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Dielectric studies of Goldstone mode and soft mode in the vicinity of the A-C* transition

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Abstract. — We report the results of dielectric studies on three ferroelectric liquid crystals exhibiting the A-C* transition. Two relaxation modes viz., the soft mode and the Goldstone mode have been observed in the frequency domain covered. Careful measurements have allowed us to observe the soft mode relaxation in the C* phase, even in the absence of a bias field, over a larger temperature range than in any previous study. The results are discussed in the light of the predictions of the generalised mean-field model.

1. Introduction.

The temperature and frequency dependence of the complex dielectric constant of ferroelectric liquid crystals has been studied quite extensively [1-4]. The results of these studies may be briefly summarised as follows. When the sample is cooled the low frequency static dielectric constant increases steeply as the temperature approaches the smectic A-smectic C* (A-C*) transition and reaches a broad maximum a few degrees below the transition point ($T_\text{c}$). The dispersion regime exhibits two important relaxation modes, viz., the Goldstone mode and the soft mode. The former, appearing only in the C* phase, owes its existence to the presence of phase (or azimuthal) fluctuations of the tilt order parameter. The latter is due to the amplitude fluctuations of the tilt angle and exists, in the absence of any bias field, only very close to the transition. Most of these studies have been done on compounds having low spontaneous polarisation ($P_s$). In order to study the effect of the magnitude of $P_s$ on dielectric properties, we have carried out static and dispersion studies on materials which are structurally similar, but exhibit varying magnitudes of $P_s$. The results are discussed in the light of the predictions of the generalised Landau model [4-6]. The effect of bias field on the soft mode relaxation is also studied.

2. Experimental.

The structural formulae and phase transition temperatures of the substances [7] investigated — for convenience referred to as I, II and III — are given below.
The $P_s$ values measured [8] at $T_c$-10 °C are 1 500 µC/m², 720 µC/m² and 370 µC/m² for I, II and III respectively.

The preparation of the sample cell (typical thickness ~ 20 µm) has been described in an earlier paper [8] The ITO treated glass plates were coated with a polymer solution and rubbed unidirectionally to get planar orientation of the molecules The samples were aligned by cooling from the isotropic phase at a slow rate (~ 1 °C/h) and the alignment was checked by optical microscopy The capacitance and the dielectric loss were measured using an Impedance Analyser (HP4192A). During any dispersion measurement the temperature of the cell was maintained to a constancy of ± 5 mK The data acquisition was handled by a microcomputer which was also used for storage and analysis of the data.

3. Results and discussion.

As mentioned earlier, in the C* phase orientational fluctuations of the director give rise to two relaxation modes, the Goldstone and soft modes Thus the complex dielectric constant can be written as

$$
\varepsilon^*(f) = \varepsilon' - j\varepsilon'' = \frac{\Delta\varepsilon_G}{1 + (f/f_G)\frac{1 - h_G}{h_G}} + \frac{\Delta\varepsilon_s}{1 + (f/f_s)\frac{1 - h_s}{h_s}} + \varepsilon_\infty
$$

(1)

where $f_G$ and $f_s$ are the Goldstone and soft mode relaxation frequencies, $\Delta\varepsilon_G$ and $\Delta\varepsilon_s$ their respective strengths, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts and $\varepsilon_\infty$ represents the sum of the dielectric strengths of all other high frequency modes, $h$ is the distribution parameter of the mode.

In the A phase the amplitude and phase fluctuations are degenerate and hence only the second and third terms on the right hand side of equation (1) remain

Before presenting the results of our experiments, it may be relevant to recall some of the predictions of the generalised Landau model [5]

A phase

$$
\Delta\varepsilon_s = \frac{\varepsilon^2 C^2}{\alpha (T - T_c) + (K_3 - \varepsilon \mu^2) q_0^2}
$$

(2)

$$
 f_s = \frac{1}{2 \pi \gamma_1} [\alpha (T - T_c) + (K_3 - \varepsilon \mu^2) q_0^2]
$$

(3)

$$
 f_s \Delta\varepsilon_s = \frac{1}{2 \pi \gamma_1} \varepsilon^2 C^2
$$

(4)
C* phase

neglecting the $\varepsilon \mu^2$ term,

\[
\Delta \varepsilon_G = \frac{1}{2 K_3} \left( \frac{P}{q \theta} \right)^2
\]

\[
f_G = \frac{K_3}{2 \pi \gamma_1} q^2
\]

\[
f_G \Delta \varepsilon_G = \frac{1}{4 \pi \gamma_1} \left( \frac{P}{\theta} \right)^2
\]

where the subscripts $s$ and $G$ denote soft mode and Goldstone mode respectively; $f$ and $\Delta \varepsilon$ are the relaxation frequency and dielectric strengths of the mode, $K_3$ is the elastic constant, $\varepsilon$ represents the high temperature dielectric susceptibility, $\mu$ and $C$ are the coefficients of the flexoelectric and piezoelectric bilinear coupling, $\alpha$ is the coefficient of the temperature dependent term in the Landau expansion, $P$, $\theta$ and $q$ are respectively the polarisation, tilt angle and inverse pitch in the C* phase, and $q_0 = q$ at $T_c$. $\gamma_1$ represents the rotational viscosity of the modes.

The experimental data of $(\varepsilon^*(f), f)$ was fitted to equation (1) using a non-linear least square technique by varying the parameters $\Delta \varepsilon_i$, $\varepsilon_{\alpha i}$, $f_i$ and $h_i$ (here $i$ represents different modes — Goldstone and soft mode) [9] The distribution parameter $h$, was found to be small ($\approx 0.1$). Figure 1a-c shows Cole-Cole diagrams, for the compound II figure 1a in the A phase, figure 1b in the C* phase close to $T_c$ and figure 1c in the C* phase away from $T_c$. Plots in figure 1a and 1c exhibit single relaxation behaviour and are due to soft mode and Goldstone modes respectively. But figure 1b shows the presence of relaxations due to both the modes. Normally it is very difficult to resolve the soft mode from the Goldstone mode because as seen in these figures the strength of the former is smaller compared to the latter. Also, as will be discussed later, the strength of the soft mode rapidly decreases as $|T_c - T|$ is increased. However, owing to the large polarization in compound I we have been able to resolve the two over a temperature range of 0.8°C in the C* phase. For the same reason the soft mode could be studied up to 3°C above the transition. In fact, this point is quite clear when we note that for the three materials these ranges are 0.8, 3.0 for I, 0.5, 1.5 for II and 0.07, 0.5 for III respectively. Temperature variation of the soft mode dielectric strength and relaxation frequency are plotted in figures 2-4. The salient features seen are (i) $f_s$ decreases linearly with reduced temperature $(T - T_c)$, the value of $f_s$ at $T_c$($f_0$) is considerably different for different materials — $(f_0)_{II} > (f_0)_{II} > (f_0)_{III}$. (ii) the inverse dielectric strength $1/\Delta \varepsilon_s$, unlike $f_s$, is non-linear in the A phase, indeed it appears to have a power-law behaviour, but has a linear temperature dependence in the C* phase. Most of the earlier experiments have also shown the linear behaviour of $f_s$, but only a few observations of non-linear variation of $1/\Delta \varepsilon_s$ exist. From equation (2) we see that $1/\Delta \varepsilon_s$ will linearly decrease with temperature only if temperature dependence of the piezoelectric coefficient $C$, elastic constant $K_3$ and the flexoelectric term $\mu^2$ are negligible. Experimentally it is known that the value of the piezoelectric coefficient $C$ remains constant in the A phase in materials possessing low as well as high polarization [10]. Thus, one possible explanation for a non-linear variation of $1/\Delta \varepsilon_s$ could be that the twist to piezo energy ratio may be changing with temperature (We will see later that this is true in the C* phase.) But if the ratio of elastic to viscosity terms is weakly temperature dependent [11], then only the term $(\alpha (T - T_c)/2 \pi \gamma_1)$ will influence the thermal variation of $f_s$. This could be the reason for the linear behaviour of $f_s$. Multiplying equations (2) and (3) to eliminate the elastic term, we get equation (4). Based on the arguments presented above we can expect the product $\Delta \varepsilon_s f_s$ to be non-linear only in the immediate proximity of the transition. This is indeed the experimental behaviour as seen in
Fig 1 — Representative Cole-Cole diagrams for compound II in a) A phase, b) C* phase near $T_c$, c) C* phase away from $T_c$.

Fig 2 — Temperature dependence of soft mode relaxation frequency ($f_s$) and inverse dielectric strength ($\Delta \varepsilon_s^{-1}$) for compound I.
Fig 3 — Thermal variation of $f_s$ and $\Delta \varepsilon_s^{-1}$ for compound II.

Fig 4 — Thermal variation of $f_s$ and $\Delta \varepsilon_s^{-1}$ for compound III.

Fig 5 — Plot of the product $\Delta \varepsilon_s f_s$ vs temperature for compound I.
figures 5-7 It must be pointed out that all these effects are seen over a very small range for compound III, the range itself being much bigger for materials I and II, understandably due to increased piezoelectric coupling. Following Gouda et al [12], we have tried to describe the temperature variation of the product $\Delta \varepsilon f_s$ with a power-law $\Delta \varepsilon f_s \propto (T - T_c)\beta$, $\beta$ values obtained for I, II and III are 0.45, 0.37 and 0.19 respectively.

The figures 8 to 10 show the variation of $\Delta \varepsilon G$ and $f_G$ as a function of temperature. The qualitative behaviour is in very good agreement with the theoretical prediction [6]. In particular, it is seen that the minimum in $f_G$ occurs not at the transition, but slightly below it. Using equation (7) and knowing the parameters $f_G$, $\Delta \varepsilon G$, $P$ and $\theta$ and the relation $\gamma_{\phi} = \gamma_1 \sin^2 \theta$, $\gamma_\phi$ can be calculated. Such a calculation done at $T_c - 3$ ($P$ and $\theta$ values are taken from Ref [8]) for the compound II gives $\gamma_{\phi} = 10$ mPas. This may be compared with the value of 25 mPas for the same compound obtained [8] by employing a field-reversal method. The discrepancy may probably be attributed to the fact that the parameters involved have been obtained by different techniques. According to Legrand and Parneix [13] the relative twist to piezo-energy parameter $Q^2$ can be defined as $Q^2 = (Kq^2/x_\infty C^2)$ (where $K$ is the renormalized twist elastic constant, $x_\infty = \frac{1}{4\pi} (\varepsilon_\infty - 1)$) These authors also give a more practical definition for $Q^2$:

$$Q^2 = \frac{2\pi x_\infty}{\Delta \varepsilon G}$$
Fig 8 — Temperature dependence of Goldstone mode frequency \( f_G \) and dielectric strength \( \Delta\varepsilon_G \) for compound I.

Fig. 9 — Thermal variation of \( f_G \) and \( \Delta\varepsilon_G \) for compound II.

Fig 10 — Thermal variation of \( f_G \) and \( \Delta\varepsilon_G \) for compound III.
Using this relation, we have calculated $Q^2$ for the compound II at two different temperatures, the values are 0.004 at $T = T_c - 6$ °C and 0.009 at $T = T_c - 0.02$ °C. These numbers may be compared with the value $Q^2 = 0.2$ for DOBAMBC [1] ($P_s = 30 \mu$C/m$^2$) and $Q^2 = 0.003$ for a material [13] with $P_s = 500 \mu$C/m$^2$. This appears to suggest that the value of $Q^2$ is inversely proportional to the magnitude of $P_s$ (and hence the piezoelectric coefficient). But more systematic measurements need to be carried out in order to establish this relationship.

As mentioned earlier in the C* phase the dielectric strength of the Goldstone mode drowns that due to the soft mode even slightly away from $T_c$. One well known technique to suppress the Goldstone mode, so that the soft mode effect can be clearly observed, is to apply a DC bias field which is high enough to unwind the helical structure. We have used this method to study the soft mode relaxation in one material, viz., compound II. Figures 11 and 12 are plots of $1/\Delta \varepsilon$ and $f_s$ as a function of temperature obtained using a bias value of 20 kV/cm; for the sake of comparison the zero bias values are also plotted. While the zero bias data show sharp minima at the transition, the minimum is broad in the presence of a bias voltage. As expected the values obtained at the transition are also different in the two cases $(\Delta \varepsilon)_E = 43.5$; $(\Delta \varepsilon)_E = 58$, $(f_s)_E = 3.8$ kHz, $(f_s)_E = 53.7$ kHz, here $E$ denotes the value of the bias field applied.

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**Fig 11** — Plot of $\Delta \varepsilon_s^{-1}$ versus temperature with no bias (O) and 20 kV/cm bias field (X) for compound II

**Fig 12** — Plot of $f_s$ versus temperature with no bias (O) and 20 kV/cm bias field (X) for compound II
Static dielectric constant measurements were also made on these materials. We present the results for a representative case, viz., compound II. Figures 13 and 14 show static measurements at different frequencies and applied bias respectively. The features seen here are similar to the ones observed by other authors, viz., (1) at higher frequencies or high bias voltages, the Goldstone mode vanishes and only the soft mode remains, (2) there is a maximum in the dielectric constant at the transition when measured either at high frequencies or with high bias voltages.

Fig 13 — Influence of the frequency of measurement on the dielectric constant of compound II

Fig 14 — Effect of bias field on the static dielectric constant of compound II

We have studied the effect of the magnitude of $P_s$ on the soft mode and Goldstone mode relaxations. Because of the large $P_s$ value in one of the three materials used, we could study the soft mode relaxation in the C* phase over a temperature range as high as 0.8 °C from $T_c$. The results obtained compare well with the predictions of the generalised mean-field model.

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References

[9] For the sake of curve fitting, the first two terms on the right handside of equation (1) have been used in their rationalised form (see e.g., N. E. Hill, W E Vaughan, A H Price and M Davies, Dielectric Properties and Molecular Behaviour, Van Nostrand, 1969, p 49 ff)