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NON-CHIRAL FERROELECTRIC SMECTIC-C FILMS

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Free standing films of non-chiral liquid crystal compound have been studied by optical-reflectivity measurements. In the temperature range above the smectic-C – smectic-A bulk transition the existence of macroscopic ferroelectric properties and orientation of the tilt plane parallel to an electric field is demonstrated.

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Since the discovery, by Meyer et al. [1] of ferroelectric liquid crystals it is assumed usually that the phenomenon (ferroelectricity) is possible only in the chiral smectic-C^* phase (SmC^*), having the polar symmetry group C_2. In this case polarization can be written as $\mathbf{P} = P[\mathbf{n} \times \mathbf{z}]$, where $\mathbf{n}$ is director [2] and $\mathbf{z}$ is a unit vector orthogonal to smectic layers (Fig. 1). Thus the necessary conditions for $\mathbf{P} \neq 0$ are a finite tilt angle ($\theta \neq 0$) and the presence of a molecular dipole perpendicular to the long axis of molecules.

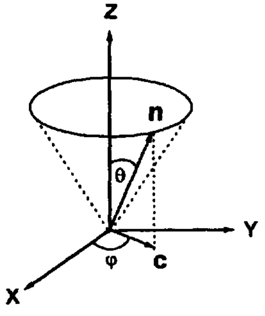

Fig.1. Schematic structure of SmC phase; $\mathbf{z}$ is the unit vector of the layer normal, $\mathbf{n}$ is the director, $\mathbf{c}$ is c-director

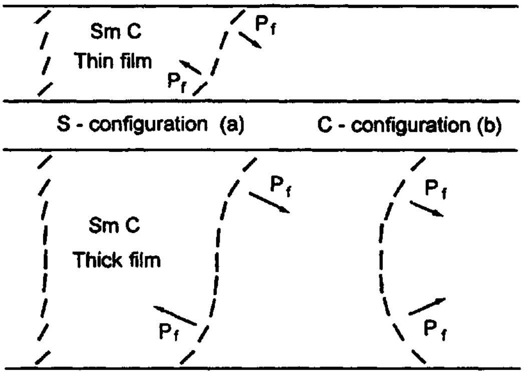

Fig.2. Orientation of the molecules in thin and thick SmC films above the bulk transition temperature. S-like and C-like configurations are shown for a thick film. $\mathbf{P}$ is ferroelectric polarization

Orientational order in tilted smectic phases (SmC^* and SmC) can be characterized by two-components order parameter $\psi = \theta\exp(i\varphi)$ or equivalently by vector $\mathbf{c}$ (so-called

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c-director [2]) determining the preferred (due to the tilt) direction in a layer. In SmC^* phase, each successive layer is rotated through a certain angle relative to the preceding one. So that a twisted structure with a certain pitch (determining by chirality) is formed. Therefore when going along the z – coordinate the director **n** (as well as **c**-director) and the polarization vector directed along the C_2 axis (i.e. orthogonal to the tilt plane), rotate.

Note however that there is no direct correspondence between chirality of molecules and the existence of macroscopic ferroelectric properties or structures they formed. It is well known for example non-chiral and non-ferroelectric smectic -A structures in chiral materials. A search of opposite examples (namely non-chiral analogous of ferroelectric liquid crystals) "is still a challenge to researchers" [3].

In this paper we demonstrate the existence of a simple non-chiral smectic – C structure possessing ferroelectric properties, e.g. having macroscopic polarization **P** which (unlike SmC^*) is parallel to the tilt plane. Let us imagine that due to certain specific conditions (see below) the module $|\mathbf{c}|$ of **c**-director is continuously varied from layer to layer, while the orientation of **c** does not rotate (since we have no chirality). In such a structure the ferroelectric polarization **P** parallel to the tilt plane should appear. Surprisingly the structure can be realized easily in freely suspended smectic films.

Freely suspended films consist of an integer number of smectic layers. The plane of the smectic layers are aligned parallel to the film surface. Usually due to surface tension and specific interactions on the surface the large effect of surface ordering are observing above the bulk SmC – SmA transition temperature T_c [4–8]. The surface tilt appears at the temperature about 20°C above the bulk transition temperature [4, 5]. It has been shown also that above T_c the SmC phase occurs in the films [4, 6]. In this temperature range the tilt is a function of the distance from the surface.

Fig.2a illustrates the essential features of freely suspended SmC films above T_c. Let us note that it is exactly the same structure as we need for our model of non-chiral ferroelectric smectics. The symmetry of the structure allows the existence of ferroelectric polarization **P** parallel (!) to the tilt plane. For S-like configuration the direction of **P** is different at the top and at the bottom of the film. Above the bulk transition temperature the tilt angle θ decays with the distance from the surface and becomes very small (nearly zero) for distances larger than bulk correlation length (at the centre of the film if film thickness is larger than this correlation length). As a result the orientations of **c**-director in the layers of the top part of the film are not coupled (or negligeably coupled) with the orientations of **c**-director for the layers of the bottom part of the film.

In the presence of an electric field **E**, two parts of the film can be oriented independently. Consequently for thick films a C-like configuration is favoured in the electric field above the bulk transition temperature. The tilt arrangement of C-like configuration is anticlinic (see also [9]), i.e. the top and the bottom of the film are tilted in opposite directions. The net polarization **P** is parallel to the tilt plane (and to the vector **c**). In thin films (with thickness less than the bulk correlation length) there is a tilt at the centre of the film (Fig. 2) and in this case C-like configuration can not be realised.

Our model was tested with optical-reflectivity measurements. The experimental techniques have been described elsewhere [9, 10]. Optical reflection from the film was measured in the "backward" geometry. The incident light was linearly polarized. An electric field from 3 to 20 V/cm was applied in the plane of the film. Our sample was the compound p-decyloxybenzoic acid-p-n-hexyloxyphenyl ester (DOBHOP). In optical measurements bulk samples showed the following phase transitions: SmC (78°C) – SmA (83°C) – nematic (89 °C) – isotropic. Free-standing films were spread across a 6 mm hole in a glass holder. The bulk SmA – nematic transition temperature and the step-by-step thinning of the film [11, 12] determine the stability limit of thick films. So, for thick films (several tens of layers) the maximum temperature of the measurements was restricted to about 83°C. X-ray diffraction measurements of θ on a bulk sample were made using a curved linear position sensitive multidetector and a curved quartz monochromator ($\lambda = 1.5406$Å).

When the light is normally incident on the film, the reflection intensity is given by [13]

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

where d is the interlayer distance ($d \simeq 3\,nm$ in the SmA phase), n is the index of refraction and N is the number of layers. In the SmC films with an in-plane anisotropy of the reflectivity index, two reflection spectra can be measured (for the polarization plane of the light oriented parallel and orthogonal to the tilt plane). The reflected intensity and the wavelength of the reflectivity minimum for thick film ($\lambda_{min} = 2nNd/k$, $k = 1, 2, 3, \ldots$) depend on the index of refraction and should differ for the two polarizations. The reflection spectra were measured for electric field oriented parallel ($\mathbf{E}_{||}$) and perpendicular ($\mathbf{E}_{\perp}$) to the light polarization plane. This method enabled us to investigate the orientation of the tilt plane and the behaviour of the average tilt angle θ.

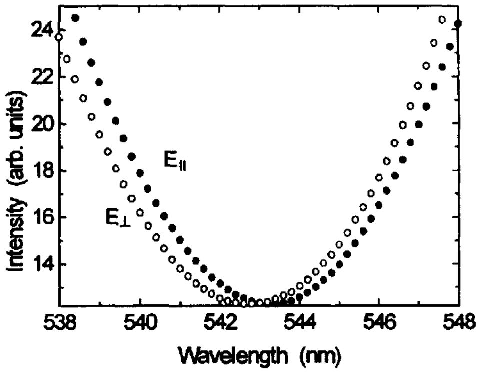

Fig.3. Field induced tilt plane orientation in a SmC film ($N \simeq 60$, $T = 81.2°$ C). The wavelengths of the reflectivity minima λ_{min} differ for two directions of the electric field $\mathbf{E}$ (parallel, $\mathbf{E}_{||}$, and perpendicular, $\mathbf{E}_{\perp}$, to the plane of polarization of light)

We found that above T_c thick films are oriented by a weak electric field ($\simeq 3\,$V/cm). Fig.3 provides evidence for the field induced orientation. The wavelengths of the reflectivity minima λ_{min} are different for the two polarizations of the light. It means the orientation of the tilt planes. When the direction of the electric field is switched ($\mathbf{E}_{||} \to \mathbf{E}_{\perp}$) the reflection spectra exchange theirs positions. Fig.4a shows the response of the optical reflection intensity when the direction of the electric field is switched.

Let us stress that the electro-optic response was observed above the bulk transition temperature T_c. Near the phase transition we observed that the orientation of the film differed from the orientation at high temperature. This behavior DOBHOP was connected with deformation of S-configuration in an electric field. Below T_c at low temperature uniformly oriented films could not be obtained in a weak electric field for the DOBHOP molecules with a small dipole. Fig.4b shows typical results (three runs) at low temperatures. The time dependence of the reflected intensity is related to a change with time of

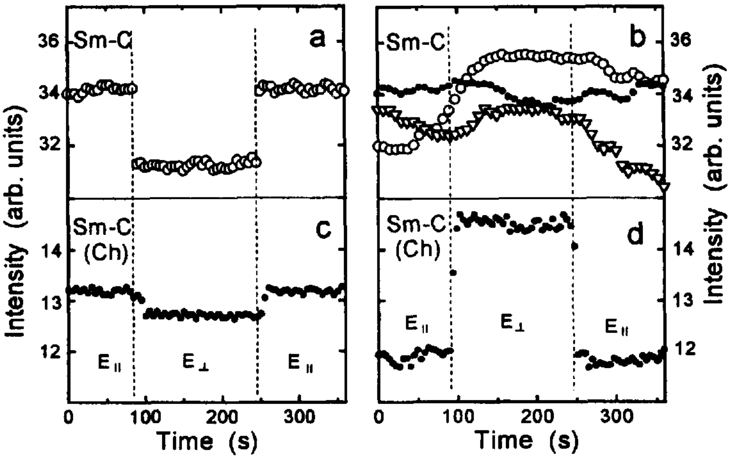

Fig.4. Optical reflectivity intensities for non-chiral smectic film (DOBHOP) at the temperature above ((a) , 80 °C) and below ((b) , 77 °C) the bulk SmC - SmA transition temperature ($\lambda_{min} - \lambda \simeq 20\,\mathrm{nm}$). Smectic liquid crystal DOBHOP with chiral component above ((c) , 78.3 °C) and below ((d) , 72.3 °C) the bulk transition temperature ($N \simeq 60$). Electric field is applied parallel ($\mathbf{E}_{||}$) and perpendicular ($\mathbf{E}_{\perp}$) to the light polarization plane

the tilt plane direction. The orientation in a weak field was not observed for thin films ($N < 20$) both below and above T_c. Such kind of behaviour correlates with our model.

Consider now results for thick films above the bulk transition temperature (Fig. 3). The wavelength of reflectivity minimum λ_{min} for the field $\mathbf{E}_{||}$ is larger than λ_{min} for $\mathbf{E}_{\perp}$. The refraction index for the polarization of the light along the tilt plane is larger than the ordinary refraction index n_o (i.e. perpendicular to the tilt plane). From this fact it follows (see (1), $\lambda_{min} = 2nNd$) that the orientation of the tilt plane and c-director are parallel to the electric field.

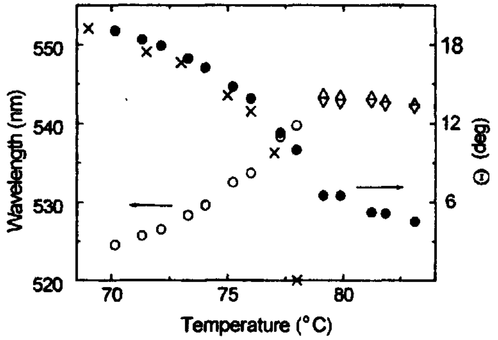

Fig.5. Temperature dependence of the reflectivity minimum λ_{min} in the electric field applied parallel ($\mathbf{E}_{||}$, upright triangles) and perpendicular ($\mathbf{E}_{\perp}$, inverted triangles) to the direction of the light polarization ($N \simeq 60$). Open circles show averaged data for reflectivity minimum at the temperature below the bulk transition. Temperature dependence of θ for the film (closed circles, optical reflectivity data) and for the bulk sample (x)

Fig.5 shows the temperature dependence of λ_{min}. Below T_c the average data for the two light polarizations are shown. To find the tilt angle from the optical spectra one should calculate θ from the positions of the reflectivity minima λ_{min} using Eq. (1) and the known relation [13] between the reflectivity indices and the tilt angle (details are described in [10]). Fig.5 shows also the temperature dependence of θ taken from our

X-ray measurements on a bulk sample. Below T_c the magnitude of θ in the bulk sample is slightly smaller, it is indicated also the additional surface ordering in the film.

For thick films, non zero tilt first appears at the surface for temperatures about 20 °C above the bulk transition temperature [4, 5]. When the temperature is only few degrees above T_c the surface layers exhibit already a tilt angle of the order of $20 - 30°$ [4, 5]. In the temperature range (79-83 °C) the average tilt angle is about $4 - 6$ ° (see Fig. 5). It is clear that the tilt angle has to be very small (practically zero) at the centre of the film and so, the C-like configuration takes place in the electric field.

Let us estimate now the magnitude of the ferroelectric polarization. Note that the change of the tilt angle in our model implies bending of the director **n**. It is well known (see e.g. [2, 14]) that in nematics splay and bend deformations of the director field induce a polarization, so-called flexoelectric effect. In ideal bulk, smectics deformations leading to the flexoelectric polarizations are strongly suppressed by layer structures. However it is not the case in our model where the tilt angle is not a constant. The dependence of θ on the distance from surface even in the frame work of the Landau theory may be quite sophisticated [15, 16] Moreover the spatial variation of θ and of the polarization may result in a space charge and polarization contribution to the elastic constants [1, 17]. However in any case the relevant space scale is the bulk correlation length and the integrated polarization density of the film depends only on the difference between the surface tilt angle θ_s and the tilt angle in the centre of the film θ_c. Using the natural estimation for the flexoelectric coefficients $e \simeq 10^{-11}$,C/cm [2], $\theta_s = 20°$, and $\theta_c = 0$, we get using the standard expression for the flexoelectric polarization [2, 14] $P \simeq 0.4 \cdot 10^{-4}\,\mathrm{C/m^2}$ for $N = 60$. So this polarization P found for non-chiral free standing SmC films is fairly large (of the order of spontaneous polarization for chiral smectics).

Thus in our model the ferroelectric polarization is parallel to the tilt plane, whereas for chiral smectics it is perpendicular to this plane. To study the competition of both mechanisms, we investigated the mixture of DOBHOP with chiral component (Looch 15, NIOPIC, 10%). Below T_c, in contrast to pure DOBHOP, free standing films of the mixture are oriented by a weak field electric field (Fig.4d) and as it takes place for classical chiral ferroelectric the tilt plane is oriented perpendicularly to the electric field. However above T_c the tilt plane is oriented parallel to **E** (Fig.4c). It confirms that for small tilt (remind that $T > T_c$) our mechanism of non-chiral polarization dominates.

The main conclusion we draw is that under appropriate conditions a non-chiral SmC structure displaying ferroelectric properties may exist in free standing films. The most distinctive feature of this structure is that the polarization is parallel to the tilt plane. The physical mechanism responsible for ferroelectricity of non-chiral smectics is the surface ordering and phase transition leading to spatial variation of the tilt angle.

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