Available online at www.sciencedirect.com
ScienceDirect
Physica B 400 (2007) 292–296
PHYSICA B
www.elsevier.com/locate/physb

Influence of pressure on the isotropic to smectic-E phase transition

Prabir K. Mukherjee[a,*], Sylwester J. Rzoska[b]

[a]Haldia Government College, P.O.-Debhog, Dist.-Purba Medinipur, 721657, India
[b]Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

Received 9 June 2007; received in revised form 27 July 2007; accepted 30 July 2007

Abstract

A phenomenological approach to the description of the pressure effect on the isotropic to smectic-E phase transition is proposed. The influence of pressure on the isotropic to smectic-E transition is discussed by varying the coupling between order parameters and pressure. The pressure dependence of the non-linear dielectric effect in the isotropic phase above the isotropic to smectic-E transition is calculated. The theoretical predictions are found to be in good agreement with experimental results.

Keywords: Liquid crystals; Phase transition in liquid crystals

1. Introduction

In recent years the transitions from the isotropic to smectic phases have attracted much attention. The isotropic to smectic-E (I-SmE) phase transition is one such phase transition which has current interest. The SmE phase is a soft crystal characterized by a two-dimensional hexagonal lattice and strong herringbone packing [1,2]. Because of the herringbone arrangement the free rotation around the molecular director is frozen. The first order behavior of the I-SmE transition was probably the first quantitative test in non-linear dielectric effect (NDE) studies on 4-*n*-4′-isothiocyanatobiphenyl (nBT from $n = 2$–10) by Rzoska and coworkers [3,4]. The clear evidence for the pretransitional anomaly was obtained in the isotropic phase above the I-SmE transition. The simple mean-field type behavior of NDE takes place only in the static case i.e. if the relaxation time of premesomorphic fluctuations $\tau \gg 1/f$, where f is the measuring frequency of NDE—whose reciprocal defines the time scale of measurements. This relaxation time is related to the relaxation time of pretransitional fluctuations—not to the single molecule relaxation time, detected for instance in "linear" dielectric spectroscopy [5]. The observed pretransitional behavior of the NDE in the isotropic phase of the I-SmE transition give the critical exponents $\gamma = 1$ and $\alpha = 0.5$. It was further found that pressure initially reduces the discontinuity of the I-SmE transition similar to the isotropic to smectic-A (I-SmA) transition, but contrary to the isotropic to nematic (I-N) transition. The I-SmE transition temperature increases with rising pressure.

On the theoretical side there is only one attempt [6] to study the I-SmE phase transition. In this recent work one of the present author developed a Landau model to describe the I-SmE transition. In this work all the key features of the I-SmE transition was discussed. The present paper now focuses on the pressure effect on the I-SmE transition. We further analyze the effect of the pressure on the NDE in the isotropic phase above the I-SmE transition.

2. Theory

The starting point of our approach is to write down the Landau free energy near the I-SmE transition. The existence of the pretransitional anomaly [3,4] for the permittivity in the isotropic phase above the I-SmE transition proves the existence of the nematic order parameter S in the SmE phase. Thus a direct transition from the isotropic to SmE phase requires that nematic, SmA, bond-orientation and herring-bone orders are established at the transition. All these order parameters

---

*Corresponding author. Tel.: +91 3224 252278; fax: +91 33 28480781.
E-mail address: pkmukherje@yahoo.co.in (P.K. Mukherjee).

0921-4526/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2007.07.025

jump simultaneously at the I-SmE transition. The orientational order parameter originally proposed by Ref. [7] is a symmetric, traceless tensor described $Q_{ij} = (S/2)(3n_in_j - \delta_{ij})$. The quantity S defines the strength of the nematic ordering. The layering in the SmE phase is described by the order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-\mathrm{i}\Psi)$ is a complex scalar quantity whose modulus ψ_0 is defined as the amplitude of a one dimensional density wave characterized by the phase Ψ. The local order parameter associated with bond-orientational order (BOO) in the SmE phase is defined by Ref. [8] $\chi_6 = \chi \exp(\mathrm{i}6\theta)$. The bond angle θ is the orientation relative to any fixed laboratory axis of a bond between two nearest neighbor molecules. The herring-bone order parameter is described by Ref. [9] $\Phi = \phi \exp(\mathrm{i}2\omega)$, where ω is the angle between the local herring-bone axis and a reference direction. The Ginzburg–Landau free energy should be invariant under the transformation $\theta \to \theta + m(2\pi/6)$ and $\omega \to \omega + n\pi$, where m and n are integers. Considering the above described order parameters, the total Gibbs free energy near the I-SmE transition can be written as [6]

$$\begin{aligned} g(P,T) = {} & g_0(P,T) + \tfrac{1}{3}aQ_{ij}Q_{ij} - \tfrac{4}{9}bQ_{ij}Q_{jk}Q_{ki} + \tfrac{1}{9}c(Q_{ij}Q_{ij})^2 \\ & + \tfrac{1}{2}\alpha_1|\psi|^2 + \tfrac{1}{4}\beta|\psi|^4 + \tfrac{1}{2}p_1|\chi_6|^2 + \tfrac{1}{4}q_1|\chi_6|^4 + \tfrac{1}{2}p_2|\Phi|^2 \\ & + \tfrac{1}{4}q_2|\Phi|^4 + \tfrac{1}{3}\delta Q_{ij}Q_{ij}|\psi|^2 + \tfrac{1}{3}\gamma_1|\chi_6|^2Q_{ij}Q_{ij} \\ & + \tfrac{1}{3}\gamma_2|\Phi|^2Q_{ij}Q_{ij} + \tfrac{1}{2}\eta_1|\psi|^2|\chi_6|^2 + \tfrac{1}{2}\eta_2|\psi|^2|\Phi|^2 \\ & + \tfrac{1}{2}w|\chi_6|^2|\Phi|^2 + \tfrac{1}{2}d_1|\nabla_i\psi|^2 + \tfrac{1}{2}d_2|\Delta_i\psi|^2 \\ & + \tfrac{1}{2}eQ_{ij}(\nabla_i\psi)(\nabla_j\psi^*), \end{aligned} \tag{2.1}$$

where g_0 is the free energy of the isotropic phase. The coefficients $a, b, c, \alpha_1, \beta, p_1, q_1, p_2, q_2, d_1, d_2, e, \gamma_1, \gamma_2, \eta_1, \eta_2$, and w are material parameters. All parameters are assumed to be a function of pressure. The coupling constant δ is negative for the smectic phases. The negative values of η_1 and η_2 favors the SmE phase over the other phases. The gradient terms associated with the coefficients d_1 and d_2 guarantee a finite wave vector q_0 for the smectic density wave. The gradient term $\sim e$ involving Q_{ij} governs the relative direction of the layering with respect to the director. A negative value of e favor the stability of the smectic phases. There is no direct linear coupling terms $\sim|\psi|^2Q_{ij}$, $\sim|\chi_6|^2Q_{ij}$ and $\sim|\Phi|^2Q_{ij}$ in the free energy (2.1), since such a term would preclude the existence of the isotropic phase [10]. The material parameters a, α_1, p_1 and p_2 can be assumed as $a = a_0[T - T_1^*(P)]$, $\alpha_1 = \alpha_{10}[T - T_2^*(P)]$, $p_1 = p_{10}[T - T_3^*(P)]$ and $p_2 = p_{20}[T - T_4^*(P)]$. T_1^*, T_2^*, T_3^* and T_4^* are the super cooling temperatures. a_0, α_{10}, p_{01} and p_{20} are constants. The above free energy describes the first order I-SmE phase transition.

In accordance with the experimental phase diagram (shown in Fig. 1), $T_1^*(P)$, $T_2^*(P)$, $T_3^*(P)$ and $T_4^*(P)$ can be expanded as

$$T_1^*(P) = T_1^0 + u_1P + v_1P^2, \tag{2.2}$$

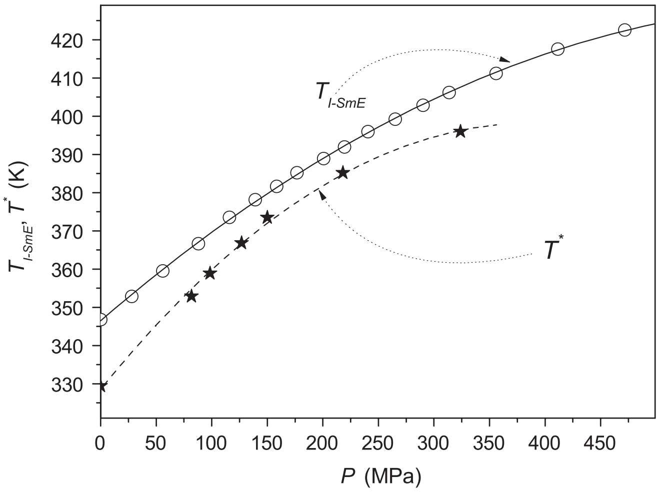

Fig. 1. The pressure dependence of the I-SmE transition temperature (open circles) and the temperature of the hypothetical continuous phase transition (stars) of 5BT. The solid line is the best fit of Eq. (2.10).

$$T_2^*(P) = T_2^0 + u_2P + v_2P^2, \tag{2.3}$$

$$T_3^*(P) = T_3^0 + u_3P + v_3P^2, \tag{2.4}$$

$$T_4^*(P) = T_4^0 + u_4P + v_4P^2, \tag{2.5}$$

where u_1, u_2, u_3, u_4, v_1, v_2, v_3 and v_4 are constants.

For the determination of the thermodynamic quantities near the I-SmE transition we consider a spatially uniform system in which the order parameter values are spatially invariant. Then the substitution of Q_{ij}, ψ, χ_6 and Φ into Eq. (2.1) gives

$$\begin{aligned} g(P,T) = {} & g_0(P,T) + \tfrac{1}{2}aS^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4 + \tfrac{1}{2}\alpha\psi_0^2 + \tfrac{1}{4}\beta\psi_0^4 \\ & + \tfrac{1}{2}p_1\chi^2 + \tfrac{1}{4}q_1\chi^4 + \tfrac{1}{2}p_2\phi^2 + \tfrac{1}{4}q_2\phi^4 + \tfrac{1}{2}\delta S^2\psi_0^2 \\ & + \tfrac{1}{2}\gamma_1S^2\chi^2 + \tfrac{1}{2}\gamma_2S^2\phi^2 + \tfrac{1}{2}\eta_1\psi_0^2\chi^2 + \tfrac{1}{2}\eta_2\psi_0^2\phi^2 \\ & + \tfrac{1}{2}w\chi^2\phi^2. \end{aligned} \tag{2.6}$$

It is clear that $S_E \neq 0$, $\psi_0 \neq 0$, $\chi \neq 0$ and $\phi \neq 0$ are the equilibrium conditions realized in the SmE phase. In order to ensure the condition of the SmE phase to be stable, it is required that

$$\frac{\partial^2 g}{\partial x^2}\frac{\partial^2 g}{\partial y^2} - \left(\frac{\partial^2 g}{\partial x\,\partial y}\right)^2 > 0, \tag{2.7}$$

where $x, y \in \{S, \psi_0, \chi, \phi\}$. Now the elimination of the equilibrium values of ψ_0, χ and ϕ from Eq. (2.6), leads to the Gibbs free energy as a function of S alone can be written as [6]

$$g(P,T) = g_0^* + \tfrac{1}{2}a^*S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}c^*S^4, \tag{2.8}$$