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Thermodynamic Model to Study the Phase Transition Properties of SmC_A^* Phase in Antiferroelectric Mesogen W-358 Series

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Employing the thermodynamic model which is centred on Landau-de-Gennes theory, the electro-optical properties of the SmC_A^* phase in antiferroelectric mesogen has been studied. The wave vector q, the polarisation vector P, and the couplings between these order parameters are used to express the system's free-energy density. The Landau coefficients involved in the free-energy density have been computed using experimental data of tilt angle and spontaneous polarisation in the SmC_A^* phase of chiral compounds (6F2OBi and 3F5HBM6(S)). Theoretical and experimental data have been compared in investigations

Keywords: Antiferroelectric Liquid Crystal; Thermodynamic Model; Landau-de-Gennes Theory

1 Introduction

In the meantime, after the detection of antiferroelectricity by Chandani *et al.*[1] a lot of theoretical and experimental studies (dielectric, electro-optic properties) have been done to realize its origin and nature[3-10]. The anticlinic SmC_A^* phase and various subphases can be found in antiferroelectric liquid crystals[2]. In the antiferroelectric (Sm C_A^*) phase, the molecules in the adjoining layers tilt in the opposite directions, and thereby the direction of the spontaneous polarizations reverses from one layer to the succeeding in the opposite directions. The first phenomenological theory for antiferroelectric phase transition were suggested by Orihara and Isibashi[11]. They introduced the antiferroelectric and ferroelectric order parameters namely ξ_a and ξ_f in their free-energy density expansion and effectively explained the Sm C*-SmC_A^* and Sm A- SmC_A^* phase transition. Later on, different theoretical models were developed to explain the different sub phases in antiferroelectric liquid crystal[12-18]. In order to characterise the antiferrolelectric smectic phases, most theoretical models require order parameters such as tilt ξa, ξ_f and polarisation P_a and P_f. In any of the models, the orientational order parameter Q_{ij} and the smectic order parameter ψ have not been incorporated. Mukherjee and Gielesselmann[19] were the first to include these order parameters in their free-energy density expansion for the explanation of phase transition properties of IL - SmC_A^* phase. Later on Singh *et al.*[20] have framed thermodynamic model involving Q_{ij}, ψ, P, q and the coupling between these order parameters for the description of Sm A*- SmC_A^* phase in antiferroelectric liquid crystal. In this article we have analyzed the electro-optical properties of antiferroelectric mesogen 6F2OBi and 3F5HBM6(S) mixed in various proportions such as 1:3, 1:1 and 3:1 named as W-358-n series (n = 1,2,3)[21], a promising material in LCD devices, by utilizing the thermodynamic model established by us[20].

2 Thermodynamic model and the working equations

For a thorough explanation of the SmC_A^* phase and Sm A*- SmC_A^* transition[20], the order parameters Q_{ij}, ψ, P, the wave vector of the helix, and their coupling terms are essential. Since ξ is presided over by Q_{ij}, no term involving should be included in the free-energy density expansion.

The scalar order parameter ψ defines the stacking in the SmC_A^* phase.

$$\psi(r) = \psi_0 \exp(-i\Phi) \quad ...(1)$$

where ψ_0 is the amplitude of the one-dimensional density wave given by phase Φ. $d = 2\pi/q_0$

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represents the layer spacing. q_0 has a value that is not zero: $q_0 = |\nabla\Phi|$

In the SmC_A^* phase, the tilt direction changes from layer to layer by a phase angle ϕ. In view of this, the orientational order parameter $Q_{ij}^{(m)}$will be unlike in adjacent layers,

$$Q_{ij}^{(m)} = \frac{1}{2}S\left(3\hat{n}_i^{(m)}\hat{n}_j^{(m)} - \delta_{ij}\right) \quad \ldots(2)$$

In the above equations S signifies the modulus of Q_{ij}. $\hat{n}_i^{(m)}$can be defined as

$$\hat{n}_i^{(1)} = e_x sin\theta cos\phi(z) + e_y sin\theta sin\phi(z) + e_z cos\theta \quad \ldots(3)$$

$$\hat{n}_i^{(2)} = -e_x sin\theta cos\phi(z) - e_y sin\theta sin\phi(z) + e_z cos\theta \quad \ldots(4)$$

where ϕ denotes the average position of molecules in the cone that varies with the coordinate z as ϕ = qz, and θ represents the angle between the director $\widehat{n}$ and the layer normal. The helix's wave vector is q, where q << q_0 is the density modulation's wave vector P_1 and P_2, respectively, are the polarizations in subsequent layers 1 and 2, and P_1 = -P_2.

$$P_1 = P_0(-sin\phi, cos\phi, 0) \quad \ldots(5)$$

$$P_2 = P_0(sin\phi, -cos\phi, 0) \quad \ldots(6)$$

The Landau free-energy density can be inscribed as for an acceptable description of the SmC_A^* phase and Sm A – Sm C_A^* transition[21]

$$F = F_0 + \frac{1}{2}d_1|\nabla_i\psi|^2 + \frac{1}{2}d_2|\Delta\psi|^2 + \frac{1}{4}\chi_1(P_1^2 + P_2^2) + \frac{1}{2\chi_2}\left(P_{1x}P_{2x} + P_{1y}P_{2y}\right) + \frac{1}{16}h(P_1^2 + P_2^2) + \frac{1}{2}\eta Q_{ij}^{(1)}Q_{ij}^{(2)} + \frac{1}{4}\lambda\left(Q_{ij}^{(1)}Q_{ij}^{(2)}\right)^2 + \frac{1}{4}L_1\left(\nabla_i Q_{jk}^{(1)}\nabla_i Q_{jk}^{(1)} + \nabla_i Q_{jk}^{(2)}\nabla_i Q_{jk}^{(2)}\right) + \frac{1}{4}L_2\left(\nabla_i Q_{ik}^{(1)}\nabla_j Q_{jk}^{(1)} + \nabla_i Q_{ik}^{(2)}\nabla_j Q_{jk}^{(2)}\right) + \frac{1}{2}L_3\varepsilon_{ijk}\left(Q_{il}^{(1)}\nabla_k Q_{jl}^{(1)} + Q_{il}^{(2)}\nabla_k Q_{jl}^{(2)}\right) + \frac{1}{4}g'_{ijkl}\left(P_{1l}\nabla_k Q_{ij}^{(1)} + P_{2l}\nabla_k Q_{ij}^{(2)}\right) + \frac{1}{4}g''_{ijkl}\left(P_{2l}\nabla_k Q_{ij}^{(1)} + P_{1l}\nabla_k Q_{ij}^{(2)}\right) + \frac{1}{2}\gamma'\left(Q_{ij}^{(1)}P_{1i}P_{1j} + Q_{ij}^{(2)}P_{2i}P_{2j}\right) + \frac{1}{2}\gamma''\left(Q_{ij}^{(1)}P_{2i}P_{2j} + Q_{ij}^{(2)}P_{1i}P_{1j}\right) + \frac{1}{2}\Omega'_{ijklmn}\left(Q_{ij}^{(1)}Q_{kl}^{(1)}P_{1m}P_{1n} + Q_{ij}^{(2)}Q_{kl}^{(2)}P_{2m}P_{2n}\right) + \frac{1}{2}\Omega''_{ijklmn}\left(Q_{ij}^{(1)}Q_{kl}^{(1)}P_{2m}P_{2n} + Q_{ij}^{(2)}Q_{kl}^{(2)}P_{1m}P_{1n}\right) + f\left(Q_{il}^{(1)}Q_{jl}^{(1)} + Q_{il}^{(2)}Q_{jl}^{(2)}(\nabla_i\psi)(\nabla_j\psi^*)\right) \quad \ldots(7)$$

Where F_0, χ_1 χ_2.η, λ and h represents are the free - energy density of Sm A phase, the dielectric susceptibilities and positive constants. L_1 and L_2 are used to represent elastic constants. The antisymmetric third rank tensor is ε_{ijk}. The coefficient L_3 in the SmC_A^* phase corresponds to the coefficient of the Lifshitz-invariant term which causes helical modulation.

The coefficients f associated to the gradient terms constituting Q_{ij}, which determine the relative direction of the layering with respect to the director, determine the tilt angle of the SmC_A^* phase.

g'_{ijkl} is defined as $g'_{ijkl} = g'\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right)$. The coefficient g' and g" are similar to the flexoelectric coefficient.

Substituting Q_{ij}, ψ and P in equation (7) and introducing new variables

$$\frac{1}{\chi_0} = \frac{1}{\chi_1} - \frac{1}{\chi_2}, \gamma = \gamma' + \gamma'', \Omega' = \Omega'_1 + 6\Omega'_2, \Omega'' = \Omega''_1 + 6\Omega''_2, \Omega = \Omega' + \Omega'', L' = L_1 + \frac{1}{2}L_2, g = g' + g''$$

Assuming that the tilt angle is small, sin θ≈θ_0 and cos θ≈ 1, equation (7) reads,

$$F = F_0 + \frac{1}{2\chi_0}P_0^2 + \frac{1}{4}hP_0^4 + \frac{9}{4}L'S^2q^2\theta_0^2 - \frac{9}{8}L_2S^2q^2\theta_0^4 + \frac{9}{4}L_3S^2q\ \theta_0^2 - \frac{1}{2}\gamma P_0^2S + \frac{3}{2}gSP_0q\theta_0 + \frac{1}{2}d_1\psi_0^2q_0^2 + \frac{1}{2}d_2\psi_0^2q_0^4 + f\psi_0^2q_0^2S^2 + \frac{1}{4}b_3\psi_0^4q_0^2 + \frac{1}{4}\Omega P_0^2S^2 - \frac{9}{2}\eta S^2\theta_0^2 + \frac{27}{4}\lambda S^4(4\theta_0^4 - \theta_0^2) \quad \ldots(8)$$

In the above equation $1/\chi_0$ = a_0 (T_c -T), T_c represents the transition temperature for SmC_A^* $phase$.

The constraint that F should be minimum with respect to S, ψ_0, q, P_0 and θ_0 determines the equilibrium value of these quantities, and for the phase stability its second derivative with respect to the variables should be positive.

Minimization of the equation (8) with respect to ψ_0 and q_0 give, respectively,

$$\psi_0^2 = -\frac{1}{b_3}[d_1 + d_2q_0^2 + 2fS^2] \quad \ldots(9)$$

and $q_0^2 = -\frac{1}{2d_2}\left(d_1 + 2fS^2 + \frac{1}{2}b_3\psi_0^2\right)$ ...(10)

Elimination of q_0^2 from the equation (9), and then ψ_0^2 from the equation (10) lead to the following equations, respectively,

$$\psi_0^2 = -\frac{2}{3b_3}(d_1 + 2fS^2) \quad \ldots(11)$$

$$q_0^2 = -\frac{1}{3d_2}(d_1 + 2fS^2) \quad \ldots(12)$$

Substituting equations (11) and (12) into equation (8), we obtain

$$F = F_0 + \frac{1}{2\chi_0}P_0^2 + \frac{1}{4}hP_0^4 + \frac{9}{4}L'S^2q^2\theta_0^2 - \frac{9}{8}L_2S^2q^2\theta_0^4 + \frac{9}{4}L_3S^2q\theta_0^2 - \frac{1}{2}\gamma P_0^2S + \frac{3}{2}gSP_0q\theta_0 + \frac{1}{4}\Omega P_0^2S^2 - \frac{9}{2}\eta S^2\theta_0^2 + \frac{27}{4}\lambda S^4(4\theta_0^4 - \theta_0^2) + \frac{2}{27}b_3d_2(d_1^3 + 6d_1^2fS^2 + 12d_1f^2S^4) \quad \ldots(13)$$

Minimization of the equation (13) with respect to θ_0, P_0, q gives the following order parameters relations,

$$\frac{27}{4}\lambda S^4(16\theta_0^3 - 2\theta_0) + \frac{9}{2}L'S^2q^2\theta_0 - \frac{9}{2}L_2S^2q^2\theta_0^3 + \frac{9}{2}L_3S^2q\theta_0 + \frac{3}{2}gSP_0q - 9\eta S^2\theta_0 = 0 \quad \ldots(14)$$

$$\frac{P_0}{\chi_0} + hP_0^3 + \frac{3}{2}gSq\theta_0 - \gamma P_0S + \frac{1}{2}\Omega P_0S^2 = 0 \quad \ldots(15)$$

$$q = -\left(\frac{3}{2}L_3S^2\theta_0 + gSP_0\right) / \left(3L'S^2\theta_0 - \frac{3}{2}L_2S^2\theta_0^3\right) \quad \ldots(16)$$

Introducing following new Landau coefficients λ_1 and λ_2,

$$\lambda_1 = \frac{d_1^2f}{b_3d_2}, \text{ and } \lambda_2 = \frac{d_1f^2}{b_3d_2} \quad \ldots(17)$$

So, 14 Landau coefficients have been reduced to 12 in terms of these new Landau coefficients.

3 Experimental Results and Discussion

From the application point of view the mesogens exhibiting ferroelectric and antiferroelectric phases offer significant improvement in LCDs in comparison with the twisted nematic LCD. In this article the electro-optical properties have been analysed for the chiral compounds 6F2OBi and 3F5HBM6(S) which are mixed in various ratios 1:3, 1:1 and 3:1 indicated as W-358-n series (n=1,2,3)[21]. The molecular structure of 6F2OBi-3F5HBM6(S) system is depicted in Fig. 1 and the phase sequence is shown in the table below.

W-358 mixture exhibits the following phase sequence on cooling

Mixture	Phase Sequence
W-358-1	I (132) Sm A* (120) Sm C* (62) SmC_A^* (29) Cr
W-358-2	I (159) Sm A* (139) Sm C* (68) SmC_A^* (30) Cr
W-358-3	I (160) Sm A* (130) Sm C* (54) SmC_A^* (45) Cr

3.1 Numerical calculation and comparison between theoretical and experimental results

The free - energy density (equation 13) is conveyed in terms of 14 Landau coefficients. 14 Landau coefficients have been reduced to 12 in terms of new Landau coefficients λ_1 and λ_2. Minimization of the equation (13) tends to couple the equation for P_0, θ_0 and q. To study the theoretical value of P_0, θ_0 as a function of temperature for W-358-n series; the values of these 12 coefficients are required. All the twelve coefficients have been calculated by simultaneously solving equation (15), (16) and (17) and utilizing the experimental data of polarization and tilt angle for W-358-n series. In Table 1, the values of these

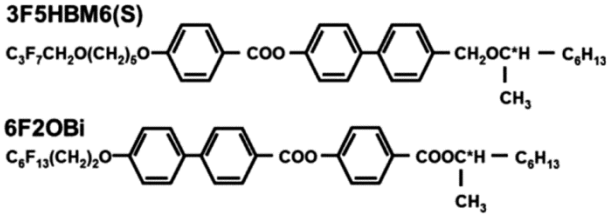

Fig.1 — Molecular structure of 6F2OBi-3F5HBM6(S)[21].

Table 1 — Values of the Landau coefficients of the thermodynamic model for W-358-n series

Coefficients	Units	W-358-1	W-358-2	W-358-3
a_0	10^{11} m/FK	0.25	0.24	0.23
h	10^{19} Jm^5/C^4	2.8	2.7	2.5
L_3	10^{-3} J/m^2	1.5	1.0	0.99
L'	10^{-10} N	2.4	2.4	2.1
L_2	10^{-10} N	4.8	4.6	4.2
g	V	-6.4	-5.2	-3.9
γ	$10^9$$Jm/C^2$	0.5	0.3	0.1
Ω	$10^8$$Jm/C^2$	2.5	2.2	2.1
λ_1	10^4 J/m^3	5.2	5.3	5.0
λ_2	10^3 J/m^3	6.7	3.5	2.2
λ	10^3 J/m^3	1.5	1.05	0.98
η	10^3 J/m^3	0.17	0.12	0.11
T_c	K	335	341	327

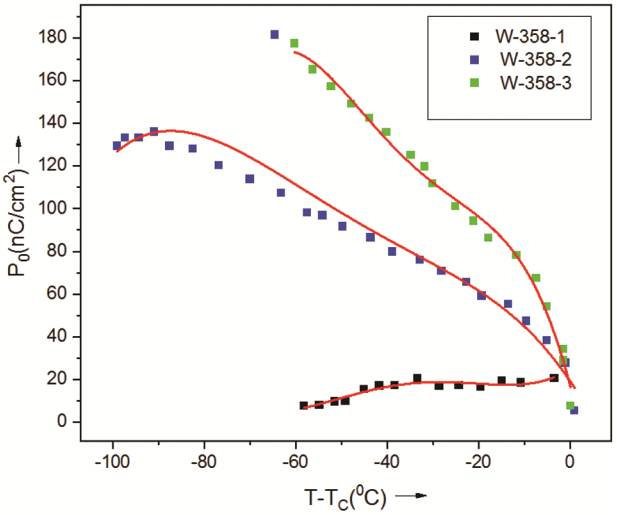

Fig. 2 — Comparison of the theoretical results (solid lines) with the experimental data[21] of W-358-n (n=1,2,3) for the temperature variation of polarization. Other symbols are mentioned in the figure.

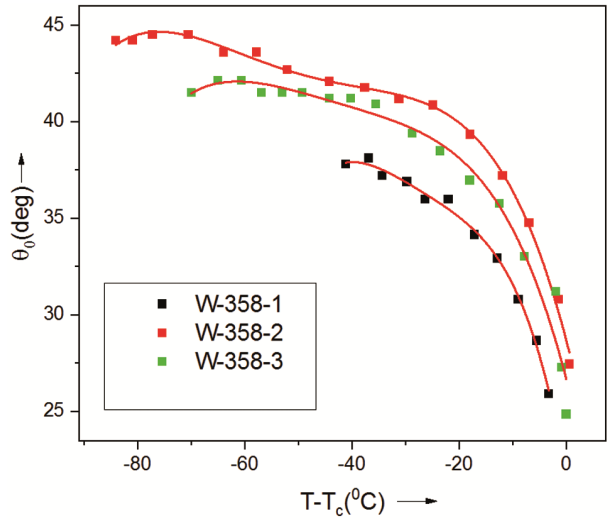

Fig. 3 — Comparison of the theoretical results (solid lines) with the experimental data[21] of W-358-n (n=1,2,3) series for the temperature variation of tilt angle. Other symbols are mentioned in the figure.

coefficients are tabulated. All the calculations have been performed using MATLAB software, utilizing these values of the coefficients which are mentioned in Table 1.

The temperature variation of P_0 and θ_0 has been calculated for W-358-n series by solving the equations (15), (16) and (17). The temperature variation of spontaneous polarization and tilt angle have been shown in Figs. 2 & 3 for W-358-n series. As obvious from the Figs. 2 & 3 as the temperature is increasing, the value of spontaneous polarization and tilt angle goes on decreasing.

4 Conclusion

The thermodynamic model provided by us has been used to investigate electro-optical properties such as tilt angle and spontaneous polarisation of antiferroelectric liquid crystal mixtures. The temperature variations of spontaneous polarisation P_0 and tilt angle θ_0 for the antiferroelectric mesogen W-358-n series were estimated using experimental data. These mesogens' Landau coupling coefficients, which are required for the estimate of P_0, θ_0, were obtained by fitting their experimental data. The terms containing orientational and smectic positional order parameters that emerge in the free energy density expansion are crucial. The theoretical and experimental results are in close accord. In conclusion, we believe that all phenomenological models based on the two degrees of freedom P and ξ order parameters are insufficient and do not account for physical reality. The thermodynamic model proposed here in terms of Q_{ij}, ψ and P order parameters is conceptually exact, takes into consideration the real situation, and is capable of explaining the antiferroelectric mesogen's characteristic properties while illustrating the Sm $\boldsymbol{C_A^*}$ phase.

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References

1 Chandani ADL, Gorecka E & Ouchi Y, *Jpn J Appl Phys*, 28 (1989) L1265.
2 Chandani ADL, Ouchi Y, Takezoe H & Fukuda A, *Jpn J Appl Phys*, 28 (1989) L1261.
3 Musevic I, Blinc R & Zeks B, *World Sci*, 46 (2000) 215.
4 Lagerwall S T, Ferroelectric and Antiferroelectric Liquid Crystals, Willey-VCH, Weinheim, (1999).
5 Dardas D, Kuczynski W, Hoffmann J, Jezewski W, Nowicka K & Malecki J, *Opto-Electron Rev*, 17 (2009) 25.
6 Perkowski P, Ogrodnik K, Piecek W, Zurowska M, Raszewski Z, Dabrowski R & Jaroszewicz L, *Liq Crystals*, 38 (2011) 1159.
7 Marzec M, Fryn P & Tykarska M, *Phase Trans*, 87 (2014) 1011.
8 Pandey M B, Dabrowski R & Dhar R, *Adv Energy Matter*, 10 (2014) 389.
9 Takezoe H, Gorecka C & Cepic M, *Rev Mod Phys*, 82 (2010) 897.
10 Dwivedi A, Dhar R, Dabrowski R & Tykarska M, *J Phys D*, 42 (2009) 095402.
11 11Orihara H, Kawada K, Yamada N & Ishibashi Y, *Mol Cryst Liq Cryst*, 303 (1997) 159.
12 Zeks B & Cepi M, *Liq Cryst*, 14 (1993) 445.
13 Lorman V L, Bulbitch A A & Toledano P, *Phys Rev E*, 49 (1994) 1367.
14 Yamashita M & Miyajima S, *Ferroelectrics*, 148 (1993) 1.

15 Yamashita M, *Mol Cryst Liq Cryst*, 263 (1995) 93.
16 Yamashita M, *Ferroelectrics*, 181 (1996) 201.
17 Roy A & Madhusudana N V, *Euro Phys Lett*, 36 (1996) 221.
18 Dolganov P V, Zhilin V M, Dolganov V K & Kats E I, *Phys Rev E*, 67 (2003), 041716-1.
19 Mukherjee P K & Giesselmann F, *J Chem Phys,* 121 (2004) 12038.
20 Singh A & Singh S, *J Mater Chem*, 21 (2011) 1991.
21 Fitas J, Jaworska G T, Deptuch A, Tykarska M, Kurp K, Zurowska M & Marzec M, *Phase Trans*, 91 (2017) 199.