Optical rotation and structure of ferrielectric smectic phases

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We analyze the measured optical rotation in three- and four-layer smectic ferrielectric phases within the matrix approach to the light propagation. We show that ''perfect'' three- and four-layer structures with 120° and 90° phase rotation of the director in neighboring layers give negligible optical rotation of polarized light travelling along the normal to the smectic layers. Significant optical rotation is obtained in deformed three- and four-layer smectic phases. The analysis of the measured optical rotatory power clearly shows that three-layer ferrielectric phases of [4-(1-methylheptyloxycarbonylphenyl)-octylbiphenyl-4-carboxylate] and 4-[(4-{[1(*)-methyl]heptycarboxy}phenyl)carboxy]phenyl-4′-decyloxy-1-benzencarbatioate (10OTBBB1M7) are deformed with the deformation angle of 35°–45°. The deformation angle in the four-layer smectic phase of 10OTBBB1M7 is 70°–90°. This is in reasonable agreement with other experiments and suggests the validity of the ''deformed clock model.''

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I. INTRODUCTION

The resonant x-ray experiment of Mach *et al.* [1] has shown that tilted phases of chiral smectics are preferentially organized in a clocklike manner, where the molecular direction precesses along the normal to the smectic layers, as we move from one layer to another. In the ferroelectric smectic-C^* phase this precession is slow on the molecular scale and the angle between the in-plane projections of the director ξ_i and ξ_{i+1} in the neighboring smectic layers denoted by i and $i+1$ is of the order of 1°. As a result, a helical superstructure is formed with a helical period p in the range of a micrometer.

In the smectic-C^*_α phase, the angle between the in-plane projections ξ_i and ξ_{i+1} is of the order of 60°, which results in a short-pitch structure with a incommensurate helical period of the order of 6–7 smectic layers, as shown in Fig. 1. By decreasing the temperature one usually enters the two ferrielectric phases. The ferrielectric smectic-C^*_{FI2} (i.e., smectic-$C^*_{1/4}$) is a four-layer structure (Fig. 1), where the angle between the in-plane projections of the director ξ_i and ξ_{i+1} in the neighboring smectic layers changes by an angle close to 90° according to the first resonant x-ray experiments of Mach *et al.* [1]. The ferrielectric smectic-C^*_{FI1} (smectic-$C^*_{1/3}$ or smectic-C^*_γ) is a three-layer unit cell structure (Fig. 1), where the angle between the in-plane projections of the director ξ_i and ξ_{i+1} in the neighboring smectic layers changes [1] by an angle close to 120°. In the antiferroelectric smectic-C^*_A phase this angle is close to 180° and we obtain a structure with a unit cell of two smectic layers.

Whereas the x-ray experiment gives an elegant and unified classification of structures of tilted smectics that are consistent with the ''clock'' model [2], several salient experimental observations remain unexplained. In particular, rather large magnitudes of the optical rotatory power (ORP), measured in the two ferrielectric phases [3–5,10], are several orders of magnitude larger than what one would expect for ''perfect'' three- and four-layer structures. In view of this experimental fact, a ''deformed clock'' model has been proposed [5,6], which is a ''mixture'' of *XY* [7] and one-dimensional (1D) Ising theoretical models [2]. The results of recent ellipsometric experiment on freely suspended ferrielectric films [8] strongly support the deformed clock model and have been recently also supported by higher resolution resonant x-ray experiments [9].

The motivation for this paper is an apparent lack of complete and accurate analysis of high resolution optical rotatory power experiments in intermediate smectic phases. So far, the analysis of the measured temperature dependence of ORP was either based on the de Vries approximation for the antiferroelectric and ferroelectric phase of 4-[(4-{[1(*)-methyl]heptycarboxy}phenyl)carboxy]phenyl-4′-decyloxy-1-

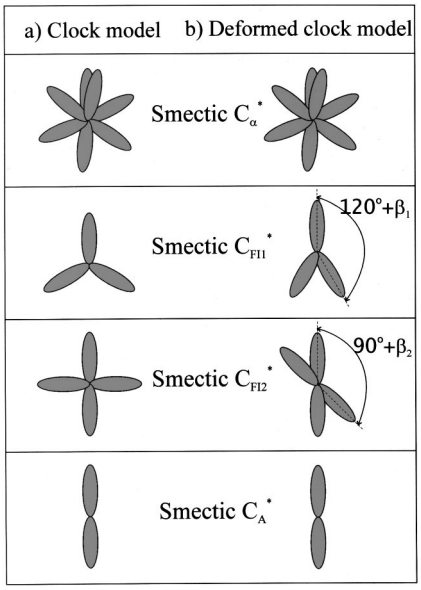

FIG. 1. (a) The set of tilted phases of polar smectics, as reproduced within the ''clock'' model of Čepič and Žekš. (b) The proposed structures, based on experimental evidence from ellipsometry and ORP measurements.

benzencarbatioate (10OTBBB1M7) and 11OTBBB1M7 [10], or concentrated on the analysis of ORP in the four-layer ferrielectric phase using 4×4 matrix analysis [5] at a given temperature. To our knowledge, a complete and detailed analysis of the measured temperature dependence of ORP, helical period, and their relation to the structure of ferrielectric phase over a large temperature interval has not yet been performed. We therefore concentrate our analysis on the optical rotation of these phases, because it is without doubt a very sensitive function of the structure of their unit cell.

The theory of optical rotation in chiral birefringent media is one of the most intensively studied problems in liquid crystals [11]. Most of the theoretical considerations are based on the solutions of Maxwell equations for the propagation of light along the helical axis, using macroscopic forms of dielectric tensor. Among them, the de Vries theory was successfully applied to the calculation of the optical rotation in ferroelectric liquid crystals [12]. Some studies also connect the microscopic picture of molecular ordering with the macroscopic dielectric tensor, using quantum statistical techniques [13]. In this paper we use two different matrix formalisms for the calculation of the ORP: the Jones matrix formalism (see, for example, Ref. [11]) and the 4×4 transfer-matrix method developed by Yeh [14]. Within these two approaches, one divides a layer of a liquid crystal into N thin layers, which is in our case a single smectic layer. Optical properties of the liquid crystal as a whole are then calculated by transfer-matrix multiplication, as described elsewhere. We present quantitative comparison between the transfer-matrix approach, the de Vries theory, and the results of ferrielectric phases. We show that Yeh's 4×4 matrix formalism exactly reproduces the analytical de Vries expression for the ORP in ferroelectric smectic-C^* phase. We also show that various approximations of the de Vries theory in antiferroelectric and ferrielectric phases overestimate ORP in these phases. We also calculate the ORP as a function of the angle between the in-plane projections of the director ξ_i and ξ_{i+1} in the neighboring smectic layers. The comparison of the theory and experiment undoubtedly shows that the unit cells of three- and four-layer ferrielectric structures must be distorted, which is in agreement with the results of ellipsometric measurements in freely suspended ferrielectric films [8] and supports previous analysis of ORP [5,6,10].

II. THEORY

The optical properties of ferroelectric chiral smectic liquid crystals for light propagation along the helical axis are very similar to the optical properties of cholesterics, which has been quantitatively proven in high resolution ORP measurements [12]. It has been shown that the continuum theory of de Vries can successfully be applied to the analysis of ORP in the chiral ferroelectric smectic-C^* phase, and only qualitatively to the optical properties of the antiferroelectric smectic-C_A^* phase [10]. Although the generalization of the analysis of the optical properties of three- and four-layer unit cell ferrielectric phases is straightforward, it deserves some precaution, as it implies optical rotation in short-pitch helical structures. It has been shown by Oldano and Rajteri [15] that in short-period helical smectic structures, optical rotation shows in some cases unexpected results. We shall therefore compare the results of the first-order approximation to the de Vries theory, Jones matrix calculus, and Yeh transfer-matrix method and compare these calculations to each other and to the experimental results.

A. Jones matrix calculation of ORP

Within the 2×2 matrix Jones calculation of the optical rotation in helicoidally ordered birefringent media [11], one regards the medium as being composed of a large number of infinitesimally thin sections. In our case this thin section is a single smectic layer and the z axis is directed along the layer normal. The retardation matrix J_i that relates the input and output polarization of light transversing the ith thin section and travelling along the z axis is

$$J_i = S_i G S_i^{-1}. \tag{1}$$

Here,

$$S_i = \begin{bmatrix} \cos\beta_i & -\sin\beta_i \\ \sin\beta_i & \cos\beta_i \end{bmatrix}, \quad G = \begin{bmatrix} \exp(-i\gamma) & 0 \\ 0 & \exp(i\gamma) \end{bmatrix}, \tag{2}$$

and β_i is the angle between the direction of the principal axis of the ith layer with respect to the x, y coordinates, whereas γ describes phase retardation of each layer, i.e., $\gamma = \pi\delta n\Delta/\lambda$. Here $\delta n = n_a - n_b$ is the birefringence of a single smectic layer of thickness Δ and λ is the vacuum wavelength. We assume that layer birefringence is equal for all layers, whereas S_i actually depends on the type of structure under consideration. The displacement vectors of the input light wave $\overline{D}_{\rm in}$ and output light wave $\overline{D}_{\rm out}$ are coupled via a simple equation $\overline{D}_{\rm out} = \underline{J}\cdot\overline{D}_{\rm in}$. Here $\underline{J}$ is a Jones matrix for the system of N layers, which is obtained by successive multiplication of the Jones matrices for each layer,

$$\underline{J} = (S_N G S_N^{-1})(S_{N-1} G S_{N-1}^{-1})\cdots(S_2 G S_2^{-})(S_1 G S_1^{-1}). \tag{3}$$

In a simple case of a helically modulated ferroelectric smectic-C^* phase, the angle β_i is equal for all layers and the Jones matrix is simplified to $\underline{J} = (S_i G S_i^{-1})^N$. In the more general cases of three- and four-layer ferrielectric phases, the expression (3) can also be greatly simplified by grouping individual Jones matrices to a set of smectic layers that form a unit cell. For example, in the case of a smectic structure with a unit cell of three smectic layers, one first calculates the Jones matrix for a unit cell,

$$\underline{J}_{\rm unit} = (S_3 G S_3^{-1})(S_2 G S_2^{-1})(S_1 G S_1^{-1}). \tag{4}$$

The Jones matrix J for a system of M unit cells, rotated with respect to each other by a small angle is

$$\underline{J} = (S J_{\rm unit} S^{-1})^M \tag{5}$$

Here, S is the matrix that describes the rotation of a given unit cell to its neighbor and is equivalent to Eq. (2), where β

is in this case the angle of rotation of a unit cell with respect to the previous cell. By writing the Jones matrix for a whole stack in a form

$$\underline{J}=\begin{bmatrix} a & b \\ c & d \end{bmatrix} \tag{6}$$

and following general principles of optical rotation and retardation in birefringent structures [11], the angle of rotation ψ of the stack of layers is given by

$$\Psi = -\arctan\left(\frac{\mathrm{Re}[b]}{\mathrm{Re}[a]}\right). \tag{7}$$

For a given structure one therefore has to calculate the Jones matrix and then the calculation of optical rotation from the elements of this matrix is straightforward.

B. Yeh's transfer-matrix method

The formulation of the Jones matrix method implies some simplification of the problem of light propagation because (i) it does not consider reflection of light at the interface between neighboring liquid crystalline layers, (ii) the optical axis lies within the plane of the smectic layers, i.e., the E_z component of a light wave propagating along the layer normal z equals zero. Clearly, this is not fulfilled in alternating tilted smectic structures, where the optical axis of an individual layer is tilted at a tilt angle of 20°–30° and changes its direction in space from layer to layer.

On the other hand, the transfer-matrix method of Yeh [14] is superior in comparison to the Jones method because (i) it is based on exact solutions of Maxwell's equations and (ii) it considers continuity of electric and magnetic fields at the interface between the neighboring layers. Briefly, Yeh's method considers a stack of $i=1,...,N$ birefringent layers, which is in our case an individual smectic layer. This idealized dielectric layered structure is therefore the only approximation within Yeh's approach. The dielectric permitivity tensor $\underline{\varepsilon}(i)$ in each smectic layer is given by

$$\underline{\varepsilon}(i)=\underline{A}_i\begin{bmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{bmatrix}\underline{A}_i^{-1}. \tag{8}$$

Here ε_i denotes principal values of the dielectric tensor of a single tilted smectic layer (equal for all layers) and $\underline{A}_i$ is the coordinate rotation matrix, which depends on the phase and the tilt angle of an individual smectic layer [16]. In the next step, the wave equation is solved for individual smectic layers, which gives us two pairs of wave vectors together with the eigensolutions of the propagating waves. This is followed by imposing continuity relations for the transverse components of $\overline{E}$ and $\overline{H}$ at each interface. This leads to the 4×4 transfer matrix $T_{n-1,n}$ for the nth layer

$$T_{n-1,n}=D^{-1}(n-1)D(n)P(n), \tag{9}$$

which relates the amplitudes A_j of the four eigenwaves in the neighboring layers,

$$\begin{pmatrix} A_1(n-1) \\ A_2(n-1) \\ A_3(n-1) \\ A_4(n-1) \end{pmatrix} = T_{n-1,n}\begin{pmatrix} A_1(n) \\ A_2(n) \\ A_3(n) \\ A_4(n) \end{pmatrix}. \tag{10}$$

The elements of the transfer matrix $T_{n-1,n}$, i.e., $D(n)$ and $P(n)$ are calculated from the eigensolutions of the wave equation for a particular layer [14]. The transfer matrix for a series of smectic layers with arbitrary orientation of the principal axis of the dielectric tensor in each layer is obtained by subsequent multiplication of individual transfer matrices. For a given polarization of the input light wave, the electric field amplitude of a transmitted wave is calculated as a vector sum of the electric field amplitudes of four eigenwaves. The optical rotation of a stack of smectic layers is then calculated similarly to the Jones method, i.e., following the Eq. (7).

C. de Vries's theory of optical rotation

Within de Vries's calculation of optical rotation of helical birefringent structures, one solves Maxwell equations for the light propagating along the helical axis. The calculation is based on the macroscopic dielectric tensor $\underline{\varepsilon}$, which has a complicated form in ferroelectric and antiferroelectric helical phases [16]. It has been shown experimentally [12] that optical rotatory power ρ *in the ferroelectric phase* is given by a modified de Vries expression

$$\rho=\frac{\Psi}{d}=-\frac{2\pi}{p}\frac{\alpha^2}{8\lambda'^2(1-\lambda'^2)}. \tag{11}$$

Here, Ψ is the angle of the rotated output polarization with respect to the input polarization, d is the thickness of the sample, p is the helical period, $\lambda'=\sqrt{2}\lambda_0/p\sqrt{\varepsilon_\parallel+\varepsilon_\perp}$ is the reduced wavelength, λ_0 is the wavelength in vacuum, and $\alpha=(\varepsilon_\parallel-\varepsilon_\perp)/(\varepsilon_\parallel+\varepsilon_\perp)$. Here $\varepsilon_\parallel=\varepsilon_2\varepsilon_3/(\varepsilon_2\sin^2\theta+\varepsilon_3\cos^2\theta)$ and $\varepsilon_\perp=\varepsilon_1$ are the dielectric constants in the direction perpendicular to the plane of the tilt (i.e., along the direction of polarization) and in the direction of the projection of the tilt onto the smectic layers, respectively. ε_1, ε_2, and ε_3 are the eigenvalues of the dielectric tensor defined elsewhere [16] and θ is the tilt angle.

For the calculation of the ORP in the antiferroelectric and ferrielectric phases, de Vries description can be modified by considering a unit cell of the ferrielectric phase as *a single birefringent layer with dielectric tensor that is equal to an average of the dielectric constant tensor* within the unit cell [10,16]. For example, let us consider a four-layer distorted unit cell, as shown in Fig. 1(b). Let us denote the dielectric tensor of the individual smectic layer by $\underline{\varepsilon}(i)$, $i=1,...,4$. In the first step we calculate the space average of the dielectric tensor of a four-layer unit cell and obtain a new tensor that describes average birefringence of the unit cell as a whole. After solving the wave equation using this unit-cell-averaged

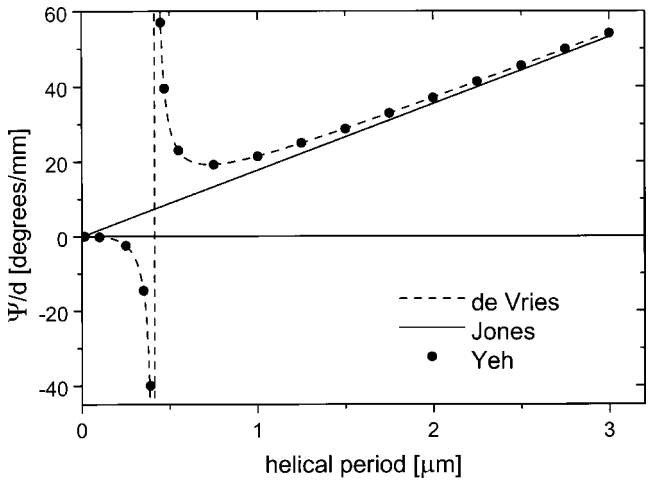

FIG. 2. Comparison of optical rotatory power of ferroelectric smectic-C^* phase, calculated from de Vries's analytical solutions of the wave equation, Yeh's 4×4 matrix approach, and Jones matrix formalism as a function of helical period. The tilt angle is 16.2°, whereas the eigenvalues of the dielectric tensor are $\varepsilon_1=2.28$ and $\varepsilon_3=2.89$, the wavelength of light is 632.8 nm.

dielectric tensor, ORP of a deformed four-layer helical structure is again given by the Eq. (11), where

$$\alpha=\frac{\frac{1}{2}(\varepsilon_3-\varepsilon_1)\sin^2\theta}{\varepsilon_1+\frac{1}{2}(\varepsilon_3-\varepsilon_1)\sin^2\theta}\cos\beta \tag{12}$$

and $\lambda=\lambda_o/(p\sqrt{\varepsilon_1+\frac{1}{2}(\varepsilon_3-\varepsilon_1)\sin^2\theta})$. As the ORP is proportional to the square of the angle of distortion β, it is therefore quite sensitive to the distortion of the unit cell. This enables us to directly determine the magnitude of the orientational distortion of the unit cell of ferrielectric phases.

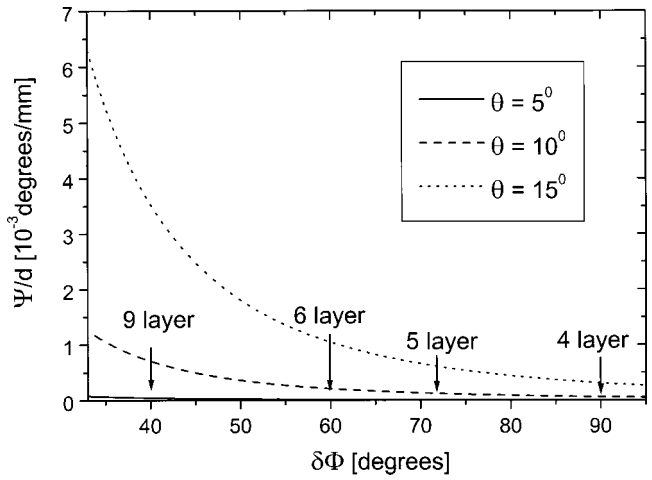

FIG. 3. Optical rotatory power of smectic-C^*_α phase as a function of the phase difference between the directions of directors in neighboring smectic layers $\delta\Phi$, calculated for different values of the tilt angle. The wavelength of light is 632.8 nm and the eigenvalues of the dielectric tensor are $\varepsilon_1=2.28$ and $\varepsilon_3=2.89$, ORP was calculated within Yeh's 4×4 matrix formalism.

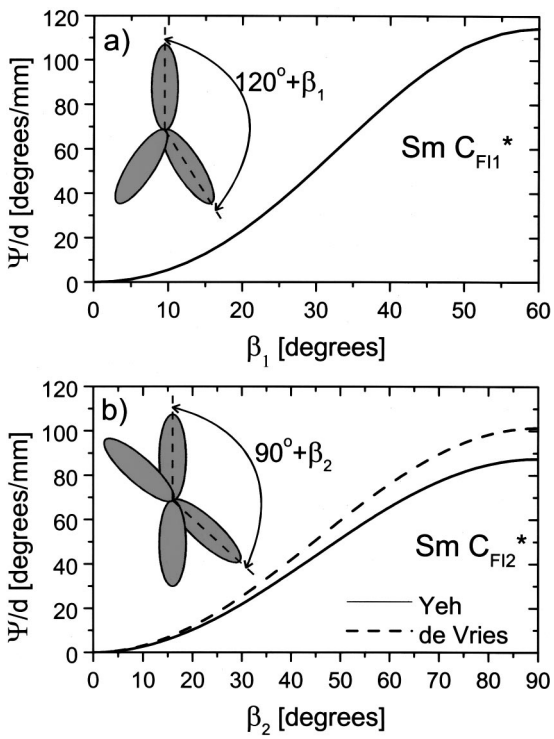

FIG. 4. Optical rotatory power of (a) the three-layer smectic-C^*_{FI1}, (b) the four-layer smectic-C^*_{FI2} ferroelectric phase as a function of the angle of distortion of a unit cell, indicated in the inset. Yeh's formalism was used with $\lambda=632.8$ nm, $\varepsilon_1=2.28$, $\varepsilon_3=2.89$, $p=3$ μm, and $\theta=17°$. The dashed line in Fig. 4(b) is de Vries's calculation according to Eqs. (11) and (12) with the same set of parameters.

III. RESULTS AND DISCUSSION

Figure 2 shows a comparison of the ORP of the ferroelectric smectic-C^* phase, calculated from the de Vries expression, Jones matrix, and Yeh matrix formalism. As expected, de Vries's and Yeh's formalisms give practically identical results, whereas Jones method typically gives underestimated values of the ORP. This is most remarkable in the vicinity of the Bragg selective reflection peak, which is very well reproduced by Yeh's method and totally absent in Jones calculus. These can be understood by noting that the Bragg reflection peak is a result of the interference of traveling light waves that are reflected back and forth in the medium. As these reflections are not considered in Jones's formalism, Bragg reflection is absent too. We therefore conclude that Yeh's formalism is superior for the analysis of the ORP in three- and four-layer ferrielectric phases.

The optical rotary power calculated using Yeh's formalism for the incommensurate smectic-C^*_α phase is shown in Fig. 3 for different values of the tilt angle and for different periodicities. One can see that ORP in smectic-C^*_α is practically unobservable, which is in agreement with high resolution experiments that show negligible ORP in this phase.

The optical rotatory power for three- and four-layer ferrielectric phases, calculated from the Yeh matrix formalism, are shown in Fig. 4 as a function of the angle of orientational distortion β and for a typical value of the helical period of

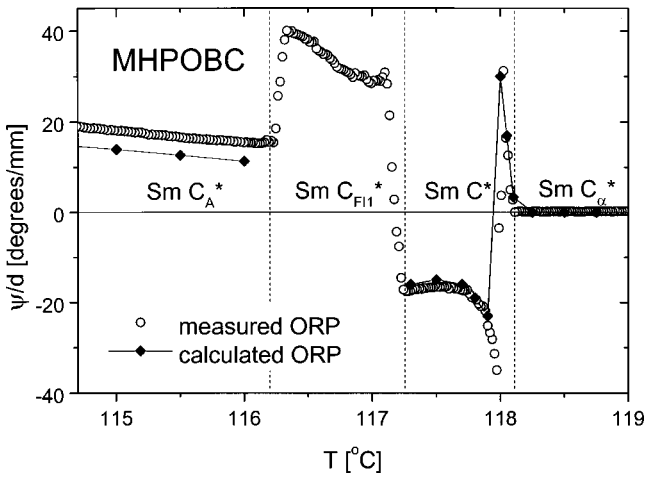

FIG. 5. Temperature dependence of the measured ORP (○) in MHPOBC [4] together with the calculated ORP (◆). The calculations were made within Yeh's formalism.

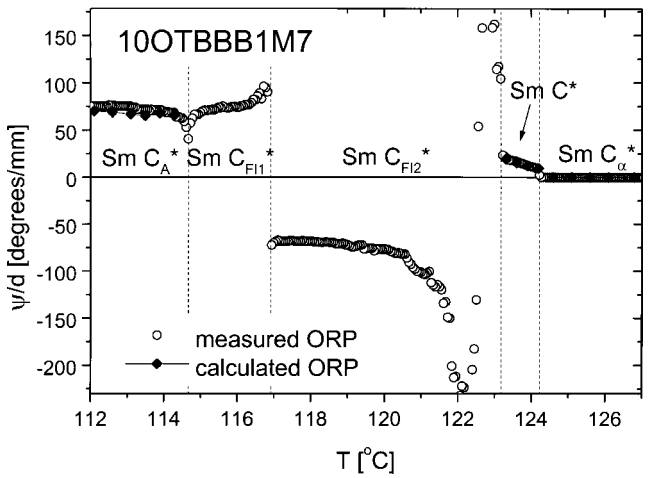

FIG. 6. Temperature dependence of the measured ORP (○) in 10OTBBB1M7 [18] together with the calculated ORP (◆). The calculations were made within Yeh's formalism.

$p=3\ \mu$m and tilt angle $\theta=17°$. As one can see, the ORP of these phases is extremely sensitive to the distortion of the structure. For an undistorted case (i.e., $\beta=0$) the ORP is in both cases very small and well below experimental resolution of $\Psi\approx 0.02°$ for a sample of thickness 100 μm. The ORP then increases strongly with the angle of deformation β. It reaches maximum value for the maximum angles of deformation, $\beta_1=60°$ for a three-layer structure and $\beta_2=90°$ for a four-layer structure. These maximum distorted structures correspond to the three-and four-layer structures of the 1D Ising models.

The dashed line in Fig. 4(b) shows the ORP calculated using de Vries's expressions [Eqs. (11) and (12)] and the same set of parameters. One can see that de Vries's expression, which is based on the space-averaged tensor for a four-layer unit cell, significantly overestimates ORP in comparison to Yeh's method. The reason for this difference is in the fact that averaged dielectric tensor of the antiferroelectric phase is in this case equal to the dielectric tensor of a cholesteric liquid crystal. As a consequence, the E_z component of the electric field calculated from the wave equation is zero. This artificially increases the value of the parameter α and consequenty leads to an increased ORP. The difference between Yeh's and de Vries's values for the ORP depends linearly on the dielectric anisotropy $\varepsilon_3-\varepsilon_1$ and becomes smaller than 10% for very low birefringent materials with $\Delta n<0.04$.

In order to test the overal procedure, we present in Figs. 5 and 6 the comparison between the experiment and the theory of ORP in the ferroelectric and antiferroelectric phases of 10OTBBB1M7 and MHPOBC. The calculation of ORP is not presented in ferrielectric phases, since the distortion angle β is, in principle, not known. The high resolution birefringence and ORP experiment has been described elsewhere and we have also used our measurements of the temperature dependence of the tilt angle and indices of refraction [4,19]. The temperature dependencies of the pitch in these materials have been taken either from literature [17] or have been determined either directly by microscope observations or indirectly from our additional electro-optic response experiments. In these experiments, we have measured the relaxation rates of the phase mode, which is given by $\tau^{-1}=(K_3/\gamma)q_c^2$, where $q_c=2\pi/p$ [16]. Whereas the ferroelectric and the antiferroelectric phases give an excellent and quantitative agreement between the measured and calculated ORP values, such a good agreement can only be obtained in three- and four-layer ferrielectric structures if they are strongly distorted. If the ferrielectric structures are not distorted, the calculated value is several magnitudes less than the measured values.

We have therefore used the measured ORP data for the calculation of the distortion angle β in the ferrielectric phases. For this calculation, reliable values of the helical pitch in the ferrielectric phases are necessary. We have de-

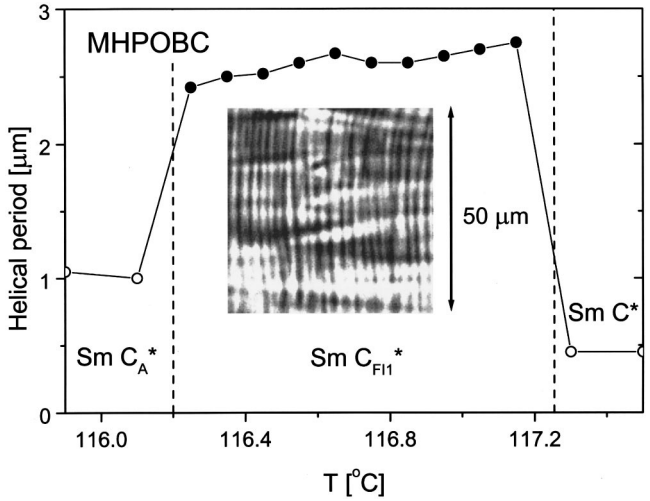

FIG. 7. Temperature dependence of the helical period in the smectic-C^*_{FI1} phase of MHPOBC, measured by the observation of disclination lines (filled circles). The values in the smectic-C^* and smectic-C^*_A phase are from Ref. [17] (open circles). The inset shows a picture of disclination lines of the smectic-C^*_{FI1} phase under polarizing microscope at the temperature of 116.5 °C.

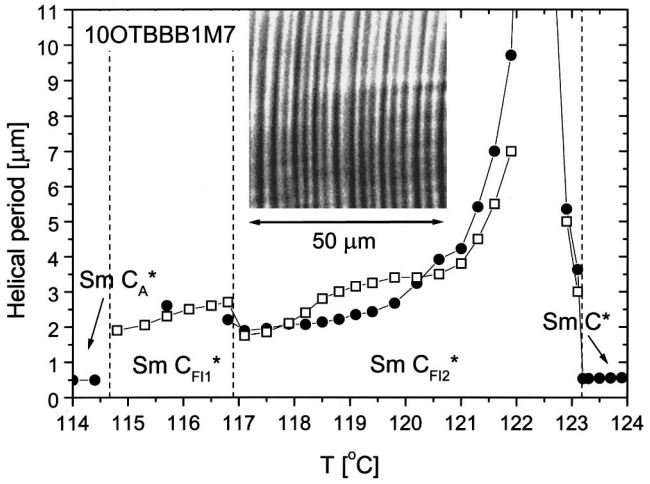

FIG. 8. Temperature dependence of the helical period in the smectic-C^*_{FI1} and smectic-C^*_{FI2} phases of 10OTBBB1M7, measured directly by the observation of disclination lines (open squares) and determined indirectly from relaxation rates of the phase mode (filled circles). The inset shows a picture of disclination lines under polarizing microscope in the smectic-C^*_{FI2} phase at the temperature of 118.5 °C.

termined the temperature dependencies of the pitch in the ferrielectric phases by observing the homogeneously oriented samples under a polarizing microscope and by measuring the distance between the disclination lines. In Figs. 7 and 8, the measured temperature dependencies of the pitch in the ferrielectric phases of MHPOBC and 10OTBBB1M7 are shown together with a polarizing microscope image of the structures. In the smectic-C^*_{FI2} phase of 10OTBBB1M7, helical period has been also determined from electro-optic response measurements. We have observed that the relaxation rate in the smectic-C^*_{FI2} goes to zero at the temperature 0.8 K below the transition from the smectic-C^* phase. This is explained by the change of sign of ORP in the smectic-C^*_{FI2} phase, accompanied with the unwinding and rewinding the helix.

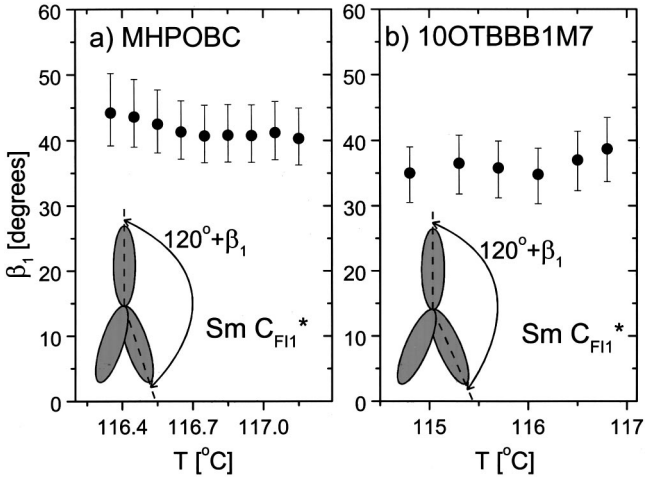

FIG. 9. Temperature dependence of the calculated distortion angle β in the smectic-C^*_{FI1} phase of MHPOBC and 10OTBBB1M7.

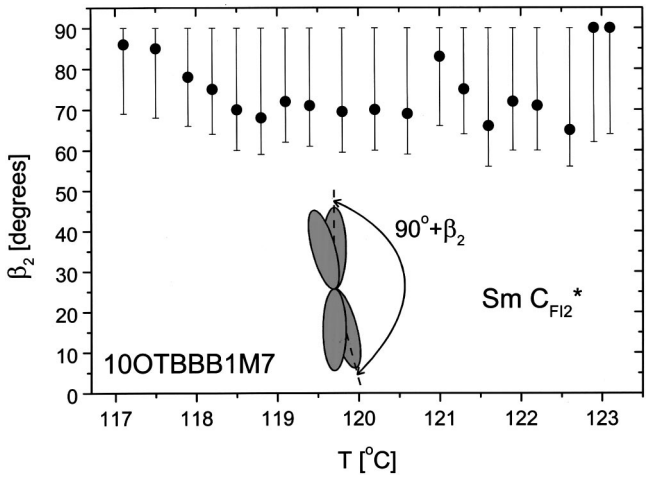

FIG. 10. Temperature dependence of the calculated distortion angle β in the smectic-C^*_{FI2} phase of 10OTBBB1M7.

Finally, combining all these data, we show in Figs. 9 and 10 the temperature dependence of the calculated distortion angle β in the smectic-C^*_{FI1} and *smectic*-C^*_{FI2} phases. The error bars have been calculated by considering errors of all data, entering into calculation, which are (i) the tilt angle $\delta\theta = 0.2°$, (ii) length of the helical period $\delta p/p = 0.04$, (iii) index of refraction $\delta\varepsilon_3 = 0.01$, and (iv) ORP $\delta\psi/\psi = 0.04$.

Figure 9, shows the distortion angle β_1 for a three-layer ferrielectric structure and one can see that β_1 is nearly temperature independent. In the three-layer smectic-C^*_{FI1} phase of MHPOBC, the average value of the distortion angle is $\overline{\beta_1} = 41° \pm 5°$, and in the smectic-$C^*_{FI1}$ phase of 10OTBBB1M7 it is equal to $\overline{\beta_1} = 36° \pm 5°$. Both values are close to $\beta_1 = 32°$ in [4-(1-methylheptyloxycarbonyl)phenyl-4′-octylbipheny]-4-carboxylate (MHPBC) reported by Johnson *et al.* [8]. This analysis clearly shows that the three-layer smectic-C^*_{FI1} phase is significantly distorted and the angle of distortion is nearly temperature independent. It is however also clear that this structure is not Ising-like.

In the smectic-C^*_{FI2} phase of 10OTBBB1M7 the average value of the distortion angle is $\overline{\beta_2} = 75° + 15° - 11°$, and again the distortion angle is nearly temperature independent. However, due to rather large uncertainty in $\overline{\beta_2}$, we cannot say whether the smectic-C^*_{FI2} phase is completely distorted ($\beta_2 = 90°$) and consequently Ising-like, or not. The observed average value is however very close to the values $\beta_2 = 83°$ in MHPBC and $\beta_2 = 72°$ in MHDDOPTCOB [20] reported by Johnson *et al.* [8].

IV. CONCLUSIONS

In conclusion, we have shown that Yeh's 4×4 matrix formalism for the propagation of light in modulated birefringent structures gives a good quantitative agreement with the analytic de Vries expression for optical rotation only in the ferroelectric smectic-C^* phase. Jones matrix method and various approximations of de Vries's theory show significant deviations from Yeh's method in the case of antiferroelectric

and ferrielectric phases. These deviations are smaller than 10% for low birefringence material of $\Delta n < 0.04$.

We have clearly shown that high optical rotatory power, observed in three-and four-layer smectic structures is inconsistent with ''perfect'' orientational structure, suggested from the first resonant x-ray experiments. A distortion of the orientation of the molecules in the unit cell is necessary to describe quantitatively the high value of ORP from optical experiments. In this sense, our analysis of ORP in the ferrielectric phases of MHPOBC and 10OTBBB1M7 completely supports the analysis of ellipsometric experiments in the ferrielectric phases of MHPBC and MHDDOPTCOB [8] and is also consistent with recent higher-resolution resonant x-ray experiments, reported by Pindak [9]. The angle of the distortion of the unit cell in MHPOBC is estimated to $\beta_1 = 41(1 \pm 0.13)$deg in the smectic-C^*_{FI1} (i.e., smectic-$C^*_{1/3}$ or smectic-C^*_γ). In 10OTBBB1M7 the angle of distortion is estimated to $\beta_1 = 36(1 \pm 0.13)$deg in the smectic-C^*_{FI1} (i.e., smectic-$C^*_{1/3}$ or smectic-C^*_γ) and to $\beta_2 = 75(1 + 0.2 - 0.15)$deg in the smectic-$C^*_{FI2}$ (i.e., smectic-$C^*_{1/4}$). Consequently, the three-layer ferrielectric phases are clearly not consistent with the proposed 1D Ising model, whereas the four-layer ferrielectric phases are more consistent with 1D Ising model. However, as the model has to generally describe the structure of ferrielectric phases of a given substance, it is clear that the Ising model is ruled out. However, we would also like to point out that the present clock model has to be modified and completed in order to generate (i) large, alternating phase distortions and (ii) temperature-independent distortion angles.

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