05

Effect of electric fields on the formation of solid phase nuclei in metal melts

© S.A. Nevskii, S.V. Konovalov, L.P. Bashchenko, V.E. Gromov, D.D. Mikhailov, A.Yu. Granovskii

Siberian State Industrial University, Novokuznetsk, Russia
e-mail: nevskiy.sergei@yandex.ru

Received November 15, 2024
Revised March 3, 2025
Accepted March 9, 2025

The effect of an electric field on the crystallization process of metallic materials is studied on the basis of the idea that the nuclei of the solid phase are formed as a result of nonadiabatic Landau–Ziner transitions and transitions due to vibrational degrees of freedom. It is assumed that the splitting of energy levels by an electric field leads to an increase in the probability of these transitions and the appearance of dynamic displacements, the amplitude of which is one of the order parameters that describe the crystallizing system. The second parameter of the order is the amplitude of elastic displacements, which characterizes the volume change during the phase transition. Based on the analysis of the equations of kinetics of formation and growth of solid phase nuclei for two order parameters, it is established that constant and pulsed electric fields lead to the fact that a static autosolithon, which corresponds to a solid phase embryo, is formed in less time than in the absence of a field. At the same time, with an increase in the amplitude value of the field strength, this effect increases. This is explained by the fact that the potential barrier between two stable states of the system decreases, and when the critical value of the field is reached, it completely disappears. The same effect occurs when the pulse duration increases at a constant amplitude. In the mode of a damped autosoliton, the electric field leads to a change in the type of this solution to an oscillating autosoliton, and then, with an increase in its intensity, to a static one. When switching to the oscillating autosolithon mode, the electric field also leads to a change in the type of this solution, first to a damped autosolithon, and then to a static one. In the case of diffusive phase transformations, which are described by a switching wave, the effect of an electric field leads to an increase in the propagation velocity of this wave. The established effect depends only on the amplitude of the pulsed electric field and does not depend on its duration.

Keywords: liquid–solid phase transitions, electric field, nonadiabatic Landau–Ziner transitions, thermal fluctuations, autosolitons.

DOI: 10.61011/TP.2025.07.61454.422-24

Introduction

The phase transformations „liquid–solid body“ are widely spread in natural and man-made systems. They play a key role in forming a material microstructure and, ultimately, its physical-mechanical properties. Therefore, scientists are just more and more interested in these transformations [1]. By now, the most effective method of studying these transformations is a phase field method [2,3]. Its essence is that in order to describe behavior of the systems during phase transitions of the first and the second kind, order parameters are introduced [4]. Their physical meaning is determined by a type and a structure-scale level of a problem being solved. Usually, the order parameter is a volume portion of the new phase [5] or an amplitude of the most unstable mode of inelastic atomic displacements [6,7]. By now, the biggest success of this method was achieved when modeling crystallization of two-phase systems [8,9]. Kinetics of formation of the new phase in these papers is described by the Cahn–Hillard equations. Kinetic models of cellular and dendrite crystallization can be given as an example [10,11]. For the multi-phase systems, the situation is complicated by the fact that it is not possible to describe formation of new phases by means of equations of the two-phase models [11,12]. It is caused, as the authors think [13], by a holonomic constraint between the order parameters, which makes it impossible to assume that they are independent variables. To remove this disadvantage, the paper [13] proposes to use antisymmetric combinations of the phase field as such variables. The model of directional solidification created by means of this approach allows evaluating its kinetics by the example of a melt. It was shown that first the phase with a HCP lattice is formed, and then the phase with a BCC lattice is formed to displace, in turn, the liquid phase. Crystallization of binary alloys is theoretically studied in the papers [14–16]. The papers [14,15] have investigated influence of an oncoming melt flow on crystallization of supercooled liquids with a two-phase layer. It is established that it substantially affected characteristics of this layer and its internal structure. The volume fraction of the solid phase in this layer increases, while its permeability and interdendrite distance decrease with increase of intensity of the entering melt flow [15]. Application of the phase field method in the paper [16] showed that with directional solidification equilibrium compositions at the interface were invariant in relation to selecting diffusion constant matrices. In this case, it is easy to determine a change of concentration

gradients before the interface, as a velocity of the interface is known [16]. For the case of solidification in isothermal conditions, this problem has no stationary solution that is characterized by a constant velocity of the system. The interface growth coefficient as well as the equilibrium compositions depend on selecting the diffusion constant matrix as well as the melt composition. These characteristics of the phase transition affect a growth of morphological disturbances and, therefore, a process of formation of the material structure in various size ranges.

The above phase field method does not provide a full answer regarding the behavior of the material at initial stages of crystallization, namely, mechanisms of formation of nuclei. To answer this question, the studies at an atom-molecular level are required. They are especially relevant in the context of developing methods of control of the said process by means of electromagnetic fields. Presently, a thermofluctuation mechanism of formation of nuclei is reliably established [17]. Its essence is that an atom transits from the metastable phase without a nucleus into the metastable phase with the nucleus by thermal fluctuation. With a big height of the potential barrier, probability of formation of nuclei is sharply reduced [17] and this mechanism does not adequately explain appearance of a first-order phase transition. It should also be noted that this mechanism is applicable when the system is in conditions close to equilibrium ones, for example, at low rates of heating and cooling [18]. If the system is under any external effects (mechanical, electromagnetic, etc.), then, as the results of the studies [18,19] demonstrate, it experiences nonadiabatic Landau–Zener transitions and thermofluctuation transitions. According to the author of the paper [19], formation of the new phase nuclei is caused by two mechanisms: a thermally activated one and an athermal one, which is caused by these transitions. In accordance with these mechanisms, construction of the nucleus formation model requires use of two order parameters. The first one has the meaning of the most unstable mode of dynamic atomic displacements, while the second one has the meaning of the amplitude of the most unstable mode of their elastic displacements. As shown by the results of the study [20], in the two-component system, depending on ratios of spatial and time scales, the development scenarios may be both switching waves and static autosolitons as well. As the authors of the paper [19] believe, the latter correspond to formation of the new phase nuclei.

The electric fields and currents substantially affect the process of crystallization of the materials. Thus, the papers [21,22] have studied influence of the electric field on a process of crystallization of thin films of amorphous silicon as induced by presence of aluminum. It was shown that application of the currents from 3 to 6 A contributes to increase of film porosity and formation of large grains. It is shown in the paper [23] that effect of the electric current on crystallization of steel castings results in more uniform distribution of carbide-generating elements across its cross section, thereby improving operating characteristics of cast parts. It is found in the study [24] that irradiation of the AA511 alloy by nanosecond electromagnetic pulses contributes to substantial refinement of structural components and redistribution of alloying elements, which is manifested in two-time increase of microhardness. According to the authors of the paper [24], effect of the pulse electromagnetic field results in reduction of critical values of the Gibbs free energy, which are required for initiation of processes of formation of nuclei and reduction of surface tension at the „melt–crystal“ interfaces, thereby facilitating the crystallization process. The results of the studies [25,26] show that the electric field ambiguously affects crystallization of the dielectric liquids. The authors of the paper [25,26] explain this behavior of the crystallization process by the fact that during formation of the nucleus in the electric field the Gibbs free energy changes by a value ΔW_E, which, in turn, is a difference of the electric field energies after formation of the nucleus and before its formation. The change of the electrostatic field energy calculated in approximation of the spherical nucleus is $\Delta W_E = c_e E^2$, where

$$c_e = \frac{3\varepsilon_0\varepsilon_m(\varepsilon_c - \varepsilon_m)v_0}{2(\varepsilon_c - \varepsilon_m)},$$

v_0 — the nucleus volume; ε_0 — the dielectric constant; ε_m and ε_c — permittivities of the melt and the crystals, respectively; E — the electric field strength. A value of the work of formation of the nucleus as obtained within the framework of the thermofluctuation theory will be as follows

$$W^* = \frac{16\pi v_0^2\gamma^3}{3(\Delta\mu_0 + c_e E^2)^2},$$

where γ — the surface tension; $\Delta\mu_0$ — the change of the chemical potential of the system before application of the field. If $\varepsilon_c > \varepsilon_m$, then $c_e > 0$ and the work of formation of the nucleus is reduced, otherwise $c_e < 0$ and the value of W^* increases. For conducting liquids, such manifestation of effect of the electric field [27] is observed with the only difference that the work of formation of the nucleus will be as follows:

$$W^* = \frac{16\pi\gamma^3}{3\left(\Delta G_0 - (1/4)E^2(\sigma_c - \sigma_m)\right)^2},$$

where ΔG_0 — the change of the Gibbs free energy density before application of the field; σ_c and σ_m — the conductivities of the crystal and the liquid phase, respectively. It follows that if $\sigma_c < \sigma_m$, then the work of formation of the nucleus will be reduced, thereby resulting in reduction of a critical size of the nuclei to the nanoscale range [27]. Thus, the thermodynamic theory only qualitatively explains formation of the solid phase nuclei under impact of the electric fields. The question about the field effect mechanisms at the atom-molecular level remains open. In our view, to answer this question, it may be useful to take representations about field splitting of the electron subsystem energy levels during the „liquid–solid“

phase transitions. This splitting contributes to reduction of the value of a potential barrier that divides two states of the system (the metastable state without the nucleus and the metastable state with the nucleus), thereby increasing probability of the transition from one state into another. It should be noted that these representations were successfully applied in the study [28] when describing mechanisms of an electroplastic effect, which showed that due to this splitting a value of the material's yield strength was reduced.

Summarizing all of the above, we formulate the aim of the study, which is to establish the mechanism of crystallization in the electric field based on the representations about splitting of the atom energy levels.

1. Problem formulation

We will consider crystallization of the conducting liquids in the electric field. Following the study [18], we will consider that formation of the new phase nucleus is in two stages. The first stage includes excitation of dynamic atomic displacements due to the nonadiabatic Landau–Zener transitions. At the second stage, when the critical temperature is reached, the homogeneous distribution of the dynamic displacements becomes unstable in relation to disturbances with a wavelength exceeding an interatomic distance. The development of this instability is accompanied by origination of displacements modes with wavelengths that are close to the most unstable mode. The localized displacement distribution will represent the new phase nuclei [18]. According to the paper [29,30], the probability of the Landau–Zener transitions is determined as

$$P = \exp\left(-\frac{2\pi W_0^2}{\hbar v|(dU/dx)_1 - (dU/dx)_2|}\right),$$

where v — the velocity of atomic displacement; $2W_0$ — the width of the band gap; $\hbar$ — the Planck constant; $(dU/dx)_1$ and $(dU/dx)_2$ — the derivatives of the potential energy with respect to a coordinate near the point of intersection of the energy levels. Under impact of the electric field, due to splitting of the energy levels the width of the energy level is reduced by a value $\Delta W_E = a_p E^2$ (the Stark quadratic effect), where a_p is a magnitude that characterizes polarizability of the system atoms in the electric field [20]. This representation is justified in case of transmission of an pulse or constant electric current through the melt. As a result, the probability of the Landau–Zener transitions increases, so does the probability of appearance of the dynamic displacements and of formation of the new phase nucleus, respectively. As in the papers [18,19], in order to describe the phase transition, we will adhere to an approach proposed in the theory of nonlinear systems [31], which is based on a Landau expansion of the free energy along the order parameters near an instability threshold. Let the distribution of the atoms in the liquid phase along the coordinates is characterized by a continuous function $\rho_0(\mathbf{r})$, then as the material temperature decreases, the atom coordinates are shifted by the value $\mathbf{u}$, which includes dynamic inelastic displacements $\mathbf{u}_d$ and elastic displacements $\mathbf{u}_{el}$. When the temperature approaches a critical point, the equilibrium distribution of the atoms becomes unstable in relation to inelastic displacements [18,27,31]. Then the field of these displacements is as follows:

$$u_d(x,t) = \overline{u}_d + u_d^0\big(\varphi(x,t)\big(\exp(ik_1x) + \exp(-ik_1x)\big)\big),$$

where $\varphi(x,t)$ is an amplitude value of the most unstable mode of dynamic inelastic atomic displacements with a wave vector k_1. The magnitude u_d^0 is determined by medium properties. If $\varphi(x,t) > 0$, then the localized distributions of dynamic displacements will be the new phase nuclei, whose formation is accompanied by reduction of the free energy [18,27]. Formation of the nucleus also includes a change of the material volume $\Delta V = V_n - V_0$, where V_n — the nucleus volume, V_0 — the liquid phase volume. This change results in appearance of elastic displacements in the liquid phase. Near the stability threshold, the change of the volume is characterized as follows:

$$\Delta V(x,t) = V_d^0\big(\eta(x,t)\big(\exp(ik_2x) + \exp(-ik_2x)\big)\big),$$

where $\eta(x,t)$ — the amplitude value of the most unstable mode of elastic displacements with the wave vector k_2, V_d^0 — the parameter determined by the medium properties. As the change of the material volume is small ($\sim 10\%$) during the phase transformations, then $\varphi \ll 1$ and $\psi \ll 1$ [18,27].

The metastable medium with the new phase nuclei is bistable, i.e. at the same temperature value a parent phase with $\varphi = 0$ (the liquid without the nucleus) and a new phase with $\varphi > 0$ (the liquid with the nucleus) can be in equilibrium. A potential energy of this system has two minimums (a double-well potential). Taking into account this fact, expansion of the free energy along the order parameter φ is as follows

$$F = F_0 + \frac{\alpha|\varphi|^2}{2} + \frac{q_2(\varphi+\varphi^*)|\varphi|^2}{3} - \frac{q_3|\varphi|^4}{4} - \frac{q\psi|\varphi|^2}{2} - \frac{l_1^2}{2}(|\nabla\varphi|^2). \quad (1)$$

The third summand of (1) takes into account bistability of the medium. The sign „$*$“ means complex conjugation. The secondary mode that corresponds to elastic displacements is excited when there are dynamic displacements without the potential barrier that divides the two states. In this case, expansion of the free energy along the order parameter ψ is as follows

$$F_2 = F_0 - \frac{a|\psi|^2}{2} - \frac{b|\psi|^4}{4} + \frac{p\varphi|\psi|^2}{2} - \frac{l_2^2}{2}(|\nabla\psi|^2). \quad (2)$$

To clarify a qualitative picture of the crystallization phenomenon, we take into account changes of only moduli of the order parameters. Then (1), (2) take the following form

$$F = F_0 + \frac{\alpha\varphi^2}{2} + \frac{q_2\varphi^3}{3} - \frac{q_3\varphi^4}{4} - \frac{q\psi\varphi^2}{2} - \frac{l_1^2}{2}(|\nabla\varphi|^2),$$

$$F_2 = F_0 - \frac{a\psi^2}{2} - \frac{b\psi^4}{4} + \frac{p\varphi\psi^2}{2} - \frac{l_2^2}{2}(\nabla\psi^2). \quad (3)$$

Evolution of the order parameters is described by means of the Landau–Khalatnikov equations.

$$t_1 \frac{\partial\varphi}{\partial t} = \frac{\delta F_1}{\delta\varphi}, \quad t_1 \frac{\partial\psi}{\partial t} = \frac{\delta F_1}{\delta\psi}. \quad (4)$$

Under impact of the electric field, the value of the free energy is reduced by the magnitude $a_p E^2$. As a result, we obtain

$$F_{1e} = F_1 - a_p E^2. \quad (5)$$

Taking into account (5), the equations (4) will take the following form:

$$t_1 \frac{\partial\varphi}{\partial t} = (\alpha - q\psi) + q_2\varphi^2 - q_3\varphi^3 + l_1^2\Delta\varphi + \theta(t, E),$$

$$t_2 \frac{\partial\psi}{\partial t} = (-a + p\varphi)\psi - b\psi^3 + l_2^2\Delta\psi, \quad (6)$$

where

$$\theta(t, E) = \frac{\delta a_p}{\delta\varphi} E^2.$$

The parameters α, q, q_2, q_3 are determined by the body properties, t_1 — the characteristic time of the Landau–Zener transitions, l_1 — the spatial period of localized disturbances of dynamic displacements, t_2 — the characteristic time of the thermofluctuation transitions, l_2 — the spatial period of disturbances of elastic displacements. For convenience of the calculations, in (6) we proceed to dimensionless variables:

$$\tilde{\varphi} = \varphi q_3^{1/2}, \quad \tilde{\psi} = \psi b^{1/2} a^{-1/2}, \quad \tilde{t} = at/t_2,$$

$$\tilde{x} = x/l_2, \quad \tilde{E} = E q_3^{-1/2}, \quad \tilde{a}_p = a_p/l_2. \quad (7)$$

In the variables (7) the equations (6) will take the form

$$\tau \frac{\partial\varphi}{\partial t} = (\alpha - c\psi)\varphi + \beta\varphi^2 - \varphi^3 + l^2\Delta\varphi + \theta(t, E),$$

$$\frac{\partial\psi}{\partial t} = (-1 + d\varphi)\psi - \psi^3 + \Delta\psi, \quad (8)$$

where

$$\tau = \frac{t_1}{t_2} a, \quad l = \frac{l_1}{l_2} a^{1/2}, \quad \beta = q_2/q_3^{1/2},$$

$$c = q\left(\frac{a}{b}\right)^{1/2}, \quad d = \frac{p}{a q_3^{-1/2}}.$$

The sign „∼“ of (7) will be omitted for further convenience.

2. Results and discussion

In order to find stationary solutions, in the first equation of (8) we discard inertial and diffusion components and we also assume that $\psi = 0$. As a result, we obtain

$$\alpha\varphi + \beta\varphi^2 - \varphi^3 + \theta(t, E) = 0. \quad (9)$$

Without taking into account effect of the electric field, the stationary solutions of (8) take the form [19]:

$$\varphi_0 = 0, \quad \varphi_1 = \frac{\beta}{2} + \sqrt{\frac{\beta^2}{4} + \alpha}, \quad \varphi_2 = \frac{\beta}{2} - \sqrt{\frac{\beta^2}{4} + \alpha}. \quad (10)$$

Regions of stability of the solutions (10) are known [18,19]. When $\alpha < -(\beta^2/4)$, the solution $\varphi_0 = 0$ is the only one, which occurs for the parent liquid phase at the temperatures far from the critical one. If

$$-\frac{\beta^2}{4} < \alpha < 0,$$

then the system will be in the bistable state. When

$$-\frac{\beta^2}{4} < \alpha < -\frac{2\beta^2}{9}$$

the solution φ_0 is stable, while φ_1 is unstable. Within the interval

$$-\frac{2\beta^2}{9} < \alpha < 0$$

the solution φ_1 is stable, while φ_0 is metastable. When

$$\alpha = -\frac{2\beta^2}{9}$$

the solutions φ_0 and φ_1 have the same stability. The critical temperature can be found from this relationship. The condition $\alpha = 0$ determines loss of stability of the parents liquid phase. It should be also noted that the solution φ_2 is always unstable. As mentioned above (see Introduction), formation of the nucleus is matched with formation of the static autosoliton. This type of the waves can occur when $\tau < 1$, $l \ll 1$, $\tau > l$ [18,20]. At this, an amplitude of initial disturbance shall be less than φ_2. An important role in formation of the autosolitons is played by the parameters c and d, which are included in the first and the second equations of the system (7), respectively, and determine a type of the resulting autosoliton. When $d < 1/\varphi_2$, there will be oscillating and static autosolitons [18].

The effect of the electric field changes the conditions of stability of the stationary solutions of the equation (8). A special role here is played by a sign of the variation derivative $\delta a_p/\delta\varphi$, which determines a sign of the governing parameter $\theta(t, E)$. If

$$\frac{\delta a_p}{\delta\varphi} > 0,$$

then we are dealing with growing polarizability of the system atoms with increase of the amplitude of inelastic

dynamic displacements. As a result, the height of the potential barrier that divides two states is reduced, thereby resulting in the change of the critical temperature of the phase transition. Otherwise

$$\frac{\delta a_p}{\delta \varphi} < 0$$

there is reduction of polarizability of the system atoms and, respectively, reduction of a rate of formation of the nuclei due to increase of the height of the potential barrier that divides the two metastable states. To find the conditions of stability of the solutions (9) in the electric field, we note that it describes motion of a material particle in the field with potential energy

$$V = -\frac{\alpha\varphi^2}{2} - \frac{\beta\varphi^3}{3} + \frac{\varphi^4}{4} - \varphi\theta(t, E). \qquad (11)$$

The minimums of the function (11) will indicate the stable states of the system, while their position is determined by roots of the equation (8). The nature of the roots of the equation (8) depends on the sign of the expression $p^3 + q^2$, where

$$p = -\frac{\beta^2}{9} - \frac{\alpha}{3}, \quad q = -\left(\frac{1}{27}\beta^3 + \frac{\alpha\beta}{6} + \frac{\theta}{2}\right).$$

If $p^3 + q^2 > 0$, then (8) has one real root and two complex conjugate roots. Otherwise, all the three roots are real. In the space of the parameters (p, q) or (α, β, θ), these modes are separated by a curve $p^3 + q^2 = 0$, in which (9) has one single real root and one double root. The three-time real root will also be observed when $p = 0$ and $q = 0$, which is equivalent to $\beta_{\min} = \sqrt{-3\alpha}$ and $\theta_{\min} = \beta^3/27$ when $\alpha < 0$ [32]. In order to obtain values of the parameter θ, at which (8) has real roots, we present the expression $p^3 + q^2 = 0$ as

$$\frac{\theta^2}{4} + \left(\frac{\beta^3}{27} + \frac{\alpha\beta}{6}\right)\theta - \frac{\alpha^2\beta^2}{108} - \frac{\alpha^3}{27} = 0. \qquad (12)$$

The roots of the equation (12) are as follows

$$\theta_1 = -\frac{2}{27}\sqrt{(\beta^2 + 3\alpha)^3} - \frac{\alpha\beta}{3} - \frac{2\beta^3}{27},$$

$$\theta_2 = \frac{2}{27}\sqrt{(\beta^2 + 3\alpha)^3} - \frac{\alpha\beta}{3} - \frac{2\beta^3}{27}. \qquad (13)$$

The dependences of θ on β (13) at the fixed value of α are shown on Fig. 1.

It follows from this figure that within the region I between the curves θ_1 and θ_2 the equation (10) will have real roots that correspond to various stationary states. This interval will exhibit a local minimum of the dependence (11) in the point $\varphi_E \approx 0$ and a global minimum in the point $\varphi_1 > 0$, which are separated by the potential barrier (Fig. 2, *a*, the curve *1*)). As the strength of the electric field increases, there is reduction of the height of the potential barrier that

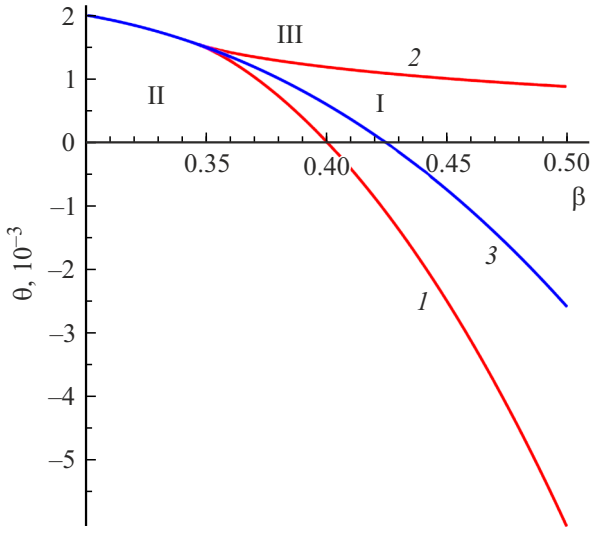

Figure 1. Dependences θ on β: *1* — the first equation of the system (12); *2* — the second equation of the system (12); *3* — the condition (13).

divides the states φ_E and φ_1, up to full disappearance. The only stable state is still φ_1 (Fig. 2, *a*, the curve *2*). As shown by the results of the study [32], which are obtained for the simple autocatalytic reactions, the region I can be divided into two subregions of the curve (Fig. 1, the curve *3*), in which the potential (11) has two quantum wells of the same depth, i.e. the solution φ_E and φ_1 will have the same stability (Fig. 2, *a*, the curve *3*). This curve will be formed provided that $p \neq 0$ and $q = 0$, which is equivalent to

$$\theta_3 = -\frac{\alpha\beta}{3} - \frac{2\beta^3}{27}. \qquad (14)$$

It is possible to determine from the condition (14) threshold values of the electric field E_c and the critical temperature T_c, above which there is a stable state $\varphi_1 > 0$ resulting in formation of the solid phase nucleus.

If the system is in the liquid phase (the region II of Fig. 1), then when $\theta = 0$ the only stable condition is the state $\varphi_0 = 0$ (Fig. 2, *b*, the curve *4*). The electric field results in formation of a local maximum near φ_0 (Fig. 2, *b*, the curve *5*). Dynamic inelastic displacements do not develop and the new phase nuclei are not formed. Within the region III ($\theta > \theta_3$ and $\theta > \theta_2$, Fig. 1), only one global minimum is formed. In indicates that strong electric fields contribute to development of dynamic displacements and, respectively, stimulate the crystallization process.

Fig. 3 shows the distributions of the order parameters in the electric field, which are obtained when $\alpha = -0.04$, $c = 0.4$, $d = 15$, $\tau = 0.9$, $l = 0.05$, $\varphi_m = 0.1$, $\psi_m = 0.001$, $\sigma_\varphi = \sigma_\psi = 1$, $x_0 = 1.5$ and with the various values of β by solving the system of equations (8) with the periodic boundary conditions. The initial disturbances were predefined as

$$\varphi(x, 0) = \varphi_0 + \varphi_m \exp\left(-\sigma_\varphi (x - x_0)^2\right)$$

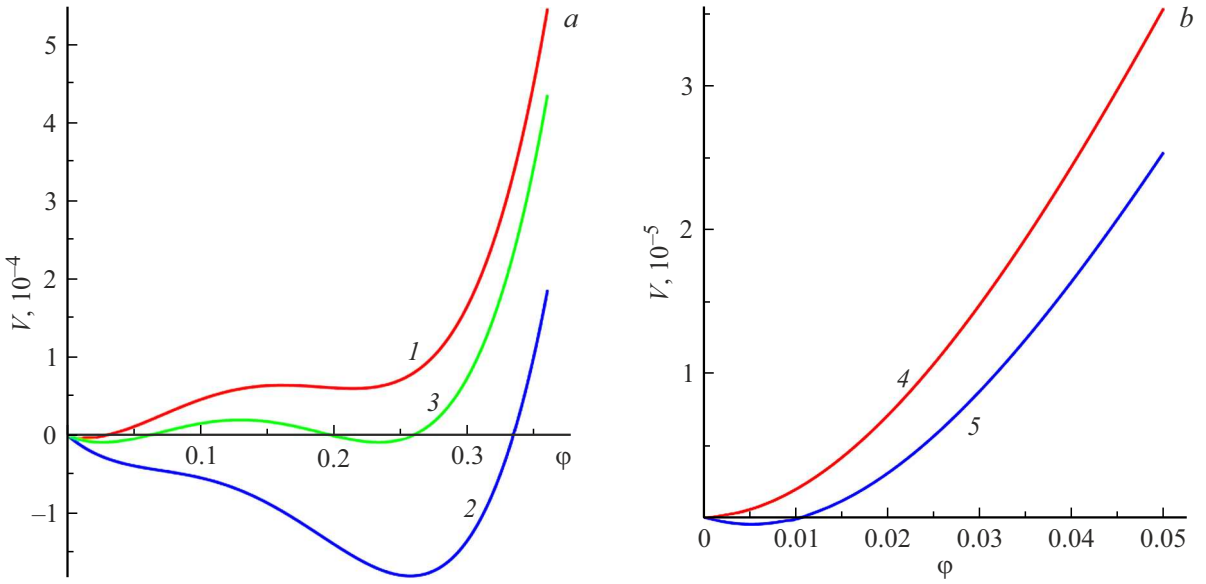

Figure 2. The dependences V on the order parameter φ when $\alpha = -0.04$ and $\beta = 0.39$. *1* — the function $V(\varphi)$ when $\theta = 0.0005$ $(\theta_1 < \theta < \theta_2)$; *2* — the function $V(\varphi)$ when $\theta = 0.0015$ $(\theta > \theta_2)$, *3* — the function $V(\varphi)$ when $\theta = 0.0008$ $(\theta = \theta_3)$ (a); *4* — $\theta = 0$; *5* — $\theta = 0.0002$ (b).

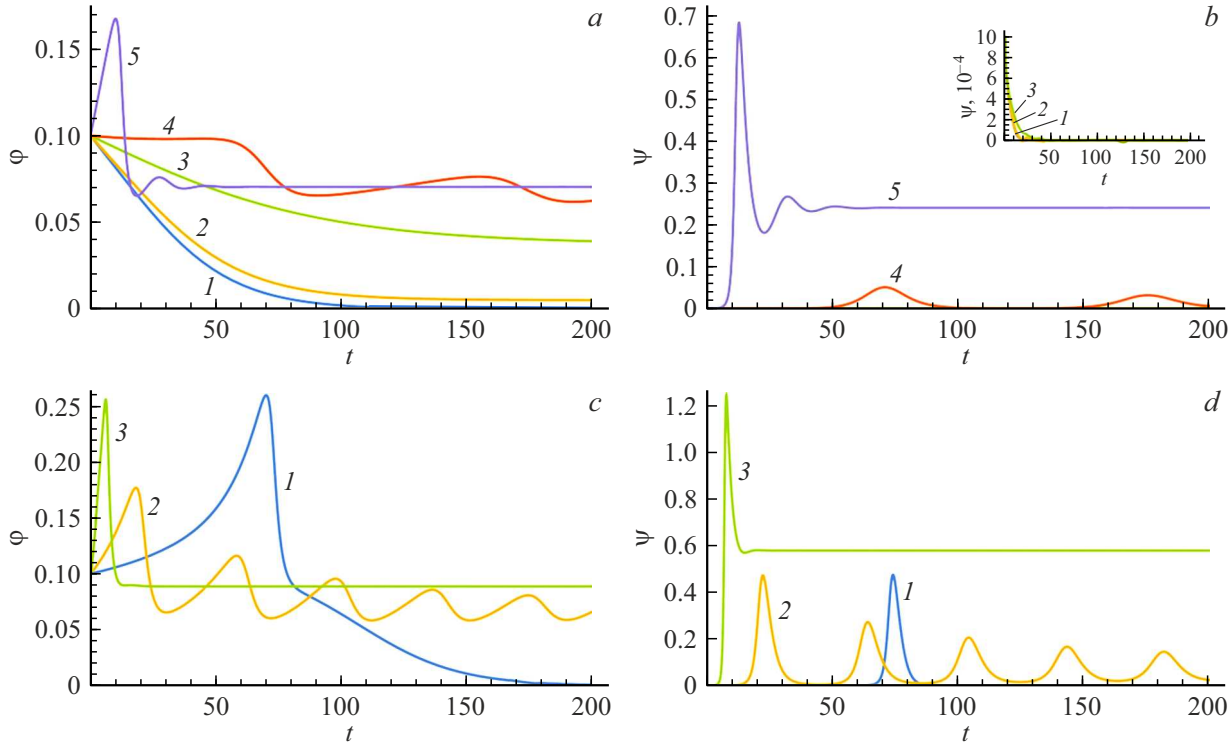

Figure 3. Dependences of the order parameters φ and ψ on time when $c = 0.4$; a, b — $\beta = 0.39$, c, d — $\beta = 0.6$. *1* — $\theta(t, E) = 0$; *2* — $\theta(t, E) = 0.0002$; *3* — $\theta(t, E) = 0.0008$; *4* — $\theta(t, E) = 0.0015$; *5* — $\theta(t, E) = 0.008$ (a, b). *1* — $\theta(t, E) = 0$; *2* — $\theta(t, E) = 0.002$; *3* — $\theta(t, E) = 0.02$ (c, d).

and

$$\psi(x, 0) = \psi_0 + \psi_m \exp\left(-\sigma_\psi (x - x_0)^2\right).$$

At the same time, $\varphi_m \gg \psi_m$ and $\varphi_0 = \psi_0 = 0$. It follows from the figure that when $\beta = 0.39$ and $\theta = 0$ (the region II of Fig. 1) there will be relaxation of the order parameter φ (Fig. 3, a, the curve *1*). The stationary state $\varphi_{st} = 0$ is obtained for $t = 150$, whereas the electric effect reduces the depth of relaxation, thereby resulting in that $\varphi_{st} > 0$ (Fig. 3, a, the curve *2*). The same behavior is observed in

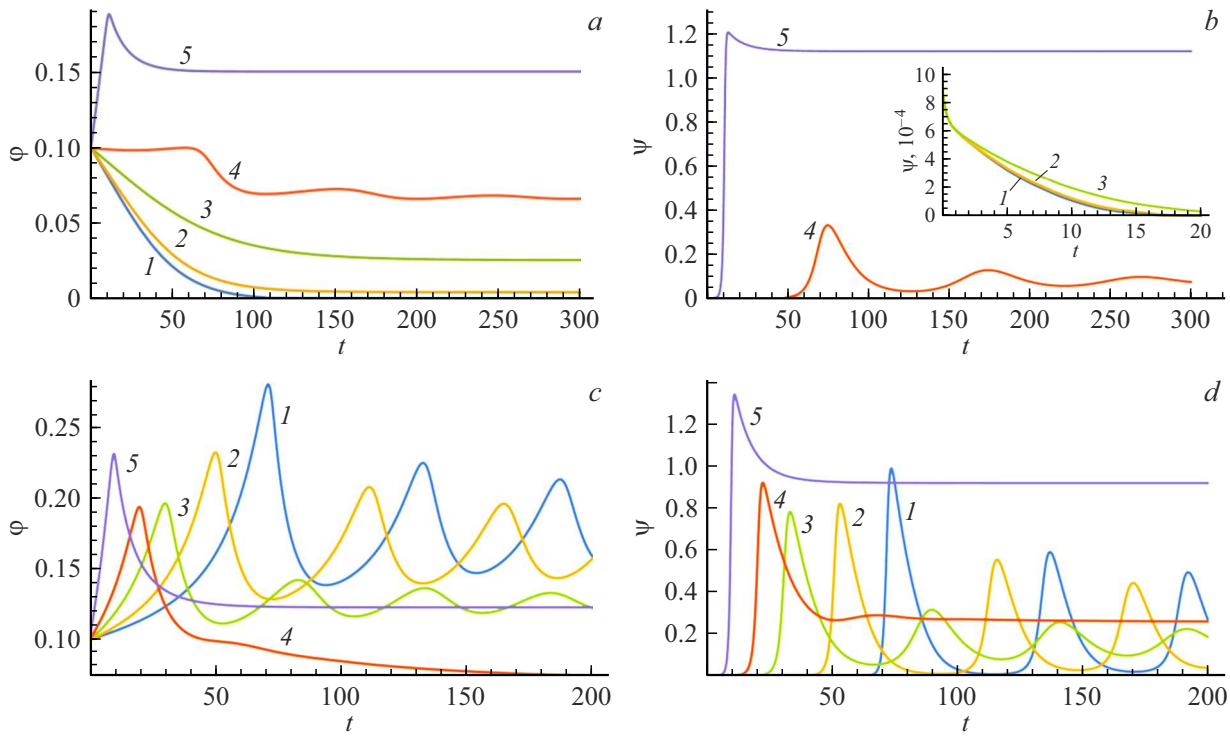

Figure 4. Dependences of the order parameters φ (a) and ψ (b) on time when $c = 0.05$; *1* — $\theta(t, E) = 0$; *2* — $\theta(t, E) = 0.0002$; *3* — $\theta(t, E) = 0.0008$; *4* — $\theta(t, E) = 0.002$; *5* — $\theta(t, E) = 0.009$.

the interval $\theta_1 < \theta < \theta_2$ (Fig. 3, *a*, the curve *3*). When $\theta > \theta_2$ (the region III of Fig. 2), first the oscillating autosoliton is formed (Fig. 3, *a*, the curve *4*), and then the static autosoliton is formed (Fig. 3, *a*, the curve *5*). The similar behavior is observed for the order parameter ψ, but it decreases faster than φ (Fig. 3, *b*). Increase of the value of β to 0.6 (the region I, the subregion $\theta_3 < \theta < \theta_2$ of Fig. 1) results in formation of a damped autosoliton in the absence of the electric field (Fig. 3, *c*, the curve *1*). As shown by results of the study [18], it is formed and evolves in three stages. In the first stage, the order parameter φ increases to the maximum value φ_m, while the parameter ψ is close to zero. When $(-1 + d\varphi) > 0$, there is the second stage, and ψ starts growing sharply, while φ slightly varies within the interval $\Delta t \sim 1$. In the third stage, both the order parameters decrease, but φ decreases slower than ψ. Application of the electric field ($\theta(t, E) = 0.002$) results in the change of the autosoliton to the oscillating one (Fig. 3, *c, d*, the curve *2*). Further increase of the value of $\theta(t, E)$ to 0.02 results in formation of the static autosoliton (Fig. 3, *c, d*, the curve *3*). It should be noted that a transition from the damped autosoliton to the oscillating one in the electric field also occurs when $\theta > \theta_2$.

If the value of c is reduced to 0.05, then when the value $\beta = 0.39$ a pattern of distribution of the order parameters will not be fundamentally changed as compared to the previous case (Fig. 4, *a, b*). The only difference is that the amplitude values of the order parameter φ in the oscillating autosoliton decrease much faster (Fig. 4, *a, b*, the curve *4*). When $c = 0.05$ and $\beta = 0.6$, in conditions in the absence of the electric field there will be the oscillating autosoliton (Fig. 4, the curve *1*). At this, the amplitude values of the order parameter φ decrease with time. As a result, a stationary localized state is set. With the values $\theta(t, E) = 0.0002$ and $\theta(t, E) = 0.0008$, there is acceleration of this process (Fig. 4, the curves *2* and *3*). Increase of the value of θ by one order results in formation, first, of the damped autosoliton (Fig. 4, the curve *4*), and, then, of the static autosoliton (Fig. 4, the curve *5*).

Now we proceed to consideration of influence of an oscillation period of the external electric field on the crystallization process. For this, we present this dependence of the electric field on time in the following form: $E(t) = E_m \sin\big((2\pi/T)t\big)$, where T — the period of oscillations. This dependence occurs, for example, during magnetic pulse processing [33]. In this case: $\theta(t, E) = \theta_m \sin^2\big((2\pi t/T)\big)$. Fig. 5 shows the distribution of the order parameters when $\theta_m = 0.0002$, $\beta = 0.6$ and $T = 10^{-4}$, 10^{-3} and 10^{-2} along the mode of formation of the damped autosoliton. It follows from the figure that increase of the oscillation period of the external electric field result in the fact that the time of reaching the maximum value φ_m decreases from $t = 70.1$ in the absence of the field to 68.2 with the value of the period $T = 10^{-4}$ and to 57.3 and 57.5 when $T = 10^{-3}$, 10^{-2} , respectively. At the same time, the third stage of development of the damped autosoliton proceeds faster than without effect of the field.

Thus, it can be concluded that with increase of the oscillation period of the electric field a rate of autosoliton damping increases.

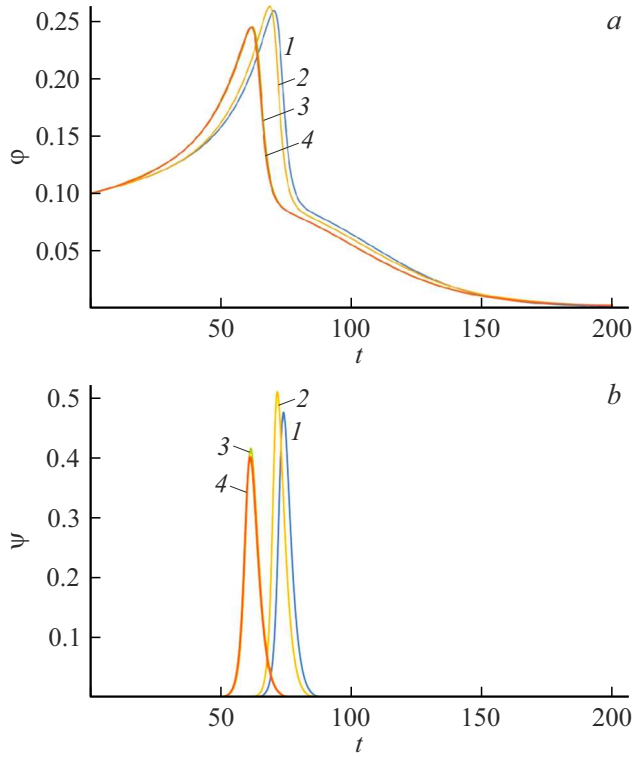

Figure 5. Dependences of the order parameters φ (a) and ψ (b) on time in the damped autosoliton mode (when $c = 0.4$ and $\theta_m = 0.0002$): *1* — without effect of the field; *2* — $T = 10^{-4}$; *3* — $T = 10^{-3}$; *4* — $T = 10^{-2}$.

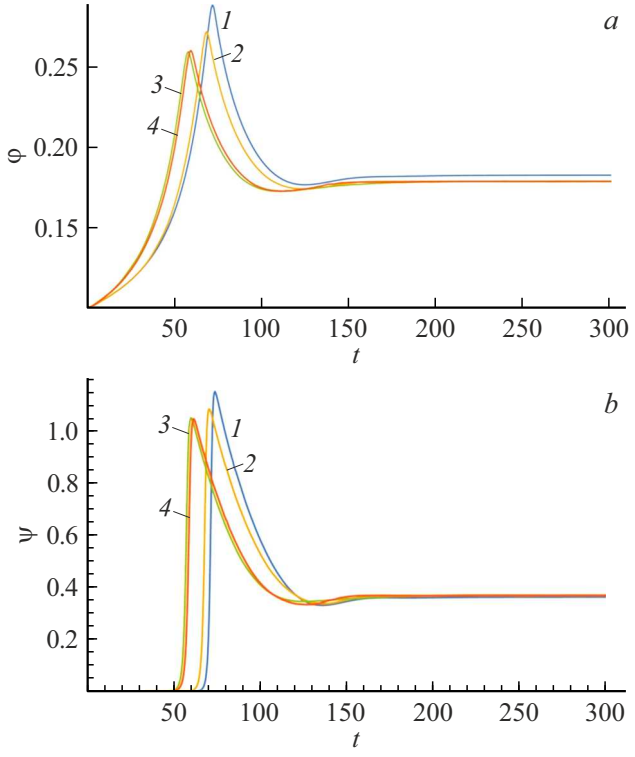

Figure 6. Dependences of the order parameters φ (a) and ψ (b) on time in the mode of formation of the static autosoliton (when $c = 0.05$ and $\theta_m = 0.0002$): *1* — without the effect of the field; *2* — $T = 10^{-4}$; *3* — $T = 10^{-3}$; *4* — $T = 10^{-2}$.

In the mode of formation of the static autosoliton, which is matched with the new phase nucleus, the increase of the oscillation period of the electric field results in the fact that it is formed in less time than in the absence of the field (Fig. 6).

Now we consider influence of pulse duration of the electric field. For this, the dependence of θ on time we present in the following form:

$$\theta(t) = \begin{cases} \theta_m, & 0 < t < \tau_i, \\ 0, & \tau_i < t < T, \end{cases} \qquad (15)$$

where τ_i — the pulse duration; T — the pulse period. The results of the calculations of Fig. 7 have shown that with increase of the pulse duration, with a constant period of the pulsed electric field the static autosoliton is formed faster than in the absence thereof. Thus, when $\tau_i = 5$, $\theta_m = 0.0002$ and $T = 20$ the maximum value of the order parameter φ_m is reached for the time $t = 65$, whereas when $\tau_i = 10$ and 15 the maximum of the order parameter falls on the value $t = 55$ and 53, respectively.

The above-listed facts make it possible to conclude that due to splitting of the energy levels and reduction of time of the Landau–Zener transition the electric field contributes to formation of the new phase nuclei at the temperatures that exceed the temperature of the phase transformation in the initial state (without effect of the field).

We proceed to consideration of influence of the electric field on diffusive phase transformations. These transformations occur at low rates of cooling at the interface of the parent and the new phase. In this case, the time of the phase transformation as per the thermofluctuation mechanism is much less than the time of the Landau–Zener transition. Therefore, it can be presumed that the diffusive transformations proceed as per the mechanism of thermal fluctuations [19]. The atomic displacements and the medium strain will be determined by vibrational degrees of freedom. The coefficient d in the second equation of the system (8) shall be small in comparison with the previous case. As shown by the results of the study [19], these transformations are accompanied by origination of the switching wave that appears under the condition $\tau \leq l$ and $\tau < 1$, $l < 1$. Fig. 8 shows the distribution of the order parameters in the switching wave when $\tau = 0.01$; $l = 0.05$, $d = 3$, $c = 0.4$ and at various values of θ. It follows from the figure that the switching wave develops in three stages regardless of whether the electric field is connected or not. The first stage includes sharp growth of the order parameter φ (Fig. 8, a), while $\psi \approx 0$ (Fig. 8, b). As the time t^* is reached, there is the second stage that is characterized by weak variation of φ and sharp growth of the order parameter ψ. At the third stage, the value of the order parameter φ will be reduced until a stationary value. The order parameter ψ will proceed to saturation.

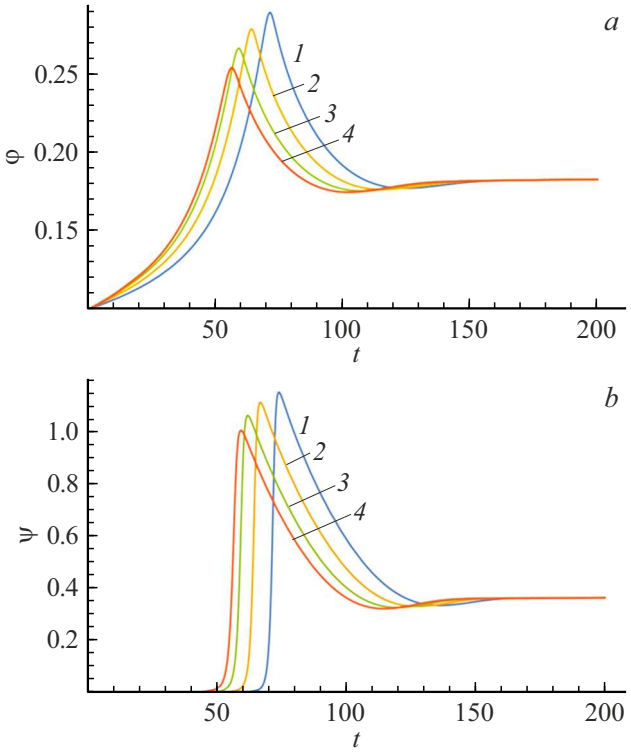

Figure 7. Dependences of the order parameters φ (a) and ψ (b) on time in the mode of formation of the static autosoliton (when $c = 0.05$ and $\theta_m = 0.0002$) with the various pulse duration: *1* — without effect of the field; *2* — $\tau_i = 5$; *3* — $\tau_i = 10$; *4* — $\tau_i = 15$.

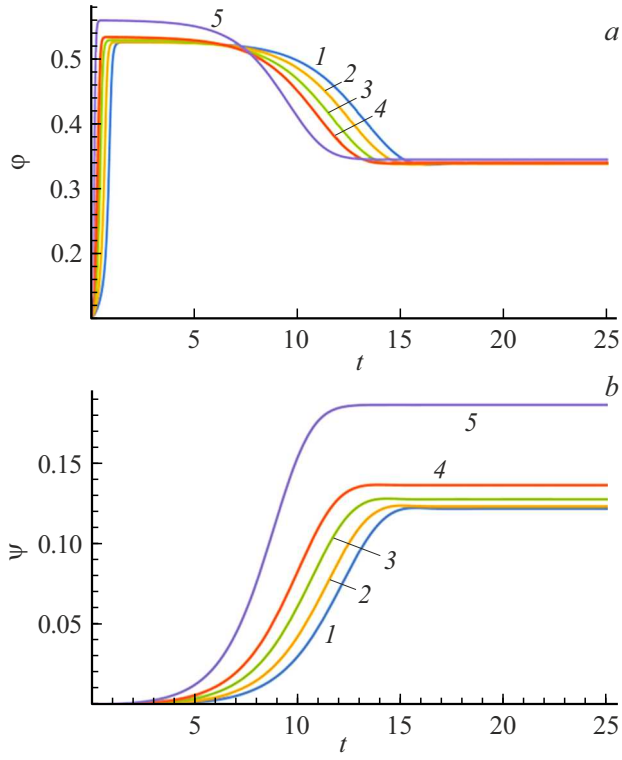

Figure 8. Distribution of the order parameters φ (a) and ψ (b) along time in the switching wave: *1* — $\theta(t, E) = 0$; *2* — $\theta(t, E) = 0.0002$; *3* — $\theta(t, E) = 0.0008$; *4* — $\theta(t, E) = 0.002$; *5* — $\theta(t, E) = 0.009$.

As in case of the autosoliton, the electric field accelerates processes of formation and propagation of the switching wave. If in the absence of the field reaching the stationary values φ and ψ takes the time $\Delta t = 17$ (the curve *1*), then when $\theta(t, E) = 2 \cdot 10^{-4}$ and $8 \cdot 10^{-4}$ the stationary states are obtained for $\Delta t = 16.2$ and 15.8, respectively (the curves *2* and *3*). The stationary values of φ slightly vary at small θ. These changes are the most pronounced are when the values of θ increase by one order (the curves *4* and *5*). Thus, for example, when $\theta(t, E) = 9 \cdot 10^{-3}$ (the curve *5*) the value $\varphi_{st} = 0.346$, whereas when $\theta(t, E) = 0$ $\varphi_{st} = 0.338$. And vice versa, the stationary value of the order parameter ψ, monotonically increases from 0.1213 when $\theta(t, E) = 0$ to 0.1851 when $\theta(t, E) = 9 \cdot 10^{-3}$. Let us evaluate the speed of the switching wave on the example of the order parameter. For this, we will use the formula proposed in the study [34]:

$$V = (l/\tau)(\varphi_0 + \varphi_1 - 2\varphi_2)/2. \qquad (16)$$

If in the absence of the electric field the dimensionless speed of the switching wave $V = 0.037$, then when $\theta(t, E) = 0.0002$ its value is 0.039, thereby confirming the fact of increase of the speed of propagation of the switching wave.

For the case when the dependence $\theta(t, E)$ is described by the equation (14), a role of pulse duration of the electric field is shown on Fig. 8. It follows from the figure that propagation of the switching wave in the electric field does not depend on the pulse duration, but it depends only on its amplitude, which is manifested in superimposition of the curves *2*–*4* to each other. The stationary valuesφ_{st} and ψ_{st} in the presence of the field are 0.3560 and 0.2579, respectively.

This acceleration of the diffusive phase transformations is related to decrease of the time of thermal fluctuation due to splitting of the energy levels and reduction of the value of the potential barrier. If in the initial state $t_{th} \propto \exp(U/kT_s)$, where U — the activation energy; k — the Boltzmann constant; T_s — the temperature, then under impact of the field $t_{th} \propto \exp\big((U - a_p E^2)/kT_s\big)$.

Conclusion

1. It is found that application of the external electric field results in splitting of the energy levels of the atoms, which is manifested in increase of the probability of the nonadiabatic Landau–Zener transitions and the transitions caused by thermal fluctuations. As a result, dynamic displacements occur and result in formation of the nuclei at the temperature higher than the temperature of the phase transition in the absence of the field.

2. The equations of kinetics of the order parameters were analyzed to show that there is the change of the type of their solution in an area to the right of the curve θ_3. If the interval

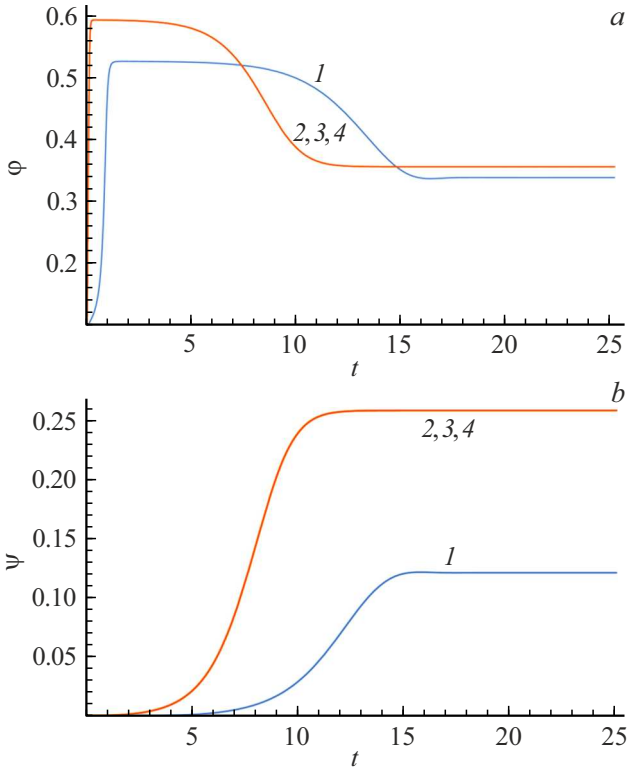

Figure 9. Distribution of the order parameters φ (a) and ψ (b) along time in the switching wave with various pulse duration (the amplitude value $\theta_m = 0.02$): *1* — without effect of the field; *2* — $\tau_i = 5$; *3* — $\tau_i = 10$; *4* — $\tau_i = 15$.

$\theta_1 < \theta < \theta_3$ exhibits relaxation of the order parameters φ and ψ, then the damped autosoliton is formed in the interval $\theta_3 < \theta < \theta_2$, which is due to formation of the new global minimum of potential energy of the crystallizing system.

3. The effect of the electric field results in the change of the type of the autosoliton solutions when $\theta(t, E) > \theta_2$ from the damped autosoliton to the oscillating autosoliton. Further increase of the field results in appearance of the static autosoliton, which corresponds to the new phase nucleus. This is due to disappearance of the potential barrier that divides the stationary states $(\varphi_E,\ \psi = 0)$ and $(\varphi_1,\ \psi = 0)$.

4. The pulse duration τ_i of the electric field, with its constant period and amplitude, substantially affects formation and development of the static autosoliton. It is manifested in acceleration of its development. The time of reaching the maximum of the order parameter φ_m monotonically decreases with increase of τ_i.

5. It is found for the case of diffusive phase transformations that the electric field accelerates these transformations, which is manifested in the increase of the rate of formation and evolution of the switching wave. It is related to reduction of the time of thermal fluctuation due to decrease of the potential barrier as a result of splitting. This effect depends on the amplitude only and does not depend on the pulse duration.

Funding

The study was supported by the Russian Science Foundation grant no. 22-79-10229, https://rscf.ru/project/22-79-10229/.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Ghosh, J. Zollinger, M. Zaloznik, D. Banerjee, C.K. Newman, R. Arroyave. Additive Manufacturing, **78**, 103845 (2023). DOI: 10.1016/j.addma.2023.103845
[2] Y. Chen, X.B. Qi, D.Zh. Li, X.H. Kang, N.M. Xiao. Comp. Mater. Sci., **104**, 155 (2015). DOI: 0.1016/j.commatsci.2015.04.003
[3] Ch.-Sh. Zhu, Sh. Xu, L. Feng, D. Han, K.-M. Wang. Comp. Mater. Sci., **160**, 53 (2019). DOI: 10.1016/j.commatsci.2018.12.058
[4] X. Zhang, H. Wang, W. Kuang, J. Zhang. Acta Mater., **128**, 258 (2017). DOI: 10.1016/j.actamat.2017.02.026
[5] J. Kundin, E. Pogorelov, H. Emmerich. Acta Mater., **83**, 448 (2015). DOI: 10.1016/j.actamat.2014.09.057
[6] P.P. Kaminskii, Yu.A. Khon. Theor. Appl. Fracture Mechan., **51**, 161 (2009). DOI: 10.1016/j.tafmec.2009.05.006
[7] E.E. Slyadnikov. Metals, **11**, 1390 (2021). DOI: 10.3390/met11091390
[8] X. Yang, J. Zhao. Comput. Phys. Commun., **235**, 234 (2019). DOI: 10.1016/j.cpc.2018.08.012
[9] A.G. Khachaturyan. *Theory of structural transformations in solids* (Wiley, NY., 1983)
[10] D.V. Alexandrov, G.Y. Dubovoy, A.P. Malygin, I.G. Nizovtseva, L.V. Toropova. Russ. Metallurgy, **2017**, 127 (2017). DOI: 10.1134/S0036029517020021
[11] D.V. Alexandrov, P.K. Galenko. Phys.-Usp., **57** (8), 771 (2014). DOI: 10.3367/UFNe.0184.201408b.0833
[12] B. Nestler, A.A. Wheeler. Comp. Phys. Commun., **147**, 230 (2002). DOI: 10.1016/S0010-4655(02)00252-7
[13] V.G. Lebedev. ZhTF, **92** (2), 187 (2022) (in Russian).
[14] D.V. Alexandrov, L.V. Toropova. Scientific Reports, **12**, 17857 (2022). DOI: 10.1038/s41598-022-22786-w
[15] D.V. Aleksandrov, I.V. Aleksandrova, A.A. Ivanov, I.O. Starodumov, L.V. Toropova. Rasplavy, **1**, 37 (2020). DOI: 10.31857/S0235010620010028
[16] A. Lahiri, A. Choudhury. J. Crystal Growth, **459**, 1 (2017). DOI: 10.1016/j.jcrysgro.2016.11.046
[17] S.A. Kukushkin, A.V. Osipov. Prog. Surf. Sci., **151** (1), 1 (1996). DOI: 10.1016/0079-6816(96)82931-5
[18] Yu.A. Khon. FTT, **65** (8), 1263 (2023) (in Russian).
[19] Yu.A. Khon. FTT, **66** (3), 342 (2024) (in Russian).
[20] B.S. Kerner, V.V. Osipov. Phys.-Usp., **32** (2), 101 (1989).
[21] Y.J. Choi, K. Ryu, H.-L. Lee, S.J. Moon. Thin Solid Films, **779**, 139919 (2023). DOI: 10.1016/j.tsf.2023.139919
[22] K. Ryu, J.-Y. Park, S.J. Moon. Mater. Sci. Semicond. Process., **158**, 107352 (2023). DOI: 10.1016/j.mssp.2023.107352
[23] I.F. Selyanin, S.N. Starovatskaya, A.A. Kutsenko, A.I. Kutsenko. Steel in Translation, **42** (12), 814 (2012).

[24] V.B. Deev, E.Kh. Ri, E.S. Prusov, M.A. Ermakov, A.V. Goncharov. Izvestiya vuzov. Tsvetnaya Metallurgiya, **27** (4), 32 (2021) (in Russian). DOI: 10.17073/0021-3438-2021-4-32-41
[25] A.L. Fiona, N. Radacsi. Cryst. Eng. Comm., **21**, 5014 (2019). DOI: 10.1039/c9ce00755e
[26] D. Kashchiev. *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, NY., 2000)
[27] J. Tang, S. Li, X. Mao, Y. Du. J. Phys. D: Appl. Phys., **38**, 729 (2005).
[28] P.P. Kamisnkii. *Neobratimaya deformatsiya kristallov kak strukturnoe prevrashchenie, initsiiruemoe izmeneniem mezhatomnogo vzaimodeistvi* (Dokt. diss., 2015) (in Russian).
[29] O.V. Ivakhnenko, S.N. Shevchenko, F. Nori. Phys. Reports, **995**, 1 (2023). DOI: 10.1016/j.physrep.2022.10.002
[30] L.D. Landau, E.M. Lifshits. *Kurs teoreticheskoi fiziki. Kvantovaya mekhanika (nerelyativistskaya teoriya)* (Fizmatlit, M., 2004). t. III (in Russian).
[31] P.C. Hohenberg, A.P. Krekhov. Phys. Reports, **572**, 1 (2015). DOI: 10.1016/j.physrep.2015.01.001
[32] G. Nicolis, I. Prigogine. *Self-Organization in Non-equilibrium system* (Wiley, NY., 1977)
[33] G.R. Li, B.W. Zhao, H.M. Wang, Z.J. Ji, X.F. Ding, H. Nan, J.J. Zhang, T.T. Wu, S.M. Chen. Mater. Characterization, **211**, 113919 (2024). DOI: 10.1016/j.matchar.2024.113919
[34] A.Yu. Loskutov, A.S. Mikhailov. *Vvedenie v sinergetiku* (Nauka, M., 1990) (in Russian).

Translated by M.Shevelev