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Low frequency dielectric spectroscopy on mixtures containing ferroelectric liquid crystals

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PRELIMINARY COMMUNICATIONS

Low frequency dielectric spectroscopy on mixtures containing ferroelectric liquid crystals

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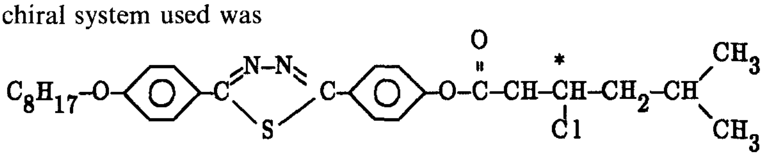
Dielectric spectroscopy (frequency range 10^{-1} Hz to 10^5 Hz, temperature range 300 K to 370 K) was employed to investigate the Goldstone mode in ferroelectric liquid-crystalline mixtures of chiral and achiral compounds. While the spontaneous polarization decreases with increasing fraction of the achiral molecules the Goldstone mode remains constant in its oscillatory strength. As expected the Goldstone mode frequency shifts to lower values with increasing amount of achiral molecules in the ferroelectric liquid-crystalline mixture.

Dielectric spectroscopy has become a versatile tool for the investigation of low molar mass [1–10] and polymeric [11] ferroelectric liquid crystals. Usually pure ferroelectric liquid crystals or a single mixture containing ferroelectric liquid crystals were studied. Whereas for display applications several ferroelectric mixtures are available and commonly used (e.g. [12]) in order to achieve a broad temperature range, a smectic A phase and a compensated cholesteric pitch for easy orientation and fast switching times can also be employed. In this preliminary communication we present a broadband dielectric spectroscopy study (frequency range: 10^{-1} Hz to 10^5 Hz, temperature range 300 K to 370 K) of chiral/achiral systems.

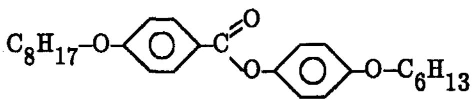
The chiral system used was



THIA

C 340 K S_C^* 422 K S_A 423 K I.

The achiral system used was



C 328 K S_C 339 K N 362 K I.

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The synthesis of the chiral liquid crystals is described in [5]. The transition temperatures and phase assignments were determined by polarization microscopy and dielectric spectroscopy. The mixing was done by stirring in the isotropic phases. The dielectric measurements covered the frequency range from 10^{-1} Hz to 10^5 Hz using a frequency response analyser (Solartron-Schlumberger FRA 1254 frequency range 10^{-4} Hz to 6×10^4 Hz) with a high impedance preamplifier of variable gain [13–15] and a Hewlett-Packard impedance analyser (HP 4192 A frequency range from 10 Hz to 10^7 Hz). The AC measuring field (200 V/cm) could be superimposed on an internal bias field obtained from the HP 4192 A or from the Solartron-Schlumberger FRA 1254. A nitrogen gas heating system covered the temperature range from 100 K to 450 K, the stability of the temperature adjustment was $\pm 0{\cdot}02$ K (i.e. the resolution of the temperature measurement was 0·01 K). The temperature gradient across the sample is estimated to be less than 0·04 K. The liquid-crystalline sample was kept between two glass plates coated with polyimid and separated by a spacer (50 ± 4 μm). The parallel rubbing direction led to the desired uniform bookshelf geometry. The alignment in the filled cell was checked by polarization microscopy. The voltage was applied by two evaporated indium–tin oxide electrodes with an area of $10 \times 10\,\mathrm{mm}^2$ (LCD-Cell from EHC, Japan).

The measured dielectric loss ε'' in its frequency and temperature dependence (see figure 1) for the 0·5 chiral (THIA)/achiral mixture reveals how much the Goldstone mode contributes in the S_C^* phase. Close to the phase transition from the S_C^* phase to the crystalline phase the Goldstone mode is shifted to lower frequency before it completely

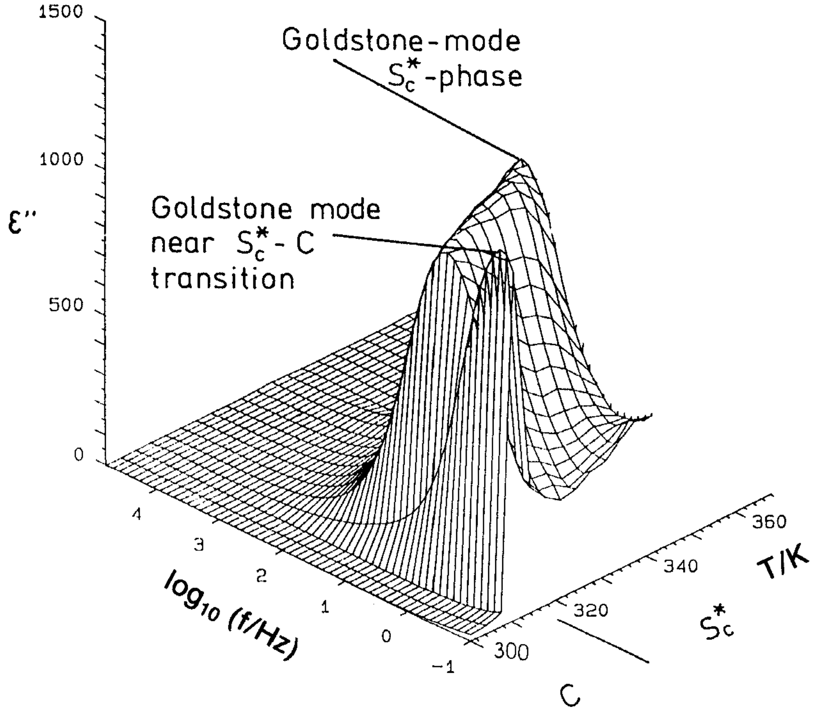

Figure 1. Dielectric loss ε'' versus frequency and temperature for a 1 : 1 mixture ($x_T = 0{\cdot}5$) of the chiral and achiral compound. The experimental accuracy of the dielectric measurement is ±5 per cent.

Liquid-crystalline phases, spontaneous polarization and dielectric increment $\Delta\varepsilon$ of the Goldstone mode for different mixtures of chiral/achiral liquid crystals. The spontaneous polarization was measured 10 K below the phase transition $T_{S_C^*S_A}$. The dielectric increment and the Goldstone mode frequency is independent of temperature in the S_C^* phase.

Mixtures x_{chiral}	Phases	Spontaneous polarization 10 K below $T_{S_C^*S_A}$ P_S/nC cm^{-2}	Dielectric increment $\Delta\varepsilon$ for the Goldstone mode at the temperature indicated
1	C 340 K S_C^* 422 K S_A 423 K I	125	3700 ± 300 at 349·1 K
0·7	C 325 K S_C^* 387 K S_A 402 K I	39·5	2600 ± 210 at 350·4 K
0·5	C 318 K S_C^* 371 K S_A 380 K N* 386 K I	19·8	3100 ± 250 at 351·0 K
0·2	C 321 K S_C^* 354 K S_A 360 K N* 374 K I	5·2	2900 ± 230 at 350·4 K

vanishes in the crystalline state, which might be a highly ordered smectic phase. Similar behaviour is found in all three mixtures ($x=0{\cdot}7, x=0{\cdot}5, x=0{\cdot}2$) and in the pure thiodiazol ($x=1$). Diluting (see the table and figure 2) the chiral component from $x=1$ to $x=0{\cdot}2$ results in a decrease of the Goldstone mode frequency from about 100 Hz for $x=1$ to about 2 Hz for $x=0{\cdot}2$ whereas the dielectric strength is unaffected within the limits of the experimental accuracy. For the spontaneous polarization measured by the field reversal method decreasing values were found with decreasing content of the chiral component in the mixtures (see the table).

For the Goldstone mode frequency ν_G, the expression

$$\frac{1}{\nu_G}=\frac{\gamma_\rho}{K_\rho q^2}$$

was derived [3 (b), 3 (c), 6 (c)] where γ_ρ is the rotational viscosity, K_ρ the coefficient in the Landau expression [1] and q the wavevector of the helical pitch Z with $q=2\pi/Z$. Diluting the initial pure chiral substance with the achiral we expect that q should depend linearly on concentration. Thus, with a dilution factor of 5 ($x=0{\cdot}2$), the peak frequency should be reduced by a factor of 25, or to 4 Hz, given that $f(x=1)=100$ Hz. This is only a factor of two higher than in the experiment, which is not striking in view of the fact that as the pitch increases the helix becomes quite susceptible to external perturbations. For example, the samples used are only 50 μm thick, so that the sample surfaces must significantly perturb the helix structure at its larger pitches. The fact, that the frequencies for $x=1$ and $x=0{\cdot}7$ are similar, is not understood.

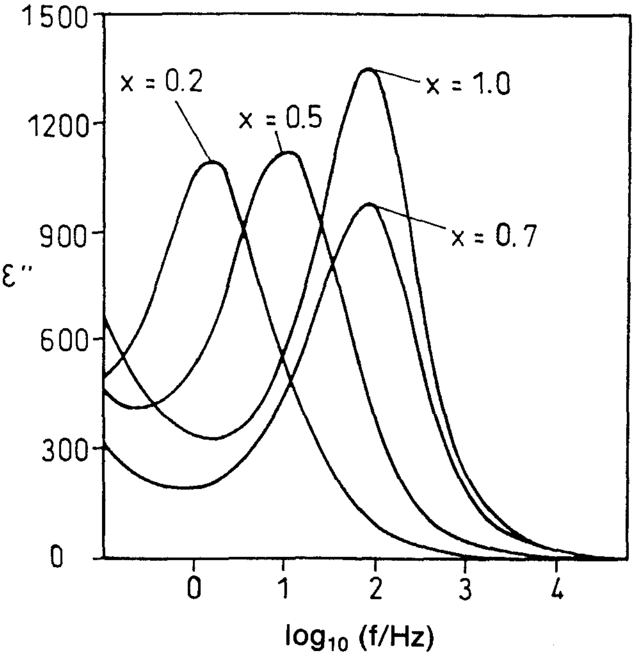

Figure 2. Dielectric loss ε'' versus frequency for different mixtures x chiral/achiral. Due to an uncertainty in the sample thickness of ±10 per cent the absolute accuracy in the comparison between two mixtures is only ±10 per cent. The sample temperatures vary between 349·1 K and 351 K (see the table).

The oscillatory strength of the Goldstone mode is, in contrast, nearly unaffected within the limits of experimental accuracy, which is unexpected in view of the decreasing values of the spontaneous polarization and the different dipole moments of the chiral and achiral compounds. Obviously, even at a concentration of $x = 0{\cdot}2$, the chiral system induces a chiral S_C phase, in which the lateral dipoles of the achiral compound can contribute to the oscillatory strength of the dielectrically observable Goldstone mode. In the classical theory of the S_C^* phase [16–18] and in the conclusion drawn by Lalanne *et al.* from their experiments [19], free rotation of the molecules in the S_A phase exists which is strongly hindered in the S_C^* phase.

Based on the direct observation of the high frequency rotation by broadband dielectric spectroscopy [20, 21], we could show that frequency and dielectric strength of the hindered rotation of the molecules, which has to be interpreted as a librational movement, is not influenced at the S_C^*–S_A transition which is in accord with the theoretical work of Brand and Pleiner [22, 23]. For the S_A phase the angle distribution of this libration is presumably isotropic, whereas inside the S_C^* phase an anisotropic distribution is present. The chiral compound would then induce in our mixtures this anisotropic distribution also for the achiral molecules, so that their dipole moments can contribute to the oscillatory strength of the dielectric Goldstone mode. The application of a DC bias field, which normally allows the suppression of the dielectrically observed Goldstone mode inside the S_C^* phase [5, 6, 8, 11 (b)] and thereby makes the soft mode observable, is not possible in the thiodiazol compound due to the occurrence of electrochemical degradation.

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