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# Soft Relaxations Near the Ferroelectric Phase Transition in Liquid Crystals

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The dispersion of dielectric and optical properties found in experiment yields the relaxation frequencies of the polarization $P$ and the tilt angle $\theta$. The temperature dependences of these frequencies are compared to those obtained from the free energy $F(P, \theta)$ describing the ferroelectric phase transition. This comparison shows that order parameters $P$ and $\theta$ are strongly coupled in the whole temperature region studied, both showing the same soft-mode relaxation frequency in the $S_A$ phase. In the ferroelectric $S_{C^*}$ phase the soft-mode relaxation frequency has been detected only when the helicoidal structure has been unwound by a d.c. electric field. On the other hand this d.c. field influences the soft-mode relaxation frequency in the vicinity of the phase transition and the soft-mode dielectric strength even in the whole $S_{C^*}$ phase.

## 1. INTRODUCTION

Dynamic properties near the ferroelectric $S_{C^*}$—$S_A$ phase transition were studied theoretically[1,2] on the basis of the free energy expansion $F$ of the Landau type.[3] It was considered that this phase transition is owing to softening of the spatially non-uniform fluctuations of the molecular tilt $\theta$ with respect to the normal to the smectic layers. Below the transition, in the ferroelectric $S_{C^*}$ phase, a spontaneous tilt $\theta_s$ of molecules appears the direction of which precesses about the smectic layer normal, a helicoidal structure being formed. The spontaneous polarization $P_s$ arises due to the interaction of $P$ with $\theta$ and is also spatially non-uniform. Physically, the origin of $P_s$ is in hindering of molecular rotation along their long axes when $\theta_s$ appears.[4]

The free energy expansion $F$ was constructed using a two-component order parameter determining the magnitude and the direction of the tilt angle $\theta$ as well as the two-component polarization $P$ of the same symmetry coupled to $\theta$. The diagonalization of the quadratic part of $F(\theta, P)$ gives the eigenvectors of normal modes which have generally both $P$ and $\theta$ components and their eigenfrequencies, which can be detected experimentally. This analysis has been done in Reference 1. The calculated temperature dependences of eigenfrequencies are shown in Figure 1 in a wide temperature region.

Far above the phase transition temperature $T_c$, there is a high frequency soft mode (vibrations of $\theta$) and a low frequency hard mode (vibrations of $P$), denoted

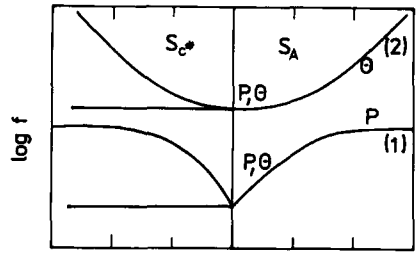


FIGURE 1 Relaxation frequencies of four modes in the $S_{C^*}$ phase and two modes in the $S_A$ phase. The horizontal axis is in arbitrary temperature units. The figure is taken from Reference 1.

as (2) and (1) resp. in Figure 1. Near above $T_c$, where the relaxation frequencies of the modes approach, both modes interact, which is expressed by the term $P.\theta$ in the free energy $F$.[3] As a result of the interaction the modes (1) and (2) do not cross but they repulse each other (anti-crossing). Consequently the hard mode becomes soft and vice versa. Moreover, in the temperature region of the interaction, both modes have $\theta$ and $P$ components. Therefore, in this temperature region both should be detected in dielectric as well as in electroclinic response.

In the $S_{C^*}$ phase both paraelectric modes are split into two modes. The low frequency couple of modes is known as the Goldstone (temperature independent) and the soft mode.

The theoretical analysis affords only qualitative results. Consequently the temperature scale in Figure 1 is arbitrary. One cannot estimate in advance the real width of the temperature interval above $T_c$ where the modes are mixed. Therefore, a temperature behaviour of modes cannot be predicted in details and can differ in various materials.

## 2. COMPARISON OF THE THEORETICAL PICTURE WITH THE AVAILABLE EXPERIMENTAL DATA

In dielectric measurements with several substances[5–8] a linear temperature dependence of relaxation frequency has been found above $T_c$. This frequency can be identified with the mode (1) in Figure 1 in the temperature region where $\theta$ and $P$ modes are mixed. Therefore the same relaxation frequency should appear in electroclinic effect, too.

A determination of the soft-mode relaxation frequency in the $S_{C^*}$ phase is impeded by the existence of very high contribution of the Goldstone mode to the dielectric and electroclinic response, which overwhelms the soft mode contribution. The Goldstone mode is eliminated only when the helicoidal structure is unwound. This can be achieved by constructing of very thin samples, but then the properties are determined mostly by boundary conditions. Unwinding the helicoidal structure by an electric or a magnetic biasing d.c. field in bulk samples is the best way to obtain a homogeneous structure, but under the biasing field $E$ the phase transition as well as the soft-mode contributions are considerably influenced.[9]

The high frequency mode in the $S_A$ phase (see Figure 1) can be identified with

the mode with a temperature independent relaxation frequency detected in the dielectric dispersion on DOBAMBC at the frequency of about 70 MHz.[10] The symmetry of this mode indicates that it is connected with the rotation of molecules around their long axes.[10] The hindering of this rotation is supposed to be a source of $P_s$. The temperature independence of this relaxation frequency suggests that even this mode was studied in the temperature region where strong $P$, $\theta$ interaction took place (see Figure 1). For this reason, the mode has both $P$ and $\theta$ components and should appear also in the dispersion of the electroclinic effect. This has not been confirmed so far because the electroclinic experiment has not been performed at such high frequencies.

Concerning the high frequency modes in the $S_{C^*}$ phase, experimental dielectric as well as electroclinic data are missing.

## 3. NEW EXPERIMENTAL RESULTS IN THE $S_A$ PHASE

With the material 4-*n*-octyloxy benzoic acid 4′|(2-methylbutyloxy) carbonyl| phenyl ester exhibiting a monotropic $S_{C^*}$ phase below $T_c = 32°C$ the dielectric and electrooptic dispersion has been studied.[9,11] Both the experiments have been performed under the same conditions, namely the sample orientation and the measuring electric field have been kept the same.[9,11]

The soft-mode relaxation frequency $f_r$ has been determined from both experiments. With increasing temperature the contribution of this mode to dielectric and to electrooptic response decreases so that the precision of determining $f_r$ also goes down being satisfactory up to $T = T_c + 2K$. Within this temperature range $f_r$ determined from dielectric and electrooptic experiment are practically equal to each other and exhibit a linear temperature dependence (see Figure 2).

Also the reciprocal value of the induced tilt angle (Figure 3) and the reciprocal soft-mode dielectric strength (Figure 4 (b)) exhibit a linear temperature dependence in the form of the Curie-Weiss law.[9,11]

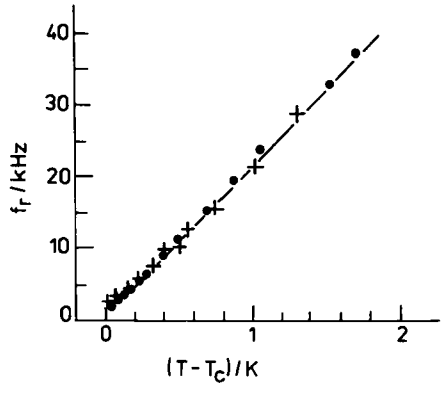


FIGURE 2 Temperature dependences of relaxation frequencies determined from dielectric dispersion (circles) and from electrooptic dispersion (crosses).

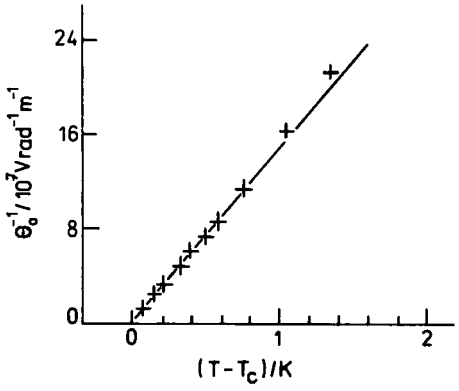


FIGURE 3 Temperature dependence of the reciprocal value of the induced angle extrapolated to zero frequency.

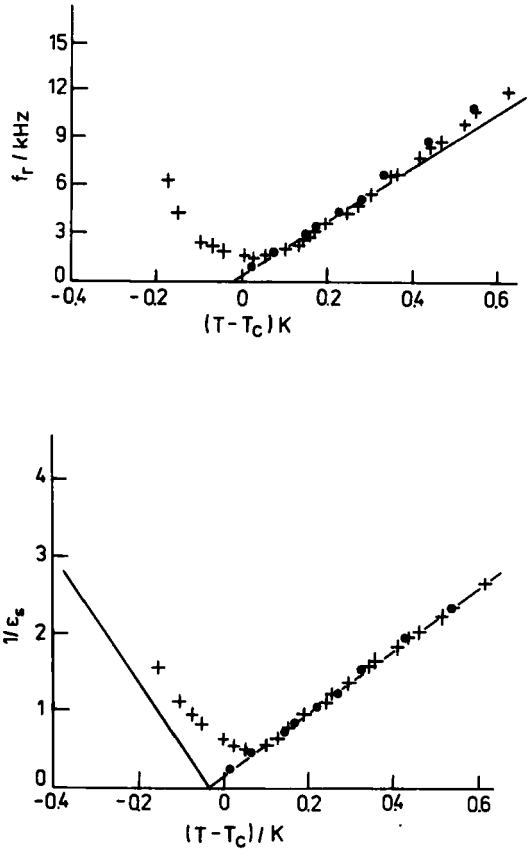


FIGURE 4 Temperature dependences of the soft-mode relaxation frequency (a) and the reciprocal of the soft-mode dielectric strength (b) at $E = 0$ (circles) and at $E = 4 \times 10^2$ k V m$^{-1}$ (crosses). The full line in (b) is a theoretical asymptote for $(\Delta\epsilon_s)^{-1}(T)$ at low temperatures.

## 4. THE EFFECT OF BIASING FIELD

To detect a soft mode in the $S_{C^*}$ phase the dielectric dispersion has been studied (with the same material as described in the previous chapter) under a biasing electric field $E = 4 \times 10^2$ k V m$^{-1}$. $E$ is higher than the critical field $E_c$ for unwinding the helicoidal structure. This biasing field influences neither $f_r$ nor the soft-mode contribution $\epsilon_s$ to permittivity above $T = T_c + 0.1$ K (cf. Figure 4). Below this temperature $\epsilon_s$ becomes lower and the temperature dependence of $f_r$ becomes non-linear under the influence of the biasing field (Figure 4(a), (b)).

The effect of the biasing field $E > E_c$ on $\epsilon_s$ can be calculated from the free energy of the Landau type

$$g = \frac{1}{2} a \theta^2 + \frac{1}{4} b \theta^4 + \frac{1}{2\chi} P^2 + C P \theta - P E, \tag{1}$$

where $a = \alpha (T - T^*)$. This free energy is similar to that derived in[3] for the $S_A - S_{C^*}$ phase transition, but here all gradient terms describing the modulation are omitted. From (1) the dielectric susceptibility of the soft mode is determined as

$$\chi_s = \frac{\chi^2 C^2}{a + 3 b\theta^2 - \chi C^2}, \tag{2}$$

where $\theta$ is the equilibrium value of the tilt angle. In the vicinity of the phase transition temperature $\theta$ can be estimated as[9]

$$\theta(T,E) \approx - \left(\frac{C\chi E}{b}\right)^{1/3} + \frac{a - \chi C^2}{3b} \left(\frac{b}{C\chi E}\right)^{1/3}, \tag{3}$$

which is nonzero even above the phase transition. Function (3) inserted to (2) gives the temperature dependence of $\chi_s$ at $E \neq 0$. It can be shown[9] that $1/\chi_s(T)$ is then non-linear around $T_c$ and far from $T_c$ it approaches asymptotes

$$\frac{1}{\chi_s} = \frac{\alpha(T - T_c) + K q^2}{\chi^2 C^2} \quad (T > T_c) \tag{4a}$$

$$\frac{1}{\chi_s} = \frac{2\alpha(T_c - T) + K q^2}{\chi^2 C^2} \quad (T < T_c), \tag{4b}$$

where $T_c = T^* + \chi C^2 + K q^2$ and $K$ is the elastic constant, $q$ is the wavevector of the space modulation when $E = 0$.[1] The asymptote below $T_c$ (shown by the full line in Figure 4(b)) has doubled and opposite slope in comparison to that above $T_c$.

It is interesting to note that $\epsilon_s$ determined in samples unwound by a biasing field differs from $\epsilon_s$ of helicoidal samples not only in the vicinity of $T_c$ but everywhere

below $T_c$. In unwound samples, far below $T_c$, $\epsilon_s = 1 + 4\pi\chi_s$ is determined by expression (4b), while in helicoidal samples it is[1]

$$\frac{1}{\chi_s} = \frac{4\alpha(T_c - T) + 2Kq^2}{\chi^2 C^2}.$$

Far above $T_c$ in both helicoidal and unwound structures $1/\chi_s$ is determined by expression (4a).

We can conclude that the behaviour of the soft mode in structures unwound by a biasing electric field does not fully reflect its behaviour in ideal helicoidal structures. It is necessary to exploit another method enabling to detect the soft mode directly in the helicoidal structure. The first step has been done in Reference 12, where the light scattering is used to detect a soft mode in the helicoidal structure together with the Goldstone mode.

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