

Research Article

Analysis of the Dielectric Constant as a Function of Temperature at Constant Electric Fields for the Smectic A-Smectic G Transition in A6

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The temperature dependence of the dielectric constant is studied under some fixed electric fields for the smectic G- (tilted-) smectic A (orthogonal) transition of the ferroelectric liquid crystal of compound A6. For this study, a mean field model with the quadrupole-quadrupole interactions is introduced. By fitting the inverse dielectric susceptibility from the mean field model to the experimental data from the literature, the observed behaviour of the dielectric constant is described satisfactorily for the smectic AG transition in A6. The transition temperature induced by an external electric field is also discussed for this ferroelectric compound.

1. Introduction

Ferroelectric liquid crystals have been the subject of various experimental and theoretical studies [1–12]. As a function of temperature under fixed pressures or concentrations, the physical quantities such as the spontaneous polarization, tilt angle, dielectric constant, specific heat, and so forth, have been studied for their phase transitions between the smectic phases of A and C (or C^{*}) in particular. Under the electric field, some of those quantities have also been investigated and the first order or second order nature of the transitions between the smectic phases has been clarified.

Among the smectic phases, smectic C (or C^{*}) and also smectic G phases are tilted since the long axes of the molecules make an angle θ with the director, whereas smectic A, B, and E phases are orthogonal ($\theta = 0$). In the presence of the chiral molecules, the smectic tilted phases possess a spontaneous polarization P_s [1]. In the chiral-racemic systems, as the spontaneous polarization increases, the ferroelectric transition temperatures are shifted. Similarly, increasing the applied electric field causes the ferroelectric transition temperatures to shift [7]. Increasing the amount

of spontaneous polarization P_s or the external electric field E then changes the phase transition from a first order towards a second order in ferroelectric liquid crystals. In some ferroelectric materials, a tricritical transition [12, 13] occurs which exhibits both the features of first order and second order transitions.

The nature of the transition among the smectic phases can be investigated by considering the coupling between the order parameters (tilt angle, spontaneous polarization, orientational order parameter, etc.) in the mean field models. A bilinear coupling between the spontaneous polarization and the tilt angle ($P\theta$ coupling) [5, 7] and the biquadratic coupling ($P^2\theta^2$ coupling) [3, 4] have been considered in the mean field models mainly for the smectic AC (or AC^{*}) transitions. We have also studied the AC or AC^{*} transitions using the biquadratic [14–18] and both the bilinear and biquadratic couplings [19, 20] in our earlier studies.

In this study, we investigate the dielectric properties of the ferroelectric liquid crystal of A6 for its smectic AG transition using our mean field model with the $P^2\theta^2$ coupling which we have introduced previously [14]. The temperature dependence of the dielectric susceptibility χ is derived from

TABLE 1: Values of the coefficients according to (7) with the definitions of a_1 and a_2 (see the text) within the temperature intervals below T_0 for the smectic AG transition of compound A6 at fixed field strengths. The transition temperatures (T_0) are also given here.

E (kV/cm)	T_0 ($^{\circ}\text{C}$)	a ($^{\circ}\text{C}^{-1}$)	a_1	a_2	$2D/e\chi_0\epsilon_0$	Temperature interval ($^{\circ}\text{C}$)
0	77.8	0.435	15.66	63.04	0.118	$77.56 < T < 77.80$
17	78.0	-0.053	1.37	108.40	0.115	$77.69 < T < 77.95$
33	78.1	-0.041	1.05	89.85	0.122	$77.76 < T < 78.10$
50	78.2	-0.044	1.16	100.95	0.125	$77.88 < T < 78.19$
67	78.4	-0.013	0.37	168.68	0.125	$78.03 < T < 78.36$

our mean field model and it is fitted to the experimental data [7] for the phase transition, ransition between the tilted smectic G phase and the orthogonal smectic A phase of compound A6. This analysis of the dielectric constant ϵ (or dielectric susceptibility χ) is performed for the applied electric field strengths of 0, 17, 33, 50, and 67 kV/cm using the experimental data for A6 [7].

Below, in Section 2, we give an outline of our mean field model regarding the dielectric susceptibility. In Section 3 our calculations and results are presented. Sections 4 and 5 give our discussion and conclusions.

2. Theory

The smectic A-smectic G (AG) transition in ferroelectric liquid crystals can be studied by the mean field models where the free energy of the smectic G phase can be expanded in terms of the order parameters. Since the smectic G phase is the tilted phase such as smectic C and C* phases, the free energy of this phase can be expanded in terms of the tilt angle θ and the spontaneous polarization (order parameters) as follows:

$$g = \frac{1}{2}a(T - T_0)\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 + \frac{1}{2\chi_0\epsilon_0}P^2 - DP^2\theta^2 + \frac{1}{4}eP^4. \quad (1)$$

In this mean field model (1) as we have introduced in our previous study [14], the quadrupole-quadrupole interactions ($P^2\theta^2$) between the molecules are taken into account (D is the biquadratic coupling constant). The coefficients a , b , c , and e are independent of temperature, χ_0 is the dielectric susceptibility at fixed θ , and ϵ_0 is the vacuum permittivity. When b is negative, smectic AG transition is of a first order, for $b = 0$, the tricritical AG transition occurs and this transition is of a second order when b is positive.

The temperature dependence of the order parameters (tilt angle θ of the smectic G phase, and the spontaneous polarization P of the smectic A and G phases) and the susceptibility χ can be derived from the free energy (1).

By minimizing the free energy (or $\partial g/\partial\theta = 0$ and $\partial g/\partial P = 0$), one gets

$$a(T - T_0)\theta + b\theta^3 + c\theta^5 - 2DP^2\theta = 0, \quad (2)$$

$$\frac{1}{\chi_0\epsilon_0}P - 2DP\theta^2 + eP^3 = 0. \quad (3)$$

By solving P^2 in terms of θ^2 in (3) and substituting it to (1), we can express the free energy g in terms of the tilt angle θ only, as given below:

$$g = \left[\frac{1}{2}a(T - T_0) + \frac{2D}{e\chi_0\epsilon_0} \right] \theta^2 + \frac{1}{4} \left(b - \frac{4D^2}{e} \right) \theta^4 + \frac{1}{6}c\theta^6. \quad (4)$$

Equations (2) and (3) give, respectively, the temperature dependence of the tilt angle of the smectic G phase and the spontaneous polarization of the smectic G and A phases (when substituted (3) in (2) for P^2).

The temperature dependence of the dielectric susceptibility χ can also be derived, as stated above, according to

$$\chi_{\theta}^{-1} = \frac{\partial^2 g}{\partial \theta^2}, \quad (5)$$

or

$$\chi_P^{-1} = \frac{\partial^2 g}{\partial P^2}. \quad (6)$$

Using (5) for the tilt angle susceptibility through (1), we find

$$\chi_{\theta}^{-1} = a(T - T_0) + \frac{2D}{e\chi_0\epsilon_0} + 3 \left(b - \frac{4D^2}{e} \right) \theta^2 + 5c\theta^4. \quad (7)$$

The temperature dependence of the tilt angle θ can be obtained from the molecular field theory [21] as

$$\theta = \left[3 \left(1 - \frac{T}{T_0} \right) \right]^{1/2} \quad 0 < (T_0 - T) \ll T_0. \quad (8)$$

Equation (8) can be used in (7) and the coefficients in the expansion of the inverse susceptibility can then be determined.

3. Calculations and Results

The temperature dependence of the inverse susceptibility χ_{θ}^{-1} was analyzed according to (7) for the smectic AG transition of compound A6 using the experimental data for the dielectric constant ϵ [7]. This analysis was conducted for constant bias field strengths of 0, 17, 33, 50, and 67 kVcm $^{-1}$ [7]. Equation (7) was fitted to the experimental data for ϵ for the field strengths studied using the variables $a_1 = 3(b - 4D^2/e)$ and $a_2 = 5c$, as given in Table 1 within the temperature intervals in the smectic G phase ($T < T_0$)

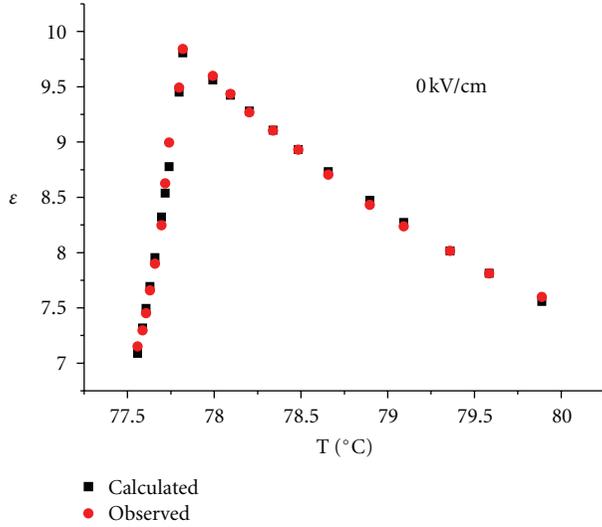


FIGURE 1: Dielectric constant ϵ calculated as a function of temperature at 0 kVcm^{-1} according to (7) fitted to the observed data [7] for the smectic AG transition of compound A6.

for A6. Values of the coefficients which we obtained from our analysis above T_0 in the smectic A phase ($\theta = 0$) are tabulated in Table 2. In both tables, $2D/e\chi_0\epsilon_0$ represents the experimental values [7] of the inverse susceptibility when $\theta = 0$ at the critical temperature ($T = T_0$). Our calculated (7) and the observed data [] for the dielectric constant ϵ are plotted as a function of temperature for the bias field strengths of 0, 17, 33, 50, and 67 kVcm^{-1} in Figures 1, 2, 3, 4, and 5, respectively, for the smectic AG transition of compound A6.

4. Discussion

The dielectric constant ϵ was calculated from the inverse dielectric susceptibility χ_θ^{-1} according to (7) using the experimental data [7] for both the smectic AG transition of compound A6 at various temperatures for fixed field strengths, as shown in Figures 1, 2, 3, 4, and 5. For all the fixed electric fields by fitting (7) to the observed data [7], the fitted parameters were deduced within the temperature intervals studied (Tables 1 and 2). As seen in Figures 1, 2, 3, 4, and 5, our fits are reasonably good for the smectic AG transition as the transition temperature (T_0) is shifted to higher values with increasing the bias field strength (Tables 1 and 2). We also estimated the temperature difference between the observed temperature T_c and the transition temperature T_0 ($\Delta T = T_c - T_0$) for the smectic G phase at zero electric field ($E = 0 \text{ kVcm}^{-1}$) in the case of a first order smectic AG transition of compound A6. We found that $\Delta T = 0.7^\circ\text{C}$ for $E = 0$, which increases to considerably much larger values as the bias field strength increases towards 67 kVcm^{-1} . This indicates that a first order smectic AG transition can occur at zero electric field which changes toward a second order one with increasing the field strength in A6. This is also demonstrated experimentally (Figures 1, 2, 3, 4, and 5) that

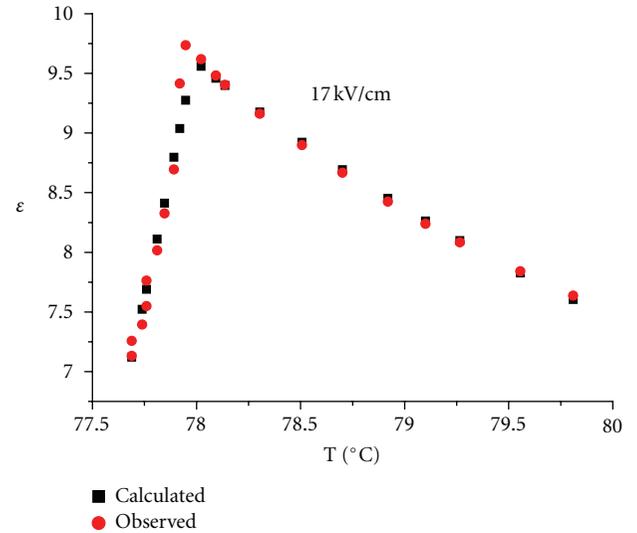


FIGURE 2: Dielectric constant ϵ calculated as a function of temperature at 17 kVcm^{-1} according to (7) fitted to the observed data [7] for the smectic AG transition of compound A6.

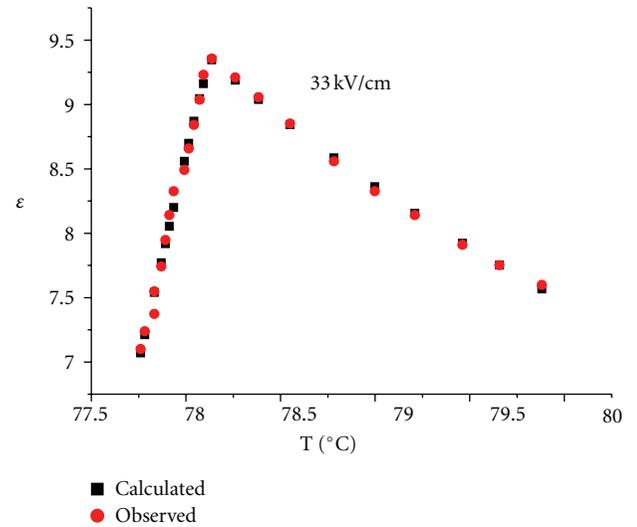


FIGURE 3: Dielectric constant ϵ calculated as a function of temperature at 33 kVcm^{-1} according to (7) fitted to the observed data [7] for the smectic AG transition of compound A6.

the dielectric constant ϵ decreases in magnitude as the field strength increases with the transition temperature shifted. This decrease in the dielectric constant ϵ indicates most likely a second order smectic AG transition in A6. In the smectic A phase, the dielectric constant ϵ increases with decreasing temperature due to the electroclinic soft mode behaviour of the smectic A phase of chiral molecules [7]. As the electric field decreases (with decreasing temperature), the electroclinic soft mode behaviour of the smectic A phase of chiral molecules becomes more effective, which causes a sudden decrease of the dielectric constant ϵ in the tilted smectic G phase, as observed experimentally [7].

TABLE 2: Values of the coefficients according to (7) within the temperature intervals above T_0 for the smectic AG transition of compound A6 at fixed field strengths. The transition temperatures (T_0) are also given here.

E (kV/cm)	T_0 ($^{\circ}\text{C}$)	a ($^{\circ}\text{C}^{-1}$)	$2D/e\chi_0\varepsilon_0$	Temperature interval ($^{\circ}\text{C}$)
0	77.8	0.019	0.113	$77.82 < T < 79.89$
17	78.0	0.019	0.116	$78.02 < T < 79.81$
33	78.1	0.019	0.119	$78.14 < T < 79.88$
50	78.2	0.018	0.122	$78.22 < T < 79.91$
67	78.4	0.019	0.124	$78.45 < T < 79.90$

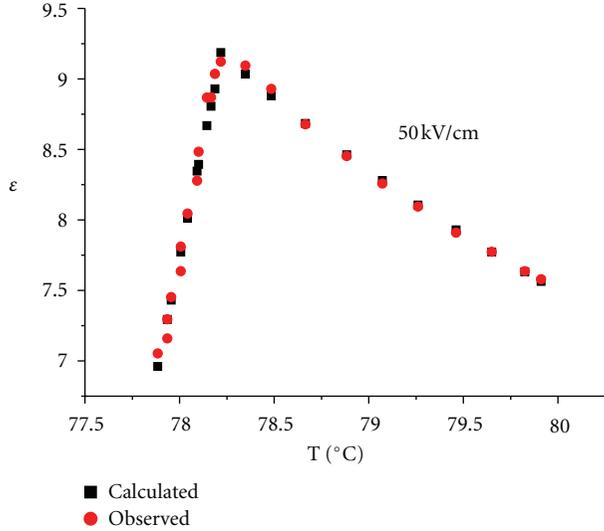


FIGURE 4: Dielectric constant ε calculated as a function of temperature at 50 kVcm^{-1} according to (7) fitted to the observed data [7] for the smectic AG transition of compound A6.

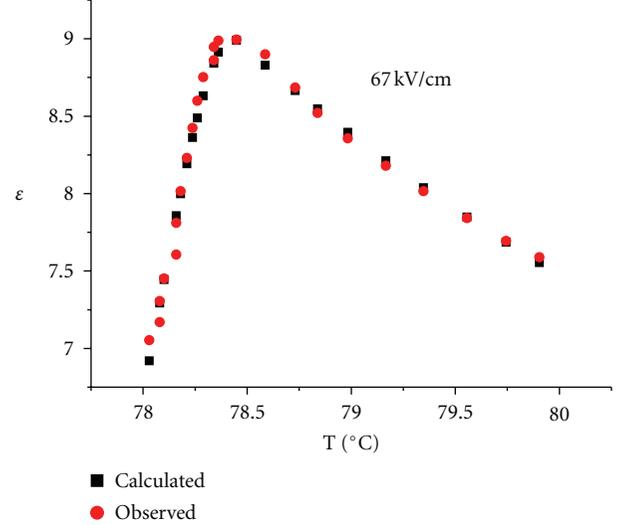


FIGURE 5: Dielectric constant ε calculated as a function of temperature at 67 kVcm^{-1} according to (7) fitted to the observed data [7] for the smectic AG transition of compound A6.

It has been reported [7] that a linear relation between the induced temperature shift and the applied field strength can be established, as studied for A6. Also, an analogy between the shift of the transition temperature induced by an external electric field and the shift induced by the spontaneous polarization can exist for ferroelectric liquid crystals [7], in particular, for compound A6. In fact, the ferroelectric transition temperatures are shifted by the increasing amount of the spontaneous polarization in the chiral-racemic systems, as pointed out previously [7]. By considering a bilinear coupling between the spontaneous polarization P and the tilt angle θ ($P = C\chi_0\varepsilon_0\theta$ with the coupling constant C) in the mean field model, the difference in the transition temperature between the chiral compound and its racemate has been obtained [7] as

$$T_{\text{chi}} - T_{\text{rac}} = \frac{C^2\chi_0\varepsilon_0}{a}. \quad (9)$$

In our mean field model (1) with the biquadratic coupling $DP^2\theta^2$ (D is the coupling constant), this difference in the transition temperature can be obtained as

$$T_{\text{chi}} - T_{\text{rac}} = -\frac{2D}{e\chi_0\varepsilon_0}. \quad (10)$$

This can be applied to the smectic G (chiral)-smectic A (racemic) on the assumption that the spontaneous polarization P_s refers to the smectic G phase only. In order to estimate the difference in the transition temperature ($T_{\text{chi}} - T_{\text{rac}}$), we used (10) at zero electric field ($E = 0 \text{ kV/cm}$) and we obtained the value of 0.3 K which can be compared with the value of 1.0 for the smectic AG transition of compound A6. We also calculated the difference ($T_{\text{chi}} - T_{\text{rac}}$) at higher field strengths up to 67 kV/cm (Table 1). We obtained that the values of $T_{\text{chi}} - T_{\text{rac}}$ increased enormously for the smectic AG transition of A6 as the bias field strength increases. We conclude that the transition temperatures are shifted by the increasing amount of the spontaneous polarization in the case of zero electric field for the chiral-racemic systems, as studied here for the compound A6. This gives rise to a first order smectic AG transition at zero electric field for A6. Regarding the dielectric susceptibility (χ_P) induced by the spontaneous polarization P_s , its temperature dependence can also be studied for ferroelectric liquid crystals, particularly for compound A6. Here, the spontaneous polarization P_s can be defined as the total polarization of both smectic phases of A and G or for the tilted phase G only. This then requires the temperature dependence of the spontaneous polarization P_s as we used that dependence of the tilt angle

θ (8) from the molecular field theory. Within the biquadratic $P^2\theta^2$ coupling (with the coupling constant D) from our mean field model (1), χ_p^{-1} can be obtained as a function of temperature. In this case, the spontaneous polarization which induces the temperature shift can be considered as an internal electric field similar to the applied electric field that induces a tilt angle in ferroelectric liquid crystals.

5. Conclusions

The dielectric constant was studied at various temperatures for the smectic A- smectic G transition of compound A6 in the presence of constant electric fields. The inverse dielectric susceptibility deduced from our mean field model with the biquadratic $P^2\theta^2$ coupling, was fitted to the experimental data from the literature for the AG transition of this ferroelectric liquid crystal. It was found that the mean field model studied here describes adequately the observed behaviour of the dielectric constant as a function of temperature.

It is concluded that the smectic A-smectic G transition in A6 is of a first order at zero electric field. As the field strength increases, it changes toward a second order transition in this ferroelectric liquid crystal.

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