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Z. Raszewski[a]; J. Rutkowska[a]; J. Kedzierski[a]; J. Zieliński[a]; J. Żmija[a]; R. Dabrowski[a]; P. Perkowski[a]
[a] Institute of Technical Physics WAT, Warsaw, Poland

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The Goldstone mode in mixtures containing ferroelectric liquid crystals

by Z. RASZEWSKI*, J. RUTKOWSKA, J. KEDZIERSKI, J. ZIELIŃSKI,
J. ŻMIJA, R. DĄBROWSKI and P. PERKOWSKI
Institute of Technical Physics WAT, 00-908 Warsaw, Poland

Measurements of complex electric permittivity of room temperature ferroelectric liquid crystal mixtures have been made on aligned samples with the electric measuring field being parallel to the layer planes. The spontaneous polarization, the tilt angles and pitch have been measured in these mixtures. By theoretical fitting of the experimental points of electric permittivity for the Cole–Cole modification of the Debye equation dielectric parameters, the dielectric strength, relaxation frequency, and distribution parameter for the Goldstone mode have been computed. The dielectrically observed Goldstone mode in our mixtures is shown to have both DC bias field and AC field dependences.

1. Introduction

In recent years considerable theoretical and experimental work has been devoted to the study of the dielectric response of ferroelectric liquid crystals with a S_C^*–S_A phase transition. It was shown [1] that the perpendicular component of the complex dielectric permittivity $\varepsilon_\perp$ reveals, in addition to normal molecular relaxation, two spectacular relaxation regions, the so-called Goldstone mode and soft mode. The Goldstone mode contribution to $\varepsilon_\perp$ is due to phase fluctuations of the azimuthal orientation of the director, whereas the soft mode comes from tilt angle amplitude fluctuations.

To describe the relaxation of the dielectric permittivity in the S_C^* phase, which usually does not relax within a single relaxation time, Cole and Cole [2] have extended the Debye equation by introducing the distribution parameter h. Frequency dependence of the $\varepsilon_\perp$ component in the S_C^* phase can thus be written as follows:

$$\varepsilon_\perp^*(\omega)=\varepsilon_{\perp\infty}+\frac{\varepsilon_{\perp 0}^{G}-\varepsilon_{\perp\infty}^{G}}{1+(i\omega\tau_G)^{1-h_G}}+\frac{\varepsilon_{\perp 0}^{S}-\varepsilon_{\perp\infty}^{S}}{1+(i\omega\tau_S)^{1-h_S}}, \qquad (1)$$

where $\varepsilon_{\perp\infty}$ is the high frequency limit of the electric permittivity, $\Delta\varepsilon_\perp^G=\varepsilon_{\perp 0}^G-\varepsilon_{\perp\infty}^G$, $\Delta\varepsilon_\perp^S=\varepsilon_{\perp 0}^S-\varepsilon_{\perp\infty}^S$ are the dielectric increments resulting from the Goldstone mode and from the soft mode, respectively, τ_G, τ_S are the corresponding relaxation times, and h_G, h_S are the empirical parameters of the relaxation time distribution.

In this paper we present results of experiments in which dielectric spectra of room temperature ferroelectric liquid crystal mixtures have been studied as a function of chiral dopant concentration and electric measuring field magnitude.

2. Experimental

Measurements of complex electric permittivity, spontaneous polarization, tilt angle and pitch have been performed on aligned samples of room temperature ferroelectric liquid crystal mixtures [3, 4].

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* Author for correspondence.

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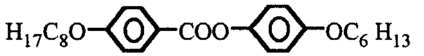
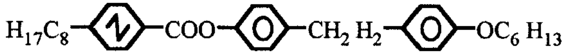
The basic mixtures consists of the following compounds:



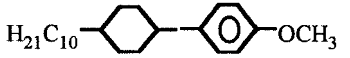
23·55 wt%

18·80 wt%

24·41 wt%

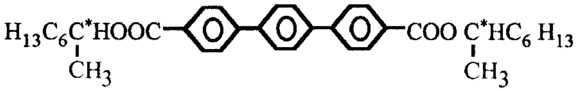


32·44 wt%



4·00 wt%

the chiral dopant



was introduced with gradually increasing concentration.

Transition temperatures and phase assignments were determined employing polarization microscopy and dielectric spectroscopy techniques. Phase diagrams obtained from these experiments have already been presented and discussed in [3, 4]. Some data for the mixture containing 6 wt%, 12 wt%, 20 wt%, and 25 wt% of chiral dopant are listed in the table. The mixtures with these chiral dopant concentrations were studied by us.

The measurements were performed in a shielded plate condenser described previously [5, 6]. The alignment of the molecules was checked optically and the applied procedure resulted in the bookshelf geometry being obtained.

Empty cells were calibrated with toluene and cyclohexane to calculate stray capacitance C_M and empty cell capacitance C_0. Then the cells were filled, using the capillary method.

The spontaneous polarization, tilt angle and the real and imaginary parts of the complex dielectric permittivity were measured in the cells of 17·6 μm, 14·1 μm, 12·3 μm and 8 μm thickness for mixtures A, B, C and D, respectively. The pitch was measured in the cell of 50 μm thickness for all mixtures.

The real ε' and imaginary ε'' parts of the complex dielectric permittivity have been studied in the frequency range from 20 Hz to 300 kHz employing a Precision Component Analyser WAYNE KERR 6425. In our experiment a time dependent measuring voltage from 10 mV to 5 V was applied in a direction parallel to the smectic layers (i.e. perpendicular to the helical axis) and thus we measured the perpendicular component of the dielectric permittivity $\varepsilon_\perp^*$. The real and imaginary parts of $\varepsilon_\perp^*$ were calculated from measured capacitance and conductance values using the relations:

$$\varepsilon'_\perp = \frac{C - C_M}{C_0}, \qquad \varepsilon''_\perp = \frac{G}{\omega C_0}, \tag{2}$$

where C and G are the capacitance and conductance of a cell filled with liquid crystal and ω is the measuring field frequency. The effect of dielectric absorption, due to freely moving ions being predominant at low frequencies, was corrected for in dielectric measurements [7]. A measuring voltage could be superimposed on an internal bias voltage from zero to 20 V, obtained from a WAYNE KERR 6425 analyser.

The spontaneous polarization was measured by a Diamant AC bridge technique and the tilt angle was derived from the optical switching angle of the sample [5, 6]. To

Concentration of chiral dopant wt%	Transition temperature/°C	Mixtures
6	$S_C^*62S_A72N^*110{\cdot}5I$	A
12	$S_C^*63S_A75{\cdot}5N^*106I$	B
20	$S_C^*63S_A79{\cdot}5N^*93{\cdot}5I$	C
25	$S_C^*63{\cdot}7S_A80{\cdot}6N^*88{\cdot}7I$	D

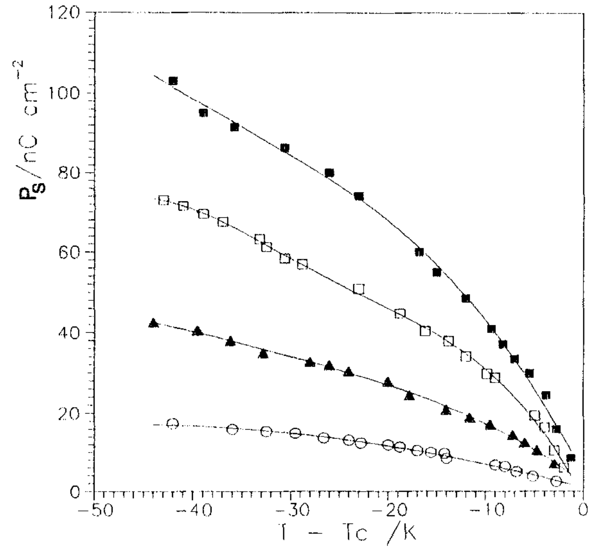


Figure 1. Temperature dependence of the spontaneous polarization of mixtures A, B, C and D containing 6 wt% (○), 12 wt% (▲), 20 wt% (□), 25 wt% mixtures of chiral dopant, respectively.

measure the helical pitch we used the technique of direct microscopic observation of the strip's spacing [5].

3. Results and discussion

The spontaneous polarization P_S and the tilt angle θ of each mixture were measured as a function of temperature. These results are given in figures 1 and 2. The accuracy of spontaneous polarization and tilt angle measurements is $1{\cdot}5\,\mathrm{nC\,cm^{-2}}$ and $0{\cdot}5°$, respectively. From these data we derived the concentration dependence of P_S and θ at constant temperature below the S_C^*–S_A phase transition (see figures 3 and 4). Summarizing these results we can see that there is a linear dependence of P_S on the concentration of this chiral dopant and the tilt angle is found to be nearly unaffected, within the limits of experimental accuracy.

The tilt angle values is correlated directly with the existing range of the smectic A phase above the smectic C* phase. A broader temperature interval of the existence of the smectic A phase is connected with a smaller value of the tilt angle. It was found from a study of the phase diagram [3, 4] that this chiral dopant induces a smectic A phase concentrations exceeding 4 wt%. For the concentrations of 6 wt%, 12 wt%, 20 wt% and 25 w%, the existing range of the smectic A phase is nearly independent of the concentration. Therefore, the basic mixture doped with 6 wt%, 12 wt%, 20 wt%, 25 wt% of the chiral compound reveals no significant change of the tilt angle. This dopant was

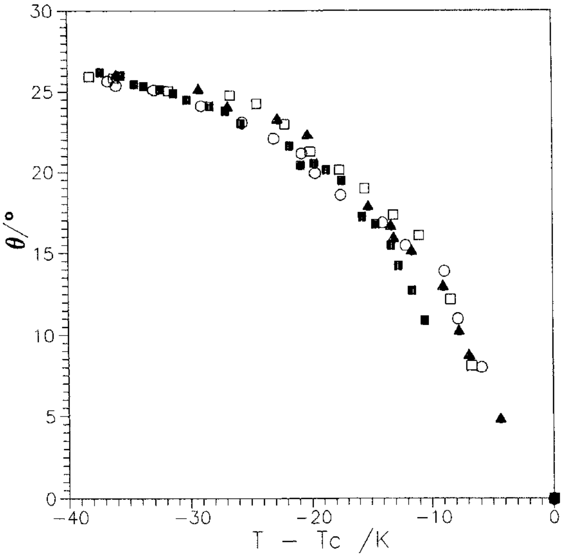


Figure 2. Temperature dependence of the tilt angle of mixtures A, B, C and D containing 6 wt% (○), 12 wt% (▲), 20 wt% (□), 25 wt% (■) of chiral dopant, respectively.

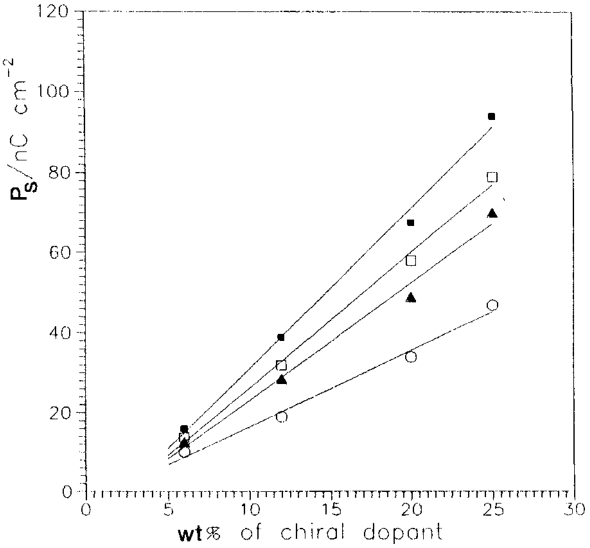


Figure 3. The spontaneous polarization as a function of chiral dopant concentration at 36 K (■), 26 K (□), 20 K (▲) and 10 K (○) below the S_A–S_C^* transition (T_c).

used not only to induce the smectic A phase, but in principle to induce simultaneously chiral properties.

The emergence of spontaneous polarization is due to induced dipole–dipole interactions at low concentration of chiral dopants in an achiral smectic C matrix. Therefore the spontaneous polarization originates from the average transverse dipole moments of all chiral molecules in the tilted matrix and we expect an approximately linear increase of P_S with the concentration of chiral molecules. It is worth mentioning that the linear P_S dependence for this concentration range, observed by us, is in good

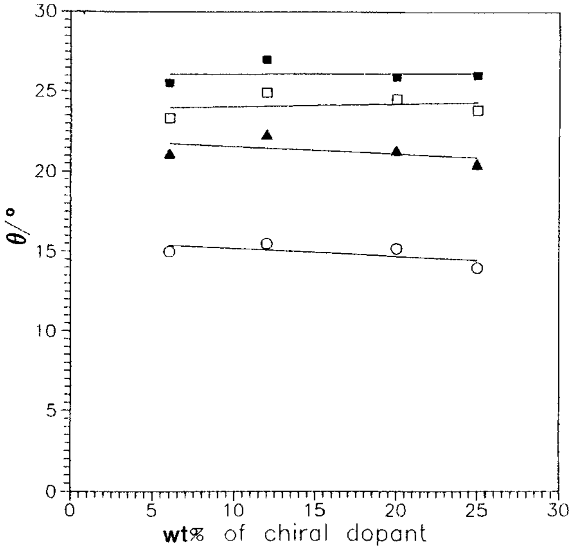


Figure 4. The tilt angle as a function of chiral dopant concentration at 36 K (■), 26 K (□), 20 K (▲) and 10 K (○) below the S_A–S_C^* transition (T_c).

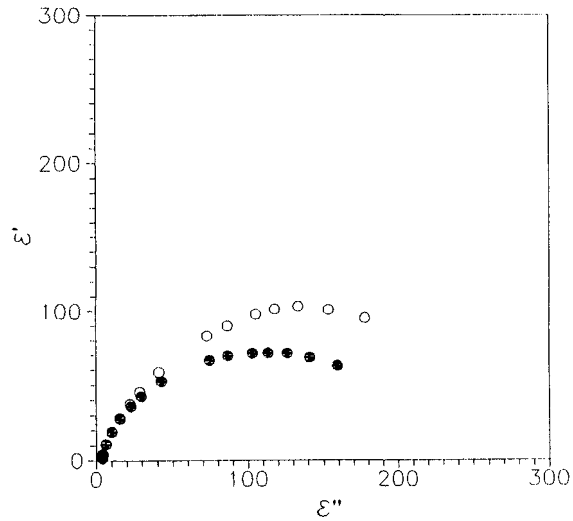


Figure 5. The Cole–Cole diagram for the Goldstone mode of mixture C at 36 K below the S_A–S_C^* transition at AC measuring voltages of 0·6 V (●) and 1·8 V (○), respectively.

agreement with results presented by Loseva *et al.* [8]. These authors also maintain that further increase of this chiral dopant concentration above 30 wt% in the smectic matrix HOPOOB leads to a decrease in spontaneous polarization.

On the other hand, addition of this chiral compound at concentrations of 12 wt%, 20 wt% and 25 wt% to an achiral smectic C basic mixture results in mixtures B, C, D having pitches 4·2 μm, 2·5 μm and 2 μm respectively, at a temperature of 36 K below the transition temperature S_A–S_C^* (hereafter denoted as T_c).

Using the previously described set-up, dielectric spectra in the S_C^* phase of mixtures A, B, C and D have been measured in the frequency range from 20 Hz to 300 kHz. In order to show the Goldstone mode dielectric contribution, all dielectric measurements were made made at temperatures 36 K below T_c, because at this temperature the soft mode is suppressed by the Goldstone mode. For all investigated mixtures the dielectric spectra connected with the Goldstone mode were measured between 20 Hz and 10 kHz. For example in figure 5 such a dielectric spectrum is presented in the form of Cole–Cole diagram, for mixture C containing 20 wt%. of chiral compound.

When a bias DC electric field is applied parallel to the smectic layers, it affects the S_C^* phase in different ways. As predicted theoretically, sufficiently strong electric fields can unwind the helix and thus quench the Goldstone mode [9, 10]. Figure 6 shows the values of $\Delta\varepsilon'_\perp = |\varepsilon'_\perp(U_{DC}=0) - \varepsilon'_\perp(U_{DC})|$ as a function of internal bias DC field from 0 to 20 000 V cm^{-1}. Increasing the bias field to 4000 V cm^{-1} removes the Goldstone mode, which exhibits a dramatic bias field dependence.

To discover the AC field dependence of the Goldstone mode, the following dielectric parameters have been computed by fitting the Cole–Cole modification of the Debye equation to the experimental data: $\varepsilon^G_{\perp 0}$, the static dielectric constant; $\varepsilon^G_{\perp\infty}$, the high frequency limit of the electric permittivity mode; f_G, the dielectric relaxation frequency; h_G, the distribution parameter for the Goldstone mode. These values were computed from experimental data for mixtures A, B, C and D at $(T - T_c) = -36$ K and a AC measuring field strength from 100 V cm^{-1} to 4000 V cm^{-1}.

Figure 7 shows the calculated values of the dielectric strength, $\Delta\varepsilon^G = (\varepsilon^G_{\perp 0} - \varepsilon^G_{\perp\infty})$, of the Goldstone mode, and figure 8 the calculated values of dielectric relaxation frequency f_G as a function of AC measuring field strength. The parameter h_G, governing the shape of the relaxation was found to vary from 0 to 0·25 for all mixtures and these

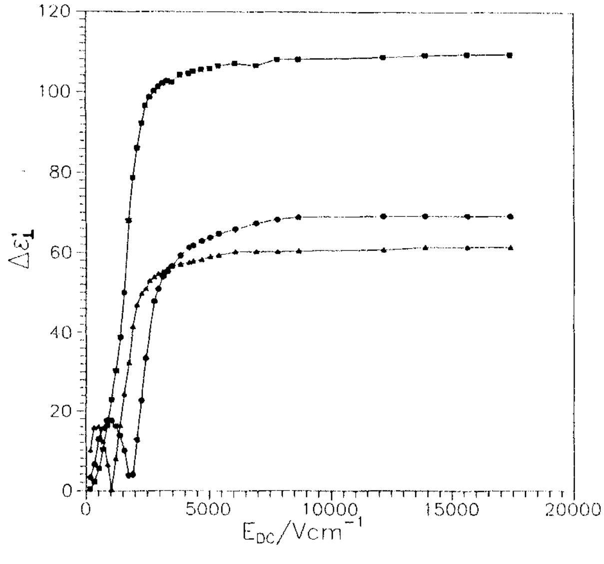


Figure 6. The DC bias field dependence of the real part of the complex dielectric permittivity ($\Delta\varepsilon'_\perp = |\varepsilon'\ (U_{DC}=0) - \varepsilon'_\perp(U_{DC})|$) of mixture C at 36 K below the S_A–S_C^* transition, at AC measuring voltages 0·6 V (▲), 1·8 V (■), and 4·2 V (●) and a frequency of 50 Hz. 50 Hz is the relaxation frequency for the Goldstone mode for mixture C (see figure 8).

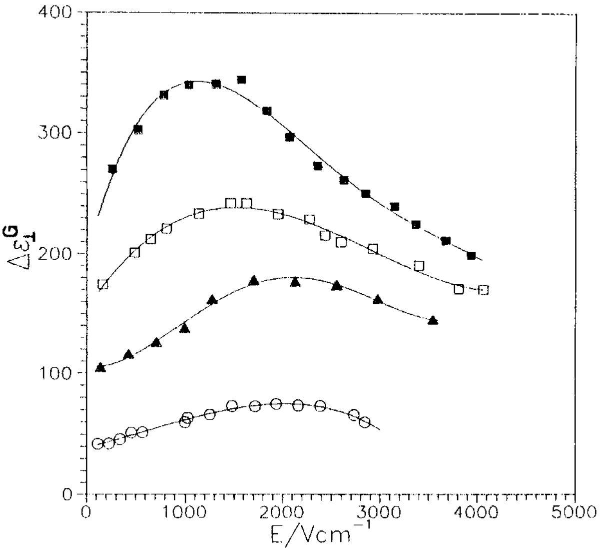


Figure 7. The AC measuring field dependence of the dielectric strength of the Goldstone mode for mixtures A, B, C and D, containing 6 wt% (○), 12 wt% (▲), 20 wt% (□), and 25 wt% (■), of chiral dopant respectively, at 36 K below the S_A–S_C^* transition.

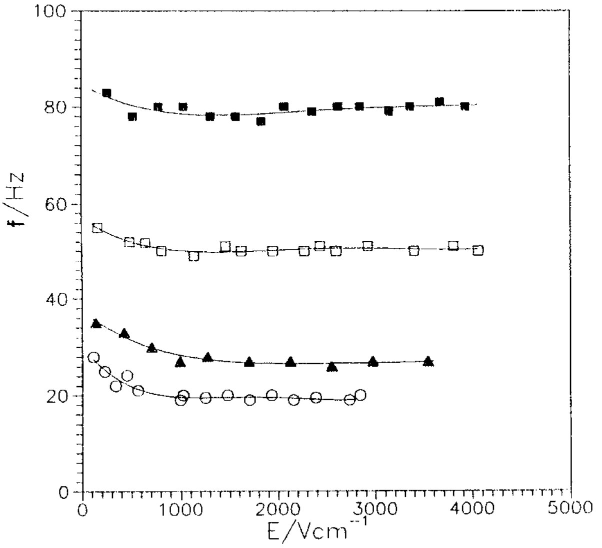


Figure 8. The AC measuring field dependence of the dielectric relaxation frequency of the Goldstone mode for mixtures A, B, C and D, containing 6 wt% (○), 12 wt% (▲), 20 wt% (□) and 25 wt% of chiral dopant, respectively, at 36 K below the S_A–S_C^* transition.

results will be published elsewhere. From results presented in figures 7 and 8 we can see that:

(i) an increase in the concentration of the chiral dopant from 6 wt% to 25 wt% leads to an increase of the Goldstone mode dielectric strength;

(ii) an increase in the concentration of the chiral dopant from 6 wt% to 25 wt% results in an increase of the Goldstone mode relaxation frequency;

(iii) the measuring AC field dependence of the Goldstone mode dielectric strength is strong.
(iv) the AC measuring field dependence of the Goldstone mode relaxation frequency is very weak and almost constant above 400 V cm^{-1}.

The Goldstone mode dielectric strength increases linearly with chiral dopant concentration, i.e. with the spontaneous polarization, indicating that this relaxation is due to the bulk relaxation of the electric dipoles connected with the chiral dopant molecules in our mixtures. This result might be expected, in view of the increasing values of the spontaneous polarization and the different dipole moments of the chiral dopant and smectic C matrix, but it does not agree with results published in [11].

For the Goldstone mode it is possible to derive an expression for the relaxation frequency in terms of the wavevector of the pitch q ($q = 2\pi/\lambda$), rotational viscosity γ and elasticity coefficient K [12]

$$\frac{1}{2\pi f_G} = \frac{\gamma}{Kq^2}. \tag{3}$$

Thus when the helical pitch increases from 2 μm to 2·5 μm to 4·2 μm (for mixtures D, C, and B respectively), the relaxation frequency should decrease from 80 Hz to 51·2 Hz to 18·4 Hz. We can see that these theoretical values of f_G are in good agreement with values obtained from Cole–Cole plots, specially for mixtures D and C.

The AC field dependence of the Goldstone mode has not yet been analysed systematically. First it has been considered by Kremer *et al.* in [13]. In our experiment, the Goldstone mode dielectric strength is also shown to have an AC field dependence. In agreement with [13] we have found that for increasing spontaneous polarization the AC field dependence of $\Delta\varepsilon_\perp$ becomes stronger. Our results, i.e. the dielectric strength increases linearly with the spontaneous polarization and the relaxation frequency is unaffected by the AC field, confirm that it is bulk relaxation.

The difference in bulk relaxation behaviour for small and large AC field strengths is due to the fact that in the former case the response of the molecules for small deviations around their equilibrium configuration is measured. In the latter case, the dipoles switch their orientations from one electrode to the other and thus the dielectric response is characteristic of large deviations from molecular equilibrium positions.

4. Conclusions

The structure of the chiral dopant is such that its introduction into a basic mixture induces the useful phase sequence (I–N*–S_A–S_C^*), tilt angle values suitable for applications and a linear concentration dependence of the spontaneous polarization.

It is important to know that analysis of the Goldstone mode, based on linear theory, is restricted to sufficiently small AC fields.

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