring energy.

A sensible form for the surface energy (for small θ) is

$$F_s = \tfrac{1}{2} W_\theta \theta^2 + \tfrac{1}{2} W_\phi \theta^2 \sin^2 \phi, \tag{3}$$

where W_θ and W_ϕ are the out of plane and in plane anchoring energies, respectively. If W_ϕ is large (strong anchoring) the azimuthal angle at the surface, ϕ_s, does not differ essentially from 0 or π; this leads to boundary conditions for the angles θ and ϕ

$$\begin{aligned} G_\theta \frac{d\theta_s}{dx} &= G_\theta \frac{d\phi}{dx} \\ &= \pm W_\theta \theta_s, \end{aligned} \tag{4}$$

$$\begin{aligned} G_\phi \frac{d\phi_s}{dx} &= G_\phi \,, \frac{d\phi}{dx} \\ &= \pm W_\phi \phi_s. \end{aligned} \tag{5}$$

A solution of equation (4) is

$$\theta(x) = \theta(0) \pm \frac{W_\theta}{G_\theta} \theta_s \cdot x.$$

Taking into consideration, that $\theta(\pm d/2) = \theta_s$ we obtain

$$\theta_s = \theta(0) \bigg/ \left(1 + \frac{d}{2} \frac{W_\theta}{G_\theta}\right)$$

and substitution of this into the boundary condition (4) gives

$$\frac{d\theta}{dx} = \pm 2\theta \bigg/ \left(d + 2 \frac{G_\theta}{W_\theta}\right). \tag{6}$$

In this expression we have assumed that the tilt angle $\theta(0)$ is equal to the tilt angle for the non-deformed chiral smectic C phase. The ratio $(G_\theta / W_\theta) = l$ is an extrapolation length [3] and takes into account the anchoring finiteness, in other words a cell with finite anchoring and of thickness d possesses properties equivalent to those for a cell with infinitely strong anchoring and thickness $d + 2l$.

In the same manner we can obtain an expression for the gradient of the azimuthal angle

$$\frac{d\phi}{dx} = \pm\, 2\phi \bigg/ \left(d + 2 \frac{G_\phi}{W_\phi}\right).$$

When the surface has strong anchoring $W_\phi \approx 10^{-4}\,\mathrm{J\,m^{-2}}$ [5]. On the other hand $G_\phi \sim 10^{-11}\,N$ and the corresponding extrapolation length $l' = (G_\phi/W_\phi) \approx 0{\cdot}1\,\mu\mathrm{m}$ can be neglected in comparision with $d \gtrsim 2\,\mu\mathrm{m}$. Moreover the change of ϕ in the Z direction causes the absolute value of the gradient $(d\phi/dx)$ to change from 0 to π/d (see figure 2 (*b*)) and it is not difficult to show that averaged value of $(d\phi/dx)^2$ is $\pi^2/3$:

$$\overline{\left(\frac{d\phi}{dx}\right)^2} = \frac{1}{L/4}\int_0^{L/4}\left(\frac{\phi}{d/2}\right)^2 dz = \frac{16}{Ld^2}\int_0^{L/4}\left(\frac{2\pi}{L}\cdot z\right)^2 dz = \frac{\pi^2}{3d^2}. \qquad (7)$$

Thus, by combining equations (1), (6) and (7) we obtain the free energy density as

$$\bar{F} = F_{\mathrm{A}} + \tfrac{1}{2}\left[a'(T - T_{\mathrm{AC}^*}(\infty)) + 4G_\theta\left(d + 2\frac{G_\theta}{W_\theta}\right)^{-2} + \frac{\pi^2}{3}G_\phi d^{-2}\right]\theta^2 + b\theta^4$$

From this we obtain directly that the $\mathrm{S_C^*}$–$\mathrm{S_A}$ transition temperature shifts by

$$T_{\mathrm{AC}^*}(d) - T_{\mathrm{AC}^*}(\infty) = -\left[\frac{4G_\theta}{a'}\left(d + 2\frac{G_\theta}{W_\theta}\right)^{-2} + \frac{\pi^2}{3}\frac{G_\phi}{a'}d^{-2}\right]. \qquad (8)$$

The first contribution is caused by the change in the tilt angle and, the second results from the change in the azimuthal angle in the x-direction. For sufficiently large cell thickness the second contribution can be neglected as it is clear that G_θ is greater than G_ϕ by at least one order of magnitude. In fact, at $d \gtrsim 15\,\mu\mathrm{m}$ we can describe curve 1 approximately by the formula

$$\Delta T_{\mathrm{AC}^*}(d) = -k_1(d + 2l)^{-2}$$

with $k_1 \approx 280\,\mathrm{K}\,\mu\mathrm{m}^2$ and $l \approx 4\,\mu\mathrm{m}$. The dependence

$$\Delta T_{\mathrm{AC}^*} = -\frac{4G_\theta}{a'}\left(d + 2\frac{G_\theta}{W_\theta}\right)^{-2}$$

was first obtained and verified experimentally by Pikin and Yoshino [4], in which the factor $\pi^2/2$ was obtained instead of 4. This small difference is related to the assumption that the gradient of θ is a constant.

In our experiment we have observed a systematic deviations from this dependence for the cell thickness $d \lesssim 10\,\mu\mathrm{m}$, which can be explained by the increasing importance of the second contribution. It is not difficult to separate out the ϕ gradient contribution from curve 1 (the last contribution is very small for a cell with unrubbed substrates) and to find the relation of G_ϕ/a', which equals $3\,\mathrm{K}\,\mu\mathrm{m}^2$.

At a thickness d less than 7–8 μm the liquid crystal undergoes a transition from the smectic A phase to the non-helicoidal ferroelectric phase. This behaviour also can be related to the gradient of the aximuthal angle in the x direction. Actually, it causes the deformation of the spiral structure as shown in figure 2. According to equation (6) the gradient of $d\phi/dx$ increases with decreasing cell thickness and at some critical thickness, d_c, the spiral structure disappears. It is not difficult to show that the critical thickness is determined by

$$d_c = (2/\pi)\sqrt{(G_\phi/K_{33})}L, \qquad (9)$$

where L is the helical pitch and K_{33} is the bend elastic constant.

The experimental study of the thickness dependence of the transition temperature gives us the possibility of an approximate determination of the elastic constants G_θ and G_ϕ as well as W_θ the anchoring energy by using the simple scheme:

(*a*) the ratios G_θ/a', G_θ/W_θ and G_ϕ/a' are determined from the experimental curve 1;

(*b*) to measure the critical thickness d_c in the wedge-shaped cell via equation (9) which determines the ratio G_ϕ/K_{33};

(*c*) the helical pitch and the bend elastic constants are measured independently using light diffraction in the periodic S_C^* structure and using the ferroelectric liquid crystal behaviour in an external electric field.

For the mixture studied we find $G_\theta/W_\theta \approx 4 \times 10^{-6}$ m, $G_\theta/a' \approx 7 \times 10^{-11}$ K m^2, $G_\phi/a' \approx 3 \times 10^{-12}$ K m^2, $L = 5{\cdot}5 \times 10^{-6}$ m, $K_{33} \approx 1{\cdot}2 \times 10^{-12}$ J m^{-1}. From these results we obtain $G_\theta \approx 1{\cdot}2 \times 10^{-10}$ J m^{-1}, $G_\phi \approx 5 \times 10^{-12}$ J m^{-1}, $W_\theta \approx 3 \times 10^{-5}$ J m^{-2}.

Although we have been concerned with the S_C^*–S_A phase transition the solid walls also influence other possible phase transitions occurring in the ferroelectric liquid crystal. It was confirmed that due to the cell thickness decreasing not only the second order transition, but also a weak first order transition is shifted. The transition temperature of Ch–I rises slowly with decreasing cell thickness according to the law d^{-1}. For the cell with a thickness of order 1 μm this increase reached 0·3 K. This is in a good accord with theoretical work [6–8] carried out for the nematic–isotropic transition. The S_A–Ch transition temperature also increases slightly with decreasing thickness, but in this case we could not determine any concrete dependence, since the transition is not sharp and is spread with a width ΔT, which is greater than $\Delta T_c(d)$. Similar behaviour takes place for the S_C^*–Ch transition, but if we take a point, in which the fingerprint texture emerges, we obtain curve 2 which is similar to the curve 1. Such behaviour can be explained by the assumption that the S_C^*–Ch transition preceeds with a metastable interface and S_A phase formation within a narrow temperature interval [9]. For a thickness less than 10 μm the cholesteric planar texture undergoes a transition to the chiral smectic C homeotropic texture.

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