



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

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Received 17 May 2022; accepted 18 July 2022

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 nature³⁻¹⁰. The anticlinic SmC_A^* phase and various subphases can be found in antiferroelectric liquid crystals². In the antiferroelectric (SmC_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 Isibashi¹¹. They introduced the antiferroelectric and ferroelectric order parameters namely ξ_a and ξ_f in their free-energy density expansion and effectively explained the SmC^* - SmC_A^* and SmA - SmC_A^* phase transition. Later on, different theoretical models were developed to explain the different sub phases in antiferroelectric liquid crystal¹²⁻¹⁸. In order to characterise the antiferroelectric smectic phases, most theoretical models require order parameters such as tilt ξ_a , 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 Giesselemann¹⁹ 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 SmA^* - 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 us²⁰.

2 Thermodynamic model and the working equations

For a thorough explanation of the SmC_A^* phase and SmA^* - SmC_A^* transition²⁰, 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.

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

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,

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

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

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

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

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

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

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

The Landau free-energy density can be inscribed as for an acceptable description of the SmC_A^* phase and $Sm A - Sm C_A^*$ transition²¹

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

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

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

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

Assuming that the tilt angle is small, $\sin \theta \approx \theta_0$ and $\cos \theta \approx 1$, equation (7) reads,

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

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,

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

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

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

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

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

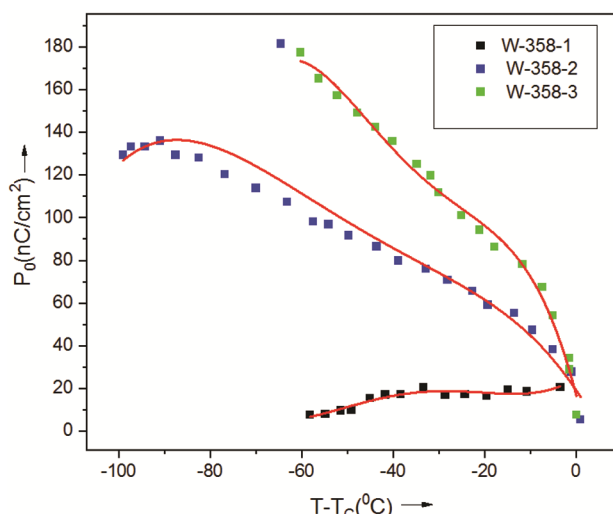


Fig. 2 — Comparison of the theoretical results (solid lines) with the experimental data²¹ of W-358-n (n=1,2,3) for the temperature variation of polarization. Other symbols are mentioned in the figure.

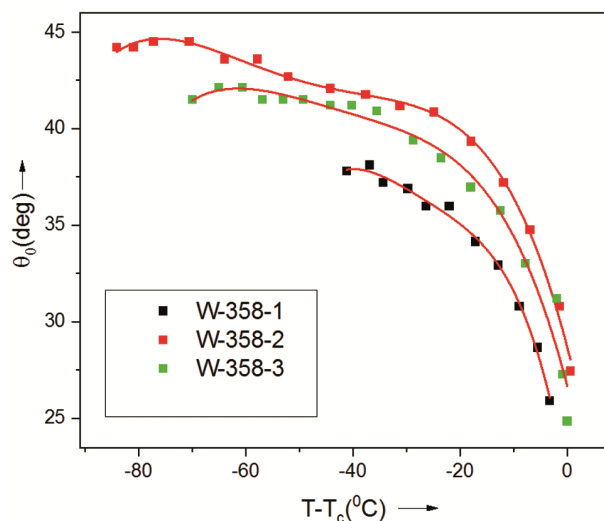


Fig. 3 — Comparison of the theoretical results (solid lines) with the experimental data²¹ of W-358-n (n=1,2,3) series for the temperature variation of tilt angle. Other symbols are mentioned in the figure.

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 $Sm C_A^*$ phase.

Acknowledgement

We would like to acknowledge JSSMVP Mysore for kind support and encouragement.

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