High-frequency dielectric behavior of a ferroelectric liquid crystal near the smectic-C^*–smectic-A phase transition

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The temperature and frequency dependence of the complex dielectric susceptibility of a ferroelectric liquid crystal (FLC) near the smectic-C^*–smectic-A phase transition has been calculated using the generalized Landau model. It is shown that, although the dielectric response of the Sm-C^* phase consists generally of four modes (soft, Goldstone, and two high-frequency polarization modes), only three bands appear in the dielectric-loss spectrum of FLC's at the Sm-A–Sm-C^* phase transition. The calculations based on the generalized Landau model show that the frequency split of the two high-frequency modes is too low to be detected as two separate relaxation processes. A special technique has to be used to split these modes. At the Sm-A–Sm-C^* phase transition this process does not split or broaden. These results are in agreement with the recent experimental data. It is shown that in the light of these calculations a revision of the theory as proposed by Pleiner and Brand [Phys. Rev. A **43**, 7064 (1991); Mol. Cryst. Liq. Cryst. Lett. **8**, 11 (1991)] is rather unnecessary.

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I. INTRODUCTION

Since the discovery of ferroelectric liquid crystals (FLC's) by Meyer *et al.* [1] in 1975, an increasing number of publications on experimental and theoretical investigations of the smectic-C^* phase have appeared in the literature. The Landau model [2] and its generalizations (see, e.g., Refs. [3–9]) are most frequently used to explain thermodynamic properties of FLC's. In particular it has explicitly been shown [3,4,8] that the generalized Landau model can explain the main experimental features of the static and the dynamic dielectric behavior of FLC's.

In order to describe the ferroelectric Sm-C^* phase, two-component order parameters [cf. Eqs. (1) and (2)] are introduced by the model. The dynamic dielectric response of the system consists generally of four modes, the two high-frequency polarization modes and the two low-frequency modes. The latter are connected to the relaxation of the director fluctuations. The low-frequency modes are commonly denoted as the soft mode and the Goldstone mode [4]. In the Sm-A phase, only two degenerate modes are observed, the high-frequency polarization mode and the soft mode [4].

In the recent experimental investigations of the broadband dielectric spectra (up to 1 GHz) of FLC's in the vicinity of the Sm-A–Sm-C* phase transition, three bands in dielectric-loss spectra have been observed [10,11]. In the low-frequency region the soft and Goldstone modes were observed as expected. However, in the microwave (high-) frequency range only one (β-relaxation) band was observed. At the Sm-A–Sm-C^* phase transition this band did not split or broaden and its dielectric strength did not decrease [10,11]. Therefore it was concluded [11] that these results did contradict the Landau model. Moreover these results have led Pleiner and Brand [12,13] to suggest a model which predicts only three modes in contrast to the four predicted by the Landau model.

In the present paper we show that there is really no contradiction between the experimental observations [10,11] and the predictions of the Landau model [2–4]. We show that for the Landau model we indeed expect only three peaks in the dielectric-loss spectrum of a FLC in the frequency range up to 1 GHz and not four as has earlier been suggested.

II. THE DIELECTRIC SUSCEPTIBILITY OF THE SMECTIC-C^* AND -A PHASES IN THE CONTEXT OF THE GENERALIZED LANDAU MODEL

In the chiral ferroelectric Sm-C^* phase, the tilt of the director vector **n** from the normal to the smectic layers precesses helically as one goes from one smectic layer to another. The projection of **n** into the plane of a smectic

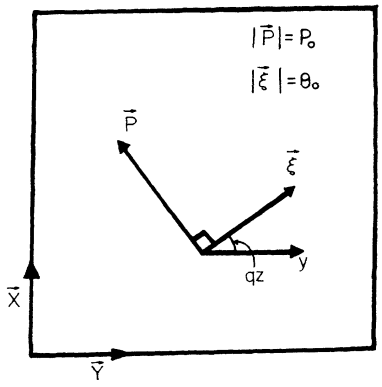

FIG. 1. The order parameters ξ and **P**; ξ is the projection of the director **n** onto the layer plane and **P** is the spontaneous polarization.

layer (which is taken to be parallel to the xy plane) is described by the order parameter $\xi=\xi_1\mathbf{x}+\xi_2\mathbf{y}$. Because of the chirality of the molecules the tilt breaks the axial symmetry around the long molecular axis and induces a transverse in plane polarization $\mathbf{P}=P_x\mathbf{x}+P_y\mathbf{y}$ perpendicular to the director $\mathbf{n}$. For small tilt angles, we can write [3,4] (Fig. 1)

$$\xi_1=\theta_0\cos(qz)\ ,\quad \xi_2=\theta_0\sin(qz)\ , \tag{1}$$

$$P_x=-P_0\sin(qz)\ ,\quad P_y=P_0\cos(qz)\ , \tag{2}$$

where z is the coordinate normal to the smectic planes, $q=2\pi/p$ is the wave vector of the pitch p, and θ_0 and P_0 are the magnitudes of the tilt angle and the spontaneous polarization, respectively. An ac electric field $\mathbf{E}(t)=\mathbf{E}\exp(i\omega t)$ applied parallel to the smectic layers induces an average macroscopic polarization $\langle\mathbf{P}(t)\rangle=\langle\mathbf{P}\rangle\exp(i\omega t)$. The complex dielectric susceptibility $\chi(\omega)$ is then defined as

$$\chi(\omega)=\lim_{\mathbf{E}\to 0}\frac{\langle\mathbf{P}\rangle}{\mathbf{E}}\ . \tag{3}$$

In order to describe the dielectric properties of a FLC we use the generalized Landau model. A full review of this model can be found elsewhere [8]. Only a summary of the model is presented below.

The free-energy density g of a chiral Sm-C^* liquid crystal in the vicinity of the Sm-C^*-Sm$-A$ transition is given by a Landau expansion in the order parameters ξ and $\mathbf{P}$ [3,4],

$$\begin{aligned} g=&\tfrac{1}{2}a(\xi_1^2+\xi_2^2)+\tfrac{1}{4}b(\xi_1^2+\xi_2^2)^2+\tfrac{1}{6}c(\xi_1^2+\xi_2^2)^3-\Lambda\left[\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right]\\ &+\tfrac{1}{2}K_3\left[\left[\frac{d\xi_1}{dx}\right]^2+\left[\frac{d\xi_2}{dz}\right]^2\right]+\tfrac{1}{2}\epsilon^{-1}(P_x^2+P_y^2)+C(P_x\xi_x-P_y\xi_1)-\mu\left[P_x\frac{d\xi_1}{dz}+P_y\frac{d\xi_2}{dz}\right]\\ &-\tfrac{1}{2}\Omega(P_x\xi_2-P_y\xi_1)^2+\tfrac{1}{4}\eta(P_x^2+P_y^2)^2-d(\xi_1^2+\xi_2^2)\left[\xi_1\frac{d\xi_2}{dz}-\xi\frac{d\xi_1}{dz}\right]-\mathbf{E}\cdot\mathbf{P}+\cdots\ , \end{aligned} \tag{4}$$

where only the term quadratic in tilt is explicitly temperature dependent and goes to zero at the "unrenormalized" transition temperature T_0 for the FLC, i.e., $a=\alpha(T-T_0)$, the other constants are temperature independent: ϵ is a generalized susceptibility, K_3 is the elastic modulus, Λ is the coefficient of the Lifshitz invariant term responsible for the helical structure, and μ and C are coefficients of the flexoelectric and piezoelectric coupling between the tilt angle θ and the polarization, respectively. Ω is the coefficient of the biquadratic coupling term inducing transverse quadruple ordering and the η term has been added to stabilize the system. The d term describes the monotonic increase of the pitch with temperature at low temperature. The c term has been added to account for the specific-heat temperature dependence of the system. Here it has been assumed that the tilt angle θ is relatively small.

An equation for the free-energy density g for the "classical" Landau model introduced by Pikin and Indenbom [2] can be obtained from Eq. (4) by setting the c, Ω, η, and d terms all equal to zero. The most essential feature of the generalized Landau model [3,4], in contrast to the classical one, is the presence of the biquadratic coupling (the Ω term) between tilt and polarization in the free-energy density. The presence of the biquadratic coupling is essential in order to correctly describe the dielectric (and also the basic thermodynamic) properties of the Sm-C^* phase [4].

As shown in [3,4,8], equations governing the behavior of the system which can be deduced from Eq. (4) are most conveniently studied by rewriting them into dimensionless form. This allows one to be able to examine the shapes of the calculated curves. By doing so the 11 material parameters introduced in Eq. (4) are transformed to six independent dimensionless constants and five scaling factors. The six constants are defined [3] as

$$\begin{aligned} &\gamma=\frac{\tilde{b}\eta}{\Omega^2}\ ,\quad \beta=\frac{\eta^{1/2}\tilde{C}\tilde{\epsilon}}{\Omega^{1/2}}\ ,\quad \rho=\frac{\tilde{c}\eta}{\tilde{\epsilon}\Omega^3}\ ,\\ &\lambda=\Lambda\left[\frac{\eta\tilde{\epsilon}}{K_3\Omega}\right]^{1/2}\ ,\quad \nu=\mu\left[\frac{\tilde{\epsilon}}{K_3}\right]^{1/2}\ ,\\ &\delta=d\left[\frac{\eta}{K_3\Omega^3\tilde{\epsilon}}\right]^{1/2}\ , \end{aligned} \tag{5}$$

where $\tilde{b}$, $\tilde{c}$, $\tilde{\epsilon}$, and $\tilde{C}$ are renormalized constants given by [3]

$$\begin{aligned} &\tilde{b}=b-\frac{4\Lambda d}{K_3}\ ,\quad \tilde{c}=c-\frac{3d^2}{K_3}\ ,\\ &\tilde{C}=C+\frac{\Lambda\mu}{K_3}\ ,\quad \frac{1}{\tilde{\epsilon}}=\frac{1}{\epsilon}-\frac{\mu^2}{K_3}\ . \end{aligned} \tag{6}$$

The physical quantities such as polarization P_0, the tilt θ_0, and the dielectric susceptibility χ will now be expressed in dimensionless form and will be denoted by a tilde above the corresponding symbol, while the characteristic units with which these are measured will be denoted by an asterisk (e.g., $\tilde{\theta}_0=\theta_0/\theta^*$). The characteristic units [8] are chosen to be

$$\begin{aligned} &\theta^*=(\tilde{\epsilon}\Omega)^{-1/2}\ ,\quad P^*=(\tilde{\epsilon}\eta)^{-1/2}\ ,\quad \chi^*=\tilde{\epsilon}\ ,\\ &T^*=\tilde{b}/(\alpha\tilde{\epsilon}\Omega)\ ,\quad E^*=P^*/\chi^*\ . \end{aligned} \tag{7}$$

From Eq. (4) one can derive [3] the equations governing the equilibrium tilt and polarization of the system, namely,

$$(\beta^2-\gamma\tau)\tilde{\theta}_0+\gamma\tilde{\theta}_0^3+\rho\tilde{\theta}_0^5-\tilde{\theta}_0\tilde{P}_0^2-(\beta+3\nu\delta\tilde{\theta}_0^2)\tilde{P}_0=0 , \quad (8)$$

$$\tilde{P}_0^3+(1+\tilde{\theta}_0^2)\tilde{P}_0-(\beta+\nu\delta\tilde{\theta}_0^2)\tilde{\theta}_0=0 , \quad (9)$$

where $\tau=(T_c-T)/T^*$ and T_c is the phase-transition temperature which is [8]

$$T_c=T_0+\frac{T^*}{\gamma}(\beta^2+\lambda^2) . \quad (10)$$

In the presence of an ac field $\mathbf{E}(t)$, a general disturbance of the equilibrium state of Eqs. (1) and (2) can be regarded to be composed of two parts [3,4]. First, the amplitudes, and secondly, the phases of the order parameters, can change. Denoting the amplitude changes by $\Delta\tilde{\theta}_1$ and $\Delta\tilde{P}_1$ and the phase changes by $\Delta\tilde{\theta}_2$ and $\Delta\tilde{P}_2$, respectively, the order parameters in the presence of ac field $\tilde{\mathbf{E}}(t)=\tilde{\mathbf{E}}\exp(i\omega t)\mathbf{x}$ applied in the $\mathbf{x}$ direction are written as [3]

$$\begin{aligned}
\tilde{\xi}_1&=\tilde{\theta}_0\cos(qz)+\Delta\tilde{\theta}_1\cos(qz)-\Delta\tilde{\theta}_2\sin(qz) ,\\
\tilde{\xi}_2&=\tilde{\theta}_0\sin(qz)+\Delta\tilde{\theta}_1\sin(qz)+\Delta\tilde{\theta}_2\cos(qz) ,\\
\tilde{P}_x&=-\tilde{P}_0\sin(qz)-\Delta\tilde{P}_1\sin(qz)-\Delta\tilde{P}_2\cos(qz) ,\\
\tilde{P}_y&=\tilde{P}_0\cos(qz)+\Delta\tilde{P}_1\cos(qz)-\Delta\tilde{P}_2\sin(qz) ,
\end{aligned} \quad (11)$$

where

$$\begin{aligned}
\Delta\tilde{\theta}_1&=\Delta\tilde{\theta}_{10}\sin(qz)\exp(i\omega t) ,\\
\Delta\tilde{\theta}_2&=\Delta\tilde{\theta}_{20}\cos(qz)\exp(i\omega t) ,\\
\Delta\tilde{P}_1&=\Delta\tilde{P}_{10}\sin(qz)\exp(i\omega t) ,\\
\Delta\tilde{P}_2&=\Delta\tilde{P}_{20}\cos(qz)\exp(i\omega t) .
\end{aligned} \quad (12)$$

As a consequence the relaxation behavior of the Sm-C^* phase consists of two director reorientation modes, the soft mode (mostly amplitude changes) and the Goldstone mode (mostly phase changes), and the two high-frequency polarization modes [3].

The dynamic (Landau-Khalatnikov) equations of the system obtained in Ref. [4] may be written down in the dimensionless form as

$$\begin{aligned}
&(\tilde{b}_1-i\omega\gamma_s\tilde{\epsilon}\eta/\Omega)\Delta\tilde{\theta}_{10}+\tilde{b}_2\Delta\tilde{\theta}_{20}+\tilde{b}_3\Delta\tilde{P}_{10}+\tilde{b}_4\Delta\tilde{P}_{20}=0 ,\\
&\tilde{b}_2\Delta\tilde{\theta}_{10}+(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)\Delta\tilde{\theta}_{20}+\tilde{b}_4\Delta\tilde{P}_{10}+\tilde{b}_6\Delta\tilde{P}_{20}=0 ,\\
&\tilde{b}_3\Delta\tilde{\theta}_{10}+\tilde{b}_4\Delta\tilde{\theta}_{20}-(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})\Delta\tilde{P}_{10}=\tilde{E} ,\\
&\tilde{b}_4\Delta\tilde{\theta}_{10}+\tilde{b}_6\Delta\tilde{\theta}_{20}-(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})\Delta\tilde{P}_{20}=\tilde{E} ,
\end{aligned} \quad (13)$$

where γ_S and γ_G are the ordinary rotational viscosities connected to the director reorientations (soft and Goldstone modes); the two viscosities γ_{PS} and γ_{PG} connected to the high-frequency polarization modes are related to the rotation of the molecules around their long axis (one can expect that close to T_c, $\gamma_S=\gamma_G$ and $\gamma_{PS}=\gamma_{PG}$ [4]), the coefficients $\tilde{b}_i$ are given by [8]

$$\begin{aligned}
\tilde{b}_1&=-\beta^2+\gamma\tau-\lambda^2-(2\lambda\delta+3\gamma)\tilde{\theta}_0^2-5\rho\tilde{\theta}_0^4+\tilde{P}_0^2\\
&\quad+8\nu\delta\tilde{\theta}_0\tilde{P}_0-2\nu\lambda\tilde{P}_0/\tilde{\theta}_0-2\nu^2(\tilde{P}_0/\tilde{\theta}_0)^2-5\delta^2\tilde{\theta}_0^4 ,\\
\tilde{b}_2&=-2\lambda\delta\tilde{\theta}_0^2+2\nu\lambda\tilde{\theta}_0/\tilde{P}_0+2\nu^2(\tilde{P}_0/\tilde{\theta}_0)^2-2\delta^2\tilde{\theta}_0^4 ,\\
\tilde{b}_3&=\beta+\nu\delta\tilde{\theta}_0^2+2\tilde{\theta}_0\tilde{P}_0+\nu^2\tilde{P}_0/\tilde{\theta}_0 ,\\
\tilde{b}_4&=-\lambda\nu-\nu\delta\tilde{\theta}_0^2-\nu^2\tilde{P}_0/\tilde{\theta}_0 ,\\
\tilde{b}_5&=-\beta^2+\gamma\tau-\lambda^2-(2\lambda\delta+\gamma)\tilde{\theta}_0^2-\rho\tilde{\theta}_0^4\\
&\quad-2\nu\lambda\tilde{P}_0/\tilde{\theta}_0-2\nu^2(\tilde{P}_0/\tilde{\theta}_0)^2-\delta^2\tilde{\theta}_0^4 ,\\
\tilde{b}_6&=\beta+\nu\delta\tilde{\theta}_0^2+\tilde{\theta}_0\tilde{P}_0+\nu^2\tilde{P}_0/\tilde{\theta}_0 ,\\
\tilde{b}_7&=1-\tilde{\theta}_0^2+3\tilde{P}_0^2+\nu^2 ,\\
\tilde{b}_8&=1+\tilde{P}_0^2+\nu^2 .
\end{aligned} \quad (14)$$

The normalized complex susceptibility $\tilde{\chi}_C(\omega)$ of the Sm-C^* phase defined as [4]

$$\tilde{\chi}_C(\omega)=-\frac{1}{2\tilde{E}}(\Delta\tilde{P}_{10}+\Delta\tilde{P}_{20})$$

is determined as the solution of the set of linear equations (13), namely,

$$\tilde{\chi}_C(\omega)=-\frac{A(\omega)}{2B(\omega)} , \quad (15)$$

where

$$\begin{aligned}
A(\omega)=&(2\tilde{b}_4\tilde{b}_6-\tilde{b}_4^2-\tilde{b}_6^2)(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)+(2\tilde{b}_3\tilde{b}_4-\tilde{b}_3^2-\tilde{b}_4^2)(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)\\
&-(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})-2\tilde{b}_2\tilde{b}_3\tilde{b}_6\\
&-(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})+2\tilde{b}_2\tilde{b}_4\tilde{b}_6\\
&+\tilde{b}_2^2(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})+\tilde{b}_2^2(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})-2\tilde{b}_2\tilde{b}_4^2+2\tilde{b}_2\tilde{b}_3\tilde{b}_4
\end{aligned} \quad (16)$$

and

$$\begin{aligned}
B(\omega)=&(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)(\tilde{b}_5-i\omega\gamma_G\epsilon\eta/\Omega)(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})+\tilde{b}_4^2(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})\\
&+\tilde{b}_6^2(\tilde{b}_1-i\omega\gamma_S\tilde{\epsilon}\eta/\Omega)(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})-\tilde{b}_2^2(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})\\
&+\tilde{b}_3^2(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})+\tilde{b}_4^2(\tilde{b}_5-i\omega\gamma_G\tilde{\epsilon}\eta/\Omega)(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon})+\tilde{b}_4^4-2\tilde{b}_3\tilde{b}_4^2\tilde{b}_6+\tilde{b}_3^2b_6^2\\
&-2\tilde{b}_2\tilde{b}_3\tilde{b}_4(\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon})-2\tilde{b}_2\tilde{b}_4\tilde{b}_6(\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon}) .
\end{aligned} \quad (17)$$

In the smectic-A phase ξ and $\mathbf{P}$ are zero at equilibrium so that fluctuations corresponding to $\Delta\theta_i$ and ΔP_i, which were introduced by Eqs. (11), can here be taken to be the components of ξ and $\mathbf{P}$ themselves. We only retain terms of second order in ξ and $\mathbf{P}$ and set $d/dz=0$ in Eq. (4) [4]. Thus the free-energy density g of the smectic-A phase is given by [4]

$$g=\tfrac{1}{2}a(\xi_1^2+\xi_2^2)+\tfrac{1}{2}\epsilon^{-1}(P_x^2+P_y^2) +C(P_x\xi_2-P_y\xi_1)-\mathbf{E}(t)\cdot\mathbf{P}+\cdots . \quad (18)$$

Introducing a time dependence of the order parameters as $\tilde{\xi}_i=\Delta\tilde{\xi}_{i0}\exp(i\omega t)$ and $\tilde{P}_i=\Delta\tilde{P}_{i0}\exp(i\omega t)$ we can obtain the set of dynamic equations [4] which may be represented in the dimensionless form as

$$\begin{aligned}
&(\tilde{a}_1-i\omega\gamma_{SA}\tilde{\epsilon}\eta/\Omega)\Delta\tilde{\xi}_{10}+\tilde{a}_4\Delta\tilde{P}_{y0}=0 ,\\
&(\tilde{a}_1-i\omega\gamma_{SA}\tilde{\epsilon}\eta/\Omega)\Delta\tilde{\xi}_{20}+\tilde{a}_4\Delta\tilde{P}_{x0}=0 ,\\
&\tilde{a}_4\Delta\tilde{\xi}_{20}-(\tilde{a}_7+i\omega\gamma_{PA}\tilde{\epsilon})\Delta\tilde{P}_{x0}=\tilde{E} ,\\
&\tilde{a}_4\Delta\tilde{\xi}_{10}-(\tilde{a}_7+i\omega\gamma_{PA}\tilde{\epsilon})\Delta\tilde{P}_{y0}=0 ,
\end{aligned} \quad (19)$$

where

$$\tilde{a}_1=-\beta^2+\gamma\tau-\lambda , \quad \tilde{a}_4=\beta-\lambda\nu , \quad \tilde{a}_7=1+\nu^2 . \quad (20)$$

Then the normalized complex susceptibility $\tilde{\chi}_A$ of the smectic-A phase defined as [8]

$$\tilde{\chi}_A(\omega)=-\Delta\tilde{P}_{x0}/\tilde{E} \quad (21)$$

is given by

$$\chi_A(\omega)=\frac{(\tilde{a}_1-i\omega\gamma_{SA}\tilde{\epsilon}\eta/\Omega)}{\tilde{a}_4^2+(\tilde{a}_1-i\omega\gamma_{SA}\tilde{\epsilon}\eta/\Omega)(\tilde{a}_7+i\omega\gamma_{PA}\tilde{\epsilon})} . \quad (22)$$

III. THE HIGH-FREQUENCY DIELECTRIC RESPONSE OF A FERROELECTRIC LIQUID CRYSTAL: DISCUSSION AND CONCLUSIONS

On using Eqs. (8), (9), (14), (16), (17), (20), and (22) we are able to calculate the dielectric susceptibility of both the smectic-C^* and -A phases. The six dimensionless parameters defined by Eqs. (5) and the four scaling factors χ^*, θ^*, P^*, and T^* enter into the calculations. The calculations have been made using the values of the material parameters introduced by Carlsson *et al.* [8] as a standard set of parameters of the Sm-C^* phase. They are $\gamma=2.0$, $\beta=-0.17$, $\rho=0.90$, $\lambda=-0.062$, $\nu=-0.060$, $\delta=-0.012$, $T^*=0.92$ [K], $\chi^*=2.66\times10^{-13}$ [C/(V m)], $\theta^*=0.20$ [rad], and $P^*=1.3\times10^{-5}$ [C/m^2]. We have not considered any temperature dependence of the rotational viscosities and have taken $\gamma_G=\gamma_S=\gamma_{SA}=0.25$ Pa S (1 S=1 cm^2/s) and $\gamma_{PG}=\gamma_{PS}=\gamma_{PA}=7400$ V m/(C s) as in [4]. In our calculations we assume $T_c=327$ K.

Results of the calculation of the imaginary part of the normalized complex dielectric susceptibility near the Sm-A–Sm-C^* phase transition as a function of frequency are shown in Fig. 2. As expected in the low-frequency region one can see the soft and Goldstone modes at $T<T_c$ (curves 1 and 2) and only the soft mode at $T>T_c$ (curves 4 and 5). The high-frequency modes observed appear to be only one band. Similar dependencies for the "classical" Landau model [2] are also shown in Fig. 3 for comparison (calculations have been made for the same set of the material parameters).

When studying the high-frequency polarization modes

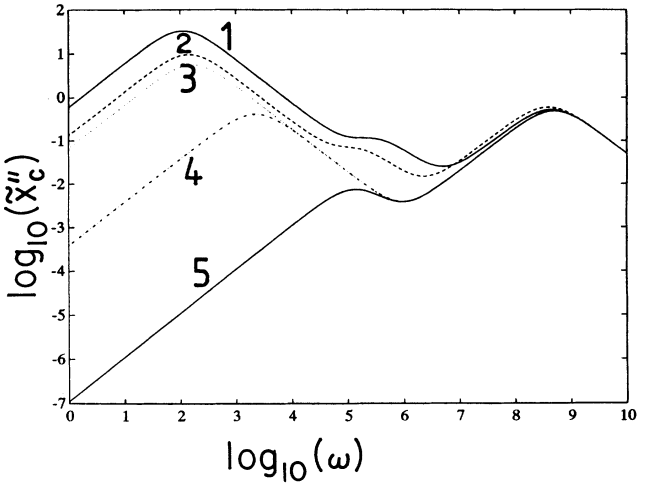

FIG. 2. The imaginary part of the normalized complex susceptibility for the generalized Landau model [4] as a function of frequency near the Sm-C^*–Sm-A transition. Curve 1: $T=326.04$ K, $\tilde{\theta}_0=0.92$, $\tilde{P}_0=-0.4442$; curve 2: $T=326.51$ K, $\tilde{\theta}_0=0.68$, $\tilde{P}_0=-0.1998$; curve 3: $T=327.0$ K (the phase-transition temperature), $\tilde{\theta}_0=0.00$, $\tilde{P}_0=0.00$; curve 4: $T=327.015$ K; curve 5: $T=327.96$ K.

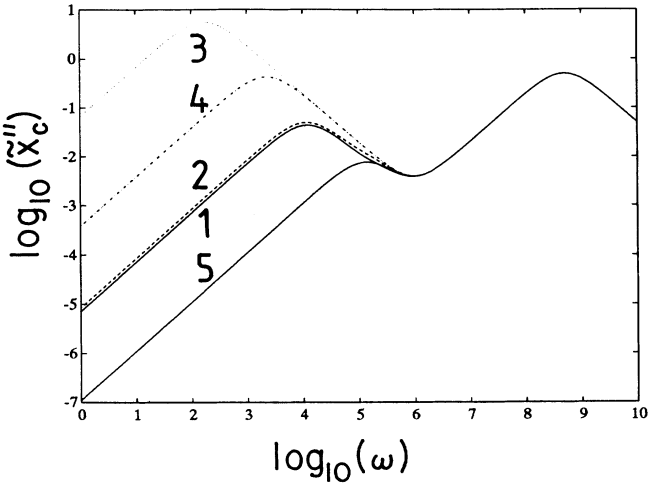

FIG. 3. The imaginary part of the normalized complex susceptibility for the "classical" Landau model [2] as a function of frequency near the Sm-C^*–Sm-A transition. Curve 1: $T=326.08$ K, $\tilde{\theta}_0=1.00$, $\tilde{P}_0=-5.8824$; curve 2: $T=326.52$ K, $\tilde{\theta}_0=0.72$, $\tilde{P}_0=-4.2353$; curve 3: $T=327.0$ K (the phase-transition temperature) $\tilde{\theta}_0=0.00$, $\tilde{P}_0=0.00$; curve 4: $T=327.015$ K; curve 5: $T=327.96$ K.

we are dealing with frequencies that are so high that the director can no longer follow the electric field, and one can therefore neglect contributions of low-frequency relaxation processes to the dielectric susceptibility [4]. Mathematically this can be expressed by setting γ_G, γ_S, and γ_{SA} equal to infinity in Eqs. (16), (17), and (22); the accuracy of this approximation is of the order $\sim 10^{-3}$ which is negligible compared to experimental errors [4]. The high-frequency dielectric response is then given by the following equations [4]:

$$\tilde{\chi}_C(\omega)=\tfrac{1}{2}\left[\frac{1}{\tilde{b}_7+i\omega\gamma_{PS}\tilde{\epsilon}}+\frac{1}{\tilde{b}_8+i\omega\gamma_{PG}\tilde{\epsilon}}\right], \tag{23}$$

and

$$\tilde{\chi}_A(\omega)=\frac{1}{\tilde{a}_7+i\omega\gamma_{PA}\tilde{\epsilon}} \tag{24}$$

for the Sm-C^* and Sm-A phases, respectively. Equations (23) and (24) may be written down in the Debye form, viz., *for smectic-C^* phase,*

$$\tilde{\chi}_C(\omega)\cong\Delta\chi_{PC}\left[\frac{g_S}{1+i\omega\tau_{PS}}+\frac{g_G}{1+i\omega\tau_{PG}}\right], \tag{25}$$

for smectic-A phase

$$\tilde{\chi}_A(\omega)\cong\frac{\Delta\chi_{PA}}{1+i\omega\tau_{PA}}, \tag{26}$$

where the dielectric strengths $\Delta\chi_{PC}$, and $\Delta\chi_{PA}$ and relaxation times τ_{PS}, τ_{PG}, and τ_{PA} are given by

$$\Delta\tilde{\chi}_{PC}=\tfrac{1}{2}\left[\frac{1}{\tilde{b}_7}+\frac{1}{\tilde{b}_8}\right],\quad \delta\chi_{PA}=1/\tilde{a}_7, \tag{27}$$

$$\tau_{PS}=\epsilon\gamma_{PS}/\tilde{b}_7,\quad \tau_{PG}=\epsilon\gamma_{PG}/\tilde{b}_8,\quad \tau_{PA}=\epsilon\gamma_{PA}/\tilde{a}_7, \tag{28}$$

and the coefficients g_S and g_G are determined as

$$g_S=1/2\tilde{b}_7\tilde{\Delta}\chi_{PC},\quad g_G=1/2\tilde{b}_8\tilde{\Delta}\chi_{PC}\quad (g_S+g_G=1). \tag{29}$$

As one can see from Eq. (25) $\tilde{\chi}_C(\omega)$ consists indeed of the two high-frequency polarization modes. [We denote the first and second terms in the right-hand side of Eq. (25) as the S and G modes, respectively.]

In the limit $T\to T_c$ when $\tilde{P}_0,\tilde{\theta}_0\to 0$, the dielectric strength $\tilde{\Delta}\chi_{PC}$ may be represented as

$$\begin{aligned}\Delta\chi_{PC}&=\frac{1}{2}\left[\frac{1}{\tilde{b}_7}+\frac{1}{\tilde{b}_8}\right]\\&=\frac{1}{2}\left[\frac{1}{1+\nu^2+3\tilde{P}_0^2-\tilde{\theta}_0^2}+\frac{1}{1+\nu^2+\tilde{P}_0^2}\right]\\&\cong\frac{1}{1+\nu^2}+\frac{1}{2}\frac{\tilde{\theta}_0^2-4\tilde{P}_0^2}{(1+\nu^2)^2}=\Delta\tilde{\chi}_{PA}+\frac{1}{2}\frac{\tilde{\theta}_0^2-4\tilde{P}_0^2}{(1+\nu^2)^2}.\end{aligned} \tag{30}$$

As follows from Eq. (30) the model may predict both the small increase and decrease of the dielectric strength $\Delta\tilde{\chi}_{PC}$. This depends on the ratio

$$\tilde{\theta}_0^2/4\tilde{P}_0^2=\eta\theta_0^2/4\Omega P_0^2$$

which is determined by the material parameters η and Ω. Also we have a similar behavior of the relaxation times τ_{PS} and τ_{PG}, namely,

$$\tau_{PS}\cong\frac{\tilde{\epsilon}\gamma_{PS}}{1+\nu^2}+\tilde{\epsilon}\gamma_{PS}\frac{\tilde{\theta}_0^2-3\tilde{P}_0^2}{(1+\nu^2)^2}, \tag{31}$$

$$\tau_{PG}\cong\frac{\tilde{\epsilon}\gamma_{PG}}{1+\nu^2}-\tilde{\epsilon}\gamma_{PG}\frac{\tilde{P}_0^2}{(1+\nu^2)^2}. \tag{32}$$

On taking into account explicit expressions for all the quantities entering in Eqs. (25)–(29) and setting $\gamma_{PG}\cong\gamma_{PS}\cong\gamma_{SA}=\gamma$ we find that at the phase-transition temperature T_c

$$\tilde{\chi}_C(\omega)=\tilde{\chi}_A(\omega)=\frac{1}{1+\nu^2+i\omega\gamma\tilde{\epsilon}}. \tag{33}$$

For the "classical" Landau model [2] when $\tilde{b}_7=\tilde{b}_8=\tilde{a}_7\equiv 1+\nu^2$ at all T Eq. (33) is valid for all temperatures in the vicinity of the Sm-C^*–Sm-A transition, that is to say, in the case under consideration the Landau model predicts the three modes only—the soft, Goldstone, and degenerate high-frequency polarization modes.

As follows from Eqs. (30)–(32) in the vicinity of the phase-transition temperature the deviations of the high-frequency part of the susceptibility $\tilde{\chi}_C(\omega)$ from that of $\tilde{\chi}_A(\omega)$ are of the order $\{\tilde{\theta}_0^2,\tilde{P}_0^2\}$. Hence there is no splitting or broadening of the band at the phase transition. Thus in full agreement with the comments of Pleiner and Brand [12,13] the frequency of the band maximum varies smoothly across the Sm-A—Sm-C^* transition not showing any jumps, cusps, or kinks (see Figs. 2 and 3).

Such a type of the high-frequency dielectric behavior of a FLC is not surprising in view of the fact that the imaginary part of the complex susceptibility $\tilde{\chi}(\omega)$ for the two relaxation processes with relaxation times τ_1 and τ_2 defined as

$$\tilde{\chi}(\omega)=\Delta\chi\left[\frac{g_1}{1+i\omega\tau_1}+\frac{g_2}{1+i\omega\tau_2}\right]\quad (g_1+g_2=1) \tag{34}$$

may have two maxima if the ratio τ_1/τ_2 is sufficiently large [14]. The minimum value of τ_1/τ_2 for the occurrence of two maxima depends on the relative weight of the two relaxation processes; for $g_1=g_2=\frac{1}{2}$ Davidson [15] calculated $\tau_1/\tau_2>3+2\sqrt{2}\cong 5.8$. When $g_1\neq g_2$, the ratio τ_1/τ_2 must be larger to obtain a separation of the maxima (see Ref. [14] for detail).

For FLC's we usually have $\tau_1/\tau_2<2$ [4]. In such a case Eq. (35) predicts always only one maximum in the spectrum of dielectric loss and the frequency dependence can be approximated by a single relaxation process

$$\tilde{\chi}(\omega)=\frac{\Delta\chi}{1+i\omega\tau} \tag{35}$$

with a single relaxation time τ which is a geometric average of τ_1 and τ_2,

$$\tau=(\tau_1\tau_2)^{1/2} \tag{36}$$

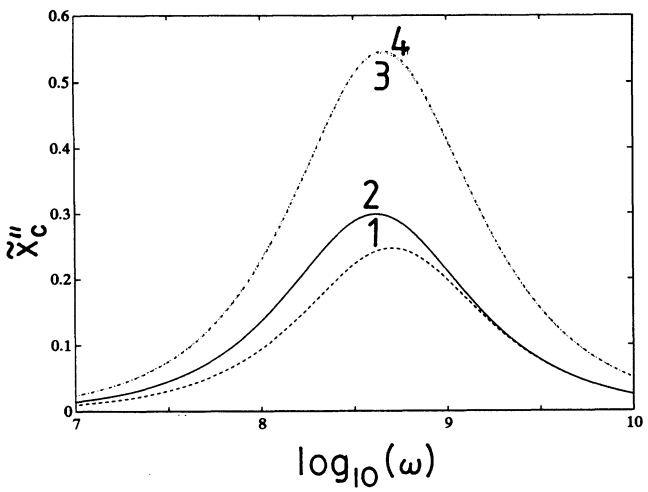

FIG. 4. The high-frequency behavior of the imaginary part of the normalized complex susceptibility for the generalized Landau model [4] as a function of frequency. The Sm-C^* phase, $T=326.81$ K, $\tilde{\theta}_0=0.44$, $\tilde{P}_0=-0.0917$. Curve 1: the high-frequency G mode; curve 2: the high-frequency S mode; curve 3: the sum of the first two curves (the resulting spectrum); curve 4: the relaxation band with the single relaxation time τ calculated from Eqs. (35) and (36). (In this case $\tau_1/\tau_2\cong 1.212$.) Curve 3 coincides with curve 4 within graphical accuracy.

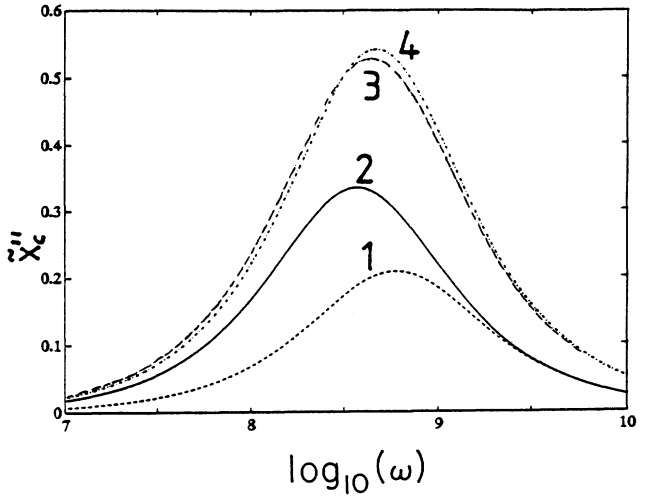

FIG. 5. The high-frequency behavior of the imaginary part of the normalized complex susceptibility for the generalized Landau model [4] as a function of frequency. The Sm-C^* phase, $T=326.0.4$ K, $\tilde{\theta}_0=0.92$, $\tilde{P}_0=-0.4442$. Curve 1: the high-frequency G mode; curve 2: the high-frequency S mode; curve 3: the sum of the first two curves (the resulting spectrum); curve 4: the relaxation band with the single relaxation time τ calculated from Eqs. (35) and (36). For this case $\tau_1/\tau_2\cong 1.60$.

[for $g_1=g_2$ this value of τ guarantees the coincidence of the frequencies of the maximum for $\chi''_C(\omega)$ predicted by Eqs. (34) and (35)].

Typical examples are illustrated by Figs. 4 and 5 and these support the above conclusions. One can see by inspection of these figures that the high-frequency band of a FLC resembles that for a single relaxation process.

However, a graphical method for the evaluation of the two relaxation times τ_1 and τ_2 if the dielectric strength $\Delta\chi$ is already known has been given by Barriol, Boule, and Diguet [16]. This method requires an arbitrary choice of a time constant τ_0 which is of the order of the relaxation times of the system under investigation. We then plot $[\Delta\chi-\chi'(\omega)]/\omega\tau_0\chi''(\omega)$ against $\omega\tau_0\chi'(\omega)/\chi''(\omega)$. It can be derived from Eqs. (34) that

$$\frac{\Delta\chi-\chi'(\omega)}{\omega\tau_0\chi''(\omega)}=\frac{\tau_1+\tau_2}{\tau_0}-\frac{\tau_1\tau_2\omega\tau_0\chi'(\omega)}{\tau_0^2\chi''(\omega)}\ , \tag{37}$$

the plot should be a straight line with the direction tangent $-\tau_1\tau_2/\tau_0^2$ and intersecting the ordinate at $(\tau_1+\tau_2)/\tau_0$, hence the values of τ_1 and τ_2 can easily be inferred [14]. It would be very interesting to apply this method to the Sm-C^* phase in order to determine the relaxation times τ_{PS} and τ_{PG} and to check the model more accurately.

It should be noted that the Landau model does not explain details of the temperature dependencies of the experimental dielectric spectra [10,11] because it has been assumed that the model parameters (excluding the term quadratic in tilt) are explicitly temperature independent and we can thus ignore the implicit temperature dependencies of the parameters. However, these assumptions are strictly valid in a very narrow temperature range, which does not satisfy the experimental conditions [10,11]. For example, under the above assumptions, the "classical" Landau model predicts that the frequency of the maximum of the β-relaxation band $f_{\max}$ does not depend on temperature (see Fig. 3). In the context of the model, if we suppose an Arrhenius behavior for the rotational viscosities γ_{PS} and γ_{PG}, i.e., $\gamma_{PS},\gamma_{PG}\sim\exp(A/T)$, which is typical for liquid systems including liquid crystals [14], we could explain the observed Arrhenius-like temperature dependence of $f_{\max}$ [an almost straight line in the coordinates $\ln(f_{\max})$ versus T^{-1}] [11]. Also, the temperature variations of the dielectric strength that have been observed [10,11] may be explained by the temperature dependence of the density, high-frequency dielectric constant, intermolecular correlations, etc. We also note that the conclusions concerning the high-frequency polarization modes are also valid for the FLC racemic mixture.

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