Molecular origin of ferroelectricity in induced smectic-C^* liquid crystalline phases

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Based on recent experimental results, a molecular model of the ferroelectric ordering in the induced smectic-C^* phase is proposed in terms of a coupling between dipole and quadrupole ordering of chiral molecules. The analysis of the correlations between the value and sign of the spontaneous polarization and the molecular structure of a broad variety of chiral dopants indicates that several new experimental results cannot be explained in the framework of the existing theory of ferroelectric ordering. In particular, the realistic theory is expected to account for the qualitative difference between the properties of the two different types of dopants that possess a chiral center either in the flexible chains or in the rigid core, respectively. The general statistical theory of ferroelectric ordering induced by a chiral dopant in the nonchiral smectic-C host phase is developed and used to obtain the expression for the spontaneous polarization in terms of the dopant molar fraction, quadrupole order parameter, molecular chirality, and the geometrical parameters that characterize the relative orientation of molecular electric and steric dipoles with respect to the molecular rigid core. The different kinds of polar interactions between chiral molecules, which can be responsible for the appearance of the spontaneous polarization, are discussed in detail. In the context of this model it is possible to explain qualitatively the difference in properties between the two types of chiral dopants used in the experiment. The results of the theory enable one to understand why the spontaneous polarization is sensitive to the molecular structure of the host phase only if the dopant molecule possesses a chiral center in the rigid core. In the context of the same model one explains also the opposite signs of the polarization induced by the same chiral dopant in the smectic-C host phases with the two different orientations of the molecular dipole. The latter result enables one also to understand the origin of the recently observed polarization sign inversion induced by a change of concentration of the chiral dopant. The theoretical conclusions are supported by some recent experimental data presented in this paper. [S1063-651X(96)03611-2]

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I. INTRODUCTION

Ferroelectric ordering in smectic-C^* liquid crystals is observed only when the material is chiral. This property is related to the C_{2h} point symmetry of the nonchiral smectic-C phase, which involves the mirror plane parallel to the plane of the director tilt. In chiral smectic-C^* phases all mirror planes are absent (point symmetry C_2) and as a result it is possible to have the spontaneous polarization in the direction perpendicular to the tilt plane [1].

The simplest ferroelectric smectic-C^* phase is formed by a one-component chiral liquid crystal. On the other hand, chirality can be induced in the nonchiral smectic-C liquid crystal by doping it with various chiral molecules [2,3]. This possibility strongly enriches the family of ferroelectric liquid crystals because the chiral dopant molecules must not necessarily be mesogenic themselves. On the other hand, the induced ferroelectric smectics-C^* liquid crystals are very important materials for applications. In such mixed systems it is much easier to combine the broad temperature range and low viscosity of the selected nonchiral smectic-C phase with the large polarization induced by the selected chiral dopant. The proper combination of these parameters is vital for the development of the new family of displays based on ferroelectric liquid crystals [3].

Traditionally, the chiral molecules that are used to induce ferroelectricity in smectic-C liquid crystals possess a rather special structure. In these molecules both the chiral center and the transverse dipoles are located in the flexible chains attached to the rigid molecular core [4,5] (see Fig. 1, type-I). The majority of induced smectic-C^* phases investigated so far belong to this class. We note that in such ferroelectric phases the reduced spontaneous polarization $P_0 = P_s/\sin\Theta$ (where Θ is the tilt angle of the director in the smectic-C^* phase) was found to be independent on the molecular structure of the nonchiral smectic-C host phase [5].

It is possible, of course, to induce ferroelectricity in the smectic-C phase using chiral molecules of a different structure [3], and recently we have performed systematic investigations of the ferroelectric properties of induced smectic-C^* phases doped with chiral molecules of the new type [6]. (See type II on Fig. 1.) In these molecules both the chiral center and the transverse dipoles are part of the rigid core. Examples of such chiral molecules are presented in Table I. It is interesting to note that the ferroelectric properties of

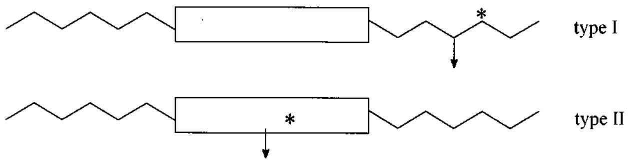
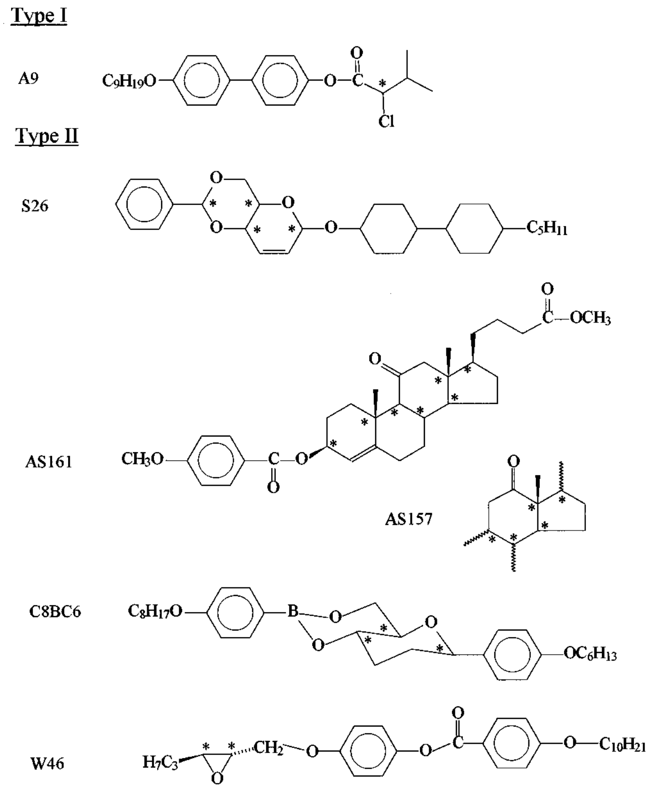


FIG. 1. Schematic structure of two types of chiral dopant molecules used to induce ferroelectricity in smectic-C phases.

TABLE I. Molecular structure of different chiral dopants.



these systems appear to be qualitatively quite different from the properties of the previously studied smectic-*C** induced phases with type-I dopants. In particular, the reduced spontaneous polarization P_0 induced by the chiral type-II dopants is very sensitive to the molecular structure of the nonchiral host phase. Strong host phase effects on P_0 have been observed both in the case of mesogenic host compounds bearing a strong transverse CN dipole perpendicular to the molecular plane and in those of different structure with an in-plane CO dipole. We note that sometimes even the sign of the polarization is different in different smectic-*C* matrices. One typical example of such behavior is shown in Fig. 2. Concerning details of the molecular structure of the host phases we refer to our earlier papers [3,6,7].

Very recently we have also observed the sign inversion of the spontaneous polarization induced by a change of concentration of the chiral type-II dopant [8]. We note that this observation became possible because the new chiral dopant used in the experiments [8], is mesogenic itself and forms a monotropic smectic-*C** phase. Thus it was possible to measure the spontaneous polarization in a broad range of concentrations of the chiral compound (see Fig. 3).

These challenging experimental results indicate that the two different types of chiral dopant molecules (cf. Fig. 1) must have qualitatively different orientational properties in nonchiral smectic-*C* host phases. We expect this to be determined by some difference in the intermolecular interactions between chiral dopant and nonchiral matrix molecules. The results can be understood only in the context of a detailed molecular-statistical theory. In this paper we make a first step and propose a simple model that can be used to explain qualitatively the most important experimental data.

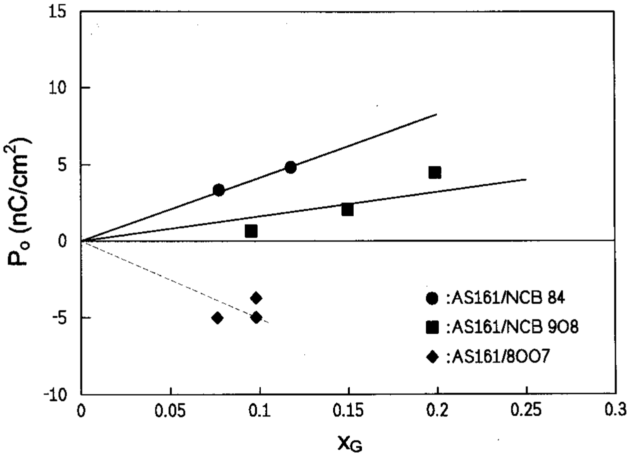


FIG. 2. Tilt angle reduced polarization P_0 vs mole fraction x_G of the dopant AS 161 in different host phases. Values refer to $\Delta T = T_c - T = 5$ K.

The model is based on the idea of the coexistence of the dipolar and quadrupolar orderings of the molecular short axes in the smectic-*C** phase [9–11]. The dipolar ordering of the short axes results in the ordering of transverse molecular dipoles, which gives rise to the spontaneous polarization. This type of ordering is determined by some specific interactions between chiral and polar molecules, which have been discussed in detail before [12–14]. We note that in the molecular theory of ferroelectric ordering, presented in [12–14], it has been assumed that there is only a small polar deviation from the isotropic distribution of molecular orientations about the long molecular axis. In this case the chiral and polar intermolecular interactions are responsible for the weak polar anisotropy of this distribution, which determines the spontaneous polarization.

Recently, however, it has been recognized that the polar ordering of transverse molecular dipoles can be strongly coupled with the quadrupolar ordering of biaxial rigid molecular cores (i.e., with the orientation of ''molecular planes'') in the smectic-*C* phase [9–11]. We note that this

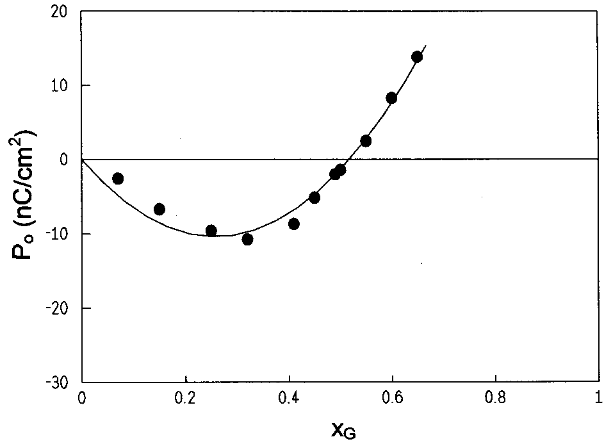


FIG. 3. Polarization P_0 vs mole fraction x_G of the dopant C8BC6 in the achiral host phase NCB808. $\Delta T = 5$ K.

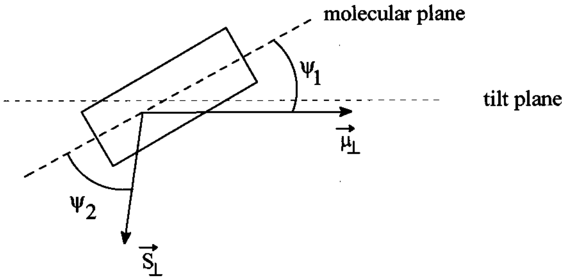


FIG. 4. Schematic representation of the orientation of the electric dipole $\boldsymbol{\mu}_\perp$ and the steric dipole $\mathbf{s}_\perp$ within a dopant molecule.

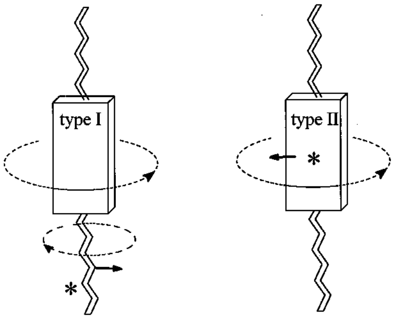


FIG. 5. Models of dopant molecules demonstrating the decoupling of $\boldsymbol{\mu}_\perp$ from the core in type-I dopants and their coupling in type-II dopants.

nonpolar ordering of flat molecular cores is not related to chirality and must exist also in the nonchiral smectic-*C* phase. In the ferroelectric smectic-*C** liquid crystals the quadrupolar ordering of the rigid cores is responsible for the flip-flop-like motion of the molecular short axes observed in the experiment [15] and strongly influences the magnitude and the temperature variation of the spontaneous polarization [11]. The values of the corresponding quadrupole order parameter extracted from polarized Fourier transform IR spectroscopy [16], from measurements of the spontaneous polarization [17,18], and from the dielectric measurements [19], appear to be rather large (of the order of 0.5 or even larger) compared to values obtained from NMR and ^{14}N nuclear quadrupole resonance measurements. However, these data refer to the ordering of single atoms [20]. The strong quadrupolar ordering of the molecular short axes can also be responsible for the large dielectric biaxiality observed in a number of smectics-*C** liquid crystals at low frequency [19]. Recently, strong quadrupolar ordering of various molecular fragments in the smectic-*C** phase has also been observed using the method of vibrational spectroscopy [16,21].

The influence of the quadrupolar ordering of the rigid cores is particularly important if the transverse electric and steric dipoles are not parallel to the main axes of the biaxial core, i.e., if the dipoles are tilted with respect to the flat core (see Fig. 4). In this case the polarization depends on the angle between the dipoles and the plane of the core and can even vanish if the dipoles are normal to the flat cores that are strongly ordered perpendicular to the tilt plane of the smectic-*C** phase [22].

In this paper we show that the idea of coupling between dipolar and quadrupolar ordering can also be used to explain the qualitative difference between the ferroelectric properties of smectic-*C** phases induced by the chiral dopants of the two different types I and II. We note that in molecules of both types the rigid cores are expected to possess some degree of quadrupolar order in the induced smectic-*C** phase. At the same time, the transverse dipoles of dopant molecules of the type II (located around the chiral center in the flexible chain) are significantly decoupled from the orientation of the core (see Fig. 5) and thus the spontaneous polarization does not depend on the quadrupole order parameter. In this case the spontaneous polarization is determined by the induction interaction between the dipole in the chiral center and the polarizability of the neighbor host phase molecules [13,14]. This polarizability is not sensitive to the details of the molecular structure of the host phase. By contrast, in the induced smectic-*C** phases of the second type the ordering of transverse dipoles in the molecular chiral centers is strongly coupled with the orientation of rigid cores and the spontaneous polarization strongly depends on the quadrupolar order parameter of the core. We note that the quadrupole order parameter is determined by short-range steric and dispersion interactions between the cores of neighbor molecules and *is* sensitive to the molecular structure of the host phase.

In this way it is also possible to understand why the same chiral dopant of type II can induce polarizations of opposite signs in different nonchiral smectic-*C* matrices. This can be a consequence of the opposite signs of the quadrupolar order parameter of the chiral molecule in different smectic-*C* phases determined by the difference in the short-range interactions. The corresponding molecular model is discussed in more detail in Sec. III B. It is also possible that the quadrupolar order parameter of the pure chiral smectic-*C** phase will have the opposite sign to that of the quadrupolar order parameter of the same chiral molecule in the selected nonchiral smectic-*C* liquid crystal. Then the sign inversion of the polarization in the mixture of chiral and nonchiral smectic-*C* liquid crystals can be related to the sign inversion of the quadrupole order parameter at some critical concentration of chiral molecules (see Fig. 3).

This paper is arranged as follows. In Sec. II A we derive a general expression for the spontaneous polarization of the induced smectic-*C** phase using the phenomenological expansion of the effective one-particle potential. This expression is then used to explain the experimental data obtained with different types of the chiral dopants. In Sec. II B we consider the influence of the molecular structure of the host phase on the value and sign of the polarization and in Sec. II C we discuss the polarization sign inversion induced by a change in the concentration of the chiral dopant. In Sec. III A we consider two different kinds of interactions between chiral dopant and nonchiral host phase molecules that can be responsible for ferroelectric ordering. In Sec. III B we derive an equation for the quadrupole order parameter and consider the influence of the molecular structure of the host phase on the sign of this parameter. This provides a basis for the understanding of the polarization sign inversion. In the Appendix we present the general molecular-statistical theory of ferroelectric ordering in the induced smectic-*C** phase and derive an expression for the one-particle effective potential that has been introduced phenomenologically in Sec. II A.

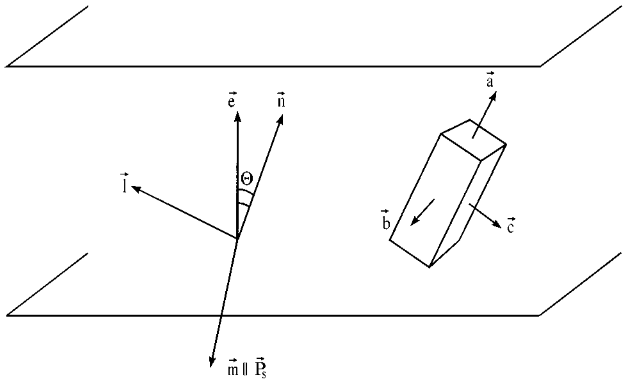


FIG. 6. Orientation of a biaxial molecule within a smectic layer (for vector notation see the text).

The results of this general theory are used in Secs. III A and III B. Finally, in Sec. IV we summarize the qualitative results of the paper.

II. SPONTANEOUS POLARIZATION OF THE INDUCED SMECTIC-*C** PHASE

A. General results

The spontaneous polarization of the smectic-*C* phase doped with chiral molecules is determined by the polar ordering of transverse molecular dipoles

$$\mathbf{P}_s = \rho_0 x_D \langle \boldsymbol{\mu}_\perp \rangle, \tag{1}$$

where ρ_0 is the average number density of molecules, x_D is the mole fraction of the chiral dopant molecules, and $\boldsymbol{\mu}_\perp$ is the transverse dipole of the dopant. The angular brackets denote the ensemble average.

We note that the transverse dipoles of the nonchiral matrix molecules can also be ordered due to the interaction with the chiral dopant [14]. However, at present there is no indication that this effect can be strong. For example, it was mentioned in the Introduction that the polarization induced by chiral dopant molecules of type I does not depend on the molecular structure of the nonchiral smectic-*C* host phase. It would be difficult to explain this result if the contribution from the dipoles of the host molecules to the total polarization were noticeable. It should be stressed that the nonchiral molecules of different smectic-*C* host phases used in the experiment [3,5–7] differ significantly in the absolute values and orientations of their transverse molecular dipoles [3].

In Eq. (1) the spontaneous polarization of the induced smectic-*C** phase is determined by the average transverse dipole of the dopant molecule

$$\langle \boldsymbol{\mu}_\perp \rangle = \int \boldsymbol{\mu}_\perp f_{1C}(\mathbf{x}) d\mathbf{x}, \tag{2}$$

where $\boldsymbol{\mu}_\perp$ is the transverse dipole of the dopant molecule, $f_{1C}(\mathbf{x})$ is the one-particle distribution function of the dopant molecules in the smectic-*C** phase, and $\mathbf{x}$ specifies the orientation of the molecule (see Fig. 6). In general, the orientation of a rigid biaxial molecule is specified by the two unit vectors $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ in the direction of the long and short molecular axes, respectively: $(\hat{\mathbf{a}} \cdot \hat{\mathbf{b}}) = 0$ (see Fig. 6). Sometimes it is convenient also to introduce the third unit vector $\hat{\mathbf{c}}$, which is parallel to the second short axis. The vector $\hat{\mathbf{c}}$ is expressed in terms of $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$: $\hat{\mathbf{c}} = [\hat{\mathbf{a}} \times \hat{\mathbf{b}}]$.

In the smectic-*C* phase the nematic order parameter is usually high [23] and, as in previous papers [9–11], we shall use the approximation of perfect orientational order of the long molecular axes. In this approximation $a_\alpha a_\beta = n_\alpha n_\beta$, where $\hat{\mathbf{n}}$ is the director. Then Eq. (2) can be rewritten as

$$\langle \boldsymbol{\mu}_\perp \rangle = \int (\mu_x \hat{\mathbf{b}} + \mu_y \hat{\mathbf{c}}) f_{1C}(\hat{\mathbf{b}}, \hat{\mathbf{c}}) d\hat{\mathbf{b}}, \tag{3}$$

where μ_x and μ_y are the two components of the transverse molecular dipole.

The distribution function $f_{1C}(\hat{\mathbf{b}}, \hat{\mathbf{c}})$ can always be written in terms of the effective one-particle potential $C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}})$,

$$f_{1C}(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = Z^{-1} \exp[-C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}})], \tag{4}$$

where Z is the normalization constant.

In the smectic-*A* phase the spontaneous polarization is absent and the short molecular axes are not ordered. Therefore, in the smectic-*A* phase $C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = \text{const}$. Thus we are interested only in the difference between the effective potentials of the smectic-*A* and smectic-*C** phases. This difference is characterized by the primary order parameter of the smectic-*C** phase, which can be represented in the form of a pseudovector $\mathbf{w} = [\hat{\mathbf{n}} \times \hat{\mathbf{e}}](\hat{\mathbf{n}} \cdot \hat{\mathbf{e}})$ [11], where $\hat{\mathbf{e}}$ is the smectic plane normal. The order parameter $\mathbf{w}$ specifies both the tilt angle Θ and the direction of the tilt in the smectic-*C* phase. The absolute value is $|\mathbf{w}| = \frac{1}{2}\sin 2\Theta$ and the direction of the vector $\mathbf{w}$ is perpendicular to the tilt plane.

The chiral smectic-*C** phase is characterized also by two secondary order parameters [11]: the spontaneous polarization $\mathbf{P}_s$ and the quadrupole (or the biaxiality [11]) order parameter $B_{\alpha\beta} = \langle b_\alpha b_\beta - c_\alpha c_\beta \rangle$, which characterizes the nonpolar ordering of the molecular short axes (i.e., the ordering of the molecular planes). The quadrupole order parameter $B_{\alpha\beta}$ is not related to molecular chirality and is nonzero also in the nonchiral smectic-*C* phase [11].

In the vicinity of the second-order smectic-*A*–smectic-*C* phase transition all these order parameters are expected to be small because they are proportional to powers of the tilt angle: $w \sim \Theta, P_s \sim \Theta$, and $B_{\alpha\beta} \sim \Theta^2$ if $\Theta^2 \ll 1$ [11]. Thus one can expand the effective one-particle potential of the smectic-*C** phase in powers of the order parameters $\mathbf{w}, \mathbf{P}_s$, and $B_{\alpha\beta}$:

$$C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = C_{1A} + (\mathbf{S} \cdot \mathbf{w}) + (\mathbf{G} \cdot \mathbf{P}_s) + (K_{\alpha\beta} w_\alpha w_\beta) + (M_{\alpha\beta} B_{\alpha\beta}) + \cdots, \tag{5}$$

where only terms of order Θ and Θ^2 have been taken into account. Here the quantities $\mathbf{S}$, $\mathbf{G}$, $K_{\alpha\beta}$, and $M_{\alpha\beta}$ are the coefficients of the expansion, which are functions of the molecular parameters, and $C_{1A} = \text{const}$ is the effective one-particle potential of the smectic-*A* phase.

The tensors $K_{\alpha\beta}$ and $M_{\alpha\beta}$ in Eq. (5) depend only on the components of the unit vectors $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$. Now it is convenient to choose the orientation of the short molecular axes in such a way that the tensors $K_{\alpha\beta}$ and $M_{\alpha\beta}$ are diagonalized:

$$K_{\alpha\beta}=K_{xx}b_{\alpha}b_{\beta}+K_{yy}c_{\alpha}c_{\beta},\quad M_{\alpha\beta}=M_{xx}b_{\alpha}b_{\beta}+M_{yy}c_{\alpha}c_{\beta}. \tag{6}$$

In this frame the vectors **S** and **G** can be written as

$$\mathbf{S}=S_x\hat{\mathbf{b}}+S_y\hat{\mathbf{c}},\quad \mathbf{G}=G_x\hat{\mathbf{b}}+G_y\hat{\mathbf{c}}. \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (5) one obtains

$$\begin{aligned}C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})={}&C_{1A}+C_{1C}^{0}+S_x(\hat{\mathbf{b}}\cdot\mathbf{w})+S_y(\hat{\mathbf{c}}\cdot\mathbf{w})+G_x(\hat{\mathbf{b}}\cdot\mathbf{P}_s)\\&+G_y(\hat{\mathbf{c}}\cdot\mathbf{P}_s)+\Delta K[(\hat{\mathbf{b}}\cdot\mathbf{w})^2-(\hat{\mathbf{c}}\cdot\mathbf{w})^2]\\&+\Delta M[(b_{\alpha}b_{\beta}-c_{\alpha}c_{\beta})B_{\alpha\beta}],\end{aligned} \tag{8}$$

where

$$C_{1C}^{0}=\frac{1}{8}(K_{xx}+K_{yy})\sin^2 2\Theta,$$

$$\Delta K=\frac{1}{2}(K_{xx}-K_{yy}),\quad \Delta M=\frac{1}{2}(M_{xx}-M_{yy}). \tag{9}$$

In the equilibrium state the quadrupole order parameter

$$B_{\alpha\beta}=B(l_{\alpha}l_{\beta}-m_{\alpha}m_{\beta}), \tag{10}$$

with

$$B=\langle(\hat{\mathbf{b}}\cdot\mathbf{m})^2-(\hat{\mathbf{c}}\cdot\mathbf{m})^2\rangle, \tag{11}$$

where $\hat{\boldsymbol{l}}$ and $\hat{\mathbf{m}}$ are the two unit vectors in the smectic-*C* plane (see Fig. 6), $\hat{\mathbf{m}}=\mathbf{w}/w$ and $\hat{\boldsymbol{l}}\perp\hat{\boldsymbol{m}}$. With the help of Eq. (10) the effective potential (8) is finally written as

$$\begin{aligned}C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})={}&+S_x(\hat{\mathbf{b}}\cdot\mathbf{w})+S_y(\hat{\mathbf{c}}\cdot\mathbf{w})+G_x(\hat{\mathbf{b}}\cdot\mathbf{P}_s)\\&+G_y(\hat{\mathbf{c}}\cdot\mathbf{P}_s)+\Delta K[(\hat{\mathbf{b}}\cdot\mathbf{w})^2-(\hat{\mathbf{c}}\cdot\mathbf{w})^2]\\&+\Delta MB[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2].\end{aligned} \tag{12}$$

The first two terms in the effective potential (12) are sensitive to the chirality of the dopant molecules. We note that the scalar products $(\hat{\mathbf{b}}\cdot\mathbf{w})$ and $(\hat{\mathbf{c}}\cdot\mathbf{w})$ change sign under space inversion because the polar vectors $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$ do change sign under inversion while the pseudovector **w** does not. At the same time the energy must be invariant under space inversion, and therefore we conclude that the coupling constants S_x and S_y must also change sign. The constants S_x and S_y are expected to be proportional to the molecular chirality because they also change sign if all chiral molecules are replaced by their enantiomers.

By contrast, the third and the fourth terms in the potential (12) are nonchiral and are determined by dipole-dipole intermolecular interactions. The last four terms in Eq. (12) are nonchiral and nonpolar and determine the quadrupolar ordering of the molecular short axes. The term $\Delta K[(\hat{\mathbf{b}}\cdot\mathbf{w})^2-(\hat{\mathbf{c}}\cdot\mathbf{w})^2]$ characterizes the nonpolar interaction of the molecular short axes with the tilt of the director. The last term in Eq. (12) is determined by some quadrupole-quadrupole-type intermolecular interactions. The relation between the various parts of the potential (12) and particular intermolecular interactions is discussed in more detail in Sec. III.

Substituting the effective potential (12) into Eq. (4) and using the modified equation (3) together with Eq. (2), one obtains from Eq. (1) the following expression for the spontaneous polarization of the induced smectic-*C** phase:

$$\mathbf{P}_s=\rho_0x_D\int(\mu_x\hat{\mathbf{b}}+\mu_y\hat{\mathbf{c}})Z_0^{-1}\exp[-C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})]d\hat{\mathbf{b}}, \tag{13}$$

where

$$Z_0=\int\exp[-C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})]d\hat{\mathbf{b}},$$

and the potential $C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})$ is given by Eq. (12).

Equation (13) can be further simplified if one takes into account that the chiral part of the potential is expected to be small. The spontaneous polarization is also relatively small because in most cases the polarization per molecule corresponds to a small fraction of the total molecular dipole [13]. Then one can expand the exponent in Eq. (13) in powers of the polar part of the potential (12) and retain the first term, which determines the spontaneous polarization. As a result, one obtains

$$\begin{aligned}\mathbf{P}_s&\approx\rho_0x_D\int(\mu_x\hat{\mathbf{b}}+\mu_y\hat{\mathbf{c}})f_0(\hat{\mathbf{b}},\hat{\mathbf{c}})d\hat{\mathbf{b}}\\&=-\frac{1}{2}\rho_0x_D[(\mathbf{S}\cdot\boldsymbol{\mu}_{\perp})+(S_x\mu_x-S_y\mu_y)B]\mathbf{w}-\frac{1}{2}\rho_0x_D\\&\quad\times[(\mathbf{G}\cdot\boldsymbol{\mu}_{\perp})+(G_x\mu_x-G_y\mu_y)B]\mathbf{P}_s,\end{aligned} \tag{14}$$

where the quadrupole order parameter

$$B=\int[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2]f_0(\hat{\mathbf{b}},\hat{\mathbf{c}})d\hat{\mathbf{b}}, \tag{15}$$

and $f_0(\hat{\mathbf{b}},\hat{\mathbf{c}})$ is the one-particle distribution function of the corresponding nonpolar system

$$\begin{aligned}f_0(\hat{\mathbf{b}},\hat{\mathbf{c}})={}&\frac{1}{Z_0}\exp\{\Delta K[(\hat{\mathbf{b}}\cdot\mathbf{w})^2-(\hat{\mathbf{c}}\cdot\mathbf{w})^2]\\&+2\Delta MB[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2]\}.\end{aligned} \tag{16}$$

From Eq. (14) one readily obtains the final expression for the spontaneous polarization P_s:

$$P_s=-\frac{1}{2}\rho_0x_D\chi_0[(\mathbf{S}\cdot\boldsymbol{\mu}_{\perp})+(S_x\mu_x-S_y\mu_y)B]\sin 2\Theta, \tag{17}$$

where $(\mathbf{S}\cdot\boldsymbol{\mu}_{\perp})=S_x\mu_x+S_y\mu_y$ and the susceptibility χ_0 is written as

$$\chi_0=\left(1+\frac{1}{2}\rho_0x_D[(\mathbf{G}\cdot\boldsymbol{\mu}_{\perp})+(G_x\mu_x-G_y\mu_y)B]\right)^{-1}. \tag{18}$$

B. Influence of the molecular structure of the host phase

Equation (17) for the spontaneous polarization has been derived in the preceding subsection using only the general properties of the induced ferroelectric smectic-C^* phase. We did not refer to any specific molecular model. We note that the polarization depends on the biaxiality order parameter B and on the quantities $\mathbf{S}$ and $\mathbf{G}$, which represent some vector properties of the chiral molecules. It will be shown in Sec. III that in the context of our molecular model the quantity $\mathbf{S}$ is proportional to the molecular transverse steric dipole $\mathbf{s}$, $\mathbf{S}=J_0\mathbf{s}$, where the coupling constant J_0 is determined by chiral intermolecular interactions. Here the transverse steric dipole $\mathbf{s}$ characterizes the polar deviation from the ''cylindrical'' molecular shape. The concept of steric dipole has been introduced by Petrov and Derzhanski [24] and used in the molecular theory of nematic and smectic liquid crystals [25,14]. The quantity $\mathbf{G}$ is determined by the dipole-dipole interaction potential and is proportional to the transverse electric dipole $\boldsymbol{\mu}_\perp$ of the dopant molecule.

Using these approximate relations, we can finally write a simple expression for the reduced polarization $P_0=P_s/\sin\Theta$:

$$P_0=-\frac{1}{2}\rho_0 x_D \chi_0[(\mathbf{S}\cdot\mu_\perp)+(S_x\mu_x-S_y\mu_y)B]. \tag{19}$$

Let us now use Eq. (19) to explain the difference between the properties of the chiral dopants of the type I and type II (see Fig. 1 and Table I). First we note that the quadrupole order parameter B in Eq. (19) strongly depends on the molecular structure of the nonchiral host phase. Indeed, according to Eq. (15), the parameter B is determined by short-range (mainly steric and dispersion) interactions between the rigid cores of the guest and (neighbor) host molecules. In particular, the value of B is very sensitive to the coupling constant ΔM in Eq. (16) [11]. Therefore, in the general case the reduced spontaneous polarization of the induced smectic-C^* phase is expected to be sensitive to the molecular structure of the nonchiral host phase.

We note, however, that Eq. (19) is valid only if the chiral dopant molecules are assumed to be rigid. This assumption can be justified for dopant molecules of type II, which contain the chiral center and the transverse dipole in the rigid core. In this case the spontaneous polarization is determined by the chiral and polar interactions between the rigid cores of guest and host molecules. Then the ordering of transverse molecular dipoles is strongly coupled with the quadrupolar ordering of flat rigid cores. In this case the dependence of the reduced polarization on the biaxiality order parameter B can be responsible for the dependence of the reduced polarization on the molecular structure of the nonchiral host phase, which has been observed in the experiments [6,7].

At the same time, in the chiral dopant molecules of type I the chiral center is located in the flexible chain and usually possesses significant rotational freedom with respect to the rigid core (see Fig. 5). In this case the short molecular axes $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$, which determine the orientation of the transverse dipole $\boldsymbol{\mu}_\perp=\mu_x\hat{\mathbf{b}}+\mu_y\hat{\mathbf{c}}$, are practically decoupled from the short axes $\hat{\mathbf{b}}'$ and $\hat{\mathbf{c}}'$, which specify the orientation of the rigid core and determine the quadrupole order parameter $B=\langle(\hat{\mathbf{b}}'\cdot\hat{\mathbf{m}})^2-(\hat{\mathbf{c}}'\cdot\hat{\mathbf{m}})^2\rangle$ in Eq. (19). Here the reduced polarization does not depend on the biaxiality order parameter of the core. On the other hand, for dopant molecules of type I we do not expect any significant quadrupole ordering of the chiral center itself. Thus the spontaneous polarization induced by a chiral dopant of type I is determined by the first term in square brackets in Eq. (19). The reduced polarization can be written approximately as

$$P_0=-\frac{1}{2}\rho_0 x_D \chi_0(\mathbf{S}\cdot\mu_\perp). \tag{20}$$

In Eq. (20) only the vector $\mathbf{S}$ can depend on the parameters of the nonchiral host molecules. However, it will be shown in Sec. III that the predominant contribution to $\mathbf{S}$ depends mainly on the average polarizability of the nonchiral host molecules, which does not differ much for the host phases used in the experiment [3]. Thus we arrive at the conclusion that the reduced polarization induced by the chiral dopant molecules of type I can only weakly depend on the parameters of the nonchiral smectic-C host phase. This conclusion is in accordance with our experimental data discussed in the Introduction.

It should be noted, however, that these results strictly apply only to chiral dopant molecules that possess a simple chiral center in the flexible chain (i.e., one chiral carbon, for example). Such a chiral dopant molecule is presented as type I in Fig. 1. As an example, the dopant $A9$ [4] is given in Table I. The majority of the existing dopant molecules are of this type [13]. There are, however, chiral dopants in which the chiral center is located in the flexible chain but is a part of some small flat fragment [26,27]. In this case the flat fragment can also possess some quadrupolar ordering in the smectic-C^* phase. As a result, the spontaneous polarization will depend on the corresponding quadrupole order parameter and therefore will depend on the molecular structure of the nonchiral host phase. This conclusion is supported by our recent experimental data on oxirane derivatives [27], which possess two neighbor chiral carbons in the flexible chain, bonded with the same oxygen atom in an epoxy ring. An example is given in Table I (dopant W46).

C. Sign inversion of the spontaneous polarization

Equation (19) can also be used to explain why the same chiral dopant of type II can induce polarizations of opposite signs in different nonchiral smectic-C host phases, as observed in experiments. We propose that this is related to the sign reversal of the quadrupole order parameter B of the chiral molecules.

We note that from symmetry reasons the average orientation of the flat molecular core in the smectic-C phase can be either parallel or perpendicular to the tilt plane. However, recently, Stegemeyer and Stockel obtained some indications from FTIP data that the benzene ring of the chiral molecule (of type I) is oriented parallel to the tilt plane [16,28]. Let us then take the short molecular axis $\hat{\mathbf{b}}$ to be perpendicular to the core. Then one can readily see from the definition of the quadrupole order parameter B [see Eq. (15)] that positive values of B correspond to the case when the equilibrium orientation of the flat core is parallel to the tilt plane. Negative values of B correspond to an average orientation of the core perpendicular to the tilt plane. The equilibrium orientation of the guest molecule is determined by the short-range interaction between the rigid cores of the guest and host molecules. These interactions are discussed in more detail in Sec. III B. Here we stress that both the steric repulsion between flat cores and the dispersion interaction between polarizable rings promote parallel orientation of the cores of the neighbor molecules. Thus the rigid core of a chiral guest molecule is normally expected to be parallel to the cores of the nonchiral host molecules.

On the other hand, the width to breadth ratio (i.e., the ''flatness'') of the typical rigid core is rather small (less than 2). In this case the equilibrium orientation can be changed by some strong specific intermolecular interaction of the opposite sign. In our systems the molecules of several smectic-*C* host phases possess the strongly polar CN group that is perpendicular to the cyclohexane ring (see the molecular structure in Ref. [6]. It will be shown in Sec. III B that the dipole-dipole induction interaction between this dipole and the polarizable core of the guest molecule can promote the perpendicular orientation of the core with respect to the cores of the nonchiral host molecules. At the same time we have used also host smectic-*C* phases composed of molecules with the C=O dipole, which is approximately *parallel* to the rigid core [6] (see Fig. 10). In the latter case the core of the guest molecule is expected to be parallel to the cores of the neighboring host molecules.

Thus we arrive at the conclusion that the rigid core of the chiral guest molecule can have different equilibrium orientations in different smectic-*C* host phases. These different orientations correspond to opposite signs of the quadrupole order parameter B in Eq. (19). As a result, the spontaneous polarization can change sign if one host phase composed of molecules with in-plane dipoles is substituted for a different smectic-*C* matrix, composed of molecules that possess large dipoles perpendicular to the flat core. This qualitative conclusion is generally supported by our experimental data [8].

We note that, according to Eq. (19), the possibility of observing the sign inversion of the spontaneous polarization caused by the sign reversal of the parameter B, depends on the relative orientation of the electric and steric molecular dipoles. The quadrupole order parameter B can vary between the values of $B=+1$ and -1 [see Eq. (16)]. For the limiting value $B=1$ we obtain $P_0^{(+)}=-\rho_0 x_D \chi_0 J_0 s_x \mu_x$, and for $B=-1$ we obtain $P_0^{(-)}=-\rho_0 x_D \chi_0 J_0 s_y \mu_y$. Thus the actual sign of the ratio $P_0^{(+)}/P_0^{(-)}=s_x\mu_x/s_y\mu_y$ is determined by the angle between the transverse steric dipole $\mathbf{s}_\perp$ and the transverse electric dipole $\boldsymbol{\mu}_\perp$. It is possible to distinguish four different cases, which are presented in Fig. 7.

Now we are in a position to interpret the sign inversion of the spontaneous polarization caused by a change in the concentration of chiral dopant molecules in the induced smectic-*C** phase [8]. This inversion can also be related to the opposite signs of the quadrupole order parameter B of the dopant molecules in the corresponding pure smectic-*C** phase and in the nonchiral smectic-*C* host phase. The different orientations of the guest molecule in these two systems are determined by the fact that in the pure smectic-*C** phase a chiral dopant molecule is surrounded by the same chiral molecules, while in the nonchiral smectic-*C* host phase (when $x_D \ll 1$) the dopant molecule is interacting only with the molecules of the host material. In this case the spontaneous polarization can also have opposite signs at $x_D \ll 1$ and at $x_D=1$ and will vanish at some critical dopant concentration x_D^0 as observed in the experiment [8].

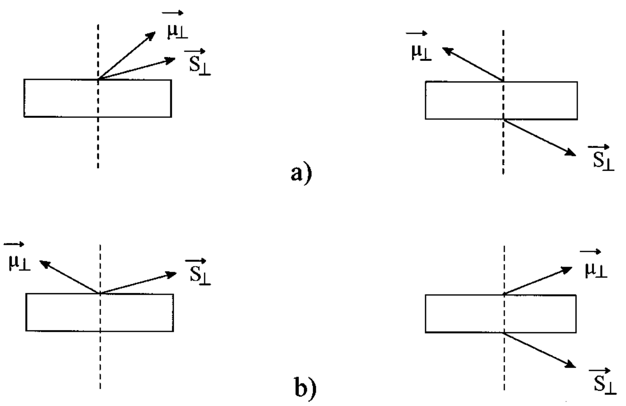


FIG. 7. Four possible relative orientations of the electric ($\boldsymbol{\mu}_\perp$) and the steric dipole ($\mathbf{s}_\perp$) within a dopant molecule.

Finally, we note that, according to Eq. (19), the spontaneous polarization can change sign when the orientation of the transverse electric dipole $\boldsymbol{\mu}_\perp$ or the steric dipole $\mathbf{s}_\perp$ is reversed with respect to the rest of the molecular structure. This result can be used to explain why the two similar chiral dopants AS161 and AS157 (the molecular structure of AS161 is given in Table I) induce polarizations of opposite signs in the same nonchiral smectic-*C* host phases as shown in Fig. 8 [7].

In the dopant AS161 the transverse C=O dipole is located in the 11th position of the steroid skeleton pointing above the core plane, whereas in AS157, with the C=O dipole in the

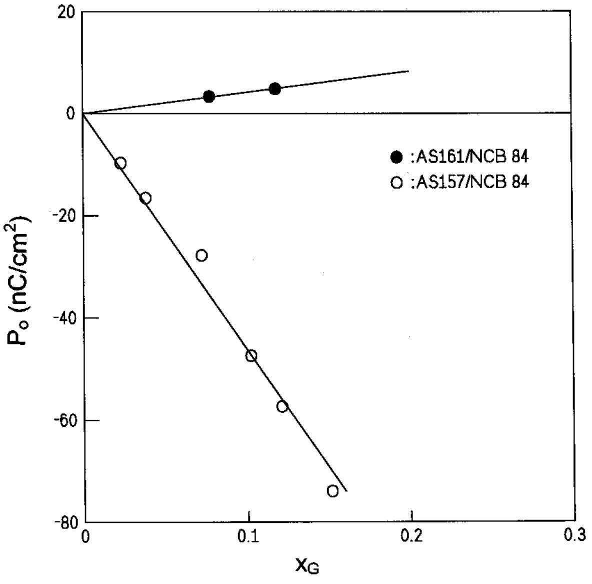


FIG. 8. Polarization P_0 vs mole fraction x_G of the steroid ketones AS157 and AS161 (see Table I) as dopants in the host NCB84. $\Delta T=5$K.

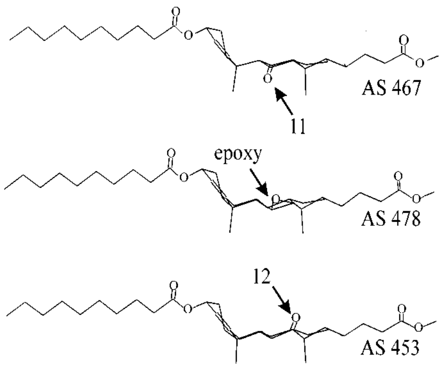


FIG. 9. Molecular skeletons of steroid ketones used as type-II dopants bearing a C=O dipole in the 11th position of the core (AS467, below the core plane) or in the 12th position (AS453, above the plane) and an epoxy ring located in plane (AS478). The polarization values (in nC/cm^2) are AS467, +109; AS478, −30; and AS453, −71 (host NCB808).

12th position, it points in the direction below the plane. This situation is illustrated in Fig. 9 for quite similar steroid skeletons with the C=O dipole in the 11th and 12th positions, respectively. These skeletons obtained by molecular modeling demonstrate that the molecular structure is practically the same, except for the orientation of the C=O dipole with respect to the core plane. In addition, in Fig. 9 we present the epoxy derivative (AS478) with the transverse dipole originating from a three-membered oxirane ring oriented nearly completely within the core plane. As expected, the value of the polarization P_s is in between the values for the 11th and 12th derivatives (see the caption for Fig. 9) [29].

We note that the different orientations of the C=O dipoles in the molecules AS161 and AS157 does have a strong effect on the transverse steric dipole, which is an integral parameter of the molecular shape. Thus the reversal of this C=O dipole (with the transverse steric dipole remaining practically the same) can change the sign of the polarization according to Eq. (19).

III. MOLECULAR THEORY OF FERROELECTRIC ORDERING IN MIXED SMECTIC-*C** PHASES

A. Interaction between polar and chiral molecules

The spontaneous polarization of the induced smectic-C^* phase is given by the general equation (17). We note that the polarization is mainly determined by the quantity **S** because the polarization vanishes when $\mathbf{S}=0$. Thus the quantity **S** is supposed to represent the specific interactions between polar and chiral molecules that are responsible for the ferroelectric ordering.

The general expression for the vector **S** is derived in Appendix. According to Eq. (A13) the vector **S** is a sum of two terms proportional to the molar fractions of dopant and host phase molecules, respectively,

$$\mathbf{S}=x_M\mathbf{S}^M+x_D\mathbf{S}^D. \tag{21}$$

In this expression the coefficient $\mathbf{S}^M$ [see Eq. (A14)] is determined by the interaction between dopant and host phase molecules, while the coefficient $\mathbf{S}^D$ represents a contribution from the dopant-dopant interaction. At small dopant concentration $x_D \ll 1$ the first term $x_M\mathbf{S}^M$ is predominant and the spontaneous polarization is determined by the interaction between a chiral dopant molecule and the neighbor molecules of the nonchiral smectic-C host phase.

In the general case the vector **S** depends on the corresponding intermolecular interactions and can be expressed in terms of some moments of the direct correlation functions $C_{MD}(1,2)$ and $C_{DD}(1,2)$ between dopant and host phase molecules [see Eqs. (A7), (A8), and (A14) for more details]. The general expansion of the corresponding correlation functions is given by Eq. (A8) of the Appendix. Taking into account that different terms in expansion (A8) are orthogonal, one obtains

$$J_x^{D\alpha}=12\int C_{D\alpha}(\hat{\mathbf{b}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_1,\hat{\mathbf{c}}_2,\mathbf{u}_{12})(\hat{\mathbf{b}}_1\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{u}}_{12}])\times(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})d\hat{\mathbf{b}}_1 d\hat{\mathbf{b}}_2 d\hat{\mathbf{u}}_{12},$$

$$J_y^{D\alpha}=12\int C_{D\alpha}(\hat{\mathbf{b}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_1,\hat{\mathbf{c}}_2,\hat{\mathbf{u}}_{12})\times(\hat{\mathbf{c}}_1\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{u}}_{12}])(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})d\hat{\mathbf{b}}_1 d\hat{\mathbf{b}}_2 d\hat{\mathbf{u}}_{12}, \tag{22}$$

where $\hat{\mathbf{u}}_{12}=\mathbf{r}_{12}/r_{12}$.

Equation (22) enables one to determine the quantity **S** using some approximations for the direct correlation functions and some model for a chiral and polar molecule of the smectic-C^* liquid crystal. However, before discussing these models, it is reasonable to consider some qualitative properties of the quantity **S**.

We note that in principle there are two possibilities to compose the pseudovector **S** using characteristic molecular parameters. The first possibility is to express **S** as

$$\mathbf{S}=\mathbf{s}_0\Delta, \tag{23}$$

where $\mathbf{s}_0$ is some polar vector, which characterizes the molecular properties (for example, $\mathbf{s}_0$ can be the molecular permanent electric or steric dipole) and Δ is a pseudoscalar that characterizes the molecular chirality.

In this case the pseudovector **S** directly represents molecular chirality and therefore is determined by chiral intermolecular interactions. The corresponding chiral interactions, which can be responsible for the ferroelectric ordering, have been discussed in detail in [12–14]. The molecular model used in [13,14] is based on the observation that the large spontaneous polarization is found in smectic-C^* liquid crystals composed of molecules with large dipoles in the chiral center. In this case the spontaneous polarization is mainly determined by the induction interaction between the dipole in the chiral center and the polarizability of a neighboring molecule. This attraction interaction is modulated by the short-range steric repulsion between molecules of asymmetric shape. In the context of this model the spontaneous polarization can be expressed as [13,14]

$$\mathbf{P}_s=(\boldsymbol{\mu}_\perp\cdot\mathbf{S})(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})[\hat{\mathbf{n}}\times\hat{\mathbf{e}}], \tag{24}$$

where

$$\mathbf{S}\approx\mathbf{s}_0 J_0 \tag{25}$$

and

$$J_0=\kappa_0\Delta\chi_M\Delta,\quad \kappa_0=-(225/4)(\rho^2/kT)(D/L)^6.$$

Here $\mathbf{s}_0$ is the transverse steric dipole that characterizes the polar deviation from the uniaxial molecular shape and Δ is a measure of molecular chirality in the context of this model

$$\Delta=(\boldsymbol{\mu}\cdot\hat{\mathbf{a}})[\boldsymbol{\mu}\times\hat{\mathbf{a}}]\cdot\mathbf{o}, \tag{26}$$

where $\boldsymbol{\mu}$ is the dipole moment of the chiral center, $\hat{\mathbf{a}}$ is the molecular long axes, and $\mathbf{o}$ is the vector pointing from the molecular center of mass to the chiral center. One can readily see that the pseudoscalar parameter Δ possesses opposite signs for left-handed and right-handed enantiomeric molecules because the product $[\boldsymbol{\mu}\times\hat{\mathbf{a}}]\cdot\mathbf{o}$ changes sign under the simultaneous transformation $\boldsymbol{\mu}\to-\boldsymbol{\mu},\hat{\mathbf{a}}\to-\hat{\mathbf{a}}$, and $\mathbf{o}\to-\mathbf{o}$.

Equations (24)–(26) have also been used in the description of the ferroelectric properties of the induced smectic-C^* phase at small dopant molar fraction [13,30]. In this case the electric dipole $\boldsymbol{\mu}$, the steric dipole $\mathbf{s}_0$, and the chirality parameter Δ are the parameters of the chiral dopant molecules. The only parameter that corresponds to nonchiral molecules of the host phase is the polarizability anisotropy $\Delta\chi_M$. Thus, in this case the dependence of the spontaneous polarization on the parameters of the smectic-C host phase is not expected to be strong. However, in the context of this model there still must be some dependence because the polarizability anisotropy is rather sensitive to the global structure of a mesogenic molecule (for example, it must be sensitive to the number of aromatic rings). However, we shall see below that there exists another contribution to the spontaneous polarization that has not been considered in [12–14]. This contribution is even less sensitive to the molecular structure of the smectic-C host phase and can be the predominant one under favorable conditions.

The new contribution to the spontaneous polarization is related to the second possible structure of the pseudovector $\mathbf{S}$. We note that $\mathbf{S}$ can also be a cross product of any two polar vectors that characterize the molecular structure. For example, one of these vectors can be in the direction of the molecular long axis $\hat{\mathbf{a}}$ while the second polar vector could be the molecular transverse electric or steric dipole. Then the pseudovector $\mathbf{S}$ could be expressed as

$$\mathbf{S}\propto\langle[\mathbf{s}_0\times\hat{\mathbf{a}}](\mathbf{s}_0\cdot\hat{\mathbf{a}})\rangle, \tag{27}$$

where we have taken into account that $\mathbf{S}$ must be even in $\hat{\mathbf{a}}$.

In order to study this possibility in more detail, let us consider the simple induction interaction between the permanent dipole $\boldsymbol{\mu}$ and the permanent quadrupole $Q_{\alpha\beta}$ of the chiral dopant molecule on the one hand and the polarizability $\chi_{\alpha\beta}$ of the host phase molecule on the other:

$$V_{dq}(i,j)=\sum_{n_j}(E^M_{oj}-E^M_{nj})^{-1}\langle o_j|U_{dq}(i,j)|n_j\rangle\langle n_j|U_{dd}|o_j\rangle + \text{c.c.}, \tag{28}$$

where $|o_j\rangle$ and $|n_j\rangle$ represent the ground state and the excited state of the host phase molecule j, respectively, $E^M_{oj}-E^M_{nj}$ is the excitation energy of the molecule j, and c.c. stands for complex conjugate. The dipole-dipole interaction potential $U_{dd}(i,j)$ and the dipole-quadrupole potential $U_{dq}(i,j)$ can be written as

$$U_{dd}(i,j)=\mu_{i\alpha}p_{j\beta}T_{\alpha\beta}(\mathbf{r}_{ij}),\quad U_{dq}(i,j)=Q_{i\alpha\beta}p_{j\gamma}T_{\alpha\beta\gamma}(\mathbf{r}_{ij}), \tag{29}$$

where

$$T_{\alpha\beta}(\mathbf{r})=\frac{1}{R^3}(\delta_{\alpha\beta}-3u_\alpha u_\beta),$$

$$T_{\alpha\beta\gamma}(\mathbf{r})=\frac{1}{2R^5}(3\delta_{\alpha\beta}u_\gamma+3\delta_{\alpha\gamma}u_\beta+3\delta_{\beta\gamma}-5u_\alpha u_\beta u_\gamma), \tag{30}$$

and $\mathbf{p}_j$ is the induced dipole of the host phase molecule $\hat{\mathbf{u}}=\mathbf{R}/R$.

Equation (28) can be rewritten in the form

$$V_{dq}=\frac{1}{2}\chi^D_{\mu\nu}T_{\mu\alpha}(\mathbf{r}_{ij})\mu_{i\alpha}T_{\nu\gamma\delta}Q_{\gamma\delta}, \tag{31}$$

where

$$\chi^D_{\mu\nu}=2\sum_{n_j}(E_{0j}-E_{nj})^{-1}|p_j|_\mu|p_j|_\nu \tag{32}$$

is the polarizability of the host phase molecule. The predominant contribution to the induction interaction (31) is one that involves the average polarizability $\chi^D=\mathrm{Tr}\chi^D_{\alpha\beta}$ Then the main contribution to the potential (31) reads

$$\overline{V}_{dq}(i,j)=\frac{1}{2}\chi^D T_{\alpha\beta}(\mathbf{r}_{ij})\mu_{i\alpha}T_{\beta\gamma\delta}(\mathbf{r}_{ij})Q_{i\gamma\delta}. \tag{33}$$

With the help of Eq. (30) the product $T_{\alpha\beta}T_{\beta\gamma\delta}$ can be expressed as

$$T_{\alpha\beta}(\mathbf{R})T_{\beta\gamma\delta}(\mathbf{R})=\frac{1}{2R^7}[3\delta_{\gamma\alpha}u_\delta+3\delta_{\delta\alpha}u_\gamma - 2\delta_{\gamma\delta}u_\alpha-5u_{\alpha\gamma\delta}].$$

Finally, the induction interaction between the permanent dipole and the quadrupole of the dopant molecule and the average polarizability of the host phase molecule can be written as

$$\overline{V}_{dq}(i,j)=\chi^D\frac{1}{4R^7}[6(\boldsymbol{\mu}_i\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}})-5(\boldsymbol{\mu}_i\cdot\hat{\mathbf{u}})(\hat{\mathbf{u}}\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}})]. \tag{34}$$

We note that the induction interaction (34) itself does not contribute to the free energy of the homogeneous smectic-C^* liquid crystal because it is odd in $\hat{\mathbf{u}}$ and therefore vanishes after integration over $\mathbf{r}_{ij}$. However, the contribution becomes nonzero if one takes into account the polar deviation from the ‘‘cylindrical’’ molecular shape that is characterized by the steric dipole $\mathbf{s}_\perp$. The same argument has already been used in [12,14] in the derivation of Eqs. (24) and (25).

The short-range repulsion between asymmetric molecules can be taken into account by using the generalized mean-field approximation for the direct correlation function

$$C_2(i,j)=-\frac{1}{kT}\exp[-\beta V_{\mathrm{st}}(i,j)]\overline{V_{dq}}(i,j), \tag{35}$$

where the potential $\overline{V_{dq}}(i,j)$ is given by Eq. (33) and $V_{\mathrm{st}}(i,j)$ is the energy of steric repulsion. The function $\exp[-\beta V_{\mathrm{st}}(i,j)]$ can be rewritten in the form of a step function $\Omega(r_{ij}-\xi_{ij})$, where ξ_{ij} is the minimum distance of approach for the two molecules i and j. The function $\Omega(r_{ij}-\xi_{ij})=0$ when the molecules penetrate each other (i.e., $r_{ij}<\xi_{ij}$) and $\Omega(r_{ij}-\xi_{ij})=1$ otherwise. Substituting Eq. (34) into Eq. (35) and then into the general equation (A6) and (A7) we obtain, in the case of the perfect nematic ordering, the following contribution to the effective one-particle potential:

$$\begin{aligned}\mathbf{C}_1(\hat{\mathbf{b}},\hat{\mathbf{c}})=&-\rho_0\frac{1}{4kT}(1-\sigma)\int d\hat{\mathbf{u}}_{ij}\xi_{ij}^{-4}\delta((\hat{\mathbf{u}}_{ij}\cdot\hat{\mathbf{e}})^2-1)\\&\times[6(\boldsymbol{\mu}_i\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}}_{ij})-5(\boldsymbol{\mu}_i\cdot\hat{\mathbf{u}}_{ij})(\hat{\mathbf{u}}_{ij}\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}}_{ij})]\\&+\rho_0\frac{1}{4kT}\sigma\int d\hat{\mathbf{u}}_{ij}\delta[(\hat{\mathbf{u}}_{ij}\cdot\hat{\mathbf{e}})]\xi_{ij}^{-4}[6(\boldsymbol{\mu}_i\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}}_{ij})\\&-5(\boldsymbol{\mu}_i\cdot\hat{\mathbf{u}}_{ij})(\hat{\mathbf{u}}_{ij}\cdot\mathbf{Q}_i\cdot\hat{\mathbf{u}}_{ij})],\end{aligned} \tag{36}$$

where we have taken the integral over r_{ij}.

In general the function ξ_{ij} depends on the orientation of the short molecular axes of the two molecules. For the molecules with parallel long axes one can approximately write

$$\xi_{ij}\approx D+(\mathbf{s}_i\cdot\hat{\mathbf{u}}_{ij})+(\mathbf{s}_j\cdot\hat{\mathbf{u}}_{ij})+\cdots, \tag{37}$$

where $\mathbf{s}_i$ and $\mathbf{s}_j$ are the transverse steric dipoles of the molecules i and j, respectively.

In the description of the ferroelectric properties of the smectic-C^* phase one can, in a first approximation, neglect the interaction between the molecules in neighboring smectic layers because the corresponding intermolecular interaction is much weaker than the interaction between neighboring molecules that belong to the same smectic layer. Substituting Eq. (37) into Eq. (36) and neglecting the first term in Eq. (36), one obtains, after integration over $\hat{\mathbf{u}}_{ij}$,

$$\begin{aligned}C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})\approx&\frac{\rho_0\chi^H\sigma}{48kTD^5}[10(\boldsymbol{\mu}\cdot\hat{\mathbf{e}})(\mathbf{s}\cdot\mathbf{Q}\cdot\hat{\mathbf{e}})-2(\mathbf{s}\cdot\hat{\mathbf{e}})\\&+5(\mathbf{s}\cdot\boldsymbol{\mu})(\hat{\mathbf{e}}\cdot\mathbf{Q}\cdot\hat{\mathbf{e}})-15(\mathbf{s}\cdot\hat{\mathbf{e}})(\boldsymbol{\mu}\cdot\hat{\mathbf{e}})(\hat{\mathbf{e}}\cdot\mathbf{Q}\cdot\hat{\mathbf{e}})].\end{aligned} \tag{38}$$

Equation (38) represents a contribution from the dipole and quadrupole induction interaction to the effective one-particle potential of the smectic-C^* phase. On the other hand, the general expansion of the one-particle potential $C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})$ is given by Eq. (5). At this stage we are interested only in the second term $(\mathbf{S}\cdot\mathbf{w})$ in expansion (5), which gives rise to the spontaneous polarization. Thus one has to single out the corresponding contribution from Eq. (38). Then it will readily be possible to derive an explicit expression for the vector $\mathbf{S}$, which is used in expressions (19) and (20) for the spontaneous polarization. A possible way to do this is to define a vector $\mathbf{p}$, parallel to the spontaneous polarization:

$$\mathbf{p}=\int d\hat{\mathbf{b}}\ \boldsymbol{\mu}_\perp\Delta C_1(\hat{\mathbf{b}},\hat{\mathbf{c}}), \tag{39}$$

For symmetry reasons [see the derivation of Eq. (14) in Sec. II] the vector $\mathbf{p}$ must have the form

$$\mathbf{p}=\frac{1}{2}(\mathbf{S}\cdot\boldsymbol{\mu}_\perp)(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})[\hat{\mathbf{n}}\times\hat{\mathbf{e}}], \tag{40}$$

and thus the vector $\mathbf{S}$ can be obtained from the explicit expression for $\mathbf{p}$. We note that not all terms in Eq. (38) contribute to the spontaneous polarization. For example, the term $(\mathbf{s}\cdot\boldsymbol{\mu})(\hat{\mathbf{e}}\cdot\mathbf{Q}\cdot\hat{\mathbf{e}})$ does not depend on the orientation of the short molecular axes if the tensor $Q_{\alpha\beta}$ is uniaxial.

Substituting Eq. (38) into Eq. (39) and assuming for simplicity that the molecular quadrupole tensor $Q_{\alpha\beta}$ is uniaxial (i.e., $Q_{\alpha\beta}=Q[a_\alpha a_\beta-(1/3)\delta_{\alpha\beta}]$) one obtains

$$\mathbf{p}=\frac{7}{396}\rho_0\frac{\chi^H\sigma}{kTD^5}Q\{\boldsymbol{\mu}_\perp\cdot[\mathbf{s}\times\hat{\mathbf{a}}](\boldsymbol{\mu}\cdot\hat{\mathbf{a}})\mathbf{w}\}. \tag{41}$$

From Eqs. (40) and (41) one obtains the final expression for the parameter $(\boldsymbol{\mu}\cdot\mathbf{s})$ in Eqs. (19) and (20) for the spontaneous polarization

$$(\boldsymbol{\mu}\cdot\mathbf{s})=\frac{7}{144}\frac{\rho_0\sigma\chi^H}{kTd^5}Q(\boldsymbol{\mu}_\perp\cdot[\mathbf{s}\times\hat{\mathbf{a}}])(\boldsymbol{\mu}\cdot\hat{\mathbf{a}}). \tag{42}$$

We note that the quantity $(\boldsymbol{\mu}_\perp\cdot\mathbf{s})$ is indeed proportional to the pseudoscalar parameter $\Delta_0=(\boldsymbol{\mu}_\perp\cdot[\mathbf{s}\times\mathbf{a}])(\boldsymbol{\mu}\cdot\hat{\mathbf{a}})$, which is a measure of molecular chirality in the context of this simple model. In this case the molecular chirality is characterized by three noncoplanar vectors: the steric dipole $\mathbf{s}$, the electric dipole $\boldsymbol{\mu}$, and the long molecular axis $\hat{\mathbf{a}}$. The chirality parameter Δ_0 is nonzero when these three vectors are not parallel to the same plane. It should also be noted that the pseudoscalar Δ_0 differs from Δ given by Eq. (23) and (26) because it is based on a different molecular model.

If the chiral center of the dopant molecule is in the flexible chain, the orientation of the molecular hard core is practically decoupled from that of the chiral center. As discussed in Sec. II, in this case the spontaneous polarization is determined by the first term in Eq. (19):

$$P_s\approx\rho_0x_D\chi_0(\boldsymbol{\mu}\cdot\mathbf{s})\sin 2\Theta. \tag{43}$$

In the general case the quantity $(\boldsymbol{\mu}\cdot\mathbf{s})$ is a sum of the two different contributions given by Eqs. (24) and (25) and Eq. (41), respectively. These contributions are determined by different intermolecular interactions. However, in the case of large molecular quadrupoles Q the contribution (41) is predominant and the spontaneous polarization can approximately be expressed as

$$P_s \approx \frac{1}{2}\rho_0^2 x_D \kappa \Delta_0 \chi^H \sin 2\Theta, \tag{44}$$

where $\kappa = (7/144)(\sigma Q \chi_0 / kTD^5)$.

We note that in this case the spontaneous polarization is approximately proportional to the average polarizability χ^H of the host phase molecule. This polarizability is related to the average refractive index of the host phase, which does not significantly depend on the molecular structure of the nonchiral smectic-*C* phase. Thus the spontaneous polarization, induced by chiral dopant molecules of type I (see Fig. 1), is not expected to depend significantly on the molecular structure of the host phase. This conclusion is in agreement with our experimental data [3,5,6].

B. Sign inversion of the quadrupole order parameter of a dopant molecule in the smectic-C^* phase

In the preceding subsection we have obtained an expression for the spontaneous polarization induced by chiral dopant molecules of type I that possess a chiral center in the flexible chain. In this case the spontaneous polarization P_0 appears to be practically independent on the molecular structure of the smectic-*C* host phase. By contrast, the spontaneous polarization induced by dopant molecules of type II is very sensitive to the molecular parameters of the host phase because it depends on the quadrupole order parameter B_D of the dopant molecule in the host phase. [See the second term in Eq. (19)]. In the general case the parameter B_D is determined by the sum of all intermolecular interactions with quadrupolar symmetry. Thus one expects that the parameter B_D must depend, for example, on the shape and polarizability anisotropy of the hard core of the host phase molecule. This conclusion enables one to understand qualitatively the host phase dependence of the spontaneous polarization observed in Refs. [2,6].

It should be noted that one and the same chiral dopant of type II can induce polarizations of opposite signs in different smectic-*C* host phases (see Fig. 2). This result is more difficult to explain in the context of the present theory. Indeed, the first term in Eq. (19) for the spontaneous polarization practically does not depend on the parameters of the smectic-*C* host phase. The second term can depend on the host phase only via the quadrupole order parameter B_D. Thus the only possibility to explain the host phase dependence of the polarization sign is to assume that the quadrupole order parameter of the dopant molecule can have opposite signs in different host phases.

This possibility seems to be in contradiction with naive expectations because, from the close-packing point of view, flat cores of dopant and host phase molecules are expected to be parallel. In this case the sign of the parameter B_D must always coincide with that of the quadrupole order parameter B_H of the host phase. Nevertheless, we are going to show that in some cases the flat core of a dopant molecule can be oriented perpendicularly to the core of the neighbor host phase molecule due to strong dipole-induced dipole interaction between the transverse dipole of the host phase molecule and the polarizability of the dopant molecule hard core.

We note that some of the smectic-*C* host phases used in [3] (see Table 2 of Ref. [3]) are composed of molecules possessing large transverse dipoles that are approximately perpendicular to the plane of the ring (e.g., CCN host compounds with a CN dipole perpendicular to the cyclohexane ring). At the same time, in other host smectic-*C* phases the molecules bear the transverse dipoles approximately parallel to the plane of the rings (e.g., host compound 8OO7 with the in-plane C=O dipole). This situation is shown in Fig. 10. From Fig. 2 one can readily see that opposite signs of the induced polarization are observed for host phases that differ significantly in the orientation of the dipole with respect to the flat core. The importance of the dipole orientation within a hard-core structure can be understood in the following simple way.

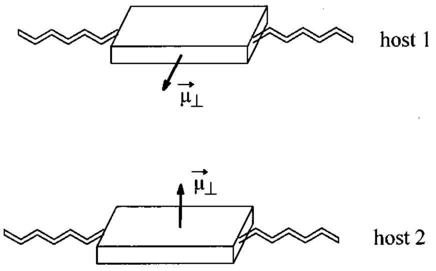


FIG. 10. Schematic structures of different host phase molecules showing the transverse dipole $\boldsymbol{\mu}_\perp$ in the core plane (e.g., host 8007) or perpendicular to the core plane (e.g., NCB808).

Let us consider the induction interaction between the permanent dipole $\boldsymbol{\mu}^H$ of the host phase molecule and the polarizability of the neighbor dopant molecule. The corresponding interaction potential can be written as

$$V_{\mathrm{ind}}(i,j) = \mu_\alpha^H T_{\alpha\beta}(\mathbf{r}_{ij}) \chi_{\beta\gamma}^D T_{\gamma\delta}(\mathbf{r}_{ij}) \mu_\delta^H, \tag{45}$$

where $T_{\alpha\beta}$ is given by Eq. (30) and $\chi_{\beta\gamma}^D$ is the polarizability of the dopant molecule. The tensor $\chi_{\alpha\beta}^D$ can be represented as a sum of its irreducible components

$$\chi_{\alpha\beta}^D = \overline{\chi^D}\delta_{\alpha\beta} + \Delta\chi^D(a_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}) + \Delta\chi_\perp^D(b_\alpha b_\beta - c_\alpha c_\beta), \tag{46}$$

where $\overline{\chi^D}$ is the average polarizability, $\Delta\chi^D$ is the anisotropy of the polarizability, and $\Delta\chi_\perp^D$ is the anisotropy of the transverse polarizability of the dopant.

In this section we consider the interaction potential between two molecules with parallel long axes. In this case one has to take into account only the last term in Eq. (46) because this is the only one that depends on the orientation of the short molecular axes $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$. Now we discuss the influence of the interaction (45) on the value and sign of the quadrupole order parameter of the dopant molecule B_D, given by

$$B_D = \int d\hat{\mathbf{b}}[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2 - (\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2] f_D(\hat{\mathbf{b}},\hat{\mathbf{c}}), \tag{47}$$

where $f_D(\hat{\mathbf{b}},\hat{\mathbf{c}})$ is the distribution function of the dopant in the smectic-C^* phase.

By contrast to the spontaneous polarization, the quadrupole order parameter does not vanish in the nochiral smectic-*C* phase. Thus, in the first approximation one can neglect the relatively weak chiral part of the total interaction in Eqs. (4) and (12) for the distribution function f_D. Then the function f_D can be expressed as [see Eqs. (4), (12), and Eq. (A13)]

$$f_D(\hat{\mathbf{b}},\hat{\mathbf{c}})=\frac{1}{Z_0}\exp\{-\beta(\Delta K\sin 2\Theta+\Delta M)\times[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2]\}, \tag{48}$$

where

$$\Delta K=x_D K^D+x_H K^H,\quad \Delta M=x_D\Delta M^D B_D+x_H\Delta M^H B_H. \tag{49}$$

We note that in the general case the distribution function of the dopant depends on the molar fractions of the dopant and host phase molecules x_D and x_H and on the corresponding quadrupole order parameters B_D and B_H. However, at small dopant molar fraction $x_D \ll 1$ one can neglect the corresponding contributions in Eqs. (49). At small tilt angles $\Theta \ll 1$ it is also possible to neglect the term $\Delta K \sin 2\Theta$ in Eq. (48). Then one obtains the following simplified equation for the quadrupole order parameter of the dopant molecule:

$$B_D\approx\frac{1}{Z_0}\int\cos 2\psi\,\exp(-\beta x_H\Delta M^H B_H\cos 2\psi)\,d\cos\psi, \tag{50}$$

where $\cos\psi=(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})$. According to Eq. (50), at small dopant concentration and small tilt angles the dopant quadrupole order parameter is determined by the quadrupole order parameter B_H of the host phase and by the coupling constant ΔM^H, which is related to the corresponding interactions between dopant and host phase molecules. We note also that the sign of the parameter B_D is reversed if the coupling constant ΔM^H changes sign.

Now we are in a position to consider the influence of the induction interaction (45) on the sign of the quadrupole order parameter B_D. For this purpose we calculate the contribution from the interaction (44) to the coupling constant ΔM^H using the mean-field approximation for the direct correlation function $C_{HD}(1,2)$. Substituting the last term of Eq. (46) for the polarizability $\chi^D_{\alpha\beta}$ into Eq. (45) for the induction interaction potential and then substituting Eq. (45) into the general Eqs. (A6) and (A7), one obtains after integration over $\mathbf{r}_{ij}$

$$\delta C_D(\cos 2\psi)\approx x_H\Delta M^H B_H\cos 2\psi, \tag{51}$$

where

$$\Delta M^H=\frac{1}{9}\rho_0\sigma\Delta\chi^D_\perp(\mu_x^2-\mu_y^2). \tag{52}$$

One can readily see from Eq. (50) that the coupling constant ΔM^H can have different signs depending on the orientation of the permanent dipole $\boldsymbol{\mu}^H_\perp$ of the host phase molecule with respect to the main axes of the molecular hard core. The sign of ΔM^H is determined by the factor $(\mu_x^2-\mu_y^2)$. According to our definition of the quadrupole order parameter, the parameter B_H is positive if the molecular short axis $\hat{\mathbf{b}}$ is approximately parallel to the direction of the spontaneous polarization. Let us assume that the axis $\hat{\mathbf{b}}$ is perpendicular to the plane of the hard core. In this case μ_x is the component of the transverse dipole that is perpendicular to the core and μ_y is the corresponding component that is parallel to the core.

In the experiments described in Ref. [7], some host phases possessed the strongly polar CN group that is approximately perpendicular to the flat hard core (see Fig. 10). In this case $\mu_x \gg \mu_y$ and the quantity $(\mu_x^2-\mu_y^2)$ is positive. It follows then from Eqs. (50) and (52) that the sign of the quadrupole order parameter B_D is opposite that of the order parameter B_H. This means that the flat core of the dopant molecules is oriented perpendicularly to the flat cores of neighboring host phase molecules. This result can readily be understood qualitatively. Indeed, the flat core of the dopant molecule is supposed to be more polarizable in the direction parallel to the core. Then the core of the dopant molecule has a tendency to be parallel to the transverse dipole of the neighbor host phase molecule. This dipole is perpendicular to the plane of the host phase molecule hard core and, as a result, the hard core of the dopant molecule is also oriented perpendicular to those of the neighboring host phase molecules.

By contrast, for host phase molecules with large in-plane dipoles (see Fig. 10) one finds $\mu_y \gg \mu_x$ and therefore the corresponding factor is negative. In this case the sign of the quadrupole order parameter B_D coincides with that of the parameter B_H and hence the flat core of the dopant molecule is oriented parallel to the flat cores of the neighboring host phase molecules. These qualitative results, obtained in the framework of a simple molecular model, enable one to explain the experimental results of Ref. [7].

Finally, we consider the case when the molar fraction of the dopant is not small. This corresponds to our recent measurements of the spontaneous polarization in a broad range of concentrations of the chiral mesogenic compound [8]. In this system the sign inversion of the polarization has been observed at relatively large dopant molar fraction $x_D \approx 0.5$ (see Fig. 3). We note that Eqs. (48) and (49) for the distribution function of the dopant molecules are valid for arbitrary concentration of the chiral dopant. Then, at small tilt angles $\Theta^2 \ll 1$ the quadrupole order parameter of the dopant can be expressed as

$$B_D=\frac{1}{Z_0}\int\cos 2\psi\,\exp\left[-\frac{1}{kT}(x_H\Delta M^H B_H+x_D\Delta M^D B_D)\cos 2\psi\right]d\cos\psi. \tag{53}$$

Here the coupling constant ΔM^H is determined by the interaction between dopant and host phase molecules, while the constant ΔM^D is determined by the interaction between two dopant molecules. At small dopant molar fraction the quadrupole order parameter B_D is determined only by the constant ΔM^H. As discussed above, this coupling constant can be negative if the host phase molecules possess large transverse dipoles that are perpendicular to the flat core. Then the quadrupole order parameter of the dopant is negative, while that of the host phase is positive.

In the opposite limiting case of high dopant molar fraction (i.e., when $x_H \ll 1$) the parameter B_D is mainly determined by the dopant-dopant interaction. It is reasonable to assume that the flat cores of two *equal* dopant molecules always have a tendency to be parallel and thus the coupling constant ΔM^D must always be positive. Then the quadrupole order parameter B_D is also positive at high dopant concentration (including the smectic-C* phase composed of dopant molecules only).

Thus we arrive at the conclusion that if the host phase molecules possess large dipoles perpendicular to the flat core, as it is the case for CCN hosts (see Fig. 10), the quadrupole order parameter of the dopant is expected to have opposite signs at small and large dopant molar fractions, respectively. Therefore the quadrupole order parameter B_D must change sign at some intermediate dopant concentration. According to Eq. (19), this sign reversal of B_D can induce a sign inversion of the spontaneous polarization (if the quadrupole order parameter is large). These qualitative arguments can be considered as an explanation of the polarization sign inversion observed in [8].

IV. DISCUSSION

In recent years the properties of induced smectic-C* phases have been extensively studied experimentally by Stegemeyer *et al.* [3] and it became clear that a number of new results cannot be explained in the framework of the existing theory [13,14]. In this paper we have made an attempt to explain qualitatively the main ferroelectric properties of induced smectic-C* phases using the general statistical theory presented in the Appendix, and a more realistic molecular model. We have also presented several very recent results that confirm some of our theoretical conclusions [7,8,23].

The molecular model used in the present theory takes into consideration the following two characteristics of the molecular structure of the dopant molecules. First, we distinguish between the chiral dopant molecules of type I and type II, which are schematically presented on Fig. 1. The difference between the two types of the dopant molecules is in the position of the chiral center and of the transverse dipole. In molecules of type I both are located in the flexible chain and possess a significant rotational freedom with respect to the molecular rigid core. In molecules of type II both are located in the rigid core.

Second, we take into account that molecular rigid cores are biaxial in shape and possess some quadrupole-type ordering in the biaxial smectic-C* phase. This quadrupole ordering of flat rigid cores is not related to chirality and exists also in the nonchiral smectic-C phase. Nevertheless, in the ferroelectric smectic-C* liquid crystals the quadrupole ordering of the core can be strongly coupled with the polar ordering of the molecular transverse dipole. However, this coupling is different for dopant molecules of different types. In molecules of type I the transverse dipole is decoupled from the rigid core and one cannot expect any significant influence of the quadrupole ordering of the core on the ordering of this dipole. We note that only the dipoles directly attached to the chiral center are important here [13] because they take part in the corresponding interaction between the chiral center and the polarizability of the neighbor molecule (see Sec. III A) that is responsible for the spontaneous polarization. By contrast, in molecules of type II the transverse dipoles are also located in the rigid core and hence there must be a strong coupling between the dipolar and quadrupolar types of ordering of such rigid cores. In Sec. II B we derived the explicit expression for the polarization induced by the dopant molecules of type II, in terms of the quadrupole order parameter. It has been shown that if the quadrupole order parameter is large, it can influence both the absolute value and the sign of the spontaneous polarization.

The polarization induced by the chiral dopant of type I is determined mainly by the induction interaction between the dipole and quadrupole of the chiral fragment of the dopant molecule and the average polarizability of the host phase molecule. The resulting polarization practically does not depend on the molecular structure of the host phase because the average polarizability is not sensitive to the details of the molecular structure. At the same time the polarization induced by the dopant of type II *is* sensitive to the molecular structure of the host phase because it depends on the quadrupole order parameter of the rigid core. At small dopant molar fraction this quadrupole order parameter is determined by the hard-core interaction between rigid cores of dopant and host phase molecules and is expected to be sensitive to the structure of both rigid fragments. In particular, it must be sensitive to the orientation of the strong permanent dipole with respect to the main axes of the hard core. As shown in Sec. III B, the strong dipole-dipole induction interaction can be responsible for the different signs of the quadrupole order parameter of the dopant depending on the orientation of the transverse dipole within the rigid core of the host phase molecule (see Fig. 10). In the context of this model it is possible to understand why one and the same chiral dopant can induce polarizations of opposite signs in two different host phases (see Fig. 2). This effect is related to the different equilibrium orientations of the dopant cores with respect to the tilt plane in different host phases. In the two different cases the transverse dopant dipole appears to be oriented above or below the tilt plane [31]. One expects opposite signs of the induced polarization in the two host phases if one of them is composed of molecules with in-plane dipoles, while in the molecules of the other phase the dipoles are perpendicular to the flat rigid core (see Fig. 10). In the same way it is possible to explain qualitatively the sign inversion of the spontaneous polarization induced by a change of concentration of the chiral dopant (see Fig. 3). In this case the polarization sign inversion is determined by the inversion of the quadrupole order parameter of the dopant molecule. This parameter is expected to have opposite signs in the two limiting cases of very small and very large dopant concentration, respectively.

The quadrupole ordering of biaxial molecules has already been taken into account in the theory of one-component smectic-C* liquid crystals [11,31,9,10]. It has been shown that the coupling between spontaneous polarization and the quadrupole order parameter can be responsible for the unusual temperature variation of the polarization to tilt ratio that is observed in some ferroelectric smectic-C* liquid crystals close to the smectic-A–smectic-C* transition point [11]. Two of the present authors have also used the simple model of quadrupole ordering in the description of the strong sensitivity of the spontaneous polarization to some changes of the rigid core structure that affect neither the molecular chirality nor the permanent dipole [31]. The results of the present paper also indicate that the molecular theory of the induced smectic-*C** phase appears to be incomplete if one does not take into account quadrupole ordering. This ordering, however, seems to influence the spontaneous polarization only if the chiral center (and the transverse dipole) of the dopant molecule is located in some rigid flat fragment that can order independently in the biaxial smectic-*C* phase.

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APPENDIX: MOLECULAR THEORY OF FERROELECTRIC ORDERING IN INDUCED SMECTIC-*C** PHASES—GENERAL RESULTS

As discussed in Sec. II, the spontaneous polarization is determined by the difference between the one-particle distribution functions of the smectic-*C** and the smectic-*A* phases:

$$\mathbf{P}_s = \rho_0 x_D \int \boldsymbol{\mu}_\perp \Delta f_1(\mathbf{x}) d\mathbf{x}, \qquad \text{(A1)}$$

where $\Delta f_1(\mathbf{x}) = f_{1C}(\mathbf{x}) - f_{1A}(\mathbf{x})$. The general expression for the difference Δf_1 can be obtained using the density-functional approach to the theory of liquid crystals [32]. In this approach the free energy of the system can be represented as a functional of the one-particle density $\rho(\mathbf{x}) = \rho_0 f_1(\mathbf{x})$. In the case of mixtures the free-energy functional depends on the densities $\rho_\alpha(\mathbf{x})$ of all components α. This functional can be written as a sum of two terms $F = \Phi + H$, where Φ is the free energy of the system without intermolecular interactions $\Phi = \Sigma_\alpha kT\rho_0 x_\alpha \int d\mathbf{x}\, f_\alpha(\mathbf{x})[\ln f_\alpha(\mathbf{x}) + 1]$, where $f_\alpha(\mathbf{x})$ are the distribution functions of the molecules of the components and α and x_α are the corresponding molar fractions. The functional derivatives of H are related to the direct correlation functions of the liquid crystal. For example,

$$\frac{\delta^2 H}{\delta f_\alpha(\mathbf{x}_1)\, \delta f_\beta(\mathbf{x})} = -kT\rho_0^2 C_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2), \qquad \text{(A2)}$$

where $C_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2)$ is the direct correlation function between the molecules of components α and β.

This relation enables one to expand the free energy of the ferroelectric smectic-*C** phase with respect to its value in the smectic-*A* phase, using the differences Δf_α as expansion parameters. One can neglect the higher-order terms in the corresponding functional Taylor expansion of the free-energy functional because for small tilt angles Θ the differences Δf_α are also small.

Now the free energy of the induced smectic-*C** phase can be written as

$$\begin{aligned} F_C \approx F_A &+ kT\rho_0 x_D \int d\mathbf{x}\, f_{CD}(\mathbf{x}) \ln[f_{CD}(\mathbf{x})/f_{AD}(\mathbf{x})] \\ &+ kT\rho_0 x_H \int d\mathbf{x}\, f_{CH}(\mathbf{x}) \ln[f_{CH}(\mathbf{x})/f_{AH}(\mathbf{x})] \\ &- (kT/2)\rho_0^2 \sum_{\alpha,\beta=H,D} x_D x_H \\ &\times \int d\mathbf{x}_1 d\mathbf{x}_2 C_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \Delta f_\alpha(\mathbf{x}_1) \Delta f_\beta(\mathbf{x}_2), \end{aligned} \qquad \text{(A3)}$$

where $f_H(\mathbf{x})$ and $f_D(\mathbf{x})$ are the one-particle distribution functions of the host phase and dopant molecules, respectively while x_H and x_D are the corresponding molar fractions.

Minimization of the free energy (A3) yields the following expression for the distribution function f_D:

$$\begin{aligned} f_D(\mathbf{x}) = f_D^A \frac{1}{Z_D} \exp\Big(& x_M \int C_{MD}(\mathbf{x}_1, \mathbf{x}_2) \Delta f_M(\mathbf{x}_2) d\mathbf{x}_2 \\ & + x_D \int C_{DD}(\mathbf{x}_1, \mathbf{x}_2) \Delta f_D(\mathbf{x}_2) d\mathbf{x}_2 \Big). \end{aligned} \qquad \text{(A4)}$$

One can readily see from Eq. (A4) that in the general case the distribution function of the dopant molecules is determined both by the correlation function $C_{MD}(\mathbf{x}_1, \mathbf{x}_2)$ between the dopant and host phase molecules and the correlation function $C_{DD}(\mathbf{x}_1, \mathbf{x}_2)$ between the dopant molecules. The latter contribution, however, is proportional to the molar fraction of the dopant and therefore it is negligible when the dopant concentration is small (i.e., when the dopant molecule is surrounded predominantly by host phase molecules).

In the case of perfect nematic order the distribution function $f_D(\mathbf{x})$ depends only on the orientation of the short molecular axes $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$ [see Eq. (4) and Fig. 6]. Then Eq. (A4) can be rewritten as

$$f_D(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = \frac{1}{Z_D} \exp[C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}})], \qquad \text{(A5)}$$

where the effective one-particle potential $C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}})$ can be represented as a sum of two terms

$$C_1(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = x_M C_M(\hat{\mathbf{b}}, \hat{\mathbf{c}}) + x_D C_D(\hat{\mathbf{b}}, \hat{\mathbf{c}}), \qquad \text{(A6)}$$

with

$$C_M(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = \int \overline{C_{MD}}(\hat{\mathbf{b}}, \hat{\mathbf{c}}, \hat{\mathbf{b}}_2, \hat{\mathbf{c}}_2) \Delta f_M(\hat{\mathbf{b}}_2, \hat{\mathbf{c}}_2) d\hat{\mathbf{b}}_2,$$

$$C_D(\hat{\mathbf{b}}, \hat{\mathbf{c}}) = \int \overline{C_{DD}}(\hat{\mathbf{b}}, \hat{\mathbf{c}}, \hat{\mathbf{b}}_2, \hat{\mathbf{c}}_2) \Delta f_D(\hat{\mathbf{b}}_2, \hat{\mathbf{c}}_2) d\hat{\mathbf{b}}_2, \qquad \text{(A7)}$$

where $\overline{C_{MD}}(\hat{\mathbf{b}}, \hat{\mathbf{c}}, \hat{\mathbf{b}}_2, \mathbf{c}_2)$ and $\overline{C_{DD}}(\hat{\mathbf{b}}, \hat{\mathbf{c}}, \hat{\mathbf{b}}_2, \hat{\mathbf{c}}_2)$ are the effective direct correlation functions averaged over all positions of neighboring molecules in the ideal smectic structure:

$$\overline{C_{\alpha\beta}}(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2)=\sigma\int C_{\alpha\beta}(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2,\mathbf{r}_{12})\times\delta((\mathbf{r}_{12}\cdot\hat{\mathbf{e}}))d^3\mathbf{r}_{12}+(1-\sigma)\times\int C_{\alpha\beta}(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2,\hat{\mathbf{e}}r_{12})r_{12}^2dr_{12}. \tag{A8}$$

Here $\alpha=D,\ M$ and σ is the fraction of nearest neighbors that are in the same plane as the central molecule. The first term in Eq. (A7) is a contribution from the correlations between the central molecule and the nearest neighbors of the same component that are in the same smectic plane. For such molecules $\mathbf{r}_{12}\perp\hat{\mathbf{e}}$. The second term is a contribution from the molecules that are in two neighboring planes. In this case $\mathbf{r}_{12}\|\hat{\mathbf{e}}$.

Equations (A5)–(A7) are the general expressions for the effective one-particle potential $C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})$, which has been introduced phenomenologically in Sec. II. In Eqs. (A5)–(A7) the effective potential is expressed in terms of the direct correlation functions between host phase and dopant molecules. Now it is also possible to derive the expressions for the quantities $\mathbf{S}$, $\mathbf{G}$, $K_{\alpha\beta}$, and $M_{\alpha\beta}$ in the expansion (5).

For this purpose we expand the functions $C_{DM}(1,2)$ and $C_{DD}(1,2)$ in terms of irreducible tensors composed of the components of the vectors $\hat{\mathbf{b}}$, $\hat{\mathbf{c}}$, $\hat{\mathbf{u}}_{12}$, and $\hat{\mathbf{n}}$ and write down the first few terms

$$\begin{aligned}C_{Dj}(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2,\mathbf{r}_{12})={}&\{(J_x^j\hat{\mathbf{b}}_1+J_y^j\mathbf{c}_1)\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{u}}_{12}](\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})\}+\{(J_x^D\hat{\mathbf{b}}_2+J_y^D\hat{\mathbf{c}}_2)\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{u}}_{12}](\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})\}+K_x^D(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{u}}_{12})\\&+K_y^D(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})(\hat{\mathbf{c}}_1\cdot\hat{\mathbf{u}}_{12})+K_x^j(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{u}}_{12})+K_x^j(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})(\hat{\mathbf{c}}_2\cdot\hat{\mathbf{u}}_{12})+I_{xx}^{Dj}(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{b}}_2)\\&+I_{yy}^{Dj}(\hat{\mathbf{c}}_1\cdot\hat{\mathbf{c}}_2)+I_{xy}^{Dj}[(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{c}}_2)+(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{c}}_1)]+G^{Dj}B_{\alpha\beta}^{(1)}B_{\alpha\beta}^{(2)}+H^{Dj}B_{\alpha\gamma}^{(1)}u_\gamma u_\beta B_{\alpha\beta}^{(2)}\\&+M^{DD}B_{\alpha\gamma}^{(1)}u_\gamma u_\beta+M^{Dj}B_{\alpha\gamma}^{(2)}u_\gamma u_\beta,\end{aligned} \tag{A9}$$

where $j=H,D$ and $B_{\alpha\beta}^{(1)}=b_\alpha b_\beta-c_\alpha c_\beta$. Substituting Eq. (A9) into Eq. (A8) and averaging over $\hat{\mathbf{u}}_{12}\perp\hat{\mathbf{e}}$ one obtains

$$\begin{aligned}\overline{C_{Dj}}(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1,\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2,\hat{\mathbf{e}})={}&\{(J_x^j\hat{\mathbf{b}}_1+J_y^j\hat{\mathbf{c}}_1)\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{e}}](\mathbf{n}\cdot\hat{\mathbf{e}})\}(1-\tfrac{3}{2}\sigma)+\{(J_x^D\hat{\mathbf{b}}_2+J_y^D\hat{\mathbf{c}}_2)\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{e}}](\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})\}(1-\tfrac{3}{2}\sigma)\\&+K_x^D(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{e}})(1-\tfrac{3}{2})+K_y^D(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{c}}_1\cdot\hat{\mathbf{e}})(1-\tfrac{3}{2})+K_x^j(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{e}})(1-\tfrac{3}{2}\sigma)\\&+K_x^j(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\mathbf{c}_2\cdot\hat{\mathbf{e}})(1-\tfrac{3}{2}\sigma)+I_{xx}^{Dj}(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{b}}_2)+I_{yy}^{Dj}(\hat{\mathbf{c}}_1\cdot\hat{\mathbf{c}}_2)+I_{xy}^{Dj}[(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{c}}_2)+(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{c}}_1)]\\&+\left(G^{Dj}+\frac{\sigma}{2}H^{Dj}\right)B_{\alpha\beta}^{(1)}B_{\alpha\beta}^{(2)}-H^{Dj}(1+\tfrac{1}{2}\sigma)B_{\alpha\gamma}^{(1)}e_\gamma e_\beta B_{\alpha\beta}^{(2)}\\&-M^{DD}(1+\tfrac{1}{2}\sigma)B_{\alpha\gamma}^{(1)}e_\gamma e_\beta-M^{Dj}(1+\tfrac{1}{2}\sigma)B_{\alpha\gamma}^{(2)}e_\gamma e_\beta,\end{aligned} \tag{A10}$$

where $j=D,H$.

Finally, one substitutes the functions $\overline{C_{DH}}(1,2)$ and $\overline{C_{DD}}(1,2)$ into Eqs. (A4)–(A7) and performs the orientational averaging with the distribution functions $\Delta f_H(\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2)$ and $\Delta f_D(\hat{\mathbf{b}}_2,\hat{\mathbf{c}}_2)$. One obtains the following expressions for the two parts of the effective one-particle potential $C_1(\hat{\mathbf{b}}_1,\hat{\mathbf{c}}_1)$:

$$\begin{aligned}C_H(\hat{\mathbf{b}},\hat{\mathbf{c}})={}&J_x^{HD}(\hat{\mathbf{b}}\cdot\mathbf{w})+J_y^{HD}(\hat{\mathbf{c}}\cdot\mathbf{w})+I_{xx}^{HD}(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{b}}\rangle)+I_{yy}^{HD}(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{c}}\rangle)+I_{xy}^{HD}[(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{c}}\rangle)+(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{b}}\rangle)]+K_x^{HD}(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})+K_y^{HD}(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})\\&+M^{HD}[(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})^2]+G^{HD}B_H[(\hat{\mathbf{b}}\cdot\mathbf{w}_0)^2-(\hat{\mathbf{c}}\cdot\mathbf{w}_0)^2]\end{aligned} \tag{A11}$$

and

$$\begin{aligned}C_D(\hat{\mathbf{b}},\hat{\mathbf{c}})={}&J_x^{DD}(\hat{\mathbf{b}}\cdot\mathbf{w})+J_y^{DD}(\hat{\mathbf{c}}\cdot\mathbf{w})+I_{xx}^{DD}(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{b}}\rangle)+I_{yy}^{DD}(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{c}}\rangle)+I_{xy}^{DD}[(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{c}}\rangle)+(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{b}}\rangle)]+K_x^{DD}(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})+K_y^{DD}(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})\\&+M^{DD}[(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})^2]+G^{DD}B_M[(\hat{\mathbf{b}}\cdot\mathbf{w}_0)^2-(\hat{\mathbf{c}}\cdot\mathbf{w}_0)^2],\end{aligned} \tag{A12}$$

where

$$J_i^\alpha=J_i^{D\alpha}(1+\tfrac{1}{2}\sigma),\quad K_i^\alpha=K_i^{D\alpha}(1+\tfrac{1}{2}\sigma),$$

$$M^{D\alpha}=M^{D\alpha}(1+\tfrac{1}{2}\sigma),$$

$$G^{D\alpha}=-2\left(G^{D\alpha}+\frac{\sigma}{2}H^{D\alpha}\right)-\sin^2\Theta H^{D\alpha}(1+\tfrac{1}{2}\sigma),$$

with $\alpha=M,D$ and $i=x,y$.

Now Eqs. (A11) and (A12) can be reduced to the form of Eq. (12) after some straightforward algebra. One can readily see that $[(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})^2]=-\cos^{-2}\Theta[(\hat{\mathbf{b}}\cdot\mathbf{w}_0)^2-(\hat{\mathbf{c}}\cdot\mathbf{w}_0)^2]$, $\langle\hat{\mathbf{b}}\rangle=(\rho_0\mu)^{-1}\mu_x\mathbf{P}$, and $\langle\hat{\mathbf{c}}\rangle=(\rho_0\mu)^{-1}\mu_y\mathbf{P}$, where μ is the absolute value of the molecular dipole and **P** is the macroscopic polarization. Using these relations the expression $M^{HD}[(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})^2-(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})^2]$ in Eq. (A11) can be transformed into $-M^{HD}\cos^{-2}\Theta[(\hat{\mathbf{b}}\cdot\mathbf{w}_0)^2-(\hat{\mathbf{c}}\cdot\mathbf{w}_0)^2]$, which corresponds to the fifth term in Eq. (12) of Sec. II. It is also possible to rewrite the sum

$$I_{xx}^{MD}(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{b}}\rangle)+I_{yy}^{MD}(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{c}}\rangle)+I_{xy}^{MD}[(\hat{\mathbf{b}}\cdot\langle\hat{\mathbf{c}}\rangle)+(\hat{\mathbf{c}}\cdot\langle\hat{\mathbf{b}}\rangle)]$$

as

$$\begin{aligned}&(\rho_0\mu^2)^{-1}(I_{xx}^{MD}\mu_x+I_{xy}^{MD}\mu_y)(\hat{\mathbf{b}}\cdot\mathbf{P})\\&+(\rho_0\mu^2)^{-1}(I_{yy}^{MD}\mu_y+I_{xy}^{MD}\mu_x)(\hat{\mathbf{c}}\cdot\mathbf{P}),\end{aligned}$$

which corresponds to the third and fourth terms in Eq. (12).

Finally, we note that the expressions $K_x^M(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})$ and $K_y^M(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})$ can also be rewritten in the familiar form [see the first two terms in Eq. (12)], using the relation $\hat{\mathbf{c}}=[\hat{\mathbf{n}}\times\hat{\mathbf{b}}]$;

$$K_x^M(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{b}}\cdot\hat{\mathbf{e}})+K_y^M(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})(\hat{\mathbf{c}}\cdot\hat{\mathbf{e}})=-K_y^M(\hat{\mathbf{b}}\cdot\mathbf{w})+K_x^M(\hat{\mathbf{c}}\cdot\mathbf{w}).$$

Now we can finally rewrite Eqs. (A11) and (A12) for the effective one-particle potential in the form of the phenomenological Eq. (12), obtained in Sec. II:

$$\begin{aligned}C_1(\hat{\mathbf{b}},\hat{\mathbf{c}})=&S_x(\hat{\mathbf{b}}\cdot\mathbf{w})+S_y(\hat{\mathbf{c}}\cdot\mathbf{w})+G_x(\hat{\mathbf{b}}\cdot\mathbf{P}_s)+G_y(\hat{\mathbf{c}}\cdot\mathbf{P}_s)\\&+\Delta K[(\hat{\mathbf{b}}\cdot\mathbf{w})^2-(\hat{\mathbf{c}}\cdot\mathbf{w})^2]+\Delta M[(\hat{\mathbf{b}}\cdot\hat{\mathbf{m}})^2\\&-(\hat{\mathbf{c}}\cdot\hat{\mathbf{m}})^2].\end{aligned}$$

The coefficients of this effective potential are now expressed as

$$\begin{aligned}S_i&=x_MS_i^M+x_DS_i^D,\\G_i&=x_MG_i^M+x_DG_i^D,\\\Delta K&=x_MM^M+x_DM^D,\\\Delta M&=x_M\Delta M^MB_M+x_D\Delta M^DB_D,\end{aligned}\qquad\text{(A13)}$$

where $i=x,y$ and

$$\begin{aligned}S_x^\alpha&=(J_x^{D\alpha}-K_y^{M\alpha})(1+\tfrac{1}{2}\sigma),\\S_y^\alpha&=(J_y^{D\alpha}+K_x^{M\alpha})(1+\tfrac{1}{2}\sigma),\\G_x^\alpha&=(\rho_0\mu^2)^{-1}(I_{xx}^{\alpha D}\mu_x+I_{xy}^{\alpha D}\mu_y),\\G_y^\alpha&=(\rho_0\mu^2)^{-1}(I_{yy}^{\alpha D}\mu_y+I_{xy}^{\alpha D}\mu_x),\\M^\alpha&=-M^{\alpha D}(1+\tfrac{1}{2}\sigma),\\\Delta M^\alpha&=-2\left(G^{\alpha D}+\frac{\sigma}{2}K^{\alpha D}\right)-\sin^2\Theta K^{\alpha D}(1+\tfrac{1}{2}\sigma).\end{aligned}\qquad\text{(A14)}$$

Here $\alpha=H,D$ and B_H and B_D are the quadrupole order parameters of the host phase and dopant molecules, respectively.

Equations (A13) and (A14) express the coefficients in the general expression of the effective one-particle potential (12) in terms of the coefficients of expansion (A9) of the direct correlation functions $C_{MD}(1,2)$ and $C_{DD}(1,2)$ between dopant-dopant and dopant-host phase molecules, respectively. The general equations (A13) and (A14) are used in Sec. III in the discussion of the influence of different intermolecular interactions on the ferroelectric properties of the induced smectic-$C*$ phase.

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