Chiroclinic effect and the phase diagram of achiral polar molecules in the antiferroelectric smectic $B_2$ phase

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The paper presents a detailed analysis of the effects of chiral doping on antiferroelectric $B_2$ subphases in bent core systems. The studied system exhibits the phase sequence $\text{SmA} \leftrightarrow \text{SmAP}_A \leftrightarrow \text{SmC}_{A} P_{A}$. The chiral dopant induces the tilt in the $\text{SmAP}_A$ phase or the tilt modulation in the $\text{SmC}_{A} P_{A}$ phase, which is known as the chiroclinic effect, but it also influences the stability ranges and the order of the transition between the phases. The order of the phase transition changes from a continuous for weak effects of chiral doping to discontinuous for strong effects. Competition of interactions results in changes of the phase sequences, which are resumed in the phase diagram. The method that leads to these findings, which could be used for the analysis of other similar systems, is briefly presented as well.

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I. INTRODUCTION

Liquid crystals with polar properties are formed of molecules with very distinctive properties. Smectic layers formed of elongated chiral molecules, which are tilted away from the layer normal, are polar, as in the $\text{SmC}^*$ phase in chiral polar smectics [1]. If smectic layers are formed of molecules with a shape that hinders molecular rotation, the molecules may orient in a way that the layer becomes polar. An example is a system made of molecules with a bent core, which are not chiral, but some phases they form have polar properties [2]. First compounds with bent-shaped molecules that formed liquid crystalline phases were intentionally designed and synthesized two decades ago [3]. Several phases were found in those systems and were named $B_1$-$B_8$, where the subscript indicates the order of their identification. Experimental studies of these phases revealed that several phases actually consist of sets of subphases with different structures and macroscopic properties. Probably the most understood is the $B_2$ phase, in which bent core molecules are ordered in layers, and are ordered polarly in an antiferroelectric or ferroelectric way. In addition, the molecules in layers are often tilted in an antclinic or synclinic way [4].

The $B_2$ phase includes six different polarly ordered subphases with different structures. Two of the phases are not tilted. Organizations of polarizations determine whether the structure is ferroelectric as in the nontilted $\text{SmAP}_F$ phase where polarizations are parallel in adjacent layers [5], in contrast to the antiferroelectric nontilted $\text{SmAP}_A$ phase where polarizations are antiparallel in the adjacent layers [6]. Moreover, four phases exist where molecules in the smectic layer are additionally to the polar order, also tilted. The tilts in adjacent layers in these subphases are either synclinic ($\text{SmC}_{A} P_A$, $\text{SmC}_{A} P_F$) or anticlinic ($\text{SmC}_{A} P_A$, $\text{SmC}_{A} P_F$). The combination of polar packing and molecular tilts results in the chirality of the smectic layer, although molecules are achiral. Several studies of influences of chiral dopants on these structures exist. The chiral dopant lifts the degeneracy between domains with opposite chiralities and suppresses the existence of one chirality [7]. Initially synclinic antiferroelectric structures transform to anticlinic antiferroelectric structures if chiral dopants are added. Finally, the chiroclinic effect predicts that a chiral dopant added to the nontilted polar phase induces the tilt in the nontilted $\text{SmAP}_A$ phase [8].

In this paper we analyze how the chiral dopant added to the system influences the temperature intervals of antiferroelectric $B_2$ subphases’ (meta)stability, their dynamics, and the order of transitions among them. The analysis is limited to the three antiferroelectric $B_2$ subphases, as the results can easily be adapted to the ferroelectric subphases. In addition, as long as with lowering the temperature, the first smectic phase is the nontilted polar phase, the chiral doping cannot change the polarity of the phase, but only its clinicity. Therefore, the separate analysis of the ferroelectric phases does not introduce new physics.

The most interesting system to study is the system that exhibits the phase sequence $\text{SmA} \leftrightarrow \text{SmAP}_A \leftrightarrow \text{SmC}_{A} P_{A}$. The chiral dopant induces the anticlinic tilt in the $\text{SmAP}_A$ phase, but the $\text{SmC}_{A} P_{A}$ phase that appears below is synclinic. Competition of chiral and synclinic interactions results in an interesting phase diagram, which explains observations from more
than a decade ago [7] and predicts new phenomena enabling the testing of the chiroclinic effect.

II. THE NONCHIRAL SYSTEM

The order of bent-shaped molecules is defined by two order parameters that are characteristic for the smectic layer. The first-order parameter $\vec{P}_j$ describes the ordering of the kink axes in $j$th layer and is always orthogonal to the layer normal (see Fig. 1). The polarization of the $j$th layer is proportional to the ordering of the cores’ kinks; however, its direction is determined by the molecular structure and is either parallel or antiparallel to this direction. Therefore, this order parameter is called the layer polarization. The tilt order parameter $\vec{\xi}_j$ in the $j$th layer gives an average molecular tilt and is associated to the director in the layer (Fig. 1). The definition reflects its quadrupolar properties:

$$\vec{P}_j = [P_{j,x}, P_{j,y}, 0],$$

$$\vec{\xi}_j = [n_{j,x}n_{j,z}, -n_{j,y}n_{j,z}, 0].$$

(1)

Although the two order parameters are usually considered as two dimensional, the third component is added explicitly to both for later use. Bent-shaped molecules form polarly ordered $B_2$ phases that are nontilted or tilted. In this study we focus on antiferroelectric structures, where the polarization order parameter has opposite directions in neighboring layers. This narrows the analysis to three possible phases: the orthogonal SmAPA phase, the anticlinically tilted SmCAPA phase, and the synclinically tilted SmCSPA phase. The tilted phases always appear below the temperature range of the nontilted phases.

Both synclinically and anticlinically tilted phases form two enantiomorphic structures. In each layer, mutual orientation of the tilt order parameter, the polarization, and the layer normal corresponds to a right-handed coordinate system, while the mirror image of these vectors corresponds to a left-handed coordinate system, indicating the chirality of the layer structure [4]. Therefore, we define a chiral order parameter of the $j$th layer as $\vec{\sigma}_j = \vec{P}_j \times \vec{\xi}_j$, which has the same magnitude in both cases, but the opposite signs [8,9]. The chiral order parameter is (anti)parallel to the layer normal in the local coordinate system. As only the $z$th component is different from zero, it has a character of the pseudoscalar, which is invariant under rotations, but changes sign under inversion, and hence disappears if the structure is achiral [10]. In the SmAPA phase, which is antiferroelectric and anticlinic, all the layers have the same sign of the chiral order parameter $\vec{\sigma}_j$ and the structure is homogeneously chiral. On the contrary, in the antiferroelectric synclinic SmCSPA phase the signs of $\vec{\sigma}_j$ alternate from one layer to another, which indicates an antichiral structure [9]. Consequently, two homochiral domains exist in the SmAPA phase and two antichiral domains in the SmCSPA phase with the same free energy and they occur with the same probability in samples (Fig. 2).

The free energy of a system made of achiral bent-shaped molecules expressed in the terms of order parameters, which allows for polar nontilted and polar tilted phases with chiral structures, has the following form:
[11]:

\[
G = \sum_j \frac{1}{2} a_0 j_j^2 + \frac{1}{2} a_0 j_j^2 + \frac{1}{2} a_0 \xi_j^2 + \frac{1}{2} a_0 \xi_j^2 + \frac{1}{2} \left( \bar{P}_j \cdot \bar{P}_{j+1} \right) + \frac{1}{2} a_1 \left( \bar{P}_j \cdot \bar{P}_{j+1} \right).
\]

In Eq. (2), the subscript 0 indicates intralayer interactions, while the subscript 1 indicates interactions between neighboring layers. We do not believe that direct interactions extend to more distant layers, as the layers are well organized and strong positional correlations between molecules in next-nearest-neighbor layers are negligible [11]. The only temperature-dependent coefficient in the free energy is the first coefficient \( a_0 = \alpha (T - T_0) \), where \( T_0 \) is the transition temperature from the orthogonal polarly disordered to the polarly ordered phase. For an antiferroelectric ordering discussed in this paper, the coefficient \( a_2 > 0 \).

To analyze the structures that minimize the free energy, we chose a domain in which the tilt order parameter has a positive direction along the \( x \) axis in the \( j \)th layer. The ansatz for the tilt and the polarization order parameters, as illustrated in Fig. 2, is

\[
\begin{align*}
\text{SmAP}_A & : \xi_j = 0, \\
\bar{P}_j & = P_0 \{0, 1, 0\}, \\
\bar{P}_{j+1} & = P_0 \{0, -1, 0\}. \\
\text{SmC}_{A/P}_A & : \xi_j = \theta_0 \{1, 0, 0\}, \\
\bar{P}_j & = P_0 \{0, 1, 0\}, \\
\bar{P}_{j+1} & = P_0 \{0, -1, 0\}, \\
\text{SmC}_{A/P}_A & : \xi_j = \theta_0 \{1, 0, 0\}, \\
\bar{P}_j & = P_0 \{0, 1, 0\}, \\
\bar{P}_{j+1} & = P_0 \{0, -1, 0\}.
\end{align*}
\]

By inserting ansatz (3) in Eq. (2) a system of two linear equations for \( \theta_0^2 \) and \( P_0^2 \) is obtained for the structures of the three phases

\[
\begin{align*}
\text{SmAP}_A & : \theta_0 = 0, \\
P_0^2 & = \frac{(a_0 + a_1)}{b_0}, \\
\text{SmC}_{A/P}_A & : \theta_0^2 = \frac{(a_0 - a_1)}{b_0} - \frac{\Omega}{b_0} P_0^2, \\
P_0^2 & = \frac{(a_0 + a_1)}{b_0} - \frac{\Omega}{b_0} \theta_0^2.
\end{align*}
\]

III. EFFECTS OF CHIRAL DOPANTS

The temperature dependence of the tilt and polarization for an example with the sequence SmA \( \leftrightarrow \text{SmAP}_A \leftrightarrow \text{SmC}_{A/P}_A \) is presented in Fig. 3(a). As seen in Fig. 3(a), the nontilted polar SmAP_A phase becomes stable at \( T_C \), which is always higher than the transition temperature to a polarly ordered structure in an isolated layer. With further cooling of the sample the molecules synclinically tilt at the phase transition temperature \( T_S \). In addition, a solution of the anticalin SmC_{A/P}_A phase exists below temperature \( T_S \) [Fig. 3(a)]. This additional solution stimulates a few questions. Is the SmC_{A/P}_A phase metastable even if the system favors a synclinc ordering? Is there a mechanism that prevails over favorable synclinic order and stabilizes the anticalinic SmC_{A/P}_A phase?

Adding a chiral dopant enhances overall chirality of the sample as interactions of bent-shaped molecules with chiral molecules favor one chiral structure and destabilize the structure with the opposite chirality [7]. Effects of chiral dopant are modeled by adding a chiral field \( h \), which is linearly coupled with the \( z \) component of the chiral order parameter of the \( j \)th layer \( h \bar{s}_{j,z} = h(\bar{P}_j \times \bar{P}_j) \). The three effects of chiral dopants—a disappearance of domains with one chirality in the anticalinic SmC_{A/P}_A phase, a modulation of amplitudes of order parameters in the SmC_{A/P}_A phase, and an induced tilt in the nontilted SmAP_A phase, also called the chiroclinic effect—were already considered in [8]. However, for stronger chiral fields the stabilization of the anticalinic SmC_{A/P}_A phase over the synclinic SmC_{A/P}_A phase can be expected. Therefore, a thorough analysis of those phases under chiral doping is needed. The temperature dependence of order parameters in the chirally doped system with favorable synclinic ordering is presented in Fig. 3(b). The results were obtained numerically as the coupling with the chiral field does not allow for theoretical expressions of order parameters. Two temperature regions are clearly identified. In the temperature region
between \( T_C \) and \( T_S \), where the nontilted SmAP\(_A\) phase is stable in a system without a dopant, a chiral dopant induces tilts in opposite directions in adjacent layers. We call this phase the induced tilt SmAP\(_A^*\) phase, where the asterisk marks that the system is doped. Chiral dopant affects the synclinic SmC\(_{SPA}\) phase similarly. It increases the amplitude of the tilt and the polarization in the layer with favorable chiral order parameter and decreases both order parameters in the layer with the opposite chiral order parameter. As a result, amplitudes of order parameters in odd layers differ from even ones. The modulated amplitudes of order parameters are characteristic for the chiral SmC\(_{SPA}\) phase.

To investigate the influence of chiral dopant on stabilities of phases we analyze dynamical properties of doped structures following the procedure used in [12], as the stability limits are the most straightforwardly obtained from the fluctuation modes. The analysis is reduced to the two neighboring layers in the continua-
tion, order parameters in odd layers are marked by a subscript 1 and in even layers by a subscript 2. Time-dependent order parameters in these two layers have two contributions, the nontilted SmAP\(_A\) phase and the thermodynamically induced fluctuations, as shown in Fig. 4:

\[
\begin{align*}
\dot{\xi}_1 &= \xi_0, \dot{\xi}_{11} + \delta \xi_{11}, \\
\dot{P}_1 &= P_0, \dot{P}_{11} + \delta P_{11} + \delta P_{11}^\parallel, \\
\dot{\xi}_2 &= \xi_0, \dot{\xi}_{21} + \delta \xi_{21}, \dot{\xi}_{21} + \delta \xi_{21}^\perp, \\
\dot{P}_2 &= P_0, \dot{P}_{21} + \delta P_{21} + \delta P_{21}^\perp, \dot{P}_{21}^\perp.
\end{align*}
\]

The unit vectors indicate the directions of fluctuations which are parallel or perpendicular to stable order parameters in the corresponding layers \( \xi_0, \dot{\xi}_0 \) and \( \xi_0, \dot{\xi}_0, \dot{\xi}_0 \), respectively (Fig. 4).

The free energy due to fluctuations \( G_2 \) is shortly written as

\[
G_2 = \frac{1}{2} \chi \mathbf{G}_2 \chi,
\]

where \( \chi = \{ \delta \xi_{11}, \delta \xi_{12}, \delta P_{11}, \delta P_{12}, \delta \xi_{21}, \delta \xi_{22}, \delta P_{21}, \delta P_{22} \} \) is an eight-dimensional vector of fluctuation amplitudes and \( \mathbf{G}_2 \) is an 8 \times 8 matrix of the form

\[
\mathbf{G}_2 = \begin{bmatrix}
A & 0 & L & 0 & I & 0 & 0 & 0 \\
0 & B & 0 & K & 0 & I & 0 & 0 \\
L & 0 & C & 0 & 0 & J & 0 & 0 \\
0 & K & 0 & D & 0 & 0 & J & 0 \\
I & 0 & 0 & 0 & E & 0 & N & 0 \\
0 & I & 0 & 0 & 0 & F & 0 & M \\
0 & 0 & J & 0 & N & 0 & G & 0 \\
0 & 0 & 0 & J & 0 & M & 0 & H
\end{bmatrix}
\]
Model coefficients are the same as in Fig. 3, while phases when (a) the system is pure and (b) the system is doped with a chiral dopant. Vertical lines mark phase transitions between phases.

with the elements

$$A = 2a_0 + 6b_0 \theta_{0,1}^2 + 2 \Omega P_{0,1}^2 , \quad Y$$

$$B = 2a_0 + 2b_0 \theta_{0,1}^2, \quad I = \mp 2a_1,$$

$$C = 2a_0 + 6b_0 P_{0,1}^2 + 2 \Omega \theta_{0,1}^2, \quad J = 2a_1,$$

$$D = 2a_0 + 2b_0 P_{0,1}^2, \quad K = 2 \Omega \theta_{1,0} P_{0,1} - 2h,$$

$$E = 2a_0 + 6b_0 \theta_{0,1}^2 + 2 \Omega P_{0,1}^2, \quad L = 4 \Omega \theta_{1,0} P_{0,1} - 2h,$$

$$F = 2a_0 + 2b_0 \theta_{0,1}^2, \quad M = 2 \Omega \theta_{1,0} P_{0,1}, \quad 2h,$$

$$G = 2a_0 + 6b_0 P_{0,1}^2 + 2 \Omega \theta_{0,1}^2, \quad N = 4 \Omega \theta_{1,0} P_{0,1} + 2h,$$

$$H = 2a_0 + 2b_0 P_{0,1}^2.$$

Stable solutions in chirally doped systems are all tilted, and they are either sinclinic (SmC_A^*) or anticlinic (SmAP_A^*, SmC_A^*). For the sincline structure, one uses the upper of the signs in matrix elements I, M, and N, while for anticlinic structures, stable tilts and polarizations are equal, and lower signs are used for I, M, and N.

In pure systems, four different fluctuation modes exist in the phases where order parameters are zero and eight fluctuation modes in the tilted phases [Fig. 5(a)]. The analysis of corresponding eigenvectors revealed that the fluctuation modes are either related to the changes of the phase or the amplitude, but never to both. In all the tilted phases, represented by dashed lines in Fig. 5, the Goldstone mode exists, reflecting the rotation symmetry of the system. Besides the Goldstone mode, three temperature-independent modes and four modes that linearly depend on temperature, exist. But, in the doped system, however, relaxation modes do not linearly depend on the temperature [Fig. 5(b)]. Furthermore, chiral dopant induces split in the amplitude modes. In addition, the analysis of the temperature dependence of the modes allows for determination of the temperature range, that is, the temperatures T_C and T_S. In this range the phases are (meta)stable, because frequencies of all modes are $\pm 0$.

The analysis of the model revealed that transitions SmA $\leftrightarrow$ SmAP_A $\leftrightarrow$ SmC_A P_A(SmC_A P_A) are all continuous when the system is not doped. Adding the chiral dopant stabilizes the SmAP_A^* range, the T_C increases, and the T_S decreases. Surprisingly, although the structures of SmC_A P_A^* and SmAP_A^* with the chiroclinically induced tilt are structurally different, the phase transition between the two phases is continuous for weak chiral fields h. However, for stronger effects of chiral dopants the phase transition becomes discontinuous.

The phase diagram for the set of coefficients given in the caption of Fig. 3, including all the subtleties, is shown in Fig. 6(a). The white region corresponds to the nontilted SmA^* phase. The light-gray region corresponds to the SmAP_A^* phase with the tilt induced by the chiroclinic effect. The dark region corresponds to the SmC_A P_A^* phase with slightly different tilts and polarizations in the neighboring layers, again due to the chiroclinic effect. In the semidark region, both the single chiral domain SmC_A P_A^* phase and the SmC_A^* phase are (meta)stable. The SmC_A P_A^* phase is stable below the temperatures indicated by the solid line. Along the short-dashed line the free energy of the SmC_A P_A^* phase and the SmC_A^* phase are equal. The SmC_A P_A^* phase is stable above, and the SmC_A^* phase is stable below this line. The metastability limit of the SmC_A P_A^* phase is indicated by the long-dashed line. The dotted line indicates the limit between the spontaneously chiral anticlinic antiferroelectric phase and the dopant-induced SmC_A P_A^* phase. The inset of the phase diagram in Fig. 6(a) shows the range of h where the SmAP_A^* $\leftrightarrow$ SmAP_A^* phase transition changes from continuous to discontinuous. A detailed analysis of temperature dependence of the lowest positive modes, marked by the long-dashed line for the SmAP_A^* phase and the short-dashed line for the SmC_A P_A^* phase, revealed the borders of hysteresis that exist between the low and high temperatures [Fig. 6(b)]. For h > h_{High}, the anticlinic SmC_A^* phase, structurally equal to the SmC_A P_A^* with high induced tilt, is (meta)stable in the whole temperature region below T_C.

How is it possible that the SmAP_A^* phase with induced anticlinic tilt continuously transforms to the structurally very different sinclinically tilted SmC_A P_A^* phase? Above the temperature T_S, the induced tilts in neighboring layers are opposite in direction and equal in magnitude. Directly below the phase transition at T_S, directions of tilts still remain the same, but in one layer the tilt gradually increases upon lowering the temperature and in the neighboring layer the tilt...
The analysis evidently shows that adding the chiral dopant to the system stabilizes the homochiral anti-clinic antiferroelectric phase in two ways. Although the sinclinity is favored due to interlayer interactions, in the SmAP$_A^*$ phase the anti-clinic tilt is induced. Next, for strong enough chiral fields the homochiral phase becomes metastable or even stable in temperature ranges where the sinclinically tilted SmC$_3$P$_A$ is stable without a dopant. As a result, the system may exhibit phase sequence SmA$^*$ ↔ SmAP$_A^*$ and the region with an induced tilt continuously develops to the region of a spontaneously chiral anti-clinic antiferroelectric phase by tilted SmC$_3$P$_A^*$ phase.

In spite of being stimulated by experiments that followed the prediction of the phenomenon [8], this study is purely theoretical. Two predictions of the model could be experimentally tested relatively easily: (a) The magnitude of the induced tilt in the SmAP$_A^*$ phase and its temperature dependence by measuring the tilt optically, and (b) the hysteresis on heating and cooling of the doped sample using differential scanning calorimetry. The observed homochirality of domains in the SmC$_3$P$_A^*$ was already discussed within this model in [8]. The effects of chiral doping, which stabilize the SmC$_3$P$_A^*$ structure in the same temperature window where the SmC$_3$P$_A^*$ is stable without a dopant [7] is also consistent with the part of the phase diagram, where both phases are metastable. Finally, the measurement of the tilt in dependence of the temperature in a system with the transition from SmAP$_A^*$ to SmC$_3$P$_A^*$ upon cooling, which was doped by different concentrations (up to 5%) of a chiral dopant, revealed the appearance of the tilt in the nontilted SmAP$_A^*$ and the shift of the transition temperature to the tilted phase [13].


