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Temperature Dependence of the Dielectric Constant Calculated Using a Mean Field Model Close to the Smectic A - Isotropic Liquid Transition

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1. Introduction

Various transitions among the phases of isotropic liquid (I), nematic (N) and smectic (SmA, SmC and SmC*) in liquid crystals have been studied extensively. The nematic-smectic A (NA) and the smectic A- smectic C (AC) or the smectic A-smectic C* (AC*) transitions are usually continuous and they are considered to belong to the three-dimensional XY universality class for the critical fluctuations (de Gennes, 1973). Experimentally, this requires a wide range of the nematic phase (Garland & Nounesis, 1994) for the NA transition, whereas at the AC transition the critical fluctuations are very large (Safinya et al., 1980).
Ferroelectric liquid crystals exhibiting transitions from the isotropic liquid (I) to the nematic (N), smectic A and the smectic C or smectic C* (with optically active molecules), have also been studied extensively, in particular, those with high spontaneous polarization such as 4-(3-methyl-2-chlorobutanoyloxy)- 4' -heptyloxybiphenyl (A7). Experimental studies on the ferroelectric liquid crystals with high spontaneous polarization (Bahr & Heppke, 1986- Mercuri et al., 2003) have been reported in the literature. The AC (or AC*) transitions in the ferroelectric liquid crystals (Bahr & Heppke, 1990- Denolf et al., 2006) and in the antiferroelectric liquid crystals (Ema,, et al., 1996) have also been studied experimentally. Theoretical studies on the AC and AC* transitions have been reported in the literature (Musevic et al.,. 1983- Mukherjee, 2009). We have also studied the AC and AC* transitions in the ferroelectric liquid crystals (A7 and C7) theoretically by using the mean field models in our previous works (Salihoğlu et al., 1998- Yurtseven 2011).
Among the various physical properties of the ferroelectric liquid crystals, the dielectric properties have been studied extensively close to the AC (or AC*) transitions (Bahr et al., 1987, Musevic et al., 1983, Yurtseven & Kilit, 2008, Kilit & Yurtseven, 2008, Benguigui, 1984). In an another ferroelectric liquid crystal known as DOBAMBC which shows a second order transition (Zeks, 1984, Indenbom et al., 1976, Carlsson & Dahl, 1983), the AC* transition is associated with an increase in the dielectric constant $\varepsilon_{\perp}$ with decreasing temperature, as observed experimentally (Bahr et al., 1987). This increase in the $\varepsilon_{\perp}$ has been attributed to the contributions from a soft mode and also a Goldstone mode of this ferroelectric material with

low spontaneous polarization. It has been observed experimentally that the ferroelectric liquid crystal 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl exhibits similar to the DOBAMBC an increase in the dielectric constant $\varepsilon_{\perp}$ with decreasing temperature from SmA to SmC* at different voltages (Bahr et al., 1987). This increase in $\varepsilon_{\perp}$ also occurs for the pure optically active compound, the 50% optically active mixture and the racemate at the SmA-I transition of 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl (Bahr et al., 1987).

A first order or second order character of the phase transitions in the ferroelectric liquid crystals can be characterized by the critical behaviour of the order parameters which occurs as the temperature decreases from the isotropic liquid to the nematic and smectic phases. There is no order parameter in the isotropic liquid phase, whereas in the nematic and smectic phases there occur orientational order parameter ψ (in the nematic and smectic phases). In the smectic phases of a ferroelectric liquid crystal, in addition to the orientational order parameter ψ, the spontaneous polarization P occurs. P can couple with ψ since the symmetry is reduced as the temperature decreases in the smectic phase. This coupling between the spontaneous polarization P and the orientational order parameter ψ can also occur in the crystal which contains optically active molecules such as 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl (A7). In this ferroelectric liquid crystal, in particular, the optically active molecules can induce the phase transition which changes towards a second order (continuous) as the temperature decreases from the isotropic liquid to the smectic phase, whereas the racemic A7 can exhibit a first order (discontinuous) transition.

In this study, a first order transition of the racemic A7 and the second order transition of the 50% optically active compound are investigated by calculating the temperature dependence of the dielectric constant $\varepsilon_{\perp}$ on the basis of the experimental results (Bahr et al., 1987). For this calculation, our mean field model which we have studied for the AC* transition ($P^2\theta^2$ coupling, θ is the tilt angle in the C* phase) previously (Salihoğlu et al., 1998), is used with the biquadratic $P^2\psi^2$ coupling between the spontaneous polarization P and the orientational order parameter ψ. For both 50% optically active compound and the racemic A7, the isotropic liquid-smectic A transition is studied by expanding the free energy in terms of the order parameters P and ψ according to the Landau phenomenological model. With the $P^2\psi^2$ coupling, our mean field model considers quadrupolar interactions for the 50% optically active compound and for the racemic A7 differently from the bilinear $P\theta$ coupling which considers the dipole-dipole interactions as studied in a previous study (Bahr et al., 1988). The mean field models with the $P^2\theta^2$ coupling have also been treated in some earlier theoretical studies (Zeks, 1984- Blinc, 1992).

In section 2, we describe our mean field model for the SmA-I transition. Section 3 gives our calculations and results which are discussed in section 4. Finally, conclusions are given in section 5.

2. Theory

Close to the smectic A-isotropic liquid transition can be investigated by a mean field model. In the smectic A phase, the order parameters are the orientational order parameter ψ and the spontaneous polarization P. So, the free energy in this phase can be expanded in terms of ψ and P as given below:

$$g = \frac{1}{2}\alpha\psi^2 + \frac{1}{4}b\psi^4 + \frac{1}{6}c\psi^6 + \frac{1}{2\chi_0\varepsilon_0}P^2 - DP^2\psi^2 + \frac{1}{4}eP^4 \tag{1}$$

This expansion of the free energy has already been introduced in our earlier study (Salihoğlu et al., 1998). In Eq.(1) the coefficient α is taken as the temperature dependent given by

$$\alpha = a(T - T_o) \tag{2}$$

where *a* is constant and T_o is the transition temperature. When the smectic A-isotropic liquid (SmA-I) transition is considered as a first order, then *b* is negative in Eq.(1) with the additional ψ^6 term and the coefficients *c, D* and *e* are taken as positive. In Eq.(1) the other constants, ε_0 is the vacuum permittivity and χ_0 describes the susceptibility at $\psi = \psi_0$. We consider a quadratic coupling $P^2\psi^2$ in our mean field model to describe the quadrupolar interactions in the liquid crystalline system studied here. The last term to the power P^4 in Eq.(1) stabilizes the system thermodynamically. Since there is no ordering in the isotropic liquid (order parameter is zero), we have

$$F_I = 0 \tag{3}$$

The free energy g (Eq.1) can be minimized with respect to the orientational order parameter ψ and the spontaneous polarization P, which gives

$$\alpha\psi + b\psi^3 + c\psi^5 - 2DP^2\psi = 0 \tag{4}$$

and

$$\frac{1}{\chi_o\varepsilon_o}P - 2DP\psi^2 + eP^3 = 0 \tag{5}$$

Eq.(5) then gives

$$P^2 = \frac{1}{e}\left(2D\psi^2 - \frac{1}{\chi_o\varepsilon_o}\right) \tag{6}$$

By substituting this expression into Eq.(4), one gets

$$c\psi^4 + b^*\psi^2 + d^* = 0 \tag{7}$$

with the definitions of the coefficients

$$b^* = b - \frac{4D^2}{e} \tag{8}$$

and

$$d^* = a(T - T_o) + \frac{2D}{e\chi_o\varepsilon_o} \tag{9}$$

When we substitute the spontaneous polarization P (Eq.6) into the free energy g (Eq.1), we then get

$$g = \frac{1}{2}\alpha'\psi^2 + \frac{1}{4}b'\psi^4 + \frac{1}{6}c'\psi^6 \tag{10}$$

where

$$\alpha' = \alpha + \frac{2D}{e\chi_o\varepsilon_o} \tag{11}$$

$$b' = b - \frac{4D^2}{e} \tag{12}$$

and

$$c' = c \tag{13}$$

In order to describe the SmA-I transition, the condition for a first order transition can be obtained according to the relation among the coefficients (Salihoğlu et al., 1998)

$$\frac{\alpha' c'}{b'^2} = \frac{3}{16} \tag{14}$$

For a first order transition, a difference occurs between the transition temperature T_o and the observed T_c, which can be given in Eq.(2) as

$$\alpha = a(T_o - T_c) \tag{15}$$

at $T=T_c$. As we have already derived in our previous study (Salihoğlu et al., 1998), this temperature difference can be obtained using Eqs.(11-14) as

$$T_c = T_o + \frac{3}{16}\frac{b'^2}{ac} - \frac{2D}{ea\chi_o\varepsilon_o} \tag{16}$$

The inverse susceptibility χ^{-1} can be derived from the free energy g (Eq. 10) according to the definition

$$\chi_\psi^{-1} = \partial^2 g / \partial\psi^2 \tag{17}$$

This second derivative then gives

$$\chi^{-1} = \alpha' + 3b'\psi^2 + 5c'\psi^4 \tag{18}$$

In Eq.(18) the coefficient α' depends on the temperature through Eq.(11) by using Eq.(2). The coefficients b' and c' are taken as constants, as before.
Since we expressed the inverse susceptibility χ^{-1} to the powers of the orientational order parameter ψ in Eq.(18), it will be determined by the temperature dependence of ψ. From the molecular field theory (Matsushita, 1976), the order parameter ψ depends on the temperature according to the relation

$$\psi = [3(1-\frac{T}{T_c})]^{1/2}, \qquad 0<(T_c - T)<<T_c \tag{19}$$

with the critical exponent $\beta = 1/2$. By using this temperature dependence of ψ (Eq.19) in Eq.(18), we obtain the inverse susceptibility χ^{-1} or the dielectric constant ($\chi = \varepsilon - 1$) as a function of temperature for the smectic A-isotropic liquid transition in our mean field model studied here.

3. Calculations and results

The inverse susceptibility χ^{-1} was calculated here as a function of temperature according to Eq.(18) on the basis of the temperature dependence of the orientational order parameter ψ (Eq.19) for the ferroelectric phase of A7. We first calculated the temperature dependence of ψ below T_c for the smectic A-isotropic liquid transition of A7. It was calculated (Eq.19) for the 50% optically active mixture (T_c=81.9^{o}C) and for the racemate (T_c=82^{o}C) at the smectic A-isotropic liquid transition.

In order to calculate the inverse susceptibility χ^{-1} from the orientational order parameter ψ as a function of temperature, we determined the coefficients α', b' and c' in Eq.(18). For this determination, the experimental data for the dielectric constant $\varepsilon_\perp$ (Bahr et al., 1987) was used ($\chi = \varepsilon_\perp - 1$). In Eq.(18), the expression for α' (Eq.11) through α (Eq.15) can be used and the inverse susceptibility becomes

$$\chi^{-1} = a(T - T_o) + \frac{2D}{e\chi_o\varepsilon_o} + a_1\psi^2 + a_2\psi^4 \tag{20}$$

where the coefficients are $a_1 = 3b'$ and $a_2 = 5c'$. The second term as a constant in Eq.(20) can be computed from the value of the inverse susceptibility at the transition temperature ($T=T_o$) where the order parameter is zero (Figs. 1 and 2). This gives

$$\chi^{-1}\Big|_{T=T_o} = \frac{2D}{e\chi_o\varepsilon_o} \tag{21}$$

Values of this constant term were obtained from the experimental values of $\varepsilon_\perp$ at $T=T_c$ for the smectic A-isotropic liquid transition of the 50% mixture and the racemic A7 compound, as given in Table 1.

A7	T_c (^{o}C)	a x 10^{-2} (^{o}C^{-1})	a_1	a_2	$\varepsilon_\perp$	χ^{-1}	$\alpha' c' / b'^2$
50% mixture	81.9	5.88	1.224	3.63	5.21	0.238	1.88
Racemic	82.0	0.48	0.152	-0.312	5.07	0.246	-11.97

Table 1. Values of the coefficients a, a_1 and a_2 which were obtained by fitting Eq.(20) to the experimental data for the dielectric constant $\varepsilon_\perp$ of the 50% mixture and the racemic A7 (Bahr et al., 1987) for the smectic A phase ($T<T_c$) close to the SmA-I transition. The experimental values of $\varepsilon_\perp$ (or χ^{-1}) at the transition temperature T_c (Bahr et al., 1987) are given here. Values of the transition temperature T_o calculated from Eq.(16) are indicated for both compounds. The temperature difference ΔT is also given here.

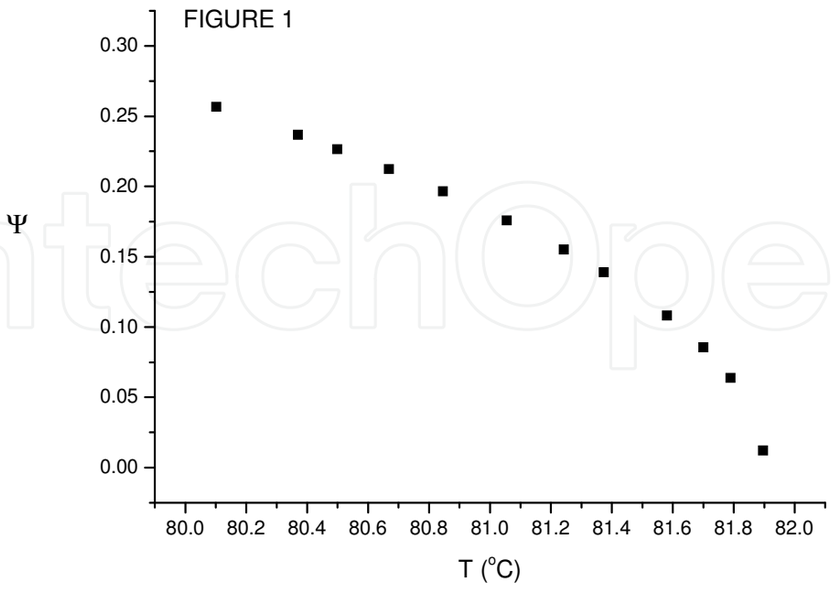


Fig. 1. The orientational order parameter ψ calculated from the mean field theory (Eq.19) as a function of temperature for the smectic A phase of the 50% optically active mixture of A7 (T_c=81.9°C).

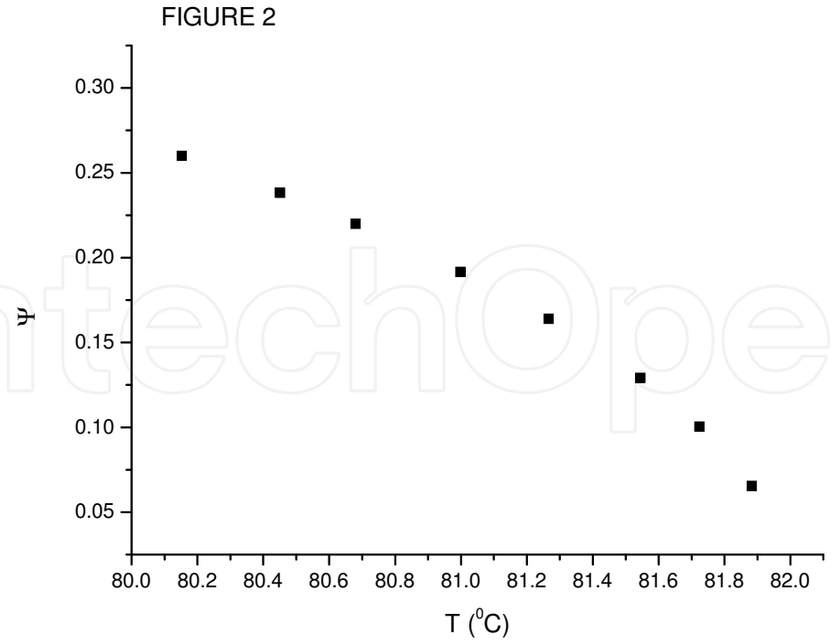


Fig. 2. The orientational order parameter ψ calculated from the mean field theory (Eq.19) as a function of temperature for the smectic A phase of the racemic A7 (T_c=82 °C).

Finally, the coefficients a, a_1 and a_2 given in Eq.(20) were determined from the temperature dependence of the orientational order parameter ψ (Eq.19) as we plotted in Figs. 1 and 2 for the 50% mixture and racemic A7, respectively. For this determination of the coefficients a, a_1 and a_2, we also used the experimental data for the dielectric constant $\varepsilon_\perp$ of the 50% mixture and the racemic A7 (Bahr et al., 1987) in Eq.(20). By fitting Eq.(20) to the experimental data for $\varepsilon_\perp$ (or χ^{-1}), the coefficients a, a_1 and a_2 were obtained for both compounds (50% mixture and racemic A7), as given in Table 1. Figs. 3 and 4 give the dielectric constant $\varepsilon_\perp$ calculated (Eq.18) with the experimental data (Bahr et al., 1987) for the 50% mixture and the racemic A7, respectively, for the smectic A-isotropic liquid transition.

The temperature dependence of the dielectric constant $\varepsilon_\perp$ was also calculated in the isotropic liquid phase for the 50% mixture and the racemic A7 according to Eq.(20) where the orientational order parameter is zero (ψ =0). Eq.(20) then becomes

$$\chi^{-1} = a(T - T_c) + \frac{2D}{e\chi_0\varepsilon_0} \tag{22}$$

for the inverse susceptibility (or the dielectric constant) in the isotropic liquid phase of A7. We first calculated the inverse susceptibility χ^{-1} for the 50% mixture of A7 as a function of temperature by using in Eq.(22) the same value of the coefficient a (=5.88x10^{-2} ^{o}C $^{-1}$) which we determined for the smectic A phase (Table 1). We also used in Eq.(22) our value of $\chi^{-1}\big|_{T=T_o}$ (Eq.21) as given in Table 1. Our calculated values of $\varepsilon_\perp$ are plotted in Fig.3 for the 50% mixture in the isotropic phase at various temperatures.

As we performed for the SmA phase, this time we followed the same procedure by fitting Eq.(22) to the experimental data for the 50% mixture in the isotropic liquid. We then determined the coefficient a for the isotropic liquid phase by keeping the value of $\chi^{-1}\big|_{T=T_o}$ the same as before (Table 1). Table 2 gives the a value determined for the 50% mixture of A7. By means of this a value (Table 2), the dielectric constant $\varepsilon_\perp$ was obtained (Eq.22), as plotted as a function of temperature for the isotropic liquid phase in Fig.3.

A7	T_c (^{o}C)	a x 10^{-2} (^{o}C^{-1})	χ^{-1}	T_c (^{o}C)	$\Delta T = T_0 - T_c$ (^{o}C)	$\alpha' c' / b'^2$
50% mixture	81.9	7.9	0.238	84.4	2.5	1.9
Racemic	82.0	4.2	0.234	87.7	5.7	-11.3

Table 2. Values of the coefficients a and $\chi^{-1}\big|_{T=T_0}$ (Eq.21), which were obtained by fitting (Eq.(22) to the experimental data for the dielectric constant $\varepsilon_\perp$ of the 50% mixture and the racemic A7 for the isotropic liquid phase (T>T$_c$) close to the SmA-I transition. The temperature difference ΔT and the ratio $\alpha' c' / b'^2$ (Eq. 14) obtained for both compounds are given.

For the racemic A7, we were unable to predict the observed $\varepsilon_\perp$ data for the isotropic liquid phase from Eq.(22) by using the same values of the coefficient a and $\chi^{-1}\big|_{T=T_o}$, which we determined for the SmA phase (Table 1). Instead, we fitted Eq.(22) to the experimental data (Bahr et al., 1987) for the isotropic liquid phase and determined the values of the coefficient a

and $\chi^{-1}\big|_{T=T_o}$, as given in Table 2. We plot the $\varepsilon_\perp$ values obtained in Fig. 4 as a function of temperature for the racemic A7 in the isotropic liquid phase.

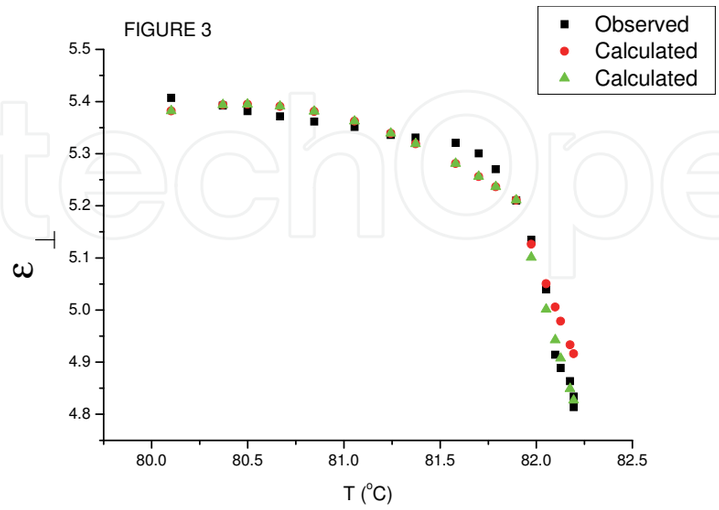


Fig. 3. Values calculated from Eqs. (20) and (22) for the smectic A and the isotropic liquid phases, respectively, for the 50% mixture of A7. The ψ values used in Eq.(20) were calculated from the mean field theory (Eq. 19). Calculated values (■) were obtained from fitting the Eq.(20) (SmA) and Eq.(22) (I) to the experimental data (Bahr et al., 1987) for the $\varepsilon_\perp$. Calculated values (▲) in the isotropic liquid phase were obtained by using the coefficients of the smectic A phase (Table 1) in Eq.(22). The observed data (Bahr et al., 1987) is also plotted here (T_c=81.9 °C).

The transition temperature T_o can also be calculated from the experimental transition temperature T_c for the 50% mixture and the racemic A7. The T_o values were calculated by using the values of the coefficients a and $\chi^{-1}\big|_{T=T_C}$ (Table 2), b' (or a_1) and c (or a_2) (Table 1) for the 50% mixture and the racemic A7, which we give in Table 2 for both compounds. The temperature range $\Delta T(=T_0-T_c)$ was determined for the 50% and the racemic A7, as tabulated in Table 2. We also obtained the ratio $\alpha' c'/b'^2$ for both compounds, as given in Tables 1 and 2. We computed this ratio for the smectic A phase (Table 1) and for the isotropic liquid (Table 2) by using the coefficients for both the 50% mixture and the racemic A7. Finally, the slope ratio from the plots of the dielectric constant $\varepsilon_\perp$ vs. temperature for the smectic A and isotropic liquid phases (SmA/I) was calculated for both the 50% mixture and the racemic A7. The slope ratio of SmA/I was computed close to the transition temperature for the 50% mixture (Fig.3) and for the racemic A7 (Fig. 4) in the temperature ranges, as given in Table 3.

A7	T_c (°C)	Slope ratio(SmA/I)	Temperature range (SmA)	Temperature range(I)
50% mixture	81.9	0.4 (≈ 1/2)	81.7 < T < 81.974	82.051 < T < 82.195
Racemic	82.0	13.8 (≈ 14)	80.451 < T < 81.724	82.27<T<82.622

Table 3. The slope ratio (SmA/I) for the calculated $\varepsilon_\perp$ vs. T plots of the 50% mixture (Fig.3) and of the racemic A7 (Fig.4) within the temperature interval indicated.

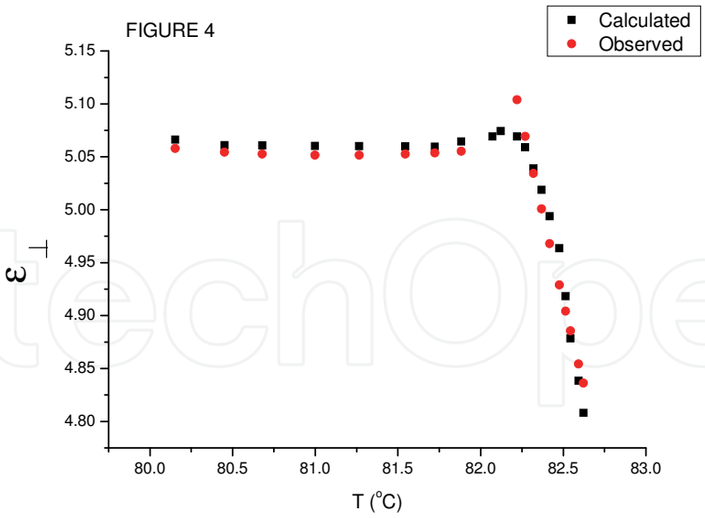


Fig. 4. Values calculated from Eqs. (20) and (22) for the smectic A and the isotropic liquid phases, respectively, for the racemic A7. The ψ values used in Eq.(20) were calculated from the mean field theory (Eq. 19). Calculated values were obtained from the fitting Eq.(20) (SmA) and Eq.(22) (I) to the experimental data (Bahr et al., 1987) for the $\varepsilon_{\perp}$. The observed data (Bahr et al., 1987) is also plotted here (T_c=82°C).

4. Discussion

The temperature dependence of the dielectric constant $\varepsilon_{\perp}$ was calculated here using our mean field model with the biquadratic coupling $P^2\psi^2$, as given by Eq.(1). For this calculation of $\varepsilon_{\perp}$ or the inverse dielectric susceptibility χ^{-1} (Eq.20), the orientational order parameter ψ was first calculated as a function of temperature from the mean field theory (Eq.19), as plotted in Figs.1 and 2 for the 50% optically active compound and the racemic 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl, respectively. The temperature dependence of the spontaneous polarization P can also be calculated from Eq.(6) which gives similar critical behaviour as the orientational order parameter ψ. It decreases smoothly with increasing temperature in the SmA phase as the smectic A- isotropic liquid (SmA-I) transition temperature (Table 1) is approached for the 50% mixture and the racemic A7.
By using the temperature dependence of the order parameter for the 50% optically active (Fig.1) and the racemic A7 (Fig.2), the dielectric constant $\varepsilon_{\perp}$ was calculated in these compounds, as plotted in Figs. 3 and 4, respectively. This calculation was carried out for the smectic A phase ($\psi \neq 0$) and for the isotropic liquid ($\psi = 0$) according to Eqs. (20) and (22), respectively, as stated above. Eqs. (20) and (22) were both fitted to the experimental data for the smectic A and the isotropic liquid phases with the coefficients given in Tables 1 and 2. We also calculated the dielectric constant $\varepsilon_{\perp}$ of the 50% mixture in the isotropic liquid by using the same values of a and the $\chi^{-1}\big|_{T=T_C}$ extracted for the smectic A phase (Table 1). Those calculated $\varepsilon_{\perp}$ values are also in good agreement with the experimental data in the isotropic phase of the 50% mixture, as plotted in Fig.3. As seen from Fig.3, variation of the dielectric constant $\varepsilon_{\perp}$ is continuous with the temperature so that the $\varepsilon_{\perp}$ decreases continuously as the

temperature increases from the smectic A to the isotropic liquid phase for the 50% optically active A7. This continuous change in the dielectric constant $\varepsilon_\perp$ indicates a second order transition between the smectic A and the isotropic liquid of the 50% mixture. In regard to the variation of the $\varepsilon_\perp$ with the temperature for the racemic A7 (Fig.4),the smectic A-isotropic liquid transition in this compound is more likely closer to the first order transition. In the smectic A phase, the dielectric constant $\varepsilon_\perp$ varies slightly within the temperature interval of nearly 2K (from about 80.5 to 82K) and then there occurs a kink just above 82K (at around 82.25K) prior to the isotropic liquid (Fig. 4). When Eqs.(20) and (22) were fitted to the experimental data (Bahr et al., 1987) for the smectic A and the isotropic liquid phases, respectively, this kink that occurs in the racemic A7 was not studied in particular, which might be the pretransitional effect. As shown in Fig.4, Eqs. (20) and (22) are adequate to describe the observed behaviour of the smectic A and the isotropic liquid phases of the racemic A7, respectively. Above T_c in the isotropic liquid phase of the racemic A7, the dielectric constant $\varepsilon_\perp$ exhibits closely a discontinuous behaviour. It drops more rapidly in a small temperature interval, as shown in Fig. 4. In fact, this first order behaviour is supported by a very large value of ≈-11 or -12 for the ratio $\alpha' c' / b'^2$ extracted (Eq.14) by using the coefficients (Table 1 and 2) for the racemic A7 in comparison with the value of 1.9 for the 50% mixture. The first order character of the smectic A- isotropic liquid transition can also be seen from the temperature difference ($\Delta T = T_0 - T_c$) which is nearly 6K for the racemic A7 compared to the value of 2.5 K for the 50% mixture (Table 2). Another comparison for the first order (racemic A7) and the second order (50% mixture) character of the smectic A- isotropic liquid transition in both compounds can be made in terms of the slope ratio of the SmA/I, as given in Table 3. Again, a very large value of ≈14 for the racemic A7 also indicates a first order SmA-I transition in this compound in comparison to the value of $\sim 1/2$ for the 50% mixture which can be considered to exhibit a second order SmA-I transition within the temperature intervals studied. This slope ratio can be used as a criterion to describe a first or second order transition exhibited by the ferroelectric liquid crystals, which was used in particular for the smectic A-smectic C* (AC*) phase transition in A7 (Bahr et al., 1987), and also in general for the ferroelectrics and related materials (Lines & Glass, 1979).

The dielectric constant $\varepsilon_\perp$ was calculated using the temperature dependence of the orientational order parameter ψ (Eq.19) from the mean field theory in Eq.(18), as stated above. According to the minimization condition, by taking the derivative of the free energy g (Eq.10) with respect to the ψ ($\partial g / \partial \psi = 0$), a quadratic equation obtained in ψ^2 can be solved, which also gives a similar functional form of the temperature dependence of ψ with the critical exponent of $\beta = 1/2$ from the mean field theory, as given by Eq.(19). This quadratic solution in ψ^2 can also be used to calculate the temperature dependence of the spontaneous polarization P (Eq.6) and of the dielectric constant $\varepsilon_\perp$ (or χ^{-1}) (Eq.18). The calculated $\varepsilon_\perp$ can then be compared with the experimental data (Bahr et al., 1987) for the SmA-I transition of 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl below T_c.

As shown in Figs. (3) and (4), the observed behaviour of the dielectric constant $\varepsilon_\perp$ is described satisfactorily by our mean field model with the $P^2\theta^2$ coupling which considers quadrupolar interactions in the 50% mixture and the racemic A7. Our results for the dielectric constant $\varepsilon_\perp$ (Figs. 3 and 4) indicate that the quadrupolar interaction ($P^2\psi^2$ coupling) is the dominant mechanism for the first order (or a weak first order) transition in the racemic A7 and the second order (or close to a second order) transition in the 50% mixture.

5. Conclusions

The dielectric constant $\varepsilon_{\perp}$ of the ferroelectric 50% optically active and the racemic compounds of 4-(3-methyl-2-chlorobutanoyloxy)- 4′ -heptyloxybiphenyl was calculated as a function of temperature for the smectic A-isotropic liquid (SmA-I) transition. A mean field model with the biquadratic coupling $P^2\psi^2$ between the spontaneous polarization P and the orientational order parameter ψ of the smectic A (SmA) phase was used to calculate $\varepsilon_{\perp}$ through the temperature dependence of the order parameter ψ.

Our mean field model describes adequately the observed behaviour of $\varepsilon_{\perp}$ for this liquid crystal with high spontaneous polarization close to the smectic A –isotropic liquid transition. It is indicated here that the 50% mixture exhibits a second order (or close to a second order) and that the racemic A7 exhibits a first order (or a weak first order) smectic A-isotropic liquid transition.

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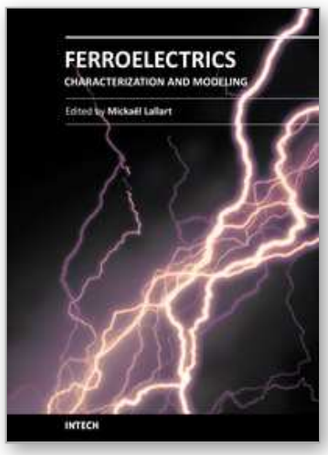
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Ferroelectrics - Characterization and Modeling

Edited by Dr. MickaÃ«l Lallart

ISBN 978-953-307-455-9
Hard cover, 586 pages
Publisher InTech
Published online 23, August, 2011
Published in print edition August, 2011

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the characterization of ferroelectric materials, including structural, electrical and multiphysic aspects, as well as innovative techniques for modeling and predicting the performance of these devices using phenomenological approaches and nonlinear methods. Hence, the aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric system characterization and modeling, allowing a deep understanding of ferroelectricity.

How to reference

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H. Yurtseven and E. Kilit (2011). Temperature Dependence of the Dielectric Constant Calculated Using a Mean Field Model Close to the Smectic A - Isotropic Liquid Transition, Ferroelectrics - Characterization and Modeling, Dr. MickaÃ«l Lallart (Ed.), ISBN: 978-953-307-455-9, InTech, Available from: http://www.intechopen.com/books/ferroelectrics-characterization-and-modeling/temperature-dependence-of-the-dielectric-constant-calculated-using-a-mean-field-model-close-to-the-s

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