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QUANTUM CONCEPT OF THE REARRANGEMENT OF A CRYSTAL LATTICE

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Using quantum considerations based on the concept of lattice rearrangement waves, we carried out an analysis of processes of rearrangement of a crystal lattice occurring on a moving front (interface) of crystal rearrangement. For the introduction and quantization of these waves we use the method of acoustomechanical analogy and the Sommerfeld quantum conditions. We calculate the energies and the propagation velocities of the lattice rearrangement waves. Along with quanta having a certain momentum, quanta that have a certain angular momentum are introduced into consideration. On the basis of the concepts developed, we suggest a new expression for calculating the probability of thermofluctuational processes in a crystal. We perform a numerical analysis of the rate of growth of the γ*-phase in iron in the process of* α*-*γ*-conversion. Satisfactory agreement with experiment is obtained. We discuss the limitations and prospects of further development of the concept suggested. For direct experimental verification of the concept we propose to investigate the diffraction of electrons and other particles on the lattice rearrangement waves, i.e., in the process of phase conversions or disintegration of crystals.*

The theoretical analysis of many physical processes occurring in crystals, for example, phase conversions of the first kind, recrystallization, deformation and disintegration on shock loading, etc., is ultimately reduced to an analysis of the rearrangement of the crystal lattice. Common to all of the processes indicated is the fact that a rearrangement of the lattice occurs as a displacement of the rearrangement front of the substance, i.e., of the interfaces that separate the initial and final regions of the crystal (in what follows, without loss of generality, we will speak of the initial and final phases). At the present time, to analyze the mobility of interfaces, use is made of various atomistic models based on dislocation concepts of the structure of boundaries [1–5]. However, despite well-known achievements of such an approach, it is also necessary to note its limitation that does not permit one to consider the nature of physical processes on an elementary level. In fact, first, the well-known atomistic theories are based on a static model of the interface and do not take into account the dynamic structure of the latter [6–8], which is important for understanding the kinetics of the process, and, second, they ignore the quantum mechanics-based representation of a crystal as a system of special waves, i.e., quasiparticles.

The aim of the present work is to justify the quantum nature of the process of lattice rearrangement, determine the energies and the propagation velocities of the lattice rearrangement waves, and apply the results obtained to an analysis of a number of basic problems of the physics of phase conversions.

Before we proceed further, we note the fundamental difference of the concept suggested in the present work from the results of [9–11], in which the processes of ordering in solid solutions were analyzed with the help of the method developed by Bogolyubov in the theory of a nonideal Bose gas [12], i.e., the method of the theory of phase conversions of the second kind. In this case one need not analyze the mechanics of the motion of interfaces, since the conversion occurs simultaneously throughout the entire volume. It is therefore not difficult to introduce waves of fluctuations of the order parameter and, what is fundamentally important in the method, to carry out computations in a momentum representation.

In the present work we introduce lattice rearrangement waves to describe the typical case where the lattice rearranges on the moving front of conversion. To introduce such waves, use is made of the method of

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acoustomechanical analogy [13, 14]. From the viewpoint of acoustics [15, 16], a moving interface can be considered as a discontinuity surface, which, incidentally, is evident, since the latter separates phases with different physical properties. At the same time, from the results of [14, 17] it follows that the discontinuity surface, whose propagation is described by a hyperbolic-type equation, represents a wave front, which is a surface of constant action according to the acoustomechanical analogy [13, 14]. It is precisely the latter fact that permits one, by analogy with de Broglie's approach [18, 19], to introduce lattice rearrangement waves.

According to the principle of least action, the trajectory of a mechanical system (for simplicity we speak about a conservative system with one degree of freedom) is determined from the condition of the action extremum

$$\delta \int (P\delta Q - E\delta t) = 0\,, \tag{1}$$

where P is the momentum; E is the energy; δQ and δt are the variations of the generalized coordinate and the time. It seems that this principle should be satisfied also by trajectories intersecting the wave front, i.e., those bringing the mechanical system to another state. According to an analysis made in [20, 21], such trajectories should satisfy the Weierstrass–Erdman condition

$$[P\delta Q - E\delta t] = 0\,. \tag{2}$$

Here, the square brackets indicate the jump in the quantities on passage across the front. We will write Eq. (2) in another form:

$$p\delta q - \varepsilon\delta\tau = \text{const}\,, \tag{3}$$

where $p = [P]$; $\delta q = [\delta Q]$; $\varepsilon = [E]$; $\delta\tau = [\delta t]$.

It is evident that ε is the difference of energies of the system in different phase states, and $\delta\tau$ is the time of the transition of the system from one quantum state to another. Therefore, on the basis of the Bohr–Sommerfeld principle [19, 22], it is possible to identify ε with the energy of the quantum of lattice rearrangement and $\delta\tau^{-1}$ with its frequency. From this it follows that for the elementary process of the absorption of one quantum of lattice rearrangement the constant in expression (3) is equal to the Planck constant h. Such a conclusion agrees with the principal postulate of the "old quantum theory," i.e., with the Sommerfeld quantum condition [19, 22], according to which the truncated action of $p\delta q$ is replaced by the Planck constant h each time the system passes from one quantum state to another.

To determine the value of ε, we will take the quantity δq to be equal to the natural parameter of crystals, i.e., to the period of the crystal lattice a. As a result, we obtain

$$p = \frac{h}{a} = \hbar G\,, \tag{4}$$

where G is the vector of the reciprocal lattice. Assuming that the mass of the lattice rearrangement quantum is equal to the mass of the ion M, we obtain the following result for the velocity of the lattice rearrangement quantum:

$$v_i = \hbar G/M\,. \tag{5}$$

The characteristic values of v_i for metals are equal to 1–10 m/sec. We note that the velocity v_B, equal numerically to v_i, was introduced heuristically earlier in [15, 16] as the critical group velocity of atoms above which the plastic flow of the crystal acquires a stochastic (turbulent) character. This result is evident within the framework of the given concept, since the process of generation of lattice rearrangement waves becomes possible when $v > v_i$.

Similar considerations can be given for the quanta of the rearrangement of the electronic subsystem of a crystal

$$v_e = \hbar G/m\,. \tag{6}$$

Here m is the effective mass of an electron. Equations (3)–(6) yield the following estimates for the quantities ε_i and ε_e:

$$\varepsilon_i = \frac{\hbar v_i}{a} = \frac{h^2}{a^2 M} = M v_i^2 , \tag{7}$$

$$\varepsilon_e = \frac{\hbar v_e}{a} = \frac{h^2}{a^2 m} = m v_e^2 . \tag{8}$$

It is evident that v_e and ε_e are close to the characteristic parameters of the electronic subsystem of the crystal, i.e., to the velocity and the Fermi energy, respectively. The estimate of the quantity ε_i is $(m/M)^{1/2}\bar{\eta}\omega_\mathrm{D} = 10^{-2}-10^{-3}\hbar\omega_\mathrm{D}$, where ω_D is the Debye frequency.

There is a certain correlation between v_i and v_e. In actual fact, using the Bohm–Stuver relation for the speed of sound [23] and taking into account Eqs. (4)-(8), we obtain

$$v_i v_e = c_s^2 , \tag{9}$$

where c_s is the speed of sound.

In much the same fashion we can construct the whole hierarchy of characteristic velocities, e.g.,

$$v_i c_s = v_M^2 . \tag{10}$$

According to [15, 16], v_M is the maximum group velocity of atoms above which the crystal disintegrates, since the pressure $p_0 = \rho c_s v_M$ (here ρ is the density) in such a wave exceeds the theoretical strength.

The results obtained make it possible to also estimate the characteristic dimensions of the regions in the crystal in which correlation in the motion of atoms is possible. Evidently, in this case the maximum possible length is of greatest interest. The following expression can be given for this length:

$$l = h v_e / \varepsilon_i . \tag{11}$$

Estimations made by expression (11) give $l \simeq 0.1-1.0$ μm, which agrees with the dimensions of the Frank dislocation grid [3], as well as with experimentally recorded dimensions of the nuclei of a new phase in crystals [6, 24, 25].

It is known that the majority of physical processes in crystals occur in a thermofluctuational fashion [1, 2]. The calculation of the probabilities of these processes is based on the theory of absolute rates of reaction [1]. We know the following estimate for the velocity of the displacement of phase interfaces:

$$v_{ph} = c_s \exp(-U/kT) . \tag{12}$$

Here $W = \exp(-U/kT)$ is the probability of fluctuation; U is the activation energy of lattice rearrangement, interpreted as the energy needed to overcome the potential barrier that separates different phases. It is assumed for deriving formula (12) that the interface moves in a jumpwise fashion, with c_s being its actual velocity and v_{ph} its mean velocity. The main problem in using expressions of type (12) for specific calculations consists in the determination of the magnitude of the activation energy U. Actually, according to the theory of absolute rates of reactions, an activated complex consists of just a single atom in contradiction to modern concepts of transfer of thermal energy in crystals, since during its lifetime an activated complex interacts with 10^2-10^3 surrounding atoms, i.e., the process has a collective nature [5, 26]. Within the framework of the quantum concept of the rearrangement of a lattice it is possible to develop a new approach to the analysis of thermofluctuational processes that is free of the above shortcomings and is based on the theory of stochastic properties of the energy spectrum of quantum systems [27].

According to Eqs. (2) and (3), during passage of a quantum system from one state to another the action acquires the finite increment h, while its energy undergoes a change by a small value $\delta E = E_i$, $\delta E/E \ll 1$, where E is the characteristic energy of the system (of the crystal). In [27] it is shown that an infinitely small change in the energy δE for stable phase trajectories of dynamic systems does not lead to a finite increment of the action $p\delta q \geq h$. For the increment of the action to be finite, it is necessary that the phase trajectories corresponding to the energies E and $E + \delta E$ be statistically independent. For this it is at least necessary that stochastic displacement occur along a single generalized coordinate. According to [27], the probability of such a process obeys the following law:

$$W = \exp(-\operatorname{const} N), \tag{13}$$

where N is the number of collisions (scatterings) needed by the system for the phase trajectory with the energy $E + \delta E$ to become statistically independent of the trajectory with the energy E.

When calculating N we will proceed from the wave concept of lattice rearrangement. In this case the problem of determining N is reduced to the standard problem of the theory of scattering of elementary excitations in a crystal. Therefore, according to [23], N can be estimated as the ratio of the length of scattering Λ to the lattice period a:

$$N = \Lambda/a. \tag{14}$$

To determine Λ we will use the Gruneisen approximation [23]. As a result, for the length of the scattering of phonons with wave vector equal to G, we obtain (we consider the case of high temperatures $T > T_D$)

$$\Lambda = \operatorname{const}/\Gamma\varepsilon_T. \tag{15}$$

Here $\Gamma \simeq 2$ is the Gruneisen parameter; ε_T is the thermal dilatation of the lattice. Finally, for the probability of fluctuation we obtain

$$W = \exp(-\operatorname{const}/\Gamma\varepsilon_T). \tag{16}$$

In accordance with the analysis performed in [28], in what follows we will take const = 1 in Eq. (16). Refinement of the numerical value of this quantity requires the development of a more detailed theory. Comparing expressions (12) and (16), for the logarithm of the probability of the thermofluctuational process we obtain

$$U/kT = 1/\Gamma\varepsilon_T. \tag{17}$$

We note that Eq. (17) can be obtained formally by performing identical transformations of the left-hand side of Eq. (17) and taking into account that $U \simeq fa^2$, $kT \simeq fx_T^2$, $\varepsilon_T \simeq x_T^2/a^2$, where f is the quasielastic force; x_T^2 is the mean square of thermal atomic vibrations [29].

Let us demonstrate the results obtained in relation to the calculation of the rate of growth of the γ-phase during α-γ-conversion in iron. Even though this problem was the subject of discussions among specialists in physical metallurgy, it cannot be regarded as solved [1, 30]. First, let us estimate the actual velocity of the interface. In this case we will proceed from the concept of cooperative rearrangement of the lattice [28, 31], according to which each atom shifts a distance $a\varepsilon_{ph}$ in passing to a new phase, where ε_{ph} is the phase dilatation. The time during which the phase rearrangement of the lattice occurs will be estimated as $\delta t_{ph} = h/\varepsilon_e$, where ε_e is determined from Eq. (8). With allowance for Eqs. (12), (16), and (17) we finally obtain

$$v_{ph} = \frac{a\varepsilon_{ph}\varepsilon_e}{h} \exp(-1/\Gamma\varepsilon_T). \tag{18}$$

In Eq. (18) the combination $a\varepsilon_{ph}\varepsilon_e/h$ will be defined as the speed of sound $c_s = 3 \cdot 10^3$ m/sec and the combination $\Gamma\varepsilon_T$ as $(\beta_\alpha + \beta_\gamma)T$, where β_α and β_γ are the coefficients of linear thermal expansion of the α- and γ-phase, respectively. According to [32], $\beta_\alpha = 1.9 \cdot 10^{-5}\ \mathrm{K}^{-1}$, $\beta_\gamma = 2.2 \cdot 10^{-5}\ \mathrm{K}^{-1}$. Finally, from Eq. (18) we obtain that the rate of growth of the γ-phase in iron at $T = 1195$ K is equal to $v_{ph} \simeq 5 \cdot 10^{-3}$ mm/sec, which agrees well with experimental data [33].

There is still much experimental data relating to various physical processes in crystals that can be constructively considered within the framework of the concept developed, but an analysis of the limitations and the means for further development of this concept seems to be more urgent. In the present work the quantization of the lattice rearrangement waves is done by superposition of quantum conditions in a manner similar to that used in the "old quantum mechanics" rather than by solving an eigenvalue problem as is the case in the Schrödinger method. This makes the interpretation of the processes easier (wave front), which makes it possible to obtain many results directly on the basis of intuitive considerations without losing the depth of the analysis. Therefore, in the future, lattice rearrangement waves should be analyzed as solutions of the Schrödinger equation for a crystal.

Speaking of experimental confirmation of the concept developed, it should be noted that the existence of lattice rearrangement waves can be proved directly by experiments in which phenomena of interference or diffraction of waves occur. These data can be obtained by employing standard methods used for the analysis of the structure and the energy spectrum of elementary excitations of a crystal. Experiments in this field are few in number. For example, the authors of [34] revealed an abnormal decrease of the Debye–Waller factor in the vicinity of the point of the martensitic transformation. Interesting data were obtained in [15, 16] on the basis of acoustic emission from zones of disintegration of crystals. In particular, the conclusion was drawn that crystals disintegrate in a spiral fashion, i.e., through formation of disk cracks. A detailed analysis of this phenomenon lies outside the scope of the present work, but nevertheless it would be logical to suppose that this problem can be analyzed constructively on the basis of the concept developed. However, it is necessary to assume for this purpose that along with lattice rearrangement quanta having a certain momentum there are also quanta with a certain angular momentum (multiple of the Planck constant h). An analysis of such (rotational) quanta can be made by the method developed above. Therefore, for the angular frequencies of rotational quanta we may write down immediately

$$\Omega_i = \varepsilon_i/h, \tag{19}$$

$$\Omega_e = \varepsilon_e/h. \tag{20}$$

The quantum concept of lattice rearrangement suggested in the present work allows the following conclusions to be drawn:

1) the rearrangement of a crystal lattice occurs in a discrete fashion by emission of lattice rearrangement quanta by one phase and their absorption by the other;

2) the energy and propagation velocity of lattice rearrangement quanta are expressed in terms of parameters of elementary excitations;

3) within the framework of the quantum concept of lattice rearrangement one can consider thermofluctuational processes; the logarithm of the probability of thermofluctuational processes is determined by the reciprocal of the lattice dilatation;

4) to verify experimentally and refine the propositions of the concept suggested, it is possible to investigate the diffraction of elementary particles (electrons, neutrons) or x-rays at lattice rearrangement waves, i.e., in the process of phase conversions or disintegration.

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