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Dielectric method for determining the electrical critical field in ferroelectric liquid crystals

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Abstract. — Both the electrical critical field and the dielectric constant ($\epsilon_0 \Delta\epsilon_G$) associated with the Goldstone mode in the ferroelectric liquid crystals are related to the helical pitch. A direct relation between these two physical quantities is established. We have calculated the electrical critical field for both DOBAMBC and DOBA-1-MPC compound from the measured temperature variation of $\epsilon_0 \Delta\epsilon_G$ and polarization without any adjustable parameter. Just below the transition temperature region, the results obtained agree qualitatively with the experimental data. Away from the transition temperature, there exist systematic deviations.

In 1975, Meyer *et al* [1] discovered pseudo-proper ferroelectric behavior in a liquid-crystal mesophase that does not display long-range translational order, namely the SmC* phase. In these studies the now widely characterized compound DOBAMBC (p-(n-decyloxybenzylidene)-p-amino-(2-methyl-butyl) cinnamate) was used. To date, ferroelectric properties have been found not only in the chiral-smectic-C (SmC*) phase but also in the chiral-smectic-I (SmI*) and chiral-smectic-F (SmF*) phases. Among these three mesophases, the most disordered one, SmC*, has been the focus of a lot of attention, because it has high potential applications for fast electro-optical switching devices [2]. Upon heating, the SmC* phase can undergo a continuous phase transition to the smectic-A (SmA) phase which has a high enough symmetry such that it does not exhibit the ferroelectric behavior. Considerable experimental and theoretical work has been carried out in the vicinity of the continuous SmA-SmC* transition to gain insight into nature of the more ordered SmC* phase. Nevertheless, only after a number of years was it realized that the sixth order terms in the mean field free energy expansion had to be included to account for the unusual temperature variation of the heat capacity and tilt angle (θ) and accurately describe the SmA-SmC* transition [3]. The necessity of the sixth order terms indicates that the transition is in the close vicinity of a mean-field tricritical point.

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Among numerous outstanding experimental efforts, one of the most celebrated works is the discovery of the anomaly in the temperature dependence of the ratio P/θ through high-resolution and simultaneous measurements of both tilt angle (θ) and spontaneous polarization (P) near the SmA-SmC* transition of DOBAMBC [4]. Since then, the similar anomalous behavior has been observed in many other ferroelectric liquid-crystal compounds by various research groups [5-7]. In order to explain the temperature dependence of the polarization, helical pitch and other physical properties (in particular the anomaly in the ratio (P/θ)), we need, at least, eleven expansion terms in the mean-field free energy expansion (the so called, generalized mean-field model [4, 8, 9]).

So far detailed experimental tests of this generalized mean-field model have only been carried out on DOBAMBC [9], DOBA-1-MPC [6] and HDOBAMBC [5] which have very similar chemical structures. All of these compounds are Schiff-based compounds which are not stable at elevated temperature. Many new and stable chiral smectic-C liquid-crystal compounds have been synthesized for device applications. It would be very important to demonstrate that the generalized mean-field model is not just applicable to the homologous series similar to DOBAMBC. On the other hand, the major motivation [4] of proposing the generalized mean-field model is the experimental discovery of the anomaly in the temperature variation of P/θ which has been subsequently confirmed in two other SmC* compounds [7] that are not Schiff-based compounds.

Intuitively it sounds unrealistic that eleven terms in the mean-field free energy expansion are needed to describe the SmA-SmC* transition. But judging from the number of non-trivial anomalous behaviors in physical properties to be described, the eleven-parameter fitting scheme no longer seems unwarranted. Moreover, the three leading parameters in the free energy expansion can be determined fairly precisely by fitting to both the heat capacity and tilt angle data which can be measured with very high resolution. The other independent experimental measurements give us a very good idea about the magnitude of another four coefficients. Consequently, there are only four parameters to be determined entirely from the fitting to the anomalies in P/θ and helical pitch [9]. Under these circumstances, the generalized mean-field model gives an excellent account for the temperature variation of heat capacity, tilt angle, polarization and the ratio P/θ , but only a qualitative description of the temperature dependence of the helical pitch. Meanwhile, we have tried to find a simpler model to describe all these anomalies and failed. As a result, before we add more terms to the generalized mean-field model to improve our fitting for the helical pitch, two different approaches can be taken to get further insight into the nature of the SmC* phase. First, direct, independent confirmation of these four new parameters from other experimental measurements would be extremely useful. The most important one is the biquadratic coupling term ($P^2\theta^2$) between the polarization and tilt angle. This is not an easy task, because it involves the high order terms in the free energy expansion. Secondly, it is a good idea to find some consistency check of the physical quantities which are related to the helical pitch. In this spirit we present one of these evidences from the temperature variation of the spontaneous polarization, electrical critical field (E_c) and the dielectric constant ($\epsilon_0 \Delta\epsilon_G$) associated with the Goldstone mode. Both the electrical critical field and the dielectric constant are directly related to the helical pitch. Thus these two physical quantities can be related to each other without the knowledge of the helical pitch.

The temperature dependence of electrical critical field in the SmC* phase of DOBAMBC has been measured by many research groups [10, 11]. The data reported by Dumrongrattana and Huang [10] are displayed in figure 1. Details of our experimental measurements are presented in reference [10]. Some of the important facts are listed in reference [12]. Two salient features revealed by this set of data are the following: 1) There exist hystereses

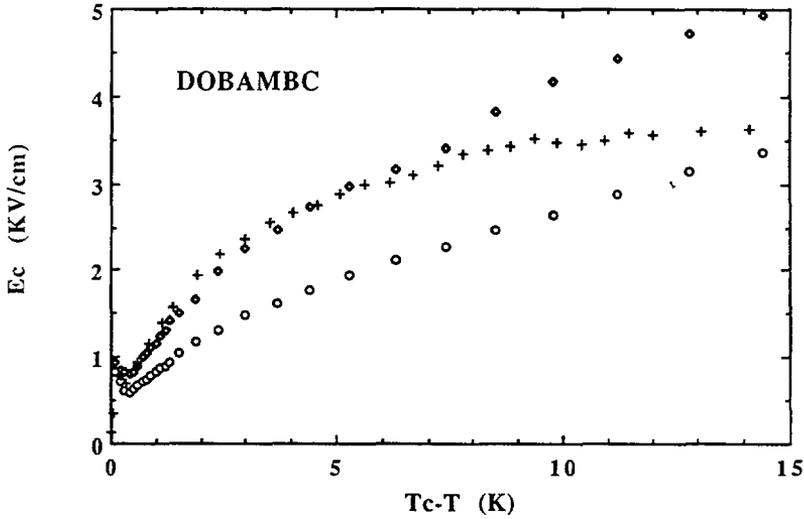


Fig 1 — Measured temperature dependence of the electrical critical field E_u (open diamonds) and E_d (open circles) for DOBAMBC. For comparison, the calculated values from equation (3) are shown as '+'.

between the disappearance and appearance of dechiralization lines while the applied electrical field is increased or decreased through the critical field region. Here E_u and E_d are the critical field for disappearance and appearance of dechiralization lines, respectively. 2) Within one degree range below the transition temperature, in a very narrow region of applied electrical field (8×10^5 V/m), the system exhibits a reentrant behavior, namely, existence of the SmC*-SmC-SmC* transition sequence as temperature decreases under a constant electrical field. One very important point should be mentioned here. Because of the hysteretical behavior of the measured electrical critical field, a concave upwards curve in the temperature dependence of E_u is not sufficient to guarantee that there exists a reentrant behavior as a function of temperature. For example, a system with temperature dependence of E_u and E_d as sketched in figure 2 will not have a reentrant behavior. The second feature, namely, the up turn of the electrical critical field in the immediately vicinity of the transition temperature is directly related to the decrease in the size of the helical pitch.

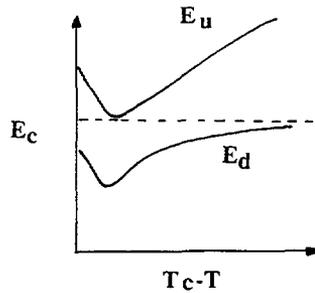


Fig 2 — A sketch of the temperature dependence of the electrical critical field E_u and E_d . The dashed line indicates the minimum of the E_u . Even though there exist upward turns near the transition temperature in both E_u and E_d , in this special case one cannot find any constant applied electrical field that will lead to a reentrant behavior as a function of temperature.

Based on the balance of elastic energy associated with the helix and electrostatic energy associated with the polarization and applied electrical field, one obtains [10] an expression for the electrical critical field to unwind the helical pitch, namely,

$$E_c = \pi^4 K \theta^2 / (4 P L^2) \quad (1)$$

Here K is the elastic constant, L the size of the helical pitch. The same expression can be obtained from one soliton solution to electrically unwind the helical pitch [13] This approach has been discussed in detail by de Gennes in the context of unwinding cholesteric pitch by an applied magnetic field [14]

Figure 3 displays the anomaly of $\Delta\varepsilon_G$ obtained from a dielectric relaxation measurement of DOBAMBC below the SmA-SmC* transition [15] The peak, located just below the transition temperature, is directly related to the anomaly in the helical pitch. Now let us derive an expression of $\Delta\varepsilon_G$ in term of relevant physical parameters. The order parameter associated with the SmA-SmC (or -SmC*) transition can be written as $\theta \times \exp(i\phi)$ where θ is the magnitude of the angle between the smectic layer normal (say the z axis) and the long axis of the molecule and ϕ the azimuthal angle of the molecule tilt with respect to, say, the y axis While the angle ϕ is fixed within a given domain in the SmC phase, it gradually changes along the z axis in the SmC* phase This leads to the formation of helical pitch Typically the pitch size is on the order of a few microns. Since the molecular length is only about 25 \AA , the change in ϕ between successive smectic layer is quite small. Consequently, in a moderate electrical field applied to unwind the helical pitch, we will assume that the magnitude of tilt angle remains constant With the applied electrical field being along the x -axis, the free-energy density in the SmC* phase can be written as

$$g = K\theta^2(d\phi/dz)^2/2 - K\theta^2 L(d\phi/dz) - EP \cos \phi$$

Here $q (= 2\pi/L)$ is the wave vector associated with the helical pitch (L) Minimizing this free energy density, one obtains

$$K\theta^2(d^2\phi/dz^2) - EP \sin \phi = 0$$

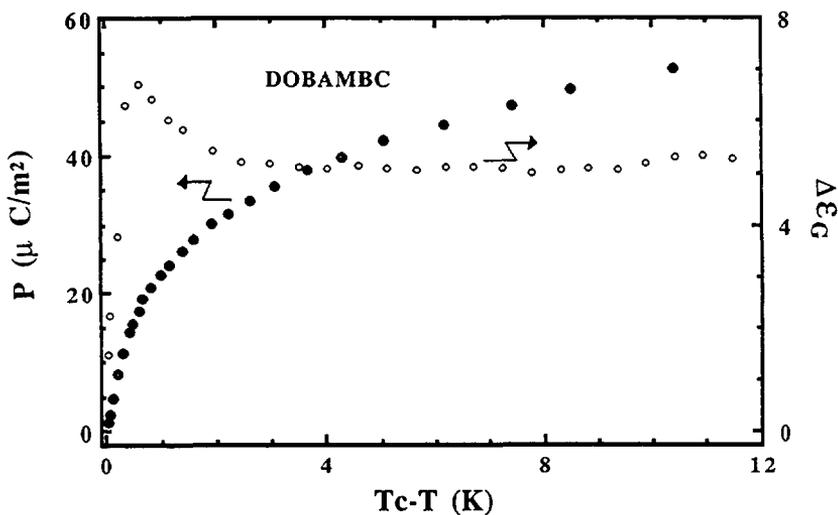


Fig. 3 — Temperature variation of polarization (solid dots) and dielectric strength (open circles) in the SmC* phase of DOBAMBC

In the case of a small applied electrical field and in the limit of the linear response region, we obtain

$$\varepsilon_0 \Delta\varepsilon_G = (PL)^2 / (8 \pi^2 K \theta^2) . \quad (2)$$

Here $\varepsilon_0 \Delta\varepsilon_G$ is the dielectric strength in the Goldstone-mode of the induced polarization due to the applied electrical field. Combining equations (1) and (2), one obtains the following relation

$$E_c = (\pi^2 P) / (32 \varepsilon_0 \Delta\varepsilon_G) \quad (3)$$

Here the electrical critical field is directly related to the polarization and dielectric strength. Near the SmA-SmC* transition of DOBAMBC and DOBA-1-MPC, we have measured the temperature variation of both polarization [4, 6, 15] and dielectric strength [15]. The results are reproduced in figures 3 and 4 for DOBAMBC and DOBA-1-MPC, respectively. Without any adjustable parameters, equation (3) allows us to calculate E_c from P and $\varepsilon_0 \Delta\varepsilon_G$. The calculated results are displayed in figure 1 and figure 5 for DOBAMBC and DOBA-1-MPC, respectively. The measured temperature dependence of the electrical critical field E_u and E_d near the SmA-SmC* transition of DOBA-1-MPC is shown in figure 5 (see Ref [12]). Qualitatively, equation (3) gives reasonable relation among the three physical quantities in describing the nature of the SmC* phase of both DOBAMBC and DOBA-1-MPC. The difference between the measured and calculated electrical critical field is clearly not negligible, particularly in the region away from the transition temperature. At this point, the effect of the surface treatment used for alignment on the measured results is not clear to us (Note, in the case of dielectric measurements, a magnetic field was used to align the samples). Careful measurements on the same sample for all three physical quantities, namely, E_c , P and $\varepsilon_0 \Delta\varepsilon_G$ may allow us to eliminate this plausible problem.

One final remark is that the major difference between the two compounds, we presented in this paper, is that the chiral group of DOBA-1-MPC is closer to the central part of the molecule than that of DOBAMBC. This results in an increase of factor of three in the

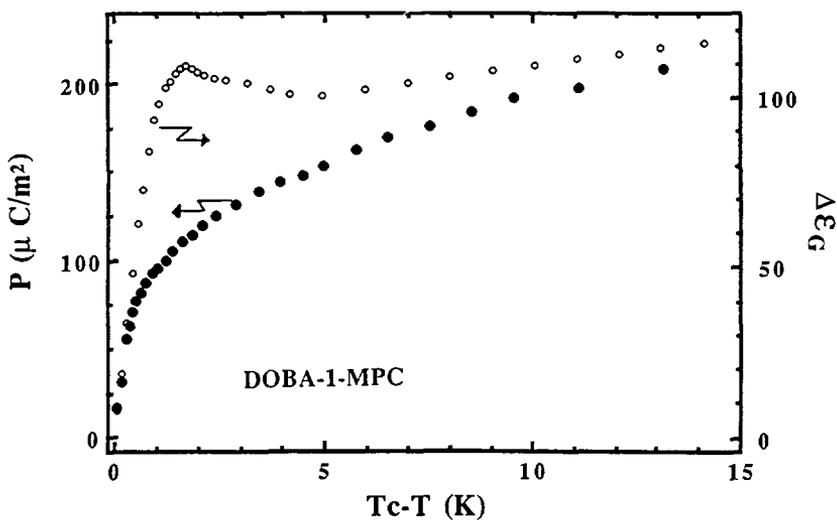


Fig 4 — Temperature dependence of polarization (solid dots) and dielectric strength (open circles) in the SmC* phase of DOBA-1-MPC

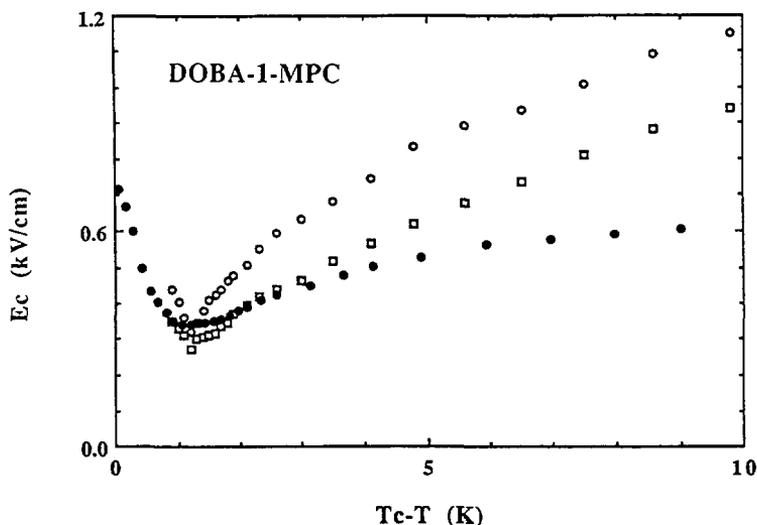


Fig 5 — Measured temperature variation of the electrical critical field E_u (open circles) and E_d (open squares) for DOBA-1-MPC. For comparison, the calculated values from equation (3) are shown as solid dots.

magnitude of polarization for DOBA-1-MPC (see Figs. 3 and 4). According to equation (1), we believe that this is the major factor that the electrical critical field for DOBA-1-MPC is about three times smaller than that for DOBAMBC.

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