Dielectric relaxation spectroscopy of a nematic liquid crystal doped with ferroelectric Sn 2 P 2 S 6 nanoparticles

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It was found that doping a nematic liquid crystal (LC) with a small amount of ferroelectric nanoparticles strongly affects the dielectric properties of the system. In particular, adding the ferroelectric particles results in a shift of the absorption bands corresponding to the rotation of liquid crystal molecules around their short axes to lower frequencies and in an increase of the amplitude and with of the absorption bands. This suggests that strong interactions occur between the LC molecules and the particles, caused by the large dipole moment and high polarizability of the ferro-particles. The ferroelectric particles affect not only dielectric losses, but also dielectric permittivity of the system. Specifically, the static dielectric permittivity and the dielectric anisotropy of the suspension are more than twice that of the pure LC.

1. Introduction

Composites based on liquid crystals (LCs) have attracted much attention over a number of years because of their unique electro- and magneto-optic properties and novel display applications. Typical examples of these systems are polymer dispersed liquid crystals [1], suspensions of aerosils in LC matrices [2] and suspensions of ferro-particles in nematic LCs [3, 4].

The inclusions in known composite LC systems produce director distortions that extend over macroscopic scales. A new approach, however, was proposed recently [5]. This is based on the idea of controlling the properties of the composites by adding a low concentration of nanoparticles into a LC matrix. These dilute nanosuspensions are stable due to the weak interactions of the particles at low concentrations. The nanoparticles are so small that they do not disturb the LC orientation and thus macroscopically homogeneous structures are obtained, i.e. the suspensions appear similar to a pure LC with no readily apparent evidence of dissolved particles. At the same time the nanoparticles are sufficiently large to maintain the intrinsic properties of the materials from which they are made (e.g. ferromagnetism or ferroelectricity) and share these properties with the LC matrix due to anchoring with the LC. In particular, it was found that embedding submicron ferroelectric $Sn_2P_2S_6$ particles in a nematic liquid crystal at a low volume concentration ($c_v < 10^{-2}$) did not change the elastic and anchoring properties of the LC, but did result in an enhanced dielectric response. In particular, we found an increase in the dielectric anisotropy by a factor >2, which resulted in a decrease of the Fréedericksz transition voltage and an acceleration of the director reorientation in the electric field. In addition, the suspension exhibited an unusual linear response to the electric vector—the direction of the director reorientation was determined by the sign of the applied electric field. Here we report studies of the dielectric properties of a nematic liquid crystal suspension containing ferroelectric $Sn_2P_2S_6$ particles. We found that embedding the submicron ferro-particles in a LC results in changes of the dielectric spectra of the matrix, caused by the strong interaction between LC and ferro-particles.

2. Experiments and discussion

We used a ferroelectric liquid crystal suspension based on a nematic LC host, ZLI-4801-000 (Merk), and containing powder of the ferroelectric thiohypodiphosphate, $Sn_2P_2S_6$ (obtained from Uzhgorod University). ZLI-4801-000 shows a moderate dielectric anisotropy, $\varepsilon_a^{ZLI} = \varepsilon_\parallel^{ZLI} - \varepsilon_\perp^{ZLI} = 8.3 - 3.2 = 5.1$. Thus, the contribution from the ferro-particles can be easily seen [5].

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ZLI-4801-000 has a transition temperature to the isotropic state, $T_{NI} = 93°C$, which is higher than the Curie temperature $T_{Curie} \approx 66°C$ of $Sn_2P_2S_6$ macrocrystals. At room temperature macrocrystals of $Sn_2P_2S_6$ have a spontaneous polarization of $14\,\mu C\,cm^{-2}$ parallel to the [1 0 1] direction of the monoclinic cell [6]. The value of the dielectric constant of $Sn_2P_2S_6$ along the main axis depends strongly on the quality of the samples and varies from 200 for a ceramic samples to 9 000 for monodomain crystals [7].

We prepared the ferroelectric liquid crystal suspension by milling microparticles of $Sn_2P_2S_6$ ($\cong 1\,\mu m$ size) mixed with oleic acid in a weight ratio of 1:2. The mixture was ultrasonically dispersed and ground in a vibration micromill (Fritsch 00-502) for 120 h. The resulting suspension was mixed with the ZLI-4801-000 in a weight ratio 1:100 and ultrasonically dispersed for 5 min. The suspension was then put in a vessel and left for a day to allow for segregation. To fill the cells the top layer of the suspension in the vessel was used. The characteristic size of the particles in the suspension was about 100 nm and their volume concentration was about 0.3% in the LC matrix.

We assembled cells filled with both the suspension and the pure LC. The cells were made from two glass substrates coated with conducting ITO layers having a resistance of about $50\,\Omega/\square$. To obtain planar alignment of the suspension and of the pure LC the conducting layers were covered with polyvinyl-cinnamate (PVCN) and irradiated with polarized UV light [8]. The value of the pretilt angle was $3.5° \pm 0.5°$ for both types of planar cells. The homeotropic alignment of the suspension and of the pure LC was obtained by covering the ITO layers with polyimide *PI-1211*. The thickness of both types of the dielectric aligning layer was about 100 nm. The cells' thickness was fixed with calibrated 13 μm polymer spacers. The cells were filled with the suspension or the pure LC at $T \approx 105°C$ by capillary effect. Both cells, filled with the suspension and with pure LC, had an identical alignment quality and visually appeared the same.

Dielectric measurements were made using a Solarton Schlumberger Impedance Analyzer SI1260 in combination with a Chelsea Dielectric Interface, equipped with a temperature controller. We measured the complex dielectric function of the samples $\varepsilon^* = \varepsilon' - i\varepsilon''$ in a frequency range $f = 0.01$–10^7 Hz. The experimental set-up was calibrated by prior measurements of the empty cells and the cells filled with cyclohexane. During the measurements the sample temperature was in the range $T = -25°C$–$105°C$ and varied in 5°C intervals. The temperature of the samples was stabilized within 0.1°C. The measurements in the cell having planar orientation gave us the values of $\varepsilon_\perp(f)$ perpendicular to the director

of the LC and the measurements in the cell with homeotropic orientation, the values of $\varepsilon_\parallel(f)$ parallel to the director.

Since the ITO layer resistance was rather high we estimated the influence of 'ITO absorption' on the dielectric properties of the cells. For the cells filled (a) with pure ZLI-4801-000 and (b) with the LC with the ferroelectric nano-particles, the capacitances were measured as 1.7 and 3 nF, respectively at 10^5 Hz, which gives relaxation times for the cells ($\tau = C \cdot R$) of about 0.85 and 1.5×10^{-7} s, respectively. The related relaxation frequencies are 1.8 and 1.06 MHz, respectively. For data interpretation one has to remember that the influence of this relaxation starts at frequencies one decade lower.

The dispersion of the dielectric permittivity, $\varepsilon'_\parallel(f)$, and dielectric losses, $\varepsilon''_\parallel(f)$, in the homeotropic cells containing pure LC and the suspension, in the range 1–10^6 Hz are shown in figure 1. These data were observed at $T = 263$ K, and the features of the dielectric spectra can be clearly seen. The data obtained at higher frequencies were strongly affected by the 'ITO relaxation' discussed already. Therefore all data at $f > 1$ MHz are omitted. Nevertheless we note that the high frequency absorption is influenced by the ITO relaxation and seen, for example, as the decrease of ε' to zero.

The dielectric measurements were analysed according to the procedure described elsewhere [9] in which the experimental value of ε' and ε'' were fitted to the real and imaginary parts of equation (1) containing absorption Cole–Cole mechanisms (terms 2 and 3), a conductivity contribution (term 4) and a description of the capacitance of the double layer at low frequencies (term 5).

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-a_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-a_2}} - \frac{iA}{f} + \frac{B}{f^N} \tag{1}$$

ε_i ($i = 1$ and 2) are the low and high frequency limits of the dielectric constant; $\omega = 2\pi f$ (f = frequency); τ is the relaxation time; α is the Cole–Cole distribution parameter; and A, B and N are fitting parameters.

Let us first consider the dielectric loss spectra. Two dielectric absorption bands (1 and 2) with maxima at $f_1^{LC} \approx 10^4$ Hz and $f_2^{LC} \approx 5 \times 10^5$ Hz are seen and can be associated with rotations of molecules of mixture components around their short axes [10]. At frequencies less then 10 Hz an absorption due to the ionic conductivity of the LC can be observed. It should be noted that ferroelectric particles do not absorb electric field in the observed frequency range: their absorption bands lie at $f > 10^7$ Hz.
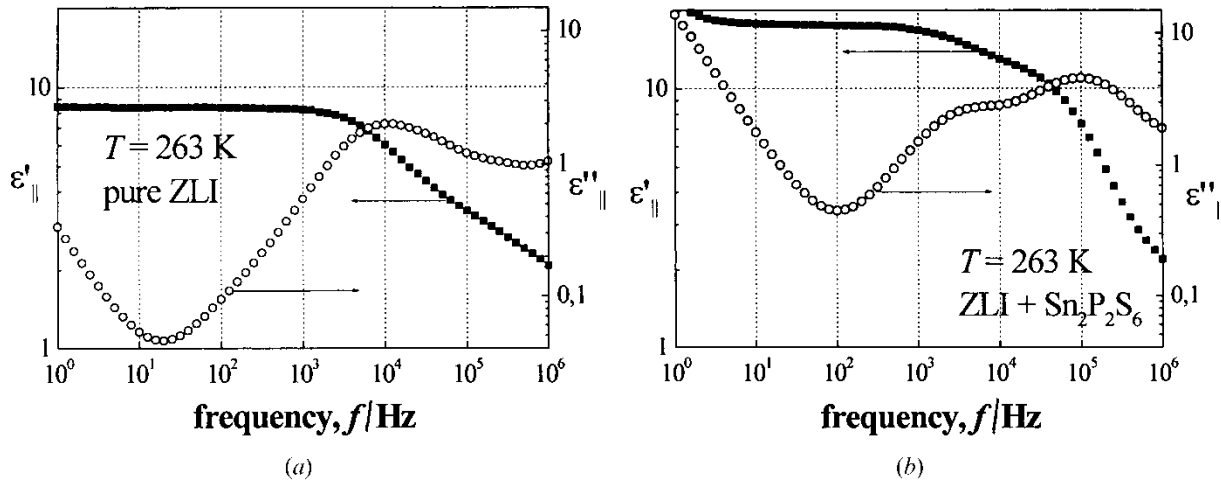
Figure 1. Comparison of $\varepsilon'_\parallel$, $\varepsilon''_\parallel$ for (*a*) pure LC ZLI-4801-000 and (*b*) the nematic ferroelectric suspension. Measurements were carried out in the homeotropic cell.

The doping of the LC with ferroelectric particles caused appreciable changes of the spectra, figure 1 (*b*). The addition of ferroelectric nanoparticles to LC led to an increase of the dielectric absorption and to a shift in the dielectric absorption peaks to lower frequencies; the band at $f_1^{LC} \approx 10^4$ Hz was shifted to $f_1^{susp} \approx 3.5 \times 10^3$ Hz, and the band at $f_2^{LC} \approx 5 \times 10^5$ Hz to $f_2^{susp} \approx 10^5$ Hz. These shifts in the frequency indicate an increase in the relaxation times for the reorientation of the molecules of the LC components: $\tau = 1/2\pi f$. The temperature dependences of the relaxation times $\tau_{1,2}^{LC,susp}$ are shown in figure 2. We have not taken into account all relaxation times $\tau < 8 \times 10^{-7}$ s because the high frequency absorption was strongly affected by the 'ITO relaxation'.

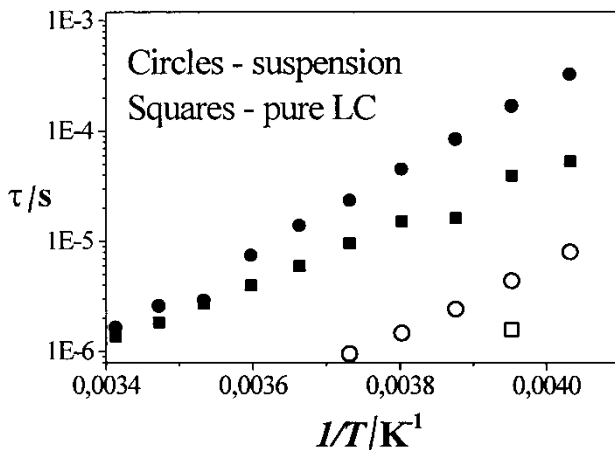One can see that the dependence of the relaxation

Figure 2. Temperature dependence of relaxation times for the dielectric absorption band-1 (filled symbols) and for band-2 (open symbols).

times $\tau^{LC,susp}$ $(1/T)$ is well described by an Arrhenius law except for the curve $\tau_2^{LC,susp}(1/T)$, and the activation energy for the pure LC E_1^{LC} is 50 kJ; and for the LC with ferro-particles $E_1^{susp} = 73$ kJ. Thus, the activation energy of the rotation of the LC molecules increases in the suspension. This, together with the increase in the relaxation times τ^{susp} suggests a strong interaction exists between the LC molecules and the ferroelectric particles. The LC molecules interact with both spontaneous and permanent dipole moments of the particles. In addition, LC molecules interact with the particle surfaces (anchoring effect). All these interactions impede the rotation of the LC molecules in the vicinity of the particles and hence result in a decrease of the absorption bands' frequencies.

In addition to the shifts in the absorption band-1 and band-2, the analyses of the spectra showed that the addition of ferroelectric particles leads to an increase both in the amplitude of the absorption bands and of their width. These changes also indicate strong interaction between the particles and the LC host. The large dipole moment of ferro-particles causes a strengthening of the local field, resulting in stronger oscillations of the molecules and, therefore, in larger absorptions of electric field by the LC molecules. The broadening of the absorption bands is due to dissipation of the energy during the reorientation of the LC molecules close to the particle surfaces.

We also observed a significant increase in the dielectric loss caused by an increase in the conductivity of the composite at low frequencies. The value of conductivity was calculated from fitting curves of dielectric permittivity and losses at frequencies less than 10 Hz. The dependences of the conductivity of the LC and the suspension on temperature are shown in
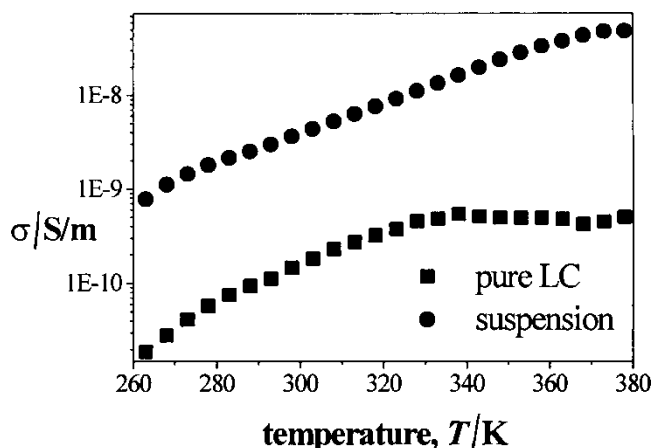
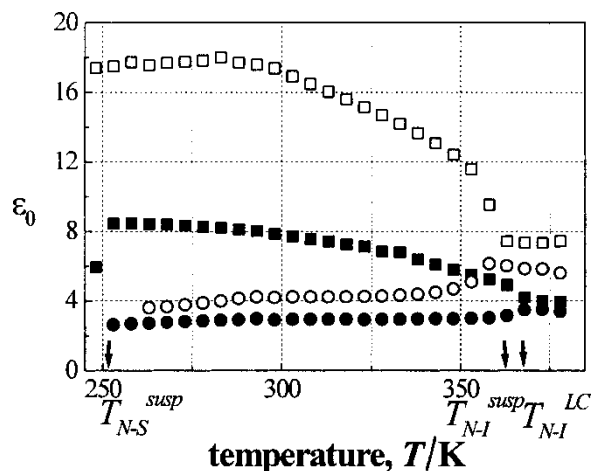Figure 3. Temperature dependence of the conductivity of the pure LC, and with ferroelectric nanoparticles.

Figure 4. Temperature dependence of $\varepsilon_{0\parallel}$ (squares) and $\varepsilon_{0\perp}$ (circles) of the pure LC (filled symbols) and of the suspensions (open symbols). T_{NS}^{susp} = transition temperature of suspension from nematic to smectic phase; T_{NI}^{susp} = transition temperature of suspension from nematic to isotropic phase; T_{NI}^{LC} = transition temperature of pure LC from nematic to isotropic phase.

figure 3. It can be seen that the conductivity of the suspension increases by two orders of magnitude with respect to that of the LC and has an unusual temperature dependence. The nature of the elevated conductivity of the suspension deserves additional study. We found that the mixture of LC with only the surfactant, in a concentration which was much larger than that present in the suspension, did not increase the conductivity of the LC. Thus the increased conductivity is not directly caused by the surfactant but is connected with the ferro-particles, which are semiconductors.

The ferroelectric particles affect not only dielectric losses, $\varepsilon''(f)$, but also the dielectric permittivity, $\varepsilon'(f)$. The fitting of the curves $\varepsilon'(f)$ using equation (1), measured at different temperatures in homeotropic and planar cells, allowed us to plot the temperature dependences $\varepsilon_{0\parallel}(T)$ and $\varepsilon_{0\perp}(T)$ for the pure LC and for the suspension (figure 4). At room temperature $T = 300\,\text{K}$, $\varepsilon_{0\parallel}^{LC} = 7.8$, $\varepsilon_{0\perp}^{LC} = 2.9$; and $\varepsilon_{0\parallel}^{susp} = 17.1$, $\varepsilon_{0\perp}^{susp} = 4.2$ is, close to estimates obtained from the measurements of the Freedericksz transition [5]. One can see that not only components $\varepsilon_{0\parallel}$, $\varepsilon_{0\perp}$ but their anisotropy $\varepsilon_a = \varepsilon_{0\parallel} - \varepsilon_{0\perp}$ increase significantly. This suggests that the anisotropic ferroelectric particles are ordered in the suspension.

If the dielectric permittivity of the particles is large compared with that of the host, the effective dielectric permittivity of the suspension is largely determined by the dielectric permittivity of the host.† We believe that the clear increase in the dielectric permittivity of the nematic ferroelectric suspension is caused by the permanent dipole moments and geometrical anisotropy of the ferroelectric nanoparticles, which are not taken

into account in the theory of dielectric properties of heterogeneous systems.

3. Conclusions

In summary, doping a nematic LC with a small amount of ferroelectric nanoparticles strongly affects the dielectric properties of the system. In particular, the ferroelectric particles result in a shift of the adsorption bands corresponding to the rotation of LC molecules around their short axes to lower frequencies, and increases in the amplitude and width of the absorption bands. This suggests that strong interactions occur between the LC molecules and the particles, resulting from the large dipole moment and high polarizability of the ferro-particles. The ferroelectric particles affect not only the dielectric losses, but also the dielectric permittivity of the system: the static dielectric permittivity and its anisotropy for the suspension are more than twice those of the pure LC. Thus, a strong increase of the static dielectric permittivity may be associated with the permanent dipole moments of the ferro-particles.

†Logarithm law of alligation by K. Lichtenecker.

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