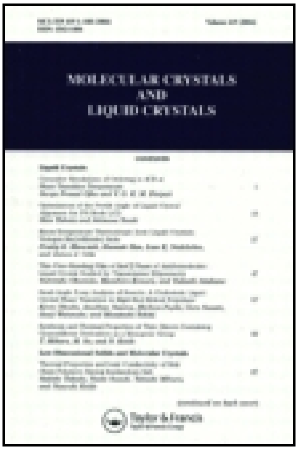

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Enhanced Dielectric Response of Liquid Crystal Ferroelectric Suspension

O. Buchnev [a], E. Ouskova∗ [a], Yu. Reznikov [a], V. Reshetnyak [a b], H. Kresse [c] & A. Grabar [d]

[a] Institute of Physics, Kyiv, Ukraine

[b] Kyiv National Taras Shevchenko University, Kyiv, Ukraine

[c] Halle-Wittenberg, Martin-Luther Universität, Halle, Germany

[d] Institute of Solid State Physics and Chemistry of Uzhgorod National University, Uzhgorod, Ukraine

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ENHANCED DIELECTRIC RESPONSE OF LIQUID CRYSTAL FERROELECTRIC SUSPENSION

O. Buchnev, E. Ouskova, and Yu. Reznikov*
Institute of Physics, Pr. Nauki 46, Kyiv 03039, Ukraine

V. Reshetnyak
Institute of Physics, Pr. Nauki 46, Kyiv 03039, Ukraine and Kyiv National Taras Shevchenko University, Pr.Glushkova 6, Kyiv 03022, Ukraine

H. Kresse
Martin-Luther Universität, Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, D-06108, Halle, Germany

A. Grabar
Institute of Solid State Physics and Chemistry of Uzhgorod National University, Pidhirna 46, 88000, Uzhgorod, Ukraine

It was found that doping of tiny ferroelectric particles to a nematic liquid crystal (LC) strongly affects dielectric properties of the system. The doping increases dielectric response of the LC due to interaction between LC molecules and particles, which possess large dipole moment and high polarisability. The suspension reveals high dielectric response on either side of the Curie temperature, T_{Curie}, and peculiarity at the vicinity of T_{Curie}. This result points at retention of dipole ordering above Curie temperature that may be a result of a memory effect.

Keywords: dielectric properties; ferroelectric particles; liquid crystal suspension; nematic liquid crystal ferroelectric suspension

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*Corresponding author. Tel.: 38044–2650779, Fax: 38044–2650830, E-mail: ouskova@iop.kiev.ua

1. INTRODUCTION

Liquid crystal (LC) suspensions have attracted much attention in the last decades because of their unique electro- and magneto-optics and possible interesting applications. Suspensions of aerosil in LC matrices [1,2] and suspensions of ferro-particles in nematic LC's [3,4] are a typical example of these systems.

Traditional LC suspension are highly heterogeneous systems, where suspending materials have weight concentration of tens percents. Recently it was found that low concentrated suspensions of nano-ferromagnetic and nano-ferroelectric particles in nematic LC possess unique properties [5,6]. The nano-particles have certain size in order not to disturb the LC orientation producing macroscopically homogeneous structure, and at the same time to maintain the intrinsic properties of the materials from which they are made (e.g., ferromagnetism or ferroelectricity) and to share their intrinsic properties with the LC matrix due to anchoring with LC. Obtained stable nano-suspensions appeared similar to pure LC with no readily apparent evidence of dissolved particles were studied.

In Reference [5] it was found that embedding of ferroelectric nano-particles $Sn_2P_2S_6$ in nematic LC at a small volume concentration ($c_v < 10^{-2}$) did not change their elastic and anchoring properties, but resulted in enhanced dielectric response. The essential decrease of the Freedericksz transition voltage and acceleration of the director reorientation in the electric field were also observed in [5]. The following measurement of the complex dielectric function $\varepsilon^* = \varepsilon' - i\varepsilon''$ of the suspension of ferroelectric nano-particles $Sn_2P_2S_6$ in nematic LC (frequency range $f = 0.01 \div 10^7$ Hz; temperature range $T = 105°\mathrm{C} \div -25°\mathrm{C}$ with 5 degree interval) revealed a shift of the dielectric absorption peaks to lower frequencies, increase of the amplitude of the absorption bands and their broadening in comparison with pure LC. It points at strong interaction between LC molecules and the particles caused by large dipole moment and high polarisability of the ferro-particles. The doping of LC with ferroelectric particles strongly increased the value of dielectric permittivity, $\varepsilon'(f)$, of the system. The data of the dielectric measurements were analyzed accordingly to the procedure [7] where experimental points ε' and ε'' were fitted together to the real and imaginary parts of Eq. (1) having absorption Cole-Cole mechanisms (term 2 and 3), conductivity contribution (term 4) and term 5 for the description of the capacitance of the double layer at low frequencies.

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}} - \frac{iA}{f} + \frac{B}{f^N}, \qquad (1)$$

where 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 fit parameters. The calculated value of real dielectric permittivity (ε_0) of the suspension was almost two times higher that one of LC (Fig. 1) [6].

The evident increase of the dielectric permittivity of LC after doping with ferroelectric particles is rather uncommon fact. It is well known that doping of dielectric media with particles which dielectric constant is much higher than that of the matrix (that is our case) does not result in notable increase of the effective dielectric constant of the suspension [8]. A natural cause of the observed effect may be a permanent dipole moment of the particles in a ferroelectric state, which is not taken in account in known models of suspensions' dielectric properties. The permanent dipole moment of the ferro-particles vanishes above Curie temperature, T_{Curie}. Besides, the dielectric constant of ferroelectrics reveals a peculiarity around T_{Curie}. Therefore, the investigation of the dielectric properties of the LC ferroelectric suspensions nearby T_{Curie} is very actual to set the origin of the unique dielectric properties of ferroelectric LC suspensions.

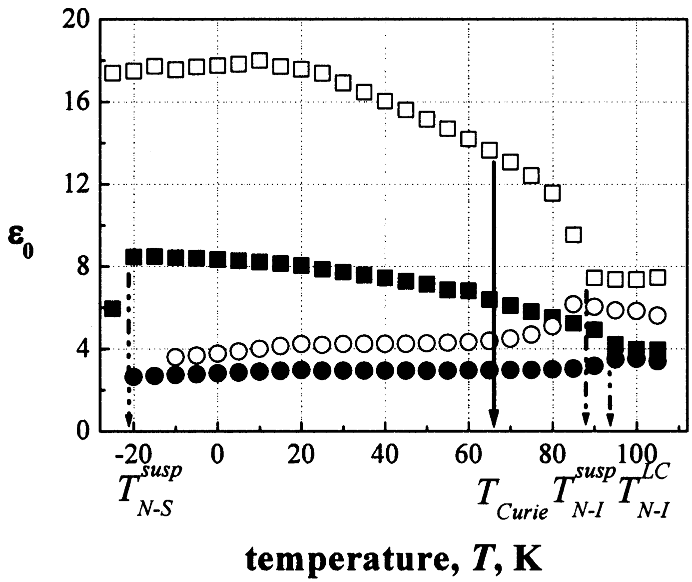

FIGURE 1 Temperature dependence of dielectric permittivity $\varepsilon_{0||}$ (squares) and $\varepsilon_{0\perp}$ (circles) of the pure LC (filled symbols) and of the suspensions (transparent symbols). T^{susp}_{N-S} – transition temperature of suspension from nematic to smectic phase; T^{susp}_{N-I} – transition temperature of suspension from nematic to isotropic phase; T^{LC}_{N-I} – transition temperature of pure LC from nematic to isotropic phase; T_{Curie} – Curie temperature of ferroelectric nano-particles $Sn_2P_2S_6$.

In the present publication we report on the studies of dielectric properties of the nematic ferroelectric liquid crystal suspension near Curie temperature of ferroelectric particles $Sn_2P_2S_6$ and introduce a model that takes into account dipole moment and geometrical anisotropy of ferroelectric nano-particles and explains the dielectric properties of LC heterogeneous system.

2. MATERIALS AND EXPERIMENTS

We used the ferroelectric liquid crystal suspension consisted of nematic LC ZLI-4801-000 (Merk) (temperature of the transition to isotropic state, $T_{N\text{-}I} = 93^\circ\mathrm{C}$, dielectric anisotropy – $\varepsilon_a^{ZLI} = \varepsilon_{||}^{ZLI} - \varepsilon_{\perp}^{ZLI} = 8.3 - 3.2 = 5.1$) and powder of ferroelectric thiohypodiphosphate, $Sn_2P_2S_6$, (Uzhgorod University). Curie temperature of $Sn_2P_2S_6$ is $T_{Curie} \approx 66^\circ\mathrm{C}$ and spontaneous polarization at room temperature is $14\,\mu\mathrm{C/cm^2}$ parallel to the [101] direction of the monoclinic cell [9]. The value of dielectric constant of $Sn_2P_2S_6$ along the main axis strongly depends on the quality of the samples and varies from 200 for ceramics sample to 9000 for monodomain crystals [10].

The suspension was prepared by milling micro-particles of $Sn_2P_2S_6$ ($\cong 1\,\mu$m size) mixed with oleic acid in a weight ratio of 1:2. The method of suspension preparation is fully described in Reference [6]. The characteristic size of the particles in the suspension was about 100 nm and their volume concentration, f_v, was about 0.03% in the LC matrix.

We produced the cells filled with the suspension or pure LC. The cells were made from two flat glass substrates coated with guard conducting ITO layers. To get planar alignment of the suspension and LC, the conducting layers were covered with polyvinyl-cinammate irradiated with polarized UV-light [11]. The value of the pretilt angle was $3.5 \pm 0.5^\circ$. The homeotropic alignment of the suspension and the pure LC was obtained by covering the ITO layers with polyimide PI−1211. The thickness of both types of the dielectric aligning layers was about 100 nm. The thickness of the cells was given with calibrated 13 μm polymer spacers. The cells were filled with the suspension and LC at $T \approx 110^\circ\mathrm{C}$ by capillary effect.

The temperature of the cells was controlled with HS1 hot stage, which is operated by Instec MK2 temperature controller (HS1-I), within 0.01°C accuracy. The temperature of the samples was set in a range $T = 60^\circ \div 70^\circ\mathrm{C}$ with 0.5 degree interval (while our previous measurements [6] were made with 5 degree interval). We measured the impedance of the cell, that is the complex dielectric permittivity of the samples, $\varepsilon = \varepsilon' + \varepsilon''$, at a frequency $f = 10^3$; 10^4 Hz with National Instruments data acquisition board with standard auto balancing bridge method. The frequencies were chosen with correspondence to the frequency dependencies of $\varepsilon'_{||}, \varepsilon''_{||}, \varepsilon'_{\perp}, \varepsilon''_{\perp}$ of nematic ferroelectric suspension obtained in [6]. In the Reference [6] it was found that at the chosen frequencies there was no dielectric absorption of ferroelectric liquid crystal suspension and there was no influence of the double electric layers. The experimental set-up was calibrated by the prior measurements of the empty cells.

The obtained temperature dependence of the dielectric constant $\varepsilon_{||}$ for $f = 10^3$ and 10^4 Hz in homeotropic cell is shown on Figure 2, and the dependence of $\varepsilon_{\perp}$ in planar cell at the same frequencies is shown on Figure 3.

One can point the following particular features of these dependencies:

- There is an evident peculiarity in behavior of both $\varepsilon_{||}^{susp}$ and $\varepsilon_{\perp}^{susp}$ in the vicinity of the Curie point, T_{Curie}.
- Both $\varepsilon_{||}^{susp}$ and $\varepsilon_{\perp}^{susp}$, as well as $\Delta\varepsilon^{susp}$ are almost twice larger than the same values of pure LC. It is valid as for $T > T_{Curie}$ as for $T < T_{Curie}$.

3. DISCUSSION

To find the effective dielectric permittivity of inhomogeneous medium is rather hard task. The most used theory is Maxwell–Garnett theory [8]. According to it, scalar dielectric permittivity of a medium consisted of inclusions (e.g., particles) with dielectric permittivity ε^p and the matrix with dielectric permittivity ε^{matrix} is

$$\varepsilon = \frac{(1 - f_v)\varepsilon^{matrix} + f_v \beta \varepsilon^p}{1 - f_v + f_v \beta}, \tag{2}$$

where f_v is a volume fraction of the inclusions; β depends on the shape of the inclusions.

If the inclusions are spherical, then

$$\beta = \frac{3\varepsilon^{matrix}}{\varepsilon^p + 2\varepsilon^{matrix}} \tag{3}$$

and Exp.(2) will be

$$\varepsilon = \varepsilon^{matrix}\left[1 + \frac{3f_v\left(\frac{\varepsilon^p - \varepsilon^{matrix}}{\varepsilon^p + \varepsilon^{matrix}}\right)}{1 - f_v\left(\frac{\varepsilon^p - \varepsilon^{matrix}}{\varepsilon^p + \varepsilon^{matrix}}\right)}\right]. \tag{4}$$

If $\varepsilon^p \gg \varepsilon^{matrix}$ then Exp.(4) turns into $\varepsilon \approx \varepsilon^{matrix}(1 + 3f_v)$ that is dielectric permittivity of the suspension of low concentrated spherical particles is determined by permittivity of the matrix and ε, and does not really differ from ε^{matrix}. Geometrical anisotropy of the particle changes the resulting effective dielectric function of suspension, but not significantly.

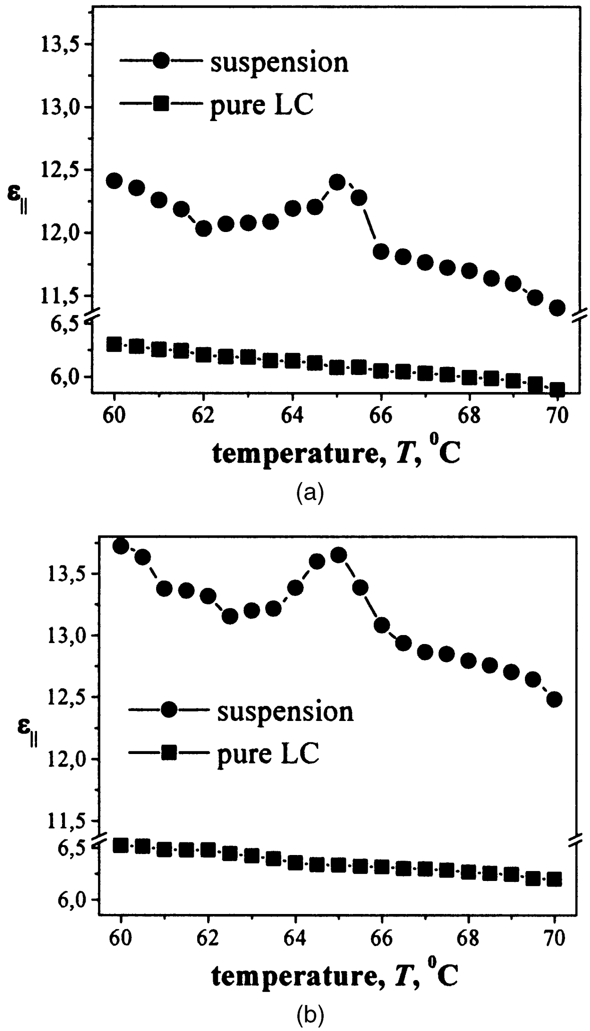

FIGURE 2 Temperature dependence of the effective dielectric constant $\varepsilon_{||}$ at f = 10 kHz (a) and f = 1 kHz (b), U = 0.6 V. Homeotropic cell.

If inclusions are *ferroelectric particles* then another possibility to get increased dielectric permittivity is to take into account spontaneous polarization of the particles in the ferroelectric phase. It has been done recently by Reshetnyak [12]. He considered a suspension of ferroelectric ellipsoidal particles oriented in nematic LC matrix along a local director, suggesting permanent polarization $\vec{d}$ of each particle to be parallel or anti-parallel to

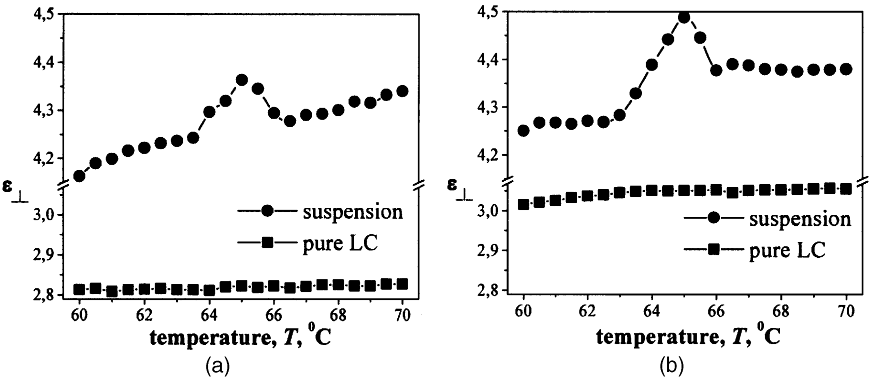

FIGURE 3 Temperature dependence of the effective dielectric constant $\varepsilon_\perp$ at $f = 10\,\mathrm{kHz}$ (a) and $f = 1\,\mathrm{kHz}$ (b), $U = 0.6\,\mathrm{V}$. Planar cell.

the director. It was also supposed that the main axes of the polarisability tensor of the particles coincided with particles long axis and local LC director. At these assumptions Reshetnyak got the following expressions for dielectric constant of ferroelectric suspension:

$$\varepsilon_\perp^{susp} = \frac{f_v T_\perp \varepsilon_\perp^P + (1 - f_v)\varepsilon_\perp^{LC}}{1 - f_v + f_v T_\perp}, \tag{5}$$

$$\varepsilon_{||}^{susp} = \frac{f_v T_{||} \varepsilon_{||}^P + (1 - f_v)\varepsilon_{||}^{LC} + f_v \frac{d^2 v}{\varepsilon_0 k_B T} \frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})}}{1 - f_v + f_v T_{||}}. \tag{6}$$

Here $\tilde{\varepsilon}^P = \frac{1}{3} Sp\varepsilon^P$ and $\tilde{\varepsilon}^{LC} = \frac{1}{3} Sp\varepsilon^{LC}$; v is a volume of the particles; $T_\perp$, $T_{||}$ are matrix components of the dependence $\langle \vec{\boldsymbol{E}}^P \rangle = \hat{T} \langle \vec{\boldsymbol{E}}^{LC} \rangle$, $\langle \vec{E}^p \rangle$ and $\langle \vec{E}^{LC} \rangle$ are averaged over physically small volume values of electric field inside particles and LC; $\lambda_{||} = \frac{1-e^2}{e^3}(\mathrm{arth}e - e)$ and $\lambda_\perp = \frac{1}{2}\left(1 - \lambda_{||}\right)$ are the depolarization factors, $e = \sqrt{1 - b^2/a^2}$ is the eccentricity, and $a, b (a > b)$ are the semi-axes of spheroid particles.

The parallel component of the dielectric constant, $\varepsilon_{||}^{susp}$, contains the additional term related to contribution due to permanent polarisation:

$$\delta\varepsilon_{||}^{susp} = f_v \frac{d^2 v}{\varepsilon_0 k_B T} \frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})}. \tag{7}$$

Thus, both components, $\varepsilon_\perp^{susp}$ and $\varepsilon_{||}^{susp}$, can have increased values compared to pure LC. If the component $\varepsilon_\perp^{susp}$ is increased only due to higher polarizability of particles, permanent, induced polarisations and geometric anisotropy can give the contribution to the increase of $\varepsilon_{||}^{susp}$.

Let us consider the experimental results from the standpoint of the conclusions [12]. As seen from Figure 1, both values $\varepsilon_\perp$, $\varepsilon_{||}$, and anisotropy $\Delta\varepsilon$ increase with the doping of LC. At first glance it means that both geometric anisotropy and ferroelectricity give contribution to $\varepsilon_{||}^{susp}$. Nevertheless, a sufficient contribution of the geometric anisotropy of the particles to the dielectric permittivity is doubtful to expect. Really, if consider very elongated particles ($b/a = 0.1$), then $\lambda_{||} \approx 0.02$ [13]. For small volume fraction of particles and neglecting permanent polarisation we get approximately $\varepsilon_{||}^{susp} \approx f_v \frac{\tilde{\varepsilon}^{LC}}{\lambda_{||}\tilde{\varepsilon}^{P}} \varepsilon_{||}^{P} + (1 - f_v)\varepsilon_{||}^{LC} \approx \varepsilon_{||}^{LC}(1 + 50 f_v)$ that is in our case ($f_v \approx 3 \cdot 10^{-4}$) the value $\delta\varepsilon_{||}^{susp} \approx 1.5 \cdot 10^{-2}$ is almost in 3 orders less then the experimental value $\delta\varepsilon_{||}^{susp} \approx 9.5$. For our experimental parameters ($\vec{d} \approx 14 \cdot 10^{-2} C/m^2,\ T = 22^\circ$C) and realistic value $\lambda_{||} = 0.3$ the experimental increase $\delta\varepsilon_{||}^{susp} \approx 9.5$ corresponds in accordance with (7) to reasonable value $\varepsilon^p \approx 730$. Thus, the contribution of the ferroelectricity to the dielectric constant $\varepsilon_{||}^{susp}$ is dominant in our experiments.

One can see two discrepancy between the theory [12] and the experimental results. The first one is the evident increase of the component $\varepsilon_\perp$. We believe that it is due to that the theory [12] considers perfectly oriented particles with permanent polarisation parallel to the particles long axis that may be not the case. In reality, the order parameter of the particles in LC, $S^p \leq S^{LC} \approx 0.4$ and there may be non zero angle of permanent polarisation with particles long axis. It should result in appearance of the term being analogous to (7) in the expression for $\varepsilon_\perp^{susp}$. The second difficulty is that in contradiction to the Exp.(7) the increased dielectric permitivity keeps even above the Curie point. This fact can be explained if to suppose that a permanent dipole moments keep exist in the suspension when the particles structure transfers to paraelectric phase. This situation could be realized when the dipole LC molecules adsorb on the ferroparticles surface forming a dipole oriented layer, which does not disappear after particles loose their ferroelectricity.

4. CONCLUSIONS

We found that doping of tiny ferroelectric particles to a nematic liquid crystal (LC) strongly affects dielectric properties of the system. The doping increases dielectric response of the LC due to interaction between LC molecules and particles, which possess large dipole moment and high polarisability. The suspension reveals high dielectric response on either side of the Curie temperature, T_{Curie}, and peculiarity at the vicinity of T_{Curie}. This result points at retention of dipole ordering above Curie temperature that may be a result of a memory effect.

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