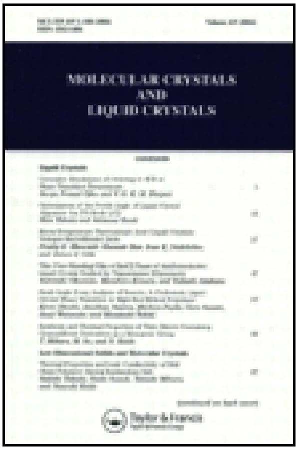

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Investigations of the Non-Linear Dielectric Response in the Smectic C*, Smectic I* and Smectic F* Phases of a Chiral Liquid Crystal

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Investigations of the Non-Linear Dielectric Response in the Smectic C*, Smectic I* and Smectic F* Phases of a Chiral Liquid Crystal

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We report the variation of the linear and non-linear dielectric constants across the smectic A-smectic C*, smectic C*-smectic I* and smectic I*-smectic F* transitions of a chiral liquid crystal. Clear changes are seen for both the parameters across all the three transitions. Interestingly, at the transition between the two tilted hexatic phases, viz., smectic I* and smectic F* phases, the non-linear dielectric constant shows a steeper variation than the linear one indicating that it is more sensitive to the change of sign of the bond orientational order occurring across this transition.

Keywords: Nonlinear dielectric response; tilted hexatic phases; chiral liquid crystal

INTRODUCTION

Measurements of the dielectric constant in the vicinity of various liquid crystalline transitions have been carried out very extensively [1–9]. But most of these studies have been done only in the linear regime where the sample response is linear with the applied electric field. Further, the only ferroelectric mesophase in which the non-linear response has been studied is the chiral smectic C (Sm-C*) phase [7–10]. Thus, it is interesting to determine the non-linear response in other ferroelectric phases like the Smectic I (Sm-I*) and Smectic F (Sm-F*) phases. To obtain information on the structures of the Sm-I* and Sm-F* phases, several synchrotron X- ray studies have been performed using freely suspended films [11,12]. These studies have shown that both the mesophases are tilted hexatic

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* Corresponding Author.

phases in which the molecules that are tilted with respect to the smectic layer normal exhibit long range bond orientational (BO) order but possess only short range positional order. In the Sm-I* phase the molecular tilt direction is towards a nearest neighbour while in the Sm-F* phase it is between two nearest neighbours. The diminution of the BO order alone can cause either of these phases to transform into the Sm-C* phase. In contrast to the wealth of information available on the structural details, dielectric studies near the Sm-I* to Sm-F* phase transition had not been reported till recently [13]. Further, to our knowledge, no measurements of the non-linear dielectric constants in the two hexatic phases have been reported. In this paper we present the temperature dependence of the first, third and fifth harmonics of the dielectric response near the Sm-C* – Sm-I* and Sm-I* – Sm-F* transitions and compare it with the data near the smectic A (Sm-A) – Sm C* transition. Here the third and fifth harmonics represent the non-linear part of the response.

EXPERIMENTAL

The compound used for the study is 4-(2′-methylbutyl) phenyl 4-(n-octyl) biphenyl-4-carboxylate (from E-Merck), showing the phase sequence Isotropic-Blue phase-Cholesteric – Smectic A – Sm-C* – Sm-I* – Sm-F* – Crystal J* [14,15]. The samples were taken between two ITO coated glass plates treated with a polyimide solution and uni-directionally rubbed. Mylar Spacers were used to define the cell thickness (~ 4 μm). To get a uniform planar orientation of the molecules, the sample was cooled slowly (6K/hour) from the isotropic phase through the cholesteric phase into the Smectic A (Sm-A) phase. The sample alignment was monitored during the measurements using an optical polarizing microscope. The dielectric experiments were carried out using a technique that we have recently developed [9]. To describe it briefly, a small amplitude (0.5Vrms) ac probing electric field was applied to the sample and its charge response was converted to a voltage signal using a very low loss, good high frequency performance capacitor that was calibrated using a standard frequency response analyzer (Solatron 1260). The analog output of the capacitor was digitized and is then analyzed using a fast Fourier transform algorithm to extract the multi-harmonic responses. The waveform generation, Sample &Hold, analog-to-digital conversion and the Fourier transform functions were all handled by a digital lock-in amplifier (EG&G PAAR model 7260). The samples were kept in a hot stage, which was controlled by an INSTEC temperature controller. The entire process of data acquisition and control was handled by a PC.

RESULTS AND DISCUSSION

Previous studies have shown that the dynamics of the system slows down on transforming from the Sm-C* to Sm-I* phase [16,17] and further has a strong softening near the Sm-I* – Sm-F* transition [13,18]. Hence, we performed the measurements at a relatively low frequency of 12 Hz. If the amplitude of the field is E_0 and the angular frequency is ω, then the different components of the displacement can be written as

$$\begin{aligned} D_1 &= \varepsilon_1 E_o + \frac{3}{4}\varepsilon_3 E_o^3 + \dots \\ D_2 &= \frac{1}{2}\varepsilon_2 E_o^2 + \frac{1}{2}\varepsilon_4 E_o^4 + \dots \\ D_3 &= \frac{1}{4}\varepsilon_3 E_o^3 + \frac{5}{16}\varepsilon_5 E_o^5 + \dots \end{aligned} \tag{1}$$

and so forth. Since the applied electric field is weak, the practice [7–9] is to neglect the higher order terms on the right hand side of each of the expressions in equation (1) and retain only the first terms. As we shall see later, this assumption is supported by the raw values obtained for the first and third harmonic signals [19]. Hence $D_1$is considered to be the linear response, D_2 and D_3 to be the second and third harmonic responses. Correspondingly, ε_1 is the linear dielectric constant and ε_2 and ε_3, the non-linear dielectric constants. It should be mentioned here that the present set up measures only the magnitude of the nonlinear response but not its sign. Therefore, we can not extract any information regarding the nature of the transition, which requires the determination of the sign of the response. All the three tilted phases studied here, viz., Sm-C*, Sm-I* and Sm-F* phases possess a helical structure. Therefore, if the sample thickness is larger than the helical pitch, the global symmetry of the all these phases will be the same as that of the Sm-A phase, i.e., $\mathcal{D}_\infty$, and the system has a centre of symmetry. Thus ε_2 and other even harmonics which can be present only in non-centrosymmetric systems will be absent. For the sample used in the present study the helical pitch in the three tilted phases varies from 0.8 μm to 1.7 μm [20] and thus always smaller than the cell thickness of 4 μm. Hence the magnitude of the even harmonics will be negligibly small.

Sm-A – Sm-C* transition

Figure 1 shows the temperature dependence of the first, third and fifth harmonic dielectric constants near the Sm-A – Sm C* transition. The value of the linear dielectric constant (first harmonic) in the Sm-A phase is comparable to that observed by Cava *et al* [21], while in the Sm-C* phase it is slightly higher. This is not sur-

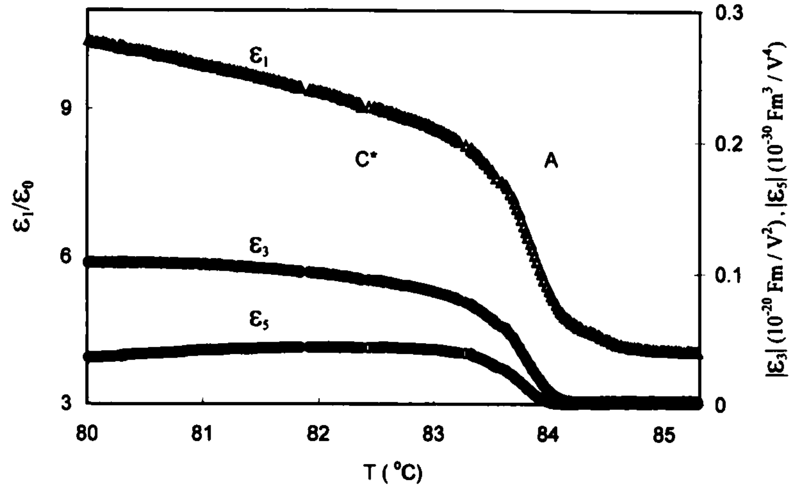

FIGURE 1 Temperature dependence of the linear ε_1 (Δ) and the non-linear dielectric constants, ε_3 (•) and ε_5 (O) near the sm-A – Sm-C* transition

prising as the measuring frequency used by Cava *et al* [21] is quite close to the relaxation frequency of the Goldstone mode. Owing to its paraelectric nature, the Sm-A phase has only a linear dielectric response, except close to the transition to the Sm-C* phase. In the Sm-C* phase, the non-linear electric displacement parameters D_3 and D_5 are about a factor of 20 and 100 lower compared to the linear displacement D_1. In the Sm-A phase D_3 and D_5, are further smaller by another 2 orders of magnitude. These features are in agreement with the observations made on other materials exhibiting a Sm-A – Sm C* transition [7–9]. The values of the non-linear dielectric constants obtained in the Sm-C* phase are similar to the values in other ferroelectric liquid crystalline (FLC) materials, but are much larger than in crystalline ferroelectric polymers, although the spontaneous polarization is much smaller in FLCs [22]. For instance, in FLCs, the polarization is smaller by about 3 orders of magnitude, while ε_3 is larger by 4 to 6 orders of magnitude. To explain this feature the following reasoning has been proposed [8]. The non-linear permittivity reflects the *softness* of the environment of the dipoles. In the case of the non-liquid crystalline ferroelectric substances, the dipoles are in a crystalline environment and therefore their fluctuations are suppressed by the strong interactions between the dipoles. In FLCs, the helical structure with a macroscopic pitch (~ μm) is responsible for large fluctuations of dipole moments. Hence, just the thermal fluctuations of the molecules can cause a significant deformation of the helical structure, resulting in large magnitude of the non-linear dielectric constants.

Sm-C* – Sm-I* transition

The onset of the Sm-C* – Sm-I* transition is indicated (fig. 2) by a sharp drop in the value of the linear and the fifth harmonic data, while the third harmonic shows only a change in the slope. As mentioned in the Introduction, although both the Sm-C* and Sm-I* phases are BO ordered, the magnitude of this order is very small in the Sm-C* phase and increases to a large value in the Sm-I* phase. In addition to this, the positional order, which although is short ranged in both the phases, also increases in the Sm-I* phase [11]. This in turn should lead to increase in the cooperative motion of the dipoles and therefore one should expect the dielectric constants to show an increase across the Sm-C* – Sm-I* transition. Figure 2 shows that on the contrary there is a decrease in the measured values. This can be understood in the following manner. It has been reported that the dynamics of the system slows down when the material transforms from the Sm-C* to the Sm-I* phase [16,17]. A detailed measurement of the response time τ associated with the ferroelectric switching has shown that there is a simple scaling relationship between τ and the magnitude of the BO order [16]. For example, τ reaches a value of ~ 4 ms at ~ 1°C below the Sm-C* – Sm-I* transition. Thus the measuring frequency of ~ 12Hz, used in the current studies, would fall in the dispersion region of the switching process, with a relaxation frequency of (= $1/2\pi\tau$) 40Hz and consequently the dielectric constants can show a decrease through the transition to the Sm-I* phase. Another feature to be mentioned is that in the Sm-I* phase, the ratios of D3 and D5 to D1 also decreases and becomes comparable to those observed in the Sm-A phase, indicating that the increase in the magnitude of the bond orientational order reduces the non-linearity of the response.

Sm-I* – Sm-F* transition

The two relevant parameters that describe the Sm-I* – Sm-F*transition are ϕ, the azimuthal angle of the tilt and θ, the "bond" angle representing the 6-fold BO order [23]. In this terminology, θ-ϕ is 0° (mod 60°) in the I phase and 30° (mod 60°) in the F phase. The tilt-bond coupling gives rise to two dynamic modes: first, a hydrodynamic or acoustic mode corresponding to the in-phase fluctuations of bond plus tilt and the second, a non-hydrodynamic or optic mode corresponding to the out-of-phase fluctuation of bond plus tilt. The optic mode shows a critical slowing down of the frequency with a concomitant increase in the susceptibility on approaching the Sm-I – Sm-F transition from either side [18]. In both these phases the molecules are tilted in the layer and hence they exhibit a spontaneous in-plane ferroelectric polarization, whose direction is coupled to the

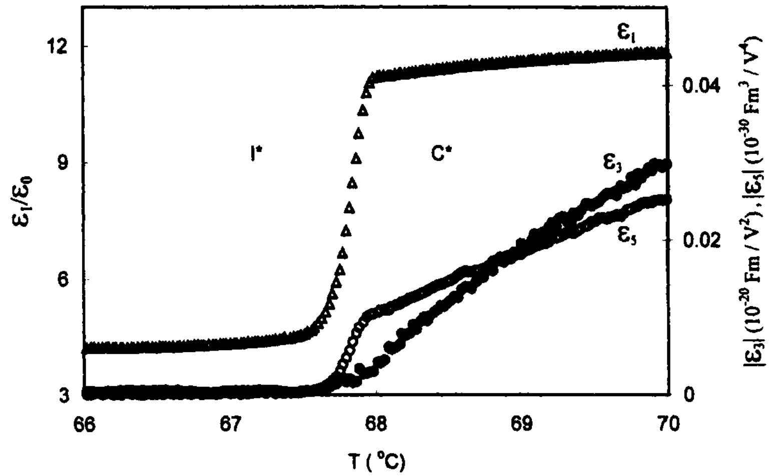

FIGURE 2 Thermal variation of ε_1 (Δ), ε_3 (•) and ε_5 (O) across the Sm-C* – Sm-I* transition. The drop in the values at the transition is due to the slowing down of the dynamics of the system

azimuthal angle of the tilt. This makes it amenable to study by using dielectric spectroscopy especially to probe the dynamics in such systems. Recently, we reported results of the linear dielectric investigations near the Sm-I* – Sm-F* transition [13]. Although the transition appears to be first order, strong pre-transitional effects are observed. On approaching the transition, the softening of the relaxation frequency was accompanied by an enhancement of the associated amplitude.

Let us now look at the temperature variation of the non-linear dielectric constants in comparison with that of the linear one, across the Sm-I* – Sm-F* transition (Figure 3). As expected the linear dielectric constant shows a strong increase on approaching the transition from either of the phases. But more interestingly, the third harmonic shows a similar behaviour, with a much sharper and symmetric variation. Since the two phases differ in the sign of the BO order with the crossover in the sign occurring at the transition, the observed feature clearly shows that the behaviour of the dielectric constant is strongly correlated with that of the BO order. The steeper variation and a factor of 40 increase at the transition indicates that ε_3 is more sensitive to the sign of the BO order than ε_1. Notice, however, that even the maximum value of $\sim 4 \times 10^{-23}$Fm/V^2 for ε_3 is about two orders of magnitude smaller than the value in the Sm-C* phase. Perhaps for this reason it is difficult to observe any change in the $\varepsilon 5$ value at the transition. Dispersion measurements are underway, which are expected to throw more light on the influence of the critical slowing down of the mode on the non-linear dielectric constant.

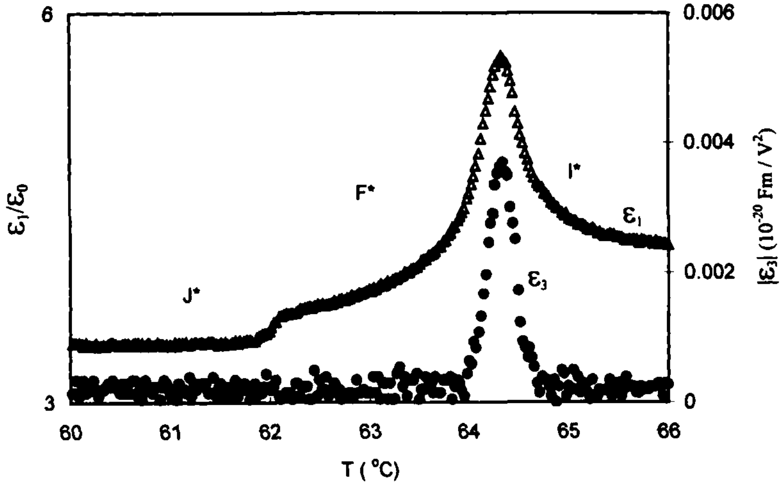

FIGURE 3 Plot of temperature versus ε_1 (Δ) and ε_3 (●) across the Sm-I* – Sm-F* transition. At the transition, ε_3 shows a steeper variation than ε_1 indicating that ε_3 is more sensitive to the sign of the BO order. Notice that even the maximum value of ~ 4×10^{-23} Fm/V^2 for ε_3 is about two orders of magnitude smaller than the value in the Sm-C* phase. The ε_5 data is not shown here as it hardly has any change across the transition

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