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Dielectric and optical rotatory power investigations of an antiferroelectric liquid crystal 12OF1M7 in a homeotropic cell: implications for models of the structure of ferrielectric phases

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The antiferroelectric liquid crystal (AFLC) under investigation possesses different helical smectic phases. Measurements of the optical rotatory power (ORP) of these phases have elucidated the quality of this method for finding the phase transitions between several phases and for investigating their helical structure. The optical rotatory power as a function of temperature for seven wavelengths of light in the range 441 to 665 nm was measured for different phases of the AFLC material investigated, (*R*)-1-methylheptyl 4-(4′-*n*-dodecyloxybiphenyl-4-yl-carbonyloxy)-3-fluorobenzoate, with acronym 12OF1M7. The values of the pitch and the optical anisotropy in the plane of the smectic layers for the FiLC (SmC$^*_{\rm FI3}$) phase and SmC$^*_{\rm A}$ phase have been calculated from the ORP data. The results of the ORP rule out the simple clock model for describing the structure of the SmC$^*_{\gamma}$ (SmC$^*_{\rm FI1}$) and AF (SmC$^*_{\rm FI2}$) phases. The results for these phases can be explained either in terms of the modified Ising model or the highly distorted clock model. The ORP measurements establish the existence of SmC$^*_{\rm FI3}$ found already from dielectric, polarization and polarized IR spectroscopy.

1. Introduction

Several different theoretical approaches have been advanced for explaining a variety of the chiral phases between paraelectric smectic A (SmA*) and antiferroelectric smectic C$_{\rm A}$ (SmC$^*_{\rm A}$) and these postulates are based mostly on the Landau model [1–4] or on the one-dimensional Ising model [5] and the ANNNI (axial next-nearest neighbour Ising) model [6, 7].

All these models consider a molecular tilt angle θ_j with respect to the smectic layer normal to be constant in all layers at a given temperature. The most important point at issue for these models is the kind of layer-to-layer progression of the azimuthal molecular alignment ϕ_j in the ferrielectric SmC$^*_{\gamma}$ (SmC$^*_{\rm FI1}$) and antiferroelectric AF (SmC$^*_{\rm FI2}$) phases. This progression is clear for ferroelectric SmC* ($\delta\phi=\phi_{j+1}-\phi_j\approx 0$) and for antiferroelectric SmC$^*_{\rm A}$ ($\delta\phi\approx 180°$) phases, but is still being debated for SmC$^*_{\gamma}$ and AF phases. The resonant X-ray technique has recently confirmed [8, 9] the existence of the three- and four-layer superlattices in the SmC$^*_{\gamma}$ and AF phases, respectively, that were postulated by existing models. These X-ray results were explained in terms of a uniaxial clock model [2] because the planar Ising model [5] (where the plane of the azimuthal molecular alignment is the same for all of the smectic layers in a unit cell) is unable to describe most of them correctly. On the other hand, some of the optical results [10, 11] cannot be explained in terms of the uniaxial clock model. Now it seems that only the highly biaxial models such as a modified Ising model [10] or the distorted clock model [11, 12] may explain most of the recently obtained experimental results.

In the present work, the light transmitted through a homeotropically aligning LC cell placed between crossed and parallel polarizers was measured, and the optical rotatory power calculated from these results. The transmission as a function of temperature was measured in the different smectic phases of the AFLC material at several wavelengths of light. Dielectric spectroscopy and polarizing optical microscopy were also carried out to complement the optical transmission results. The helical pitch of the structures and the optical anisotropy in

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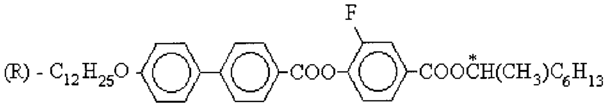
the plane of the smectic layers were obtained from the optical rotatory power for some of the phases of the AFLC material. The various models for the structure of the ferrielectric phases were examined in the light of these experimental results.

In the previous work reported on this material and reviewed recently [13], investigations were carried out on homogeneously planar aligned samples, and the work was directed towards investigating the phase transition temperatures and establishing that FiLC (SmC^*_{FI3}) was distinct from the SmC* phase. The results for a homeotropic cell are not affected by the surfaces as in a planar cell and these should be comparable with those obtained for free-standing films.

2. Experimental

The AFLC material used in our experiments was synthesized at Hull and is (*R*)-1-methylheptyl 4-(4′-*n*-dodecyloxybiphenyl-4-yl-carbonyloxy)-3-fluorobenzoate, with the acronym 12OF1M7. The molecular structure is:



The following phase transition sequence has been found for this material under cooling conditions on homogeneously aligned samples, using dielectric and pyroelectric measurements [13, 14]:

$$\mathrm{SmC}^*_{\mathrm{A}}\ 78\ \mathrm{SmC}^*_{\gamma}\ 81\ \mathrm{AF}\ 84.5\ \mathrm{FiLC}\ 92\ \mathrm{SmC}^*\ 93\ \mathrm{SmC}^*_{\alpha}\ 94.4\ \mathrm{SmA}^*\ 106\ \mathrm{I}\ (^\circ\mathrm{C}).$$

In a previous paper [15] we reported that in an optically pure sample of this material, the SmC^*_{α} phase exists in the temperature range 94.4–93°C. The FiLC phase exists in planar samples over a wide range of temperature and characteristics different from those of SmC*. The temperature of the phase transition from SmC* to FiLC obtained by the pyroelectric method (92°C) differs from that (90°C) found using conoscopy and spontaneous polarization measurements [16]. Our results from the ORP measurements presented in this paper show that the temperature of 90°C is probably the more correct one.

It may be stated here that DSC determines only some transitions, especially SmC*–SmC^*_{α}, SmC^*_{α}–SmC^*_{γ}, SmC^*_{γ}–SmC^*_{A}; and that the transition temperatures normally depart from those found using other techniques, since the cooling rate ($\sim 10^\circ C\ min^{-1}$) is much greater than that used in most other experiments, on account of the large temperature hysteresis between the phase transitions and the long relaxation times [13].

In the following text, SmC^*_{γ}, AF and FiLC phases are denoted by SmC^*_{FI1}, SmC^*_{FI2} and SmC^*_{FI3}, respectively, in keeping with the notations adopted recently.

The cell of 15 μm sample thickness, used for the dielectric and optical measurements, consisted of two glass plates with indium tin oxide (ITO) layers as electrodes and thin-film strips of Mylar as spacers. Homeotropic orientating films of a carboxylatochromium complex (chromolane) were coated onto the ITO electrodes. These were cured for 30 min at 120°C and then used without rubbing. The cell was heated and filled with the antiferroelectric compound in its isotropic phase and cooled slowly to give the SmA* phase. The textures of the different smectic phases were observed with a polarizing microscope. Dielectric measurements in the frequency range 100 Hz to 10 MHz were made using the impedance analyser HP-4192A. The temperature measurements were carried out during continuous cooling at a rate of $0.1^\circ C\ min^{-1}$.

To calculate a tilt angle θ in the SmC^*_{α}, SmC* and SmC^*_{FI3} phases from the maximum value of the dielectric losses ε''_{max} measured on a homeotropically aligned sample, a dielectric method [17] was used. According to this method the value of the tilt angle $\theta(T)$ is calculated from the equation

$$\theta(T) = \cos^{-1}\left[\frac{\varepsilon''_{max}(T)}{\varepsilon''_{ext}(T)}\right]^{1/2} \tag{1}$$

where $\varepsilon''_{max}(T)$ is the measured maximal value of the dielectric loss at the temperature T and $\varepsilon''_{ext}(T)$ is the maximal value of the dielectric loss extrapolated from the SmA* phase to the same temperature.

The optical rotatory power (ORP) was calculated from the ratio of the light transmitted through the homeotropic liquid crystal cell when the polarizers were crossed to that when they were parallel to each other. For the case of a pure optical rotation, i.e. the light transmitted through the cell remains linearly polarized, the ratio of these transmissions R_T is given by a simple expression $R_T(\psi) = \tan^2 \psi$. Here ψ is a rotation angle of the light transmitted through the cell with respect to the polarizer direction. ORP (Ψ) is expressed in terms of the optical rotation per unit length ψ/d, where d is a cell thickness, and can be calculated from the transmission ratio using the expression

$$\Psi = \frac{\tan^{-1}[R_T(\psi)]^{1/2}}{d}. \tag{2}$$

This method gives only the absolute value of the ORP. The sign of the ORP for a given wavelength of light in several smectic phases was determined by rotating the analyser until the minimum transmission was achieved. Turning of the analyser clockwise (with respect to the reference position where it is crossed with the polarizer) is considered as indicating a positive ORP and anticlockwise as negative.

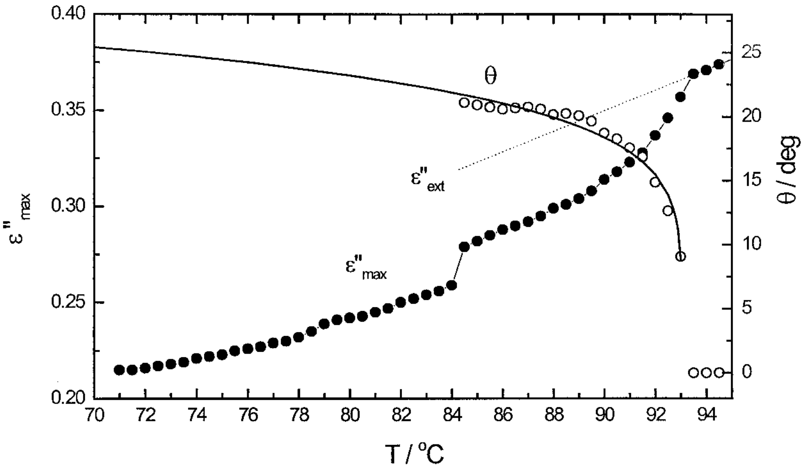


Figure 1. Left scale: dependence on temperature of the maximum dielectric loss $\varepsilon''_{\mathrm{max}}$ measured on a homeotropic sample in several smectic phases and the maximal dielectric loss $\varepsilon''_{\mathrm{ext}}$ extrapolated from the SmA* phase (dotted line). Right scale: the tilt angle θ in the SmC* and $\mathrm{SmC}^*_{\mathrm{FI3}}$ phases calculated using equation (1) from dielectric data and the best fit curve (solid line) obtained with the power law $\theta(T) \approx 15.4 \times (T_c - T)^{0.27}$.

3. Results and discussion

In figure 1 the temperature dependence of the maximal dielectric losses $\varepsilon''_{\mathrm{max}}(T)$ measured in the SmA* and in the tilted smectic phases of 12OF1M7, as well as the $\varepsilon''_{\mathrm{ext}}(T)$ obtained by the extrapolation of $\varepsilon''_{\mathrm{max}}(T)$ from the SmA* phase, are shown. In the same figure, the values of the tilt angle $\theta(T)$ in the SmC* and $\mathrm{SmC}^*_{\mathrm{FI3}}$ phases, calculated using equation (1), are presented. It is clear that this method cannot be applied to ferri- and antiferro-electric phases for calculation of their tilt angles because it gives a large stepwise increase of the tilt angle at the transition from $\mathrm{SmC}^*_{\mathrm{FI3}}$ to $\mathrm{SmC}^*_{\mathrm{FI2}}$. This behaviour was not confirmed by an optical method [17] for the tilt angle measurement, and our results for the tilt angle are about 2° lower than those obtained by the optical method in Ref. [18] for this AFLC. This discrepancy is explained by the fact that the dielectric method can be considered as the zero-field method applied to the undisturbed helical structure, in contrast to the optical method which uses a high field for helix unwinding. The temperature dependence of $\theta(T)$ in the SmC* (from 93 to 90°C) is found to obey the power law $\theta(T) \approx 15.4 \times (T_c - T)^{\beta}$, presented in figure 1 by a solid line, with the transition temperature $T_c = 93.03$°C and a critical exponent $\beta = 0.27$. This critical exponent is surprisingly low for the ferroelectric phase. At the transition point from SmC* to $\mathrm{SmC}^*_{\mathrm{FI3}}$, the tilt angle gives a small stepwise increase and in the $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase its temperature dependence is characterized by a critical exponent $\beta = 0.07$. This also confirms that the $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase is different from the SmC* phase. The discontinuity in ε'' at 90°C, and therefore in the tilt angle, is really very small. It is not demonstrative of a phase transition when considered on its own; however, when combined with our earlier results, obtained using dielectric spectroscopy, pyroelectric and FTIR techniques, this small discontinuity in ε'' gives additional evidence that the transition from SmC* to $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase exists at 90°C. Recently, through FTIR dichroic measurements [19] for this phase, it has been established that trends in the molecular tilt angle with bias voltage follow a behaviour different from that for the SmC* phase.

The ORP calculated from the light transmission using equation (2) and shown in figure 2 demonstate a characteristic change in each phase. The sign of ORP in the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases is opposite for all wavelengths. This means that the handedness of the chiral structure is changed during the transition from the $\mathrm{SmC}^*_{\mathrm{FI2}}$ to $\mathrm{SmC}^*_{\mathrm{FI1}}$ phase. The sign of ORP in the $\mathrm{SmC}^*_{\mathrm{A}}$ phase is the same for the long wavelengths (485, 494 and 588 nm) but is opposite for the short wavelength (441 nm). According to equation (3), this implies that the wavelength of the selective reflection is located between 441 and 485 nm. This fact is confirmed by visual observation (bright reflection of blue–green light from the sample).

The ORP in a cholesteric LC is given as [20]

$$\Psi \equiv \frac{\psi}{d} = \frac{2\pi}{8P}\left(\frac{n_e^2 - n_o^2}{n_e^2 + n_o^2}\right)^2 \frac{1}{\lambda'^2(1-\lambda'^2)} \tag{3}$$

$$n = \left(\frac{n_e^2 + n_o^2}{2}\right)^{1/2} \tag{4}$$

$$\lambda' = \frac{\lambda}{nP} \tag{5}$$

where P is the helical pitch, λ is the wavelength in vacuo, and n_e and n_o are the refractive indices parallel and perpendicular to the director, respectively. This expression can be extended to the tilted smectic phases using the relations [10]

$$n_e^2 = \frac{\varepsilon_{10}\varepsilon_{30}}{\varepsilon_{10}\cos^2\theta + \varepsilon_{30}\sin^2\theta} \tag{6}$$

$$n_o = (\varepsilon_{20})^{1/2} \tag{7}$$

where ε_{10}, ε_{20} and ε_{30} are the principal values of the dielectric tensor for the chiral tilted smectics at optical

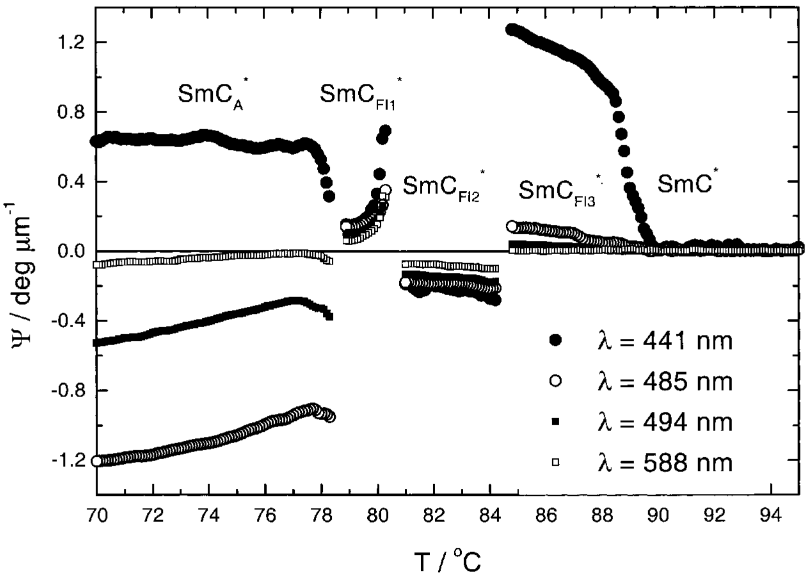


Figure 2. Temperature dependences of ORP for 12OF1M7 measured in the homeotropic cell on cooling for various wavelengths of light.

wavelengths, and θ is a tilt angle of the director with respect to the smectic layer normal.

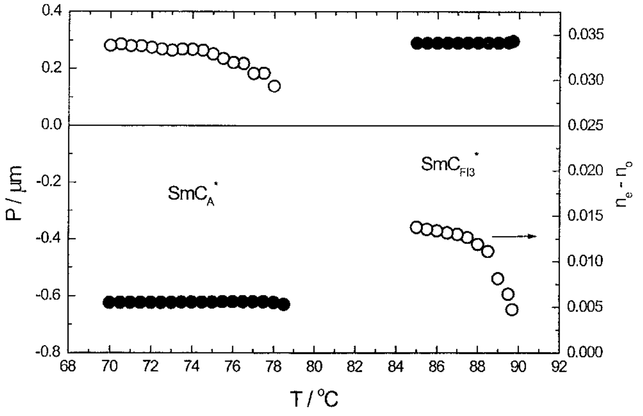


Figure 3. The values of the pitch P of the helical structures (left scale) and the optical anisotropy in the plane of the smectic layers (right scale) in the SmC^*_{FI3} and SmC^*_A phases of 12OF1M7 obtained by fitting the ORP data with the use of equation (3). Open circles refer to the data on refractive index anisotropy, closed circles refer to the pitch.

The temperature dependences of the ORP obtained at eight fixed wavelengths of light, 441, 485, 495, 525, 588, 619 and 665 nm (only four of them are presented in figure 2) can be transformed into the wavelength dependences of the ORP at fixed temperatures. These dispersion dependences of ORP were fitted using equation (3) to obtain the temperature dependences of the optical anisotropy $n_e - n_o$ and the parameter nP. The latter is equal to the wavelength of the selective reflection (SR) in several smectic phases. In this fitting procedure we neglect the dispersion of the refractive indices since its influence on the ORP dispersion is much smaller than that of denominator $\lambda'^2\,(1-\lambda'^2)$. The observed colours of the selective reflected light for the SmC^*_{FI3} and SmC^*_A phases allow for a check on the calculated SR wavelength values. The pitch value can be estimated from the SR wavelength by assuming that the wavelength of the SR light is related to the full pitch in the SmC^*_{FI3} phase and to the half pitch in the SmC^*_A phase, and that the mean refractive index n is about 1.5. A fitting of the ORP experimental data gave very reasonable values for the SR wavelength and the optical anisotropy in the SmC^*_A phase and in the SmC^*_{FI3} phase (figure 3). In the SmC* phase, the ORP is very low and this implies that the helical pitch in this phase is rather low. In the SmC^*_{FI3} phase, the pitch is about 0.29 μm; the corresponding colour of the selective reflected light is violet–blue. In the SmC^*_A phase the SR light is blue–green, and the corresponding pitch is -0.62 μm. In the SmC^*_A phase, the sense of the helix is left-handed, opposite to that observed for the SmC^*_{FI3} phase. The reversal of the helix sense occurs during the phase transition from SmC^*_{FI2} to SmC^*_{FI1}. This fact allows the two phases to be distinguished. It may be emphasized that pitch inversion inside a given phase usually occurs in liquid crystalline materials which are mixtures of LC compounds with opposite handedness. This can mean that the temperature dependences of the pitches for the left-handed and the right-handed compounds are different. In this case the pitch goes to infinity at the inversion temperature and decreases when the temperature moves away from the inversion temperature. This results in the temperature dependence of the ORP being symmetric with respect to the inversion temperature; that is, the ORP will have approximately the same absolute values but the opposite signs below and above the inversion temperature. Our ORP results do not demonstrate this kind of behaviour inside any phase of the investigated compound. The inversion in the sign of the ORP at the transition from $\mathrm{SmC}^*_{\mathrm{FI2}}$ to $\mathrm{SmC}^*_{\mathrm{FI3}}$ is connected with an increase in the pitch value in the $\mathrm{SmC}^*_{\mathrm{FI2}}$ phase and not with pitch inversion. In our case we have an optically pure compound. The existence of the phases SmC^*_{α}, $\mathrm{SmC}^*_{\mathrm{FI1}}$ and $\mathrm{SmC}^*_{\mathrm{FI2}}$ confirms its optical purity.

In the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases, no reasonable results for the pitch and the optical anisotropy could be obtained using the fitting procedure with the aid of the de Vries expression (3). It seems that in these phases the pitch is too large and the condition of pure optical rotation [19] $\lambda > P(n_e - n_o)$ is not fulfilled.

An ORP spectrum at 85.5°C in the $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase was simulated numerically using Berreman's matrix method [21]. The simulated curve (solid line) and the experimental points are presented in figure 4, as well as the best fit curve (dotted line) obtained using the de Vries expression (3). The absolute values are taken for the sake of using the logarithmic scale to present the ORP data in the figure. In the same figure the simulated ellipticity of the transmitted light versus wavelength is shown. The ellipticity is defined here as the ratio of the shortest axis of the elliptically polarized transmitted light to the largest axis. One can see that the transmitted light remains linearly polarized for all wavelengths except a very narrow range around the wavelength of selective reflection. This fact confirms the validity of our procedure used for the ORP measurements. The parameters used for this simulation were: the sample thickness $d = 15\,\mu\mathrm{m}$; the layer spacing $h = 3\,\mathrm{nm}$; the indices of refraction $n_3 = 1.639$ along the director, $n_2 = 1.497$ perpendicular to the tilt plane and $n_1 = 1.495$ along the third principal axis; the tilt angle of the director $\theta = 19.5°$; the pitch of the helix structure $P = 0.28\,\mu\mathrm{m}$.

In both the Ising [5, 10] and the clock [2, 12] models the structures of the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases involve unit cells consisting of four and three smectic layers, respectively. In the Ising model the azimuthal distribution of the director in the smectic layers forming the unit cell leads to the optical anisotropy of the unit cell in a plane parallel to the smectic layers. This optical anisotropy in the case of a simple clock model [2] is absent due to symmetry in the azimuthal distribution of the director in the unit cell. The simple clock model for the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases implies very short pitch values P_S with periods of four and three layers; therefore in this case a very small ORP of the order P_S^3/λ^4 should be produced for $P_S \sim 12$–$16\,\mathrm{nm}$ and $\lambda \sim 500\,\mathrm{nm}$. When in the simple clock model the long pitch chirality is superimposed, then the structure becomes slightly incommensurate because an additional long pitch helix slightly increases the increment of the azimuthal angle between the adjacent smectic layers in a unit cell. But even in this case, a very small ORP is expected because of the evanescent optical anisotropy of the unit cell in the plane parallel to the smectic layers. This has been confirmed by using the 4×4 matrix method [21]. The calculations of the ORP in the $\mathrm{SmC}^*_{\mathrm{FI2}}$ phase for the structures proposed by the Ising [10], the distorted clock [12] and the simple clock [2] models are presented in figure 5. The parameters used for these simulations were the same as for $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase, except for the tilt angle of the director and the pitch of helix structure; these were $\theta = 22.5°$ and $P = 2.15\,\mu\mathrm{m}$, respectively. The distorted clock model with a symmetric sequence of azimuthal angles $\varphi_j = (\pi/2)j - \delta/2 + (-1)^j\delta/2$, where $0 \leqslant j \leqslant 3$, has the following sequence of azimuthal angles: -0, $\pi/2 - \delta$, π, $3\pi/2 - \delta$. The simple Ising and clock models are the particular cases of the distorted clock model with $\delta = \pi/2$ and $\delta = 0$, respectively. If a long pitch chirality is added, then the azimuthal angle progression becomes: 0, $\pi/2 - \delta + \varphi_{\mathrm{FI}}$, $\pi + 2\varphi_{\mathrm{FI}}$, $3\pi/2 - \delta + 3\varphi_{\mathrm{FI}}$. Here $\varphi_{\mathrm{FI}} = 2\pi h/P$ is the rotation angle between adjacent layers and h is the thickness of the smectic layer. This model, named the 'highly biaxial model', was used for describing the ellipsometric data obtained in the $\mathrm{SmC}^*_{\mathrm{FI1}}$ and $\mathrm{SmC}^*_{\mathrm{FI2}}$ phases of free-standing films [11]. It was shown

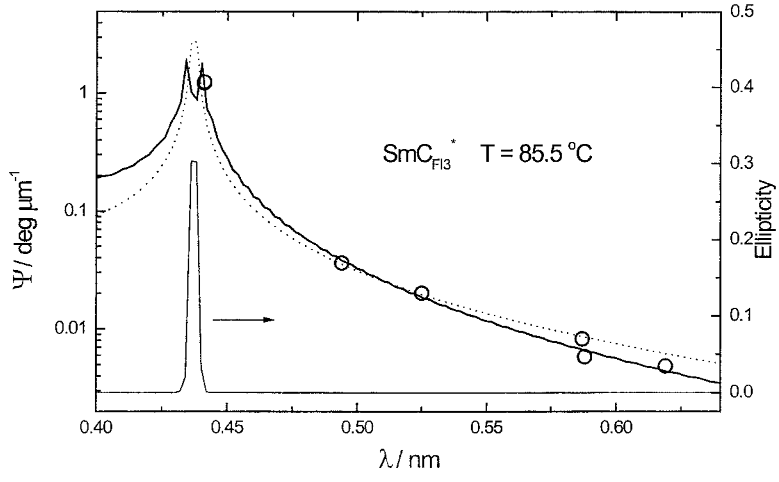


Figure 4. Left scale: ORP data of 12OF1M7 in the $\mathrm{SmC}^*_{\mathrm{FI3}}$ phase at 85.5°C for several wavelengths of light, the best fit curve (dotted line) of these data using equation (3) and the simulated ORP spectra (solid line) calculated with the aid of Berreman's matrix method. Right scale: the simulated ellipticity spectra of the light transmitted through the sample; the parameters used for simulation are $d = 15\,\mu\mathrm{m}$, $h = 3\,\mathrm{nm}$, $n_3 = 1.639$, $n_2 = 1.497$, $n_1 = 1.495$, $\theta = 19.5°$, $P = 0.28\,\mu\mathrm{m}$.

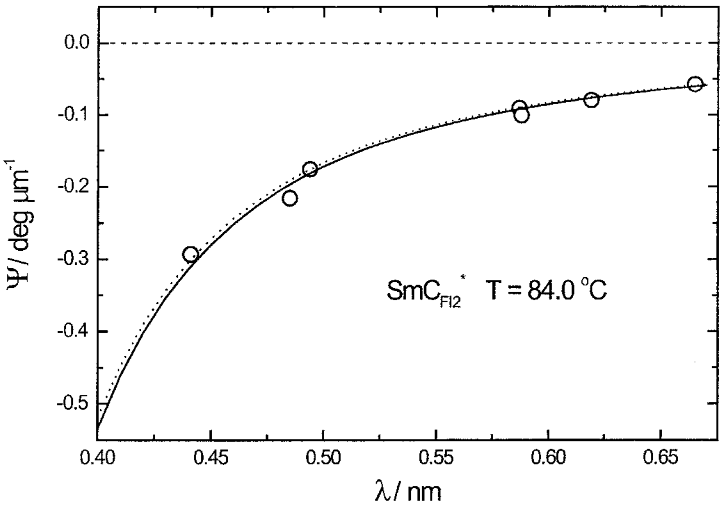


Figure 5. Experimental data at 84.0°C and simulated ORP spectra in the $\mathrm{SmC}^*_{\mathrm{FI2}}$ phase of 12OF1M7 for the Ising (solid curve, $\delta = 90°$), distorted clock (dotted curve, $\delta = 80°$) and simple clock (dashed line, $\delta = 0°$) models; $\theta = 22.5°$, $P = 2.15$ μm.

that this structure is also able to explain the resonant X-ray diffraction results. The simulation of the ORP in this case is presented in figure 5 (dotted curve) for the distortion parameter $\delta = 80°$. When the parameter δ becomes less than 70° the ORP value decreases rapidly and in the case of the simple clock model ($\delta = 0°$), the ORP (figure 5, dashed line) is about 10^{-6} of the ORP value for the Ising model.

Now it seems that the modified Ising model [10] or the distorted clock model [11, 12], i.e. the highly biaxial models, can correctly explain the experimental optical results (both the ORP and the ellipsometric data [11]) and the results of the resonant X-ray diffraction [8, 9] in the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases. To determine which of these two models is actually valid, it is necessary to make more accurate experimental investigations of both the structural and optical properties of the $\mathrm{SmC}^*_{\mathrm{FI2}}$ and $\mathrm{SmC}^*_{\mathrm{FI1}}$ phases in different AFLC compounds. The FiLC phase or $\mathrm{SmC}^*_{\mathrm{FI3}}$ is established as distinct from the SmC* phase, the former having the characteristics of a ferrielectric phase.

It is concluded that in agreement with our recent work [22] on 11OTBBB1M7, a homologue of the AFLC compound (10OTBBB1M7) reported by Mach *et al.* [9], the simple clock model is ruled out as the structure of $\mathrm{SmC}^*_{\mathrm{FI2}}$ for the material 12OF1M7. The highly distorted clock model, with $\delta \sim 80°$, or a distortion angle of 10°, can however explain these experimental results.

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