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# TRANSIENT CURRENTS IN PHOTOCHROMIC LITHIUM NIOBATE CRYSTALS

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In the studies of the photovoltaic effect in photochromic lithium niobate crystals the transient currents, that accompany the processes of induction and relaxation of the photochromic effect, are revealed. The mechanism of initiation of these currents is proposed on the basis of the model of the optical energy dissipation by impurity centres taking into account the kinetic theory of irreversible processes.

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## 1. Introduction

An influence of doping with various impurities and their combinations on photorefractive properties of lithium niobate crystals was investigated in [1]. It was found that some combinations of impurities lead to the initiation in a crystal of the photochromic effect – a photoinduced reversible change of the absorption coefficient. In [2, 3] a model of the photochromic effect was proposed based on the recharging between impurity centres and on the balance of electrons. In our last paper we reported on the production of bulk periodically poled $LiNbO_3$ crystals [4]. In present paper the photoelectric characteristics of photochromic crystals are investigated, in particular, the transient currents, which are observed at an induction and relaxation of the photochromic effect. The influence of the photovoltaic effect on the photochromic properties of lithium niobate crystals is also studied. The mechanisms of the photochromic and photovoltaic effects and their interrelation are discussed. A possible model of the transient currents' initiation at recharging of impurity centres of various types is proposed.

## 2. Experimental results

In experiments the dependencies of the photovoltaic and photochromic effects on the light intensity ($\lambda$ = 488 nm) were investigated. The kinetics of the above-mentioned effects was also studied at a fixed level of the light radiation, as well as relaxation currents observed after the light switching off. Doped lithium niobate crystals ($LiNbO_3$:Fe:Cu) grown by the Czochralski technique were used as samples. Crystals contained 0.05 wt % of Fe impurity and 0.03 wt % of Cu impurity. Under the assumption of a randomly distributed impurity the above-mentioned concentrations are rather small to cause a direct interaction between impurity ions in crystal. The samples had the form of parallelepipeds, and the electrodes were deposited on the sides perpendicular to the spontaneous polarisation axis. The obtained experimental dependencies are presented in Fig. 1 and 2. As it is seen from the curve 1 in Fig. 1 the absorption coefficient $\alpha$ increases with the increase of the light intensity.

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At the same time the linear dependence of the stationary photovoltaic current on the light intensity is maintained (curve 2). Since the value of the photovoltaic current in the outer circuit is $j = k\alpha I$ (*k* is the photovoltaic constant, $\alpha$ is the coefficient of light absorption, *I* is the light intensity), then it is obvious that in the LiNbO3:Fe:Cu crystal the glass constant depends nonlinearly on the light intensity, namely, it decreases with the increase of the intensity. This decrease is connected with the change of the absorption coefficient.

Let us consider now the experimental results presented in Fig. 2. The curves 1 and 2 show temporal dependencies of short-circuited currents in the lithium niobate crystal at the light switching on and switching off. Measurements were carried out at two intensities of light, namely, the curve 1 corresponds to the intensity, at which there is not a change of the absorption coefficient, and the curve 2 corresponds to the intensity, at which the photochromic effect is observed. To compare the curves the values of currents are normalised on the incident light intensity. Stationary values of normalised photovoltaic currents have just the same value, however, transient components are different. The transient component of the short-circuited current presented on the curve 1 corresponds to the typical transient component in measurements of photovoltaic currents and is caused by the pyroeffect. However, on the curve 2, besides the usual transient pyrocomponent, we observe also a slower transient component of the short-circuited current (both at switching on and switching off of the light). It is natural to connect these transient currents with the process of an induction and relaxation of the optically induced change of the absorption coefficient, i.e. with the photochromic effect. Really, as it was shown in [1, 2], at the induction of the photochromic effect a redistribution of electrons between Fe and Cu impurity centres takes place, i.e. under the light action a part of electrons passes from Fe level to Cu level which leads to the unbalanced state. At the light switching off a relaxation of this unbalanced state takes place and electrons return from Cu level to Fe level. In this case the relaxation time is not connected with the Maxwell's time which is a characteristic time for other photoinduced phenomena in lithium niobate crystals (photorefraction, photovoltaic effect, pyroeffect, etc.).

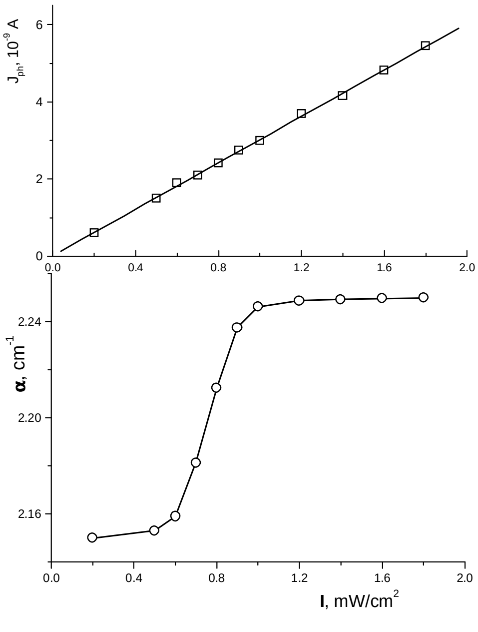

Fig. 1. Experimental dependencies of absorption and photovoltaic current on the light intensity in the LiNbO$_3$:Fe:Cu crystal.

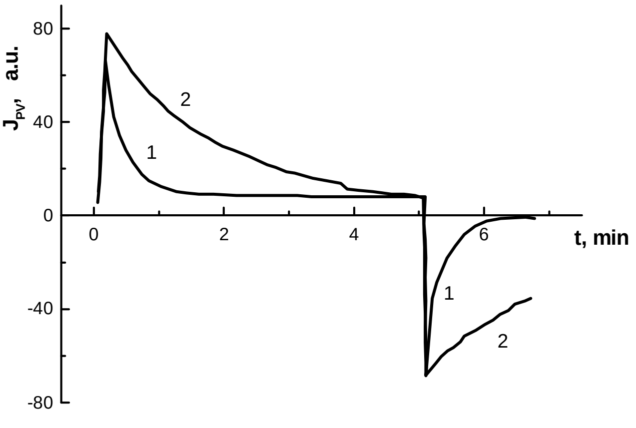

Fig. 2. Photocurrent kinetics in LiNbO$_3$:Fe:Cu crystal: 1 – light intensity does not induce the photochromic effect; 2 – light intensity exceeds the threshold and is sufficient for change of the absorption coefficient.

Since the formation and relaxation of the unbalanced state take place in a crystal without a symmetry centre and are connected with photovoltaic centres, it is natural to expect that these processes will be accompanied by the passing of currents through the crystal and external registering circuit and these currents are necessarily transient which fact is observed in experiment. Thus, we consider that detected transient currents accompanying induction and relaxation processes of the photochromic effect are relaxational currents having the photovoltaic nature and conditioned by the recharging processes between the impurity photovoltaic centres. Similar currents caused by the γ-centre's decay in lithium niobate crystals under the light action and therefore called photorelaxational have been earlier found in [5]. Below we will try to substantiate these conclusions by the model calculation of the photovoltaic effect in photochromic crystals.

## 3. Theoretical model

As it was shown in [6] at an excitation of the impurity centre a change of the centre dipole moment takes place since the dipole moment is generally different in ground and excited states. A mechanism of the dipole moment change for Er impurity in lithium niobate crystals was proposed in [7]. In ferroelectrics this change has just the same direction. Therefore for these crystals a total polarisation change may be presented as $\Delta P=n\mu$, where $n$ is number of impurities at the excited state, $\mu$ is the change of the impurity centre's dipole moment. In this case the electric current in the external measuring circuit is equal to $I = dP/dt$. In the above-mentioned references the intraatomic optical transitions were considered. However, since the photochromic effect is conditioned by the recharging processes between Fe and Cu centres through the conduction band [1], we will consider the mechanism of the transient currents' formation under the excitation of electrons to the conduction band.

The origin of the change of the local dipole moment at the recharging of centres Fe ↔ Cu can be illustrated on the basis of the one-dimensional asymmetrical potential [8]. Using the Born-Oppenheimer approximation, one can separate the Schroedinger equation [9] for an isolated photoactive centre into two independent equations for the photoelectron and nucleus. We denote by $li$ and $mi$ the $i$-th vibrational modes of the unexcited ($l$) and excited ($m$) states. The complete wave function $\Psi$ of the photoactive centre in the unexcited ($l$) and excited ($m$) states may be presented as a product of the electronic wave function $F(q,r)$ and vibrational wave function $F(r)$ of the lattice:

$$\begin{aligned} \Psi_{li}(q,r) &= F_l(q,r).F_{li}(r) \\ \Psi_{mi}(q,r) &= F_m(q,r).F_{mi}(r) \end{aligned} \tag{1}$$

where $q$, $r$ are the "electronic" and "nuclear" co-ordinates, respectively. Below we consider only the electronic wave functions and Schroedinger equation for photoelectrons, whereas the lattice wave functions are considered as invariable.

The transition dipole moment or the matrix element of electric dipole moment between two states $\Psi_{li}$ and $\Psi_{mi}$ are calculated from the relation

$$M(mi\rightarrow li) = <\Psi_{li}|Z|\Psi_{mi}> = <F_m|Z|F_l><F_{mi}|F_{li}> , \tag{2}$$

where $Z$ is the spatial co-ordinate.

The model potential functions $V_{\mathrm{Cu}}(z)$ and $V_{\mathrm{Fe}}(z)$ for an electron at the excitation energy $E$ are shown in Fig. 3. An asymmetry is conditioned by the lack of the inversion centre in the crystal. In our calculations the model potential well is represented by a piecewise-smooth function with the discontinuities of derivative. It is assumed that along with the relaxation through the conduction band, electronic transitions are possible from the Cu level to the Fe level bypassing the conduction band, by the tunnelling through a barrier separating these states. Values of energy levels presented in Fig. 3, are approximated from spectral data (spectra of the absorption and photoconductivity for crystals doped only with the Fe or Cu ions). The value of the asymmetrical barrier is calculated from the spectral dependence of the photovoltaic current.

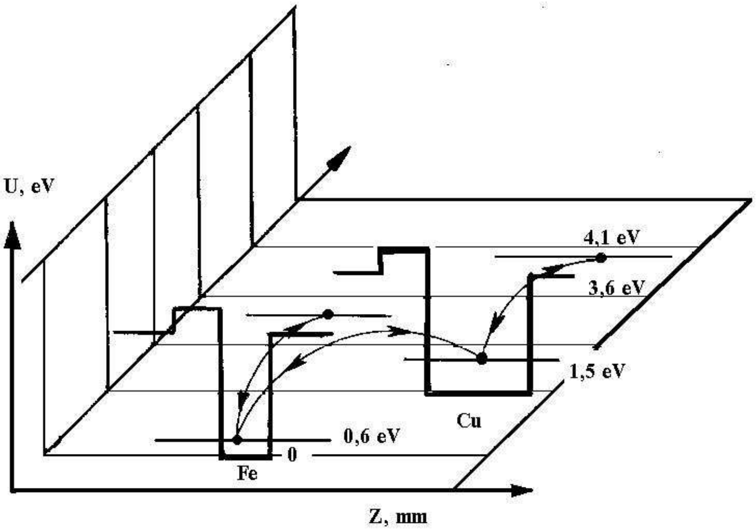

Fig. 3. Model of potential well for Fe and Cu impurities.

The Schrödinger equation for an electron in a potential well has the form

$$\frac{d^2\Phi(z)}{dz^2} + \frac{2m}{\hbar^2}[E - V(z)] = 0, \quad (3)$$

where $V(z)$ is the potential of an impurity centre, $m$ is the particle mass. A solution of the equation for the potential shown in Fig. 3 can be presented in the form of a piecewise-smooth analytical function [9]. Though values of the wave function in the whole space may be obtained analytically, however, because of the cumbersome expressions, we will use a numerical method. Suppose that the potential well width for Fe impurity equals $10^{-7}$ cm and for Cu is $2 \times 10^{-7}$ cm. It should be noted that the value of the potential well width weakly influences the value of the dipole moment change. Integrating numerically the wave function by the Simpson method in the whole space, we obtain the mean value of the spatial co-ordinate of the wave function. The wave function for the ground state is calculated analytically, and, thus, the mean value of the spatial co-ordinate is also calculated analytically. Calculating the wave function for the excited states of the Fe and Cu centres ($E$ = 3.1 eV) we can determine both the charge centre for these centres and the charge centres for an electron on the bottom of the conduction band.

Calculating the dipole moment change for Fe by the formulas (2) and (3) we obtained that the excitation from the ground state to the conduction band ($h\nu = 3.1$ eV) leads to the dipole moment change by 40 D. Under the recombination from the bottom of the conduction band to the ground level the change of the dipole moment equals 37 D, and an excitation from Fe level to Cu level leads to the local dipole moment change by 4 D. In these calculations a transition trajectory is not significant, since the system is potential, except the process of the photoelectrons scattering on phonons in the conduction band. Owing to the temporal invariance, the above-mentioned values of dipole moments, for transitions without a scattering on phonons, are the same by the absolute value for the excitation and relaxation.

Consider a specific model of the photovoltaic electrons scattering. As it is known, the elastic scattering on a random static potential is one of the simplest types of scattering. The probability $W(k,k')$ of the transition for electron with the momentum $k$ to electron with the momentum $k'$ is determined by the Fokker-Planck equation [11]. As it was mentioned, for transitions without the scattering the dipole moment value is invariant relatively to the time inversion. This is reflected in the equality of the time inversion and in the equality of the transition probabilities $W(k,k')=W(k',k)$. The relaxation of photoelectrons to the bottom of the conduction band caused by the phonon scattering is determined by the kinetic theory of irreversible processes. An irreversibility of processes in the kinetics appears by the averaging of the expansion coefficients of the wave function over time. This averaging is based on the hypothesis of random phases, which is the background of the kinetic theory of the scattering. In this case, for the elastic scattering processes, electron after the first interaction completely losses a preferential moving direction [11].

Thus we assume that electrons passed to the conduction band are isotropized (chaotized) by the momentum due to the strong electron-phonon interaction, which is inherent for ferroelectrics. Then, owing to the inelastic electron-phonon interaction, a slow relaxation by energy to the bottom of conduction band takes place without a change of mean value of spatial co-ordinate of wave function.
Assuming that in the conduction band, owing to the scattering on phonons, a loss of the photovoltaic momentum occurs without a change of spatial co-ordinates we obtain a difference of mean values of electronic wave functions at the excitation and relaxation. The photovoltaic current is conditioned just by this difference of the charge localisation co-ordinates. The mean distance between impurities does not enter the obtained result, which is obvious and is due to the translational invariance.

From the above-mentioned it can be shown that along with the usual photovoltaic current under the illumination the transient currents must be observed, which have a photovoltaic nature and are conditioned by a change of Cu level population. Actually, as it is shown in the photochromic effect model [1], processes of the induction and relaxation of the photochromism are conditioned by a recharging between Fe and Cu impurity centres. This means a redistribution of electrons between these impurity centres and hence a change of the dipole moment of the system, which leads to the transient currents at the induction and relaxation of the photochromic effect.

Below we consider the process of electronic subsystem relaxation without light excitation. Assuming that a release of traps takes place as a result of the interaction of thermal phonons conditioned by thermodynamic temperature of crystal and is subject to the Gauss-Markov conditions, one can calculate the probability $R$ of the transition from Cu level to Fe level by solving Fokker-Planck equation:

$$\frac{\partial R(z,t)}{\partial t} = \frac{\partial [V(z)R(z,t)]}{\partial z} + D\,\frac{\partial^2 R(z,t)}{\partial z^2}\,. \tag{4}$$

Further considerations will be based on the following assumption: a probability of occurrence in the state $\xi$ during the time $\Delta t$ is completely determined by the value of the state $\xi$ and does not depend on a way how the system came to the state $\xi$, i.e. it does not depend on the prehistory of the process. We will find a solution of the equation (4) in the case of the asymptotic limit which does not depend on time ($\partial R/\partial t = 0$) [11]. In the equilibrium case a solution of this type is reduced to the Maxwell distribution. A stationary solution with account of boundary conditions has the following form:

$$R = (\sigma / D)\ \exp(-V_o / kT)\ [1 - \exp(-\Delta V / kT)] \tag{5}$$

where $V_O$ is the transition barrier height satisfying the inequality $kT << V_O$, $\Delta V$ is the difference of the Fe-Cu energy levels, $D$ is the diffusion coefficient which is equal to $D = kT\mu^*/e$ [15], where $\mu^*$ is the mobility of charge carriers, $\sigma$ is the interaction cross-section.

Having the transition probability and using the balance equations for the photoelectron concentration at Cu level [1] we get the transient (relaxational) current's dependence on time at fixed temperature:

$$j(t)=RN_{\mathrm{Cu}}(t)\Delta P, \tag{6}$$

where $N_{Cu}$ is the density of captured electrons at the Cu level; $\Delta P$ is the change of the impurity centre's dipole moment. The equation obtained describes exactly the relaxation dynamics of currents conditioned by the recharging of the Fe ↔ Cu centres, as well as it allows to predict the decay dynamics for other impurities introduced into a crystal using the energy levels values in the forbidden band and the decay dynamics in the range of low and room temperatures. From the solution (5) of the

Fokker-Planck equation one can determine the relaxation time. It was seen that some modes have a low relaxation time, whereas the other ones have a large relaxation time. We are dealing with systems with two temporal scales.

Thus, on the basis of have the kinetic theory of irreversible processes with the use of the analytical-numerical model we shown the possibility of the initiation of transient currents during induction and relaxation of the photochromic effect in ferroelectric crystals.

## 4. Conclusions

Transients currents that accompany the induction and relaxation of the photochromic effect were revealed in lithium niobate crystals.

A mechanism based on the model of dissipation of optical energy on impurity centers was proposed.

## References

[1] E. S. Vartanyan, R. K. Hovsepyan, A. R. Pogosyan, Kristallografiya **35**, 900 (1990).
[2] G. T. Avanesyan, E. S. Vartanyan, R. S. Mikaelyan, R. K. Hovsepyan, A. R. Poghosyan, phys. stat. sol. (a) **126**, 245 (1991).
[3] G. T. Avanesyan, E. S. Vartanyan, R. S. Mikaelyan, R. K. Hovsepyan, A. R. Poghosyan, J. of Contemp. Physics **28**, 1, 19 (1993).
[4] I. A. Ghambaryan, R. Guo, R. K. Hovsepyan, A. R. Poghosyan, E. S. Vardanyan, V. G. Lazaryan, J. Optoelectron. Adv. Mater. **5**(1), 61 (2003).
[5] E. S. Vartanyan, R. K. Hovsepyan, A. R. Poghosyan, A. L. Timofeev, Fizika Tverdogo Tela (Russ.) **26**, 2418 (1984).
[6] D. H. Auston, A. M. Glass, Phys. Rev. Lett. **28**, 897 (1972).
[7] V. G. Babadjanyan, G. G. Demirchanian, R. B. Kostanyan, Opt. Comm. **95**, 269 (1993).
[8] M. Born, Kun Huang, Dynamical Theory of Crystal Lattices, Clarendon Press, Oxford (1954).
[9] S. Flugge, Practical Quantum Mechanics, Springer Verlag, Berlin-Heidelberg-New York (1971).
[10] C. W. Gardiner, Handbook of Stochastic Methods for Physics, Berlin (1984).
[11] A. Isihara, Statistical Physics, Academic Press, New York – London (1971).