Gyrotropy problem in nonhomogeneous media: The case of short-pitch chiral-smectic-*C* liquid crystals and incommensurate structures

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The question about the existence of macroscopic models for gyrotropy in inhomogeneous materials is examined. We have carried out a detailed polarimetric study on a short-pitch chiral-smectic-*C* liquid crystal, which has been taken as an example of an inhomogeneous optical medium. In accordance to the theoretical predictions, we have found that, as a first approximation, the inhomogeneous liquid crystal can be modeled as a homogeneous uniaxial medium with huge optical activity in a direction perpendicular to the optic axis. However, some deviations have been determined in the precise values of the optical activity predicted by the theory. These discrepancies have been attributed to higher-order gyrationlike effects, which are usually negligible and have not been considered in previous theoretical approaches. The agreement improves when these higher-order effects are incorporated. In the light of the above results, the theory is applied to the case of incommensurate structures. The origin of gyrotropy in these materials is clarified, and it is shown that this quantity can be described by a usual macroscopic tensor. If the incommensurate structure has an inversion center we deduce that all gyration effects rigorously vanish, contrary to the opinion maintained by several authors.

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I. INTRODUCTION

Optical activity (OA) in crystals is a nonlocal property that explicitly depends on some spatial periodicity p relevant in the structure, a molecular size or any other characteristic length. This fact was already recognized by Boltzmann on the basis of a molecular model for OA, finding that gyrotropy scales as a/λ, where a is a molecular size and λ the light wavelength. This characteristic indicates that OA is a clear manifestation of the molecular structure of matter. However, as usually $a \ll \lambda$, OA is described in terms of macroscopic constitutive relations that are valid for homogeneous models.

This approach to the problem of OA can seem somewhat paradoxical, in the sense that it is not obvious to what extent a homogeneous model can describe a property that is entirely due to the inhomogeneous nature of the medium, especially in crystals with long periodicities. In fact, the search or even the existence of macroscopic models for some gyrotropic crystals is still a controversial problem.

Recently this question has received attention from the theoretical viewpoint [1,2]. The problem has been addressed on the basis of a simple optical model coming from the field of liquid crystals. Despite its simplicity, the model is however realistic for several liquid crystalline phases of interest, and in particular for chiral-smectic-*C* (SmC*) phases with short helical pitches. Under several conditions that are easily met in practice, it can be shown that these inhomogeneous mesophases can behave as homogeneous optical media, and the refractive index and gyrotropy tensors are described by simple analytical expressions.

The main aim of this paper is to test empirically these predictions in actual materials, since, up to now, the limits of validity of the model have been essentially established theoretically by comparison of the analytical results with exact numerical calculations [3].

In Sec. II, we briefly review the homogeneous optical model for short-pitch SmC* materials and give the expressions for the effective dielectric tensor. The experiment is described in Sec. III. In view of the results, further extensions of the theory are developed (Sec. IV), and applications to other inhomogeneous materials are proposed (Sec. V). More specifically, we show that the optical properties of incommensurate crystal structures can be described by macroscopic tensors in a very good approximation. In particular, if the incommensurate structure is centrosymmetric, we deduce that the gyration effects are strictly zero, contrary to the opinion maintained by several authors. This puts an end to a controversy opened in the literature 15 years ago.

II. HOMOGENEOUS MODEL FOR SHORT-PITCH SmC* STRUCTURES

Consider a locally uniaxial and nongyrotropic medium in which the optical indicatrix uniformly rotates about the z axis. The orientation of the optic axis is described by a unit vector $\mathbf{n}$, with components

$$n_y = \sin\theta \cos\varphi(z); \quad n_y = \sin\theta \sin\varphi(z); \quad n_z = \cos\theta. \quad (1)$$

This optical model corresponds to the usual description of a SmC* phase. Here, $\mathbf{n}$ is identified with the molecular director, θ is the molecular tilt angle, and $\varphi(z) = qz + \varphi_0$ is the azimuthal angle, where $q=2\pi/p$ being p the helical pitch. The local dielectric tensor is given by:

$$\varepsilon(z)=\varepsilon_0 I+\varepsilon_a \mathbf{n}\otimes\mathbf{n}, \tag{2}$$

where I is the 3×3 identity matrix, $\varepsilon_a=\varepsilon_e-\varepsilon_0$ is the local dielectric anisotropy, and $\varepsilon_0,\varepsilon_e$ are the principal values of ε.

An analysis of the light propagation in a medium defined by Eq. (2) was carried out by Oldano and Rajteri [1] using the Berreman formalism. A perturbative procedure that converges rapidly when $p\ll\lambda$ indicates that, under this condition, the material behaves as an homogeneous [4], optically active, and uniaxial medium. The OA scales as p/λ (in accordance with Boltzmann) and is maximal for light propagating orthogonally to the helix axis. The effective dielectric tensor is given in first order by

$$\varepsilon_{\mathrm{eff}}=\begin{pmatrix}\tilde{\varepsilon}_0 & 0 & 0\\ 0 & \tilde{\varepsilon}_0 & 0\\ 0 & 0 & \tilde{\varepsilon}_e\end{pmatrix}+ig_\perp\begin{pmatrix}0 & 0 & -m_y\\ 0 & 0 & m_x\\ m_y & -m_x & 0\end{pmatrix}, \tag{3}$$

where

$$\tilde{\varepsilon}_e=\varepsilon_0+\varepsilon_a\cos^2\theta,\quad \tilde{\varepsilon}_0=\varepsilon_0(1+\varepsilon_e/\tilde{\varepsilon}_e)/2, \tag{4}$$

$$g_\perp=-\frac{p}{\lambda}\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e}\sin^2 2\theta, \tag{5}$$

and $\mathbf{m}=\mathbf{k}/k_0$, where $\mathbf{k}$ is the light wave vector in the material and $k_0=2\pi/\lambda$.

Equation (3) defines a homogeneous uniaxial medium with the optic axis parallel to z. The optical behavior is similar to that found for crystal classes C_n,D_n, with $n>2$, except for one peculiarity: there is no OA along the optic axis, i.e., $g_\parallel=0$. This is somewhat unexpected since, as is well known, SmC* phases have usually large optical rotations along the helix axis, in agreement with the de Vries equation. However, a simple analysis of the de Vries equation shows that for small p, $g_\parallel$ scales as $(p/\lambda)^3$, vanishing for all practical purposes for $\lambda>5p$.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The existence of a unique gyration coefficient perpendicular to the optic axis can only be proven by using nonstandard polarimetric techniques. The problem arises because the modifications in the polarization state of light due to gyration are usually very small corrections of the main birefringence effects. In other words, OA is extremely difficult to detect along birefringent crystal sections, and its effects can often be confused with those due to imperfections of the optical measuring system and sample surface defects. We have solved this difficulty by using the so-called high-accuracy universal polarimeter (HAUP) technique [5]. The HAUP method permits us to control possible imperfections of the optical equipment, and to measure reliably the values of the birefringence, OA, indicatrix rotation, and linear and circular dichroism, when all these effects appear simultaneously. The most critical components of the equipment are two motorized high-quality polarizers that should be rotated during the measurements with high accuracy and reproducibility (0.001° in our case). The technical details of the apparatus and experimental procedure can be found in Ref. [6].

The studied material is a commercial liquid crystal (Rolic FLC10854, whose phase sequence above room temperature is isotropic $\xrightarrow{91\,^\circ\mathrm{C}}$ chiral nematic $\xrightarrow{79\,^\circ\mathrm{C}}$ SmC*. At room temperature, this compound is a ferroelectric mixture with short pitch, designed for fabrication of devices based on the so-called deformed helix ferroelectric effect [7]. The measurements were performed in the SmC* range above 25 °C. A glass cell of thickness $d=18.0\pm0.3\,\mu$m, coated with lecithines to promote homeotropic alignment (helix axis perpendicular to the cell plates) was used. The alignment was excellent over the whole sample area. In contrast, the quality of the planar cells (which seem more appropriate to measure $g_\perp$) was not so high, independent of the sample thickness or electric-field treatment. In these cells, a texture of fine stripes parallel to the aligning direction, which seem to be characteristic of short-pitch SmC* materials [8,9], was always observed.

In order to detect $g_\perp$, the homeotropic cell was illuminated at oblique incidence $\alpha_i=23.5°$. The light wavelength was $\lambda=632.8$ nm. The material parameters directly determined from the experiment were the optical retardation

$$\Delta=\frac{2\pi}{\lambda}\Delta\tilde{n}d, \tag{6}$$

and the ellipticity of the normal modes

$$e=\frac{G}{2\Delta\tilde{n}}. \tag{7}$$

Here, $\Delta\tilde{n}$ and G are the birefingence and OA along the illumination direction, respectively [10].

The HAUP data were supplemented with additional measurements of θ and p versus temperature in order to get the material parameters required to check Eqs. (4) and (5). The tilt angle was determined on a planar cell of 2 μm with the usual electro-optic method using a polarizing microscope. The pitch was deduced from the de Vries equation (adapted to SmC* materials [11]) by measuring the optical rotation of the homeotropic cell at normal incidence. In the last case, the HAUP device working as a standard polarimeter was used. Figures 1 and 2 show the temperature dependence of θ and p. The behavior of both quantities is classical. The pitch is remarkably small. As can be seen, $p/\lambda<1/4$ below 50 °C, which indicates the suitability of the material for our purposes.

Figures 3 and 4 show the results obtained from the HAUP measurements. The birefringence in Fig. 3 corresponds to the value of the optical anisotropy $\sqrt{\tilde{\varepsilon}_e}-\sqrt{\tilde{\varepsilon}_0}$. The increasing tendency of this quantity is due to the decrease of θ as temperature rises. The data are in good agreement with Eq. (4) if the local birefringence is almost independent of temperature and takes the value $\sqrt{\varepsilon_e}-\sqrt{\varepsilon_0}=0.14$. This value is consistent with the birefringence found for a sample with the helix unwound by an electric field. On the other hand, Fig. 4 indi-

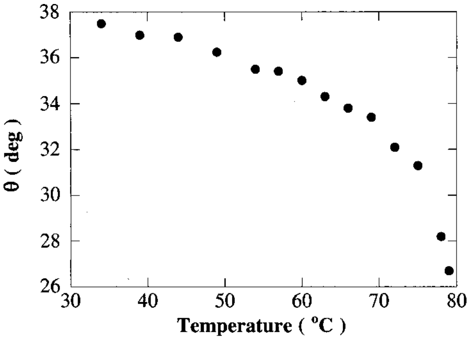

FIG. 1. Temperature dependence of the tilt angle in the SmC* phase of FLC10854. The measurements were carried out on a 2 μm thickness planar sample.

cates the existence of a remarkable gyration. Open squares represent the measured ellipticities. The size of e would correspond to an order of magnitude $G \approx 10^{-3}$ for light propagating in a direction perpendicular to z. This is a huge OA since in the absence of birefringence it would imply a rotatory power larger than 600°/mm.

Open circles in Fig. 4 represent the elipticity deduced from Eqs. (3)–(5) and (7) using the θ, p, and $\Delta\tilde{n}$ values of Figs. 1–3. The experimental data are in agreement qualitatively, though the quantitative comparison is not completely satisfactory. As can be seen, the disagreement is not large, but the experimental ellipticity is systematically higher by an amount larger than the error bars. Obviously, one should not expect a complete accordance with the theory, especially in the region of high temperatures, where certainly p is not much smaller than λ. In addition, since the illumination direction is not far from the optic axis (the angle of refraction was $\alpha_r = 14.5°$), it seems reasonable to consider the effects of $g_\parallel$ in G. It is not evident the way in which $g_\parallel$ should be incorporated to G since $g_\parallel$ is not a true OA [1,2]. Anyway, if the $g_\parallel$ contribution is removed in the usual way like a true gyration (solid circles in Fig. 4), the discrepancies are similar at low temperatures and become greater at high temperatures (where $g_\parallel$ is as large as 20°/mm), because $g_\perp$ and $g_\parallel$ have opposite signs.

We therefore conclude that although Eqs. (3)–(5) provide a good first approximation for modeling, the optical behavior

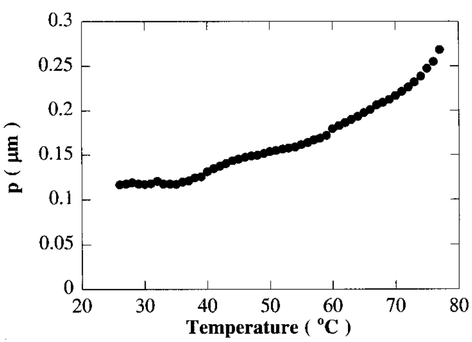

FIG. 2. Pitch versus temperature in the SmC* phase of FLC10854. The depicted values were obtained from measurements of the pseudorotatory power along the optic axis, by using the de Vries expression.

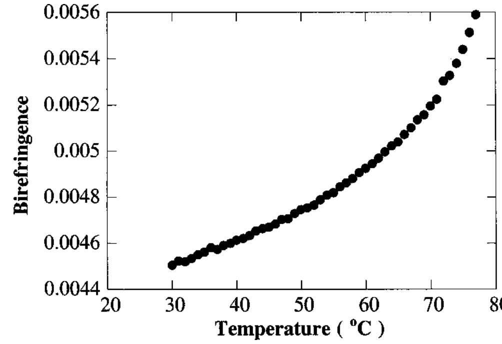

FIG. 3. Temperature dependence of the birefringence in the SmC* phase of FLC10854. Measurements were carried out using the HAUP technique on a homeotropically aligned sample at an oblique incidence $\alpha_i = 23.5°$.

of SmC* materials, they are not enough to fully describe the gyration effects we have found experimentally. This is not surprising since the degree of inhomogeneity of our material is rather large (at high temperatures, p/λ is as large as 0.42). We are then forced to consider higher-order terms in the expansion of ε_{eff} in powers of p/λ. These are presented in the next section.

IV. HIGHER-ORDER CONTRIBUTIONS TO ε_{eff}

Higher-order corrections for ε_{eff} can be obtained by means of an extension of the perturbative treatment reported in Ref. [1]. Here, however, we will follow a different procedure, which is simpler, and is based on a paper by Galatola [2]. The complexity of the analysis of Ref. [1] is due to its generality, accounting even for optical effects that are sample dependent. However, both approaches [1] and [2] are practically equivalent provided that the validity of a homo-

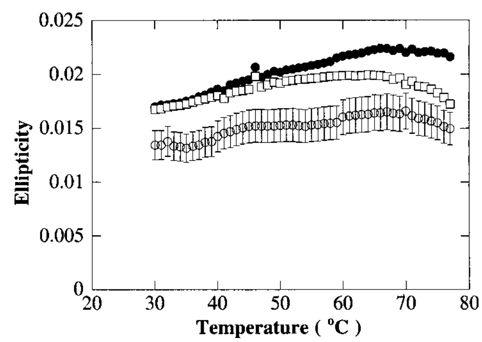

FIG. 4. Experimental ellipticity of the normal modes versus temperature of FLC10854 in the SmC* phase (square symbols). Measurements were carried out on an 18 μm thickness sample at an incidence angle $\alpha_i = 23.5°$ using the HAUP technique. Solid circles were obtained after removing the $g_\parallel$ contribution, using the birefringence, θ, and p data and the de Vries equation for evaluating this quantity. The error bars in both cases are smaller than the symbol size. Open circles represent the theoretically predicted ellipticity assuming a gyration tensor contribution given by expression (5). The measured birefringence, θ, and p values were also used to calculate this quantity. The error bars are due to error propagation, starting from the experimental errors in the birefringence, θ, and p.

geneous model for the SmC* phase is assumed [4].

According to Ref. [2], a short-wavelength periodic medium can be described as a homogeneous medium with $\varepsilon_{\rm eff}$ given by

$$\varepsilon_{\rm eff}(\mathbf{k})=\varepsilon(0)+k_0^2\sum_{q\neq 0}\varepsilon(-\mathbf{q})G(\mathbf{q})\varepsilon(\mathbf{q}), \tag{8}$$

where $\varepsilon(\mathbf{q})$ are the Fourier components of $\varepsilon(z)$ and

$$G(\mathbf{q})=[(\mathbf{k}+\mathbf{q})^2I-(\mathbf{k}+\mathbf{q})\otimes(\mathbf{k}+\mathbf{q})-k_0^2\varepsilon(0)]^{-1}. \tag{9}$$

In our case, $\mathbf{q}=(2\pi m/p)\hat{\mathbf{z}}$, with m an integer.

The expansion of Eq. (8) in powers of p/λ is equivalent to the classical expansion of the dielectric tensor in powers of the light wave-vector $\mathbf{k}$, which is used to treat the spatial dispersion phenomenon

$$\varepsilon_{{\rm eff},i,j}(\mathbf{k})=\varepsilon^{(0)}_{{\rm eff}_{i,j}}+i\gamma^{(1)}_{i,j,l}k_l+\gamma^{(2)}_{i,j,l,m}k_lk_m+i\gamma^{(3)}_{i,j,l,m,n}k_lk_mk_n+\cdots, \tag{10}$$

being $\varepsilon^{(0)}_{{\rm eff}_{i,j}}=\varepsilon_{{\rm eff}_{i,j}}(0)$.

The first two terms of Eq. (10) are explicitly written in Eq. (3) for a SmC* phase, and describe the refractive index and OA, respectively. Further-order terms are expressed in terms of tensors of increasing rank and are corrections to the symmetric (real) and antisymmetric (imaginary) components of $\varepsilon_{\rm eff}$. As will be shown below, successive corrections in Eq. (10) scale as increasing powers of p/λ. Their effects are usually negligible in the optical region and, due to the small size of $(p/\lambda)^n$, $n=2,3,...$, are seldom considered in the literature [12]. Here, however, in view of our p/λ values, some of these terms will be retained.

From Eq. (2), the Fourier components of $\varepsilon(z)$ are easily found:

$$\varepsilon(0)=\begin{bmatrix}\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta & 0 & 0\\ 0 & \varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta & 0\\ 0 & 0 & \varepsilon_0+\varepsilon_a\cos^2\theta\end{bmatrix}, \tag{11}$$

$$\varepsilon(\pm 1)=\frac{\varepsilon_a}{2}\sin\theta\cos\theta\begin{bmatrix}0 & 0 & 1\\ 0 & 0 & \mp i\\ 1 & \mp i & 0\end{bmatrix}e^{\pm i\varphi_0}, \tag{12}$$

$$\varepsilon(\pm 2)=\frac{\varepsilon_a}{4}\sin^2\theta\begin{bmatrix}1 & \mp i & 0\\ \mp i & -1 & 0\\ 0 & 0 & 0\end{bmatrix}e^{\pm 2i\varphi_0}, \tag{13}$$

Using Eqs. (8), (9), and (11)–(13), a rather complicated expression for $\varepsilon_{\rm eff}(\mathbf{k})$ results. By expanding this expression in powers of p/λ, the series (10) is obtained. The first two terms of the series coincide with those given by Eq. (3). The third term represents a very small correction to the optical indicatrix and will not be written here. The next-order contribution is a gyrationlike term, which is given by

$$i\gamma^{(3)}_{i,j,l,m,n}k_lk_mk_n=\begin{bmatrix}0 & \Gamma_{1,2} & \Gamma_{1,3}\\ \Gamma_{2,1} & 0 & \Gamma_{2,3}\\ \Gamma_{3,1} & \Gamma_{3,2} & 0\end{bmatrix}, \tag{14}$$

with

$$\Gamma_{2,1}=-\Gamma_{1,2}=-i\left(\frac{p}{\lambda}\right)^3\left\{\frac{1}{16}\varepsilon_a{}^2\sin^4\theta(\bar{n}\cos\alpha)+\left[\frac{\varepsilon_a^2}{32\tilde{\varepsilon}_e}\sin^4\theta-\frac{\varepsilon_a^2}{4\tilde{\varepsilon}_e^2}\left(\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta\right)\right]\bar{n}^3\sin^2\alpha\cos\alpha\right\}, \tag{15}$$

$$\Gamma_{3,1}=-\Gamma_{1,3}=-i\left(\frac{p}{\lambda}\right)^3\left\{\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e}\left[\left(\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta\right)+\bar{n}\right]\bar{n}\sin\alpha-\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e^2}\left(\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta\right)\bar{n}^3\sin^3\alpha\right\}\sin\xi\sin^2 2\theta, \tag{16}$$

$$\Gamma_{3,2}=-\Gamma_{2,3}=i\left(\frac{p}{\lambda}\right)^3\left\{\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e}\left[\left(\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta\right)+n^2\right]\bar{n}\sin\alpha-\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e^2}\left(\varepsilon_0+\frac{\varepsilon_a}{2}\sin^2\theta\right)\bar{n}^3\sin^3\alpha\right\}\cos\xi\sin^2 2\theta. \tag{17}$$

where we have expressed the components of $\mathbf{k}$ as

$$k_x=\bar{n}k_0\sin\alpha\cos\xi,\quad k_y=\bar{n}k_0\sin\alpha\sin\xi,\quad k_z=\bar{n}k_0\cos\alpha, \tag{18}$$

being $\bar{n}$ a mean refractive index.

Obviously, the property described by $\gamma^{(3)}$ is not a true OA, since it is a fifth-rank tensor (antisymmetric in its first two indices) instead of a third-rank one. However, for small α angles (as in our experiment, where the angle inside the material was $\alpha=14.5°$), the imaginary part of $\varepsilon_{\rm eff}$ can be approximately written as a true OA, namely,

$$\gamma^{(1)}_{i,j,l}k_l+\gamma^{(3)}_{i,j,l,m,n}k_lk_mk_n\approx\begin{bmatrix}0 & g_\parallel^{\rm eff}m_z & -g_\perp^{\rm eff}m_y\\ -g_\parallel^{\rm eff}m_z & 0 & g_\perp^{\rm eff}m_x\\ g_\perp^{\rm eff}m_y & -g_\perp^{\rm eff}m_x & 0\end{bmatrix}, \tag{19}$$

with

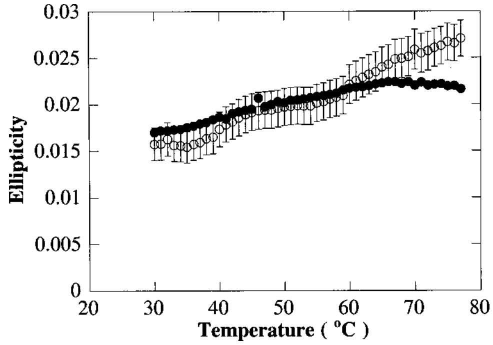

FIG. 5. Theoretical temperature dependence of the ellipticity of the normal modes assuming an OA $G=g_{\perp}^{\mathrm{eff}}\sin^2\alpha$, with $g_{\perp}^{\mathrm{eff}}$ given by Eq. (20) (open circles). Solid circles are the same as those in Fig. 4, i.e., are obtained from the raw experimental ellipticities by subtracting the $g_{\parallel}$ contribution assuming a tensor behavior for this quantity

$$g_{\perp}^{\mathrm{eff}}=-\frac{\varepsilon_a^2}{8\tilde{\varepsilon}_e}\left[\frac{p}{\lambda}+\left(\frac{p}{\lambda}\right)^3[\varepsilon_0+\varepsilon_a\sin^2\theta+\overline{n^2}]\right]\sin^2 2\theta, \tag{20}$$

and

$$g_{\parallel}^{\mathrm{eff}}=\frac{1}{16}\left(\frac{p}{\lambda}\right)^3\varepsilon_a^2\sin^4\theta. \tag{21}$$

Equation (20) introduces an additional term to $g_{\perp}$ in Eq. (5) that scales as $(p/\lambda)^3$. On the other hand, it can be checked that $g_{\parallel}^{\mathrm{eff}}$ is just the first term of the expansion of the de Vries equation in powers of p/λ. Therefore, even when neither $g_{\parallel}^{\mathrm{eff}}$ nor the higher-order term in $g_{\perp}^{\mathrm{eff}}$ are genuine OA's, their interpretation as true gyrations for small α is reasonably justified. With these corrections in mind, a new interpretation of the experimental results must be carried out.

In Fig. 5, a comparison between the experimental and theoretical values of the eigenmode ellipticities is depicted. Solid circles in this figure are obtained by removing from the raw experimental data the $g_{\parallel}$ contribution, assuming a usual tensor behavior for this quantity. Open circles represent the ellipticities deduced form expression (20) in which $(p/\lambda)^3$ contributions have been included. As can be seen, a good agreement is obtained up to 65 °C. However, above this temperature, a clear discrepancy between both curves appears, which can be interpreted as a limitation of the model due to the rise of the pitch length with temperature. For temperatures higher than 65 °C the ratio (p/λ) is larger than 0.3, which, indeed, is a value surprisingly high for the validity of any homogeneous model. However, at least below this limit, the optical properties of this material can be properly described in terms of the zero Fourier component of the electromagnetic Bloch wave.

V. OA IN INCOMMENSURATE STRUCTURES

Having established the adequacy of the homogeneous model to describe the optical properties of short-pitch SmC* phases, we now turn to apply this approach to other inhomogeneous materials. More specifically, we will examine the case of incommensurate (IC) phases, where some features about their optical properties have been in dispute in the literature for more than one decade.

As is well known, IC structures can be described in terms of a basic crystal structure, which is distorted by a modulation wave whose period is IC with the periodicity of the basic structure. This gives rise to long-range structural distortions in comparison to the dimensions of the unit cell of the basic structure. Optical properties of IC structures, and more especially, the question of the OA, have become an interesting subject since the report in 1985 of a nonnull gyration in the centrosymmetric [13] IC phase of $(NH_4)_2BeF_4$ [14]. After this preliminary result, the existence of OA has been claimed in other centrosymmetric IC materials, most of them belonging to the A_2BX_4 family [15–19]. On the other hand, other authors [20–24] disagree with these surprising results, finding null gyrations in some of the materials in which OA had been previously detected. They argue that the apparent gyrations determined in some experiments are due to the presence of systematic errors in the measurement process.

As will be shown below, the OA in IC structures (centrosymmetric or not) can be described using the formalism presented here. The local dielectric tensor is spatially inhomogeneous $\varepsilon(\mathbf{r})$, and expression (8) for $\varepsilon_{\mathrm{eff}}(\mathbf{k})$ is formally valid, with wave-vectors $\mathbf{q}$ of the form [25]

$$\mathbf{q}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\gamma\mathbf{c}^*, \tag{22}$$

where, for simplicity, a one-dimensional (1D) IC structure is considered. Here $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ describe the reciprocal lattice of the basic structure and γ is a temperature-dependent irrational number, while h,k,l,m are integers. The Fourier wave vectors given by $(0,0,l,-m)$ with $l/m\approx\gamma$ are the responsible of the longest modulations, with a period $p\approx c/(l-m\gamma)$. In practice, the modulations with relevant structural information have periods as large as some tens times the cell parameter c. Evidently, this is a rather long-range modulation in comparison to the unit cell of the basic structure, but it is still small compared to the optical wavelength. Therefore, one can expect that the optical properties of these phases are those of a homogeneous medium with an effective dielectric tensor given by an expression similar to Eq. (8).

The homogeneous model for IC phases is even more realistic than for short-pitch SmC* phases, because here, apart from the shorter modulation scale, the Fourier components $\varepsilon(\mathbf{q})$ with $q\neq 0$ are usually small corrections to the main homogeneous contribution $\varepsilon(0)$. This greatly contrasts with the SmC* case, where the inhomogeneity of the structure is more evident.

We turn now to the particular case of centrosymmetric IC structures. In general, $\varepsilon(\mathbf{r})$ should fulfill the symmetry restrictions imposed by the superspace group G_x of the IC structure [25]. This group has elements of the form $g_S=\{R_E,R_I|t_s\}$, and is defined in a 4D space. Here, $R_S=(R_E,R_I)$ where R_E is the usual 3D orthogonal transformation and R_I the internal transformation, while $t_S=(\mathbf{t_E},\mathbf{t_I})$ is the superspace translation. More explicitly, it can be shown that the symmetry requirements imply the relation [26]

$$\varepsilon(\mathbf{q}) = R_E \otimes R_E \varepsilon(R_E^{-1}\mathbf{q}) \exp[i(R_S^{-1}h_S)\cdot t_s], \quad (23)$$

where $h_s = (\mathbf{h_E}, \mathbf{h_I})$, with $\mathbf{h}_E = (h,k,l)$ defined in the 3D external subspace and $\mathbf{h}_I = (m)$ defined in the 1D internal subspace, perpendicular to the external one. In particular, if the IC phase has an inversion center, then $g_S = \{-I,-1|0000\}$, and Eq. (23) implies $\varepsilon(\mathbf{q}) = \varepsilon(-\mathbf{q})$.

On the other hand, since in a nonabsorbing medium $\varepsilon_{\mathrm{eff}}$ must be hermitian (in accordance to the general symmetry requirements [27]), it can be easily shown from Eq. (8) that this implies that $\varepsilon(\mathbf{r})$ is real $[\varepsilon(\mathbf{q}) = \varepsilon(-\mathbf{q})^*]$ and symmetric.

Now, taking together both requirements for $\varepsilon(\mathbf{q})$, we have $\varepsilon(\mathbf{q}) = \varepsilon(\mathbf{q})^*$ in the centrosymmetric case. Therefore, from Eqs. (8) and (9), it can be straightforwardly concluded that $\varepsilon_{\mathrm{eff}}(\mathbf{k})$ is a real tensor, which excludes the possibility of true OA or any pseudogyration effect. More general, it can be shown from Eq. (23) that $\varepsilon_{\mathrm{eff}}(\mathbf{k})$ as well as the material tensors $\gamma^{(i)}$ in Eq. (10) satisfy the Neumann Principle with a symmetry group equal to the point group of the basic structure $G_P = \{R_E\}$. This remarkable conclusion represents a theoretical support to the experimental data first obtained by Ortega *et al.* in 1992 [20], and clarifies a long controversy in recent studies of crystal optics.

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