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Experimental and theoretical study of the influence of a bias electric field on the dielectric properties of the chiral smectic A* phase

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The influence of a bias electric field on the temperature and frequency dependence of the soft mode part of the complex dielectric constant of the chiral smectic A* phase has been studied experimentally. It was found that only close to $T_{S_C^*S_A^*}$ does the bias field have any influence on the experimentally determined quantities. Here the relaxation frequency increased with increasing bias field, while the corresponding dielectric strength decreases. We also present a theoretical calculation of the influence of a bias field on the complex dielectric constant of the chiral smectic A* phase which, apart from minor details, is in accordance with the observed behaviour. Finally we discuss how the nature of the electroclinic effect can be correlated with the influence of the bias field on the smectic A* dielectric constant.

1. Introduction

When characterizing the properties of ferroelectric liquid crystals [1] near the chiral smectic A (S_A^*)–chiral smectic C (S_C^*) transition the determination of the complex dielectric constant is of great interest, because in the same experiment the statics (low frequency dielectric constant) as well as the dynamics (frequency dependence of the dielectric constant) of the system can be studied. Today a vast number of papers dealing with both experimental and theoretical aspects of the dielectric properties of S_C^* and S_A^* liquid crystals can be found in the literature [2–21]. In general two two-component vectors are introduced [22, 23] as order parameters when describing the system which we have studied. These are the primary order parameter $\boldsymbol{\xi} = (\xi_1, \xi_2)$ describing the tilt of the director from the normal to the smectic layer, and the secondary order parameter, the in-plane polarization $\mathbf{P} = (P_x, P_y)$. Thus the dielectric response of the system consists (apart from the usual electronic contribution) of four modes [3, 20]. Two of these are associated with director fluctuations and have

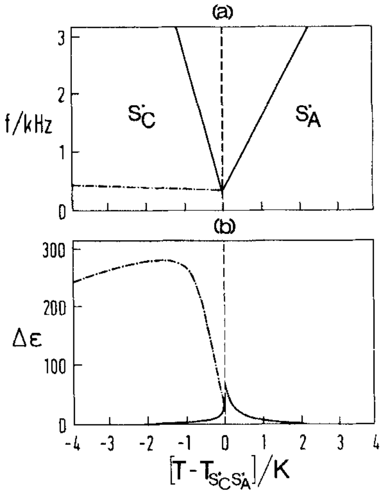


Figure 1. Typical behaviour of (*a*) the relaxation frequency and (*b*) the dielectric strength of the soft mode denoted by the solid line and the Goldstone mode indicated by the broken line close to the S_C^*–S_A^* transition.

relaxation frequencies which lie in the Hz and kHz range [14, 16]. The other two are associated with fluctuations of the polarization order parameter and exhibit relaxation frequencies which have been reported [8] to be of the order of 500 MHz. In this paper we shall only study the director modes and thus we incorporate the contribution from polarization modes into the high frequency part of the dielectric constant, ε_∞. Further we have only studied the case when the electric field is applied parallel to the smectic planes.

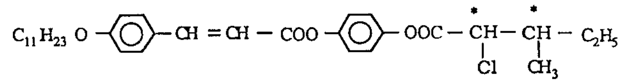
The two director modes of S_C^* liquid crystals are commonly denoted [14] the soft mode and the Goldstone mode. The Goldstone mode is associated with distortion of the helix (i.e. the phase of the director) due to the probing electric field. Typical relaxation frequencies of the Goldstone mode are of the order of 10–500 Hz with a relatively weak temperature dependence. The corresponding dielectric strength increases rapidly as the temperature of the system is lowered from the S_C^*–S_A^* transition temperature $T_{S_C^*S_A^*}$, and adopts a plateau-like maximum a few degrees below $T_{S_C^*S_A^*}$. The soft mode is associated with the change of the tilt of the molecules and exhibits relaxation frequencies which vary almost linearly with $T_{S_C^*S_A^*}$, typically in the range 1 kHz–1 MHz. The corresponding dielectric strength shows a pronounced decrease as $T_{S_C^*S_A^*} - T$ is increased. In the S_A^* phase the Goldstone mode is absent and the system exhibits a doubly generate soft mode. In figure 1 we have sketched the behaviour of the relaxation frequencies and the dielectric strengths of the director modes for a typical system near the S_C^*–S_A^* transition.

As we can see from figure 1 the intensity of the soft mode is rapidly drowned in that of the Goldstone mode as the temperature of the system is lowered from $T_{S_C^*S_A^*}$. This makes it possible to separate [14, 16, 18] the contribution from the two modes only in a temperature interval which is of the order of a few tenths of a degree below $T_{S_C^*S_A^*}$. One way to study the soft mode in a broader temperature interval into the S_C^* phase is to apply a static electric bias field parallel to the smectic layers. If the bias field is strong enough the helix of the system is unwound and thus the Goldstone mode is suppressed. Different types of studies of the dielectric properties under a bias field near the S_C^*–S_A^* transition have been performed by, among others, Hoffman *et al.* [11], Bahr *et al.* [12], Pavel *et al.* [15] and Gouda *et al.* [19]. One question which immediately arises when this type of experiment is performed, is in which way does the bias field influence the behaviour of the soft mode dielectric response of the system. It is well known that close enough to $T_{S_C^*S_A^*}$ the tilt is affected [13, 24–26] by the bias field in both the S_C^* as in the S_A^* phase. This change of tilt should, of course, also be expected to influence the dielectric properties of the system.

It is the purpose of the present paper to investigate to what extent the soft mode part of the complex dielectric constant is influenced by applying a bias field to the system. In the S_C^* phase when applying a bias field, the major change of the dielectric constant is attributed to the gradual unwinding of the helix, resulting [12] in a decrease of the dielectric strength of the Goldstone mode. Thus it is difficult to extract any information about the influence of the bias field on the soft mode, especially when the bias field is much less than the critical (unwinding) field. Therefore, we have chosen to perform a careful study of the field dependence of the complex dielectric constant in the S_A^* phase. Here, only the soft mode is present, and so in this case all of the changes of the dielectric constant can be attributed to the soft mode behaviour. In §2 we give the experimental details. We present measurements of the functional dependence of the complex dielectric constant on the strength of the applied bias field for a sequence of temperatures between 0·15–2·14 K above $T_{S_C^*-S_A^*}$. In §3 we then present a theoretical calculation of the complex dielectric constant of the S_A^* phase in the presence of a bias field. The outcome of this calculation is found to be in good agreement with the experimental results.

2. Experimental results

The liquid crystal used in this work has been synthesized by Nguyen *et al.* [27] and has the formula,



The measuring cell consists of two conducting glass plates separated by Mylar spacers of 100 μm thickness. The capacitance and conductance were measured in the frequency range 0·5–200 kHz using the HP 4192 LF impedance analyser. At first the capacitance of the empty cell was measured, later the cell was filled with the liquid crystal in vacuum to avoid air bubbles. A planar orientation (bookshelf sample geometry) was obtained by cooling the sample slowly in a magnetic field of 1·2 T from the isotropic phase to the S_A^* phase. A measuring field of 0·3 V_{pp}/100 μm was applied parallel to the smectic layers. The measuring field was superimposed on the internal bias field obtained from the HP bridge. The value of the bias field was varied between zero and 35 V/100 μm for each temperature.

The aim of the experiment is to investigate the influence of the bias field on the complex dielectric constant in the S_A^* phase. Assuming a single Debye relaxation, this can be written as

$$\varepsilon^*(\omega, T) = \frac{\Delta\varepsilon_{SA}(T)}{1 + i\omega t_A} + \varepsilon_\infty(T), \qquad (1)$$

where ω is the angular frequency of the applied measuring field, $\Delta\varepsilon_{SA}$ is the dielectric strength of the S_A^* soft mode and $t_A = 1/2\pi f_A$ is the corresponding relaxation time.

The constant ε_∞ represents the sum of the contributions from the S_A^* polarization mode and all other high frequency mechanisms which might be present in the system. The experimental data were analysed by the use of Cole–Cole plots [28]. The details of this analysis for ferroelectric liquid crystals have been discussed by us elsewhere [14]. In figure 2 (*a*) we have plotted the Cole–Cole diagrams obtained for zero bias field at different temperatures in the S_A^* phase while in figure 2 (*b*) we demonstrate the effect of applying an increasing bias field to the system at one of these temperatures.

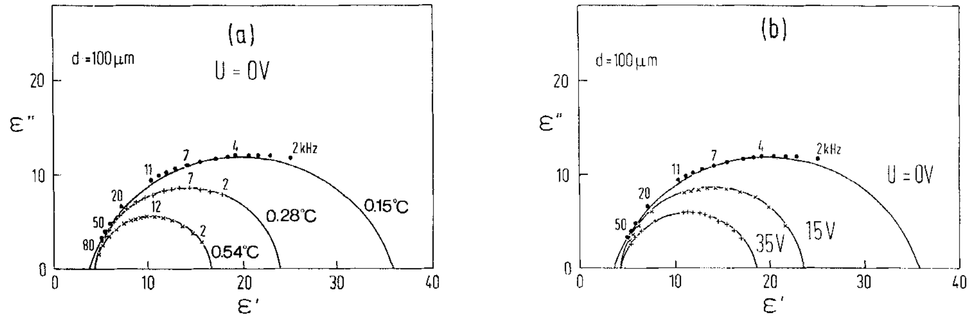


Figure 2. Cole–Cole plots of the soft mode in the S_A^* phase. In (*a*) a sequence of plots for different temperatures, $T - T_{S_C^*S_A^*}$, at zero bias field is shown, while in (*b*) a sequence of plots for different bias fields at a fixed temperature, $T - T_{S_C^*S_A^*} = 0{\cdot}15\,\mathrm{K}$, is shown.

In figure 3 the relaxation frequency, the inverse of the dielectric strength and the product of the relaxation frequency and the dielectric strength are plotted, for several temperatures, as a function of the strength of the applied bias field. We note that close to $T_{S_C^*S_A^*}$ the relaxation frequency increases with increasing bias field towards a limiting value. The same is true for the inverse of the dielectric strength. Above a temperature, which in our case is approximately 1 K from $T_{S_C^*S_A^*}$, the bias field does not have any influence on neither the relaxation frequency, nor the dielectric strength of the system. Concerning the product of the relaxation frequency and the dielectric strength, there is no influence of the bias field except at the temperature which is the closest to $T_{S_C^*S_A^*}$ ($T - T_{S_C^*S_A^*} = 0{\cdot}15\,\mathrm{K}$). At this temperature the product is almost constant, except when the bias field approaches zero where it exhibits a small drop.

3. Theory

In this section we present a calculation of the complex dielectric constant of the S_A^* phase when the system is affected by a static electric bias field. As a starting point of the calculation we use the generalized Landau expansion of the free energy density of the system discussed by us elsewhere [14, 21, 23]. Expanding the free energy density, $g_0(z)$, in the order parameters $\boldsymbol{\xi}$ and $\mathbf{P}$, we write in the absence of any applied external field,

$$\begin{aligned} g_0(z) = {} & \tfrac{1}{2}a(\xi_1^2 + \xi_2^2) + \tfrac{1}{4}b\,(\xi_1^2 + \xi_2^2)^2 + \tfrac{1}{6}c(\xi_1^2 + \xi_2^2)^3 - \Lambda\left(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}\right) \\ & + \tfrac{1}{2}K_3\left[\left(\frac{d\xi_1}{dz}\right)^2 + \left(\frac{d\xi_2}{dz}\right)^2\right] + \frac{1}{2\varepsilon}(P_x^2 + P_y^2) - \mu\left(P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz}\right) \\ & + C(P_x\xi_2 - P_y\xi_1) - \tfrac{1}{2}\Omega\,(P_x\xi_2 - P_y\xi_1)^2 + \tfrac{1}{4}\eta\,(P_x^2 + P_y^2)^2 \\ & - d(\xi_1^2 + \xi_2^2)\left(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}\right). \end{aligned} \qquad (2)$$

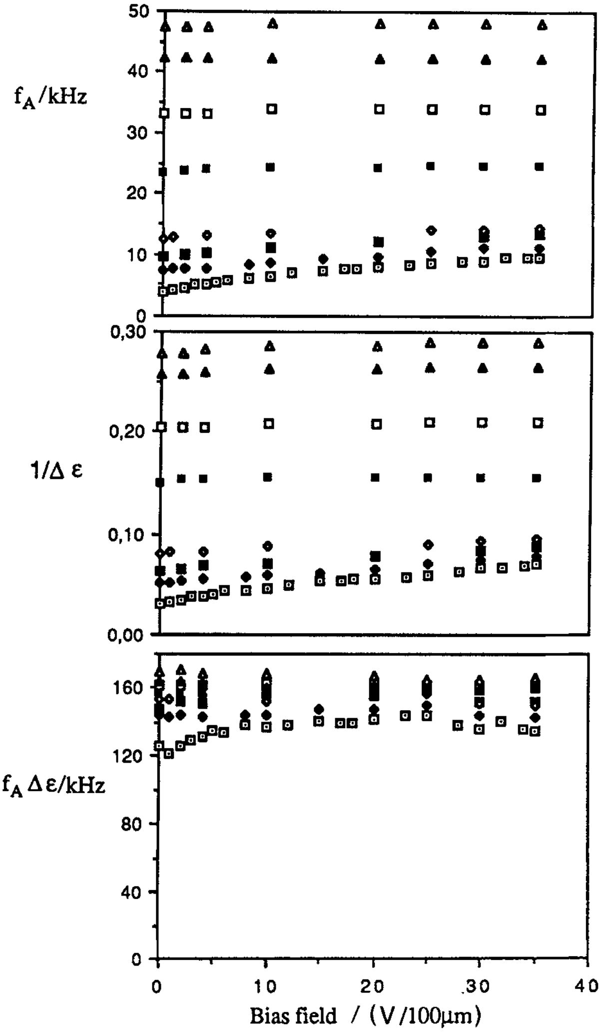


Figure 3. Experimentally determined relaxation frequency, inverse of the dielectric strength and product of relaxation frequency and dielectric strength of the soft mode at different temperatures in the S_A^* phase as a function of the applied bias field. □, ΔT = 0·15°C; ◆, ΔT = 0·28°C; ■, ΔT = 0·40°C; ◇, ΔT = 0·54°C; ■, ΔT = 0·99°C; □, ΔT = 1·46°C; ▲, ΔT = 1·93°C; △, ΔT = 2·14°C.

A full review of the generalized Landau model can be found in any of the three papers [14, 21, 23] where the meaning of the eleven material parameters introduced through equation (2) is discussed in detail. By applying a bias electric field $\mathbf{E}_B = E_0\hat{y}$ and a measuring field $\mathbf{E}_m = \delta E \exp(i\omega t)\hat{y}$ we obtain an additional contribution $-(\mathbf{E}_B + \mathbf{E}_m) \cdot \mathbf{P}$ to the free energy density of the system, which in this case is written as

$$g(z) = g_0(z) - [E_0 + \delta E \exp(i\omega t)]P_y, \tag{3}$$

where $g_0(z)$ is given by equation (2). As we are studying the system in the S_A^* phase, a homogeneous electric field will induce spatially uniform changes of the order parameters. We thus write the order parameters $\boldsymbol{\xi}$ and $\mathbf{P}$ as

$$\boldsymbol{\xi} = (\xi_0 + \delta\xi)\hat{x}, \qquad (4a)$$

$$\mathbf{P} = (P_0 + \delta P)\hat{y}. \qquad (4b)$$

Here ξ_0 and P_0 denote the equilibrium values of the tilt and the spontaneous polarization which correspond to the bias field E_0, while $\delta\xi$ and δP are the time dependent fluctuations of the order parameters which are due to the measuring field $\delta E \exp(i\omega t)$. The way in which $\boldsymbol{\xi}$ and $\mathbf{P}$ are introduced in equations (4) (i.e. $\boldsymbol{\xi} \times \mathbf{P} \propto \hat{z}$) imply that if we are dealing with what Clark and Lagerwall denote a (+) substance [29], a positive value of the constant C corresponds [21] to positive polarization P_0. Putting $d/dz \equiv 0$ and taking the linear response of the system we find from equations (2)–(4), by expanding to second order in $\delta\xi$ and δP,

$$g(z) = g_0 + g_1 + g_2 + g_E, \qquad (5)$$

where

$$g_0 = \tfrac{1}{2}a\xi_0^2 + \tfrac{1}{4}b\xi_0^4 + \tfrac{1}{6}c\xi_0^6 + \frac{1}{2\varepsilon}P_0^2 + \tfrac{1}{4}\eta P_0^4 - CP_0\xi_0 - \tfrac{1}{2}\Omega P_0^2\xi_0^2 - E_0P_0, \qquad (6a)$$

$$g_1 = (a\xi_0 + b\xi_0^3 + c\xi_0^5 - CP_0 - \Omega\xi_0 P_0^2)\delta\xi + \left(\frac{1}{\varepsilon}P_0 + \eta P_0^3 - C\xi_0 - \Omega\xi_0^2 P_0 - E_0\right)\delta P, \qquad (6b)$$

$$g_2 = (\tfrac{1}{2}a + \tfrac{3}{2}b\xi_0^2 + \tfrac{5}{2}c\xi_0^4 - \tfrac{1}{2}\Omega P_0^2)\delta\xi^2 + \left(\frac{1}{2\varepsilon} + \tfrac{3}{2}\eta P_0^2 - \tfrac{1}{2}\Omega\xi_0^2\right)\delta P^2 - (C + 2\Omega P_0\xi_0)\delta P\delta\xi, \qquad (6c)$$

$$g_E = -\delta E \exp(i\omega t)\,(P_0 + \delta P) \qquad (6d)$$

The equations governing the equilibrium values of the tilt, ξ_0, and the polarization, P_0, of the system in the presence of the bias field are obtained by minimizing the expression of equation (6a) with respect to ξ_0 and P_0, respectively

$$a\xi_0 + b\xi_0^3 + c\xi_0^5 - CP_0 - \Omega P_0^2\xi_0 = 0 \qquad (7a)$$

$$\frac{1}{\varepsilon}P_0 + \eta P_0^3 - C\xi_0 - \Omega\xi_0^2 P_0 - E_0 = 0. \qquad (7b)$$

These two equations imply $g_1 \equiv 0$ (cf. equation (6b)). We now introduce the renormalized constants

$$\bar{a} = a + 3b\xi_0^2 + 5c\xi_0^4 - \Omega P_0^2, \qquad (8a)$$

$$\frac{1}{\bar{\varepsilon}} = \frac{1}{\varepsilon} + 3\eta P_0^2 - \Omega\xi_0^2 \qquad (8b)$$

and

$$\bar{C} = C + 2\Omega P_0\xi_0. \qquad (8c)$$

With the use of these renormalized constants the extra free energy density due to the measuring field $\delta E \exp(i\omega t)$, which is given by $g_2 + g_E$ (equations (6 *c*) and (6 *d*) can be written

$$g_2 + g_E = \tfrac{1}{2}\bar{a}\delta\xi^2 + \frac{1}{2\bar{\varepsilon}}\delta P^2 - \bar{C}\delta P\delta\xi - \delta E \exp(i\omega t)\,(P_0 + \delta P). \tag{9}$$

To study the dynamical response of the system we now apply the Landau-Khalatnikov equations of motion

$$\dot{\delta\xi} = -\Gamma_S \frac{\partial(g_2 + g_E)}{\partial(\delta\xi)}, \tag{10a}$$

$$\dot{\delta P} = -\Gamma_P \frac{\partial(g_2 + g_E)}{\partial(\delta P)}, \tag{10b}$$

where Γ_S and Γ_P are the S_A^* phase kinetic coefficients of the director soft mode and the polarization mode, respectively. Assuming the eigenfrequency of the polarization mode to be much larger compared to that of the director mode, we take the limit $\Gamma_P \to \infty$ in equation (10 *b*). We shall also introduce the soft mode rotational viscosity, γ, which is just the reciprocal of Γ_S. By introducing a time dependence of $\delta\xi$ and δP according to

$$\delta\xi = \delta\xi_0 \exp(i\omega t) \tag{11a}$$

$$\delta P = \delta P_0 \exp(i\omega t) \tag{11b}$$

we find the set of equations governing the amplitudes of the fluctuations, $\delta\xi_0$ and δP_0, by using equations (9)–(11)

$$(\bar{a} + i\gamma\omega)\,\delta\xi_0 - \bar{C}\delta P_0 = 0, \tag{12a}$$

$$-\bar{C}\delta\xi_0 + \frac{1}{\bar{\varepsilon}}\delta P_0 = E. \tag{12b}$$

From the first of these we find

$$\delta\xi_0 = \frac{\bar{C}}{\bar{a} + i\omega t}\delta P_0 \tag{13}$$

which gives the relation between the induced tilt and induced polarization due to the measuring field. By substituting equation (13) into equation (12 *b*) we shall find

$$\delta P_0 = \left[\frac{\bar{\varepsilon}^2\bar{C}^2}{\bar{a} + i\omega t - \bar{\varepsilon}\bar{C}^2} + \bar{\varepsilon}\right]\delta E \tag{14}$$

a relation which can be rewritten as

$$\frac{\delta P_0}{\delta E} = \frac{\bar{\varepsilon}^2\bar{C}^2}{\bar{a} - \bar{\varepsilon}\bar{C}^2}\,\frac{1}{1 + i\omega\dfrac{\gamma}{\bar{a} - \bar{\varepsilon}\bar{C}^2}} + \bar{\varepsilon}. \tag{15}$$

Neglecting all other contributions to the dielectric constant than those connected to the ferroelectric behaviour of the system, equation (1) can be written as

$$\varepsilon^*(\omega, T) = \frac{\Delta\varepsilon_{SA}}{1 + i\omega t_A} + \Delta\varepsilon_{PA}, \tag{16}$$

where $\Delta\varepsilon_{PA}$ is the dielectric strength of the S_A^* phase polarization mode. By comparing equations (15) and (16) we obtain

$$\varepsilon_0 \Delta\varepsilon_{PA} = \bar{\varepsilon}, \qquad (17a)$$

$$\varepsilon_0 \Delta\varepsilon_{SA} = \frac{\bar{\varepsilon}^2 \bar{C}^2}{\bar{a} - \bar{\varepsilon}\bar{C}^2}, \qquad (17b)$$

$$f_A = \frac{1}{2\pi\gamma}(\bar{a} - \bar{\varepsilon}\bar{C}^2), \qquad (17c)$$

where ε_0 is the permittivity of free space. In the absence of the bias field the equilibrium values of ξ_0 and P_0 are zero. From equations (8) we see that in this case $\bar{a} \rightarrow a$, $\bar{\varepsilon} \rightarrow \varepsilon$, $\bar{C} \rightarrow C$ and the expressions of equations (17) transform to those of the S_A^* phase previously presented [7, 20] in the literature. The influence of the bias field is introduced through the renormalization of the constants according to equations (8), where the equilibrium values of ξ_0 and P_0 due to the bias field are given by equations (7).

In order to compare the results of equations (17) with the experimental data presented in figure 3 we must introduce some values of the material coefficients which enter the equations. In order to determine these parameters we need [21, 23] to perform a full set of measurements of other physical quantities such as tilt, polarization, pitch and heat capacity of the system. As all of these data do not exist for the present compound, we cannot determine all of the material parameters which are needed in the calculation. We must, therefore be content to make a qualitative comparison between theory and experiment by performing the calculations with a set of parameters which has been determined by us previously [21] for another liquid crystal and which will be used as a standard set of parameters of the S_C^*–S_A^* system. In figure 4 we have plotted the calculated relaxation frequency and the calculated inverse of the dielectric strength as a function of the bias field according to equations (7), (8) and (17) for a sequence of reduced temperatures. All of the scales as well as the reduced temperature $\tau \sim T - T_{S_C^* S_A^*}$ are chosen to be given as arbitrary units since we are only making a qualitative comparison between figures 3 and 4. We note that for small values of τ the calculated relaxation frequency and the calculated inverse of the dielectric strength have the same general dependences as those determined

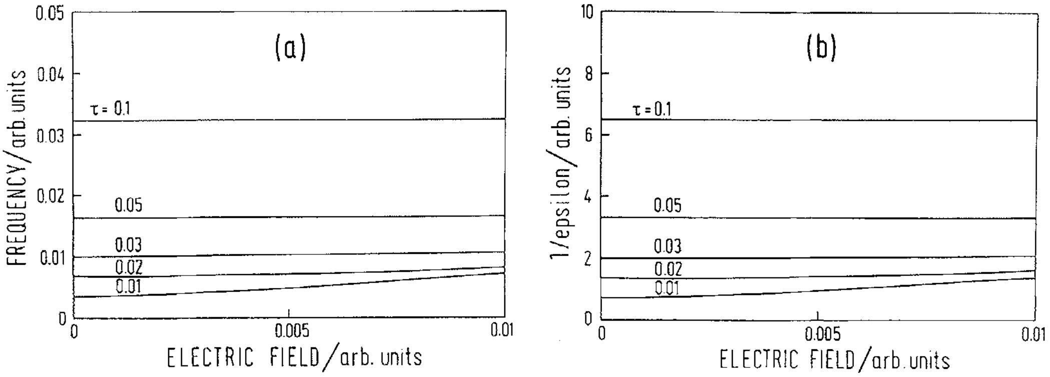


Figure 4. Calculated (see equations (7), (8) and (17)) relaxation frequency and inverse of the dielectric strength of the soft mode at different temperatures in the S_A^* phase as a function of the applied bias field.

experimentally. For larger values of τ, the bias field does not have any influence on the calculated values, this is also in accordance with experiment. The calculated values of the product of the relaxation frequency and the dielectric strength does not, for our set of parameters, exhibit any observable influence of the electric field, not even close to $T_{S_C^*S_A^*}$, and so it is not plotted in the figure. This discrepancy between the experimental and theoretical behaviour of this product will be discussed in the next section.

4. Discussion

In this work we have made a detailed study of the influence of a bias electric field upon the complex dielectric constant of the chiral S_A^* phase. The experimental results are summarized in figure 3, where the relaxation frequency, the inverse of the dielectric strength and the product of the relaxation frequency and the dielectric strength are plotted. The conclusion we draw from this figure is that only close to $T_{S_C^*S_A^*}$ does the bias field have any influence upon the behaviour of the quantities in question.

In order to understand the physics behind the observed behaviour of the dielectric constant, we first discuss the nature of the electroclinic effect [24], i.e. the phenomenon that a bias electric field in the S_A^* phase induces a tilt as well as a polarization in the sample. By solving equations (7) we calculate the induced tilt as function of the applied bias field E_0. In figure 5 we show the result of such a calculation performed with the same set of parameters as we have used for the calculation of the dielectric constant presented in figure 4. We have plotted the induced tilt as function of the bias field for the same sequence of temperatures in both cases, i.e. the five curves in figure 5 are those corresponding to the five curves in figure 4. We see that away from $T_{S_C^*S_A^*}$, the electroclinic effect shows a linear dependence with the bias field while close to $T_{S_C^*S_A^*}$ we notice a non-linear behaviour with a tendency to saturate for large enough electric fields. This performance of the electroclinic effect is in accordance with what is observed experimentally by Nishiyama *et al.* [30]. It is easy to understand this behaviour of the electroclinic effect qualitatively. As long as the field induced tilt and polarization are not too large, only linear effects play a role and we can neglect all higher order terms in equation (7), which in this case have the solution

$$\xi_0 = \frac{\varepsilon C}{\alpha(T - T_{S_C^*S_A^*}) + (K_3 - \varepsilon\mu^2)q_0^2} E_0, \qquad (18)$$

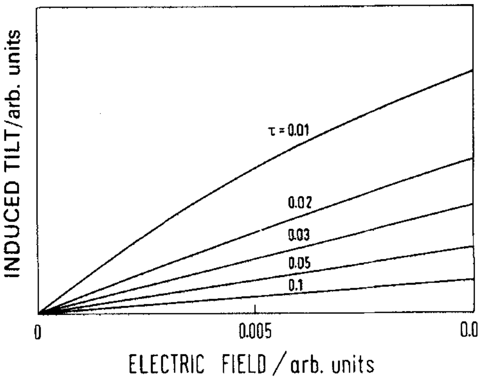


Figure 5. Calculated (see equations (7)) induced tilt at different temperatures in the S_A^* phase as a function of the applied electric field.

where q_0 is the wavevector of the pitch at $T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}$ and where we have used the relation [20]

$$a - \varepsilon C^2 = \alpha(T - T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}) + (K_3 - \varepsilon\mu^2)q_0^2. \tag{19}$$

The closer to $T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}$ the system is, the larger is the induced tilt for a given applied electric field and thus the higher order terms in equations (7) will become more important. This is the reason why we expect a non-linear behaviour of the induced tilt only close to $T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}$. As we have discussed, this behaviour is also confirmed by the calculations presented in figure 5 and by the experimental results of Nishiyama *et al.* [30].

We can understand the behaviour of the relaxation frequency under a bias field with the aid of the previous discussion, in the following way. When investigating the dielectric response of the system under a bias field, we are studying small oscillations of the director around a tilted equilibrium ξ_0. The relaxation of the system back to this equilibrium is driven by a torque, which for small deviations from ξ_0 can be linearized and generally written as $-k\delta\xi$, where $\delta\xi$ is the deviation of the system from equilibrium and k is an effective force constant. This torque is balanced by a viscous torque $-\gamma\delta\dot{\xi}$ and the relaxation back to equilibrium is given therefore by the differential equation

$$-k\delta\xi - \gamma\delta\dot{\xi} = 0 \tag{20}$$

which has the solution

$$\delta\xi = \delta\xi_0 \exp\left(-\frac{k}{\gamma}t\right), \tag{21}$$

where $\delta\xi_0$ is the deviation from equilibrium at time $t = 0$. The relaxation frequency $f_a = 1/2\pi t_\mathrm{A}$ for such a system is given by

$$f_\mathrm{A} = \frac{k}{2\pi\gamma}. \tag{22}$$

When we apply the bias field we create a tilt in the system. If this tilt is linear with the applied field, the restoring torque acting on the system is associated with a harmonic potential, the force constant of which is proportional to the inverse of the slope of the graph of induced tilt versus bias field. It is well known that adding a constant force to a harmonic potential just displaces the equilibrium of the system leaving the eigenfrequency unchanged. Thus, we do not expect any influence on the relaxation frequency of the system as long as the electroclinic effect shows a linear behaviour with the field. Closer to $T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}$, where the electroclinic effect is non-linear, the torque acting on the system can no longer be associated with a harmonic potential but with some more general form. Anyhow, for a given bias field, as we are studying only small oscillations around the equilibrium position we can approximate the potential with a harmonic one, the force constant of which is proportional to the inverse of the slope of the graph of induced tilt versus bias field taken for the bias field in question. From figure 5 it is easy to understand therefore that close enough to $T_{\mathrm{S}_\mathrm{C}^*\mathrm{S}_\mathrm{A}^*}$, where an increasing bias field is associated with a decreasing slope of this graph, the force constant of the system and thus the relaxation frequency will increase with increasing bias field. Qualitatively it is clear, that an increased stiffness of the system results in a smaller response and so we expect the dielectric strength to behave in the opposite way to that of the relaxation frequency. This is also what is observed in figure 3. The correlation between the linearity of the electroclinic effect and the influence of a bias electric field on the complex dielectric constant of the S_A^* phase have later been confirmed experimentally by Andersson *et al.* [31].

By comparing figures 3 and 4 we conclude that our theoretical model permits us to predict the behaviour of the complex dielectric constant in the presence of a bias field in agreement with the experimental observations. From the previous discussion of this section it is also clear how we can obtain a good physical understanding of the system. At one point, however, theory and experiment do not agree completely. From equations (17) we calculate a value of the product $f_A \Delta\varepsilon_{SA}$ which is almost temperature as well as field independent. We see in figure 3 that, close to $T_{S_C^*S_A^*}$, this product is constant for large bias fields but shows a pronounced drop when the bias field approaches zero. The corresponding behaviour has also been observed [18, 19] by us when this product is plotted as function of temperature if the experiment is performed without a bias field. In neither of these cases there is any theoretical explanation for this drop, we just conclude that our theory fails to predict the drop which is found to occur experimentally as soon as the system approaches the origin of the electric field-reduced temperature plane. Disregarding this discrepancy, the understanding of which probably would be a step towards a better understanding of the S_C^*–S_A^* transition, we conclude that theory and experiment are in good agreement.

When studying the temperature and frequency dependence of the complex dielectric constant in the S_C^* phase, we face the problem of resolving the soft mode contribution from that of the Goldstone mode. Studies of the soft mode in the S_C^* phase are therefore most often limited [14, 16] to a very narrow temperature interval just below $T_{S_C^*S_A^*}$. However, this difficulty can be eliminated by studying dielectric relaxation in the S_C^* phase using [12, 15] a bias field applied parallel to the smectic layers. The bias field unwinds the helix and thus the Goldstone mode is suppressed allowing the soft mode to be studied separately. The problem when performing such an experiment is, of course, that we do not know to what extent the bias field influences the soft mode part of the dielectric constant in the S_C^* phase. Assuming that the bias field affects the soft mode in a temperature interval below $T_{S_C^*S_A^*}$ which is comparable to that we have determined above $T_{S_C^*S_A^*}$, we thus obtain an indication of how close to $T_{S_C^*S_A^*}$ in the S_C^* phase we can perform a dielectric experiment under a bias field without influencing the properties we want to study. Such a study of the soft mode part of the complex dielectric constant in the S_C^* phase has been performed by us recently, the details of the experimental results have been published elsewhere [19].

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