BIOFERROELECTRICITY AND RELATED PROBLEMS: HYDROGEN-BONDED FERROELECTRIC-LIKE SYSTEMS

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Short review of bioferroelectricity and related problems is presented. One of the important cases the hydrogen-bonded systems, are analysed in detail. The proposed model describes the soliton-like dynamics of hydrogen-bonded ferroelectrics with two interacting subsystems (protons and ordered ferroelectric) in the vicinity of phase transition. As a results, the shift of the phase transition point is obtained. The results are compared with experimental data on microwave irradiation of triglycine sulphate.

Key words: biological systems; hydrogen-bonded systems; proton; soliton; ferroelectrics; phase transition; ion channels.

INTRODUCTION

Bioferroelectricity is a branch of ferroelectricity concerning studies of ferroelectric phenomena in biological objects and application of the ferroelectric effects to biophysics. The idea to apply the ferroelectric approach to biological systems was first proposed in 1980s by Richard Leuchtag, when he investigated the nature of ion channels in excitable biomembranes [1-3] and then developed by V. Bystrov and R.Leuchtag [4-7]. A recent review of direction has been presented in [8, 9]. Now the field is extended and includes various studies: the piezoelectric, pyroelectric and ferroelectric properties of biomaterials (Sidnay B. Lang [10]), ferroelectricity in cell microtubules (J.D.Tuszynski [11,12]), propagation of action potential (Alex Gordon et al. [13]) , self-organized model of membrane excitation (K. Shirane et al. [14]) flexoelectricity of biomembranes (A. G. Petrov [15]) and a number of other new applications.

One of the most important problems is that of hydrogen-bonded ferroelectric-like systems.

THE TWO-COMPONENT MODEL OF HYDROGEN-BONDED FERROELECTRICS AND ORDERED BIOLOGICAL SUBSYSTEMS

The connection between phase transition (PT) conditions and transport of electrical charge (such as protons and ions , electrons and holes) in ferroelectrics, molecular and biological hydrogen-bonded systems is a long-standing problem which has been extensively studied [8, 16]. The proton conductivity in hydrogen-bonded molecules is remarkably high and, in some cases, the proton subsystem may be considered as a subsystem of quasi non-equilibrium carriers [16,17], which can affect the phase transition point. This effect is very similar to the one seen in photoferroelectrics where the phase transition point is affected by the electron subsystem [18]. The only difference between two cases is that the electron subsystem is excited by UV or visible irradiation while the proton subsystem - by microwave irradiation which has a direct effect on the hydrogen bonds of these systems through the soliton mechanism proposed here. Here we are going to present a theoretical interpretation of interaction between the two sublattices in hydrogen-bonded ferroelectrics presented hereafter is based on a soliton-like motion of protons in a two component model and considered together with experimental data on microwave irradiated triglycine sulphate (TGS). By this approach we try to understand the mechanism of proton motion in the voltage-gated ion channels of excitable biomembranes [8, 9, 16].

In the case of the continuum representation, when the negative ion sublattice is frozen, the single-component proton Hamiltonian is [18]

$$H_1 = \int dx \left\{ \frac{1}{2} m \left(\frac{\partial u}{\partial t} \right)^2 + \frac{1}{2} m c_0^2 \left(\frac{\partial u}{\partial x} \right)^2 + V[u(x,t)] \right\}, \quad (1)$$

where m - is the proton mass, $c_0 = \omega_0 l_0$ - is the proton motion velocity ("proton sound"), in which ω_0 is the characteristic proton-proton vibration (tunnelling) frequency, l_0 - is the proton sublattice period, u - is displacement of the proton from the middle of a fixed distance between two neighbouring frozen negative ions when the proton moves in the double-well nonharmonic potential V(u)

$$V(u) = \frac{1}{2}Au^2 + \frac{1}{4}Bu^4 \quad (A<0, B>0). \tag{2}$$

This simple but general continuum form Hamiltonian (1) allows to study the nature of non-linear solitary-waves (kink, soliton) which arise as solutions of the Euler-Lagrange motion equation for $u=u(x,t)$, following from (1)

$$m\frac{\partial^2 u}{\partial t^2} - mc_0^2 \frac{\partial^2 u}{\partial x^2} + \frac{dV(u)}{du} = 0. \tag{3}$$

The only restriction on the local (on-site) potential $V(u)$ is that it should have at least two degenerated minima (for example, $V=0$ for $u=u_1$ and $u=u_2$). This is sufficient to admit that the partial soliton or solitary-wave (kink) solutions of (3) correspond to two proton positions in a double-well potential - left and right. By introducing velocity v for a kink motion and by transforming the coordinate frame to a moving one $s=x-vt$ the solution can be obtained by integrating equation (3) under appropriate boundary conditions

$$\frac{du(s)}{ds} (s = \pm\infty) = 0, \quad u(s = \pm\infty) = u_{1,2} = \pm u_0 = \pm(-A/B)^{1/2}. \tag{4}$$

In a more general case that includes dissipation (or relaxation) with a damping coefficient $\Gamma = 1/\lambda$ and external force F the motion equation is

$$mc_0^2\left(1 - \frac{v^2}{c_0^2}\right)\frac{d^2u}{ds^2} + mv\lambda\frac{du}{ds} - \frac{dV(u)}{du} + F = 0. \tag{5}$$

In the case of hydrogen-bonded ferroelectrics, chiral molecular ferroelectric liquid crystals, and ferroelectric biological systems (for example, membrane proteins such as ion channel biomacromolecules, DNA etc.) we have both the rigid ordered subsystem and the lighter hydrogen bonded one. The first is characterised by an order parameter ξ (which describes polarization P, or tilt angle   ) and a conformational phase transition from $\xi=\xi_1$ to $\xi=\xi_2$ at a certain temperature $_0$.

The interaction between hydrogen-bonded subsystem and ordered (ferroelectric) subsystem in the first approximation can be described by introducing the interaction Hamiltonian in the form

$$H_{\text{int}} = D\xi^2(u^2 - u_0^2) + Q\xi(u - u_0). \tag{6}$$

Kinetics of both first and second order phase transitions (PT1 and PT2) can be described in the framework of condensed matter physics approach [7] by using the Landau-Ginzburg-Devonshire expression for free energy density (which corresponds to a second Hamiltonian component $H_2 = v_c F$, when v_c is the volume of a unit cell)

$$F = F_0 + \frac{1}{2}\alpha\xi^2 + \frac{1}{4}\beta\xi^4 + \frac{1}{6}\gamma\xi^6 + \delta\left(\frac{\partial\xi}{\partial x}\right)^2, \quad (7)$$

and the time-dependent Ginzburg-Landau equation for evolution of the order parameter ξ [7, 16] (including the interaction term divided on vc $F = F + Hint/vc$) from which we obtain the equation for the phase transition moving boundary (kink) between two values $\xi_2(s \Rightarrow -\infty)$ and $\xi_1(s \Rightarrow +\infty)$ with velocity v_2 in the moving coordinates $s = x - v_2 t$

$$2\delta\frac{d^2\xi}{ds^2} + \lambda_2 v_2\frac{d\xi}{ds} - \left[\left(\alpha + Du^2\right)\xi + \beta\xi^3 + \gamma\xi^5 - E + Qu\right] = 0. \quad (8)$$

Here $\Gamma = 1/\lambda_2$ - is the Landau-Khalatnikov damping coefficient which is assumed to depend noncritically on temperature, the interacting coefficient D is D/v_c and Q is Q/v_c,

$$\alpha = \alpha_0' + \alpha_0(T - T_0) = \alpha_0(T - T_c), \ \alpha_0 = 4\pi/C_w, \quad (8a)$$

when α, α_0', $\gamma > 0$, $\beta < 0$ are the F- expansion coefficients, T_0 - is the phase transition temperature, T_c and C_w are Curie-Weiss temperature and constant, δ - is a gradient term coefficient and E – external field. For PT2 $\gamma = 0$, $T_0 = T_c$ and $\xi_0^2 = -\alpha/\beta$ in the case of $E=0$ ($D=Q=0$).

For the first component – the proton hydrogen-bonded subsystem – with regard to an interaction term ($H=H1+Hint$) and an external field force $F=qE$ (when q – is effective proton charge, qu – polarization of the proton subsystem) in the moving variables $s=x-v_1t$ both equations (3) and (7) come to the following form

$$mc_0^2\left(1 - \frac{v_1^2}{c_0^2}\right)\frac{\partial^2 u}{\partial s^2} + m\lambda_1 v_1\frac{\partial u}{\partial s} - \left[\left(A + D\xi^2\right)u + Bu^3 - (qE - Q\xi)\right] = 0. \quad (9)$$

In the absence of external field ($E=0$), dissipation ($\lambda=0$) and interactions ($D=0$, $Q=0$) equations (8) and (9) turn into the case (3) of the homogeneous "domain wall" motion between two equilibrium positions of the proton $u=\pm u_0$ in the double-well potential (2) or $\xi=\pm \xi_0$ for order parameter and have the simple soliton solution .

It was shown in [16] by renormalization of coefficients A and $\square$ in the form of

$$A^* = A + D\xi^2, \quad \alpha^* = \alpha + D(u^2 - u_0^2), \quad (10)$$

that the soliton (kink) motions are possible only if the external field does not exceed a critical value $E \leq E_k$ and the critical value was estimated to be $E_k \sim 10^7 V/m$.

The phase transition temperature shift $\Delta T_0^* = T_0^* - T_0$, owing to the Hamiltonian (6), is determined by condition $\alpha^*(T_0^*) = 0$. From (8a) and (10) for the PT2 case and $Q=0$

$$\Delta T_0^* = T_0^* - T_0 = -\left(\frac{4\pi\varepsilon_0}{v_c}\right)\frac{D}{\alpha_0}(u^2 - u_0^2), \quad (11)$$

where $\varepsilon_0 = 8,85*10^{-12}$ C/(V*m). Without microwave irradiation, when the proton is in equilibrium asymmetric position $u = u_0$, this value is $\Delta T_0^* = 0$. After microwave irradiation, when the proton is excited into a new symmetric position $u=0$, the value of ΔT becomes

$$\Delta T_0^* = (4\pi\varepsilon_0 / v_c)Du_0^2 / \alpha_0 > 0. \quad (11a)$$

Preliminary estimations of both energy and phase transition temperature shifts for TGS crystals are made in [16] using the data $C_w = 3305\ grad$ and $\alpha_0 = 3,8\cdot10^{-3}\ grad^{-1}$, $v_c \sim 1\div0.26*10^{-27}$ m^3, $u_0 \sim 0.4*\ 10^{-10}$ m and $D \sim 50$ J·m^2/C^2 $\sim 3*10^{20}$ eV*m^2/C^2. The estimations give the temperature shift $\Delta T_0^* \sim 2\div9\ grad$ and the shift in energy introduced by the interaction term in (6) $\Delta E \sim 0.25*D*(u_0*\xi_0)^2 \sim 0.0002$ eV, that corresponds to the microwave frequency of ~ 50 GHz. It means that microwave irradiation of a TGS crystal may cause a phase transition shift of the estimated value. Detailed calculations of soliton widths and velocities made in [20] are presented in Figure 1 (a – nonradiated, b – irradiated cases) show a phase transition temperature shift of 2...3 grad.
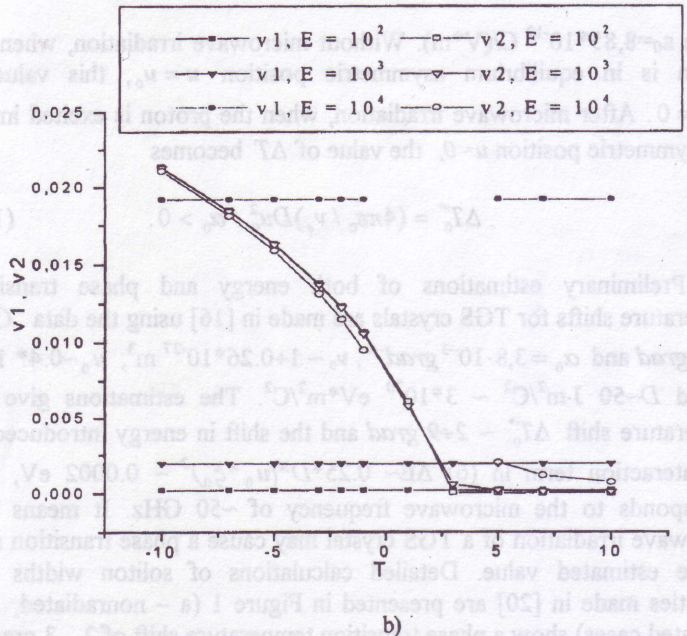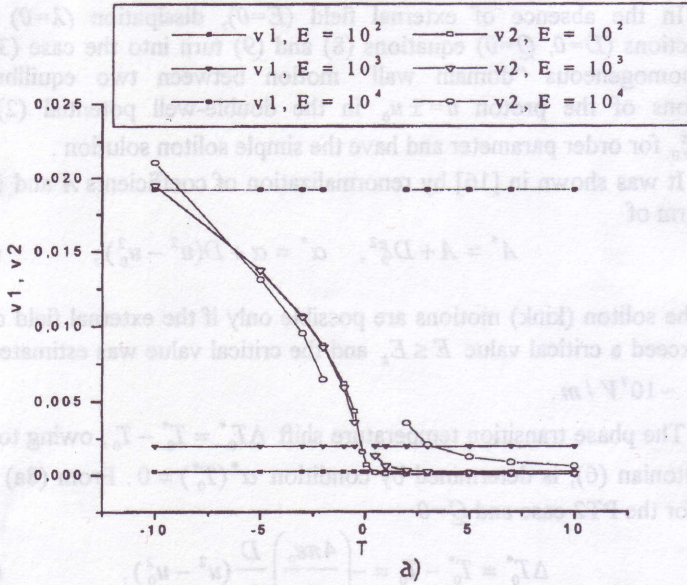
a)

b)

Figure 1.

RESENT EXPERIMENTS AND DISCUSSION

Here we presented some recent experimental data [19]. Since the theoretically estimated interaction energy was of the order of 0,0002 eV the frequency of 40 GHz was chosen for measurements. The typical hydrogen-bonded ferroelectric TGS was subject to microwave irradiation. To estimate the effect of microwave influence low frequency dielectric permittivity was measured as function of temperature in the vicinity of phase transition.

Samples of rectangular parallelepiped configuration were shaped out of TGS crystals grown in the ferroelectric phase - $5,2 \times 2,5$ mm^2 of cross, in accordance with the waveguide size, and 4 mm long. Samples were cut out with polar axis oriented along the 2,5 mm side of crystals thereby the external electric force and the spontaneous polarization were directed along the same axis. For further measurements $2,5 \times 4$ mm^2 sides of samples were covered with leaf-silver.

The samples were placed at the short-circuit end of the wave guide and irradiated for 5 hours with 40 GHz pulses from a G4-141 high-frequency generator, the samples being at a distance of 4 cm from generator attachment flange. The samples in the wave-guide were heated to the temperature of 40 °C. The low-frequency measurements were carried out in a thermostabilizer camera connected to polarization and dielectric permittivity measuring devices.

Dielectric permittivity was measured at 1 kHz on an R551AC bridge. Polarization was calculated from finite-increment data of pyroelectric coefficient.

Figure 2 shows dependence of $1/\varepsilon'$ on the temperature for irradiated and nonirradiated TGS crystals. The shift of the phase transition temperature can be seen (curve 2). A similar shift is manifested by polarization measurements (Figure 3). The observed shift is $2,5 \div 3$°C and is consistent with the preliminary estimations made above. It is very important considering the TGS crystals as a model hydrogen-bonded object for such biological systems as voltage-dependent ion channels of excitable biological membranes.
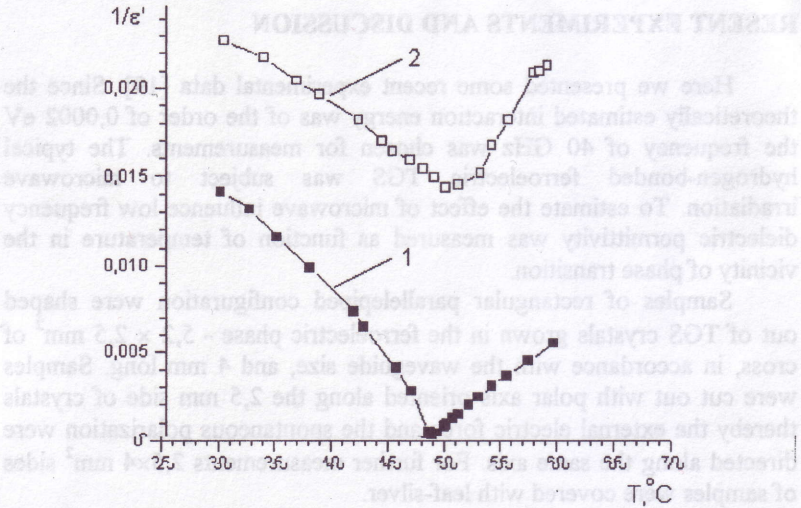
FIGURE 2 $1/\varepsilon'$ as a function of temperature: 1-nonirradiated crystal; 2-irradiated crystal.

From the $1/\varepsilon'(T)$ curve of the nonirradiated crystal we obtained the following values of coefficients for Curie-Weiss constant $C_w = 2000$ and $\alpha_0 / \varepsilon_0 = 4\tilde{\pi}/C_w = 6,28\cdot10^{-3}$ *1/grad* for $T > T_C$ and $C_w = 700$ and $\alpha_0 / \varepsilon_0 = 17,94\cdot10^{-3}$ *1/grad* for $T < T_C$. The ratio 2,86 between C_w in paraelectric and ferroelectric phases is comparable with 2,7 known for a second order phase transition.

In this case we can easy obtain the value of coefficient ☐from $\xi_0^2 = P_0^2 = -\alpha/\tilde{\beta}$. Taking the experimental value of polarization $P = 0,01$ C/m^2 at $T = 20°C$ we obtain $\beta = (T_0 - T)/\varepsilon_0 C_w P_0^2 = 164\cdot10^{11} V\cdot m^5\cdot C^{-3}$.

The data are close to values of biological membranes and ion channels structures found from biological experiments by R. Leuchtag [8]. This result is very important for the bioferroelectric approach and interpretation of the ferroelectric effects in biological systems.
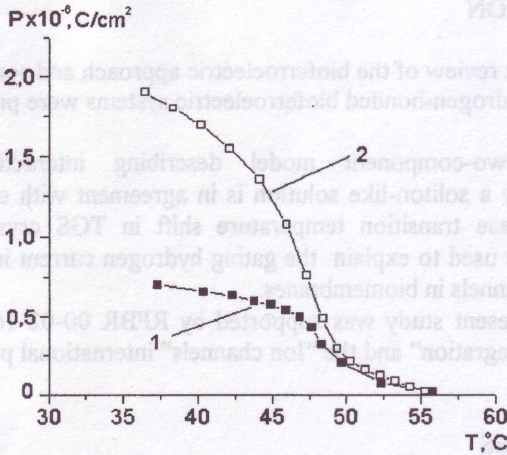
FIGURE 3 Polarization as a function of temperature: 1-nonirradiated crystal; 2-irradiated crystal.

Now we can calculate the effect of temperature on the experimental data and values of D, v_c, u_0 used in the previous section. We obtained the $\Delta T = 1,4 \div 5,5$ grad which is in a good agreement with the experimentally observed shift of $\Delta T = 2,5 \div 3$ grad.

After microwave irradiation the Curie-Weiss constant changed to $C_{wm} = 875$ and $\alpha_0 / \varepsilon_0 = 4\pi/C_w = 14,36 \cdot 10^{-3}$ $1/grad$ for $T > T_c$. Polarization became $P = 0,021$ C/m^2 and coefficient $\beta = 85 \cdot 10^{11}$ $V \cdot m^5 \cdot C^{-3}$. Assuming these changes forced by arising internal electric field as a result of proton motion by soliton mechanism, we estimated the field from relation $E_i = \beta(P_e / 0,73)^3$, where P_e is the value of polarization at the point of inflection. In our case the point corresponds to $T = 51,5°C$, $P_e = 0,001$ C/m^2 and $E \sim 10^5$ V/m. Estimating from our experiments the electrocaloric constant $k_e = dT / dE = \varepsilon_0 C_w / P_e = 2 \cdot 10^{-5}$ $grad/(V/m)$ we calculated the temperature shift caused by internal electrical field as $\Delta T_e \sim 2°C$, which is in a good agreement with our experimental data. Since the value of critical field is $E_k = 10^7$ V/m $\geq E_i$, we can conclude that proton transfer by soliton mechanism is possible in this case.

It means that we have the new proton-voltaic effect , which is similar to photo-voltaic effect in ferroelectric-semiconductors [6], but has a different carriers' nature of the non-equilibrium mobile charges - electrons in semiconductors and protons in our case. This effect may play a role as a possible gating mechanism of the ion channels biomembranes [8,9].

CONCLUSION

A short review of the bioferroelectric approach and some new results for hydrogen-bonded bioferroelectric systems were presented and discussed.

The two-component model describing interaction between sublattices by a soliton-like solution is in agreement with experimentally observed phase transition temperature shift in TGS crystals and this model can be used to explain the gating hydrogen current in the voltage-gated ion channels in biomembranes.

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