PHYSICAL REVIEW E VOLUME 59, NUMBER 4 APRIL 1999

Polarization in free standing chiral and nonchiral smectic films

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(Received 8 September 1998)

There is no fundamental reason that nonchiral liquid crystals should not be ferroelectric. In this paper nonchiral flexoelectric effects (particularly leading to the specific orientation phenomena for smectic films in electric fields) are investigated in freely suspended films. Optical reflectivity measurements are presented for the region near the smectic-C^*–smectic-A and smectic-C–smectic-A phase transitions. Temperature dependences of the tilt angle are determined for two kinds of smectic structures where polarization is either perpendicular or parallel to the tilt plane. [S1063-651X(99)03104-9]

PACS number(s): 61.30.Eb, 64.70.Md, 68.10.Cr, 77.84.Nh

I. INTRODUCTION

A variety of molecules form liquid crystalline phases (see, e.g., the Ref. [1]). Many mesogen molecules have symmetries consistent with the formation of ferroelectric phases and nonzero dipole moments. Ferroelectric ordering is, however, extremely rare in positionally disordered liquids or liquid crystals, and, since the discovery of ferroelectric liquid crystals [2], it has been assumed usually that ferroelectricity is possible only in a chiral smectic-C^* phase (SmC^*) that has a polar symmetry group C_2. In this case the polarization can be written as $\mathbf{P}=P[\mathbf{n}\times\mathbf{z}]$, where $\mathbf{n}$ is the director [3] and $\mathbf{z}$ is the smectic layer normal. The necessary conditions for the existence of nonzero polarization are a finite tilt angle ($\theta \neq 0$) and a molecular dipole perpendicular to the long axis of molecules. In racemic mixtures, which contain both enantiomers (that is, molecules that are mirror images of each other) in equal amounts, the electric polarization vanishes. Obviously, the electric polarization is directly connected with molecular chirality in the SmC^* ferroelectric liquid crystals.

Orientational order in both tilted smectic phases (namely, SmC^* and SmC) can be characterized by the two-component order parameter $\psi=\theta\exp(i\phi)$ or by so-called $\mathbf{c}$ director (projection of the director $\mathbf{n}$ onto the layer plane) [3]. In the SmC^* phase, molecular chirality induces a twisted structure with a certain pitch. When going along the z coordinate the director $\mathbf{n}$ (as well as the $\mathbf{c}$ director) and the polarization $\mathbf{P}$ rotate. Therefore, strictly speaking, the smectic-C^* phases can be considered as ferroelectric only in two dimensions because the direction of the polarization varies helically in the direction orthogonal to the smectic layers. A spiral structure of such type is typical for chiral systems.

Intuitively it is clear why ferroelectricity is a rather rare and specific phenomenon in liquid crystals in spite of the fact that their molecules almost always possess nonzero dipole moments. Typically the free energy is larger when dissimilar chemical parts (e.g., hydrophobic and hydrophilic) of molecules are in contact. Thus interactions between chemically dissimilar parts of molecules (as well as steric ones) in a general case are expected to discourage ferroelectricity. Moreover, in liquid crystals the polar interactions are usually rather small. Coulomb interaction results only in a weak tendency toward polar order, depending, however, on the pair distribution function. Nevertheless this tendency can lead to a ferroelectric order in systems with at least partially freezing molecular motions, as is the case in smectic-C^* phases.

Note that there is no unambiguous correspondence between the chirality of molecules and the existence of the macroscopic ferroelectric properties or structures they formed. Attempts at observation of ferroelectricity in nonchiral liquid crystals are, as a rule, centered around synthesis and investigations of nonconventional liquid crystalline structures [4]. Recently [5,6], we observed an anomalous orientation of conventional smectic structures in electric fields (for example, in the SmC^* free standing film the tilt plane of the molecules is oriented parallel to an electric field). The present paper is devoted to investigations of this ''unusual'' orientation, and to nonchiral origin of the polarization in the SmC^* and SmC structures. These phenomena are demonstrated to be typical of the smectic liquid crystalline films. We have determined the order parameters (tilt angles) for the different types of films (polarization is either perpendicular or parallel to the molecular tilt plane).

Note that free standing smectic films are interesting in their own right, but in addition are a new thermodynamical state of matter (like liquids or solids). Free standing films exist only for smectic phases having some tendency to construct layer structures. The large effects of surface ordering were observed above the bulk SmC-SmA transition temperature T_c [7–13]. The SmC ordering appears in films at a temperature about 20 °C above T_c [7,8]. The thinnest free standing films have just two smectic monolayers. But even two monolayers experience certain internal forces fixing both monolayers close to each other. Without such forces, free standing films do not exist (as in the case of isotropic liquids or nematic phases). There is also another demonstration of this statement. For thin films there is a definite temperature stability region for each thickness, or in others words, there are definite thinning transitions temperatures $T(N)$ [14,15]. Upon increasing the temperature the film undergoes layer thinning transitions before it finally ruptures at a certain temperature which is usually $20-30\,^{\circ}\mathrm{C}$ higher than the bulk smectic-isotropic liquid or smectic-nematic phase transition temperatures.

The organization of our paper is as follows. In Sec. II we formulate our model and introduce (in the framework of the Landau theory) the basic thermodynamics necessary for our discussions. In this section we present expressions for the spatially dependent order parameter profiles in the vicinity of so-called ordinary, extraordinary, and surface phase transitions in free standing smectic films. Section III contains our experimental results including optical-reflectivity measurements in chiral and nonchiral free standing films, which allowed us to find the reorientation temperature, its dependences on the film thicknesses, and an average tilt angle (i.e., the order parameter). Section IV is devoted to a discussion and summary of our main results.

II. THEORETICAL MODEL

The Sm*C* structure is distorted in the Sm*C** phase with a spatial variation of the order parameter. In any layer the order parameter is equal in magnitude $|\mathbf{c}|$ (tilt angle θ), but slightly different in direction (angle ϕ). The order parameter is a two-component vector, and, as we mentioned above, the Sm*C** phase has a polar axis (and therefore may have a ferroelectric polarization) perpendicular to the tilt plane. However, there is also the following principal possibility to prepare ferroelectric structures: the orientation of $\mathbf{c}$ is the same in neighboring layers, while the magnitude of the order parameter $|\mathbf{c}|$ (angle θ) is continuously varied from layer to layer. This is a nonchiral ferroelectric smectic structure. The polarization $\mathbf{P}$ should appear in the tilt plane. The structure of such type can be realized in freely suspended smectic films.

In fact, since the bend of $\mathbf{c}$ removes the $\mathbf{c}$-$\mathbf{z}$ mirror symmetry plane, it produces a local chiral symmetry breaking. This breaking of chiral symmetry can occur on two distinct length scales (microscopic or macroscopic). The distinction between microscopic and macroscopic chiral symmetry breaking is similar to the distinction between spontaneous and induced order parameters. As we will see below, we deal with an induced order.

There are two effects related to the existence of the surface in free standing films. The first is a pure geometrical one (finite size effects). The surfaces break the translational and rotational invariances (because any specific surface breaks the translational invariance, and the normal to the surface is a specific direction which breaks the rotational invariance). In addition, certainly, there are physical modifications of the system due to the existence of the surface (surface effects). The surface can suppress the bulk ordering (this case is traditionally called the ordinary phase transition), the surface can enhance the bulk ordering (this is called the extraordinary phase transition), or as a third possibility the surface can experience an intrinsic critical behavior. There is also a so-called special phase transition which is intermediate between ordinary and extraordinary transitions.

Thus for any finite system having boundaries (and particularly for free standing films) one can introduce at least three types of specific local characteristics of the system; among these the most convenient are susceptibilities: the bulk susceptibility χ_b which is a response function with respect to the bulk field H (i.e., external action, conjugate to the bulk order parameter ψ), the local surface susceptibility χ_1 which is a response function of surface ordering with respect to the same bulk field, and the local surface susceptibility $\chi_{1,1}$ which is a response function with respect to the local surface field H_1. In addition, we should distinguish these local properties from the surface contribution, which is in fact a nonlocal property, describing, roughly speaking, the difference between the energy of a given system and the energy for the same system but without surfaces. Thus there is a fourth susceptibility χ_s. It is necessary to keep all these susceptibilities in mind when considering a theoretical description of experimental data.

In order to escape a conflict between experiment and theory, we suggest that generalized fields H and H_1 (they are not necessary magnetic or electric fields; e.g., the most relevant local action on the surfaces of free standing films is an anchoring field) do not depend on coordinates in the plane of a film, and H_1 is coupled only to the module of the order parameter θ. In this case the theory is reduced to the well known Landau theory for a scalar order parameter [16]. However due to its importance for the present context (and for convenience) we mainly repeat known results but apply these to our concrete case (the smectic-*A*–smectic-*C* transition in free standing films). This is just the case where it is easy and more useful to derive these results for the concrete system under consideration than to try to find the suitable references, and to modify all expressions to apply them to the case.

Let us first consider an ordinary phase transition. For $T > T_c$ (let us remember that this is the most relevant case for our systems) one can obtain the following profile of the order parameter [7]:

$$\theta(x)=\theta_b-(\theta_b-\theta_1)\frac{\cosh[x-(L/2\xi_b)]}{\cosh(L/2\xi_b)}, \tag{1}$$

where $x\equiv z/\xi_b$, ξ_b is the bulk correlation length, θ_b is the bulk value of the order parameter, and

$$\theta_1=\frac{(\lambda/\xi_b)\,\theta_b\tanh(L/2\xi_b)+H_1(\lambda/C)}{1+(\lambda/\xi_b)\tanh(L/2\xi_b)}. \tag{2}$$

Here λ is a constant having the dimension of length; it is called the extrapolation length, C is the Landau coefficient at the gradient term (‘‘elastic modulus’’), and H_1 is a local surface field.

The expression given below assumes that the smectic-*A* order parameter (i.e., smectic-*A* density modulation) is a constant through the film thickness. This is not always the case for free standing smectic films, where the smectic-*A* order parameter [as well as smectic-*C* one (i.e., the tilt angle)] varies spatially. In this case, instead of Eq. (1) one can derive a rather bulky expression, having the form of a certain convolution of two functions of the type (1). However, the qualitative behavior in both cases is not much different, and we will not discuss the phenomenon further.

For $T=T_c, H=0, H_1\neq 0$ (in fact it requires $\xi_b \gg L$) we have a nonexponential behavior. For small H_1 and near $z=0$, θ changes linearly with distance from the surface:

$$\theta(x)=\theta_1-\frac{z}{\lambda}(\theta_b-\theta_1).$$

Note that extrapolating this behavior to negative z one finds $\theta(z)=0$ at $z=-\lambda$. Due to this fact the constant λ is called the extrapolation length.

Let us define now an average order parameter over the thickness of the film,

$$\bar{\theta}=\frac{1}{L}\int_0^L \theta(z)dz=\theta_b-\frac{2}{L}\,\frac{\xi_b(\theta_b-H_1(\lambda/C))}{\coth(L/2\xi_b)+(\lambda/\xi_b)}. \tag{3}$$

It has a rather evident structure, including both bulk and surface contributions

$$\bar{\theta}\equiv\theta_b-\frac{2}{L}\theta_s,$$

where

$$\theta_s=\tfrac{1}{2}\int_0^L dz[\theta_b-\theta(z)], \tag{4}$$

and from Eq. (4) one can obtain in the limit $\xi_b \gg L$,

$$\theta_s=\xi_b(\theta_b-\theta_1)=\frac{\xi_b(\theta_b-(H_1\lambda/C))}{1+(\lambda/\xi_b)}. \tag{5}$$

For extraordinary phase transitions (i.e., if $\lambda<0$) the surface enhances the ordering, and therefore on the surface one can expect the onset of ordering before (i.e., at higher temperatures) it occurs in the bulk. Thus in this case one can expect a surface transition for temperatures $T_{cs}>T_c$. But of course at T_c, due to the onset of the bulk order, the surface will experience some critical behavior as well. In the regime of $T_c<T<T_{cs}$ the bulk correlation length ξ_b is finite, and the order decays exponentially quickly from its maximum value θ_1 at the surface toward zero in the bulk. One can find the transition temperature for the surface layer (see, e.g., Ref. [16]):

$$\frac{T_{cs}}{T_c}-1=\frac{C}{T_c}\lambda^{-2}. \tag{6}$$

In this case the profile of the order parameter can be found again from Eq. (1) but θ_1 is not zero now even at $H_1=0$. At T_c (or as we mentioned above at $\xi_b \gg L$) the order parameter profile decays algebraically, from θ_1 at the surface to zero in the bulk.

Note that the response $\bar{\chi}$ of the total order parameter of a sample to a uniform external field is often experimentally more accessible than either χ_1 or $\chi_{1,1}$. If $\bar{\chi}$ is measured in a sample with $\lambda<0$, two divergences should appear as the temperature is lowered. The first will appear at T_{cs} with $\bar{\chi} \propto (T-T_{cs})^{-1}A\xi_b$, (in the mean-field approximation) where A is the surface area of the sample. The second divergence appears at T_c with the mean-field Curie law $\bar{\chi}\propto(T-T_c)^{-1}V$, where V is the volume of the sample.

Thus there are two mechanisms of smectic-C ordering in free standing films above the bulk smectic-C–smectic-A transition temperature. That is, for the ordinary phase transition ($\lambda>0$) the only mechanism inducing ordering is connected with the surface field H_1 (most plausibly it is an anchoring field), and the order parameter profile is determined by Eq. (1). For the extraordinary phase transition ($\lambda<0$) the surface phase transition takes place at the temperature T_{cs} found above Eq. (6). For $\lambda<0$ both surface and bulk fluctuations contribute equally to thermodynamic (e.g., ferroelectric) properties, and therefore these properties appear as the sum of two independent parts which diverge at different temperatures.

In both cases the spatial variation of the order parameter allows for free standing films, the bending deformations of the director strongly being suppressed in the bulk smectic phases. In turn these deformations can create a polarization $\mathbf{P}_f$ due to the well known flexoelectric effect [17,1,3]

$$\mathbf{P}_f=e_1(\mathbf{n}\,\mathrm{div}\,\mathbf{n})+e_3(\mathrm{rot}\,\mathbf{n})\times\mathbf{n}. \tag{7}$$

It involves two coefficients with the dimensions of an electric potential. Rough estimations of these coefficients, based on the calculation of the fraction of the molecules which achieve the ordering of their dipoles to ensure the maximum packing density, give

$$e\simeq\mu_d K\frac{N^{1/3}}{T},$$

where μ_d is the molecular dipole moment, K is elastic Frank constant, and N is the number of molecules per unit volume.

So in our geometry the polarization vector $\mathbf{P}_f$ should be parallel to the tilt plane, and the absolute value of the polarization is given as

$$|\mathbf{P}_f|\simeq e\frac{\partial\theta}{\partial z},$$

where the function $\theta(z)$ can be found from Eq. (1). Among the symmetry groups admitting a flexoelectric relation between the deformation and the polarization in the plane of the ferroelectric axis, let us mention groups D_2 and D_{2d} which are the plausible symmetry groups for free standing films of smectic-C phases.

In Sec. III we will see that the consequences of this simplest model are consistent with our experimental data. In order to say more, we require a further knowledge of a number of parameters entering the Landau theory. Unfortunately using only our data we are not able to extract values of all necessary parameters. Therefore, we will not quantitatively compare our data with this theory, since with too many unknown parameters the theory tends to become an exercise in curve fitting. Note, however, that there is a qualitative agreement. For example, more likely, the smectic-C ordering in the free standing films under consideration is induced by surface phase transitions (so we are dealing with extraordinary phase transitions at T_c) and the transition temperature

T_{cs}, according to Eq. (6), is inversely proportional to λ^2. Thus we have the following tendency: the greater the difference between the bulk and the surface transition points, the less λ is, and one can expect the specific configuration of the film (which we will call the *C* configuration) which was really observed in our experiments (see also Sec. III and discussions in Sec. IV, where we will see that dipole-dipole interactions also favor the *C* configuration of the film).

III. EXPERIMENTAL RESULTS

In this section we report results of optical-reflectivity measurements in linearly polarized light on freely suspended films of chiral and nonchiral liquid crystal compounds near Sm*A*-Sm*C* transitions. This method enables us to determine directly the orientation of the optical axis in the films and the temperature behavior of the tilt angle. Our samples were chiral liquid crystalline compound *n*-noniloxybenzylidene-*n*'-amino-2-methylbutylcinnamate (NOBAMBC) and nonchiral *p*-decyloxybenzoic acid *p*-*n*-hexyphenyl ester (DOBHOP). Bulk samples had the following phase transition temperatures: 91 °C (SmC*-Sm*A*, NOBAMBC) and 78 °C (SmC-Sm*A*, DOBHOP). Some measurements were made on a mixture of DOBHOP and nonchiral Sm*A* liquid crystal NO_2-hexyloxyphenyl ester of hexylhydroxybenzoic acid (C2). X-ray diffraction measurements of the layer spacing and tilt angle of the molecules in the Sm*C** and Sm*C* phases of the bulk samples were made using a curved linear position sensitive multidetector ($\lambda=1.5406$ Å). Thick free standing films for optical measurements were prepared by drawing the liquid crystal in the Sm*A* phase across 4- or 6 mm holes in a glass plate. Thin films were obtained by layer-by-layer thinning transitions above bulk Sm*A*-*I* or Sm*A*-*N* phase transition temperatures [14,15]. The incident light was linearly polarized. Optical reflection was measured in the ''backward'' geometry. The thickness of the film was determined from the intensities and spectral dependence of the optical reflection in the Sm*A* phase [18,19],

$$I(\lambda)=\frac{(n^2-1)^2\sin^2(2\pi nNd/\lambda)}{4n^2+(n^2-1)^2\sin^2(2\pi nNd/\lambda)}, \tag{8}$$

where *d* is the interplanar distance, *n* is the refraction index, and *N* is the number of smectic layers.

An electric field was applied in order to fix the polarization direction **P** in the Sm*C* phases. Our setup allows one to change the direction of the electric field in the plane of the film. Because of the coupling between **P** and the tilt plane, the electric field aligns the direction of the tilt plane. For a uniformly oriented Sm*C* film with an in-plane anisotropy of the refractive index, the reflection spectra with the light polarization plane oriented parallel (I_p) and orthogonal (I_o) to the tilt plane can be measured. In our experiments the electric field was applied parallel ($E_\parallel$) and perpendicular ($E_\perp$) to the direction of the light polarization (corresponding reflection intensities are denoted by $I_\parallel$ and $I_\perp$, respectively). Two types of measurements were performed. In thin films we determined the temperature dependence of the relative optical reflection intensities ($I_\perp/I_\parallel$). In thick films we measured the wavelengths of the reflectivity minima for the reflective spectra $I_\perp$ and $I_\parallel$.

For films with $N>40$, the orientation of the tilt plane was determined from a comparison of the optical spectra for two polarizations ($I_\perp$ and $I_\parallel$). The wavelength of the reflectivity minimum depends on the refraction index ($\lambda_m=2nNd/k, k=1,2,3,\dots$). Since the refraction index n_p (parallel to the tilt plane) is larger than n_o (perpendicular to the tilt plane), the larger value of λ_m corresponds to the light polarization which is parallel to the tilt plane. For thick films we also measured the optical reflectivity at the wavelength near the reflectivity minimum λ_m. In this case the sensitivity of the optical measurements could be essentially improved [20]. For thin films the reflected intensity is proportional approximately to $(n^2-1)^2$:

$$I(\lambda)\simeq N^2\pi^2d^2(n^2-1)^2/\lambda^2. \tag{9}$$

Hence the larger value of the reflected intensity corresponds to the light polarization parallel to the tilt plane.

The average tilt θ is more easily determined for the films with reflectivity minima ($N>40$) and for thin films. Considering the molecules as rigid rods, the layer spacing d_C in the Sm*C* phase may be taken as

$$d_C=d_A\cos\theta, \tag{10}$$

where d_A is the layer spacing in the Sm*A* phase. The refractive index in the direction perpendicular to the tilt plane does not depend on the tilt angle (ordinary refraction index n_o). Thus, for ordinary waves, λ_m is proportional to *d*. Within these approximations, the tilt angle can be found from the ratio

$$\cos\theta=\lambda_{mC}/\lambda_{mA}, \tag{11}$$

where λ_{mC} and λ_{mA} are the wavelengths of the reflectivity minima for the tilted and untilted smectic phases, respectively.

For thin films the ratio I_p/I_o depends only on the refraction coefficients n_p and n_o. When n_o is known, n_p can be determined from the values I_p/I_o. Then, using the results derived for uniaxial crystals [18,21] (i.e., neglecting rather weak biaxiality of Sm*C* phases), θ can be found from

$$\cos^2\theta=\frac{n_o^2(n_e^2-n_p^2)}{n_p^2(n_e^2-n_o^2)}. \tag{12}$$

For the determination of θ in films with an intermediate thickness (8–40 layers) we used Eqs. (8), (10), and (12) and the measured $I_\perp/I_\parallel$ values. For calculation of θ averaged over the thickness of the film, in the case of NOBAMBC, we used the values of n_e and n_o for DOBAMBC [22] whose molecules are similar to the molecules of NOBAMBC. The value of the layer spacing in the Sm*A* phase d_A was taken from the x-ray measurements. Using the techniques and methods described above we have investigated the following systems.

A. Chiral liquid crystal with the ferroelectric SmC* phase in a bulk sample

Orientation of the films can clearly be observed for thick films with minima in the reflection spectra. Figure 1 shows

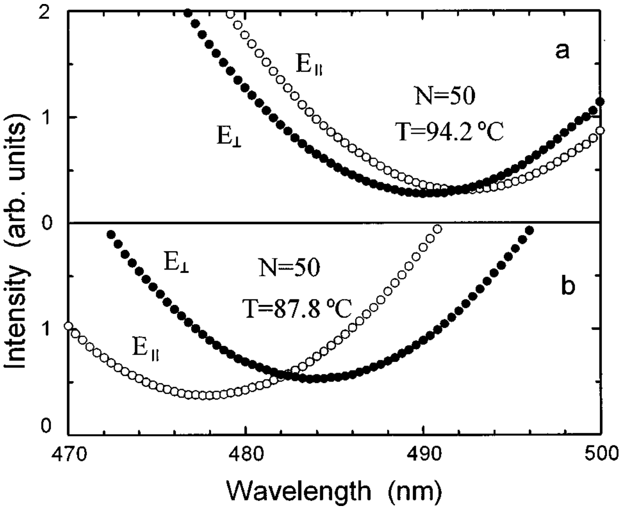

FIG. 1. An example of reflection spectra at a temperature above (a) and below (b) the bulk transition temperature. The relative positions of the reflectivity minima for $E_\perp$ and $E_\parallel$ are different for temperatures above (a) and below (b) the bulk transition temperature (NOBAMBC).

the reflection spectra of the 50-layer film near the reflectivity minima for two directions of the electric field. At low temperatures for the $\mathbf{E}_\perp$ field λ_m is larger than corresponding minimum for the $\mathbf{E}_\parallel$ field (tilt plane is perpendicular to the electric field). This is exactly what is expected for the SmC^* type structure. The relative position of the minima at high temperatures is different from that at low temperatures, implying a reorientation of the tilt plane by 90° upon heating.

Figures 2(a) and 2(c) shows the behavior of the reflected intensity for the 25-layer film near T_i when the electric field, stabilizing the **c**-director orientation, changes by 90°. Below T_i the reflected intensity $I_\perp$ is larger than $I_\parallel$ that means that the **c** director is perpendicular to the electric field (usual orientation). Above T_i the intensity $I_\perp$ is smaller than $I_\parallel$, i.e., the **c** director is parallel to the electric field (unusual orientation). Figure 2(b) shows the temperature range near T_i (heating of the sample). The tilt plane of the molecules changes its orientation abruptly. The cooling run also shows the step in the intensity curve, but at a lower temperature than for the heating one.

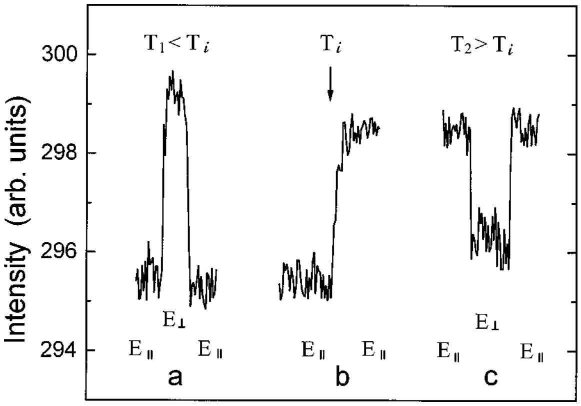

FIG. 2. Optical reflection intensity ($\lambda = 630$ nm) for smectic-C^* films in the electric fields applied parallel ($E_\parallel$) and perpendicular ($E_\perp$) to the light polarization direction from $T_1 = 93.9\,°\mathrm{C}$ (a) to $T_2 = 94.6\,°\mathrm{C}$ (c). (b) shows the temperature range from $T = 93.9\,°\mathrm{C}$ to $T = 94.3\,°\mathrm{C}$ (heating of the sample). Around $T_i = 94.1\,°\mathrm{C}$ an abrupt change of the orientation is observed (NOBAMBC, $N = 25$).

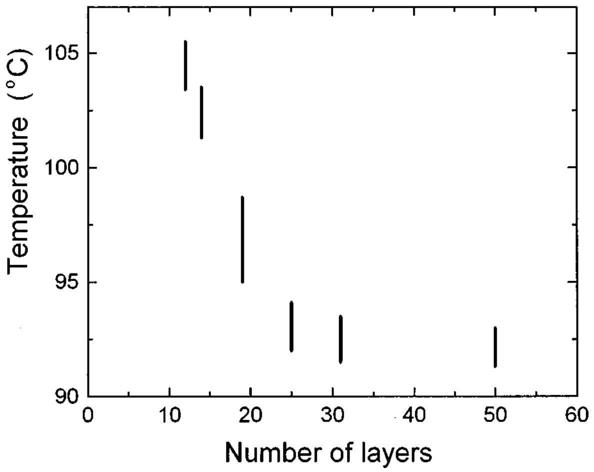

FIG. 3. Temperatures T_i, where the change of the orientation of ferroelectric smectic-C^* films takes place for different film thicknesses. The uncertainty of the temperatures (lines in the figure) is due to reorientation hysteresis (NOBAMBC).

For thick films ($N > 11$) two temperature regions with different **P** orientations with respect to the tilt plane are observed. At low temperatures ($T < T_i$) electric fields orient the SmC^* films analogously to the bulk samples: the tilt plane is perpendicular to the electric field. At high temperatures ($T > T_i$) the unusual orientation is observed: the tilt plane is parallel to the electric field. T_i decreases with an increase of the film thickness. The temperatures where the reorientation of the films occurs are shown in Fig. 3. The lines in the figure indicate the temperature ranges of the thermal hysteresis. For thin films we observed that the tilt plane was always perpendicular to the electric field (the ferroelectric polarization **P** is perpendicular to the tilt plane). The temperature dependences of θ for films without reflectivity minima were calculated using our optical data ($I_\perp / I_\parallel$), as described in this section. Figure 4 shows the values of θ for the three-, five-, and 19-layer films.

Figure 5 shows the temperature dependence of the measured λ_m values for the 50-layer film in electric fields applied

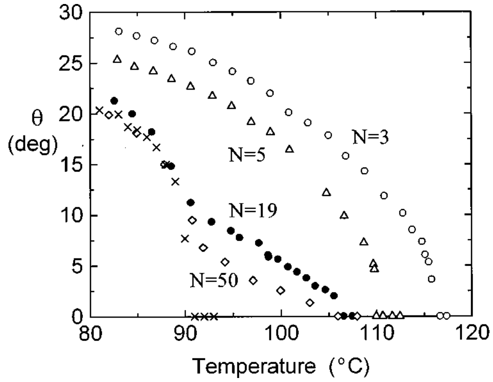

FIG. 4. Temperature dependence of the average tilt for film thicknesses of three, five, 19, and 50 smectic layers, and for the bulk sample (x), NOBAMBC.

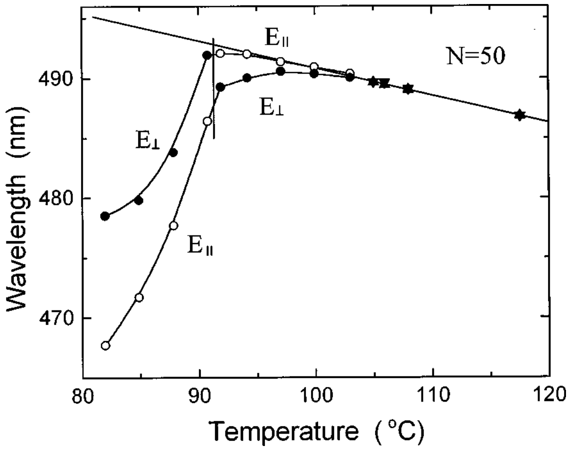

FIG. 5. Temperature dependence of the reflectivity minimum λ_o in the electric field applied parallel ($E_{\|}$, open circles) and perpendicular ($E_{\perp}$, closed circles) to the light polarization direction (NOBAMBC). The straight line was drawn according to the data for temperatures above the surface transition temperature ($E_{\|}$, upright triangles, $E_{\perp}$ inverted triangles).

parallel and perpendicular to the direction of the light polarization. One can see the increase of λ_m in the Sm*A* phase of the film ($T > 105\,°\mathrm{C}$), followed by the decrease at low temperatures in the chiral Sm*C** phase. A splitting in λ_m appears at the surface phase transition into the Sm*C** phase. When the temperature decreases, the difference $\Delta\lambda_m$ for two directions of the electric field increases, showing Sm*C** ordering. The increase of λ_m in the Sm*A* phase is related partially to the temperature dependence of the layer spacing that was observed in our x-ray measurements on the bulk sample. The wavelengths λ_m in the Sm*A* phase were fitted with a linear law and extrapolated into the tilted smectic phase (Fig. 5). The resulting λ_{mA} was used [see Eq. (11)] for the determination of θ in Sm*C** phase for the 50-layer film. For these calculations, λ_{mC} were taken for the direction of the ordinary refraction index, that is, λ_{mC} for the $\mathbf{E}_{\perp}$ field at $T > T_i$ and λ_{mC} for the $\mathbf{E}_{\|}$ field at $T < T_i (T_i$ is denoted by the vertical line in Fig. 5). The values of θ for the 50-layer film are shown in Fig. 4. Figure 4 also shows the temperature dependence of θ taken from our x-ray measurements on the bulk sample. Below T_c, the magnitudes of θ in thick films and in the bulk sample are in good agreement.

B. Nonchiral Sm*C* liquid crystals

In the high temperature range of the Sm*C* phase, thick films of nonchiral Sm*C* liquid crystals are oriented by weak electric fields. The orientation of the tilt plane is the same as for ferroelectric Sm*C** films: the applied electric field orients **n** so that the tilt plane and **E** are parallel. In thick nonchiral Sm*C* (as well as in ferroelectric Sm*C**) films we observed an abrupt change in the tilt plane orientation near T_c. Figure 6 demonstrates the change of the optical reflection intensity near the reorientation temperature of the film. At $T < T_i$ the tilt plane is oriented perpendicular to the direction of the electric field. In Sm*C* films of DOBHOP, such a behavior is observed below T_i in a narrow temperature range ($\Delta T < 1\,°\mathrm{C}$).

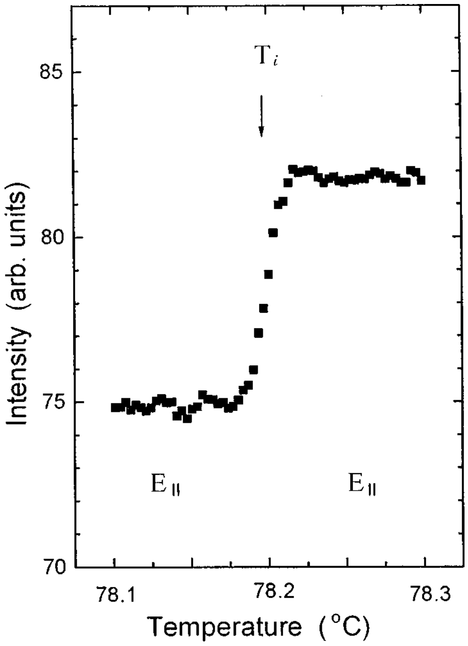

FIG. 6. Optical reflection intensity for DOBHOP near $T_i = 78.2\,°\mathrm{C}$ (heating of the sample, $N = 70$). The measurements were made at a wavelength near the reflectivity minimum ($\lambda \simeq \lambda_m - 20$ nm).

DOBHOP molecules have a small dipole moment. To study the dependence of the orientation of the Sm*C* films on the value of molecular dipoles, we investigated the mixture of DOBHOP with a C2 compound possessing a relatively large dipole moment perpendicular to the long molecular axis. At high temperatures the tilt plane is oriented parallel to **E** (Fig. 7). Below the reorientation temperature (T_i), thick aligned films may be obtained in the whole temperature range of the Sm*C* phase.

At high and low temperatures we did not observe any orientation of the two-layer film in weak electric fields. This means that the possible mechanisms of the smectic-*C* film orientation in weak electric fields have to be applied for thick films.

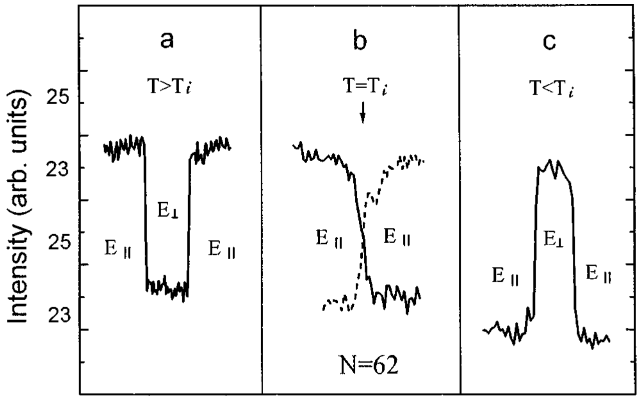

FIG. 7. Optical reflection intensities for the Sm*C* liquid crystal DOBHOP with the smectic compound C2 (12%) at $T = 76.4\,°\mathrm{C}$ (a) and $T = 75.5\,°\mathrm{C}$ (c). (b) The solid curve shows the temperature range from $T = 75.9$–$T = 75.7\,°\mathrm{C}$ (cooling of the sample). The change in the orientation of the film is observed (solid line, $E_{\|}$). The dotted line is the change of the intensity for the $E_{\perp}$ field. $\lambda \simeq \lambda_m - 20$ nm and $N = 62$.

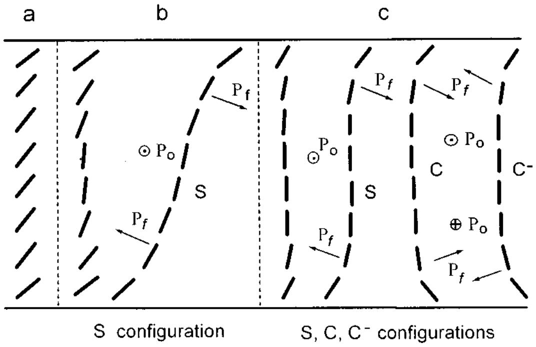

FIG. 8. Orientation of the molecules in thick Sm*C* films below (a) and above (b) and (c) the bulk transition temperature. *S*- and *C*-like configurations are shown for a thick film. $\mathbf{P}_o$ is the ferroelectric polarization. $\mathbf{P}_f$ is the flexoelectric polarization.

IV. DISCUSSION

Due to surface, tension (suppressing bending fluctuations) and specific interactions on the surface, the molecules tilt at a temperature about 20 °C above the bulk transition temperature [7,8]. One can most plausibly say that in free standing smectic-*C* films we have extraordinary phase transitions in the presence of a surface field H_1, and therefore the expressions given in Sec. II for this case can be applied. Unfortunately, we can find no guidance from experimental or theoretical sources for choosing all phenomenological coefficients that appear in these expressions. Thus the primary function of this section must be to give a qualitative interpretation of our results, and to demonstrate the possibility of ferroelectric ordering in basically nonchiral systems, as opposed to proving exactly its existence.

As we have already said, the inhomogeneous smectic-*C* ordering taking place in free standing films is responsible for ferroelectric properties. This inhomogeneous ordering physically means that over a large region of thicknesses of free standing films, the films can be considered as some effective interfaces. It is typical for liquid crystals [23] that the width of the interface of experimental mesogenes is 40–100 times the length of molecules. We observed an example of how the presence of an interface may induce a type of ordering in the inhomogeneous region (for free standing films it may be the whole thickness of the system) that does not occur in the bulk phases. Analogous phenomena are also known for Langmuir monolayers where chiral symmetry can be spontaneously broken [24], and this leads to a chiral phase composed of nonchiral molecules. In fact, for a thick free standing film the top and bottom layers are each equivalent to Langmuir monolayers.

Let us proceed further to describe theoretically the results presented above (Sec. III) concerning the behavior of Sm*C* and Sm*C** films in electric fields. Our interpretation of these results is based on the configurations shown in Fig. 8. Here we indicate the layer structures of the films below (a) and above [(b) and (c)] the bulk transition temperature. Everywhere over the Sm*C* temperature range of the film the tilt is a function of the distance from the surface. The symmetry of the structure allows the existence of a polarization **P** parallel to the tilt plane. The distinctive features of the structure and polarization properties of the free standing film depend essentially on the temperature. According to the experimental observations, and remembering the theory presented above, several temperature regions may be distinguished (Fig. 8): (a) low temperatures, below the bulk transition temperature; (b) a temperature range above the bulk transition temperature, where Sm*C* ordering is essential in the whole thickness of the free standing film; and (c) high temperatures, where Sm*C* ordering at the center of the film is negligibly small.

We start our discussion with the high temperature range. In the framework of the Landau theory, the tilt is given by expressions (1), and (6) presented in Sec. II. At high temperatures the tilt angle θ decays with the distance from the surface, and becomes very small (nearly zero) for distances larger than the bulk correlation length (at the center of the film if its thickness is larger than this correlation length). As a result the orientations of the **c** director in the layers of the top part of the film are not coupled to the orientations of the **c** director for the layers of the bottom part. In this case, with respect to the Sm*C* ordering, two parts of the film may be considered independently of one another. Let us estimate the magnitude of the flexoelectric polarization (7). The dependence of θ on the coordinates even in the framework of the Landau theory may be quite sophisticated (see the expressions given in Sec. II and Refs. [16,25,26]). However in any case the integrated polarization density of the film depends mainly on the difference between the surface tilt angle θ_s [see Eq. (5)] or θ_1 [see Eq. (2)], and the tilt angle in the center of the film θ_c which can be estimated from Eq. (1) putting $x = L/2\xi_b$ and $\theta_b = 0$. From the data for the bulk smectic-*A*–smectic-*C* transition, one can obtain T_c, ξ_b, and *C*, and from T_{cs} and Eq. (6) we can extract λ. The results allow us to neglect θ_c and to estimate $\theta_s \simeq 0.2$ rad. Using the natural estimation for flexoelectric coefficients $e \simeq 10^{-11}$ C/m [3,21], we obtain $P_f \simeq 3\times 10^{-5}$ C/m^2 for $N = 50$. This polarization P_f does not depend on chirality, and has to appear both in Sm*C* and Sm*C** films. However, Sm*C** films have a spontaneous ferroelectric polarization $\mathbf{P}_o$. Let us compare the magnitudes of $\mathbf{P}_o$ and $\mathbf{P}_f$. For the 50-layer film the average tilt angle θ is less than 7° (Fig. 4). For such small angles the ferroelectric polarization $\mathbf{P}_o$ is less than 1×10^{-5} C/m^2 for substances of the NOBAMBC type [22]. Our estimations show that the nonchiral (bend-induced) polarization $\mathbf{P}_f$ exceeds the chiral-induced polarization $\mathbf{P}_o$. One can say that the angle between the orientations of nearest molecules due to the bending deformation is larger than that due to the chiral (twist) deformation (the helical pitch p_c in the Sm*C** phase is larger than 1 μm). Moreover, one may speculate that it is always the case that $P_f > P_o$ when, at a high temperature range (c), the effective surface correlation length ξ_s is less than the helical pitch p_c. So the behavior of Sm*C* and Sm*C** films in electric fields at high temperatures are determined mainly by the bend-induced polarization $\mathbf{P}_f$.

In principle one can imagine configurations of two types depicted schematically in Fig. 8(c). In the *S*-like configuration the orientation of $\mathbf{P}_f$ is different at the top and bottom of the film. Therefore, an electric field inevitably leads to a certain elastic deformation of the structure. This deformation in smectic-*C* phases (unlike nematic phases) have a threshold, i.e., to observe the orientation, the electrostatic energy (the interaction of the dipole polarization with the external electric field) should be larger than the elastic deformation energy. Comparing both energies one can estimate the threshold field

$$E_{th} \simeq \frac{K}{e}\frac{1}{L}\int_0^L \frac{\partial\theta}{\partial z}dz, \tag{13}$$

where K and e are the characteristic values of the elastic and flexoelectric coefficients respectively, and $\partial\theta/\partial z$ is determined from the order parameter profiles found in Sec. II. It is clear that the threshold field (and the electric field orientation of free standing smectic-C films) depends essentially on the material parameters and temperature.

In the C-like configuration $\mathbf{P}_f$'s are oriented in the same direction. Since two parts of the film can be oriented independently, the C-like configurations are favored in the electric field. The tilt arrangement of the C configuration is anticlinic, i.e., the top and bottom of the film are tilted in opposite directions. Note also recent ellipsometric studies [27] where new phases of liquid crystals have been investigated. Among these are antiferroelectric SmC_A structures where the tilt direction alternates when going from layer to layer. It is a microscopic analog of our macroscopically anticlinic C configuration. However it is not possible to distinguish between the both types of anticlinic structures, since in Ref. [27] only an average tilt was measured. The direction of the polarization $\mathbf{P}_f$ relative to $\mathbf{n}$ depends on the sign of the flexoelectric constants (C or C^- configuration [Fig. 8(c)]). For the ideal smectic-C^* structure only the second term in Eq. (7) makes a contribution to the flexoelectric polarization. The sign of this contribution is the same as the sign of e_3 for the right-handed spiral, and is opposite to it for the left-handed one.

In any case the net polarization $\mathbf{P}_f$ is parallel to the tilt plane (and $\mathbf{c}$ director). Thick SmC^* and SmC films are oriented at high temperatures by relatively weak electric fields (see Sec. III). The direction of the tilt plane for both phases is parallel to the electric field (an ''unusual'' orientation for SmC^* phases). It is clear from these data that we are dealing with orientation phenomena of the same kind. So the experimental behavior of films at high temperatures [Fig. 8(c)] is in agreement with our model. However further structure studies are needed to prove the proposed C-like structure.

Consider now the behavior of films at intermediate temperatures [Fig. 8(b)]. In this region of parameters we observe the ''usual'' (with respect to the bulk SmC^* samples) orientation: the tilt plane is perpendicular to the direction of the electric field. Such behavior can be attributed to the fact that in this temperature region the SmC ordering is not small at the center of the film, and therefore a rather strong interlayer interaction stabilizes the S-like configuration. The characteristic temperature (T_i), where the change of the film orientation takes place, depends on the number of layers (Fig. 3). In thin films (of thickness less than the bulk correlation length) there is a finite tilt at the center of the film, which can be estimated from Eq. (1) for $x = L/\xi_b$, and in this case the unusual orientation cannot be realized in the whole SmC stability region.

In the SmC^* phase at low temperatures [$T < T_c$, Fig. 8(a)], the usual orientation of the films is observed in electric fields (Sec. III). The mechanism of the orientation is the same as for the bulk samples. However the behavior of the SmC films in electric fields is not the same for different substances. Thick films of DOBHOP and C2 mixture are oriented by a weak electric field (about 3 V/cm), whereas DOBHOP is not oriented (Sec. III). However, in this temperature range the usual orientation for DOBHOP can be achieved in much larger ac fields. The magnitude of the ac electric field used for the orientation depends on the temperature and increases as the temperature decreases [the amplitude of the ac field (2×10^2 Hz) is about 60 V/cm at $T_c - T = 5$ °C]. Let us emphasize that when using an ac field the orientation of SmC^* films can also be observed in optical reflection experiments. Qualitatively it corresponds to the estimation of E_{th} by Eq. (13), since as the temperature decreases K/e (and E_{th}) should increase. In addition, we should bear in mind that at $T < T_c$ we may not use a linear approximation leading to the order parameter profiles presented in Sec. II. Taking into account the fourth order term in the Landau expansion, one can find, instead of Eq. (1), the more complicated implicit expression

$$\frac{z}{\xi_b} = \int_{\theta_1}^{\theta} d\theta \left[\frac{1}{4}\left(1-\left(\frac{\theta}{\theta_b}\right)^2\right)^2 + \frac{\chi_b H}{\theta_b}\left(\frac{\theta}{\theta_b}-1\right)\right]^{-1/2}. \tag{14}$$

This profile (as well as the profiles presented in Sec. II for $T > T_c$) leads to a flexoelectric polarization according to Eq. (7). However, its dependences on the material parameters and temperature are more rich and sophisticated. The orientation of the SmC films at low temperatures can also be explained by the following mechanisms.

(1) Surface (for instance flexoelectric) polarization may still be retained at low temperatures in SmC films. This polarization has to lead to the deformation of the structure of the film in electric fields (a twisting of the top and bottom parts of the films in different directions). As a result, the net polarization is directed perpendicularly to the tilt plane. A deformation of such type may exist also in SmC^* phases above the bulk transition temperature when P_o is rather small. Note also that the spatial variation of the polarization may result in a space charge and polarization contribution to the elastic constants [28].

(2) Domains (striped texture) [29–31] can appear on the surfaces of the films. The orientation of the films may depend on the structure of these domains. The physical mechanism which is responsible for these domain structures is related to the dipolar interactions. In addition, polarization can modify the order parameter profiles (found in Sec. II) due to dipolar interactions. One should add the interaction of the order parameter with the so-called depolarization field:

$$-\frac{1}{2}\mathbf{E}_d \cdot \mathbf{P}_f(z),$$

where $\mathbf{E}_d$ is the depolarization field. For a thin film of thickness L and otherwise infinite linear dimensions, this field is nonzero only if the direction of the $\mathbf{P}_f$ is not parallel to the film. Introducing the angle φ between the normal vector at the film surface and $\mathbf{P}_f$, one can find

$$\mathbf{E}_d(z) = -4\pi\varepsilon\cos^2\varphi\left(\mathbf{P}_f(z) - \frac{1}{L}\int_0^L \mathbf{P}_f(z)dz\right),$$

where ε is the corresponding component of the dielectric susceptibility. While previously (in Sec. II) the order parameter profile was governed by interplay of the extrapolation length λ and the correlation length ξ_b which diverges at T_c, it is now a length Λ^{-1} which takes over the role of ξ_b:

$$\Lambda=\left(\xi_b^{-2}+\frac{4\pi\varepsilon\cos^2\varphi}{C}\right)^{1/2}.$$

It is very important that this length Λ^{-1} remains finite at T_c and it leads to the following modification of the profile of the order parameter (1). In the case without depolarization field, the order parameter in the center of the film $\theta(z=L/2)$ differs from θ_b by exponentially small contribution only $[\propto\exp(-L/2\xi_b)]$. In the case with dipolar interaction, taking into account the order parameter, $\theta(z=L/2)$ is depressed by a correction of the order $1/L$.

Note that in the presence of a depolarization field a negative sign of the extrapolation length is not sufficient to ensure the order at the surface for temperatures exceeding T_c. The surface ordering occurs only if $|\lambda^{-1}|$ exceeds a critical value

$$\lambda_c^{-1}=-\cos\varphi\left(\frac{4\pi}{C}\right)^{1/2}\varepsilon,$$

and the critical temperature at the surface is [16]

$$\frac{T_{cs}}{T_c}-1=\frac{C}{T_c}(|\lambda^{-1}|^2-|\lambda_c^{-1}|^2).$$

Thus the stronger the dipolar forces are, the more pronounced is the reduction of the order parameter profiles at the center of the free standing films.

(3) Dielectric anisotropy may be also essential in the case of absence (or small) ferroelectric polarization. At the moment the main orientation mechanism for Sm*C* films at low temperatures [Fig. 8(a)] is not yet clear. Further experimental and theoretical investigations have to be performed.

The conclusion we draw is that a nonchiral Sm*C* structure displaying flexoelectric properties may exist in free standing films. The most distinctive feature of this structure is that the tilt plane is parallel to the direction of the electric field. A nonchiral mechanism responsible for the flexoelectricity of smectics is the surface ordering, leading to spatial variation of the tilt angle. Let us stress out that in free standing films the correlation length is relevant not only for the specific thermodynamic features of the phase transition, but also for the polarization, macroscopic structure, and orientation of the film in electric fields (for example, we have seen that if $\xi_s<p_c$, one has $P_f>P_o$, and for $\xi_s<L/2$ the ‘‘unusual’’ orientation is observed). We suggest that further experimental work on free standing smectic films over a wider range of film thickness can reveal these interesting features.

Let us also again point out that the physical mechanisms providing the polarization properties of nonchiral and chiral free standing films are very different. For nonchiral systems the polar order is in fact induced by the steric packing of anisotropic (but nonchiral) molecules, whereas in ordinary (chiral) ferroelectric liquid crystalline phases the polar order is a consequence of the molecular chirality.

ACKNOWLEDGMENTS

This work was supported in part by RFFR Grant No. 98-02-16639 and by the Russian State Program ‘‘Statistical Physics.’’ E.K. thanks Professor M. Vallade and M. Mezard for supporting his stay at the Laboratoire de Spectrometrie Physique, Joseph Fourier University, Grenoble 1, and Professor J. Lajzerowicz for fruitful discussions. The Laboratoire de Dynamique et Structure des Moleculaires is a Unite de Recherche Associee au CNRS No. 801.

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