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Sign inversion of the spontaneous polarization in induced liquid crystalline smectic-C^* phases

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Ferroelectricity can be induced in nonchiral smectic-C liquid crystal phases by different chiral guest molecules. We observed a sign inversion of the spontaneous polarization P_s as a function of the guest molecule concentration. In addition, in mixtures near the inversion concentration a temperature induced sign inversion of P_s occurs. These inversions can be qualitatively explained by the elementary theory of ferroelectric mixtures, taking into account the difference in the interactions between guest and host molecules.

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Ferroelectric smectic liquid crystals are the only ferroelectric materials in which the appearance of the spontaneous polarization is intimately related to molecular chirality. The symmetry of the tilted smectic phases allows for the spontaneous polarization if the medium is chiral [1]. One important way to obtain new ferroelectric liquid crystal materials is to use achiral smectic-C phases doped with various chiral molecules [2]. So far, only chiral dopants of special molecular structure have been employed. In these molecules both the chiral centers and the transverse dipoles are located in the flexible chains attached to the rigid molecular core (Fig. 1, type I). As a result, the reduced polariztion $P_0 = P_s/\sin\Theta$ was found to be independent of the nature of the achiral smectic-C host phase [3,4]. Recently, we have investigated ferroelectric smectic-C^* phases induced by chiral dopants of a new type, in which the chiral centers and the transverse dipoles are part of the rigid core (Fig. 1, type II) [5,6]. The properties of these systems appear to be very sensitive to the structure of these new chiral molecules. As a result, the magnitude and sometimes even the sign of the spontaneous polarization depend on the nature of the host phase.

The temperature variation of the spontaneous polarization in some ferroelectric liquid crystals differs significantly from the "classical" behavior typical for the order parameter in the second order phase transition [7.8]. In particular, a temperature induced sign inversion of the spontaneous polarization has recently been observed in some one-component smectic-C^* phases [9–12].

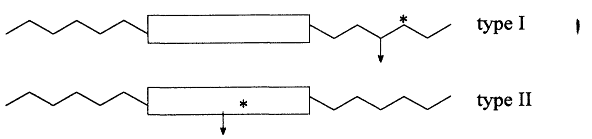

FIG. 1. General molecular structure of chiral dopants in induced smectic-C^* phases. ↓, transverse dipole; *, chiral center.

In this paper, we report a type of polarization sign inversion in the smectic-C^* phase induced by the change of the concentration of chiral guest molecules (of the type II mentioned above). In the same system, the temperature induced sign inversion of the spontaneous polarization is also observed, but the origin of this effect is different from the one described by Patel and Goodby [9]. We present a qualitative explanation of these effects using the generalized version of the molecular theory of ferroelectric liquid crystal mixtures [13,14].

The dependence of the spontaneous polarization on the molar fraction x_G of the chiral dopant is presented in Fig. 2. The values correspond to temperatures 5 and 15 K below the Sm-A-Sm-C^* transition temperature T_{AC}. The most interesting result here is the sign inversion of the polarization P_s at some value of the molar fraction

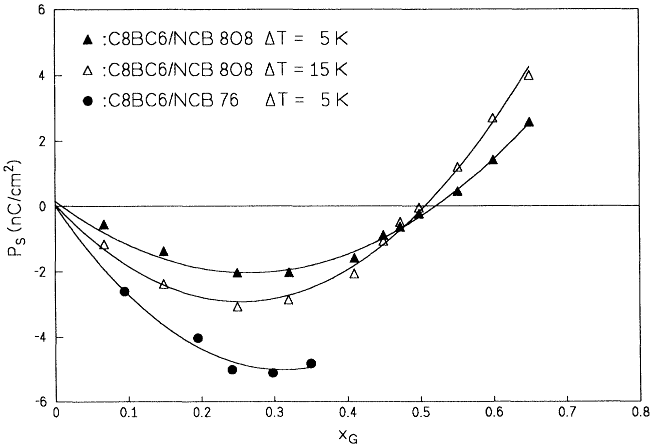

FIG. 2. Spontaneous polarization P_s vs mole fraction x_G of the chiral compound C8BC6 in different host phases.

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x_G. We note that a tendency toward this sign inversion has already been indicated in induced smectic-C^* phases (see Fig. 3 of Ref. [5]). It can also be seen that the polarization strongly depends on the nature of the achiral host phase and the concentration dependence of P_s is nonlinear. The second result is the temperature induced sign inversion of the polarization that is observed in mixtures with the mole fraction x_G close to but below the inversion value x_G^0. The corresponding temperature variation of the spontaneous polarization is presented in Fig. 3. We note that this temperature effect is very sensitive to the molar fraction of the chiral dopant. At a slightly lower fraction $x_G = 0.473$ one observes only the tendency toward the sign inversion (see Fig. 4). Values of the spontaneous polarization at temperatures below the sign inversion could not be obtained due to crystallization problems. It is important to stress that these temperature effects are observed only if the molar fraction x_G is smaller than x_G^0. At higher concentrations of chiral molecules the polarization does not show any tendency toward sign inversion.

In the present experimental studies we have used the mesogenic chiral dopant C8BC6, which bears the chiral centers and the transverse dipole in the rigid core. The molecular structure of this dopant is shown in Fig. 5. The advantage of this dopant is the fact that it is mesogenic and forms both smectic-A and the monotropic smectic-C^* phases. As a result, we were able to investigate the ferroelectric properties of the mixture up to high dopant concentration, where the sign inversion is observed. We have used the achiral smectic-C host phases composed of molecules of the NCB type (Merck, Darmstadt), which possess large CN dipoles perpendicular to the molecular plane. These host phases are of particular interest in the present context because the ordering of these dipoles can also contribute to the spontaneous polarization. Further details about the molecular structure of the host phases and the experimental procedures can be found in [5].

According to the microscopic theory of ferroelectric liquid crystals, the spontaneous polarization in the chiral smectic-C^* phase is determined by the ordering of transverse molecular dipoles. The spontaneous polarization in the chiral smectic-C^* phase can be written as $P_s = \rho\mu_\perp\langle\cos\psi\rangle$ where ρ is the number density of molecules and ψ is the angle between the molecular dipole $\mu_\perp$ and the direction of the spontaneous polarization [15]. The brackets $\langle\ \rangle$ denote the ensemble average.

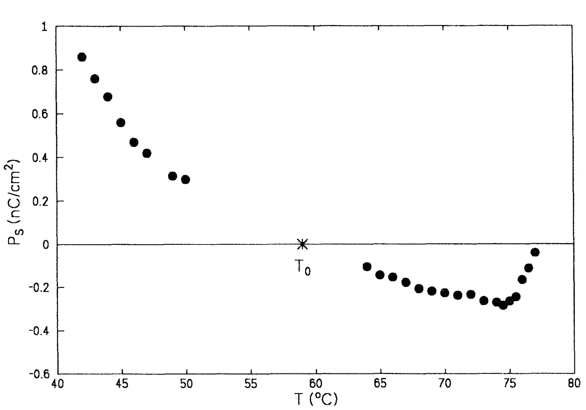


FIG. 3. Temperature dependence of the spontaneous polarization P_s in a mixture of C8BC6 in the host phase NBC 808 ($x_G = 0.499$). T_0 is the inversion temperature obtained by means of texture observations.

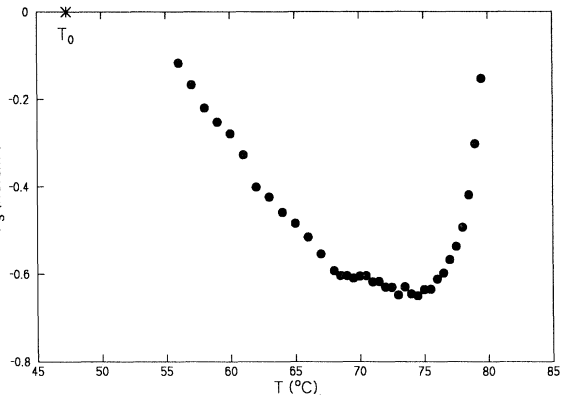


FIG. 4. Temperature dependence of the spontaneous polarization P_s in the same system as in Fig. 3, but with $x_G = 0.473$.

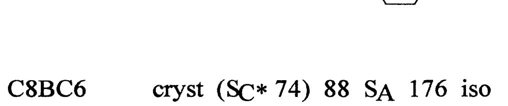
In the general case, the polarization of a mixture is determined by contributions of all components. At the same time, according to the Landau–de Gennes theory of ferroelectric smectic-C^* [13], the spontaneous polarization can be written in the general phenomenological form

$$P_s = g \sin 2\Theta \ . \qquad (1)$$

The expression is valid at small tilt angles $\Theta \ll 1$, i.e., close to the Sm-A–Sm-C^* transition. At lower temperatures the coefficient g can also depend on the tilt angle Θ. In the case of mixtures the coefficient g depends on the molar fractions x of the components. According to the molecular theory of ferroelectric liquid crystal mixtures [13,14], the constant g is determined by pair interaction between the molecules of all components. For a smectic-C host phase (H) with chiral guest molecules (G), the constants g can be written as

$$g = x_H^2 g_{HH} + x_H x_G g_{HG} + x_G^2 g_{GG} \ , \qquad (2)$$

where the constants g_{HG} and g_{GG} are determined by the interaction between guest and host and between two guest molecules, respectively. Here x_H and x_G are the molar fractions of the host and guest molecules. The first term in Eq. (2) vanishes because there is no spontaneous



C8BC6 cryst (S_C* 74) 88 S_A 176 iso

FIG. 5. Molecular structure and phase transition temperatures of the chiral dopant.

polarization in the achiral smectic-*C* phase (i.e., for $x_G=0$). Thus, $g_{HH}=0$ and Eq. (1) can be rewritten as

$$P_s=(x_G g_{HG}+x_G^2 g_{GG}^*)\sin 2\Theta \; , \tag{3}$$

where $g_{GG}^*=g_{GG}-g_{HG}$.

It follows from Eq. (3) that at small concentrations of chiral guest molecules ($x_G \ll 1$) the second term, related to the guest-guest interaction, can be neglected. In this case the spontaneous polarization of the mixture is determined only by the interaction between the chiral guest molecules and their neighbor achiral host molecules [13,14]. In this region, the polarization depends linearly on the concentration x_G. By contrast, in the pure chiral guest smectic-C^* phase the polarization is given by $P_s=g_{GG}\sin 2\Theta$.

The linear concentration dependence of the polarization at $x_G \ll 1$ is confirmed by the present experimental results. At higher molar fractions of the chiral guest molecules, the second (quadratic) term in Eq. (3) becomes more important. This means that the contribution from the guest-guest intermolecular interaction to the spontaneous polarization increases. Finally, the balance between the two terms in Eq. (3) leads to the observed sign inversion of the spontaneous polarization at some critical molar fraction x_G^0. It should be stressed, however, that the sign inversion of P_s can take place only if the constants g_{HG} and g_{GG}^* have opposite signs. Formally, in this case the guest-host interaction aligns the transverse molecular dipoles behind the tilt plane ($P_s<0$), whereas the guest-guest interaction promotes the orientation of dipoles in front of the tilt plane ($P_s>0$). For sign convention of P_s, cf. Fig. 5 of Ref. [16].

These different orientations can be understood in terms of the microscopic theory of ferroelectric ordering [15,16]. According to this theory, the spontaneous polarization is determined by polar ordering ($\langle \cos\psi \rangle \neq 0$) of the transverse dipoles around the molecular long axes. The rotational mean-field potential $V(\psi)$ of a given guest molecule is determined mainly by its hard core interaction with the neighbor molecules [13]. In molecules with complex structure, the dipole $\mu_\perp$ does not necessarily coincide with the reference polar axis of the guest molecule that can be related to its steric dipole [14]. The transverse dipole $\mu_\perp$ can deviate from this reference axis by an angle ψ_0. In this case, it is more convenient to rewrite the related equation in the following form [16]: $P_s=\rho\mu_\perp\langle\cos(\psi'+\psi_0)\rangle$, where ψ' is the angle between the molecular polar axis (transverse steric dipole) and the spontaneous polarization. We note that the magnitude of P_s in the present system is very small compared to the typical values expected from the value of the molecular dipole $\mu_\perp$. This means that the angle ψ_0 is close to $\pi/2$, i.e., the transverse dipoles are, on the average, oriented nearly parallel to the tilt plane. This results in the small values of P_s observed in the present systems. Then it seems reasonable to assume that the expectation value $\langle\cos(\psi'+\psi_0)\rangle$ can have opposite signs due to small differences in the interaction potential of a guest molecule surrounded by either host or guest molecules. Consequently, different signs of the interaction parameters in Eq. (3) seem to be plausible.

Now we are in a position to propose a qualitative explanation of the observed temperature induced sign inversion of P_s in mixture with $x_G<x_G^0$. In the general case, one can expand the coefficients g_{HG} and g_{GG} in Eq. (2) in powers of the tilt angle Θ. In our experiments, the tilt angle was only weakly dependent on the molar fraction x_G and therefore we can write phenomenologically

$$g_{HG}=g_{HG}^0+g_{HG}^{(2)}\Theta^2+\cdots, \quad g_{GG}=g_{GG}^0+g_{GG}^{(2)}\Theta^2+\cdots \; . \tag{4}$$

Finally, we obtain the following equation for the spontaneous polarization:

$$P_s=[G_0(x_G)+G_2(x_G)\Theta^2]\sin 2\Theta \; , \tag{5}$$

with

$$\begin{aligned} G_0&=g_{HG}^0 x_G(1-x_G)+g_{GG}^0 x_G^2, \\ G_2&=g_{HG}^{(2)} x_G(1-x_G)+g_{GG}^{(2)} x_G^2 \; . \end{aligned} \tag{6}$$

The temperature dependence of Eq. (5) is determined by the tilt angle: $\Theta\sim(T_{AC}-T)^\beta$ [7,8]. Let us note that the magnitude and the sign of the parameters G_0 and G_2 are sensitive to the molar fraction of the guest molecules.

Now we can explain the observed temperature induced sign inversion. Let us first consider the mixture with $x_G=0.499$ (see Fig. 3). Close to the transition temperature, the spontaneous polarization is determined by the first term G_0 in Eq. (5). In this temperature range the polarization is negative and thus $G_0<0$. By contrast, due to the values $g_{HG}^{(2)}$ and $g_{GG}^{(2)}$ the constant G_2 for $x_G=0.499$ is positive. At lower temperatures, with increasing tilt angle, the second term in Eq. (5) becomes more important and the absolute value of P_s decreases. Finally, at a particular temperature T_0, the second term $G_2\Theta^2$ compensates the first term G_0. The polarizations changes sign and for $T<T_0$ to the polarization P_s is positive. From texture observations with an applied dc electric field, we found the sign inversion to occur at $T_0=59\,^\circ\mathrm{C}$, which corresponds to $\Delta T=T_{AC}-T_0=18$ K (cf. Fig. 2).

As has already been stressed, this temperature induced sign inversion is very sensitive to the composition of the mixture. In Fig. 4 the polarization P_s is given for a mixture with a slightly lower concentration of chiral dopant ($x_G=0.473$). The spontaneous polarization remains negative over the whole measured temperature range. We observed a decrease of P_s with decreasing temperature, but positive values of P_s could not be measured. However, by means of texture observations we could determine the sign inversion of P_s at $T_0=47.3\,^\circ\mathrm{C}$ ($\Delta T=32.5$ K). The different behavior of this mixture can be understood if we take into account that at a lower molar fraction of the guest molecules, the constant G_0 is larger and G_2 is smaller than the corresponding constants in the mixture with $x_G=0.499$. Then the negative contribution of G_0 in Eq. (5) is compensated by the positive term $G_2\Theta^2$ at larger values of ΔT in comparison to the mixture with $x_G=0.499$.

In mixtures with $x_G>x_G^0$, neither the temperature induced sign inversion nor a tendency toward this effect has been observed. This behavior also seems to be plausible because at $x_G > x_G^0$ the contribution from the guest-guest interaction compensates the one from the guest-host interaction already at $T=T_{AC}$, resulting in a positive sign of G_0. Taking into account the positive sign of G_2, only a continuous increase of the polarization is possible.

This qualitative explanation of the temperature induced sign inversion of P_s is also supported if we compare the two functions. $P_s(x_G)$ at different temperatures as presented in Fig. 2. At lower temperatures (with ΔT increasing from 5 to 15 K), x_G^0 is shifted to lower values. This means that the equilibrium between $G_0(x_G)$ and $G_2(x_G)\Theta^2$ and, hence, the appearance of the sign inversion can be obtained at smaller fractions of the guest molecules due to the increasing influence of the second term $G_2\Theta^2$ at lower temperatures.

The observed concentration dependent sign inversion of P_s is different from the sign inversion in the mixtures reported in [17] and is understood in terms of different interactions between host and guest molecules and between two guest molecules. The origin of the temperature induced sign inversion of P_s observed in our mixtures seems to be quite different from those reported for pure compounds [9–12]. Patel and Goodby [9] have taken into account the competition between different structural conformers of the same chiral compound which can be excluded in our case because of the rigid core structure of the dopant. By contrast, Meister and Stegemeyer consider an influence of the quadrupolar ordering of the molecular transverse dipoles [18]. The latter explanation, however, is based on the general effect, which is not sensitive to the composition of the mixture that is important in our experiment.

We conclude that the present experimental results can only be explained taking into account different chiral interactions between the guest and host molecules. Development of the corresponding detailed molecular theory is in progress now and will be published elsewhere.

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