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Optical probe, local fields, and Lorentz factor in ferroelectrics

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An optical probe is suggested that allows measurements of the local field and Lorentz factor (L) in ferroelectric medium. The copolymer poly (vinyliden fluoride/trifluoroethylene) is mixed with Pd-tetraphenylporphyrin (TPP-Pd) that has a very narrow absorption band. Thus TPP-Pd serves as a molecular optical probe of the local field. During the switching of the electric field lower than the coercive one the factor L of a non-polarized ferroelectric mixture is found to be of about $1/3$ that corresponds to the random distribution of molecular dipoles in the ferroelectric. With increasing field the dipole orientation acquires a lower symmetry and L tends to zero as predicted by lattice sum calculations for vinyliden-fluoride. The knowledge of the field dependence of L and the usage of the optical probe makes it possible to measure directly the local and macroscopic fields in the individual elements of various ferroelectric-dielectric heterostructures.

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The modern physics of ferroelectrics is now being confronted with an acute problem of measuring internal electric fields in nanoscale devices. The study of internal fields is very important for novel practical applications of both inorganic and organic ferroelectric heterostructures such as memory cells, transistors [1], solar cells [2], tunable resistors [3], and many others [4]. However, it is very difficult to measure correctly macroscopic fields even in a simplest heterostructure that comprises of ferroelectric and dielectric layer placed between two metal electrodes connected to the voltage source. In this case, Maxwell equation $\operatorname{div}\mathbf{D} = \rho/\varepsilon_0$ can't be resolved because the space distribution of density of charge ρ across the layers or near electrodes, as a rule, is unknown. The problem can be solved with different local field optical probes located in dielectric Langmuir–Blodgett layers [5], polymers [6], organic semiconductors [7], and other heterostructures [8]. In all these cases, only dyes with absorption spectra sensitive to the electric field were used as the probes. By using an electroabsorption technique it was possible to find the strength of the local field and then the macroscopic field in the *isotropic dye layers* with Lorentz factor $L = 1/3$.

The aim of the present paper is to suggest a new method of macroscopic fields measurements in ferroelectric heterostructures with the help of an optical molecular probe incorporated into the volume of the ferroelectric. The probe measures the local field of the ferroelectric medium which is not isotropic and, to find the macroscopic field, we need the corresponding Lorentz factor. It seems that up to now there was no discussion concerning the dependence of the Lorentz factor upon a strong field applied to the initially non-polarized ferroelectric so that the field could change a symmetry of the material. To begin the discussion of this problem, we have chosen a ferroelectric copolymer polyvinylidene-fluoride (70 %) with trifluoroethylene (30 %), P(VDF-TrFE) [9], particularly attractive for Langmuir–Blodgett film technology [10]. For this copolymer the Lorentz factor was estimated just for a particular voltage [11] and the other available information deals only with the lattice sum calculations of the Lorentz factor in the ideally polarized polyvinylidene-fluoride, the material very similar to P(VDF-TrFE) [12, 13].

As an optical probe for ferroelectric medium a *meso*-substituted Pd-tetraphenylporphyrin (TPP-Pd, Fig. 1 Inset) studied earlier in detail [14] has been adopted. It was mixed with the copolymer in the ratio of 1:30 in cyclohexanone. The mixed solution was spread on the surface of ultrapure distilled water in a Langmuir trough and compressed to a surface pressure of 4.4 mN/m. Then, cyclohexanone was evaporated and fifty layers of the mixture were transferred by the horizontal lift technique from the water surface onto the glass substrate equipped with a vacuum evaporated, semitransparent aluminium stripe electrode. After annealing at 110 °C for 45 min, the three top Al stripes were evaporated perpendicularly to the bottom stripe forming three capacitors with an electrode area of $S = 14\,\mathrm{mm}^2$. The thickness of the samples was measured by a Linnik interferometer.

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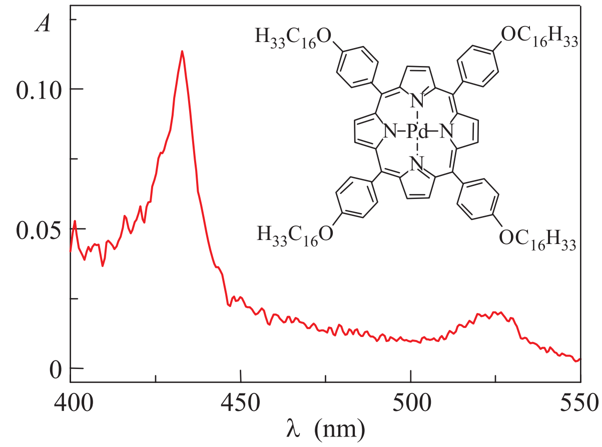

Fig. 1. Inset – molecular structure of meso-substituted palladium-tetraphenylporphirin (TPP-Pd). Main panel – absorption band of TPP-Pd mixed with ferroelectric copolymer P(VDF-TrFE) after annealing the mixture. $A_{\max} = 0.1$ (at 433 nm), $\partial A/\partial\lambda = -1.27\cdot 10^7\,\mathrm{m}^{-1}$ ($\lambda = 436$ nm)

Sawyer–Tower technique were used. The latter provides the hysteresis displacement loops of which few are shown in Inset to Fig. 2. The maximal displacement values D_m for all measured loops are represented by Curve *1* in Fig. 2. The displacement amplitude $D_m = \varepsilon_0\varepsilon E_m + P_{z,m}$

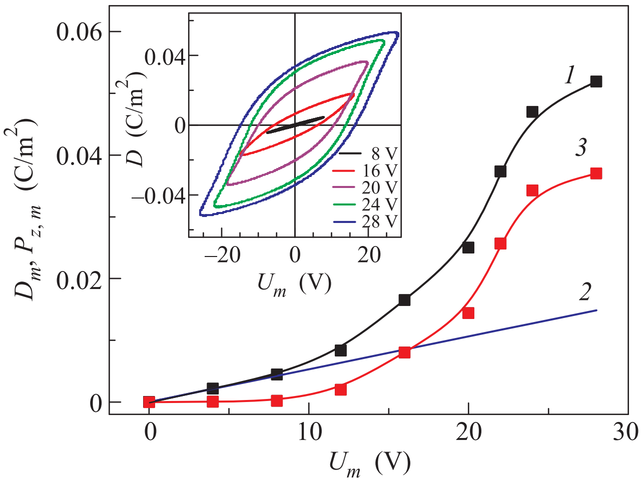

Fig. 2. Inset – selected displacement loops measured by the Sawyer–Tower technique (amplitudes $U_m = 8$, 16, 20, 24, and 28 V). Main panel – applied voltage (U_m) dependencies of the dielectric displacement D_m (curve *1*), linear part of displacement D_{lin} (straight line *2*), and switched spontaneous polarization $P_{z,m}$ (curve *3*)

has both a linear part and a field dependent switchable part of spontaneous polarization $P_{z,m}$. Indeed, at the voltage amplitudes $U_m < 10$ V curve *1* is evidently linear that marked off by straight line *2*. From this line $D_{m,\mathrm{lin}} = \varepsilon_0\varepsilon E_m$ ($\varepsilon_0 = 8.85\cdot 10^{-12}$ F/m) we find $\varepsilon = 9$ because the macroscopic field $E_m = U_m/d$ is known (here, a sample thickness is $d = 150$ nm and U_m is the amplitude of voltage $U_m \sin\omega t$ applied across the electrodes at frequency $f = \omega/2\pi = 30$ Hz). After subtracting the linear contribution from D_m the amplitude values of the switchable part of polarization $P_{z,m}(U_m)$ were found and shown by curve *3*.

It is essential that the displacement loops were recorded along with the electroabsorption increment loops necessary for local field measurements. The pristine TPP-Pd is an isotropic material [14] with Lorentz factor $L = 1/3$. Its molecule has no dipole moment and possesses an individual, very narrow (7 nm at the half-width) absorption band with the maximum at a wavelength of $\lambda = 433$ nm. This band is characterized by a difference in molecular polarizabilities $\Delta\alpha = \alpha_e - \alpha_g = 9\pm 2$ Å^3 of the excited and the ground states. In solid solution with copolymer P(VDF-TrFE), even after annealing, the absorption spectrum of TPP-Pd holds its generic shape, as shown in Fig. 1. Since the molecule is non-polar, one can use a simple formula, which relates the spectral shift $\Delta\nu$ ($\nu = 1/\lambda$ is a wave number) to the square of the local field [15]

$$hc\Delta\nu = -\frac{1}{2}\Delta\alpha E_{\mathrm{loc}}^2. \qquad (1)$$

Here, h and c are Planck constant and light velocity in vacuum, respectively. The spectral shifts $\Delta\nu$ can be easily converted to $\Delta\lambda$ and the field-induced change of an absorbance amplitude $\Delta A(\lambda)$ using the experimental value of derivative $\partial A/\partial\lambda$,

$$\Delta A = -\frac{\Delta\alpha(\lambda^2\partial A/\partial\lambda)}{2hc}E_{\mathrm{loc}}^2. \qquad (2)$$

Due to very high value of derivative $\partial A/\partial\lambda = -1.27\times 10^7\,\mathrm{m}^{-1}$, the field-induced spectral shift of the band $\Delta\lambda$ results in a significant change of the absorbance at a wavelength of $\lambda = 436$ nm. The values of ΔA are founded by the electroabsorption technique [6–8] and the local field E_{loc} acting on a TPP-Pd molecule in the ferroelectric medium is deduced from Eq. (2).

The measurements of the Lorentz factor were carried out both in the course of the ferroelectric switching (*dynamic mode*) and during local field relaxation after poling the ferroelectric with voltage pulses of $\Delta t = 1$ s duration (*static mode*). In the first experiment, an external a.c. voltage $U_m \sin\omega t$ at frequency $f = \omega/2\pi = 30$ Hz applied to the electrodes provides a macroscopic field of amplitude $E_m = U_m/d$ (in this sample $d = 140$ nm) and causes the local field acting on the guest molecule of TPP-Pd. The hysteretic values of ΔA are measured at $\lambda = 436$ nm for each particular voltage amplitude U_m using the electroabsorption technique. Few such hysteresis loops are shown in the Inset to Fig. 3. Note that

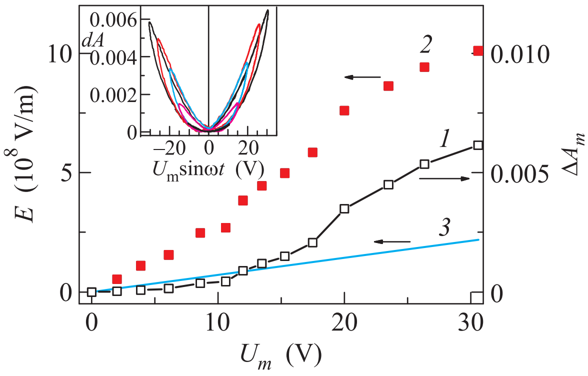

Fig. 3. Inset – selected electroabsorption loops of absorption increment ΔA of ferroelectric mixture at a wavelength $\lambda = 436$ nm as functions of voltage $U_m \sin\omega t$ applied to the electrodes (selected amplitudes U_m = 11, 15, 20, 26, and 30 V). Main panel – maxima of absorption increment ΔA_m as functions of the external voltage amplitudes U_m (curve *1*, right scale); local field amplitudes $E_{\mathrm{loc},m}$ (curve *2*, left scale), and macroscopic field amplitudes E_m (curve *3*, left scale) as functions of U_m

due to the quadratic dependence of ΔA on the applied voltage electroabsorption loops are always positive and have a butterfly shape. Here we are only interested in the maximal values of these loops. Curve *1* in Fig. 3 combines all amplitude values ΔA_m dependent on voltage amplitude U_m. Then, the local field amplitudes $E_{\mathrm{loc},m}$ acting on the probe were directly calculated using Eq. (2) (curve *2* in the same figure). For comparison the macroscopic field E_m in the mixture is represented by curve *3*. The ratio $\gamma_z = E_{\mathrm{loc},m}/E_m$ is a component of the local field tensor or enhancement factor [12] and within the linear part at $U_m < 10$ V the factor $\gamma_z = 3.7$.

As soon as the local and macroscopic fields in the ferroelectric mixture were found as functions of the voltage across the electrodes we can raise an issue of the Lorentz factor voltage dependence in the dynamic switching experiment. Consider an equation for the local field that is valid for a homogeneous ferroelectric structure with a material of not necessarily cubic [16] but of any symmetry [12, 17]:

$$E_{\mathrm{loc}} = E + L_z\frac{P}{\varepsilon_0} = E + L_z(\varepsilon - 1)E + L_z\frac{P_z}{\varepsilon_0}. \qquad (3)$$

Here, L_z is a z-component of Lorentz tensor along the axis perpendicular to the electrodes, P is the total polarization, and P_z is the switchable part of the spontaneous polarization. The macroscopic field $E = E_0 + E_{\mathrm{dep}}$ includes the field E_0 of the free charges outside of the ferroelectric and depolarization field $E_{\mathrm{dep}} = NP/\varepsilon_0$ where $N = 1$ corresponding to the "coin" geometry of our thin film. The linear part of Eq. (3) may be written as $\gamma_z = E_{\mathrm{loc}}/E = 1 + L_z(\varepsilon - 1)$, and with $\varepsilon = 9$ and $\gamma_z = 3.7$ found above we obtain the expected value of $L_z = 0.33$ for isotropic medium.

Now we have amplitudes E_m and $E_{\mathrm{loc},m}$ for macroscopic and local fields, respectively, calculated from all the electroabsorption hysteresis loops and polarization $P_{z,m}$ from the displacement loops (on account of different sample thickness). Using these data and solving Eq. (3) for L_z we have found a voltage dependence of the Lorentz factor for the ferroelectric mixture:

$$L_z(U_m) = \frac{E_{\mathrm{loc},m}(U_m) - E_m(U_m)}{(\varepsilon - 1)E_m(U_m) + P_{z,m}(U_m)/\varepsilon_0}. \qquad (4)$$

Curve *1* shown in Fig. 4 seems intriguing. At a low volt-

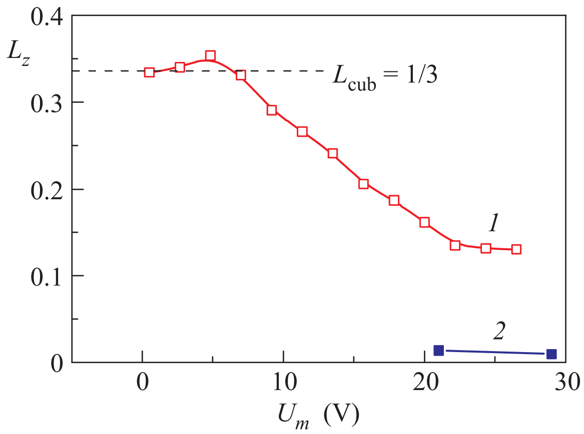

Fig. 4. Lorentz factor L_z for a ferroelectric mixture of copolymer P(VDF-TrFE) with a TPP-Pd probe as a function of the voltage (U_m) applied to electrodes. Curve *1* corresponds to the dynamic mode experiment. Short line *2* corresponds to the static mode experiment

age, we deal with a non-polarized, ceramic-type ferroelectric with randomly oriented C–F and C–H dipoles. In such a case the Lorentz factor should be close to 1/3 as in crystals with cubic symmetry. Indeed, taking into account the dispersion of the experimental data (of about ± 10 %) the obtained value of about ≈ 1/3 is very good. On the other hand, the dipole sums calculation of a Lorentz factor in polyvinylidene-fluoride [12, 13] having orthorhombic symmetry with ideally oriented dipoles offers the values of $L_z \approx 0$ (and even $L_z < 0$ for a particular dipole length). Indeed, with increasing applied voltage, we see a strong decrease of L_z down to the value of 0.132.

To ensure that Lorentz factor, indeed, is close to zero we have carried out an additional experiment we call *static mode*. The idea was to pole the ferroelectric mixture by voltage pulses $U_p \approx \pm(20{-}30)$ V with duration of $\Delta t = 1$ s and then to measure the local d.c. field under the short circuit conditions when by definition the d.c. macroscopic field is zero:

$$E_{\text{loc}} = L_z \frac{P_z}{\varepsilon_0}. \tag{5}$$

In the static mode the ferroelectric sample was again connected to the voltage source providing a low probe a.c. voltage ($U_m \le 6$ V) without d.c. offset. The d.c. component of the local field $E_{\text{loc,DC}}$ before and after poling can be calculated from comparison of the increments of absorption at the fundamental (1ω) and double (2ω) frequencies [18],

$$E_{\text{loc,DC}} = -\frac{E_{\text{loc},m}}{4}\frac{\Delta A_{m,\omega}}{\Delta A_{m,2\omega}}. \tag{6}$$

The result is shown in Fig. 5. Here the local a.c. field amplitude $E_{\text{loc},m}$ was measured at frequency 2ω

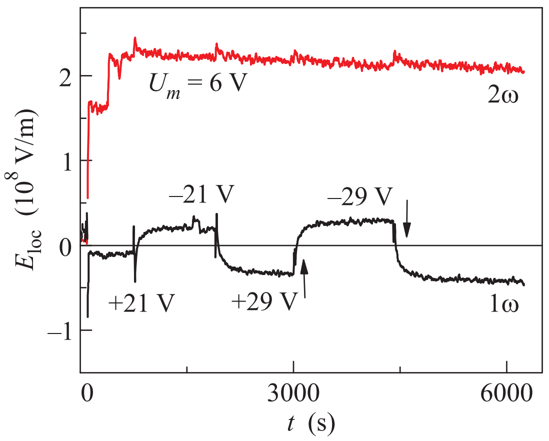

Fig. 5. Time evolution of the local field amplitudes seen by TPP-Pd probe at $\lambda = 436$ nm in P(VDF-TrFE) medium at the fundamental (curve 1ω) and double (curve 2ω) frequencies. A.c. probe voltage amplitude $U_m = 6$ V. Voltage poling pulses $U_p = \pm 21$ and ± 29 V with duration 1 s cause local d.c. field $E_{\text{loc,DC}}$ calculated with the help of Eq. (5)

(curve *1*) and the static local field $E_{\text{loc,DC}}$ was measured at frequency 1ω (curve *2*), both at the wavelength of $\lambda = 436$ nm. Before poling $E_{\text{loc,DC}}$ had a value of $9 \cdot 10^6$ V/m but after application of voltage pulses ($\Delta t = 1$ s, $U_p = \pm 21$ and ± 29 V), the field reaches one of the stable values within 300 s. For the calculations of Lorentz factor, the stable values of $E_{\text{loc,DC}} = -3.2 \cdot 10^7$ and $-4.15 \cdot 10^7$ V/m (both directed from the bottom to top Al contact) were selected and the data on P_z were taken from curve *3* in Fig. 2. Unfortunately, for $U_p < 20$ V the stable states could not be achieved and the data on the Lorentz factor are not available. The found values of $L_z = \varepsilon_0 E_{\text{loc,DC}}/P_z = 0.014$ and 0.097 for $U_p = -21$ and -29 V, respectively, were added to Fig. 4 (curve *2*) for the sake of comparison with curve *1*. Evidently, the high-voltage data complement each other although the results of the static mode experiment are closer to zero as predicted by theory [13]. We believe that the difference in the results of the two experiments come about by incomplete amplitude of the switchable polarization (at maximum $P_{z,m} = 0.038$ C/m^2) when we operate at a frequency of 30 Hz. However, at 0.2 Hz the switchable polarization is twice larger (at maximum $P_{z,m} = 0.08$ C/m^2) [19]. Our estimations show that, with such a value for $P_{z,m}$ and a similar amplitude of the applied voltage (≈ 30 V), in the dynamic mode the Lorenz factor could reach the level of about 0.05, much closer to the results of the static mode experiment.

In conclusion, we suggested a non-destructive spectral technique of electroabsorption for the study of internal fields in ferroelectric structures. For this purpose, an optical probe of the local field (*meso*-substituted Pd-tetraphenylporphyrin or TPP-Pd) was introduced into ferroelectric copolymer polyvinylidene-fluoride P(VDF-TrFE). The probe measured the local field of the ferroelectric mixture whereas the macroscopic field in the sample was known. Therefore, a Lorentz factor could be found for different voltages applied to a sample. The measurements of the Lorentz factor were carried out both in the course of the ferroelectric switching (dynamic mode) and during local field relaxation after poling the ferroelectric by voltage pulses of 1 s duration (static mode). During the switching of the applied field lower than the coercive one, the Lorentz factor of a non-polarized ferroelectric mixture was found to be of about 1/3 that corresponded to random distribution of C–F and C–H molecular dipoles in the ferroelectric. With increasing field the dipole orientation acquired a lower symmetry and Lorentz factor decreased down to the value of about 0.15. After poling by voltage pulses the local field stabilized and the Lorentz factor reduced down to the values close to zero as follows from the theory for vinyliden-fluoride. It is important that using optical probe and the field dependence of Lorentz factor one can directly measure the local and macroscopic fields in individual elements of ferroelectric-dielectric heterostructures.

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