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Temperature difference between bulk and surface transition in freely suspended smectic films

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We report an ellipsometric study of freely suspended films of a chiral liquid-crystal compound possessing the phase sequence smectic-*C*–smectic-*A*–isotropic with a very broad (67 K) smectic-*A* phase range. We observe a smectic-*C*–smectic-*A* surface transition which is situated more than 60 K above the bulk smectic-*C*–smectic-*A* transition temperature. Possible reasons for this unusually large temperature shift are discussed. [S1063-651X(99)06405-3]

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Most condensed matter systems are expected to be less ordered at the surface than in the bulk [1]. Exceptions are simple chain molecules such as alkanes and alcohols, and thermotropic liquid crystals. These compounds can show, at temperatures above a bulk phase transition, a distinct surface phase transition, at which the low-temperature phase is formed at the surface whereas the bulk remains in the high-temperature phase. In the case of alkanes and alcohols, where a crystalline surface layer on an isotropic melt is formed a few degrees K above the bulk melting point, this behavior has been observed fairly recently [2–4], whereas for liquid crystals the corresponding behavior is known for more than 15 years. The free surface of liquid crystals has been studied in two kinds of samples: Thick films on a substrate have been used to investigate the behavior at phase transitions involving the isotropic and nematic phase [5–7] (in these cases, however, the surface phase develops often continuously without a distinct transition). By far the most studied systems are freely suspended smectic films which provide ideal systems for the investigation of transitions between different smectic phases at free surfaces.

Freely suspended smectic films consist of an integral number (adjustable between several hundred and only two) of molecular smectic layers which are arranged parallel to the two free surfaces. If a transition between two smectic phases is approached from above, the layers at the surface transform into the low-temperature phase usually well above the bulk transition temperature (recent reviews are [8,9]). On further approaching the bulk transition temperature, the low-temperature phase grows into the interior of the film, in most cases via a series of layer-by-layer transitions. Finally, when the bulk transition temperature is reached, the complete film has adopted the structure of the low-temperature phase.

We are concerned here with the temperature difference $\Delta T = T_S - T_B$ between the surface transition and the transition in the corresponding bulk sample; in some cases, phases appear at the surface which are not present in the bulk sample (see, e.g., [10]); we do not regard these cases in the following. For most transitions ΔT amounts to a few degrees K, with some variation from compound to compound (Table I gives an overview). The transition between the two simplest smectic phases, smectic-*A*(Sm-*A*) and smectic-*C*(Sm-*C*), occurs for most compounds at the surface of freely suspended films about 10 to 15 K above the bulk transition temperature. Sm-*A* and Sm-*C* phases can be considered as stacks of molecular layers, each layer corresponding to a two-dimensional fluid in which the rodlike molecules are with their long axis aligned on average parallel (Sm-*A*) to the layer normal or tilted (Sm-*C*) by an angle θ with respect to the layer normal.

Recently, it was observed that in compounds possessing fluorinated alkyl chains the Sm-*A*–Sm-*C* surface transition temperature is situated unusually close (only 1–2 K above) to the bulk transition [20,11]; the small value of ΔT in these compounds is probably a result of the low surface tension of fluorinated compounds. We report here our observation of an unusual *large* value (>60 K) of ΔT in a compound possessing a very broad Sm-*A* phase above its Sm-*C* phase. The large ΔT value is probably a consequence of a large tilt susceptibility in the Sm-*A* phase of this compound.

The compound under investigation (designated as ‘‘9HL,’’ the molecular structure is shown at the top of Fig. 1) is a chiral lactate derivative [21]. The bulk phase sequence of our sample is Sm-*C* 64 °C Sm-*A* 138 °C isotropic. Freely suspended films are drawn in the Sm-*A* phase using a rectangular, variable-area frame described in [22]. The typical film area is $5\times10\ \mathrm{mm}^2$.

The Sm-*A*–Sm-*C* transition at the film surface is detected by ellipsometry. The beam of a HeNe laser transmits the film

TABLE I. Typical values of ΔT for different smectic transitions.

Transition	ΔT (K)	
Smectic-*C*–smectic-*A*	1–16	[11–13]
Hexatic-*B*–smectic-*A*	7–8	[14–16]
Crystal-*B*–smectic-*A*	9–13	[17,18]
Hexatic-*I*–smectic-*C*	5	[19]
Crystal-*E*–hexatic-*B*	5	[15]

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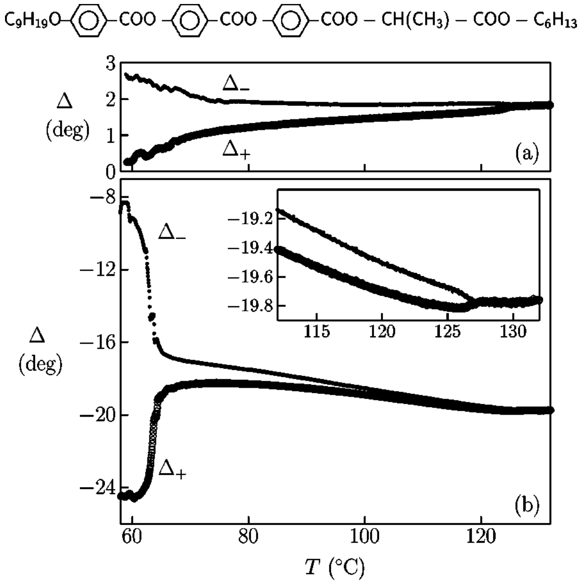

FIG. 1. Temperature dependence of the ellipsometric quantity Δ for freely suspended films with thicknesses of 25 layers (a) and >300 layers (b) of the compound 9HL. The bulk Sm-*A*–Sm-*C* transition temperature is 64 °C, the surface Sm-*A*–Sm-*C* transition occurs at 127 °C; see inset in (b).

under an angle of incidence of 45 °. Using a null ellipsometer (details can be found in [23]) we determine the quantities Δ and Ψ which describe the state of polarization of the transmitted light. Δ and $\tan\Psi$ correspond to the argument and the magnitude of the ratio of the complex field amplitudes E_p and E_s of the *p*- and *s*-polarized components of the transmitted light: $E_p/E_s = \tan\Psi \exp(i\Delta)$, i.e., Δ gives the phase difference and $\tan\Psi$ the amplitude ratio of the *p* and *s* components. The polarization of the incident light is described by $\Delta = 0$ and $\Psi = \pi/4$. A weak dc electric field (8 V/cm) is applied in the film plane and perpendicular to the plane of incidence (the plane containing the film normal and the incident laser beam). Values of Δ and Ψ are continuously collected while the temperature is changed at a constant rate of about 2 K/h. For each field polarity one measurement run is conducted.

The value of Δ is sensitive to the magnitude and direction of the optical axis of the film. Because 9HL is a chiral compound, there is a spontaneous electric polarization $\vec{P}_s$ in each layer. The direction of $\vec{P}_s$ is coupled to the tilt direction, and the applied dc field, which aligns $\vec{P}_s$, is used to predetermine the tilt direction: In our experimental geometry, the molecules in the ferroelectric Sm-*C* phase tilt, depending on the polarity of the applied field, within the plane of incidence either towards the incident laser beam or away from it, giving rise to two values Δ_- and Δ_+. The difference $|\Delta_- - \Delta_+|$ is a measure of the average tilt angle in the film. This method is sensitive enough to detect a nonzero tilt even if only a few layers of the film are tilted, regardless of whether the film consists of only a few or hundreds of smectic layers [12,24,25].

Figure 1 shows the temperature dependence of Δ_+ and Δ_- for a freely suspended 9HL film with a thickness of about 25 layers and a very thick film consisting of several hundred layers. The signature of the bulk transition is seen around 64 °C where the difference $|\Delta_- - \Delta_+|$ shows an increase with decreasing temperature which becomes very pronounced in thick films. Above the bulk transition temperature, a finite difference between Δ_+ and Δ_- remains over a wide temperature range until, at 127 °C, the surface transition takes place where Δ_+ becomes equal to Δ_-. Thus, for 9HL the temperature difference ΔT between the surface and the bulk Sm-*A*–Sm-*C* transition amounts to 63 K. To our knowledge, the largest value of ΔT reported so far for freely suspended films consisting of at least ten layers [26] is that of the compound 2-methylbutylester of 4-decyloxybenzylidene-4′-aminocinnamic acid (DOBAMBC) for which $\Delta T = 16$ K was found [12]. There are also several cases [23,27] where ΔT cannot be measured since the Sm-*C*–Sm-*A* surface transition is shifted beyond the bulk Sm-*A*–isotropic transition temperature, i.e., the surface layers remain tilted with increasing temperature until the film ruptures; however, in these compounds the temperature range above the bulk Sm-*A*–Sm-*C* transition, in which freely suspended films are stable, is relatively narrow (7–15 K).

Since for many different types of smectic phase transitions a surface transition at the free surface occurs at higher temperatures compared to the bulk transition, the detailed structures of the involved phases do not seem to play a major role. An important origin of the enhanced surface order is the surface tension γ which can damp the displacement fluctuations of the smectic layers near the surface. The smectic layer fluctuations consist of two contributions (bending and dilatation/compression of the layers) and their magnitude is determined by the values of the bend elastic constant *K* and layer compressibility constant *B*. If $\gamma > \sqrt{BK}$, the fluctuations at the surface are expected to be smaller compared to the bulk, otherwise they should be larger [28,29]; both cases were experimentally confirmed by x-ray reflectivity studies [30,31]. Supposing that the depression of the fluctuations by the surface tension γ is the primary reason of the enhanced surface transition temperature, the experimental behavior may be described by a very simple Landau model if we introduce a coupling between the order parameter of the transition (in our case the tilt angle θ) and γ, or, more precisely, $\gamma - \sqrt{BK}$. The Landau free energy *g* then reads in its simplest form for a second-order transition

$$g = g_0 + \tfrac{1}{2} a (T - T_B)\theta^2 + \tfrac{1}{2} b \theta^4 - C(\gamma - \sqrt{BK})\theta^2. \quad (1)$$

Here, T_B is the bulk Sm-*A*–Sm-*C* transition temperature, *C* describes the strength of the coupling between γ and θ, and *a* and *b* are positive constants. Equation (1) yields a transition temperature T_S, corresponding to the surface transition temperature, as

$$T_S = T_B + \frac{2C(\gamma - \sqrt{BK})}{a}. \quad (2)$$

Primary reasons for a large value of $\Delta T = T_S - T_B$ could be a large value of γ or a small value of *a*. The magnitude of the surface tension γ depends mainly on the composition of the alkyl chains of the liquid-crystal molecules. Compounds possessing simple alkyl chains with no other substituents than hydrogen show γ values in the range of 21–28 dyn/cm [32,33]; compounds with fluorinated alkyl chains show smaller values [34,35]. There is no reason why 9HL should show a considerably larger γ value than, e.g., the compound DOBAMBC.

The coefficient a of the Landau free energy expansion is a measure of the inverse susceptibility of the order parameter. In the case of the Sm-*A*–Sm-*C* transition, a corresponds to the inverse tilt susceptibility, i.e., a describes how easily the Sm-*A* phase could be tilted by external fields: the smaller the value of a, the ''softer'' (easier to tilt) the Sm-*A* phase. The large temperature range of the bulk Sm-*A* phase provides some indication that 9HL is likely to possess a small value of a. It is well known that the width of the Sm-*A* phase is connected with the nature of the Sm-*A*–Sm-*C* transition: decreasing the Sm-*A* width shifts the transition from simple second order towards tricritical behavior [36,37]; the transition can even become first order [38,39]. Thus, the magnitude of pretransitional effects, i.e., the magnitude of the tilt susceptibility, can be expected to be large in compounds with a large Sm-*A* phase width. Indeed, the compound 9HL possesses a large tilt susceptibility and an extraordinarily small a value: for many compounds a is in the range of 20 to $200\times10^3\ \mathrm{J\,m^{-3}\,K^{-1}}$ [40–44], but for 9HL a value of $a=11\times10^3\ \mathrm{J\,m^{-3}\,K^{-1}}$ was determined [45].

Among the compounds, for which the values of $\Delta T=T_S-T_B$ are known, DOBAMBC is the only one for which the Landau coefficients were also determined. The observed a values for DOBAMBC are between 23 and $50\times10^3\ \mathrm{J\,m^{-3}\,K^{-1}}$ [40,41], i.e., two to four times larger than the value of 9HL. According to Eq. (2), the difference ΔT between the Sm-*A*–Sm-*C* surface and bulk transition temperature for 9HL should be two to four times larger than in DOBAMBC [provided the other quantities of Eq. (2) are of similar magnitude in both compounds]. Indeed we find experimentally $\Delta T_{\mathrm{9HL}}/\Delta T_{\mathrm{DOBAMBC}}=3.9$.

In conclusion, we have reported our observation of an unusual large temperature difference ΔT between a Sm-*A*–Sm-*C* surface and bulk transition in freely suspended films of the smectic liquid crystal 9HL. The large value of ΔT is probably not the consequence of an unusually large surface tension but rather the result of a large tilt susceptibility in the Sm-*A* phase. The compound 9HL provides a system with a well separated surface transition, the correlation length associated with the second-order bulk Sm-*A*–Sm-*C* transition is probably very small at the surface transition temperature. High-resolution studies of this Sm-*A*–Sm-*C* surface transition are in progress.

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