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Nonadiabatic transitions of atoms and the formation of new phase nuclei in solids

© *Yu.A. Khon*

Institute of Strength Physics and Materials Science SB RAS,
Tomsk, Russia

E-mail: khon@ispms.tsc.ru

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A mechanism for the formation of nuclei of a new phase in a solid is proposed, determined by nonadiabatic Landau–Zener transitions in an open system of nuclei and electrons. Based on the analysis of the equations of nonadiabatic molecular dynamics, two order parameters are identified. The dynamics of the nucleation and growth of the embryo is determined by two related nonlinear parabolic equations for order parameters. The conditions for the formation of stable and unstable embryos are found. It is shown that the formation of the embryo can proceed in an auto-oscillatory mode. The influence of the heating (cooling) rate on the formation of new phase nuclei is considered.

Keywords: Phase transformations, non-adiabatic dynamics of atoms, dynamic displacements, localization of displacements.

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1. Introduction

Phase transformations (PT) in solids (polymorphic, martensitic transformations, crystallization of the amorphous phase, decomposition of a solid solution, etc.) are widespread in nature and play a key role in changing the microstructure and properties of various materials. For this reason, they have important fundamental and applied value in physics, materials science and other sciences. It is not surprising that much attention has been paid and is being paid to the study of phase transformations in solids [1–20]. It was found that the phase transition of the first kind is a complex multistage process determined and accompanied by various nonlinear phenomena. The first fastest stage is the stage of a formation of a new phase nucleus, the size of which exceeds the critical value. The equation describing the kinetics of the origin of a new phase was first obtained by Zeldovich [13]. The kinetics of nucleation is determined by the rate of transition of atoms from the metastable phase to the nucleus, and the rate itself depends on the mechanisms of growth of the nucleus. There were no restrictions of the mechanisms of nucleus growth in Zeldovich's theory. The probability of realization of one or another mechanism in the system depends on the conditions under which the phase transition occurs, and is ultimately determined by the dynamics of atoms. And there are two possible cases here.

In the first case, when the phase transformation takes place under conditions close to equilibrium (low heating/cooling rates, absence of external forces), the solid is considered as an isolated system. The Born–Openheimer adiabatic approximation is applicable for such systems [14] (electrons instantly adjust to the slow movement of nuclei). The dynamics of atoms is determined by vibrational degrees of freedom, the displacements of atoms are completely determined by the gradients of a single potential energy surface (PES) $E(R)$. Here $R = \{R^1, \dots, R^N\}$ — the coordinates of the nuclei in $3N$-dimensional space, N — the number of atoms. PSE represents a hypersurface in $3N$-dimensional space with its minima and potential barriers separating them. One of these minima corresponds to the potential energy of the metastable phase, and the other — to the metastable phase with the nucleus. According to [9], the probability of formation of a nucleus

$$w(a) \propto \exp\left(-\frac{R_{\min}}{k_{\mathrm{B}}T}\right),$$

where a — nucleus size, k_{B} —Boltzmann constant, T — temperature, $R_{\min}$ — the minimum work that must be expended to form a nucleus of a given size. When a critical nucleus is formed, the trajectories of the shifting atoms (in phase space) should be near the top of the potential barrier separating the metastable phase without a nucleus and with an nucleus. The atoms are displaced due to thermal fluctuations. The value of w for the considered mechanism of nucleation may be small at a high height of the potential barrier. Taking into consideration the mechanisms of transition through potential barriers of intermediate states increases the probability of nucleation [12]. Defects of various types present in the metastable phase can lower the height of the potential barrier, increasing the probability of formation of an nucleus.

Nuclear displacements with Landau–Zener (LZ) non-adiabatic transitions [15–20] with PES $E_j(R)$ to PES

$E_{j'}\big(R(t)\big)$ are possible in an open system (finite heating/cooling rates, the amplitude of external forces depends on time, etc.). Here j, j' — sets of quantum numbers characterizing the state of electrons at fixed values of nuclei R, t — time. There are no such transitions in the adiabatic approximation. For this reason, the dynamics of atoms in open systems is called non-adiabatic (see, for example, [21–23]). In solids, the electronic energy levels form a quasi-continuous spectrum, adjacent PES are located close to each other. For example, $E_j(R)$ and $E_{j'}\big(R(t)\big)$ shift relative to each other and intersect when PES R change. Under these conditions, in the area of intersection with the dimension $N-2$, the trajectories of atoms located initially on the PES $E_j(R)$, with a probability $P > 0$ may appear on the surface of the PES $E_{j'}(R)$ with other coordinates of the nuclei [21], which may coincide with the coordinates of the atoms in the nucleus of the new phase. The probability of P displacements of atoms does not depend on temperature and increases with an increase in the rate of displacement of energy levels. Therefore, the nucleation is possible at any temperature and the potential energy of the system always decreases in this case. Thus, the origin of a new phase in an open system is determined not only by thermal fluctuations during atomic vibrations, but also by displacements of atoms during non-adiabatic transitions. The latter type of displacement can manifest itself in the deviation of the characteristics of the phase transition occurring in equilibrium and nonequilibrium conditions. There are experimental data that, apparently, can confirm what has been said. Here are some of them [24–29] as the most indicative.

A phase transition of the first kind occurs at a temperature of $T_{c0} = 28-30\,\mathrm{K}$ in a proustite crystal ($\mathrm{Ag_3AsS_3}$) under equilibrium conditions [24]. The temperature of the nonequilibrium phase transformation T_c decreases in case of heating at a constant rate. The temperature difference $\Delta T = T_c - T_{c0}$ depends on the heating rate $\dot{T}$. There is a minimum at $\dot{T} \approx (8-10)\,\mathrm{K/min}$ on the dependence curve $\Delta T = \Delta T(\dot{T})$. At the minimum point $\Delta T \approx 3\,\mathrm{K}$. If we consider the mechanisms of nucleation determined only by thermal fluctuations, then the temperature of the phase transition ($28-30\,\mathrm{K}$), on the contrary, should increase. It was found that the nonequilibrium phase transformation is preceded by the excitation of a metastable short-range order, whose lifetime at a constant temperature is estimated at $\sim 16\,\mathrm{min}$. That is, the nucleus of a new phase against the background of this short-range order are formed in less time. In fact, the metastable short range order acts as an intermediate state, increasing the probability of the nucleation [12]. The origin of this short-range order is still unclear. The structural relaxation of an amorphous alloy $\mathrm{Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5}$ was studied in papers [25–27] under the action of cyclic stretching with different amplitudes A and frequency f. Only the topological short-range order changes in this alloy. The structural relaxation is not observed in the sample at a temperature of 25°C and $f = 0$. Non-spherical clusters with a size of $3-5\,\mathrm{nm}$ are formed at $A = 4\,\mu\mathrm{m}$, $f = 20\,\mathrm{Hz}$ after 10 min, the short-range order in which is characteristic of the crystal. The deformation of the sample does not exceed 10^{-4} at $A = 4\,\mu\mathrm{m}$. If we assume that all the work of the external force is performed for heating the sample, then with an elastic modulus of the order of 1 eV/atom, work of the order of 10^{-8} eV/atom is performed in one deformation cycle, and for 10 min — of the order of 10^{-4} eV/atom. The temperature change in this case will not exceed 10 K. When an amorphous metastable phase turns into a crystalline one, a mode is possible in which the system does not have time to remove the released heat from the nucleus, which leads to a sharp increase of temperature in the area of the interphase boundary „nucleus−amorphous phase“ and to „explosive crystallization“ [30.31]. But it is difficult to talk about a local temperature increase during deformations of the order of 10^{-4} in solids due to the ambiguity of the mechanism of heat localization on the scales of several nanometers. In liquids, such a mechanism exists, and it is associated with the formation of cavitation bubbles [31]. It should be noted that nanoclusters in the amorphous phase are also observed with a cyclic temperature change from cryogenic to room [28,29].

Thus, the question of the mechanisms of the nucleation of a new phase in nonequilibrium conditions remains debatable. It is no coincidence that the identification of the laws of the formation of nanoclusters in nonequilibrium systems is among the priorities of the „physical minimum“ XXI century [33]. The aim of this work is to solve the problem of the origin of a new phase taking into account the displacements of atoms determined by both thermal fluctuations and non-adiabatic transitions of Landau−Zener atoms.

2. A model of the new phase nucleation

A homogeneous isotropic solid in which only the topological short-range order changes at PT is considered. A solid can be either single-component or multicomponent, both crystalline and amorphous. Heating/cooling rate $\dot{T} = dT/dt$ (here T — temperature). The free energies of the two phases are equal at $T = T_0$. In the future, bearing in mind both heating and cooling, the phase in which the nucleus is formed will be called the parent. Then, the parent phase will be stable at $T > T_0$ in case of cooling, and at $T < T_0$ in case of heating. Let us introduce a dimensionless temperature

$$\theta = \frac{T - T_0}{T_0} \quad \left(\theta = \frac{T_0 - T}{T_0}\right)$$

and its rate of change $\dot{\theta} = \dot{T}/T_0$ when heating (cooling) the system. Introduction θ allows considering both heating and cooling. Let us denote the volume of the parent phase via V_0. The equation of state $V_0 = V_0(\theta)$ is assumed to be known. The parent phase is in a stable state at $\theta < 0$ with its characteristic short-range order in the distribution of atoms.

2.1. Equations of nonadiabatic molecular dynamics

It is necessary to recall the equations of non-adiabatic molecular dynamics for clarity of further presentation. The wave function of nuclei and electrons is written in form in representation [34]:

$$\Psi(\mathbf{R},\mathbf{r},t)=\sum_i^{\infty}\Omega_i(\mathbf{R},t)\Phi_i(\mathbf{r};\mathbf{R}),\tag{1}$$

where $\mathbf{r}$ — the set of electron coordinates, $\Omega_i(\mathbf{R},t)$ — the wave function of the nuclei, $\{\Phi(\mathbf{r};\mathbf{R})\}$ — the complete system of orthonormal wave functions of electrons ($\langle\Phi_i|\Phi_j\rangle=\delta_{ij}$), which are solutions the stationary Schrodinger equation

$$H_{\text{el}}(\mathbf{r};\mathbf{R})\Phi_i(\mathbf{r};\mathbf{R})=E_i(\mathbf{R})\Phi_i(\mathbf{r};\mathbf{R}).\tag{2}$$

Here H_{el} — electron Hamiltonian, the notation „;$\mathbf{R}$“ means that $\mathbf{R}$ is included in the Hamiltonian and the wave function as a parameter. After substituting (1) into the nonstationary Schrodinger equation

$$\left(H\Psi(\mathbf{R},\mathbf{r},t)=i\hbar\frac{\partial\Psi(\mathbf{R},\mathbf{r},t)}{\partial t}\right),$$

multiplication on the left by Φ_j^* and integration by the coordinates of the electrons, there is an equation describing the motion of the nuclei:

$$i\hbar\frac{\partial\Omega_j(\mathbf{R},\mathbf{t})}{\partial t}=\left[-\sum_\gamma\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2+E_j(\mathbf{R})\right]\Omega_j(\mathbf{R},t)+\sum_i^{\infty}F_{ji}(\mathbf{R})\Omega_i(\mathbf{R},t).\tag{3}$$

Here M_γ — the mass of the nucleus with the number γ ($\gamma=1,\ldots,N$), $E_j(\mathbf{R})$ is determined by the equation (2), matrix elements

$$F_{ji}(\mathbf{R})=\int d\mathbf{r}\,\Phi_j^*(\mathbf{r};\mathbf{R})\left[-\sum_\gamma\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2\right]\Phi_i(\mathbf{r};\mathbf{R})+\sum_\gamma\frac{1}{M_\gamma}\left\{\int d\mathbf{r}\,\Phi_j^*(\mathbf{r};\mathbf{R})-\left[i\hbar\nabla_\gamma\right]\Phi_i(\mathbf{r};\mathbf{R})\left[i\hbar\nabla_\gamma\right]\right\}.\tag{4}$$

In the adiabatic approximation ($F_{ji}=0$), the dynamics of the nuclei is completely determined by the vibrational degrees of freedom. The various electronic states turn out to be connected if the coordinates of the nuclei depend on time ($t=\theta/\dot\theta$), and the non-diagonal elements F_{ji} are not zero. The last term in the right part (3) at $F_{ji}\neq 0$ determines the contribution of electronic degrees of freedom to the dynamics of nuclei. They lead to non-adiabatic transitions of LZ atoms.

2.2. Dynamic displacements of atoms and order parameters

System of nonlinear equations (2), (3) describes the dynamics of nuclei taking into account vibrational and electronic degrees of freedom. The value θ is a control parameter. The square of the wave function $\Omega_j(\mathbf{R},t)$ determines the distribution function of the nuclei

$$\rho_j(\mathbf{r},t)=|\Omega_j(\mathbf{R},t)|^2=\sum_i\delta[r-R_i(t)]$$

in the j-m electronic state. The equilibrium positions of the nuclei in this state are equal to R_j. Let us denote the nuclei distribution function with coordinates $\mathbf{R}_0(t)$ in the parent phase via $\rho_0(\mathbf{r},t)$ when there are no non-adiabatic transitions ($F_{ji}=0$, $P=0$) or they are not taken into account. If we neglect the probability of the new phase nucleation due to thermal fluctuations, then the parent phase at $\theta>0$ will be stable up to a certain value θ_{in}, above which the parent phase becomes unstable relative to small perturbations during thermal fluctuations. If $P>0$ (at $\theta>0$), then $n=P(N{-}2)$ atoms are shifted by the amount of $\mathbf{u}_d=\{u_{d1},\ldots,u_{dn}\}$. The distribution function $\rho_n(\mathbf{r},t)$ determines the coordinates of the nuclei

$$\mathbf{R}_n(t)=\mathbf{R}_0(t)+\mathbf{u}_d(t)+\mathbf{u}_{\text{el}}(t),\tag{5}$$

where $\mathbf{u}_{\text{el}}$ — elastic displacements of atoms caused by dynamic displacements $\mathbf{u}_d$. A short-range order is formed, uncharacteristic of the parent phase. Following [35], this type of short-range order will be called dynamic short-range order (DSRO), and the displacement $\mathbf{u}_d$ — dynamic displacements (DD). The formation of DSRO in the parent phase is accompanied by a decrease in the potential energy of the system. It should be noted that in the classical approach, the displacements $\mathbf{u}_d$ are given by „hands“, and the displacements $\mathbf{u}_{\text{el}}$ are calculated based on the elasticity theory. A cluster(s) of dynamically displaced atoms represent(s) the germ of a new phase.

Due to the nonlinearity of the equations and the probabilistic nature of the DD, finding the distribution function $\rho_n(\mathbf{r},t)$ by solving the equations (2), (3) on large spatial and temporal scales is hardly possible. Nevertheless, the qualitative features of the distribution of atomic displacements at different values θ can be defined using the methods developed in the theory of nonlinear systems [36]. Next, the one-dimensional case is considered.

We denote a homogeneous stationary solution of a system of equations (2), (3) at $\theta>0$ through $\bar\rho_n(\theta)$, and the DD distribution — through $\bar u_d$. The task is to study the stability of this solution with respect to small perturbations $\propto\exp[i(kx{-}i\omega t)]$. Here the frequency is $\omega=\omega_{\text{re}}+i\omega_{\text{im}}$, ω_{re}, ω_{im} — real and imaginary parts, respectively, k — wave vector. Linear stability analysis is a standard procedure and is described in detail in [36]. The homogeneous solution is stable at $\theta<\theta_1$, $\omega_{\text{re}}<0$ with all k. The homogeneous solution is unstable at $\theta>\theta_1{-}\omega_{\text{re}}>0$. There is an unstable displacement mode with $\omega_{\text{re}} = 0$ at the stability threshold $(\theta = \theta_1)$. The threshold value $\theta = \theta_1(k)$ is found from the condition $\omega_{\text{re}}(k, \theta) = 0$, and the wave vector k_1 and the frequency $\omega_1 = \omega_{\text{im}}(k_1, \theta_1)$ of the unstable mode are found from the minimum condition $\theta_1(k)$. The classification of spatio-temporal instabilities is based on the values of ω_1, k_1. The transition from one stationary state to another takes place if $\omega_1 = 0$, $k_1 = 0$. This situation occurs with homogeneous displacements of atoms in the parent phase with a change of θ. A stationary inhomogeneous displacement distribution is formed at $\omega_1 = 0$, $k_1 > 0$. Near the dimensionless stability threshold

$$a_1 = \frac{\theta - \theta_1}{\theta_1} \ll 1$$

solution of the equations (2), (3) is searched for as a superposition of plane waves with wave vectors $k = k_1 \pm \Delta k \left(\frac{\Delta k}{k_1} \ll 1\right)$. The spatial distribution of displacements u_d can be written as [36]:

$$u_d(x, t) - \bar{u}_d = u_d^0[\varphi(x, t)\exp(ik_1x) + \text{CC}], \tag{6}$$

where $\varphi(x, t)$ — the complex amplitude of an unstable mode with a wave vector k_1, u_d^0 — a parameter defined by the properties of the medium, CC means complex conjugation. The amplitude of the unstable mode $\varphi(x, t)$ characterizes the displacements u_d on spatial scales

$$l_1 \propto \frac{1}{k_1} > l_0,$$

where l_0 — interatomic distance. The frequency of the unstable mode ω determines the characteristic time $t_1 \propto 1/\omega$. In stable parent phase $\varphi = 0$. Localized displacement distributions with an amplitude of $\varphi > 0$ and a spatial period of l_1 represent the nuclei of a new phase. Their formation is accompanied by a decrease in the potential energy of the system $U_d(\varphi)$. The relative volume change at PT, as a rule, does not exceed ten percent. Therefore, the amplitude $\varphi < 1$, i.e. φ is a small parameter. Note that in addition to the distribution of DD (6), other distributions are possible. But frequency ω is the highest of all possible. Therefore, the time of distribution formation (6) is the smallest of all possible. And in the experiment, the fastest processes manifest themselves.

The atoms in the matrix are displaced from the equilibrium positions by u_{el} due to the difference in the volumes of the nuclei and the matrix. If the elastic deformation energy is $\Delta U_{\text{el}} > \Delta U(\varphi)$, then such a state is energetically unprofitable, the nucleus must disappear. If $\Delta U_{\text{el}} < \Delta U(\varphi)$, then the nucleus will grow. The problem is again reduced to analyzing the stability of a system with excited DD relative to small perturbations of the volume of the medium during the propagation of a longitudinal displacement wave. The wave vector and the frequency of the unstable mode at the stability threshold $\theta_2 > \theta_1$ of the parent phase with DD will be denoted through k_2 and ω_2. The development of instability at $\theta > \theta_2$ leads to a change in volume by $\Delta V_n = V_n - V_0 \neq 0$. The nuclei grow at $\theta > \theta_2$, while the potential energy decreases. Near the dimensionless stability threshold

$$a_2 = \frac{\theta(\varphi) - \theta_2}{\theta_2} \ll 1,$$

the value ΔV_n can be written as

$$\Delta V_n(x, t) = V_n^0[\eta(x, t)\exp(ik_2x) + \text{CC}]. \tag{7}$$

Here $\eta(x, t)$ — the complex amplitude of an unstable longitudinal mode with a wave vector k_2, V_n^0 — a parameter determined by the properties of the medium. It is assumed that the dependence $\Delta V_n(t)$ is known from the experiment. The values

$$l_2 \propto \frac{1}{k_2}, \quad t_2 \propto \frac{1}{\omega_2}$$

determine the spatial period and time of change η. The case of real values η is considered below. In physics, the amplitudes of unstable modes characterizing changes in the structure, following Landau, are commonly called order parameters (OP). This name for the variables φ, η will be retained further.

3. Dynamics of nucleus formation

Considering that φ is a small parameter, the dimensionless stability threshold a_2 in a linear approximation can be written as

$$a_2 = -1 + p\varphi, \quad p = \frac{1}{\theta_2}\frac{d\theta}{d\varphi}. \tag{8}$$

The equation for OP η represents the real Ginzburg–Landau equation [36]

$$t_2\partial_t\eta = (-1 + p\varphi)\eta - b\eta^3 + l_2^2\partial_x^2\eta. \tag{9}$$

Here $b > 0$. Equation (9) with $p = 0$ has a unique stable solution $\eta_0 = \eta = 0$. There is a solution $\eta > 0$ for $p > 1/\varphi$, which corresponds to a lower value of potential energy $(\propto -\int \partial_t\eta d\eta)$.

A metastable phase with nuclei is bistable, with the same value θ, the regions with $\varphi = 0$ and with $\varphi > 0$ can be in equilibrium state. The simplest equation for a bistable medium has the following form

$$t_1\partial_t\varphi = [\alpha - g\eta]\varphi + q_2\varphi^2 - q_3\varphi^3 + l_1^2\partial_{x^2}^2\varphi. \tag{10}$$

Here $q_2(\theta) > 0$, $q_3(\theta) > 0$, $g(\theta) > 0$ are coefficients. The parameter $\alpha(\theta)$ can have different signs. The parameters α, g, q_2 and q_3 are determined by the properties of the solid. The characteristic time t_1 is determined by the time of LZ non-adiabatic transitions. It is easy to see that at $\alpha > 0$, the potential energy of $\varphi d\varphi$ $(\propto -\int \partial_t\varphi d\varphi)$ decreases. The sign „–“ before the coefficient g on the right side of equation (10) shows that the excitation of the dynamic short-range order is accompanied by elastic displacements of atoms. This leads to an increase of the potential energy of the system.

In dimensionless variables

$$\tilde{t} = t/t_2,\ \tilde{x} = x/l_2,\ \tilde{\eta} = \eta b^{1/2},\ \tilde{\varphi} = \varphi q_3^{1/2} \tag{11}$$

equations (9) and (10) become (the sign „$\sim$“ is omitted in further):

$$\partial_t \eta = (-1 + d\varphi)\eta - \eta^3 + \partial^2_{x^2}\eta, \tag{12}$$

$$\tau\,\partial_t \varphi = (\alpha - c\eta)\varphi + \beta\varphi^2 - \varphi^3 + l^2\partial^2_{x^2}\varphi. \tag{13}$$

Here

$$\tau = \frac{t_1}{t_2},\ l = \frac{l_1}{l_2},\ \beta = q_2 q_3^{-1/2},\ d = p q_3^{-1/2},\ c = g b^{-1/2}. \tag{14}$$

Equation (13) for $\eta = 0$ has three homogeneous stationary solutions:

$$1)\ \varphi_0 = 0,$$

$$2)\ \varphi_{\mathrm{h}} = \frac{\beta}{2} + \left(\frac{\beta^2}{4} + \alpha\right)^{1/2},$$

$$3)\ \varphi_{\mathrm{in}} = \frac{\beta}{2} - \left(\frac{\beta^2}{4} + \alpha\right)^{1/2}.$$

The solution φ_{in} is always unstable. The solution φ_0 is unique with $\alpha < -\beta^2/4$, which is the case for the stable parent phase at $\theta \ll \theta_c$. The medium is in a bistable state with $-\beta^2/4 < \alpha < 0$. If $-\beta^2/4 < \alpha < -2\beta^2/9$, then the solution φ_0 is stable, and φ_{h} — is metastable. The solution $\varphi_{\mathrm{h}}(\varphi_0)$ is stable (metastable) with $-2\beta^2/9 < \alpha < 0$. Both solutions have the same stability with $\alpha = -2\beta^2/9$. The temperature θ_c can be found from this equation. The solution $\varphi_{\mathrm{h}}(\varphi_0)$ is stable (unstable) with $\alpha > 0$, any small disturbance φ increases. The equation $\alpha = 0$ determines the temperature of the loss of stability of the parent phase. The homogeneous stationary solutions of $\varphi_{\mathrm{h}} > 0$, $\eta_{\mathrm{h}} > 0$ equations (12), (13) were analyzed in [37,38].

Equations (12), (13) always have a homogeneous stationary solution η_0, φ_0. Standard analysis shows that the solution of η_0, φ_0 is stable with respect to small homogeneous and inhomogeneous disturbances with a frequency of ω and a wave vector of k at

$$-\tau + \alpha < 0, \tag{15}$$

$$-\alpha > 0. \tag{16}$$

These inequalities always hold with $\alpha < 0$. Small homogeneous and inhomogeneous disturbances do not lead to structural relaxation. But the solution η_0, φ_0 may be unstable with respect to perturbations of finite amplitude. The development of instability leads to the excitation of localized solutions $\varphi(x,t)$, $\eta(x,t)$, called autosolitons (AS) in [39]. They are nonequilibrium localized states of a nonlinear medium. Kinetic variables change sharply inside the autosoliton, and on its periphery they are equal to stationary values (in this case equal to zero). There are running and static AS. Static AS are of interest, which represent the mathematical image of the nuclei of a new phase. Static AS can be excited when the following inequalities are met [39]:

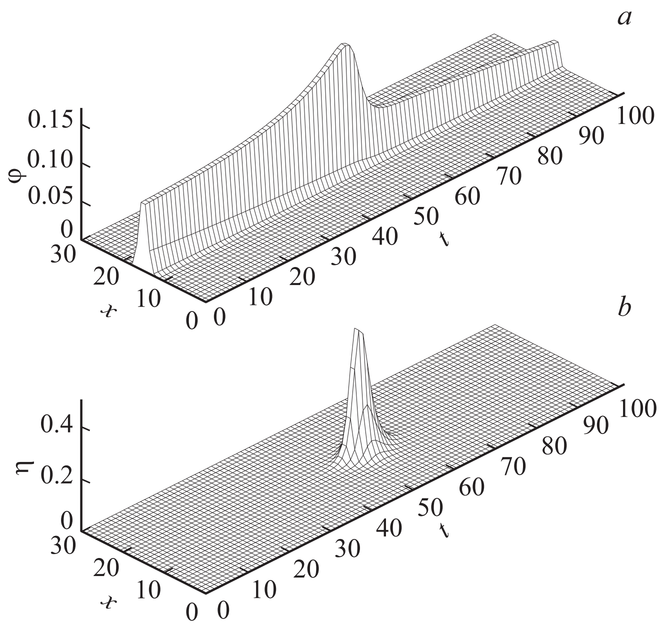

Figure 1. Spatio-temporal distribution of parameters of the order φ, η in a damped autosoliton.

$$\tau < 1, \quad l \ll 1, \quad \tau > l. \tag{17}$$

According to the last inequality $l_1/t_1 < l_2/t_2$. That is, the characteristic rate of change of DSRO should be less than the characteristic rate of longitudinal displacements. This is always the case in solids.

The analysis of equations (12), (13) shows the following. First of all, the amplitude of the initial disturbance $\Delta\varphi_0$ should satisfy the inequality to excite a static autosoliton

$$\Delta\varphi_0 > \varphi_{\mathrm{in}}. \tag{18}$$

Further, the damped and oscillating AS can be excited with $d > 1/\varphi_{\mathrm{in}}$, while oscillating and static AS can be excited with $d < 1/\varphi_{\mathrm{in}}$.

The equations (12), (13), describing the dynamics of the origin and development of various types of AS can be solved only by numerical methods. The equations (12), (13) were numerically solved using the finite-difference method with a completely implicit scheme in the interval $0 \le x \le X$. The system is in the state η_0, φ_0 with $t = 0$. The initial perturbation for the variable φ was given as $\Delta\varphi = \Delta\varphi_0 \exp[\sigma_\varphi(x - x_0)^2]$. Here $\Delta\varphi_0, \sigma_\varphi, x_0$ is the amplitude, variance and coordinate of the initial disturbance, respectively. The initial perturbation for the variable η is taken stochastic with an amplitude of $0 \le \Delta\eta(x) \le 10^{-3}$. Periodic boundary conditions were set.

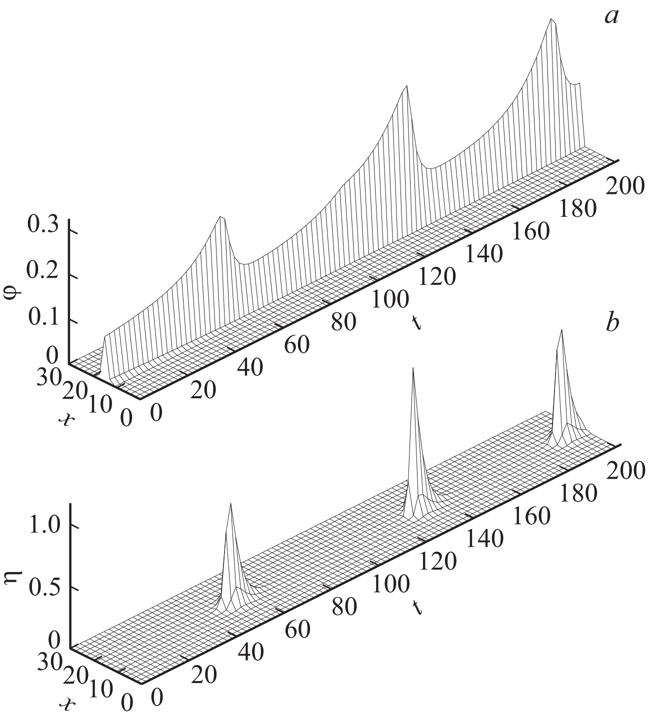

Figure 2. spatial-temporal distribution of parameters of the order φ, η in an oscillating autosoliton.

As an example, Fig. 1–4 shows the dynamics of the origin and development of various types of AS at

$$\beta = 0.6,\ \tau = 0.9,\ l = 0.05,\ \Delta\varphi_0 = 0.1,\ \sigma_\varphi = 1,\ x_0 = 15 \tag{19}$$

and different values of α, c, d. With $\alpha = -0.04$ $\varphi_{\text{in}} \approx 0.08$, $\varphi_{\text{h}} \approx 0.52$. A damped AS is formed with $d = 15 > 1/\varphi_{\text{in}}$, $c = 0.4$. Fig. 1 shows the spatio-temporal distributions of OP. There are three stages. At the first stage OP φ increases to the value $\varphi_{\max} \approx 0.24$ during $t \approx 44$, OP η is close to zero. The second stage occurs when the value $(-1 + d\varphi)$ becomes positive. OP η starts to grow rapidly. Its growth rate is determined by the value $(-1 + d\varphi)$. This can be seen from equation (12), in which $\dot{\eta} \propto (-1 + d\varphi)\eta$. At this stage, the OP φ hardly changes during $\Delta t \approx 1$. At the third stage, both OP decrease. But OP φ decreases slower η. Physically, this means that a slowly decreasing perturbation φ can act as an initial perturbation with a further temperature change.

An oscillating AS is excited when c decreases. A typical spatial and temporal distribution of OP is shown in Fig. 2 at $c = 0.2$. Each AS is excited against the background of $\eta = \varphi = 0$. Additional analysis shows that the amplitude of the AS decreases with time. The number of oscillations depends on the value of c, the oscillation period decreases with a decrease of c. This means that the nucleus is formed in an auto-oscillatory mode with a decreasing amplitude over time.

With $\alpha = -0.02$, $\varphi_{\text{h}} \approx 0.56$ $\varphi_{\text{in}} \approx 0.04$. At $d = 10 < 1/\varphi_{\text{in}}$, $c = 0.3$ an oscillating AS is excited (Fig. 3), but the spatio-temporal distribution of OP differs from that shown in Fig. 2. The amplitude of the oscillations decreases with time, but a stationary localized state is established $\varphi > 0$, $\eta > 0$. At the same time, the maximum values of OP are not equal to stationary values. The number of oscillations decreases with a decrease of c. A static AS is formed almost immediately with $c = 0.1$ (Fig. 4).

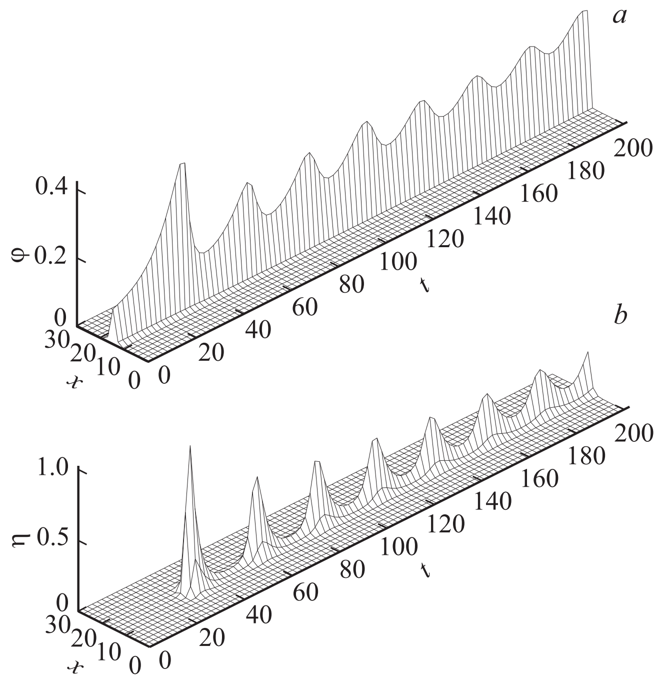

Figure 3. Spatio-temporal distribution of parameters of the order φ, η in a damped autosoliton.

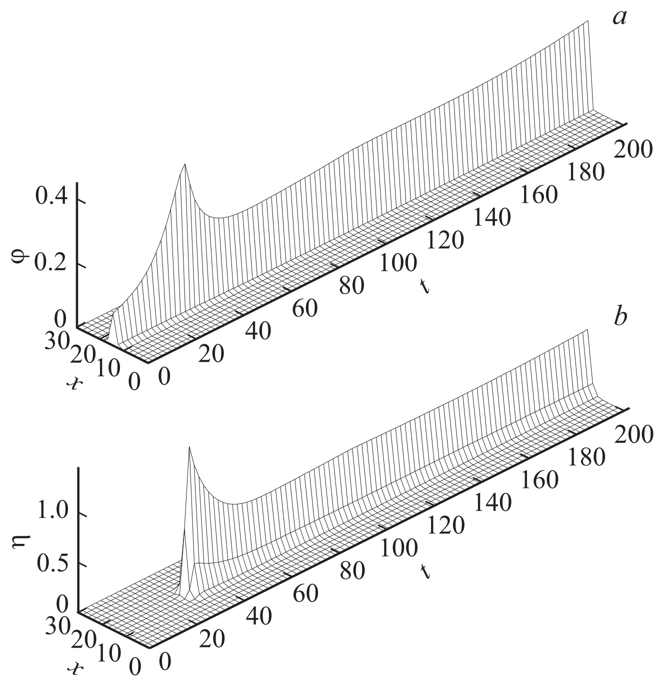

Figure 4. Spatio-temporal distribution of parameters of the order φ, η when a static autosoliton is excited.

4. Discussion of results

The excited AS describes the dynamics of the formation of unstable and stable nuclei in the metastable phase. An initial disturbance is required to excite the AS, the amplitude of which is $\Delta\varphi_0 > \varphi_{\text{in}}$. The value of φ_{in} at a given value θ is determined by the probability of a non-adiabatic transition of atoms P. For a system of two atoms whose energy levels near the intersection point have the same signs of derivatives of potential energy at the coordinate [15]:

$$P = \exp\left(-2\pi W_0^2/(\hbar v|F_2 - F_1|)\right). \qquad (20)$$

Here v — the displacement velocity of atoms determined by the rate of volume change during heating/cooling, F_1, F_2 — derivatives of potential energy at the coordinate near the intersection point of energy levels 1 and 2, respectively, $2W_0$ — the width of the energy gap between the levels. It can be seen from formula (20) that the probability of transition from temperature does not depend, increases with a decrease in W_0 and an increase in the displacement velocity of atoms $v\, dV/dt\, v \propto dV/dt$. The probability of displacement of several hundred atoms remains a finite value in a system with a large number of atoms and a continuous energy spectrum of electronic states. Therefore, there is no need to introduce any defects for the formation of the nucleus. Although their presence, leading to an increase in the potential energy of the metastable phase, may contribute to the formation of the nucleus. The energy interval between the PES increases with a decrease in the volume of the system (the number of atoms), the probability of non-adiabatic transitions decreases. As a consequence, PT in such systems may be difficult, or may not occur at all. The dynamics of the system is determined by the vibrational degrees of freedom at $v \to 0$ $P \to 0$. In the absence of inhomogeneities, the parent phase will remain metastable up to the temperature of its loss of stability with respect to small perturbations of the medium density.

It follows from the formula (18) that the characteristic time of the non-adiabatic transition

$$t_{\text{LZ}} = W_0/(v|F_2 - F_1|). \qquad (21)$$

The characteristic time of nucleus formation $t_1 \approx t_{\text{LZ}}$ does not depend on temperature. This explains the fact that phase transitions of the first kind also occur at low temperatures. For example, a phase transition of the first kind occurs at a temperature of $T_{c0} = 28-30\,\text{K}$ in a proustite crystal (Ag_3AsS_3) under equilibrium conditions [24].

Let the formation of a critical nucleus of a new phase under equilibrium conditions ($v \approx 0$) be determined by the time $t_1 = t_1^0$. The critical size of the nucleus will be reached within $t_1 < t_1^0$ under nonequilibrium conditions ($v > 0$). This is equivalent to the fact that the temperature of the nonequilibrium phase transition will be higher than θ_c when cooled and lower than θ_c when heated. This pattern is observed experimentally [24].

5. Conclusion

In the proposed model, the metastable phase is considered as an open system of nuclei and electrons, in which the dynamics of nuclei is non-adiabatic. The nucleus of a new phase is formed in two stages, at each of which the potential energy of the system decreases. The dynamic displacements of atoms are excited at non-adiabatic Landau–Zener transitions at the first stage. When the temperature threshold value is reached, the homogeneous distribution of dynamic displacements becomes unstable relative to displacements with a wavelength exceeding the interatomic distance. The development of instability is accompanied by an increase in the number of displacement modes with wavelengths close to the wavelength of the unstable mode. The localized displacement distribution represents the germs of a new phase. The presence of any defects in the metastable phase is not required for their formation. Nuclei are stable if their formation is accompanied by a decrease in the elastic part of the potential energy of the system.

The dynamics of nuclei formation is described by two nonlinear parabolic equations for order parameters (amplitudes of unstable modes). The solutions of the equations describing the resulting nuclei are static autosolitons. Depending on the temperature, the nuclei can be attenuated, stable, and exist in self-oscillating mode. An increase of the rate of heating (cooling) of a solid facilitates the nucleation, as a consequence, a decrease (increase) of the temperature of the phase transformation.

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Conflict of interest

The authors declare that they have no conflict of interest.

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