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PRELIMINARY COMMUNICATION

Critical behaviour of the order parameters at the SmC* to SmA phase transition in a ferroelectric liquid crystal mixture

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Critical behaviour of the order parameters has been investigated in the ferroelectric liquid crystal mixture ZLI-3654 in a 7.5 μm thick planar cell. The temperature dependence of the primary (tilt angle) and secondary (spontaneous polarisation) order parameters is considered. The critical exponent (β) has been evaluated from the fitting of the temperature dependence of the experimental data for both tilt angle and spontaneous polarisation. Experimental results are compared with the predictions of the de Gennes and Landau models.

Keywords: order parameter; critical exponent; ferroelectric liquid crystal mixture; tilt angle; spontaneous polarisation

1. Introduction

The liquid crystalline smectic A (SmA) to chiral smectic C (SmC*) phase transition is characterised by a change of orthogonal molecular structure to a layered tilted structure (with polarisation helix). The tilt angle in the SmC* phase (with respect to the smectic layer normal) is considered as the relevant primary order parameter, whereas the spontaneous polarisation is considered as the secondary order parameter. There are two main theoretical approaches describing the SmC–SmA transition. In the first one, de Gennes suggested that the SmA–SmC phase transition can be described by critical exponents by introducing a two-component, helium-like order parameter, $\psi=\theta\exp(i\phi)$, where θ is the molecular tilt angle and ϕ defines its azimuthal position (*1, 2*). The de Gennes model gives a value for the critical exponent (β) of about 0.35, whereas a second approach based on the mean field model gives a value of β of about 0.50 (*3*).

The aim of the present work was to study the critical behaviour of a ferroelectric liquid crystal (FLC) mixture exhibiting SmA and SmC* phases. Experimental results for the temperature variations of both tilt angle and spontaneous polarisation (P_s) are presented for a room temperature FLC mixture. An attempt is made to determine the experimental value of the critical exponents by measuring P_s and tilt angle. The results are compared with data reported by other authors on liquid crystalline mixtures.

2. Experimental

Critical behaviour studies were carried out on a novel room temperature FLC mixture, ZLI-3654 (obtained from E. Merck, Darmstadt), with a phase sequence is given by

$$\text{Crystal} \xrightarrow{-30^\circ\text{C}} \text{SmC}^* \xrightarrow{62^\circ\text{C}} \text{SmA} \xrightarrow{76^\circ\text{C}} \text{N}^* \xrightarrow{86^\circ\text{C}} \text{Isotropic}$$

This material has a wide temperature range in its ferroelectric (SmC*) liquid crystalline phase. The sample cells consisted of conducting indium tin oxide (ITO)-coated glass substrate pre-treated with a polyamide (spin coating ~1000 rpm) at the surfaces. The sample cell was assembled in the planar orientation and then filled with FLC mixture by capillary action in the isotropic phase (~88°C). Mylar was used as a spacer to maintain the sample thickness (7.5 μm). The cell temperature was controlled using a Linkam TP92 and THS600 temperature hot stage with an accuracy of ±0.1°C. The optical texture of the FLC phase was observed using a Getner polarising optical microscope.

The measurements of the temperature dependence of the order parameters were performed using an electro-optical set-up (tilt angle, θ) and the polarisation reversal technique (P_s) (*4–7*). The tilt angle in the SmC* phase at the temperature of interest was determined by placing the FLC sample cell on the rotating stage of the Getner polarising optical microscope. A low-frequency (50–100 mHz) bipolar square wave of 10 $V_{p\text{-}p}$ was applied to the sample cell filled with the FLC material to switch it on and off (between crossed polarisers) in its SmC* phase using a function generator (HIL-2821). The observed angular separation between the two positions of its

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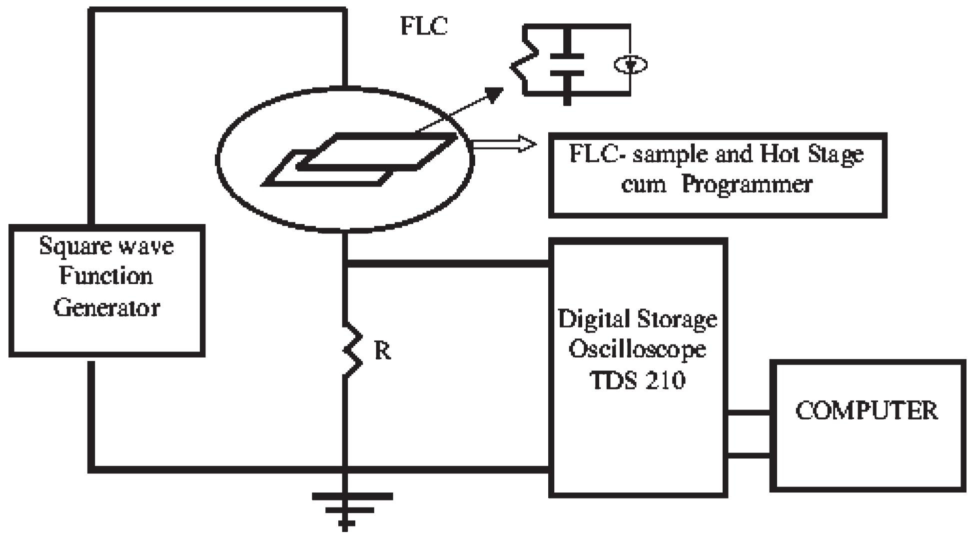

Figure 1. Experimental set-up for measuring spontaneous polarisation using the field reversal technique.

optical extinction (Φ_1, Φ_2) accounts for half of tilt angle as follows:

$$\theta = \frac{\Phi_2 - \Phi_1}{2}. \tag{1}$$

The experimental set-up for the measurement of spontaneous polarisation is shown in Figure 1.

The current–time transient across the resistance in series with the sample cell was observed using a digital storage oscilloscope (Tektronix TDS 210). The FLC sample cell is regarded as a parallel combination of the resistance, capacitor and an molecular reorienting device. On application of a field across the sample cell, the induced current is the sum of the ion flow (I_i), charge accumulation of the capacitor (I_c) and charge induced due to the polarisation realignment current (I_p) as follows (*8*):

$$I(t) = I_i + I_C + I_p = \frac{V}{R} + C\frac{dV}{dt} + A\frac{dP}{dt}, \tag{2}$$

where $R=R_{st}+R_{dc}$ (R_{st} is standard resistance (1 MΩ); R_{dc} is the effective dc resistance of the sample) and A is the area of the substrate surface.

3. Results and discussion

Tilt angle

The observed temperature variation of the tilt angle in the SmC* phase is shown in Figure 2. It can be

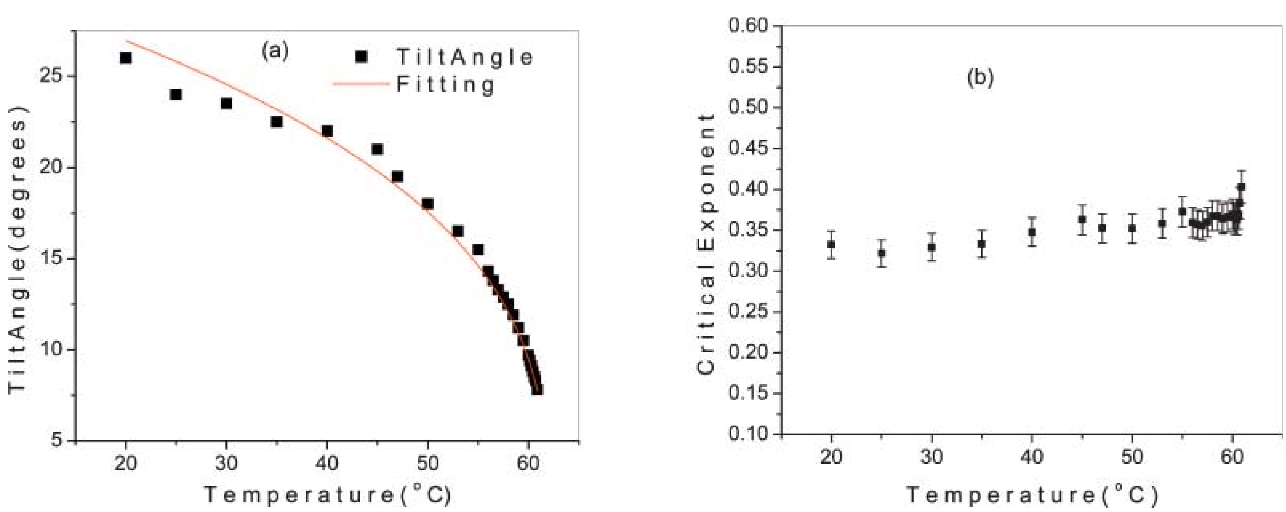

Figure 2. Temperature dependence of (a) the tilt angle (θ) and its (b) critical exponent (β).

Table 1. Dependence of the critical exponent (β) on the fitting temperature range.

Entry	Method	T_C–T/K	β	Liquid crystal compound	Ref.
1	Conoscopy	~29	0.335	terephthalbis(4-*n*-butylaniline)	(*22*)
2	X-ray	~1	0.48–0.49	4-*n*-pentylphenylthiol 4′-*n*-octyloxybenzoate	(*23*)
3	NMR	~25	0.40 ± 0.04	terephthalbis(4-*n*-butylaniline)	(*18*)
4	Dielectric	~8	0.32–0.36	ferroelectric ester compound	(*24*)

seen that the increase in tilt angle with decreasing temperature reflects the growth of fluctuations in the primary order parameter relevant to SmC* phase. The tilt increases and is found to saturate at ~23° towards ambient temperature. Although the value of the saturated maximum tilt angle is found to be in the range of reported values for other ferroelectric materials (*9, 10*), it increases relatively steeply in the first ~14°C of the SmC* phase. It should be noted that the observed temperature dependence of the relevant order parameter (θ) follows (*11, 12*) the relation:

$$\theta(T) = k(T_{C*A} - T)^{\beta}, \tag{3}$$

where k is a constant and T_{C*A} is the SmC*–SmA transition temperature. The value of the critical exponent (β) obtained from fitting of the experimental results (Figure 2(a)) was found to be 0.342 ± 0.03, which is closer to the theoretical value of 0.35 obtained by de Gennes. The temperature dependence of β (Figure 2(b)) shows a tendency to increase to a value of 0.403. The high-temperature data are rather noisy due to the increase of experimental error and may involve additional tilt due to the electric field. The values of the β from the tilt angle temperature dependence are in agreement with de Gennes model. The reported exponents vary from complying with the mean field model (*13–15*) to the de Gennes model (*1, 16, 17*) or have intermediate values (*18–21*). The reported data are summarised in Table 1.

Spontaneous polarisation

The temperature variation of P_s was computed in the SmC* phase from the area under the current–time profile (*4, 5*). The temperature variation of P_s, which reflects the secondary order parameter of the SmC* phase, is shown in Figure 3(a). It should also be noted that the temperature dependence of the secondary order parameter, P_s, in the SmC* phase follows the relation:

$$P_s(T) = k(T_{C*A} - T)^{\beta}. \tag{4}$$

The value of β deduced from the above fitting is also dependent on the fitting range, but not so strongly as in case of optical tilt angle. The temperature dependence of the critical exponent lies within the range 0.521 ± 0.02, which is closer to the theoretical value 0.5 obtained from mean field theory. The temperature dependent behaviour of the critical exponent is reported as being different for various liquid crystalline materials and its published value

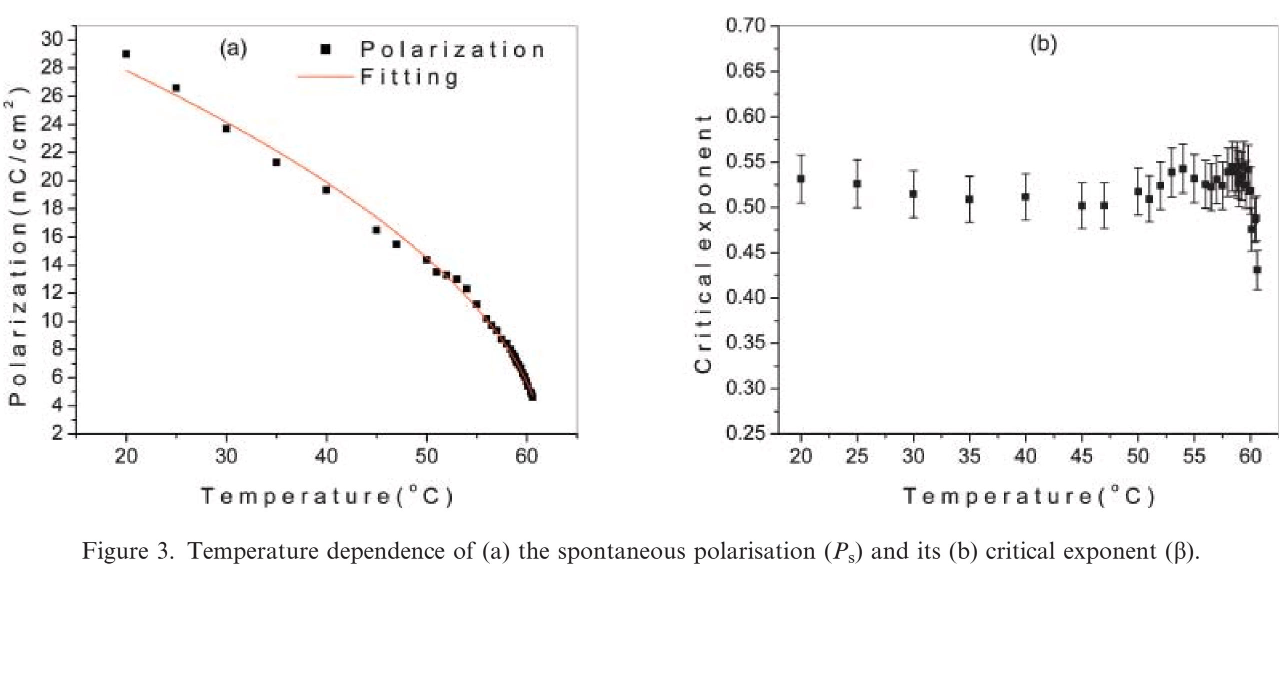

Figure 3. Temperature dependence of (a) the spontaneous polarisation (P_s) and its (b) critical exponent (β).

varies from 0.3 (*22*) to 0.55 (*15*). The inconsistency of the results might be due to different temperature ranges of measurements and/or fitting (*25, 26*).

4. Conclusions

The critical exponent obtained from the primary order parameter measurements (tilt angle) is closer to the de Gennes model, whereas the critical exponent obtained from secondary order parameter measurements gives a value closer to the Landau approach. It is believed that value obtained from the primary order parameter is more realistic and that the SmA–SmC* transition can be better explained by the de Gennes model as compared with the Landau model.

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