PHYSICAL REVIEW E **72**, 051711 (2005)

Test of clock model in ellipsometric study of thin and thick free-standing films of an antiferroelectric liquid crystal

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(Received 5 May 2005; published 16 November 2005)

The temperature dependences of the ellipsometric parameters in a weak dc external field are studied in thin and thick free-standing films of MHPOBC. The results for thin films consisting of two, three, and four layers are analyzed within the discrete phenomenological model. We find very good quantitative agreement between the theory and experiment, which indicates an odd-even effect. We find that the *XY* structures are stable for an odd number of layers, whereas planar, Ising-like structures are stable for an even number of layers. The experiments on thick (several tens of layers) films show a combination of bulklike and free-surface behavior. This is most pronounced at high temperatures, where the interior of the film is not tilted, whereas the layers at the air interfaces show qualitatively similar temperature dependance of the ellipsometric parameters as in the four-layer film.

DOI: 10.1103/PhysRevE.72.051711 PACS number(s): 61.30.Hn, 68.08.−p, 61.30.Pq, 68.08.Bc

I. INTRODUCTION

Since the discovery of ferroelectricity and antiferroelectricity in smectic phases, chiral and polar smectic liquid crystals [1–4] have attracted considerable attention. One of the very intriguing aspects related to the smectic and polar nature of these materials is an extraordinary rich variety of phases that have been observed in the antiferroelectric liquid-crystalline materials. Today, we know that these phases can be understood and classified using the concept of a unit cell, which was first used to understand light scattering on phase fluctuations in antiferroelectric liquid crystals [5]. On this basis, the unit cell of the ferroelectric phase consists of a single, tilted, and polar smectic layers. The unit cell of the antiferroelectric phase consists of two tilted smectic layers with opposite directions of the molecular tilt and antiparallel spontaneous polarization of each layer. The two "intermediate" phases, sometimes called the "ferrielectric" phases, have unit cells of three and four tilted and polar smectic layers, respectively. And, finally, the smectic-C_α^* phase is an incommensurate phase, where, strictly speaking, there is no unit cell.

The existence of such a rich variety of phases is very challenging from the theoretical point of view. There have been several theoretical studies in this direction, starting with Sun *et al.* [6], who first introduced the "discrete phenomenological model." Within this model, individual smectic layers are considered independent thermodynamic systems, undergoing their own phase transitions. Then, a coupling is introduced between the smectic layers, that substantially influences phase behavior and phase stability of a system of *N* smectic layers. The discrete phenomenological model was further analyzed by Čepič *et al.* [7] and Roy *et al.* [8]. The symmetry properties of possible structures were analyzed by Lorman *et al.* [9]. The most elaborated, "distorted clock" model of Čepič and Žekš can describe well the phase stability, as well as phase transitions in intermediate phases of antiferroelectric liquid crystals [10].

It is then natural to consider that free-standing smectic films of antiferroelectric liquid crystals are promising candidates to study the validity of different proposed theoretical models. These films are almost perfect two-dimensional systems, being an excellent experimental system for probing the physics of different phenomenological models. The films can be made free of any defects, the number of smectic layers can be varied and determined with great precision, and the structure of the films can be determined with great accuracy using x rays and optical ellipsometry. This is the main reason why free-standing smectic films have been extensively studied in the past [11]. The main interest in those studies was the effect of reduced dimensionality on phase transitions and phase stability, surface wetting, and surface-enhanced order [12], whereas there have been only two systematic analysis of the agreement between the theory and experiment [13,14]. Recently, we have reported a combined theoretical and experimental analysis of phase stability and phase transitions in free-standing films, consisting of two, three, and four layers of an antiferroelectric liquid crystal 4-(1-methylheptyloxycarbonyl-phenyl)4′ - octylbiphenyl-4-carboxylate (MHPOBC) [15]. We have applied a clock model to describe quantitatively the measured temperature dependences of the ellipsometric parameters, and we have found a good quantitative agreement. Moreover, we have determined for the first time the set of phenomenological parameters that are necessary for the calculations within discrete model of Čepič and Žekš.

Whereas very thin films consisting of only several smectic layers are perfect candidates for testing the basic premises of the phenomenological models, the question is to what extent can we extrapolate the physical properties from thin to thick films for which we expect properties characteristic of a bulk.

In order to clarify the dilemma about the similarities and differences between thick and thin free-standing smectic films, we present in this paper an extension of our previous studies [15] of phase stability and phase transitions to thick

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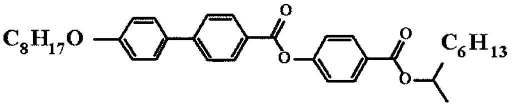

FIG. 1. The chemical structure of the antiferroelectric liquid crystal MHPOBC.

free-standing films of an antiferroelectric liquid crystal MHPOBC. We first present a detailed quantitative analysis of thin films consisting of two, three, and four smectic layers. Whereas we could not find any phase transition in a two-layer film in a rather large temperature interval, we observe a single phase transition in a three-layer film and a rich phase sequence in a four-layer film. We apply the clock model to describe quantitatively the measured temperature dependence of the ellipsometric parameters. We reproduce not only the phase structures, phase transition temperatures, and phase sequences in films of different thickness, but also find good quantitative agreement of measured ellipsometric parameters using a minimum set of adjustable thermodynamic parameters. Surprisingly, the data could be fit only by considering an even-odd effect: whereas films with an even number of layers are planar (Ising like), films with an odd number of layers seem to be twisted (*XY* like). This is consistent with recent predictions of Rovšek *et al.* [16] and strongly supports the distorted clock model.

In thick films, we observe a phase sequence that is typical for bulk MHPOBC. But in addition to that we observe some characteristic details of the ellipsometric parameter that are characteristic of thin films and free surfaces. This is pronounced in the high-temperature region, which never appears in the form of a nonpolar Sm-*A* phase. We observe qualitatively similar behavior as in a four-layer film, suggesting the existence of a thin surface layer that is decoupled from the bulk and behaves independently of the film thickness.

II. EXPERIMENT

The experiments were performed in the antiferroelectric liquid crystal 4-(1-methyl-heptyloxycarbonyl-phenyl) 4′-octylbiphenyl-4-carboxylate (MHPOBC; see the chemical structure in Fig. 1) with the following bulk phase sequence: Isotropic (145 °C) Sm-A^* (120.7 °C) Sm-C_α^* (119.3 °C) Sm-C^* (118.4 °C) Sm-C_γ^* (116.7 °C) Sm-C_A^* (65 °C) Sm-I_A^* (32 °C) crystal. The liquid crystal was spread across a 3-mm circular opening etched in a 150-μm glass slide. Two parallel metal electrodes separated by 3.5 mm were deposited on each side of the opening to apply an electric field along the layers of the freely suspended smectic film. The film holder was put in a closed chamber with several windows for optical access that was temperature controlled to ±0.02 K.

After spreading, the film was heated close to the isotropic phase and let to homogenize until it was uniformly colored. The lateral structure and homogeneity of the film were checked by observing it in a reflected white light using a video camera. After homogenization, the thickness of the film and its refractive indices were determined using three independent optical methods [17]: (i) reflection of a He—Ne laser light, (ii) spectral analysis of the reflected white light using a fiber coupled spectrophotometer, and (iii) ellipsometry. Further on, a procedure similar to Ref. [18] is applied on a large number of smectic films to determine the refractive indices and the thickness of a single smectic layer of MHPOBC by independently fitting data obtained by three methods. The best overall agreement was obtained for $n_e=(1.73\pm0.01)$ and $n_o=(1.47\pm0.01)$, and the thickness of a single MHPOBC Sm-*A* layer is (3.5 ± 0.5)nm, which is in good agreement with x-ray data [19].

In our transmission ellipsometry measurements, a 632-nm laser light was incident on a free-standing film at an angle of 45°. A photoelastic modulator (PEM) based ellipsometer [3] was used to measure the ellipsometric parameter Δ with the resolution of ±0.01°.

The ellipsometric parameter Δ measures the phase difference between the $\hat{p}$ (parallel to the plane of incidence) and $\hat{s}$ (perpendicular to the plane of incidence) components of the transmitted light [20]. In ellipsometry, the second ellipsometric parameter Ψ is also measured, which is equal to the arctangent of the ratio of p and s polarizations of the transmitted (or reflected) light. It therefore represents the ellipticity of the detected light. In our experimental arrangement, which is dedicated to the precise and fast measurement of Δ, the sensitivity to Ψ is rather low—i.e., of the order of 0.1°—and was therefore not used in the interpretation of our data.

It is straightforward to see that Δ carries information about the thickness of the sample, as the phase difference between the p and s polarization should increase with increasing thickness of the free-standing film. However, it turns out that the situation is slightly more complicated in thin films. Namely, in addition to the directly transmitted beam, also the multiply reflected beams, originating from the direct beam and subsequent reflections, have to be considered as well. As the length of propagation and the relative orientation of the dielectric tensor is different for each beam and the polarization state can also be changed upon reflection, the ellipsometric parameter Δ does not simply increase linearly with increasing thickness (see Fig. 2). Instead, Δ can be considered as a combination of a linearly increasing function of thickness and an oscillatory part that appears due to the multiple reflections of the incident beam. Note that due to this oscillatory part, the sign of Δ can change at very small thicknesses of the free-standing film. For example, in Fig. 2, the change of sign of Δ is observable around $N=25$ for a simple, nontilted Sm-*A* structure.

In a typical experimental run, the sample was cooled in a temperature interval of 30–40 K at a rate of 0.4 K/min, starting from the Sm-A^* phase and ending in the antiferroelectric phase at low temperatures. No influence of the cooling rate on the structures and phase transitions was observed. In the experiments, a weak dc electric field (4 V/cm) was applied in the plane of the smectic layers and perpendicular to the plane of incidence of the laser light [see Fig. 3(a)]. In this way, the energetically invariant rotation of the sample around the normal to the smectic layers was removed through the coupling of the electric polarization of the sample with the applied electric field. In each experiment, the temperature dependence of the ellipsometric parameter Δ

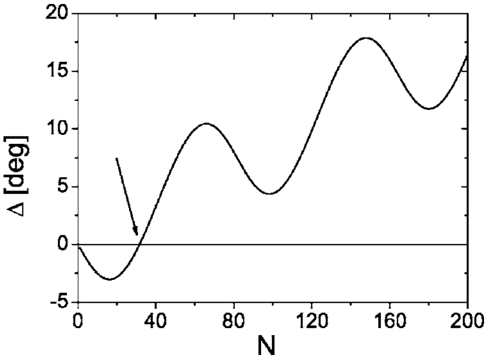

FIG. 2. The ellipsometric parameter Δ as a function of the number of smectic layers forming a free-standing smectic film in the Sm-*A* phase, calculated via the 4×4 matrix method by Yeh [21]. The refractive indices are $n_o=1.47$ and $n_e=1.73$, and the thickness of each smectic layer is 3.5 nm. The arrow indicates the point where Δ changes sign.

was first measured for one direction of the applied field (let us say Δ_+), and immediately after that the measurement of Δ was repeated at the reverse direction of the applied electric field (let us say Δ_-). In this way, a set of two different ellipsometric parameters (Δ_+ and Δ_-), which correspond to two different spatial orientations of the smectic film structure, was obtained as a function of temperature for each film thickness. The experiments were repeated on several samples over extended period of time, giving essentially identical results.

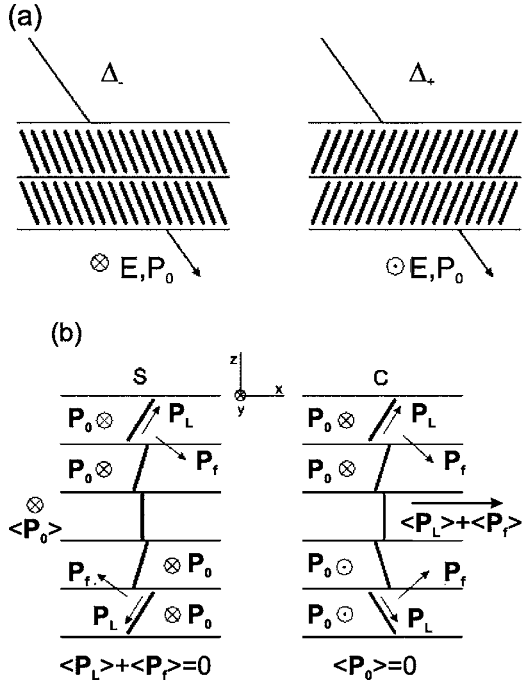

FIG. 3. (a) Experimental geometry and the definition of the two ellipsometric parameters Δ_+ and Δ_- (shown here for a two-layer film). Depending on the polarity of the orienting field **E**, the "average" molecular tilt is either towards (Δ_-) or away from (Δ_+) the laser beam. (b) Schematic drawings of the tilt profiles of the synclinic *S* structure (left) and anticlinic *C* structure (right). In the *S* structure, the tilt direction is the same in all layers, and consequently $\mathbf{P}_0\neq\mathbf{0}$ and $\mathbf{P}_L+\mathbf{P}_f=\mathbf{0}$. On the contrary, in the *C* structure, the tilt directions in the two halves of the film are opposite, thus $\mathbf{P}_0=\mathbf{0}$ and $\mathbf{P}_L+\mathbf{P}_f\neq\mathbf{0}$.

Some of the observed structures could straightforwardly be identified due to their characteristic response to the change of the direction of the external electric field. For example, there are two typical structures that are very often observed in free-standing films: the synclinic *S* structure and the anticlinic *C* structure [22], which have quite a specific electro-optic response.

In the synclinic structure, there is a large average component of the transverse spontaneous polarization $\mathbf{P}_0$, since the tilt direction is the same in all layers [Fig. 3(b), left]. The components of the longitudinal $\mathbf{P}_L$ and flexoelectric $\mathbf{P}_f$ polarization cancel out due to the even symmetry of the central layer in a synclinic structure. In an external dc electric field, the synclinic structure will orient in such a manner that the plane of the average molecular tilt is perpendicular to the direction of the external electric field. Reversing the direction of the field reverses the direction of the average molecular tilt.

The situation is opposite in the anticlinic structure [Fig. 3(b), right]. Due to the odd symmetry of the anticlinic free-standing film, the components of the longitudinal $\mathbf{P}_L$ and flexoelectric $\mathbf{P}_f$ polarization are nonzero and the component of the transverse spontaneous polarization $\mathbf{P}_0$ cancels out, because the tilt directions in the two halves are opposite [Fig. 3(b), right]. In an external dc electric field, the anticlinic structure will orient in such a manner that the plane of the molecular tilt coincides with the direction of the electric field. Reversing the direction of the field will reverse the overall conformation of the anticlinic structure. In general, a given stable structure in the tilted and polar smectic free-standing film is neither of pure anticlinic nor synclinic type. The spatial orientation of such a structure will depend on the relative magnitudes of the spontaneous transverse polarization and the components of the longitudinal and flexoelectric polarization.

The measured temperature dependences of Δ_+ and Δ_- in a two-layer film of MHPOBC are shown in Fig. 4(a). The magnitude of the two ellipsometric parameters $\Delta_\pm$ suggests that the molecules are tilted, and a weak temperature dependence of the ellipsometric parameters suggests a weak temperature dependence of a nearly saturated tilt angle. We can see that both ellipsometric parameters are nearly identical in the temperature range of more than 20 K, suggesting that the two-layer MHPOBC film has no component of the spontaneous polarization $\mathbf{P}_S$ in a direction perpendicular to the plane of the molecular tilt. Based on these observations we conclude that the structure which is stable in a two-layer film is an anticlinic, *C* structure [22]. Here, the molecules in successive layers are tilted in opposite directions and the transverse electric dipole moments cancel out. Quite probably the structure has some longitudinal polarization (in the plane of the tilt), which unfortunately cannot be resolved in the geometry used.

In a three-layer MHPOBC film [Fig. 4(b)] we already observe one structural transition. In the high-temperature phase the two ellipsometric parameters Δ_+ and Δ_- are nearly

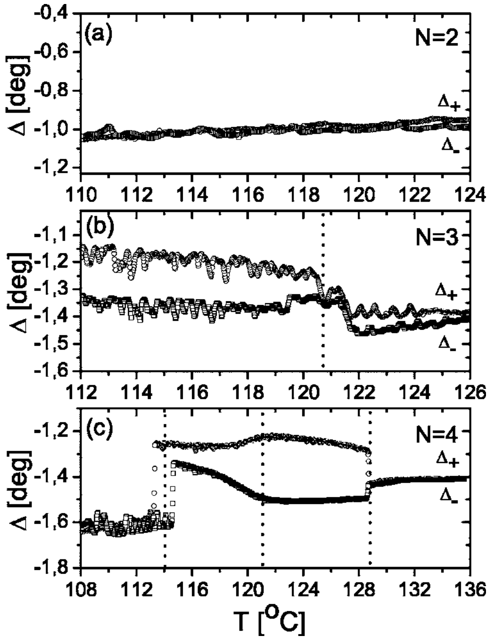

FIG. 4. Measured temperature dependence of the two ellipsometric parameters Δ_+ (○) in Δ_- (□) in (a) $N=2$ layer film, (b) $N=3$ layer film, and (c) $N=4$ layer film. The two ellipsometric parameters are defined in the text to Fig. 3. We observe an increased richness of the phase sequence with increasing number of smectic layers.

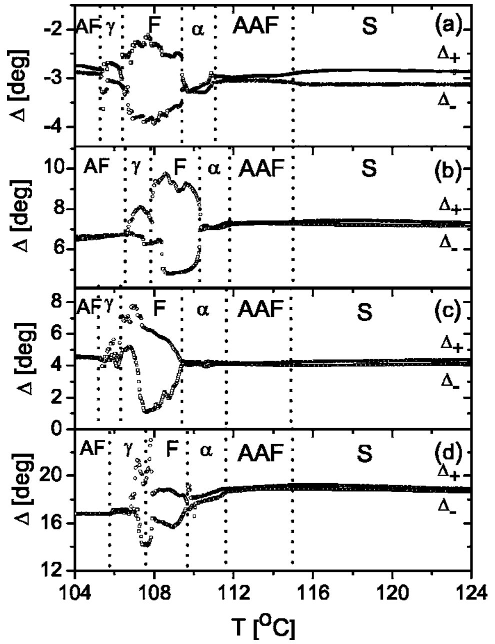

FIG. 5. The evolution of the phases towards the bulklike phase sequence, as the number of smectic layers is increased from (a) $N=21$, (b) $N=44$, (c) $N=69$, and (d) $N=285$. The two ellipsometric parameters are defined in the text to Fig. 3. Note the change of the sign of the ellipsometric parameter between $N=21$ and $N=44$, which is due to the crossover of the sign, as indicated by the arrow in Fig. 2.

equal; however, they are different and nearly temperature independent below the phase transition. Following similar reasoning as for the two-layer film, we conclude that the high-temperature phase is an anticlinic *C* phase with opposite—i.e., the anticlinic—surface tilt and no transverse spontaneous polarization. At this point of observation we cannot be sure about the structure in the low-temperature phase of the three-layer film, as there are several options that have to be analyzed quantitatively. The experiment, however, clearly shows the existence of an overall molecular tilt that is coupled to the transverse polarization in this phase. This scenario, for example, is possible in either synclinic phase or in a three-layer antiferroelectric phase, where the electric polarization of smectic layers is not compensated.

The phase diagram becomes reacher with increasing number of smectic layers. In a four-layer film [Fig. 4(c)] we observe four different phases. In the high-temperature phase the two ellipsometric parameters are nearly identical, which suggest that this phase is a tilted *C* phase with anticlinic surface layers and no transverse electric polarization. Below the *C* phase we measure a very large difference $|\Delta_+ - \Delta_-|$, clearly indicating a net molecular tilt that is coupled to a net transverse polarization. This temperature region corresponds to a synclinic *S* phase. At the temperature of ~121 °C, the *S* phase undergoes a phase transition into a region with nonmonotonous behavior of the two ellipsometric parameters, similar to those in Ref. [23]. We observe that the difference $|\Delta_+ - \Delta_-|$ in this phase decreases; however, the structure retains some finite value of a net molecular tilt that is coupled to a net transverse polarization. Unfortunately, the experiment itself does not give us enough information to directly determine the structure in this phase. We observe a first-order transition into a low-temperature phase at $T \sim 114$ °C. The new phase is the antiferroelectric phase with no transverse polarization and zero difference between Δ_+ and Δ_-, which confirms the theoretically predicted odd-even effect [16]. We should note that understanding the phase diagram of a four-layer film is very important, because it hides the key to our understanding of structures and phase transitions in thin and thick films, as we are going to see in the following paragraphs.

Let us now have a quick look at the results for thick free-standing films, in which the volume interactions start overcoming the surface interactions, thus bringing the film into the limit of a bulk. The limit of thick films is characterized by the appearance of the phase sequence that is observed in bulk MHPOBC. We estimate that free-standing films can be considered as thick for the number of smectic layers, $N > 20$. This is illustrated in Figs. 5(a)–5(d) for the number of smectic layers $N=21$, 44, 69, and $N=285$, respectively.

The onset of the characteristic phase sequence Sm-A^*–Sm-C^*_α–Sm-C^*–Sm-C^*_γ–Sm-C^*_A can be recognized already at $N=21$ and this phase sequence is present with minor changes up to the bulk. However, no matter what the thickness of the film is, it is clearly seen that at temperatures above the Sm-C^*_α phase, the film retains some very characteristic details that we have already seen in the four-layer film. It is then natural to consider that above the bulk Sm-A^*–Sm-C^*_α transition temperature there is a combination of the nontilted, nonpolar Sm *A*-like core and tilted surface

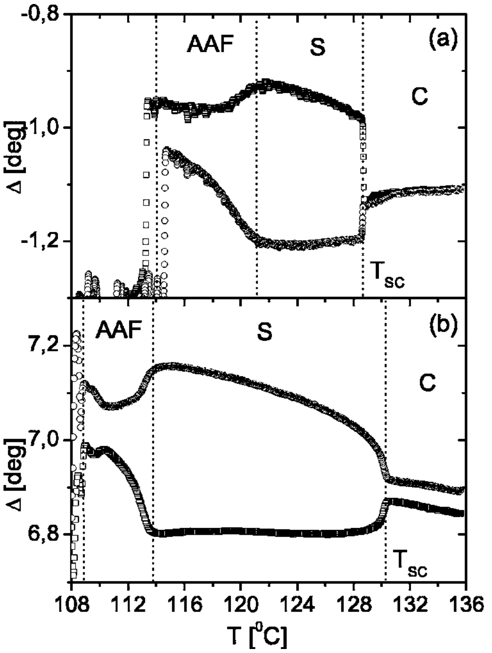

FIG. 6. Measured temperature dependence of the two ellipsometric parameters Δ_+ (○) and Δ_- (□) in the high-temperature region in (a) $N=4$ layer and (b) $N=47$ layer film. The two ellipsometric parameters are defined in the text to Fig. 3. We observe similar behavior of the parameters $\Delta_\pm$ in thin and thick films, which suggests that the surface layers of thick films behave like layers in thin films. This means that in the high-temperature region (i.e., above the bulk phase transition into tilted phases), the surface layers in thick films undergo the same phase sequence as thin films: $C \rightarrow S \rightarrow$ AAF.

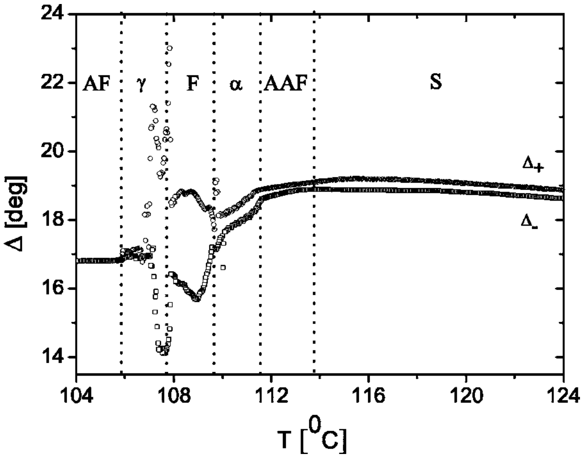

FIG. 7. Measured temperature dependence of the two ellipsometric parameters Δ_+ (○) and Δ_- (□) in $N=285$ layer film. The two ellipsometric parameters are defined in the text to Fig. 3.

layers that behave very similarly to the four-layer free-standing film [see Figs. 4(c) and 6(b)]. We therefore analyze in more details the high-temperature region of thick films in order to compare their properties to the thin four-layer film.

Figure 6 shows a comparison of the ellipsometric parameters $\Delta_\pm$ for a 4-layer (a) and 47-layer (b) free-standing film of MHPOBC in the temperature region above the bulk phase transition into the tilted Sm-C_α^* phase. One can immediately observe a striking quantitative similarity, which leads to the following conclusion: above the phase transition into the Sm-C_α^* phase, thick free-standing films of MHPOBC can be considered as a combination of the interior layers, which are of the Sm-A type—i.e., nontilted and nonpolar—and the outermost layers that are tilted in the same manner as in a 4-layer film. The quantitative agreement of the ellipsometric parameters of 4- and 47-layer film suggests that the range of the surface interactions is of the order of two layers in MHPOBC. In thick films and above T_C^{bulk}, the two surface layers therefore undergo the following phase transitions: planar $C \rightarrow$ planar $S \rightarrow$ planar AAF phase. In our experimental geometry, nearly identical ellipsometric parameters $\Delta_\pm$ in the C phase above $T_{CS} \sim 128$ °C suggest that there is no component of the spontaneous polarization $\mathbf{P}_S$ in the system. The synclinic—i.e., S—phase below $T_{CS} \sim 128$ °C is characterized by a constant difference between the two parameters $|\Delta_+ - \Delta_-| \sim 0.3°$, which appears to have the same value as in a 4-layer film [see Fig. 6(a)]. In a temperature region ~ 4 °C above the bulk transition temperature T_C^{bulk} we observe a nonmonotonous decrease of the difference between $\Delta_\pm$, suggesting that the S phase undergoes a phase transition into a similar phase, as observed in a 4-layer film, shown in Fig. 6(a).

As can be seen from Fig. 7, thick films undergo a phase transition into the Sm-C_α^* phase at T_C^{bulk}. The Sm-C_α^* phase is characterized by specific oscillations (see details in Fig. 7) of the ellipsometric parameters that reflect the temperature dependence of the period of the Sm-C_α^* phase and increasing tilt with decreasing temperature [13,24]. It has been shown that the period of the Sm-C_α^* phase of MHPOBC increases drastically at the phase transition into the Sm-C^* phase. In the Sm-C^* phase we measure the largest difference between $\Delta_\pm$, which corresponds to the ferroelectric order in this phase and to the largest component of the spontaneous polarization $\mathbf{P}_S$, coupled to a net molecular tilt. At this temperature, the increase of the ellipsometric parameters with decreasing temperature reflects the increase of the overall molecular tilt. A characteristic noisy signal is always observed in the ferrielectric Sm-C_γ^* phase, which is probably due to the high instability of the short-pitch three-layer phase. The low-temperature phase is the antiferroelectric phase with zero or very small and constant difference $|\Delta_+ - \Delta_-|$, depending on the odd and even number of smectic layers [22].

III. DISCRETE PHENOMENOLOGICAL MODEL

The experimental observations were analyzed within discrete phenomenological (clock) model, as described in detail before [25]. The goal of the analysis was to reproduce the observed temperature dependences of both ellipsometric parameters in thin films, using a minimum set of model parameters, and then extrapolate the model to the thick films system, that is numerically very demanding. We should emphasize, as was already emphasized before by different authors [18,23,26,27], that the two ellipsometric parameters are extremely sensitive to the overall configuration of the c directors in individual smectic layers. This extreme sensitivity results in a very strong constraint on possible structures and therefore their unique identification.

When considering such a model, we restricted our choice of model properties to those already observed in other experiments. For example, we consider that the molecules in the outer layers can spontaneously tilt at higher temperatures compared to the layers in the interior [20]. Furthermore, we consider that the tilting direction of the inner layers can be in some cases opposite to the outer layers, as observed recently by Han *et al.* [23].

The analysis of the temperature dependences of the ellipsometric parameters was carried out in two steps. First we calculated the equilibrium structures in the model films at various temperatures. This was done by analyzing the stability of the N-layer free-standing film by expanding the free energy of a system of N coupled smectic layers:

$$G = \sum_{i=1}^{N} \frac{a_0^i}{2}\vartheta_i^{\,2} + \frac{b_0^i}{4}\vartheta_i^{\,4} + \frac{a_1}{2}\vartheta_i\vartheta_{i+1}\cos(\varphi_i - \varphi_{i+1}) + \frac{a_2}{8}\vartheta_i\vartheta_{i+2}\cos(\varphi_i - \varphi_{i+2}) + CE\vartheta_i\cos\varphi_i. \qquad (1)$$

The coefficients $a_0^i = \alpha(T - T_0)$ and b_0^i describe the intralayer interactions and to the largest extent determine the value of the tilt angle in the ith layer. These interactions can be different for inner and outer layers, respectively.

We should note here that the values of the coefficients a_0^i and b_0^i cannot be considered equal to those determined experimentally within the phenomenological continuum models (see, for example, Ref. [1]). This is because the coefficients a_1 and a_2 also influence the magnitude of the tilt angle through the coupling of the tilt magnitude with the phase. In simple words, when the structure is highly twisted or otherwise distorted, the equilibrium values of the tilt angle are different from those in a homogeneous configuration. We should also note that the values of these coefficients were determined for the first time in this and our preceding work [15].

The next two terms with coefficients a_1 and a_2 are the lowest-order terms describing the interactions between the neighboring layers and are set equal for all layers. The last term is the coupling of the spontaneous polarization of each layer with the external electric field. The surface interactions of the outer layers are properly taken into account by defining the order parameter to be $\vartheta_i = 0$ for $i < 1$ and $i > N$. Physically, this means that the first and last smectic layers (i.e., the two outer layers), as well as their first interior neighbors, interact only with the layers in the interior of the film, whereas there is no molecular interaction with empty space outside the film.

Before starting the minimization procedure, the free-energy density was normalized to the parameter α, so that consequently all the expansion parameters in Eq. (1) were also normalized to α. The starting values of the expansion parameters were determined as follows: the ratios of b_0/α and α were determined from the temperature dependence of $\Delta_\pm$ in a two-layer film. These values, which determine to the largest extent the magnitude of the tilt in a given layer, had to be varied slightly for individual layers in three- and four-layer films, to obtain the best overall agreement. The starting values of the coefficients a_1 and a_2 were taken from previous theoretical studies [16], and only a_1 was fine-tuned after comparing the calculated temperature dependence and phase transitions with those measured. a_2 was kept at a constant value.

The free energy is then minimized following the standard procedure as described in Ref. [25] and can be done analytically in $N=2$ and partially analytically in $N=3$ layer films. The results of the first step was a set of the equilibrium values of the tilt angle for each smectic layer and the set of the phase angles of the c director for each layer, uniquely defining the equilibrium structure in a free-standing film.

In the second step, we have calculated the temperature dependences of both ellipsometric parameters $\Delta_\pm$ for the calculated equilibrium structure using the 4×4 matrix method of Yeh [21]. The calculated temperature dependence was compared to the measured one, and then the procedure was iterated by fine-tuning b_0 and a_1, whereas keeping a_2 constant, until an overall agreement was obtained for two-, three-, and four-layer films. We should stress that at the initial stage, the analysis was very time consuming (time scale of several months), until we traced the basic structures and corresponding phase transitions. From there on, the analysis converged very rapidly to the set of parameters that could describe quantitatively the measured temperature dependences and observed phase transition. We should stress again that the two measured temperature dependences of the ellipsometric parameters (including the number of observed phases and the temperatures of phase transitions) have a very strong constraining effect on possible structures and make us confident that the structures that we have calculated indeed correspond to those that exist in our films.

IV. DISCUSSION

In a two-layer film the analytically calculated equilibrium structure is planar anticlinic with the tilt angles of $\vartheta_1 = \vartheta_2 \sim 23°$. The corresponding ellipsometric parameters, as calculated by the 4×4 matrix method, confirm the experimental temperature dependence of $\Delta_\pm$ [Figs. 8(a) and 4(a)]. The slight temperature dependence of the tilt angle and consequently of the two ellipsometric parameters indicates the nearly saturated regime, and the phase transition temperature into the tilted phase is estimated to be 161 °C.

The temperature dependence of the ellipsometric parameters in a three-layer film is analyzed partially analytically and partially numerically. First, the free energy is minimized analytically with respect to the phase angles of individual layers, which is followed by a numerical minimization with respect to the tilt angles. The experimental data can be fitted well if we assume the following: (i) the outer layers tilt spontaneously at higher temperatures compared to the inner layers, (ii) the parameter a_1 is small and depends on temperature, and (iii) we allow the possibility that the structure in the low-temperature region is nonplanar—i.e., twisted. In this case the measured and calculated ellipsometric parameters agree very well [Fig. 8(b)]. We conclude that the high-temperature phase is indeed an anticlinic C phase and the low-temperature phase is a twisted structure with the phase

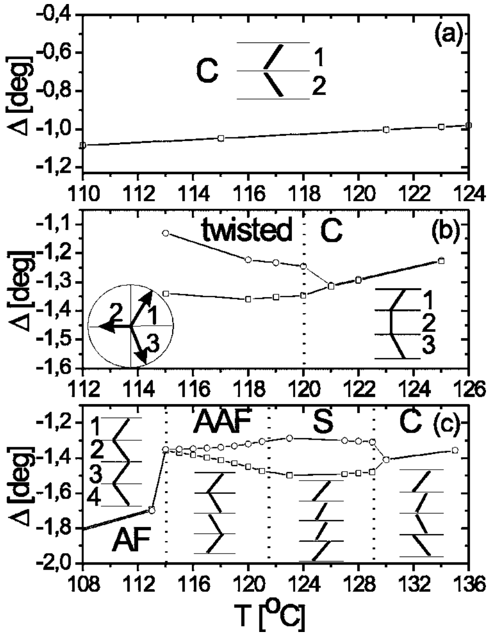

FIG. 8. The temperature dependence of the two ellipsometric parameters Δ_+ (○) and Δ_- (□), obtained from the minimization of the clock model free energy. The model parameters are normalized to α (see [10]) and slightly differ for $N=2$, 3, and 4 layers: (a) $N=2$: the model parameters are $a_1/\alpha=0.025$ K, $b_0^{1,2}/\alpha=230$ K, $\alpha=4000$ J/m^3. (b) $N=3$: the model parameters are $(a_0^{1,3}-a_0^2)/\alpha=13$ K, $a_2/\alpha=0.25$ K, $b_0^{1,3}/\alpha=55$ K, $b_0^2/\alpha=330$ K, $\alpha=4000$ J/m^3. The nearest-neighbor interaction a_1 is temperature dependent, $\Delta a_1/\alpha/\Delta T=0.01$, $a_1/\alpha(T=126\ ^\circ\mathrm{C})=0.07$ K. (c) $N=4$: the model parameters are $a_0^{1,4}-a_0^{2,3}/\alpha=15$ K, $a_2/\alpha=0.25$ K, $b_0^{1,4}/\alpha=140$ K, $b_0^{2,3}/\alpha=200$ K, $\alpha=4000$ J/m^3. Again, a weak temperature dependence of the nearest-neighbor interaction coefficient a_1 was considered: $\Delta a_1/\alpha/\Delta T=0.01$ and $a_1/\alpha(T=135\ ^\circ\mathrm{C})=-0.16$ K.

difference between neighboring c directors of ≈40°. The phase transition between the two phases appears at $T_C\sim 121$ °C. The stability of a twisted structure is consistent also with an odd-even effect, which was predicted recently [16]. We observe, however, a small discrepancy between the experiment and theory close to the transition, where we could not reproduce completely a small difference between Δ_+ and Δ_- in the C-phase region and a small jump at the phase transition. The first can be explained by the influence of the applied electric field, which makes the originally planar C structure slightly nonplanar and therefore polar, with a nonzero difference between the two ellipsometric parameters. The second is a consequence of a slightly first-order transition, discussed in [3].

In a four-layer film, we can easily reproduce the anticlinic C, the synclinic S phase, as well as the low-temperature antiferroelectric phase. The most interesting is, however, the temperature interval between 114 and 128 °C, where we observe the nonmonotonous behavior of the two ellpsometric parameters. The analysis in this region was performed numerically [25] and several possible scenarios were tested to describe the unusual T dependence of the ellipsometric parameters. The twisted structures were eliminated, because Δ_+ and Δ_- could not be reproduced at all. The difference between Δ_+ and Δ_- was always far too small due to spatial averaging of the optical anisotropy in the case of twisted structures. We then concentrated on the stability analysis of possible planar phases [28] by setting the phase angles to zero. The observed nonmonotonous behavior of Δ_+ and Δ_- could be well reproduced in a four-layer film if we considered similar assumptions as in a three-layer film: (i) the outer layers spontaneously tilt at higher temperatures compared to the interior two layers, (ii) the inner layers tilt in the opposite direction compared to the outer layers, and (iii) the neighboring layer coupling parameter a_1 is small and temperature dependent. Due to the symmetry properties of the phase in the nonmonotonous region, we called this phase the antiantiferroelectric (AAF) phase, where the antiferroelectric unit pairs are ordered in an antiferroelectric manner. These assumptions automatically generate the sequence of structures as well as phase transitions, which give a very good quantitative agreement with the observed ellipsometric parameters, as shown in Fig. 8(c). The anticlinic C phase first transforms via the first-order phase transition into a synclinic S phase at $T_{SC}\sim 128$ °C. Then, the S phase transforms into the AAF phase at $T\sim 121$ °C. Finally, the AAF phase transforms into the antiferroelectric (AF) phase at $T_{AS}\sim 114$ °C by collective rotation of the antiferroelectric molecular pairs. The most important result here is the reproduction of the characteristic narrowing of the part of the Δ_+-Δ_- in the AAF phase, which could not be reproduced in any other scenario that was considered. The stability of planar phases in an even four-layer film is confirmation of the odd-even effect [16] and supports the clock model.

Before discussing thick films, let us comment on the values of the expansion parameters, as they are different for different film thicknesses. First, the parameter a_0 is in all cases smaller for the outer layers. This means they are already tilted at higher temperatures, which is in agreement with other experiments that have been performed so far [20,22,23,29]. Second, the parameters b_0 are different for the outer and inner layers. As a consequence of this, the tilt of surface layers is larger compared to the interior layers, which is also in agreement with other experiments. The fact that the difference between b_0's of exterior and interior layers is smaller for larger N is also consistent, as it indicates less influence of the surface in the interior layers for thicker films. Third, the parameter a_1 is temperature dependent, which is the most crucial issue in our analysis. Fortunately, there is a direct evidence of this temperature dependence (suggesting its intrinsic nature) from the critical field for the unwinding of the bulk AF phase into the ferroelectric phase, which is $E_c(T)=2a_1(T)\vartheta/P(T)$ and $P(T)$ is the electric polarization of a single tilted smectic layer. The analysis of available data for bulk MHPOBC [30] shows that a_1 increases linearly with decreasing temperature, in good agreement with our premise. Interestingly, the crossover temperature, where this parameter changes sign, is at lower temperatures for thicker films. This is also consistent, as positive a_1 favors the AF phase and this phase appears at lower temperatures in thicker films (compare $N=2$ and $N=4$). The observed thickness dependence of the free-energy expansion parameters is in fact not surprising, as they depend in a complicated way on the nematic and smectic order parameters, which are strongly influenced by the confining surfaces and therefore number of layers.

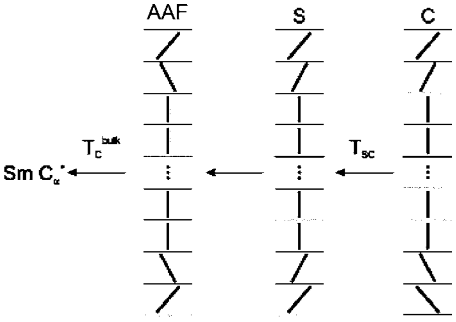

FIG. 9. Proposed phase sequence in the high-temperature region of thick films. Comparison of the temperature dependance of the ellipsometric parameters in a four-layer film and thick films suggests that above T_C^{bulk} in thick films planar phases with an overall molecular tilt in the two outermost smectic layers are stable. The interior of the thick films remains in the form of the Sm-*A* phase. Note that the surface layers can be either anticlinic or synclinic and consequently oriented by external electric field into either planar *C*, planar *S*, or AAF structure.

Let us now see to what extent can we extrapolate the scenario of a four-layer film to the high-temperature region of thick films—i.e., above T_C^{bulk} (see Fig. 9). Very similar behavior of the temperature dependences of the two ellipsometric parameters in thin and thick films suggests that the surface layers in thick films behave similarly as thin free-standing films. This leads to the conclusion that in thick films the crucial contribution to the calculated values of $\Delta_\pm$ originates from the structure of the two outermost layers at both surfaces. If the two outermost layers are tilted in the same manner as in the four-layer film, the interior of the thick film has to remain in the form of a nonpolar Sm-*A* phase. Our conclusion is that in the high-temperature region of thin and thick films (i.e., above T_C^{bulk}), the surface layers undergo the following phase sequence: planar $C \rightarrow$planar $S \rightarrow$planar AAF phase (see Fig. 6).

We have observed many similarities between our ellipsometric experiment and others. For example, we have observed that above the bulk phase transition into the tilted Sm-C_α^* phase, thick free-standing films can be considered as a combination of tilted surface layers and nonpolar and nontilted cores. We find that these tilted surface layers undergo the same phase sequence as the four-layer thin free-standing film, indicating that the range of surface interaction is of the order of two smectic layers. Similar findings were reported in other experiments that have been performed so far [20,22,23,29]. Further on we have observed the new planar AAF phase besides the well-known planar anticlinic and synclinic structures in thin films. This phase was also observed nearly simultaneously in recent ellipsometric experiments of Chao *et al.* [27] and Han *et al.* [23]. Similar to our experiments, they have reported stable structures in thin free-standing films, where the molecules in inner layers tilt in opposite directions compared to the surface layers.

We can conclude that the simple clock model is indeed very successful not only in reproducing the phase stability and phase sequences but also in giving a good quantitative agreement between measured and calculated ellipsometric parameters of two-, three-, and four-layer free-standing films of MHPOBC. The present work represents a direct test of the clock model and the first (to our knowledge) determination of a consistent set of free-energy expansion parameters of the clock model.

ACKNOWLEDGMENTS

This work was supported by the European Commission through the project ALCANDO and by the Slovenian Ministry of Higher Education and Science through Project No. J1-6560-0106-05.

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