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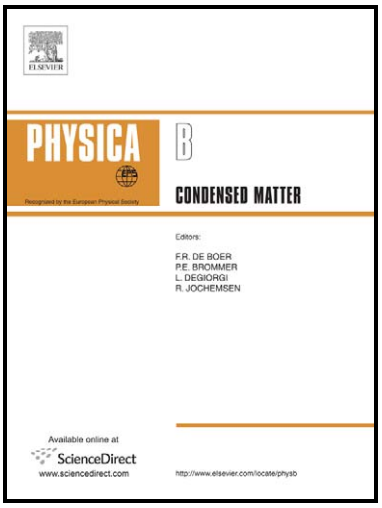

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Non-linear dielectric effect in the isotropic phase of antiferroelectric liquid crystals

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Abstract

We have theoretically studied the non-linear dielectric effect in the isotropic phase of antiferroelectric liquid crystals on the basis of phenomenological theory. We find an analytical expression for the non-linear dielectric effect in the isotropic phase of the I-SmC$^*_A$ transition. The temperature dependence of the non-linear dielectric effect is presented in the isotropic phase of the I-SmC$^*_A$ transition.

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I. INTRODUCTION

Since it's discovery by Chandani et al [1–3], much progress has taken place in the field of antiferroelectric liquid crystals (AFLC). The most frequently studied and best understood AFLCs is the chiral antiferroelectric smectic (SmC^*_A) phase. This phase is a chiral smectic C (SmC^*) phase where the molecules in adjacent layers are tilted from the layers normal in almost opposite directions and, thereby, the direction of the spontaneous polarization reverses from one layer to the next and the net polarization is vanishing over two successive layers.

In recent years the transitions from the isotropic phase to the smectic phases have been attracted much attention. The isotropic to SmC^*_A (I-SmC^*_A) is one such transition which has a considerable current interest. There are relatively few papers [4–8] on the I-SmC^*_A transition. The most interesting aspect of their results is that the optical activity becomes nearly linear with temperature near the I-SmC^*_A transition when the chirality is high. Uchiyama etal [4] studied the dielectric properties in AFLC with the I-SmC^*_A transition. Gorecka et al [6] studied the properties of the induced SmC^*_A phase by doping ferroelectric liquid crystals with Bent-shaped molecules. The temperature stability of the SmC^*_A phase increases quickly with increasing dopant concentration and for higher concentration the direct I-SmC^*_A transition is observed. In an another study [8], the binary mixture of the (S,R)-enantiomer of the M7BBM7 AFLC mesogen with the non-chiral SmC-forming compound HOAB also shows a direct I-SmC^*_A phase transition. The temperature dependence of the spontaneous polarization in the SmC^*_A phase close to the I-SmC^*_A transition was measured. Experimentally, the I-SmC^*_A phase transition is found to be first order.

On the theoretical studies there is only one attempt [9] to study the I-SmC^*_A transition. In this work one of the present author with his coworker developed a Landau model to describe the direct I-SmC^*_A transition and explained the key features of the I-SmC^*_A transition.

The first order behavior of the I-SmC^*_A transition can also be verified by the quantitative test in the non-linear dielectric effect (NDE). The SmC^*_A phase is accompanied anomalous behavior in the dielectric properties. The pretransitional behavior is rather complex in the isotropic phase of the chiral liquid crystal compounds [10]. There is so far practically no experimental as well as no theoretical observation of the NDE near the I-SmC^*_A transition.

The purpose of the present paper is to explain the pretransitional behavior of the NDE in the isotropic region of the I-SmC^*_A transition within the framework of Landau theory. Following the approach in [9, 11] we calculate directly the temperature dependence of the NDE in the isotropic phase of the I-SmC^*_A transition.

II. THEORY

The construction of the Landau free energy for the I-SmC$^*_A$ transition is rather complex, since one needs four different order parameters: the modulus of the orientational order parameter, S, the smectic order parameter characterizing the density wave, ψ, the tilt angle, θ and the antiferroelectric polarization, $\mathbf{P_a}$ as well as the wave vector q of the helix to describe the I - SmC$^*_A$ phase transition. The layering in the SmC$^*_A$ phase is described [12] by the order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-i\Phi)$, whose modulus ψ_0 is defined as the amplitude of a one-dimensional density wave characterized by the phase Φ. The wave vector $\nabla_i\Phi$ is parallel to the director n_i in the smectic-A phase. The anticlinic tilt in the SmC$^*_A$ phase can be described by the tensor order parameter [9, 11, 13, 14].

According to the previous paper [9], the two tensorial order parameters $Q^{(1)}_{ij}$ and $Q^{(2)}_{ij}$ which represent, respectively the orientations of molecules in the alternatively odd-numbered and even numbered layers are defined as

$$Q^{(m)}_{ij} = \frac{S}{2}(3n^{(m)}_i n^{(m)}_j - 1) \tag{2.1}$$

where $m = 1, 2$ and n_i is the director in the ith layer and the z-axis is set to be parallel to the layer normal. Here $n^{(m)}_i$ is not parallel to $\nabla_i\Phi$. The quantity S defines the strength of the orientational ordering.

The director $n^{(m)}_i$ in terms of the tilt angle θ and the azimuthal angle ϕ can be expressed as

$$n^{(1)}_i = e_x \sin\theta\cos\phi + e_y \sin\theta\sin\phi + e_z\cos\theta \tag{2.2}$$

$$n^{(2)}_i = -e_x \sin\theta\cos\phi - e_y \sin\theta\sin\phi + e_z\cos\theta \tag{2.3}$$

where θ is the angle between the layer normal and the director n_i. While the tilt direction is varying from layer to layer, the layer normal (z-axis) is fixed. The azimuthal angle ϕ which describes the average position of the molecules on the tilt cone changes with the coordinate z as $\phi = qz$, q being the wave vector of the helix.

The spontaneous polarization in the neighboring layers are opposite in the SmC$^*_A$ phase. If $\mathbf{P}_1$ and $\mathbf{P}_2$ are the polarization in the neighboring layers "1" and "2", then the anti-ferroelectric polarization in the SmC$^*_A$ phase can be expressed as

$$\mathbf{P}_a = \{P_y\} = \sum_{i=0}^{m-1} (\mathbf{P}_1^{2i} - \mathbf{P}_2^{2i+1}) \tag{2.4}$$

where the subscript i runs over the number of layers m and $\mathbf{P}_1 = \frac{1}{2m} P_0 \hat{\mathbf{P}}$ and $\mathbf{P_2} = -\mathbf{P_1}$ are the alternating polarizations in the sublayers (1 and 2) and $\hat{\mathbf{P}}$ denotes the preferred direction within the

layers. The staggered polarization $\mathbf{P_a} = P_0\hat{\mathbf{P}}$ has the same properties as the polarization $\mathbf{P}$ in the ferroelectric case. The procedure outlined closely parallels that well-known for anti-ferromagnets.

All these order parameters jump simultaneously at the I-SmC$^*_A$ transition.

Following Kittel [15], we assume that when we apply a small electric field $\Delta\mathbf{E}$ in the helical modulated SmC$^*_A$ phase, a small but finite macroscopic polarization $\Delta\mathbf{P_a} = \mathbf{P}_1 + \mathbf{P}_2$ is produced in the unit cell in the helical modulated SmC$^*_A$ phase. In this case we assume $\mathbf{P}_1 \cong -\mathbf{P}_2$. This is justified since the direction of the in-plane spontaneous polarization in the helical modulated SmC$^*_A$ phase is changing from layer to layer by a phase angle slightly less than 180^o. This macroscopic polarization $\Delta\mathbf{P_a}$ couples with electric field $\Delta\mathbf{E}$.

Considering the above described order parameters, the total free energy density near the I - SmC$^*_A$ transition in the presence of an electric field can be expanded as [9]

$$\begin{aligned}
F \;=\; & F_0 + \frac{1}{6}a\left(Q^{(1)}_{ij}Q^{(1)}_{ij} + Q^{(2)}_{ij}Q^{(2)}_{ij}\right) - \frac{4}{18}b\left(Q^{(1)}_{ij}Q^{(1)}_{jk}Q^{(1)}_{ki} + Q^{(2)}_{ij}Q^{(2)}_{jk}Q^{(2)}_{ki}\right) \\
& + \frac{1}{18}c_1\left(Q^{(1)}_{ij}Q^{(1)}_{ij} + Q^{(2)}_{ij}Q^{(2)}_{ij}\right)^2 + \frac{1}{18}c_2\left(Q^{(1)}_{ij}Q^{(1)}_{jk}Q^{(1)}_{kl}Q^{(1)}_{li} + Q^{(2)}_{ij}Q^{(2)}_{jk}Q^{(2)}_{kl}Q^{(2)}_{li}\right) \\
& + \frac{1}{2}\alpha\left|\psi\right|^2 + \frac{1}{4}\beta\left|\psi\right|^4 + \frac{1}{2\chi_a}(\Delta\mathbf{P_a})^2 + \frac{1}{2}d_1\left|\nabla_i\psi\right|^2 + \frac{1}{2}d_2\left|\Delta\psi\right|^2 \\
& + \frac{1}{18}\eta Q^{(1)}_{ij}Q^{(2)}_{ij} + \frac{1}{108}\lambda\left(Q^{(1)}_{ij}Q^{(2)}_{ij}\right)^2 + \frac{1}{4}L_1\left(\nabla_i Q^{(1)}_{jk}\nabla_i Q^{(1)}_{jk} + \nabla_i Q^{(2)}_{jk}\nabla_i Q^{(2)}_{jk}\right) \\
& + \frac{1}{4}L_2\left(\nabla_i Q^{(1)}_{ik}\nabla_j Q^{(1)}_{jk} + \nabla_i Q^{(2)}_{ik}\nabla_j Q^{(2)}_{jk}\right) + \frac{1}{2}L_3\varepsilon_{ijk}\left(Q^{(1)}_{il}\nabla_k Q^{(1)}_{jl} + Q^{(2)}_{il}\nabla_k Q^{(2)}_{jl}\right) \\
& + \frac{1}{6}\mu\left(Q^{(1)}_{ij}Q^{(1)}_{ij} + Q^{(2)}_{ij}Q^{(2)}_{ij}\right)\left|\psi\right|^2 + \frac{1}{4}e\left(Q^{(1)}_{ij} + Q^{(2)}_{ij}\right)(\nabla_i\psi)(\nabla_j\psi^*) \\
& + \frac{1}{2}\gamma(Q^{(1)}_{ij} + Q^{(2)}_{ij})\Delta P_{ai}\Delta P_{aj} + \frac{1}{4}g_{ijkl}(\nabla_k Q^{(1)}_{ij} + \nabla_k Q^{(2)}_{ij})\Delta P_{al} - \Delta\mathbf{P_a}\cdot\Delta\mathbf{E} \qquad (2.5)
\end{aligned}$$

where F_0 is the free energy of the isotropic phase. Here $a = a_0(T - T^*_1)$, and $\alpha = \alpha_0(T - T^*_2)$. T^*_1 and T^*_2 are the critical temperature for a hypothetical second-order transition. a_0, α_0, c_1, c_2, β, d_1, d_2, η, λ, and γ are positive constants. μ is a coupling constant. A negative value μ increases the smectic ordering and favors the SmC$^*_A$ phase. χ_a is the relevant dielectric susceptibilities. L_1 and L_2 are the orientational elastic constants. Here ε_{ijk} is an antisymmetric third rank tensor. The chiral character of the SmC$^*_A$ phase results in the pseudoscalar first-order spatial derivative term in the free energy. Thus the coefficient L_3 is analogous to the coefficient of the Lifshitz-invariant term and induces the helical modulation of the SmC$^*_A$ phase. The gradient terms $\sim e$ and $\sim h$ involving Q_{ij} govern the relative direction of the layering with respect to the director and lead to the tilt angle of the SmC$^*_A$ phase. In general a negative value of e favors the stability of the SmC$^*_A$ phase. There is no direct linear coupling term $\sim|\ \psi\ |^2\ Q^{(1,2)}_{ij}$ in the free energy (2.5), since such a term cannot exist in the isotropic phase [16]. Here g_{ijkl} takes the form $g_{ijkl} = g(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$

with δ_{ik} the Kronecker symbol. The coefficient g is analogous to the flexoelectric coefficient. The above free energy describes the direct first order I-SmC$^*_A$ transition in the absence of an electric field. The detailed analysis of the I-SmC$^*_A$ transition was described in Ref [9].

The pretransitional anomaly of the NDE near the I-SmC$^*_A$ transition can appear only when the antiparallel cancellation of dipole within fluctuations occurs which is the basic results of the directors $-\mathbf{n}$ and $\mathbf{n}$ equivalence. Now we consider the phases in which the nematic and smectic order are spatially homogeneous, *i.e.* S =const. and ψ_0=const. for simplicity of the calculation. The system being in the isotropic phase, a homogeneous electric field will couple to $q = 0$ changes of the order parameters. Accordingly all spatial derivatives of Q_{ij} in Eq. (2.5) is zero. The substitution of Q_{ij}, ψ and $\mathbf{\Delta P_a}$ in Eq. (2.5), and eliminating the equilibrium value of θ from Eq. (2.5), leads to the free energy density

$$\begin{aligned} F \;=\; & f_0 + \frac{1}{2}a'S^2 - \frac{1}{3}bS^3 + \frac{1}{4}c'S^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 + \frac{1}{2\chi_a}(\Delta P_a)^2 \\ & + \frac{1}{2}\mu S^2\psi_0^2 - \frac{1}{2}\gamma(\Delta P_a)^2 S - \Delta P_a \Delta E \end{aligned} \tag{2.6}$$

where $a' = a + 3\eta/4$, $c' = c + 3\lambda/2$, and $c = (c_1 + c_2/2)$.

After minimizing the free energy (2.6) with respect to ΔP_a and ψ_0, the polarization and the translational order parameter are obtained to be

$$\Delta P_a = \Delta E \chi_a M \tag{2.7}$$

where $M = (1 - \gamma\chi_a S)^{-1}$.

$$\psi_0^2 = -\frac{1}{\beta}(\alpha + \mu S^2) \tag{2.8}$$

After inserting these results into the free energy density (2.6), we obtain the free energy density as a function of S alone as:

$$F = F_0^* + \frac{1}{2}a^*S^2 - \frac{1}{3}b^*S^3 + \frac{1}{4}c^*S^4 - \frac{1}{2}\gamma\chi_a^2(\Delta E)^2 S \tag{2.9}$$

where $F_0^* = F_0 - \frac{\alpha^2}{4\beta} - \frac{(\Delta E)^2\chi_a}{2}$,

The renormalized coefficients are

$$a^* = a + \frac{3}{4}\eta - \frac{\alpha}{\beta} - \gamma^2\chi_a^3(\Delta E)^2, \tag{2.10}$$

$$b^* = b - \frac{9}{2}\gamma^3\chi_a^4(\Delta E)^2, \tag{2.11}$$

$$c^* = c + \frac{3}{2}\lambda - \frac{\mu^2}{\beta}. \tag{2.12}$$

The analysis of Eq. (2.10) shows that the influence of the electric field produces a shift of the transition temperature $T^*_{I-SmC^*_A}$ which is proportional to the square of the electric field

$$\Delta T^*_{I-SmC^*_A} = W(\Delta E)^2 \tag{2.13}$$

with $W = \gamma^2\chi_a^2\left(a_0 - \frac{\mu\alpha_0}{\beta}\right)^{-1}$. The electric field also induces weak orientational ordering in the isotropic phase. The orientational order parameter induced by an electric field in the isotropic phase is calculated to a first approximation ($b^* = 0$ and $c^* = 0$) and can be expressed as

$$S(\Delta E) = \frac{U}{(T - T^*_{I-SmC^*_A})}(\Delta E)^2 + \frac{V}{(T - T^*_{I-SmC^*_A})^2}(\Delta E)^4 \tag{2.14}$$

where

$U = \frac{\gamma\chi_a^2}{2}\left(a_0 - \frac{\mu\alpha_0}{\beta}\right)^{-1}$,
$V = \frac{\gamma^3\chi_a^4}{2}\left(a_0 - \frac{\mu\alpha_0}{\beta}\right)^{-2}$,
$T^*_{I-SmC^*_A} = \left(a_0T_1^* - T_2^*\frac{\mu\alpha_0}{\beta} - 3\eta/4\right)\left(a_0 - \frac{\mu\alpha_0}{\beta}\right)^{-1}$.

Note that in the first approximation $S(\Delta E) = \frac{U}{(T-T^*_{I-SmC^*_A})}(\Delta E)^2$. The NDE denotes the change in the dielectric permittivity of a material that originates from the application of strong static electric field $\Delta\mathbf{E}$. The NDE is widely analogous to the electro-optic Kerr effect which applies to the case of optical frequencies. Transitions from the isotropic to the SmC^*_A state are associated with a pronounced pretransitional NDE since the aligning electric field $\Delta\mathbf{E}$ couples to the critical fluctuations and, thereby, induces a certain long range orientational order $S(\Delta E)$ of mesogenic units in the originally disordered isotropic phase [17]. This electric field-induced orientational order gives rise to an induced dielectric anisotropy which in turn changes the dielectric permittivity observed in the direction of the measuring field. Hence the dielectric permittivity in the isotropic phase to a first approximation can be expressed as [18, 19]

$$\Delta\varepsilon(\Delta E) = \varepsilon(\Delta E) - \varepsilon(0) = (\Delta\varepsilon_f)_{max}\ S(\Delta E). \tag{2.15}$$

where $\varepsilon(\Delta E)$ and $\varepsilon(0)$ are the dielectric permittivities in a strong ($\Delta\mathbf{E}$) and weak (measuring) electric field. $(\Delta\varepsilon_f)_{\max}$ denotes the anisotropy of the dielectric permittivity for the given frequency f. Combining Eqs. (2.14) and (2.15) we find

$$\varepsilon_{NDE} = \frac{\varepsilon(\Delta E) - \varepsilon(0)}{(\Delta E)^2} = \frac{W}{(T - T^*_{I-SmC^*_A})}, \tag{2.16}$$

where $W = (\Delta\varepsilon_f)_{\max}U$.

The temperature dependence of the NDE in the isotropic phase is shown in Fig.1. This is done for a set of phenomenological parameters for which a direct I-SmC$^*_A$ transition is possible. Units of the NDE and temperature are arbitrary. The form of Eq. (2.16) shows that there are several unknown phenomenological parameters. We have, therefore used $(\Delta\varepsilon_f)_{\max}$ and U as reduced unknown parameters to draw the Fig.1. Fig.1 shows the temperature dependence of the NDE in the isotropic phase with parameter values $(\Delta\varepsilon_f)_{\max} = 0.87$ and $U = 1.45$.

III. CONCLUSION

We have theoretically shown that the NDE in the isotropic phase of the I-SmC$^*_A$ transition can be observed by an electric field through linear coupling with the polarization. We would like to point out that the obtained results in this paper, which were based on the free energy density Eq. (2.6) leading to a first order I-SmC$^*_A$ transition will be valid also in the case of the second order transition. Furthermore, the critical exponent exponent $\gamma' = 1$ indicate the fluid like analogy in the isotropic phase of the I-SmC$^*_A$ transition similar to that at the isotropic-nematic, isotropic-Smectic A and isotropic to SmC* transitions. We hope that the present theoretical analysis of the NDE in the isotropic phase of the I-SmC$^*_A$ transition will stimulate a closer look at this problem. Clearly the detailed experiments on the antiferroelectric liquid crystals are highly desirable to check the phase diagrams presented here is actually accessible experimentally.

IV. ACKNOWLEDGMENTS

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Figure captions:

FIG. 1: The temperature dependence of the NDE in the isotropic phase of the I-SmC$^*_A$ transition.

FIG.1