RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 51, NUMBER 5 MAY 1995

Experimental indication of a devil's staircase structure in a smectic liquid crystal

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(Received 21 February 1995)

Free-standing films of a chiral liquid-crystal compound have been studied by ellipsometry. In the temperature range between the ferroelectric smectic-*C* and the paraelectric smectic-*A* phase we observe in thick films a sequence of alternating antiferroelectric and ferrielectric states. The number of these states depends strongly on the number of the molecular layers of which the film consists. Our results suggest the existence of a large number of different states in the corresponding bulk sample which may be a confirmation of the devil's staircase structure proposed for these compounds.

PACS number(s): 61.30.Eb, 64.70.Md

One of the most interesting findings concerning the study of ferroelectric liquid crystals in recent years was the discovery of an antiferroelectric modification, smectic-C_A(Sm-C_A) [1], of the conventional ferroelectric smectic-*C* (Sm-*C*) phase.

In both phases, Sm-*C* and Sm-C_A, the rodlike molecules are arranged in layers with their long axes tilted with respect to the layer normal. If the molecules are chiral, there exists by symmetry a spontaneous ferroelectric polarization $\vec{P}_s$, directed along the layer plane and perpendicular to the tilt direction, in each layer [2]. Whereas in the usual ferroelectric Sm-*C* phase the direction of the molecular tilt (and thus of $\vec{P}_s$) is the same [3] in neighboring layers, the tilt direction (and thus the $\vec{P}_s$ direction) in the antiferroelectric Sm-C_A phase alternates by $\pm 180°$ when going from layer to layer. This structure, which was initially proposed on the basis of electro-optic and conoscopic studies of bulk samples [1,4], was confirmed by ellipsometric studies of thin freely suspended films consisting of only a few molecular smectic layers [5].

Besides the Sm-C_A phase, a number of several other Sm-*C* subphases, which displays not only antiferroelectric but also ferrielectric behavior, have been observed, mainly in studies by Fukuda, Takezoe, and co-workers [6]. Of particular interest is the so-called Sm-C_α phase which occurs usually between the Sm-*C* and the Sm-*A* phase [the Sm-*A* phase, in which the amount of the tilt angle (and thus of $\vec{P}_s$) is zero, is usually the high-temperature phase to Sm-*C*]. Because Sm-C_α is a tilted phase behaving in an antiferroelectric way at its high-temperature limit, and in a ferroelectric way at its low-temperature limit, and ferrielectric in between, a structural model [7] was proposed bearing features of a devil's staircase [8]. In this model, it is assumed that Sm-C_α is not a single phase; rather, it is proposed that a sequence of different structural states, which may be antiferroelectric or ferrielectric, occurs in the temperature range of Sm-C_α. Each state is assumed to consist of a periodic arrangement of ferroelectric and antiferroelectric ordered layer pairs (same or opposite tilt direction in two neighboring layers) and can be characterized by a single rational number q corresponding to the fraction of, e.g., ferroelectric ordered layer pairs within one period. If one allows arbitrarily long periods, an infinitely large number of different states, constituting a devil's staircase, is possible.

Experimentally, however, the situation is not clear: Whereas studies in external electric fields yielded some indication of a sequence of different structural states occurring with increasing field strength [7], the intrinsic zero-field structure of Sm-C_α is not clarified; especially a sequence of discrete structural states, which should occur when varying the temperature, has not been observed to date. A reason for this may be that in a bulk sample the difference between two subsequent states is beyond the resolution of the corresponding experimental methods.

In this Rapid Communication we report on ellipsometric studies of freely suspended films of a chiral smectic liquid crystal. A freely suspended film consists of an integral number (between some thousands and only two) of molecular smectic layers, the layer planes being parallel to the two free surfaces; thus one can realize samples consisting of a small and exactly defined number of smectic layers. If the above described model of the Sm-C_α phase is correct, one should expect that in thin films only a few different states occur and that the number of states increases with increasing film thickness. We report results indicating such a behavior.

Our sample is the compound (R)-1-methylheptyl-4-(4′-*n*-dodecyloxybiphenyl-4-yl carbonyloxy)-3-fluorobenzoate, abbreviated in the following as 12F1M7. Whereas in the bulk sample the phase sequence Sm-*A*–Sm-*C*–Sm-C_γ [9] –Sm-C_A was observed [10], preliminary studies [11] of freely suspended films of this compound have shown that in a temperature interval between the Sm-*A* and the Sm-*C* phase an additional phase occurs (at least in freely suspended films) showing characteristics of the Sm-C_α phase.

Free-standing films were drawn in the Sm-*A* phase over a 3×12 mm^2 rectangular opening in a 0.15-mm-thick glass plate. The details of our ellipsometric setup are given in [12]. We determine the ellipsometric parameters Δ and Ψ of laser light ($\lambda = 633$ nm) transmitting the film under an angle of incidence of 45°; here, $\Delta = \delta_p - \delta_s$ is the phase difference between the *s*- and *p*-polarized components of the transmitted light and Ψ is related to the ratio of the amplitudes

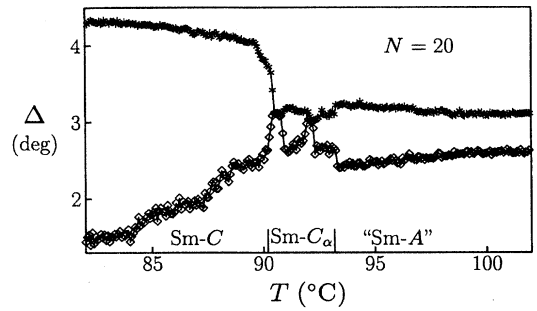

FIG. 1. Temperature dependence of the ellipsometric parameter Δ for the two polarities of a dc aligning field (*: Δ_-, i.e., tilt direction in the Sm-C phase towards the incident laser beam; ◇: Δ_+, i.e., tilt direction away from the incident beam) for a 20-layer film of 12F1M7.

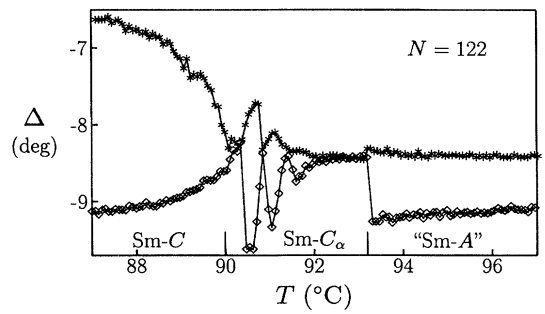

FIG. 2. Temperature dependence of the ellipsometric parameter Δ (*: Δ_-; ◇: Δ_+) for a 122-layer film of 12F1M7. As to be expected for thicker films, the Δ values are now negative (details of the thickness and tilt dependence of Δ can be found in [12]). At first sight, the difference $|\Delta_+ - \Delta_-|$ in the Sm-C phase, where all layers are tilted, should be in a 122-layer film at least 40 times larger than in the "Sm-A" phase, where only a few surface layers are tilted. In our experiment we find $|\Delta_+ - \Delta_-|$ in the Sm-C phase only 2–3 times larger than in the "Sm-A" phase because a 122-layer film possesses already a partially developed helical superstructure which reduces the difference between Δ_+ and Δ_- in the Sm-C phase.

$|T_s|$ and $|T_p|$ of the s and p components as $\tan\Psi = |T_p|/|T_s|$. Our setup determines Δ and Ψ with an accuracy of $\approx 0.01°$. From the Δ and Ψ values of the transmitted light, measured in the Sm-A phase, we obtain (as described in [12]) the thickness of our films.

For the present study we use our ellipsometer mainly to distinguish between ferroelectric, antiferroelectric, and ferrielectric Sm-C structures in freely suspended films. We do this by determining the temperature dependence of Δ [13] for the two polarities of a dc electric field applied along the film plane and perpendicular to the plane of incidence. In the Sm-A phase, the external field has no effect and we expect $\Delta_+ = \Delta_-$. In the ferroelectric Sm-C phase, the external field aligns the direction of $\vec{P}_s$ and thus the tilt direction. Depending on the field polarity, the tilt direction will be either away from or towards the incident laser beam and thus Δ_+ will be different from Δ_-. In the antiferroelectric Sm-C_A phase with its layer-by-layer alternation of tilt and polarization, the field has no effect and $\Delta_+ = \Delta_-$ provided that the film consists of an even number of molecular layers; an odd-numbered-layer film bears a nonzero net polarization and an "excess tilt" corresponding to one layer, hence we will measure $\Delta_+ \neq \Delta_-$ but with a much smaller difference than in the Sm-C phase of the same film [5]. For a ferrielectric Sm-C modification we expect a similar behavior as for an odd layered Sm-C_A film. It is important to point out here that the strength (6 V/cm) of the applied dc field is just sufficient to align a finite net polarization of a film; it is three orders of magnitude too small to cause changes of the internal structure such as a transition from antiferroelectric to ferroelectric; therefore our experiment probes, at least to a very good approximation, the zero-field structures of the phases in question.

Figure 1 shows our results for a 20-layer film. We can distinguish three different regions: At temperatures above 93 °C, where the bulk sample shows its Sm-A phase, we measure in freely suspended films nevertheless $\Delta_+ \neq \Delta_-$ because the surface layers start to tilt at temperatures 20–30 K above the corresponding bulk transition, as was already observed for a number of other compounds [5,12,14]. We label this Sm-A phase with tilted surface layers in the following as "Sm-A" [15]. The ferroelectric Sm-C phase is seen for $T < 90$ °C where the amount of the difference $\Delta_+ - \Delta_-$ is, at the low-temperature limit of the Sm-C phase, eight times larger than at the high-temperature limit of the "Sm-A" phase. Between the Sm-C and "Sm-A" phases, Δ_+ and Δ_- exhibit a kind of oscillation behavior; we can distinguish four different regions: two where $\Delta_+ = \Delta_-$, and two where $\Delta_+ \neq \Delta_-$. This oscillation behavior of the Δ values becomes more pronounced in thicker films: in a 122-layer film (cf. Fig 2), we find between the Sm-C and the "Sm-A" phase four regions where $\Delta_+ = \Delta_-$ and three regions where $\Delta_+ \neq \Delta_-$, i.e., states, where the field polarity does not affect the value of Δ and where the net polarization is obviously zero, and states, where Δ depends on the field polarity and where a finite net polarization is present, are succeeding one another. If we identify states where $\Delta_+ = \Delta_-$ with an antiferroelectric and states where $\Delta_+ = \Delta_-$ with a ferrielectric structure, the 122-layer film shows between its Sm-C and "Sm-A" phase an alternating sequence of four antiferroelectric and three ferrielectric states.

Unfortunately, we could not study films with more than 122 layers because thicker films adopted a strong tendency to retain an inhomogeneous thickness [16]. When we decrease the film thickness, we find the behavior displayed in Fig. 3, which shows the temperature dependence of Δ_+ (the changes of Δ_- in the Sm-C_α phase are, especially in thin films, much less significant) for various films: the number of different states in the Sm-C_α phase decreases until, in an 8-layer film, only one antiferroelectric state remains; also, the temperature interval of this state is considerably expanded to higher temperatures and the range of the "Sm-A" phase is shifted beyond the stability limit (the Sm-A–isotropic transition temperature of the bulk) of the film. In the thin films (10 and 8 layers), we have made sure by direct optical observation through a telescope that in the states designated as antiferroelectric no optically observable switching occurs when the field is inverted.

As shown in Fig. 3, the number of different states in the Sm-C_α phase increases with increasing film thickness. In this context, it is interesting to note that the bulk sample, when observed by differential scanning calorimetry (DSC) and op-

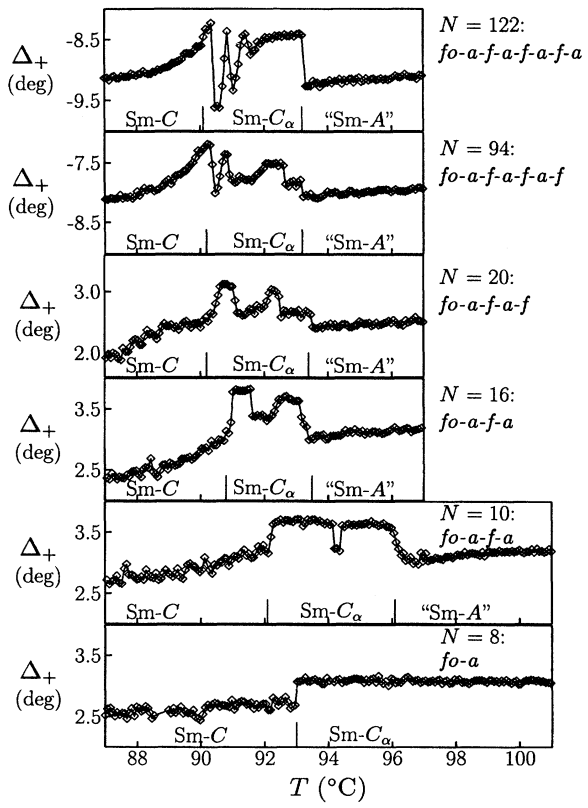

FIG. 3. Temperature dependence of Δ_+ for films of various thicknesses (N= number of molecular layers) and phase sequence in the Sm-C_α range; a: antiferroelectric state, i.e., $\Delta_+=\Delta_-$; f: ferrielectric state, i.e., $\Delta_+\neq\Delta_-$; fo: ferroelectric state (=Sm-C phase).

tical microscopy, seems to show only one transition, which appears like a Sm-C–Sm-A transition, around 90 °C. If the Sm-C_α phase exists in bulk 12F1M7 also, it may be "hidden" at the low-temperature limit of the phase which appears in the microscope like a usual Sm-A phase. In bulk, the Sm-C_α phase may show a large number of different states possessing extremely narrow stability intervals so that the structure changes quasicontinuously and no effects can be observed by DSC or microscopy.

The theoretical model of Takanishi *et al.* [7] for the Sm-C_α phase is based on a one-dimensional Ising model described by Bak and Bruinsma [17]. The Hamiltonian of this Ising model is given by

$$H=-\sum_i HS_i+\tfrac{1}{2}\sum_{i,j} J_{|i-j|}(S_i+1)(S_j+1).$$

S_i are the spins which may be equal to ± 1, $J_{|i-j|}$ is a convex long-range repulsive interaction between two $+1$ spins at sites i and j, and H is an external field aligning the spins in the $+1$ state. The competition between J and H produces a complete devil's staircase in the phase diagram, i.e., for every rational number q between 0 and 1, corresponding to the fraction of $+1$ spins, there is a finite stability interval ΔH; the total H scale is completely filled up by the ΔH intervals and the q vs H curve shows an infinity of steps.

In order to apply this Ising model to the Sm-C_α phase, the $+1$ state was identified with a ferroelectric ordered layer pair and the -1 state with an antiferroelectric ordered pair [7], i.e., $q=1$ corresponds to the usual ferroelectric Sm-C phase and $q=0$ to the antiferroelectric layer-by-layer alternating Sm-C_A phase; H would correspond to a ferroelectric ordering field the strength of which increases with decreasing temperature and the repulsive interaction $J_{|i-j|}$ was recently proposed [18] to result from thermally excited polarization waves.

At finite (nonzero) temperature one cannot expect an infinity of steps or states because the long-period structures, which possess only extremely narrow stability intervals on the H scale, will be destroyed. In our experiment, this effect will be amplified by the reduction of the number of layers of the sample and we expect in thin films only the most stable structures to occur. Besides the structures with $q=0$ (antiferroelectric Sm-C_A phase) and $q=1$ (ferroelectric Sm-C phase), which possess infinitely large stability intervals on the H scale, the most stable state is that with $q=\frac{1}{2}$ corresponding to an antiferroelectric two-layer-by-two-layer alternating structure. In thin films, we expect therefore a phase sequence corresponding to either 1-0 or 1-$\frac{1}{2}$-0 on the q scale (with increasing temperature) and indeed we observe in films with $N<10$ only antiferroelectric behavior above the Sm-C phase. With the present ellipsometric setup, however, we can hardly distinguish between a layer-by-layer ($q=0$) or a two-layer-by-two-layer ($q=\frac{1}{2}$) antiferroelectric structure; probably we would even fail to detect a transition between these two states because both produce nearly the same values of the ellipsometric parameters.

The next-most-stable states are first those with $q=\frac{1}{3}$ (ferrielectric) and $q=\frac{2}{3}$ (antiferroelectric) and then those with $q=\frac{1}{4}$ and $q=\frac{3}{4}$ (both antiferroelectric). A phase sequence, in which all states with periodicities ≤ 8 layers are allowed to occur, would thus read 1-$\frac{3}{4}$-$\frac{2}{3}$-$\frac{1}{2}$-$\frac{1}{3}$-$\frac{1}{4}$-0, or, denoting ferroelectric states by fo, ferrielectric ones by f, and antiferroelectric ones by a, *fo-a-a-a-f-a-a*. Provided that transitions between two adjacent a states are not detected by our measurements, we could interpret our results for the 10- and 16-layer films as such a sequence. In thicker films, however, a ferrielectric state appears adjacent to the paraelectric Sm-A phase; such a behavior is in accordance with the Ising model only if one assumes that the whole sequence between $q=1$ and $q=0$ is not necessarily to pass. Further, we have to keep in mind that in the simple considerations described above we have neglected any boundary effects near the free surfaces of our films.

In conclusion, we have presented an ellipsometric study of the Sm-C_α phase in freely suspended films. Whereas in bulk samples only an apparently continuous change of the properties with temperature is established to date, we have shown that a sequence of discrete ferrielectric and antiferroelectric states may occur when the number of molecular layers of the sample is limited to a relatively small value. The number of states increases with increasing number of molecular layers, thereby indicating that most states possess probably long-period structures extending over several smectic layers. Such a behavior is in qualitative agreement with the devil's staircase model based on a one-dimensional Ising model with long-range repulsive interactions in a field. How-

ever, other theoretical models, such as an Ising model with competing nearest-neighbor and next-nearest-neighbor interactions (axial next-nearest-neighbor Ising model) [19] or a mean field model [20] also based on competing nearest- and next-nearest-neighbor interactions, also show a large number of different phases and the situation on the experimental side is not clear enough to draw a definite conclusion on the proper theoretical model. Clearly, further structural investigations of the Sm-C_α phase are needed.

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335). Stimulating discussions with G. Heppke are gratefully acknowledged.

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