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A CONTRIBUTION TO THE DIFFUSION THEORY IN SOLIDS

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Abstract—A statistical method for calculating the diffusion coefficient D in solids is discussed. The method reveals strong dependence of D on the measurable parameters characteristic of the structure and vibrational spectrum of particles in a solid body. The probability is calculated of a large short-time energy fluctuation (of mean life-time $\bar{\tau}$) at one of the interacting particles with allowance for a change in the state of surrounding particles whose motion provides the supply of necessary energy to the place of its casual concentration at distances $l \approx v_0\tau/2$.

Time change of the coordinates and impulses of particles as well as energy fluctuations in macroscopic volumes are described in terms of the theory of steady random functions.

In the final equations the time–space scales of large energy fluctuation at individual particles, their probability, diffusion coefficient and pre-exponential factor D_0 are related with the measurable parameters of a solid (E, $\varkappa$, θ, λ_D, Q, γ); here D_0 appears to be an exponential function of these parameters.

A procedure is shown of applying the relationships obtained for processes of self-diffusion and diffusion of admixtures in solids of different structures. A comparison is made with the corresponding experimental data.

NOMENCLATURE

D,	diffusivity;
D_0,	pre-exponential factor;
E,	activation energy
E_v,	energy of vacancy formation;
T,	absolute temperature;
R,	gas constant;
h,	Planck constant;
K,	Boltzmann constant;
t,	time;
θ,	Debye temperature;
$\varkappa$,	coordinational number;
λ_D,	Debye wavelength;
v_0,	rate of energy transfer over "grid" degree of freedom;
Q,	volume of elementary crystal cell;
γ,	number of degrees of freedom in elementary crystal cell;
$q_i(t)$,	particle coordinates;
$P_i(t)$,	components of particle impulse;
m,	mass of particles;
ρ,	root-mean-square displacement of particle passing through the barrier.

As is well known the temperature dependence of the diffusivity may be expressed as

$$D = D_0 \exp\left(-\frac{E}{RT}\right). \quad (1)$$

Here it is supposed that D_0 and E practically do not depend on T and $E \gg RT$. Comparison of the theoretical and experimental values of D_0 often reveals a sharp disagreement between them (see for example [1–4]). Such a disagreement is thought to be caused by some reasons connected with the fundamentals of the diffusion theory (and other activation processes) in solids [5–12]. One of these reasons lies in the fact that in the diffusion theory the so-called "individualistic" description of particles passing through a potential barrier is assumed [13].

The "individualistic" description of an elementary diffusion act does not take into account a collective character of motion of interacting solid particles but consider the behaviour and state of those particles which directly pass over the potential barrier. Ya. I. Frenkel [13] noted that the systematic diffusion theory for solids should allow for the appropriate changes in the solid state which accompany a single process of particle passing over the potential barrier.

In this connection the author undertook some attempts [5–8] to consider this problem which required investigation of the probability of large energy fluctuations on separate particles of a solid when the thermodynamic fluctuation theory cannot be applied. On the basis of the approach proposed in [5, 6] a method [7, 8] has been developed for calculation of the probability of large energy fluctuations on individual particles in the systems of strong interacting particles. The method allows for changes in the system due to large fluctuation on an individual solid particle.

The proposed method was applied [5–12] for consideration of the kinetics of some processes (including diffusion [8, 11, 12]) in condensed bodies. In these cases the final equations include interaction between crystal particles in terms of the measured parameters characterizing the process and system (E, $\varkappa$, θ, λ_D, Q and γ).

In the present paper the above method is reported in application to diffusion processes in solids.

STATEMENT OF THE PROBLEM

For the diffusion theory, the problem of the motion of those relatively few particles of which the fluctuation energy casually increases up to $E' \geqslant E \gg kT$ due to large fluctuation, is of substantial interest. In each of these relatively unusual cases within some small region of a body (of the order of atom sizes) a short-time local state appears when particle motion is considerably nonlinear. There are no general methods for description of such nonlinear motions of interacting particles. Besides, the probability of great energy fluctuations at a crystal particle cannot be calculated by direct application of the fluctuation theory to an individual particle. Usually these questions are not considered by the diffusion theory, but it is assumed* that while calculating the probability of particle passage over the barrier the state and behaviour of the surrounding particles is neglected. Frenkel [13] formulated the assumptions which are the basis of such an "individualistic" description of an elementary diffusion act (and other activation processes) in solids (the so-called hypothesis of "instantaneous" energy concentration on a particle and "instantaneous" discarding of the excess energy). Such assumptions are presumably specified by the fact that a number of problems connected with formation of large energy fluctuation on one of the strong interacting solid particles and its passage over the barrier are not yet investigated.

Let us consider some of them. In many cases the energy $E' \geqslant E \gg kT$ which is necessary for the particle to pass over the barrier may considerably exceed the mean energy of thermal motion of all the near neighbours of the particle considered. Under such conditions a random energy increase in one of the particles up to $E' \geqslant E$ may occur only due to the fact that the energy necessary for it will be transmitted to the particle from some distance l (for the time $\bar{\tau}^{(1)} \approx l/v_0$, on the average) as a result of collective motion of many surrounding particles supplying energy to the region of its random concentration at average velocity v_0 (of the order of sound velocity). The question arises about the value of average time-space scales l and $\bar{\tau}^{(1)}$ characterizing formation of such great energy fluctuations, their dependence on E, crystal structure and so on. Another problem deals with the method of predicting the probability of large energy fluctuation on one of the many interacting particles, i.e. when the usual fluctuation theory cannot directly be applied to this particle. These problems are discussed below without dwelling upon the details of mechanical motion of the solid particles (which eliminates the difficulties of solving the mechanical problem of non-linear

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*The appropriate references and literature analysis on the diffusion theory in condensed bodies may be found in many works (see for example [1–4, 8, 13–16]).

particle motion within the region of formation of large energy fluctuations). We completely assume the theoretical probability point of view while expressing the motion of solid particles in terms of the statistical theory of fluctuations with continuous spectrum, and describe the collective fluctuations of solid particles using the concept of multidimensional vector steady random functions [17, 18].

DESCRIPTION OF THE MODEL

First we shall consider an equilibrium system consisting of N_0 interacting similar particles of mass m which oscillate around the equilibrium with the coordinates q_i where $i = 1, 2, \ldots, 3N_0$. Assume that $3N_0 = N$ of the coordinates $q_i|t, \xi|$ of all the particles form a continuous $3N_0$—dimensional stationary (in a narrow sense) vector process [17, 18] $\boldsymbol{R}(t, \xi) = \{q_i(t, \xi)\}$ which is believed to be ergodic and almost everywhere at least twice-differentiable with respect to time t. Here ξ is the space variable of elementary events. The correlation between the coordinates q_i and q_k at arbitrary time moments t_1 and t_2 is characterized by the correlation matrix with the elements

$$D_{ik}(\Delta t) = \overline{[q_i(t + \Delta t) - \bar{q}_i][q_k(t) - \bar{q}_k]}$$

which are assumed to be absolutely integrated and possess the correlation interval t_0' satisfying the condition $|D_{ik}(t_0')| \ll a^2$, where $a^2 = D_{ii}(0)$. Time differentiation of the random function $\boldsymbol{R}(t, \xi)$ yields $3N_0$—dimensional steady random vector function $\dot{\boldsymbol{R}}(t, \xi) = \{\dot{q}_i(t, \xi)\}$ possessing ergodic property and describing random fluctuations of $3N_0$ components of $\dot{q}_i$ velocities of N_0 solid particles. By using this function we build $3N_0$—dimensional continuous random steady vector function $\mathscr{P}(t, \xi) = \{P_i(t, \xi)\}$ that describes the correlated fluctuations N of the components $P_i(t, \xi) = m\dot{q}_i(t, \xi)$ of pulses of N_0 particles. The random process $\mathscr{P}(t, \xi)$ possesses the correlation matrix with the absolutely integrated elements $B_{ik}(\Delta t)$ with the correlation interval t_0 satisfying the conditions $|B_{ik}(t_0)| \ll S^2$, where $S^2 = B_{ii}(0)$. Differentiation of the function $\mathscr{P}(t, \xi)$ over t yields N-dimensional steady random function $\boldsymbol{F}(t, \eta) = \{\dot{P}_i(t, \eta)\}$ which describes random oscillations of the forces acting upon solid particles. The correlation of $\dot{P}_i(t_1)$ and $\dot{P}_k(t_2)$ values is characterized by the correlation matrix with the absolutely integrated elements $C_{ik}(\Delta t)$ and correlation interval t_0'' satisfying the condition

$$|C_{ik}(t_0'')| \ll C_{ii}(0).$$

Next we suppose that the spectra of the random functions $\boldsymbol{R}(t, \xi)$, $\mathscr{P}(t, \xi)$, $\boldsymbol{F}(t, \eta)$ are practically broken by the Debye frequency $\nu_D = K\theta/h$, and the body temperature T is high enough and satisfies the condition $T \gg \theta/4$. Then the values with dimensions of time, pulse length and force characterizing motion of individual particles of the body are as follows

$$t_0 \approx t_0' \approx t_0'' \approx \frac{h}{K\theta}; \qquad a_0 \approx \frac{h}{\sqrt{(mK\theta)}}$$

$$S_0 \approx \sqrt{(mK\theta)}; \qquad \sigma_0 = \frac{\sqrt{[m(K\theta)^3]}}{h}. \tag{2}$$

The above model may be applied to non-equilibrium systems with rather slow (in particular, diffusive) processes whose relaxation time T_a satisfies the condition

$$T_a \gg \Delta\tau \gg t_0 \tag{2a}$$

wherein $\Delta\tau$ is the time interval for small enough changes in the parameters of the system. Generally speaking, in this case the random functions $\boldsymbol{R}(t, \xi)$, $\mathscr{P}(t, \xi)$ and $\boldsymbol{F}(t, \xi)$ will be unsteady. However, when fulfilling condition (2a), to realize the random functions whose duration is of the order of $\Delta\tau$, the above considerations involving steady random functions may be used with sufficient accuracy.*

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* If the accuracy of determining the coordinates and particle pulses is prescribed by the values a_0 and S_0 from (2), then the general relationships for the entropy of continuous distributions [18, 19] may be employed to build the entropy expressions which correspond to simultaneous single-time, two-time, etc. multipartial density of probability of distribution of coordinates and pulses $\rho\ (q, p)$ etc., solid particles, distribution of coordinates or particles (as well as of forces acting upon them) separately [7, 8]. Similar relationships may also be constructed for an unsteady-state case.

SPACE-TIME EVALUATION FOR LARGE ENERGY FLUCTUATION ON ONE OF THE INTERACTING PARTICLES

The random energy concentration $E' \geqslant E$ on an individual (for example j-th) solid particle means peak of some realization $P_j^{\xi}(t)$ of the random function $P_j(t, \xi)$ up to $P(E') \geqslant P(E) = \sqrt{(2mE)}$ (see Fig. 1, solid line).* From this point of view an elementary event of particle transition over the barrier comprises the following stages: (a) increase in energy (pulse) of particle for the time $\bar{\tau}^{(1)}$, on the average, from the values which are considerably less than E (less than $P(E)$) to the values $E' \geqslant E$ (or $P(E') \geqslant P(E)$); (b) transition over the potential barrier; (c) decrease in energy (pulse) of a particle from the values $E' \geqslant E$ ($P(E') \geqslant P(E)$) to the value of the order of its mean energy (mean pulse) of thermal motion for the time $\bar{\tau}^{(2)}$, on the average. When calculating $\bar{\tau}$, $\bar{\tau}^{(1)}$ and $\bar{\tau}^{(2)}$ we proceed from energy determination of the durability of the function $P_j^{(\xi)}(t)$ peak [22]

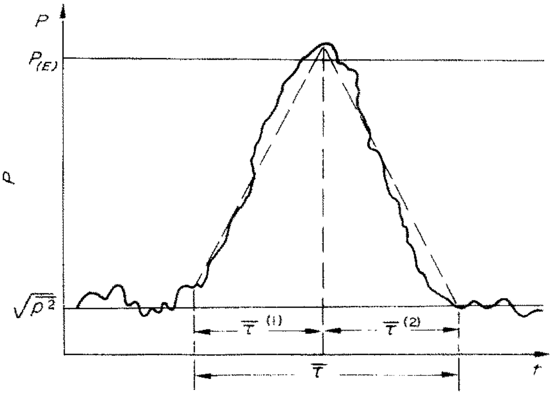

FIG. 1.

$$\frac{1}{2m\tau}\int_{t'}^{t'+\tau}[P_j^{(\xi)}(t)]^2\,dt = fE \tag{3}$$

where f is the constant of the order of unity depending on the shape of the peak, and τ is a random value. An exact form of the function peak $P_j^{(\xi)}(t)$ is unknown in every case. Therefore to estimate the average values of $\bar{\tau}^{(1)}$ and $\bar{\tau}$ we approximate the peak of the function $P_j^{(\xi)}(t)$ by the triangular peak with angular coefficient $\zeta(\bar{\tau})$ (see Fig. 1, broken line). Bearing in mind that energy is supplied to a particle by its near neighbours whose number is $\varkappa^*$, the value $\zeta(\bar{\tau})$ may be estimated (using (2)) as $\zeta(\bar{\tau}) = \varkappa\sigma_0$. With the above assumptions and supposing $\bar{\tau}^{(1)} \approx \tau/2$, we get from (2), (3)

$$\bar{\tau}^{(1)} \approx \frac{p(E)}{\zeta(\bar{\tau})} \quad \text{or} \quad \bar{\tau}^{(1)} = \beta\frac{h}{\varkappa_K\theta}\sqrt{\left(\frac{E}{K\theta}\right)};$$

$$\bar{\tau} \approx \beta\frac{2h}{\varkappa_K\theta}\sqrt{\left(\frac{E}{K\theta}\right)} \tag{4}$$

where β is a dimensionless coefficient of the order of unity. Consequently, an energy increase to the values $E' \geqslant E$ for the time $\bar{\tau}^{(1)}$ is accompanied by energy supply from other particles at distances

$$l = \bar{\tau}^{(1)}\ v_0 = \beta\frac{\lambda_D}{\varkappa}\sqrt{\left(\frac{E}{K\theta}\right)} \tag{5}$$

i.e. from the surrounding region with an average volume (in an isotropic case) equal to

$$\Omega = \frac{4\pi}{3}l^3 = 4\beta^3\frac{\lambda_D^3}{\varkappa^3}\left(\frac{E}{K\theta}\right)^{\frac{3}{2}}. \tag{6}$$

This region possesses the number of degrees of freedom

$$n = 4\beta^3\frac{\gamma\lambda_D^3}{\varkappa^3 Q}\left(\frac{E}{K\theta}\right)^{\frac{3}{2}}. \tag{7}$$

If the condition $\sqrt{(n)} \gg 1$ is satisfied, then the volume Ω may be described in terms of statistical

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* The peaks of some random functions were investigated in connection with different physical and engineering problems [20, 21] neglecting peaks of some components of the multidimensional vector random process provided that the appropriate conservation laws are satisfied.

* It is not the same for a number of cases. For instance, in ionic crystals where the interaction forces between particles decrease rather slowly, a definite contribution is made by the second and consequent coordination spheres. Similar situation appears in some crystals where various groups of neighbours are at somewhat different distances, etc.

thermodynamics that will be assumed below. The only parameter $\beta \approx 1$ entering formulae (4)–(7) may be found by comparing the provided and experimental data.

CALCULATION OF THE PROBABILITY OF LARGE ENERGY FLUCTUATION ON A SOLID PARTICLE

The probability of the random energy overshoot on a solid particle is mainly determined by local conditions existing at certain time moments in the surrounding region μ of mean volume Ω. Contribution of more removed regions and conditions existing in the region earlier, quickly decreases with an increase of the appropriate space and time intervals. For description of random energy fluctuations of the region μ we introduce the continuous normal four-dimensional random field $u_0(t, r)$ [17, 21] of the bulk density of energy which is assumed to be steady in time t, uniform along the coordinates r, ergodic and differentiable almost throughout. The energy of the region μ of the mean volume Ω is described by the random function $U(t) = \int U_0(t, r)\, \mathrm{d}r$ which is continuous and almost everywhere differentiable by a steady normal random function possessing an ergodic property. It is assumed that its auto-correlational function $A(\Delta t)$ is absolutely integrated and allows introduction of the correlation interval t_k which satisfies the condition $A(t_k) \ll \alpha^2 = A(0)$.

The probability of change in the energy $\Delta U(\Delta t)$ of the region μ for the time Δt due to energy transfer between the region μ and the rest of the system parts is determined by the probability density

$$f[\Delta U(\Delta t)] = \frac{1}{\sqrt{\{4\pi\alpha^2[1 - \lambda(\Delta t)]\}}} \times \exp\left\{-\frac{[\Delta U(\Delta t)]^2}{4\alpha^2[1 - \lambda(\Delta t)]}\right\} \tag{8}$$

where $\lambda(\Delta t) = A(\Delta t)/\alpha^2$. Since the spectrum of the random function $U(t)$ is practically broken from above by the frequency $\nu_0 \approx 1/\bar{\tau}^{(1)}$ then $t_k \approx \bar{\tau}^{(1)}$. Now from (8) we find the mean-root-square energy change of the region μ for the time $\bar{\tau}^{(1)}$

$$\{[\Delta U(\bar{\tau}^{(1)})^2]\}^{\frac{1}{2}} = b(\bar{\tau}^{(1)}) \approx \alpha^2 \text{ where}$$

$$\alpha = \sqrt{(KCT^{(2)}}; \qquad C = Kn = K\gamma\frac{\Omega}{Q}. \tag{9}$$

For calculation of the probability W of energy fluctuation to the level $E' \geqslant E$ per unit time on one of the particles of the region μ with regard to changes in this region which accompany formation of such fluctuation, we consider two modes of fluctuations: (a) relatively slow fluctuations (whose frequency does not exceed $\bar{\tau}^{(1)}$) due to energy changes in the region μ because of energy exchange between the region and other parts of the system; (b) fast fluctuations due to energy redistribution within the region μ during time not longer than τ. If $W(E/U)\bar{\tau}^{(1)}$ is the probability of the fact that for the time $\bar{\tau}^{(1)}$ on one of the particles of volume Ω possessing energy U, energy $E' \geqslant E$ is accumulated by chance, then for W we have

$$W = \int W(E/U) f(U)\, \mathrm{d}U \tag{10}$$

where

$$W\left(\frac{E}{U}\right) = \int_{E' \geqslant E} W_1\left(\frac{E'}{U}\right) \mathrm{d}E';$$

$$f(U) = \frac{1}{\sqrt{(2\pi\alpha^2)}} \exp\left[-\frac{(U - \bar{U})^2}{2\alpha^2}\right]. \tag{11}$$

Here $W_1(E'/U)$ is the probability of forming a random energy overshoot to some definite value E' on $\Delta n = n - n' \ll n$ degrees of freedom of the region per unit time and unit energy interval and equal to

$$W_1\left(\frac{E'}{U}\right) = \frac{1}{h_1} \exp\left(\frac{S_A - S_C}{K}\right) \tag{12}$$

where h_1 is a value with the dimension of action; $S_C = S(U')$ is the maximum value of the entropy of $n' = n - \Delta n$ degrees of freedon possessing the energy U'; $S_A \approx S[U' - E' + b(\bar{\tau}^{(1)})]$ is the value of the entropy n' of degrees of freedon of the region provided that the energy E' appeared to be accidentally concentrated on $\Delta n = (n - n') \ll n$ degrees of freedom of this region. On the other

n' degrees of freedom this energy loss is somewhat compensated by the energy supply $b \equiv b(\bar{\tau}^{(1)})$ into the region from other regions of the system.* Then from (10) to (12) we get

$$W = \frac{1}{h\sqrt{(2\pi\alpha^2)}} \iint\limits_{(M)E' \geqslant E} \left\{\frac{S[U' - E + b] - S(U')}{K}\right\} \times \exp\left[-\frac{(U - \bar{U})^2}{2\alpha^2}\right] \mathrm{d}U\,\mathrm{d}E'. \qquad (13)$$

The mean time between two successive energy fluctuations to the level $E' \geqslant E$ on one and the same Δn degrees of freedom is equal to

$$\tau_d = \frac{n}{2W} = \frac{\gamma\Omega}{3QW} \qquad (14)$$

(since the probability W refers to one of $n/3$ particles of volume Ω). To reduce equation (13) to a more convenient form we expand the function $S[U_{n'} - E + b]$ into series over the powers of the value $(E' - b)$ provided that heat capacity is independent of temperature. Then (if we neglect deviation ΔU of energy U from the average value $\bar{U}$) from (13) with respect for (4) and (7) we obtain†

$$W = W_0 \exp\left(-\frac{E}{kT}\right) \qquad (15)$$

where the pre-exponential multiplier is

$$W_0 = \frac{1}{\tau}\mathrm{e}^{\sqrt{(n)}} = \frac{K\theta\varkappa}{2\beta h}\left(\frac{K\theta}{E}\right)^{\frac{1}{2}} \exp\left[\delta\left(\frac{E}{K\theta}\right)^{\frac{3}{4}}\right],$$

$$\delta = 2\beta^{\frac{3}{2}}\left(\frac{\gamma\lambda_D^3}{\varkappa^3 Q}\right)^{\frac{1}{2}}. \qquad (16)$$

It was assumed above that the body consists of similar particles. However the reported method of calculating the probability of large energy fluctuation on separate particles of the system of interacting particles is also generally valid (within some calculation details) if the body consists of different particles (solid solutions, etc.).

CALCULATION OF DIFFUSIVITY IN SOLIDS

Let us consider the following two cases.

1. *Diffusion of particles proceeds without any defects.* In this case transition of a particle (particles) over the potential barrier occurs with the probability $a \leqslant 1$ if energy fluctuation on a particle (particles) reaches the value $E' \geqslant E$. Particular mechanisms of particle transition over the potential barriers are not dealt with in this paper and E is assumed to be known.

2. *Diffusion proceeds over vacancies (or other defects).* In this case two conditions should be satisfied in order than an elementary event of diffusion takes place: (a) formation of appropriate energy fluctuation on a particle (particles); (b) presence of vacancy (or other defect) in the vicinity of a particle with the developed energy fluctuation.

We consider first self-diffusion without defects. Using (6), (14)–(16) we get for the diffusion coefficient

$$D = \frac{a\eta\rho^2}{6\tau d} = D_0 \exp\left(-\frac{E}{kT}\right) \qquad (17)$$

$$D_0 = \frac{a\eta\rho^2 Q W_0}{2\gamma\Omega} = D_{00}\mathrm{e}^{\sqrt{(n)}} = D_{00} \exp\left[\delta\left(\frac{E}{K\theta}\right)^{\frac{3}{4}}\right] \qquad (18)$$

$$\delta = 2\beta^{\frac{3}{2}}\left(\frac{\gamma\lambda_D^3}{\varkappa^3 Q}\right)^{\frac{1}{2}}, D_{00} = \frac{a\eta\rho^2 Q}{2\Omega\bar{\tau}}$$

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[*] The process of energy removal b from the volume Ω which accompanies formation of energy fluctuation on a particle and is not considered here makes negligible contribution to the probability of the process under consideration [8].

[†] If we take into account deviations of u from $\bar{u}$, then in (16) additional multipliers

$$\exp\left[q\left(\frac{E - b}{K\theta}\right)^{\frac{1}{2}}\right] \quad \text{and} \quad \exp\left[-\frac{\theta}{r\delta}\left(\frac{E - b}{K\theta}\right)^{\frac{1}{4}}\right]$$

appear where

$$q = \frac{1}{8\beta^3}\left(\frac{\varkappa^3 Q}{\gamma\lambda_D^3}\right)\left(\frac{\theta}{T}\right)^2.$$

However as these multipliers partially compensate each other and $T > \theta$, their contribution is relatively small.

$$= \frac{a\eta\varkappa^4 Q}{16\pi\gamma\beta^4\lambda_D^3}\left(\frac{K\theta}{E}\right)^2 \frac{\rho^2 K\theta}{h} \tag{19}$$

where η is a factor depending on the type of crystal lattice. Introducing dimensionless values we derive from (17)–(19) the following expressions

$$D = D_0 \exp\left(-\frac{\varepsilon}{T_r}\right) \tag{20}$$

$$D_0 = D_{00} \exp(\delta\varepsilon^{\frac{3}{4}}); \quad D_{00} = \frac{a\eta\rho^2 K\theta\varkappa^4}{16\pi\gamma\beta^4\lambda_r^3\varepsilon_r^2 h};$$

$$\delta = 2\beta^{\frac{3}{2}}\left(\frac{\lambda_r^3\gamma}{\varkappa^3}\right)^{\frac{1}{2}}. \tag{21}$$

The equations obtained may also be used when considering diffusion in mixtures, etc. If in this case a crystal retains the structure of the basis substance, then when calculating D it is necessary to take into account the position of the diffusible foreign particle in it, since a number of its near neighbours $\varkappa_{ef}$ may noticeably differ from $\varkappa$, etc.

When diffusion proceeds in the form of replacing vacancies by a particle, it is necessary to allow for the probability of vacancies present in the vicinity of this particle which is equal to $\psi_v \approx \varkappa \exp[-(E_v/kT)]$ (where E_v is an energy of vacancy formation) as well as decrease in the effective coordinational number at least by unity (for a particle diffusing). Then substituting the value a by $a\psi_v$ and the appropriate parameters by $\varkappa_v$, θ_v, λ_{D_v}, Q_v and γ_v in (17) we arrive at

$$D_v = D_{0v} \exp\left(-\frac{E + E_v}{kT}\right) \tag{22}$$

$$D_{0v} = D_{00v} \exp\left[\delta_v\left(\frac{E}{K\theta_v}\right)^{\frac{3}{4}},\right.$$

$$\delta = 2\beta^{\frac{3}{2}}\left(\frac{\gamma_v\lambda_{D_v}}{\varkappa_v^3 Q_v}\right)^{\frac{1}{2}} \tag{23}$$

$$D_{00v} = \frac{a\eta\varkappa_v^5 Q_v}{16\varkappa\beta^y\gamma_v\lambda_{D_v}^3}\left(\frac{K\theta_v}{E}\right)^2 \cdot \frac{\rho_v^2 K\theta_v}{h}. \tag{24}$$

In expressions (22)–(24) the dependence of D_v on T is determined by the total energy $E + E_v$ and the pre-exponential factor D_{0v} is controlled only by the "threshold" energy E necessary for a "jump" over the barrier.

DISCUSSION OF RESULTS

Comparison of the predicted and experimental values of D_0 and D for metals with cubic and hexagonal lattices for ion crystals and semiconductors of various types showed that at $\beta \approx 1$ the equations obtained lead to agreement between the predicted and experimental data in the cases when activation energy and pre-exponential factors D_0 are not too small. The reasons for the anomalous small values D_0 observed are not quite clear though the relationships obtained above are likely to discover new possibilities for their consideration. Below we confine ourselves to some results describing the case when the pre-exponential factor is not too small.

From (18), (19), (21), (23), (24) it is clear that according to [1] factor D_0 slightly depends on temperature. These expressions also show a strong (exponential) dependence of D_0 not only on the energy E but on a number of parameters of a solid ($\varkappa$, Q, etc.). We consider some conclusions following from this dependence.

1. It follows from (18)–(21), (23) and (24) that D_0 is an exponential function of the dimensionless relation $\varepsilon = E/K\theta$, where θ and E while changing from one body to another may vary within a wide range, and energy E may also vary with changing conditions and diffusion direction. These are some examples.

(a) Self-diffusion in crystals with equal crystal lattices (equal $\varkappa$ and γ). In this case, in spite of considerable difference in activation energy, the values of ε and D_0 may differ a little, which often takes place in practice (for example, at self-diffusion in γ-Fe and Pb [3]).

(b) At remarkable anisotropy of self-diffusion the values of E for diffusion in various directions are different. The calculations by equations

(17)–(19) for hexagonal closely packed lattices and a number of other systems yield coincidence with experimental data at $\beta \approx 1$. It was taken into account that the effective coordinational number $\varkappa_{ef}$ may be larger than $\varkappa$, since the most remote neighbours may contribute to a definite degree to $\varkappa_{ef}$ [23].

(c) Diffusion of low admixtures in substitutional solid solutions, where the observed values of activation energy E_1 and pre-exponential factor D'_0 may considerably differ from the appropriate values observed at self-diffusion of the basic lattice-forming element.

The facts like these may be explained using the relationships obtained, since $E_1 \neq E$ and $\varepsilon_1 \neq \varepsilon$.*

2. According to (18), (21) and (23) the factor D_C is an exponential function of the value $\delta \sim \gamma^{\frac{1}{2}}\varkappa^{-\frac{1}{2}}$. Because of it, other conditions being equal, its relatively small changes may noticeably affect the values of D_0, which may explain the corresponding experimental facts taking into account the change in crystal structure.

(a) Diffusion in interstitial solid solutions. It was taken into consideration that the admixture atoms settle at interjunctions and the number of their nearest neighbours may differ markedly in coordinational number of the main lattice. The calculations for a number of interstitial solid solutions showed agreement with experimental values of D_0 at $\beta \approx 1$.

(b) Diffusion in ion crystals is closely connected with ion conductivity where experimental data are usually described by the sum of two summands of the type (I) [13, 24, 25]. In these summands the activation energy E_1 and E_2 may differ two to three times, and pre-exponential factors, by several orders of magnitude. The above equations for moderate values of D_0 yield coincidence with the experimental data if account is taken of relatively slow decrease in the forces of interaction between particles of ion crystals, which leads to increase in the effective coordinational number $\varkappa_{ef}$ because of contribution of other coordinational spheres.

We assume that the above examples will illustrate the essential difference between the relationships obtained and conventional equations for diffusion coefficients and will show the possibility of experimental check of the above relationships.

CONCLUSIONS

The comparison with experimental data showed that equations (17)–(24) open some new possibilities for better understanding the laws and peculiarities observed in diffusional processes, as well as for setting closer relationship between the kinetics of these processes and the structure of a solid, processes of energy transfer, and so on.

We shall point out that the above method of calculating the rates of activation processes allows to account for the effect exerted by external variables and constant electric fields and mechanic stresses on the rates of activation processes [5, 8]. Here the concepts of mechanics and solid electrodynamics as well as the thermodynamic perturbation theory may be used because the condition $\Omega U_e \ll nkT$ is usually satisfied where Ω and n are determined in accordance with [6, 7] and U_e is bulk density of the external field. The volume Ω may be described in terms of thermodynamics.

The implicit account of the finite rate of energy transfer by "lattice" degrees of freedom as well as of macroscopically small volume in the process of generation of great fluctuation energy on an individual particle of the system of strong-interacting particles (rather than the hypothesis of instantaneous concentration of energy on the particle and its instantaneous overshoot by the particle) is generally peculiar of the calculation of the rates of various activation processes in similar systems at sufficiently high activation energies. In this connection the above method of calculating the probabilities of large energy fluctuations may be also applied to other

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*The calculations of the coefficients of self-diffusion in hexagonal crystals and diffusion in substitutional and interstitial solid solutions were carried out together with V. M. Beilin.

activation processes (both bulk and surface) with crystal and amorphous bodies and, presumably, of liquids at moderate temperatures. In case of amorphous bodies and liquids the values $\varkappa$, γ etc. are determined by the structure corresponding to the nearest order, and for surface processes, by the structure of the condensed body surface.

To conclude I wish to express my appreciation to the corresponding member of the USSR Academy of Sciences S. Z. Roginsky and Prof. L. S. Polak for fruitful discussion of the problems under consideration.

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UNE CONTRIBUTION A LA THEORIE DE DIFFUSION DANS DES SOLIDES

Résumé—On discute une méthode statistique de calcul du coefficient de diffusion D dans des solides. La méthode révèle une forte dépendance de D vis-à-vis des paramètres mesurables caractéristiques de la structure et du spectre vibrationnel de particules dans un corps solide. On a calculé la probabilité d'une grande fluctuation d'énergie à temps court (avec $\bar{\tau}$ durée de vie moyenne) pour l'une des particules en interaction, avec éventualité d'un changement d'état des particules environnantes dont le mouvement fournit le supplément d'énergie nécessaire à la plaque pour une concentration casuelle à des distances $1 = v_0\tau/2$.

Les changements dans le temps des coordonnées et des pulsations des particules aussi bien que des fluctuations d'énergie dans des volumes microscopiques sont décrits par la théorie des fonctions aléatoires stationnaires.

Dans les formulations finales les échelles espace-temps de grande fluctuation d'énergie pour des particules individuelles, le coefficient de diffusion et le facteur pré-exponentiel D_0 sont reliés aux paramètres mesurables d'un solide (E, x, θ, λ_D, Q, γ); ici D_0 est une fonction exponentielle de ces paramètres.

On donne la procédure d'application des relations obtenues pour des processus d'auto-diffusion et de diffusion de mélanges dans des solides de structure différente. Une comparaison est faite avec les résultats expérimentaux correspondants.

BEITRAG ZUR DIFFUSIONSTHEORIE IN FESTKÖRPERN

Zusammenfassung—Eine statistische Methode zur Berechnung des Diffusionskoeffizienten D in Festkörpern wird behandelt. Die Methode zeigt eine starke Abhängigkeit des Koeffizienten D von den messbaren Parametern, die charakteristisch für die Struktur und das Schwingungsspektrum der Teilchen in einem Festkörper sind.

Für grosse Werte einer Kurzzeit-Energieschwankung ist die Wahrscheinlichkeit berechnet (mittlere Lebensdauer $\bar{\tau}$) und zwar an einem Teilchen bei Berücksichtigung der Zustandsänderung der umgebenden Teilchen, deren Bewegung die nötige Energie zur Konzentration im Abstand l $\approx v_0\tau/2$ liefert.

Die zeitliche Änderung der Koordinaten und Impulse der Teilchen sowie Energieschwankungen im mikroskopischen Volumen werden durch die Theorie der stetigen Zufallsfunktionen beschrieben.

In den Endgleichungen werden die Zeit-Raum-Skalen der grossen Energieschwankungen bei Einzelteilchen, ihre Wahrscheinlichkeit, der Diffusionskoeffizient und der vorexponentielle Faktor D_0 auf die messbaren Parameter eines Festkörpers (E, κ, λ_D, Q, γ) bezogen. Hier erscheint D_0 als Exponentialfunktion dieser Parameter.

Es wird ein Verfahren gezeigt, wie man diese Beziehungen auf Prozesse anwenden kann, wie Selbst-Diffusion und Diffusion von Beimischungen in Festkörpern verschiedener Struktur. Die Ergebnisse werden mit entsprechenden experimentellen Daten verglichen.

К ТЕОРИИ ДИФФУЗИИ В ТВЕРДЫХ ТЕЛАХ

Аннотация—Рассматривается статистический метод расчета коэффициента диффузии D в твердых телах, который устанавливает сильную зависимость D от измеримых параметров, характеризующих структуру и спектр колебаний частиц твердого тела. Вычисляется вероятность большой кратковременной флуктуации (со средним временем жизни τ) энергии на одной из взаимодействующих частиц с учетом, сопровождающих эту флуктуацию изменений состояния окружающих частиц, коллективной движение которых обеспечивает подвод необходимой энергии к месту ее случайной концентрации с расстояний $l \approx v_0\tau/2$.

Описание изменений со временем координат и импульсов частиц тела, а также флуктуаций энергии в микроскопически малых объемах проводится в терминах теории стационарных случайных функций.

В окончательных формулах пространственно-временные масштабы больщих флуктуаций энергии на отдельных частицах, их вероятность, коэффициент диффузии и предэкспоненциальный множитель D_0 связывается с измеримыми параметрами твердого тела (E, κ, θ, λ_D, Q, γ); причем D_0 оказывается экспоненциальной функцией этих параметров.

Показана методика применения полученных соотношений к процессам самодиффузии и диффузии примесей в твердых телах различной структуры и проведено сравнение с соответствующими экспериментальными данными.