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DYNAMICS OF SYSTEMS ALLOWING STRUCTURAL PHASE TRANSITIONS*

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The dynamics of active atoms that determine structure phase transitions in a solid body is considered in the context of the previously presented atom interaction model based on a special type of three-minimum potential. Periodical and soliton-like solutions of nonlinear differential equation of motion were obtained. The value of the bond energy of active atoms with respect to the potential barrier height in a single-particle potential with a triple minimum determines the character of a phase transition. Crystals of the $Me^{I}Me^{II}BX_4$ kind, as well as crystals and metals, on the surface of which atoms of gases and metals are absorbed, are considered as objects, in which the obtained results can be used.

Keywords: *oscillation, three-minimum potential, structural phase transition, dynamics of systems.*

Introduction

Solid-state physics studies a variety of compounds (ferroelectrics, superconductors, magnetic materials, etc.), the most interesting properties of which are due to structural transformations occurring in them. Structural phase transitions arise when the crystallographic structure of a substance changes. Such transitions usually break the symmetry of the crystals only by the rearrangement of some atoms, whereas the positions of all the other atoms remain invariable [1, 2]. It is commonly assumed that phase transitions can be divided into two main classes: disorder-order type and displacive type [3]. In the first case the phase transition consists in statistical ordering of active atoms with respect to several equilibrium positions determined in each elementary cell by other atoms. In the second case the phase transition is caused by dynamic instability of the lattice with respect to collective displacement of active atoms with respect to symmetric positions in the cell.

In most cases (see, for example, [4, 5]) the model of structural transition is described in the simplest case by a Hamiltonian in the form of the sum of one-partial energies determined by a double-minimum potential and by the harmonic bond between active atoms in different cells. The bond magnitude Величина связи (энергии связи?) in relation to the height of the potential barrier in the one-partial potential determines the nature of the phase transition. In case of a disorder-order transition collective oscillations of atoms do not play an essential role. In case of a displacive transition dynamic correlation of atomic displacements in different cells turns out to be determinative. The opportunity of occupying two equivalent positions of equilibrium by active atoms is not a solitary one. As experience shows, there are substances in which a sequence of several phase transitions is observed, so, the double-well potential model is inapplicable. The picture of the phase transition becomes much more difficult, and it is necessary to involve the multi-

well one-particle potential for its description. The theory of these transitions has been developed much less than the theory for the case of the double-well potential. This work considers the dynamics of systems in which the ordering of active atoms can occur by three equivalent positions.

Results and Discussion

When describing phase transitions, it is usually possible to distinguish a group of atoms, the nature of the motion of which significantly depends on temperature. So, they can be considered responsible also for the emergence of the phase transition. At the same time, as a first approximation, the effect of other atoms can be replaced with an average static field. Let us consider a simple quasi-one-dimensional model, in which only the motion of active atoms is taken into account:

$$\mathrm{H} = \sum_{n=1}^{N} \left\{ \frac{1}{2} m \left(\frac{du_n}{dt}\right)^2 + V(u_n) + \frac{1}{2} k_0 (u_{n+1} - u_n)^2 \right\}. \quad (1)$$

Here u_n is the displacement of an active atom of mass *m* from the equilibrium position; $V(u_n)$ is the one-partial potential created by other atoms; parameter k_0 takes into account the dipole-dipole interaction of displacements u_n of the active atoms. Potential $V(u_n)$ has two minima or more, which makes it possible to order the active atoms by these states in the cell.

The following system of motion equations corresponds to Hamiltonian (1):

$$m \frac{d^2 u_n}{dt^2} + k_0 (2u_n - u_{n+1} - u_{n-1}) + \frac{dV}{du_n} = 0. \quad (2)$$

By means of Hamiltonian (1) and motion equations (2) structural phase transitions were described in works [4–6]. It was assumed that potential $V(u)$ has two minima. This work considers the dynamics of a lattice with potential function [7, 8]

$$V(u) = \varepsilon u^2 (1 - u^2)^2 \quad (3)$$

having three minima at $u = 0, \pm 1$ and separated by potential barriers of height $4\varepsilon/27$ at $u = \pm 1/\sqrt{3}$. Let us assume further that the energy parameter $\varepsilon = 1$.

The properties of the system described by Hamiltonian (1) at value (3) depend significantly on the relative role of the potential barrier $\Delta V = 4/27$ and energy $\sim k_0 a^2$ (a is the constant of the lattice of the active atoms) of the bond between the displacements in adjacent nodes of the lattice.

1. *If the energy between the displacements in adjacent nodes of the lattice $2k_0 a^2$ is very small in comparison with the potential barrier ΔV,* the oscillations of the active atoms in different nodes are almost independent. In this case motion equations (2) reduce to the following system of independent equations:

$$m \frac{d^2 u_n}{dt^2} + \frac{dV}{du_n} = 0. \quad (4)$$

Integrating equation (4) and omitting the node index we obtain

$$\frac{1}{2} m \left(\frac{du}{dt}\right)^2 + V(u) = E, \quad (5)$$

where E is the total energy of the oscillator.

Taking into account (3) we can write solution (5) in the following form:

$$\frac{du}{dt} = \pm\sqrt{2[E - u^2(1-u^2)^2]}\,. \qquad (6)$$

Expression (6) sets phase trajectories on the plane (u, du/dt). All the phase trajectories are closed, which corresponds to oscillation motion. The separatrixes have the shape of loops beginning and ending in the same saddle points. The separatrix curves separate the trajectories corresponding to the oscillation of different character: low-amplitude oscillations with respect to minima $u = 0, \pm 1$ are separated by the separatrix from oscillations with large amplitude with respect to zero of the coordinate system.

Integrating equation (6) we obtain

$$\int_{u_0}^{u} \frac{du}{\sqrt{2[E-u^2(1-u^2)^2]}} = \frac{1}{\sqrt{2}}\int_{u_0}^{u} \frac{du}{\sqrt{P_6(u,E)}} = \pm t\,, \qquad (7)$$

where $P_6(u,E) = E - u^2(1-u^2)^2$. Integration limits u_0, u are chosen from condition $P_6(u,E) > 0$.

Replacing variables $u^2 = y$ makes it possible to depress the radicand degree in the left part of (7). Let us use this replacement to transform (7) to the following form:

$$\int_{y_0}^{y} \frac{dy}{\sqrt{P_4(y,E)}} = \pm 2\sqrt{2}t, \qquad (8)$$

where $P_4(y,E) = Ey - y^4 + 2y^3 - y^2$.

Periodic solutions (8) exist at positive energies ($E \geq 0$). If $0 \leq E \leq 4/27$, equation $P_4(y,E) = 0$ has four real roots $c_1 > c_2 > c_3 > c_4 = 0$. Constants c_i (i = 1, 2, 3) fulfill the following conditions: $c_1 + c_2 + c_3 = 2$, $c_1c_2 + c_1c_3 + c_2c_3 = 1$, $c_1c_2c_3 = E$. Polynom $P_4(y,E)$ is positive at $c_4 \leq y < c_3$, and the integral in the left part of (8) is expressed in Jacobian elliptic functions [9]:

$$\int_0^{y} \frac{dy}{\sqrt{y(c_2-y)(c_3-y)(c_1-y)}} = \frac{2}{\sqrt{c_2(c_1-c_3)}}F(\beta,r), \qquad (9)$$

where $\beta = arcsin\sqrt{\frac{(c_1-c_3)y}{(c_1-y)c_3}}$, $r = \sqrt{\frac{(c_1-c_2)c_3}{(c_1-c_3)c_2}}$.

(10)

Taking into account the left part of expression (8) we obtain

$$F(\beta,r) = \pm z, \qquad (11)$$

where $z = \sqrt{2c_2(c_1-c_3)}t$.

Expression (11) is an implicit solution of equation (8) using an elliptic integral of the first type. The explicit solution is written with the use of Jacobi sine function: $sn\,(z,r) = sin\,\beta$, so that

$$y(t) = \frac{c_1c_3sn^2(z,r)}{c_1 - c_3cn^2(z,r)}\,. \qquad (12)$$

Returning to the initial variable (y>0) we obtain

$$u(t) = \pm\frac{\sqrt{c_1c_3}sn(z,r)}{\sqrt{c_1-c_3cn^2(z,r)}}\ . \qquad (13)$$

Function $u(t)$ (13) is uneven. The period of oscillation and the oscillation frequency are determined by expressions

$$T=\frac{4K(r)}{\sqrt{c_2(c_1-c_3)}},\qquad \omega=\frac{\pi\sqrt{c_2(c_1-c_3)}}{K(r)}\ , \qquad (14)$$

where $K(r)$ is the complete elliptic integral of the first type. When the modulus of the elliptic sine is small (r^2<<1), we have *sn*(*z*,*r*)→*sinz*, *cn*(*z*,*r*)→*cosz*, and the motion is harmonic,

$$u(t) \approx \sqrt{c_3}sin(\sqrt{c_2(c_1c_1-c_3)}t)\ . \qquad (15)$$

When r^2<<1, the magnitude of $K(r)\approx\frac{\pi}{2}$. So, the oscillation frequency $\omega = 2\sqrt{c_2(c_1-c_3)}$.

When r=1 ($c_2 = c_3$), expression (13) ($sn(z,r)\rightarrow thz, cn(z,r)\rightarrow 1/chz$) leads to separatrix solution

$$u(t) = \pm\frac{\sqrt{c_1c_3}shz}{\sqrt{c_1ch^2z-c_3}}. \qquad (16)$$

The plot of function (16) is a bell-shaped curve: when z=0, displacement u=0, and when $z\rightarrow\pm\infty$, we obtain $u=\pm\sqrt{c_3}$.

Polynom $P_4(y,E)$ is positive also in the range $c_2 \le y \le c_1$. The integral in the left part of (8) has the following form:

$$\int_{c_2}^{y}\frac{dy}{\sqrt{y(y-c_3)(y-c_2)(c_1-y)}}=\frac{2}{\sqrt{c_2(c_1-c_3)}}F(\lambda,r), \qquad (17)$$

where $\lambda = arcsin\sqrt{\frac{(c_1-c_3)(y-c_2)}{(c_1-c_2)(y-c_3)}}$. (18)

Taking into account expressions (11) and (17) we obtain the following expression for the displacement:

$$u(t) = \pm\sqrt{\left[\frac{c_2(c_1-c_3)-c_3(c_1-c_2)sn^2(z,r)}{c_1-c_3-(c_1-c_2)sn^2(z,r)}\right]}\ . \qquad (19)$$

Function (19) is even. The expressions for the period of oscillation and the oscillation frequency are given by

$$T=\frac{2K(r)}{\sqrt{c_2(c_1-c_3)}},\ \omega=\frac{\pi\sqrt{c_2(c_1-c_3)}}{K(r)}\ . \qquad (20)$$

When $E\ge$4/27, polynom $P_4(y,E)$ has two real roots (y_1=0, y_2=c) and two complex ones ($y_{3,4}=a\pm ib$). In this case expression (8) has the following form:

$$\int_0^y\frac{dy}{\sqrt{y(c-y)[(y-a)^2+b^2]}}=\pm2\sqrt{2}t. \qquad (21)$$

According to [7] the integral in the left part of (21) is expressed with the use of elliptic functions so that

$$\frac{1}{\sqrt{pq}}F\left(2arcctg\sqrt{\frac{q(c-y)}{py}},\quad \frac{1}{2}\sqrt{\frac{-(p-q)^2+c^2}{pq}}\right)=\pm 2\sqrt{2}t, \tag{22}$$

where $p^2=(a-c)^2+b^2$, $q^2=a^2+b^2$.

Let us assume that $z=2\sqrt{2pq}t$. Then $z=\pm F(\gamma,k)$, where

$$\gamma = 2arcctg\sqrt{\frac{q(c-y)}{py}},\ k=\frac{1}{2}\sqrt{\frac{-(p-q)^2+c^2}{pq}}.$$

In order to write the explicit solution let us use the function inverse to the elliptic integral:

$$sn(z,k)=\sin\gamma = \sin\left(2arcctg\sqrt{\frac{q(c-y)}{py}}\right)=2\frac{\sqrt{pqy(c-y)}}{py+q(c-y)}.$$

It follows that

$$u(t)=\pm\frac{\sqrt{qc}sn(z,k)}{\sqrt{qsn^2(z,k)+p(cn(z,k)\pm 1)^2}}. \tag{23}$$

Function $u(t)$ in the form (23) is an uneven function with period $T=\frac{4K(k)}{\sqrt{pq}}$.

In the range $E\approx\frac{4}{27}$ the modulus $k^2=1$, and function (23) is approximated by a function coinciding with (16) and having an infinite period ($\omega\approx 0$) – a soft mode. When E increases, complete elliptic integral $K(k)$ decreases, and the oscillation frequency grows.

2. *If condition* $k_0a^2 \gg \Delta V$ *is fulfilled*, the oscillation state moves along the lattice and becomes essentially collective in character. In this case it is possible to use the continuum approximation by replacing the positions of the nodes na with continuous variable x. Then the Hamiltonian of the chain of active atoms (1) is transformed to the following form:

$$H=\int_{-\infty}^{\infty}\frac{dx}{a}\left\{\frac{1}{2}m\left(\frac{\partial u}{\partial t}\right)^2+\frac{1}{2}mc_0^2\left(\frac{\partial u}{\partial x}\right)^2+V(u)\right\}, \tag{24}$$

where $c_0=a\sqrt{\frac{k_0}{m}}$ is the speed of sound.

The following partial differential motion equation corresponds to Hamiltonian (24):

$$m\frac{\partial^2 u}{\partial t^2}-mc_0^2\frac{\partial^2 u}{\partial x^2}+\frac{\partial V}{\partial x}=0\,. \tag{25}$$

Let us further consider excitations that move along the chain at constant speed $V<c_0$. Let us introduce a new variable $z=x-Vt$ $\left(\text{i.e., } u(x,t)=u(x-Vt)\right)$. Then partial differential equation (25) is transformed into a usual differential equation:

$$\frac{d^2u}{dz^2}-\boldsymbol{\gamma}_0^2\frac{dV}{dZ}=0\,, \tag{26}$$

where $\boldsymbol{\gamma}_0^2 = 1/m(c_0^2 - V^2)$.

Integrating equation (26) we obtain:

$$\frac{du}{dz} = \pm\sqrt{2[E + \boldsymbol{\gamma}_0^2 u^2(1-u^2)]}. \quad (27)$$

Expression (27) sets phase trajectories on the plane (u, du/dz). The phase portrait has five basic elements: critical points of the "center" type at $u = \pm 1/\sqrt{3}$ and three critical saddle points $u = 0, \pm 1$, du/dz = 0. A trajectory leaving one saddle point and entering another – a separatrix – separates areas of the phase plane with significantly different nature of motion. In our case the separatrix curve connects three critical points and separates time-periodic solutions from aperiodic ones. Closed trajectories correspond to solutions that have the form of space-periodic waves. Infinitely growing solutions correspond to open trajectories.

Integrating equation (27) we obtain:

$$\int_{u_0}^{u} \frac{du}{\sqrt{2[E+\boldsymbol{\gamma}_0^2 u^2(1-u^2)^2]}} = \frac{1}{\sqrt{2}} \int_{u_0}^{u} \frac{du}{\sqrt{P_6(u,E)}} = \pm z, \quad (28)$$

where $P_6(u,E) = E + \boldsymbol{\gamma}_0^2 u^2(1-u^2)^2$. Integration limits u, u_0 are chosen according to condition $P_6(u,E) > 0$. Using the variable replacement u^2=y it is possible to transform expression (28) to the following form:

$$\int_{y_0}^{y} \frac{dy}{P_4(y,E)} = \pm 2\sqrt{2} z, \quad (29)$$

where $P_4(y,E) = \boldsymbol{\gamma}_0^2(y^4 - 2y^3 + y^2) + Ey$.

Periodic solutions exist at negative energies ($-4\boldsymbol{\gamma}_0^2/27 \le E \le 0$). In this case equation $P_4(y,E) = 0$ has four real roots $c_1 > c_2 > c_3 > c_4 = 0$.

Polynom $P_4(y,E)$ is positive at $c_3 < y < c_2$, and the integral in the left part of (29) is expressed in Jacobian elliptic functions [9]

$$\int_{c_3}^{y} \frac{dy}{\sqrt{y[\boldsymbol{\gamma}_0^2(y^3-2y^2+y)+E]}} = \int_{c_3}^{y} \frac{dy}{\sqrt{y(y-c_3)(c_2-y)(c_1-y)}} = \frac{2F(\delta,q)}{\sqrt{c_2(c_1-c_3)}}, \quad (30)$$

where $\delta = arcsin\sqrt{\frac{c_2(y-c_3)}{y(c_2-c_3)}}, \quad q = \sqrt{\frac{c_1(c_2-c_3)}{c_2(c_1-c_3)}}$. (31)

Taking into account the right part of expression (29) we obtain $F(\delta, q) = \pm p$, $p = \sqrt{2c_2(c_1-c_3)}z$.

The explicit solution of equation (29) is written with the use of Jacobi sine function $sn(p,q)=sin\delta$, so that $y(t)=\frac{c_2 c_3}{c_2-(c_2-c_3)sn^2(p,q)}$.

Returning to the initial variable (y>0) we find that

$u(t)=\pm\frac{\sqrt{c_3c_2}}{\sqrt{c_2-(c_2-c_3)sn^2(p,q)}}$. (32)

Function $u(t)$ of form (32) is an even function with period

$T=\frac{2K(q)}{\sqrt{c_2(c_1-c_3)}}$. (33)

When the modulus of the elliptic sine is small ($q<<1$), functions $sn(p,q)$, $K(p,q)$ can be expanded as a power series by parameter q (see [9]), and we obtain the following expressions for the displacement and the oscillation frequency:

$u(t)\approx \pm\sqrt{\frac{c_2c_3}{c_2cos^2p+c_3sin^2p}}$, $\omega \approx 2\sqrt{c_2(c_1-c_3)}\left(1-\frac{q^2}{4}\right)$. (34)

When $q\to 1$, oscillation period (33) tends to infinity ($K(q)\to ln(4/\sqrt{1-q^2})$), and frequency tends to zero. Jacobi sine becomes a hyperbolic tangent: $sn(p,q)\to thp$, and expression (32) is the following separatrix solution

$u(t)=\pm\sqrt{\frac{c_3c_2}{c_2-(c_2-c_3)thp}}$. (35)

The plot of function (35) is a bell-shaped curve: when $p=0$, displacement $u=\pm\sqrt{c_3}$, and when $p\to\pm\infty$, we obtain $u=\pm\sqrt{c_2}$.

Polynom $P_4(u,E)$ is positive also at $y>c_1$, and at the same time

$\int_{c_1}^{y}\frac{dy}{\sqrt{y(y-c_1)(y-c_2)(y-c_3)}}=\frac{2}{\sqrt{c_2(c_1-c_3)}}F(\nu,q)$, (36)

where $=arcsin\sqrt{\frac{c_2(y-c_1)}{c_1(y-c_2)}}$, $q=\sqrt{\frac{c_1(c_2-c_3)}{c_2(c_1-c_3)}}$.

Let us assume that $d=\sqrt{2c_2(c_1-c_3)}z$. Then $F(\nu,q)=\pm d$ and, therefore, $snd=sin\,\nu=\sqrt{\frac{c_2(y-c_1)}{c_1(y-c_2)}}$.

It can be easily found further that

$u(t)=\pm\frac{\sqrt{c_1c_2}cn(d,q)}{\sqrt{c_2-c_1sn^2(d,q)}}$. (37)

Taking into account that $c_1>c_2$ and $|sn(d,q)|\le 1$ we obtain from expression (37) that, if condition $c_2-c_1sn^2(d,q)\le 0$ is fulfilled, oscillation states of collective character cannot be propagated.

Conclusion

The range of fluctuations of systems allowing structural phase transitions was determined for the accepted model of interatomic interaction. Periodic and soliton-like solutions of the nonlinear differential motion equation were obtained. The nature of the phase transition (disorder-order type and displacive type) is determined by the ratio of the bond energy of active atoms to the height of the potential barrier in the single-particle potential with a triple minimum. Possible objects of application of the obtained results can be crystals of $Me^{I}Me^{II}BX_4$ family, as well as crystals or metals, on the surface of which atoms of gases or metals are absorbed (for example, hydrogen on a tungsten surface).

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