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Dielectric spectroscopy of an antiferroelectric liquid crystal showing an antiferroelectric–ferrielectric transition

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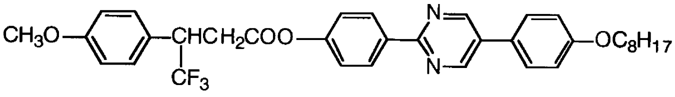
We report the dielectric relaxation behaviour in the antiferroelectric SmC_A^* and ferrielectric SmC_γ^* phases of the antiferroelectric liquid crystal 4-[5-(4-octloxyphenyl)-2-pyrimidinyl]phenyl 4,4,4-trifluoro-3-(methoxyphenyl)butanoate which shows an antiferroelectric transition at around 88 ± 0.1°C. In the SmC_A^* phase, two dielectric relaxation modes have been found, namely the usual antiferroelectric Goldstone mode and another arising from molecular rotation around its short axis. In the SmC_γ^* phase, one dielectric relaxation mode has been observed due to the ferrielectric Goldstone mode. Dielectric increments and relaxation frequencies of the antiferroelectric and ferrielectric phases are estimated from the fits of the Cole–Cole function of the dielectric spectrum. The dependence of the bias field in the ferrielectric phase is also discussed.

1. Introduction

The discovery of the chiral antiferroelectric (AFE) smectic C phase (SmC_A^*) in a liquid crystal compound [1] showed that interlayer antiferroelectric ordering can be stabilized in the mesophase without long range positional order. Smectic liquid crystals show a variety of phases such as the ferroelectric (SmC^*), antiferroelectric (SmC_A^*), ferrielectric (SmC_γ^*) and SmC_α^* phases [1–5]. The characterization of these phases was first made by switching measurements [3,6] and also by conoscopic observations [4,5]. The relaxation processes and the phase transitions between these smectic phases have been studied by dielectric [7–9] or by electro-optic spectroscopic techniques [10,11]. The present understanding of dielectric relaxation behaviour in the AFE phase is at a rather rudimentary stage, although some contributions devoted to detailed dielectric measurements of antiferroelectric liquid crystals (AFLCs) have been published [12,13]. The results obtained so far showed a complex relaxation behaviour in the AFE SmC_A^* phase. In the dielectric spectrum of the ferrielectric (FI) SmC_γ^* phase, there is a low frequency mode which appears due to the ferrielectric Goldstone (G) mode [13–16]. A high frequency absorption has also been observed in the SmC_γ^* phase which is due to the soft mode [17].

In this work, the temperature, frequency and bias field dependence of the dielectric properties of the AFLC compound 4-[5-(4-octloxyphenyl)-2-pyrimidinyl]phenyl 4,4,4-trifluoro-3-(methoxyphenyl)butanoate (TFMB), which shows an AFE transition well above room temperature, has been investigated.



By fitting these data, we have attempted to evaluate the characteristic features of each of the relaxation modes present in the system.

2. Experimental

The synthesis and phase behaviour of TFMB have already been discussed by Aoki and Nohira [18,19]. The liquid crystal cell used in our measurements consisted of two indium tin oxide (ITO) coated parallel transparent glass plates with an active area $A = 17.5\,\mathrm{mm}^2$. The glass plates were separated using mica spacers of thickness $t = 11\,\mu\mathrm{m}$. A uniformly aligned (planer alignment) sample was obtained by depositing a thin film of polyvinyl alcohol (PVA) on the ITO plate. The plates were then dried in an oven at a

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temperature of 140.0–150.0°C for about 60–70 min and then the film was rubbed in only one direction of the plates as described elsewhere [20]. The cells were first calibrated using air and toluene as a standard reference, allowing us to calculate the absolute value of the dielectric permittivity. The AFLC compound TFMB, used in this study, was introduced into the cell in the isotropic phase by means of the capillary action technique. TFMB has the phase sequence: Cr–60.2°C –SmC$^*_A$–88.1°C–FI(SmC$^*_\gamma$)–90.8°C–TGBA–107.5°C–Iso.

The temperature (55.0–110.0°C) of the sample was controlled with an accuracy of ± 0.1°C. Cooling and heating cycles were repeated several times to obtain a better molecular alignment. The frequency dispersion of the complex dielectric permittivity $\varepsilon^*(\omega)=(\varepsilon', \varepsilon'')$ was measured in the frequency range 10 Hz–1 MHz and bias field 0–25 V using a computer controlled HP 4192A impedance analyser.

3. Results and discussion

By definition, the AFE SmC$^*_A$ phase has no net polarization due to an effective cancellation of the dipole moments of adjacent layers. Two relaxation modes are found in the AFE SmC$^*_A$ phase [21]. According to Panarin *et al.*, the first is assigned as the antiferroelectric Goldstone mode arising from the fluctuation of the azimuthal orientation of the director; the other is due to the molecular rotation around its short axis [22,23]. These modes are distinguished from each other by the temperature-dependent behaviour of their relaxation times. By contrast, only one relaxation mode is observed in the FI SmC$^*_\gamma$ phase, which is due to the ferrielectric Goldstone mode showing some kind of ferroelectric G mode like behaviour. No relaxation modes are observed in the TGBA phase [24]. For each relaxation mode in the AFE and FI phases, the strength of the dielectric mode $\Delta\varepsilon$ and its relaxation frequency ν were obtained from fitting the complex permittivity to the Cole–Cole equation [25]

$$\varepsilon^* = \varepsilon_{\infty j} + \frac{\varepsilon_{Sj} - \varepsilon_{\infty j}}{1 + \left(i\omega\tau_j\right)^{1-\alpha_j}} \qquad (1)$$

where $\Delta\varepsilon_j = \varepsilon_{Sj} - \varepsilon_{\infty j}$, ($j$ = G for G mode, S for S mode); ε_{Sj} is the static dielectric constant, $\varepsilon_{\infty j}$ is the high frequency dielectric permittivity, τ_j ($=1/2\pi\nu_j$) and α_j are the dielectric relaxation time and the distribution parameter, respectively, and ν_j is the relaxation peak frequency. For a distribution of relaxation times, one has $\alpha_j \in [0,1]$ .The effect of α_j is to produce a semicircular Cole–Cole plot, the centre of which is depressed below the abscissa. The larger α_j is, the larger is the extent of the distribution of relaxation times. If the parameter α_j is equal to zero, the dielectric behaviour has only one relaxation time.

Using equation (1), dielectric strength $\Delta\varepsilon$ and relaxation frequency ν_C are calculated for TFMB. Figure 1 (*a*) shows the temperature-dependent dielectric strength of the antiferroelectric G-mode and that of the other (molecular) mode resulting from molecular rotation

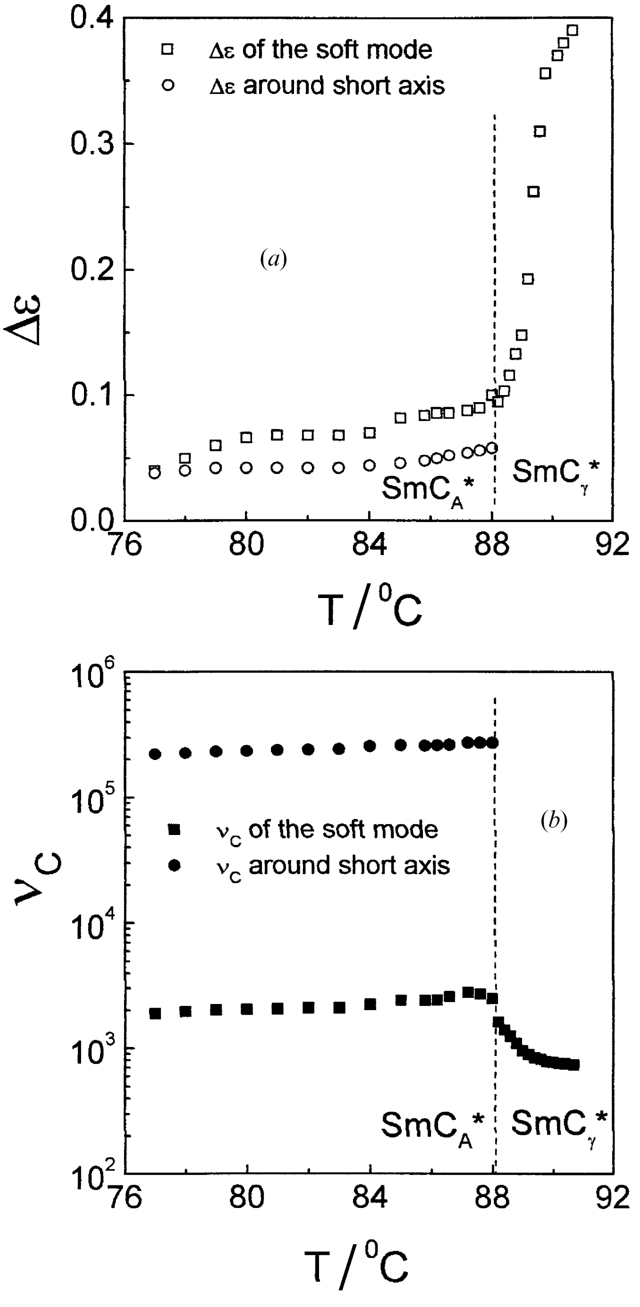

Figure 1. (*a*) Variation of dielectric strength $\Delta\varepsilon$ of the G mode and the mode due to molecular rotation around the short axis with temperature. (*b*) Variation of relaxation frequency ν of the G mode and the mode due to molecular rotation around the short axis with temperature in the SmC$^*_A$ and SmC$^*_\gamma$ phases for TFMB.

around its short axis in the AFE SmC$_A^*$ and FI SmC$_\gamma^*$ phases. Figure 1 (*b*) shows the temperature dependent behaviour of ν_C of the antiferroelectric G mode and that of the other molecular mode in the AFE SmC$_A^*$ and FI SmC$_\gamma^*$ phases. It is seen from Figures 1 (*a*) and 1 (*b*) that the relaxation frequencies in the two modes are almost constant, while the dielectric strengths increases slightly in the SmC$_A^*$ phase with increasing temperature. In the SmC$_\gamma^*$ phase, the dielectric strength increases rapidly but the relaxation frequency first decreases and then attains a constant value. It is also seen that the relaxation frequency of the G mode decreases with increasing temperature from the SmC$_A^*$ to SmC$_\gamma^*$ phase, and that a sudden jump appears near the SmC$_A^*$–SmC$_\gamma^*$ transition temperature T_C ($\sim$88.1°C). This jump in the relaxation frequency at T_C is due to the change of the activation energy with the phase transition. This discontinuous change of the relaxation frequency at the transition point is likely to be first order in nature [19]. Indeed, the first order nature of the SmC$_A^*$–SmC$_\gamma^*$ transition for TFMB was reported by Aoki and Nohira [19].

The effect of biasing voltage [26] on the ferrielectric G mode in the SmC$_\gamma^*$ phase at T=89.0°C has been studied using a planar aligned cell. The variation of the imaginary parts of the dielectric permittivity (ε'') with frequency for different bias voltages is shown in figure 2. In the ferrielectric SmC$_\gamma^*$ phase, the absorption of the G mode contribution first increases at very low bias voltages, and is then suppressed gradually on further increasing of the bias voltage. The relaxation frequency of this mode is almost constant at low bias voltage and starts to increase at a bias field of $\sim$3 V. The change of the relaxation parameters with bias field is due to the structural change of the SmC$_\gamma^*$ phase [26]. ε'' increases rapidly on the low frequency side of the frequency spectrum due to the presence of ions in the cell [26]. At the high frequency side the value of ε'' again increases; this is due to the resistance of the ITO film [17]. The variation of dielectric strength and relaxation frequency with bias voltage at fixed temperature T=89.0°C is shown in figure 3.

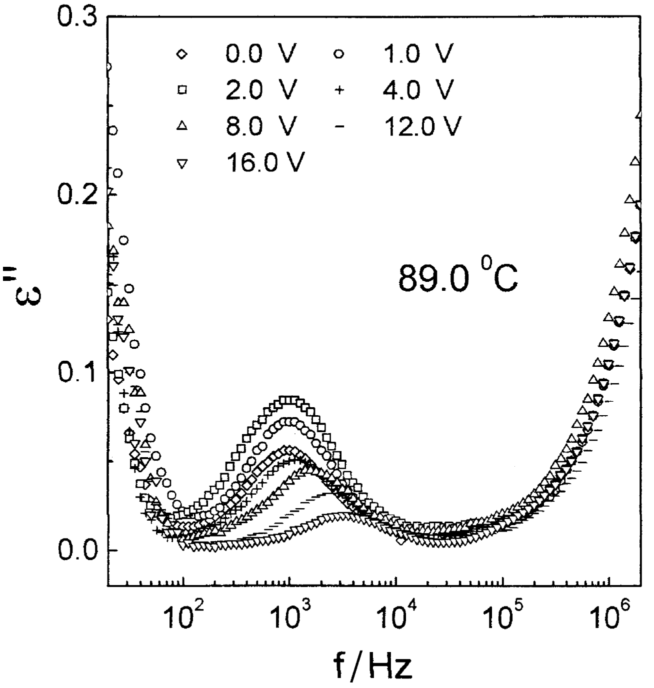

Figure 2. Variation of the imaginary part of the dielectric permittivity ε'' with frequency for different fixed bias voltages at 89.0°C in the SmC$_\gamma^*$ phase for TFMB.

4. Conclusion

The frequency and temperature-dependent dielectric relaxation behaviours of the AFLC compound TFMB have been examined. From the analysis of the complex dielectric constant data and by fitting the data we observed; in the SmC$_A^*$ phase, two dielectric relaxation modes. One is related to the antiferroelectric G mode, the other is due to molecular rotation around its short axis. In the SmC$_\gamma^*$ phase, only one dielectric relaxation mode has been found due to the ferrielectric G mode. We also note that in the SmC$_\gamma^*$ phase, the ferrielectric S mode is strongly dependent on the bias field.

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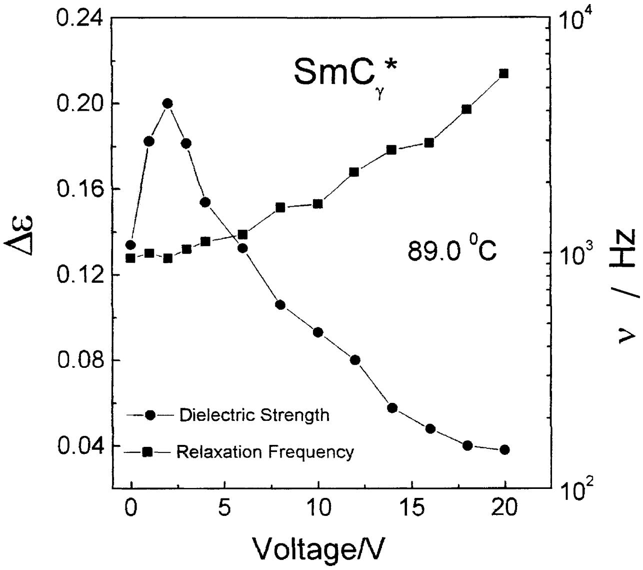

Figure 3. Variation of dielectric strength $\Delta\varepsilon$ and relaxation frequency ν with bias field at 89.0°C in the SmC$_\gamma^*$ phase for TFMB.

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